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THREE NEW THIOCYANATO-BRIDGED COMPLEXES OF CADMIUM(II): SYNTHESSES, X-RAY CRYSTAL STRUCTURES AND THERMAL PROPERTIES

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Three new thiocyanato-bridged polymers of cadmium(II), [Cd(me₄dpt)(SCN)₂]_n (**1**) [me₄dpt = 3,3'-iminobis(*N,N*-dimethylpropylamine)], [Cd(me₂tn)(SCN)₂]_n (**2**) (me₂tn = *N,N'*-dimethyl-1,3-propanediamine) and [ampyH] {Cd(SCN)₃]_n (**3**) (ampyH = 4-aminopyridinium cation), have been synthesized and their molecular structures determined through X-ray crystallography. In Complex **1** each square pyramidal mononuclear fragment is H-bonded (N–H··S) to form a 1D supramolecular chain. Complex **2** is a 1D coordination polymer in which each distorted octahedral cadmium(II) ion is linked with the four bridging thiocyanates and one diamine. The structure of **3** reveals anionic [Cd(SCN)₃][–] zigzag chains arranged in an approximately hexagonal array with the 4-aminopyridinium cations occupying triangular channels. Each chain is H-bonded (N–H··N) to form a 2D supramolecular network. Upon heating, **1** and **2** melt and transform to transparent solid masses at ambient temperature over a few days. On scratching, these turn to a fine powder. This phenomenon is repeatable. Complex **3** upon heating loses a 4-aminopyridine molecule and transforms to [H][Cd(SCN)₃] at ~195°C.

Keywords: Cadmium(II); Thiocyanato-bridged complexes; Crystal structures; Thermal studies

INTRODUCTION

Coordination polymers of one-, two- and three-dimensional infinite frameworks involving cadmium(II) have been of great interest in recent years owing to their potential applications in various fields [1–8]. The d¹⁰ configuration and softness of cadmium(II) permit a wide variety of geometries and coordination numbers [9–12]. In our studies of the supramolecular chemistry of metal complexes, we have reported a number of complexes of cadmium(II) using halides (Cl[–], Br[–], I[–]) and pseudohalides

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(SCN⁻, SeCN⁻, etc.) as bridging anions and which were observed to control the structural diversity and stereochemistry at the cadmium(II) centre [13–18]. Reaction of Cd(SCN)₂ with (2-aminoethyl)(3-aminopropyl)(apa) produced a 2D hyperbranched polymeric network [15] in which each apa moiety acted as a chelating as well as a bridging ligand whereas reaction with bis(2-aminoethylamine)(baa) and *N*²-methyl-bis(2-aminoethylamine) (mebaa) yielded unique three-dimensional complexes, [Cd(baa/mebaa)₂(NCS)₆]·*n*H₂O with two types of cadmium environment; one involved only N-donor atoms and the other only S-donor atoms, whereas baa/mebaa acted as a chelating ligand only [14,16]. On the other hand, reaction of Cd(SeCN)₂ with mebaa/*N'*-isopropyl-diethylenetriamine (iprdien) produces two novel architectures [17]; one as a 2D supramolecular network and the other is a 2D coordination polymer with alternating octahedral and tetrahedral environments. These findings suggest that chain length as well as substitution at carbon/nitrogen of the triamine ligand in the Cd(SCN/SeCN)₂ system play key roles in generating novel polymer architectures. Similarly, variation of substitution in diamines results in different polymeric networks [10,18]. Based on this idea we have chosen three different ligands, a tridentate, 3,3'-iminobis(*N,N*-dimethylpropylamine) (me₄dpt), a bidentate, *N,N'*-dimethyl-1,3-propanediamine (me₂tn) and a monodentate, 4-aminopyridine (ampy) to react with Cd(SCN)₂ for synthesizing novel coordination polymers. We now present the syntheses, X-ray crystal structures and thermal properties of three new thiocyanato-bridged, 1D compounds of cadmium(II), [Cd(me₄dpt)(SCN)₂]_{*n*} (**1**), [Cd(me₂tn)(SCN)₂]_{*n*} (**2**) and [ampyH]{Cd(SCN)₃]_{*n*} (**3**).

EXPERIMENTAL

Materials

3,3'-Iminobis(*N,N*-dimethylpropylamine), *N,N'*-dimethyl-1,3-propanediamine and 4-aminopyridine were purchased from the Aldrich Chemical Company and used as received. All other chemicals used were of AR grade.

Physical Measurements

Elemental analyses (carbon, hydrogen and nitrogen) were carried out using a Perkin-Elmer 240C instrument and cadmium(II) contents were estimated gravimetrically [19]. IR spectra (4000–400 cm⁻¹) were recorded on a Perkin-Elmer IR 783 spectrophotometer where KBr was used as medium/reference material. Thermal analyses (TGA) were carried out using a Shimadzu DT-30 instrument under flowing nitrogen (30 cm³ min⁻¹). The sample (particle size 50–200 mesh) was heated at a rate of 10°C min⁻¹ with inert alumina used as a reference.

