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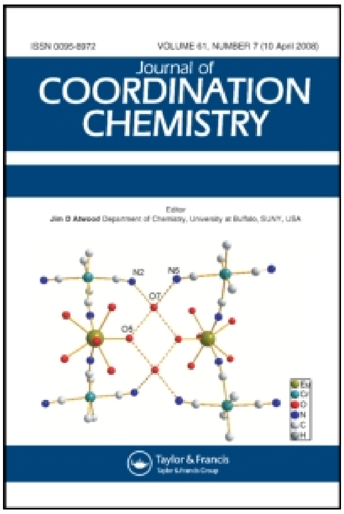

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Synthesis and spectral studies on mixed ligand complexes of Cd(II) dithiocarbamates with nitrogen donors: single crystal X-ray structure of <i>bis</i>(4-methylpiperidinecarbodithioato-S,S')(1,10-phenanthroline)cadmium(II)

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Synthesis and spectral studies on mixed ligand complexes of Cd(II) dithiocarbamates with nitrogen donors: single crystal X-ray structure of *bis*(4-methylpiperidinecarbodithioato-S,S′) (1,10-phenanthroline)cadmium(II)

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The current article describes the synthesis and characterization of the following adducts: [Cd(2-mpipdtc)$_2$(1,10-phen)], [Cd(2-mpipdtc)$_2$(bipy)], [Cd(4-mpipdtc)$_2$(1,10-phen)], [Cd(4-mpipdtc)$_2$(bipy)] (where 2-mpipdtc$^-$ = 2-methylpiperidinecarbodithioate anion, 4-mpipdtc$^-$ = 4-methylpiperidinecarbodithioate anion, 1,10-phen = 1,10-phenanthroline and bipy = 2,2′-bipyridine). A single crystal X-ray structural analysis was carried out for [Cd(4-mpipdtc)$_2$(1,10-phen)]. IR spectra of the complexes show the contribution of the thioureide form to the structures. Reduction in ν_{C-N}(thioureide) for the mixed ligand complexes is attributed to the change in coordination number from four to six and the steric effect exerted by 1,10-phenanthroline or 2,2′-bipyridine. Deshielding of the protons adjacent to nitrogen in the ^{1}H NMR spectra is attributed to drift of electrons from the nitrogen of NR$_2$, forcing electron density towards sulfur via the thioureide π-system. Single crystal X-ray structural analysis of [Cd(4-mpipdtc)$_2$(1,10-phen)] showed that the cadmium is in a distorted octahedral environment with a CdS$_4$N$_2$ chromophore. The presence of 1,10-phenanthroline in the coordination sphere of Cd(dtc)$_2$ increases the Cd–S distances and decreases the S–Cd–S angles. VBS analysis supports the determined structure.

Keywords: Dithiocarbamates; Cadmium; X-ray structure; VBS analysis

1. Introduction

Group XII dithiocarbamates (DTC) represent a large and interesting class of inorganic compounds [1, 2]. Cadmium dithiocarbamate complexes have been used as precursors for synthesis of CdS nanoparticles [3, 4]. Applications of dithiocarbamate ligands have been demonstrated in construction of new supramolecular structural motifs including polymetallic nanosized macrocycles, cryptands, and catenane [5]. The high affinity of cadmium for sulfhydryl groups in proteins makes it one of the most hazardous ecotoxicants [6–8]; cadmium readily substitutes for zinc in metalloproteins and blocks zinc-containing enzymes. Cadmium accumulates in the liver and kidneys forming stable complexes with intracellular proteins causing cumulative effects and extremely slow removal of cadmium from the organism. Cadmium (even in extremely low

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concentrations) is able to trigger some forms of tumors and inhibit the DNA mismatch repair mechanism [9, 10]. Therefore, the synthesis and study of complexes that firmly fix cadmium can be important in the content of the search for efficient antidotes for cadmium intoxication [11, 12]. To understand the influence of 1,10-phenanthroline and 2,2′-bipyridine on coordination around cadmium and on the thioureide bond, we report the syntheses and spectral characterizations of four new adducts along with the single crystal X-ray structural analysis of [Cd(4-mpipdtc)$_2$(1,10-phen)].

2. Experimental

All reagents and solvents were commercially available high-grade materials (Sigma-Aldrich/Sd fine/Spectrochem) and used as received.

2.1. *Physical measurements*

The C, H, N, and S contents were determined by elemental analysis using an Elementar Analysensysteme Gmbh Vario El V3.00. IR spectra were recorded on a Thermo NICOLET AVATAR 330 FT-IR spectrophotometer (range: 400–4000 cm^{-1}) as KBr pellets. The NMR spectra were recorded on a JEOL GS X 400 spectrometer operating at 400 MHz.

