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Six-Coordinated Cd(II) Centers as Four- or Six-Connected Nodes in Coordination Polymer Networks Containing Bis(4-pyridyl)amine

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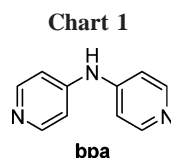
ABSTRACT: The networks for **2** and **3** were 4-fold interpenetrated and isotopological. The reaction of CdSO₄ with **bpaH**⁺ led to the formation of a two-dimensional (2D) hydrogen-bonded net (**4**). Complex **4** consisted of discrete six-coordinate mononuclear units linked into a 2D network by a number of different hydrogen-bonding interactions. The topological analysis of this network showed it to be reminiscent of a 2D diagonal section of an α -polonium network.

Introduction

Much of the early work carried out on coordination polymers was focused on the use of linear ligands with few degrees of freedom, such as 4,4'-bipyridine and related compounds.¹ The aim of this was to attempt to minimize the competing factors working to produce the final polymer. More recently, ligands with a greater number of degrees of freedom have been used,² including some that are very flexible indeed.³ However, flexibility, while offering advantages such as access to a greater range of structural motifs and an increased ability to form additional supramolecular interactions, has the downside of decreasing the predictability of the resulting architectures.⁴ Alternative methods for increasing the supramolecular possibilities available while maintaining a reasonable degree of predictability might include extending ligands such as 4,4'-bipyridine, incorporating an inflexible bend, or incorporating further functional groups into these ligands.⁵ One such ligand with an inflexible bend achieved by the presence of an amine group is bis(4-pyridyl)amine (**bpa**) (Chart 1). As well as the hydrogen-bonding synthon introduced by the presence of the amine, in the solid state **bpa** contains a chiral axis and can behave as a two-bladed molecular propeller.⁶

One of the challenges currently being addressed in the crystal engineering of coordination polymers is that of controlling the connectivity of the overall network. This can be achieved either by the use of metal nodes with different coordination preferences⁷ or by ligands with sufficient connectivity to act as multiple-connected nodes rather than just simple linkers.⁸ The difficulties in this area can be exemplified by the fact that although pseudo-octahedral coordination geometries are common among transition metal complexes relatively few coordination polymers display true six-connected nodes based on the metal (*vide infra*). In part, this relates to the steric environment about the metal ion and the electronic makeup of that ion together with the nature of the linking ligand and the presence of auxiliary ligands such as anion or solvent.

Previous syntheses of supramolecular systems involving **bpa** have been primarily concerned with the hydrothermal synthesis of molybdenum and vanadium oxide materials augmented by



the incorporation of **bpa** or protonated **bpaH**⁺ and additional metal cations.⁹ In many of these materials, the metal oxide anions formed networks rather than acted as discrete counterions, and all of these systems were prepared hydrothermally. In contrast to this, we have carried out non-hydrothermal preparations of complexes of **bpa** using a variety of common metal salts. Reactions with Ag(I) salts gave a series of one-dimensional (1D) coordination polymers,¹⁰ while reaction with both Cu(I) and Cu(II) salts gave two-dimensional (2D) nets.¹¹ It was also found that the monoprotonated **bpaH**⁺ could be produced under non-hydrothermal conditions and resulted in the formation of a neutral discrete complex that formed hydrogen-bonded networks.¹¹ Recently, a 1D zigzag polymer [Zn(S₂P(OiPr)₂)₂-(**bpa**)_{0.5}]_∞ has also been prepared by conventional means from a zinc(II) dithiophosphate complex and **bpa**.¹² This polymer could be extended to a 2D network by hydrogen bonding.

We now report the reaction of **bpa** with Cd(II) salts to form 3D coordination-polymeric networks. With SCN[−] pseudo-octahedral Cd(II) ions were able to act as six-connected nodes, whereas with SO₄^{2−} and NO₃[−] the pseudo-octahedral Cd(II) ions acted as four-connected pseudo-pentagonal nodes. This resulted in the formation of an α -polonium net and adamantoid nets, respectively. Because of the 3D nature of these architectures, the hydrogen-bonding motifs did not play as overtly significant a role as they had in the previously prepared complexes.^{10,11} In an attempt to increase the role played by hydrogen bonding, **bpa** was monoprotonated and reacted with CdSO₄. This resulted in the formation of a discrete neutral complex. As expected, hydrogen bonding played a significant role in the network structure formed by this complex. Our hydrogen-bonded system differs subtly from previously designed systems using bipyridinium or related cations and metal anions in that the cation is directly bound to the metal.¹³

Experimental Section

General. The ligand bis(4-pyridyl)amine was prepared by the literature method.^{9c} IR spectra were measured with a Perkin-Elmer

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Table 1. Crystallographic Data for Complexes

	1·1/5iPrOH	2	3·3H₂O	4·2MeCN
formula	C _{12.6} H _{10.6} CdN ₅ O _{0.2} S ₂	C ₄₀ H ₄₀ CdN ₁₆ O ₁₄	C ₂₀ H ₂₆ CdN ₆ O ₈ S	C ₂₄ H ₃₀ CdN ₈ O ₁₀ S ₂
<i>M</i>	411.78	1193.68	622.93	767.10
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
space group	<i>C2/c</i> (No. 15)	<i>Cc</i> (No. 9)	<i>Pbca</i> (No. 61)	<i>C2/m</i> (No. 12)
<i>a</i> /Å	21.9952(10)	24.0569(12)	17.268(5)	23.4891(16)
<i>b</i> /Å	10.1725(5)	16.0840(8)	15.465(5)	6.9729(5)
<i>c</i> /Å	7.6396(3)	16.5679(6)	17.929(5)	9.0414(6)
β /°	97.608(3)	132.762(2)		105.212(4)
<i>U</i> /Å ³	1694.28(13)	4706.6(4)	4788(2)	1428.98(17)
<i>Z</i>	4	4	8	2
<i>T</i> /K	123(2)	123(2)	113(2)	123(2)
μ /mm ⁻¹	1.535	0.987	1.059	0.985
reflections collected	6531	9089	16487	3141
unique reflections (<i>R</i> _{int})	1920 (0.0418)	9082 (0.0308)	4869 (0.0303)	1753 (0.0551)
<i>R</i> 1 indices [<i>I</i> > 2σ(<i>I</i>)]	0.0332	0.0449	0.0332	0.0565
<i>wR</i> 2 (all data)	0.0997	0.0788	0.0835	0.1479
crystal size/mm	0.35 × 0.32 × 0.24	0.4 × 0.15 × 0.1	0.72 × 0.43 × 0.39	0.32 × 0.09 × 0.09
theta range	3.38 to 27.44	3.01 to 27.48	2.10 to 26.42	3.06 to 27.49
data/restraints/parameters	1920/0/93	9082/2/650	4869/6/372	1753/0/147

Spectrum BX FTIR system, with samples in KBr disks. Elemental microanalyses were carried out at the Campbell Microanalytical Laboratory at the University of Otago. Samples were predried under vacuum to remove volatile solvent residues.

