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Article

Flexible Ligands and Structural Diversity: Isomerism in $Cd(NO_3)_2$ Coordination Polymers

**David B. Cordes,[†] Andrew S. Bailey,[‡] Paula L. Caradoc-Davies,[†] Duncan H. Gregory,[‡]
Lyall R. Hanton,*,[†] Kitty Lee,[†] and Mark D. Spicer[§]**

*Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand,
School of Chemistry, University of Nottingham, University Park, Nottingham, U.K. NG7 2RD, and
Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street,
Glasgow, Scotland G1 1XL*

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The ligands 1,4-bis(2-pyridylmethylsulfanylmethyl)benzene (**L1**) and 2,5-bis(2-pyridylmethylsulfanylmethyl)pyrazine (**L2**) were treated with $Cd(NO_3)_2 \cdot 4H_2O$ in metal-to-ligand ratios of 1:1 and 2:1, respectively; **L2** was also treated with $CdCl_2 \cdot 2.5H_2O$ in a 2:1 ratio. All products were found to be coordination polymers. The crystal structures of $\{[Cd(\mathbf{L1})(NO_3)_2] \cdot CH_2Cl_2\}_\infty$ (**1a**), $\{[Cd(\mathbf{L1})(NO_3)_2] \cdot {}^4/_3CH_3CN\}_\infty$ (**1b**), $\{[Cd_2(\mathbf{L2})(NO_3)_4] \cdot 2CH_3CN\}_\infty$ (**2**$\cdot 2CH_3CN$), and $\{[Cd_2(\mathbf{L2})Cl_4] \cdot 2CH_2Cl_2\}_\infty$ (**3**$\cdot 2CH_2Cl_2$) were determined. Compounds **1a** and **1b** were found to be conformational supramolecular isomers. The structure of **1b** displayed topological isomerism with two isomeric polymer chains, **1b(1)** and **1b(2)**, in the one crystal forming a single supramolecular array. The structure of **2**$\cdot 2CH_3CN$ showed Cd_2(**L2**) units linked together by nitrates bridging between the Cd(II) centers in a mode previously not seen in Cd(II) compounds. The overall structure of **3**$\cdot 2CH_2Cl_2$ was found to be similar to that of **2**$\cdot 2CH_3CN$ despite the presence of different anions and solvent molecules. Powder X-ray diffraction was used to investigate the nature of bulk preparations of compounds **1**–**3**.

Introduction

The use of conformationally flexible ligands with multiple donor sites to engineer coordination polymer arrays has a number of inherent challenges.[1,2] First, the flexibility of the ligands could lead to polymers with structures that are more difficult to predict and that do not readily fit into a current paradigm.[3] Second, the arrangement of donor atoms in the chelating compartments of polytopic ligands makes it difficult to avoid array structures of low dimensionality.[4,5] Finally, conformational flexibility and different binding modes could enhance the possibility of forming supramolecular isomers.[1,6] However, the propensity toward structural diversity in such systems brings opportunities to probe their conditions of formation and to gain a greater understanding of the factors leading to this structural variety. As an area of research, coordination polymer chemistry has developed rapidly in recent years.[1,7] However, as some of the important principles that underpin this area of research are those of classical coordination chemistry, it is not surprising that the

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* To whom correspondence should be addressed. E-mail: lhanton@alkali.otago.ac.nz.
[†] University of Otago.
[‡] University of Nottingham.
[§] University of Strathclyde.

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various types of isomerism found there are also exemplified in coordination polymer chemistry. These phenomena are expected to have enhanced or extended consequences in a supramolecular array and result in polymorphism and/or supramolecular isomerism.[1,8] Zaworotko and co-workers have examined the occurrence of supramolecular isomerism[1,9] in network solids and, in particular, have investigated a number of isomeric two- and three-dimensional arrays formed with the flexible ligand 1,2-bis(4-pyridyl)ethane.[10] Other workers[6,11] have consolidated supramolecular isomerism as a factor to be considered when designing ligands for supramolecular arrays.

We have been investigating the use of flexible ligands based on aromatic spacers linked to thioether−pyridine arms to build coordination polymer arrays.[4,12,13] Recently we identified a rare example of two isomeric Ag(I)-containing polymer chains in the same crystal.[14] Other workers have reported an additional example of this type of isomerism, which involved $Cd(NO_3)_2$-containing polymer chains.[15] Even more remarkable, three types of coordination polymers, again involving $Cd(NO_3)_2$, have been reported in the same crystal.[16] This form of topological isomerism has parallels in classical coordination chemistry where complexes of two different stereochemistries are found in the same crystal.[17] We now report an additional, if less extreme, example of the same phenomenon in a $Cd(NO_3)_2$ system. The two different one-dimensional polymer chains, **1b(1)** and **1b(2)**, have essentially the same arrangement, with the difference between them arising from differences in the coordination of the NO_3^- anions to the central Cd(II) ion. This is akin to the commonly encountered property of having two chemically identical but crystallographically distinct species in the same crystal. In addition to this topological isomerism, we found that the flexible ligand **L1** was able to adopt gauche and anti conformations with $Cd(NO_3)_2$ (Chart 1). This led to the formation of two complexes, **1a** and **1b**, containing different solvent molecules, related to each other as conformational supramolecular isomers.

Chart 1

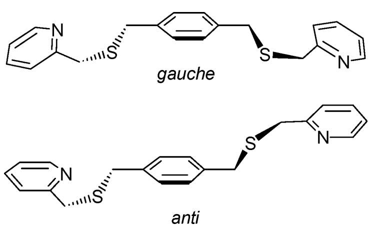
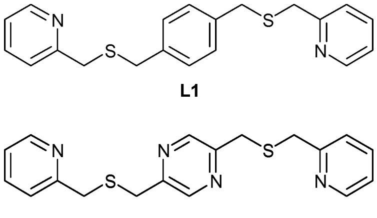


Chart 2



We have also investigated the effect of restricting the flexibility of the ligand system upon coordination to Cd(II). Replacing the benzene central spacer of **L1** with pyrazine (Chart 2) led to facial binding of **L2**, and we isolated the closely related $Cd(NO_3)_2$ and $CdCl_2$ polymer arrays **2**$\cdot 2CH_3CN$ and **3**$\cdot 2CH_2Cl_2$, respectively. In the former structure, the polymer is generated by an unusual NO_3^- dimeric bridging mode previously unknown in Cd(II) complexes. In contrast to the arrays of the less restricted ligand **L1**, the array structures of **2**$\cdot 2CH_3CN$ and **3**$\cdot 2CH_2Cl_2$ do not seem to be significantly affected by the nature of the incorporated solvent.