Syntheses

[Cd(me₄dpt)(SCN)₂] (**1**)

A methanol solution (5 cm³) of 3,3'-iminobis(*N,N*-dimethylpropylamine) (me₄dpt) (1 mmol, 0.187 g) was added dropwise to a well-stirred methanol solution (10 cm³) of

$\text{Cd}(\text{SCN})_2$ (1 mmol, 0.228 g). The resulting mixture was stirred for 30 min, then it was filtered and the filtrate kept in a CaCl_2 desiccator. After a few days the desired complex was obtained in the form of shiny single crystals (yield 80%). Anal. Calcd. for $\text{C}_{12}\text{H}_{25}\text{CdN}_5\text{S}_2$ (%): C, 34.6; H, 6.0; N, 16.9; Cd, 27.1. Found: C, 34.7; H, 6.2; N, 16.8; Cd, 27.3.

$[\text{Cd}(\text{SCN})_2(\text{me}_2\text{tn})_2]_n$ (2)

Complex **2** was synthesized using the same procedure adopted for Complex **1** (yield 70%). Anal. Calcd. for $\text{C}_7\text{H}_{14}\text{CdN}_4\text{S}_2$ (%): C, 18.2; H, 4.2; N, 16.9; Cd, 34.0. Found: C, 18.1; H, 4.3; N, 16.8; Cd, 34.3.

$\{\{\text{ampyH}\}\{\text{Cd}(\text{SCN})_3\}\}_n$ (3)

A methanol solution (5 cm^3) of 4-aminopyridine (ampy) (1 mmol, 0.094 g) was added dropwise to a well-stirred methanol solution (10 cm^3) of cadmium nitrate tetrahydrate (1 mmol, 0.308 g) and the resulting reaction mixture was allowed to stir for 15 min. Then, an aqueous solution (5 cm^3) of ammonium thiocyanate (2 mmol, 0.152 g) was added to the reaction mixture, which was refluxed for 1 h, cooled, filtered and the filtrate kept in a CaCl_2 desiccator. After a week, needle-shaped, shiny crystals suitable for X-ray structure determination were obtained. These were collected by filtration, washed and dried (yield 60%). Anal. Calcd. for $\text{C}_8\text{H}_7\text{CdN}_5\text{S}_3$ (%): C, 25.2; H, 1.6; N, 18.4; Cd, 29.5. Found: C, 25.1; H, 1.7; N, 18.5; Cd, 29.3.

Crystal Structure Determinations

Suitable single crystals of Complexes **1**, **2** and **3** were mounted on a Siemens CCD diffractometer equipped with graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.711073\text{ \AA}$) radiation. Crystallographic data, conditions for data collection and some features of the structure refinements of all the complexes are listed in Table I. Unit cell parameters and crystal-orientation matrices were determined for the complexes by least-squares refinements of all reflections. Intensity data were corrected for Lorentz and polarization effects [20] and empirical absorption corrections were also employed using the SAINT program for all complexes [21]. A total of 5508 [unique data, 2193; $R_{\text{int}} = 0.030$], 3882 [unique data, 1508; $R_{\text{int}} = 0.032$] and 8322 [unique data, 1718; $R_{\text{int}} = 0.029$] reflections was measured and 2019, 1232 and 1606 reflections were assumed to be observed applying the condition $I > 2\sigma(I)$ for Complexes **1**, **2** and **3** respectively. All structures were solved by direct methods followed by successive Fourier and difference Fourier syntheses. Full-matrix least-squares refinements on F^2 were carried out using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon or nitrogen atoms with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement of their parent atom in all cases. During refinement of Complex **2**, the diamine and the thiocyanate ligands are found to occupy two orientations [N(1), S(1), N(2), C(2), C(4), N(1A), S(1A), N(2A), C(2A), C(4A)] with 0.6/0.4 occupancy. The atom C(3) has symmetry-constrained disorder and C(1) is common to both orientations of the thiocyanate ligand. The refinement converged to residual indices

TABLE I Crystal data and structure refinement details for Complexes **1**, **2** and **3**

	1	2	3
Formula	C ₁₂ H ₂₅ CdN ₅ S ₂	C ₇ H ₁₄ CdN ₄ S ₂	C ₈ H ₇ CdN ₅ S ₃
Formula weight	415.92	330.77	381.77
<i>a</i> /Å	12.6115(9)	13.0985(15)	10.4399(5)
<i>b</i> /Å	9.6098(7)	8.9202(10)	9.5507(4)
<i>c</i> /Å	7.4312(5)	10.8952(12)	13.2644(6)
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
β /°		99.802(2)	
<i>T</i> /K	294	293	293(2)
<i>Z</i>	2	4	4
<i>V</i> /Å ³	900.62(11)	1254.4(2)	1322.57(10)
<i>F</i> (000)	424	656	744
λ (Mo K α)/Å	0.71073	0.71073	0.71073
<i>D</i> _{calc} /g cm ⁻³	1.534	1.752	1.917
μ (Mo K α)/mm ⁻¹	1.442	2.045	2.108
θ _{range} (Mo K α)/°	2.1–28.3	2.8–28.3	2.48–28.30
Total data	5508	3882	8322
Unique data; <i>R</i> _{int}	2193, 0.030	1508, 0.032	1718, 0.029
Observed data [<i>I</i> > 2 σ (<i>I</i>)]	2019	1232	1606
<i>R</i>	0.0300	0.0499	0.0227
<i>wR</i>	0.0623	0.0932	0.0630

