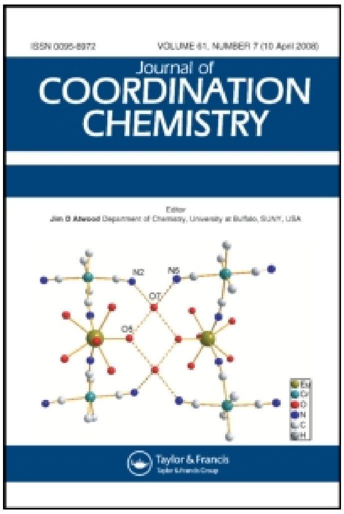

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SYNTHESIS AND CHARACTERIZATION OF *BIS*(*N*-METHYL-*N*-ETHANOL-DITHIOCARBAMATO)M(II) (M = Zn, Cd, Hg) AND *BIS*(*N,N*-(IMINODIETHYLENE)-*BIS*PHTHALIMIDEDITHIOCARBAMATO)M(II) (M = Zn, Cd, Hg) COMPLEXES. SINGLE CRYSTAL X-RAY STRUCTURE OF *BIS*(DI(2-HYDROXYETHYL)-DITHIOCARBAMATO)ZINC(II)

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S. THIRUMARAN[a], V. VENKATACHALAM[a], A. MANOHAR[a], K. RAMALINGAM[a,*], G. BOCELLI[b] and A. CANTONI[b]

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M(nmedtc)$_2$ and M(padtc)$_2$ (where nmedtc$^-$ = *N*-methyl-*N*-ethanol-dithiocarbamate anion; padtc$^-$ = *N,N'*-(iminodiethylene)*bis*phthalimidedithiocarbamate anion; M = Zn(II), Cd(II), Hg(II)) complexes were synthesized and characterized. Zinc and cadmium complexes are tetrahedral. Splitting of the νC–S band in Cd(nmedtc)$_2$ indicates anisobidentate coordination of the ligand. The mercury analogue is polymeric. Thioureide νC–N bands for Cd(nmedtc)$_2$ and Hg(padtc)$_2$ appear at relatively low energy due to the large sizes of the cadmium and mercury ions in comparison with zinc. Thermal studies have been carried out. Unit cell constants of Zn(deadtc)$_2$ are $a = 29.017(2)$ Å, $b = 8.611(4)$ Å, $c = 14.045(2)$ Å, $\beta = 103.2(1)°$, space group *C2/c*. The coordination polyhedron is a distorted trigonal bipyramid. Thioureide C–N is 1.489(5) Å, which is significantly longer than observed in the corresponding diethyl analogue (1.325(9) Å). Zn–Zn' is 3.485(3) Å compared to 3.546(3) Å observed in the diethyl analogue.

Keywords: Dithiocarbamates; zinc; cadmium; mercury; X-ray structure

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INTRODUCTION

Specific studies of metal complexes of sulfur-containing ligands have formed the basis for many reviews.[1-3] Studies of first and second row d^{10} complexes have been made to understand the interaction between metal ion and ligands; forces other than crystal field effects are responsible for stabilization in these cases.[4] Most d^{10} dithiocarbamato complexes have been found to be stable and of tetrahedral geometry.[5] The tetrahedral complexes are known to form adducts which have been well characterized.[6] In the present study, syntheses and characterization of $M(dtc)_2$ complexes (where M = Zn(II), Cd(II), Hg(II); dtc^- = *N*-methyl-*N*-ethanoldithiocarbamate, *N*,*N*′-(iminodiethylene)*bis*pthalimidedithiocarbamate anions) are reported for the first time. Only a related dithiocarbamate, *bis*(diethanoldithiocarbamato)zinc(II), could be obtained in the form of single crystals. Hence, we report the crystal structure of *bis*(diethanoldithiocarbamato)zinc(II) also in this paper. Spectroscopic characteristics of this complex have been reported earlier.[7]

EXPERIMENTAL

M(nmedtc)$_2$

N-methyl-*N*-ethanoldithiocarbamic acid (nmedtcH) was prepared by mixing 4 cm^3 of *N*-methyl-*N*-ethanolamine and 2 cm^3 of carbon disulphide diluted with ethanol (20 cm^3) at 5°C. To the yellow dithiocarbamic acid solution (20 mmol), 10 mmol of metal salt dissolved in water was added with constant stirring. Pale yellow dithiocarbamate complex separated, and which was washed with water and alcohol and then dried.

