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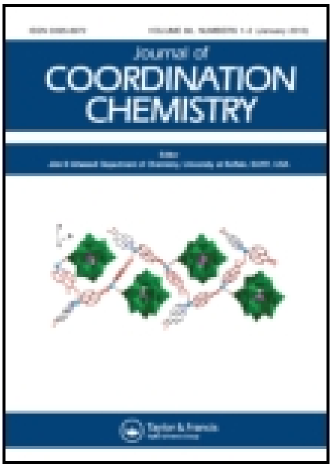

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A family of double-layered coordination polymers containing Cd^{2+}, N,O-chelating ligands, and bridging SCN^- and Cl^-

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A family of double-layered coordination polymers containing Cd^{2+}, N,O-chelating ligands, and bridging SCN^- and Cl^-

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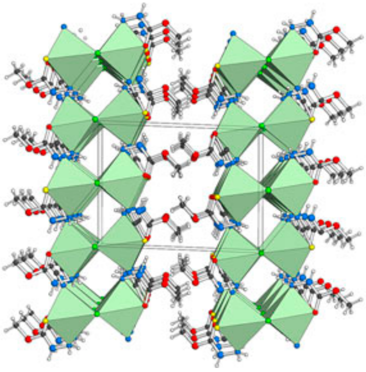

The syntheses, structures, and characterization (IR, TGA/DTA) of a family of layered coordination polymers containing Cd^{2+}, bridging anions (SCN^- and Cl^-), and chelating $C_2H_6N_2O_2$ methyl carbazate (mc) and $C_3H_8N_2O_2$ ethyl carbazate (ec) ligands are described, viz: $Cd(SCN)_2(C_2H_6N_2O_2)$, $Cd(SCN)Cl(C_2H_6N_2O_2)$, $Cd(SCN)_2(C_3H_8N_2O_2)$, and $Cd(SCN)Cl(C_3H_8N_2O_2)$. Single-crystal structures show them to contain distorted CdN_3OS_2 (for the thiocyanate) and CdN_2OCl_2S (for the thiocyanate/chloride) octahedra, in which the mc and ec ligands adopt an N,O-bidentate coordination mode, and the four anions bridge adjacent metal ions, which leads to polymeric sheets built up from double-octahedral layers propagating in the (1 0 0) plane. The topological linkage of the metal ions, which is the same in each structure, can be described as a distorted hexagonal grid. The crystal structures are completed by weak N–H⋯O, N–H⋯N, N–H⋯Cl, and N–H⋯S hydrogen bonds, which all occur within the (1 0 0) polyhedral layers.

Keywords: Layered coordination network; Bridging ligand; Bidentate ligand; Crystal structure

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Introduction

A remarkable variety of functional materials containing different types of molecular and supramolecular architectures incorporating strong metal–ligand covalent bonds and non-covalent weak interactions have been synthesized [1, 2]. Extensive investigations have been made into the roles of different types of organic and inorganic ligands in establishing these networks [3, 4]. An important strategy for generation of new supramolecular architectures involves the use of neutral ligands having both hydrogen bond donor and acceptor capabilities [5, 6].

One interesting family of donor/acceptor ligands that have been less explored are alkyl carbazates, i.e. the alkyl esters of hydrazine carboxylic acid, $NH_2NHCOOH$. These usually show N,O-bidentate coordination to the metal [7], their NH_2 and NH groups can act as hydrogen bond donors, and their N and O can act as hydrogen bond acceptors. As part of our ongoing studies of metal–organic network solids constructed from bridging ligands combined with neutral organic blocking (chelating) units [8], we now describe the syntheses, crystal structures, and results of physical characterization of a family of structurally related layered coordination polymers, $Cd(SCN)_2(C_2H_6N_2O_2)$ (**1**), $CdCl(SCN)(C_2H_6N_2O_2)$ (**2**), $Cd(SCN)_2(C_3H_8N_2O_2)$ (**3**) and $CdCl(SCN)(C_3H_8N_2O_2)$ (**4**), where $C_2H_6N_2O_2$ = methyl carbazate (mc) and $C_3H_8N_2O_2$ = ethyl carbazate (ec).

Experimental

Physical measurements

All reagents were of analytical grade and used as received. Elemental analyses (C, H, and N) were measured on a Perkin-Elmer–240B CHN element analyzer. The metal contents were determined by using EDTA complexometric titrations. Hydrazine and thiocyanate contents were determined volumetrically using a standard KIO_3 (0.025 M) solution [9, 10]. IR spectra were recorded from 4000 to 400 cm^{-1} on a Shimadzu FTIR 8000 spectrometer using KBr pellets. Solid-state fluorescent studies were conducted at room temperature on a JY-Fluorolog-FL3-1 spectrofluorometer. Combined thermogravimetric/differential thermal analyses were performed on a Perkin-Elmer Pyris Diamond thermal analyzer from room temperature to 850 °C under oxygen with a heating rate of 20 °C min^{-1}.

Synthesis and characterization

Preparation of $Cd(SCN)_2(C_2H_6N_2O_2)$ (1). Methyl carbazate (0.178 g, 0.002 M) was dissolved in 30 mL of an aqueous solution containing ammonium thiocyanate (0.152 g, 0.002 M). To this, cadmium nitrate tetrahydrate (0.308 g, 0.001 M) dissolved in 30 mL of water was added. The resultant colorless solution was concentrated on a water-bath to about one third of its initial volume and then left at room temperature in an open container. After a week, colorless blocks of **1** were recovered by vacuum filtration and rinsing with water and acetone. Yield based on metal = 72%. Analysis: found (Calcd) %: N_2H_4 9.90 (10.05); SCN^- 36.30 (36.43); Cd 35.10 (35.30); C 14.98 (15.07); N 17.43 (17.59); H 1.87 (1.88).