TABLE II Selected bondlengths (Å) and angles (°) for Complex **1**

Cd–N(1)	2.255(5)	Cd–N(2)	2.208(6)
Cd–N(3)	2.378(3)	Cd–N(4)	2.329(4)
N(1)–Cd–N(2)	108.0(2)	N(1)–Cd–N(3)	85.53(14)
N(1)–Cd–N(4)	151.00(17)	N(1)–Cd–N(3) ^a	85.53(14)
N(2)–Cd–N(3)	102.28(9)	N(2)–Cd–N(4)	101.00(18)
N(2)–Cd–N(3) ^a	102.28(9)	N(3)–Cd–N(4)	88.39(16)
N(3)–Cd–N(3) ^a	155.39(11)	N(3) ^a –Cd–N(4)	88.39(16)
Cd–N(1)–C(1)	179.1(5)	Cd–N(2)–C(2)	141.3(5)
Cd–N(3)–C(3)	114.0(3)	Cd–N(3)–C(6)	107.9(2)
Cd–N(3)–C(7)	108.2(4)	Cd–N(4)–C(5)	113.5(2)
Cd–N(4)–C(5) ^a	113.5(2)	S(1)–C(1)–N(1)	178.5(6)
S(2)–C(2)–N(2)	179.4(6)		

^aSymmetry code: $-x, y, z$.TABLE III Hydrogen bonds (Å, °) for Complex **1**

<i>D</i> – <i>H</i> ··· <i>A</i>	<i>D</i> – <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> – <i>H</i> ··· <i>A</i>
N(4)–H(4)···S(1) ^a	0.91	2.664	3.564(4)	170.26
N(4)–H(4)···S(1) ^b	0.91	2.664	3.564(4)	170.26

Symmetry code: ^a $x, y, -1+z$; ^b $-x, y, -1+z$.

$R=0.030$ and $wR=0.062$; $R=0.050$ and $wR=0.093$; $R=0.023$ and $wR=0.063$ for Complexes **1**, **2** and **3**, respectively. Complex neutral atom scattering factors were used throughout for all cases. All calculations were carried out using SHELXS 97 [22], SHELXL97 [23], PLATON 99 [24] and ORTEP-3 [25] programs. Selected bondlengths and angles are given in Tables II, IV and VI and H-bonding parameters are listed in Tables III, V and VII for Complexes **1**, **2** and **3**, respectively.

TABLE IV Selected bondlengths (Å) and angles (°) for Complex 2

Major part			
Cd–S(1)	2.788(3)		
Cd–N(1)	2.294(10)		
Cd–N(2)	2.300(9)		
S(1)–Cd–N(2)	89.0(2)	N(1) ^b –Cd–N(1) ^c	174.1(4)
S(1)–Cd–S(1) ^a	88.05(8)	S(1)–Cd–N(2) ^a	176.3(3)
S(1)–Cd–N(1) ^b	91.9(3)	S(1) ^a –Cd–N(1) ^b	83.9(3)
S(1) ^a –Cd–N(2)	176.3(3)	N(2)–Cd–N(2) ^a	94.0(3)
S(1) ^a –Cd–N(2) ^a	89.0(2)	N(1) ^b –Cd–N(2) ^a	90.2(4)
N(1) ^b –Cd–N(2)	93.8(4)	C(2)–N(2)–C(4)	94.4(9)
Cd–N(2)–C(2)	114.3(7)	Cd–S(1)–C(1)	99.4(2)
Cd–N(2)–C(4)	111.1(7)	S(1)–C(1)–N(1)	175.5(7)
Cd ^b –N(1)–C(1)	161.6(8)		
Minor part			
Cd–S(1A)	2.917(4)		
Cd–N(1A)	2.229(12)		
Cd–N(2A)	2.430(17)		
S(1A) ^b –Cd–S(1A) ^c	162.88(13)	N(1A)–Cd–N(2A)	95.0(5)
Cd–N(2A)–C(2A)	118.9(16)	N(1A)–Cd–N(1A) ^a	92.1(4)
C(2A)–N(2A)–C(4A)	116.8(19)	N(1A)–Cd–N(2A) ^a	168.9(5)
S(1A) ^b –Cd–N(1A)	91.3(3)	S(1A) ^c –Cd–N(1A)	100.6(3)
N(1A) ^a –Cd–N(2A)	168.9(6)	N(2A)–Cd–N(2A) ^a	79.4(6)
S(1A) ^b –Cd–N(2A)	87.8(5)	S(1A) ^c –Cd–N(2A)	79.0(5)
S(1A)–C(1)–N(1A)	173.5(7)	N(1A) ^a –Cd–N(2A) ^a	95.0(5)
S(1A) ^b –Cd–N(1A) ^a	100.6(3)	S(1A) ^c –Cd–N(1A) ^a	91.3(3)
S(1A) ^b –Cd–N(2A) ^a	79.0(5)	S(1A) ^c –Cd–N(2A) ^a	87.8(5)
Cd ^b –S(1A)–C(1)	96.2(3)	Cd–N(2A)–C(4A)	107.6(10)
Cd–N(1A)–C(1)	159.6(8)		

Symmetry code: ^a1 – x, y, $\frac{3}{2}$ – z; ^b1 – x, 1 – y, 1 – z; ^cx, 1 – y, $\frac{1}{2}$ + z.

