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Dicyanidobis(thiourea-*κS*)cadmium(II) monohydrate

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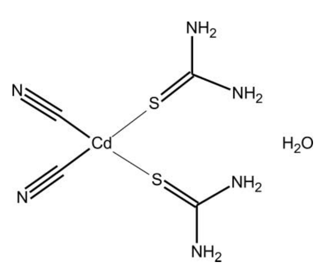
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(N–C) = 0.003 Å; R factor = 0.018; wR factor = 0.043; data-to-parameter ratio = 16.6.

In the title compound, $[Cd(CN)_2(CH_4N_2S)_2]\cdot H_2O$, the Cd atom lies on a twofold rotation axis and is bonded to two S atoms of thiourea and two C atoms of the cyanide anions in a distorted tetrahedral environment. The crystal structure is stabilized by N—H···N(CN), N—H···O, O—H···N and N—H···S hydrogen bonds.

Related literature

For background to cadmium(II) complexes of thiourea-type ligands, see: Corao & Baggio (1969); Malik *et al.* (2010); Marcos *et al.* (1998); Nawaz *et al.* (2010*a*,*b*); Wang *et al.* (2002). For the non-linear optical properties and semi-conducting applications of Cd–thiourea complexes, see: Rajesh *et al.* (2004); Stoev & Ruseva (1994). For the structures of cyanido complexes of d^{10} metal ions, see: Ahmad *et al.* (2009); Hanif *et al.* (2007); Yoshikawa *et al.* (2003).



Experimental

Crystal data

$[Cd(CN)_2(CH_4N_2S)_2]\cdot H_2O$
M_r = 334.70
Monoclinic, $P2/n$
a = 10.5955 (6) Å
b = 4.0782 (3) Å
c = 13.4127 (8) Å
β = 98.738 (1)°
V = 572.84 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.25 mm^{-1}
T = 294 K
0.29 × 0.28 × 0.24 mm

Data collection

Bruker SMART APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.561, T_{max} = 0.614
7211 measured reflections
1430 independent reflections
1376 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.043
S = 1.10
1430 reflections
86 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −0.74 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H5···O1^{i}	0.72 (4)	2.26 (4)	2.961 (2)	166 (3)
N3—H4···S1^{i}	0.90 (4)	2.61 (4)	3.470 (2)	159 (3)
N2—H3···N1^{ii}	0.84 (3)	2.22 (3)	3.035 (2)	163 (3)
N2—H2···N1^{iii}	0.78 (3)	2.51 (3)	3.286 (3)	171 (3)
O1—H1···N1^{iv}	0.83 (3)	2.16 (3)	2.988 (2)	176 (3)

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

Data collection: *SMART* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2290).

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supplementary materials

Acta Cryst. (2010). E**66**, m997 [**doi:10.1107/S1600536810028710**]

Dicyanidobis(thiourea-*κS*)cadmium(II) monohydrate

M. Fettouhi, M. Riaz Malik, S. Ali, A. A. Isab and S. Ahmad

Comment

The interest in cadmium(II) complexes of thiourea (Tu) arises because some of them exhibit non-linear optical properties (Rajesh *et al.*, 2004) and they are useful for the convenient preparation of cadmium sulfide based semiconducting materials by their thermal decomposition in air (Stoev *et al.*, 1994). Several crystallographic reports about cadmium(II) complexes of thiourea reveal that it coordinates to cadmium(II) *via* the sulfur atom (Corao *et al.*, 1969; Marcos *et al.*, 1998; Wang *et al.*, 2002). Recently, we have reported the crystal structures of cadmium(II) complexes of *N*,*N*'-dimethylthiourea (Dmtu), $[Cd(Dmtu)_2Cl_2]$ (Malik *et al.*, 2010) and tetramethylthiourea (Tmtu), $[Cd(Tmtu)_2Br_2]$ (Nawaz *et al.*, 2010*a*) and $[Cd(Tmtu)_2I_2]$ (Nawaz *et al.*, 2010*b*). Herein, we report the crystal structure of a cadmium cyanide complex of thiourea, biscyanidobis(thiourea-kS)cadmium(II) monohydrate, $[Cd(Tu)_2(CN)_2].H_2O$. The present investigation was carried out in view of our continuous interest in the structural chemistry of cyanido complexes of d^{10} metal ions with thiourea type ligands (Ahmad *et al.*, 2009; Hanif *et al.*, 2007).

