CrystEngComm

COMMUNICATION

Cite this: *CrystEngComm*, 2016, **18**, 1883

Received 18th December 2015, Accepted 3rd February 2016

DOI: 10.1039/c5ce02490k

www.rsc.org/crystengcomm

Topology analysis reveals supramolecular organisation of 96 large complex ions into one geometrical object†‡

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It is shown that the highly complex crystal structure of [Ag(4-(pyrrolidin-1-yl)pyridine)$_2$]NO_3·1/2H_2O, **1**, with 12 symmetry-independent Ag^+ ions and 96 units of complex ions in a unit cell can be understood by the ubiquitous **srs** topology, reducing thousands of atom positions into a single geometrical object in one go.

Modern technology is dependent on the understanding of the solid state.[1] Two examples are inorganic LEDs[2] and organic semiconductors,[3,4] and there is no reason to believe that future inventions will be any less reliant on information from crystal structures and diffraction data.

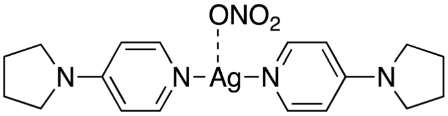
Currently, there are three main levels of interpretation of the solid state as measured by such methods. First, there is the space group and the positions of atoms and molecules in a unit cell. Then, we analyse the structure in more detail to reveal intermolecular interactions. By doing those things, we may perhaps arrive at one of the variations of close packing or at a known type structure. Some of these are found in basic chemistry textbooks and include, for example, the rock salt structure and the perovskite structure, wherein the latter is recently of solar cell relevance.[5]

The third level deserves to be known better and does not have an agreed upon name, but we will call it network topology analysis. First and foremost, it is associated with robust network solids such as diamond, quartz and zeolites, but topology analysis has the last two decades also been of immense value in understanding, categorising and even in synthesis planning of a new class of materials known as metal–organic frameworks.[6,7]

However, the significance of network topology goes well beyond these types of materials. For example, it was recently suggested,[8] and subsequently shown,[9] that nets are good starting points for screening possible allotropes of the group 14 elements. However, hydrogen-bonded systems can also be profitably viewed this way,[10–13] and we note that a recently suggested ice polymorph[14] has the same topology as the proposed "T12" allotrope[8] of the group 14 elements, which is the already known **cdp**-net (see the ESI‡). The method also offers a convenient way to classify and name compounds, reducing the need to reinvent the same wheel in different areas of solid state chemistry and physics.

In this communication, we demonstrate how network topology can be used to make sense of the crystal structure of [Ag(4-(pyrrolidin-1-yl)pyridine)$_2$]NO_3·1/2H_2O (**1**) having 12 symmetry-independent silver ions and 96 units of the complex ion in a 45 747(5) Å^3 unit cell.

Silver(I) compounds have attracted interest as versatile components especially in supramolecular compounds,[15,16] and for antimicrobial purposes[17] and we prepared [Ag(4-(pyrrolidin-1-yl)pyridine)$_2$]NO_3·1/2H_2O (**1**) (Scheme 1) by direct combination of silver nitrate and 4-(pyrrolidin-1-yl)pyridine in a 10 : 15 water–ethanol solvent mixture giving needle-shaped crystals in 88% yield. **1** crystallizes with tetragonal body-centered symmetry in the space group $I4_1$ and a complete structure description with selected interatomic distances and bond angles can be found in the ESI.‡



Scheme 1 [Ag(4-(pyrrolidin-1-yl)pyridine)$_2$] unit in [Ag(4-(pyrrolidin-1-yl)pyridine)$_2$]NO_3·1/2H_2O (**1**).

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† Dedicated to the memory of our longtime friend, collaborator and colleague, Prof. Dr. Yousry M. Gohar, 1950–2015.

‡ Electronic supplementary information (ESI) available: Additional crystal structure information, Hirshfeld plots, experimental details and biological testing. CCDC 1058723–1058725. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ce02490k

The degree of disorder in the structure is astonishingly low. Only one of 24 ligand molecules in the asymmetric unit shows orientation disorder of the pyrrolidine ring. Three of 12 nitrate ions showed orientation disorder and the protons of the crystal water molecules could not be located properly, thus only the positions of the oxygen atoms were refined. The asymmetric unit contains 12 formula units of this complex, thus the complete unit cell comprises 96 $[AgL_2]^+$ complex cations, 96 nitrate anions and 48 crystal water molecules. The coordination geometry of all the $[AgL_2]^+$ ions is similar – for this reason, only one dimeric molecular unit is shown in Fig. 1.

Overall, the structure shows an intriguing molecular packing, and the view along the *c*-axis (see Fig. 2, top) reveals some kind of cylindrical arrangement with half of the nitrates bridging between cylinders, as described in Fig. 1, and disordered water and the remaining nitrate ions inside the cylinders, which can be seen from the side (Fig. 2, bottom).

