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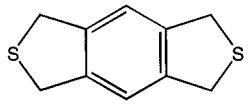
Self-Assembly of Lamellar and Expanded Lamellar Coordination Networks**

George K. H. Shimizu,* Gary D. Enright, Chris I. Ratcliffe, John A. Ripmeester, and Danial D. M. Wayner

The construction of infinite solid-state arrays by employing coordinate covalent bonding and the principles of self-assembly has resulted in numerous metal–ligand networks with fascinating structural topologies.[1] Among the framework types that have resulted are PtS analogues,[1a] honeycomb structures,[1b] α-Po analogues,[1c] diamondoid networks,[1f, j] and $SrSi_2$ analogues.[1g] With these metallo-organic networks, one hopes to realize the wealth of applications known for solely inorganic frameworks, which range from separations[2] to catalysis[3] to devices.[4] The preponderance of infinite arrays formed by metal coordination chemistry employ either aromatic N-donor ligands[1a, d, i, j, 5] or cyano-derived ligands[1b, e, 6] as the metal-chelating point of contact. Thioethers have been largely neglected as ligands in this sense,[7] probably due to the relatively poor metal-complexing ability of nonchelating thioethers.[8] Herein, we introduce a family of layered coordination networks, structurally reminiscent of anionic clays,[9] generated by the self-assembly of a novel dithia ligand with $AgBF_4$. Single-crystal data on two lamellar arrays are presented which illustrate the formation and expansion of the layers. Differential scanning calorimetry (DSC) results reveal thermal stability to over 180 °C, which is attributed to a "lamellar chelate effect."

The dithia ligand **1** contains two sulfurs linked by a rigid durene unit, which prohibits chelation of both donors to a single metal center. The ligand **1** was synthesized in excellent yield by the reaction of tetrabromodurene with sodium sulfide. An equimolar mixture of **1** and $AgBF_4$ was stirred for three hours in MeCN, and then benzene was diffused into this solution to afford colorless platelike crystals of $[\{Ag(\mathbf{1})(MeCN)_2\}_\infty][BF_4]_\infty$ (**2**), suitable for X-ray diffraction analysis. An infinite two-dimensional layered structure is formed by the cationic $\{Ag(\mathbf{1})(MeCN)_2\}$ building blocks while the BF_4 anions reside between the parallel layers (Figure 1).



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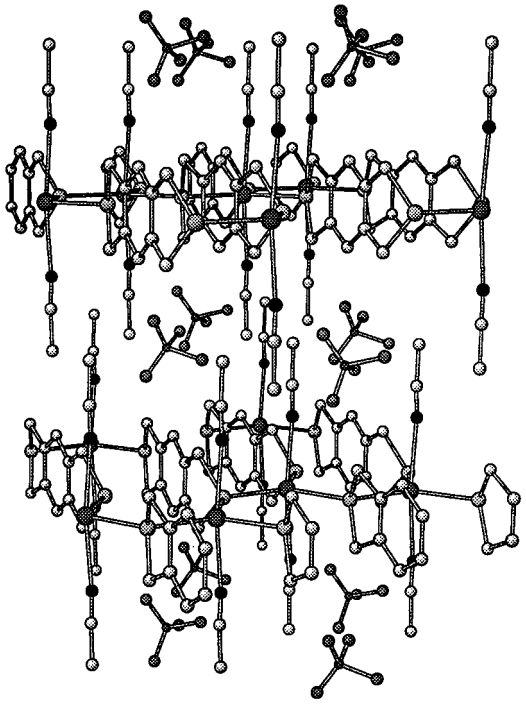

Figure 1. Structure of **2** in the crystal, showing the lamellar network with interlayer BF_4 ions and MeCN molecules that point into the interlayer region. Hydrogen atoms are omitted for clarity.