M(padtc)$_2$

N,*N*-(iminodiethylene)*bis*phthalimide ‘pa’[8] in acetonitrile was added to carbon disulphide in acetonitrile in equimolar ratio. After an hour, fine yellow crystals separated out (yield 70%, m.p. 165°C). Single crystal X-ray analysis of paH^+padtc^- has been reported from our laboratory.[9] The structure of paH^+padtc^- is shown in Figure 1. $M(padtc)_2$ (where M = Zn, Cd, Hg) complexes were prepared by mixing the corresponding metal salt and PaH^+ $padtc^-$ in a 1 : 2 ratio.

Zn(deadtc)$_2$

Diethanoldithiocarbamic acid (deadtcH) was freshly prepared by mixing 20 mmol of diethanolamine and 20 mmol of carbon disulphide (each in

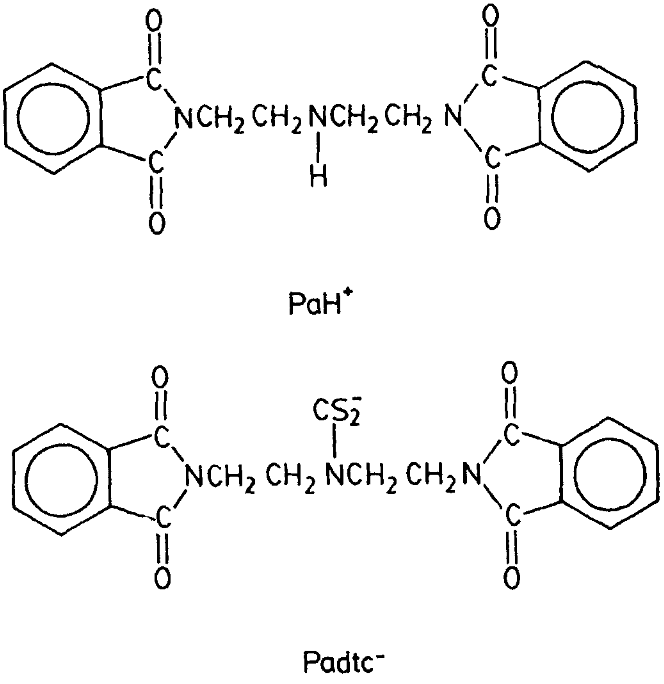

FIGURE 1 Structure of PaH^+ $Padtc^-$.

$20\,cm^3$ of methanol) under ice cold condition (5°C). $ZnSO_4 \cdot 7H_2O$ (10 mmol) in water was added to the ligand solution with continuous stirring to result in a solid complex. Crystals for data collection were obtained by recrystallization of the complex from ethanol at room temperature.

Analytically pure chemicals (Merck/BDH) were used in the study. IR spectra were recorded on a Jasco IR-700 infrared spectrophotometer, and the electronic spectra were recorded on a Jasco UVIDEC-340 double beam spectrophotometer.

RESULTS AND DISCUSSION

Important absorptions in the dithiocarbamate complexes are due to the νC–N and νC–S stretching modes; νC–N has been used as a measure of the contribution of the thioureide group to the structure of the dithiocarbamate. Depending on the nature of the substituent, R, whether it be electron releasing or withdrawing, the extent of contribution of the thioureide structure is decided.

