

# The Cambridge Structural Database in chemical education: analysis of hydrogen-bonded networks in salts of hexaaqua metal ions with organic counter-ions

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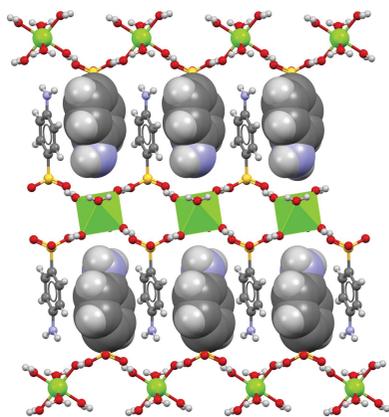
**Supporting information:** this article has supporting information at journals.iucr.org/j

This paper describes a laboratory course that introduces basic crystallographic data analysis to chemistry students encountering for the first time the world of crystals and crystal structures. The aim of the course is to provide students with direct contact with crystal structures and hands-on experience in structure analysis. To this end, a set of appropriately simple inorganic molecular structures was selected, consisting of salts of hexaaqua metal ions with organic counter-ions. By exploiting the crystallographic tools available in the Cambridge Structural Database program *Mercury*, students learn how to visualize and analyse a set of atomic coordinates. In this way they learn how to extract bonding and structural information concerning intramolecular interactions in both salt components. Intermolecular interactions are next analysed by looking closely at supramolecular motifs and packing patterns generated by hydrogen bonds. This pragmatic approach turned out to be effective and extremely useful for summarizing many chemical concepts learned by students during a bachelor degree course in chemistry. The experience provides at the same time some basic capabilities for properly managing crystal structure analysis.

## 1. Introduction

During the past ten years, inorganic chemistry teaching at the Università di Milano – Bicocca has been performed with a focus on amorphous and crystalline solid materials. The backbone of the course comprises classroom lectures complemented by a computer-based laboratory component. Students attend the course in the second semester of the third and final year, having at that time almost finished their training in general, inorganic, organic and physical chemistry. The approach followed by the laboratory supervisor (the present author) is to summarize and exploit all chemical information acquired by students during the previous five semesters to study simple inorganic crystalline solids.

Since the beginning, this aim has been pursued by exploring the rich chemistry stored in crystallographic databases. Due to the complexity of purely inorganic structures present in the Inorganic Crystal Structure Database (Belsky *et al.*, 2002), the author chose to make use of the large amount of chemical information stored in the Cambridge Structural Database (CSD; Allen, 2002; Groom *et al.*, 2016), which is constantly updated and validated. The relevance of the CSD in research and education is highly appreciated worldwide due to its overall performance and potential in different fields (Taylor & Wood, 2019). Numerous papers have been published that



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specifically address teaching activities based on the full crystal data available in different databases (Glasser, 2016). For example, there are a number of education-oriented papers discussing molecular geometry, stereochemistry, solid-state chemistry (Boldyreva, 2010), reaction pathways (Wackerly *et al.*, 2009; Battle, Ferrence *et al.*, 2010) and intermolecular interactions (Battle, Ferrence *et al.*, 2010; Battle & Allen, 2012; Vologzhanina, 2019). Inorganic systems are also considered, even though their geometrical and bonding features are more complex than those of organic molecules. The teaching proposals regarding inorganic compounds deal with the geometry of metal centres, high/low spin systems, back-bonding and the Jahn–Teller effect (Davis *et al.*, 2002; Orpen, 2002; Reglinski *et al.*, 2004; Battle *et al.*, 2011*a,b*). These articles are furthermore integrated in a collection of ‘Teaching Modules’ (Battle *et al.*, 2010*a,b*; Battle, Ferrence *et al.*, 2010) easily found in the ‘Help/Tutorial’ menu of *Mercury*, the graphical and analytical tool for molecular and crystal structures distributed with the CSD suite of programs (Macrae *et al.*, 2020).

The present paper reviews ten years of inorganic chemistry teaching through the analysis of crystal structures and their relationship to chemistry topics learned during a chemistry curriculum. In addition to raising awareness of the existence of huge amounts of crystallographic (and therefore chemical) data (Glasser, 2016), by the analysis of crystal structures, students are provided with an opportunity to summarize the chemical knowledge absorbed in previous classes, and to merge concepts formally coming from different chemical fields. Moreover, X-ray crystallography is seldom present in undergraduate curricula (Pett, 2010), and students hardly have a chance to learn the role of crystallography in science, and, even less, to develop basic skills in crystal structure analysis.

To fulfil these requirements, the choice of case studies was restricted to inorganic solids comprising hexaaqua ions having organic counter-ions. These were found to be simple enough for inexperienced students but nonetheless chemically very rich, with varied and interesting packing motifs arising from networks of strong hydrogen bonds (Allen & Motherwell, 2002). It is shown here that, for the selected molecular inorganic solids, classical hydrogen bonds, thanks to their strength and directional properties, are dominant in determining many features of the proposed crystal structures and are at the same time a very effective teaching tool.

## 2. Retrieval of case studies with *ConQuest*

The subset of molecular inorganic structures suitable for the course is updated every year before assigning the final report task to each student. The latest search has been performed on CSD Version 5.41 with March and May 2020 updates using *ConQuest 2.0.5* (Bruno *et al.*, 2002). The retrieved crystal structures satisfied the following constraints:

(i) Connectivity search for hexa-coordinated metal cations with any positive charge and bonded to non-bridging water molecules.

(ii) Crystal structures must contain exactly two chemical residues, in order to exclude other solvates and thus limit structural complexity, *i.e.* just one hexaaqua ion and one organic counter-ion.

(iii) ‘Residual factor’  $R < 0.1$  (minimum, maximum and average values in the final data set are 0.0188, 0.0867, 0.0397).

(iv) No disorder, no errors, no polymeric structures, coordinates from single-crystal data only (268 hits including also metal anions).

(v) Structures with metal-containing anions were discarded (64 hits).