TABLE V Hydrogen bonds (Å, °) for Complex 2

<i>D</i> – <i>H</i> ··· <i>A</i>	<i>D</i> – <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> – <i>H</i> ··· <i>A</i>
N(2)–H(2)···S(1)	0.91	2.578	3.350(10)	143.02

Symmetry code: $\frac{3}{2}$ – x, $-\frac{1}{2}$ + y, $\frac{3}{2}$ – z.

TABLE VI Bondlengths (Å) and angles (°) for Complex 3

Cd–N(2) ^a	2.292(2)	Cd–N(1) ^b	2.3649(18)
Cd–N(1) ^c	2.3649(18)	Cd–S(2)	2.6965(7)
Cd–S(1)	2.7209(5)	Cd–S(1) ^d	2.7209(5)
Cd ^a –N(1)	2.3649(18)	Cd ^c –N(2)	2.292(2)
N(2) ^a –Cd–N(1) ^b	88.05(6)	N(2) ^a –Cd–N(1) ^c	88.05(6)
N(1) ^b –Cd–N(1) ^c	88.44(10)	N(2) ^a –Cd–S(2)	176.58(6)
N(1) ^b –Cd–S(2)	89.50(4)	N(1) ^c –Cd–S(2)	89.50(4)
N(2) ^a –Cd–S(1)	92.98(4)	N(1) ^b –Cd–S(1)	177.71(5)
N(1) ^c –Cd–S(1)	89.56(5)	S(2)–Cd–S(1)	89.387(15)
N(2) ^a –Cd–S(1) ^d	92.98(4)	N(1) ^b –Cd–S(1) ^d	89.56(5)
N(1) ^c –Cd–S(1) ^d	177.71(5)	S(2)–Cd–S(1) ^d	89.387(15)
S(1)–Cd–S(1) ^d	92.42(3)	C(1)–S(1)–Cd	98.64(6)
N(1)–C(1)–S(1)	178.55(18)	N(2)–C(2)–S(2)	179.6(2)

Symmetry code: ^ax + $\frac{1}{2}$, y, –z + $\frac{1}{2}$; ^bx – $\frac{1}{2}$, –y + $\frac{1}{2}$, –z + $\frac{1}{2}$; ^cx – $\frac{1}{2}$, y, –z + $\frac{1}{2}$; ^dx, –y + $\frac{1}{2}$, z.

TABLE VII Hydrogen bonds (Å, °) for Complex 3

<i>D-H...A</i>	<i>D-H</i>	<i>H...A</i>	<i>D...A</i>	<i>D-H...A</i>
N(4)–H(4A)···N1 ^a	0.86	2.498	3.318(2)	159.79
N(4)–H(4B)···N1 ^b	0.86	2.499	3.318(2)	159.44

Symmetry code: ^a2 - *x*, -½ + *y*, 1 - *z*; ^b2 - *x*, 1 - *y*, 1 - *z*.

RESULTS AND DISCUSSION

Infrared Spectra

Several strong bands in the range 3240–3360 cm⁻¹ are observed, which can be assigned to the ν(NH) stretch of the me₄dpt, me₂tn and ampy ligand in **1**, **2** and **3**, respectively. Complexes **1** and **2** show several bands in the range 2800–3000 cm⁻¹ assigned to aliphatic ν(CH) vibrations. The most intense split ν(CN) bands are observed at 2031 and 2072 cm⁻¹ (**1**), at 2101 cm⁻¹ (**2**) and at 2085 and 2107 cm⁻¹ (**3**). The higher frequencies are consistent with the bridging thiocyanato group whereas the lower frequency may be assigned to a terminally bound thiocyanato group [26]. All other bands appear at usual positions.

Crystal Structures

[Cd(me₄dpt)(SCN)₂]_n (**1**)

A ZORTEP drawing of the asymmetric unit with the atom numbering scheme of **1** is shown in Fig. 1. The structure determination reveals that in the mononuclear fragment each cadmium(II) centre is linked with one triamine (me₄dpt) and two thiocyanate ligands to give a CdN₅ chromophore. The coordination environment of each cadmium(II) ion is best described as a highly distorted square pyramid with N(1), N(3), N(3*) (* = -*x*, *y*, *x*), N₄ atoms in the equatorial plane and N(2) at the axial site. Equatorial bondlengths are Cd–N(1) 2.255(5), Cd–N(3) 2.378(3) and Cd–N₄, 2.329(4) Å and the axial bondlength is Cd–N(2) 2.208(6) Å. The Cd–N(3) and Cd–N(3*) bondlengths are higher than the corresponding equatorial bondlengths owing to steric effects exerted by the two methyl groups attached to N(3) and N(3*) atoms. The deviation of the cadmium atom from the mean square plane is about 0.539 Å. Bond angles in the equatorial plane are in the range 85.5–88.4° and the axial bond angles are in the range 101.0–108.0° and reflect distortions from ideal square pyramidal geometry. The most interesting feature of this structure is the orientation of the two pendent thiocyanate ligands; Cd–N(1)–C(1)–S(1) is almost linear 179.1(5)° and Cd–N(2)–C(2)–S(2) is bent 141.3(3)°. Each mononuclear fragment is engaged in intermolecular H-bonding through S(1) of one pendent thiocyanate ligand with an H-atom of the secondary N atom of me₄dpt (N(4)–H(4)···S(1), 2.664 Å, 170.3°, *x*, *y*, -1 + *z*) forming a 1D supramolecular chain (Fig. 2). This chain lies along the crystallographic *z* direction. The shortest distance between the two Cd centres in the supramolecular array is 9.610 Å.