The polar $\nu C{=}N^+$ thioureide band of the dithiocarbamate appears at an intermediate value between the two extremes of (1250–1350 cm^{-1}) and (1650–1690 cm^{-1}).[3,4] $\nu C{-}N$ bands are observed at 1502, 1488, 1510 cm^{-1} for Zn(nmedtc)$_2$, Cd(nmedtc)$_2$, Hg(nmedtc)$_2$ complexes, respectively. Similarly, for Zn(padtc)$_2$, Cd(padtc)$_2$ and Hg(padtc)$_2$, bands are observed at 1490, 1477, 1480 cm^{-1}, respectively. Lower $\nu C{-}N$ values associated with Cd(nmedtc)$_2$ indicates poor delocalization of the lone pair of electrons of the nitrogen atom. This is probably due to the relatively larger size of the cadmium ion. In related structures, Cd-S distances are longer than those observed in corresponding zinc complexes[10] and this causes an increase in thioureide distance leading to reduction in $\nu C{-}N$ values. However, the same effect is not seen in the mercury analogue because of the polymeric nature of the complexes.[11] The $\nu C{-}S$ band appears at 988 and 970 cm^{-1} in the complexes of Zn(II) and Hg(II), but in Cd(II) complexes, two bands are observed at 946 and 974 cm^{-1}. The splitting is due to the anisobidenticity of the dithiocarbmate moiety. C–S vibrations are not observed in the case of Zn(II), Cd(II) and Hg(padtc)$_2$ complexes as they are masked by moderate absorptions of the parent amine 'pa'. $\nu O{-}H$ frequencies in all the *N*-methyl-*N*-ethanoldithiocarbamato complexes appear in the range 3200 to 3500 cm^{-1}. Important ir bands and analytical data for the complexes are given in Table I.

All complexes are diamagnetic and are of pale colour with featureless electronic spectra. There is strong charge transfer absorption at 300 and 425 nm. High insolubility associated with Cd and Hg analogues indicates the polymeric nature of the complexes.

Thermal decomposition of M(nmedtc)$_2$ and M(padtc)$_2$ confirmed the proposed formulae. Decomposition of Zn(nmedtc)$_2$ is similar to that of Zn(padtc)$_2$, leaving ZnS as the final product. Cd(nmedtc)$_2$ and

TABLE I Important ir bands and analytical data for the complexes

Complexes	*Bonds*			*M%*		*N%*	
	$\nu O{-}H$	$\nu C{-}N$ (*thioureide*)	$\nu C{-}S$	*Calcd.*	*Found*	*Calcd.*	*Found*
Zn (nmedtc)$_2$	3324	1502	988	17.9	17.6	7.6	7.4
Cd (nmedtc)$_2$	3386	1488	974	27.4	27.3	6.7	6.6
Hg (nmedtc)$_2$	3446	1510	970	40.1	39.8	5.6	5.4
Zn (padtc)$_2$		1490		6.9	6.7	8.9	8.7
Cd (padtc)$_2$		1477		11.3	11.0	8.5	8.3
Hg (padtc)$_2$		1480		18.6	18.4	7.8	7.6
Zn (deadtc)$_2$	3400	1487	990	15.3	15.1	6.6	6.4

$Hg(nmedtc)_2$ are stable to 200°C and above 200°C there is a single step decomposition. In the case of $Cd(nmedtc)_2$ and $Cd(padtc)_2$, the final residue was found to be CdS, as observed earlier.[5] In the case of $Hg(nmedtc)_2$ and $Hg(padtc)_2$, there is continuous loss of mass and only 10% of the initial mass remained as 650°C. The volatility of mercury dithiocarbamates around 650°C is well documented.[12]

X-ray Crystal Structure of Bis(Diethanoldithiocarbamato)Zinc(II)

Data collection and refinement parameters are given in Table II. Fractional atomic coordinates are given in Table III. Important bondlengths and angles are listed in Table IV and a molecular diagram of the complex is shown in Figure 2.