Complexes. {[Cd(**bpa**)(SCN)₂]_∞} (**1**). Cd(SCN)₂ (67 mg, 0.29 mmol) dissolved in H₂O (10 mL) was added to **bpa** (50 mg, 0.29 mmol) dissolved in 2,2,2-trifluoroethanol (TFE) (5 mL) and stirred 1 h. The white solid that precipitated was filtered and dried in vacuo (yield 92 mg, 79%). Despite extended drying times, the microanalytical data of **1** always showed the presence of residual solvent, specifically half an equivalent of TFE. Anal. Calcd. for C₁₂H₉N₅S₂Cd·0.5TFE: C, 34.70; H, 2.35; N, 15.57%. Found: C, 34.51; H, 2.75; N, 15.11%. Selected IR (KBr)/cm⁻¹: 3422s br (**bpa**), 2107 (SCN⁻), 2073m sh (SCN⁻), 2009m (SCN⁻), 534m (**bpa**). Colorless X-ray quality crystals of **1·1/5iPrOH** were grown from the slow diffusion of an *i*PrOH solution of **bpa** layered with ethyl acetate and a H₂O solution of Cd(SCN)₂.

[[Cd(**bpa**)₂(NO₃)(H₂O)](NO₃)_∞] (**2**). Cd(NO₃)₂·4H₂O (45 mg, 0.15 mmol) dissolved in degassed MeCN (5 mL) was added via cannula to **bpa** (50 mg, 0.29 mmol) dissolved in degassed MeCN/H₂O (5 mL, 3:1, v/v) and stirred for 2 days. The white solid that precipitated was filtered and dried in vacuo (yield 38 mg, 45%). Anal. Calcd. for C₂₀H₂₀N₈O₇Cd: C, 40.24; H, 3.38; N, 18.78%. Found: C, 40.26; H, 3.25; N, 18.75%. Selected IR (KBr)/cm⁻¹: 3414m (**bpa**), 1515s (NO₃⁻), 1399m (NO₃⁻), 1354s br (NO₃⁻), 529m br (**bpa**). Colorless X-ray quality crystals of **2** were grown from the slow diffusion of an MeCN/H₂O (3:1, v/v) solution of **bpa** layered with an MeCN/H₂O (3:1, v/v) solution of Cd(NO₃)₂·4H₂O. Crystals were light sensitive but did not appear to decompose.

[[Cd(**bpa**)₂(SO₄)(H₂O)]_∞] (**3**). CdSO₄·8/3H₂O (38 mg, 0.15 mmol) dissolved in H₂O (20 mL) was added to **bpa** (50 mg, 0.29 mmol) dissolved in MeCN/H₂O (20 mL, 3:1, v/v) and stirred for 1 h. The white solid that precipitated was filtered and dried in vacuo (yield 52 mg, 64%). Anal. Calcd. for C₂₀H₂₀N₈O₅SCd·H₂O: C, 40.92; H, 3.78; N, 14.32; S, 5.46%. Found: C, 40.67; H, 3.77; N, 14.33; S, 5.40%. Selected IR (KBr)/cm⁻¹: 3424s br (**bpa**), 1215m br (SO₄⁻), 1096s br (SO₄⁻), 508m br (**bpa**). Colorless X-ray quality crystals of a block morphology (**3·3H₂O**) were grown from the slow diffusion of an MeCN/H₂O (3:1, v/v) solution of **bpa** layered with a H₂O solution of CdSO₄·8/3H₂O.

[Cd(**bpa**)₂(SO₄)₂(H₂O)₂] (**4**). HCl (1 M, 0.29 mL, 0.29 mmol) was added to **bpa** (50 mg, 0.29 mmol) dissolved in MeCN/H₂O (10 mL, 3:1, v/v) and stirred for 1 h. An excess of (NH₄)₂SO₄ (330 mg, 2.9 mmol) dissolved in H₂O (10 mL) was added with vigorous stirring. CdSO₄·8/3H₂O (37 mg, 0.15 mmol) dissolved in H₂O (10 mL) was added, and the resulting solution was stirred for 3 days. The white solid which precipitated was filtered and dried in vacuo (yield 41 mg, 43%). Anal. Calcd. for C₂₀H₂₀N₈O₈S₂Cd·2.5H₂O: C, 34.60; H, 3.63; N, 12.11; S, 9.24%. Found: C, 34.36; H, 3.91; N, 12.53; S, 9.70%. Selected IR (KBr)/cm⁻¹: 3418s br (**bpa**), 3080m (N⁺-H), 1198m br (SO₄⁻), 1095s br (SO₄⁻), 526m (**bpa**). Colorless X-ray quality crystals of a needle morphology (**4·2MeCN**) were grown from the slow diffusion of an MeCN/H₂O (3:1, v/v) solution of **bpa** layered with a H₂O solution of CdSO₄·8/3H₂O.

X-ray Crystallography. Diffraction data were collected either at the University of Strathclyde, Scotland, on a Nonius Kappa-CCD diffractometer (for **1·1/5iPrOH**, **2** and **4·2MeCN**), or at the University of Canterbury, New Zealand, on a Bruker SMART CCD diffractometer (for **3·3H₂O**). Both diffractometers had graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. Intensities were corrected for Lorentz polarization effects,¹⁴ and a multiscan absorption correction was applied to the data collected at the University of Canterbury.¹⁵ The structures were solved by direct methods (SHELXS¹⁶ or SIR-97¹⁷) and refined on *F*² using all data by full-matrix least-squares procedures (SHELXL 97).¹⁸ All calculations were performed using the WinGX interface.¹⁹ Crystallographic data for the four structures are listed in Table 1. In **1·1/5iPrOH**, the highly disordered solvent molecule could not be satisfactorily modeled, so it was removed from the atom list for refinement and the PLATON SQUEEZE²⁰ procedure was applied. The structure of **2** was investigated in the space group *C2/c* and gave an unsatisfactory result. In **3·3H₂O**, the SO₄²⁻ anion was disordered by translation over two sites, one SO₄²⁻ anion having a site occupancy factor of 0.70 and the other a factor of 0.30. The three noncoordinated water molecules were also disordered by translation over five sites, two of them having site occupancy factors of 0.80, two of 0.50, and one of 0.40. Because of this disorder, these H₂O molecules were only refined with isotropic thermal parameters. In **4·2MeCN**, a MeCN solvent molecule was disordered by reflection, the N and adjacent C atoms occupying the same sites in the two disordered forms. As a result, these two atoms were only refined with isotropic thermal parameters.

Results and Discussion

Synthesis and Structure of {[Cd(bpa**)(SCN)₂]·1/5*i*PrOH}_∞ (**1·1/5iPrOH**).** The 1:1 molar reaction of Cd(SCN)₂ in H₂O and **bpa** in TFE produced a white solid that was isolated in good yield and gave microanalytical data consistent with a 1:1 metal-to-ligand ratio with half a molecule of TFE solvent. The complex was found to be insoluble in common organic solvents. The IR spectrum showed three features in the SCN⁻ stretching region: a strong peak at 2107 cm⁻¹ with a shoulder of moderate intensity at 2073 cm⁻¹ and another peak of moderate intensity at 2009 cm⁻¹, consistent with the SCN⁻ anion bridging between Cd(II) ions in a linear fashion, and as a result displaying both N- and S-binding.²¹ Also present were peaks indicative of the ligand, at 3422 and 534 cm⁻¹.

