program package for multipurpose crystallochemical analysis

ToposPro

Version 5.0

PRACTICAL MANUAL 1.1.4

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Preface

The ToposPro program package has been developed since 1989 by Prof. Vladislav A. Blatov (Samara State University) under the name TOPOS. Within 1989-2005, the second TOPOS author, Dr. Alexander P. Shevchenko (SSU), created the TOPOS IsoCryst, Dirichlet, and StatPack programs as well as a part of the Database Management System (DBMS). Since 2013 A.P. Shevchenko is again in the TOPOS team and now elaborates ToposPro. Within 1989-1998, Prof. Victor N. Serezhkin (SSU) actively participated in discussions of the TOPOS methods relating to use of atomic Voronoi partition of the crystal space. Since 2003 the topological algorithms of TOPOS have been developing with essential contribution and stimulation of Prof. Davide M. Proserpio (University of Milan). Some procedures in TOPOS were written by Vladimir A. Pol’kin and Maxim V. Peskov (SSU).

During 1989-2000 TOPOS was developed as a MS DOS application written in Borland Pascal (versions 1.0, 2.0) with using Turbo Vision library (versions 3.0, 3.1, and 3.2). Version TOPOS 3.2 was supported until 2005. In 2000, the Windows-based application programmed with Borland Delphi was started as version TOPOS 4.0. In 2005, it covered all abilities of the MS DOS version and since that time TOPOS 4.0 has been distributing for free. In 2007, we launched the project with the TOPOS topological collections (i.e. sets of databases containing the information on topological properties of crystal structures). Now six types of collections are supported (TTD, TTO, TTR, TTL, TTM, TTN).

The history of the TOPOS methods is rather strictly subdivided to two parts: in 1989-2000 the geometrical methods based on atomic and molecular Voronoi polyhedra were mainly developed in the programs IsoCryst, Dirichlet, and ADS, while since 2000 the topological approaches began to be implemented and realized in the ADS program. The geometrical methods allowed estimating form, size, and coordination number of atoms and molecules and were important for developing the topological part. These methods are used to determine the connectivity of crystal structure within the AutoCN program. The Voronoi approach was also used to develop the method of determination of migration paths in solid electrolytes (2006-2007).

The TOPOS topological methods come from 1991 when the labeled quotient graph approach was applied for the first time to represent the adjacency matrix of crystal structure. They started to be intensively developed in 2000, when the program IsoTest was created that allowed to compare the overall topologies of different crystal structures. At that time, only coordination sequences were used as topological indices to discriminate the overall topologies. The other indices, circuits, rings, and strong rings, were introduced within 2003-2005. In the same period, the main algorithms to analyze entanglements were implemented. In 2006-2007, the tiling approach was realized, which extended the TOPOS methods to microporous compounds. At the same period, the group-subgroup relations were implemented and special procedures to generate subnets were developed. In 2008, a very important procedure of searching for any finite fragment in infinite periodic network was written. In 2009, the nanocluster approach was proposed and intensive exploration of intermetallic compounds started. In 2012, the algorithm to analyze topology of polynuclear coordination compounds was proposed and the Hopf ring net approach was implemented to classify the entanglements in crystal structures.

Now, in 2014, we declare a new stage of development of the TOPOS software and databases. We are going to essentially improve them within a new brand ToposPro. As well, we propose a number of new services, which we hope will make the topological methods more popular in the crystallographic community.

Samara, August 01, 2014

Vladislav A. Blatov
Davide M. Proserpio
Alexander P. Shevchenko

List of practical works on ToposPro

Module 1. Working with DBMS (DataBase Management System). (pages 9-16)
General crystallographic information.
   a. Creating a database from CIF, SHELX or Systre formats.
   b. Copying, moving, deleting and undeleting records.
   c. Creating and editing records.
Applications: import your data, or data from another databases into ToposPro format.

Module 2. Working with the program AutoCN. Computing and editing an adjacency matrix. Organic, inorganic, metal-organic frameworks and artificial nets. (pages 17-25)
   a. Computing adjacency matrices for various types of chemical compounds and some artificial nets.
   b. Editing an adjacency matrix in DBMS.
Applications: An automated determination of all types of bonding. No atomic radii or distances are required!

   a. Visualizing 0D, 1D, 2D and 3D structures. Geometrical calculations.
   b. Analysis of molecular packings (nearest environment, molecular coordination numbers).
   c. Search for a given finite fragment in the net.
Applications: Creating images of crystal structures. Performing all standard geometrical calculations (distances, angles, RMS planes, etc.). Analysis of molecular crystals, including H-bonded ones and supramolecular complexes. Searching for clusters (also of nano-size) in intermetallides and other structures.

Module 4. Working with the program ADS. Simplification of crystal structures. (pages 43-70)
Applications: Representing complicated structures with much simpler nets by replacing atomic groups with their centroids keeping the structure connectivity. Facilitating further visual analysis and comparison of the structures. Preparing the data for a subsequent topological analysis.

Module 5. Working with the program ADS, TTD, TTO, and TTR collections. Identification and taxonomy of nets. (pages 71-86)
   a. Computing topological indices (coordination sequences, point and vertex symbols).
   d. Different structure representations
Applications: An automated assignment of a net to a topological type. No visual analysis is required! World databases, RCSR and EPINET, and much more topological types are included. Obtaining a list of known crystal structures that have a given topology.

Module 6. Working with the program ADS. Searching for and analysis of entanglements. (pages 87-110)
   a. Analysis and classification of interpenetrating nets.
   b. Searching for polycatenation, self-catenation and polythreading.
Applications: Comprehensive and fast analysis of all types of entanglements.
Module 7. Working with the program ADS. Computing and analysis of natural tilings. (pages 111-122)

b. Constructing and storing dual nets.

Applications: Search for all minimal cavities and cages in the net. Constructing migration paths within the framework. Determination of cavities and cages in zeolites and other micro- and mesoporous materials.

Module 8. Working with the program Dirichlet. Constructing Dirichlet domains and their characteristics. (pages 123-136)

b. Computing and analysis of migration maps for solid electrolytes.

Applications: Obtaining relative sizes and forms of atoms and molecules in the crystal field. Determination of possible ion conductors and exchangers.

Module 9. Working with large groups of structures. Data filtering. (pages 137-142)

a. Working with DBMS filters. Searching for a given finite fragment.
b. Simplification and taxonomy of nets.

Applications: Searching for common regularities in groups of crystal structures. Distribution of nets by topology.

Module 10. Searching for topological relations between nets. (pages 143-150)

Searching for topological relations between nets and working with the net relation graph.

Applications: Searching for the shortest transformation paths within a given set of nets.

Module 11. Searching for building units. The Nanoclustering procedure. (pages 151-166)

Searching for building units and the corresponding underlying net.

Applications: automatic description of the crystal structure as a set of non-interpenetrating building units (clusters).

Module 12. Analysis of coordination compounds. (pages 167-176)

Analysis of chemical composition and coordination types of ligands

Applications: automatic recognition and description of ligands and complex groups in coordination compounds.

Module 13. Analysis of polynuclear coordination clusters. (pages 177-184)

Classification of metal skeletons in polynuclear coordination clusters

Applications: automatic recognition and topological identification of polynuclear coordination clusters and their metal skeletons.
Appendices within the text:
App. 1. Details of the AutoCN algorithms.  page 25
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## Practical courses to learn different parts of crystal chemistry

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Module 1. Working with DBMS (DataBase Management System).
General crystallographic information

**Task 1**: standard operations to work with ToposPro databases.
**Tools**: commands from menu sections Compound, DataBase and Window.
**Example 1**: creating a new database from CIF, SHELX or Systre formats.

**Algorithm**:
1. Run ToposPro.
2. Go to the Database menu section and select Import.

(3) Select type of files (*.cif) to be converted.
(4) Select files to be converted (you may select as many files as you need using Ctrl-Click or Shift-Click).
   In the present case you should select two files: task 1_1 and task 1_2
(5) Click Open (or, if you selected only one file, Double-Click on the file name) and type the name of the database (e.g. CIF) to store the compounds processed.
(6) Click Open again, or hit Enter.
(7) Answer Yes when ToposPro asks you 'Create database...' and enter 1 as default user code, hit Enter.
(8) ToposPro informs you on the number of the compounds processed:

(9) Click OK and the database with the compounds processed will be opened.
(10) Repeat steps (2)-(9) to create a database Systre with the records from Systre *.cgd files.
(11) Repeat steps (2)-(9) to add records from SHELX *.res files to the CIF database. For this purpose choose the name CIF from the list of the database at step (5). Click Yes as an answer to the request. For possible error during converting see the file Report.txt.
(12) Rename the database CIF to CIF_RES using Rename command from the Database menu section.

**Example 2:** Copying, moving, deleting and undeleting database records.

**Algorithm:**
1. Tile windows of the databases CIF_RES and Systre (Window/Tile Vertically command) (or click on the corresponding icon in the menu bar - the last on the right).
2. Order the records in the CIF_RES window alphabetically (clicking the title/bar Compounds on top of the list), select the first 5 records using Insert key and drag them into the Systre window holding Alt key. Answer Yes to the window/question: Move compound(s) to:... The records will be moved to the Systre database.
3. Select all records in the Systre database (press “+” key on the numerical part of the keyboard or use the local menu by right-clicking).
4. Drag the selected records to the CIF_RES window not holding Alt key. The records will be copied.

(5) Delete the Systre database (DataBase/Delete command, enter 1 as default user code). The window of the database should be active.

(6) Order the records in the CIF_RES window by the record/code number. Click the title/bar Compounds with the right button and select Code Column click now on the bar Code to order according the to record number. Please notice that the record numbers do not correspond to the numbers of lines visible: Topos keep record of the files deleted/moved. To restore the records moved before we use the Show Deleted command of the local menu to show the list with removed records.
(7) Notice the negative Code number for deleted records. Select all records and perform the Compound/(Un)delete command (answer Yes to the question "Undelete XX records?"). Turn to the main list of records (the Show Main command of the local menu).

(8) Order the records alphabetically and find the duplicates. Select duplicated records and remove them using the Compound/(Un)delete command. (answer Yes to the question "Delete XX records?").
(9) Clean the database out of the records removed by the **Database/Refresh** command (enter 1 for user code and answer Yes). Be sure that the removed records have really been cleaned out (the list with removed records must be empty, if you check the “show deleted” command is no more active). Notice that the Code numbers remain unchanged. The total number of entries is reported at the bottom left [7:0:2 means 7 records with the 2nd record, with code 9, selected].

![Database/Refresh interface](image-url)
Task 2: viewing, editing and creating database records.
Tools: Crystal Data window.
Example 1: viewing and editing crystallographic information.
Algorithm:
(1) Open the database Examples and double click on the first record to open a Crystal Data window with four main tabs collecting all the crystallographic information on this compound the database contains:

- **General** information on the compound: name, chemical composition, crystallographic data (unit cell and space group), possible bibliographic data.

- **Atoms**, a window with the complete list of the independent atoms present in the unit cell (asymmetric unit) with name, list number, oxidation state (if available), site symmetry, crystallographic coordinates x-y-z, site occupation (important in disordered structures), coordination number of the atom.

Adjacency Matrix. Lists all the atoms with all the other atoms connected/interacting with them, ordered by type of interaction. From this window is possible to modify the kind of connection type: we scroll the list of possible interaction (clicking on +); with the mouse right button we open the local menu and we can change or delete a specific interaction. Changing the type the display of the atom interacting will change too: Valence // Hydrogen bonded // Specific (secondary interactions) // Van der Waals // No bond //; different types of bonds are marked in different colours by V, H, S or W symbols, respectively. Pay attention to the field in the Adjacent Matrix tree:

**Root** (all inequivalent atoms A in the unit cell):
- **CN** – coordination numbers for valence (V, first number) and non-valence (second number H, S or W) contacts;
- **Rsd** – radius of spherical domain value (Å) (see Appendix 1);

**Branch** (all atoms B connected to a particular atom from the root):
- **SA** – solid angle in percentage of the total solid angle of 4π steradian (see Appendix 1);
- **R** – interatomic distance A–B (Å);
- **BV** – bond valence for A–B;
- **Mult** – multiplicity of the bond.

- **Comment.** All the notes may be written here.
(2) Press **Symmetry** button to look at the lists of symmetry operations, minimal supergroups and maximal subgroups of the space group of the structure. Pay attention that you may easily transform any non-conventional setting (e.g. \( F1 \to P1 \) or \( Pbnm \to Pnaa \)) of a space group into the conventional one by clicking the **Change Setting** button. The button is active only in the case when the current setting is non-conventional. To transform the space-group symmetry into the symmetry of a subgroup you have to select the subgroup in a bottom list and click the **Change Group** button. Close the **Symmetry** window.
(3) Now let's perform the **Compound/Add** command. Fill the window fields with the data for NaCl given below. To enter the authors' names press **Enter** key after typing every name in the line **Authors**. The journal name should be chosen from the **Journal** dropping list. After entering the whole information, determine the composition of the unit cell by going to the **General** tab and pressing **Calculate** button. Be sure that VolCell =177.50 Å³. Press **Save** button.

<table>
<thead>
<tr>
<th>Data</th>
<th>NaCl</th>
<th>CsCl</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Space group</strong></td>
<td>Fm $\overline{3}$m</td>
<td>Pm $\overline{3}$m</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>5.620</td>
<td>4.120</td>
</tr>
<tr>
<td><strong>Atoms</strong></td>
<td>Na: (0,0,0)</td>
<td>Cs: (0,0,0)</td>
</tr>
<tr>
<td></td>
<td>Cl: (0.5,0.5,0.5) or (1/2,1/2,1/2)</td>
<td>Cl: (0.5,0.5,0.5) or (1/2,1/2,1/2)</td>
</tr>
</tbody>
</table>

(4) Duplicate the record by right-clicking and choosing **Duplicate** command.

(5) Change the information in the duplicated record using the data for CsCl. For this purpose use the **Compound/Edit** (or double left-click on entry) command and change the content of the fields. To remove the authors' name select it by left-click, then right-click on the name and choose **Delete Author**. Save the changes.

**Exercise**: Create a database with your own structures from CIF or SHELX formats. Copy them into another database. Create a new record in the database manually using crystallographic data from a journal paper.

**Questions/Hints**: Why the "Composition" field in the **Crystal Data** Window shows Fe0 Cl0 N0 H0 C0 ? Click on the **Calculate** button and see/explain what happens.
Module 2. Data filtering. Working with the program AutoCN. Computing and editing an adjacency matrix. Inorganic, organic, metal-organic frameworks and artificial nets.

**Task 1:** searching for compounds in a database. Computing and saving an adjacency matrix containing the information on valence and non-valence bonding in the crystal structure. Automated storing coordination numbers of atoms in the database.

**Tools:** DBMS filters, the program AutoCN.

**Example:** filtering different modifications of lithium sulfate including hydrates, computing and saving adjacency matrices for them.

**Algorithm:**

1. Open the database Li_S_Se (66 entries). Using the filter **Filter/Fragment/Name** find all compounds with the substring “lithium sulfate” in the compound name. Type the name to be searched and click on **Add**, then click **Ok** (or simply click **Ok**; if the list of filters is empty the current filter will be added automatically). 58 compounds are found. Selected them all and copy into the database Li2SO4. (see Example 2 in the previous Module 1) (If you want to see again all the 66 entries in Li_S_Se right-click in the window of the selected database and go on **Show Main** in the local menu.)
(2) Open the database Li2SO4 and filter the structures containing the atoms other than Li, S, O or H. For this purpose, use the filter *Filter/Composition/Element*, clear from previous filters by click on “Clear” button and now set the filter fields: Elements: ‘Li S O H’; Only; One Filter Operator: *Without*. Click on Add, then Ok. Select all the 35 records found and remove them (use Del key, or F8, or (Un)Delete in the local menu)

![Image of database filter settings]

Go to the main list of the database Li2SO4 (use *Show Main* command of the database local menu). 23 compounds are left

(3) Filter and remove the records containing no coordinates of atoms. For this purpose use the filter *Filter/Composition/CompFlags* and check the *No Coordinates* flag (after clear from previous filters check that One Filter Operator is set to *With*).

![Image of filter settings]

Select them all, remove, *Show Main*. How many structures are left? 23–4=19

How many hydrates does lithium sulfate form? (use filter to look for “hydrate”, you will find 11)

(4) Using *Crystal Data* window find a hydrate in the list in whose structure the hydrogen atoms are allocated. (For example, Ref. Code 22347)
(5) Open the window of the program AutoCN (Programs/AutoCN) or click on the window.
(6) Specify the following AutoCN options (Options/Matrix):

- **Method**: Domains; **Save**: Atoms (to store coordination numbers in the Li2SO4.cd file and adjacency matrix in the Li2SO4.adm file);
- **Matrix Data**: Spec. Cont., vdW Cont., Dist. + Rsds to store the information on specific and van der Waals bonding as well as interatomic distances.

Check the options for computing hydrogen bonds (**H bonds** tab). Consider also the possibility to search for hydrogen bonding also when the hydrogen atoms are disordered or allocated too close to each other (use the option **Resonance bonds for disordered**). Leave the Default selections in **Common** and **VDP Calculations**.

Press **Ok** button.
(7) Run the program by the command **Run** to get the output like follows.

At the bottom part of the output the computed connectivity is resumed in columns, pay attention to three of them:

- **CN** contains the number of covalent bonds connecting the listed **Atom**;
- **Hb** contains the number of hydrogen bonds connecting the listed **Atom**;
- **Sp** and **vdW** contain information on non-valence specific and van der Waals interactions.

For example atom O2 is connected to 2 atoms (Li and S) and is involved into one hydrogen bond.

**ATTENTION:** Sometimes you may get the message **Inconsistent contacts: A-B** which means that AutoCN has found wrong A…B contact that will not be included into the adjacency matrix. The point is that two AutoCN algorithms, **Domains** and **Solid Angles**, use some parameters of Dirichlet domains to determine type of interatomic bonds. These parameters are computed with some errors and it may occur that for a contact A-B the method gives the bond type, say, valence, if the Dirichlet domain of atom A is considered, but if we rest upon the Dirichlet domain of atom B, the contact will be classified as, say, van der Waals. It occurs when parameters of the contact are very close to accepted limits separating bond types, ordinarily for non-valence types (specific or van der Waals) and most frequently for H atoms as they are often wrongly allocated. In other words AutoCN requires that the 'semi'-bonds A- and -B must obey the 'self-consistency' principle: they must be of the same type. Otherwise an error message is output and such 'bond' is broken. It is not crucial in most cases but rarely (especially if one of such 'semi'-contacts is valence) can indicate some inconsistency in the structural data (e.g. disordering, wrong atomic coordinates, etc.).

The main AutoCN algorithm, **Domains**, is universal and be applied to both inorganic and organic (including metal-organic) compounds. The method **Solid Angles** is useful in the case of compounds with undirected interactions, such as intermetallides, noble gases, ionic compounds. The method **Ranges** is designed for artificial nets like sphere packings, RCSR nets or epinets. For more details of the methods see **Appendix 1**.

(8) Close the program window with the **Quit** command.

(9) Open the **Crystal Data** window and be sure that the adjacency matrix was saved (see the **Adjacency matrix** tab).

(10) Select all records and run AutoCN again (options should not be changed, but you may uncheck **Data/Show Data** flag to toggle off the output and speed up the calculation). As a result, adjacency matrices will be stored for all the structures.
Exercises:
(a) perform the algorithm to find all structures of lithium selenate in the Li_S_Se database and to compute adjacency matrices for them. Do lithium sulfate and selenate have similar hydrates?
(b) compute adjacency matrices for organic and metal-organic compounds contained in the Org_MOF database. Use the method Domains (Options/Matrix).
(c) compute adjacency matrices for your own structures converted in Module 1.

Task 2: looking through and editing adjacency matrix.
Tools: Crystal Data window.
Example: determining typical interatomic distances for hydrogen bonds in a lithium sulfate hydrate.
Removing all van der Waals contacts from the adjacency matrix.

Algorithm:
(1) Open a Crystal Data window for a lithium sulfate hydrate (Ref. Code 22347) with all allocated hydrogen atoms (Compound/Edit or double left click or click F4).
(2) Open Adjacency matrix tab and find all hydrogen bonds (H) in the list. Find typical interatomic distances for the hydrogen bonds O-H…O. What range do they vary in? (see the values of R in Å)
(3) Find all contacts H…O corresponding to Van der Waals bonding. What are their distances?
(4) Remove all the "non H" H…O contacts using local menu (Delete Selected or Change Type/No bond commands). Save the changes. Pay attention that the Reference Code field contains the Collection Code of the structure in ICSD.

(5) Open a Crystal Data window for a lithium sulfate hydrate without allocated hydrogen atoms. Look at the typical interatomic distances corresponding to O…O hydrogen bonds. For example, compound with Ref. Code 18173 shows O1…O5 2.870 Å vdW
(6) If instead of going on Change Type (step 4 above) you click on Information, you will get, e.g. for structures 22347 (with H, left) and 18173 (without H, right) the following self-explanatory windows:

\[\begin{array}{c}
\text{Exercise}: \text{perform the algorithm for lithium selenate hydrates. Are there any differences in interatomic distances } O\ldots O \text{ for hydrogen bonds in lithium sulfate and selenate hydrates?} \\
\text{Answer}: \text{the distances } O\ldots O \text{ for hydrogen bonds in lithium selenate is } 2.87 \text{ Å; } 3.00-2.881 \text{ Å are typical ranges for } O\ldots O \text{ distances in hydrogen bonds in lithium sulfate.}
\end{array}\]
Task 3: building the adjacency matrix for an artificial net.

Tools: the program AutoCN, Crystal Data window.

Example: building the adjacency matrix for the vab net. Producing subnets for the nbo net.

Algorithm:
(1) Open the database art_net. There is one entry named "Unknown distribution of points".

(2) Open the window of the program AutoCN and set the following options: Method: Ranges; Dist. Ranges: C-C 0:1.01 to store all carbon-carbon contacts of length 0–1.01 Å. In general, for the range you need to use the format A-B x.x:y.y; several different bonds could be searched simultaneously. For all other types of contacts, not mentioned in the Dist. Ranges window AutoCN will use the standard distance criterion: a contact A–B is stored in adjacency matrix if its distance is less than the sum of Slater's radii of the atoms A and B multiplied by (1+ Extra Dist.). If you want to ignore some A–B contacts you have to type A-B 0:0.

(3) Run AutoCN, then close the window.

(4) Open the Crystal Data window and go to Adjacency matrix tab. You have got a 4-coordinated net (You will learn later how to identify a net, this one is with the nbo topology.)

(5) Expand the list of contacts of the carbon atom and right-click on the contact. Choose Mark Equivalent. If two contacts are selected, the two contacts are equivalent by symmetry
Repeat the procedure for the next unselected contact until the message here below appears.

(6) Right-click again and change the type of the contact to **No bond**.

To summarize the 4 bonds are grouped in three independent sets 1+1+2. Two are related by symmetry

(7) Save the changes.

(8) Duplicate the record and open **Adjacency matrix** tab again. Restore the type for the broken contact to **Valence**. Assign the type **No bond** to another contact. Save changes. You have got two 3-coordinated nets. Call them e.g. "3-c A derived from 4-c" and "3-c B derived from 4-c", later you will be able to identify the nets and see that one is single **vab** and the other is an array of two interpenetrated nets with the **bmn** topology. Pay attention that you cannot get the two derived 3-c nets by an analysis of interatomic distances: the nearest neighbor are always 4 at the same distances of 1.00Å

**Summary:** With this last Task, you found a possible relation between 3-c net **vab** or 2-fold interpenetrated **bmn** nets to 4-c **nbo**. This may be related to some transformations in solid-state. Keep the database to be analyzed later.

**Questions:** Could you derive other subnets form the original 4-c one? 2D or 1D (rod packings)? Is the 4-c net found a sphere packing? Are the derived 3-c nets also sphere packings?
Appendix 1. Details of the AutoCN algorithms.

The **Domains** algorithm mimics the way of how the crystal chemist determines interatomic interactions and classifies them, however, instead of the human intuition, it rests upon a strict sequence of steps, and clearly defined numerical parameters.

1. For each non-equivalent atom A its Voronoi-Dirichlet polyhedron (VDP, Fig. 1) is constructed, and only the atoms X that are *direct neighbors* of A (the lines connecting them with A cross the corresponding VDP faces) are taken into account at the subsequent steps.

   ![Figure 1](image1.png)

   **Figure 1:** Voronoi-Dirichlet polyhedron (left) and partition (right) for the body-centered lattice.

2. For all contacts A-X, the solid angles $\Omega_i$ of pyramids with the basal VP face corresponding to the A-X contact (Fig. 2) are computed. If $\Omega_i < \text{MinOm}$ (see the AutoCN parameters; default value is 1.5% of the total solid angle $4\pi$ steradian) the contact is referred to as non-valence and its classification to H bonds, halogen bonds, or van der Waals interactions is performed according to additional geometrical criteria.