The coordination geometry about the Ag^I ions is a trigonal bipyramid comprising three equatorial sulfur donors and two axially bound MeCN molecules. Remarkably, in order to achieve such a structure, it is necessary for the highly symmetrical **1** to be asymmetrically coordinated to three Ag^I ions. Figure 2 clearly shows that one thioether group of **1** coordinates a single Ag^I center, while the sulfur atom on the

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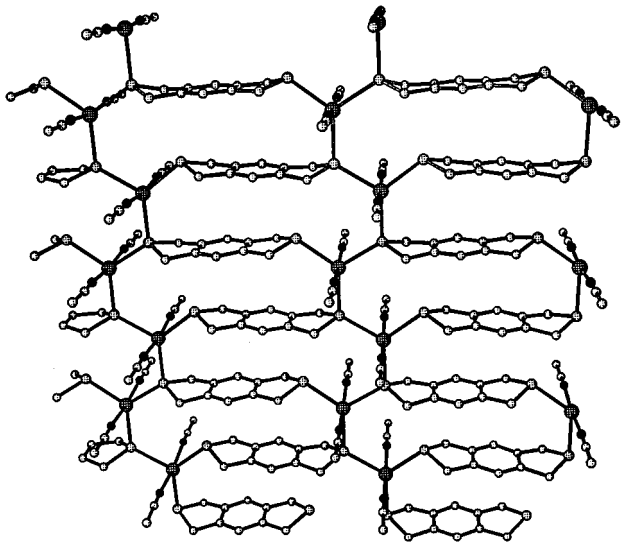

Figure 2. View down onto a single lamella of the structure of **2**. BF_4 ions and hydrogen atoms are omitted for clarity.

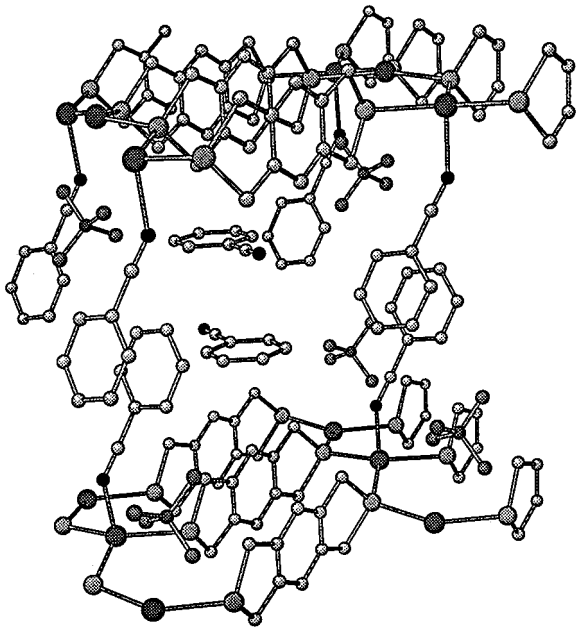

Figure 3. The "swelled" interlayer region in the structure of **3**. The π-stacked PhCN pseudo-pillars and the PhCN guest molecules[15] are clearly visible.

opposite side of the ligand employs both lone pairs to coordinate to two different Ag^I centers.

The cationic layers lie perpendicular to the crystallographic *c* axis with an interlayer separation of 10.085(1) Å.[10] The axial MeCN molecules are ligated in a linear fashion and protrude directly into the interlayer region. The ligand **1** may adopt either a *syn* or *anti* conformation with respect to the orientation of the sulfur donors, owing to inversion at the benzylic carbon atoms, but **1** is observed exclusively in the *syn* conformation. Throughout the structure, the *syn* sulfur atoms are oriented towards the same crystal face. Adjacent layers are offset by 3.672(2) Å along the *b* axis. The calculated surface area of the layered structure ($S_t = 1160\ m^2 g^{-1}$ [11]) and the fixed charge density ($(fcd) = 5.58 \times 10^{13}\ e^{-1} cm^{-2}$ [12]) are both comparable to other classes of layered compounds.[13]