(vi)  $X-H$  ( $X = C, N, O$ ) bond distances were renormalized using default values built into the CSD software and corresponding to average internuclear distances to improve clarity for students.

The remaining 204 hits were further sieved by hand to exclude strange/difficult structures based on the supervisor’s judgement (*e.g.* complex boron cages) and structures with missing hydrogen atoms, especially water hydrogens whose position cannot be determined from the local stereochemistry. A few structures have been discarded because of space-group errors or because they were duplicates. All structures have been checked and provided with a complete set of hydrogen atoms.

The final data set comprises 134 hits and shows a variety of anions giving rise to multiform crystal structures based on the following metal centres:  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $V^{2+}$ ,  $Zn^{2+}$ ,  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Ru^{3+}$ . A list of accepted structures is available in the supporting information for this paper as a spreadsheet file which also includes for each structure CSD refcode, metal cation, organic anion, a short description of the hydrogen-bond network, the presence of hydrogen bonds between cations or anions, labelling of isomorphous structures, polymorphs, space group,  $R$ -factor value and useful remarks. By filtering and sorting on each of these columns the user can select subsets for programming her/his own teaching activities.

## 3. Description of the teaching activity

### 3.1. Overall view of the working scheme

In the following sections the laboratory course and its timing will be discussed in detail, providing all information required to replicate the activity. Chemistry students attend 28 academic hours of classroom lectures supplemented by 48 h of hands-on activities in the laboratory, spanning 12 days of 4 h slots. The computer-based activity for students is a bottom-up approach from molecules to crystal structures. The working scheme has been refined over the years to provide practical skills in crystal chemistry of simple inorganic compounds to students with little or no previous crystallographic training; this poses several challenges to the teacher and to students as well. Before coming to grips with the analysis and description of a crystal structure, students must learn some basic concepts such as point-group symmetry, space-group symmetry, unit cell and asymmetric unit, and Miller indices with crystal directions;

these topics are presented in a stepwise fashion by the laboratory supervisor, keeping formal language and derivations to a minimum.

Importantly, the newly introduced concepts are promptly investigated by using available free software to acquire the necessary skills. For analysis of molecular point-group symmetries the interactive collection of chemical species available at <https://symotter.org/> (by D. H. Johnston) is extensively used. In order to get students acquainted with unit cells, asymmetric units, crystallographic symmetry elements and packing diagrams, the core of the course, the CSD program *Mercury* and its associated Teaching Database subset of crystal structures are employed. By using the rich set of user-friendly tools available in *Mercury* [for a description of recent developments see the article by Macrae *et al.* (2020)] students can quickly learn how to display and analyse molecules in crystals, and how to measure different bonding and conformational parameters. At the end of the learning process they should be able to extract fundamental chemical information at the intramolecular level. Previous applications of the CSD to molecular inorganic systems can be found in the work of Orpen (2002).

Students are introduced to the beauty (and perils) of solid-state chemistry, by means of a few revealing examples, illustrating in particular chemical information that cannot be extracted from chemical formulae. (a)  $\text{Cu}^{\text{II}}$  acetate monohydrate  $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$  is actually built by dimers with five-coordinate copper centres bridged by four carboxylate groups plus a terminal water molecule. (b)  $\text{NiSO}_4$  heptahydrate easily loses water because one of the water molecules does not belong to the octahedral inner coordination sphere of the cation, and the associated hydrogen bonds are not strong enough to stabilize the structure even at room temperature; in contrast,  $\text{NiSO}_4$  hexahydrate is fairly stable because all water molecules are linked to the metal centre. (c) Borax, quoted in older books as  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , is really  $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  as shown by its crystal structure.

After these introductory concepts about chemical compounds in the crystalline state have been established, students are instructed on how to analyse crystal structures and how to gradually extract several relevant features from crystal data (unit-cell parameters, space-group symmetry, atomic coordinates) with the program *Mercury*. Then, they begin moving to interactions between molecules at the supramolecular level, as is the case for crystals.

In summary, students are asked to analyse a set of atomic coordinates to extract the following chemical data:

- (i) Number of cations and anions in the unit cell (unit-cell content).
- (ii) Oxidation state of metal centres and net anionic charges.
- (iii) Chemical formula of the crystalline compound as deduced from the unit-cell content with an explicit description of the cationic and anionic components.
- (iv) Intramolecular features of anions (bond order, delocalization, molecular geometry described by bond distances and angles, torsion angles, ring conformation, stereocentres, intramolecular hydrogen bonds).

(v) Intramolecular bonding features of aqua cations (inner sphere coordination geometry including possible Jahn–Teller distortions).

(vi) Intermolecular contacts due to hydrogen bonds involving cations and anions.

(vii) Packing motif as determined by extended hydrogen-bond networks.

As already pointed out, hydrogen bonds are prominent among intermolecular interactions and this is the reason for them being frequently exploited in crystal chemistry education. In the selected crystal structures, hydrogen bonds, whose potential energy contribution is in the 30–50  $\text{kJ mol}^{-1}$  range, really play a fundamental directional role at a supramolecular level, and students are required to explore them and summarize all their findings in a detailed written report. For completeness, a brief preliminary mention is made of other packing forces, namely Coulombic potential interactions between ionic centres (amounting to 136  $\text{kJ mol}^{-1}$  for two ions 10 Å apart), and weaker dispersive forces between organic moieties.