Table 1. Crystallographic and data-collection parameters.

	1	**2**	**3**	**4**
Empirical formula	$C_4H_6CdN_4O_2S_2$	$C_3H_6CdClN_3O_sS$	$C_5H_8CdN_4O_2S_2$	$C_4H_8CdClN_3O_2S$
Formula weight	318.65	296.02	332.67	310.05
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	14.6089(5)	12.4985(8)	16.0202(9)	13.4764(13)
b (Å)	7.3152(3)	7.4837(5)	7.4452(4)	8.0603(8)
c (Å)	9.4400(3)	9.5271(6)	9.5184(5)	9.1887(9)
β (°)	91.870(2)	92.128(2)	92.5120(10)	92.204(2)
V (Å^3)	1008.29(6)	890.50(10)	1134.20(11)	997.37(17)
Z	4	4	4	4
T (K)	120	298	298	298
ρ_{Calcd} (g cm^{-3})	2.099	2.208	1.948	2.065
μ (mm^{-1})	2.554	2.943	2.275	2.633
Data scanned	12,626	7693	7607	6577
R_{Int}	0.044	0.056	0.019	0.023
Unique data	2318	2196	2591	2260
S (goodness of fit)	1.07	1.10	1.04	1.07
R (F)	0.024	0.026	0.026	0.026
wR (F^2)	0.057	0.067	0.069	0.070
$\Delta\rho$ limits (e Å^{-3})	−0.74, +0.69	−0.72, +0.88	−0.40, +0.53	−0.45, +0.83

Preparation of $CdCl(SCN)(C_2H_6N_2O_2)$ (2). This compound was prepared as described above for **1** by using cadmium chloride (0.183 g, 0.001 M) as a starting material instead of cadmium nitrate. The well-shaped colorless blocks of **2** obtained after five days were separated as before. Yield: 73%. Analysis: found (Calcd) %: N_2H_4 11.00 (10.82); SCN^- 19.70 (19.60); Cd 38.10 (37.99); C 11.99 (12.17); N 14.03 (14.20); H 1.98 (2.03).

Preparation of $Cd(SCN)_2(C_3H_8N_2O_2)$ (3). This compound was prepared as above for **1** by using ethyl carbazate (0.208 g, 0.002 M) in place of methyl carbazate. The colorless blocks of **3** obtained after five days were separated as before. Yield: 78%. Analysis: found (Calcd) %: N_2H_4 9.80 (9.63); SCN^- 33.80 (34.93); Cd 33.20 (33.82); C 18.34 (18.05); N 16.06 (16.85); H 2.82 (2.41).

Preparation of $CdCl(SCN)(C_3H_8N_2O_2)$ (4). This compound was prepared as above for **1** by using $CdCl_2$ (0.183 g, 0.001 M) in place of cadmium nitrate and ethyl carbazate (0.208 g, 0.002 M) in place of methyl carbazate to yield colorless blocks of **4** after five days. Yield: 82%. Analysis: found (Calcd) %: N_2H_4 10.10 (10.33); SCN^- 18.20 (18.73); Cd 36.70 (36.28); C 15.20 (15.49); N 13.68 (13.55); H 2.13 (2.58).

Crystal structure determinations

Intensity data for **1** (colorless block, 0.38 mm × 0.31 mm × 0.16 mm) were collected on a Nonius KappaCCD diffractometer at 120 K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical (multi-scan) absorption correction was applied during data reduction and the structure was routinely solved in space group $P2_1/c$ (No. 14) by direct methods with SHELXS97 and the structural model developed and refined against $|F|^2$ by full-matrix non-linear least squares with SHELXL97 [11]. The hydrogens were located in difference maps and then relocated to idealized locations and refined as riding (C–H = 0.98 Å;

N–H = 0.88–0.92 Å) with the constraint U_{iso}(H) = 1.2U_{eq} (carrier) [1.5U_{eq}(C) for methyl H atoms] applied. Data for **2** (colorless block, 0.35 mm × 0.30 mm × 0.25 mm), **3** (colorless block, 0.35 mm × 0.30 mm × 0.25 mm), and **4** (colorless chunk, 0.30 mm × 0.30 mm × 0.20 mm) were collected at room temperature using a Bruker APEXII diffractometer (Mo Kα radiation). The data reduction, structure solution, and refinement steps were the same as for **1** and the space group was found to be $P2_1/c$ in each case. The methyl group of the ec ligand in **3** was disordered over two sets of sites in a 0.753(9) : 0.247(9) ratio. Key crystallographic parameters are summarized in table 1 and full details are available in the Supplementary material (cif files).

Results

IR spectroscopy

IR spectra for **1–4** resemble each other (figures S1–S4, see online supplemental material at http://dx.doi.org/10.1080/00958972.2013.867038) and the bands were assigned by comparison to literature data [12]. All spectra show a very strong SCN$^-$ band at ~2100 cm^{-1}. The spectra each exhibit a band around 1695 cm^{-1}, which is characteristic of the C=O (ester group) stretch of ethyl carbazate. The shift to lower frequency in these metal complexes compared to the free ligand (1735 cm^{-1}) indicates that the carbonyl oxygen is coordinated [13]. Besides these, absorptions centered around 3240 and 1120 cm^{-1} are in accord with N–H and N–N stretching vibrations, respectively, of the carbazate ligand, signifying coordination of the terminal nitrogen to the metal [14].