As with any layered material, the prospect of "swelling" the structure to afford greater access to the interlayer region is highly appealing.[14] The presence of labile coordination sites on the metal directed into the interlamellar region makes the use of a larger coordinating ligand, such as PhCN, a logical choice. Therefore, a dried sample of **2** was dissolved in PhCN, and then benzene was diffused into this solution to give colorless, needlelike crystals of $[\{Ag(\mathbf{1})(PhCN)\}_\infty][BF_4]_\infty \cdot \infty$ PhCN (**3**), where one molecule of PhCN is coordinated to the silver ion and the second is present as a guest molecule. The structure of **3** (Figure 3) is a remarkable illustration of a swelled lamellar solid. It is noteworthy that only a single molecule of PhCN is coordinated to each Ag^I ion, necessitating a shift in metal ion geometry from a five-coordinate trigonal bipyramid to a severely distorted four-coordinate tetrahedron (N1-Ag-S1 = 93.9(1)°, N1-Ag-S2 = 102.2(1)°, N1-Ag-S2′ = 79.8(1)°). The individual {Ag(**1**)} lamellae of **3**, however, are completely planar and identical to the individual layers observed in **2**. Therefore, despite the strained geometry at the metal and the change in metal coordination number, an analogous lamellar structure is retained. The coordinated PhCN molecules, which serve to swell the layers, are coordinated to the metal in a bent orientation (Ag-N1-C11 = 141.3(4)°). Furthermore, the phenyl moiety of each coordinated PhCN molecule participates in a π-stacking interaction with another PhCN molecule from an adjacent layer to form a "pseudo-pillar". This results in a swelling of the interlayer region and an increase in the *d* spacing from 10.085(1) Å to 13.890(1) Å.[10, 15] The void space generated by this interlamellar expansion is occupied by a single PhCN molecule per repeat unit.[16] An additional effect of the pseudo-pillar is to align adjacent layers in the crystal structure. The lamellae are offset by only 0.624(2) Å, primarily in the *a* direction, which is considerably different from the 3.672(2) Å offset observed in **2**. Interestingly, all molecules of **1** are again in a *syn* conformation, but the ligands in adjacent layers are oriented in opposite directions.

The individual cationic lamellae formed by $AgBF_4$ and **1** are quite robust in nature. DSC and thermogravimetric (TG) measurements reveal the loss of the nitrile molecules for both **2** and **3** below 100 °C; however, the desolvated complexes do not undergo any further phase changes until an endothermic transition with an onset temperature of 188 °C is observed in both complexes.[17]

Monodentate thioethers are notoriously poor ligands for transition metal ions.[8] In fact, homoleptic transition metal complexes of Me_2S are quoted as "virtually impossible to prepare".[18] Thus, it is interesting to note that **1**, which can be pictured as two molecules of Me_2S linked by a benzene ring, forms complexes stable to over 180 °C with the air- and light-sensitive $AgBF_4$ salt. As this stability stems from the regimented coordination environment about the Ag^I center enforced by the layered structure, we refer to this as a "lamellar chelate effect". Work in progress has shown that these complexes undergo anion exchange reactions and that some of these anions serve to pillar the interlayer region.[19] This observation further extends the analogy of these lamellar networks to claylike solids.

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Experimental Section

1:[20] Tetrabromodurene (1.99 g, 4.44 mmol) was added to a solution of $Na_2S \cdot 9H_2O$ (2.14 g, 8.88 mmol) in ethanol (100 mL) and refluxed for 6 h. Removal of solvent resulted in an off-white residue that was partitioned between CH_2Cl_2 (100 mL) and H_2O (50 mL). The aqueous layer was separated and further extracted with CH_2Cl_2 (2×100 mL). The organic fractions were combined and dried ($MgSO_4$). Yield: 0.84 g (4.34 mmol, 97%), >95% purity by ^1H NMR; m.p. 220–223 °C; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.08$ (s, 2H, arom.), 4.19 (s, 8H, CH_2S); $^{13}C\{^1H\}$: $\delta = 139.66$, 120.50 (arom.), 37.31 (CH_2S); CPMAS SS ^{13}C NMR (75 MHz): $\delta = 140.6$, 120.7 (arom.), 39.1 (CH_2S); FAB-MS: *m/z*: 194.2 [M^+]; C, H analysis: calcd: C 61.81, H 5.19; found: C 61.59, H 5.14.