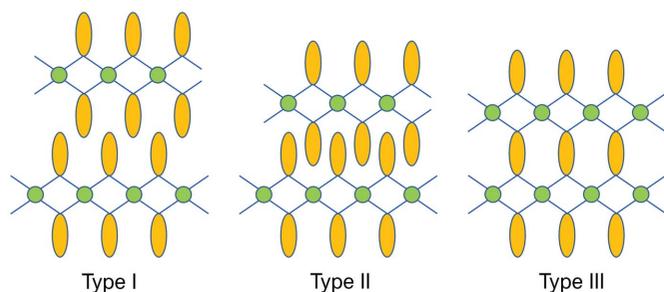
### 3.2. Description of the selected crystal structures

When planning this course, the CSD has been mined to extract inorganic crystal structures with extended hydrogen-bond networks, while representing a level of structural complexity suitable for undergraduate students. The 134 crystalline structures that passed the selection stage, all comprising  $M(\text{H}_2\text{O})_6^{n+}$  cations, show a great variety of organic anions and of local and crystal environments due to intermolecular hydrogen bonds. All structures exhibit segregation of cations in layers [cations arranged in rows or isolated aqua ions have been excluded; the spreadsheet file in the supporting information reports an example of a chain of metal centres (see refcode FEYTIN; Ma *et al.*, 2005)]. These layers represent an easily visualized structural motif for inexperienced students. All selected structures comprise multiple layers consisting of two sheets of anions with a layer of  $M(\text{H}_2\text{O})_6^{n+}$  cations sandwiched in between. A net of hydrogen bonds links the coordinated water molecules to acceptor atoms in the anions with no direct coordination to the metal centres. The organic anions fall into numerous different categories and bear one or more functional groups able to act as hydrogen-bond acceptors (and in some cases as donors as well), producing extended networks of mostly strong hydrogen bonds (see Section 4 for a simple interatomic distance criterion for evaluation of the strength of hydrogen bonds). Anions linked to hexaaqua ions adopt a wide variety of configurations, giving rise to anion/cation/anion three-tiered layers (henceforth referred to as ‘triple layers’) characterized by (a) simple stacking on top of adjacent triple layers according to the bumps-into-hollows rule with weak interlayer interactions, (b) deep interdigitation of adjacent anionic sheets or (c) interconnected sheets by bridging anions in 3D architectures. In several cases direct cation–cation and/or anion–anion hydrogen bonds are also present, thus increasing the variety of structural motifs available in the data set. All

$D-H \cdots A$  ( $D$  = hydrogen-bond donor;  $A$  = hydrogen-bond acceptor) interactions comprise nitrogen and oxygen atoms, with nitrogen coming only from anionic units. Only two structures are based instead on  $D-H \cdots S$  interactions.

A manual inspection of the structures with *Mercury* led to identification of the three aforementioned main types of hydrogen-bonded triple layers which were named as 'stacked layers', 'interdigitated layers' and 'interconnected layers'. To improve the teaching process, the instructor illustrates to students the packing motifs observed for the chosen class of compounds and detailed in the following sections. This somewhat arbitrary classification introduces a minimum of common language for the description of the hydrogen-bond frameworks and is easily understood and applied by students when analysing their own structures. In the following, some examples of these structural types are briefly described to illustrate their potential in teaching inorganic structural chemistry. Intramolecular details are not reported here but are a mandatory part of the final assessment procedure for students (see Section 4). A schematic picture of the three different structural types is reported in Fig. 1. It should be understood that a layer is formed as the ribbons of aqua ions or of organic anions are extended in a direction perpendicular to the plane of Fig. 1.

**3.2.1. Type I – stacked layers.** A total of 27 CSD hits out of 134 share the type I architecture comprising different metal centres and anions; among them four different isomorphous series are present, based on the BENBIG01 (Johnston & Tinapple, 2018), FABWEM (Riedel *et al.*, 2011), LIJSOM (Henderson & Nicholson, 1995) and TOKBUR (Chagas *et al.*, 2008) structures (see column ISOMORPHS in the spreadsheet file in the supporting information). This structural type (Fig. 1, left) is the simplest one among the hexaaqua metal ions with organic counter-ions. It is characterized by anion/cation/anion triple layers with different corrugation degrees of the contacting surfaces but without any significant interdigitation of the anionic layers with the adjacent ones. Therefore, triple layers are simply stacked on top of each other and held

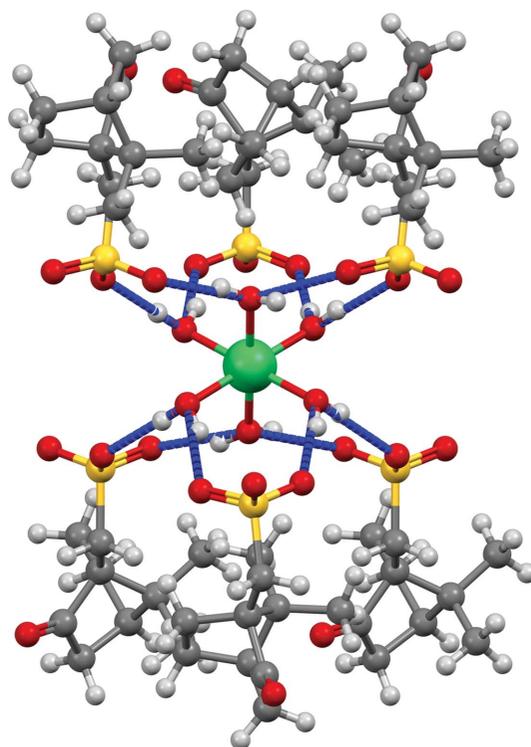


**Figure 1**  
Schematic configurations of triple anion/cation/anion layers as observed for the accepted 134 hits showing stacked layers (type I), interdigitated layers (type II) and interconnected layers (type III). Layers are formed as the ribbons of aqua ions connected by organic anions are extended in a direction perpendicular to the plane of the figure. The same projection, tangential to the triple layers, is maintained in all the following packing diagrams. Hexaaqua ions are symbolized as green spheres, anions as orange ellipsoids and hydrogen bonds as blue lines.