   ![Figure 2](image2.png)

   **Figure 2:** The solid angle ($\Omega_i$) of the shaded VDP face in the body-centered lattice is equal to the shaded segment of the unit sphere being cut off by the pyramid with the VDP atom at the vertex and the face in the base.

3. For each atom type two kinds of radii are determined: Slater's radius, $r_s$, (it is a constant that is predetermined in the ToposPro parameters) and averaged *radius of spherical domain* ($R_{sd}$, the radius of a sphere of the VDP volume, averaged over all atoms of a given sort in the structure). The former radius characterizes the size of the atom accepted in crystal chemistry; the latter one estimates the real size of a given atom depending on the atoms in the particular structure.

4. For each pair A-X the reference distance $D(A-X)$ is determined, which is equal to the minimum of two sums: $R_{sd}(A) + R_{sd}(X)$ or $[r_s(A) + r_s(X)](1 + \delta)$, where $\delta = 0.25$ by default (it can be changed in the ToposPro parameters; **Extra Dist.** value). $D(A-X)$ means the maximal distance, at which the contact A-X should be considered as strong (valence) bond.
5. The D(A-X) values are modified to take into account the features of the structure. For this purpose, if A is a metal atom or both A and X are non-metals, all distances \(d(A-X)\) are grouped if they do not differ more than the Min. Interval value (see the AutoCN parameters; default value is 0.3 Å). If after this the D(A-X) value falls within one of the groups, it increases up to the maximal value of the group. This operation allows to avoid the situation when the contacts, whose distances are very close to but larger than D(A-X), are not considered as bonds.

6. If A is a metal atom and it does not form any valence bond or forms just one bond according to the D(A-X) values obtained at the previous steps, the corresponding D(A-X) value is increased up to the maximal distance value of the closest group of contacts. As a result, the closest contacts A-X will be considered as valence (the metal atom cannot have zero coordination number or be one-coordinated).

7. If both A and X are metals and at least one of them is \(s\) or \(p\) metal then the valence contact between them can exist only if there are no valence bonds between them and non-metal atoms, otherwise D(A-X) is specified to zero. This prevents \(s\) or \(p\) metal atoms from valence bonds with other metals except the structures of intermetallic compounds. It also assumes that \(s\) or \(p\) metal atoms do not form clusters; strong bonding between them and other metals can exist only in intermetallic compounds.

8. If A is a metal and X is a boron atom connected to O or F atoms then the bond A-X (if any) is broken (D(A-X) = 0).

9. If there are several non-equivalent pairs (A, X) and, hence, several D(A-X) values have been chosen at the previous steps, then the maximal D(A-X) is chosen as the final reference distance for all contacts of a particular A-X type.

10. All contacts A-X with \(d(A-X) < D(A-X)\) are considered as valence. Other contacts are assumed non-valence and their classification to H bonds, halogen bonds, or van der Waals interactions is performed according to additional geometrical criteria.

Thus, in contrast to standard crystallochemical approach, when the bonds A-X, are determined according to just one fixed parameter D(A-X), in the Domains method, three criteria are used: (i) the sign of direct neighbor, (ii) the solid angle value \(\Omega_i\) (both of them estimate the screening of X_i from A by other atoms), and (iii) the floating D(A-X_i), which essentially depends on a particular structure and takes into account all non-equivalent contacts A-X_i in it. The Domains algorithm was tested for thousands of structures from the CSD and ICSD, and showed a good agreement with the chemical models.

The Solid Angles algorithm is useful for intermetallic compounds; here \(\Omega_i > MinOm\) is the only criterion to select connected net nodes from surrounding ones; it;

The Ranges algorithm is mainly intended for artificial nets with nodes, not atoms; the nodes are considered connected if the distance between them falls into specified range(s); no VDPs are constructed in this case. If the user does not specify the distance range the standard distance criterion will be used: a contact A–B is stored in adjacency matrix if its distance is less than \([r_s(A) + r_s(X)](1 + \delta)\).

With these three algorithms the user can compute adjacency matrices in an automated mode, which is very important for the analysis of large amounts of crystal structures.
Module 3. Working with the program IsoCryst. Visualizing crystal structures. Geometrical and topological analysis.

Task 1: drawing an image of a crystal structure, performing standard geometrical calculations, analysis of the system of chemical bonds.

Tools: the programs AutoCN and IsoCryst, Crystal Data window.

Example 1: analysis of the crystal structure of $\beta$-UO$_2$SO$_4$.

Algorithm:
(1) Open the database UO2SO4 that contains one record corresponding to $\beta$-UO$_2$SO$_4$ and compute the adjacency matrix with the AutoCN program (Method: Domains).

(3) Run IsoCryst (Programs/IsoCryst). Or click the button 

(4) Perform the following operations with the crystal structure image:

- Press to draw the unit cell composition.
- Grow the network (i.e. extend the content of the unit cell by the atoms connected to the one inside the cell). Use the command Ctrl+W or push the button one time. The image looks as follows

![Crystal Structure Image]

- Click on the button or on the button to choose the OpenGL or API modes, respectively.
- Try different plot styles: Wire - Cylinder - Sphere & Wire - Sphere & Cylinder
- Try coloured bonds versus uncolored (white)
• Toggle on/off: Show crystal axes - Show legend - Show cell edges.
• Move the image with the tools Rotate - Z Rotate - Magnify/Shrink - Translate. To rotate or magnify by a precise value, double-click the tool icon and enter the value.
• Some of the other bottom buttons allow to display/orient the view according to some predefined directions/projection defined by the crystallographic hkl: 100, 010 or 001 (along the axis a, b or c). Clicking on hkl you should specify the hkl values for the direction on which to project the view, for example 1,0,1 or 0,-1,3 etc.
• Show atom names by clicking the button .
• Click on the button to use the Select tool. Select one of uranium atoms and leave it alone on the picture by pressing the button .
• Grow the structure one time by clicking and put the image into the centre by pushing the Space key.
• Draw the coordination polyhedron for the uranium atom (it should be selected) by clicking . Remove the polyhedron using the button .
• Compute interatomic distances U–O. For this purpose, having selected an uranium atom, select oxygens one-by-one, every time unselecting the previous oxygen. Read the distance value in the status line. For example, (O1-U1) r = 2.361 Å, (O5-U1) r = 1.796 Å
• Compute bond angles O–U–O by selecting triples of atoms. What are the angle values for equatorial and apical oxygens? For example, angle (O5-U1-O6) = 176.11° for apical, and 83.76° for equatorial.
• Unselect all atoms by right-clicking in an empty space of the window.
• Compute the root-mean-square deviation (σ) from the RMS plane for equatorial oxygens of the uranium coordination shell including the uranium atom. For this purpose, select all these atoms and perform the Calculate/Selected Atoms command. The resulting value should be σ = 0.15Å. Compute the distance from the uranium atom to the RMS plane by magenta-selecting the atom (holding Ctrl key). You should select oxygen atoms of the equatorial plane by yellow (left click) and uranium atom by magenta (left click + Ctrl key) The resulting value in the status line should be equal 0.0492Å. Unselect all atoms by right-clicking in an empty space of the window.
- Compute the angle between equatorial plane of the uranium coordination polyhedron and the uranyl O–U–O group. You should select oxygens of the equatorial plane and uranyl group by yellow and magenta, respectively. The resulting value should be 88.80°.

- Restore the initial image by clicking .
- Perform the Growth command one time. Select all atoms in a sphere of radius 3Å around one of the uranium atoms. For this purpose, set the sphere selection mode ( ), select an uranium atoms and left-drag the sphere of required radius. You should have 8 atoms selected. Click to leave visible the selected atoms only.
- Perform the Growth command one time and compute the torsion angles O–U–O–S. Find the angle equal to 148.08°. Answer: O3-U1-O2-S1.
- Compute the angle between equatorial planes of a pair of uranium atoms connected via bridge oxygen atom. For this purpose, select the oxygen atoms of the two planes in yellow and magenta. The resulting value should be equal 61.16°.
- Restore the initial image by clicking  and perform the Growth command several times.
- Select chains of the uranium coordination polyhedra connected by vertices (oxygen atoms). For this purpose, draw the legend by clicking the button, then select in magenta all sulfur atoms by clicking the sulfur atom in the legend holding the Ctrl button. Remove the selected sulfur atoms by pressing the Delete button. Then select all atoms in a chain by specifying the selection mode and clicking any atom of the chain.
- Restore the initial image by clicking  and perform the Growth command several times.
- Select pseudo-layers by removing O(2) atoms. For this purpose, choose the “Magic Wand” tool , click one of the O(2) atoms and specify Command: Delete, Do for: Cryst. Sort. Select one layer and leave it alone on the image. Arrange the layer perpendicular to [001] using the button .
- Select other pseudo-layers by removing O(3) atoms. What direction is perpendicular to them? Answer: (100)
- Restore the initial image and perform the Growth command several times. Select all uranium and sulfur atoms and draw the structure in a polyhedral representation using the button . Try different options for drawing polyhedra in the IsoCryst options window (use the button , the Polyhedra tab).
- Remove polyhedra from the image, select all uranium atoms and remove them. Use Undo command (the button ) to cancel the removal.
- Close the IsoCryst window.
**Example 2**: analysis of a hydroquinone polymorph.

**Algorithm**:

1. Open the database C₆H₆O₂ and compute the adjacency matrices for all the 11 compounds of C₆H₆O₂ composition considering hydrogen bonds (AutoCN Method: Domains).
2. Go to the second record in the list (Ref. Code HYQUIN), open the Crystal Data window and be sure that this is a hydroquinone polymorph.

![Crystal Data window](image)

Press Calculate button and find that the composition of the unit cell corresponds to the composition of hydroquinone. Press Yes button.

![Information dialog](image)

3. Open the window of the program IsoCryst (Programs/IsoCryst). Perform the following operations:
   - Display one unit cell clicking on the yellow pencil button.
   - Grow the network (i.e. extend the content of the unit cell by the atoms connected to the one inside the cell). Use the command Ctrl+W or push the button. The image looks as follows.
• Click on the button or on the button to choose the OpenGL or API modes, respectively.

• Try different plot styles: Wire - Cylinder - Sphere & Wire - Sphere & Cylinder.

• Toggle on/off: Show crystal axes - Show legend - Show cell edges.

• Move the image with the tools Rotate - Z Rotate - Magnify/Shrink - Translate.

• Some of the other bottom buttons allow to display/orient the view according to some predefined directions/projection defined by the crystallographic hkl. Clicking on you should specify the hkl values for the direction on which to project the view, for example 1,0,1 or 0,-1,3 etc.

Click on the button to use the Select tool. Select one group of atoms connected together. For this purpose push/activate the button “select polymeric chain” and then click on an atom, all the others connected to it will be selected and shown/coloured in yellow. This will immediately show if a compound is made of 0D, 1D or 3D subnets.
- Choose to display only the selected subnet clicking on "Show selection only" and display both
  the atom names and the bond/interaction distances with a click on some of the buttons on the bottom
  left: "Atoms labels" and "Show Bond Distances". Click on the "All" button to show unselected
  atoms.
- Show different kinds of bonds/interactions. You have to go into the Options window following
  Image/Options, or click on the right button. Go to Bonds tab and select which kind of
  interaction to visualize, e.g. hydrogen bonds (Show column). Press Ok.

The hydrogen bonds are dot-dashed.
• Click on \( \text{ } \) and release \( \text{ } \) and \( \text{ } \). Then open the Options window again. Check Hydrogen bonds box in the Take column to consider hydrogen bonds as possible growth of the network.

Press Ok and perform one time the Growth operation to show the atoms connected with the selected molecule by hydrogen bonds.
Now uncheck Hydrogen bonds box, unselect the molecule by right-clicking on any of its atoms or on an empty space in the window and perform the Growth operation a few more times to show the molecules connected with the selected molecule by hydrogen bonds.

Check Hydrogen bonds box again and grow the net. Then press Space key or button to fit the view to the window size. Rotate the image to be sure that the net is 2D.
Press **Undo** button several times to go back to the previous view.

- To compute distances, bond or dihedral angles toggle on selection mode and select pairs, triples or quadruples of atoms and read the value in the status line. For example below the angle for the hydrogen bond O2–H4…O2 is equal to 154.23° (see status line at the bottom of the window).

To compute a dihedral angle between two RMS planes select the atoms lying in one plane (yellow selection) and then select atoms of the other plane holding Ctrl key (magenta selection). Thus, the dihedral angle between two hydroquinone molecules is equal 66.79°. To unselect the magenta selection hold Ctrl key and right-click on atoms or on an empty space in the window.
Select a hydroquinone molecule in yellow and click on the button. A molecular Voronoi-Dirichlet polyhedron will be constructed. Open the Information window by selecting Calculate/Selected Atoms and find the volume of the molecule in the solid \( V = 131.99 \) or \( 132.88 \, \text{Å}^3 \) for two non-equivalent molecules. Click Ok to close the window.

Now unselect the molecule, to get the following picture.
Remove the Voronoi-Dirichlet polyhedron by clicking button.

(4) Close the IsoCryst window.

**Exercise:** analyze your own structures with IsoCryst.

**Hints:** Play with the other button on the bottom bar:

- Increase Atom radius. Change **Radii System** to *Sph. Domain* to get the atom size close to fill the space. With a bit of play you can get CPK picture-like as shown below.

- Show Vertices and Fill Faces, take effect on the Voronoi-Dirichlet polyhedron.
**Task 2:** Search for a given finite fragment in the net.

**Tools:** the program IsoCryst, DBMS filters.

**Example:** search for hydroquinone polymorphs.

**Algorithm:**

1. Open the window of the program IsoCryst again and draw a hydroquinone molecule. Select it.
2. Perform **Select/Save Selection** command and choose the file type **Graph files (*.gph)**. Type the name **hydroquinone** and save the data. **IMPORTANT!** By default the *.gph* files are stored in the GPH directory that can be assigned in **System/TOPOS Parameters** window (see also **Appendix 9**).

   ![TOPOS Parameters](image)

   (3) Close the IsoCryst window.

   (4) Choose **Filters/Topology/Subgraph**, press **Load** button and load **hydroquinone.gph** file.

   ![Topology](image)

   Press **View** button to look at the molecule. Close the IsoCryst window.

   (5) Press **Ok** button. Four hydroquinone polymorphs out of 11 C₆H₆O₂ compounds will be found.

   (6) Go to the second polymorphs in the list, open an IsoCryst window and perform **Select/Load Tint File** command. Choose **Graph files (*.gph)** and load **hydroquinone.gph** file. A **Tint file data** window will be open. There are three independent hydroquinone molecules in the structure. Perform **Growth** command in the IsoCryst window until all three records become bold.
Select all the three records (using Ctrl+Click or Shift+Click), set **Options: Hide all atoms** and click on **Apply** button. The three molecules will be selected (in yellow) in the IsoCryst window.

Close **Tint file data** and IsoCryst windows.
Notes: Options: Hide none – in the figure all molecules will be kept and 3 among them will be selected by yellow. Options: Hide all atoms – in the IsoCryst window only 3 molecules will be presented, to be selected by yellow.

(7) Select all four records in the database window and copy them into a new database **Quinol**.

**Exercise**: search for an arbitrary fragment in your own structures.
**Task 3**: Analyzing interpenetrated arrays.

**Tools**: the program IsoCryst.

**Example**: analysis of an interpenetrated hydroquinone polymorph.

**Algorithm**:
1. Open the database Quinol and go to HYQUIN05 in the list (show Ref.Code names).
2. Open an IsoCryst window. Be sure that hydrogen bonds are checked in the Take column and in the Show column of the Options/Bonds tab.
3. Grow the structure several times and fit the image to the window.
4. Toggle on mode and select one net in yellow and the second net in magenta (holding Ctrl) or green (holding Shift). There are two interpenetrated 3D H-bonded nets.

**Exercise**: Go back to your CIF_RES database of Module 1 and examine the interpenetrations there. You will find several cases up to 7-fold! But we will see how to compute interpenetration correctly in Module 6.
**Task 4:** Determining molecular coordination numbers, analysis of molecular packing and intermolecular bonds.

**Tools:** the programs AutoCN and IsoCryst.

**Example:** analysis of $\alpha$-S$_8$ crystal structure.

**Algorithm:**
1. Open the database S8_P4_Cl2 and compute an adjacency matrix for the first record.
2. Run the program IsoCryst.
3. Be sure that in Options/Bonds tab only valence bonds are checked in the Take column.
4. Grow the structure to get the whole molecules.
5. Select a molecule and show only the selected one.
6. Check Specific and van der Waals boxes in the Show and Take columns.

(7) Perform growth *one time only* to get all atoms connected with the selected molecule by non-valence interactions.
(8) Uncheck **Specific** and **van der Waals** boxes, unselect the molecule and perform growth a few more times to get all surrounding molecules.

(9) Select all molecules (click outside the molecules, or use the mouse with the tools and find total number of selected atoms (128) in the status line.

So there are $128/8=16$ molecules in the image and, hence, the central molecule is surrounded by 15 other molecules (the molecular coordination number is 15)

**Exercise:** compute molecular coordination numbers for phosphorus $P_4$ ($56/4=14$) and chlorine $Cl_2$ ($28/2=14$) molecules (see the database **S8_P4_C12**).

**Questions:** Examine the differences between **Specific** and Van der Waals contacts looking at the distances values in the **Adjacency Matrix** of chlorine $Cl_2$. Using only vdW contacts the neighbor molecules are 10, and 4 using only **Spec**. This indicate that there are 4 halogen bonds at work. By default, ToposPro detects halogen bonds and classify them as **Specific bonds**. For more on analysis of molecular packing see:

Module 4. Working with the program ADS. Simplification of crystal structures.

**Task 1**: standard methods to simplify valence-bonded, hydrogen-bonded and specific-bonded structures.

**Tools**: the programs ADS, AutoCN and IsoCryst, **Crystal Data** window.

**Example 1**: simplification of CaCO₃ polymorphs.

**Algorithm**:
1. Open the database **CaCO₃** and compute the adjacency matrices for all the CaCO₃ polymorphs with the **Domains** method.
2. Analyze successively the crystal structure of each polymorph with IsoCryst. Determine the number of carbonate ions connected to Ca atoms. For this purpose, select a Ca atom, leave it only in the picture and perform **Growth** command until carbon atoms emerge. Then select carbons by clicking on the carbon atom in the legend and grow the structure one time again. Select all oxygens and leave selected atoms (central Ca, all carbons and oxygens) in the picture. Calculate the number of carbonate ions (it is equal to the number of selected carbons in the status line).

![Image of CaCO₃ molecule](image)

Determine in the same manner the number of Ca atoms connected to carbonate ions.

3. Simplify the crystal structure of aragonite to get its underlying net in standard representation (metal atoms and centroids of ligands are the nodes of the “simplified underlying net”; see **Appendix 2** for details and definitions). For this purpose, open a window of the program ADS, click **Options**, clear all checkboxes on **Common** and **Topology** tabs, set **Topology/Coord. Seq.** = 1 (this is just to make it faster), check the option **Common/Save Simplified Net** and **Simplification Method** = Standard.
Press Ok and run the program.

(4) Answer Yes to the request to create the database CaCO₃_c that will contain the simplified structure. Then enter your user code 1.

(5) Select Ca atoms as central and press Ok.

After the program finishes look at the coordination numbers of the nodes in the simplified structure, open a Crystal Data window and compare with the numbers determined at step (2). Go to Comment tab and draw attention that the nodes ‘ZA’ designate centroids of carbonate ions, while ‘ZB’ correspond to metal atoms (the line entitled SIMPLIG contains the description of which structural units were used to construct the underlying net).
(6) Turn to the window of the database CaCO$_3$ and simplify the crystal structures of calcite and vaterite by one step. For this purpose, select the records pressing Insert key or Shift+$\downarrow$ or Ctrl-mouse click. Open one more ADS window and go to Options/Continuous tab. Press El button at Central Atoms line.

In the Periodic Table window click All Up button and then Me button to select all metals. (To make it faster, you can just type "Me" in the Central Atom window)
Press Ok and then Ok in the ADS Options window. Then run the program and answer Yes to reload the database with simplified structures.

Check the resulting simplified structures. You will notice that the three derived underlying nets are 6-coordinated but (after classification) of only two distinct topological type *pcu* and *nia*, however aragonite and vaterite, belonging to the same topological type (*nia*), are antitypes (cations and anions are topologically exchanged).

**Exercise**: simplify the structures of MgCO₃ and SrCO₃ from the Mg_SrCO₃ database.

**Answer**: MgCO₃ and SrCO₃ can be simplified to 6-coordinated underlying nets with topological type *pcu* and *nia* respectively.
Example 2: simplification of the H$_2$S crystal structure.

**Algorithm:**

(1) Open the database **H2S** and compute the adjacency matrix taking into account S–H…S hydrogen bonds. For this purpose, include sulfur atoms into the lists of A and B atoms in the AutoCN options.

(2) Simplify the crystal structure of H$_2$S to its *standard* representation (centroids of molecular groups are the nodes of the simplified net). For this purpose, set the ADS options: **Topology/Bond Types/Valence** = *At.*; **H bonds** = *Mol.* This means that any group of atoms connected by valence bonds is considered as a molecule, and the isolated molecules are linked by hydrogen bonds.

Run ADS and press the **Whole Molecule** button to choose no central atoms and to consider all atoms equally composing molecules.
To simplify the molecular structures in one step select the records pressing Insert key or Shift↓ or Ctrl-mouse click, open ADS window and leave empty the line Central Atoms in ADS Options/Continuous tab.

Check the coordination number of nodes in the simplified net and molecular coordination number for H₂S in initial structure. What numbers of molecules are H-bonded with an H₂S molecule? Find that there are two interpenetrated 3D nets in the simplified structure using IsoCryst, and find the two nets also in the not simplified representation. One single net is shown here:

Try to change the colors of the atoms with the Magic wand (selected in the figure above) and the thickness of the H-bonds in the IsoCryst Option / Bonds window clicking on the left column (Thick).

**Exercise:** simplify the structures of H₂O polymorphs from the H₂O database. Set Resonance bonds for disordered AutoCN option to take into account resonance O–H↔H–O hydrogen bonds. To simplify the molecular structures at one step remember to leave empty the line for Central Atoms in ADS Options/Continuous tab.

**Answer:** The polymorphs I, II, III, IV, and VII for H₂O have 4-coordinated underlying nets with topological types lon, ict, kea, icf, and 2-fold interpenetrated dia respectively.
**Example 3**: simplification of the crystal structure of SAKNAU, 4,4'-bipyridinium tetracyano-platinum.

**Algorithm:**
1. Open the database SAKNAU and compute the adjacency matrix using the AutoCN method **Domains** and standard set of other options:

   ![AutoCN Options](image1)

   File Name: C:\TOPOS\module6\SAKNAU.acn

   ![IsoCryst](image2)

2. Look at the structure in IsoCryst and find \([\text{Pt(CN)}_4]^2-\) complex groups and bipyridinium cations connected by hydrogen bonds.

3. Simplify the crystal structure to its standard representation. Run ADS and press the **Whole Molecule** button.

4. Look at the simplified underlying net and be sure that it contains two 4-coordinated nodes corresponding to different molecular groups. Find two interpenetrating 3D nets composing the total structure.
Example 4: simplification of the crystal structure of ACOKIM, 4-iodo-2,3,5,6-fluoro-benzonitrile.

Algorithm:
(1) Open the database ACOKIM and compute the adjacency matrix using the AutoCN methodDomains. Check the options to determine specific bonds A-X...B with participation of iodine atoms.
(2) Open IsoCryst and find the 4-iodo-2,3,5,6-fluoro-benzonitrile connected by specific C-I…N bonds. Check the IsoCryst option **Bonds/Show/Specific** to see the specific bonds. Compute the C-I…N angle that is equal to 167.28°.

(3) Simplify the crystal structure to its underlying net in standard representation. Check the ADS option **Topology/Bond Types/Specific = Mol.** Run ADS and press the **Whole Molecule** button.

(4) Look at the simplified net and be sure that it contains inclined chains of molecular centroids. Come back to the initial structure and find the chains in it.
**Exercise:** simplify the structures from the database CYANAM_TISRAO. Which structures contain hydrogen or specific bonds? Which of them is interpenetrating?

**Answer:** Structure of CYANAM01 contain two interpenetrated H-bonded frameworks (hydrogen bonds H1-N2, H2-N2) with topology of 4-coordinated net dia. Structure of TISRAO contain a Halogen bonded framework (Halogen bonds = Specific bonds I1-I2, I1-I3) with topology of 4-coordinated net cds (to obtain cds topology you should remove 2-c nodes using the simplify adjacency matrix, see Task 2, Example 2).

