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# Two-Dimensional Frameworks Based on Ag(I)–N Bond Formation: Single Crystal to Single Molecular Sheet Transformation

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S Supporting Information

ABSTRACT: A series of new two-dimensional coordination framework materials, based on Ag(I)-N bond formation, has been synthesized and structurally characterized by single crystal methods. Reactions between the poly-monodentate bridging ligand N,N'-((1r,4r)-cyclohexane-1,4-diyl)bis-(1-(pyridin-3-yl)methanimine), L1, and silver salts yield compounds  $\{[Ag(L1)(MeCN)](CF_3SO_3^{-})\}_n, 1, \{[Ag(L1)(PF_2O_2^{-})]:H_2O\}_n, 2, and$  $\{Ag_2(L1)(tosylate)_2\}_{n'}$  3. The frameworks of these materials exhibit two distinct net topologies:  $3^{6}.4^{6}.5^{3}$  (1 and 2) and  $4^{4}.6^{2}$  (3). In all cases, L1 ligands are found to be fully saturated, in terms of metal ion binding, with both sets of pyridyl and imino N atoms involved, though in 1 and 2, crystallographically independent L1 moieties also display pyridyl-only binding. Either solvent (1) or the anion (2 and 3) acts as a terminal ligand to support interlayer interactions in the solid state. For 2 and 3 the



molecular sheet orientation lies in the plane of the largest crystal face, indicating that crystal growth is preferentially driven by coordinate bond formation. Despite the relatively labile nature, typical of such Ag(I)-N bonds, solvent-based exfoliation of crystals of 3 was shown to provide dispersions of large,  $\mu m^2$ , flakes which readily deposit on oxide surfaces as single-molecule sheets, as revealed by atomic force microscopy.

## INTRODUCTION

In this "post-graphene" era there is an enormous interest in two-dimensional or layered materials due to their potential for applications in electronic, display, and sensor technologies, etc.<sup>1-3</sup> Metal-organic, or coordination polymer, frameworks<sup>4</sup> provide a useful means to realize this type of structure. Moreover, in contrast to graphene and binary inorganics, e.g., boron nitride (BN) and molybdenum disulfide ( $MoS_2$ ), such a molecular-based approach offers an extensive level of functionalization and diversity of architecture due to the building-block nature of coordination chemistry.

Notably, it has been demonstrated that two-dimensional (2D) coordination framework materials comprising a few layers or even a single molecular sheet can be obtained. Recent efforts in this area include both "bottom-up" synthesis<sup>6-10</sup> and "top-down" exfoliation approaches.<sup>11-16</sup> The successful and reproducible preparation of these materials is an important processing step for developments such as thin-film applications<sup>17,18</sup> and membrane technologies.<sup>19</sup>

Ag(I)-N bond formation is very well established as a basis for the synthesis of coordination polymers.<sup>20-28</sup> The d<sup>10</sup> electronic configuration of Ag(I) ensures a diversity of coordination number and geometries though there is a general tendency toward low-coordination-number, chainlike, systems with many studies specifically aimed at producing one-dimensional (1D) materials.<sup>21,29,30</sup> Two-dimensional, sheet,

polymers represent a somewhat smaller fraction, though many examples are known, exhibiting a variety of topologies.<sup>22,31,3</sup> While these materials have been shown to be capable of catalysis,<sup>33</sup> reversible anion binding<sup>33</sup> and luminescence<sup>34</sup> reports of Ag-based frameworks being prepared as single molecular sheets are lacking.

With these factors in mind, we have begun to explore the coordination chemistry of Ag(I) with poly-monodentate ligands based on bis(1-pyridin-3-yl)methanimine. The labile nature of the Ag–N bond  $^{21,22,35-39}$  means that high-quality crystalline materials can be prepared at or below ambient temperature, as well as by the hydrothermal methods<sup>40-43</sup> typically used for metal-organic framework (MOF) materials.<sup>44</sup> However, this lability may have consequences for any subsequent top-down exfoliation processing designed to isolate single layer molecular sheets.

