A unique example of a high symmetry three- and four-connected hydrogen bonded 3D-network†

Morsy A. M. Abu-Youssef,[*a] **Vratislav Langer**[b] **and Lars Öhrström**[*b]

We present a three- and four-connected 3D-net based on 4-aminopyridine coordinated to Ag(I) and hydrogen bonded to nitrate with the unusual, high symmetry, topology $(8^3)(8^6)_2$-tfa.

The examples of possible practical applications of three-dimensional coordination polymers ("metal–organic frameworks") and hydrogen bonded analogous systems are growing.[1] However, such systems have to a large extent been based on highly symmetric building blocks and this has resulted in a high number of structures containing **srs**‡ (or (10,3)-a),[2] **dia** (or diamond), **nbo** (or boronnitride) and **pcu** (or α-polonium), and a number of other high symmetry nets.[3–5]

More recently, the use of unsymmetrical building blocks or combining "tectons" with different connectivities is now leading to the synthesis of a growing number of "less common nets". The use of specifically tailored building blocks in order to prepare these nets has also been identified as an important synthetic strategy.[4,6]

Nets containing both three- and four-connected nodes form one such class of networks where we can envisage controlling the structure *via* both the geometry of the building blocks (most trivially by the choice of tetrahedral or square planar four-connected nodes) and the stoichiometry of the nodes. Arguably the most symmetric of these is the $(8^3)(8^6)_2$-**tfa** net, see Fig. 1. It contains only eight-membered rings, has two different types of nodes, two different types of links (edges) and is of *genus* 3 (thus one of the eight minimal nets[7]).
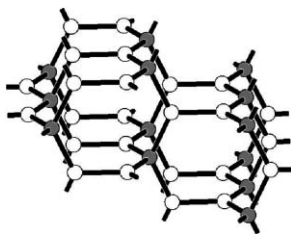

Fig. 1 The $(8^3)(8^6)_2$-**tfa** net is arguably the most symmetric net containing both three- and four-connected nodes. Note that the stoichiometry is 1 : 2.

[a]Chemistry Dept., Alexandria University, P.O. Box 426 Ibrahimia, 21321 Alexandria, Egypt. E-mail: morsy5@link.net; Fax: +2 03 3911794; Tel: +2 03 4264443
[b]Dept. of Chemical and Biological Engineering, Chalmers Tekniska Högskola, SE-412 96 Göteborg, Sweden. E-mail: langer@chalmers.se; ohrstrom@chalmers.se; Fax: +46 31 772 28 46; Tel: +46 31 772 1000
† Electronic supplementary information (ESI) available: Histogram from the CSD analysis. Additional exp. and structural data for **1**. See DOI: 10.1039/b515399a

Given the abundance of all other high symmetry nets it is somewhat surprising that the **tfa** net has not been observed among the three-dimensional coordination polymers and hydrogen bonded nets so far.[4,5] In fact, prior to this study on aminopyridines, we knew of only one example of this net, the borate net in $Cs(B_9O_{14})$.[8,9]

The aminopyridines can act as three-connected nodes through hydrogen bonding and coordination (one could also consider the Ag(I) ion as a hydrogen bond mimicker[10]) and nitrate can accept several hydrogen bonds, making it a potential three- or four-connected node.[11] However, while the reactions of 2- and 3-aminopyridine with $AgNO_3$ gave only 2D nets,[12] in [Ag(4-aminopyridine)$_2$]NO$_3$§ **1** (Scheme 1), we found a hydrogen bond pattern corresponding to the **tfa** net, see Fig. 2.¶ The reason for this difference in behaviour may lie in the higher symmetry of the 4-aminopyridine and the possibility of the other compounds to "fold back" and form discrete or 2D units.

As the geometry of the complex ion [Ag(4-aminopyridine)$_2$]$^+$ is unsurprising,[13] we will concentrate on the intermolecular interactions and the interpretation of these in the form of a net.

