

## КРАТКИЕ СООБЩЕНИЯ

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STRUCTURAL CHARACTERIZATION OF DICYANIDOBIS(*N,N'*-DIMETHYLTHIOUREA-κS)CADMIUM(II)M.R. Malik<sup>1</sup>, T. Ruffer<sup>2</sup>, H. Lang<sup>2</sup>, A.A. Isab<sup>3</sup>, S. Ali<sup>1</sup>, S. Ahmad<sup>4</sup>,  
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A cadmium(II) complex dicyanidobis(*N,N'*-dimethylthiourea-*S*) cadmium(II) [Cd(Dmtu)<sub>2</sub>(CN)<sub>2</sub>] (**1**) is prepared and its structure in the solid state is determined by single crystal X-ray structural analysis. The cadmium(II) ion is four-coordinate having a distorted tetrahedral geometry composed of two cyanide C atoms and two thione S atoms of *N,N'*-dimethylthiourea (dmtu). The molecular structure is stabilized by intermolecular N—H⋯N(CN) hydrogen bonding interactions that lead to a 3D network structure. The complex was also characterized by IR and NMR spectroscopy.

**Keywords:** cadmium cyanide, *N,N'*-dimethylthiourea, crystal structure.

Cadmium(II) complexes featuring thiourea-type ligands are of significant interest because of their semiconducting and non-linear optical properties [1–6]. With thioureas, cadmium(II) is known to form a variety of complexes with the composition [LCdX<sub>2</sub>]<sub>n</sub> [7], [L<sub>2</sub>CdX<sub>2</sub>] [7–21] or [L<sub>4</sub>Cd]X<sub>2</sub> [22, 23] (where X is halide or pseudohalide). Except polymeric [L<sub>2</sub>CdX<sub>2</sub>] complexes, the coordination environment around Cd(II) is tetrahedral in these complexes. In polymeric [L<sub>2</sub>CdX<sub>2</sub>], the structural arrangements are based on a distorted octahedral geometry [19–21]. Some examples of [L<sub>4</sub>CdX<sub>2</sub>] type complexes, in which cadmium(II) shows significant distortions from the octahedral geometry, have also been reported [24, 25]. Whereas numerous adducts of cadmium halides with thiourea ligands have been structurally characterized [9–19, 24], the number of complexes defined with Cd(CN)<sub>2</sub> is much more limited [8]. We are particularly interested in studying the coordination chemistry of cyanido complexes of *d*<sup>10</sup> metals such as silver(I), gold(I), and mercury(II), and in this regard we have already reported the spectroscopic and structural characterization of a number of silver(I) and gold(I) cyanide complexes of thiones [26–33]. As a part of our continuing interest in the coordination chemistry of thione and cyanide ligands, we report here the spectral and structural characterization of a cadmium(II) cyanide complex of *N,N'*-dimethylthiourea (Dmtu).

**Experimental. Materials.** Cadmium chloride (CdCl<sub>2</sub>·H<sub>2</sub>O) was obtained from Merck Chemical Company, Germany and *N,N'*-dimethylthiourea (Dmtu) was purchased from Acros Organics, Belgium.

**Synthesis of [Cd(Dmtu)<sub>2</sub>(CN)<sub>2</sub>] (**1**).** Complex **1** was prepared by adding 2 mmol of Dmtu dissolved in 15 ml of methanol to an aqueous solution (15 ml) of cadmium chloride (1.0 mmol, 0.2 g) followed by the addition of 2 mmol of KCN in water. The mixture was stirred for 15 min at ambient

temperature. The colorless solution was filtered and the filtrate was kept at room temperature for crystallization. As a result, white crystalline product **1** was obtained, which was washed with methanol and dried. Yield = 35 %; M.P. = 158—159 °C.

**IR and NMR measurements.** The IR spectra were recorded with a Perkin—Elmer FTIR 180 spectrophotometer using KBr pellets over the range 4000—400  $\text{cm}^{-1}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in  $\text{DMSO-}d_6$  were obtained on a Jeol JNM-LA 500 NMR spectrometer at frequencies of 500.00 MHz and 125.65 MHz respectively at 297 K. The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were measured relative to TMS.