Normally, one would now leave the structure and not analyse it further, but we were convinced that, for a simple molecular coordination compound, there was a more regular underlying pattern to this extremely complex structure. We used Hirshfeld surfaces[18] (Fig. S1‡) to analyse the intermolecular interactions and found that both the "flatter" part of the coordination entity and the end $-CH_2-CH_2-$ units have significant dispersion type ($C-H\cdots H$ and $C-H\cdots C$) interactions with identical units. The most regular of these are $-CH_2-CH_2-\cdots-CH_2-CH_2-$ "embraces" connecting the ends of ligands, visible in Fig. 2.

The attractive nature of the $-CH_2-CH_2-\cdots-CH_2-CH_2-$ "embraces" can be deduced from analysis of the Cambridge Structural Database[19] where a linear arrangement of five-membered rings of this type in a similar fashion shows a broad maximum at 3.7–4.0 Å for C–C centroid distances (Fig. S2‡) quite similar to the distances in **1**. This interaction is, however, less clear in the structure of the free ligand, **2**, because the basic pyridine type nitrogen is now unprotected and tends to interact with these $-CH_2$ groups as well. On the other hand, in **2**, the flatter type of interaction is quite obvious.

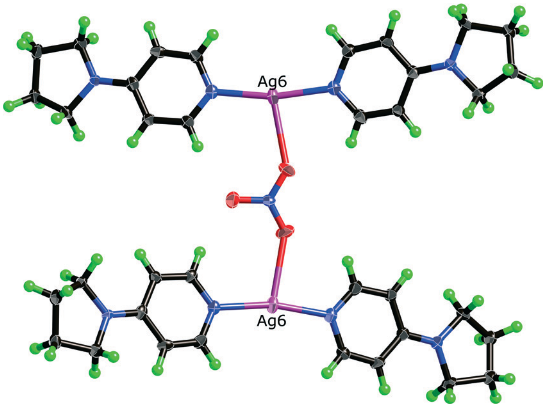

Fig. 1 Structure and atom numbering scheme of one of the twelve dimeric silver complex units in $[Ag(1\text{-pyrrolidinyl)pyridine})_2]NO_3\cdot 1/2H_2O$ (**1**). All ellipsoids are drawn at the 50% probability level. What is shown has two-fold crystallographic symmetry with one Ag6 at (*x*, *y*, *z*) and the other at (1 − *x*, −*y*, *z*).

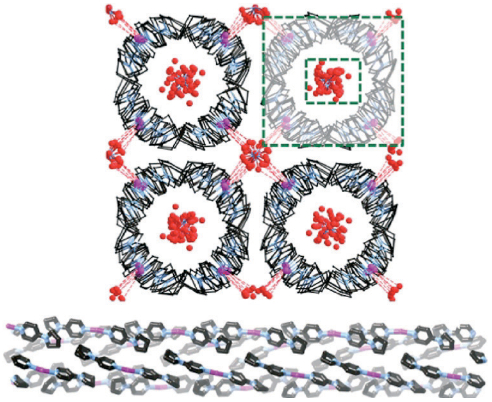

Fig. 2 Molecular packing of $[Ag(4\text{-(pyrrolidin-1-yl)pyridine})_2]NO_3\cdot 1/2H_2O$ (**1**).

Without passing judgement on the relative strength of these two interactions, we chose to connect the coordination entities with the $-CH_2-CH_2-\cdots-CH_2-CH_2-$ "embraces" to see if this could help us understand the overall structure. The result is shown in Fig. 3 and reveals a hexaplet helix forming a cylinder through the less well-defined "flatter" interactions. (If we take the "flatter" interactions as our organizing principle, we get a structure model that is as complicated as the structure itself and gives no additional insight.)

Since the cylinders and individual helices are connected with each other through the dimers shown in Fig. 2, the complete structure, ignoring the disordered H_2O and NO_3^- inside the helices, can now be described as intertwined three-connected networks, as each silver complex connects to two other complexes through the $-CH_2-CH_2-\cdots-CH_2-CH_2-$ "embraces" and to one other complex through the bridging nitrates. The topology of these 3D-nets is astonishingly simple: what we have in the structure is the most common and most symmetric of all the three-connected nets, namely the **srs**-net,[20] also known as the (10,3)-a (Wells[21]) or $SrSi_2$ net. This topology is inherently chiral, and as can be seen in Fig. 4, all the helices in one cylinder have the same chirality. However, the overall topology is achiral because the six helices in one cylinder, all simply related by translation, are balanced by six helices of opposite chirality in a neighbouring cylinder, all related by a mirror plane, see Fig. 4 (bottom).