Here we report the synthesis and structural characterization of a series of 2D coordination framework materials, {[Ag(L1)- $(MeCN)](CF_3SO_3^{-})_n$ , 1,  $\{[Ag(L1)(PF_2O_2^{-})] \cdot H_2O\}_n$ , 2, and  $\{Ag_2(L1)(tosylate)_2\}_n$ , 3, (Scheme 1; L1 =  $N_nN'-((1r_n4r)$ cyclohexane-1,4-diyl)bis(1-(pyridin-3-yl)methanimine)). These illustrate different ligand binding modes, metal:ligand stoichiometry, and network topology. In addition, we demonstrate,



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Scheme 1. Metallo-Ligand Frameworks All Prepared with (1E,1'E)-N,N'-((1r,4r)-Cyclohexane-1,4-diyl)bis(1-(pyridin-3-yl)methanimine), L1



for 3, that despite any relative lability of individual Ag–N bonds, the material is amenable to solvent-based exfoliation and provides dispersions of flakes of individual molecular sheets up to several  $\mu$ m<sup>2</sup> in size.

## EXPERIMENTAL SECTION

**General Methods and Reagents.** All reagents were purchased from Sigma-Aldrich or Alfa Aesar. Fourier transform infrared (FTIR) spectra were recorded in air on a Shimadzu IRAffinity-1S or Varian 800 Scimitar Series. <sup>1</sup>H NMR spectra were recorded on a Bruker AC300 spectrometer at 300 MHz in  $\text{CDCl}_3$  (Sigma-Aldrich) unless reported otherwise and referenced to residual non-deuterated solvent ( $\delta$  7.26). High-resolution electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Waters Micromass LCT Premier TOF mass spectrometer. Microanalyses were carried out by the Elemental Analysis Service in the School of Human Sciences, London Metropolitan University. Powder X-ray diffraction (XRD) data were collected using a Panalytical X'pert MPD equipped with an X'Celerator detector. Samples were mounted onto an oblique-cut Si wafer as the substrate.

Atomic force microscopy (AFM) images were acquired in air using a MultiMode 8 atomic force microscope with a NanoScope V controller (Bruker). The microscope was controlled by Nanoscope software, version 9.1. The AFM was operated in ScanAsyst in air mode as a peak force tapping mode at ultralow forces to minimize damage to crystal surfaces. An isolation table (TMC) was used to reduce vibrational noise. The probes used for AFM were silicon tips on silicon nitride cantilevers (ScanAsyst, Bruker) with a nominal tip radius of approximately 2 nm, resonant frequency 150 kHz, and spring constant k = 0.7 N m<sup>-1</sup>. The AFM data was processed with NanoScope Analysis 1.50 software (Bruker). For imaging, P-type silicon wafers  $\langle 100 \rangle$ oriented 1–10  $\Omega$  cm B-doped were used as substrates that were cleaned by plasma ashing for 15 min at 8 kV followed by sonication in ethanol for 15 min.

Synthesis of L1. (1E,1'E)-N,N'-((1r,4r)-Cyclohexane-1,4-diyl)bis-(1-(pyridin-3-yl)methanimine), L1, was prepared based on literature methods.<sup>45,46</sup> trans-1,4-Diaminocyclohexane (25 mmol, 2.85 g) was dissolved in ethanol (50 mL) and dichloromethane (50 mL). While stirring, nicotinaldehyde (50 mmol, 5.36 g) was added to the solution followed by two drops of formic acid. The solution was stirred at room temperature overnight. The sample was evaporated under reduced pressure until precipitation was observed. The solution was left to stand, and vacuum assisted filtration followed by washing with ethanol (10 mL) and hexane (10 mL) gave a white crystalline powder, L1 (5.4 g, 72%). mp: 160–162 °C. FTIR: 2920 m (CH), 2860 s (CH), and 1641 cm<sup>-1</sup> vs (imine CN). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.79–1.88 (8H, m), 3.28–3.42 (2H, m), 7.34 (2H, dd, J 7.9, 4.8), 8.12 (2H, dt, J 7.9, 1.9), 8.41 (2H, s), 8.64 (2H, dd, J 4.8, 1.7), 8.86 (2H, d, J 1.6).

Silver Complexes 1–3. The general method used to obtain crystalline samples was a liquid/liquid diffusion technique. Briefly, L1 was dissolved in dichloromethane (10 mL) and the corresponding silver salt was dissolved in acetonitrile (10 mL). Reactions were typically performed for 1:1, 1:2, and 1:3 metal:ligand stoichiometric ratios, and those yielding single crystals were examined further. All solutions were cooled in dry ice during and after the layering of the relevant solutions. The crystallization vessels were stored in the freezer (-20 °C), in a dark container, for 3 days before transfer to a refrigerator for a further week.