**X-ray structural determination.** X-ray diffraction data of **1** were collected with an Oxford Gemini S diffractometer ( $\text{MoK}_\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ )) at 110 K. The structure was solved by direct methods with SHELXS-97 [41] and refined by full-matrix least squares procedures on  $F^2$  using the SHELXL-97 program [41]. All non-hydrogen atoms were refined anisotropically. All hydrogen atom positions, except the *N*-bonded hydrogen atoms, were refined using a riding model. The positions of *N*-bonded hydrogen atoms were taken from the difference Fourier map and refined isotropically. Crystal data and details of the data collection are summarized in Table 1.

**Results and discussion. IR and NMR studies.** The reactions of  $[\text{CdCl}_2 \cdot \text{H}_2\text{O}]$  with Dmtu in a 1:2 molar ratio followed by the addition of 2 equivalents of KCN resulted in a product of the composition  $[\text{Cd}(\text{Dmtu})_2(\text{CN})_2]$  (**1**). In the IR spectrum of **1**, the characteristic bands observed were typical of coordinated Dmtu  $\nu(\text{C}=\text{S})$  at  $619 \text{ cm}^{-1}$  and  $\nu(\text{N}-\text{H})$  at  $3240 \text{ cm}^{-1}$ . For free Dmtu these bands were ob

Table 1

Crystal data and refinement details for compound **1**

Formula	$\text{C}_8\text{H}_{16}\text{CdN}_6\text{S}_2$
Formula weight	372.79
Crystal system	Monoclinic
Space group	$P2(1)/c$
$a, b, c, \text{ \AA}$	9.8118(4), 15.5109(5), 9.7056(4)
$\beta$ , deg.	93.183(3)
$V, \text{ \AA}^3$	1474.82(10)
$Z$	4
$\rho_{\text{calc}}, \text{ g/cm}^{-3}$	1.679
$\mu(\text{MoK}_\alpha), \text{ mm}^{-1}$	1.753
$F(000)$	744
Crystal size, mm	0.2×0.15×0.15
Temperature, K	110(2)
$\lambda\text{MoK}_\alpha, \text{ \AA}$	0.71073
$2\theta$ range, deg.	3.16—25.04
$h, k, l$ limits	−11:11, −12:18, −11:11
Reflections; collected / Uniq.	5915 / 2549 [ $R(\text{int}) = 0.0217$ ]
Reflections: observed [ $I > 2\sigma(I)$ ]	1549
$T_{\text{min}}, T_{\text{max}}$	0.79088, 1.00000
Data / restraints / parameters	2549 / 4 / 170
$R_1, wR_2, S$ [ $I > 2\sigma(I)$ ]	0.0252, 0.0584, 0.943
Largest diff. peak, hole, $\text{e/\AA}^{-3}$	1.755, −0.554

$$w = [\sigma^2(F_0^2) + (0.0372P)^2 + 0.000P]^{-1} \text{ where } P = (F_0^2 + 2F_c^2)/3.$$

Fig. 1. Molecular structure of  $[\text{Cd}(\text{Dmtu})_2(\text{CN})_2]$  (**1**) with displacement ellipsoids drawn at the 50 % probability level

served at  $641\text{ cm}^{-1}$  and  $3203\text{ cm}^{-1}$  respectively. A low frequency shift in the  $\nu(\text{C}=\text{S})$  band and a high frequency shift in  $\nu(\text{N}-\text{H})$  indicate the existence of the thione form of Dmtu in the solid state. The  $\nu(\text{C}\equiv\text{N})$  band is observed at  $2122\text{ cm}^{-1}$ , which for  $\text{Cd}(\text{CN})_2$  appears at  $2146\text{ cm}^{-1}$ . A decrease in the frequency of the  $\text{C}\equiv\text{N}$  band is associated with a decrease in triple bond character of the  $\text{C}\equiv\text{N}$  bond due to a shift of the electron density from cadmium to empty  $\pi^*$  orbitals of cyanide upon the coordination of Dmtu to  $\text{Cd}(\text{CN})_2$ .

