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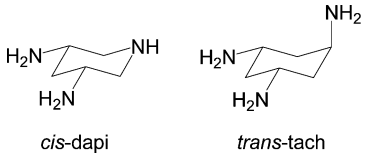
Controlling dimensionality of silver(I) coordination networks with rigid aliphatic amino ligands: from a 2D to a 3D network of unprecedented topology comprising helical channels

Georg Seeber, Alexandra L. Pickering, De-Liang Long and Leroy Cronin*
Department of Chemistry, The University of Glasgow, University Avenue, Glasgow, UK G12 8QQ.
E-mail: L.Cronin@chem.gla.ac.uk; Fax: +44 141 330 4888; Tel: +44 141 330 6650

Received (in Cambridge, UK) 8th May 2003, Accepted 30th June 2003
First published as an Advance Article on the web 15th July 2003

Ligand-directed 2D and 3D Ag(I) coordination networks are self-assembled from the rigid, topologically related tri-amino ligands *cis*-3,5-diaminopiperidine (*cis*-dapi) and *cis,trans*-1,3,5-triaminocyclohexane (*trans*-tach), yielding two networks of differing dimensionality including a 3D network of unprecedented topology comprising helical channels.

The rational approach to coordination polymers with network structures through ligand design is of great interest due to the expectation that the topology of the network may be manipulated to dramatically influence the overall physical properties and functions of the material.[1–2] For example, the utilization of rigid multidentate poly-pyridyl-based ligands, of which 4,4′-bipy is an ubiquitous example,[3] in combination with metal centres of varying geometries can give rise to a large number of network architectures and interpenetrating structures as a function of reaction conditions and stoichiometry.[4] Indeed, complexation of the relatively soft pyridyl-based ligands with soft metals such as silver has been particularly fruitful in producing arrays of coordination polymers with interesting topologies.[5a] For example, a range of diverse 1D, 2D and 3D infinite networks,[6] as well as discrete complexes[7] such as molecular grids, cages and helicates with coordination numbers between two and six have been observed for the Ag(I) ion. Although there is an extremely large number of coordination networks based upon Ag-N combinations where N is a pyridyl-based donor, examples of rigid frameworks of non-aromatic ligands are limited to few examples of primarily tertiary amino ligands such as hexamethylenetetramine[8] and 1,4-diaza-bicyclo[2.2.2]octane.[4] Here we report the first two examples of polymeric Ag(I) coordination networks with aliphatic amines, based on the related rigid tri-amino ligands *cis*-3,5-diaminopiperidine (*cis*-dapi), $[Ag(cis\text{-dapi})]_n(NO_3)_n$ **1**, and *cis,trans*-1,3,5-tri-aminocyclohexane (*trans*-tach), $[Ag(trans\text{-tach})]_n(NO_3)_n$ **2**. Furthermore it appears that, despite the related topologies of the ligands and the identical trigonal planar coordination geometry of the Ag(I) ions in each complex, **1** is a 2D network with a well known hexagonal (6,3) topology[9] whereas **2** has an unprecedented 3D network topology comprising helical channels. Moreover, these are the first examples of coordination networks based on rigid aliphatic tri-amino ligands with a transition metal ion.[10]†



cis-dapi *trans*-tach

Both the ligands utilized in **1** and **2** are sterically constrained cyclic polyamines, which limits potential metal–ligand interactions. For instance, *cis*-dapi acts predominantly as a facially coordinating tridentate ligand in octahedral complexes,[11] with the endocyclic nitrogen forming elongated bonds to the metal centres, whereas *trans*-tach provides two non-interacting binding modes[12] with increased binding flexibility due to the third exocyclic amino residue. Complexation of *cis*-dapi and *trans*-tach with $Ag(NO_3)$ yields two coordination networks of 2D (**1**) and 3D (**2**) dimensionality, respectively, with no solvent molecules incorporated in either framework. The well known hexagonal topology exhibited by **1** is facilitated by the *cis*-dapi geometry, having three coordinating amines coplanar with the piperidine ring, and comprises a metal to ligand composition of 1 : 1. The asymmetric unit of **1** consists of one *cis*-dapi ligand and one Ag(I) ion as well as one nitrate counterion. Each Ag(I) adopts a trigonal planar coordination sphere by coordinating one secondary and two primary amines of three different ligands (N–Ag–N angles: 133.8, 115.2 and 103.4°, respectively. Σ = 352.4°). The metal coordination occurs exclusively in two dimensions (perpendicular to the *c* axis), forming layers which are separated by 6.3 Å and held together by hydrogen bonded interactions with the nitrate counterions (Fig. 1).