Crystal structures

Structure of 1. Selected geometrical data for $Cd(SCN)_2(C_2H_6N_2O_2)$ (**1**) are given in table 2. Its asymmetric unit consists of one cadmium ion, two thiocyanates, and a methyl carbazate (figure 1). The Cd^{2+} adopts a substantially distorted $CdON_3S_2$ octahedral coordination geometry, arising from an N,O-bidentate mc ligand (bite angle = 68.37(7)°), two N-bonded thiocyanates, and two S-bonded thiocyanates. The three nitrogens are meridional within the octahedron (with the two thiocyanate nitrogens *cis*), sulfurs are *cis*, and the mc

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cd1–N2	2.264(3)		Cd1–N1	2.285(3)
Cd1–N3	2.394(2)		Cd1–O1	2.4226(19)
Cd1–S2$^{\mathrm{i}}$	2.6249(8)		Cd1–S1$^{\mathrm{ii}}$	2.7492(7)
N2–Cd1–N1	91.25(10)		N2–Cd1–N3	92.86(9)
N1–Cd1–N3	150.50(9)		N2–Cd1–O1	96.62(8)
N1–Cd1–O1	82.14(8)		N3–Cd1–O1	68.37(7)
N2–Cd1–S2$^{\mathrm{i}}$	95.89(7)		N1–Cd1–S2$^{\mathrm{i}}$	104.46(7)
N3–Cd1–S2$^{\mathrm{i}}$	104.15(6)		O1–Cd1–S2$^{\mathrm{i}}$	165.72(5)
N2–Cd1–S1$^{\mathrm{ii}}$	175.72(7)		N1–Cd1–S1$^{\mathrm{ii}}$	84.47(7)
N3–Cd1–S1$^{\mathrm{ii}}$	90.95(6)		O1–Cd1–S1$^{\mathrm{ii}}$	82.96(5)
S2$^{\mathrm{i}}$–Cd1–S1$^{\mathrm{ii}}$	85.07(2)			
N3–H3A···N2$^{\mathrm{iii}}$	0.92	2.55	3.336(4)	144
N3–H3B···S2$^{\mathrm{iv}}$	0.92	2.84	3.659(3)	149
N4–H4···O1$^{\mathrm{iii}}$	0.88	2.29	2.935(3)	130

Symmetry codes: (i) $2-x$, $1-y$, $-z$; (ii) x, $3/2-y$, $1/2+z$; (iii) x, $1/2-y$, $1/2+z$; (iv) $2-x$, $1/2+y$, $1/2-z$.

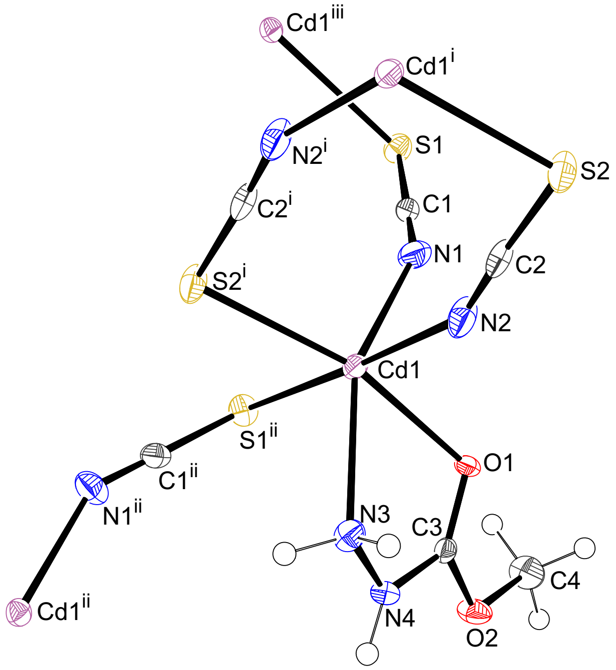

Figure 1. The asymmetric unit of **1** expanded to show the full coordination sphere of the cadmium and links to nearby Cd^{2+} ions (50% displacement ellipsoids for the non-hydrogen atoms). Symmetry codes: (i) $2-x$, $1-y$, $-z$; (ii) x, $3/2-y$, $1/2+z$; (iii) x, $3/2-y$, $z-1/2$.

O is *trans* to a thiocyanate S. A PLATON [15] analysis of the metal coordination polyhedron indicated that the bond-valence sum for Cd^{2+} is 2.13 (expected 2.00), the octahedral volume is 18.88 $Å^3$, and the X–Cd–Y angular variance [16], which is a measure of distortion of the *cis* octahedral bond angles from 90°, has the value of $103.0°^2$.

The conformation of the five-membered –Cd1–N3–N4–C3–O1– chelate ring in **1** is well described as an envelope with the metal as the flap, considerably displaced by −0.859(5) Å from the mean plane of the four ligand atoms, which are almost coplanar (rms deviation = 0.018 Å). The geometrical parameters for the thiocyanates are unexceptional; the N–C–S bond angles are 179.1(3)° and 176.7(3)°. However, the Cd–N–C and Cd–S–C bond angles are very different: the former have values of 151.6(2)° and 155.5(2)°, whereas the latter are 94.21(10)° and 99.16(10)° for the N1- and N2-containing ions, respectively.