X-ray structural analysis revealed that this complex formed a 3D coordination polymer and crystallized in the monoclinic space group *C2/c*. The asymmetric unit consisted of half of a Cd(II) cation, half of a **bpa** ligand, one SCN⁻ anion, and disordered solvent molecules (Figure 1). Since the solvent molecules could not be satisfactorily modeled, they were removed from the atom list for refinement and the PLATON SQUEEZE²⁰ procedure was applied. The residual electron

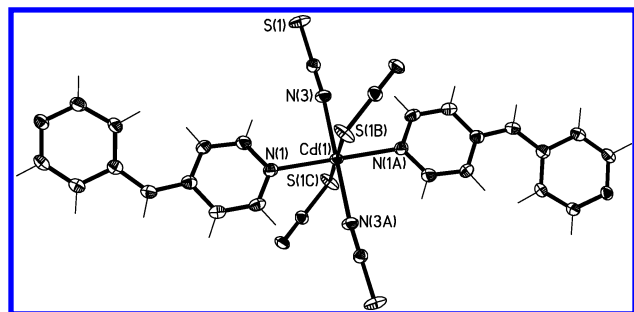


Figure 1. A view of the coordination environment of the Cd(II) ions in **1** (crystallographic numbering) with the thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Cd(1)–N(3) 2.328(2), Cd(1)–N(1) 2.313(2), Cd(1)–S(1B) 2.7648(7); N(1A)–Cd(1)–N(3) 90.30(8), N(1)–Cd(1)–N(3) 89.70(8), N(1A)–Cd(1)–S(1B) 91.49(6), N(1)–Cd(1)–S(1B) 88.51(6), N(3)–Cd(1)–S(1B) 90.02(6), N(3A)–Cd(1)–S(1B) 89.98(6) (symmetry codes: A $-x + 1/2, -y + 1/2, -z$, B $x, -y, z - 1/2$, C $-x + 1/2, y + 1/2, -z + 1/2$).

density in the asymmetric unit was assigned to one-tenth of a molecule of *i*PrOH solvent. Despite the small amount of electron density removed using SQUEEZE, *i*PrOH was considered a better assignment for this electron density than H₂O, as during early attempts to model the solvent short sections of apparent C-chains had been found.

The pyridine rings of the **bpa** ligand were somewhat twisted, at an angle of 30.7° with respect to each other. The C–N–C angle across the amine was found to be 130.4(3)°. Each ligand was bound to two symmetry-related, six-coordinate Cd(II) ions via the N_{py} donors. The Cd(II) ions in turn coordinated to one further **bpa** ligand and four SCN[−] ligands, two via the N donor, and two via the S. This led to a pseudo-octahedral coordination environment for the Cd(II) ions (Figure 1). All four of the N donors were found to lie in the same equatorial plane of the Cd(II) ion, which itself was on an inversion center. The Cd–N_{py}, Cd–NCS, and Cd–SCN bond distances were found to be close to the middle of the range (2.19–2.55 Å, 2.18–2.62 Å, and 2.56–2.89 Å, respectively) for similar six-coordinate Cd–N_{py}, Cd–N_{SCN}, and Cd–S_{SCN} systems found in a search of the CSD (version 5.26).²²

Both **bpa** ligands and SCN[−] ions were found to bridge between Cd(II) ions. The **bpa** ligands were able to link Cd(II) ions to form linear chains that propagated along the [1 0 1] diagonal axis (Figure 2). As the Cd(II) ion was located on an inversion center, adjacent **bpa** ligands were of different enantiomers, which led to an achiral structure. The SCN[−] anions in turn linked the Cd(II) centers to form 2D Cd(SCN)₂ sheets in the (1 0 0) plane (Figure 2). These sheets were linked together by the **bpa** ligands, leading to a three-dimensional (3D) structure.

The resulting 3D coordination polymer was seen to be moderately porous, with a set of pores formed along the crystallographic *c*-axis (Figure 3). These pores were approximately rectangular and had dimensions of 9 × 6 Å. The combined volume of these pores and other small pores along different axes was found to be 22.0% of the unit cell volume, calculated using PLATON from the SQUEEZED data.²⁰ Early attempts at modeling the disordered solvent molecules had shown that solvent was residing in the pores and occupying most of the residual volume. The small amount of electron density able to be removed using SQUEEZE and the significant disorder of the solvent molecules it represented may have been indicative of partial loss of solvent by the crystals.

Syntheses and Structures of {[Cd(bpa)₂(NO₃)(H₂O)]·

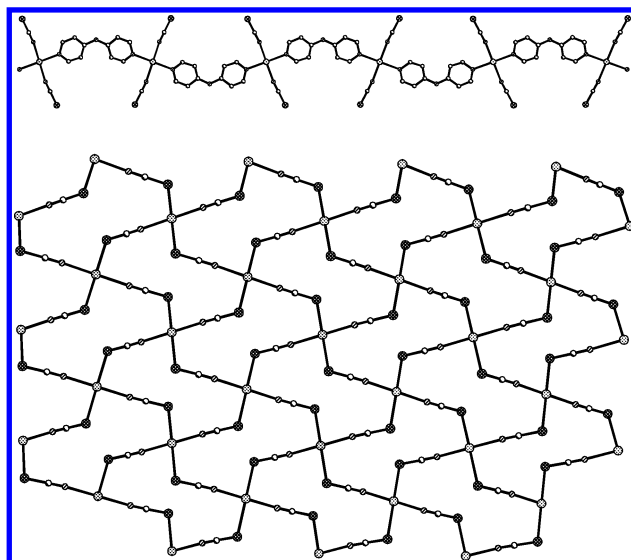


Figure 2. Views of polymeric motifs in **1**. Hydrogen atoms are omitted for clarity. (Top) view of a one-dimensional Cd–**bpa**–Cd chain running along the crystallographic [1 0 1] diagonal axis. (Bottom) view of a two-dimensional Cd(SCN)₂ sheet lying in the (1 0 0) plane.

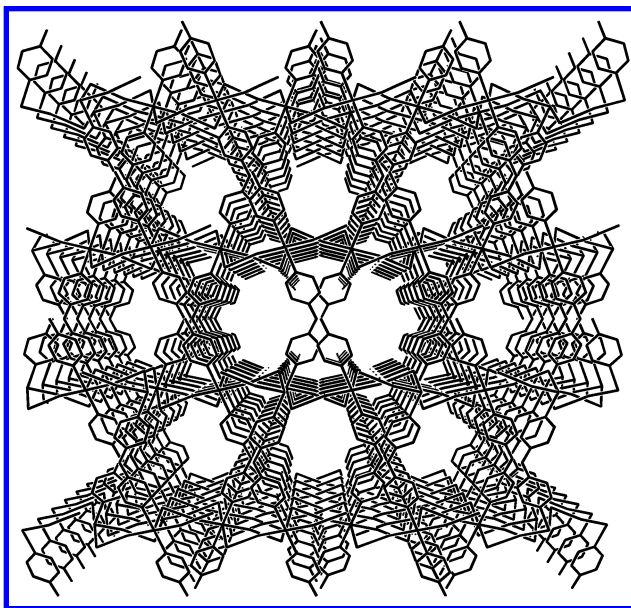


Figure 3. View down the crystallographic *c*-axis of the three-dimensional network formed by **1** showing the pores formed. Two-dimensional Cd(SCN)₂ sheets can be seen (horizontally) linked together by **bpa** ligands to form the three-dimensional network.