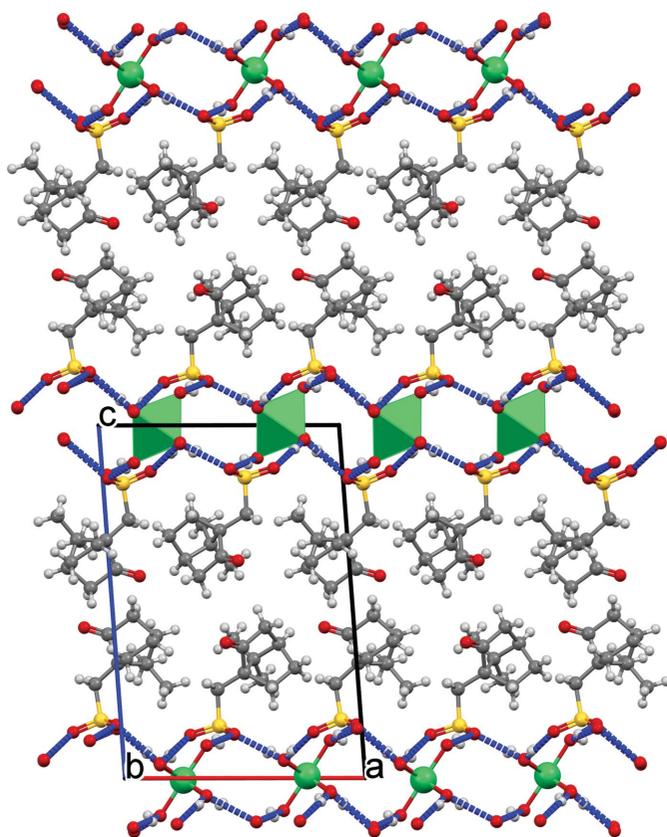
together by forces which are generally weaker than the 2D extended hydrogen-bond networks and Coulombic forces between cations and anions.

A typical type I crystal structure is that of hexaaquanickel(II) bis(*D*-camphor-10-sulfonate) (CSD refcode LIJSOM; Henderson & Nicholson, 1995). The local environment around a cationic unit in LIJSOM is shown in Fig. 2. Six anions are hydrogen-bonded to the cation water molecules through the sulfonate oxygen atoms. The sulfonate groups bridge different cationic centres using all their oxygen atoms. The ketonic oxygen atom of the anion is not involved in any hydrogen bond. Cations act as hydrogen-bond donors while anions behave as acceptors. Thanks to hydrogen bonds between anions and cations, layers are formed running parallel to (001) planes. In this case, no direct cation–cation hydrogen bonds are present. As can be easily appreciated by viewing a packing diagram down [100] and, more effectively, down the [010] (Fig. 3) direction, adjacent layers are stacked one onto another without interdigitation, leaving weak forces to glue together the triple anion/cation/anion layers. From this structural feature a reasonable assumption is the presence of an easy cleavage parallel to (001).

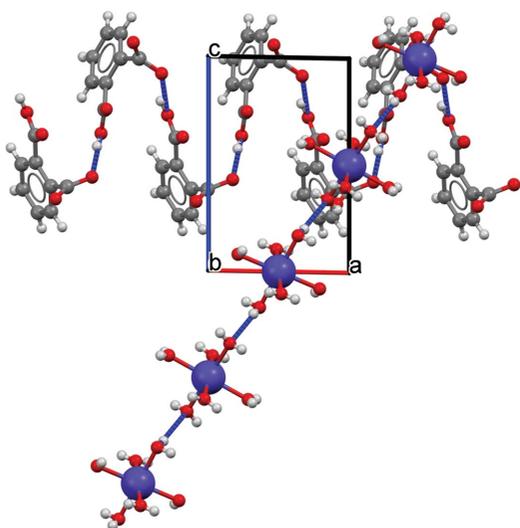
Several type I structures also have direct cation–cation or anion–anion hydrogen bonds, respectively, mediated by water molecules acting as acceptors or due to the presence of hydrogen-bond donor sites on the anions. An interesting case



**Figure 2**  
Local environment around the cation in hexaaquanickel(II) bis(*D*-camphor-10-sulfonate) (CSD refcode LIJSOM; Henderson & Nicholson, 1995). Hanging  $O-H \cdots O-S$  contacts, not shown here for the sake of clarity, are responsible for the formation of infinite (001) layers by further connecting cations.



**Figure 3**  
Packing diagram for hexaaquanickel(II) bis(D-camphor-10-sulfonate) (CSD refcode LIJSOM; Henderson & Nicholson, 1995) viewed along [010], *i.e.* parallel to the triple layers. The green octahedra represent the nickel ion coordination shell viewed edge-on. Layers of cations parallel to (001) are held together by hydrogen bonds (highlighted with blue lines) between anions (acceptors) and cations (donors). No direct cation–cation hydrogen bonds are present. Adjacent layers are stacked one onto another without interdigitation.



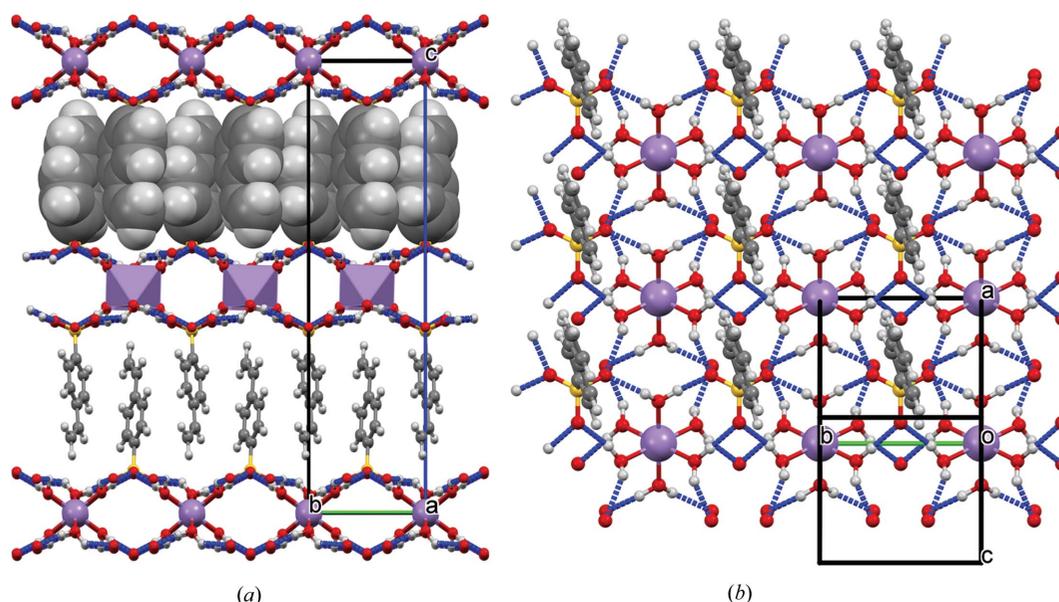
**Figure 4**  
View down [010] of the [100] anionic zigzag chains and the [101] cationic straight chains built from hydrogen bonds as observed in COHDPH (Adiwidjaja *et al.*, 1978).