In the extended structure of **1**, both the thiocyanates bridge to adjacent cadmium ions: the N2/C2/S2 anion and its inversion-related partner link two Cd ions (separation = 5.7510 (4) Å) to generate an eight-membered $Cd_2(SCN)_2$ ring (figure 1). The ring has a shallow "extended chair" conformation, with metals displaced by ±0.515(4) Å from the thiocyanates. The other SCN^- links the metal ions into [0 0 1] chains, with the mc ligands all lying to the same side of the chain. Each nitrogen + sulfur pair (N1 + S1^{ii} and N2 + S2^{i} for the unique Cd; see figure 1) from the same crystallographically independent thiocyanate ion have a *cis* conformation about any particular metal.

When the linkages of both thiocyanates are considered together, a polymeric, layered network propagates parallel to (1 0 0). In terms of the metal coordination polyhedra, double-octahedral layers result (figure 2), with the methyl groups of the mc ligands projecting into

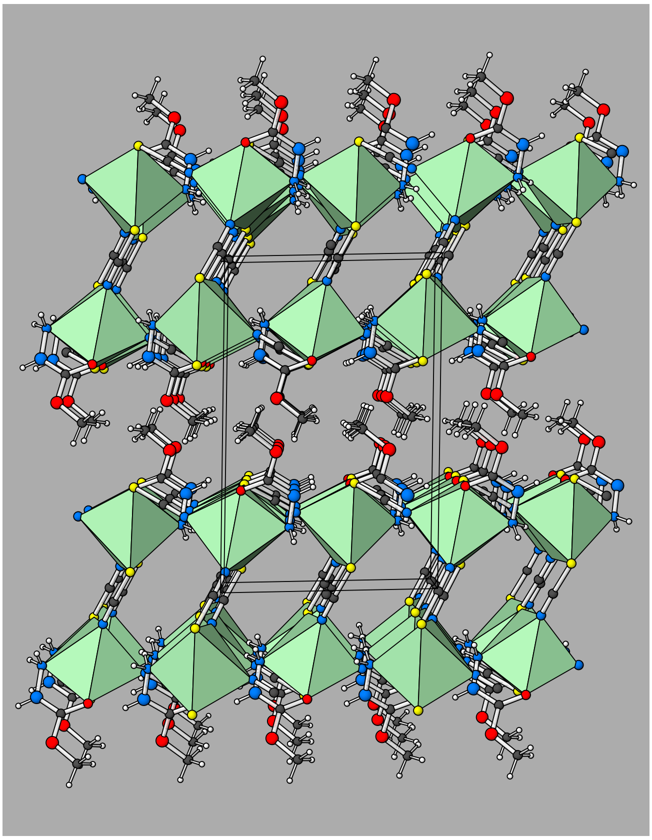

Figure 2. Polyhedral view approximately down [0 1 0] of the structure of **1** showing the linkage of cadmium octahedra into double layers propagating in (1 0 0).

the inter-layer regions. Topologically, in terms of metal–metal connectivity, a highly puckered hexagonal network arises (figure 3). The structure of **1** also features N–H···O, N–H···N, and weak N–H···S hydrogen bonds (table 2), which all occur within a layer.

Structure of 2. Key distance and angle data for $CdCl(SCN)(C_2H_6N_2O_2)$ (**2**) are given in table 3. Its asymmetric unit contains one cadmium ion, one chloride, one thiocyanate, and a chelating methyl carbazate (figure 4). The Cd^{2+} adopts a distorted $CdON_2Cl_2S$ octahedral coordination geometry, arising from the N,O-bidentate mc (bite angle = 70.44(7)°), two chlorides, an N-bonded thiocyanate, and an S-bonded thiocyanate. The chlorides are *cis* (Cl1–Cd1–Cl2 = 89.06(2)°) and the nitrogens are *trans* (N1–Cd1–N2 = 158.81(10)°). The bond-valence sum for Cd is 2.11, the octahedral volume is 19.77 $Å^3$, and the X–Cd–Y angular variance is $64.1°^2$, indicating a significantly lower degree of angular distortion within the octahedron than for **1**. The conformation of the –Cd1–N1–N2–C1–O1– chelate ring of mc in **2** is an envelope with the metal as the flap, displaced by −0.528(5) Å from the almost coplanar ligand atoms (rms deviation = 0.003 Å). The Cd–N–C, Cd–S–C and

