Structural influence of *cis* and *trans* coordination modes of multi-modal ligands upon coordination polymer dimensionality †

Neil S. Oxtoby, Alexander J. Blake, Neil R. Champness* and Claire Wilson

School of Chemistry, The University of Nottingham, University Park, Nottingham, UK NG7 2RD. E-mail: Neil.Champness@nottingham.ac.uk

Control over ligand donor arrangement leads to structural discrimination between one- and two-dimensions in two coordination frameworks, $\{[AgNO_3]_2L\}_\infty$, formed between $AgNO_3$ and hexadentate multi-modal ligands.

The construction of coordination frameworks is an extremely topical area of inorganic and materials chemistry[1] due to the possibility of targeting desired molecular arrangements in the solid-state and hence specific materials properties.[2] The most commonly employed synthetic design strategy that is used to assemble coordination frameworks is the building-block methodology[3] which relies upon utilising the specific geometries of both metal cations and ligands. Typically uni-modal ligands, such as 4,4′-bipyridine, have been used to construct coordination polymers by acting as simple bridges between metal centres. Such ligands offer little influence over the metal centre or upon the overall framework topology except to serve to separate metal cations by a given distance, defined by the inter-donor separation. Multi-modal ligands differ from simpler uni-modal systems in that they offer both more than one binding site, usually both monodentate and chelating multidentate donor sites, and in some cases more than one bridging mode. Previous examples of coordination polymers constructed using multi-modal ligands have demonstrated the potential for control over the coordination sphere of a metal and the relative placement of donor groups and hence fine tuning of network structures.[4,5] We now report a study which illustrates that precise control over the relative positioning of donors within a multi-modal ligand can be used to determine the dimensionality of the resultant coordination polymer.

Two novel coordination polymers have been prepared from $AgNO_3$ and either 3,6-di-pyrazin-2-yl-(1,2,4,5)-tetrazine (dpztz) or the novel 3,6-di-pyrazin-2-yl-pyridazine (dpzpy), two very similar multi-modal ligands. Dpzpy is closely related to the uni-modal 3,6-di-pyridin-2-yl-pyridazine, which, along with extended analogues, has been extensively utilised in supramolecular chemistry.[6] Both dpztz and dpzpy control the relative arrangement of up to four metal ions. In the case of dpzpy, the pyridazine ring forces a *cis* arrangement of the chelating sites. In contrast, previous reports[4,7] have shown that dpztz exhibits a significant preference for a *trans* arrangement of the chelating sites (Scheme 1). By using these particular ligands we show that through ligand design a degree of control over the arrangement of metal ions within a coordination polymer is achieved. We also illustrate the influence of the *cis* or *trans* arrangement of the chelating sites upon the overall polymer structure. We recently reported four polymeric structures formed *via* the complexation of dpztz with three silver salts containing relatively non-coordinating anions (BF_4^-, PF_6^- and SbF_6^-).[4] The NO_3^- anion is known to have a much greater propensity for coordination than BF_4^-, PF_6^- or SbF_6^- and can be anticipated to occupy one coordination site of the Ag(I) cation.

Analogous reaction conditions were used for the synthesis of the two coordination polymers. In particular, reaction of
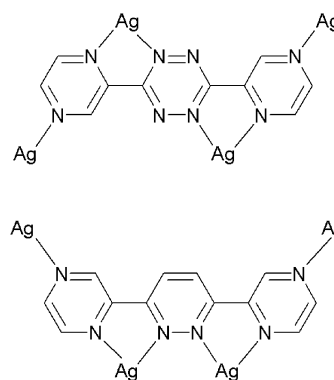
Scheme 1 The *trans* coordination mode of dpztz (top) and the *cis* coordination mode of dpzpy (bottom).