Experimental Section

General. The ligands **L1**[4] and **L2**[14] were prepared by literature methods. Infrared spectra were measured on a Perkin-Elmer Win-IR Spectrum BX FT-IR System (samples in KBr disks). Powder X-ray diffraction (PXD) data were collected using a Philips XPERT $\theta-2\theta$ diffractometer with Cu Kα radiation in flat-plate Bragg−

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Table 1. Crystallographic Data for Complexes

	1a	**1b**	**2**·2CH$_3$CN	**3**·2CH$_2$C
empirical formula	$C_{21}H_{22}CdCl_2N_4O_6S_2$	$C_{34}H_{36}Cd_{1.5}N_8O_9S_3$	$C_{22}H_{24}Cd_2N_{10}O_{12}S_2$	$C_{20}H_{22}Cd_2Cl_8N_4S_2$
M_w	673.85	965.49	909.43	890.94
crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	9.7818(2)	12.463(5)	8.739(3)	12.505(4)
b/Å	12.0119(2)	12.611(5)	9.603(3)	8.072(2)
c/Å	12.6382(4)	12.999(5)	10.239(3)	15.225(4)
α/deg	102.076(1)	82.141(5)	73.759(4)	
β/deg	91.909(1)	89.839(5)	79.778(4)	100.691(4)
γ/deg	112.308(1)	89.758(5)	77.533(4)	
U/Å^3	1332.95(5)	2024(1)	799.2(4)	1510.1(7)
Z	2	2	1	2
T/K	293(2)	168(2)	158(2)	158(2)
μ/mm^{-1}	1.220	1.011	1.536	2.274
reflections collected	8103	25695	10266	18849
unique reflections (R_{int})	6054 (0.0173)	8107 (0.1025)	3196 (0.0174)	3085 (0.0179)
R1 indices [$I > 2\sigma(I)$]	0.0384	0.0949	0.0185	0.0250
wR2 (all data)	0.0913	0.2666	0.0516	0.0678

Brentano geometry. Diffraction data were collected over a duration of 16 h in the range 5−80° 2θ with a step size of 0.02° 2θ at 298 K. Theoretical powder patterns were calculated with POWDER-CELL 2.0[18] using the single-crystal diffraction data generated for **1a**, **1b**, **2**·2CH$_3$CN, and **3**·2CH$_2$Cl$_2$ as models. Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago. Samples were predried under vacuum to remove volatile solvent residues. Melting points were measured on a Gallenkamp melting-point apparatus.

Complexes. [Cd(L1)(NO$_3$)$_2$]$_\infty$, 1. Cd(NO$_3$)$_2$·4H$_2$O (44 mg, 0.14 mmol) dissolved in MeCN (5 mL) was added to **L1** (50 mg, 0.14 mmol) dissolved in CH$_2$Cl$_2$ (5 mL), and the mixture was allowed to stir for 1 h. The cream-colored solid that precipitated was filtered and dried in vacuo (yield 77 mg, 92%). (Found: C, 40.7; H, 3.3; N, 9.5; S, 10.9%. Calcd for $C_{20}H_{20}N_4O_6S_2Cd$: C, 40.8; H, 3.4; N, 9.5; S, 10.9%.) Mp > 180 °C (decomp). Selected IR (KBr)/cm^{-1}: 1481 (s, NO$_3^-$), 1439 (br, NO$_3^-$), 1296 (br, NO$_3^-$).

{[Cd(L1)(NO$_3$)$_2$]·CH$_2$Cl$_2$}$_\infty$, 1a. Cd(NO$_3$)$_2$·4H$_2$O (44 mg, 0.14 mmol) dissolved in MeCN (10 mL) was added to **L1** (50 mg, 0.14 mmol) dissolved in CH$_2$Cl$_2$ (10 mL), and the mixture was allowed to stir for 1 h. The cream-colored solid that precipitated was filtered and then transferred to a sample tube and stored in the presence of mother liquor (yield 86 mg, 87%). (Found: C, 37.4; H, 3.4; N, 8.7, S 9.3%. Calcd for $C_{20}H_{20}N_4O_6S_2Cd\cdot CH_2Cl_2$: C, 37.4; H, 3.3; N, 8.3; S, 9.5%.) Mp > 180 °C (decomp).

{[Cd$_2$(L2)(NO$_3$)$_4$]}$_\infty$, 2. Cd(NO$_3$)$_2$·4H$_2$O (87 mg, 0.28 mmol) dissolved in MeCN (5 mL) was added to **L2** (50 mg, 0.14 mmol) dissolved in MeCN (5 mL), and the mixture was allowed to stir for 1 h. The pale brown solid that precipitated was filtered and dried in vacuo (yield 62 mg, 53%). (Found: C, 26.4; H, 2.3; N, 13.3; S, 7.5%. Calcd for $C_{18}H_{18}N_8O_{12}S_2Cd_2$: C, 26.1; H, 2.2; N, 13.6; S, 7.8%.) Mp > 200 °C (decomp). Selected IR (KBr)/cm^{-1}: 1493 (s, NO$_3^-$), 1474 (s, NO$_3^-$), 1452 (s, NO$_3^-$), 1326 (s, NO$_3^-$), 1284 (s, NO$_3^-$), 1266 (s, NO$_3^-$).

{[Cd$_2$(L2)Cl$_4$]}$_\infty$, 3. CdCl$_2$·2.5H$_2$O (64 mg, 0.28 mmol) dissolved in MeOH (20 mL) was added to **L2** (50 mg, 0.14 mmol) dissolved in CH$_2$Cl$_2$ (20 mL), and the mixture was allowed to stir for 8 days. The pale brown solid that precipitated was filtered and dried in vacuo (yield 81 mg, 71%) (Found: C, 29.9; H, 2.3; N, 7.5; S, 8.5; Cl, 19.7%. Calcd for $C_{18}H_{18}N_4S_2Cl_4Cd_2$: C, 30.0; H, 2.5; N, 7.8; S, 8.9; Cl, 19.7%.) Mp > 146 °C (decomp).

X-ray Crystallography. Diffraction data for **1a** were collected on a Nonius Kappa-CCD diffractometer and data for **1b**, **2**·2CH$_3$CN and **3**·2CH$_2$Cl$_2$ were collected on a Bruker SMART CCD diffractometer; both had graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Intensities were corrected for Lorentz-polarization effects,[19] and a multiscan absorption correction[20] was applied, except in the case of **1a**, which was not corrected for absorption. The structures were solved by direct methods (SHELXS)[21] and refined on F^2 using all data by full-matrix least-squares procedures (SHELXL 97).[22] All calculations were performed using the WinGX interface.[23] The data for **1a** were collected at room temperature. The CH$_2$Cl$_2$ molecule in **1a** was disordered over two sites with site occupancy factors of 0.54 and 0.46. For **1b**, a potential monoclinic system was carefully evaluated with PLATON and other programs available through the WinGX interface and rejected, as the transformed data showed no systematic absences and structure solutions made no chemical sense. Crystals of isomer **1b** were of poor quality, had a high mosaicity, and lost solvent very quickly. This was reflected in the poor but unambiguous structure solution. Consequently, the structure showed three peaks of about 2 e Å^{-3}, possibly Fourier ripples, located at about 0.7 Å from the Cd atom. In **3**·2CH$_2$Cl$_2$, the CH$_2$Cl$_2$ molecule was disordered over two sites about a C−Cl bond with site occupancy factors of 0.88 and 0.12. Crystallographic data for the four structures are listed in Table 1.

