

One-dimensional polymeric chain structure of bis(aniline)dithiocyanato-cadmium(II)

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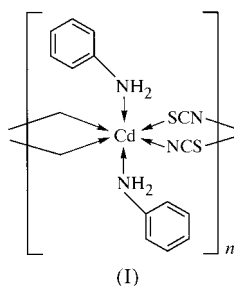
Received 7 September 1999

Accepted 5 January 2000

In the title compound, *catena*-poly[[bis(aniline-*N*)cadmium(II)]-di- μ -thiocyanato-*S:N:N:S*], $[\text{Cd}(\text{SCN})_2(\text{C}_6\text{H}_7\text{N})_2]$, the Cd^{II} atom lies on an inversion centre and is in a distorted octahedral geometry. The coordination sphere contains two thiocyanate (SCN) S atoms, two isothiocyanate (NCS) N atoms and two aniline N atoms. The six-coordinated Cd atoms run parallel to the *b* axis and are doubly bridged with neighbouring Cd atoms by SCN and NCS ligands. Thus, this complex has a one-dimensional coordination polymeric chain structure in which the aniline ligand is in the *trans* conformation.

Comment

The supramolecular architecture of multi-dimensional networks has become of great interest recently. It has been reported that these networks may have electronic, magnetic, optical or catalytic applications (Batten & Robson, 1998; Dunbar & Heintz, 1997). For designing infinite inorganic organic frameworks, we and others (Kim *et al.*, 1999; Cortes *et al.*, 1997; Demunno *et al.*, 1997) have used various pseudohalide ions, such as CN^- , OCN^- , SCN^- , SeCN^- , CNO^- and N_3^- , and complementary organic ligands. Due to the terminal and bridging bonding properties, multi-dimensional framework



structures linking alternately one metal atom *M* to another *M'* could be built by using pseudohalide ions (Wells, 1984). As an extension of the study, we have introduced thiocyanate and aniline as complementary ligands. We report here the one-

dimensional inorganic organic composite coordination polymeric structure of $[\text{Cd}(\text{SCN})_2(\text{C}_6\text{H}_5\text{NH}_2)_2]$, (I).

As shown in Figs. 1 and 2, each Cd^{II} atom lies on an inversion centre and is hexacoordinated by the two thiocyanate S atoms, two isothiocyanate N atoms and two aniline N atoms. Pairs of the same kinds of ligands are all in *trans* configurations. The coordination environment of the central Cd^{II} atom adopts a distorted octahedral geometry. The bond length of $\text{Cd}-\text{S}_{\text{SCN}}$ is longer than that of $\text{Cd}-\text{N}_{\text{NCS}}$ in the corresponding cation [2.7485 (6) *versus* 2.283 (2) Å]. The bond length of $\text{Cd}-\text{N}_{\text{NCS}}$ is shorter than that of $\text{Cd}-\text{N}_{\text{aniline}}$ [2.283 (2) *versus* 2.358 (2) Å]. The variations in the $\text{Cd}-\text{S}-\text{C}_{\text{SCN}}$ and $\text{Cd}-\text{N}-\text{C}_{\text{NCS}}$ bond angles are all within the reported range (Wells, 1984). The bond lengths and angles of the SCN and aniline ligands of (I) are unexceptional and similar to those reported in the literature (Zukerman-Schpector *et al.*, 1988).

As shown in Fig. 2, the octahedral Cd centres run parallel to the *b* axis and are doubly bridged with neighbouring Cd centres by the SCN and NCS ligands to form an eight-membered ring with a repeating unit of $\text{Cd}-\text{S}-\text{C}-\text{N}-\text{Cd}-\text{S}-\text{C}-\text{N}-$ and a centre of inversion at the centre of the ring. Thus, (I) forms a one-dimensional infinite polymeric linear chain structure. In comparison with other similar systems, the coordination geometry and crystal structure of (I) are very different. In the crystal structure of cadmium dithiocyanate itself, the Cd atom is six-coordinated by four S and two *trans*-N atoms (Cannas *et al.*, 1976*a*). Treatment with an amine such as tetramethylethylenediamine furnishes an adduct in which adjacent Cd atoms are bridged by a pair of NCS/SCN bridges (Zukerman-Schpector *et al.*, 1988). 1,2,4-Triazole can be used for the purpose of forming the $[\text{Cd}(\text{NCS})_2]_n$ chains (Haasnoot *et al.*, 1983; Biagini Cingi *et al.*, 1986). On the other hand, with 2,2'-bipyridine, the resulting complex exists as a monomer and the bridges are absent (Rodesiler *et al.*, 1984). When a triamine is used, the resulting complex has the Cd atom bonded