(NO₃)₃ (2) and {[Cd(bpa)₂(SO₄)(H₂O)]·3H₂O} (3·3H₂O). The 1:1 molar reactions of Cd(NO₃)₂·4H₂O and CdSO₄·8/3H₂O with **bpa** produced white solids in moderate yields, which gave microanalytical data consistent with 1:2 metal-to-ligand ratios. Despite careful workup of the reaction solids and filtrates, the 1:1 products could not be isolated. Both of these complexes were obtained in better yield from the 1:2 molar reaction of Cd(NO₃)₂·4H₂O and CdSO₄·8/3H₂O with **bpa**. The complexes were found to be insoluble in common organic solvents. The IR spectrum of **2** showed three features in the NO₃[−] stretching region: a strong peak at 1515 cm^{−1}, a peak of moderate intensity at 1399 cm^{−1}, and a strong and broad band at 1354 cm^{−1}, consistent with the NO₃[−] anion adopting more than one binding mode.²¹ Also present were peaks indicative of the ligand, at 3414 and 529 cm^{−1}. The IR spectrum of **3** showed two features in the SO₄^{2−} stretching region: a broad peak of moderate

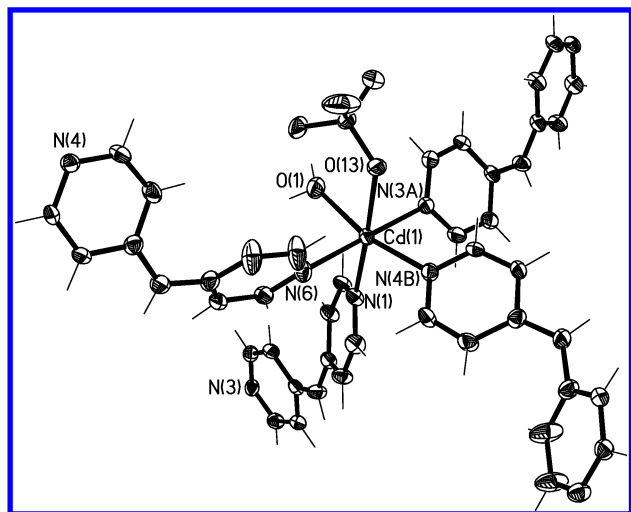


Figure 4. A view of the coordination environment of the Cd(II) ions in **3·3H₂O** (crystallographic numbering) with the thermal ellipsoids drawn at the 50% probability level. Noncoordinated water molecules and one of the disordered forms of the SO₄²⁻ anion are omitted for clarity. Selected bond lengths (Å) and angles (°): Cd(1)–N(1) 2.352(3), Cd(1)–N(3A) 2.341(3), Cd(1)–N(4B) 2.322(3), Cd(1)–N(6) 2.343(3), Cd(1)–O(1) 2.355(3), Cd(1)–O(13) 2.291(11); O(13)–Cd(1)–N(4B) 86.2(3), O(13)–Cd(1)–N(3A) 86.8(2), N(4B)–Cd(1)–N(3A) 87.62(10), O(13)–Cd(1)–N(6) 95.0(2), N(4B)–Cd(1)–N(6) 93.40(11), N(3A)–Cd(1)–N(6) 178.05(11), O(13)–Cd(1)–N(1) 172.0(3), N(4B)–Cd(1)–N(1) 100.23(11), N(3A)–Cd(1)–N(1) 88.80(11), N(6)–Cd(1)–N(1) 89.38(11), O(13)–Cd(1)–O(1) 84.3(3), N(4B)–Cd(1)–O(1) 167.64(11), N(3A)–Cd(1)–O(1) 84.00(10), N(6)–Cd(1)–O(1) 95.24(11), N(1)–Cd(1)–O(1) 88.70(12) (symmetry codes: A *x*, *−y* + 1/2, *z* + 1/2, B *x* + 1/2, *−y* + 1/2, *−z*).

intensity at 1215 cm^{−1} and a strong and broad peak at 1096 cm^{−1}, consistent with the SO₄²⁻ anion coordinating to the Cd(II) ion in a monodentate fashion.²¹ Also present were peaks indicative of the ligand, at 3424 and 508 cm^{−1}. For **3**, colorless X-ray quality crystals of block and needle morphologies were able to be grown. The crystals of a block morphology were found to be {[Cd(**bpa**)₂(SO₄)(H₂O)]·3(H₂O)}_∞ (**3·3H₂O**), while those of a needle morphology were found to be [Cd(**bpaH**)₂(SO₄)₂(H₂O)₂]·2MeCN (**4·2MeCN**).

X-ray structural analyses revealed that **2** and **3·3H₂O** were isotopological, 4-fold interpenetrated, 3D pseudo-adamantoid coordination polymers. Although the complexes were isotopological, they were found to belong to different space groups. Complex **2** crystallized in the monoclinic space group *Cc*, whereas **3·3H₂O** crystallized in the orthorhombic space group *Pbca*. As a result of the difference in space groups, the asymmetric units of the complexes were seen to be different. In **2**, the asymmetric unit consisted of two Cd(II) cations, four complete **bpa** ligands, four NO₃[−] anions, two of which were coordinated, and two molecules of H₂O solvent. In **3·3H₂O**, however, the asymmetric unit consisted of one Cd(II) cation, two complete **bpa** ligands, one SO₄²⁻ anion, and four molecules of H₂O solvent, one that was coordinated and three that were not (Figure 4). The refined Flack *x*-parameter²³ [0.55(3)] of **2** revealed that racemic twinning had occurred in this crystal.

In **2**, the two Cd(II) ions had identical pseudo-octahedral coordination environments made of four pyridine N donors from four different **bpa** ligands, one O donor from coordinated H₂O and one O donor from a monodentate coordinated NO₃[−] anion. The other NO₃[−] anions were not coordinated to a Cd(II) ion. The coordinated NO₃[−] anions were clearly bound in a monodentate fashion, as the Cd(1)···O(12) distance of 3.7293(2) Å and the Cd(2)···O(22) distance of 3.7038(2) Å were both longer

than the sum, 3.10 Å, of the van der Waals radii.²⁴ In **3·3H₂O** the coordination sphere of the Cd(II) cation was almost the same as in **2**, with coordination of four pyridine N donors, one H₂O molecule, and a monodentate SO₄²⁻ anion (Figure 4). The coordination mode of the SO₄²⁻ anions was unambiguously established as the positioning of the closest noncoordinating SO₄²⁻ O atom relative to the Cd(II) cation showed a longer Cd···O distance [Cd(1)···O(11) = 3.589(4) Å] than the sum (3.10 Å) of the van der Waals radii.²⁴ Both structures showed anion-binding or interaction modes consistent with the interpretation of the IR spectra of the complexes. In both complexes, those ligands other than **bpa** were found to coordinate with a cis relationship to each other.

The pyridine rings of the **bpa** ligands of both complexes were somewhat twisted with respect to each other, having angles of 20.5°, 30.0°, 41.9°, and 44.9° for **2** and 29.1° and 46.3° for **3·3H₂O**. The C–N–C angles across the amine were found to be 126.2(5)°, 126.3(5)°, 129.1(5)°, and 131.2(5)° for **2** and 126.4(3)° and 131.2(3)° for **3·3H₂O**. All Cd–N_{py}, Cd–OH₂, and Cd–ONO₂ bond distances were found to be close to the middle of the range (2.19–2.55 Å, 2.21–2.43 Å, and 2.25–2.60 Å, respectively) for similar six-coordinate Cd–N_{py}, Cd–OH₂, and monodentate Cd–ONO₂ systems found in a search of the CSD.²² In **3·3H₂O**, the Cd–N_{py} and Cd–OH₂ bond distances were again found to be close to the middle of the range. The Cd–OSO₃ bond distances varied for the two disordered SO₄²⁻ anions, with one Cd–OSO₃ bond in the middle of the range (2.19–2.45 Å) and the other at the maximum end of the range found in a search of the CSD.

