Two-fold interpenetration of 3-D nets assembled *via* three-co-ordinate silver(I) ions and amide–amide hydrogen bonds

Christer B. Aakeröy, Alicia M. Beatty and Brian A. Helfrich

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, USA

The combination of isonicotinamide with AgBF$_4$ or AgClO$_4$, respectively, led to isostructural compounds [tris(isonicotin-amide)silver(I) tetrafluoroborate and tris(isonicotinamide)-silver(I) perchlorate], containing two 3-D interpenetrating nets of three-co-ordinate silver(I) ions linked by N–H⋯O hydrogen bonds between adjacent isonicotinamide ligands.

Crystal engineering is a rapidly developing field of structural and supramolecular chemistry, and a wide range of assemblies that are relevant to areas ranging from biochemistry to materials science has been conceived and characterized.[1] Although much of the inspiration for these efforts originates in organic solid-state chemistry,[2] the inorganic equivalent is quickly defining its own possibilities, strategies and boundaries. The most common approach to inorganic crystal engineering has been to propagate the co-ordination geometry of a specific metal ion into infinite architectures using co-ordinate–covalent bonds, leading to co-ordination polymers of varying dimensionality and topology.[3] The result has been a plethora of extended assemblies, *e.g.* squares,[4] ribbons,[5] grids,[6] helices,[7] and interpenetrating or porous diamondoid networks.[8] Far less common has been the use of non-covalent *intermolecular* interactions as a guide to the assembly of co-ordination complexes into extended networks.[9] Although such structures can be expected to have less rigid connectors (compared to strong co-ordinate–covalent bonds), the flexibility inherent in an assembly built upon, *e.g.* hydrogen bonds, may lead to materials with improved solubility and structural agility.

Employing a strategy using a combination of covalent and non-covalent synthesis, we now present two isostructural compounds, tris(isonicotinamide)silver(I) tetrafluoroborate **1**,* and tris(isonicotinamide)silver(I) perchlorate **2**,† where each structure is dominated by a three-dimensional network created by triligated silver(I) ions and short N–H⋯O hydrogen bonds between adjacent amide functionalities. Compound **1** was obtained by adding AgBF$_4$ (1.1 mmol) in ethanol–water (40 ml, 1:1 v/v) to isonicotinamide (2.2 mmol) in ethanol–water (40 ml, 1:1 v/v). Compound **2** was obtained by adding AgClO$_4$ (4.82 mmol) in water (10 ml) to an aqueous solution (30 ml) of isonicotinamide (9.82 mmol). Transparent colourless crystals

(m.p. **1**: 238–240 °C, **2**: 230–235 °C) were obtained after several days through slow evaporation at ambient temperature.‡ These salts are stable in air and apparently do not decay upon continuous exposure to light.

As the two compounds are isostructural, the salient features of their molecular geometries and crystal structures will be discussed together. Although the co-ordination number and geometry of silver(I) complexes can vary considerably, the presence of a three-co-ordinate silver(I) ion is somewhat unexpected since there are relatively few reported crystallographically characterized examples of such complexes involving monodentate ligands [a recent survey found three trigonal planar silver(I) structures out of a total of 90 complexes examined].[10] The geometry of the complex ion is distorted trigonal planar with N–Ag–N bond angles of *ca.* 105, 120 and 135°, Fig. 1. The choice of isonicotinamide as a ligand was made for two reasons. First, silver(I) ions have a high affinity for softer, nitrogen-containing ligands, which encourages covalent–co-ordinate bonds between silver and the ring nitrogen atom in preference to co-ordination to the carbonyl oxygen. Secondly, amide moieties have a well established propensity to engage in complementary hydrogen bonds resulting either in infinite ribbons (through head-to-head interactions), or in infinite chains *via* equivalent N–H⋯O interactions.§ In the case of **1** and **2** the latter motif is observed, and the structures contain three short, near-linear crystallographically inequivalent N–H⋯O hydro-
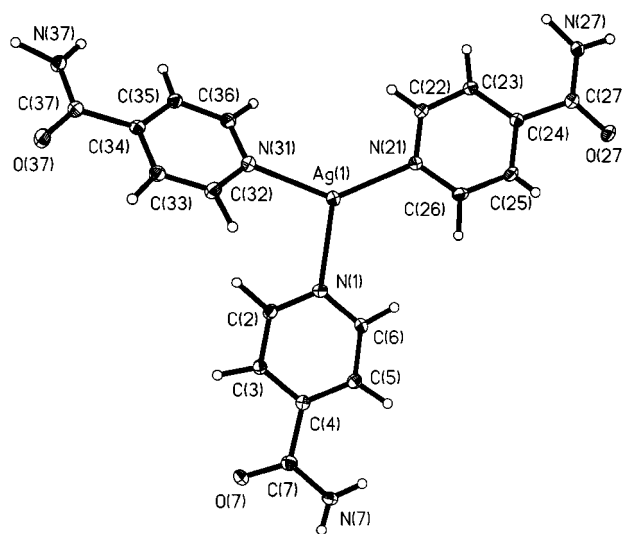