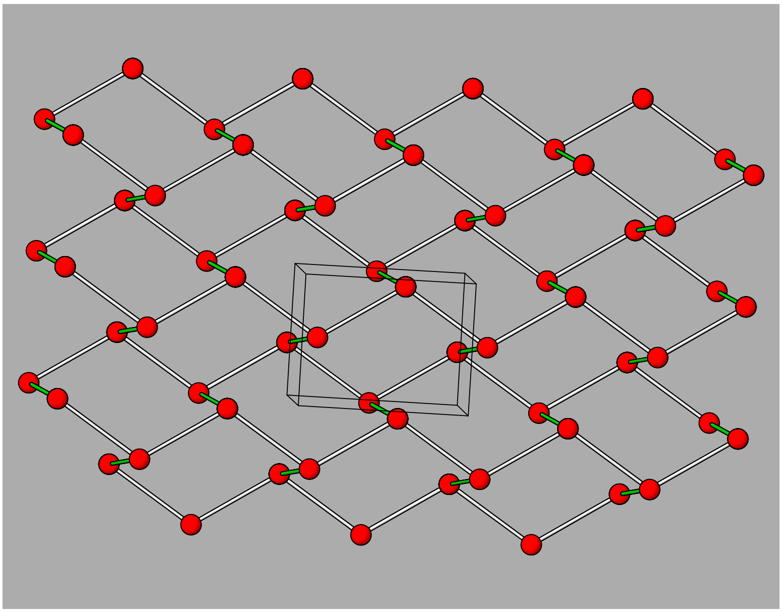

Figure 3. View approximately down [1 0 0] of the topological connectivity of the cadmium nodes in **1**, showing the resulting distorted hexagonal grid. The same connectivity also occurs in **2**, **3**, and **4**. The green line represents the pairs of Cd^{2+} ions bridged by pairs of thiocyanates in **1** and **3** and by pairs of chlorides in **2** and **4**.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Cd1–N3	2.258(3)		Cd1–O1	2.3605(17)
Cd1–N1	2.375(2)		Cd1–Cl1	2.5508(6)
Cd1–Cl1$^{\mathrm{i}}$	2.6218(6)		Cd1–S1$^{\mathrm{ii}}$	2.7331(7)
N3–Cd1–O1	88.60(8)		N3–Cd1–N1	158.81(10)
O1–Cd1–N1	70.44(7)		N3–Cd1–Cl1	96.98(7)
O1–Cd1–Cl1	174.26(4)		N1–Cd1–Cl1	103.92(6)
N3–Cd1–Cl1$^{\mathrm{i}}$	96.22(8)		O1–Cd1–Cl1$^{\mathrm{i}}$	91.72(5)
N1–Cd1–Cl1$^{\mathrm{i}}$	87.68(6)		Cl1–Cd1–Cl1$^{\mathrm{i}}$	89.06(2)
N3–Cd1–S1$^{\mathrm{ii}}$	85.89(8)		O1–Cd1–S1$^{\mathrm{ii}}$	86.97(5)
N1–Cd1–S1$^{\mathrm{ii}}$	89.86(6)		Cl1–Cd1–S1$^{\mathrm{ii}}$	92.03(2)
Cl1$^{\mathrm{i}}$–Cd1–S1$^{\mathrm{ii}}$	177.49(2)		Cd1–Cl1–Cd1$^{\mathrm{i}}$	90.94(2)
N1–H5···Cl1$^{\mathrm{iii}}$	0.90	2.55	3.319(2)	144
N1–H4···S1$^{\mathrm{iv}}$	0.90	3.01	3.639(2)	128
N2–H3···O1$^{\mathrm{v}}$	0.86	2.37	3.084(3)	140
N2–H3···S1$^{\mathrm{iv}}$	0.86	2.93	3.433(2)	119

Symmetry codes: (i) $2 - x$, $1 - y$, $1 - z$; (ii) x, $3/2 - y$, $z - 1/2$; (iii) $2 - x$, $y - 1/2$, $1/2 - z$; (iv) x, y, $z - 1$; (v) x, $1/2 - y$, $z - 1/2$.

S–C–N bond angles of 154.8(3)°, 98.04(9)° and 178.9(3)°, respectively, are comparable to the equivalent data in **1**.

In the extended structure of **2**, centrosymmetric Cd_2Cl_2 squares occur; these are almost regular with a Cd–Cl–Cd bond angle of 90.94(2)° and they are, of course, constrained to be planar by symmetry. The Cd···Cd separation across the diagonal of the square is 3.6879(3) Å, equivalent to edge-sharing of the $CdON_2Cl_2S$ octahedra via the Cl1···Cl1 edge. The thiocyanate in **2** bridges two adjacent metal ions into [0 0 1] chains in the same way that the

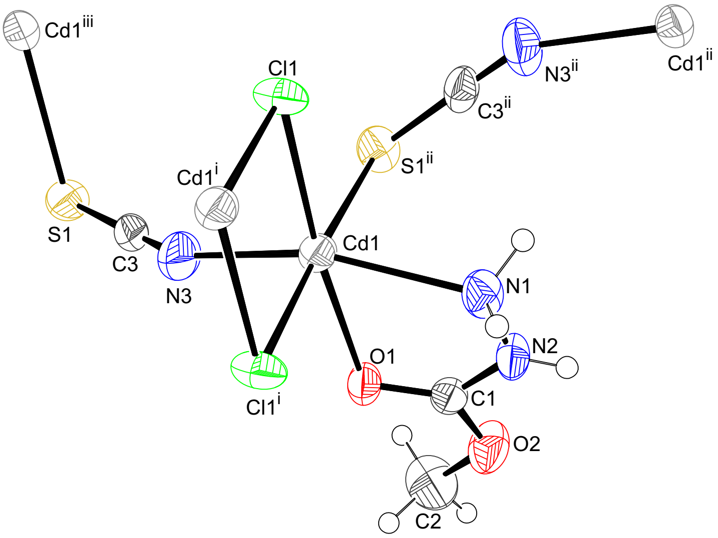

Figure 4. The asymmetric unit of **2** expanded to show the full coordination sphere of cadmium and links to nearby Cd^{2+} ions (50% displacement ellipsoids for the non-hydrogen atoms). Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $x, 3/2-y, z-1/2$; (iii) $x, 3/2-y, z+1/2$.