Both complexes formed 3D, 4-fold interpenetrated adamantoid coordination polymers (Figure 5). The anion and H₂O ligands adopted a cis coordination geometry, and, as a consequence of this, the octahedral Cd(II) ions were able to behave as pseudo-tetrahedral connectors. The individual adamantoid cages that made up the overall coordination polymer were found to be somewhat distorted from their idealized geometry. This was most likely due to the **bpa** donor atoms being coordinated to a distorted octahedral Cd(II) site, rather than a tetrahedral metal center, and also to the use of angular **bpa** ligands, instead of rigid linear ligands. In **2**, the two Cd(II) ions were found to be coordinated by two **bpa** ligands of one enantiomer and one of the other, with the two Cd(II) centers being bridged by another **bpa**. This would have been expected to lead to the structure as a whole being chiral; however, when the interpenetrated coordination polymers were examined there were found to be two symmetry-related pairs of nets, leading to an overall achiral structure. In **3·3H₂O**, the Cd(II) was coordinated by three **bpa** of one enantiomer and one of the other, which would again have been expected to lead to an overall chiral structure. However, adjacent Cd(II) ions were found to be coordinated by **bpa** ligands of opposite stereochemistry, hence again giving an achiral structure.

There were a large number of interactions that helped to hold the noncoordinated NO₃[−] anions in **2** in place in the framework and also to hold the interpenetrated frameworks of both structures together. The most important of these were networks of hydrogen bonds. In **2**, hydrogen bonds formed between all four independent amine N–H and the O atoms of both coordinated and noncoordinated NO₃[−] anions. The O···H–N distances were in the range 1.958(5)–2.202(4) Å, with corresponding O···N separations of 2.802(8)–3.014(6) Å and angles across O···H–N in the range 150.5(5)–161.1(3)°. Hydrogen-bonding interactions also occurred between the H atoms of the coordinated H₂O molecules and both of the noncoordinated

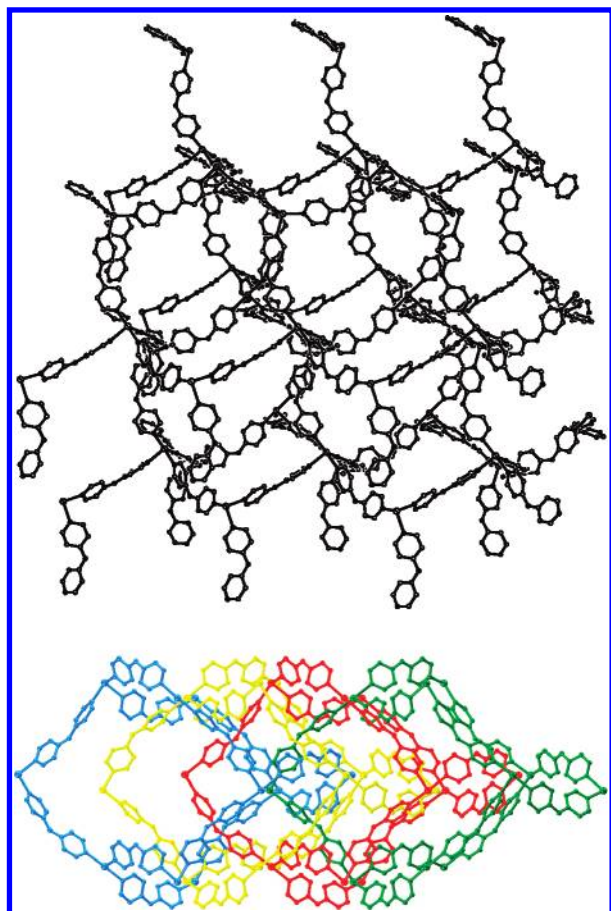


Figure 5. Views of the three-dimensional network structures formed by **2** and **3·3H₂O** with hydrogen atoms, anions, and water molecules omitted for clarity. (Top) view of one of the independent adamantoid coordination polymers of **3·3H₂O**. (Bottom) view of sections of the four independent interpenetrating arrays of **2**.

NO_3^- anions, with one O—H found to be interacting with two NO_3^- O atoms in one case and one in the other. The $\text{O}\cdots\text{H}-\text{O}$ distances were 1.895(3) and 2.315(5) Å, with corresponding $\text{O}\cdots\text{O}$ separations of 2.682(6) and 2.979(10) Å and angles across $\text{O}\cdots\text{H}-\text{O}$ varying between 141.2(3)° and 178.5(3)°. In addition, both coordinated H_2O molecules were able to form intramolecular hydrogen bonds to the O atom of the NO_3^- anions coordinated to the same Cd(II) ion. The $\text{O}\cdots\text{H}-\text{O}$ distances were 2.077(5) and 2.187(6) Å, with $\text{O}\cdots\text{O}$ separations of 2.754(6) and 2.764(8) Å and $\text{O}\cdots\text{H}-\text{O}$ angles of 125.8(4)° and 136.6(3)°. In **3·3H₂O**, two sets of hydrogen bonds also formed between the amine N—H and the O atoms of SO_4^{2-} anions of adjacent interpenetrating polymer chains. The $\text{O}\cdots\text{H}-\text{N}$ distances were in the range 1.865(14)–2.473(15) Å, with corresponding $\text{O}\cdots\text{N}$ separations of 2.721(15)–3.257(16) Å. The coordinated H_2O molecule was also able to form hydrogen bonds involving both its hydrogen atoms. The first was to an O atom of a SO_4^{2-} anion of another polymer chain, with an $\text{O}\cdots\text{H}-\text{O}$ distance of 1.92(7) Å, corresponding $\text{O}\cdots\text{O}$ separation of 2.719(6) Å, and $\text{O}\cdots\text{H}-\text{O}$ angle of 159(6)°. The second was an intramolecular hydrogen bond to an O atom of the SO_4^{2-} anion coordinated to the same Cd(II) ion. The $\text{O}\cdots\text{H}-\text{O}$ distance was 1.88(4) Å, with an $\text{O}\cdots\text{O}$ separation of 2.679(6) Å, and an $\text{O}\cdots\text{H}-\text{O}$ angle of 159(3)°.

The noncoordinated NO_3^- anions in **2** were further held in place in the overall framework by a number of interactions with aryl H atoms. The $\text{O}_2\text{N}-\text{O}\cdots\text{H}-\text{C}$ separations were in the range 2.412(4)–2.858(8) Å, with corresponding $\text{O}\cdots\text{C}$ distances of

2.930(15)–3.275(13) Å. Since the noncoordinated H_2O molecules in **3·3H₂O** were disordered hydrogen-bonding interactions were not considered.

Despite the interpenetration of these frameworks, interactions involving π -systems were not a major factor in holding the network structures together. In **2** no $\pi-\pi$ interactions occurred, the shortest centroid-to-centroid distance being 4.085(4) Å;²⁵ in **3·3H₂O** however a $\pi-\pi$ interaction was found between pyridine rings of two of the interpenetrated frameworks. The centroid-to-centroid distance was 3.852(2) Å, and the two pyridine rings were close to parallel, with an angle between the ring planes of 21°. No other π -interactions occurred in this complex.

