

## *catena*-Poly[[bis(thiocyanato- $\kappa$ N)-cadmium(II)]-di- $\mu$ -thiourea- $\kappa^4$ S:S]

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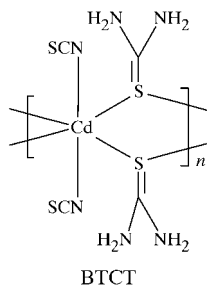
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The Cd<sup>II</sup> ion in the title complex, [Cd(SCN)<sub>2</sub>{SC(NH<sub>2</sub>)<sub>2</sub>]<sub>∞</sub>, is situated at a centre of symmetry, and is bound to two N atoms belonging to thiocyanate groups and to four S atoms of bridging thiourea ligands. The structure consists of infinite chains of slightly distorted edge-shared Cd-centred octahedra. The bridging S atoms of two thiourea ligands comprise the common edge. Some thermal properties are described.

### Comment

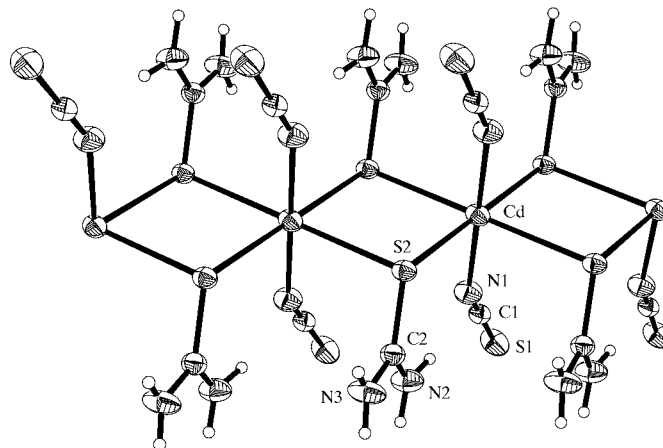
From a chemical and structural point of view, cadmium complexes have been extensively studied due to the ability of cadmium to adopt different modes of coordination determined by considerations of size, as well as electrostatic and covalent bonding forces. The presence of the thiocyanate (SCN<sup>-</sup>) ion as a ligand introduces some additional degrees of freedom, because of its versatility in acting as a monodentate,



bidentate or bridging ligand. Recently, coordination compounds formed by thiourea and cadmium have received renewed attention (Alia *et al.*, 1999). This interest arises for two main reasons: (i) the non-linear optical (NLO) properties of these compounds (Yu *et al.*, 2001) and (ii) the convenient preparation of semiconducting materials through the thermal decomposition of these complexes (Krunks *et al.*, 1997; Semenov & Naumov, 2001). As part of these investigations, the title complex, *catena*-poly[[bis(thiocyanato- $\kappa$ N)-cadmium(II)]-di- $\mu$ -thiourea- $\kappa^4$ S:S] (abbreviated as BTCT, here-

inafter), has been prepared and its thermal properties are described here.

The Cd<sup>II</sup> atom, which is situated at a centre of symmetry, is bound to two thiocyanate N atoms and to four thiourea S atoms (Fig. 1). The structure consists of infinite chains of slightly distorted edge-shared Cd-centred octahedra. The bridging S atoms of two thiourea ligands comprise the common edge. The Cd—S distances [2.7217 (5) and



**Figure 1**

The molecular structure of BTCT showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

2.7985 (6) Å] are much longer than the sum (2.52 Å) of the single-bond covalent radii (Pauling, 1960), indicating a relatively weak covalent interaction. The Cd—N bond lengths [2.258 (2) Å] are much shorter than the sum of Shannon's ionic radii (2.41 Å; Shannon, 1976), which is probably because the assumed valences of the N and S atoms are not appropriate, for the charges on the SCN<sup>-</sup> ions are delocalized. The N—Cd—S and S—Cd—S angles (between adjacent atoms) are in the ranges 84.15 (6)–95.85 (6) and 86.023 (16)–93.977 (16)°, respectively, which are somewhat different from typical octahedral angles. The thermal decomposition results (under nitrogen flux) indicate that two thiourea molecules are lost initially; the decomposition of Cd(SCN)<sub>2</sub> occurs subsequently, and the final product is CdS crystalline powder.

### Experimental

Cd(SCN)<sub>2</sub> was prepared by the reaction of CdX<sub>2</sub> (where X = Cl, NO<sub>3</sub> or CH<sub>3</sub>COO) and ASCN (where A = K, Na or NH<sub>4</sub>) (molar ratio 1:2) in water. The crystalline powders of Cd(SCN)<sub>2</sub> and thiourea were dissolved in water in stoichiometric proportions at about 313 K. The mixture was left to stand at room temperature, producing colourless crystals of BTCT which were used for X-ray structure determination.

#### Crystal data

[Cd(SCN)<sub>2</sub>(CH<sub>4</sub>N<sub>2</sub>S)<sub>2</sub>]

*M<sub>r</sub>* = 380.85

Triclinic, *P*1

*a* = 4.0368 (3) Å

*b* = 7.7237 (4) Å

*c* = 10.1355 (5) Å

$\alpha$  = 84.607 (4)°

$\beta$  = 80.825 (5)°

$\gamma$  = 75.318 (5)°

*V* = 301.31 (3) Å<sup>3</sup>

*Z* = 1

*D<sub>x</sub>* = 2.099 Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation

Cell parameters from 37 reflections

$\theta$  = 5.9–15.5°

$\mu$  = 2.48 mm<sup>-1</sup>

*T* = 293 (2) K

Prism, colourless

0.18 × 0.15 × 0.10 mm

## Data collection

Bruker P4 diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (XSCANS; Siemens, 1996)  
 $T_{\min} = 0.640$ ,  $T_{\max} = 0.782$   
 2433 measured reflections  
 1757 independent reflections  
 1637 reflections with  $I > 2\sigma(I)$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.022$   
 $wR(F^2) = 0.065$   
 $S = 1.14$   
 1757 reflections  
 86 parameters  
 All H-atom parameters refined

$R_{\text{int}} = 0.015$   
 $\theta_{\text{max}} = 30.0^\circ$   
 $h = -1 \rightarrow 5$   
 $k = -10 \rightarrow 10$   
 $l = -14 \rightarrow 14$   
 3 standard reflections  
 every 97 reflections  
 intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 0.1999P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.60 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.66 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Cd—N1	2.258 (2)	Cd—S2 <sup>i</sup>	2.7985 (6)
Cd—S2	2.7217 (5)		
N1—Cd—S2	95.85 (6)	N1—Cd—S2 <sup>ii</sup>	91.72 (6)
N1—Cd—S2 <sup>i</sup>	88.28 (6)	S2—Cd—S2 <sup>ii</sup>	93.977 (16)
S2—Cd—S2 <sup>i</sup>	86.023 (16)		

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

All H atoms were refined and N—H distances were in the range 0.81 (4)–0.92 (4)  $\text{\AA}$ .

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXTL (Bruker, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL.

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A $\cdots$ N1	0.92 (4)	2.15 (4)	3.051 (3)	166 (3)
N2—H2B $\cdots$ S1 <sup>i</sup>	0.90 (4)	2.94 (4)	3.513 (3)	123 (3)
N3—H3A $\cdots$ S2 <sup>ii</sup>	0.84 (5)	2.66 (5)	3.471 (3)	165 (5)

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1373). Services for accessing these data are described at the back of the journal.

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