Fig. 3 To visualize the structure of **1**, the $-CH_2-CH_2-\cdots-CH_2-CH_2-$ "embraces" have been used to connect the $[Ag(4\text{-(pyrrolidin-1-yl)pyridine})_2]^+$ units, revealing a hexaplet helix forming cylindrical shapes with additional interactions (not shown) between the individual helices.

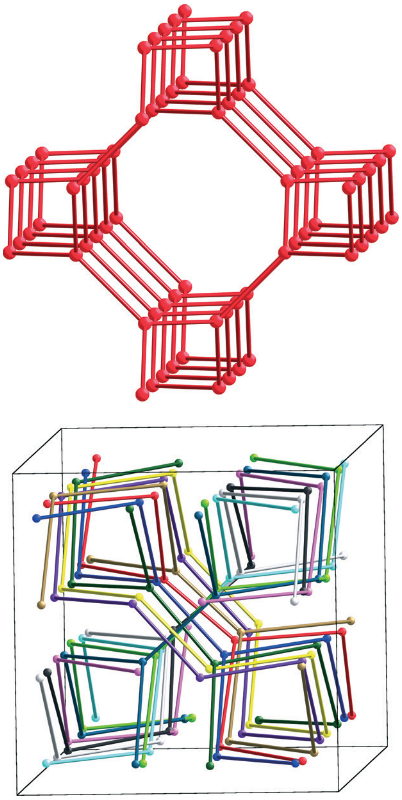

Fig. 4 Top: the three-connected **srs**-net in its most symmetric form showing four helices; bottom: the twelve interpenetrated **srs**-nets of [Ag(4-(pyrrolidin-1-yl)pyridine)$_2$]NO$_3$·1/2H$_2$O (**1**) displaying two helices each.

We find that we now have a way of interpreting, understanding and communicating the structure of **1**. The 12 symmetry-independent silver ions represent the 12 individual **srs**-nets and the 96 coordination entities in the unit cell represent 8 entities in each type of helix. As two of these individual helices, each with four entities, are present in the unit cell, the length of the *c*-axis exactly matches one pitch of the four-fold helix of an **srs**-net. The only space available in this interpenetrated structure is inside each hexaplet helix and there we find the remaining counter ions and solvent molecules.

While the overall topology of the interpenetration is achiral, **1** was refined in the chiral space group $I4_1$ and the structure is thus chiral. The reason for this apparent discrepancy is that all the individual helices in **1** are crystallographically independent and the mirror planes present when interpenetrating 6 + 6 helices with full symmetry are not present.

Why then should this **1** adapt this extraordinary structure? We note that the corresponding perchlorate compound prepared in the same way, [Ag(4-(pyrrolidin-1-yl)pyridine)$_2$]ClO$_4$ (**3**), has a more ordinary structure: exactly linear N–Ag–N coordination geometry and π–π stacking in a much smaller unit cell.

We have suggested rules of thumb for the structure of silver complexes with nitrate counter ions.[11,22–24] In general, it seems that the "problem" is that the nitrate ion is very hard, so it does not automatically bond with the silver ion but does not favourably interact with organic ligands, either. Thus, if we have hydrophobic ligands with hydrophilic substituents, the nitrate groups tend to be either coordinated to the Ag(I) ions or, preferably, hydrogen-bonded to the hydrophilic substituents of the ligand. In the absence of hydrogen bond donating substituents, we either find the nitrate ion bonded to Ag$^+$ or there is solvent water in the structure to which it can hydrogen bond instead. In certain cases, we have also found particular, but apparently favourable, weak hydrogen bond patterns or other special arrangements around polar groups that are not hydrogen bond donors that can contain nitrate ions.[22]

The present case with the 4-(pyrrolidin-1-yl)pyridine ligand present some difficulties with molecular packing: the pyridine parts could perhaps π–π stack but cannot really interact favourably with the five-membered ring, and the nitrate ion has no polar or hydrogen bond donors to interact with, so it needs to either bond to silver or assemble around waters of crystallisation. If, as indeed in the case of **1**, Ag(I) coordinates the nitrate ion, then the complex becomes nonlinear and π–π stacking of the pyridine groups becomes less evident. We believe that this is the key to this extraordinary structure and the difference compared to the perchlorate compound is that this anion is non-coordinating, giving a linear complex ion that can easily π–π stack, and as ClO$_4^-$ is also more symmetric and softer in character than NO$_3^-$, it is more compatible with the non-polar organic groups.