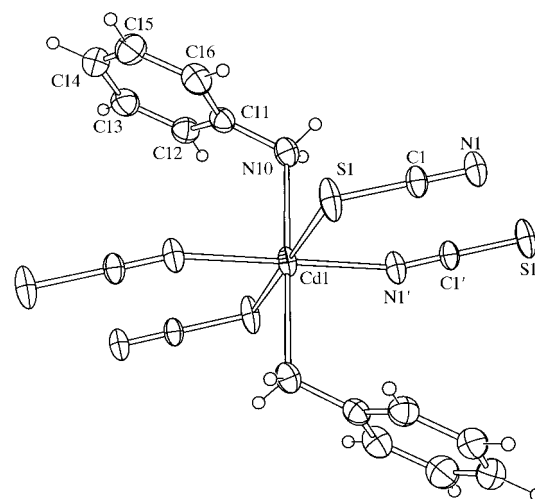


Figure 1

The coordination environment around the Cd^{II} atom in (I) with ellipsoids at the 30% probability level. H atoms are shown as small circles of arbitrary radii.

to five N atoms (Cannas *et al.*, 1976*b*). These observations indicate that the crystal structure of the thiocyanate complexes is significantly affected by the bonding properties of the thiocyanate group and the skeleton of the organic ligand.

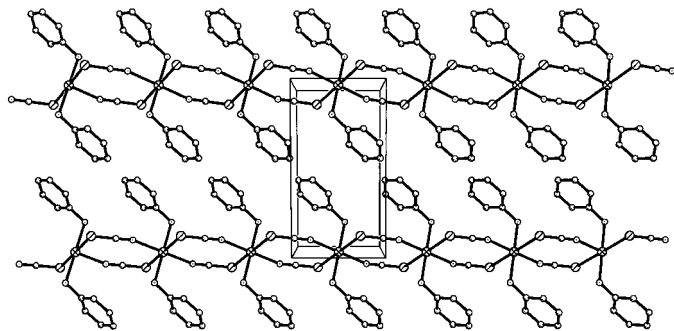


Figure 2

A perspective view of the unit cell of (I) along the *c* axis. H atoms have been omitted for clarity.

Experimental

To a 30 ml aqueous solution containing CdCl₂·2.5H₂O (1.45 g, 5 mmol) and KSCN (2.91 g, 10 mmol), aniline (1.9 ml, 20 mmol) was added; the pH of the solution was adjusted to 9 by adding 2-aminoethanol and citric acid. After a small amount of the precipitate had been filtered off, the aqueous solution was allowed to stand in a refrigerator at 278 K. After a few weeks, pale-yellow crystals were obtained.

Crystal data

[Cd(SCN)₂(C₆H₇N)₂]

M_r = 414.81

Monoclinic, *P*2₁/*c*

a = 11.1132 (13) Å

b = 5.8547 (6) Å

c = 13.1706 (13) Å

β = 100.466 (9)°

V = 842.68 (16) Å³

Z = 2

D_x = 1.635 Mg m⁻³

D_m = 1.64 Mg m⁻³

D_m measured by flotation in

mesitylene–bromoforn

Mo *K*α radiation

Cell parameters from 39 reflections

θ = 4.68–12.50°

μ = 1.541 mm⁻¹

T = 293 (2) K

Block, pale yellow

0.40 × 0.31 × 0.22 mm

Data collection

Siemens *P*4 diffractometer

2θ/ω scans

Absorption correction: empirical

(North *et al.*, 1968)

T_{min} = 0.510, *T_{max}* = 0.712

2664 measured reflections

1943 independent reflections

1616 reflections with *I* > 2σ(*I*)

R_{int} = 0.021

θ_{max} = 27.50°

h = -1 → 14

k = -1 → 7

l = -17 → 17

3 standard reflections

every 97 reflections

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.025

wR(*F*²) = 0.068

S = 1.046

1943 reflections

98 parameters

H atoms constrained

w = 1/[σ²(*F_o*²) + (0.0289*P*)² + 0.2220*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.248 e Å⁻³

Δρ_{min} = -0.474 e Å⁻³

Extinction correction: *SHELXL97*

(Sheldrick, 1997)

Extinction coefficient: 0.0317 (14)

Table 1

Selected geometric parameters (Å, °).

Cd1—N1 ⁱ	2.283 (2)	C11—C16	1.368 (3)
Cd1—N10	2.358 (2)	C11—C12	1.379 (4)
Cd1—S1	2.7485 (6)	C12—C13	1.368 (4)
S1—C1	1.646 (2)	C13—C14	1.384 (6)
C1—N1	1.139 (3)	C14—C15	1.358 (5)
N10—C11	1.434 (4)	C15—C16	1.391 (4)
N1 ⁱ —Cd1—N10	94.27 (8)	C16—C11—N10	119.8 (3)
N1 ⁱ —Cd1—S1	86.63 (5)	C12—C11—N10	120.0 (2)
N10—Cd1—S1	87.96 (6)	C13—C12—C11	119.9 (3)
C1—S1—Cd1	98.36 (8)	C12—C13—C14	120.7 (3)
N1—C1—S1	179.2 (2)	C15—C14—C13	118.8 (3)
C1—N1—Cd1 ⁱⁱ	163.1 (2)	C14—C15—C16	121.3 (3)
C11—N10—Cd1	115.59 (16)	C11—C16—C15	119.1 (3)
C16—C11—C12	120.1 (3)		

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

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JA1012). Services for accessing these data are described at the back of the journal.

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