In the title compound, the Cd atom is situated on a twofold axis of symmetry and is bonded to two cyanide carbon atoms and two sulfur atoms of thiourea (Figure 1). The four coordinate metal ion adopts a severely distorted tetrahedral geometry, the bond angles being in the range of 95.76 (4) - 143.5 (1) °. The Cd—S and Cd—C bond lengths are 2.6363 (5) Å and 2.211 (2) Å respectively. These are in agreement with those reported for related compounds (Marcos *et al.*, 1998; Malik *et al.* 2010; Nawaz *et al.*, 2010*a*,*b*; Wang *et al.*, 2002; Yoshikawa *et al.*, 2003). The two C—N bond lengths in thiourea, C2—N2 and C2—N3, are 1.312 (2) Å and 1.305 (2) Å respectively. The CNH_2 fragments of the two thiourea molecules are essentially planar, the maximum deviation from the mean plane being for the nitrogen atoms with 0.03 (1) Å. These values are consistent with a significant CN double bond character and electron delocalization in the SCN_2 moiety. To the best of our knowledge, this is the first X-ray structure of a cadmium complex having both sulfur containing ligands and cyanide in its coordination sphere.

The molecules pack to form columns parallel to the b direction (Figure 2). Within these columns, each metal ion interacts with two sulfur atoms of a neighboring molecule (Cd···S: 3.3140 (5) Å), hence extending the tetra-coordinate inner-sphere to a hexa-coordinate outer-sphere with a distorted octahedral environment. These interactions confer to the molecular columns a polymeric chain character.

Intermolecular hydrogen bonding takes place through N—H···S as well as N—H···N(CN) interactions (Table 1). The complex molecules also interact with the water molecules through C—N···H—O and N—H···O bonds. In this scheme the water molecule is tetrahedrally hydrogen bonded to four complex molecules. This generates a three-dimensional hydrogen bonding network where the molecular chains are interconnected through hydrogen bonding either directly or through the water molecules.

Experimental

To 0.17 g (1.0 mmol) cadmium(II) cyanide (prepared by the reaction of $CdCl_2.H_2O$ and KCN in 1:2 molar ratio in water) suspended in 15 mL water was added 2 equivalents of thiourea in methanol. Yellow precipitates formed, were filtered and the filtrate was kept for crystallization. Crystals were grown by slow evaporation of a water/methanol solution at room temperature.

Refinement

All non-H atoms were refined anisotropically. Hydrogen atoms were located in a difference Fourier map and freely refined isotropically.

Figures

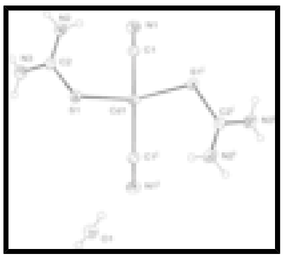

Fig. 1. The molecular structure of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level (Symmetry code: i = 0.5-x, y, 0.5-z).

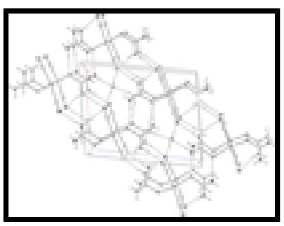

Fig. 2. Packing diagram of the title complex showing the H-bonding interactions.