**Tools**: the programs ADS, AutoCN and IsoCryst, Crystal Data window, Simplify Adjacency Matrix procedure.

**Example 1**: edge-net simplification of the crystal structure of SAYNAI, 3-(chloroacetamido)pyrazole.

**Algorithm**:
1. Open the database SAYNAI and compute the adjacency matrices for the crystal structure of 3-(chloroacetamido)pyrazole (AutoCN Method: Domains; hydrogen bonds have to be found).
2. Simplify the crystal structure to its underlying net in standard representation using the method Whole molecule. What is the coordination number of the molecule?
3. Turn to the initial SAYNAI database. Run IsoCryst and find the three molecules connected with a given one. For this purpose, toggle off Take Hydrogen bonds, select a molecule and grow it. Then toggle on Take Hydrogen bonds and grow the structure one time. Toggle off Take Hydrogen bonds again and grow surrounding molecules. Show atom names.

Pay attention that the molecules form dimers with pairs of molecules connected by H-bonds.

4. Get a simplified net were the nodes are the centroids of the dimers (synthon simplification, see e.g. Baburin, I. A.; Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. Cryst. Growth Des.; 2008; 8; 519-539). For this purpose we will change the type of the hydrogen bonds N2…H2 (in valence, specific or Wan der Waals bond type) to distinguish it from other hydrogen bonds. Duplicate the entry so you can make any changes and save the original structure: right-click and choose Duplicate command (or also form the top menu bar: Compound/Duplicate). Open a Crystal Data window for the duplicate entry. Go to Adjacency Matrix tab and change the type of the bonds to valence. Add also some comments on the General/Formula field separated by a slash, for example write: "/ dimers ". This allows keeping track of all the changes made.
Save the changes and simplify the structure again using the *Whole Molecule* approach, now the "isolated" molecules are dimers (related by the synthon). What is the coordination number of the dimer?

(5) We can obtain the net of dimers starting from the simplified net in the standard representation. We need to find the "dimers", here represented by the shortest connection. Also the other two long connections are related by symmetry, so the set of "bonds" is divided in 1+2. The single independent "bond" must be the dimer. Now we can do a simplification, changing the two equivalent bonds into H-bonds, making the "dimer" isolated, hence the standard representation can be done. Turn to the SAYNAl_c database and open a *Crystal Data* window for the first record. Change the type of two equivalent bonds to *H bond*.

Save the changes and simplify the net (Choose Whole Molecule while simplification procedure). The resulting net is a partial edge net with dia topology with respect to the initial net since its nodes correspond to some edges of the initial net. And in this case is equal to the "dimer" net. See *Appendix 2* for details and definitions.
Example 2: ring-net simplification of the crystal structure of XEHKIE, 2,3,5,6-tetrachloro-trans-1,4-diethynylcyclohexa-2,5-diene-1,4-diol.

Algorithm:

1. Open the database XEHKIE and compute the adjacency matrices for the crystal structure of it (AutoCN Method: Domains; hydrogen bonds have to be found).
2. Simplify the crystal structure to its standard representation using the method Whole molecule. What is the coordination number of the molecule?
3. Turn to the initial XEHKIE database. Run IsoCryst and look for H-bonded tetrameric synthons (O–H)_4.

Close IsoCryst and separate the synthons in the structure. For this purpose, change the type of hydrogen bonds to valence, and the type of C4–O1 bonds to H bond. Save the changes and run IsoCryst again to be sure that the synthons are really separated.

(4) Simplify the crystal structure and pay attention that there are 2-coordinated nodes corresponding to the residues of the molecules connecting the synthons. Contract the 2-coordinated nodes transforming them into edges. For this purpose duplicate the record, go to the duplicate and run Compound/Auto Determine/Simplify Adjacency Matrix procedure.
In the column **Remove** is possible to select the nodes/atoms to be removed

- Selecting **0–connected** the atoms/nodes isolated are removed;
- Selecting **1–connected** all atoms/nodes connected only with one link (terminal) are removed (e.g. all the hydrogens of benzene rings, all "dangling" atoms).
- Selecting **2 – connected** all bridge atoms/nodes will be transformed into edges.

All the procedures are cyclic, i.e. if new 0-, 1- or 2-connected nodes emerge during the simplification, they will be removed in turn.

In the column **Type** is possible to select on which kind of interaction the simplification above applies. All the interaction left unselected will not be considered, and will be discarded in the final picture. For example if we want to simplify a network built by H-bonds (we want to keep all the H-bonds in the final simplified net) we must select both **Valence** and **H bonds**.

**WARNING**: it is better to make a duplicate of the structure in use before doing any simplification; the process is irreversible.

Press **Ok** and be sure that the 2-coordinated nodes are contracted. The resulting net is a **partial ring net** with respect to the simplified net in the standard representation since its nodes correspond to some rings of the initial net. Pay attention that both standard representation and the partial ring net are 4-coordinated, but have different topologies that will be proved in Module 5. See **Appendix 2** for details and definitions.

**Tips**: The **Compound/Auto Determine/Simplify Adjacency Matrix** procedure is a very useful procedure to be used quite often, even at the beginning. It is always easy to look at a molecule if all the dangling atoms (1-connected) are removed. So, after all the bonds/contacts/H-bonds are found via AutoCN, it may be useful to duplicate your structure and simplify it. The IsoCryst representation will be more legible. See for example the simplified picture for XEHKIE (with some bond/color changed... try!), the complex 2,3,5,6-tetrachloro-*trans*-1,4-diethynylcyclohexa-2,5-diene-1,4-diol $\text{C}_{10}\text{H}_4\text{Cl}_4\text{O}_2$ is represented by a much simpler $\text{C}_6(\text{OH})_2$. 
Example 3: cluster simplification of the crystal structure of NAPFUG, a Metal-Organic Framework Zn₄O(NBT)₂, H₃NBT= 4,4′,4″-nitrilotrisbenzoic acid.

Algorithm:
(1) Open the database cluster_repr and compute the adjacency matrices for the crystal structures (default parameters for AutoCN, no Hydrogen Bonds are present).
(2) Duplicate the entry C42 H24 N2 O13 Zn4 (NAPFUG) so you can make any changes and save the original structure: right-click and choose Duplicate command (or also from the top menu bar: Compound/Duplicate).
(3) Following the Tips of the previous example, remove all the 1-connected atoms to get a simpler view of the content of the unit cell.
(4) Open the IsoCryst window and with the button on, select one atom to check if there are one or more nets. This will show that for NAPFUG there are more than one nets.
(5) Choose to display only the selected subnet clicking on (Show selection only).

Pay attention that the standard representation will not be appropriate here, instead we need to simplify the whole polynuclear groups (clusters) as a single node using “cluster representation”: the nodes are the Zn₄O(COO)₄ clusters and the tri-benzoic ligands, hence the underlying net could be described as 6-c (cluster) and 3-c (ligand).

(6) The long way will be to change (one by one) selected bonds into H-bonds as to “isolate” the cluster by H-bonds, then do the standard representation as illustrated in the previous example 1 for SAYNAI. But there is a semiautomatic mode. Open a window of the program ADS, click Options, check the option Common/Save Simplified Net and Simplification Method = Cluster. Be sure that the Cluster Rings limits are set to zero (default values), otherwise only rings within the specified limits will be considered in the simplification procedure.
Press Ok and run the program.

(7) Select All atoms (this is essential, because the program look for rings of all bonds, see Appendix 2 for details and definitions), and run. You will get a new entry in the cluster_repr_c database where the bonds that define the boundary of the cluster are changed into H-bonds (as in the figure below).
(8) Now we can apply the standard simplification for H-bonded molecules (the **Whole molecule** selection) and all the clusters and 6-rings will be changed into single points.

The database `cluster_repr_c_c` of the next level of simplification will be created.

The final net contains 5 pseudoatoms (nodes): a 6-c (ZB) pseudoatom represents the barycenter of \( \text{Zn}_4\text{O}(\text{COO})_6 \) cluster, 2-c (ZA) pseudoatoms are the benzene rings centroids, and 3-c (ZC) pseudoatoms are the nitrogen atoms of the \( \text{H}_3\text{NBT} \) ligand (these information is written in the **Comment** window under SIMPLIG: \( \text{ZA} = \text{C6H4} \) \( \text{ZB} = \text{C6O13Zn4} \) \( \text{ZC} = \text{N} \)).

Check with ADS and you will find that there are two interpenetrated underlying nets `pyr` (see Module 5).
A good exercise is to reproduce the representations of FOXRAM as illustrated here below from figure 2 and supplementary in “Underlying nets in three-periodic coordination polymers: topology, taxonomy and prediction from a computer-aided analysis of the Cambridge Structural Database” E. V. Alexandrov, V. A. Blatov, A. V. Kochetkov and D. M. Proserpio *CrystEngComm*, 2011, 13, 3947-3958.

The different possible methods of simplification of the coordination framework in FORXAM. (top) Standard representation; (middle) cluster representation with intercluster bonds belonging to 24- and 39-cycles; (bottom) cluster representation with intercluster bonds belonging to only 39-cycles

In the next page is reported a fragment of the ToposPro output for the FORXAM crystal structure showing the table of symmetry independent bonds with the size (N) of the minimum (shortest) circuits to which each of them belong shown in the last column. The bonds of groups (i)-(iv) are selected by green, yellow, cyan, and grey, respectively.

(i) grey N=0 are dangling bonds: typically C-H, and here also Zn-O (water).
(ii) yellow N=3,4,6,8 are bonds belonging to small cycles.
(iii) cyan N=24 gives cluster representation 1 ubt.
(iv) green N=39 gives alternative cluster representation 2 fcu.
<table>
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<tr>
<th>No</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Dist.</th>
<th>N</th>
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</tbody>
</table>

**24-circuit for C1-C2**

(C-H removed)

**39-circuit for Zn2-N1**

(C-H removed, one ligand is disordered)


### Answer:

<table>
<thead>
<tr>
<th>RefCode</th>
<th>Types of bonds considered</th>
<th>Shortest circuit defining cluster</th>
<th>D*</th>
<th>Underlying net</th>
<th>Entanglement</th>
<th>Comments</th>
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<td>ACUHOV</td>
<td>H-bonds, valence</td>
<td>8</td>
<td>0D</td>
<td>3-c hcb</td>
<td>2-fold interp.</td>
<td>3-c nodes - H-bonded dimers</td>
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<td>0D</td>
<td>3,8-c the</td>
<td>2-fold interp.</td>
<td>3-c nodes - central triazine-rings of ligands; 8-c nodes - clusters {MnClO4(CN)8}</td>
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<td>CUSXIV</td>
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<td>6</td>
<td>0D</td>
<td>3,6-c qom</td>
<td>-</td>
<td>3-c nodes - central benzene-rings of ligands; 6-c nodes - clusters {Zn4O(CO2)6}</td>
</tr>
<tr>
<td>MOF-180</td>
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<td>0D</td>
<td>3,6-c toz</td>
<td>-</td>
<td>3-c nodes - central benzene-rings of ligands; 6-c node - clusters {Zn4O(CO2)6}; note that some {Zn4O(CO2)6} clusters are disordered, but cluster simplification works well</td>
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<td>3,24-c rht</td>
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<td>0D</td>
<td>3,6-c ith-d</td>
<td>-</td>
<td>3-c nodes - central benzene-rings of one ligand; 6-c nodes – clusters {Zn4O(CO2)6}; note that naphthalene-groups are disordered, but cluster simplification works well</td>
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<td>0D</td>
<td>3,6-c qom</td>
<td>-</td>
<td>3-c nodes - central benzene-rings of the ligand; 6-c nodes – {Zn4O(CO2)6}; note that the {Zn4O(CO2)6} clusters are disordered, but cluster simplification works well</td>
</tr>
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<td>FOPFAS</td>
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<td>24</td>
<td>0D</td>
<td>3,6-c qom</td>
<td>-</td>
<td>3-c nodes - central benzene-rings of the ligand; 6-c nodes – {Zn4O(CO2)6}; note that the {Zn4O(CO2)6} clusters are disordered, but cluster simplification works well</td>
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<td>6-c pcu</td>
<td>-</td>
<td>6-c nodes – {Zn4O(CO2)6}</td>
</tr>
</tbody>
</table>

* Dimensionality of cluster
**Example 4:** skeleton simplification of the crystal structure of ACUCIK, $(5-[2-(3\text{-}pyridyl)ethenyl]thiophene-2\text{-}carboxylato)_2\text{Zn}$.

**Algorithm:**

1. Open the database **skeleton** and compute the adjacency matrices for the crystal structure (default parameters for AutoCN).
2. Run IsoCryst for the ACUCIK record and be sure that there are 4-, 5-, and 6-rings in the structure.
3. Run ADS in the simplification mode, **Simplification Method = Skeleton, Cluster Rings <= 4.** See **Appendix 2** for details.
4. In the generated database **skeleton.c** run IsoCryst and be sure that all 4-rings have been transformed to the net edges (C5-Zn1).
(5) Go back to the database **skeleton** and repeat simplification steps with **Cluster Rings** <=5 and 6. Pay attention to successive simplification of the coordination network.

What is the dimensionality of this network? Is there entanglement in this structure?

**Exercise**: simplify the other structures from the database **skeleton**. Determine the dimensionality of the simplified networks and check them for entanglement.

**Answer**: Structure of ARIBOS consists of 3 interpenetrated frameworks, which contains 5-rings \{Cd\_2CO\_2\}, if bonds Cd-Cd are taken into account (or 8-rings \{Cd\_3(CO\_2)\}_2\}, if they are not) and 6-rings (benzene-rings). Structure of ACOVEU is a framework, which contains only one type of 5-rings \{Co\_2O\_2\}. Structure of GIMGIT consists of corrugated polycatenated layers, which contains 4-rings \{ZnCO\_2\} (if long bonds Zn1-O4 are taken into account), 5-rings \{C\_3N\_2\}, and 6-rings \{C\_6\}.
**Example 5**: building Hopf ring net for the crystal structure of GULBAR, \([\text{Zn(atz)}(\text{isonic})] \cdot 0.5\text{Hisonic}, \text{atz} = 5\text{-amino-tetrazolate}, \text{Hisonic}=\text{isonicotinic acid.}\

**Algorithm:**

1. Open the database **Hopf ring nets** and compute the adjacency matrices for the crystal structure (default parameters for AutoCN).
2. Build standard representation for the record GULBAR. Be sure that the resulting simplified net consists of 4-coordinated Zn atoms. (do not forget to remove 2-c nodes by means of the Simplify Adjacency Matrix procedure)
3. For the simplified structure run ADS in the **Ring Net** simplification mode with the following options specified (remember to select all atoms as “central atoms”):

   - (4) Open **Crystal Data** window for the simplified structure and be sure that there are six links marked as “H bonds” per each ring center (node of the ring net).

   ![Crystal Data window](image)

   Using the ADS classification mode (see Module 5) you may determine the topology of the Hopf ring net (the net of H bonds) as 6-c hXg. (Tip: set in **Topology/Bond Types**: H-bonds: At. / Valence: None)

**Exercise**: simplify another structure in the **Hopf ring nets** database (LAYKOM). Build a Hopf ring net for LAYKOM. Does the coordination of nodes in the Hopf ring net differ from GULBAR? Is the topology of 2-fold interpenetration of the diamondoid nets the same in GULBAR and LAYKOM?

**Answer**: HRN for LAYKOM consist of 6-c and 10-c nodes (in ratio 1:1), while HRN for GULBAR is constructed with only 6-c nodes, so their topologies (rather as topology of interpenetration) are completely different. This shows different modes of entanglements for dia nets rings.

Example 6: generate the augmented version of a given net. Open the idealnets database available in the root folder. This database contain all RCSR nets and some more sphere packings. It is quite useful when you want to examine a given net in its maximum symmetry embedding. Let’s build gsi-a from gsi.

Algorithm:

1. Open the idealnets database, select gsi and copy it in a new database called augmented

2. Let the initial net contain carbon atoms only. Use the Compound/Auto determine/Bond Midpoints procedure to add one extra atom as “bond midpoint”. You get boron atoms as midpoints.

3. Apply Bond Midpoints again to the resulting structure. You get nitrogen atoms as additional midpoints.
(3) Run ADS in the standard simplification mode (Save Simplified Net /Standard), BUT having checked the Topology/Contract Atom flag. After running choose in the subsequently appeared windows: Central Atoms - all EXCEPT carbon atoms; Atoms to Contract to - NITROGEN atoms; Atoms to Contract – CARBON atoms. Of course, you can do it in the batch (Continuous) mode too - you have to specify properly atoms in the "Contract to" and "Atoms to Contract" lines. You will get a new database augmented_c with the augmented net almost ready…

(4) Now remove all 2-c BORON atoms with the Compound/Auto Determine/Simplify Adjacency Matrix

It may happen that you need to remove some extra bond in the final net in order to get the correct coordination figure.
Appendix 2. The concept of “underlying net” and crystal structure representation. Methods of simplification

When we explore the topological properties of Coordination Polymers / Metal Organic Frameworks (CP/MOFs) the key notion is the concept of underlying net. While the whole structure topology is reflected by an atomic net including all atoms as nodes and all interatomic bonds as edges, the nodes and edges of the underlying net correspond to structural groups and connections between them. In fact, any structure representation that separates building blocks (for instance, molecules in molecular packings or ligands in coordination compounds) implicitly applies the underlying net concept. The resulting simpler representation allows one to find structural resemblances between chemically quite different compounds.

In ToposPro where a number of structure representations can be built in an automated mode; each representation can be transformed to an underlying net by simplification procedures (see Module 4). Any structure representation in ToposPro corresponds to a particular way to choose structural units; this way depends on the task under consideration. For any class of chemical compounds some standard representation can be proposed that conforms to a conventional crystallochemical description (see Table below). The standard representation of valence-bonded CP/MOFs considers metal atoms and organic ligands as structure units, ignoring guest ions and molecules. Then the procedure of contracting multiatomic groups to their centroids is applied to all ligands to obtain a primary simplified net. This net can be directly transformed to the underlying net by the procedure of secondary simplification that consists in successive removing 0-coordinated nodes (intraframework molecular moieties), 1-coordinated nodes (terminal/dangling ligands) and transforming 2-coordinated nodes (bridge $\mu_2$ ligands or metal atoms connected to only two bridge ligands) into edges. If the bridge $\mu_n$ ligands are connected with more than two metal atoms ($n>2$) they form additional nodes of the underlying net.

### Standard representations for some types of crystal structures

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<tr>
<th>Structure type</th>
<th>Structure units = simplified net nodes</th>
<th>Type of bond within the structure units</th>
<th>Type of bond between the structure units = simplified net edges</th>
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<td>metal atoms, ligands</td>
<td>valence</td>
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<td>H-bonded CP/MOFs</td>
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<td>organic molecules</td>
<td>valence</td>
<td>intermolecular: H-bonds, specific (e.g. Halogen Bond), van der Waals</td>
</tr>
</tbody>
</table>

The standard representation is not the only way to obtain the primary simplified net for a CP/MOF. If the metal atoms form a cluster or a polynuclear coordination group this group can be considered as a structure unit and a node of a simplified net. To recognize these groups automatically, ToposPro uses the following criterion for distinguishing intra- and intercluster bonds. Let us determine for each $k$th bond the size $N_k$ of the minimal ring of bonds to which the $k$th bond belongs ($N_k$ is the number of bonds in the ring) and arrange all bonds in ascending order of $N_k$:

$$N_1 \leq N_2 \leq N_3 \ldots$$

If in this sequence there is such $N_m$ that

$$N_{m+1} - N_m > 2 \quad (1)$$

then all bonds with $k \leq m$ are referred to as intracluster, the other bonds are considered intercluster. Condition (1) means that intracluster bonds belong to small rings, i.e. they are allocated rather compactly forming clusters, while intercluster bonds connect the clusters together and become edges of the simplified net. If several pairs of $N_k$ obey (1), there are several ways to cluster the bonds and several cluster representations of the CP/MOF. In most cases only one representation corresponds to finite complex groups, and the resulting underlying net can be unambiguously obtained.

A modification of cluster representation is the skeleton representation. In this case the user should specify the maximal size ($N$) of rings that will be accounted to determine the atoms belonging to the structure skeleton. If the atom belongs to at least one ring of size more than $N$, this atom is included into the skeleton, otherwise it is contracted to the skeleton atoms. In practice, this means that atoms belonging only to small rings (e.g. benzene rings) are removed from the structure, and the small rings are replaced by edges of the simplified skeleton net. The larger $N$ the simpler is the skeleton. This representation is especially useful when analyzing...
entanglements since in this case small rings being impossible to be catenated just hinder the topological analysis.

Special structure representations are *edge nets* and *ring nets*. Edge net can be constructed by placing new nodes in the middle of the edges of the initial net, connecting new nodes by new edges and removing old nodes and edges. The edge net is *complete* if all the edges in the initial net are centered by new nodes and all old nodes and edges are removed; otherwise the edge net is *partial*. Similarly to edge net, one can construct a ring net by putting nodes in the centers of rings of the initial net, removing the nodes of the initial net belonging to the centered rings, and adding new edges between the centers of adjacent rings. Depending on whether all rings are centered or not, the ring net can be complete or partial. A special kind of ring net is Hopf ring net. That is the net whose nodes and edges correspond to rings and Hopf links (interlocking of 2 rings) between them. By default, ToposPro marks Hopf links as “H bonds” between the ring centers.

Hopf, multiple crossing, and the three simplest three-component links. The corresponding edges of the ring nets that connect the ring net nodes are shown by arrows. For the Borromean link, the ring net fragment contains an additional node in the center of the link. The program Knotplot (R. G. Scharein; http://www.knotplot.com/) was used to draw the link pictures.

Hopf ring net directly characterizes the catenation pattern, *i.e.* the method of catenation of the rings for the whole system of entangled nets, if the kind of network and the degree of interpenetration are fixed. For example, if a set of structures containing two interpenetrating diamondoid networks is under consideration, it is sufficient to compare their Hopf ring nets to find the differences in their catenation patterns.

**IMPORTANT:**

Pay attention, that 0, 1, 2-coordinated nodes of simplified net should be deleted. You will obtain the underlying net with nodes of coordination > 2, which can then be classified by means of the ADS program. Otherwise, you would not properly classify the net topology.

The 2-c nodes may be kept in the underlying net only in the rare cases where the entanglement is formed between 2-member rings (called also loops), see: Yang J., Ma J.-F, Batten S. Polyrotaxane metal-organic frameworks (PMOFs) *Chem. Comm.* 2012, **48**, 7899-7912.
Module 5. Working with the program ADS, TTD, TTO, and TTR collections. Identification and taxonomy of nets. Different structure representations

**Task 1: Computing and checking topological indices** (coordination sequences, point and vertex symbols).

**Tools:** the program ADS, the TTD collection tools.

**Example 1:** computing topological indices for simplified CaCO$_3$ polymorphs.

**Algorithm:**

1. Open the database CaCO$_3$ generated in Module 4 and open an ADS window for the first record (Aragonite).
2. Specify the ADS Topology options as shown in the picture below. All Common options may be unchecked.

To classify atomic nets in crystals ToposPro uses the following conventional topological descriptors:

**Coordination sequence (CS)** \{N$_k$\}, $k=1$–$n$, is a sequence of numbers N$_1$, N$_2$, N$_3$,... counting the atoms in the 1st, 2nd, 3rd etc. coordination shells of any given atom in the net. The length of CS to be computed, $n$, has to be specified as Coord. Seq. parameter.

**Point symbol** lists the numbers (amount) and sizes of shortest circuits (closed chains of connected nodes) starting from any non-equivalent node in the net. A Total Point Symbol for net (TS) summarizes all the point symbols for the non-equivalent nodes with their relation/weight. The terminology Schl{"a}fli Symbol SHOULD BE ABANDONED because of the use of this term in mathematics with a different definition.

**Extended point symbol (ES)** lists all shortest circuits for each angle for any non-equivalent atom. To compute point symbols, TS and ES, check the Point Symbol option.

**Vertex symbol (VS)** gives similar information as ES, but only for rings (circuits without shortcuts). Specify Max. Ring parameter more than zero to find the shortest rings or no more than Max. Ring size.

These descriptors for all non-equivalent atoms are collected in the binary .ttd (TOPOS Topological Database) files that form the TTD collection to be considered below.

