

КРАТКИЕ СООБЩЕНИЯ

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STRUCTURAL CHARACTERIZATION OF DICHLORIDOBIS(*N,N'*-DIMETHYLTHIOUREA-*S*)CADMIUM(II)© 2010 M.R. Malik¹, S. Ali¹, M. Fettouhi², A.A. Isab², S. Ahmad^{3*}¹Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan²Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia³Department of Chemistry, University of Engineering and Technology, Lahore 54890, Pakistan

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A cadmium(II) complex, dichloridobis(*N,N'*-dimethylthiourea-*S*)cadmium(II), [Cd(Dmtu)₂Cl₂] (**1**), was prepared and its structure was determined by X-ray crystal structure analysis. The cadmium(II) ion is four-coordinated and the complex has a distorted tetrahedral geometry. The bond angles are in the range of 108.18(3)—110.45(2)°. The metal ion is bonded to two chloride ions and two dimethylthiourea molecules through the sulfur atoms. The crystal structure shows both intra- and intermolecular hydrogen bonds. The new complex was also characterized by IR and NMR spectroscopy and the spectroscopic data are discussed in terms of the nature of bonding.

Key words: Cadmium chloride, *N,N'*-dimethylthiourea, crystal structure.

Cadmium(II) complexes of thiones are important as simple structural models for metal binding sites in metallothioneins [1—6]. As a softer and more thiophilic metal ion, cadmium(II) may displace cysteine-coordinated zinc from its enzymes [7, 8]. Cadmium(II) complexes with thiones possess a variety of structures ranging from four- to six- coordinated species with tetrahedral and octahedral geometries, respectively [4—6, 10—18]. These studies further demonstrate that thiones can act as monodentate, bidentate or bridging ligands and, because of this versatility in binding modes, in some cases the monomeric complexes further aggregate to form polymeric structures [11—14] such as [Cd(Metu)₂Cl₂]_n [11]. The present report describes the spectroscopic data and the crystal structure of dichloridobis(*N,N'*-dimethylthiourea-*S*)cadmium(II), [Cd(Dmtu)₂Cl₂] (**1**).

Experimental. Materials. Cadmium chloride monohydrate (CdCl₂·H₂O) was obtained from Merck Chemical Company, Germany and *N,N'*-dimethylthiourea (Dmtu) was purchased from Acros Organics, Belgium.

Synthesis of [Cd(Dmtu)₂Cl₂] (1**).** The complex **1** was prepared by adding 2 mmolar methanolic solution of Dmtu to an aqueous solution of cadmium chloride (1.0 mmol, 0.20 g). The reaction mixture was stirred for 30 minutes. The colorless solution was then filtered and the filtrate was left at room temperature for crystallization. As a result, a white crystalline product was obtained, that was washed with methanol and dried. Yield 40 %. Melting point 221—223 °C.

IR and NMR Measurements. FT-IR spectra were recorded on a Thermo Nicolet Nexus 6700 USA in the 4000—450 cm⁻¹ range. The ¹H and ¹³C NMR spectra of the ligands and their complexes in DMSO-*d*₆ were obtained on Bruker Avance 300 MHz NMR spectrometer operating at frequencies of 300.00 MHz and 75.47 MHz, respectively, at 300 K. The conditions were: 32 K data points, 1.822 s acquisition time, 2.00 s pulse delay and 6.00 μs pulse width. The chemical shifts were measured relative to TMS.

* E-mail: saeed_a786@hotmail.com

Table 1

<i>Crystal and structure refinement data</i>			
Gross formula	C ₆ H ₁₆ CdCl ₂ N ₄ S ₂	θ min—max, deg.	2.78—28.33
<i>M</i>	391.65	<i>h, k, l</i> limits	−17/17, −11/11, −16/16
Temperature, K	297	Reflns: total, unique, <i>R</i> _{int}	6104, 1705, 0.0234
Crystal system, space group	Monoclinic, <i>C2/c</i>	Observed data [<i>I</i> > 2σ(<i>I</i>)]	1553
<i>a, b, c</i> , Å	13.323(2), 9.012(1), 12.779(2)	Absorption: <i>T</i> _{min} / <i>T</i> _{max}	0.5220 / 0.7990
β, deg.	108.712(2)	Refined parameters	101
<i>V</i> , Å ³	1453.2(3)	<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0270, 0.0639
<i>Z</i>	4	<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0308, 0.0655
<i>d</i> _{calc} , g/cm ³	1.790	GOOF on <i>F</i> ²	1.106
μ (MoK _α), cm ^{−1}	21.35	Residual max/min, e/Å ³	0.697 / −0.282
Crystal dimensions, mm	0.35×0.25×0.11	CCDC deposition no.	731813