Fig. 1 The central silver(I) ions are co-ordinated by three isonicotinamide ligands in a distorted trigonal fashion in both complexes **1** and **2**

‡ Satisfactory elemental analyses were obtained, and X-ray powder diffraction showed that the single crystals were representative of the bulk materials.
§ Amide–amide interactions in organic molecular solids typically involve 'head-to-head' R$_2^2$(8) or catemer C$_1^1$(4) hydrogen bonds.[11]
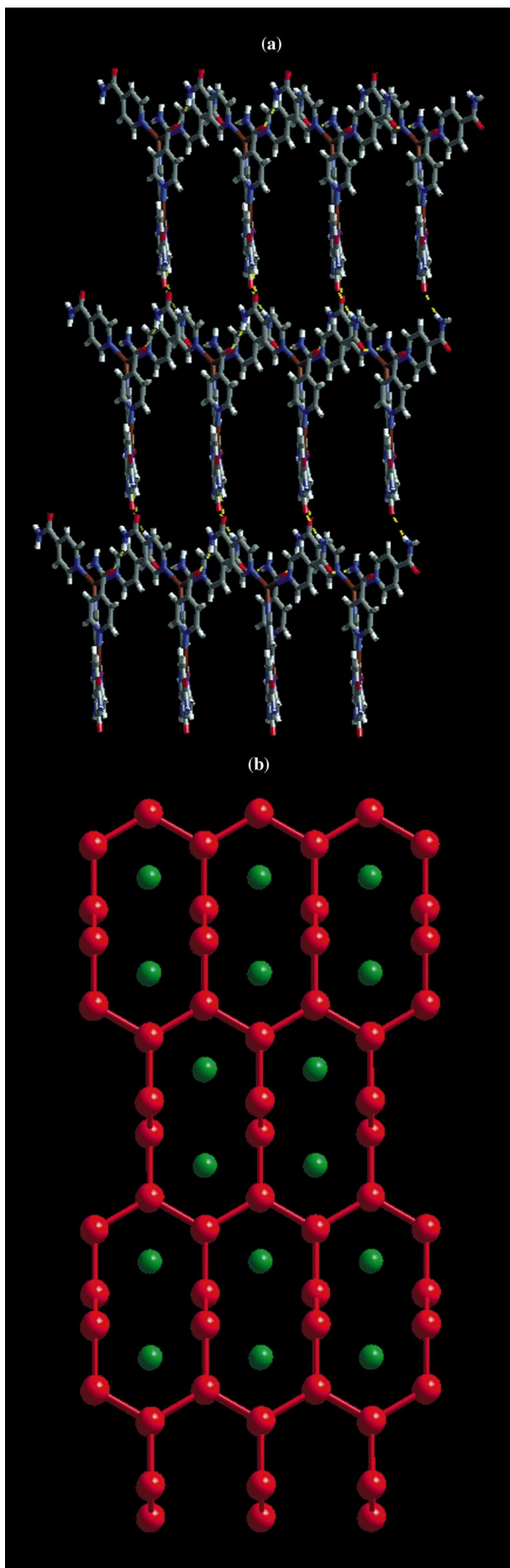
Fig. 2 (a) One of the 3-D cationic nets in the isostructural complexes **1** and **2**. (b) The crystal lattice in α-ThSi₂
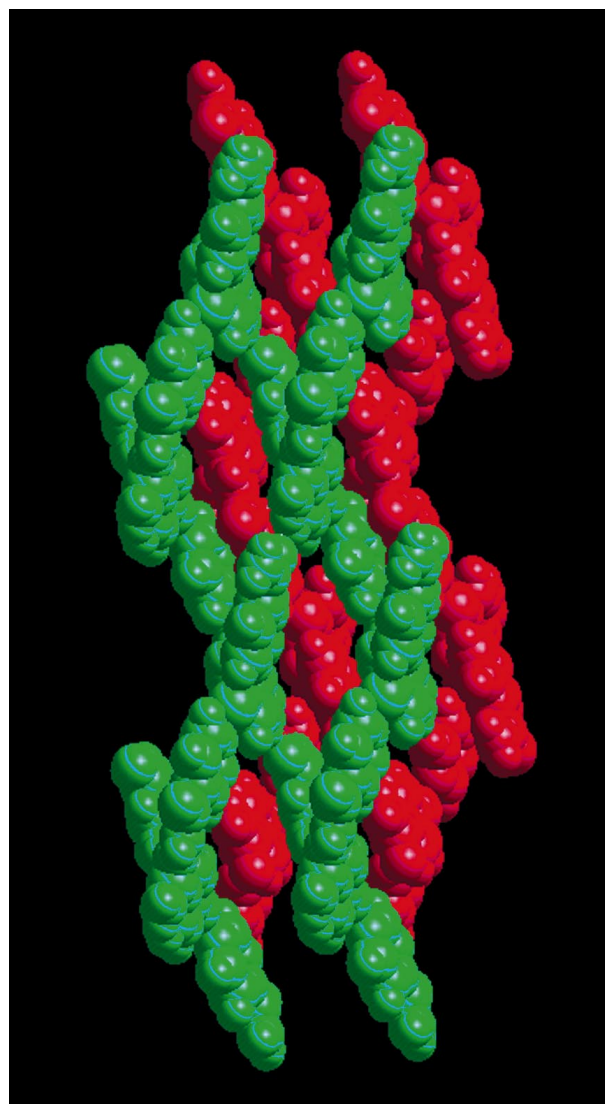
Fig. 3 The two-fold interpenetration of 3-D nets in complexes **1** and **2**