The *bis*(diethanoldithiocarbamato)zinc(II) complex exists as a dimer. Zinc is bonded to five sulfur atoms; four of them are short [mean 2.387(1) Å] and

TABLE II Crystal data, data collection and refinement parameters for $Zn(deadtc)_2$

Crystal data	
$C_{10}H_{20}N_2O_4S_4Zn$	MoKα radiation
$Mr = 425.9$	$\lambda = 0.71073$Å
Monoclinic	Cell Parameters from 24 reflections
$C2/c$	
$a = 29.017(2)$ Å	$\theta = 6.12$–18.1
$b = 8.611(4)$ Å	$\mu = 18.46\,\mathrm{cm}^{-1}$
$c = 14.045(2)$ Å	T = 293K
$\beta = 103.17(4)°$	Prism
	0.29 × 0.33 × 0.81 mm
$V = 3417.06\ (10)$ Å^3	Yellow
$Z = 8$	
$Dx = 1.655$ Mg m^{-3}	
Data collection	
Enraff Nonius CAD4 diffractometer	$Rint = 0.0282$
	θ max = 30°
θ–2θ scans	$h = -50 \rightarrow 50$
Absorption correction (empirical)	$k = 0 \rightarrow 50$
	$l = 0 \rightarrow 50$
10910 measured reflections	(2 4 8) standard reflection monitored for every 100 reflections
3234 Observed reflections $[I > 2\sigma(I)]$	
Refinement	
Refinement on F^2	(Δ/σ) max = 0.02
$R = 0.0492$	
$R_w = 0.0592$	
$S = 1.2$	
H-atom parameters not refined	
$w = 0.3070/\sigma^2(F) + 0.02482(F)^2$	

one is relatively long (2.812(1) Å. The long Zn–S bond is due to the interaction of the sulfur atom from the other molecular unit. The coordination geometry can be described as a distorted trigonal bipyramid. C–S distances are asymmetric as a result of distortion. Average C–N is 1.337(4) Å, which indicates the contribution of 'thioureide' bond to the structure. Adjacent typical single N–C bonds [mean, 1.489(5) Å] provide support for delocalization of the electron density on nitrogen between the 'thioureide' N–C bond. Other C–C and C–O bond distances are normal. A short intermolecular O···O distance of 2.630(6) Å is observed, indicating a hydrogen bond.

Diethyl[5] and dimethyl[13] analogues of the present compound are similar with respect to coordination geometry. However, the presence of electron withdrawing C_2H_4OH groups manifests itself in the lengthening of thioureide N–C and Zn–S distances [mean N–C (thioureide) 1.325(9) Å diethyl; mean Zn–S 2.375(6) Å dimethyl]. Due to steric and intermolecular interactions, Zn–Zn′ and the long Zn–S (intermolecular) distances are also affected in the present compound. Valence bond sum analysis of the structure helps to describe the state of the central atom.[14,15] The valence, v_{ij}, of a bond between two atoms i and j is defined so that the sum of all valences from a given atom i with valence V_i obeys the relation $V_i = \sum_j v_{ij}$. The relationship involving the bond distance d_{ij} and the bond valence v_{ij} is defined as $v_{ij} = \exp[(R_{ij} - d_{ij})/B]$ where B is a constant equal to 0.37. Values for the zinc ion in

TABLE III Fractional atomic coordinates (× 10^4) and U_{eq} (× $10^4 A^2$) for Zn(deadtc)$_2$

	x/a	y/b	z/c	U_{eq}
Zn	376(1)	4095(1)	5989(1)	384(2)
S1	1149(1)	4437(1)	5766(1)	447(3)
S2	894(1)	3349(1)	7573(1)	408(3)
C3	1321(1)	3748(4)	6951(3)	339(10)
N4	1781(1)	3573(4)	7367(2)	414(10)
C5	2158(2)	4224(5)	6913(3)	474(14)
C6	2314(2)	3040(7)	6287(4)	568(17)
O7	2680(1)	3711(6)	5892(3)	728(14)
C8	1934(1)	2783(5)	8326(3)	455(13)
C9	2022(1)	3861(6)	9176(3)	456(14)
O10	2468(1)	4577(5)	9264(3)	571(11)
S1′	−28(1)	6478(1)	6044(1)	374(3)
S2′	−208(1)	2145(1)	5726(1)	409(3)
C3′	310(1)	7763(4)	5522(3)	314(10)
N4′	624(1)	8709(4)	6080(2)	373(10)
C5′	671(1)	8818(6)	7155(3)	477(14)
C6′	1060(2)	7844(7)	7750(3)	559(16)
O7′	1512(1)	8538(10)	7813(3)	981(25)
C8′	884(1)	9885(5)	5624(3)	442(13)
C9′	1295(2)	9190(6)	5258(4)	536(15)
O10′	1679(1)	8798(6)	6056(3)	763(15)