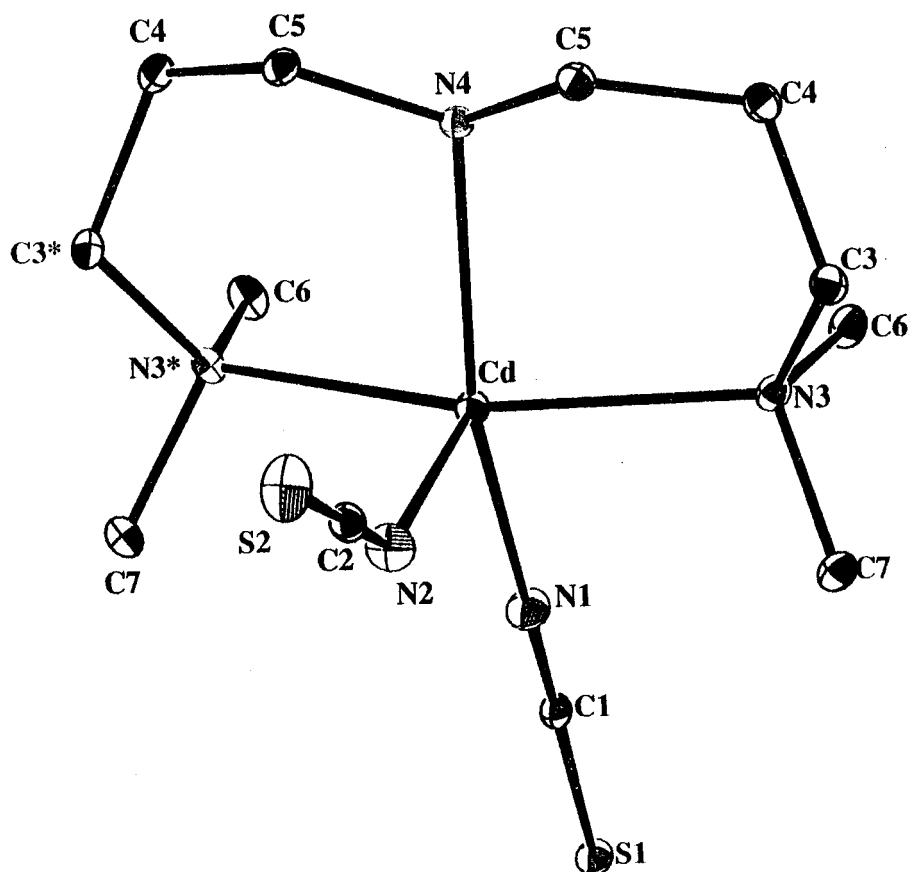


FIGURE 1 ORTEP diagram of [Cd(me₄dpt)SCN]₂, 1, with the atom labelling scheme, showing 50% probability thermal ellipsoids for all non-hydrogen atoms.

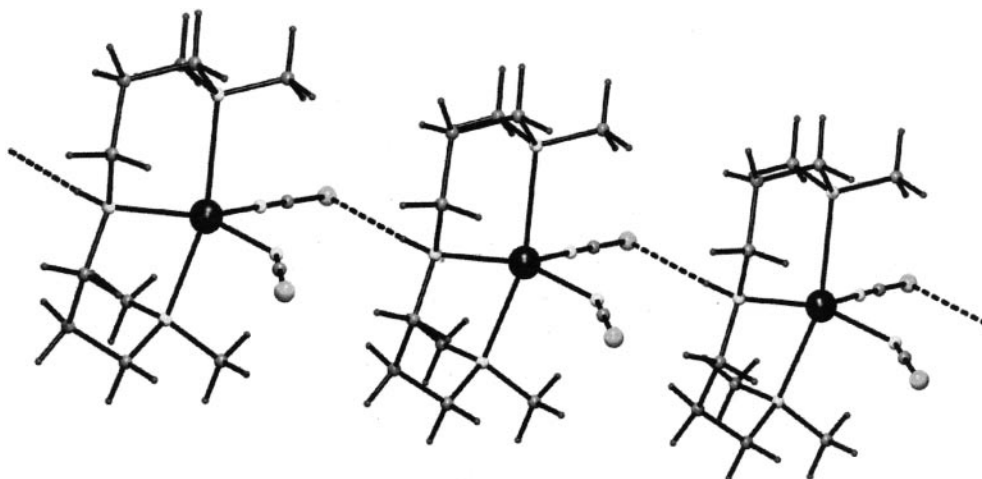


FIGURE 2 Infinite 1D supramolecular view of 1 showing H-bonding motifs along the *z* direction.