Preparation of  $\{[Aq(L1)(MeCN)](OTf)\}_n$  (1). Silver trifluoromethanesulfonate (0.1 mmol, 25.7 mg) and L1 (0.2 mmol, 58.5 mg) were reacted using previously the described method and colorless single crystals suitable for X-ray analysis were obtained upon standing. MPt: decomposed to a dark brown material, 206–208 °C. FTIR: 1642 cm<sup>-1</sup> (imine C=N). ESI-MS (ESI, H<sub>2</sub>O): calcd for AgC<sub>4</sub>H<sub>6</sub>N<sub>2</sub>, 188.9582  $([Ag + (MeCN)_2]^+)$ ; found, 188.9581  $([Ag + (MeCN)_2]^+$ , 38.3). Calcd for C<sub>18</sub>H<sub>21</sub>N<sub>4</sub>, 293.1766 ([L1 + H]<sup>+</sup>); found, 293.1766 ([L1 +  $H^{+}_{1}$ , 100.0). Calcd for AgC<sub>18</sub>H<sub>20</sub>N<sub>4</sub>, 399.0739 ([Ag + L1]<sup>+</sup>); found, 399.0738 ( $[Ag + L1]^+$ , 1.5). Calcd for  $AgC_{20}H_{23}N_5$ , 440.1004 ( $[Ag + L1]^+$ )  $L1 + MeCN^{+}$ ; found, 440.1007 ([Ag + L1 + MeCN]<sup>+</sup>, 7.7). Calcd for  $AgC_{19}F_{3}H_{21}N_{4}O_{3}S_{5}$  549.0337 ([Ag + L1 + OTf + H]<sup>+</sup>); found, 549.0340 ( $[Ag + L1 + OTf + H]^+$ , 0.9). Calcd for  $AgC_{21}F_3H_{24}N_5O_3S$ , 590.0603 ([Ag + L1 + MeCN + OTf + H]<sup>+</sup>); found, 590.0604 ([Ag + L1 + MeCN + OTf + H]<sup>+</sup>, 0.9). Calcd for AgC<sub>36</sub>H<sub>40</sub>N<sub>8</sub>, 691.2427 ([Ag +  $(L1)_2$ ]<sup>+</sup>); found, 691.2426 ([Ag +  $(L1)_2$ ]<sup>+</sup>, 4.7). Elemental anal. calcd for AgC19H20N4O3SF3: C, 41.54; H, 3.68; N, 10.20; found C, 41.65; H, 3.51; N, 10.23. Data indicates loss of solvent. Crystals of 1 were also obtained from reactions performed at L1:Ag(I) ratios of 1:1 and 3:1.

Preparation of  $\{[Aq(L1)(PF_2O_2)] \cdot H_2O\}_n$  (2). Silver diffuorophosphinato (0.12 mmol, 25.3 mg) and L1 (0.2 mmol, 58.5 mg) were reacted as described above and gave colorless single crystals suitable for X-ray analysis upon standing. [The anion, initially identified through X-ray crystallography, is a hydrolysis product of  $PF_6^{-.47}$  Crystals of 2 were also obtained from reactions with  $\sim$ 1:3 ratio alongside free ligand. No crystalline material was obtained from ratios of ~1:1. 2 MPt: decomposed to a dark brown material, 190-192 °C. FTIR: 1635  $cm^{-1}$  (imine C=N). ESI-MS (ESI, H<sub>2</sub>O): calcd for AgC<sub>4</sub>H<sub>6</sub>N<sub>2</sub>, 188.9582 ( $[Ag + (MeCN)_2]^+$ ); found, 188.9581 ( $[Ag + (MeCN)_2]^+$ , 100.0). Calcd for  $C_{18}H_{21}N_4$ , 293.1766 ([L1 + H]<sup>+</sup>); found, 293.1767  $([L1 + H]^+, 38.8)$ . Calcd for AgC<sub>18</sub>H<sub>20</sub>N<sub>4</sub>, 399.0739  $([Ag + L1]^+)$ ; found, 399.0743 ([Ag + L1]<sup>+</sup>, 1.2). Calcd for AgC<sub>20</sub>H<sub>23</sub>N<sub>5</sub>, 440.1004  $([Ag + L1 + MeCN]^{+});$  found, 440.1001  $([Ag + L1 + MeCN]^{+}, 14.2).$ Calcd for AgC<sub>36</sub>H<sub>40</sub>N<sub>8</sub>, 691.2427 ([Ag +  $(L1)_2$ ]<sup>+</sup>); found, 691.2425  $([Ag + (L1)_2]^+, 0.8)$ . Satisfactory elemental analysis could not be obtained. The structure was confirmed by single crystal X-ray crystallography.