TABLE IV Bond distances (Å) and angles (°) for Zn(deadtc)$_2$

Zn–S1	2.353(1)	N8–C9	1.488(6)
Zn–S2	2.469(2)	C9–O10	1.413(5)
Zn–S1′	2.373(1)	S1′–C3	1.747(4)
Zn–S2′	2.354(1)	C3′–N4′	1.335(4)
S1–C3′	1.730(4)	N4′–C5	1.488(5)
S2–C3	1.706(4)	N4′–C8′	1.492(5)
C3–N4	1.338(4)	C5′–C6′	1.499(7)
N4–C5	1.495(7)	C6′–O7′	1.426(7)
N4–C8	1.484(5)	C8′–C9′	1.525(7)
C5–C6	1.483(8)	C9′–O10′	1.429(6)
C6–O7	1.428(7)		
S1′–Zn–S2′	106.0(0)	N4–C5–C6	110.3(4)
S2–Zn–S2′	103.0(0)	C5–C6–O7	107.9(4)
S2–Zn–S1′	113.5(0)	N4–C8–C9	113.8(3)
S1–Zn–S2′	137.9(1)	C8–C9–O10	109.2(3)
S1–Zn–S1′	112.9(0)	Zn–S1′–C3′	101.8(1)
S1–Zn–S2	75.5(0)	S1′–C3′–N4′	120.9(2)
Zn–S1–C3	84.5(1)	C3′–N4′–C8′	120.4(3)
Zn–S2–C3	81.4(1)	C3′–N4′–C5′	121.8(3)
S1–C3–S2	118.5(2)	C5′–N4′–C8′	117.0(2)
S2–C3–N4	121.5(2)	N4′–C5′–C6′	114.4(3)
S1–C3–N4	119.9(2)	C5′–C6′–O7′	111.4(4)
C3–N4–C8	120.7(3)	N4′–C8′–C9′	112.9(3)
C3–N4–C5	121.7(3)	C8′–C9′–O10′	111.0(4)
C5–N4–C8	117.5(3)		

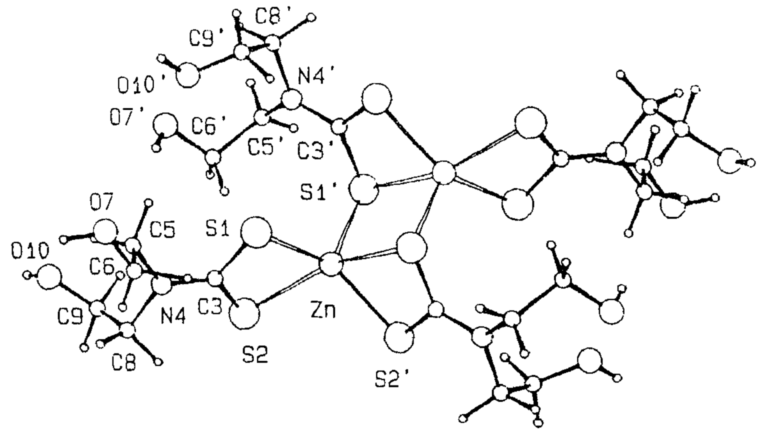

FIGURE 2 Molecular structure of Zn(deadtc)$_2$.

dimethyl, diethyl and diethanoldithiocarbamato (present compound) complexes are 1.978, 1.974 and 1.905 respectively. Very large reductions in valence sum for the diethanol complex reflect the electron withdrawing effect of the C_2H_4OH group conclusively.

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