Results and Discussion

Synthesis and Structures of [Cd(L1)(NO$_3$)$_2$]$_\infty$, 1. A 1:1 molar ratio of Cd(NO$_3$)$_2$·4H$_2$O and **L1** yielded a cream-colored solid. It was insoluble in most common organic solvents, suggesting formation of a coordination polymer. Microanalytical data were consistent with the solid having a 1:1 metal-to-ligand ratio. X-ray-quality crystals were grown by the slow diffusion of a CHCl$_3$ solution of **L1** layered with a solvent blank of CH$_2$Cl$_2$ and a MeCN solution of Cd(NO$_3$)$_2$·4H$_2$O. After 1 week, crystals of needle and platelike morphologies were found growing in the same regions of the crystal jars. Infrared spectra recorded for individual samples of the bulk material, the needle-shaped

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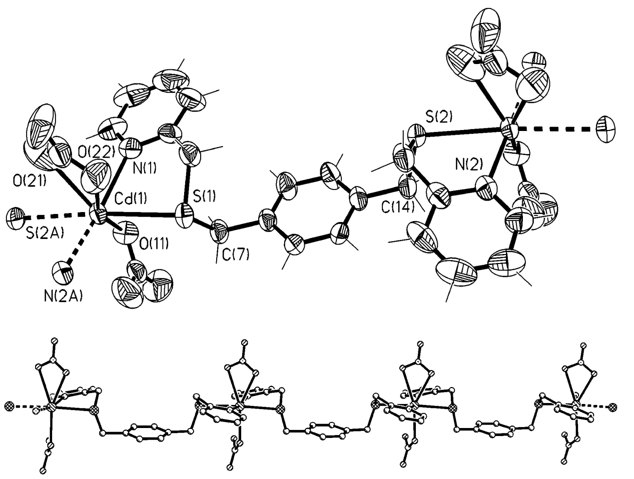

Figure 1. Views of polymer **1a**. The CH_2Cl_2 molecule is not shown. (Top) Perspective view of **1a** (crystallographic numbering) showing the coordination sphere of the Cd(II) ion. Thermal ellipsoids are drawn at the 50% probability level. (Bottom) View of a polymer chain showing the corrugated conformation of the ligand **L1** (H atoms omitted). Selected bond lengths (Å) and angles (deg): N(1)−Cd(1) 2.320(3), O(11)−Cd(1) 2.473(3), O(21)−Cd(1) 2.618(4), O(22)−Cd(1) 2.708(4), S(1)−Cd(1) 2.6848(7), Cd(1)−N(2A) 2.305(2), Cd(1)−S(2A) 2.6961(8), O(12)···Cd(1) 2.813(4); N(2A)−Cd(1)−N(1) 167.97(9), N(2A)−Cd(1)−O(11) 115.41(9), N(1)−Cd(1)−O(11) 76.54(9), N(2A)−Cd(1)−O(21) 89.9(1), N(1)−Cd(1)−O(21) 80.6(1), O(22)−Cd(1)−O(21) 46.7(1), O(22)−Cd(1)−O(11) 160.0(1), O(11)−Cd(1)−O(21) 141.2(1), N(2A)−Cd(1)−O(22) 78.5(1), N(2A)−Cd(1)−S(1) 101.08(6), N(1)−Cd(1)−S(1) 76.29(7), N(1)−Cd(1)−O(22) 89.6(1), O(11)−Cd(1)−S(1) 91.33(6), O(21)−Cd(1)−S(1) 113.20(7), O(22)−Cd(1)−S(1) 71.23(8), N(2A)−Cd(1)−S(2A) 76.54(6), N(1)−Cd(1)−S(2A) 106.91(7), O(11)−Cd(1)−S(2A) 86.00(6), O(21)−Cd(1)−S(2A) 71.16(7), O(22)−Cd(1)−S(2A) 112.05(8), S(1)−Cd(1)−S(2A) 175.19(3). (Symmetry code: A $x + 1$, $y + 1$, z.)

crystals, and the platelike crystals were very similar and gave little indication of structural differences between the two crystal morphologies. X-ray structural analysis of both crystal types revealed that they were one-dimensional coordination polymers related to each other as conformational supramolecular isomers.[1] Different solvent molecules were associated with each polymer.

Conformational Supramolecular Isomer $\{[Cd(L1)(NO_3)_2]\cdot CH_2Cl_2\}_\infty$, 1a. For the crystals with needle morphology, the asymmetric unit consisted of a Cd(II) ion, a complete ligand (**L1**), two NO_3^- counterions, and one molecule of CH_2Cl_2 (Figure 1). The CH_2Cl_2 solvent molecule was disordered over two sites with approximately equal occupancy. Each ligand was joined to an adjacent symmetry-related ligand by a seven-coordinate Cd(II) ion to form a one-dimensional polymer chain running in the [1 1 0] direction (Figure 1). Each Cd(II) ion was bound by a NSN′S′O$_2$″O‴ donor set in which one of the NO_3^- anions was considered to be bidentate and the other monodentate. Although one of the NO_3^- ions was bidentate, it had a small bite angle and effectively occupied only one coordination site, allowing a pseudo-octahedral description of the geometry. The Cd−O distances (Figure 1) and analysis by PLATON[24] supported the assignment of bidentate and monodentate NO_3^- anions, although the distinction is not clear-cut. For the monodentate NO_3^- anion, the Cd(1)···O(12) distance of 2.815(4) Å was not considered bonding as it was close to the longest value of 2.92 Å for Cd−O distances found for bidentate NO_3^- ions in a search of the Cambridge Crystallographic Database (CSD version 5.25).[25] However, the distance was still shorter than the sum of the van der Waals radii, 3.10 Å.[26] The NO_3^- anions were bound in an asymmetric fashion with very disparate Cd−O bond distances (Figure 1). The infrared spectrum showed three peaks in the NO_3^- stretching region at 1487 (m), 1427 (s), and 1299 (s) cm^{-1}, consistent with the NO_3^- anions displaying more than one binding arrangement.[27]

The ligand was folded in a cis fashion such that the pyridine arm groups were positioned on the same side with respect to the central arene ring, giving an overall gauche conformation [torsion angle across the benzene ring S(1)−C(7)···C(14)−S(2) = −29.1°] (Chart 1, Figure 1). The pyridine N donors pointed in opposite directions in a trans arrangement with respect to each other. In the gauche conformation of **L1**, all three rings were approximately parallel to each other (Figure 1), with one pyridine ring twisted by 9.6° relative to the central ring and the other twisted by 16.6°. The corrugated polymer chain did not contain a center of symmetry, and as a result, the chain was generated by a simple symmetry translation in the [1 1 0] direction. Adjacent parallel chains were related to each other in a centrosymmetric fashion by a translation of one-half of a unit cell.