Preparation of {[Ag<sub>2</sub>(L1)(Tos)<sub>2</sub>]]<sub>n</sub> (3). Silver tosylate (0.1 mmol, 27.9 mg) and L1 (0.1 mmol, 29.2 mg) were reacted as described above and gave colorless single crystals suitable for X-ray analysis upon standing. 3 MPt: decomposed to a light brown material, 215–217 °C. FTIR: 1641 cm<sup>-1</sup> vs (imine C=N). ESI-MS (ESI, H<sub>2</sub>O): calcd for AgC<sub>4</sub>H<sub>6</sub>N<sub>2</sub>, 188.9582 ([Ag + (MeCN)<sub>2</sub>]<sup>+</sup>); found, 293.1767 ([L1 + H]<sup>+</sup>, 13.0). Calcd for AgC<sub>20</sub>H<sub>23</sub>N<sub>5</sub>, 440.1004 ([Ag + L1 + MeCN]<sup>+</sup>); found, 440.1006 ([Ag + L1 + MeCN]<sup>+</sup>, 2.3). Calcd for AgC<sub>25</sub>H<sub>28</sub>N<sub>4</sub>SO<sub>3</sub>, 571.0933 ([Ag + Tos + L1 + H]<sup>+</sup>); found, 571.0927 ([Ag + Tos + L1 + H]<sup>+</sup>, 0.7). Calcd for AgC<sub>36</sub>H<sub>40</sub>N<sub>8</sub>, 691.2427 ([Ag + (L1)<sub>2</sub>]<sup>+</sup>); found, 691.22426 ([Ag + (L1)<sub>2</sub>]<sup>+</sup>, 0.3). Elemental anal. calcd for Ag<sub>2</sub>C<sub>32</sub>H<sub>34</sub>N<sub>4</sub>O<sub>6</sub>S<sub>2</sub>: C, 45.19; H, 4.03; N, 6.59; found C, 45.28; H, 4.16; N, 6.59. Crystals of 3 were also obtained from reactions with a 1:3 ratio.

**Single-Crystal X-ray Diffraction.** Crystal structure data for 1, 2, and 3 were collected at 150 K on an Xcalibur, Atlas, Gemini ultra diffractometer equipped with a sealed X-ray tube ( $\lambda_{Cu \ Kar} = 1.541 \ 84 \ Å$ ) and an Oxford Cryosystems CryostreamPlus open-flow N<sub>2</sub> cooling device. Cell refinement, data collection, and data reduction were undertaken via the software CrysAlisPro.<sup>48</sup> Intensities were corrected for absorption analytically using a multifaceted crystal model created by indexing the faces of the crystal for which data were collected.<sup>49</sup>

Crystal structure data for L1 were collected at 120 K on a Bruker D8 Venture diffractometer equipped with a Photonic CMOS detector, microfocus sealed X-ray tube ( $\lambda_{Mo K\alpha} = 0.71073$  Å) and an Oxford Cryosystems CryostreamPlus open-flow N<sub>2</sub> cooling device. An empirical absorption correction using spherical harmonics was applied to the intensities using the program SADABS.

All structures were solved using  $XT^{50}$  and refined by  $XL^{51}$  using the Olex2<sup>52</sup> interface. Hydrogen atoms were positioned with idealized geometry, with the exception of those bound to heteroatoms which

were located from peaks in the Fourier difference map. The thermal parameters of the hydrogen atoms were constrained using the riding model with  $U_{\rm (H)}$  set at  $1.2 U_{\rm eq}$  for the parent atom.

While the structure of L1 was collected at a different temperature from those of 1, 2, and 3, the experimental collection conditions are not significantly different and hence comparisons between the bond geometries of the free ligand and the coordination complexes are valid.

**Preparation of Single Molecular Sheet by Solvent-Based Exfoliation.**<sup>16</sup> A crystalline sample of 3 (ca. 50 mg) was transferred to filter paper. This was washed with hexane  $(2 \times 10 \text{ mL})$  and ethanol  $(2 \times 10 \text{ mL})$  and allowed to dry in air for 5 min. The sample was added to toluene (1.5 mL) and the mixture was sonicated at 40 kHz using a Langford Sonomatic 475H. Sonication times varied between 30 s and 5 min, with increased sonication time generally producing smaller flakes. The sonicated material was centrifuged for 5 min at 8000 rpm, and the supernatant was pipetted onto silicon wafer, allowed to dry, and analyzed by AFM.