In the  $^1\text{H}$  NMR spectrum of **1**, a downfield shift in the N—H resonance signals was observed compared to uncomplexed Dmtu (7.56 ppm vs 7.38 ppm). This downfield shift is related to an increase in the  $\pi$  electron density in the C—N bond upon coordination. In the  $^{13}\text{C}$  NMR spectrum of **1** the main change brought about by complexation is the shifting of the C=S resonance towards lower field by 3.5 ppm as compared to the free ligand resonance (182.7 ppm). The appearance of the carbon cyanide atom at 143.85 [35] further confirms the complex formation.

**X-Ray structure description.** The molecular structure of compound **1** in the solid state, along with the numbering scheme is shown in Fig. 1. Selected bond distances and bond angles are given in Table 2. The crystal structure consists of discrete molecular species having a cadmium atom bound to two cyanide carbon atoms and two sulfur atoms of *N,N'*-dimethylthiourea in a distorted tetrahedral geometry, as demonstrated by bond angles of  $97.77(7)$ – $129.39(9)^\circ$  involving the metal centers and the donor atoms. The C—Cd—S and C—Cd—C bond angles of  $97.77(7)^\circ$  and  $129.39(9)^\circ$  respectively are significantly different from those expected for the ideal geometry. The Cd—S (2.5807(7) Å and 2.5696(8) Å) and Cd—C (2.212(3) Å and 2.192(3) Å) bond distances are clearly different, unlike the analogous Hg complex showing identical bond distances. However, these values are in agreement with those found in cadmium complexes of thiones [8–19]. The Cd—S bond distances in **1** are significantly shorter than the average values (2.5186(19) Å and 2.5192(7) Å respectively) found for the corresponding distances in six-coordinate complexes, suggesting that the metal—ligand bond distances are dependent on the coordination number of the metal. The shorter C—N distances of the SCN<sub>2</sub> moiety,

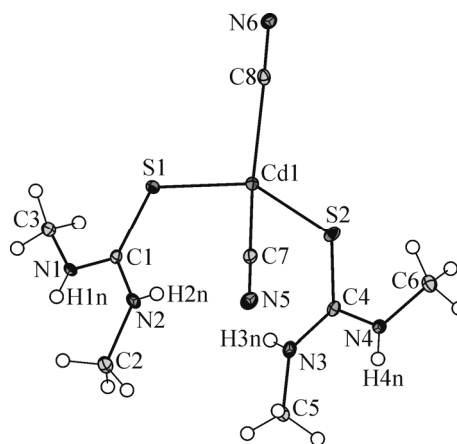


Table 2

Selected bond distances (Å) and bond angles (deg.) for **1**

Bond distance		Bond angles	
Cd(1)—S(1)	2.5807(7)	S(1)—Cd(1)—S(2)	107.43(2)
Cd(1)—S(1)	2.5696(8)	C(7)—Cd(1)—C(8)	129.39(9)
Cd(1)—C(7)	2.212(3)	S(1)—Cd(1)—C(7)	110.17(7)
Cd(1)—C(8)	2.192(3)	S(1)—Cd(1)—C(8)	97.77(7)
C(1)—S(1)	1.719(3)	S(2)—Cd(1)—C(7)	100.17(7)
C(4)—S(2)	1.739(3)	S(2)—Cd(1)—C(8)	110.77(7)
C(1)—N(1)	1.320(3)	Cd(1)—C(7)—N(5)	173.1(2)
C(1)—N(2)	1.340(3)	Cd(1)—C(8)—N(6)	178.7(2)
C(2)—N(2)	1.453(3)	Cd(1)—S(1)—C(1)	109.76(9)
C(3)—N(1)	1.457(3)	Cd(1)—S(2)—C(4)	96.23(9)
C(7)—N(5)	1.135(3)	N(1)—C(1)—S(1)	119.6(2)
C(8)—N(6)	1.136(3)	N(1)—C(1)—N(2)	118.2(2)

Table 3  
Selected bond lengths (Å) and angles (deg.)  
of intermolecular hydrogen bonds for **1**

D—H···A	D···A	D—H···A
N1—H1N···N6	2.935(3)	150(3)
N3—H3N···N6	3.118(3)	153(3)
N4—H4N···N5	2.931(3)	158(3)

as compared to the N—C(CH<sub>3</sub>) distances, correspond to a partial double bond character of the C—N bond in the SCN<sub>2</sub> moiety and the significant *sp*<sup>2</sup> character of the two nitrogen atoms. The Cd—C≡N moieties are nearly linear with an angle of 173.0°.