There were no significant interactions between adjacent chains. The aromatic rings of neighboring chains were too distant to take part in $\pi-\pi$ interactions, with the shortest distance between centroids being 4.21 Å.[28] The stacking of the corrugated chains provided spaces large enough to contain the associated disordered CH_2Cl_2 solvent molecules (potential solvent-accessible volume 18.0%).[24]

Conformational Supramolecular Isomer $\{[Cd(L1)(NO_3)_2]\cdot{}^4/_3(CH_3CN)\}_\infty$, 1b. X-ray structure analysis of the crystals with platelike morphology showed that two isomeric polymer fragments were present in the same crystal. They were one-dimensional coordination polymers related to each other as topological isomers.[14−16,29] The asymmetric unit contained four separate residues: two MeCN solvent molecules and the two polymer chains **1b(1)** and **1b(2)**. With respect to the asymmetric unit, isomer **1b(1)** contained a Cd(II) ion, two NO_3^- anions, and a complete ligand (**L1**), whereas isomer **1b(2)** contained one-half of a Cd(II) ion, one NO_3^- anion, and one-half of a ligand (**L1**) (Figure 2). The infrared spectrum showed three peaks in the NO_3^- stretching region at 1481 (m), 1439 (s), and 1296 (br) cm^{-1}, consistent with the NO_3^- anions binding in both monodentate and bidentate fashions.[27]

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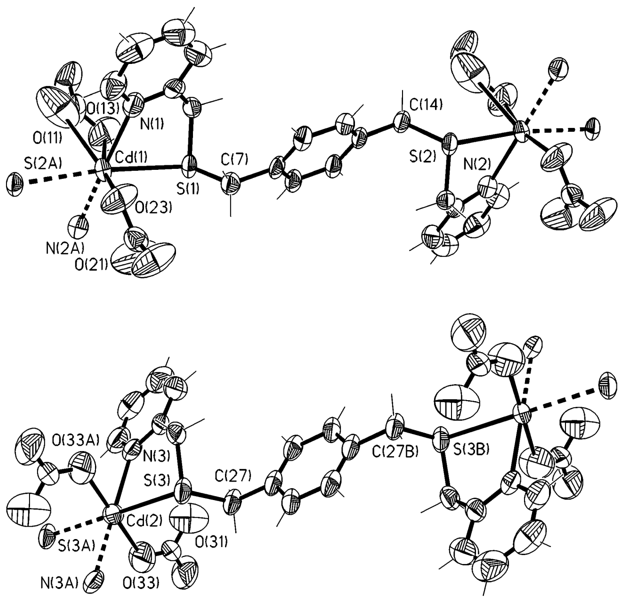

Figure 2. Perspective views of the two different chains in **1b** showing the coordination sphere of the Cd(II) ions (crystallographic numbering). The CH_3CN molecules are not shown. Thermal ellipsoids are drawn at the 50% probability level. (Top) View of **1b(1)** showing bidentate and monodentate NO_3^- anions. Selected bond lengths (Å) and angles (deg): N(2A)−Cd(1) 2.301(6), O(11)−Cd(1) 2.57(1), O(13)−Cd(1) 2.64(1), O(23)−Cd(1) 2.388(7), S(2A)−Cd(1) 2.722(2), Cd(1)−N(1) 2.338(7), Cd(1)−S(1) 2.723(2); N(2A)−Cd(1)−N(1) 172.8(2), N(2A)−Cd(1)−O(23) 108.7(2), N(1)−Cd(1)−O(23) 77.6(3), N(2A)−Cd(1)−O(11) 98.5(3), N(1)−Cd(1)−O(11) 78.1(3), O(23)−Cd(1)−O(11) 137.8(3), N(2)−Cd(1)−O(13) 79.3(3), N(1)−Cd(1)−O(13) 93.9(3), O(23)−Cd(1)−O(13) 167.2(3), O(11)−Cd(1)−O(13) 46.9(3), N(2A)−Cd(1)−S(2A) 77.3(2), N(1)−Cd(1)−S(2A) 107.9(2), O(23)−Cd(1)−S(2A) 78.5(2), O(11)−Cd(1)−S(2A) 76.9(2), O(13)−Cd(1)−S(2A) 113.6(2), N(2A)−Cd(1)−S(1) 99.7(2), N(1)−Cd(1)−S(1) 75.8(2), O(23)−Cd(1)−S(1) 96.7(2), O(11)−Cd(1)−S(1) 110.0(2), O(13)−Cd(1)−S(1) 71.7(2), S(2A)−Cd(1)−S(1) 172.94(5). (Symmetry code: A *x*, *y*, *z* − 1.) (Bottom) View of **1b(2)** showing monodentate NO_3^- anions. Selected bond lengths (Å) and angles (deg): N(3)−Cd(2) 2.308(8), O(33)−Cd(2) 2.39(1), S(3)−Cd(2) 2.694(2); N(3)−Cd(2)−N(3A) 180.0, N(3)−Cd(2)−O(33A) 81.5(3), N(3)−Cd(2)−O(33) 98.5(3), O(33A)−Cd(2)−O(33) 180.0(1), N(3)−Cd(2)−S(3A) 102.4(2), N(3A)−Cd(2)−S(3A) 77.6(2), O(33A)−Cd(2)−S(3) 75.0(3), O(33)−Cd(2)−S(3) 105.0(3), S(3A)−Cd(2)−S(3) 180.00(2). (Symmetry code: A −*x*, −*y*, −*z*.)

Topological Isomer 1b(1). The Cd(II) ion of **1b(1)** adopted a seven-coordinate geometry with each Cd(II) ion bound by a NSN′S′O$_2$″O‴ donor set. Each type of donor species was arranged in a trans manner about the central Cd(II) ion. One of the NO_3^- anions was bound in a bidentate fashion, and the other was bound in a monodentate fashion (Figure 2). Although one of the NO_3^- ions was bidentate, it had a small bite angle and effectively occupied only one coordination site, allowing a pseudo-octahedral description of the geometry. The Cd−O distances (Figure 2) and analysis by PLATON[24] showed clearly that one nitrate anion was bidentate and the other was monodentate. Also, the Cd(1)···O(21) distance of 2.94(1) Å was at the limit of values found for bidentate nitrate ions in a search of the Cambridge Crystallographic Database (CSD version 5.25).[25] The Cd−S distances fell approximately in the middle of the range of Cd−thioether S bond lengths (2.61−2.98 Å).[25] The ligand was arranged in a stepped anti conformation [torsion angle across the benzene ring S(1)−C(7)···C(14)−S(2) = −170.7°] (Chart 1, Figure 2) such that the pyridine arm groups were positioned on opposite sides with respect to the central arene ring in a trans fashion. The pyridine N donors pointed in opposite directions in a trans configuration with respect to each other. The three rings were approximately parallel to each other, with one pyridine ring twisted by 8.0° relative to the central ring and the other twisted by 9.9°.

