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An unusual chain cadmium(II) coordination polymer: *catena*-poly[[(2,2′-bipyridyl-κ^2N,N')cadmium(II)]-di-μ-chlorido-[(2,2′-bipyridyl-κ^2N,N')-cadmium(II)]-di-μ-thiocyanato-$\kappa^2N{:}S;\kappa^2S{:}N$]

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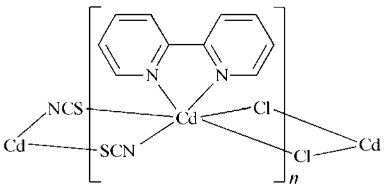
The title complex, $[\mathrm{CdCl(NCS)(C_{10}H_8N_2)}]_n$, represents an unusual Cd^{II} coordination polymer constructed by two types of anionic bridges and 2,2′-bipyridyl (bipy) terminal ligands. These two types of bridges are arranged around inversion centers. The distorted octahedral coordination of the Cd^{II} center is provided by two chloride ions, one N- and one S-donor atom from two thiocyanate ions, and a pair of N atoms from the chelating bipy ligand. Interestingly, adjacent Cd^{II} ions are interconnected alternately by paired chloride [Cd$\cdots$Cd = 3.916 (1) Å] and thiocyanate bridges [Cd$\cdots$Cd = 5.936 (1) Å] to generate an infinite one-dimensional coordination chain. Furthermore, weak interchain C—H$\cdots$S interactions between the bipy components and thiocyanate ions lead to the formation of a layered supramolecular structure.

Comment

Currently, metallo-supramolecular crystalline architectures with the incorporation of the 2,2′-bipyridyl (bipy) ligand have attracted considerable research interest as a result of their interesting structural features and physicochemical properties (Kaes *et al.*, 2000; Ye *et al.*, 2005, and references therein; Liu *et al.*, 2006). With regard to the Cd^{II} species, quite a few coordination arrays with extended structures have been addressed, in which the metal centers are commonly connected by small anionic bridging ligands such as SCN$^-$ (Yang & Ng, 2004), Cl$^-$ (Zhou *et al.*, 2003), CN$^-$ (Kim & Kim, 2000), $\mathrm{N_3}^-$ (Abu-Youssef, 2005), $\mathrm{SO_4}^{2-}$ (Harvey *et al.*, 2003), $\mathrm{CH_3COO}^-$ (Ye *et al.*, 2000) and $\mathrm{C_2O_4}^{2-}$ (Xia *et al.*, 2004), as well as various polycarboxylate linkers (Ye *et al.*, 2005, and references therein). Within this family, two similar one-dimensional chain complexes with bis-chloride (Zhou *et al.*, 2003) or bis-thiocyanate (Yang & Ng, 2004) bridges constitute a pair of interesting examples. In this context, we present here a relevant Cd^{II} coordination polymer, $[\mathrm{Cd}(\mu_2\text{-Cl})(\mu_2\text{-SCN})(\mathrm{bipy})]_n$, (I), which shows an unusual chain array derived from alternate anionic bridges of chloride and thiocyanate ligands. Complex (I) was obtained by using a diffusion method; notably, a concomitant crystalline phase that has been confirmed to be a known mononuclear complex $[\mathrm{Cd(SCN)_2(bipy)_2}]$, (II) (Rodesiler *et al.*, 1984), was also afforded.



(I)

X-ray structural analysis of (I) reveals a neutral polymeric coordination compound in which each Cd^{II} center is surrounded by a pair of N-donor atoms from bipy, a pair of chloride anions, and one N- and one S-donor atom from two thiocyanate anions (Fig. 1) to constitute a distorted octahedral coordination (Table 1). The two Cd—Cl bond lengths differ significantly [2.750 (1) and 2.552 (1) Å], and the Cd—N$_{\mathrm{NCS}}$ bond distance [2.319 (2) Å] is slightly shorter than those of the Cd—N$_{\mathrm{bipy}}$ bonds [2.358 (2) and 2.359 (2) Å]. The Cd^{II} ion lies 0.176 Å out of the least-squares basal plane [N1/N2/Cl1^{ii}/S1; symmetry code: (ii) $-x, -y+1, -z$]. The bipy ligand forms a five-membered chelate ring with the Cd^{II} ion, and the resulting N—Cd—N bite angle is 69.92 (7)°. The N1—C1—C6—N2 torsion angle within the bipy ligand is −2.6 (3)°, and the two conjugated pyridyl rings make a dihedral angle of 8.5 (1)°.