Alternately orientated linear chains are observed within the layer, which arrange in a hexagonal fashion. Linear, *intra*-chain coordination occurs between Ag(I) and one secondary piperidine nitrogen and one primary amino group (*intra*-chain Ag···Ag distance: 6.2 Å). The chains are held together by *inter*-chain coordination with the remaining primary amino group (average *inter*-chain Ag···Ag distance: 6.5 Å). The difference in orientation of the AB strands results exclusively from the orientation of the endocyclic piperidine ring nitrogen along the crystallographic *b* axis (Fig. 1, RHS). The macrocycles formed upon 3 : 3 Ag(I) to *cis*-dapi coordination contain 16 ring atoms.

In contrast, Ag(I) complexation with *trans*-tach results in a 3D network due to the additional exocyclic axial amino group providing coordination out of the cyclohexane plane. The asymmetric unit consists of two crystallographically independent *trans*-tach ligands and two Ag(I) ions as well as two nitrate counter ions. Each Ag(I) adopts a trigonal planar coordination sphere by coordinating two equatorial and one axial primary amino group of three different ligands (N–Ag1–N angles: 144.5, 109.8, 105.3°, Σ = 359.6° and N–Ag2–N angles: 149.3, 107.0, 103.7°, Σ = 360.0°).

The two crystallographically independant Ag(I) ions have different coordination environments; two Ag1 centres coordinate to two *trans*-tach units *via* their composite four equatorial amino groups, forming a macrocyclic subunit by 2 : 2 Ag1 to *trans*-tach coordination (shown in blue in Fig. 2). The

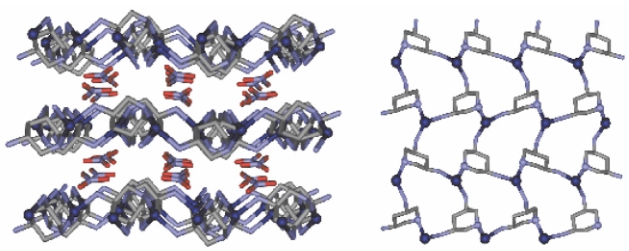


Fig. 1 Representations of the structure of **1**. **LHS**: View along the *a* axis showing the anions separating the 2D layers. **RHS**: View along the *c* axis showing the hexagonal topology of **1**. Ag(I) ions are represented as dark blue spheres and nitrogens are light blue with the endocyclic piperidine nitrogen as spheres.

DOI: 10.1039/b305188a

Ag1···Ag1 distance is 5.3 Å in the macrocycle and each cyclic unit consists of 12 ring atoms with an inversion centre. Instead of forming macrocyclic subunits, Ag2 forms linear chains running along the crystallographic *b* axis with coordination to one of the equatorial amino groups of each *trans*-tach ligand. Ag2···Ag2 distances are 5.5 Å along the chain. The Ag1 macrocyclic subunits are linked to Ag2 centres *via* the remaining *trans* amino group in axial position. Additionally, two helical channels are observed within the three dimensional coordination network along the crystallographic *b* axis. The nitrate counterions, located in the octagonal channels, form hydrogen bonded interactions with the primary amino groups (Fig. 2).