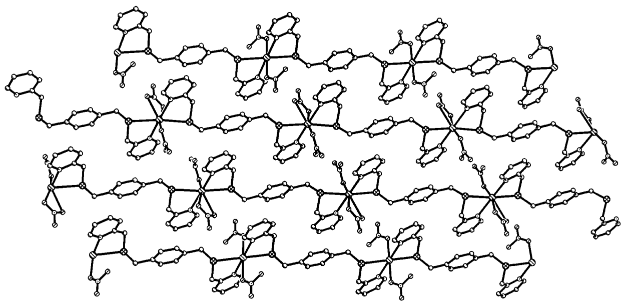

Figure 3. View of **1b** with hydrogens and solvent molecules omitted for clarity. The isomeric chains are shown packed in a **1b(1)−1b(1)−1b(2)** pattern forming a two-dimensional sheet in the *ac* plane.

Topological Isomer 1b(2). In isomer **1b(2)**, the Cd(II) ion was positioned on a center of symmetry and adopted a distorted octahedral geometry. The Cd(II) ion was bound by a NSN′S′O″O‴ donor set, with symmetry-related donor atoms binding trans to each other. The Cd(2)−O(33) bond distance of 2.39(1) Å together with the Cd(2)···O(31) distance of 3.305(9) Å clearly showed that the NO_3^- anion was monodentate (Figure 2). The Cd−O distance was identical to that for the monodentate nitrate of isomer **1b(1)**. The Cd−S distance was slightly shorter than that found in **1b(1)** (Figure 2). The three rings of the ligand adopted the same stepped anti arrangement found for isomer **1b(1)** [torsion angle across the benzene ring S(3)−C(27)···C(27B)−S(3B) = −180.0°]. Both pyridine arms were twisted by 10.6° relative to the central ring. A fit of all non-hydrogen atoms of the ligand in **1b(1)** to all those in **1b(2)** gave a weighted root-mean-squared deviation of 0.36 Å.

The polymeric isomers **1b(1)** and **1b(2)** were essentially the same in all respects except for the coordination arrangement about the Cd(II) ions and the torsion angles of the anti arrangement of **L1**. In **1b(1)**, one of the NO_3^- anions was bidentate, leading to seven-coordinate Cd(II) ions and slightly longer metal−ligand bonds compared to **1b(2)**. In addition, the two NO_3^- anions and the Cd(II) cation of each isomer lay approximately in a plane with mean deviations of 0.185 Å for **1b(1)** and 0.016 Å for **1b(2)**. The planar $Cd(NO_3)_2$ moiety in **1b(1)** was arranged in an approximately orthogonal fashion relative to the same moiety in **1b(2)** despite the two chains running parallel to each other. The angle between the $Cd(NO_3)_2$ mean planes was 106.5°.

The chains of both isomers propagated along the *c* axis and the adjacent chains were weakly held together to form sheets in the *ac* plane with a repeating **1b(1)−1b(1)−1b(2)** pattern (Figure 3). The chains were held together by two sets of interactions. The stronger was a variety of interactions of the type $O_2N{-}O{\cdots}H{-}C$ involving both aryl and alkyl hydrogens with separations in the range 2.33−2.55 Å and corresponding O···C separations of 3.12−3.48 Å. The remaining type of interaction was a very weak C(alkyl)−H···arene(pyridine) interaction at a distance of 2.96 Å. This distance was at the conventional van der Waals limit, but CH/π interactions have been suggested to be effective at distances beyond this value.[30] Each chain in the sheet was offset from its neighbors by approximately one-half of a ligand so that pyridine rings overlay with arene rings from adjacent chains. The aromatic rings of neighboring chains were too distant to take part in $\pi-\pi$ interactions, with the shortest distance between centroids being 4.23 Å.[28] The sheets were held together in a three-dimensional array by further $O_2N-O\cdots H-C$ interactions. A potential solvent-accessible volume of 18.2% was occupied by MeCN molecules[24] and was the same as the volume occupied by the CH_2Cl_2 molecules in **1a**.

Synthesis and Structure of $\{[Cd_2(\mathbf{L2})(NO_3)_4]\cdot 2CH_3CN\}_\infty$, $\mathbf{2}\cdot 2CH_3CN$. A 1:1 molar reaction of $Cd(NO_3)_2\cdot 4H_2O$ and **L2** gave a pale brown solid in low yield. The complex had a microanalysis consistent with a 2:1 metal-to-ligand ratio. Subsequently, a pale brown powder was obtained from a 2:1 molar reaction of $Cd(NO_3)_2\cdot 4H_2O$ and **L2** in moderate yield. Despite careful workup of the reaction solid and filtrate, a 1:1 product could not be isolated. X-ray-quality crystals were grown by the slow diffusion of a $CHCl_3$ solution of **L2** layered with a solvent blank of CH_2Cl_2 and a MeCN solution of $Cd(NO_3)_2\cdot 4H_2O$. Orange crystals of block morphology were found after 1 month.

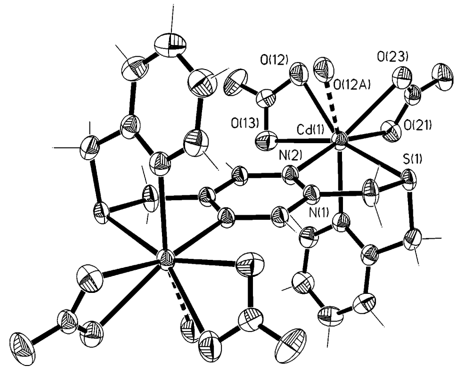

Figure 4. Perspective view of $\mathbf{2}\cdot 2CH_3CN$ (crystallographic numbering) showing the coordination sphere of the Cd(II) ion and the conformation of ligand **L2**. The CH_3CN solvent molecule is not shown. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): N(1)−Cd(1) 2.369(2), N(2)−Cd(1) 2.405(2), O(12)−Cd(1) 2.484(2), O(13)−Cd(1) 2.456(2), O(21)−Cd(1) 2.405(2), O(23)−Cd(1) 2.477(2), S(1)−Cd(1) 2.6701(8), Cd(1)−O(12A) 2.542(2); N(1)−Cd(1)−N(2) 81.19(6), N(1)−Cd(1)−O(21) 83.83(6), N(2)−Cd(1)−O(21) 164.24(6), N(1)−Cd(1)−O(13) 83.03(6), N(2)−Cd(1)−O(13) 86.47(5), O(21)−Cd(1)−O(13) 96.60(6), N(1)−Cd(1)−O(23) 129.04(5), N(2)−Cd(1)−O(23) 137.63(5), O(21)−Cd(1)−O(23) 52.22(5), O(13)−Cd(1)−O(23) 121.76(5), N(1)−Cd(1)−O(12) 128.85(5), N(2)−Cd(1)−O(12) 112.03(5), O(21)−Cd(1)−O(12) 81.36(6), O(13)−Cd(1)−O(12) 50.85(5), O(23)−Cd(1)−O(12) 74.33(5), N(1)−Cd(1)−O(12A) 152.09(6), N(2)−Cd(1)−O(12A) 71.87(6), O(21)−Cd(1)−O(12A) 122.14(5), O(13)−Cd(1)−O(12A) 102.04(6), O(23)−Cd(1)−O(12A) 71.65(5), O(12)−Cd(1)−O(12A) 70.23(7), N(1)−Cd(1)−S(1) 77.07(4), N(2)−Cd(1)−S(1) 75.86(4), O(21)−Cd(1)−S(1) 96.04(4), O(13)−Cd(1)−S(1) 155.08(4), O(23)−Cd(1)−S(1) 82.80(4), O(12)−Cd(1)−S(1) 152.96(4) and O(12A)−Cd(1)−S(1) 89.18(5). (Symmetry code: A $-x$, $-y$, $-z$.)