3. Run ADS and select all atoms in the Choose Central Atoms window. You will get the following output:

```
Coordination sequences
----------------------
ZA1: 1 2 3 4 5 6 7 8 9 10
Num  6 18 42 74 115 162 222 290 366 450
Cum  7 25 66 141 255 417 639 929 1295 1745
----------------------
ZB1: 1 2 3 4 5 6 7 8 9 10
Num  6 20 42 74 114 164 222 290 366 452
```
The following topological parameters have been computed here:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Num – N_i values</td>
<td>–</td>
</tr>
<tr>
<td>Cum – cumulative numbers of the coordination sequence including the central atom;</td>
<td></td>
</tr>
<tr>
<td>TD10 – topological density, TD_{10}, a round averaged Cum_{i} for all central atoms in the asymmetric unit;</td>
<td></td>
</tr>
<tr>
<td>Point symbol – the record like {4^9;6^6} corresponds to the point symbol (4^6), i.e. nine angles at Ca atom contain the shortest 4-circuits and six angles contain 6-circuits;</td>
<td></td>
</tr>
<tr>
<td>Extended point symbol – ES; thus, for the ZA (Ca) atom ES looks like [4.4.4.4.4.4.4.4.4.6.6.6.6.6.6], i.e. eight 6-circuits meet in any of the six angles, in three other angles two 4-circuits meet and other angles are occupied by one 4-circuit;</td>
<td></td>
</tr>
<tr>
<td>Vertex symbol – VS; thus, for the ZB atom (carbonate ion centroid) VS = [4.4.4.4.4.4.4.4.4.\infty.\infty.\infty], i.e. three angles contain no rings of size 10 or smaller. Remember that the rings were computed up to size 10 (Max. Ring = 10). So possibly larger rings may exist - ToposPro does not know this!</td>
<td></td>
</tr>
<tr>
<td>Point symbol for net – TS; {4^12;6^3}{4^9;6^6} summarizes point symbols {4^12;6^3} and {4^9;6^6} for two non-equivalent 6-coordinated nodes contained in the net with equal ratio.</td>
<td></td>
</tr>
<tr>
<td>6-c net – the net is 6-connected or 6-coordinated (all vertices are of degree 6);</td>
<td></td>
</tr>
<tr>
<td>2-nodal net – the net is binodal (contains two topologically inequivalent nodes; they have different CS+ES+VS sets).</td>
<td></td>
</tr>
</tbody>
</table>

The last message remind the user that topological classification of the net will not be provided – for this purpose one has to check the Classification flag (see the next example).

(4) Save the results in a textual CaCO3_c.ado file (Data/Save). Close the ADS window.
(5) Repeat the procedure for the remaining two records in a batch mode. Select them, open an ADS window and set Options/Continuous/Central Atoms = El. Run ADS.

Example 2: checking topological indices for nia and pecu topological types and comparing them with those for the simplified CaCO3 polymorphs.

Algorithm:
(1) Be sure that you have the TTD collection (see Appendix 3 for details) on your computer and the path TTD in System/TOPOS Parameters/Paths is correct. You may find a frequently updating collection of .ttd files on the ToposPro official site. For the sources of the TTD collection see Appendix 4. All .ttd files have to be copied into the TTD subdirectory. The path to the TTD collection can be changed in System/TOPOS Parameters/Paths.
(2) Load the TTD collection as shown in the next figure. ToposPro automatically loads all the .ttd files from the TTD folder, so you may easily expand your library of topological types by copying new .ttd files into ToposPro directory. IMPORTANT: if you have copied a new .ttd file you must reload TTD collection to accept this file. Wait until the collection is loaded.
The format of the .ttd files can be changed in new ToposPro versions. If the current TTD Collection does not fit the new ToposPro the following message appears:

![Error Message]

You have to update your TTD Collection from the ToposPro website.

(3) Open the TTD collection content by Database/TTD Collection/Content command. In the upper list of the TTD Collection window you have all .ttd files loaded together with the number of records in the files and the ranges of internal identifiers of topological types. Select one or several .ttd names and press Create List button; in the list Topological Types you will get all topological types stored in the .ttd files selected. Select any topological type (you may simply type the name of the topological type to find it quickly in the list); you will have all the topological indices in the lower window. In the example below a TTD collection of 11 databases with 76154 topological types is loaded (the number of topological types change frequently with updates).
(4) Select **TOPOS&RCSR** .td file, create list and find the nia topological type as shown above. Compare all nia topological indices with the indices computed for aragonite and vaterite. What are the differences between aragonite and vaterite in this relation?

(5) Find the pcu topological type and compare it with calcite. Why does calcite have no antitype?
Task 2: Taxonomy of nets. Working with the TTO and TTR collection.
Tools: the program ADS, the TTD, TTO, and TTR collections.
Example 1: classification of the simplified CaCO₃ polymorphs.
Algorithm:
(1) Open the database CaCO₃_c generated in Module 4 and open an ADS window for the first record. Go to the ADS Topology options and check the Classification flag. The following parameters will also be specified:

- **Dimen. Calc.** (Common tab) – to recognize all non-bonded (separated) structural components (molecules, chains, layers, 3D frameworks and interpenetration). This flag may be unchecked to speed the analysis if you are sure that the crystal structure consists of a single net.
- **Point Symbol** (Topology tab) – to calculate ES.
- **Coord. Seq.** (Topology tab) – to calculate CS (default number of coordination shells is 10).

Other flags in Common and Topology tabs will be unchecked. Pay attention that you may not set a smaller value of Coord. Seq. and uncheck Point Symbol until the Classification flag is unchecked. You may specify non-zero Max. Ring parameter to use extended CS+ES+VS set of indices for classification. However, in most cases CS+ES set is sufficient to recognize nets and it works much faster than CS+ES+VS. We recommend to use the default set for the first time, then you may toggle to CS+ES+VS set and check the results of the first classification. See below.

(2) Run ADS and select all atoms in the Choose Central Atoms window. You will get the output like in Task 1, but the last line will contain the information about topological type:


You see that the topological type of the simplified aragonite is nia indeed. Pay attention that the size of rings in VS is not larger than 6. So you may check CS+ES+VS set with Max. Ring = 6.

(3) Return to ADS options, specify Max. Ring = 6 and run ADS again. Be sure that the CS+ES+VS set gives the same result.

(4) Repeat the procedure for the remaining two records in a batch mode. Select them, open an ADS window, specify Options/Continuous/Central Atoms = El and check Standard Ring Limits flag. This ensures that ToposPro will use standard Max. Ring values for different nets depending on the net coordination:

<table>
<thead>
<tr>
<th>Coordination</th>
<th>Max. Ring</th>
<th>Coordination</th>
<th>Max. Ring</th>
</tr>
</thead>
<tbody>
<tr>
<td>3- or 4-coordinated</td>
<td>26</td>
<td>7-coordinated</td>
<td>12</td>
</tr>
<tr>
<td>5-coordinated</td>
<td>20</td>
<td>8- or 9-coordinated</td>
<td>10</td>
</tr>
<tr>
<td>6-coordinated</td>
<td>16</td>
<td>&gt;9-coordinated</td>
<td>8</td>
</tr>
</tbody>
</table>
These values will be applied instead of the Max. Ring value specified in the Topology tab only if CS+ES+VS set is used (Max. Ring > 0). Pay attention that Standard Ring Limits flag as well as all other options on the Continuous tab are valid only in the batch mode, when there are selected records in the database and the flag Common/Cont. Calc. is checked.

Run ADS.

**Example 2:** looking for the topological types for C₆H₆O₂ isomers and for all known nets with the diamond (dia) topology.

**Algorithm:**

1. Be sure that you have the TTO and TTR collections (see Appendix 3 for details) on your computer and the path TTO in System/TOPOS Parameters/Paths is correct. You may find a frequently updating collection of .tto and .ttr files on the ToposPro official site. All .tto and .ttr files and TTOReprTypes.txt file have to be copied into a separate subdirectories (/TTO within the ToposPro folder by default). In alternative, the path to the TTO and TTR collections can be changed in System/TOPOS Parameters/Paths.

2. Find all topologies for all representations of C₆H₆O₂ isomers. For this purpose open the database C6H6O2 from Module 3 and open a Crystal Data window for the first record. Go to Comment tab and push Representations Topology button. You will find that the topology for the RESORA13 isomer is known in one representation, in which H-bonded molecules are considered as whole; the topology of the resulting 3D single (Z=1) net is cds (also known as 4/6/i4 sphere packing or sqc5 net). For the nomenclature of topologies see Appendix 5.

Pay attention that you need no simplification of the structure and use of the ADS classification procedure. The data on the representation topology are stored in the TTO collection and related to a given structure by its Ref. Code.
(3) Look for the topologies if other C₆H₆O₂ isomers. Pay attention that in many cases the data on the structures are not contained in the TTO collection; you will get the message

Currently TTO collection contains the data on 3D structures only; not all of them have yet been processed.

(4) Find all known nets with the diamond (dia) topology. For this purpose open TTD Collection window, find the dia topology in TOPOS&RCR .ttl file and press Examples button. You will get 1138 examples in the bottom list. Right-click in the list, select all records, right-click again and save the Ref. Codes. They will be stored in RefCodes.gcd file located in the /TTO folder. Then you may use TopoPro Acquisition Data/Ref. Code filter to find the crystallographic data on the structures (this works only if you have a large database with many structures from CSD). Otherwise you can search CSD with ConQuest program, loading the .gcd list of Ref. Codes (File/Open/Refcode List). You may also save the whole table (Save Table) as a formatted textual file Table.txt located in the /TTO folder, or copy the information in the Clipboard. You may order the table by any column by clicking its header.

The column Occur. contains the numbers of symmetry-inequivalent nets of a given topology stored in the TTO Collection. Such a number can be more than the number of crystal structures (as for dia: 1153 compared to 1138) because some structures can contain several inequivalent nets of the same topology. A net is bold-selected if it has at least one occurrence. To leave in the list only the nets with occurrence, right-click in the net list and choose Show with Examples. To show all related nets for the selected nets use the item Show Relations. All the relations will appear in the Topological Types Relations list. You may use also the Relations button to show the entire TTR Collection.
Example 3: Working with the TTO Collection window.

Algorithm:
(1) Load the TTO collection as shown in the next figure. ToposPro automatically loads all the .tto files from the TTO folder, so you may easily expand your library of topological types observed by copying new .tto files into ToposPro directory. IMPORTANT: if you have copied a new .tto file you must reload TTO collection (Clear it and Load again) to accept this file. Wait until the collection is loaded and the TTO collection window appears.

(2) In the upper list of the TTO Collection window you have all .tto files loaded together with the number of records in the files and the ranges of internal identifiers of topological types. In the example below a TTO collection of 10 databases with 37932 examples is loaded (the number of records change frequently with updates). Any .tto database contains the information of underlying nets of crystal structures in a particular representation type (see Appendix 2 for definitions). Select one or several .tto names and press Create List button; in the bottom list you will get all examples of crystal structure topologies stored in the .tto files selected. This list contain RefCode of the crystal structure, topological type name as given in the TTD collection, periodicity of the underlying net (Dimen), degree of interpenetration (Z) that is equal to 1 for non-interpenetrating nets and the representation type.
Right-click in the list, select all records and save RefCodes or the whole table in the files `RefCodes.gcd` or `Table.txt`, respectively, that are located in the /TTO folder. You may order the table by any column by clicking its header.

**Exercise**: determine the topology of your own structure simplified according to one of algorithms from Module 4. Check that the topology of RESORA13 is indeed cds single: Could you think of a different representation? Try to describe it as 3-c cutp.

**Answer**: The cds topology for the structure RESORA13 can be obtained according to standard representation (see Module 4, Task 1, Example 2; nodes of the underlying net correspond to H-bonded resorcinol molecules), but to get the utp net you should use Simplify Adjacency Matrix (see Module 4, Task 2, Example 2) procedure to remove all 0-, 1-, and 2-c atoms that are connected with hydrogen and valence bonds. In the first case each resorcinol molecule is a node of the underlying cds net and in the second case we have dimers isolated with H-bonds.

What should you do if you have got a topology unknown to ToposPro? Read Appendix 6!
Task 3: Generating different structure representations.

Tools: the program ADS, the TTD collection, Generate Representations procedure.

Example 1: Generating different structure representations for $\alpha$-SrSi$_2$: metallic and covalent bonding.

Algorithm:

1. Open the database repres and compute the adjacency matrix for the $\alpha$-SrSi$_2$ structure. What AutoCN method should you use? Be sure that Solid Ang. and Dist. + Rsd options are checked. After the calculation close the AutoCN window and look at the adjacency matrix. Are there differences between distances and solid angles (SA) for different bonding? The solid angles as well as interatomic distances are the parameters of relative strength of interatomic bonds; the larger is the value for the solid angle, the stronger is the bond.

2. Open Compound/Generate Representations window and click Ok. Specify the name repres_all to create a new database with different representations of the structure.

3. Open the repres_all database and be sure that there are two records corresponding to solid angle levels 8.5% and 19.5%.

4. Run ADS with the Classification flag checked and determine the topological type for each representation.

Exercise: Build the representations of the $\alpha$-SrSi$_2$ structure considering different levels of interatomic distances (use the Distance and Solid Angle mode in the Representation Parameters window). Are there any differences with the previous method?

Answer: Solid angle levels 8.5% and 19.5% belong to 7,8T3 and srs nets. Distance mode generate three levels: Distance = 3.38 Å net 7,8T3; Distance = 3.26 Å a new 6,6-c net with point symbol \{3^3.4^3.5^6.6^3\}; Distance = 2.40 Å srs net.
Example 2: Generating different structure representations for $\gamma$-CaSO$_4$: ionic and covalent bonding.

Algorithm:
1. Open the database repres and compute the adjacency matrix for the $\gamma$-CaSO$_4$ structure.
2. Build the representations in the Solid Angles mode and store them in the repres_all database.
3. Open the repres_all database and simplify all the three $\gamma$-CaSO$_4$ representations using standard simplification procedure for compounds with metal atoms (central atoms are metals).
4. Determine the topological type for each simplified representation.

Example 3: Generating different structure representations for MAFXAT, 3-amino-1H-pyrazolo(3,4-c)pyridazine: hydrogen bonding.

Algorithm:
1. Open the database repres and compute the adjacency matrix for the MAFXAT structure taking into account hydrogen bonds. What AutoCN method should you use?
2. Build the representations in the Solid Angles mode for H bonds only and store them in the repres_all database.
3. Open the repres_all database and simplify all the three MAFXAT representations using standard simplification procedure for molecules (central atoms are none, H bonds = Mol).
4. Determine the topological type for each simplified representation.
5. Check if the Distances mode produces other list of representations.

Appendix 3. TTD, TTO, and TTR collections

The TTD collection

To classify atomic nets in crystals ToposPro uses the following conventional topological descriptors (see for more details: “Vertex-, face-, point-, Schl"afli-, and Delaney-symbols in nets, polyhedra and tilings: recommended terminology”. Blatov V.A., O’Keeffe M., Proserpio D. M. *CrystEngComm*, 2010, 12, 44-48):

**Coordination sequence (CS)** \(\{N_k\}\) is a sequence of numbers \(N_1, N_2, N_3, \ldots\) counting the atoms in the 1st, 2nd, 3rd etc. coordination spheres of any given atom in the net.

**Point Symbol** lists the numbers and sizes of shortest *circuits* (closed chains of connected atoms) starting from every angle of every non-equivalent atom in the net. A Total Point Symbol for net (TS) summarizes all the Point Symbols for the non-equivalent atoms with their relation/weight. The terminology “Schläfli Symbol” SHOULD BE ABANDONED because of the use of this term in mathematics with a different definition.

**Extended Point symbol (ES)** lists all shortest circuits for each angle for any non-equivalent atom.

**Vertex symbol (VS)** gives similar information as ES, but only for rings (circuits without shortcuts).

These descriptors for all non-equivalent atoms are collected in the binary *ttd* (TOPOS Topological Database) files. The following structure corresponds to the *ttd* file, and is realized in the textual *nnt* (New Net Topology) file:

An NNT and TTD entry example: TiO\(_2\), Rutile, rtl topological type

\[
\begin{align*}
'Stio2', \\
'(4;6^2)2(4^2;6^10;8^3)', \\
'3 14 19 62 51 144 99 254 163 400', \\
'[4.6(2).6(2)]', \\
'[4.6(2).6(2)]', \\
'6 10 38 34 102 74 198 130 326 202', \\
'[4.4.6.6.6.6.6.6.6.6.6.6(2).6(2).8(2).8(4).8(4)]', \\
'[4.4.6.6.6.6.6.6.6.6.6(2).6(2).**.*.**]', \\
\end{align*}
\]

**Detailed description:**

\[
\begin{align*}
'Stio2', \\
Name of the record with the ‘$’ prefix \\
'(4;6^2)2(4^2;6^10;8^3)', \\
TS, Total point symbol for the whole net: \{4.6^2\}.\{4^2.6^{10}.8^3\}. \\
In this case the numbers of the two non-equivalent nodes (O and Ti) relate as 2:1 \\
'3 14 19 62 51 144 99 254 163 400', \\
CS, Coordination sequence \(N_k\) for the first non-equivalent node (oxygen atom); \(k=1–10\) \\
'[4.6(2).6(2)]', \\
ES, Extended point symbol: \{4.6,6.\} for the first non-equivalent node \\
'[4.6(2).6(2)]', \\
VS, Vertex symbol for the first non-equivalent node (here coincides with the Extended point symbol) \\
'6 10 38 34 102 74 198 130 326 202', \\
'[4.4.6.6.6.6.6.6.6.6.6(2).6(2).8(2).8(4).8(4)]', \\
'[4.4.6.6.6.6.6.6.6.6.6(2).6(2).**.*.**]', \\
Similar triples for other non-equivalent nodes (Ti atom) \\
‘**’ means that there are no rings for this angle: \{4.4.6.6.6.6.6.6.6.6.6.6.6.6.*.**\} \\
(alternatively to * the \(\infty\) symbol could be used in the Vertex symbol notation)
\end{align*}
\]
The TTO Collection

Beside the classification of a net via the TTD collection, starting from December 2007 a new collection is being created – TTO (Topological Types Observed). In short, TTO collection matches topological types of abstract nets with examples of real crystal structures. TTO files contain the records of the following format:

- **RefCode** – the Reference Code of a particular structure;
- **Dimen** – dimensionality of the underlying net;
- **Z** – number of nets;
- **TopType** – topology of the net (its code in TTD collection);
- **ReprType** – code of representation type of the structure.

The correspondences between **ReprType** codes and the description of representations are given in the textual file **TTOReprTypes.txt**. Having TTO collection the user may now perform the following operations:

1. Find all topologies for all representations of a particular crystal structure.
2. Find all structures with a particular topology of underlying net.
3. Find all structures with a particular topology in a given database.

All .ttd and .tto files have to be copied into separate subdirectories (/TTD and /TTO by default) within the ToposPro folder. **TTOReprTypes.txt** file has to be copied into /TTO directory. In alternative, the paths to TTD and TTO collections can be changed in System/TOPOS Parameters/Paths.

The TTR Collection

Starting from April 2011, ToposPro includes the TTR collection (Topological Types Relations). This collection is based on the TTO collection and lists all ways of transformation from one net to another that are realized in crystal structures. If for a given crystal structure there are at least two possible representations in the TTO collection, and these representations have different topology, a pair of the corresponding nets appears in the TTR collection. In other words, these nets can be transformed to each other if the structure groups are chosen in different ways in the initial crystal structure. For example a diamond (**dia**) net can be transformed to a **srs** net by an appropriate choice of dimers (edges) in **dia** and matching them to **srs** vertices.

The TTR collection consists of .ttr files that are allocated in the /TTO directory.
Appendix 4. Sources of the TTD collection

The TTD collection has been built using the following sources:


- Data on the sphere packings derived by Fischer, Koch & Sowa; the data were published in a number of papers (see, e.g. and references therein Sowa, H. & Koch, E. (2005). Acta Cryst. A61, 331-342).

- Crystallographic data from CSD (Cambridge Structural Database) and ICSD (Inorganic Crystal Structure Database).

- Atlas of Zeolite Framework Types, the original data are available for free at http://www.iza-structure.org/databases/.

Appendix 5. Nomenclatures for topologies

In the TTD collection the net topologies are designated according to the following nomenclatures (see for a general introduction “Vertex-, face-, point-, Schläfli-, and Delaney-symbols in nets, polyhedra and tilings: recommended terminology”. Blatov V.A., O’Keeffe M., Proserpio D. M. CrystEngComm, 2010, 12, 44-48):

- **TOPOS symbols** \(N_Dn\), where \(N\) is a sequence of degrees (coordination numbers) of all independent nodes; \(D\) is one of the letters \(C\), \(L\), or \(T\) designating the dimensionality of the net (\(C\) – chain, \(L\) – layer, \(T\) – three-periodic); \(n\) enumerates non-isomorphic nets with a given \(ND\) sequence. For instance, the symbol \(3,3,4T3\) denotes the 3\(^{\text{rd}}\) (by the order) three-periodic trinodal net with two 3-coordinated and one 4-coordinated independent nodes. For finite (molecular) graphs the symbols \(NMk\,-\,n\) are used, where \(k\) is the number of vertices (atoms) in the graph.


- **CSD Reference Codes or ICSD Collection Codes.**


- **Subnet s-d-G-n symbols** (Blatov, V. A. (2007). Acta Cryst. A63, 329–343), where \(s\) is a conventional name of the initial net, \(d\) is a set of ascending integers equal to degrees of all inequivalent nodes in the subnet, \(G\) is the space group for the most symmetrical embedding of the subnet, \(n\) is optional and enumerates non-isomorphic subnets with a given \(s\)-\(d\)-\(G\) sequence. Examples: **scu**-3,6-P42/mnm-2 (is a 3,6-c net derived from 4,8-c **scu**); **acs**-4-Pbcn (is a 4-c net derived from 6-c **acs**)

- **Subnet transformation symbols** \(s/G\rightarrow S1\rightarrow…\rightarrow Sn;BS\) where \(s\) is a conventional name of the initial net, \(G\) is the space group of the initial net, \(S1,\ldots,Sn\) is the sequence of group-subgroup transformations to obtain the symmetry of the resulting subnet, \(Sn,\ BS\) is the set of numbers of non-equivalent edges to be retained in the subnet. For instance, the notation **fny/P 63/m cm–>P 63 2 2 (0,0,1/4);Bond sets: 2,3,4,5** means that the subnet is derived from the RCSR net **fny** by decreasing its space-group symmetry from \(P6_3/mcm\) to \(P6_322\) with shifting the origin by \((0, 0, 1/4)\) vector and breaking all non-equivalent edges in the resulting net except the edges No 2, 3, 4 and 5.

Subnet transformation symbols can be found for uninodal and binodal nets depending if the transformation start from uninodal or binodal nets. The subnet transformation symbols are being gradually replaced in the TTD collection with **s-d-G-n** symbols whenever an example is found in crystal structures;

**ATTENTION:** if you have obtained ToposPro output with a subnet transformation symbol, this means that the topology has not yet been found in crystal structures. Let ToposPro authors know about this case!

Some nets fall into different nomenclatures, in this case ToposPro outputs all possible symbols separated by semicolons with the RCSR name first (if available). For example:

dia Diamond; 4/6/c1; sqc6
crs/dia-e; 6/3/c2; sqc889
fau/faujasite/FAU;infinite polyhedron; 4/4/c17; sqc13519
eth; jbw-3,3-Pmna-1
Appendix 6. What to do with new topologies?

Exploration of the crystal structure topology becomes more and more popular and researchers often encounter topologies not described in the TTD collection. How to designate them, how to refer to them and how to be sure that your colleagues will be advised about them? Here we announce a strategy to resolve these problems.

1. If you have found the message

New topology, please, contact the authors

in the ADS output please email a ToposPro database (*.adm, *.cd and *.cmp files) with this structure to one of the authors of this manual.

2. After checking the data we assign a code abcN to the topology, where abc (italic) is your three-letter personal identifier and N is the ordinal number of the topology you have discovered (e.g. smi12 that means '12th topology discovered by Smith'). If you have no identifier you can propose a name that will be assigned for all the structures deposited.

3. The structure should be reported in papers always adding the number after the three letter in order to avoid any confusion with the three letter code of RCSR. It may be also useful to add the point symbol before the name to make the whole name more informative. E.g. (8^3)(6.5^8)-smi12

4. The list of authors' personal identifiers together with contact information will be available at the ToposPro website. We also kindly ask the authors to provide us with the final reference where the structure will be reported.

5. The novel topology will be included into the TTD collection and published in a two-week update of the personal.ttd database. Anyone who will download the database will be aware of the new topology.

6. If the topology will further be included into other databases it will get other names according to the nomenclatures described above, but the initial abcN name will be retained as a proof of priority.
Module 6. Working with the program ADS.
Searching for and analyzing entanglements.

**Task 1:** Analysis and classification of interpenetrating nets.

**Tools:** the programs AutoCN, ADS and IsoCryst.

**Example 1:** Analysis of interpenetration of valence-bonded networks in QOZDOY, \([\text{Zn}(\mu_2\text{-L})_2]\cdot\text{G} (\text{L} = 3-(4\text{-pyridyl})\text{propenoato-O}), \text{G} = \text{trans}-2\text{-butene}).

**Algorithm:**
1. Open the database entangle, right-click on the title of the list and choose **Ref. Code** to show Reference Codes in the list.

Click on the **Ref. Code** title to order the records by Reference Codes. The type of ordering is indicated as **R** in the status line.

Choose the record QOZDOY and compute the adjacency matrix with default AutoCN parameters.
(2) Simplify the structure taking metal atoms as central. For this purpose, after running ADS with **Save Simplified Net** option checked and **Simplification Method = Standard**, scroll the **Choose Central Atoms** window to find all the metals and select them with the **Insert** key (for QOZDOY is only Zn(1)), OR click **Element** button and click **Me** button in the **Periodic Table** window.