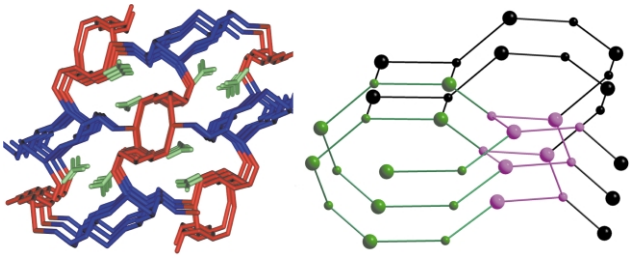


Fig. 2 View along the crystallographic *b* axis. **LHS**: Arrangement of the macrocyclic Ag1 subunits (blue) along the Ag2 coordination chain (red). Nitrate counterions are represented in green. **RHS**: The topology of the network is shown whereby the *trans*-tach ligand is subsituted by a three coordinate node at the centroid of the cyclohexane ring. The helical channels are shown in pink and green and run parallel to the crystallographic *b* axis.

The topology of **2** is interesting because, in analogy with **1**, the structure has a 3 : 3 (metal : ligand) composition but is connected in three dimensions. Each Ag(I) ion has a trigonal planar geometry while each ligand functions as a μ_3-bridging group with non-planar geometry; both the Ag(I) ion and ligand act as 3-connected nodes and form the unprecedented 3D binodal topology (4.8.10)(8.10^2) (Fig. 2, RHS). To understand this topology it is informative to consider the nets shown in Fig. 3. Fig. 3a shows a uniform 2D (4.8^2) topology,[5b] in which every 3-connected node is shared by one tetragon and two octagons. Fig. 3b demonstrates a uniform 3D (10.3)-a topology[5] which could be described as one of the 'derivatives' of the 2D (4.8^2) net with lines broken and crosslinked to its adjacent layers (in this case *each* tetragon has one side broken). However, alternative arrangements of breaking and re-crosslinking may lead to other 'derivatives'. In the case of **2**, breaking *half* of the tetragons and subsequent crosslinking to neighbouring layers results in the new topology (Fig. 3c). The tetragonal and octagonal channels involving the broken sides are therefore individually helical (Fig. 2, RHS).

In summary, we report the first two examples of transition metal-based coordination networks incorporating rigid aliphatic tri-amino ligands. The influence of the geometry of these ligands demonstrates the relationship between the ligand and the dimensionality of the network formed. This is because the only difference between both structures is the ligand itself; the stoichiometry, metal coordination environment and anions incorporated are identical, and no solvent is incorporated in either network. It is therefore interesting that small changes in the ligands' flexibility alter the network topology from the well known honeycomb type 2D net to an unprecedented 3D topology comprising helical channels. We are presently designing other rigid ligands that can expand the cavity size and extend our design concept further.

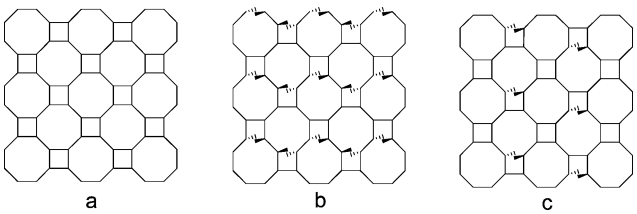


Fig. 3 Network topology of **2** is shown in *c* along with the associated topologies *a* and *b*.

We would like to thank Dr B. M. Kariuki for his collaboration and the Universities of Glasgow and Birmingham, the EPSRC and the Leverhulme Trust for funding.