Dicyanidobis(thiourea-κ*S*)cadmium(II) monohydrate

Crystal data

$[Cd(CN)_2(CH_4N_2S)_2]\cdot H_2O$	$F(000) = 328$
$M_r = 334.70$	$D_x = 1.940$ Mg m^{-3}
Monoclinic, *P*2/*n*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -P 2yac	Cell parameters from 7211 reflections
a = 10.5955 (6) Å	θ = 2.3–28.3°
b = 4.0782 (3) Å	μ = 2.25 mm^{-1}
c = 13.4127 (8) Å	*T* = 294 K
β = 98.738 (1)°	Parallelepiped, yellow
V = 572.84 (6) Å^3	0.29 × 0.28 × 0.24 mm
Z = 2	

Data collection

Bruker SMART APEX area-detector diffractometer	1430 independent reflections
Radiation source: normal-focus sealed tube	1376 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.017$
ω scans	$\theta_{max} = 28.3°$, $\theta_{min} = 2.3°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -14\rightarrow14$
$T_{min} = 0.561$, $T_{max} = 0.614$	$k = -5\rightarrow5$
7211 measured reflections	$l = -17\rightarrow17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.018$	All H-atom parameters refined
$wR(F^2) = 0.043$	$w = 1/[\sigma^2(F_o^2) + (0.0181P)^2 + 0.3434P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} < 0.001$
1430 reflections	$\Delta\rho_{max} = 0.73$ e Å^{-3}
86 parameters	$\Delta\rho_{min} = -0.73$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.072 (2)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Cd1	0.2500	−0.06581 (5)	0.2500	0.03756 (9)
S1	0.35766 (4)	0.31297 (11)	0.39821 (3)	0.03220 (11)
C1	0.06927 (16)	−0.2357 (5)	0.29604 (12)	0.0340 (3)
C2	0.28176 (16)	0.2070 (4)	0.49904 (12)	0.0322 (3)

N1	−0.02293 (17)	−0.3264 (6)	0.31974 (14)	0.0499 (4)
N2	0.16014 (18)	0.2695 (6)	0.49815 (14)	0.0535 (5)
N3	0.3466 (2)	0.0687 (6)	0.57851 (14)	0.0518 (5)
O1	0.7500	0.2524 (6)	0.2500	0.0451 (5)
H1	0.811 (3)	0.376 (7)	0.267 (2)	0.059 (8)*
H2	0.121 (3)	0.355 (8)	0.451 (2)	0.068 (9)*
H3	0.127 (3)	0.243 (7)	0.551 (2)	0.056 (7)*
H4	0.429 (4)	0.021 (8)	0.578 (3)	0.078 (10)*
H5	0.313 (3)	0.013 (7)	0.619 (3)	0.064 (9)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.02792 (11)	0.05064 (14)	0.03652 (12)	0.000	0.01265 (7)	0.000
S1	0.0315 (2)	0.0395 (2)	0.02651 (18)	−0.00063 (16)	0.00713 (14)	0.00102 (16)
C1	0.0321 (8)	0.0416 (9)	0.0291 (7)	0.0028 (7)	0.0072 (6)	0.0029 (7)
C2	0.0352 (8)	0.0371 (8)	0.0249 (7)	−0.0004 (7)	0.0063 (6)	−0.0031 (6)
N1	0.0367 (8)	0.0677 (12)	0.0477 (9)	−0.0040 (8)	0.0145 (7)	0.0077 (9)
N2	0.0403 (9)	0.0892 (16)	0.0338 (8)	0.0155 (10)	0.0148 (7)	0.0124 (9)
N3	0.0417 (9)	0.0832 (15)	0.0319 (8)	0.0100 (9)	0.0099 (7)	0.0164 (9)
O1	0.0373 (10)	0.0563 (13)	0.0423 (10)	0.000	0.0076 (8)	0.000

Geometric parameters (Å, °)