You will get a net where bridge (CN=2) 3-(4-pyridyl)propenoato ligands and solvate (CN=0) trans-2-butene molecules are designated as ZA and ZB, respectively.

(3) Simplify the net more by removing zero-coordinated ZB nodes and contracting bridge ZA nodes.
(4) Open one more ADS window and check Classification flag. Run ADS and select all atoms as central. You will get the following output:

-------------------------
Structural group No 1
-------------------------
Structure consists of 3D framework with Zn
There are 4 interpenetrating nets
TIV: Translating interpenetration vectors
[0,0,1] (12.01A)
-------------------------
NISE: Non-translating interpenetration symmetry elements
1: -1
-------------------------
PIC: [0,0,2][1,0,1][0,1,1] (PICVR=2)
Zt=2; Zn=2
Class IIIa  Z=4[2*2]
Coordination sequences
--------------------
Zn1:  1  2  3  4  5  6  7  8  9  10
Num  4 12 24 42 64 92 124 162 204 252
Cum  5 17 41 83 147 239 363 525 729 981
--------------------
TD10=981
Vertex symbols for selected sublattice
--------------------------------------
Zn1 Point symbol:{6^6}
Extended point symbol:[6(2).6(2).6(2).6(2).6(2).6(2)]
--------------------------------------
Topological type: dia Diamond; 4/6/c1; sqc6 {6^6} - VS [6(2).6(2).6(2).6(2).6(2).6(2)] (66833 types in 9 databases)
Elapsed time: 1.50 sec.

ToposPro informs you that the structure is three-periodic, and there are four (Z=4) interpenetrating nets in the array. The nets are all symmetry-equivalent and related both by translations [001] and by inversion. So Zt = 2 and Zn = 2; Z = Zt Zn and the interpenetration belongs to a rare Class IIIa. For the nomenclature of interpenetration parameters see Baburin I.A., Blatov V.A. Carlucci L., Ciani G. & Proserpio D. M. (2005). J. Solid State Chem. 178, 2452-2474 and Appendix 7. All the interpenetrating nets have the topology of diamond (dia) net. Remember that you may construct Hopf ring net to strictly determine the method of catenation (see Appendix 2 and Module 4).

(5) Close the ADS window and use IsoCryst to draw the interpenetrating array of nets.
Example 2: Analysis of a H-bonded net for XEMZUK, 4,4'-Bipyridinium pentachloro-iron.

Algorithm:
(1) Go to XEMZUK record. Run AutoCN with the default options to compute the adjacency matrix. From the output you see that there are Hb (hydrogen bonds) involving Cl1 and H1, H2.

![Output from AutoCN showing adjacency matrix and coordination numbers]

(2) Plot the structure with IsoCryst.

![Structure plotted with IsoCryst]

At first look the structure appears complicated, so it will be very useful to proceed with the Simplify Adjacency Matrix procedure eliminating all the 0 and 1 connected atoms, keeping the H-bonds. Store the simplified structure in a new database XEMZUK and rename/add comments in the Formula field, to keep track of all the operations.
(3) Display the simplified structure with IsoCryst. Grow the network (type few times Ctrl+W) then select the subnets after activate the button "select polimeric chain". Three different selections are possible: yellow just clicking on one atom, green with Shift+click, magenta with Ctrl+click (If you need more than 3 colours you will learn later how to get them, at the present just select all the subnets repeating the 3 colours). For XEMZUK we see that 3 colours are enough to select all the subnets. A possible entanglement (interpenetration or polycatenation) is present.

(4) Close IsoCryst and open an ADS window. In the Common tab of ADS options check Save Simplified Net (Simplification method = Standard). In our example the H-bonds are connecting isolated molecules, so the node of the network will be the barycenter of the molecule. Therefore we must select for Bond types Valence = At. and H bonds = Mol. (all the others are None).
(5) Now run ADS and click **Whole Molecule** in the window **Choose Central Atoms**, so the whole molecule is represented by its barycenter. XEMZUK is formed by two molecules/ions \([\text{FeCl}_5]^2-\) and \([\text{bipyH}_2]^2+\) 1:1. The ADS simplification will describe the net with two nodes, one is called ZA for the centroid of \([\text{bipyH}_2]^2+\) and the other is ZB for the centroid of \([\text{FeCl}_5]^2-\). Both nodes are 4-connected. Classify the underlying net with ADS program. Open an ADS window/ADS options and set the **Classification** in **Topology** tab. Pay attention that you cannot use the **Save Simplified Net** and **Classification** options into one step (at the same time), answer **Yes** in appearing window **Confirm**. Now run ADS and select all atoms in the window **Choose Central Atoms**.

From the output is already possible to see that the structure is interpenetrated. What symmetry operations relate the three interpenetrating **pts** nets?

---

**3D framework with ZA2B**

There are 3 interpenetrating nets

**FIV: Full interpenetration vectors**

\([0,1/2,1/2]\) (6.88Å)
\([0,1/2,-1/2]\) (6.88Å)

**PIC: \([0,3/2,3/2]\) \([0,3/2,3/2]\) \([0,1,0]\) \([0,0,0]\) (PICVR=3)**

\(Z_t=3; Z_n=1\)

**Class Ia  \(Z=3\)**

92
Coordination sequences
--------------------
ZA1:  1  2  3  4   5   6   7   8   9  10
Num   4 10 24 42  64  92 124 162 204 252
Cum   5 15 39 81 145 237 361 523 727 979
--------------------
ZB1:  1  2  3  4   5   6   7   8   9  10
Num   4 10 24 42  64  90 124 162 204 250
Cum   5 15 39 81 145 235 359 521 725 975
--------------------
TD10=977

Vertex symbols for selected sublattice
--------------------------------------
ZA1 Point symbol:{4^2.8^4}
Extended point symbol: [4.4.8(2).8(8).8(8)]
--------------------------------------
ZB1 Point symbol:{4^2.8^4}
Extended point symbol: [4.4.8(7).8(7).8(7).8(7)]
--------------------------------------
Point symbol for net: {4^2.8^4}
4,4-c net with stoichiometry (4-c)(4-c); 2-nodal net
Topological type: pts PtS, Cooperite; sqc183 (topos&RCRR.tdd) {4^2.8^4} - VS
[4.4.8(7).8(7).8(7).8(7)] [4.4.8(2).8(2).8(8).8(8)] (76154 types in 11 databases)

(5) Display the new fully simplified network from the XEMZUK_c database and select the subnets to show that they are just 3.

Exercise: Analyze the interpenetration in SAVMUB01, bis(benzene-1,3,5-tricarboxylic acid) tris(1,2-bis(4-pyridyl)ethane). What bonds provide the three-periodic array? Determine the interpenetration parameters and topological type of nets. Simplify the structure and plot it in IsoCryst drawing different nets by different colors as shown below.

Answer: Molecules are connected with H-bonds to construct 18 interpenetrated frameworks. The two step simplification for H-bonded net is needed. Resulting 18-fold underling nets srs are related by translational (4 partial interpenetration vectors) and non-translational ("-1") symmetry operations according to class of interpenetration IIIb.
To paint a net with a non-standard color, select it, toggle to the Magic Wand tool \( \mathcal{M} \) and click on any atom of the selected net. In the Magic Wand window toggle to Selected mode to apply the action to selected atoms only, then open the Change Color window and select a color. Click Ok and unselect all the atoms.

This net array is a rare example when some nets of the array have no atom in a given unit cell. Therefore, starting from a single unit cell and growing the structure you will not get all nets in the picture. To show all of them, start from a set of unit cells specifying non-zero values for the IsoCryst Translations parameters.
Task 2: Analysis of self-catenation.

Tools: the programs AutoCN, ADS and IsoCryst.

Example: Analysis of self-catenation in coesite, SiO$_2$.

Algorithm:
(1) Go to the SiO$_2$/Coesite (the database entangle) record and compute the adjacency matrix.
(2) Open an ADS window and check the option Write Data to .tnt to store the information on rings in the file entangle_r.tnt and the option Entanglement to find entanglements.

(3) Run ADS and select all atoms as central. You will get the output with the following fragments:

---

Circuit No 5; Type=16a; Centroid: (0.000,0.000,0.500)

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>0.0000</td>
<td>0.0000</td>
<td>1.0000</td>
</tr>
<tr>
<td>Si1</td>
<td>0.1404</td>
<td>0.1083</td>
<td>0.5724</td>
</tr>
<tr>
<td>O3</td>
<td>0.2664</td>
<td>0.1231</td>
<td>0.9402</td>
</tr>
<tr>
<td>Si2</td>
<td>0.4933</td>
<td>0.1580</td>
<td>0.9594</td>
</tr>
<tr>
<td>O2</td>
<td>0.5000</td>
<td>0.1162</td>
<td>0.7500</td>
</tr>
<tr>
<td>O4</td>
<td>0.3109</td>
<td>0.1037</td>
<td>0.3280</td>
</tr>
<tr>
<td>Si1</td>
<td>0.1404</td>
<td>0.1083</td>
<td>0.0724</td>
</tr>
<tr>
<td>O1</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Si1</td>
<td>-0.1404</td>
<td>-0.1083</td>
<td>0.4276</td>
</tr>
<tr>
<td>O3</td>
<td>-0.2664</td>
<td>-0.1231</td>
<td>0.0598</td>
</tr>
<tr>
<td>Si2</td>
<td>-0.4933</td>
<td>-0.1580</td>
<td>0.0406</td>
</tr>
<tr>
<td>O2</td>
<td>-0.5000</td>
<td>-0.1162</td>
<td>0.2500</td>
</tr>
<tr>
<td>O4</td>
<td>-0.3109</td>
<td>-0.1037</td>
<td>0.6720</td>
</tr>
<tr>
<td>Si1</td>
<td>-0.1404</td>
<td>-0.1083</td>
<td>0.9276</td>
</tr>
</tbody>
</table>

Crossed with bonds

<table>
<thead>
<tr>
<th>No</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Dist.</th>
<th>N Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>*</td>
<td>O1</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.5000</td>
<td>Si1</td>
<td>0.1404</td>
<td>-0.1083</td>
<td>0.5724</td>
<td>1.595</td>
<td>16a/6 16a/6</td>
</tr>
<tr>
<td>*</td>
<td>O1</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.5000</td>
<td>Si1</td>
<td>-0.1404</td>
<td>0.1083</td>
<td>0.4276</td>
<td>1.595</td>
<td>16a/6 16a/6</td>
</tr>
</tbody>
</table>

Ring links

Cycle 1 | Cycle 2 | Chain | Cross | Link | Hopf | Loop | Mult
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>16a</td>
<td>16a</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>8+8</td>
<td>2</td>
</tr>
</tbody>
</table>

---
The first part of the output indicates that 16a-circuit is crossed by two Si1–O1 bonds; each bond belongs to two other 16a-circuits, and each 16a-circuit is connected with the crossed 16a-circuit by a shortest chain of 6 bonds. The asterisk * at the beginning of each line means that the crossing circuits/rings are linked together (belong to the same structure group). Pay attention that in this session Max. Ring = 0, i.e. we consider entanglements between circuits, not rings.

The last part contains the summary table on all types of circuits/rings crossings. We see that there is only one type of crossing: between 16a-circuits; the circuits are interconnected by a shortest chain of 6 bonds; each circuit crosses another circuit one time forming one link (knot) of Hopf type; each circuit is crossed by two other circuits (Mult = 2).

(4) Draw the knots in IsoCryst. For this purpose, click Image/Rings (on the top of the ADS window), expand the tree and grow the structure several (seven) times to get all records bold in the Tint file data window. Select 16a-ring and one of the Hopf links and click the Apply button. You will get two interweaved rings (Hopf link) in the picture.

Select both Hopf links in the list and click Apply again. You will plot both circuits/rings crossing a given one.

Use the Magic Wand tool to paint the atoms in red. Unselect magenta circuits (Ctrl-right-click) and paint the central circuit in green. Grow the structure one time. Select the central circuit and repeat growth. Repeat selecting and growing until the crossing rings are united by chains of bonds. Be sure that the shortest chain between crossing circuits contains 6 bonds.
Select the crossing rings again using the **Tint file data** window. Pay attention that if you have accidentally closed the window you may open it again using **Select/Load Tint File** command. Use **Select/Complement Selection** to toggle the selection.
Apply **Sphere and Wire** model to the selected atoms. Now you see more clearly the entangled part of the structure.

**Exercise:** Analyze the self-catenation in XASDUQ, bis(µ₂-2-ethylpyrazine-N,N')-Ag(I) hexafluoroantimonate in database entangle. The structure is already simplified.

**Answer:** Ring links are formed with 8c circles (that are also rings); the shortest chain between them contain 3 bonds; each circuit crosses another circuit one time forming one link of Hopf type; each circuit is crossed by two other circuits… so you recognize that this net is again **coe**.

<table>
<thead>
<tr>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Chain</th>
<th>Cross</th>
<th>Link</th>
<th>Hopf</th>
<th>Loop</th>
<th>Mult</th>
</tr>
</thead>
<tbody>
<tr>
<td>8c</td>
<td>8c</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>
Task 3: Analysis of catenation, polycatenation, low-dimensional interpenetration and polythreading.

Tools: the programs AutoCN, ADS and IsoCryst.

Example 1: Analysis of 0D catenation in CIVBOY.

Algorithm:
(1) Go to the CIVBOY (database entangle) record and compute the adjacency matrix. Using IsoCryst look at the structure that seems weird. Is composed of cyclic complex molecules.

(2) Click on one atom and get one single macrocycle.

(2) Duplicate the record and simplify the structure removing 0- and 1-coordinated atoms (add some information on the Formula field to keep track of all the modifications).
(3) Open the CIVBOY simplified record and compute entanglements with ADS selecting All Atoms as central. Pay attention to some fragments of the output.

Circuit No 19; Type=25g; Centroid: (0.743,0.635,0.279)

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.1515</td>
</tr>
<tr>
<td>C49</td>
<td>0.5002</td>
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</tr>
<tr>
<td>C50</td>
<td>0.4261</td>
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<tr>
<td>O3</td>
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<td>0.1723</td>
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<td>C51</td>
<td>0.4465</td>
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<td>0.2057</td>
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<tr>
<td>C53</td>
<td>0.4123</td>
<td>0.4973</td>
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<td>C55</td>
<td>0.4513</td>
<td>0.4484</td>
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<td>C56</td>
<td>0.5239</td>
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<td>C57</td>
<td>0.5605</td>
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<tr>
<td>C58</td>
<td>0.6619</td>
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<td>0.3239</td>
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<tr>
<td>C60</td>
<td>0.7065</td>
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<td>C62</td>
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<td>0.3861</td>
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<tr>
<td>C63</td>
<td>0.8473</td>
<td>0.4449</td>
<td>0.3767</td>
</tr>
<tr>
<td>C64</td>
<td>0.9372</td>
<td>0.4635</td>
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</tr>
<tr>
<td>C66</td>
<td>1.0401</td>
<td>0.6561</td>
<td>0.3713</td>
</tr>
<tr>
<td>Au4</td>
<td>0.9775</td>
<td>0.7340</td>
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</tr>
<tr>
<td>C70</td>
<td>1.1146</td>
<td>0.8180</td>
<td>0.2506</td>
</tr>
<tr>
<td>C69</td>
<td>0.9229</td>
<td>0.8521</td>
<td>0.3153</td>
</tr>
<tr>
<td>C68</td>
<td>0.9734</td>
<td>0.8966</td>
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<td>C67</td>
<td>0.8917</td>
<td>0.9154</td>
<td>0.2350</td>
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<tr>
<td>P3</td>
<td>0.7454</td>
<td>0.9836</td>
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</tr>
<tr>
<td>Au3</td>
<td>0.6449</td>
<td>0.8492</td>
<td>0.1925</td>
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Crossed with bonds

<table>
<thead>
<tr>
<th>No</th>
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<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>Dist.</th>
<th>N Cycles</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.6890</td>
<td>0.3074</td>
<td>C22</td>
<td>0.7590</td>
<td>0.6400</td>
<td>0.2370</td>
<td>1.507</td>
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Ring links

<table>
<thead>
<tr>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Chain</th>
<th>Cross</th>
<th>Link</th>
<th>Hopf</th>
<th>Loop</th>
<th>Mult</th>
</tr>
</thead>
<tbody>
<tr>
<td>25a</td>
<td>25e</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25a</td>
<td>25f</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25a</td>
<td>25g</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25a</td>
<td>25h</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25b</td>
<td>25e</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25b</td>
<td>25f</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25b</td>
<td>25g</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25b</td>
<td>25h</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25c</td>
<td>25e</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25c</td>
<td>25f</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25c</td>
<td>25g</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25c</td>
<td>25h</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25d</td>
<td>25e</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25d</td>
<td>25f</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25d</td>
<td>25g</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25d</td>
<td>25h</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25e</td>
<td>25a</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25e</td>
<td>25b</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25e</td>
<td>25c</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25e</td>
<td>25d</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25f</td>
<td>25a</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25f</td>
<td>25b</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
<tr>
<td>25f</td>
<td>25c</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td>6+6</td>
<td>1</td>
</tr>
</tbody>
</table>
We see that crossing 25-circuits do not linked together (the shortest chain between them is ‘infinite’, \textit{inf}). So this is a real catenation. Pay attention that although there are two independent macrocycles (how to confirm it with ToposPro?) the number of 25-circuits is 8 (25a..25h) because in each macrocycle one can find four 25-circuits differently passing through the benzene rings.

(4) Draw the catenating circuits with the ADS command \texttt{Image/Rings}. Draw other atoms belonging to the catenating molecules. Be sure that the molecules are really not connected with each other.
**Example 2**: Analysis of 1D+1D→3D polycatenation in **SEQMUW**, [Cd₂L₃(NO₃)₄]·G (L = (μ₂-1,4-bis(4-pyridylmethyl)benzene), G = 1,4-dibromobenzene).

**Algorithm:**
(1) Go to the **SEQMUW** record and compute the adjacency matrix. It is a ladder coordination polymer.

(2) Simplify the crystal structure in the standard representation (Choose as central atom the metal Cd and the ligand will be represented by its barycenter). Remove 0- and 1-coordinated atoms in the simplified structure (see figure above right). The 2-coordinated atoms should be retained because they often play an important role in forming catenation.

(3) Open an ADS window for the simplified structure and check the following ADS options.

(4) Run ADS. You will get the following output.

```
Ring links

Cycle 1 | Cycle 2 | Chain | Cross | Link | Hopf | Loop | Mult
--------|--------|-------|-------|------|------|------|-------
 8a     | 8a     | inf.  | 1     | 1    | *    | 4+4  | 4
 8a     | 12a    | inf.  | 1     | 1    | *    | 4+4  | 8
12a     | 8a     | inf.  | 1     | 1    | *    | 4+4  | 8
12a     | 12a    | inf.  | 1     | 1    | *    | 6+6  | 16

Polycatenation

Groups
1: 1D, ZA2ZB3 (Zt=1); [1,1,0]; [1,-1,0]

Types

<table>
<thead>
<tr>
<th>Group 1</th>
<th>Orient.</th>
<th>Group 2</th>
<th>Orient.</th>
<th>Angle</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,1,0</td>
<td>1</td>
<td>1,-1,0</td>
<td>85.0</td>
<td>1D+1D, inclined; zone=[0,0,1]</td>
</tr>
</tbody>
</table>
```
ADS informs you that there is a **polycatenation** 1D+1D between two chains [110] and [1 1 0] with the angle 85.0° between the chain directions. So the polycatenation is **inclined**, not parallel. Pay attention that ADS does not recognize **polycatenation** and **low-dimensional interpenetration**; in the former case the resulting extended array of entangled nets has a higher dimensionality than each of the nets, in the latter case the dimensionalities coincide. At the same time **inclined** entanglement is always a **polycatenation**. About other differences between polycatenation and interpenetration see “Polycatenation, polythreading and polyknotting in coordination network chemistry” Carlucci L., Ciani G. & Proserpio D. M. (2003). *Coord Chem. Rev.* **246**, 247-289 and **Appendix 8**.

(5) To ensure that the array has an increased dimensionality, run IsoCryst and find catenating ladders.

![Image](image1.png)

To ensure that the ladders form an infinite array use **Select/Translation** tool and enter *1,1,1* to generate the copies if the selected ladders by all translations in the range from 1 1 1 to 1 1 1 (i.e. 1 1 1, 1 1 0, 1 1 1, etc.). If you want to generate only one copy of selected atoms by a separate translation, omit asterisk, i.e. enter 1,1,1 to generate one copy by the 1,1,1 translation.

![Image](image2.png)

It is easy to see for the picture after some rotation that the final entanglement is a 3D array. We cannot find any plane that separates it in disjoint parts.

(6) Try to simplify the structure more by contracting 2-coordinated atoms. Does the simplification influence the polycatenation in this case?
**Example 3:** Analysis of 2D+2D→3D inclined polycatenation in CAFSUY, [CuL2(NO3)2]·G (L = (μ-1,4-bis(4-pyridyl)butadiyne), G = dichloromethane).

**Algorithm:**
(1) Go to the CAFSUY record and do the same procedures as in Example 2. You should get an output like follows.

---

**Ring links**

<table>
<thead>
<tr>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Chain</th>
<th>Cross</th>
<th>Link</th>
<th>Hopf</th>
<th>Loop</th>
<th>Mult</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>4a</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>4a</td>
<td>4a</td>
<td>inf.</td>
<td>2</td>
<td>0</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>4a</td>
<td>6a</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>4a</td>
<td>6a</td>
<td>inf.</td>
<td>2</td>
<td>0</td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>6a</td>
<td>4a</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>6a</td>
<td>4a</td>
<td>inf.</td>
<td>2</td>
<td>0</td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>6a</td>
<td>6a</td>
<td>inf.</td>
<td>1</td>
<td>1</td>
<td>*</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>6a</td>
<td>6a</td>
<td>inf.</td>
<td>2</td>
<td>0</td>
<td></td>
<td></td>
<td>8</td>
</tr>
</tbody>
</table>

---

**Polycatenation**

Groups

1: 2D, Cu (Zt=1); (2,0,-1); (2,0,1)

Types

<table>
<thead>
<tr>
<th>Group 1</th>
<th>Orient.</th>
<th>Group 2</th>
<th>Orient.</th>
<th>Angle</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,0,-1</td>
<td>1</td>
<td>2,0,1</td>
<td>77.4</td>
<td>2D+2D, inclined; zone=[0,1,0]</td>
</tr>
</tbody>
</table>

Here there is 2D+2D→3D polycatenation of (201) and (201) two-periodic nets with dihedral angle 77.4°. The planes cross through the line [010].

(2) Draw the catenating nets in IsoCryst.

(3) Simplify the structure removing the 2-coordinated nodes. Run ADS with the Classification flag checked. You will find that the catenating nets belong to the topological type sql.

**Topological type:** sql/Shubnikov tetragonal plane net \{4^4;6^2\} - VS \{4.4.4.4.*.*\} (66833 types in 9 databases)
(4) A more detailed classification could be done running ADS on the fully simplified sql nets obtained in the previous step. This time check also the Max. Ring, giving a value of 10, so only the catenation among rings (excluding the 6-circuits analogues of the 12-circuits above) will be computed.

<table>
<thead>
<tr>
<th>Ring links</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle 1</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>4a</td>
</tr>
<tr>
<td>4a</td>
</tr>
</tbody>
</table>

Polycatenation
---------------
Groups
1: 2D, Cu (Zt=1); (2,0,-1); (2,0,1)

Types
-----------------------------------
Group 1 | Orient. | Group 2 | Orient. | Angle | Type
-----------------------------------
1 | 2,0,-1 | 1 | 2,0,1 | 77.4 | 2D+2D, inclined; zone=[0,1,0]

You see here that there are listed two kinds of possible ring links, only one is Hopf. If you draw them you will see the difference, on the left the 4-4 Non-Hopf, on the right the 4-4 Hopf link:

Moreover from the picture we can see that the square intersect diagonal-diagonal (d-d type) and with a bit of practice you can also show that 2 sql are catenated by each 4-ring in one given sql: it follows that the Density of catenation (doc) is 2/2 (This is reflected in the Mult.= 4 of the Hopf links in the table above).
**Example 4**: Analysis of 2D+2D→2D borromean entanglement in GUWXIF, [Ni(µ-t-cyc)]₃L₂·6G·4H₂O (cyc = cyclam, L = (1,3,5-tris(2-(4-carboxyphenyl)-1-ethynyl)benzene), G = pyridine).

**Algorithm**:

1. Go to the GUWXIF record and do the same procedures as in Example 2, but also delete 0,1,2-coordinated nodes. You should get an output like follows.