The molecular structure is stabilized by intermolecular N—H···N(CN) hydrogen bonds involving the thiourea N—H atoms and cyanide nitrogen atoms (Table 3). This gives rise to the formation of a three-dimensional network (Fig. 2).

The present report describes the synthesis and structural characterization of a cadmium cyanide complex of *N,N'*-dimethylthiourea (Dmtu) in which the Cd(II) ion adopts a distorted tetrahedral geometry. The compound studied in this work is closely related with [Cd(Tu)<sub>2</sub>(CN)<sub>2</sub>] (Tu = thiourea) [ 8 ] and [Hg(Dmtu)<sub>2</sub>(CN)<sub>2</sub>] [ 31 ].

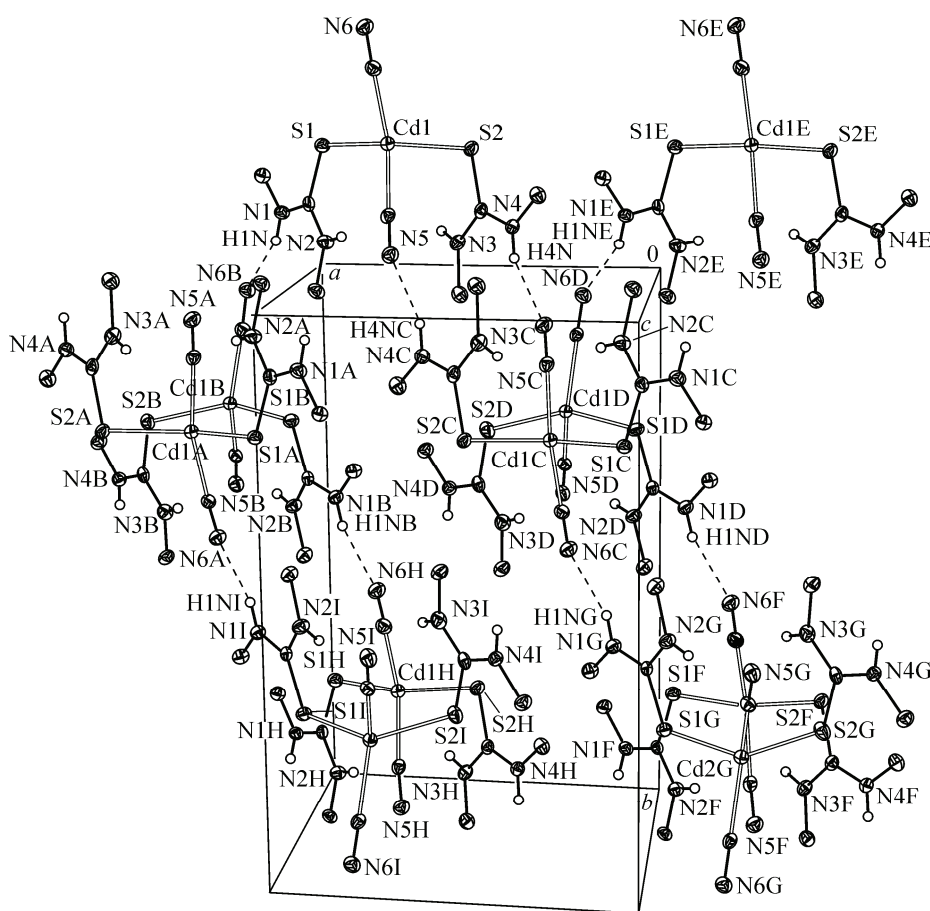


Fig. 2. Part of the 3D network formed by **1** in the solid state due to intermolecular hydrogen bonds. All C-bonded hydrogen atoms are omitted for clarity. Lable 'A' to 'I' refers to a first to the ninth symmetry generated molecule of **1**

**Supplementary data.** Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Center under CCDC No. 866931. Copies of the data can be obtained free of charge on application to CCDS, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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