Cd1—C1^{i}	2.2108 (17)	C2—N2	1.312 (2)
Cd1—C1	2.2108 (17)	N2—H2	0.78 (3)
Cd1—S1	2.6363 (5)	N2—H3	0.84 (3)
Cd1—S1^{i}	2.6363 (5)	N3—H4	0.90 (4)
S1—C2	1.7300 (17)	N3—H5	0.72 (4)
C1—N1	1.134 (2)	O1—H1	0.83 (3)
C2—N3	1.305 (2)		
C1^{i}—Cd1—C1	143.47 (10)	N3—C2—S1	119.80 (15)
C1^{i}—Cd1—S1	95.76 (4)	N2—C2—S1	121.13 (14)
C1—Cd1—S1	105.48 (5)	C2—N2—H2	120 (2)
C1^{i}—Cd1—S1^{i}	105.48 (5)	C2—N2—H3	120.4 (19)
C1—Cd1—S1^{i}	95.76 (4)	H2—N2—H3	119 (3)
S1—Cd1—S1^{i}	108.26 (2)	C2—N3—H4	119 (2)
C2—S1—Cd1	104.11 (6)	C2—N3—H5	119 (3)
N1—C1—Cd1	179.22 (18)	H4—N3—H5	122 (3)
N3—C2—N2	119.05 (18)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H5···O1^{ii}	0.72 (4)	2.26 (4)	2.961 (2)	166 (3)
N3—H4···S1^{ii}	0.90 (4)	2.61 (4)	3.470 (2)	159 (3)

N2—H3···N1^{iii}	0.84 (3)	2.22 (3)	3.035 (2)	163 (3)
N2—H2···N1^{iv}	0.78 (3)	2.51 (3)	3.286 (3)	171 (3)
O1—H1···N1^{v}	0.83 (3)	2.16 (3)	2.988 (2)	176 (3)

Symmetry codes: (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*, −*y*, −*z*+1; (iv) *x*, *y*+1, *z*; (v) *x*+1, *y*+1, *z*.

Fig. 1

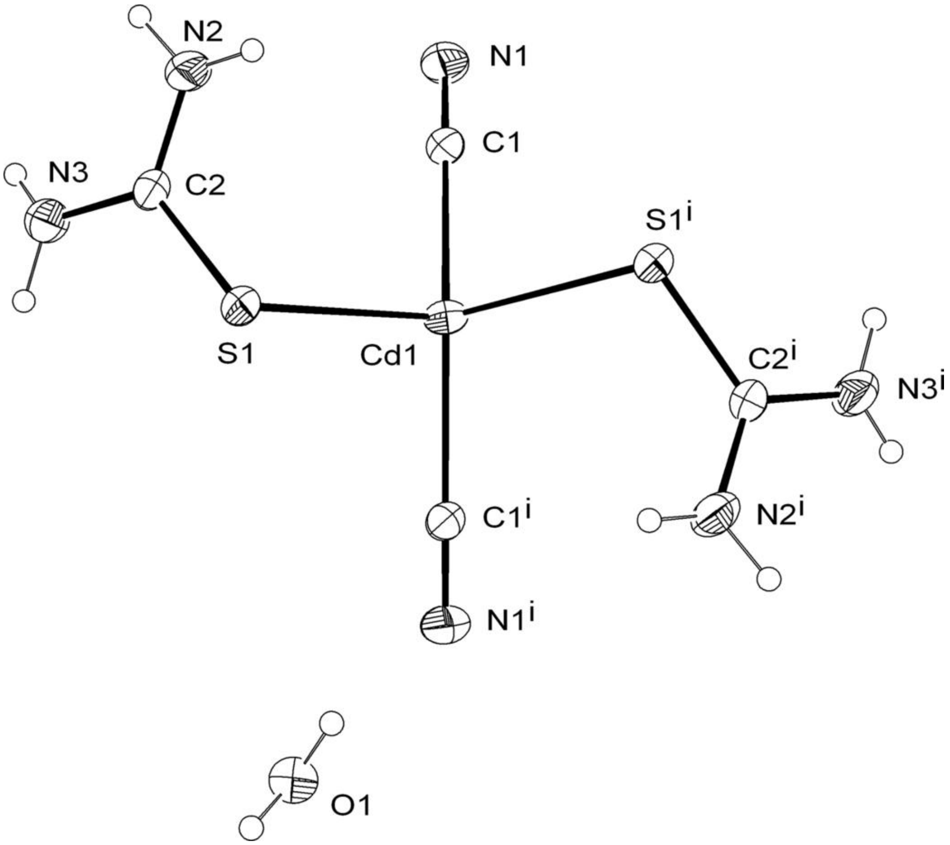

Fig. 2