   Topological type: hcb; Shubnikov hexagonal plane net/(6,3) {6³} - VS [6.6.6] (66833 types in 9 databases)

   -------------------------
   Structural group No 1
   -------------------------
   Structure consists of layers (1 0 2) with ZB

   Ring links

<table>
<thead>
<tr>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Chain</th>
<th>Cross</th>
<th>Link</th>
<th>Hopf</th>
<th>Loop</th>
<th>Mult</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>6a</td>
<td>inf.</td>
<td>2</td>
<td>0</td>
<td></td>
<td></td>
<td>6</td>
</tr>
</tbody>
</table>

   You notice that “Polycatenation” is no more detected, we only see that nets have the topology hcb (honeycomb), BUT pay attention that there are no Hopf links in the array, so any pair of the nets do not catenate each other. The nets has the same orientation (102) and, hence, are parallel. This is a sign of a possible borromean entanglement. You should check carefully with IsoCryst to confirm the borromean nature of the entanglement. Read more about borromean entanglements in “Borromean links and other non-conventional links in ‘polycatenated’ coordination polymers: re-examination of some puzzling networks” L. Carlucci, G. Ciani, D. M. Proserpio *CrystEngComm*, 2003, 5(47), 269–279.

2. Run IsoCryst and specify all **Translations** parameters equal to 1 since not all nets have atoms in the initial unit cell. Grow the structure several times to see layers.

   ![Image of IsoCryst interface](image)

   Rotate structure to orient the layers vertically, toggle to **Select atoms in a rectangle region** mode and select a set of parallel layers.
Perform **Show selection only** command and orient the layers along the (102) direction. For this purpose, click the \textbf{hkl} button and enter 1,0,2. Then grow the structure if required and paint the three entangled nets with different colors.

We have so-called **borromean** entanglement when any pair of the three nets do not catenate each other (have no Hopf links), but they are interlinked by a third net. 0D examples of the Hopf link and the borromean link are shown below.

**Exercise:** Study the entanglement in the crystal structure of \textbf{AJOSUN}, ZnL\textsuperscript{3}L\textsubscript{3}(H\textsubscript{2}O); (\(\mu_2\)-terephthalato-O,O')-(\(\mu_2\)-1,4-diazabicyclo(2.2.2)octane-N,N')-aqua-Zn. Is it polycatenation or interpenetration?

**Answer:** Net topology is \textbf{sql}; 2-fold interpenetration, layers are parallel in orientation 0,1,0; Hopf links is for 4-rings.
**Z - Total degree of interpenetration**  
Total number of 3D interpenetrating nets. It is the product of translational \((Z_t)\), and non-translational \((Z_n)\) interpenetration.

**FIV - Full interpenetration vector**  
The shortest vector defining the direction along which all the interpenetrating nets exactly superimpose and that, applied \(Z-1\) times to a single net, generates the whole entanglement.

**TIV – Translation interpenetration vector**  
When translational \((Z_t>1)\) and non-translational \((Z_n>1)\) operations are present we called TIV the shortest vector that relates all the \(Z_t\) interpenetrating nets.

**PIV – Partial interpenetration vectors**  
When there is no FIV or TIV but more than one translational operation, different partial interpenetration vectors (PIVs) relate subgroups of \(Z_p\) independent nets. PIVs could be of two kinds: \(Z_{it}\) for integral translations and \(Z_{ct}\) for centering translations.

**FISE - Full interpenetration symmetry element**  
Single space group symmetry element that generates all \(Z\) equivalent interpenetrating nets. No translational operations relating the nets are present (no FIV, TIV or PIV). The only \(Z\) allowed are 2, 3, 4, 6.

**NISE - Non-translating interpenetration symmetry element**  
When \(Z_t>1\) (TIV is present) a NISE symmetry element can exist that generates all \(Z_n\) interpenetrating nets.

**PISE - Partial interpenetration symmetry element**  
Any space group symmetry element that generates \(Z_s\) (two or more) equivalent interpenetrating nets (but not all \(Z_n\) nets). If \(Z_s=Z_n\) PISE is equivalent to NISE \((Z_t>1)\) or to FISE \((Z_t=1)\).

**PIC - Primitive interpenetration cell**  
Any cell that contains the same number of atoms for each individual (coloured) net is an “interpenetration cell”. Among the possible minimum volume interpenetration cells we select the PIC as the one based on the vectors between atoms of the same net. Thus, PIC can be considered as the minimum primitive crystallographic cell constructed with one of the nets, i.e. the primitive cell to be assigned to the structure if it contains a single network.

**PICVR - PIC volume ratio**  
The ratio of the PIC volume \((V_{PIC})\) divided by the primitive unit cell volume \((V_0)\), \(PICVR=V_{PIC}/V_0\). PICVR is integer, greater than or equal to unity.

<table>
<thead>
<tr>
<th>Class</th>
<th>Nets relationships</th>
<th>(Z)</th>
<th>PICVR</th>
<th>Sub-class</th>
<th>Interp. Vector</th>
<th>Symm. Elem.</th>
<th>(Z) symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Only translations (integral or centering)</td>
<td>(Z_t)</td>
<td>(= Z)</td>
<td>Ia</td>
<td>FIV</td>
<td>none</td>
<td>(Z_t)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ib</td>
<td>PIV</td>
<td>none</td>
<td>(Z(\sum Z_{it} \ast \sum Z_{ct}))</td>
</tr>
<tr>
<td>II</td>
<td>Space group symmetry operations</td>
<td>(Z_n)</td>
<td>(= 1)</td>
<td>IIa</td>
<td>none</td>
<td>FISE</td>
<td>(Z_n)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>I Ib</td>
<td>none</td>
<td>PISE</td>
<td>(Z(\prod Z_{it}))</td>
</tr>
<tr>
<td>III</td>
<td>Translations + symmetry operations</td>
<td>(Z_t \times Z_n)</td>
<td>(= Z_t)</td>
<td>IIIa</td>
<td>TIV</td>
<td>NISE</td>
<td>(Z(Z_t \ast Z_n))</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IIIb</td>
<td>PIV</td>
<td>NISE</td>
<td>(Z(\sum Z_{it} \ast \sum Z_{ct}) \ast Z_n)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IIIc</td>
<td>TIV</td>
<td>PISE</td>
<td>(Z(Z_n \ast \prod Z_{it}))</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IIId</td>
<td>PIV</td>
<td>PISE</td>
<td>(Z(\sum Z_{it} \ast \sum Z_{ct}) \ast \prod Z_{it}))</td>
</tr>
</tbody>
</table>
# Appendix 8. Interpenetration vs. polycatenation

<table>
<thead>
<tr>
<th>Interpenetration</th>
<th>Polycatenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>The component motifs are infinitely extended 1D, 2D or 3D nets</td>
<td>The motifs can be 0D and 1D (with closed circuits) or 2D, of the same or of different types</td>
</tr>
<tr>
<td>The individual motifs have an identical topology</td>
<td>The individual motifs may have different topology</td>
</tr>
<tr>
<td>The number of the entangled motifs is finite</td>
<td>Infinite number of entangled motifs</td>
</tr>
<tr>
<td>The resulting dimensionality is the same of the component motifs</td>
<td>The resulting dimensionality is increased (for at least one motif)</td>
</tr>
<tr>
<td>Each motif is interlaced with all the other ones forming the array</td>
<td>Each motif is never interlaced with all the other ones of the array</td>
</tr>
</tbody>
</table>

The resulting entangled array is infinite periodic

---

**Inextricable Entanglement via Hopf links**

- **Interpenetration**
  - Dimensionality unchanged: **INTERPENETRATION**
  - $1D + 1D \Rightarrow 1D$
  - $2D + 2D$ (parallel) $\Rightarrow 2D$
  - $3D + 3D \Rightarrow 3D$
  - $kD + kD \Rightarrow kD$
  - $mD + nD \Rightarrow kD$ where $m \leq k ; n < k$
  - The whole has the SAME dimensionality of the components
  - The number of entangled components is finite ($n$-fold)
  - Each component is interlaced with ALL the others

- **Polycatenation**
  - Increase of dimensionality: **POLYCATENATION**
  - $0D + 0D \Rightarrow 1D, 2D$ or $3D$
  - $0D + 1D \Rightarrow 1D, 2D$ or $3D$
  - $0D + 2D \Rightarrow 2D$ or $3D$
  - $0D + 3D \Rightarrow 3D$
  - $1D + 1D \Rightarrow 2D$ or $3D$
  - $1D + 2D \Rightarrow 2D$
  - $1D + 3D \Rightarrow 3D$
  - $2D + 2D$ (inclined) $\Rightarrow 3D$
  - $2D + 2D$ (parallel) $\Rightarrow 3D$
  - $2D + 3D \Rightarrow 3D$
  - The whole has HIGHER dimensionality of at least one component
  - The number of entangled components is infinite
  - At least one component is not interlaced with all the others
Module 7. Working with the program ADS. Computing and analyzing natural tilings.

**Task:** Computing natural tiling, dual net, determining combinatorial types of tiles, visualizing tiles, storing the information for the 3dt program.

**Tools:** the programs ADS and IsoCryst.

**Example 1:** Computing the natural tiling for the zeolite LTA, visualizing tiles and storing the information for the 3dt program.

**Algorithm:**

1. Open the database LTA_SOD and open an ADS window for the first record (Si framework for the zeolite LTA). Specify the ADS options in Common, Topology and Tiling tabs as shown below. The options Write Data to .tnt and Essential Rings for 3dt provide the information for visualizing tiles in IsoCryst and 3dt, respectively. The information will be stored in the files LTA_SOD_t.tnt and LTA_SOD_3dt.cgd, respectively. The option All Rings ensures that all rings up to size Max. Ring, not only the shortest, will be found. In the Tiling tab specify first the maximal number of tile faces (Max. Tile Size = 200 is sufficient for most of nets), then check Natural Tiles. Other options to obey the natural tiling rules will be checked automatically.

   ![ADS Options](image)

2. Run ADS and select all atoms in the Choose Central Atoms window. You will get the following output:

   ![Choose Central Atoms](image)


(a) the tiling must have the symmetry of the net (be *proper*);
(b) the faces of tiles must be locally strong rings (no tile has one face larger than the rest);
(c) a tile does not have non-face strong rings that do not intersect other such rings;
(d) when rules (a)-(c) result in multiple tilings because of intersecting strong rings, we use only the smaller of a pair if the intersecting rings are unequal in size and reject both if the intersecting rings are equal in size.

(2) Run ADS and select all atoms in the **Choose Central Atoms** window. You will get the following output:
Vertex symbols for selected sublattice

--------------------------------------
Si1 Point symbol: {4^3;6^2;8}
With circuits: [4.6.4.6.4.8(3)]
With rings: [4.6.4.6.4.8]
All rings (up to 12): [(4,6),(6,12(3)),(4,6),(6,12(3)),(4,6,12(2)),8]
All rings with types: [(4b,6a),(6b,12a(3),12b),(4b,6a),(6b,12a(3),12b),(4a,6a,12a(2))]

Point symbol for net: {4^3.6^2.8}
4-c net; uninodal net

Database with topological types was not loaded. Check 'Classification' flag.

Essential rings by homocrossing: 4a,4b,6b,8
Inessential rings by homocrossing: 6a,12a,12b

Primal proper tiling No 1

Essential rings by heterocrossing: 4a,4b,6b,8
Inessential rings by heterocrossing: none

8/6:[4^6]; [4a^2.4b^4]; Centroid: (0.000, 0.000, 0.500); Volume=29.622; G3=0.083349
24/14:[4^6.6^8]; [4a^6.6b^8]; Centroid: (0.000, 0.000, 0.000); Volume=336.020; G3=0.078576
48/26:[4^12.6^8.8^6]; [4b^12.6b^8.8^6]; Centroid: (0.500, 0.500, 0.500); Volume=1268.358; G3=0.077817

Tiling: 3[4^6]+[4^6.6^8]+[4^12.6^8.8^6] = 3[4a^2.4b^4]+[4a^6.6b^8]+[4b^12.6b^8.8^6]
Transitivity: [1343]
Simple tiling
D-size: 12
Average ring size: 4.97

All proper tilings (S=simple)
Rules a,b,c,d are applied

<table>
<thead>
<tr>
<th>Tiling</th>
<th>Essential rings</th>
<th>Transitivity</th>
<th>D-size</th>
<th>Ring Size</th>
<th>Comments</th>
<th>Tiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPT 1/NT</td>
<td>4a,4b,6b,8a</td>
<td>[1343]</td>
<td>12</td>
<td>4.97</td>
<td>MPT S</td>
<td>3[4^6]+[4^6.6^8]+[4^12.6^8.8^6]</td>
</tr>
</tbody>
</table>

Elapsed time: 7.36 sec.

The line **All rings (up to 12)** means that not only 4-, 6- or 8-rings, but also larger 12-rings meet at the same angle of the node. The **all ring VS** could be reported as: [(4,6),(6,12),(4,6),(6,12),(4,6,12)],.8. Moreover, 6- and 12-rings are not all equivalent by symmetry. ToposPro distinguishes them in the line **All rings with types** by uniting in equivalent groups. The groups are designated by one or more letters: a-z, aa-az, ba-bz, etc, e.g. 4a, 12ab, 20xaz. As a result, an **all-ring labelled VS** is calculated. Here there are two inequivalent 6-rings, 6a and 6b, and two inequivalent 12-rings, 12a and 12b. Not all rings are **essential**, i.e. are tile faces. In this case the whole tiling is constructed of four kinds of rings: 4a, 4b, 6b and 8. There are three kinds of tiles in the natural tiling: [4^6], [4^6.6^8] and [4^12.6^8.8^6]. The line corresponding to each tile contains the following information on the tile:

8/6: [4^6]; [4a^2.4b^4]; Centroid: (0.000, 0.000, 0.500); Volume=29.622; G3=0.083349

8/6 – number of vertices/faces;
[4^6] – face symbol, [4^6];
[4a^2.4b^4] – face symbol with ring types;
Centroid – coordinates of the center of gravity;
Volume – volume, Å³;
G3 – normalized second moment of inertia, G3.

The line **Tiling** shows the formula of the tiling: the stoichiometric ratio [4^6]:[4^6.6^8]:[4^12.6^8.8^6] = 3:1:1.
**Transitivity** give the transitivity of the tiling p.q.r.s, where p, q, r and s are numbers of inequivalent vertices, edges, faces and tiles in the tiling.
Some other features of the tiling are indicated, in particular, this tiling is **simple**. The table consolidates the main data on all possible **proper** tilings, the NT label indicates natural tiling.

(3) Perform **Image** command to invoke IsoCryst.
(4) Grow the net several times until the PPT label in the Tint file data window becomes bold. This means that all vertices of the tiles are shown in the picture.

(5) Go to the Tint file data window, expand the tiling tree, select a tile and click Apply button. You will get the main cavity (α-cage) in the LTA framework.

(6) Expand the tiling tree. Hold down the “ctrl” and choose all tiles and click Apply again. All tiles will be shown.
(7) Check that all atoms were not selected. Grow up a structure (2 clicks). In the Tint window select the option **Hide none** (all the tiles must still be selected). In IsoCryst three tiles will be selected. Use a magic wand and change the color of the selected atoms.

Further, use Cylinder model. Then deselect all atoms. Three types of tiles will show as green.

(8) Close the IsoCryst and ADS windows and run the 3dt program ([http://www.gavrog.org](http://www.gavrog.org)). Use the *LTA_SOD_3dt.cgd* file to draw the tiling.
**Example 2:** Computing natural tiling, dual net, determining combinatorial types of tiles for the zeolite SOD (sodalite).

**Algorithm:**
1. Go to the SOD record and open an ADS window. Check **Dual Nets, Determine Tile Topology** and **Save Tile Topology** flags (The flags on the **Common** tab and on the **Topology** tab are the same that in the Example 1).

2. Run ADS. Reply "No" to append the information on the tiling to the *LTA_SOD_3dt.cgd* file.

3. Create the database **LTA_SOD#** to save the data on the dual net.

4. Overwrite the *LTA_SOD_t.tnt* file.
(5) Choose all atoms in the **Choose Central Atoms** window and save all new combinatorial types of tiles (they will be stored in **Polyhedron Library** in the current folder with the name **tile_lib** by default).

(6) Pay attention that a new database is created with the record **SOD/sod;PPT 1** containing both initial **sod** and dual net. The nodes of the dual net are designated as **ZA**. The degree of the node is 14 (equal to the number of faces in the sodalite cage).

(7) Determine the topology of the dual net. For this purpose, open one more ADS window, uncheck all **Common** options and check **Classification** flag. Run ADS. Select all atoms as central. You will get the output:

```
------------------------
Structural group No 1
------------------------
Structure consists of 3D framework with Si

Coordination sequences
----------------------
Si1:  1  2  3  4   5   6   7   8   9  10
Num  4 10 20 34  52  74 100 130 164 202
Cum 5 15 35 69 121 195 295 425 589 791

TD10=791

Vertex symbols for selected sublattice
--------------------------------------
Si1 Point symbol:{4^2;6^4}
```
Pay attention that there are two structural units (interpenetrating 3D nets) of the topological types sod (initial net) and bcu-x (dual net).

(8) Close the ADS window and look at the initial and dual nets in IsoCryst. Select the central node of the dual net and grow it one time to get all its neighbors. Pay attention that all edges of the dual net pass through the faces of the tile in the initial net.
(9) Close the IsoCryst window and the database LTA_SOD#, then select both records in the database LTA_SOD. Uncheck Write Data to .tnt and Essential Rings for 3dt options and specify Topology and Tiling options as shown below. Uncheck Continuous/Standard Ring Limits option to speed up the calculation (the rings up to size 8 will be checked only). Specify Continuous/Central Atoms = E1.

(10) Run ADS. Pay attention that now ADS has determined the $[4^6.6^8]$ combinatorial type (truncated octahedron) both in SOD and in LTA.

$$24/14: [4^6.6^8]; [4^6.6b^8]$$; Type: $[4^6.6^8]$

To let ADS recognize other combinatorial types in LTA you have to check Save Tile Topology flag and store the types in Polyhedron Library.

**Exercise:** compute the natural tiling and dual net for your own crystal structure simplified in Module 4.

**Example 3:** Computing dual net and determining migration paths of cations in the $\alpha$-KAIO$_2$ crystal structure.

**Algorithm:**
(1) Open the database KAIO2, the record KAIO2/alpha and compute the adjacency matrix in the Domains mode with MinOm=5 (to consider only strong bonds).
(2) Open an ADS window and check Dual Nets flag. Run ADS.
(3) In the **Choose Central Atoms** window select all but potassium atoms to build the tiling for the framework only, ignoring mobile cations. Click **Ok**.

(4) Run IsoCryst for the record in the resulting **KAlO2#** database and be sure that the nodes of the dual net (ZA) almost coincide with the positions of potassium cations. For this purpose, specify the radius of potassium atoms 1.2Å (that is equal to the default radius of ZA atoms) using IsoCryst options, **Atoms** tab, **Radii** button, then click the **K** button, specify the required value and click the **Apply** and **Ok** buttons.

The result looks like as follows.
(5) Close the IsoCryst window, open the Crystal Data window. The dual net is formed by two types of voids, ZA1 and ZA2. Analyze the channel radii (distances from the edges of the dual net to the oxygen atoms). Break the narrowest channels, where such distances do not exceed 2.2Å. In following Figure example of removing the connection ZA1-ZA2 (for which oxygen is too close) is showed.

After breaking the narrowest channels the voids ZA1 and ZA2 have CN 2 and 3, respectively. Save the changes.

(6) Check with IsoCryst and ADS that the resulting migration map of potassium atoms is two-dimensional (010). Try to draw a picture like as follows.
**Exercise:** analyze in the same way the migration map of \(\beta\)-KAlO\(_2\) (the record KAIO2/beta). What are the channel radii, migration map dimensionality and topology? Which KAlO\(_2\) modification should possess higher ionic conductivity?

**Answer:**
The net of structure \(\beta\)-KAlO\(_2\) (the record KAIO2/beta) is formed by one type of voids ZA1.

The average channel radius is 2.972 Å. The migration map of potassium cation is three-dimensional.

The topology of dual net is dia (check with ADS). The \(\beta\)-KAlO\(_2\) should possess higher ionic conductivity, because his system of migration paths extended into three dimensions.
Module 8. Working with the program Dirichlet. Constructing Dirichlet domains and computing their characteristics.

**Task 1:** Constructing and drawing atomic and molecular Dirichlet domains (Voronoi-Dirichlet polyhedra, VDP).

**Tools:** the programs AutoCN, Dirichlet, ADS and IsoCryst.

**Example 1:** Determination of coordination numbers and oxidation state of uranium atoms in β-U₃O₈.

**Algorithm:**
(1) Open the database Dirichlet. Choose U3O8/beta and compute Adjacency matrix for it. Open a Dirichlet window Program/Dirichlet (or Ctrl-D or click on the menu bar) and use the default options (Click on Default in the Dirichlet Option window).
(2) Run Dirichlet, choose all atoms as sublattice (the atoms that will form faces of Dirichlet domains) and uranium atoms as origin (the atom for which Dirichlet domains will be constructed).

You will get the output like follows.

---

Central atom:U1 CN:7 0.500 0.489 0.250 Rad:1.326
D(CP):0.129 ( 0.5000 0.4778 0.2500 )
D(VDP):0.087 ( 0.5000 0.4814 0.2500 )
Atom:2.014 < r < 2.396 <r>=2.219 Top: 1.714 < R < 1.811 <R>=1.758
CN=7:0 0 0 NV=10 V=9.761/16.864 S=26.610 Cpac=0.438 Ccov=2.548
G3=0.082546286
Face distribution: {4/5 5/2 } Vertex distribution: {3/10 }

Atom   x      y      z     Dist.  SAng.
1  O  3  0.500  0.665  0.250  2.014  16.17
2  O  1  0.500  0.500  0.000  2.080  17.38
3  O  1  0.500  0.500  0.500  2.080  17.38
4  O  4  0.818  0.524  0.250  2.283  12.82
5  O  4  0.182  0.524  0.250  2.283  12.82
6  O  5  0.681  0.312  0.250  2.396  11.71
7  O  5  0.319  0.312  0.250  2.396  11.71

Central atom:U2 CN:7 0.000 0.350 0.250 Rad:1.288
D(CP):0.124 ( 0.0000 0.3609 0.2500 )
D(VDP):0.032 ( 0.0000 0.3528 0.2500 )
Atom:1.885 < r < 2.371 <r>=2.175 Top: 1.688 < R < 1.722 <R>=1.703
CN=7:0 0 NV=10 V=8.952/15.564 S=25.195 Cpac=0.392 Ccov=2.389
G3=0.082546286
Face distribution: {4/5 5/2 } Vertex distribution: {3/10 }

Atom   x      y      z     Dist.  SAng.
1  O  2  0.000  0.352  0.023  1.885  19.50
2  O  2  0.000  0.352  0.477  1.885  19.50
3  O  3  0.000  0.165  0.250  2.117  14.91
4  O  5  0.319  0.312  0.250  2.297  12.20
5  O  5  0.319  0.312  0.250  2.297  12.20
6  O  4  0.182  0.524  0.250  2.371  10.85
7  O  4  0.182  0.524  0.250  2.371  10.85

Central atom:U3 CN:6 0.500 0.832 0.750 Rad:1.350
D(CP): 0.058  ( 0.5000 0.8371 0.7500 )
D(VDP): 0.024  ( 0.5000 0.8299 0.7500 )

Atom: 2.086 < r < 2.278  <r>=2.152   Top: 1.668 < R < 2.050  <R>=1.901
CN=6:0:0  NV=8  V=10.302/12.781  S=28.776  Cpac=0.462  Ccov=3.501
G3=0.085421212
Face distribution: {4/6 }  
Vertex distribution: {3/8 }  

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Dist.</th>
<th>SAng.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O 5</td>
<td>0.681</td>
<td>0.688</td>
<td>0.750</td>
<td>2.086</td>
</tr>
<tr>
<td>2</td>
<td>O 5</td>
<td>0.319</td>
<td>0.688</td>
<td>0.750</td>
<td>2.086</td>
</tr>
<tr>
<td>3</td>
<td>O 4</td>
<td>0.682</td>
<td>0.976</td>
<td>0.750</td>
<td>2.091</td>
</tr>
<tr>
<td>4</td>
<td>O 4</td>
<td>0.318</td>
<td>0.976</td>
<td>0.750</td>
<td>2.091</td>
</tr>
<tr>
<td>5</td>
<td>O 2</td>
<td>0.500</td>
<td>0.852</td>
<td>0.477</td>
<td>2.278</td>
</tr>
<tr>
<td>6</td>
<td>O 2</td>
<td>0.500</td>
<td>0.852</td>
<td>1.023</td>
<td>2.278</td>
</tr>
</tbody>
</table>

Pay attention to the atoms forming the Dirichlet domains; they all have large (> 10%) values of solid angles of corresponding Dirichlet domain faces; this means that all of them are strongly connected with uranium atoms and, hence the coordination numbers of U1, U2 and U3 are 7, 7 and 6, respectively.