It should be noted that while the 12-fold interpenetration of the **srs**-net seems to be unique, it is not a record: in 2011, a 54-fold interpenetrated silver coordination polymer was reported[25] and in 2005, an 18-fold interpenetrated hydrogen bonded system of trimesic acid and 1,2-bis(4-pyridyl)ethane was published.[26]

Minimum inhibitory concentrations (MIC) for **1** against multidrug-resistant diabetic foot bacteria compared to a number of commercial antibiotics can be found in the ESI.‡ [Ag(4-(pyrrolidin-1-yl)pyridine)$_2$]NO$_3$·1/2H$_2$O is active against all microorganisms including the fungus *C. albicans*, and has higher, or the same activity, as the best antibiotics against *P. aeruginosa* and *P. mirabilis*.

In conclusion, we have used network topology analysis to show that the complexity of the crystal structure of [Ag(4-(pyrrolidin-1-yl)pyridine)$_2$]NO$_3$·1/2H$_2$O (**1**) can be understood by 12-fold interpenetration[27,28] of the ubiquitous **srs** topology, also known as (10,3)-a or SrSi$_2$-nets, thus reducing thousands of atom positions into one geometrical object in one go.

Notes and references

1 Editorial, *Nat. Mater.*, 2014, **13**, 757–757.

2 S. Ye, F. Xiao, Y. X. Pan, Y. Y. Ma and Q. Y. Zhang, *Mater. Sci. Eng., R*, 2010, **71**, 1–34.

3 A. Saeki, Y. Koizumi, T. Aida and S. Seki, *Acc. Chem. Res.*, 2012, **45**, 1193–1202.

4 T. Lee, C. A. Landis, B. M. Dhar, B. J. Jung, J. Sun, A. Sarjeant, H. J. Lee and H. E. Katz, *J. Am. Chem. Soc.*, 2009, **131**, 1692–1705.

5 M. Gratzel, *Nat. Mater.*, 2014, **13**, 838–842.

6 M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2011, **112**, 675–702.

7 S. R. Batten, N. R. Champness, X. M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M. P. Suh and J. Reedijk, *Pure Appl. Chem.*, 2013, **85**, 1715–1724.

8 L. Öhrström and M. O'Keeffe, *Z. Kristallogr. - Cryst. Mater.*, 2013, **228**, 343–346.

9 I. A. Baburin, D. M. Proserpio, V. A. Saleev and A. V. Shipilova, *Phys. Chem. Chem. Phys.*, 2015, **17**, 1332–1338.

10 I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *Cryst. Growth Des.*, 2008, **8**, 519–539.

11 M. A. M. Abu-Youssef, V. Langer and L. Öhrström, *Chem. Commun.*, 2006, 1082–1084.

12 A. F. Wells, *Three-dimensional nets and polyhedra*, John Wiley & Sons, New York, 1977.

13 L. Öhrström, in *Encyclopedia of supramolecular chemistry*, ed. L. Barbour, Wiley Chichester, UK, 2012, vol. 8, Supramolecular materials chemistry.

14 J. Russo, F. Romano and H. Tanaka, *Nat. Mater.*, 2014, **13**, 733–739.

15 J. Burgess and P. J. Steel, *Coord. Chem. Rev.*, 2011, **255**, 2094–2103.

16 H. Schmidbaur and A. Schier, *Angew. Chem., Int. Ed.*, 2015, **54**, 746–784.

17 S. Medici, M. Peana, V. M. Nurchi, J. I. Lachowicz, G. Crisponi and M. A. Zoroddu, *Coord. Chem. Rev.*, 2015, **284**, 329–350.

18 J. J. McKinnon, M. A. Spackman and A. S. Mitchell, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2004, **60**, 627–668.

19 F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380–388.

20 S. T. Hyde, M. O'Keeffe and D. M. Proserpio, *Angew. Chem., Int. Ed.*, 2008, **47**, 7996–8000.

21 A. F. Wells, *Acta Crystallogr.*, 1954, **7**, 535–544.

22 A. A. Massoud, V. Langer, Y. M. Gohar, M. A. M. Abu-Youssef, J. Jänis, G. Lindberg, K. Hansson and L. Öhrström, *Inorg. Chem.*, 2013, **52**, 4046–4060.

23 M. A. M. Abu-Youssef, S. M. Soliman, V. Langer, Y. M. Gohar, A. A. Hasanen, M. A. Makhyoun, A. H. Zaky and L. R. Öhrström, *Inorg. Chem.*, 2010, **49**, 9788–9797.

24 M. A. M. Abu-Youssef, V. Langer and L. Öhrström, *Dalton Trans.*, 2006, 2542–2550.

25 H. Wu, J. Yang, Z.-M. Su, S. R. Batten and J.-F. Ma, *J. Am. Chem. Soc.*, 2011, **133**, 11406–11409.

26 T. R. Shattock, P. Vishweshwar, Z. Wang and M. J. Zaworotko, *Cryst. Growth Des.*, 2005, **5**, 2046–2049.

27 S. R. Batten, *CrystEngComm*, 2001, **3**, 67.

28 L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247–289.