#### RESULTS AND DISCUSSION

Ligand L1 (1E,1'E)-N,N'-((1r,4r)-cyclohexane-1,4-diyl)bis(1-(pyridin-3-yl)methanimine) (Scheme 1) was prepared according to previously described methods.<sup>45,46</sup> This molecule offers two pairs of distinct, monodentate N-donor types: the pyridyl and imino functionalities. Combined with the 3-substitution, a range of metal binding site distances and metal–ligand bond vectors can be brought about by simple rotation of the Py–C bond. Single crystal X-ray diffraction studies reveal that L1 has an *E*-arrangement with *anti-anti-anti* conformation (as shown in Scheme 1) in the solid state at both 223 K<sup>53</sup> and 120 K as measured in this work.

Metal Complex Formation. As our primary interest was to establish unambiguous structural detail of the compounds through X-ray diffraction analysis, a liquid/liquid diffusion method for preparation of complexes 1-3 as single crystals was used. Solutions of dichloromethane containing L1 and acetonitrile containing the corresponding silver salt, Ag(OTf), Ag(Tos), or  $Ag(PF_2O_2)$  (where OTf = trifluoromethanesulfonate and Tos = *p*-toluenesulfonic acid), were prepared, cooled in dry ice, and then layered using a pipet. Reactions were typically performed for 1:1, 1:2, and 1:3 metal:ligand ratios, though a lack of stoichiometric control, quite common to the coordination chemistry of Ag(I) ions,<sup>54,55</sup> was apparent (vide infra). The reaction mixtures were stored in a freezer  $(-20 \degree C)$ for 3 days before transfer to a refrigerator. This method typically provided samples suitable for single crystal X-ray diffraction after 4-7 days. ESI-MS analysis of the solid material collected from the respective reactions indicated metal ion binding by the presence of species corresponding to [AgL1]<sup>+</sup>,  $[AgL1(MeCN)]^+$ ,  $[AgL1(anion) + H]^+$ , and  $[AgL1_2]^+$ . No degree of higher oligomerization was observed in solution, however, consistent with a rather labile nature of the Ag-N bond.

 ${[Ag(L1)(MeCN)](OTf)}_n$  (1). Reactions of L1 with Ag(OTf) at 1:1, 1:2, and 1:3 metal:ligand ratios yielded colorless crystalline material; representative single crystals isolated from each solution were identified by X-ray diffraction as the 1:1 complex {[Ag(L1)(MeCN)](OTf)}\_n 1. Compound 1 has a 2D coordination polymer structure based on distorted tetrahedral metal ion geometry about a single unique Ag(I) ion. The Ag(I) is bound by the pyridyl groups of two crystallographically independent L1 moieties (Ag–N<sub>Pyr</sub> 2.258(1) and 2.330(1) Å for N1 and N3, respectively), an imine nitrogen atom (Ag–N<sub>Im</sub> 2.318(1) Å), and the nitrogen atom of an MeCN solvent

molecule (Ag $-N_{MeCN}$  2.400(1) Å). Details of the coordination sphere are illustrated in Figure 1.



Figure 1. Structural details of 1 with (upper) the coordination sphere about the Ag ion and (lower) the different metal-binding patterns of the crystallographically independent L1 groups.

The twist angles between the mean planes of the pyridyl rings and cyclohexyl groups differ significantly between ligand–N1 and ligand–N3 at 62.8(1) and  $36.8(1)^{\circ}$ , respectively. The twist angle of ligand–N1 more closely matches that of the crystal structure of free ligand L1 ( $58.2(1)^{\circ}$ ), suggesting that Ag(I)–N<sub>Im</sub> coordination causes the deviation in ligand–N3. As with the free ligand, both independent L1 ligands have the same *anti-anti-anti* conformation with both pairs of imine and pyridyl ring N-donor atoms (N1/N2) and (N3/N4) oriented in opposite directions.