In **2**, a further interaction involving π -systems was identified as a $\text{O}_2\text{N}-\text{O}\cdots\pi$ interaction between a noncoordinated NO_3^- anion and a pyridine ring of one of the **bpa** ligands, with an $\text{O}\cdots$ centroid distance of 3.560(6) Å. Interactions between electron-poor π -systems and anions have only been recognized recently,²⁶ and in most of the cases investigations have involved aromatic systems that have multiple electron-withdrawing substituents. The $\text{O}_2\text{N}-\text{O}\cdots$ centroid distance here was longer than that seen for the $\text{O}_3\text{Cl}-\text{O}\cdots\pi$ interaction in a previously reported complex of AgClO_4 and **bpa**,¹⁰ although it was slightly shorter than the distance reported in the only other $\text{O}_2\text{N}-\text{O}\cdots$ pyridine interaction (3.58 Å).^{26c}

When the array of **2** was viewed along the *c*-axis, small ($<5 \times 5$ Å) rectangular pores were visible. There were also smaller and less regular pores along the *b*-axis. However, the array of **3·3H₂O** did not show any regular pores, but did show small voids in the complex. The combined volumes of the pores in **2** and small voids in **3·3H₂O** were found to be 11.1 and 11.9% of the unit cell volumes, respectively.²⁰ When the structures were considered as a whole, these voids were found to be filled with anions in the case of **2**, and disordered H_2O molecules in the case of **3·3H₂O**. This led to **3·3H₂O** having no residual solvent accessible volume, and **2** having 1.1% of unit cell volume vacant.

Synthesis and Structure of $[\text{Cd}(\text{bpaH})_2(\text{SO}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{MeCN}$ (4·2MeCN**).** After crystals of **4·2MeCN** were identified, the complex was synthesized in bulk. The **bpa** ligand was deliberately monoprotonated by the addition of one equivalent of HCl, after which an excess of SO_4^{2-} anion was added in the form of $(\text{NH}_4)_2\text{SO}_4$. Following this, $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ was added in a 1:2 metal-to-ligand ratio. The white solid that precipitated was isolated in moderate yield and gave microanalytical data consistent with a formation of the complex. The complex was found to be insoluble in common organic solvents. The IR spectrum showed two features in the SO_4^{2-} stretching region: a broad peak of moderate intensity at 1198 cm^{-1} and a strong and broad peak at 1096 cm^{-1} , consistent with the SO_4^{2-} anion coordinating to the Cd(II) ion in a monodentate fashion.²¹ Also present were peaks indicative of the ligand, at 3424 and 508 cm^{-1} . A previously unseen strong and broad peak was also present at 3080 cm^{-1} , indicative of the pyridinium N—H.²⁷

X-ray analysis revealed that this structure was a discrete, mononuclear complex, crystallized in the monoclinic space group $C2/m$. The asymmetric unit consisted of one-quarter of a Cd(II) cation, half a monoprotonated **bpa** ligand (**bpaH⁺**), half a SO_4^- anion, half a molecule of H_2O solvent, and half a molecule of MeCN solvent (Figure 6). The SO_4^{2-} anion and the H_2O molecule were coordinated to the Cd(II) center and were disordered due to the Cd(II) residing on a $2/m$ site. The MeCN solvent molecule was also disordered by reflection, the N and adjacent C atoms occupying the same sites in the two

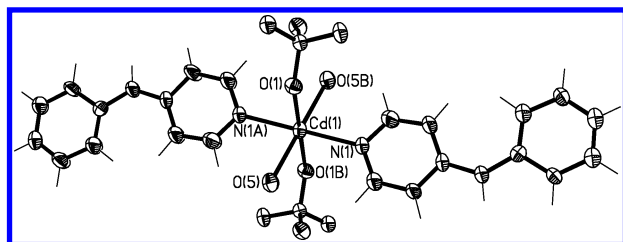


Figure 6. A view of the coordination environment of the Cd(II) ions in **4·2MeCN** (crystallographic numbering) with the thermal ellipsoids drawn at the 50% probability level. The noncoordinated solvent molecules and one of the symmetry-disordered forms of the coordinated H₂O molecules and SO₄²⁻ anions are omitted for clarity. Selected bond lengths (Å) and angles (°): Cd(1)–N(1) 2.297(5), Cd(1)–O(1) 2.318(7), Cd(1)–O(5) 2.338(7); N(1)–Cd(1)–O(1) 89.96(18), N(1)–Cd(1)–O(1B) 90.04(18), N(1A)–Cd(1)–O(5) 86.4(2), N(1A)–Cd(1)–O(5B) 93.6(2), O(1B)–Cd(1)–O(5) 93.5(2), O(1)–Cd(1)–O(5) 86.4(2), (symmetry codes: A $-x, y, -z$, B $-x, -y, -z$).

disordered forms. Each ligand was monoprotonated at one pyridine N atom, and also bonded to one, six-coordinate Cd(II) ion by coordination of the other pyridine N donor. The Cd(II) cation was in turn coordinated to another symmetry-related **bpaH**⁺ ligand. The Cd(II) ion had a slightly distorted octahedral coordination sphere, made up of two pyridine N donors from the two symmetry-related **bpaH**⁺ ligands, two O donors from two symmetry-related coordinated H₂O molecules, and two O donors from two symmetry-related, monodentate coordinated, SO₄²⁻ anions (Figure 6). The way in which the SO₄²⁻ anions were bound was unambiguously determined as the closest noncoordinating SO₄²⁻ O atom relative to the Cd(II) cation showed a longer Cd···O distance [Cd(1)···O(4) = 3.5863(2) Å] than the sum (3.10 Å) of the van der Waals radii.²⁴ The binding mode observed for the anion was found to be consistent with the interpretation of the IR spectrum of the complex. All Cd–N_{py}, Cd–OH₂, and Cd–OSO₃ bond distances were found to be close to the middle of the range for similar six-coordinate systems (vide supra).²²

The **bpaH**⁺ ligand did not display the chirality in this structure that was seen in all other complexes of **bpa**, as the ligand was strictly planar, lying as it does in a mirror plane (Figure 7). The C–N–C angle across the amine was found to be 132.3(7)°. The four coordinated, but disordered O atoms, two from H₂O and two from SO₄²⁻, and the Cd(II) ion also formed a plane due to the *2/m* site symmetry, which was orthogonal to the plane formed by the two **bpaH**⁺ ligands and the Cd(II) ion. After examining the symmetry-related disorder of the coordinated SO₄²⁻ anions and H₂O solvent molecules, it was assumed that each symmetry-related pair of SO₄²⁻ anions and H₂O solvent molecules would coordinate trans to each other.¹⁰ Similarly, adjacent complexes were assumed to be arranged such that SO₄²⁻ anions were closest to H₂O solvent molecules, rather than other SO₄²⁻ anions.