2: A solution of **1** (48.3mg, 0.249 mmol) in MeCN (40 mL) was added to a solution of $AgBF_4$ (48.3 mg, 0.249 mmol) in MeCN (10 mL). The solution was stirred for 12 h and then concentrated to about 10 mL. Diffusion of benzene into this solution resulted in the growth of platelike crystals suitable for an X-ray analysis. C, H analyses:[21] calcd: C 35.70, H 3.42; found: C 32.97, H 2.99. Crystal data:[22] $C_7H_8Ag_{0.5}B_{0.5}F_2NS$, $M_r = 235.54$, colorless plates, orthorhombic, space group *I2cm*, $a = 7.6520(2)$, $b = 11.7135(4)$, $c = 20.1711(7)$, $V = 1808.0(1)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.731$ g cm^{-3}, $R = 0.033$, $R_w = 0.041$ and GOF = 3.14 for 113 parameters, 1287 reflections with $F_o > 2.5\sigma(F_o)$.

3: Benzene was diffused into a saturated, filtered solution of **2** in PhCN. This resulted in the growth of colorless needles suitable for X-ray analysis. C, H analyses:[21] calcd: C 48.43, H 3.39, found: C 45.82, H 3.15. Crystal data:[22] $C_{24}H_{20}AgBF_4N_2S_2$, $M_r = 595.23$, colorless needles, monoclinic, space group $P2_1/c$, $a = 10.1909(5)$, $b = 27.780(1)$, $c = 8.6870(5)$, $\beta = 94.96(1)$, $V = 2450.1(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.600$ g cm^{-3}, $R = 0.051$, $R_w = 0.038$ and GOF = 2.11 for 387 parameters, 4032 reflections with $F_o > 2.5\sigma(F_o)$.

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[10] In both crystal structures, the interlayer separation was defined as the perpendicular distance between planes of silver ions since the metals are on special positions.

[11] Calculated from the expression (1);

$$S_t = N a b \times 10^{-18} n M_c^{-1} \quad (1)$$

where *N* is the Avogadro constant, *a* and *b* are the surface area of one side of the unit cell, *n* is the number of such exposed sides in the interlayer region, and M_c is the formula weight of the unit cell: G. Alberti, U. Costantino in *Comprehensive Supramolecular Chemistry*, *Vol. 7* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle), Elsevier, New York, **1996**, pp. 1–24.

[12] Calculated as $n'(a\,b\,n)^{-1}$, where n' is the number of charges, *a*, *b* and *n* are defined as in ref. [11].

[13] For comparison, typical values of S_t and fcd for a $Zr(HPO_4)_2$ structure are 965 m^2 g^{-1} and 4.1×10^{14} e^{-1} cm^{-2}, respectively, and for a smectite clay, 759 m^2 g^{-1} and 47.4×10^{13} e$^-$ cm^{-2}, respectively.[11]

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[15] In both structures **2** and **3**, the interlayer spacing corresponds to exactly half the length of one of the principal axes: the *c* axis for **2** and the *b* axis for **3**.

[16] Upon loss of solvent or attempts to exchange the PhCN for benzene, the crystals become opaque and no longer diffract.

[17] For **2**, a steady loss of MeCN is observed between room temperature and 95 °C. For **3**, loss of PhCN occurs, as expected, in two stages. The first, steady loss from room temperature to 52 °C corresponds to the unbound PhCN, followed by a second mass change from 62–97 °C for the Ag-bound PhCN. No further changes in the DSC or TG are observed for both **2** and **3** until a transition with an onset temperature of 188 ± 1 °C occurs. All mass changes are within reasonable limits (5%) of the expected values given that the room temperature desolvation of **2** and **3** made an accurate determination of the initial mass impossible. The value of 188 °C is comparable to other Ag coordination arrays with ligands generally accepted to be better donors than thioethers. See: F.-Q. Liu, T. D. Tilley, *Inorg. Chem.* **1997**, *36*, 5090–5096.

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[21] Elemental analyses were performed on single crystals of both **2** and **3** as expeditiously as possible. However, some loss of the nitrile solvent was unavoidable resulting in the slightly low observed C, H values.

[22] General crystallographic information: $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu(Mo_{K\alpha}) = 1.04$ mm^{-1}. $T = -100$ °C, Siemens SMART CCD diffractometer, ω scan mode ($3° < 2\theta < 57.3°$), solved with the NRCVAX suite of programs.[23] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101137. Copies of the data can be obtained free of charge on application to: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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