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2.2. *X-ray crystallography*

Details of the crystal data[1] and structure refinement parameters for [Cd(4-mpipdtc)$_2$(1,10-phen)] are summarized in table 1. The intensity data were collected at ambient temperature on a Bruker axis kappa apex 2.CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by SIR 92 [13] and refined by full matrix least squares with SHELXL-97 [14]. All non-hydrogen atoms were refined anisotropically and the hydrogens were fixed geometrically. Selected bond distances and angles are presented in table 2.

2.3. *Preparation of the complexes*

The *bis*(2-methylpiperidinecarbodithioato-S,S′)cadmium(II), [Cd(2-mpipdtc)$_2$] and *bis*(4-methylpiperidinecarbodithioato-S,S′)cadmium(II), [Cd(4-mpiptc)$_2$] were prepared using the established procedure [15]. Adducts were prepared by adding a hot solution of 1,10-phenanthroline (2 mmol) or 2,2′-bipyridine (2 mmol) in ethanol to a hot solution of [Cd(2-mpipdtc)$_2$] or [Cd(4-mpipdtc)$_2$] (1 mmol) in chloroform. The resulting solution was cooled and then petroleum ether (boiling range 40–60°C) was added. Yellow precipitate of the adducts was separated out. Single crystals of [Cd(4-mpipdtc)$_2$(1,10-phen)]

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[1] CCDC-671821 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK, Fax: +44 1223 366 033, E-mail: deposit@ccdc.ac.uk or at www: http://www.ccdc.cam.ac.uk].

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Table 1. Crystal data, data collection and refinement parameters for [Cd(4-mpipdtc)$_2$(1,10-phen)].

Crystal data	
$C_{26}H_{32}CdN_4S_4$	Mo-Kα
$Mr = 641.20$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 24 reflections
$P\bar{1}$	$\theta = 1.50$–25.00°
$a = 10.8122(3)$ Å	$T = 293(2)$ K
$b = 12.3877(4)$ Å	Prism
$c = 14.8965(4)$ Å	$0.30 \times 0.30 \times 0.20\,\mathrm{mm}^3$
$\beta = 82.4670(10)^\circ$	Yellow
1722.15(9) Å^3	$R_{\mathrm{int}} = 0.0195$
$Z = 2$	$h = -12 \rightarrow 12$
$D_x = 1.237\,\mathrm{mg\,m^{-3}}$	$k = -14 \rightarrow 14$
Data collection	$l = -17 \rightarrow 17$
Bruker axis kappa apex 2	
CCD diffractometer	
θ–2θ scans	
Absorption correction (empirical)	
15729 measured reflections 6028 observed reflections $[I > 2\sigma(I)]$	
Refinement	
Refinement on F^2	
$R = 0.0618$	
$R_w = 0.1939$	

Table 2. Selected bond lengths (Å) and angles (°) for [Cd(4-mpipdtc)$_2$(1,10-phen)].

Cd–S1	2.6979(16)	S4–Cd–S3	67.75(4)
Cd–S2	2.6061(14)	S2–Cd–S3	102.98(5)
Cd–S3	2.6961(16)	S4–Cd–S1	102.98(5)
Cd–S4	2.6033(15)	S2–Cd–S1	67.71(4)
Cd–N4	2.3283	S3–Cd–S1	164.27(5)
Cd–N3′	2.361(4)	S1–Cd–S2	118.3(3)
Cd–N4′	2.426(4)	S3–C22–S4	118.3(3)
Cd–N3	2.4403	N4–Cd–N3′	60.90(10)
S4–Cd–S2	110.91(5)	N4–Cd–N4′	9.04(9)

were obtained by recrystallization from a solvent mixture of chloroform and toluene. Yield, melting points, and analytical data are given in table 3.

3. Results and discussion

3.1. *Infrared spectral studies*

Stretching frequencies associated with the C–N bonds are listed in table 4. The $\nu_{\mathrm{C–N}}$ has been used as a measure of contribution of the thioureide form to the complexes [16]. In the present study, $\nu_{\mathrm{C–N}}$(thioureide) bands are observed at 1429 and 1445 cm^{-1} for [Cd(2-mpipdtc)$_2$] and [Cd(4-mpipdtc)$_2$], respectively. The reduction in $\nu_{\mathrm{C–N}}$(thioureide) for the adducts is attributed to the change in coordination number from four to six and

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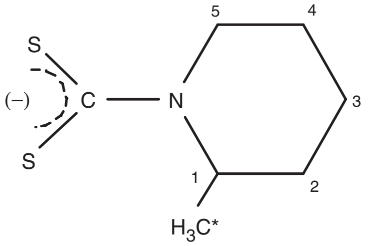
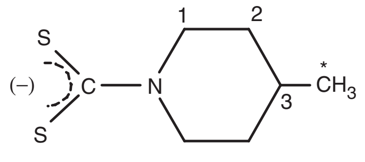
Table 3. Yield, melting points, and microanalytical data.