$[Cd(me_2tn)(SCN)_2]_n$ (**2**)

The structure determination of Complex **2** reveals that cadmium(II) ions are bridged by end-to-end thiocyanate ligands to form a 1D polymeric infinite chain. A ZORTEP drawing of the chain with the atom labelling scheme is shown in Fig. 3. Each cadmium(II) is linked with two of its neighbouring, symmetry-related counterparts (Cd^*), by two thiocyanate ligands, i.e., each cadmium(II) is ligated by four bridging ligands. This feature makes the structure unique. The coordination environment of each cadmium(II) is best described as a distorted octahedron with a CdN_4S_2 chromophore. The two nitrogen atoms [N(2), N(2*), * = 1 - x, y, 3/2 - z] of the diamine ligand and the sulfur atoms [S(1), S(1*)] from the two bridging thiocyanate ligands form the equatorial plane around the cadmium(II) centre. The trans axial sites are occupied by N(1) and N(1*) (* = 1 - x, 1 - y, 1 - z) from the other two bridging thiocyanate ligands. The cadmium atoms lie on a two-fold axis and sit perfectly in the equatorial plane without any deviation; the maximum deviation of any equatorial atoms [N(2)] from the mean plane around cadmium(II) is 0.054 Å. Cd(II)-N bond lengths are 2.294(10)-2.300(9) Å for the major part, 2.229(12)-2.430(7) Å for the minor part and the bridging Cd(II)-S distances are Cd-S 2.788(3), Cd-S(1A) 2.917 Å. Though these distances for the most part of the disordered structure are consistent with corresponding values of the cadmium(II) thiocyanate bridging system, values for the minor part show elongation. Cd-S-C, Cd-N-C angles in the bridge are 99.4(2), 161.6(8)° for the major part and 96.2(3), 159.6(8)° for the minor part, respectively. From the available structural data for polynuclear μ -thiocyanato cadmium(II) complexes, bridging Cd-S-C and Cd-N-C angles are in the range 99-101.4° and 159-168.4°, respectively [13-16]. The bridging N(1)-C(1)-S(1) ligand is *quasilinear* at 175.5(7)°, \angle N(1A)-C(1)-S(1A) 173.5(7)°. The nearest Cd...Cd distance within the chain is 5.933 Å and the shortest intermolecular Cd...Cd separation

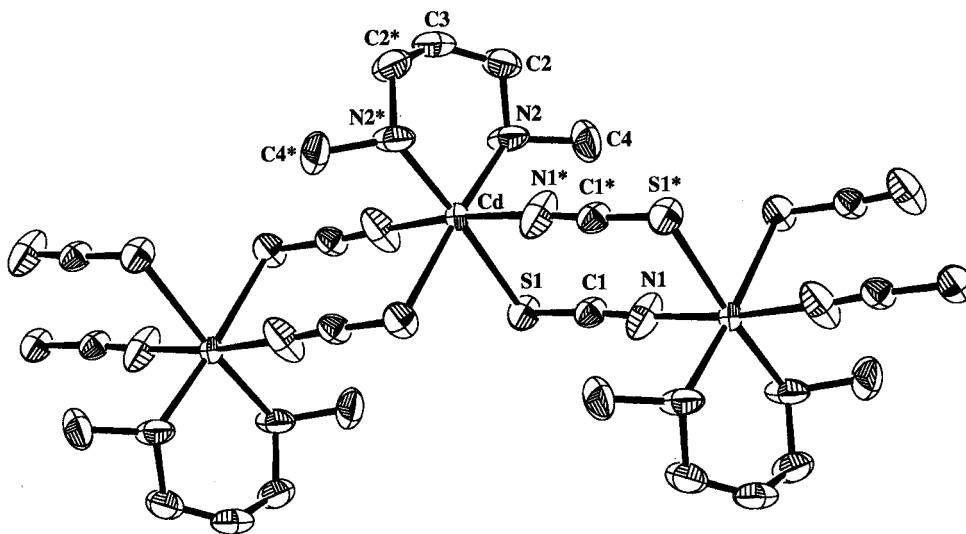


FIGURE 3 ORTEP diagram of $[Cd(me_2tn)(NCS)_2]_n$, **2**, with the atom labelling scheme, showing 50% probability thermal ellipsoids for all non-hydrogen atoms.

is 7.924 Å. Other bond distances and angles are close to expected values. Intramolecular (H(2):S1 2.578 Å, \angle N2–H(2):S(1) 143.02°) H-bonding interactions stabilize the overall conformation.

[{*amplyH*}{Cd(SCN)₃}]_n (3)