Both the chloride and thiocyanate anions act as bridging ligands, which connect metal centers to generate a one-

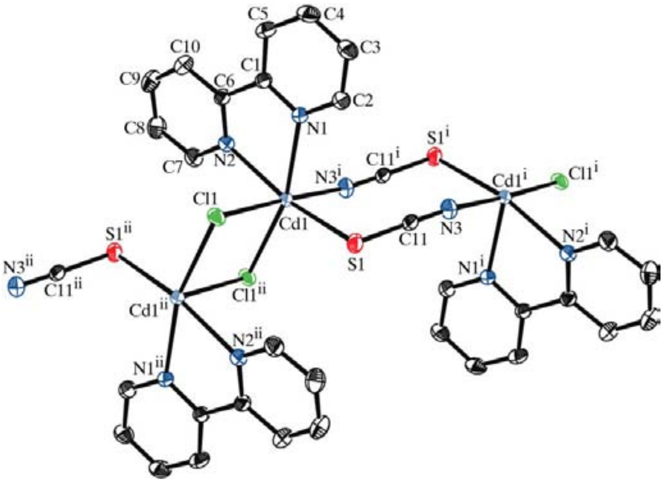


Figure 1
Part of the polymeric chain of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, -y+2, -z$; (ii) $-x, -y+1, -z$.]

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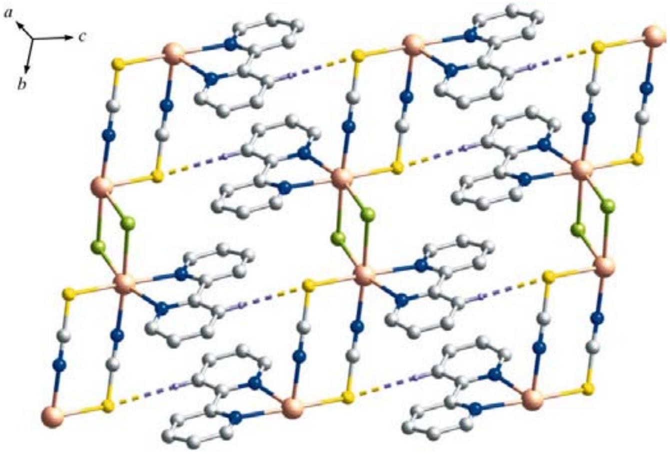

Figure 2
A perspective view of (I), showing the weak interchain C—H···S interactions. All irrelevant H atoms have been omitted for clarity.

dimensional infinite chain along the [010] direction (Fig. 1). Each linear thiocyanate ligand [S—C—N = 178.0 (2)°] adopts an *N*:*S*-bidentate bridging linking mode, with a Cd···Cd separation of 5.936 (1) Å, which is significantly longer than the Cd···Cd separation [3.916 (1) Å] bridged by the chloride anion. Notably, polymeric complexes supported by two such anionic bridges are rare; a survey of the Cambridge Structural Database (CSD; Version 5.28; Allen, 2002) revealed only five hits [refcodes EQUHAZ (Yi *et al.*, 2004), LOLWOY (Kuang *et al.*, 2000), LEMPIC (Pickardt *et al.*, 1994), VEJREH (Fan *et al.*, 1989) and ZASLOU (D'yachenko *et al.*, 1995)]. The most fascinating structural feature of complex (I) is that the adjacent Cd^{II} ions in each chain are combined alternately by paired chloride and thiocyanate ligands, and so far only one such structural example has been observed in an inorganic chain, *viz*. [Hg(μ_2-Cl)(μ_2-SCN)(SCN)]$^-$ (CSD refcode ZASLOU).