is represented by hexaaquacobalt(II) bis(hydrogenphthalate) salt, known with three monoclinic polymorphs [CSD refcodes COHDPH (Adiwidjaja *et al.*, 1978), COHDPH01 (Küppers, 1990) and COHDPH02 (Kariuki & Jones, 1993)]. Polymorph COHDPH01 is characterized by an intramolecular hydrogen bond within the hydrogenphthalate anion which also acts as a sixfold acceptor with all oxygen atoms and connecting to four cations. The remaining polymorphs both show hydrogen bonds involving adjacent anions and giving rise to zigzag chains that develop parallel to [100]. The configuration found in COHDPH is close to that observed in potassium hydrogenphthalate (CSD refcode KHPHAL01; Eremina *et al.*, 1993) along [001]. In addition to these features, COHDPH displays hydrogen bonds between cations, leading to straight chains of hexaaquacobalt(II) ions aligned along [101] (Fig. 4).

Type I structures, due to weak interactions between facing anionic sheets, are likely to be easily cleaved when shear forces parallel to the triple layers are applied. Students in Milano – Bicocca are prompted to assess the possible presence of cleavage in their structures due to the relevance of this property in low-dimensional materials. A computational approach based on a topological analysis of crystal structures supported by energy evaluation has been demonstrated to be robust enough to extract 2D hydrogen-bond networks giving rise to perfect cleavage in a specific class of organic crystals (Zolotarev *et al.*, 2016). Unfortunately, a random check of the scientific literature pertinent to the 134 hexaaqua systems described here revealed no discussion of this fundamental property.

**3.2.2. Type II – interdigitated layers.** The type II category is represented by 32 structures, out of the selected 134 hits, involving many different anions and cations, again characterized by the triple-layer motif described above. These architectures are characterized by a significant degree of interdigitation of the triple layers with the adjacent ones. The interdigitation is generated by the anionic groups that fit between the anions of the two adjacent layers through the molecular sides not involved in hydrogen bonds (Fig. 1, centre). This is the second easy-to-recognize pattern for students and represents the intermediate step on going from type I to type III structures (see the next section) in terms of relevance of interaction between adjacent triple layers.

An example of a type II structure is hexaaquamanganese(II) bis(4-styrenesulfonate) (CSD refcode SUVBOA; Leonard *et al.*, 1999) which shows segregation of cations in planes parallel to (001) and held together by bridging anions with Mn–O–H···O–S interactions. Focusing on a cationic layer, on moving parallel to [010], anions are alternately connected through hydrogen bonds to one cationic layer or to the next cationic layer in a comb-like structure [Fig. 5(a)]. The same view also illustrates the network developing within (002) slabs and responsible for the existence of strongly bonded triple layers. In Fig. 5(b) a top view of a triple layer shows the molecular trenches available for interdigitation by the adjacent anionic sheet. In fact, owing to the large separation between hydrogen-bonded anions along [010], there is room for inserting [100] rows of anions hydrogen-bonded to the next



**Figure 5**  
 (a) Packing diagram for hexaaquamanganese(II) bis(4-styrenesulfonate) (CSD refcode SUVBOA; Leonard *et al.*, 1999) viewed down [100], *i.e.* parallel to the triple layers. Cations are sandwiched between (001) layers of anions by means of hydrogen bonds between anions (acceptors) and cations (donors). No direct cation–cation hydrogen bonds are present. Adjacent layers show deeply interdigitated anionic groups. (b) Perpendicular view of a cationic layer with bridging anions (only top side ones are shown) producing the 2D network with widely spaced [100] rows available for interdigitation.

layer. In type II structures cleavage is likely to be more difficult but this is presently unknown.

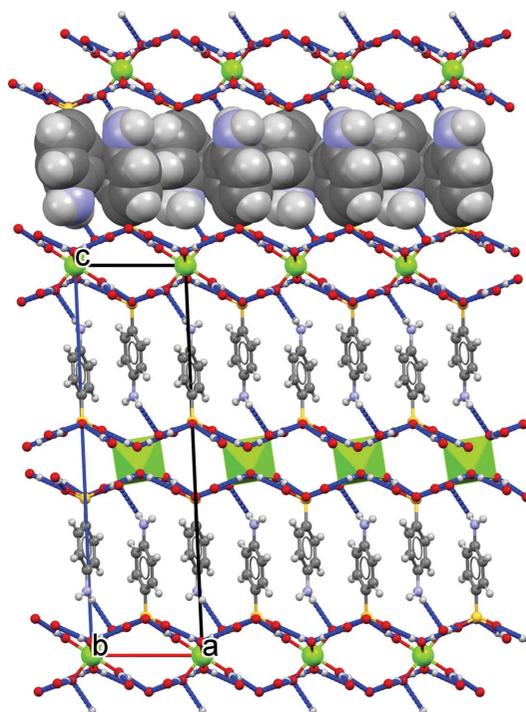
Of course with long anions, such as those of CSD refcodes FAFYIX (Oh *et al.*, 2016), KURWOK (Tai & Zhang, 2010) and RIHFVEV (Astbury *et al.*, 2013), the fingers of the comb-like structure become more entangled, probably preventing an easy cleavage along the pertinent crystallographic planes.

Only a few cases of type II structures comprise direct cation–cation or anion–anion hydrogen bonds (see the supporting information for a list). Type II structures show six different isomorphous groups and one isostructural but not isomorphous series, all listed in the supporting information.

