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Synthesis and Characterization of Heterobinuclear Cadmium-Tungsten Complexes of Dithiocarbamates

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The heterobinuclear complexes [$CdWO_2(L)_3(H_2O_2)$] (L = diethyldithiocarbamate, 4-morpholinyldithiocarbamate, 1-piperidinyldithiocarbamate) were prepared by the interaction of cadmium tungstate with the respective ligands in aqueous DMF. The magnetic moment (1.7 BM) and EPR studies suggested the presence of tungsten in the pentavalent state. The IR spectral bands suggested the presence of ν(W═O) (900 cm^{-1}) and ν(Cd—O—W) (790 cm^{-1}) and bidentate dithiocarbamate ligands (1500 and 960 cm^{-1}) in the molecule. The IR and thermal decomposition studies confirmed the presence of coordinated water molecules. The ^1H NMR chemical shifts indicated non-identical environment of protons coming closer due to rigidity in rotation around C—N bond of dithiocarbamate ligand and coordination to the heterometal atoms. The mass spectral data showed 16 lines at m/z 808–824 and subsequent peaks correspond to the fragmentation of water and dithiocarbamate ligands in steps from the complex. The proposed structure consists of a tetrahedral cadmium(II) and octahedral tungsten(V) bridged by an oxo group.

Key Words: Cadmium-tungsten complexes, Dithiocarbamates.

INTRODUCTION

The dimeric tungsten(V) complexes are rare and that the di-μ-oxo structure of W(V) $[W_2O_4]^{2+}$ has been reported[1–3]. Yamamoto[4] reported the purification of first naturally occurring tungstoenzymes from one of the acetogens. The tungstoenzymes[5] belong to *aldehyde oxidoreductases* (AOR), *formate dehydrogenases* (FDH) and *N-formylmethanofuran dehydrogenases* (FMDH). The crystal structures of two enzymes isolated from *Pyrococcus furiosus, aldehyde oxidoreductase* and *formaldehyde oxidoreductase*, have been determined by Rees and coworkers[6]. The possibility emerges that active FMDH enzymes resemble *Rhodobacter sphaeroides* DMSO reductase (DMSOR)[7] by having two pterin dithiolenes and one endogenous protein ligand in the W(IV) oxidation state. Tungsten plays a key role in the biological activity of enzymes like *Pyrococcus furiosus*, *Thermococcus littoralis, Clostridium thermoautotrophicum* and *Pelobacter acetylencicus* have been reported[8].

Several Fe-W-S and Cu-W-S heterobimetallic complexes[9–12] and the binuclear oxo bridges in iron-tungsten and manganese-tungsten complexes[13] have been reported. Mixed olefin-alkyne complexes of molybdenum and tungsten dithiocarbamate have also been reported[14]. We hereby present the preparation and characterization of cadmium-tungsten complexes of dithiocarbamates, which may be used as bench models in the bioinorganic chemistry of tungsten.

EXPERIMENTAL

Sodium tungstate, cadmium nitrate, sodium diethyldithiocarbamate, solvents and chemicals used are of pure G.R. grade. The salts of 4-morpholinyldithiocarbamate and 1-piperidinyldithiocarbamate were prepared by the reported[15] procedures.

Synthesis of $[CdWO_2L_3(H_2O)_2]$ (1–3) (L = dithiocarbamate): $CdWO_4$ was prepared by mixing cadmium nitrate (1.5 g) in water (20 mL) with sodium tungstate (1.65 g) in water (20 mL). Cadmium tungstate was filtered and dried under vacuum. $CdWO_4 \cdot H_2O$ (0.5 g) was dissolved in DMF (20 cm^3) and conc. HCl (2.0 mL) digested over a water bath for 0.5 h. The solution was filtered and an aqueous solution of sodium diethyldithiocarbamate (1.6 g) in water (80 mL) was added with constant stirring under ice-cold conditions. The brown coloured complex was filtered, washed with water and MeOH and dried under vacuum. Yield 68%.

The CHN analyses were carried out on a Heraeus CHN-O-Rapid analyzer. Cadmium and tungsten were determined[16] by wet chemical analyses. TG-DTA measurements were carried out on Seiko SII thermal analyzer. The samples were heated in air at a rate of 5°C min^{-1} in Pt crucibles. The TLC measurements were carried out on a silica gel plate using a mixture of CH_2Cl_2 and CH_3OH (2 : 1) as eluants. The conductivity measurements of the complexes in DMF were carried out on a Metzer 440 digital conductivity bridge. The redox titrimetnc procedure was adopted to assign the oxidation state of tungsten. The magnetic susceptibility measurements of the powder complexes were determined at room temperature using VSM technique. The EPR spectra of the complexes were recorded in powder form at room temperature on a Varian E-4 X-band EPR spectrometer in quartz tubes. The g values were calculated using DPPH as the standard (g = 2.0036). The FT-IR spectra for the complexes were recorded as KBr matrix on Bruker IFS 66V FT-IR spectrometer. The ^1H NMR of complex **1** was studied using a Hitachi R-600 high resolution NMR spectrophotometer. The cyclic voltammetric measurements for the complex were conducted in DMF using tetraethylammonium perchlorate (0.1 M) as the supporting electrolyte.

RESULTS AND DISCUSSION

The elemental analyses (Table-1) suggested the proposed composition of the complexes. The complexes are insoluble in water and in common organic solvents. A lower molar electrical conductivity value 8 ohm^{-1} cm^2 mol^{-1} in DMF suggested the non-ionic nature of the complexes. A single spot obtained in TLC indicated that the complexes were pure and discrete in nature. Thermal decomposition data (Table-2) of the complexes **1–3** in the first step indicated the loss of coordination water molecules in the temperature range 90–130°C.