The individual mononuclear complexes were held together by a number of interactions (Figure 7). The first of these was hydrogen bonds between the disordered H₂O molecules and SO₄²⁻ anions coordinated to the Cd(II) ions. The H atoms on the H₂O molecules could not be located, but the O···O distance was found to be 2.776(7) Å. These hydrogen bonds linked complexes so that they formed 1D metallamacrocyclic polymers propagating along the *b*-axis. A second set of hydrogen bonds existed between the protonated pyridinium of one **bpaH**⁺ ligand and one of the O atoms of the SO₄²⁻ anions. The N–H···O distance was found to be 1.816(5) Å, with a N···O separation of 2.696(9) Å and N–H···O angle of 177.8(5)°. This set of

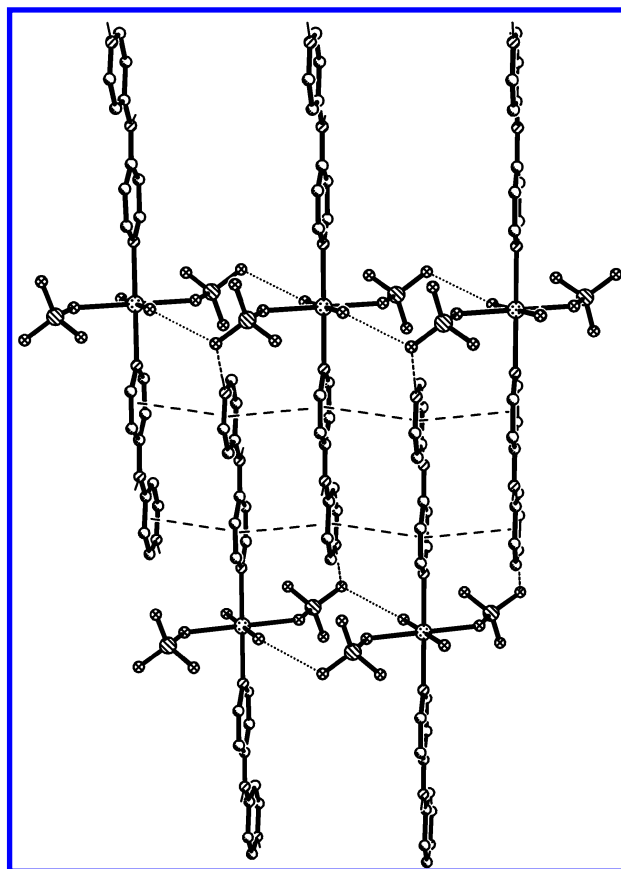


Figure 7. View of the interactions between discrete complexes of **4·2MeCN**, leading to formation of two-dimensional hydrogen-bonded sheets in the (2 0 1) plane. Hydrogen bonds between pyridinium N–H and SO₄²⁻ and π -stacking interactions are shown dashed. Hydrogen bonds between coordinated H₂O and SO₄²⁻ are shown dotted. Hydrogen atoms not involved in hydrogen bonding, disordered solvent molecules and symmetry-disordered forms of coordinated water and SO₄²⁻ anions are omitted for clarity.

hydrogen bonds formed 1D polymers propagating along the [1 0 2] diagonal axis, and the combination of these two sets of hydrogen bonds led to the formation of 2D polymeric sheets in the (2 0 1) plane. Another set of hydrogen bonds, between the amine of the **bpaH**⁺ ligand and the MeCN solvent molecule, helped to hold the MeCN firmly in place in the overall structure. The N–H···N distance was 2.114(7) Å, with a corresponding N···N separation of 2.962(10) Å and N–H···N angle of 161.59(17)°. The first two sets of hydrogen bonds were able to link individual mononuclear complexes together into 2D polymeric sheets.

As well as the hydrogen bonds, a number of other interactions were involved in holding the complexes together (Figure 7). The strongest of these was a π -stacking interaction between both pyridine rings of a **bpaH**⁺ ligand and those adjacent. Because of the hydrogen bonding between pyridinium N–H and SO₄²⁻, adjacent ligands were brought into exact register with each other, with a centroid–centroid distance of 3.5129(6) Å. Also supporting these π -stacking and hydrogen-bonding interactions was a weak C–H···O interaction between one CH of the pyridinium ring and the SO₄²⁻ anion. The C–H···O distance was 2.466(6) Å, with a C···O separation of 3.279(9) Å. Additional C–H···O interactions occurred to help hold the parallel hydrogen-bonded sheets together. In this case, the C–H···O distance was 2.307(6) Å, with a C···O separation of 3.242(11) Å.

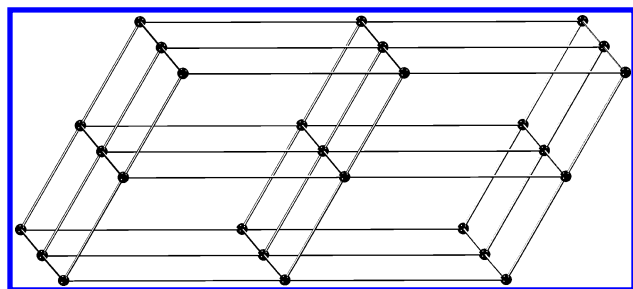


Figure 8. View of the three-dimensional topological net formed by **1** illustrating the somewhat distorted α -polonium topology (Cd nodes – black spheres).

The hydrogen-bonded polymeric sheets packed such that small (6×6 Å) rectangular pores were formed running along the b -axis. The combined solvent-accessible volume of these pores was 10.6% of the unit cell volume, but when the whole structure was considered, they were found to be filled with the MeCN solvent molecules, which led to the structure having no residual solvent-accessible volume.²⁰

Topological Analyses. The topologies of all four complexes were determined using OLEX.²⁸ In all cases, noncoordinated solvent or anions were not considered to contribute to the topological network. For complex **1**, topological analysis was carried out on the array using the SQUEEZED data. Complexes **2** and **3** were determined to be isotopological. For complex **4**, the topology of the 2D sheets formed by hydrogen bonding between mononuclear complex molecules was considered.

The topological network of **1** could be defined as a uninodal, $4^{12}, 6^3$ net, with all nodes based on Cd(II) ions (Figure 8). The nodes were six-connected to adjacent nodes via **bpa** links. This resulted in the nodes having the short topological term $4^{12}, 6^3$, which can be considered as that of the α -polonium network, by Wells' terminology a (4, 6) net.²⁹ There are comparatively few coordination polymers that display true six-connected nodes, although the number of such networks has been steadily increasing. The majority of these are related to the α -polonium net, with only six having an unrelated topology.³⁰ Those related to the α -polonium net can be divided into three major groups. The first contains those that adopt a true α -polonium type structure where all links between nodes are identical³¹ and also includes skewed frameworks that result in rhombohedral cavities,^{10,32} and the distorted α -polonium network where there are two long links and four short between identical nodes.³³ Among the α -polonium type structures also exist a subgroup of complexes based on metal–cyano salts, such as the Prussian Blue-related networks.³⁴ The second, and much smaller, group consists of those structures that adopt a network more akin to the NaCl net,³⁵ which is isotopological with the α -polonium net but consists of two equivalent octahedral nodes. The third group is made up of those networks that may be simplified easily to α -polonium nets but are more correctly described as nets with the boron topology of CaB_6 ,³⁶ which can be described as an α -polonium network with nodes replaced by octahedral clusters of nodes.^{29,37} This topological net has been seen previously for a coordination polymer containing **bpa**.¹⁰ In that structure **bpa** formed 1D helical polymer chains with Ag(I) and formed the α -polonium network by hydrogen bonding to NO_3^- anions. The net formed by the Ag(I) complex showed skewed rhombohedral cavities, while the net formed by **1** showed cavities with a slight skew and one edge almost twice as long as the other two.