**3.2.3. Type III – interconnected layers.** The type III architecture is the most populated with a total of 75 hits and a great choice of anions and cations characterized by a fully 3D supramolecular structure. In fact, these 3D architectures consist of cationic layers connected by means of hydrogen bonds with anionic moieties acting as bridging groups. Differently from type I and type II structures, the type III layers are held together by hydrogen bonds involving both ends of anionic moieties, which therefore act as pillars across two cationic sheets. The sites involved in hydrogen bonds with the cations also include for two-thirds of structures neutral functional groups of the anions, like the neutral amino group in Fig. 6, acting as a second attachment point to cations. Hydrogen bonds connecting anions through their neutral groups to cations are also sparsely present in type I and type II structures (four and two cases, respectively).

An example of an interconnected structure is shown in Fig. 6 for hexaaquamagnesium(II) bis(4-aminobenzenesulfonate) (CSD refcode VOPCEI; Shakeri & Haussühl, 1992). As usual, the sulfonate groups, the anionic moiety most frequently observed within the 134 hits, are involved in strong hydrogen

bonds but here also a donor amino group interacts with the lone pairs of water molecules. Therefore, the 4-aminobenzenesulfonate anions bridge adjacent cationic sheets (Fig. 6).



**Figure 6**  
 Packing diagram for hexaaquamagnesium(II) bis(4-aminobenzenesulfonate) (CSD refcode VOPCEI; Shakeri & Haussühl, 1992) viewed along [010], *i.e.* parallel to the triple layers. Layers of cations parallel to (001) are held together by hydrogen bonds between anions ( $\text{SO}_3^-$  acceptors) and cations ( $\text{H}_2\text{O}$  donors) plus  $\text{NH}_2 \cdots \text{OH}_2$  interactions. Direct cation–cation or anion–anion hydrogen bonds are absent.

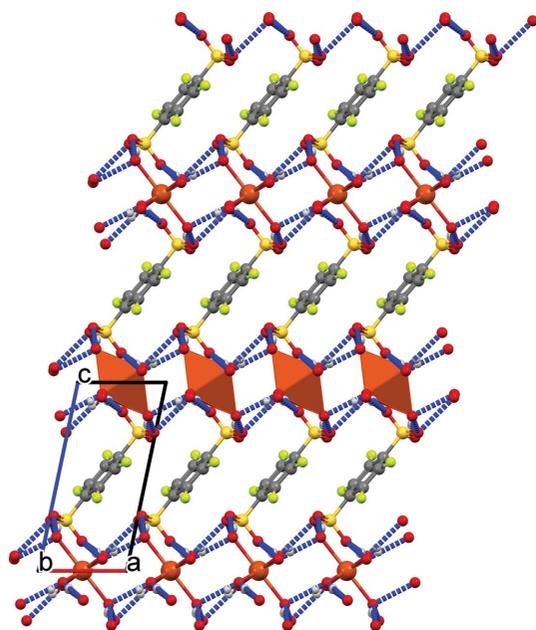


Figure 7

Packing diagram for hexaaquacopper(II) 2,3,5,6-tetrafluorobenzene-1,4-disulfonate (CSD refcode AQOXIO; Muesmann *et al.*, 2011) viewed down [010]. Layers of cations parallel to (001) develop in a direction perpendicular to the plane of the figure and are held together by dianionic bridges (hydrogen-bond acceptors) and cations (hydrogen-bond donors and acceptors). The dihedral angle between the plane of the copper atoms and the least-squares plane through the  $C_6F_4S_2$  units is  $50^\circ$ . Direct and strong cation–cation hydrogen bonds provide [100] chains with  $O \cdots O$  distances of 2.67 Å and  $O-H \cdots O$  angles of  $173.6^\circ$ . The copper cations display a relevant Jahn–Teller distortion with four short (1.948 and 1.979 Å) and two long (2.380 Å)  $Cu-OH_2$  bond distances.

Direct cation–cation or anion–anion hydrogen bonds are absent in this case.

The projections chosen for Figs. 4(a) and 5 may wrongly support the impression that anions always have the long molecular axis almost orthogonal to the layers. However, pillars are not necessarily close to being orthogonal to the triple layers. The crystal structure of hexaaquacopper(II) 2,3,5,6-tetrafluorobenzene-1,4-disulfonate (CSD refcode AQOXIO; Muesmann *et al.*, 2011) is an example of significantly tilted pillars (Fig. 7) with a dihedral angle between the plane of the copper atoms and the least-squares plane through the  $C_6F_4S_2$  units of  $50^\circ$ .

Due to the rich functionalization of anions in type III salts many crystal structures exhibit cation–cation or/and anion–anion hydrogen bonds in addition to those involving cations with anions. These interactions produce dimers (only among anions), infinite 1D structures (linear or zigzag chains) and infinite 2D structures (layers) (see the supporting information).

Finally, a couple of anions [4-hydroxy-3-nitrobenzenesulfonate (CSD refcode HEFSAM; Shubnell *et al.*, 1994) and 4-carboxybenzenesulfonate (CSD refcodes ONOSUG, ONOTAN, ONOTER; Wagner & Merzweiler, 2010)] have a functionalization suitable for giving rise to hydrogen-bonded dianionic dimers which are still able to bridge cationic sheets with hydrogen bonds between sulfonate groups and water