There are three such interactions that need to concern us. A classical coordination (or dative) bond between nitrate oxygens and
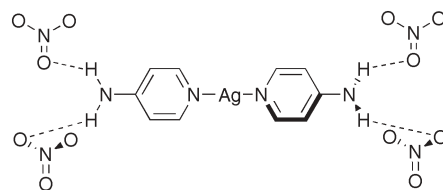
Scheme 1 The molecular unit of [Ag(4-aminopyridine)$_2$]NO$_3$. Two symmetrically independent complex ions (Ag1 in a general position and Ag2 on a twofold axis, the same applies to NO$_3^-$) are present in the structure with N–Ag–N angles 173.0(3)° and 173.4(2)°.
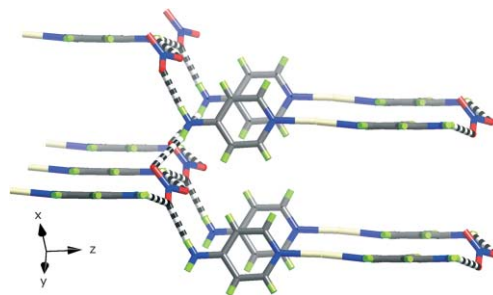

Fig. 2 Hydrogen bond pattern (striped bonds) in [Ag(4-aminopyridine)$_2$]NO$_3$ **1** giving the $(8^3)(8^6)_2$-**tfa** net. Same view as in Fig. 1.
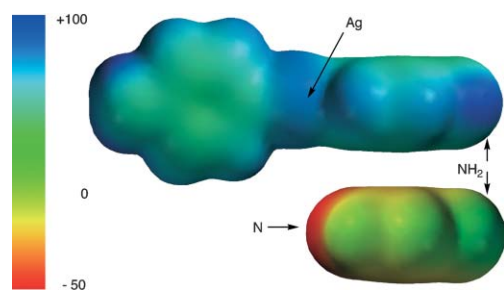
Fig. 3 Electrostatic potentials mapped on the electron density surface calculated by DFT** for [Ag(4-aminopyridine)$_2$]$^+$ (top) and 4-aminopyridine (bottom). Note the significant increase in positive potential for NH$_2$ in **1**.

Ag(I) is unlikely because of the long Ag–O distance (2.867–2.900 Å) and the near linear N–Ag–N unit,[12] but there will always be some electrostatic interaction. However, this is a long range force and its effect on individual pairs of molecules is difficult to judge.

However, the centroid–centroid distance of ~3.5 Å, a centroid offset angle of ~20° and a ~3.3 Å plane-to-plane separation clearly indicate efficient interactions between the π-systems according to a recent survey.[14] Even so, in energy terms such interactions are weak, around 2 kJ mol^{-1}, and as each molecule in the stack has two contributions we would sum this to about 4 kJ mol^{-1}.

N–H···O hydrogen bonds normally have N···O distances in the range 2.81–3.04 Å[15] so the interactions in this structure may be interpreted as weak, being 2.943(9)–3.178(9) Å. However the N–H···O angles are 154°–167° and this indicates a stronger bond[16] and a search in the Cambridge Structural Database[17] does indeed show that between organic amines and nitrate the hydrogen bonds are somewhat longer, in the range 2.85–3.15 Å.||

The energetics of these hydrogen bonds are complicated by the possibility of "charge-assisted hydrogen bonding",[18] since the positive charge from the soft silver ion may delocalise and a significant charge develop on the NH$_2$ group that will reinforce the hydrogen bond to the nitrate ion, see Fig. 3.

Nevertheless, strong, inorganic, N–H···O hydrogen bonds have been placed around 59 kJ mol^{-1}[15] and the "medium" hydrogen bonds at 17–63 kJ mol^{-1} (2.5–3.2 Å, 130°–180°).[16] We tentatively estimate our hydrogen bonds at 25 kJ mol^{-1}, giving a schematic view of the energetics in the structure as presented in Fig. 4.

This survey indicates that the links between the nodes of the net are indeed stronger than other (directional) intermolecular interactions and that the structure can justly be represented by a net.