Compound	Yield (%)	M.P. (°C)	C (%)	H (%)	N (%)	S (%)
[Cd(2-mpipdtc)$_2$(1,10-phen)]	80	288	48.13 (48.70)	5.14 (5.03)	8.70 (8.74)	19.53 (20.00)
[Cd(2-mpipdtc)$_2$(bipy)]	75	227	46.42 (46.70)	5.21 (5.23)	9.09 (9.08)	20.34 (20.78)
[Cd(4-mpipdtc)$_2$(1,10-phen)]	78	280–281	48.22 (48.70)	4.82 (5.03)	8.58 (8.74)	19.78 (20.00)
[Cd(4-mpipdtc)$_2$(bipy)]	72	244–245	46.86 (46.70)	4.98 (5.23)	9.11 (9.08)	20.42 (20.78)

Table 4. Infrared spectral data (values in cm^{-1}) and ^{1}H NMR spectral data of the complexes (chemical shifts in ppm).

	IR			
Compound	ν_{C-N}	ν_{C-S}	1,10-Phen/bipy	^{1}H NMR
[Cd(2-mpipdtc)$_2$(1,10-phen)]  (2-mpipdtc$^-$)	1420	949	1510	1.21 (d, H–*); 1.50–1.75 (m, H–2, H–3 & H–4); 3.08 (t, axial H–5); 5.27 (d, equatorial H–5); 7.27–9.42 (m, H–1,10-phen)
[Cd(2-mpipdtc)$_2$(bipy)]	1421	952	1592	1.25 (d, H–*); 1.50–1.80 (m, H–2, H–3 & H–4); 3.11 (t, axial H–5); 5.11 (d, equatorial H–5); 7.27–8.88 (m, H–bipy)
[Cd(4-mpipdtc)$_2$(1,10-phen)]  (4-mpipdtc$^-$)	1427	964	1509	0.92 (d, H–*); 1.20–1.32 (m, H–2); 1.55–1.68 (m, H–3); 3.06 (t, axial H–1); 5.21 (d, equatorial H–1); 7.18–9.32 (m, H–1,10-phen)
[Cd(4-mpipdtc)$_2$(bipy)]	1434	969	1589	0.92 (d, H–*); 1.24–1.34 (m, H–2); 1.58–1.68 (m, H–3); 3.07 (t, axial H–1); 5.19 (d, equatorial H–1); 7.27–8.98 (m, H–bipy)

steric effects exerted by 1,10-phenanthroline or 2,2′-bipyridine. The ν_{C-N} bands in the region 947–969 cm^{-1} without splitting, support bidentate coordination of the dithiocarbamate to the metal. Characteristic bands due to 1,10-phenanthroline and 2,2′-bipyridine appear around 1510 cm^{-1} (1,10-phen) and 1590 cm^{-1} (2,2′-bipy) in the