The topological networks formed by **2** and **3** could also be defined as uninodal nets, with nodes once again based on Cd-

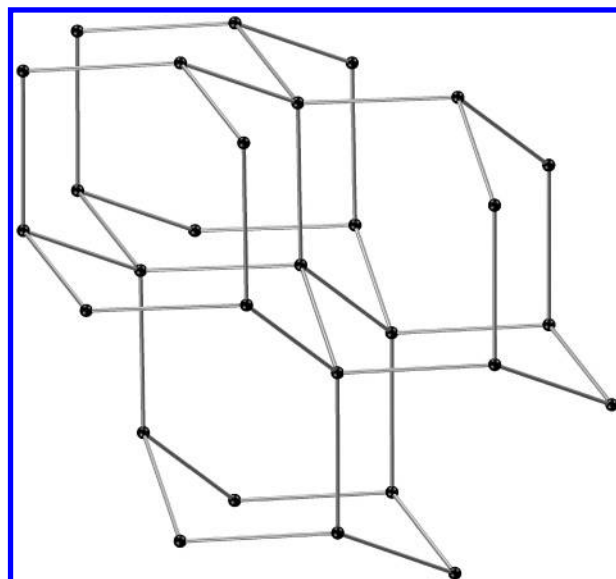


Figure 9. View of one of the topological nets formed by **2** illustrating the slightly distorted adamantoid topology.

(II) ions (Figure 9). The nodes were linked via **bpa** ligands to four other metal nodes, resulting in all nodes having the short topological term of 6^6 . This short topological term is characteristic of both the lonsdaleite and the adamantoid nets, and those nets related to them, and can also be described as a (6, 4) net.²⁹ In the case of **2** and **3**, the resulting network is the diamond net, which has been seen previously in a number of coordination polymers. Early preparations of adamantoid nets were usually based on metal ions that adopted a strictly tetrahedral geometry,³⁸ while more recent work has looked at two other possibilities: either metal clusters that take an overall tetrahedral geometry³⁹ or metal ions with higher coordination numbers than four but that adopt a pseudo-tetrahedral coordination geometry that allows them to act as four-connectors,^{9b,40} in a similar manner to that displayed by **2** and **3**. One previous example of an adamantoid net has been prepared using **bpa** and NiSO_4 .^{9b} This complex is structurally very similar to **2** and **3**· $3\text{H}_2\text{O}$, although it was described as being 2-fold interpenetrated in contrast to the 4-fold interpenetration seen here. We believe the reported analysis for this complex^{9b} is incorrect and that it is in fact 4-fold interpenetrated.

For the topological analysis of **4**, the hydrogen bonds between coordinated H_2O molecules and SO_4^{2-} anions, and SO_4^{2-} anions and pyridinium N–H were considered to be bonding interactions in the topological network.⁴¹ As there were no significant interactions between 2D hydrogen-bonded sheets of the complex, the topology was only considered for those sheets. The resulting topological network comprised two different nodes: one six-connected and based on the Cd(II) and one three-connected and based on one O atom of the SO_4^{2-} anion (Figure 10). The O nodes had links to three Cd nodes: one for the coordinated SO_4^{2-} , one for the $\text{O}=\text{H}\cdots\text{O}$ hydrogen bond to an adjacent coordinated H_2O molecule, and the third for the $\text{N}=\text{H}\cdots\text{O}$ hydrogen bond to an adjacent **bpaH**⁺ ligand. This resulted in the O nodes having a short topological term of 4^3 . The Cd nodes in turn were six-connected with short topological terms of $4^6, 6^6, 8^3$. The 4^3 node has been recognized to lead to discrete cuboid assemblies,²⁹ some of which have been synthesized as supramolecular entities.⁴² The $4^6, 6^6, 8^3$ node has been seen once before, in an isotopological complex involving **bpaH**⁺ and CuSO_4 .¹¹ The complete topological net could also be viewed

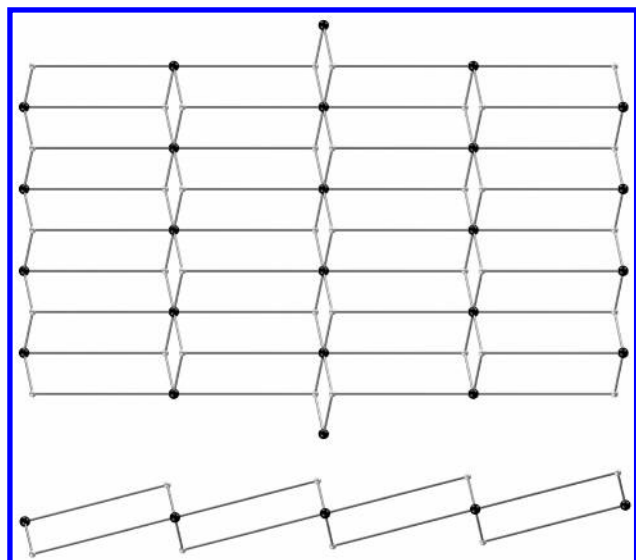


Figure 10. Views of the two-dimensional topological net formed by hydrogen bonding between discrete complexes in **4** illustrating the α -polonium-related topology (O nodes – light gray spheres).

as a 2D section of an α -polonium, $4^{12}6^3$, net, with the three-connected nodes of this network occurring at the points where the “slice” of net was removed (Figure 10).

Conclusion

The complexes **1–4** all showed octahedral coordination geometries which in **1–3** allowed for the bridging of ligands between Cd(II) centers in three dimensions. Complex **1** was the only one of **1–4** that had a 1:1 metal-to-ligand ratio, and it also showed trans coordination of the **bpa** ligands. This particular coordination mode would most likely have resulted in the formation of a 1D polymer except that the SCN^- anions also coordinated to the Cd(II) ions in a bridging manner linking the polymer into three dimensions. The isotopological complexes **2** and **3** had 1:2 metal-to-ligand ratios and both showed one coordinated anion and molecule of H_2O . These auxiliary ligands were bound to the Cd(II) in a cis fashion, which allowed the **bpa** ligands to coordinate in a pseudo-facial manner leading to tetrahedral nodes. Complex **4** had a 1:2 metal-to-ligand ratio and trans coordination of **bpa**. In this complex, the **bpa** ligands had been monoprotonated at one pyridine N, preventing coordination of that N, and thereby blocking the formation of a coordination polymer. This did however provide additional sites for the formation of hydrogen bonds.

The three polymeric Cd(II) complexes **1**, **2**, and **3** formed 3D networks, while the mononuclear complex **4** could be linked by hydrogen-bonding interactions into 2D sheets. The network structure of **1** was based on six-connected Cd(II) nodes linked by bridging **bpa** ligands and SCN^- anions into an α -polonium network. The networks formed by **2** and **3** were isotopological and displayed 4-fold interpenetration. They were based on four-connected pseudo-tetrahedral Cd(II) nodes linked by bridging **bpa** ligands into adamantoid architectures. The structure of **4** was very different as it consisted of discrete complexes linked in two dimensions by hydrogen bonding. The topological networks formed by individual 2D sheets was similar to that of an α -polonium net truncated to two dimensions.

Therefore, subtle preferences in the coordination environment adopted by a metal ion clearly influence the binding of bridging and auxiliary ligands. This has significant consequences for connectivities and as a result the types of arrays that are formed.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of **1–4** and full topological analyses for complexes **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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