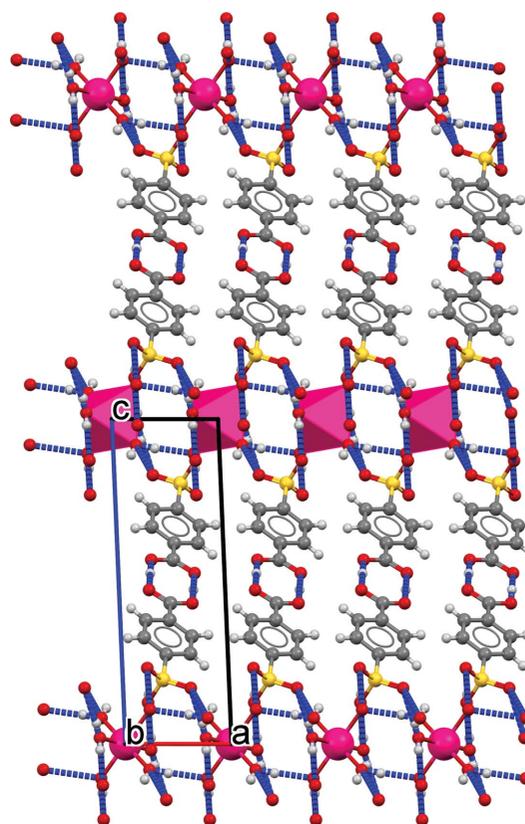


Figure 8

Packing diagram for hexaaquacobalt(II) bis(4-carboxybenzenesulfonate) (CSD refcode ONOSUG; Wagner & Merzweiler, 2010) viewed along [010] with dimeric hydrogen-bonded pillars. Layers of cations parallel to (001) are held together by hydrogen bonds involving the sulfonate groups. Direct and strong cation–cation hydrogen bonds are responsible for [100] chains with  $O \cdots O$  distances of 2.86 Å and  $O-H \cdots O$  angles of  $175.0^\circ$ . Adjacent neutral layers are further connected through hydrogen bonds involving the terminal carboxylic groups of the anions.

molecules. In this way, hydrogen-bonded dianionic layers lie between adjacent cationic sheets. Such a double layer of anionic pillars is displayed in Fig. 8 for hexaaquacobalt(II) bis(4-carboxybenzenesulfonate) (CSD refcode ONOSUG).

#### 4. Final assessment of skills: the written report

The presence of clear-cut 2D and 3D hydrogen-bond networks in the selected molecular inorganic solids allows students to unravel, understand and discuss a major component of the intermolecular interactions responsible for the packing motifs discussed here. Without neglecting the role of Coulombic charges located on cations and anions (and their long-range action), the directional character of classical hydrogen bonds has a great influence on intermolecular recognition processes and, therefore, on crystal structures. All the screened structures as detailed in Section 2 share the presence of  $M(H_2O)_6^{n+}$  cationic sheets sandwiched between two sheets of anions, resulting in electroneutral triple layers. This working data set represents a homogeneous but still varied benchmark for students' crystallographic training.

The visualization and analysis tools of *Mercury* have been extensively employed to allow inexperienced students to have a hands-on experience of crystal structures and crystal chemistry. No attempts are made to enter more deeply the complex realm of theories of the hydrogen bond (Gilli & Gilli, 2009), for instance through graph-set analysis (available in the licensed version of the CSD). Students are strongly encouraged to install the latest free version of *Mercury* on their own personal computers to integrate the laboratory classes with their homework and to prepare the study material necessary for the final written report.<sup>1</sup>

The goal of the laboratory course is to familiarize students with crystal structures and summarize all the concepts related to chemical bonding and molecules, intra- and intermolecular interactions, presented to students who are near the end of their chemistry curriculum. The final assignment asks students to apply all the chemical knowledge they have acquired, recently integrated with the fundamentals of crystallography. Through a written report, students must demonstrate having reached the teacher's expectation of being able to chemically interpret a set of atomic coordinates for a specific set of molecular inorganic solids. The report must have a good balance between visual information (easily and effectively performed with *Mercury*) and written descriptive text. Students are each assigned a different crystal structure randomly selected among the 134 CSD hits discussed here. They are also provided with a list of aspects to be discussed in the report, following a logical path from the intramolecular level to the supramolecular level of a crystal structure.

A simple template for the written report lists the mandatory topics for a satisfactory analysis of intra- and intermolecular characteristics of the assigned crystal structure: (i) unit-cell content, including the number of cations and anions in the unit cell; (ii) oxidation state of metal centres and net anionic charges; (iii) chemical formula of the crystalline compound as deduced from the unit-cell content with an explicit description of the cationic and anionic components.

First, stoichiometry must be assessed by evaluating the number of cations and anions in the unit cell, the rationale for this being provided at the first stages of the laboratory course. Although several of the actual cations cannot reveal any surprises regarding their electric charge, students are warned that the solid state is a powerful means to trap solution-unstable oxidation states of transition metals. The only safe way to establish the cationic charge is by cross examination of the organic anionic groups, the number of such groups and of cations within a unit cell. An especially critical point for

students is evaluating the number of cations and anions in the unit cell. Several structures show cations sitting on corners, on edges or across unit-cell faces, amounting to 1/8, 1/4 and 1/2 hexaaqua ions, respectively. For organic anions the situation can be frustrating and cumbersome due to complex shapes and molecules split across the bounding faces of the unit cell. In this case, a deeper analysis of translational symmetry effects helps to solve the riddle, while some students introduce molecular centroids to perform their evaluation of the unit-cell content. After the ionic charges have been determined, the chemical formula of the solid compound can be firmly established.

(iv) Intramolecular features for anions (bond order, delocalization, molecular geometry described by bond distances and angles, torsion angles, ring conformation, stereocentres, intramolecular hydrogen bonds).

The structural CIFs extracted from the CSD, prior to submission to the students, are stripped of everything but the bare crystallographic data (space group, cell parameters, elemental types, atomic coordinates), leaving just the atomic connectivity (automatically determined by *Mercury*) but without any information about type and bond order of covalent interactions. In this way, students face the task of interpreting at the intramolecular and intermolecular levels the atomic content of the unit cell. The description of molecular geometry and intramolecular characteristics of anions includes bond distances and angles, torsion angles, dihedral angles, ring conformations, stereocentres, intramolecular hydrogen bonds and a complete Lewis structural diagram. Bond distances and angles provide information about bond types and order, local stereochemistry, hybridization, delocalization, and resonance according to the valence bond theory and valence shell electron pair repulsion (VSEPR) model, all to be summarized in accordance with the Lewis structure. A brief description of numerical values after comparison with tables of typical interatomic distances (Allen *et al.*, 2004; Orpen *et al.*, 2004) completes the discussion.