Of the two crystallographically independent L1 ligands of 1, one coordinates through all four nitrogen donors, while the other coordinates via the pyridyl nitrogen donor atoms only (Figure 1). The C=N imino bond is essentially unchanged by metal binding (N4=C16 1.2695(1); N2=C7 1.2669(1); C= N bond free ligand L1 1.2662(1) Å). Similarly, the FTIR spectrum also shows little evident shift of the  $\nu_{C=N}$  observed compared to the free ligand (1641 cm<sup>-1</sup> in 1, cf. 1640 cm<sup>-1</sup>), though a slight shoulder is evident at higher wavenumber for 1 possibly due to the different imino groups (see Supporting Information, Figure S1).

The observed metal–ligand connectivity gives rise to a 2D  $3^{6}.4^{6}.5^{3}$  net topology and forms two different sized metallocyclic rings: a 12-membered disilver ring and a larger 52membered tetrasilver ring. In the smaller metallocycle, the pyridyl rings show parallel, partial, stacking with an interplanar separation of 3.34(1) Å as measured from a calculated ring centroid to ring plane (Figure 2). Also notable here is that the Ag(I) ion lies out-of-plane of the N3-containing pyridyl group (cf.  $\angle Py(N3)_{Cent}-N3-Ag = 154.5(1)^{\circ})$ ,  $\angle Py(N1)_{Cent}-N1-Ag = 173.8(1)^{\circ})$ .

The larger 52-membered metallocyle generates essentially parallelogram-shaped pores with sides of  $\sim$ 1.8 nm  $\times$  1.2 nm, as measured by the respective Ag…Ag distances, in the single



**Figure 2.** Parallel stacking of pyridyl rings that make up the smaller 12-membered metallocycle.

sheet arrangement (Figure 3). These pores are occupied by  $OTf^-$  anions. The dipyridyl moieties, L1(N1/N2) and L1(N3/N2)



Figure 3. (upper) Parallelogram-shaped pores of the 2D coordination polymer sheet of 1 as viewed essentially perpendicular to the plane. (lower) View through the (110) plane showing individual sheets in profile with a single sheet highlighted (red).

N4), make up the longer and shorter sides of the pore, respectively. Two-dimensional sheets of 1 grow in the crystallographic (101) plane and stack parallel to this (Figure 3). There is slight interdigitation of sheets involving the terminal acetonitrile molecules. Individual sheet thickness, as measured by the distance between planes calculated through the methyl groups (C21) of the coordinated MeCN, is approximately 8 Å.

 ${[Ag(L1)(PF_2O_2)]}\cdot H_2O_{n}$  (2). Single crystals isolated from reactions of L1 and Ag(PF\_2O\_2) at both 1:2 and 1:3 metal:ligand stoichiometries were analyzed by single crystal X-ray diffraction and found to be the 1:1 complex  ${[Ag(L1)-(PF_2O_2)]}\cdot H_2O_{n}$  2 (Figure 4). Compound 2 is essentially similar to 1, adopting a 2D framework structure based on a distorted tetrahedral coordinated to two pyridyl nitrogen atoms from crystallographically independent ligands (Ag–N1 2.357(1); Ag–N3 2.337(1) Å) and an imine nitrogen at a slightly shorter distance (Ag–N4<sub>Im</sub> 2.259(1) Å). In this case the fourth site is occupied by an oxygen from the terminal PF<sub>2</sub>O<sub>2</sub><sup>-</sup> counterion (Ag–O = 2.5166(1) Å), resulting in an electronically neutral layer structure.

Compared to 1, the two independent ligands are more similar with regard to the twist angles between the mean planes of the pyridyl rings and cyclohexyl groups (ligand-N1 =  $50.9(1)^{\circ}$ , ligand-N3 =  $71.2(1)^{\circ}$ ; cf. 62.8(1) and  $36.8(1)^{\circ}$  respectively for 1). However, they adopt *syn-anti-syn* (N1/N2) and *anti-anti-anti* (N3/N4) conformations, respectively. As a



**Figure 4.** Structural details of **2** showing (upper) the tetrahedral coordination sphere about the Ag ion and (lower) the different metalbinding patterns of crystallographically independent **L1** groups.

result, the intradonor atom  $N_{Py} \cdots N_{Py}$  distance for  $N1_{Py} \cdots N1_{Py}$  is shorter than  $N3_{Py} \cdots N3_{Py}$  (13.9(1) and 15.0(1) Å, respectively) with the equivalent distances in 1 being close to the latter value, at 14.9(1) and 15.1(1) Å.