The anionic [Cd(SCN)₃]_n[−] chains in the structure are very similar to those reported by Teo *et al.* [27–29]. Cd and the ligands, S(1)–C(1)–N(1) and S(2)–C(2)–N(2), reside on a crystallographic mirror plane (at $y=0.25$) while the N(3), N(4), C(5) atoms of 4-aminopyridinium cations are related by the same mirror. A ZORTEP drawing of the anionic chain, [Cd(SCN)₃]_n[−] with the atom labelling scheme is shown in Fig. 4. Cd atoms in the infinite chains are octahedrally coordinated with three S and three N atoms (in *fac* configuration) with N atoms trans to S atoms as a result of trans influences which dictate that the sulfurs are trans to the nitrogens of the thiocyanate group. The three N–Cd–S angles average 177.3°, which is higher than values reported (174.3° and 171.6°) in a similar system and very close to linearity. The Cd atoms form infinite zig-zag chains with Cd···Cd distances of 5.38 Å and Cd···Cd···Cd angles of 151.92°, a little smaller than value reported for the similar chain of 161.2° and 164.7°. The zig-zag chains are parallel to one another and run along the crystallographic *a* direction. They are arranged in an approximately hexagonal array with cations occupying triangular channels (Fig. 5). N(4) of aminopyridinium is engaged in two distinct and strong H-bonding interactions with N(1) atoms of adjacent chains [H(4A)···N(1) 2.498 Å, \angle N(4)–H(4A)···N(1) 159.8°; H(4B)···N1 2.499 Å, \angle N(4)–H(4B)···N(1) 159.4°]. As shown in Fig. 6, this arrangement results in a supramolecular 2D sheet in the *ab* plane.

Thermal Investigations

The complexes, [Cd(me₄dpt)(SCN)₂] (1) and [Cd(me₂tn)(SCN)₂]_n (2) upon heating melt as evident in DSC experiments which show a sharp endotherm (temperature range 155–170°C; peak temperature 168°C) with $\Delta H = 77.2 \text{ J g}^{-1}$ for Complex 1 and a broad endotherm (temperature range 95–135°C; peak temperature 124°C) with $\Delta H = 35.1 \text{ J g}^{-1}$ for Complex 2. Upon cooling to ambient temperatures the molten samples do not show any exotherm and do not revert on keeping them in a humid

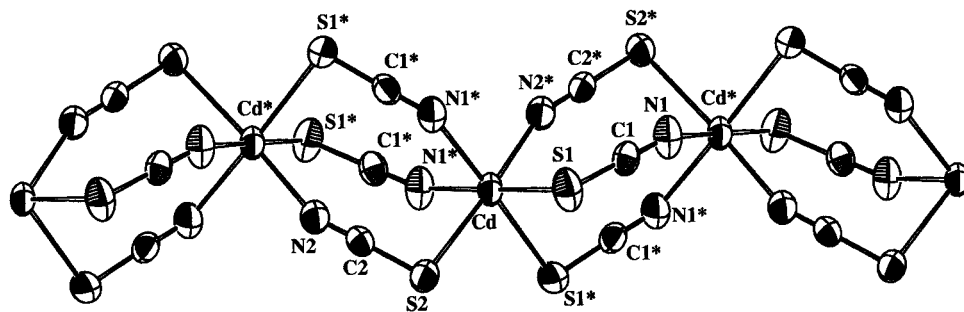


FIGURE 4 ORTEP diagram showing the infinite 1D anionic single chain of [Cd(SCN)₃]_n[−], 3.

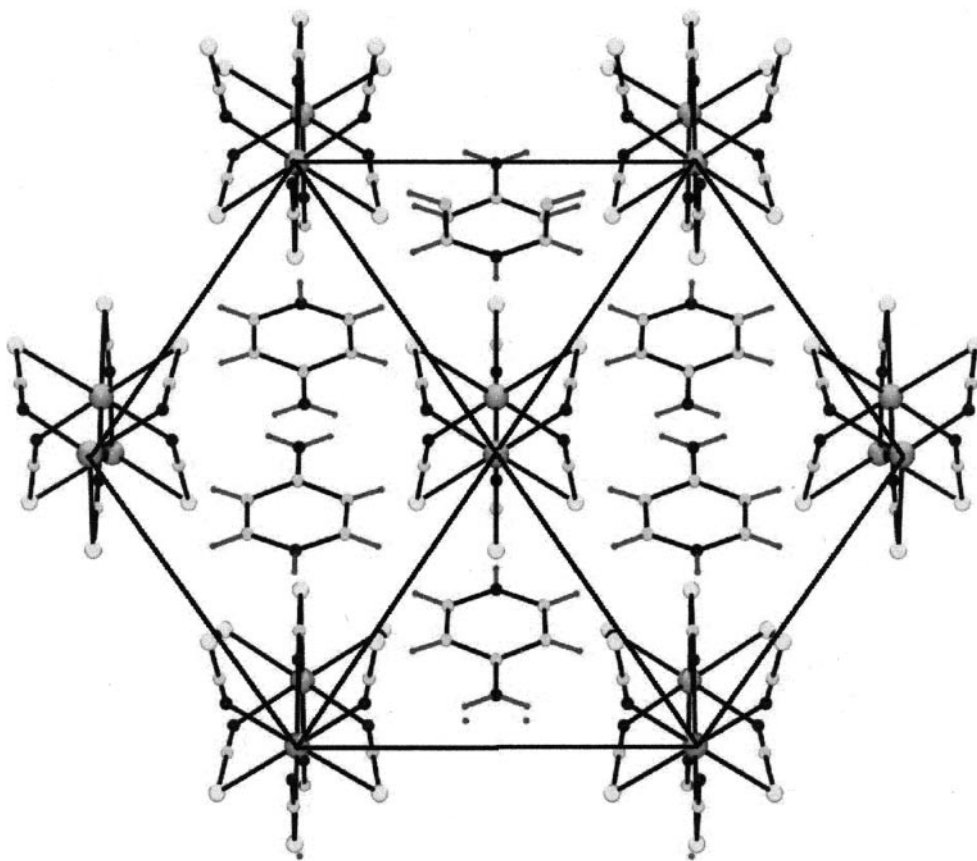


FIGURE 5 $[\text{Cd}(\text{SCN})_3]^-$ zig-zag arranged in an approximately hexagonal array with the cations, ampyH, occupying triangular channels.

atmosphere (RH \sim 60%). It is worth mentioning that molten samples transform to transparent solid masses after a few days and these, upon scratching, become white powders. Upon reheating, the same phenomenon is observed. Complex **3** upon heating loses 4-aminopyridine and transforms to $[\text{H}]\text{Cd}(\text{SCN})_3$ at $\sim 195^\circ\text{C}$ as is evident from the TGA curve.