Now look at volumes of Dirichlet domains (V, Å³) and corresponding radii of spherical domains (Rsd, Å). They are characteristic for the atoms in a given oxidation state. In particular, for U(IV), U(V) and U(VI) in oxygen environment Rsd=1.39(3), 1.33(1) and 1.30(1) Å, respectively (Blatov V.A. (2004) Cryst. Rev. 10, 249-318). Comparing these values with computed ones we find that U1, U2 and U3 occur in oxidation states V, VI and V, respectively. This obey the rule of electrostatic balance in the formula \( U^{(+6)}U^{(+5)}O^{(-2)} \).

(3) Draw the last computed Dirichlet domain together with the star of surrounding atoms by clicking Image/VDP&CP and also its Schlegel projection clicking Image/Schlegel Projection.

(4) To draw the Dirichlet domains for all uranium atoms open an additional IsoCryst window, select all uranium atoms and click button. Unselect all atoms.
Check **Polyhedra/Translucent** and **Show Vertices&Edges** option to show the interior and exterior of the Dirichlet domains.

Remove Dirichlet domains by clicking button, select uranium atoms again and construct **Coordination Polyhedra** by clicking button. Pay attention that, in general, coordination polyhedra are dual to the corresponding Dirichlet domains. Constructing coordination polyhedra for all cations you can get a polyhedral representation that is the most useful for inorganic compounds.
Example 2: Constructing molecular Voronoi-Dirichlet polyhedra for benzene molecules and estimating their sizes.

Algorithm:
(1) Go to the C6H6 record, compute the adjacency matrix and open an IsoCryst window. Grow molecules and select one of them. Click button to get the Voronoi-Dirichlet polyhedron for the molecule.

Unselect the molecule, select all domain vertices (ZA nodes) and choose the Wire model for them.

Unselect the nodes and select the molecule again.

(2) Perform Calculate/Selected Atoms and pay attention to the total volume (107.66 Å³) of the domain that estimates the volume of the molecule.
(3) Close the IsoCryst window and open an ADS window. Clear all Topology options and specify the following Common and Molecular VDP options:

Run ADS and choose the Whole Molecule mode. You will get the following output:

Central atoms: none
Structure consists of molecules (ZD1). The composition of molecule is C6H6

H 1 0.9080 0.2438 0.0067 (0 0 0)
H 1 1.0920 -0.2438 -0.0067 (2 0 0)
H 3 1.2329 -0.0880 0.2049 (2 0 1)
C 1 1.0565 -0.1450 -0.0049 (2 0 0)
H 2 0.8631 -0.1585 -0.2348 (1 0 0)
C 2 0.9165 -0.0960 -0.1399 (1 0 0)
H 3 0.7671 0.0880 -0.2049 (0 0 -1)
C 3 1.1374 -0.0530 0.1230 (2 0 1)
H 2 1.1369 0.1585 0.2348 (1 0 0)
C 2 1.0835 0.0960 0.1399 (1 0 0)
C 3 0.8626 0.0530 -0.1230 (0 0 -1)
C 1 0.9435 0.1450 0.0049 (0 0 0)
Mass=78.114; Vol=107.66; Rsd=2.951
GravityC: 1.0000 0.0000 0.0000
Centroid: 1.0000 0.0000 0.0000

Pay attention to the value of the molecular domain volume.

**Exercise:** Estimate volumes for solvate benzene molecules in the three remaining structures (WAYFAT, ZIRJUF10, WUVVOY). How large are the differences in their volumes?

**Answers:** WAYFAT  Vol = 124.33; ZIRJUF10  Vol = 127.02; WUVVOY  Vol = 130.18. The differences are not very large.
**Task 2:** Computing and analyzing migration maps for solid electrolytes.

**Tools:** the programs Dirichlet, IsoCryst and ADS, Crystal Data window.

**Example 1:** Computing and analyzing the migration map in \(\alpha\)-AgI.

**Algorithm:**

1. Open the database electrolytes, and choose AgI/alpha. Compute the adjacency matrix. Analyze the structure in IsoCryst. Determine the number of iodine atoms closest to a silver atom. For this purpose, select an Ag atom, leave it on the plot only, toggle to the \(\bigcirc\) mode and apply the \(\bigcirc\) tool to draw all atoms in the sphere of a given radius (2.85 Å) (see the value at the bottom bar).

Be sure that the Ag atom is allocated in a tetrahedral void of four I atoms.

(2) Build the system of voids and channels in the sublattice of iodine atoms ignoring Ag atoms. For this purpose, open a Dirichlet window and specify the following options in the Continuous tab:
Run Dirichlet. You will get the new electrolytes database where the data on the initial structure as well as the data on voids and channels are stored.

(3) Draw the structure from the electrolytes database in IsoCryst. Remove Ag atoms. Be sure that their positions correspond to the positions of void centers, and that the system of channels in the structure is 3-periodic (the Ag red atoms superimpose the blue ZA voids).
(4) Analyze the geometric parameters of voids and channels. For this purpose, open a Crystal Data window and go to the Adjacency Matrix tab. Extend the list of channels spreading from the void. Find the radius of the void (Rsd) and radii of the channels (Rad).

Compare the channels radius (2.661 Å) with the sum (3.0 Å) of radii of Ag and I. The values of Slater’s radii for the atoms can be found in IsoCryst options (Atoms/Radii) Ag=1.600 Å, I=1.400 Å.

The channel is assumed to be accessible for mobile ions if the sum of radii of the mobile ion and the framework atom exceeds the channel radius no more than by 10-15%. Are the channels accessible to Ag⁺ ions? Yes, the channels are accessible to Ag⁺ ions, because the radius of the channel (2.661 Å) is greater than the sum of radii of Ag and I minus 15%: (3.0 - 3.0\cdot0.15) = 2.55 Å, but smaller that 10% threshold (3-0.3 = 2.7 Å). 2.55 Å < 2.661 Å < 2.7 Å so it is likely that the conductivity is possible at high temperature.
Example 2: Computing and analyzing the migration map in $\beta$-alumina, $\text{Na}_2\text{O}(\text{Al}_2\text{O}_3)_{11}$.

Algorithm:
(1) Go to the $\text{Na}_2\text{O}(\text{Al}_2\text{O}_3)_{11}$ record. Compute the adjacency matrix. Now run Dirichlet, to ignore Na atoms you should El - Na in both lines in the Continuous tab of Dirichlet options. After running reply Yes to the request:

![Confirm dialog box](image)

After computing voids and channels duplicate the record in the electrolytes database and remove from the adjacency matrix all voids (ZA) that cannot contain Na atoms: their radius ($R_{sd}$) is less than the Na radius in oxygen environment, 1.54 Å (see Blatov V.A. (2004) Cryst. Rev. 10, 249-318). From 28 voids (ZA1-ZA28) only seven remain (ZA1-ZA7).

![Crystal Data](image)

Remove all channels inaccessible for Na atoms, they have radius less than 2.4 - 2.4·0.1 ≈ 2.15 Å. Look for the value of Rad for all ZA-ZA for each ZA. Here below we show the change for ZA2 where the channels (bonds ZA2-ZA2, ZA2-ZA3) are < 2.15 Å. Do the same for all ZA, checking all ZA-ZA Rad.
Finally, remove all the voids (ZA) having only one adjacent channel (one ZA-ZA) and all the voids that have no adjacent channels (no ZA-ZA) because they do not provide the ion migration. The final adjacency matrix contains only five voids. Save the change.

(2) Alternatively to the procedure above (1), the removal from the adjacency matrix of all voids and channels that cannot contain Na atoms can be done automatically using the Modify adjacency matrix procedure as follows:

Duplicate the initial record Na$_2$O(Al$_2$O$_3$)$_{11}$ in the electrolytes# database.

Use the option Modify adjacency matrix (Compound/Auto Determine/Modify Adjacency matrix):

In the open window select as atoms all the voids (Z). For Rsd apply the values 0:1.54 Å. In column Bonds to change select all types of bonds without bond Atom-Void. And Apply parameters to - Change bonds. As a result all voids less 1.54 Å are deprived of all contact.
Now we change to no bond all channels inaccessible for Na atoms, changing the Z-Z bonds to “none” for the ones that have radius (Rad) less than 2.15 Å, select Z both for Atom A and Atom B.

Remove all voids adjacent to one or no channel by option Simplify ADM (Compound/Auto Determine/Simplify Adjacency matrix). The final result is the same as we did with (1):
(3) Draw the migration map in IsoCryst. Select and draw only voids (ZA nodes). What is the dimensionality of the channel system? What is the orientation?

(4) Open an ADS window. Check the Common/Dimen, Calc. option and uncheck all other options. Run ADS and specify all atoms as central. You will get the following output:

```
-------------------------
Structural group No 1
-------------------------
Structure consists of 3D framework with Al11NaO17
3,4,5,6,9-c net with stoichiometry (3-c)2(4-c)18(5-c)(6-c)7(9-c)
-------------------------
Structural group No 2
-------------------------
Structure consists of layers ( 0 0 1) with ZA
2,3,4-c net with stoichiometry (2-c)6(3-c)4(4-c)3
```

Be sure that the ADS conclusion about dimensionality of the channel system coincides with the IsoCryst analysis.

**Exercise:** analyze the dimensionality of the migration map in Li₅(GaO₄). Assume \( Rsd = 1.38 \, \text{Å} \) for Li⁺ cations.

**Answer:** The system of voids contains 13 types of voids. All voids are larger than 1.38 Å.
When analyzing the channels we remove those that have Rad less than 1.8 Å (R(Li-O) – 10% R(Li-O)).

A void/channel will be available for Li-cations if it is determined only by oxygen atoms (Solid State Ionics 179 (2008) 2248–2254). We then must check for all voids that the environment does not have the other cations too close. In this case we see that many voids are located too close to Ga. We remove voids using the criteria of solid angles, specifically all bonds to cations with SA large than 10%. After this procedure do not forget remove 0-coordinated voids ZA from adjacency matrix. We get a one-dimensional system of conduction channels formed by three types of voids.

**Task 1:** Working with DBMS filters. Searching for a given finite fragment.

**Tools:** the programs AutoCN and IsoCryst, DBMS filters.

**Example:** Searching for the Bergman clusters in Cu-containing intermetallics.

**Algorithm:**

(1) Open the database intermetallics and determine adjacency matrices for all structures using the method Solid Angles and MinOm = 1.5 to consider all interatomic contacts with solid angles of corresponding Dirichlet domain faces more than 1.5%. This method is useful for the compounds with non-directional chemical bonds. Uncheck Data/Show Data to speed up the calculation and run AutoCN. After the calculation close the database.

(2) Extract all Cu-containing compounds from the database intermetallics. For this purpose, open the Composition filter, the Element tab, and type Cu in the Element line. Click Ok and choose the database to search through. You will extract 92 compounds.
(2) Open the **Topology/SubGraph** filter and load the *Bergman-44.gph* file with the adjacency matrix for a 44-atom Bergman cluster. Click the **View** button to look at the cluster.

Bergman-44 is a two-shell cluster

Close the IsoCryst window. Clear the list of filters by pushing the button **Clear** and run the filter. After some time ToposPro will find five structures.
(3) Click on the second record and open an IsoCryst window. Draw structure and open the *Bergman-44.gph* file with *Select/Load Tint File* command (choose *Graph files (*.gph)* for the file type). Click Apply button in the Tint file data window to select the cluster.
(4) Close the database window and extract the structures again using both filters at once. Use the Add button to add a new filter to the list and the Continue button to go to another filter.

Exercise: Extract all Ag-compounds containing 54-atom Mackay clusters (Mackay-54.gph) from the database intermetallides (2 structures with the 131325 and 450184 Ref. Codes).

Task 2: Simplification and taxonomy of nets.
Tools: the programs AutoCN and ADS, Microsoft Excel.
Example: classification of single 3-periodic nets in Cu-compounds by topological types.
Algorithm:
(1) Open the database Cu_3D_single (99 structures) and compute the adjacency matrices for all structures using the Domains method.

Pay attention that some compounds remain selected, click on the Filter window Acquisition Data/AcqFlags//No Adjacency Matrix you will get 7 structures which were not computed due to disordering or errors in experimental data. Remove them, we have now 92 structures.
(2) Select all records again and simplify all the structures with ADS to the standard representation (Continuous/Central Atoms = Me). Pay attention that some compounds were not simplified again due to some problems with initial crystal data.

(3) Select all records in the database Cu_3D_single_c created at the previous step (90 structures) and simplify them more by removing 0-, 1- and 2-coordinated atoms with the Simplify Adjacency Matrix procedure.
(4) Select all the records again and open an ADS window. Check the Classification and Save to Excel Format flags and specify Continuous/Central Atoms = El.

Run ADS and reply Yes to the ADS request:

(5) After the calculation finished pay attention that the structures remaining selected in the list contain nets with the topologies unknown to ToposPro (not contained in the TTD collection). Open the Cu_3D_single_c.txt file with Microsoft Excel. You will get a table with the topological types indicated for each net. Pay attention that all structures are 3-periodic (3D). Use standard Microsoft Excel filters to build a statistics on the topological types (there are 21 new topologies of the nets in the list of 90 (19 compounds weren’t calculated))

Exercise: perform the topological classification of single 3-periodic nets for the 97 Fe-compounds in the Fe_3D_single database. (results: Fe_3D_single_c – 90 structures (22 structures weren’t calculated), 23 are with new topologies)
Module 10. Searching for topological relations between nets.

**Task:** Searching for topological relations between nets and working with net relation graph.

**Tools:** the programs ADS and IsoTest, the TTD collection, *Generate Representations* procedure, DBMS filters, net relation graph tools.

**Example:** searching for all three-periodic uninodal subnets of diamond (dia) and lonsdaleite (lon) topological types. Searching for the shortest transformation paths between dia and lon.

**Algorithm:**

(1) Open the database *dia_lon*. Be sure that the adjacency matrix is computed for the first record (dia). Open *Representation Parameters* window (*Compound/Generate Representations*). Specify the options as shown below.

![Representation Parameters](image)

Press Ok and specify the database name *dia*. You will store in the database all uninodal nets (Max. NumAt = 1) with the diamond topology having an extended unit cell (MaxVolRatio = 1000, i.e. the unit cell can be 1000 times larger than the initial unit cell) and a lower symmetry of one of the subgroups of the space group $Fd\bar{3}m$ of the highest-symmetry embedding of diamond net.

(2) Open the *dia* database; there are 195 records: the initial diamond net and 194 nets with a lower symmetry. The symmetry transformations are shown in the net names.
Detailed information on the symmetry transformations is given in Comment tab of the Crystal Data window for every net. The first line shows the successive transformation path, the second one contains the cumulative transformation codes in relation to the initial symmetry. If the transformation is done in one step nothing is written in the comment tab, because the transformation itself is written in the name.

(3) Select all records in the dia database and open Representation Parameters window again. Change the parameters as shown below.

Click Ok and specify the database name dia_subnets. You will store in the database all subnets of the selected nets keeping the net symmetry. Open the dia_subnets database with 1215 records. All the subnets are obtained by breaking some sets of equivalent bonds in a dia net. For example, the net
dia/F d -3 m ->P 41 3 2 (5/8,5/8,5/8)

obtained from Fd\textsuperscript{3}m diamond by decreasing symmetry down to P4\textsubscript{1}32 and shifting the origin by the (5/8,5/8,5/8) vector, has two bond sets; therefore the initial net is stored under the name
It produces two subnets where either the second or the first set is retained; they have the names 

\[
\text{dia/F d -3 m->P 41 3 2 (5/8,5/8,5/8)}; \text{Bond sets: 2}
\]

and 

\[
\text{dia/F d -3 m->P 41 3 2 (5/8,5/8,5/8)}; \text{Bond sets: 1},
\]

respectively.

(4) Remove all the dia nets except the most symmetrical embedding. All the initial nets have a label All bond sets in the formula name, therefore they can be selected using the Formula filter. Click Filter/Fragment/Formula and type the label. Run the filter.

(5) Select all the 195 records found except the first one (select all of them and then unselect the first record). Remove selected records (Compound/(Un)Delete). Return to the main list (right-click and choose Show Main).

(6) Determine the dimensionality of the subnets. For this purpose, select all records and open an IsoTest window (Program/IsoTest). Specify the IsoTest options as shown below.
(7) Run IsoTest. You may stop the screen output to speed up the calculation by clicking Data/Show Data. After finishing the session close the IsoTest window.

(8) Search for all non-three-periodic structures. Go to Filter/Topology/Dimensionality and specify the options as shown below. Remove current (previously used) filter by clicking Remove or Clear button.

Run the filter. You will get the following message that reminds you about the records found by the previous filter. Reply Yes.

(9) Remove all the 980 found 0-, 1-, or 2-periodic structures. Return to the main list that now contains 41 records (the initial dia net and 40 its 3-periodic subnets).
(10) Obtain the information about the topology of the subnets and store it as a net relation graph. For this purpose, select all the records and open an ADS window. Specify the ADS options as shown below. Run ADS and specify the name `dia_lion` for the net relation graph file.

(11) Close the ADS window after finishing the calculation. Be sure that you have four selected records in the database list. They correspond to topologically different `dia` subnets. Other 36 subnets are different embeddings of the four distinct topologies; the four selected embeddings has maximal found symmetry. However, the topologies can have more symmetrical embeddings (that are not `pecu` subnets). To check it, use Systre program (http://www.gavrog.org). Copy the four records into a new `dia_subnets_diff` database.

(12) Open the net relation graph window.
You see that there is the initial dia net and four its three-periodic subnets (bto, srs, ths and utp) in the net relation graph. Right-click on the dia record and choose Grow Branch. You see the hierarchical relations between the nets.

(13) Repeat the whole procedure for the lon net. Store the net relations for lon in the same net relation graph. Do not forget to clear the current filter on step (4)! You have to get five lon three-periodic subnets (copy them into a new lon_subnets_diff database) and the extended net relation graph. To reload it you need to clear current net relation graph (Database/TTD Collection/Clear) and load dia_lon.nrl again (Database/TTD Collection/Net Relations). The resulting graph with 8 nets is shown in the last of the four pictures below.
(14) Look at the **dia** and **lon** subnets using **Grow Branch** command. Find the shortest transformation paths from **dia** to **lon** through their common subnets. For this purpose, select the **dia** and **lon** records (Ctrl-click), right-click and choose **Pair Relations** command. You will get three possible paths through **bto**, **ths** and **utp** subnets.

(15) Check the symmetry of the common subnets saved in the **dia_subnets_diff** and **lon_subnets_diff** databases (use ADS to identify the subnet topologies). You will find that the **ths** (**dia**/F d -3 m -> C 2/c (-5/2a-3b-5/2c, 1/2a-1/2c, a+2b+2c; 1/2a, 1/2, 1/2); Bond sets: 1, 3, 4) and **lon**/P 63/m m c -> C 2/c (a-b, c, -a-b; 0, 1/2, 0); Bond sets: 1, 2, 4) subnets have the same symmetry both for **dia** and **lon** (C 2/c and Pnna, respectively), whereas the **bto** subnet has P 32 2 1 and P 65 2 2 space groups for **dia** (F d -3 m -> P 32 2 1 (-1/2a+1/2b+1/2c, a+b+c; 1/6a, 1/2b, 5/6c); Bond sets: 1, 2) and **lon** (P 65/22 m c -> P 65 2 2 (a, b, 3c); Bond sets: 1, 3), respectively.

(16) Try to decrease the symmetry for the **bto** subnet of **lon** from P 65 2 2 down to P 32 2 1. For this purpose, open a **Crystal Data** window and click **Symmetry** button. Select the P 32 2 1 translation-equivalent subgroup and click **Change Group** button.
You will find that at this symmetry the subnet becomes binodal (see tab Atoms). So the transformation from \textit{dia} to \textit{lon} through uninodal nets is possible only with \textit{ths} and \textit{utp} subnets. Close the Crystal Data window without saving the changes.

**Exercise:** find all uninodal three periodic subnets for quartz (\textit{qtz} database). Can \textit{qtz} be transformed to \textit{dia} or \textit{lon} through uninodal subnets?

**Answer:** There is only one uninodal subnet for \textit{qtz}, it is \textit{bto} in \textit{P}$_3$21 and \textit{P}6$_2$22 space groups (totally 6 embeddings), so \textit{qtz} can be transformed to \textit{dia} through uninodal subnet \textit{bto} in symmetry \textit{P}3$_2$1, and to \textit{lon} in \textit{P}6$_2$22 space group.

Task 1: Searching for building units and the corresponding underlying net. 
**Tools:** the Nanoclustering procedure, the programs ADS, the TTD collection. 
**Example:** searching for building units and the underlying net in the crystal structure of Cu5Zn8. 

**Algorithm:**
(1) Convert the file Cu5Zn8.cif into the ToposPro database gamma-brass. Open the database and compute the adjacency matrices using AutoCN method Solid Angles (MinOm = 1.5).
(2) Having the Cu5Zn8 record active (do not select it with Insert tab), open the Nanoclustering window (Compound/Auto Determine/Nanoclustering) and specify the following options:

<table>
<thead>
<tr>
<th>Option</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. Number of Clusters</td>
<td>0</td>
</tr>
<tr>
<td>Max. Number of Shells</td>
<td>0</td>
</tr>
<tr>
<td>Search by Cations</td>
<td>Only Cations</td>
</tr>
<tr>
<td>Consider Empty Clusters</td>
<td>No</td>
</tr>
<tr>
<td>Porous Structures Units</td>
<td>Tiles</td>
</tr>
<tr>
<td>Min. Omega</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Max. Number of Clusters** – maximum number of nanoclusters in the representation; choose 0 if the number is unlimited.

**Max. Number of Shells** – maximum number of shells in each nanocluster (0 - unlimited).

**One-Atom Cluster** – permits existence of 1-atom (trivial) nanoclusters. This option is required for structures where some equivalent atoms are interconnected.

**Enumerate Layers** – consider all possible sizes for multi-shell nanoclusters, otherwise maximal possible size (maximal number of shells) will be assumed for each nanocluster.

**Save All Nets** – automatically save underlying nets in the database <database name>_c when computing several structures (continuous mode).

**Search by Cations** – if there are cations (atoms with positive oxidation degree) in the list of atoms, the centers of nanoclusters can be chosen only among them (Only Cations), or these atoms will necessarily be taken as centers of nanoclusters and some other nanoclusters will be searched among other atoms (All Cations and Other Atoms). In this case ToposPro ignores the symmetry of cation positions so you may enforce ToposPro to consider some special sets of nanoclusters that do not fit the principles of the nanocluster method (see below).

**Consider Empty Clusters** – you may consider voids as centers of nanoclusters. ToposPro treats all unoccupied Wyckoff positions without variable parameters as possible centers of nanoclusters. In the output they are designated as ZA with Wyckoff position in parentheses. You may consider only representations containing such "empty" nanoclusters (Only With Empty Clusters) or all representations both with and without "empty" nanoclusters (With All Clusters). To find the composition of the "empty" nanoclusters ToposPro considers all the contacts between ZA and atoms that have solid angle of the corresponding face of the Voronoi-Dirichlet polyhedron of ZA no less than Min. Omega value.

**Porous Structures** – a special mode to search for representation of a porous structure (like zeolite) as a set of tiles (one-shell empty clusters) and/or rings. The structure should be represented together with its dual net (see Module 7). In this mode the Porous Structures Units options are valid that allow to consider as nanoclusters only tiles, only rings, or both tiles and rings.
Consider Solutions – output all solutions, or only those where every nanocluster has at least one atom in the outer shell belonging to this nanocluster only (Without Fused Clusters), or only those where nanoclusters have no common atoms (Only Packings).

The most general set of options (largest number of representations) is: One-Atom Cluster checked; With All Clusters; other options are default. But the One-Atom Cluster option should be checked only if no representations were found with this option unchecked. So it is recommended initially try With All Clusters and other options being default. Change other options if the computation is too long (use Cancel menu item to interrupt computation). If you want to check some non-standard set of nanoclusters you may specify for their centers positive oxidation degrees and use Search by Cations options.

(3) Push Ok button and wait until the window with the list of representations appears. The representations are ordered by the number of clusters. In the Cu₄Zn₈ there are three representations, two of them consist of one-shell clusters; the one starting with ZA₁ contain “empty” cluster with the center ZA₁ in Wyckoff position 2a. Select the second representation and check the option Generate Nets if you want to obtain the underlying nets (nets whose nodes correspond to structural units; see Appendix 2 for details) for the representations. Press Ok button and wait until the calculation will be finished.