$AgNO_3$ with either dpztz **1** or dpzpy **2** in a 4 : 1 M : L ratio in an MeCN solution afforded coordination polymers of formula $\{[AgNO_3]_2L\}_\infty$.‡ Crystals of both compounds were grown by diffusion of diethyl ether vapour into MeCN reaction solutions and the products were characterised by single crystal X-ray diffraction.§ Both structures adopt a (4 + 1) Ag(I) coordination sphere consisting of a monodentate NO_3^- anion, monodentate and bidentate coordination mode from two different N-donor ligands. The combination of both coordinated monodentate and bidentate donors is consistent with previous studies on Ag(I) complexes of multi-modal ligands.[4,5] Further, long interactions with secondary NO_3^- anions are observed but these are disregarded in the following discussion for the sake of clarity. In **1**, $\{[AgNO_3]_2dpztz\}_\infty$, adopts a distorted tetrahedral environment with a dihedral angle of 81.3° defined by the planes of N1, N8 and Ag1, and O11, N4 and Ag1. In **2** the corresponding dihedral angle is 47.5° generating a significantly more distorted tetrahedral environment. In both **1** and **2** the Ag(I) cation acts, topologically, as a simple connecting rod, linking two ligands together. Thus, the ligand is considered as the only topological node.

In **1** each ligand coordinates four Ag(I) ions (Scheme 1), such that the structure consists of one-dimensional tapes composed of the previously observed[4] 2 + 2 $[Ag_2(dpztz)_2]$ metallacycles (Fig. 1). The nature of the 1-D tapes means that although each dpztz ligand coordinates four Ag(I) ions it is only connected to two other dpztz ligands.

In **2**, $\{[AgNO_3]_2dpzpy\}_\infty$, each dpzpy ligand also coordinates four Ag(I) ions (Fig. 2). However, as both the chelating sites, and consequently, both monodentate sites are *cis*, the formation of similar 2 + 2 metallacycles is precluded as this would produce a highly strained array, and thus higher connectivity is observed. Consequently in **2** each ligand is connected *via* silver ions to four other ligands resulting in a structure with exhibits higher dimensionality. Overall the structure of **2** adopts a grid structure with 4^4 topology, with the ligand acting as the only node. Such topological arrangements are common in coordination polymers,[8] however, it is normally the ligand which acts as a connecting rod, for example 4,4′-bipy, and the metal which acts as a four connecting node. As can be seen (Fig. 2) each sheet adopts a polar arrangement as a result of the
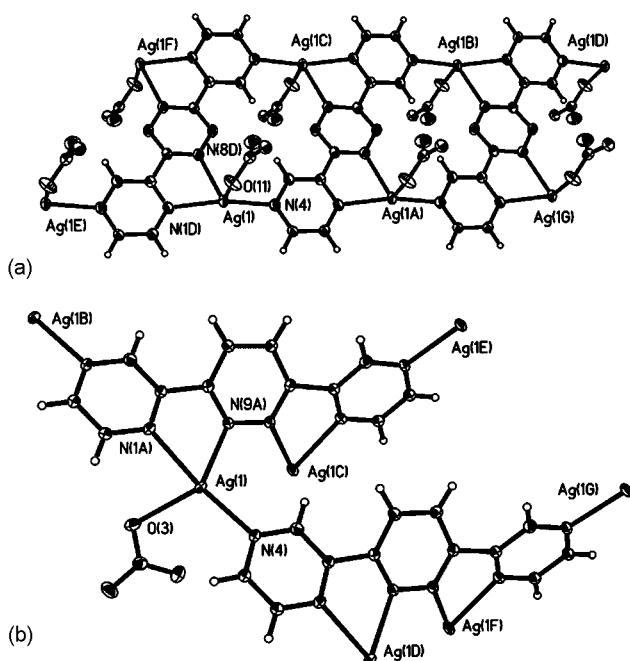
This journal is © The Royal Society of Chemistry 2003

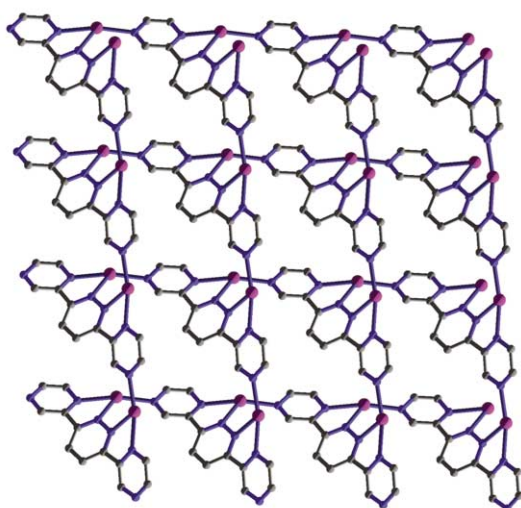**Fig. 1** Views of the localised Ag(I) and ligand geometries in (a) **1** and (b) **2**.