gen bonds that connect neighbouring amide moieties.¶ It is possible to envisage how the pseudo three-fold symmetry of the complex ions can be propagated in several ways in the crystal structure, resulting in hexagonal sheets [analogous to molecules like trimesic acid, $C_6H_3(CO_2H_3)_3$-1,3,5], or the three-fold symmetry can be maintained within a spiraling arrangement of ions. The crystal structures of **1** and **2** contain a combination of both of these possibilities resulting in the formation of a net-like array, the topology of which is analogous to the silicon framework in α-ThSi₂,‖ Fig. 2. Each structure contains two interpenetrating 3-D nets, with each net being formed through amide–amide hydrogen bonds. While the holes created by the 10-membered chair-like assembly of the silicon framework in α-ThSi₂ are occupied by thorium atoms,[13] the corresponding holes in **1** and **2** are interwoven with the second net, resulting in a tight-fitting three-dimensional assembly, Fig. 3.

¶ Intermolecular N−H···O$_{amide}$ hydrogen bond lengths (Å) and angles (°) for **1** [**2**]: N(7)···O(27) 2.869(4) [2.884(4)], N(7)−H(7A)···O(27) 157.9(1) [163.0(1)]; N(27)···O(37) 2.862(3) [2.874(4)], N(27)−H(27A)···O(37) 162.4(1) [176.9(1)]; N(37)···O(7) 2.817(3) [2.815(4)], N(37)−H(37A)···O(7) 167.08(1) [168.0(1)]. Amide−anion N−H···X hydrogen bond lengths (Å) and angles (°) for **1** (X = F) [**2** (X = O)]: N(27)···X(3) 2.947(4) [3.019(5)], N(27)−H(27B)···X(3) 159.5(1) [153.8(1)]; N(37)···X(1) 2.915(3) [2.970(5)], N(37)−H(37B)···X(1) 156.7(1) [152.4(1)].