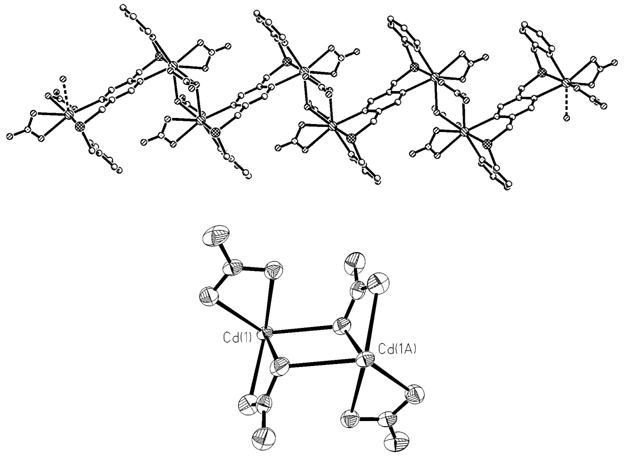

Figure 5. Views of polymer $\mathbf{2}\cdot 2CH_3CN$ with hydrogens and solvent molecules omitted for clarity. (Top) View of the zigzag polymer chain lying along the *a* axis. (Bottom) View of $\mathbf{2}\cdot 2CH_3CN$ showing the NO_3^- bridging between the Cd(II) ions to form a $\overline{\text{Cd}-\text{O}-\text{Cd}-\text{O}}$ square.

X-ray structure analysis showed that the asymmetric unit consisted of a Cd(II) ion, one-half of a ligand (**L2**), two NO_3^- anions, and a MeCN molecule. The structure was generated by a center of inversion, with the Cd(II) ion adopting an eight-coordinate geometry with each Cd(II) ion having a $N_{py}SN_{pz}O_2'O_2''O'''$ donor set (N_{py} = pyridine N donor, N_{pz} = pyrazine N donor) (Figure 4). The two NO_3^- ions chelated to the Cd(II) ion in a cis relationship to each other, with another O atom from a NO_3^- bound to an adjacent Cd(II) center also binding. The two bidentate NO_3^- anions had small bite angles and could be viewed as effectively occupying only one coordination site each, leading to a pseudo-octahedral description of the geometry. The ligand was arranged in an anti fashion, with each set of $N_{py}N_{pz}S$ donors binding to a Cd(II) ion in a pseudo-facial manner to give a centrosymmetric dinuclear $[Cd_2(\mathbf{L2})(NO_3)_4]$ moiety. The anti arrangement caused the pyridine rings to be stepped at 107.5° relative to the pyrazine ring. The structure was polymeric and consisted of repeating dinuclear $[Cd_2(\mathbf{L2})(NO_3)_4]$ units (Figure 5). The individual Cd−(**L2**)−Cd units were linked together to form a one-dimensional chain through bridging of the NO_3^- anions on each Cd(II) ion. The polymer formed a zigzag chain that propagated along the *a* axis. In addition, for one of the NO_3^- anions, one bound O atom was also used to bridge between two Cd(II) centers from different dinuclear units in a μ-1,1-*O* fashion. This formed a planar centrosymmetric $\overline{\text{Cd}-\text{O}-\text{Cd}-\text{O}}$ square that served as the polymeric link for the system (Figure 5). This was a novel structural feature both for Cd(II) systems and as a connecting group for coordination polymers. Similar examples of this motif have been found for discrete Ag(I),[31] Ca(II),[32] Nd(III),[33] Gd(III),[34] Ce(III),[35] Y(III),[36] La(III),[36] and two dif-

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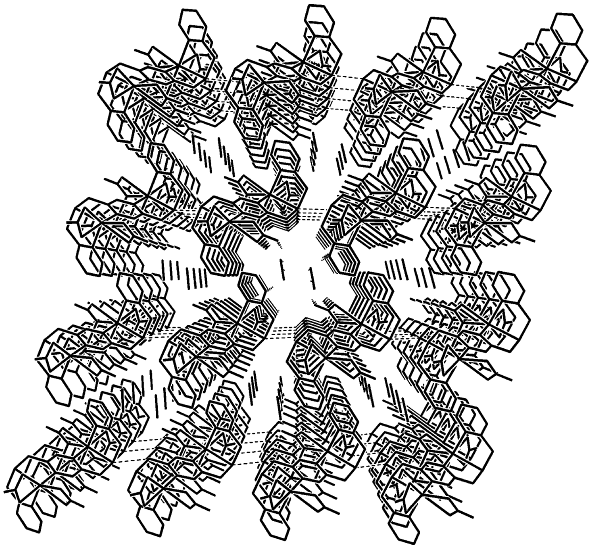

Figure 6. View along the *a* axis showing the packing of polymer **2**·$2CH_3CN$. The sheets formed by S···S interactions (indicated by dotted lines) are shown, as are MeCN solvent molecules in cavities (hydrogen atoms omitted).

ferent Hg(II) systems.[37] Except for the Ce(III) system,[35] all of these complexes had a planar arrangement for the $M_2(NO_3)_2$ moiety. In contrast, compound **2**·$2CH_3CN$ had one NO_3^- above and the other below the plane of the square Cd−O−Cd−O link, with the planes of the bridging NO_3^- anions tilted at 125° to the plane of the square. The infrared spectrum in the NO_3^- stretching region was complicated with peaks at 1493 (s), 1474 (s), 1452 (s), 1326 (s), 1284 (s), and 1266 (s) cm^{-1} consistent with the different binding modes of the NO_3^- anions found in the complex.[27,37]

The one-dimensional zigzag chains were held together to form two-dimensional sheets in the diagonal (1 −1 0) plane by interactions between the S atoms of the ligands (S···S = 3.41 Å). There were no interactions between the sheets, which packed together such that the pyridine arms of the ligands were interdigitated. This packing afforded cavities between the sheets, with a potential solvent-accessible volume of 20.6%,[24] which were able to contain MeCN solvent molecules (Figure 6). The array was held together in three dimensions by weak intermolecular interactions between the MeCN molecules residing in the solvent cavity, the O atoms on the NO_3^- ions and H atoms from three of the linear polymeric chains.