As more and more examples of 3D-nets are found, or deliberately synthesised, the classification and nomenclature become increasingly important issues.[4,5,7,9,19–22] The topology of
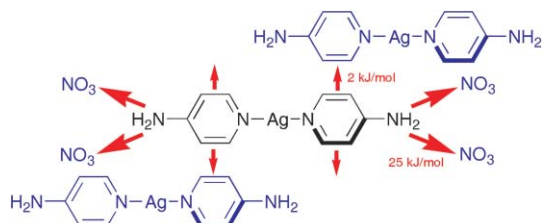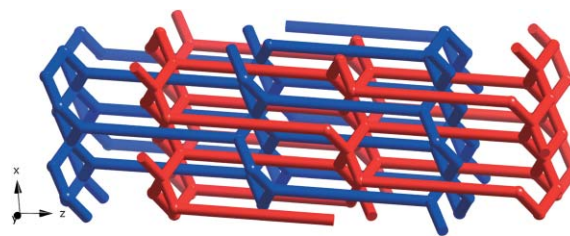

Fig. 5 The two interpenetrated three- and four-connected **tfa** nets in **1**. The four-connected nodes are NO$_3$$^-$ and the three-connected nodes are –NH$_2$.

this net was established by computing†† the vertex symbol[23] (extended Schläfli or long symbol) giving 8$_4$·8$_4$·8$_4$ for the three-connected and 8$_2$·8$_2$·8$_3$·8$_3$·8$_3$·8$_3$ for the four-connected node and comparing both the symbol and the experimental net with the ideal net.‡

However, **1** does, in fact, contain two interpenetrated nets and the overall net structure is shown in Fig. 5. Moreover, just as it is important to describe the topology of the nets formed, so it is important to describe the topology of interpenetration.[22] Recently a stringent nomenclature has been proposed,[5] where the most important distinctions are made between structures containing nets related by displacement vectors only (Class I, the most common), those where the nets are symmetry-related (Class II) and those that are related by both symmetry and displacement vectors (Class III). The interpenetration in **1** is Class II since the two nets are related by inversion (symmetry operation $-x$, $-y$, $-z$).

Finally, the attribution of nodes needs to be discussed since this is a somewhat subjective choice,[5,6a,21] and different nets may indeed be assigned to the same structure! In the case of **1** we could also consider the entire complex ion as one node and nitrate as the other giving a very distorted version (or *embedding*[19]) of the diamond (**dia**) net ("tetrahedral" angles of 50° and 140°), see Fig. 6.

There is no common practice for net assignment, but two principal ways may be distinguished. Naturally, a connectivity approach is one possibility.[24] However, connecting the centres of gravity of the tectons may result in links traversing empty space in the structure. Another possibility is to make the links in the net follow the real chemical bonds that form the structure. This can be exemplified by the two (pseudo)polymorphs of 3,3′5,5′-tetra-methyl-4,4′-bipyrazole that based on connectivity both give the **dia** net but when the directionality of the hydrogen bonds are considered two distinctly different nets can be seen in these structures; the **ths** (or (10,3)-b) and the chiral **bto** (or (10,3)-c) net.[25]

In the present case, connectivity based on the 4-aminopyridine ligand will give the **tfa** net. If we want the links of the net to follow the real bonds in the structure as closely as possible, we also get the

Fig. 4 Tentative diagram over the most important intermolecular interactions binding the "black" complex ion to its "blue" neighbours in **1**.
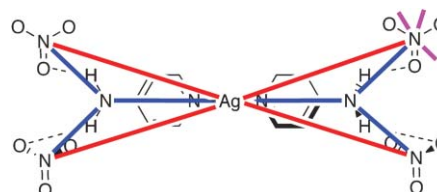

Fig. 6 Different choice of nodes giving different net topologies. Red and violet giving the **dia** net and blue and violet the **tfa** net.

tfa net. On the contrary, we get the **dia** net if we base the connectivity on the $[Ag(4\text{-aminopyridine})_2]^+$ complex ion. However, as is clear from Fig. 6, these links then pass trough empty space in the structure and moreover the resulting net is very distorted while the corresponding **tfa** net is closer to the ideal embedding.