‖ Frameworks of this type have been observed in silver(I)-containing co-ordination polymers.[12] Our thanks to the reviewer who drew our attention to this lattice type.

The formation of this framework may also be aided by the nature of the anions, which are contained within channels running through the structure. Each anion is anchored within these channels *via* two N–H · · · F or N–H · · · O interactions in **1** and **2**, respectively. There are no noteworthy close Ag · · · Ag contacts in these structures.

These structures represent relatively rare examples of 3-D metal-containing nets built around three-co-ordinate metal centers and propagated *via* intermolecular ligand–ligand hydrogen bonds. Thus, the crystal structures of **1** and **2** demonstrate how non-covalent intermolecular interactions can lead to architectures that mimic assemblies formed by both co-ordination polymers and by 'classic' inorganic lattices. We intend to further explore the supramolecular assembly of metal complexes *via* directional hydrogen bonds, and the possibilities of guiding pseudo-trigonal planar complex ions into alternate arrangements.

Acknowledgements

References

1 C. B. Aakeröy, *Acta Crystallogr.*, *Sect. B*, 1997, **53**, 569; J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; S. Subramanian and M. Zaworotko, *Coord. Chem. Rev.*, 1994, **137**, 357; F. Vögtle, *Supramolecular Chemistry: An Introduction*, Wiley, Chichester, 1991; G. R. Desiraju, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 2311; M. J. Zaworotko, *Nature* (*London*), 1997, **386**, 220.

2 G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989; G. R. Desiraju (Editor), *Perspectives in Supramolecular Chemistry*, *Vol. 2*, *The Crystal as a Supramolecular Entity*, Wiley, Chichester, 1995.

3 R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. Liu, *Supramolecular Architectures*, ACS Publication, Washington, DC, 1992, pp. 256–273.

4 C.-Y. Duan, Z.-H. Liu, X.-Z. You and T. C. W. Mak, *Chem. Commun.*, 1997, 381; M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.

5 P. Losier and M. J. Zaworotko, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 2779.

6 A. J. Blake, S. J. Hill, P. Hubberstey and W.-S. Li, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 913; O. M. Yaghi, H. Li and T. L. Groy, *Inorg. Chem.*, 1997, **36**, 4292.

7 T. M. Garrett, U. Koert, J.-M. Lehn, A. Rault, D. Meyer and J. Fischer, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 557.

8 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2755; A. J. Blake, N. R. Champness, S. S. M. Chung, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 1005; O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295; S. Subramanian and M. J. Zaworotko, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 2127; G. B. Gardner, D. Venkataraman, J. S. Moore and S. Lee, *Nature* (*London*), 1995, **374**, 792.

9 A. D. Burrows, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1996, 97; M. M. Chowdhry, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1996, 899; J.-C. Shi, B.-S. Kang and T. C. W. Mak, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 2171; C. M. Drain, K. C. Russel and J.-M. Lehn, *Chem. Commun.*, 1996, 337; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1801; C. B. Aakeröy and A. M. Beatty, *Chem. Commun.*, 1998, 1067; C. B. Aakeröy and A. M. Beatty, *Crystal Engineering*, 1998, **1**, 39.

10 D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. Hirsch, G. B. Gardner, A. C. Covey and C. L. Prentice, *Chem. Mater.*, 1996, **8**, 2030.

11 L. Leiserowitz and M. Tuval, *Acta Crystallogr.*, *Sect. B*, 1978, **34**, 1230.

12 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1995, **117**, 4562.

13 G. Brauer and A. Mitius, *Z. Anorg. Allg. Chem*, 1942, **249**, 325.