As in 1, the crystallograhically independent ligands coordinate with either all four N-sites (N3/N4) or via only the pyridyl, N1, sites. The imino bond lengths show little change upon coordination (2: N4=C16 1.2714(1) Å; N2=C7 1.2694(1) Å; L1: N=C 1.2660(7) Å) and there is little shift of the FTIR  $\nu_{C=N}$  stretch (1636 cm<sup>-1</sup>) though a shoulder on the main band is again observed (see Supporting Information, Figure S1).

The Ag–N bonding generates the same framework topology of  $3^{6}.4^{6}.5^{3}$  as in 1, but features 22-membered Ag<sub>2</sub>Ll<sub>2</sub> and 42membered Ag<sub>4</sub>Ll<sub>4</sub> metallomacrocycle rings. Figure 5 illustrates the structure of an individual molecular sheet viewed onto the plane and the packing of these sheets in the crystal structure along with dimensions for layer thickness. There is notable corrugation of the individual sheets, and interdigitation is more extensive than is the case for 1.

 ${[Ag_2(L1)(Tos)_2]}_n$  (3). Single crystals isolated from reactions of L1 and Ag(Tos) at metal:ligand 1:1 stoichiometry were found to be the 2:1 complex,  ${[Ag_2(L1)(Tos)_2]}_n$  3 (Figure 6). We note that this same compound was also isolated from reactions containing a metal:ligand 1:3 stoichiometry, alongside at least one other product. Compound 3 contains a unique Ag(I) ion 3-coordinated by donor atoms from pyridyl (Ag–N1 2.1892(1) Å) and imine nitrogen atoms (Ag–N2 2.1886(1) Å) from different L1 moieties generating a 2D coordination framework. The tosylate counterion acts as a weak terminal ligand (Ag–O1 at 2.522(1) Å). The bond angles around the metal ion indicate a distorted T-shape geometry ( $\angle N1-Ag1-N2$ N2 154.64(1)°;  $\angle O-Ag1-N1$  99.24(1)°;  $\angle O-Ag1-N2$ 



Figure 5. (upper) Single sheet of 2 viewed approximately through the (121) plane. (lower) View approximately through (100) showing sheets in profile. A single sheet is highlighted (red) and illustrates the interdigitating of layers and the corrugation of the sheets.



**Figure 6.** Structural details of **3** with (upper) the trigonal coordination sphere about the Ag ion and (lower) metal-binding pattern of **L1**. Hydrogen atoms omitted for clarity.

103.07(1)°;  $\Sigma \cong 357.0^{\circ}$ ) with the Ag ion lying slightly (0.19(1) Å) out of the mean coordination plane

The ligand adopts a *syn-anti-syn* conformation through rotation about the Py-C bond which directs the imine and pyridyl ring N-donor atoms (N1/N2) in the same direction.

Considering the rotations about the Py–C bond in structures 1 and 2, L1 appears to exhibit little conformational preference to the orientation of the N-donor atoms. The ligand L1 lies on an inversion center, and all four N-donors are involved in metal ion binding. X-ray and FTIR data indicate little change to the C=N function as a result of coordination (viz., 1: C=N 1.2685(1) Å,  $\nu_{C=N}$  1641 cm<sup>-1</sup>; L1: C=N 1.2660(7) Å,  $\nu_{C=N}$  1640 cm<sup>-1</sup>).

The resulting coordination mode forms a single type of 34membered metallocycle containing four Ag ions and four contributing ligand moieties. These generate a 2D framework with  $4^4.6^2$  topology where the centroid is a 4-connected ligand node and the silver atoms are 2-connecting linkers. Within individual layers the Ag(I) ions lie in a plane (Figure 7) and the



**Figure 7.** (upper) Details of the crystal structure of **3** illustrating the wavelike 34-membered metallocycles of individual MOF sheets viewed onto the (100) plane. (lower) Packing of sheets in the crystal as viewed onto the (010) plane with the (100) face uppermost.

layer thickness is  $\sim 14.16(1)$  Å including the coordinated tosylate anions. This is larger than the 11.5000(5) Å unit cell *a*-axis, which is the approximate sheet stacking direction and the measured interlayer spacing, due to interdigitation of the tosyl groups of adjacent sheets.