Notes and references

† Full synthetic and analytical details are given as ESI. Crystal data for **1** – $C_5H_{13}AgN_4O_3$, M = 285.06, orthorhombic, space group *Pbca*, a = 12.4470(9), b = 11.4650(7), c = 12.4929(9) Å, V = 1782(2) Å^3, Z = 8, μ(Mo–K$_\alpha$) = 2.244 mm^{-1}, 7697 reflections measured, 1562 unique which were used in all calculations. Final $R1$ = 0.041 and $wR2$ = 0.078 (all data). Data were measured at 120(2) K on a Nonius KappaCCD diffractometer [λ(Mo–K$_\alpha$) = 0.7107 Å], graphite monochromator, 221 frames were recorded in 2.0° steps, each for 120 s, crystal-detector distance 40 mm. Structure solution with SHELXS-97 and refinement with SHELXL-97 *via* WinGX.[13] Hydrogen atom positions calculated and subsequently riding. Crystal data for **2** – $C_6H_{15}AgN_4O_3$, M = 299.09, monoclinic, space group $P2_1/c$, a = 13.717(3), b = 8.9401(18), c = 16.635(3) Å, β = 93.60(3)° V = 2035.90(39) Å^3, Z = 8, μ(Cu–K$_\alpha$) = 15.857 mm^{-1}, 8413 reflections measured, 3773 unique which were used in all calculations. Final $R1$ = 0.058 and $wR2$ = 0.161 (all data). Data were measured at 293(2) K on a Bruker SMART CCD 6000 diffractometer [λ(Cu–K$_\alpha$) = 1.5418 Å], graphite monochromator, 2421 frames were recorded in 0.3° steps, each for 4 s, crystal-detector distance 40 mm, collimator 0.5 mm. Structure solution with SHELXS-97 and refinement with SHELXL-97 *via* WinGX.[13] Hydrogen atom positions calculated and subsequently riding. CCDC reference number 210477 for **1** and 210478 for **2**. See http://www.rsc.org/suppdata/cc/b3/b305188a/ for crystallographic data in .cif or other electronic format.

1 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546; S. Kawata, M. Kondo, L. Furuchi and M. Munakata, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1759.

2 A. K. Cheetham, G. Ferey and T. Louseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268; M. Kauranen, T. Verviest, C. Bouttoon, M. N. Teerenstra, K. Clays, A. J. Schouten, R. J. M. Nolte and A. Pearsons, *Science*, 1995, **270**, 966.

3 V. Niel, M. C. Munoz, A. B. Gaspar, A. Galet, G. Levchenko and J. A. Real, *Chem.-Eur. J.*, 2002, **8**, 2446; O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295; T. Soma, H. Yuge and R. Iwamoto, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1665.

4 B. F. Abrahams, S. R. Batten, B. F. Hoskins and R. Robson, *Inorg. Chem.*, 2003, **42**, 2654 and references therein.

5 (*a*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (*b*) A. F. Wells, *Three-Dimensional Nets and Polyhedra*, John Wiley & Sons, New York, 1977.

6 **1D**: M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 7287; B. F. Hoskins, R. Robson and D. A. Slizys, *J. Am. Chem. Soc.*, 1997, **119**, 2952; **2D**: . Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1088; C. V. K. Sharma and M. J. Zaworotko, *Chem. Commun.*, 1996, 2655;**3D**: L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Chem. Commun.*, 1996, 1393; B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins and R. Robson, *Chem. Commun.*, 1996, 1313.

7 S. Ottens-Hildebrandt, S. Meier, W. Schmidt and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1767and references therein.

8 S.-L. Zheng, M.-L. Tong, X.-M. Chen and S. W. Ng, *J. Chem. Soc., Dalton Trans.*, 2002, 360; L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *J. Solid State Chem.*, 2000, **152**, 211and references therein.

9 S. R. Batten, B. F. Hoskins and R. Robson, *New J. Chem.*, 1998, **22**, 173; J. Konnert and D. Britton, *Inorg. Chem.*, 1966, **5**, 1193.

10 A CSD search reveals no polymeric coordination compounds with rigid tri-amino ligands have been reported thus far.

11 J. W. Pauly, J. Sander, D. Kuppert, M. Winter, G. J. Reiss, F. Zurcher, R. Hoffmann, T. F. Fassler and K. Hegetschweiler, *Chem.-Eur. J.*, 2000, **6**, 2830.

12 G. Seeber, B. Kariuki and L. Cronin, *Chem. Commun.*, 2002, **23**, 2912.

13 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.