Synthesis and Structure of $\{[Cd_2(L2)Cl_4]\cdot 2CH_2Cl_2\}_\infty$, **3**·$2CH_2Cl_2$. A 1:1 molar reaction of $CdCl_2\cdot 2.5H_2O$ and **L2** produced a pale brown solid in moderate yield that had a microanalysis consistent with a 2:1 metal-to-ligand ratio. Subsequently, a pale brown powder was obtained in better yield from the above reactants in a 2:1 molar ratio. As in the case of **2**·$2CH_3CN$, the 1:1 product could not be obtained. X-ray-quality crystals were grown by the slow diffusion of a $CHCl_3$ solution of **L2** layered with a solvent blank of CH_2Cl_2 and a MeOH solution of $CdCl_2\cdot 2.5H_2O$. Orange crystals of block-shaped morphology were found after 2 months.

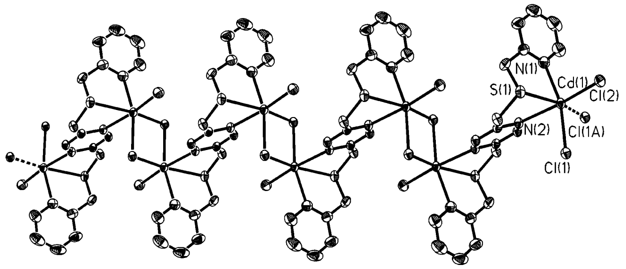

Figure 7. Perspective view of the polymeric chain **3**·$2CH_2Cl_2$ (crystallographic numbering) lying along the *b* axis, showing the coordination sphere of the Cd(II) ion. The CH_2Cl_2 solvent molecule and hydrogen atoms are not shown. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): N(1)−Cd(1) 2.350(3), N(2)−Cd(1) 2.480(2), S(1)−Cd(1) 2.6865(9), Cl(1A)−Cd(1) 2.5664(9), Cl(1)−Cd(1) 2.671(1), Cl(2)−Cd(1) 2.5132(9); N(1)−Cd(1)−N(2) 87.00(9), N(1)−Cd(1)−Cl(2) 91.60(7), N(2)−Cd(1)−Cl(2) 169.57(5), N(1)−Cd(1)−Cl(1A) 99.44(7), N(2)−Cd(1)−Cl(1A) 89.55(5), Cl(2)−Cd(1)−Cl(1A) 100.87(3), N(1)−Cd(1)−Cl(1) 164.31(7), N(2)−Cd(1)−Cl(1) 81.45(6), Cl(2)−Cd(1)−Cl(1) 97.83(3), Cl(1)−Cd(1)−Cl(1A) 91.10(2), N(1)−Cd(1)−S(1) 75.67(7), N(2)−Cd(1)−S(1) 73.17(5), Cl(2)−Cd(1)−S(1) 96.47(3), Cl(1A)−Cd(1)−S(1) 162.14(2), Cl(1)−Cd(1)−S(1) 90.76(2). (Symmetry code: A $1 - x$, $1 - y$, $1 - z$.)

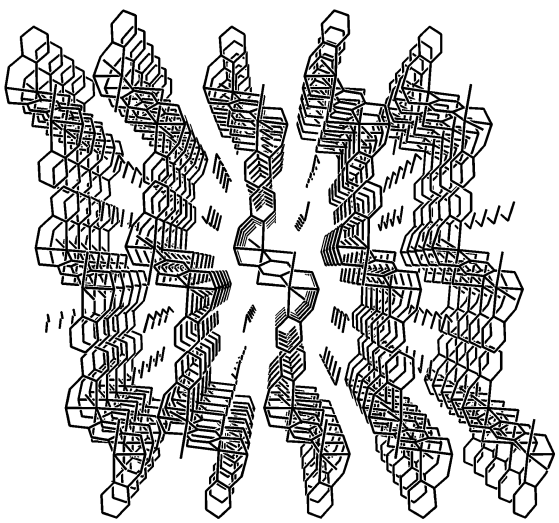

Figure 8. View along the *b* axis for polymer **3**·$2CH_2Cl_2$ showing interdigitation of chains and CH_2Cl_2 solvent molecules in cavities (hydrogen atoms omitted).

The X-ray structure of **3**·$2CH_2Cl_2$ was very closely related to that of **2**·$2CH_3CN$, except that the Cd(II) ion adopted a genuine six-coordinate geometry. The ligand was arranged in an anti fashion, with facial coordination of the Cl^- anions, to give a centrosymmetric dinuclear $[Cd_2(\mathbf{L2})Cl_4]$ moiety (Figure 7). The structure was polymeric and consisted of repeating $[Cd_2(\mathbf{L2})Cl_4]$ units linked together to form a one-dimensional chain through bridging of the Cl^- anions. The polymer formed a zigzag chain that propagated along the *b* axis. The structure showed interdigitation of the chains (Figure 8) and was packed in a manner similar to **2**·$2CH_3CN$ and to the closely related protopolymeric complex $[Cu_2(\mathbf{L2})Cl_4]$.[13] Solvent CH_2Cl_2 molecules, which were disordered over two sites about a C−Cl bond, resided in voids between the chains (potential solvent-accessible volume 27.9%),[24] and

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(36) Hudson, M. J.; Drew, M. G. B.; Foreman, M. R. St. J.; Hill, C.; Huet, N.; Madic, C.; Youngs, T. G. A. *Dalton Trans.* **2003**, 1675−1685.

(37) (a) Alyea, E. C.; Dias, S. A.; Ferguson, G.; Siew, P. Y. *Can. J. Chem.* **1983**, *61*, 257−262. (b) Krumm, M.; Zangrando, E.; Randaccio, L.; Menzer, S.; Danzmann, A.; Holthenrich, D.; Lippert, B. *Inorg. Chem.* **1993**, *32*, 2183-2189.

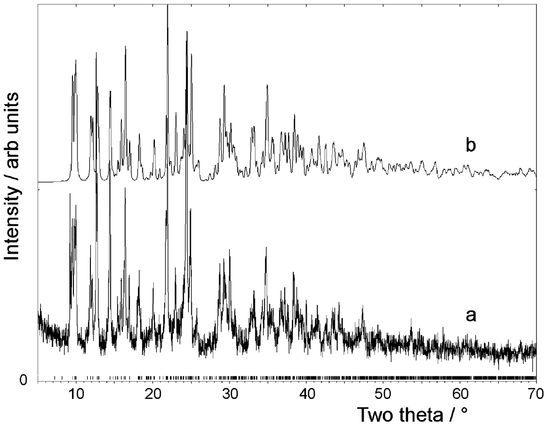

Figure 9. Comparison of (a) experimental PXD data for solvated crystals of **1a** to (b) calculated pattern from single-crystal X-ray data for **1a**.