We also note that the **tfa** assignment gives us a superior opportunity to understand the complete structure: the net designates the strongest intermolecular interactions, the long parallel links of the two nets have "π–π" interactions in between them, and the mid-points of these links (Ag^+ ions) are located right beside the "tetrahedral" links corresponding to the nitrate ions thus, at least seemingly, maximising the charge–charge interactions between nets as well, see Fig. 5. In conclusion it seems appropriate to cite A. F. Wells who in 1954 pointed out that in some sense "nets have a deeper structural significance than space groups".[26]

Notes and references

‡ Abbreviations for 3D nets have been taken from M. O'Keeffe and O. M. Yaghi, *Reticular Chemistry Structure Resource*, Arizona State University, Tucson, 2005, http://okeeffe-ws1.la.asu.edu/rcsr/home.htm, where crystallographic coordinates and other useful details for 3D-nets can be obtained. For the less common nets we recommend adding the short (Schläfli) symbol before the three-letter code for clarity, as in $(8^3)(8^6)_2$-**tfa**.[6a] This notation tells us the number of smallest rings found in the net, and also gives the stoichiometry of the nodes, and thus gives a rough idea of the type of network in question. See also ref. 6a.

§ To a 10 ml aqueous solution of $AgNO_3(s)$ (0.2 g, 1.18 mmol) 15 ml ethanolic solution of 4-aminopyridine (0.19 g, 2.0 mmol) was added dropwise. To the turbid solution 2–3 drops of 0.1 M nitric acid was added. The solution became clear and was filtered off 2 times and allowed to stand for 3 weeks. Uniform yellowish crystals were collected and dried in air (yield 85%). Elemental analysis: found: C, 33.47; H, 3.43; N, 19.38; Ag, 30.23%; calcd: C, 33.54; H, 3.38; N, 19.56; Ag, 30.12%.

¶ X-Ray data collected on a Siemens Smart CCD diffractometer at 173 K with Mo-Kα radiation. The structure was solved by direct methods and subsequent full-matrix least-squares refinement, including anisotropic thermal parameters for all non-hydrogen atoms using SHELXTL.[27] Crystals of **1** are non-merohedrally twinned by a 2-fold axis parallel with the *c*-axis; the volume ratio of the twins is 0.8806(8) : 0.1194(8) and this is a different phase from that obtained in an earlier study.[13] Hydrogen atoms were allowed for as riding atoms and the individual isotropic temperature factors were freely refined. Moiety formula: $C_{10}H_{12}AgN_4$, NO_3, $M_r = 358.12$. $Z = 12$, monoclinic, space group $C2/c$, $a = 7.1491(1)$, $b = 12.1585(2)$, $c = 44.3897(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 94.601(1)°$, $V = 3846.02(9)$ Å^3, $\mu = 1.584$ mm^{-1}, $\rho_{calc} = 1.855$ g cm^{-1}, measured refl., 14192, unique refl., 3395, $R_{int} = 0.0829$, $R(I > 2\sigma) = 0.0546$, wR_2(all) = 0.1275. CCDC 279553. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515399a

∥ Distances and angles of a C–NH₂ group to a free nitrate group were recorded for N–H···O angles >150° (*R*-values < 10%, error and disorder free, total of 469 structures). 73% of these lie within 2.85–3.15 Å.

** Calculations were made with the DFT module in Spartan5.1.3a1[28] at the BP86[29] level using the X-ray geometry and a DN** basis set including polarization and *d*-functions for C, N, O and Ag.

†† The computation was performed using the OLEX software,[30] a good alternative is the TOPOS program.[31]

1 (a) W. Lin and H. L. Ngo, in *Chemistry of Nanostructured Materials*, ed. P. Yang, World Scientific Publishing Co, Singapore, 2003, pp. 261; (b) C. Janiak, *Dalton Trans.*, 2003, 2781; (c) S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276; (d) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127; (e) J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3; (f) J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*,

2005, **44**, 4670; (g) X. B. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw and M. J. Rosseinsky, *Science*, 2004, **306**, 1012; (h) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273.

