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catena-Poly[[[bis(*N,N'*-diphenylthiourea)cadmium(II)]-di- μ -thiocyanato] dihydrate]

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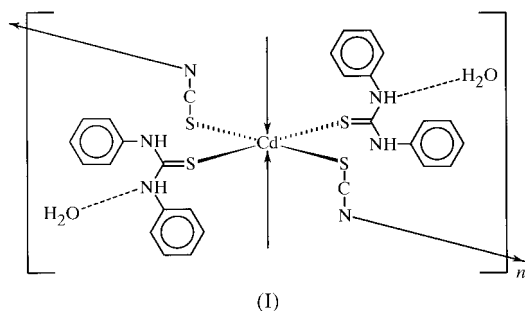
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Bridging by the two thiocyanato groups in centrosymmetric six-coordinate bis(thiocyanato)bis(diphenylthiourea)cadmium(II) dihydrate leads to the formation of eight-membered [Cd—SCN→Cd—SCN→] rings that are linked at the metal atom to furnish chains running parallel to the *a* axis, *i.e.* [[Cd(NCS)₂(C₁₃H₁₂N₂S)₂].2H₂O]_{*n*}.

Comment

In cadmium thiocyanate, bridging by both pseudohalide groups leads to the formation of eight-membered rings that are connected through the Cd atoms, which show *trans*-N₂S₄ octahedral coordination (Cannas *et al.*, 1976). In the 1/2 complexes with sulfur-donor ligands, the Cd atoms retain such a coordination characteristic, as noted in the bis(ethylene)thiourea complex (Cavalca *et al.*, 1960). The phenylthiourea complex of cadmium thiocyanate displays a one-dimensional chain structure, whereas the cadmium chloride complex exists as a monomeric entity (Yang *et al.*, 2000). Replacing the



phenylthiourea ligand by the somewhat bulkier diphenylthiourea (DPTU) donor ligand leads to the formation of a similar chain motif; however, the title compound, (I), crystallizes with lattice water that only weakly holds the chains together. There is only one hydrogen bond from the water

molecule to an N atom of the DPTU ligand.

The Cd atom is octahedrally coordinated by two S atoms of two monodentate DPTU ligands, two S atoms of two thiocyanato anions, and two N ends of other thiocyanato anions. The bridging behavior of the thiocyanato group in the formation of eight-membered rings has been documented in other systems (Chen *et al.*, 1999; Ram *et al.*, 1981; Taniguchi & Ouchi, 1987). The Cd—S and Cd—N bond distances fall within the ranges reported for other octahedral cadmium–thiocyanato complexes (Bigoli *et al.*, 1972; Cavalca *et al.*, 1960; Chen *et al.*, 1999; Ram *et al.*, 1981; Taniguchi & Ouchi, 1987; Tian *et al.*, 1997; Yang *et al.*, 2000).

Experimental

Cd(NO₃)₂·4H₂O (0.31 g, 1 mmol), KSCN (0.17 g, 2 mmol) and diphenylthiourea (0.46 g, 2 mmol) were dissolved in a small volume of ethanol. The mixture was heated until the white material which formed was completely dissolved. After filtration, the solution was allowed to evaporate slowly; crystals deposited after several days.

Crystal data

[Cd(NCS) ₂ (C ₁₃ H ₁₂ N ₂ S) ₂].2H ₂ O	<i>D_x</i> = 1.540 Mg m ⁻³
<i>M_r</i> = 721.20	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Cell parameters from 25 reflections
<i>a</i> = 5.643 (2) Å	<i>θ</i> = 7–15°
<i>b</i> = 15.625 (8) Å	<i>μ</i> = 1.007 mm ⁻¹
<i>c</i> = 17.641 (8) Å	<i>T</i> = 298 (2) K
<i>β</i> = 89.98 (4)°	Parallelepiped, colorless
<i>V</i> = 1555 (1) Å ³	0.40 × 0.22 × 0.20 mm
<i>Z</i> = 2	

Data collection

Siemens <i>R3m</i> four-circle diffractometer	<i>R</i> _{int} = 0.028
<i>ω</i> scans	<i>θ</i> _{max} = 28.91°
Absorption correction: empirical via <i>ψ</i> scans (North <i>et al.</i> , 1968)	<i>h</i> = 0 → 7
<i>T</i> _{min} = 0.609, <i>T</i> _{max} = 0.676	<i>k</i> = 0 → 20
4131 measured reflections	<i>l</i> = -24 → 23
3765 independent reflections	2 standard reflections every 120 reflections
2848 reflections with <i>I</i> > 2σ(<i>I</i>)	intensity decay: none

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0501 <i>P</i>) ² + 0.3895 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.037	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>wR</i> (<i>F</i> ²) = 0.097	(Δ/ <i>σ</i>) _{max} < 0.001
<i>S</i> = 1.037	Δρ _{max} = 0.44 e Å ⁻³
3765 reflections	Δρ _{min} = -0.40 e Å ⁻³
188 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Cd1—N1 ⁱ	2.491 (3)	Cd1—S1 ⁱⁱⁱ	2.769 (2)
Cd1—N1 ⁱⁱ	2.491 (3)	Cd1—S2	2.589 (1)
Cd1—S1	2.769 (2)	Cd1—S2 ⁱⁱⁱ	2.589 (1)
N1 ⁱ —Cd1—N1 ⁱⁱ	180	S2 ⁱⁱⁱ —Cd1—S1	94.2 (1)
N1 ⁱ —Cd1—S2 ⁱⁱⁱ	96.4 (1)	S2—Cd1—S1	85.8 (1)
N1 ⁱⁱ —Cd1—S2 ⁱⁱⁱ	83.7 (1)	N1 ⁱ —Cd1—S1 ⁱⁱⁱ	95.3 (1)
N1 ⁱ —Cd1—S2	83.7 (1)	N1 ⁱⁱ —Cd1—S1 ⁱⁱⁱ	84.7 (1)
N1 ⁱⁱ —Cd1—S2	96.4 (1)	S2 ⁱⁱⁱ —Cd1—S1 ⁱⁱⁱ	85.8 (1)
S2 ⁱⁱⁱ —Cd1—S2	180	S2—Cd1—S1 ⁱⁱⁱ	94.2 (1)
N1 ⁱ —Cd1—S1	84.7 (1)	S1—Cd1—S1 ⁱⁱⁱ	180
N1 ⁱⁱ —Cd1—S1	95.3 (1)		

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

Although the β angle is almost 90° , the cell is not orthorhombic. The checking program *PLATON* (Spek, 1990) did not find a symmetry higher than orthorhombic; indeed, if the data were averaged in an orthorhombic setting, the R_{int} exceeded 0.2. As a *TWIN* (a , $-b$, $-c$) instruction did not lower the R index much, its use was discarded. H atoms were placed in calculated idealized positions and allowed to ride on their attached non-H atoms ($\text{N}-\text{H} = 0.86 \text{ \AA}$ and $\text{C}-\text{H} = 0.93 \text{ \AA}$). The water H atoms were placed at calculated positions using the *HYDROGEN* (Nardelli, 1999) option in the *WinGX* suite (Farrugia, 1999). The slightly low completeness of the reflection data, 91.7%, is due to the incompleteness of the region of $25 < \theta < 28.91^\circ$.

Data collection: *R3m Software* (Siemens, 1990); cell refinement: *R3m Software*; data reduction: *R3m Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97*.

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