N1-thiocyanate acts in **1** and overall, a polymeric, layered double-octahedral network propagates parallel to (1 0 0), as shown in figure 5. The structure of **2** is consolidated by N–H···O, N–H···Cl, and possible very weak N–H···S hydrogen bonds (table 3), which all occur within a double layer.

Structure of 3. Geometric data for **3** $[Cd(SCN)_2(C_3H_8N_2O_2)]$ are given in table 4. Its asymmetric unit contains one cadmium ion, two thiocyanates, and a chelating ethyl carbazate (figure 6), in which the terminal CH_3 group is disordered over two orientations in an approximate 3 : 1 ratio. The Cd^{2+} adopts a distorted $CdON_3S_2$ octahedral coordination geometry, arising from the chelating ec ligand, two N-bonded thiocyanates, and two S-bonded thiocyanates. The relative disposition of the ligands in **3** is the same as with **1**. The bond-valence sum for Cd in **3** is 2.11, the octahedral volume is 18.79 Å^3, and the X–Cd–Y angular variance is 102.1$^{\circ 2}$; these data are almost identical to the equivalent values for **1**.

The five-atom chelate ring (bite angle = 68.03(7)°) of the ec ligand is an envelope with the metal as the flap, displaced by −0.798(5) Å from the mean plane of the ligand atoms (rms deviation = 0.011 Å). The Cd–N–C bond angles are 153.8(3)° and 155.4(3)° and the Cd–S–C bond angles are 95.29(10)° and 99.36(9)°. The S–C–N bond angles are 178.1(3)° and 176.7(3)°.

In the extended structure of **3**, centrosymmetric $Cd_2(SCN)_2$ loops occur (metal-atom separation = 5.7023(4) Å), involving the N4-containing anion, whereas the N3-species links Cd ions into [0 0 1] chains, just like the equivalent species in **1**, and overall, a polymeric, double-layered octahedral network propagates parallel to (1 0 0): the alkyl chains of the ec ligands project into the inter-layer region. The crystal structure of **3** is consolidated by N–H···O, N–H···N, and weak N–H···S hydrogen bonds (table 4).

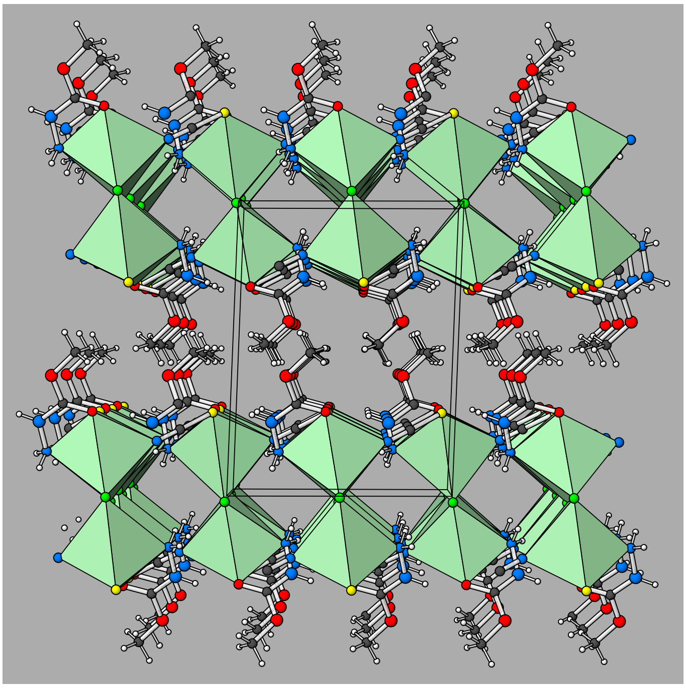

Figure 5. Polyhedral view approximately down [0 1 0] of the structure of **2** showing the linkage of cadmium octahedra into double layers propagating in (1 0 0).

Table 4. Selected bond lengths (Å) and angles (°) for **3**.

Cd1–N4	2.258(3)		Cd1–N3	2.271(3)
Cd1–N1	2.401(2)		Cd1–O1	2.4148(18)
Cd1–S2^{i}	2.6165(8)		Cd1–S1^{ii}	2.7554(8)
N4–Cd1–N3	92.26(12)		N4–Cd1–N1	92.34(11)
N3–Cd1–N1	150.33(10)		N4–Cd1–O1	94.74(9)
N3–Cd1–O1	82.38(8)		N1–Cd1–O1	68.03(7)
N4–Cd1–S2^{i}	96.81(7)		N3–Cd1–S2^{i}	104.06(8)
N1–Cd1–S2^{i}	104.47(6)		O1–Cd1–S2^{i}	166.51(5)
N4–Cd1–S1^{ii}	176.31(9)		N3–Cd1–S1^{ii}	84.08(9)
N1–Cd1–S1^{ii}	90.59(7)		O1–Cd1–S1^{ii}	84.27(5)
S2^{i}–Cd1–S1^{ii}	84.63(3)			
N1–H1A···N4^{iii}	0.90	2.61	3.383(4)	145
N1–H1B···S2^{iv}	0.90	2.92	3.713(3)	147
N2–H2···O1^{iii}	0.86	2.32	2.996(3)	135

Symmetry codes: (i) $2-x$, $1-y$, $-z$; (ii) x, $3/2-y$, $1/2+z$; (iii) x, $1/2-y$, $1/2+z$; (iv) $2-x$, $1/2+y$, $1/2-z$.