2 Nomenclature according to: A. F. Wells, *Three-dimensional nets and polyhedra*, John Wiley & Sons, New York, 1977.

3 O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705.

4 N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2005, **38**, 176.

5 V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2004, **6**, 377.

6 (a) L. Öhrström and K. Larsson, *Molecule-Based Materials: The Structural Network Approach*, Elsevier, Amsterdam, 2005; (b) L. Öhrström and K. Larsson, *Dalton Trans.*, 2004, 347.

7 C. Bonneau, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2004, **60**, 517.

8 J. Krogh-Moe and M. Ihara, *Acta Crystallogr.*, 1967, **23**, 427–430.

9 I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *J. Solid State Chem.*, 2005, **178**, 2452.

10 L. Brammer, M. D. Burgard, M. D. Eddleston, C. S. Rodger, N. P. Rath and H. Adams, *CrystEngComm*, 2002, **4**, 239.

11 See for example: K. Larsson and L. Öhrström, *CrystEngComm*, 2003, **5**, 222.

12 M. A. M. Abu-Youssef, V. Langer and L. Öhrström, *Dalton Trans.*, submitted.

13 O. Kristiansson, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2000, **56**, 165.

14 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.

15 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 2nd edn, 1997.

16 J. C. Jeffery, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, 1997.

17 (a) F. H. Allen and R. Taylor, *Chem. Soc. Rev.*, 2004, **33**, 463; (b) F. H. Allen and W. D. S. Motherwell, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 407.

18 (a) S. Ferlay, R. Holakovsky, M. W. Hosseini, J. M. Planeix and N. Kyritsakas, *Chem. Commun.*, 2003, 1224; (b) D. Braga and F. Grepioni, *Acc. Chem. Res.*, 2000, **33**, 601.

19 O. Delgado-Friedrichs, M. D. Foster, M. O'Keeffe, D. M. Proserpio, M. M. J. Treacy and O. M. Yaghi, *J. Solid State Chem.*, 2005, **178**, 2533.

20 (a) O. Delgado-Friedrichs and M. O'Keeffe, *J. Solid State Chem.*, 2005, **178**, 2480; (b) O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2003, **59**, 515; (c) O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2003, **59**, 22; (d) O. Delgado-Friedrichs, A. W. M. Dress, D. H. Huson, J. Klinowski and A. L. Mackay, *Nature*, 1999, **400**, 644; (e) L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2003, **5**, 269.

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

22 (a) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1461; (b) S. R. Batten, *CrystEngComm*, 2001, 1.

23 M. O'Keeffe, M. Eddaoudi, H. L. Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3.

24 This for example gives a **dia** net for the pentaerythrityl tetraphenyl *m*-diaminotriazine ether in: D. Laliberte, T. Maris and J. D. Wuest, *J. Org. Chem.*, 2004, **69**, 1776.

25 I. Boldog, E. B. Rusanov, A. N. Chernega, J. Sieler and K. V. Domasevitch, *Angew. Chem., Int. Ed.*, 2001, **40**, 3435.

26 A. F. Wells, *Acta Crystallogr.*, 1954, **7**, 535.

27 *SHELXTL Structure Determination Programs*, Bruker AXS Inc., Madison, Wisconsin, 2001.

28 *SPARTAN 5.1.3a1*, Wavefunction, Inc., Irvine, CA.

29 A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 3098(a) J. P. Perdew, *Phys. Rev. B: Condens. Matter*, 1986, **33**, 8822.

30 (a) O. V. Dolomanov, *OLEX*, http://www.ccp14.ac.uk/ccp/web-mirrors/lcells/index.htm,; (b) O. V. Dolomanov, A. J. Blake, N. R. Champness and M. Schroder, *J. Appl. Crystallogr.*, 2003, **36**, 1283.

31 (a) V. A. Blatov, A. P. Shevchenko and V. N. Serezhkin, *J. Appl. Crystallogr.*, 2000, **33**, 1193; (b) V. A. Blatov, *TOPOS*, http://www.topos.ssu.samara.ru/, 2004.