Further analysis of the crystal packing of (I) reveals the existence of a weak C5—H5···S1 interaction between the bipyridyl and thiocyanate ligands (Table 2). Such interchain contacts extend the one-dimensional coordination arrays into a supramolecular layer along the (100) plane (Fig. 2). Moreover, these layers are stacked in a parallel fashion along [100] without significant interlayer interactions.

Experimental

A methanol solution (5 ml) of 2,2′-bipyridyl (16 mg, 0.1 mmol) was carefully layered on to a buffer of methanol (2 ml), below which an aqueous solution (5 ml) containing a mixture of cadmium(II) dichloride 5.5-hydrate (24 mg, 0.1 mmol) and ammonium thiocyanate (16 mg, 0.2 mmol) was placed in a straight glass tube. Colorless block-shaped crystals of (I) and colorless prismatic crystals of (II) were obtained simultaneously on the tube wall after several days, and were separated manually under a microscope [yield 45–50% for (I) and 10–15% for (II)]. IR (KBr pellet, cm^{-1}) for (I): 2104 (*vs*), 1592 (*w*), 1471 (*w*), 1433 (*m*), 1310 (*w*), 1244 (*w*), 1155 (*s*), 1058 (*w*), 1013 (*m*), 764 (*m*), 733 (*w*), 647 (*w*).

Crystal data

[CdCl(NCS)($C_{10}H_8N_2$)]
M_r = 362.11
Triclinic, $P\bar{1}$
a = 8.0149 (7) Å
b = 9.2527 (8) Å
c = 9.5534 (8) Å
α = 103.031 (1)°
β = 106.938 (1)°
γ = 106.303 (1)°
V = 612.98 (9) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.15 mm^{-1}
T = 294 (2) K
0.32 × 0.26 × 0.20 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.523, $T_{\max}$ = 0.724 (expected range = 0.470–0.651)
3325 measured reflections
2126 independent reflections
2000 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.045
S = 1.04
2126 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\min}$ = −0.50 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—N3^{i}	2.319 (2)	Cd1—S1	2.6807 (7)
Cd1—N1	2.3576 (19)	Cd1—Cl1	2.7498 (6)
Cd1—N2	2.3592 (19)	S1—C11	1.651 (2)
Cd1—Cl1^{ii}	2.5519 (6)	N3—C11	1.150 (3)
N3^{i}—Cd1—N1	90.77 (7)	N3^{i}—Cd1—Cl1	175.34 (6)
N3^{i}—Cd1—N2	96.76 (7)	N1—Cd1—Cl1	89.18 (5)
N1—Cd1—N2	69.92 (7)	N2—Cd1—Cl1	87.60 (5)
N3^{i}—Cd1—Cl1^{ii}	96.36 (6)	Cl1^{ii}—Cd1—Cl1	84.858 (19)
N1—Cd1—Cl1^{ii}	164.01 (5)	S1—Cd1—Cl1	83.32 (2)
N2—Cd1—Cl1^{ii}	94.97 (5)	Cd1^{ii}—Cl1—Cd1	95.142 (19)
N3^{i}—Cd1—S1	92.03 (6)	C11—S1—Cd1	102.74 (9)
N1—Cd1—S1	93.69 (5)	C11—N3—Cd1^{i}	154.0 (2)
N2—Cd1—S1	161.41 (5)	N3—C11—S1	178.0 (2)
Cl1^{ii}—Cd1—S1	100.31 (2)		

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

Table 2
Short-contact geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···S1^{iii}	0.93	2.90	3.785 (3)	158

Symmetry code: (iii) $x, y, z+1$.

There was no evidence of crystal decay during data collection. All H atoms were placed at calculated positions, with C—H distances of 0.93 Å, and treated as riding. The $U_{\rm iso}$(H) values were set at 1.2$U_{\rm eq}$ of the parent C atoms.

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL* (Bruker, 2001).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3068). Services for accessing these data are described at the back of the journal.

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