**Crystal Habit/Molecular Sheet Alignment and Single Sheet Production.** In order to identify the method and compound most suited to produce single molecular sheets, we initially established the relationship between bulk crystal habit and the internal molecular orientation. From face-indexing of single crystals of the compounds, it was noted that the layers generally lie in the plane of the largest crystal face (see the Supporting Information for a note on 1). For 2 the principal face of the crystal was  $(01\overline{1})$ , while in 3 it was (100). Figure 8 shows the superposition of the molecular structure in relation to the individual crystal habit for 2 and 3. In the case of 3 this



**Figure 8.** Superposition of the crystal habit and the relationship of the internal molecular structure for (upper) **2** showing largest crystal face as  $(01\overline{1})$  with the corrugated sheet lying in this plane. (lower) Hexagonal crystal habit of **3** with (100) face as the large face as confirmed by AFM.



Figure 9. AFM height images (a and b) of the (100) face of a crystal of 3 and (c) corresponding line section showing the height of steps between adjacent terraces in 1(b).

corresponds exactly to the crystallographic (011) plane and stacking of sheets is then along the crystallographic [100] direction, given the  $P2_1/c$  space group. The observed relationship between crystal habit and the molecular orientation can be rationalized from the view that the stronger, Ag–N, bond formation drives crystal growth in the crystallographic (011) plane while growth in the crystallographic [100] direction is instead extended by weaker van der Waals interactions of tosylate anions. Similar arguments for crystal growth can be made for 2.

Due to issues of size and quality, as well as the smaller extent to which individual layers interdigitate, crystals of **3** were selected for further study and imaged by AFM. Scanning the dominant (100) face revealed the expected step-terrace features, with large, smooth,  $\mu$ m<sup>2</sup> terrace regions (Figure 9). The step height was persistently 1.1 nm corresponding to the intersheet separations along the crystallographic [100] direction length, viz. 11.45 Å (see Figure 7).

Despite the optimal alignment of the sheets to the crystal shape, little success was achieved with mechanical, adhesive tape, exfoliation as a means for producing flakes of single molecular sheets. However, samples of single molecular sheets were prepared by solvent-based exfoliation.<sup>16</sup> This procedure

involved sonication in toluene for several minutes. Initial indication that the procedure was successful was obtained by observing the Tyndall effect,<sup>13</sup> confirming dispersion in solvent. Powder XRD analysis further established that the exfoliation occurs with highly preferred orientation corresponding to the (100) sheet in the crystal structure of **3** with peaks corresponding to (100), (200), (300), and (400) planes in the diffraction pattern observed (Figure 10).

AFM of the reaction mixture after deposition on SiO<sub>2</sub> substrates revealed flakes ranging in size up to ~30  $\mu$ m<sup>2</sup> (Figure 11). Analysis of individual flakes shows them to very closely match the expected height of 1.4 nm for single tosylate-capped molecular sheets. The difference between the heights measured for these single sheets and the step heights on the (100) crystal face is informative. As illustrated in Figure 7, the larger of these two distances correspond to the thickness of an individual sheet with tosylate anions binding above/below the sheet plane. In the crystal, packing of these sheets involves interdigitation of the tosylate anions on adjacent sheets which has the effect of reducing the step height by ~3 Å. This AFM data indicates that after exfoliation the Ag(I)–L1 framework deposits as electrically neutral sheets with the "weak" tosylate anions bound.



Figure 10. Powder X-ray diffraction data for 3: (a) predicted bulk; (b) experimental bulk; (c) predicted pattern for a preferred 100 orientation with a March–Dollase parameter<sup>56</sup> of 0.25; (d) experimental data for exfoliated flakes.

#### CONCLUSION

In summary, we have prepared new examples of 2D coordination framework materials based on Ag-N bond formation with the poly-monodentate ligand L1. We have demonstrated that large area flakes of single molecular sheets can be obtained using a solvent-exfoliation approach despite the relative lability of the Ag-N bond. The heights measured by AFM indicate the retention of tosylate anions as part of the molecular sheet structure with deposition occurring as neutral layers onto oxide substrate. We believe these results are important in demonstrating the suitability of Ag-based coordination framework compounds as precursors for singlemolecular layer material applications, and our efforts in this area are ongoing.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b01365.

X-ray crystallographic information (CIF)

FTIR, ESI-MS, summary crystallographic data, and optical and AFM images (PDF)

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#### Notes

The authors declare no competing financial interest.

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Figure 11. AFM topography images of single layer sheets of 3 deposited on silicon substrates. Layers were deposited from the supernatant after sonicating the crystals in toluene for (a and e) 1 and (c) 2 min. The AFM image (a) shows that this procedure can produce large single layer sheets with size up to ~6.5 × ~4.5  $\mu$ m. The corresponding line sections (b and d) show the height of a single layer sheet is ~1.4 nm.

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