You will be asked about creating a new database that will contain the underlying net:

Answer Yes, enter the user code and you will get the database gamma-brass_c with the one record marked nanocluster net.
Open the file `gamma-brass.txt` that contains the output of the **Nanoclustering** procedure for the selected representation. The file looks like:

```
-----------
Nanoclusters
-----------
1:Cu5 Zn8; RefCode=137434
Total number of representations=3
1:Cu1(1) (3B12)
1:ZA1(2a) (2) (084@22)
3:ZA2(6b) (1) (086) ZA1(2a) (1) (084) Cu1(0) (1)
-----------
Representation 1:ZA1(2a) (2) (084@22)
-----------
Nanocluster #1 (084@22)
-----------
1 ZA1
-----------
4 Zn1(3^4)
-----------
(4,6,4) (3^4)
4 Cu1(6^4) (4f)
6 Cu2(6^6) (6e)
12 Zn2(3^12) (12v)
-----------
(22,48,28) (3^12,6^10) (12v,6e,4f)
-----------
Totally 26 atoms
```

The detailed information of the second representation shows that the second nanocluster is “empty” (non-centered) with the inner core ZA1 located in 2a positions. The first shell of the nanocluster consists of 4 Zn1 atoms. All four Zn1 are 3-ordinated (3\(^4\)) within the shell and presented as a tetrahedron. The (4,6,4)(3^4) line summarizes the information about the first shell of the primary nanocluster, meaning that it has 4 vertices, 6 edges, and 4 faces (4,6,4) and that the 4 vertices are 3-ordinated atoms. In the second shell, all ten Cu1, Cu2 atoms are 6-coordinated and the 12 Zn2 are 3-coordinated. The shell is now a 22 vertex polyhedron with 48 edges and 28 faces. To define the general type of the shells of nanoclusters we use the signature \(v,e,f\) where \(v\), \(e\), and \(f\) are projected to vertices, edges or faces of the previous shell or the inner core. Thus the four Cu1 6-coordinated atoms are of the type “\(f\)” [4 Cu1(6^4) (4f)], six 6-coordinated Cu2 atoms and twelve 3-coordinated Zn2 atoms have the “\(e\)” and “\(v\)” respectively [6 Cu2(6^6) (6e) / 12 Zn2(3^12) (12v)], (for the colour see below).

The numbering of atoms corresponds to the initial Cu5Zn8 structure and allows you to easily construct the nanoclusters with IsoCryst.

(4) Turn to the database **gamma-brass** and run IsoCryst for the **Cu5Zn8** record. Draw the picture ( ) and specify **Name&Index** mode for the legend view.

![IsoCryst Options](image)
Using the legend select all Zn1 atoms.

Leave only one tetrahedral core of Zn1 atoms ( ) and press one time the Growth button ( ) to obtain the second shell of the 0@4@22 nanocluster. Select the inner 0@4 core by yellow ( ) and use the corresponding signature colours for the type 4 “f”, 6 “e” and 12 “v” atoms.

As shown in the two views above, we have the nanocluster model based on the inner tetrahedral core 0@4 (yellow) and the second shell contains 22 atoms. The “onion” 0@4@22 nanocluster is fully equivalent to the common description of γ-brasses in terms of nested polyhedra as a sequence of IT+OT+OH+CO, where IT, OT, OH, CO are Inner Tetrahedron, Outer Tetrahedron, Octahedron and Cuboctahedron, respectively (see Pankova A.A., Blatov V.A., Ilyushin G.D., Proserpio D.M. “γ-Brass polyhedral core in intermetallics: the nanocluster model” manuscript in preparation).
Task 2: Searching for building units and the corresponding underlying net

Tools: the Nanoclustering procedure, the programs ADS and IsoTest, the TTD collection, the Distribution procedure.

Example: searching for building units and the underlying net in the crystal structures of ZrZn$_{22}$ and NaCd$_2$.

Algorithm:
(1) Convert the files ZrZn$_{22}.cif$ and NaCd$_2.cif$ into the ToposPro database Samson. Repeat the analysis for these records. (Set value Min. Omega=0.00 in Nanoclustering window)

(2) In the case of ZrZn$_{22}$ there are only three representations and each of them consists of two one-shell clusters; the two last representations contain “empty” cluster with the center in Wyckoff position 8b. Select the representations and check the option Generate Nets to create a new database that will contain the underlying nets.
(3) Open the **Crystal Data** window for the first record and click the Comment tab. You see the information on the cluster composition:

**CLUSTER:** Zn1=13[Zn13]; Zr1=17[Zn16Zr],

that means that atoms Zn1 and Zr1 in the underlying nets correspond to 13-atom and 17-atom clusters, respectively. Then go to the **Adjacency Matrix** tab and be sure that the cluster centered by Zn1 is in contact with 12 other clusters (6Zn1+6Zr1) while the other cluster is linked to 16 clusters (12Zn1+4Zr1).

Open the **Crystal Data** window for the second record to be sure that one of two clusters is “empty” (ZA1), moreover, some intercluster contacts in the adjacency matrix are marked as “H bonds”. Pay attention that in the underlying net each “valence” contact corresponds to a pair of “tangent” clusters having at least one common atom, while “H bond” contact designates “bounded” clusters that are connected only by bonds between their surface atoms.
Close the **Crystal Data** window and run ADS for the first record in the **Classification** mode. You will find that the underlying net has the topology of the cubic Laves phase MgCu$_2$ (mgc-x). The topology of other two underlying nets can be analyzed in two ways: ignoring or not ignoring links between “bounded” clusters. For this purpose you can set the **Bond type** option for H bonds to **None** or to **At.**, respectively.

Check that for the second underlying net the two possible topologies are diamond (**dia**) and b.c.c. (**bcu-x**), respectively, while for the last underlying net the topologies are unknown to ToposPro.

The beginning of the **Samson.txt** file looks like:

```
Nanoclusters
------------
1:ZrZn22; RefCode=457705
Total number of representations=3
2:Zr1(1) (1816) Zn3(1) (1812)
2:ZAl(8b) (1) (0010) Zr1 (1) (1016)
2:ZAl(8b) (1) (0010) Zn4 (1) (1014)
------------
Representation 2:Zr1(1) (1816) Zn3(1) (1812)
------------
Nanocluster #1 (1816)
1 Zr1
12 Zn1 (5^12) (12v)
4 Zn4 (6^4) (4v)
(16,42,28) (5^12,6^4) (16v)
------------
Totally 17 atoms
------------
Nanocluster #2 (1812)
1 Zn3
6 Zn1 (5^6) (6v)
6 Zn2 (5^6) (6v)
(12,30,20) (5^12) (12v)
------------
Totally 13 atoms
```
(6) Turn to the database **Samson** and run IsoCryst for the **ZrZn22** record. Draw the picture and select all Zr1 and Zn3 atoms.

Leave the centers of clusters only and press one time the **Growth** button to be sure that the whole structure can be constructed with one-shell clusters centered by Zr1 and Zn3 atoms. Select Zr1 atoms only and show their coordination polyhedra ( ) to see them connected by vertices. Do the same for the Zn3 coordination polyhedra.
(7) Pay attention that the number of the NaCd2 nanocluster representations is much larger (41), but there is only one with two clusters (the simplest one). Select this representation only and construct its underlying net, be sure that the topology of the net is also mge-x if both tangent and bounded cluster contacts are taken into account.
Open *Samson.txt* and be sure that both clusters are two-shell: Na1: 1@16@44 (61-atom cluster) and Cd6: 1@12@50 (63-atom cluster).

```
---
Representation 2:Na1(2)(1816044) Cd6(2)(1812@50)
---
Nanocluster #1 (1816044)
---
1 Na1
---
12 Cd12(5^12)(12v)
4 Cd9(6^4)(4v)
---
{16,42,28} (5^12,6^4) (16v)
---
4 Cd8(6^4) (4f)
4 Na2(6^4) (4v)
12 Na5(5^12) (12v)
12 Na6(6^12) (12f)
12 Na7(6^12) (12f)
---
{44,126,84} (5^12,6^32) (16v,28f) Type=vf
---
Totally 61 atoms
---
Nanocluster #2 (1812@50)
---
1 Cd6
---
6 Cd10(5^6) (6v)
6 Na8(5^6) (6v)
---
{12,30,20} (5^12) (12v)
---
12 Cd11(5^12) (12v)
6 Cd13(6^6) (6e)
12 Cd14(6^12) (12f)
2 Cd7(6^2) (2f)
6 Na3(5^6) (6v)
6 Na4(7^6) (6f)
6 Na7(6^6) (6v)
---
{50,144,96} (5^18,6^26,7^6) (24v,6e,20f)
---
Totally 63 atoms
---
```

Draw both clusters in IsoCryst and look how the atoms of the second shell are allocated relative to the atoms of the inner polyhedron:
(8) Select both records in the Samson database and open the IsoTest program. Click the option Common/Common Flags and indicate the Save Topology and Cont.Calc. mode. Then specify the following IsoTest options in Topology tab to compute coordination sequences for all atoms up to the 3rd coordination shell and store the information into the Samson.its file:

Run IsoTest and close its window after finishing the calculation. Then right-click in the database window and specify Show ITS to show information about coordination sequences in the Crystal Data window.
Open the **Crystal Data** window and go to the Structure Topology tab to see the coordination sequences.

Close the **Crystal Data** window and open the **Distribution** window (**Database/Distribution**). Press the **Subl.** button to construct the distribution of the coordination sequences.
Order the list by Property.

You see, for instance, that the clusters 1@12@50 allow four possible compositions for the third shell with 109, 113, 114 or 120 atoms, moreover, all of them occur in NaCd₂ (you may press the Select button to select the corresponding records in the database).

(9) Using the Crystal Data window, find that the cluster 1@12@50@113 is realized for Cd₁₀ and Cd₁₂ atoms of NaCd₂. Open IsoCryst and construct three-shell cluster for Cd₁₂ by two successive clicks of the Growth button. Select all atoms in the cluster and use Save Selection command (Graph files (*.gph) type of files) to store the cluster topology in the 1_12_50_113.gph file.
(10) Open IsoCryst for the NaCd2 record, draw picture and use the **Load Tint File** command (**Graph files** (*.gph) type of files) to choose the \texttt{1\_12\_50\_113.gph} file to find that there is only one independent cluster of this type.

Press the **Apply** button to show visible fragment of the cluster, press the IsoCryst **Growth** button several times until the Fragment item in the list becomes bold (all atoms are visible).
Press the **Apply** button again and center the image (**Space** key) to see the cluster required.

**Exercise**: perform the same analysis for the crystal structure of $\beta$-Mg$_2$Al$_3$ (*Mg2Al3.cif*). What are the relations between this structure and the structures of ZrZn$_{22}$ and NaCd$_2$? Note: also use **MinOm=0.00** value in **Nanoclustering** window.

(The nanocluster model can be presented as a combination of 1@16@44 and 1@12@50 nanoclusters with the Mg9 and Al14 centers, respectively. The topology of the net is **mgc-x**).
Module 12. Analysis of coordination compounds

Task 1: Analysis of chemical composition and coordination types of ligands.

Tools: the programs AutoCN, ADS, Topology/Ligands filter.

Example 1: searching for all structures containing/not containing ligands with sulfur atoms.

Algorithm:

1. Open the database ligands and compute the adjacency matrices for all structures using the AutoCN method Domains (the options concerning non-valence contacts can be unchecked since we are interested only in coordination bonds).

2. Select all structures again, open the ADS program and specify the options Cont.Calc., Dimen.Calc., Save CCF & Ligands and Central atoms = Me (other options should be unchecked for speed).

3. Show the column of RefCodes in the database window and open a Crystal Data window for the second record (BAYDIO). Be sure that according to the name of the compound it contains polymeric complex groups with cadmium atoms, succinato and aqua ligands as well as not coordinated water molecules.
(4) Open the Comment tab the **Crystal Data** window. You see the information on the central atoms and ligands after the keywords **CENTAT** and **LIGAND**:
This informs you that there are two inequivalent complexing cadmium atoms (Cd1 and Cd2), two inequivalent bridge $\mu_3$ ligands C4O4 (succinato), four inequivalent terminal ligands O (aqua) and one not coordinated molecule O (water). Pay attention that hydrogens are not allocated in the structure. The coordination types of ligands are given in square brackets; the following rules are used:

- the ligand denticity (number of donor atoms used to connect to metal atoms) is designated by capital letters M, B, T, K, P, G, H, O, N, D for mono-, bi-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, decadentate ligands, respectively; if the number of donor atoms $\geq 10$ the letter X is used;
- the integers mbtkpqghond... following after the letter show the numbers of metal atoms coordinated by one (m), two (b), three (t), ... donor atoms of the ligand. The sum of these integers is equal to the total number $n$ of metal atoms coordinated by the $\mu_n$ ligand.

(The keyword ATOMLIG contains information about atoms that compose the ligand).

For example, the coordination type M1 (M1) means that the ligand is monodentate and is connected to one metal atoms by its (one) donor atom. It is the terminal aqua ligand in our example. The coordination type K12 means that the ligand has four donor atoms and is connected to three metal atoms ($\mu_3$); for the connections with one of them it uses one donor atom and two metal atoms are coordinated by two ligand atoms each. Be sure of this using IsoCryst:

If the molecule is not connected to a metal atom, its dimensionality (0D) is given instead of coordination type.

(5) Close the Crystal Data window and open the filter Filter/Topology/Ligands. Specify the options as shown below to find all compounds with any complexing atoms and any ligand containing sulfur atoms. Click Ok. How many hits have you got? (answer: 4)

(6) Use Filter/Composition/Element to find all structures with sulfur atoms (there are 6):
Why the number of the found compounds is not equal to the number of hits at the previous step?

(7) Find all structures with sulfur-containing molecules not connected to metal atoms:

**Example 2**: searching for all structures containing ligands of a specified composition and/or coordination type.

**Algorithm**: 
(1) Specify the options of the filter **Filter/Topology/Ligands** as shown below to find all compounds containing the ligands of the C10H8N2 composition: (5 compounds)
What ligands have this composition? Do all of them have the same coordination type?

(2) Find all structures containing bridge (µ₂) C₁₀H₈N₂ ligands of the B² coordination type:

![Image of ligand search interface]

Is the number of these structures equal to the number of hits at the previous step? (4 compounds)

(3) Specify two bidentate coordination types (B² and B₀¹) for C₁₀H₈N₂ ligands:

![Image of ligand search interface]

What does the B₀¹ coordination type mean? Use IsoCryst to check on your answer. (5 compounds)

(4) Find all structures containing bridge µ₂ ligands with the following options (they are 2):

![Image of ligand search interface]

Analyze what coordination types can correspond to the µ₂ ligands.
(5) Find all structures containing disordered ligands with the following options (5 compounds):

What ligands are disordered and how? Use IsoCryst to answer the question. The disordered ligands are marked by ‘*’ in the Comment tab of the Crystal Data window:

Example 3: searching for the structures containing only a given number of kinds of ligand.
Algorithm:
(1) Specify the options of the filter Filter/Topology/Ligands as shown below to find the compounds containing only one kind of ligand:
What are these ligands and what are their coordination types? (JOMWAJ with $\mu_2$-nicotinato C6H4NO2 $[\text{T11}]$ and BEMKEJ10 with cyano CN $[\text{B2}]$)

(2) Find all structures containing one or two kinds of ligands: (14 compounds)

Exercise: perform the same analysis to find the structures containing acetato (CH$_3$COO$^-$) ligands. Do all of the ligands have the same coordination type?

Answer: You will find only JAJCUS with acetate-ligands, the coordination types are $\text{B}^2$ and $\text{B}^{11}$.

Task 2: Analysis of chemical composition, topology and dimensionality of complex groups.

Tools: the program ADS, Topology/Ligands filter, Compound/Distribution procedure.

Example 1: searching for the structures containing complex groups of a specified local topology.

Algorithm:

(1) Open Database/Distribution window and click CCF button to obtain the distribution on crystal-chemical formulas of the coordination groups.
Crystal-chemical formula (CCF) is formed of the coordination types of ligands and the symbol of the complexing atom (A) with the stoichiometric coefficients following after ')' symbol. For example the CCF \( A^*B_{2}^2)^3 \) means that the complex group consists of ligands with the \( B^2 \) coordination and metal atoms in the ratio 3:1.

Select the compounds with the \( A^*B_{2}^2)^3 \) CCF by clicking Select button.

(2) Close the Distribution window and find the same structures using the Topology/Ligands filter:

Draw all the structures in IsoCryst and understand why the namely this CCF corresponds to them.

**Example 2:** searching for the structures containing complex groups of a specified dimensionality and composition.

**Algorithm:**
(1) Select all structures in database ligands again, open the ADS program and specify the options Dimen, Calc., Save CCF & Ligands and no Central atoms to get the composition of the complex group as a whole:
Run ADS. **ATTENTION!** The information on ligands will be replaced by the information on complex groups!

(2) Find the information on the complex groups dimensionality in the **Comment** tab after the **LIGAND** keyword (the sign ‘-’ means that the polymeric moiety does not connected to any other metal atom):

(3) Find all structures containing 1D (chain) [4 compounds], 2D (layer) [7 compounds] or 3D (framework) [22 compounds] groups using the **Ligand Dimensionality** option of the **Topology/Ligands** filter. Use IsoCryst to draw some examples of the groups.
Module 13. Analysis of polynuclear coordination clusters

**Task:** Classification of metal skeletons in polynuclear coordination clusters.

**Tools:** the programs AutoCN, ADS, Modify Adjacency matrix procedure.

**Example:** separating and classifying metal skeleton in BEQXEB, \[[\text{Mn}_{42}\text{O}_{72}(\text{O}_2\text{CMe})_{78}(\text{OMe})_{24}(\text{MeOH})_{12}(\text{H}_2\text{O})_{22}(\text{OH})_{3}] \cdot \text{xH}_2\text{O} \cdot \text{yCHCl}_3\].

**Algorithm:**

1. Open the database **BEQXEB** and compute the adjacency matrix using the AutoCN method **Domains**.
2. Make a duplicate of the record, add comment **/simplified** to the formula (use **Crystal Data** window) and run the **Compound/Auto Determine/Modify Adjacency matrix** procedure with parameters: **Atom A** = Nm; **Atom B** = Nm; **Bonds to Change** = Valence; **Change To** = None; **Apply Parameters To** = Change Bonds. As a result all bonds between non-metals (X) will be broken and the cluster skeleton containing only Mn–Mn or Mn–X–Mn bonds will be separated.

3. Run **Compound/Auto Determine/Simplify ADM** with parameters: **Atoms** = Nm; **Remove** = 0-coordinated + 1-coordinated; **Type** = Valence. As a result all non-metal atoms except bridges between metal atoms will be removed.

![Modify Adjacency Matrix](image)

(3) Run **Compound/Auto Determine/Simplify ADM** with parameters: **Atoms** = Nm; **Remove** = 0-coordinated + 1-coordinated; **Type** = Valence. As a result all non-metal atoms except bridges between metal atoms will be removed.
(4) Run **Compound/Generate Representations** with parameters: \( A = \text{Me} \); **Duplicate** checked; all other parameters are default.

You generate a database with all possible representations of the clusters. In this case two representations created: the first one (Set #2) is the initial structure (all bonds have \( \Omega \geq 11.00\% \)); the second one (Set #1) does not contain weaker Mn–O bonds (all bonds with \( \Omega < 16.50 \% \) were broken). Open the **Crystal Data** window for the last record, go to the Adjacency matrix tab, right click and show the **Information** window. Be sure that the distances of the broken bonds (No bond) vary in the range 2.24–2.39\( \text{Å} \), i.e. there is no chemical reason to ignore these bonds. So we will use the first representation (Set #2).
(5) Run ADS in the Simplification mode; **Simplification Method = Standard; Topology Flags = Contract Atom.**

After running select all Mn atoms as **Central Atoms**, all Mn atoms as **Atoms to Contract to** and all oxygen atoms as **Atoms to Contract.** As a result you get the cluster skeleton in a new database **BEQXEB_c.** Draw these wheel-lite skeletons in IsoCryst.
(6) Run ADS in the **Classification** mode and be sure that the skeleton has the **3,5,6M84-1** topology (see **Appendix 5** for details of the N\(\text{M}_k\)-n nomenclature).

(7) Go back the initial record in the database **BEQXEB**. Look at the **Adjacency Matrix** tab, Information window and be sure that there are “valence” contacts C–C of length more than 3Å and O–O of length about 2.8Å. Such contacts can appear the structure is not completely solved (in this case, chloroform solvent molecules are not allocated). Break all these bonds with the **Compound/Auto Determine/Modify Adjacency matrix** procedure keeping the same options as before, but specifying **Bond AB Length = 2:100**.

(8) Run ADS with the same options as at step (5). As a result you get the cluster skeleton with additional polyatomic Mn–\(X_{n}\)–Mn bridges. Be sure that this topology is novel. Compare the coordination numbers of Mn atoms in the two skeletons. What are the differences? With IsoCryst find the Mn atoms that are linked by only polyatomic bridges.

(9) In IsoCryst, select the skeleton and save it in the **BEQXEB.gph** file (**Select/Save Selection**, file type: *.gph). You may then use this file to identify skeletons (or parts of more complex skeletons) of this topology in other compounds using the **SubGraph** filter (see Module 3, task 2).

Appendix 9. ToposPro Parameters

You can change parameters of program by modifying the System/TOPOS Parameters submenu.

The Default Radii System option determines the system of radii that is used by the IsoCryst and AutoCN programs. The colour of atoms can be changed by the Change Colours button. Select the atom and modify its colours as you want. The button Change Font allows to change the font of legend of atoms in IsoCryst program. The Min. Valid Dist. value is used as a criterion for too short interatomic distances in such procedures as Compound/Auto Determine/Errors in Distances or Remove Doubled Atoms. The ToposPro applied programs use this criterion at the initial stage to estimate if the structure is valid or not. Usually, you should not change this criterion. The Multiplier for Radii criterion (MR) is used to find “chemically” short interatomic distances: the distance \( R(A-B) \) is short if \( R < (r_A + r_B) \cdot MR \), where \( r_A \) and \( r_B \) are taken from Default Radii System. The Extra Dist. criterion (ED) is used in the AutoCN Domains and Ranges algorithms when comparing the distance \( R(A-B) \) with \((r_A + r_B)(1+ED)\) to solve if the distance corresponds to chemical bond. Bond Valence Parameters determines the data for calculation of bond valences; the parameters can be taken from the paper by Brese, N. E., O’Keeffe, M. Bond-valence parameters for solids. Acta Cryst. 1991, B47, 192-197 or from an external BVPARM.CIF file, which should be placed into the ToposPro folder.

If you want to extract the information about cell parameters and bibliography, you can select the corresponding flags in Output tab. Also the format of the output information can be chosen.
Then just select compounds and press F9 key. The window with requested information will appear.

Systre format is the input file for Systre (http://www.gavrog.org), and it is useful if you need to check new nets. CIF exports the crystallographic data to the .cif format readable with many free programs (e.g. Mercury), BUT remember that the adjacency matrix is not exported.

If you want a reproduction of exactly what you see on Isocryst window, you can export the selected view as .pdb file, readable by Mercury, Jmol, RasMol.
The tab **Paths** contains location addresses of program ToposPro/TTD collection/TTO collection/graph-files.
TOPOS Schools:

ICMR Summer School on Periodic Structures and Crystal Chemistry
University of California, Santa Barbara USA, July 2008,
http://www.icmr.ucsb.edu/programs/archive/crystalchemistry.html

Lezioni della Scuola di Dottorato in Scienze e Tecnologie Chimiche
Università degli studi di Milano, Italy, January 2009

IUCr Summer School on Mathematical Crystallography: Topological Crystal Chemistry:
Theory and Practice
Nancy Université, France, June 2010

Computer methods in crystal structure systematics
Max Planck Institute for Solid State Research, Stuttgart, Germany, September 19-22, 2011

One-day introduction to Topos
Department of Chemistry, University of South Florida (USF), Tampa, FL, USA, March 9, 2012

Computer Topological Analysis of Molecular Crystals and Coordination Networks
UIMP, Santander, Spain, July 16-18, 2012

School on computer topological analysis of MOFs and coordination networks
LBNL, Berkeley, USA, February 4-7, 2013 (with Mike O'Keeffe)

Topological methods in crystal chemistry and materials science
CECAM-HQ EPFL, Lausanne, Switzerland, September 9-13, 2013
http://www.cecam.org/workshop-869.html

Topological methods for expert systems in materials science
SCTMS, Samara State University, Samara, Russia, August 12-16, 2014

Combined topological and DFT methods for prediction of new materials
SCTMS, Samara State University, Samara, Russia, September 14-20, 2015

One-day workshop “Short course on crystal chemistry applying ToposPro”
Rutgers University, New Jersey, USA, May 11, 2016

Combined topological and DFT methods for prediction of new materials II
SCTMS, Samara State University, Samara, Russia, July 04-10, 2016

ToposPro & 13th USPEX Workshop
HPSTAR, Shanghai, China, June 16-20, 2017
Other Schools on by Prof. Mike O’Keeffe and Dr. Charlotte Bonneau where ToposPro was among the programs used:

**Design, Synthesis and topological structure analysis of porous materials**
Zhuhai college of Jilin University, China, December 5 - 9, 2010

**Design, synthesis and topological analysis of periodic structures**
PAL Workshop, Pohang Accelerator Laboratory, South Korea, January 9 - 15, 2011

**School on Topological Crystal Chemistry,**
Dept. of Materials and Environmental Chemistry Stockholm University, June 4-8, 2012