X-Ray Data Collection and Structure Determination. The crystal was mounted on a glass fiber. Diffraction data were recorded on a Bruker-AXS Smart Apex system equipped with a graphite monochromatized MoK_α radiation source ($\lambda = 0.71073 \text{ \AA}$). The data were collected using SMART [19]. The data integration was performed using SAINT [20]. An empirical absorption correction was carried out using SADABS [21]. The structure was solved by direct methods and refined by full matrix least square procedure based on *F*², using the structure determination and graphics package SHELXTL [22] based on SHELX-97 [23]. Hydrogen atoms were located on a difference Fourier map and refined isotropically. A summary of X-ray data and experimental conditions is given in Table 1.

Full crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre under CCDC No. 731813. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; web: <http://www.ccdc.cam.ac.uk>].

Results and Discussion. IR and NMR Studies. The reaction of CdCl₂·H₂O with Dmtu in a 1:2 molar ratio resulted in a product of empirical composition [Cd(Dmtu)₂Cl₂] (**1**). In the IR spectrum of **1**, characteristic bands observed due to Dmtu were ν(C=S) at 665 cm^{−1} and ν(N—H) at 3290 cm^{−1}. For free Dmtu these bands were observed at 672 and 3281 cm^{−1}, respectively. A low frequency shift in the ν(C=S) band and a high frequency shift in ν(N—H) indicate the existence of thione form of Dmtu in the solid state.

In ¹H NMR spectrum of the complex, the CH₃ signals of Dmtu were observed at 2.80 ppm, while the N—H resonance was detected at 7.75 ppm. The N—H signal of free Dmtu appears at 7.38 ppm. This downfield shift in N—H resonance is related to an increase in the π electron density in the C—N bond upon coordination. In ¹³C NMR, the >C=S resonance of Dmtu in the complex is shifted upfield by 4.15 ppm as compared to the free ligand's resonance (178.49 vs. 182.64 ppm) in accordance with the data observed for other complexes of cadmium(II) [5, 6, 18, 24, 25]. The appearance of N—CH₃ resonances at 30.63 and 31.86 ppm indicates that methyl groups are non-equivalent as observed in our previous studies for AgCN and AuCN complexes [26—28].

Crystal Structure of [Cd(Dmtu)₂Cl₂]. The molecular structure of **1** in the crystal, along with the numbering scheme, is shown in Figure 1. Selected bond distances and bond angles are listed in Table 2. The cadmium(II) ion is located on a two-fold symmetry axis and the complex adopts a distorted tetrahedral geometry. The bond angles are in the range of 108.18(3)—110.45(2)°. The metal ion is bonded to two chloride ions and two dimethylthiourea molecules. The latter ligand behaves as an S-donor and binds in a terminal mode although the bridging mode has also been observed in some other Cd-thiourea systems, e.g. in [Cd(Metu)₂Cl₂]_n (Metu = *N*-methylthiourea) [11]. The Cd—S and

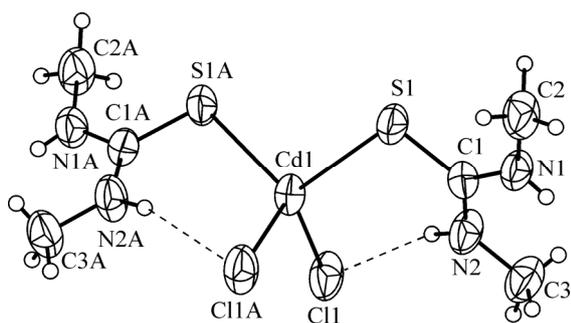


Fig. 1. Molecular structure of $[\text{Cd}(\text{Dmtu})_2\text{Cl}_2]$. Atoms with label A are generated by $1-x, y, -z+1/2$