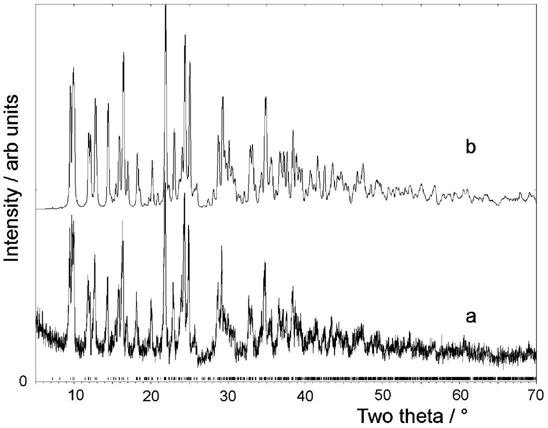

Figure 10. Comparison of (a) experimental PXD data for bulk sample of **1** to (b) calculated pattern from single-crystal X-ray data for **1a**.

were involved in linking the chains into a three-dimensional array through weak Cl···H−C interactions in the range 2.66−2.74 Å[38] corresponding to Cl···C separations of 3.58−3.67 Å.

Powder X-ray Diffraction Studies. Powder X-ray diffraction (PXD) studies were undertaken to investigate further the characteristics of these coordination polymers of cadmium(II) and, in particular, to compare the solvated forms and the bulk material of **1**. The PXD patterns were recorded for solvated and desolvated samples from bulk preparations of **1**−**3** and from samples of **1a** and **1b** prepared by slow crystallization. Comparison of the patterns for a solvated bulk sample of **1** and a sample of **1a** showed that, with the exception of a few intensity differences, the patterns were in good agreement with each other. The differences in intensity might have been due to preferred orientation of the powder samples caused during sample preparation. These two experimentally measured patterns also were in good agreement with the PXD pattern calculated from the single-crystal X-ray data for **1a** (Figures 9 and 10). Also these two solvated materials were found to decompose at the same temperature. Thus, of the two conformations for **L1** found in the structures of **1a** and **1b** (Chart 1), it was the gauche and not the anti form that was present in the bulk material. This was in contrast to previous coordination polymers of **L1** with silver or copper where only the anti form was found.[4]

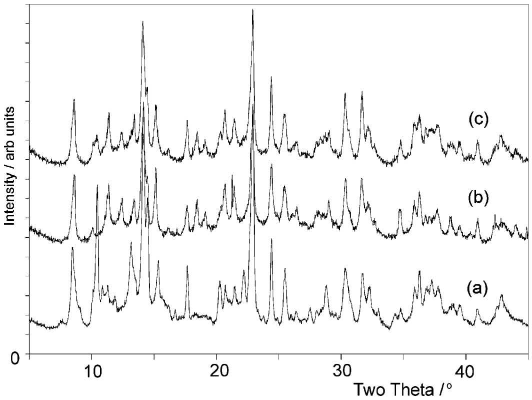

Figure 11. Comparison of the experimental PXD data for dried samples of (a) bulk **1** to those of (b) **1a** and (c) **1b**.

Interestingly, the PXD patterns for desolvated bulk samples of **1** and desolvated samples of **1a** and **1b** were all very similar (Figure 11). Again, minor differences in intensities might have arisen from the preferred orientation of certain reflections caused by sample preparation. Hence, upon desolvation, the crystalline forms **1a** and **1b** both adopted the same structure as each other and as the bulk desolvated material of **1**. The PXD patterns were completely different from the calculated or experimental patterns of any of the solvated forms of **1**. Thus, the three desolvated materials all adopted a common structure that was different from the solvated forms. This common structure must have resulted from not only rearrangement caused by loss of solvent but also, in at least some or all of the materials, from changes in the ligand conformation as well.

Unfortunately, several attempts to measure the PXD pattern of the solvated form of **1b** and to compare it with the PXD pattern calculated from the single-crystal X-ray data were unsuccessful, as all of the patterns obtained showed that the material had undergone loss of solvent. This desolvated material was found to decompose at 191 °C. For compounds **2** and **3**, the PXD patterns measured for bulk solvated samples were in good agreement with the PXD patterns simulated from the respective single-crystal X-ray data. As expected, desolvated bulk samples of **2** and **3** produced PXD patterns that were different from those obtained for the solvated forms of these materials.

Conclusion

The complexes of **L1** were found to display a remarkable degree of structural diversity for one-dimensional polymers. This was despite the fact that **L1** was predisposed to forming only one-dimensional polymers as a consequence of the arrangement of its donor groups in chelating compartments. In the solid state, complexes of **L1** were able to exist as three different polymeric chains that exhibited two different types of isomerism. The flexibility of ligand **L1** allowed the ligand to adopt different conformations[3] and gave rise to conformational supramolecular isomerism.[1] The versatility of NO_3^- coordination gave rise to topological isomerism in which two different isomeric polymer chains formed a single

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[38] Aullon, G.; Bellamy, D.; Brammer, L.; Bruton, E. A.; Orpen, A. G. *Chem. Commun.* **1998**, 653−654.

network superstructure.[14,15,29] The packing efficiency of the structures, **1b** and **2**·$2CH_3CN$, that were not disordered was analyzed using PLATON,[24] and the packing indices were calculated to be 0.69 and 0.73, respectively. For the disordered structures **1a** and **3**·$2CH_2Cl_2$, packing indices were estimated by averaging the values obtained from the structures of each of the two disordered solvent components, weighted for their occupancy. The values of 0.69 and 0.72 obtained for **1a** and **3**·$2CH_2Cl_2$, respectively, were in line with those for the related structures **1b** and **2**·$2CH_3CN$. In addition to structural diversity, a further consequence of the flexibility of **L1**, when compared with **L2**, was the slightly less efficient packing of the structures. The ligand **L2** adopted a more constrained arrangement through facial binding to the Cd(II) cation, and this resulted in analogous NO_3^- and Cl^- bridged one-dimensional polymers being formed. Surprisingly, these network superstructures were largely unaffected by the incorporation of different solvent molecules.

In addition, NO_3^- anions arranged in a cis fashion about a Cd(II) cation appeared to be more able to assist directly in forming arrays than those bound in a trans fashion.[39] This suggested that facial-directing ligands such as **L2** together with $Cd(NO_3)_2$ might have a niche role in the formation of anion-bridged coordination polymers, particularly given the variety of different bridging modes for the NO_3^- anion. However, trans NO_3^- anions themselves were found to be able to influence array formation in their own way. By being able to adopt different binding modes and relative orientations they can, as described above, give rise to topological or even types of supramolecular isomerism.

While the flexibility of the ligands allowed for supramolecular isomerism, it, in turn, meant complexes with interesting structural diversity were obtained.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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