(v) Intramolecular bonding features for cations (inner-sphere coordination geometry including possible Jahn–Teller distortions).

As to the metal centres, the homoleptic hexaaqua ions show octahedral geometry with different local symmetry and degrees of deviation with respect to the perfect octahedron, easily appreciated in terms of  $M\text{—OH}_2$  distances and  $O\text{—}M\text{—}O$  angles. Students are asked to discuss the possible presence and extent of Jahn–Teller distortions (easily identified with only  $d^9$   $\text{Cu}^{2+}$  ions with tetragonal distortions that reach up to 0.5 Å). Since water is a medium-strength ligand in the spectrochemical series (Huheey *et al.*, 1993), and due to the extended hydrogen bonds involving cations and anions, students seldom meet clear-cut evidence of Jahn–Teller distortions. Tentative decisions can be supported by crystal and ligand-field theory and a critical evaluation of metal–water bond distances (Orpen *et al.*, 2004).

After a full characterization of intramolecular parameters, students analyse the environment surrounding cations and anions. On moving to the intermolecular level, students must

<sup>1</sup> The availability of a free version of *Mercury* was vitally important. The onset of the COVID-19 pandemic in Italy overlapped with the start of the laboratory course, spanning the March–May period; this meant the course could not start in its usual form, but had to be suddenly reshaped as remote teaching and learning. A strict lockdown lasting until the middle of May 2020 prevented any chance of having at least the last lessons live. The only integration to the usual slide presentation has been the preparation of a written manual explaining the use of *Mercury* and the facilities at Otterbein University for point-group symmetry. During the writing of this article, submitted written reports were evaluated and produced high marks on average, without evidence of serious problems during the learning process.

assess (vi) the number of cations and anions interacting through hydrogen bonds with cations and (vii) the number of cations and anions interacting through hydrogen bonds with anions.

This step helps to reveal the arrangement of first neighbours around cations and anions with contacts determined by intermolecular hydrogen bonds, while Coulombic interactions have to be neglected in a visual assessment of structures. In *Mercury* the 'H-Bond contacts' tool with default settings quickly produces acceptor or donor contact atoms around a given moiety, which can be easily expanded into full hydrogen-bonded molecular shells with the 'Contacts/Expand all' command. *Mercury* default criteria for locating potential hydrogen bonds are based on donor–acceptor distances compared against standard van der Waals radii and students are warned to check for possible fake results (e.g. hydrogen bonds between highly electronegative atoms both without bonded H atoms) by activating the 'Require hydrogen atom to be present' option in the settings for hydrogen-bond searches.

At this stage of the analysis details of each  $D-H\cdots A$  interaction can be extracted by measuring  $D\cdots A$  distances and  $D-H\cdots A$  angles. These geometrical parameters allow rough estimation of the strength of each hydrogen bond, for example by comparing them with typical values discussed by Giacobuzzo (2011, in chapter 8). Such classification is necessarily a qualitative one, albeit easily handled by students and providing reasonable estimates of the robustness of hydrogen-bond networks. As already discussed in Section 3.2, all structures exhibit at least hydrogen bonds between cation water molecules and anions. In several cases direct hydrogen bonds between cations or anions are also available. Finally, for a few cases the anion also displays intramolecular hydrogen bonds.

Analysis of intermolecular patterns around cations and anions allows students to build a simplified but reasonable image of the structural motif. Each cation (anion) always interacts through many hydrogen bonds with several anions (cations). The final stage of the structural analysis must reveal (viii) the packing motif as determined by the hydrogen-bond networks.

By summarizing the hydrogen-bonding patterns around cations and anions, students are able to unravel the crystal structure built upon the patterns discovered in the previous bottom-up approach. Several options to build a suitable portion of the crystal structure with the supramolecular networks are available. One can start from a hexaaqua ion and activate the 'H-Bond contacts' tools to generate the first shell of hydrogen-bonded neighbours. Applying this procedure a second time is usually adequate to bring out the hydrogen-bond framework for each structure. The presence of cationic sheets is easily discovered and their orientation described in terms of Miller indices. Also the characteristics of the anionic sheets are in evidence and can be analysed to ascertain which type they are: triple layers with weak interlayer interactions (probably easily cleavable and 2D frameworks), interdigitated triple layers with anions linked through just one side to the cationic sheet (reduced cleavability and 2D frameworks) and bridging anions effectively connecting adjacent cationic sheets

(unlikely cleavability and 3D frameworks). This result is of significance because during the formal classes students are taught about low-dimensional solids as a very important class of materials, one example being that of layered metal phosphonates (Taddei & Costantino, 2019).

## 5. Concluding remarks

The laboratory course described in this paper has been taught for many years now and is a rewarding experience as a parallel to classroom teaching of inorganic solid-state chemistry. Being addressed to students who have no background in crystallography and with no previous experience of crystal chemistry, the course starts off with presentations of the basics of point-group and space-group symmetry, as well as of a number of essential concepts for the understanding of crystal description and constitution. As soon as this preliminary part is finished, the supervisor leaves students alone to have their own experience in dealing with molecular and crystal structures, as represented by the test cases chosen and discussed in this paper. The freeware program *Mercury* (Macrae *et al.*, 2020) is the ideal tool for the accomplishment of the proposed tasks, together with the data stored in the library of molecular symmetries available at the web site of Otterbein University (D. H. Johnston).

A further conceptual advancement provided by such an experience is the realization of the deep connection between molecular structure, as represented by a set of atomic coordinates from an X-ray diffraction experiment, and the implied chemistry, in the footsteps of the early findings gathered by the Braggs: for example, the discovery that no NaCl molecules exist as predicted by W. Barlow at the end of the 19th century. From a modern perspective, students learn from these analyses the importance of hydrogen bonding and of Coulombic and dispersive intermolecular interactions, with a glimpse of their relative strengths. The proceedings open the way to an understanding of materials science at a molecular level.

Last but not least, this laboratory course lends itself perfectly to distance learning and evaluation, as did happen due to the surge of the COVID-19 pandemic in Italy.

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