Fig. 2 The extended structure of {[AgNO₃]₂dpzpy}∞. Hydrogen atoms and nitrate anions have been omitted for clarity.

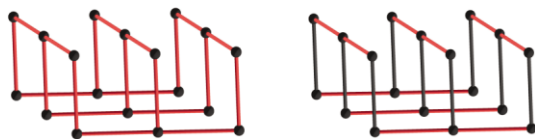**Fig. 3** The bilayer structure commonly found for T-shaped nodes (left), the structure of {[AgNO₃]₂dpzpy}∞ (right), the black part in each structure represents the ligand nodes and the red part the connecting moieties (Ag(I) cations).

cis-coordination mode but anti-parallel orientation of adjacent sheets leads to an overall centrosymmetric structure.

The structure of **2** is superficially related to that of the bilayer arrangement observed in structures containing T-shaped nodes[9] (Fig. 3). Indeed the structure of **2** can be thought of as containing I-shaped nodes, representing the dpzpy ligand, which are formed by fusing two T-shaped nodes *via* the vertical linker (Fig. 3).

By contrasting the two compounds the significant role of the ligand geometry can be readily appreciated. Whilst dpztz forms the expected [Ag₂(dpztz)₂] metallacycles[4] this arrangement is prohibited by the arrangement of donors in dpzpy. Thus, by

specific ligand design multi-modal ligands can be used to control the relative arrangement of metals and ligands within a coordination array.

Notes and references

1 A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. Schröder and M. A. Withersby, *Coord. Chem. Rev.*, 1999, **183**, 117; B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.
2 N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127; R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, K. Kindo, Y. Mita, A. Matsuo, M. Kobayashi, H. C. Chang, T. C. Ozawa, M. Suzuki, M. Sakata and M. Takata, *Science*, 2002, **298**, 2358; D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira and J. Veciana, *Nature Mater.*, 2003, **2**, 190.
3 R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. P. Liu, *ACS Symp. Ser.*, 1992, **499**, 256.
4 N. S. Oxtoby, A. J. Blake, N. R. Champness and C. Wilson, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 4905.
5 A. J. Blake, N. R. Champness, P. A. Cooke and J. E. B. Nicolson, *Chem. Commun.*, 2000, 665; A. J. Blake, N. R. Champness, P. A. Cooke, J. E. B. Nicolson and C. Wilson, *J. Chem. Soc., Dalton Trans.*, 2000, 3811; H.-P. Wu, C. Janiak, G. Rheinwald and H. Lang, *J. Chem. Soc., Dalton Trans.*, 1999, 183; C. Janiak, L. Uehlin, H.-P. Wu, P. Klüfers, H. Piotrowski and T. G. Scharmann, *J. Chem. Soc., Dalton Trans.*, 1999, 3121; O. V. Dolomanov, A. J. Blake, N. R. Champness, M. Schröder and C. Wilson, *Chem. Commun.*, 2003, 682; L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *New J. Chem.*, 2003, 483.
6 A. Marquis, J.-P. Kintzinger, R. Graff, P. N. W. Baxter and J.-M. Lehn, *Angew. Chem., Int. Ed.*, 2002, **41**, 2760; P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1978; P. N. W. Baxter, J.-M. Lehn, J. Fischer and M.-T. Youinou, *Angew. Chem.*, 1994, **106**, 2432.
7 W. Kaim, *Coord. Chem. Rev.*, 2002, **230**, 127.
8 K. Biradha and M. Fujita, *J. Chem. Soc., Dalton Trans.*, 2000, 3805; M. J. Plater, M. R. St. J. Foreman, T. Gelbrich, S. J. Coles and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 2000, 3065; R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1990, 1677.
9 S. A. Barnett and N. R. Champness, *Coord. Chem. Rev.*, 2003, in press; C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1999, 375; M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1725.
10 D. Margetic, D. N. Butler and R. N. Warrener, *Aust. J. Chem.*, 2000, **53**, 959.