Structure of 4. Geometric data for CdCl(SCN)($C_3H_8N_2O_2$) (**4**) are given in table 5. The asymmetric unit contains one cadmium ion, one chloride, one thiocyanate, and a chelating ethyl carbazate with a bite angle of 71.15(7)° (figure 7). The Cd^{2+} in **4** adopts a distorted $CdON_2Cl_2S$ octahedral coordination geometry, akin to the situation in **2** and with the same relative disposition of the bonded atoms. The bond-valence sum for the metal in **4** is 2.10, the octahedral volume is 19.88 $Å^3$ and the X–Cd–Y angular variance is 53.7$°^2$. The five-atom chelate ring of the ec ligand is an envelope with the metal as the flap, displaced by

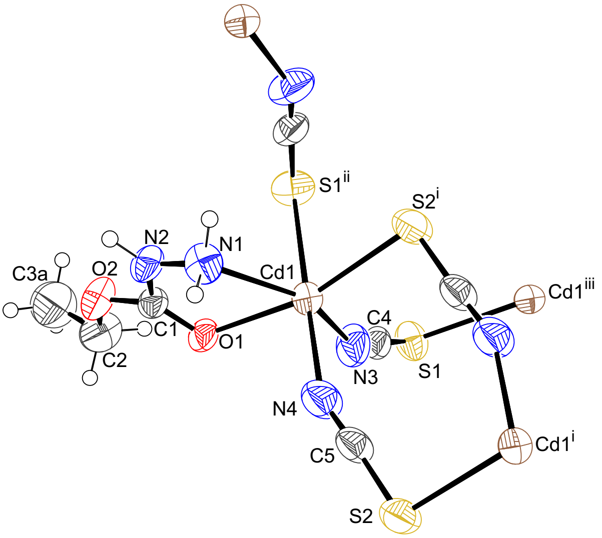

Figure 6. The asymmetric unit of **3** expanded to show the full coordination spheres of cadmium and links to nearby Cd^{2+} ions (50% displacement ellipsoids for the non-hydrogen atoms; only the major disorder component for C3 is shown). Symmetry codes: (i) $2-x$, $1-y$, $-z$; (ii) x, $3/2-y$, $1/2+z$; (iii) x, $3/2-y$, $z-1/2$.

Table 5. Selected bond lengths (Å) and angles (°) for **4**.

Cd1–N3	2.254(3)		Cd1–O1	2.3362(17)
Cd1–N1	2.381(2)		Cd1–Cl1	2.5502(7)
Cd1–Cl1^{i}	2.6533(7)		Cd1–S1^{ii}	2.7314(8)
N3–Cd1–O1	93.86(8)		N3–Cd1–N1	164.36(10)
O1–Cd1–N1	71.15(7)		N3–Cd1–Cl1	96.23(7)
O1–Cd1–Cl1	169.78(5)		N1–Cd1–Cl1	98.90(6)
N3–Cd1–Cl1^{i}	96.95(9)		O1–Cd1–Cl1^{i}	88.00(5)
N1–Cd1–Cl1^{i}	87.21(6)		Cl1–Cd1–Cl1^{i}	89.21(2)
N3–Cd1–S1^{ii}	84.61(9)		O1–Cd1–S1^{ii}	89.12(5)
N1–Cd1–S1^{ii}	90.57(6)		Cl1–Cd1–S1^{ii}	93.40(2)
Cl1^{i}–Cd1–S1^{ii}	176.81(2)		Cd1–Cl1–Cd1^{i}	90.79(2)
N1–H1A···Cl1^{iii}	0.90	2.57	3.313(2)	141
N1–H1B···S1^{iv}	0.90	3.02	3.683(3)	132
N2–H2···O1^{v}	0.86	2.39	3.115(3)	142

Symmetry codes: (i) $2-x$, $1-y$, $1-z$; (ii) x, $3/2-y$, $z-1/2$; (iii) $2-x$, $y-1/2$, $1/2-z$; (iv) x, y, $z-1$; (v) x, $1/2-y$, $z-1/2$.

0.349(5) Å from the statistically coplanar ligand atoms (rms deviation = 0.001 Å). The Cd–N–C, Cd–S–C, and S–C–N bond angles are 149.2(3)°, 99.97(9)°, and 178.9(3)°, respectively.

In the extended structure of **4**, centrosymmetric Cd_2Cl_2 squares occur that are near regular with Cl–Cd–Cl and Cd–Cl–Cd angles of 89.21(2)° and 90.79(2)°, respectively, and the Cd···Cd separation is 3.7054(4) Å. The thiocyanate bridges two adjacent metal ions in the [0 0 1] direction. Together, the bridging anions generate a (1 0 0) double-octahedral sheet, with the terminal ethyl groups of the ligands projecting into the inter-layer region. The