Complex **1**, $\text{Cd}(\text{me}_4\text{dpt})(\text{SCN})_2$, shows pentacoordinated cadmium(II) with two pendent ambidentate thiocyanate ligands, similar to the single-2 crystal structure of $\text{Cd}(\text{dpt})(\text{SCN})_2$ [dpt = bis(3-aminopropyl)amine] reported by Cannas *et al.* [30]. Complexes $\text{Cd}(\text{apa})(\text{SCN})_2$ and $\text{Cd}_3(\text{baa}/\text{mebaa})(\text{SCN})_6 \cdot n\text{H}_2\text{O}$ show 2D and 3D polymeric structures [14–16], respectively. Recently Mitra *et al.* [10] reported similar thiocyanato-bridged 2D and 1D structures of cadmium(II) with a diamine as coligand, $\text{Cd}(\text{dmen})(\text{SCN})_2$ (dmen = *N,N*-dimethylethylenediamine) and $\text{Cd}(\text{deen})(\text{SCN})_2$ (deen = *N,N*-diethylethylenediamine). Based on the above, chain length and substitution at the nitrogen/carbon atom of the linear amines play vital roles in making novel thiocyanato-bridged chain polymeric architectures. Complex **3** shows a 1D anionic thiocyanato-bridged chain in which the cations, ampyH, occupy positions between the 1D chain layers. In solution, 4-aminopyridine molecules are protonated

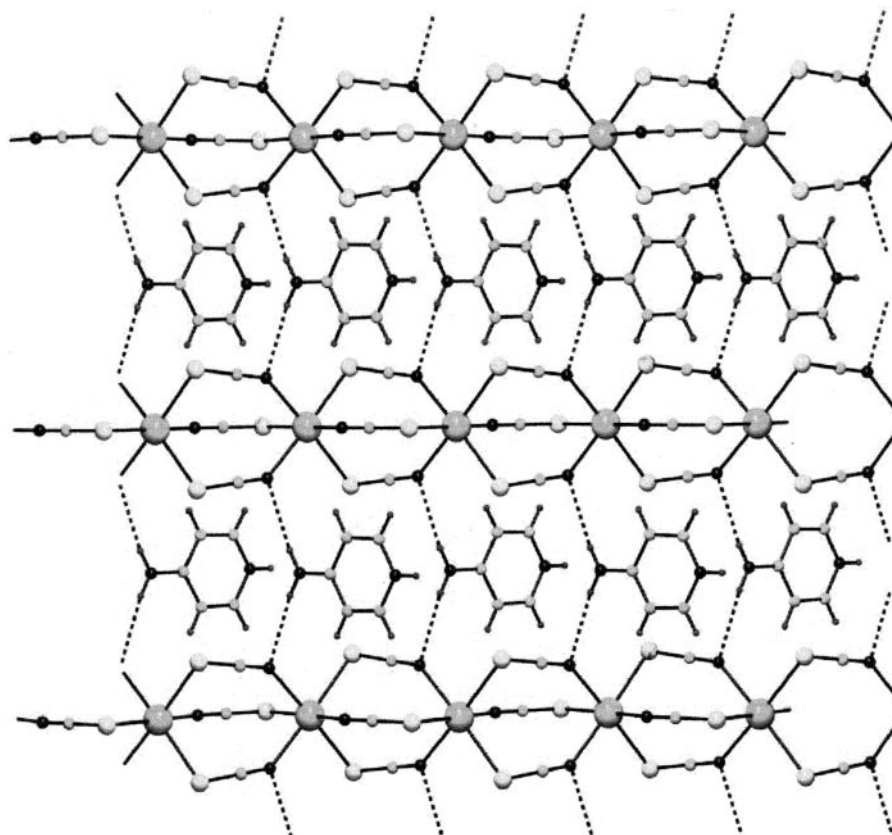


FIGURE 6 Infinite 2D H-bonded sheet of Complex 3 lying on the *ab* plane.

by water forming 4-aminopyridinium cations and OH^- anions. The formation of 4-aminopyridinium cations in solution is a key factor for the formation of the unique zig-zag arrangement of the anionic $[\text{Cd}(\text{SCN})_3]^-$ chains.

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Supplementary Material

Tables of X-ray crystallographic data in CIF format for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. 186913 (Complex 1), 186914 (Complex 2) and 186915 (Complex 3). Copies of this information may be obtained free of charge from the Director,

CCDC, 12 Union Road, Cambridge CB12 1EW, UK (fax: +44-1223-336033; e-mail: deposits@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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