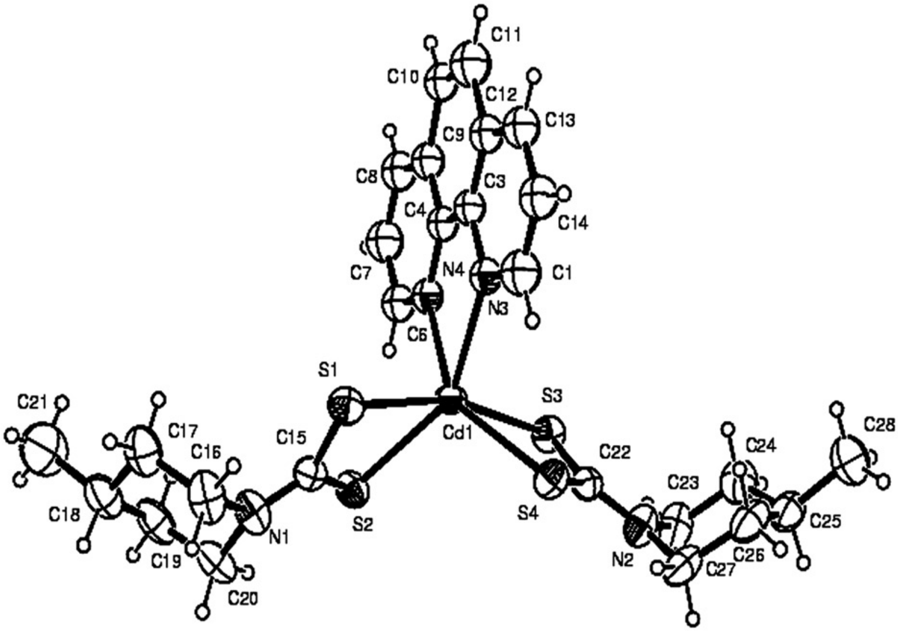


Figure 1. ORTEP diagram of [Cd(4-mpipdtc)$_2$(1,10-phen)].

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adducts, other bands due to 1,10-phenanthroline and 2,2′-bipyridine are masked by dithiocarbamate.

3.2. *^{1}H NMR spectral studies*

^{1}H NMR spectral data of all the synthesized compounds are given in table 4 along with the splitting patterns. For **1** and **2** signals around 5.60 ppm are due to the proton at C-1; a triplet observed around 3.10 ppm and a doublet observed around 5.10 ppm are due to axial and equatorial protons at C-5, respectively. A triplet at 3.06 ppm and a doublet at 5.20 ppm for **3** and **4** are due to axial and equatorial protons at C-1, respectively. The observed deshielding of the protons adjacent to nitrogen in all cases [17] is attributed to release of electrons of the NR_2 groups, forcing electron density towards the sulfur (or the metal) via the thioureide π-system. The methyl protons are more deshielded in **1** and **2** than the methyl protons in **3** and **4**, due to deshielding decrease with increase in distance from the metal center of the thioureide band. Signals at 7.18–9.42 ppm are assigned to protons present in 1,10-phenanthroline and 2,2′-bipyridine.

3.3. *Single crystal X-ray structures*

An ORTEP diagram (figure 1) shows [Cd(4-mpipdtc)$_2$(1,10-phen)] is monomeric with two molecules per unit cell. Cadmium is at the center of a distorted octahedral arrangement of four sulfurs from the chelating dithiocarbamate groups and two nitrogens from 1,10-phenanthroline. Comparisons of Cd–S, C–S, and C–N distances

Table 5. Comparative structural parameters for related cadmium compounds.

Compound	Coordination No.	S–Cd–S (°)	S–C–S (°)	Cd–S (Å)	C–S (Å)	S_2C–N (Å)	Ref.
$Cd(S_2CNEt_2)_2$	4[a]	70.9(1)	120.2(7)	2.580(4)	1.720(14)	1.33(2)	[20]
$Cd(deadtc)_2$	4[a]	68.2(1)	119.2(6)	2.591(3)	1.722(9)	1.33(1)	[21]
[Cd(4-mpipdtc)$_2$(1,10-phen)]	6	67.7(1)	118.3(3)	2.651(1)	1.721(6)	1.31(1)	This work

[a] It has been suggested that the coordination number is essentially 5 due to the presence of very long Cd–S bond in the dimer.

and the related angles with other cadmium dithiocarbamates are given in table 5. The small bite of the dithiocarbamate group results in a low S–Cd–S angle in all the complexes, but is particularly low [67.7(1)°] in the six-coordinate complex. Reduction in S–Cd–S angle necessitates either lengthening of Cd–S bond or shortening of C–S bonds or both. In the present case, only Cd–S bonds are affected with an increase in Cd–S distances [mean 2.651(1) Å].

The C–S distances [C(15)–S(1) = 1.717(5) Å and C(15)–S(2) = 1.727(6) Å] are symmetric. The short thioureide C–N distance, 1.309(8) Å, indicates that the π-electron density is delocalized over the S_2CN moiety and that this bond has double bond character comparing well with the adjacent typical single bonded N–C distance [C(16)–N(1) = 1.459(8) Å].

The C–C and C–N bond distances associated with piperidine in the dithiocarbamate fragment are normal and the piperidine ring is in the chair conformation. The methyl group in the terminal position (C(21)) is equatorially bonded to C(18).

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3.4. *VBS analysis*

In the present study, the VBS method is applied to [Cd(4-mpipdtc)$_2$(1,10-phen)] to estimate the effective valence of the metal ion from the bond lengths reported from the crystal structure, calculated by two procedures [18, 19]. The values are 2.1220 (OK/B) and 2.1624 (B/OK), confirming the valency to be 2.0 as expected.

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