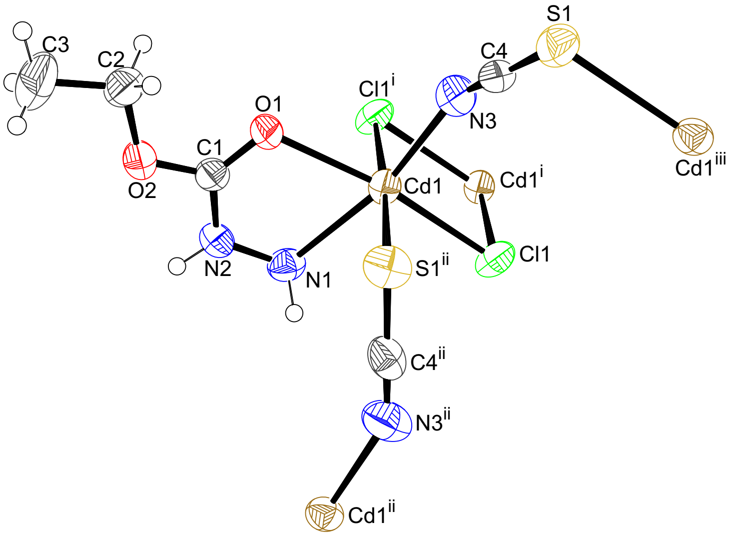

Figure 7. The asymmetric unit of **4** expanded to show the full coordination spheres of cadmium and links to nearby Cd^{2+} ions (50% displacement ellipsoids for the non-hydrogen atoms). Symmetry codes: (i) $2-x$, $1-y$, $1-z$; (ii) x, $3/2-y$, $z-1/2$; (iii) x, $3/2-y$, $z+1/2$.

structure of **4** is completed by N–H···O, N–H···Cl, and N–H···S hydrogen bonds, as listed in table 5.

Thermal studies

The thermal stability and reactivity of **1–4** were studied by simultaneous TG–DTA measurements (Supplemental figures S5–S8). All four compounds begin to decompose at about 160 °C and attain a stable residual mass at about 600 °C for **1** and about 700 °C for **2**, **3**, and **4**. The overall weight losses of 51.34% for **1** and 58.5% for **3** suggest the formation of a residue of CdS (Calcd = 54.7% for **1** and 56.6% for **3**). The large overall mass losses for **2** (80%) and **4** (72%) may correspond to reduction to Cd metal and its partial volatilization. The DTA data show that the initial weight losses are endothermic, but the decomposition steps above ~300 °C are exothermic.

Spectroscopic studies

The diffuse reflectance spectra of **1–4** are almost identical (Supplemental figure S9): in each case, a relatively sharp absorbance edge centered around 300 nm (~4.1 eV) possibly corresponds to an LMCT transition [17].

Although the uncoordinated carbazate and thiocyanate ligands are non-luminescent, **1–4** display fluorescence (Supplemental figures S10–S13). All four compounds emit around 328 nm upon excitation at 225 nm. This may be due to metal–ligand chelation [18] or an increase in the rigidity of the ligands upon coordination [19]. The emission in these complexes is tentatively assigned as intraligand ($\pi \rightarrow \pi^*$) fluorescence.

Discussion

A family of new layered coordination networks have been prepared and characterized, which, so far as we are aware, are the first compounds to contain the combination of thiocyanate/chloride ions and carbazate ligands. Their analytical and spectroscopic data are consistent with their crystal structures and with previous data.

It is notable that despite the different ligands, all four compounds can be regarded as essentially isostructural: they have similar unit cells and the connectivity of the atoms (with bridging chloride ions replacing bridging thiocyanate ions in **2** and **4**) is equivalent in each case.

The carbazate ligands in these compounds display their expected geometries and form five-membered N,O-chelate rings in each case; the ligand atoms are essentially coplanar, but the cadmium ion is significantly displaced, possibly arising due to steric blocking of the other ligands.

The CdN_3OS_2 octahedra in **1** and **3** have been seen in a few other phases, for example, $(C_{14}H_{14}N_2)\cdot[Cd_7(H_2O)_2(SCN)_{20}]$ [20], in which the O arises from water, whereas the CdN_2Cl_2OS octahedra in **2** and **4** are new, although a seven-coordinate $CdN_2Cl_2O_2S$ species have been seen with a tetradentate ligand in $[CdCl_2(C_{10}H_{12}N_4O)H_2O]\cdot H_2O$ [21].

The bridging $Cd_2(SCN)_2$ thiocyanate loops seen in **1** and **3** also occur in a number of other cadmium complexes such as $[Cd_2(SCN)_2(C_{23}H_{23}N_3)_2]^{2+}\cdot(BF_4)_2$ [22] and $[Cd_2(SCN)_4(C_{12}H_{13}N_5)_2]$ [23], which are otherwise unrelated to the compounds described here. The mean Cd–N–C and Cd–S–C bond angles (with standard deviations in parentheses) for $Cd_2(SCN)_2$ units extracted from the Cambridge Database (version 5.34 with one update) [24] are 158(7)° and 99(2)°, respectively. Bridging Cd_2Cl_2 squares are a very common structural *motif*, with almost 250 examples found in a search of the Cambridge Database; their mean Cl–Cd–Cl and Cd–Cl–Cd angles are 85(3)° and 90(6)°, respectively, which compare well with the data obtained for **2** and **4** in this study.

These results provide further indication [8] that the combination of chelating carbazate ligands with bridging anions is an effective route to new types of coordination networks and we are continuing our studies of such systems.

Supplementary material

IR spectra; TGA/DTA traces; diffuse reflectance spectra; solid-state emission spectra. Full details of the crystal structures of **1** (CCDC 931110), **2** (CCDC 931111), **3** (CCDC 931112), and **4** (CCDC 931113) in cif format are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, or Email: deposit@ccdc.cam.ac.uk.

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