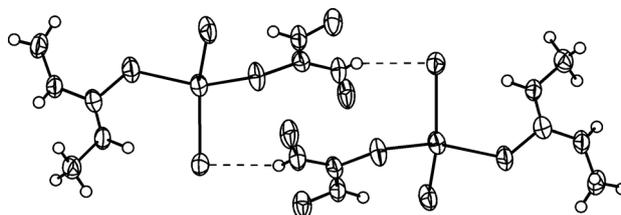


Fig. 2. Intermolecular hydrogen bonds in $[\text{Cd}(\text{Dmtu})_2\text{Cl}_2]$ (a fragment of the crystal structure). Some of the hydrogen atoms on methyl groups have been omitted for clarity

Cd—Cl bond distances are 2.5137(6) Å and 2.4682(7) Å, respectively (Table 2). These values are in agreement with those observed in other reported complexes [6, 9—17]. The SCN_2 moiety is essentially planar with bond lengths N1—C1, N2—C1 and S1—C1 of 1.315(3), 1.324(3) and 1.727(2) Å, respectively. These bond lengths correspond to intermediate bonds between single and double. This is attributed to the delocalization of electrons in the SCN_2 fragment and the significant sp^2 character of the two nitrogen atoms. As expected based on steric arguments, Dmtu ligand adopts a configuration in which one methyl group is *cis* to the sulfur atom whereas the other methyl group is *trans*. This is consistent with the solution NMR data revealing two nonequivalent methyl groups.

The crystal structure reveals both intra- and intermolecular hydrogen bonds (Table 3). Intramolecular NH...Cl hydrogen bonds involve each of the two N—H groups (N2—H2) and the chloride ions (Figure 1). This bonding pattern generates two six-membered rings, namely Cd1S1C1N2H2Cl1 and its two-fold axis symmetry equivalent Cd1S1AC1AN2AH2AC11A. Intermolecular hydrogen bonds involving N—H groups (N1—H1) with the chloride ions of adjacent molecules are also observed. This gives rise to molecular chains developing parallel to the *ac*-direction (Figure 2). The hydrogen bonding scheme is believed to stabilize the encountered distorted tetrahedral geometry.

Table 2

Selected bond distances (Å) and bond angles (deg.)

Cd(1)—S(1)	2.5137(6)	N(1)—C(1)	1.315(3)	S(1)—Cd(1)—S(1)*	108.18(3)	C(1)—S(1)—Cd(1)	106.76(8)
Cd(1)—Cl(1)	2.4682(7)	N(1)—C(2)	1.444(4)	Cl(1)—Cd(1)—Cl(1)*	108.91(4)	C(1)—N(1)—C(2)	125.5(2)
S(1)—C(1)	1.727(2)	N(2)—C(1)	1.324(3)	Cl(1)—Cd(1)—S(1)	110.45(2)	N(1)—C(1)—S(1)	119.4(2)
		N(2)—C(3)	1.447(3)	Cl(1)—Cd(1)—S(1)*	109.43(3)	N(2)—C(1)—S(1)	121.5(2)

Symmetry code (*): $1-x, y, -z+1/2$.

Table 3

Geometry of hydrogen bonds: distances (Å) and angles (deg.)

Donor—H...Acceptor	D—H	H...A	D...A	$\angle\text{D—H...A}$
N(1)—H(1)...Cl(1)*	0.77(3)	2.61(3)	3.300(2)	150(3)
N(2)—H(2)...Cl(1)	0.87(3)	2.44(3)	3.267(2)	161(3)

Symmetry code (*): $x-1/2, -y+1/2, z-1/2$.

The compound $[\text{Cd}(\text{Dmtu})_2\text{Cl}_2]$ studied in this work is isostructural with its Zn-analogue reported previously [29]. The present report shows that the interaction of *N,N'*-dimethylthiourea (Dmtu) with cadmium chloride results in a complex with a distorted tetrahedral geometry in which Dmtu is coordinating through sulfur atom in a monodentate terminal mode.

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