TABLE-1

ELEMENTAL ANALYSIS DATA OF CADMIUM-TUNGSTEN DITHIOCARBAMATES

Complex No.	Colour	Found (Calc.), %						μ_{eff} (B.M.)	g_{av}
		C	H	N	S	W	Cd		
1.	Brown	22.06 (22.78)	4.52 (4.05)	5.88 (5.31)	23.20 (22.78)	14.41 (14.22)	22.98 (23.64)	1.65	1.9978
2.	Grey	21.63 (21.63)	5.01 (5.05)	3.43 (3.12)	23.55 (23.07)	22.45 (22.10)	13.90 (13.50)	1.56	1.9943
3.	Brown	26.72 (26.14)	4.33 (3.87)	5.70 (5.08)	24.40 (23.24)	22.45 (22.25)	13.60 (13.61)	1.64	1.9635

1. $[CdWO_2(Et_2dtc)_3 (H_2O)_2]$ **2.** $[CdWO_2(1\text{-}Pipdtc)_3 (H_2O)_2]$ **3.** $[CdWO_2(4\text{-}Morphdtc)_3 (H_2O)_2]$

TABLE-2

TG-DTA DATA OF CADMIUM-TUNGSTEN DITHIOCARBAMATES

Complex	Temperature range (°C)	Weight loss (%)		DTA peaks (°C)	Probable phase formed
		Found	Calc.		
1	90–130	3.53	3.48	80 (–), 240 (+) and 525 (+)	$CdWO_2 (Et_2dtc)_3$
	200–290	51.91	51.06		$CdO + WS_3$
	300–600	55.62	54.94		$CdWO_4$
2	30–100	2.86	2.18	60 (–), 165 (+), 240 and 420 (+)	$CdWO_2(1\text{-}pipdtc)_3$
	110–200	20.83	21.54		$CdWO_2(1\text{-}pipdtc)_2$
	210–290	51.85	52.53		$CdS + WO_3$
	300–510	57.43	56.40		$CdWO_4$
3	30–100	5.40	5.24	66 (–), 160 (+), 235 (+) and 426 (+)	$CdWO_2 (4\text{-}morphdtc)_3$
	110–200	47.04	47.49		$CdO + WS_3$
	210–290	57.77	56.23		$CdS + WO_3$
	300–510	59.62	58.19		$CdWO_4$

The powder EPR spectra of the complexes **1–3** were recorded at room temperature, in the presence of W(V). The μ_{eff} values 1.56–1.65 BM indicated the presence of one unpaired electron. The lower value of the magnetic moment in the complexes may be due to the magnetic interactions between the adjacent paramagnetic centres in the complex. The redox titration of the complexes with $KMnO_4$ solution suggested the involvement of one electron oxidation of tungsten(V) to tungsten(VI).

The IR spectral data (Table-3) indicate the presence of coordinated water molecules. The bands at 3440 and 1650 cm^{-1} are attributed to $\nu(OH)$ and $\delta(H_2O)$ respectively. The bands at 1500 and 1020 cm^{-1} are attributed to $\nu(CN)$ and $\nu(CS)$ of the bidentate dithiocarbamate ligand. The band at 900 cm^{-1} is assigned to $\nu(W = O_t)$ characteristic[17] of mononuclear tungsten(V) complexes. The splitting of these bands and the shift to higher frequency (*ca.* 10 cm^{-1}) suggest the WO_2^{2+} species. The band at 785 cm^{-1} is attributed[18, 19] to ν(Cd—O—W) bridged vibration. The band at 500 cm^{-1} may be assigned[17] to $\nu(Cd—OH_2)$. The ^1H NMR spectra of **1** were recorded in $CDCl_3$ using TMS as a reference. The spectrum of **1** has a quartet peak due to $—N—CH_2$ having δ values of 3.74, 3.84, 3.93 and 4.18 ppm as expected. The triplet signal is observed at 1.18, 1.29 and 1.37 ppm due to the methyl protons. Due to resonance in the dithiocarbamate ligand, the (C—N) bond acquires partial double bond character (Fig. 1) and as a result, the free rotation on (C—N) bond is restricted.

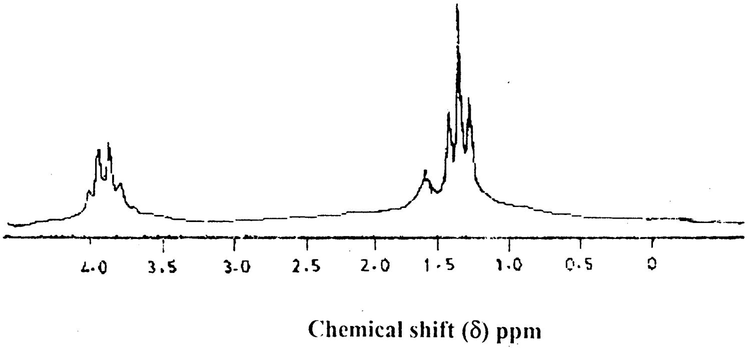

Fig. 1. ^1H NMR spectrum of $[CdWO_2(Et_2dtc)_3(H_2O)_2]$ in $CDCl_3$.

Given the geometry of the molecule, due to restriction in free rotation, the environments around the terminal $—CH_3$ groups are not the same and hence a multiplet is observed. Further, since the dithiocarbamates are attached to two different metal atoms, the electronic factors would vary, thereby bringing difference in the chemical environments of the protons.

TABLE-3

PRINCIPAL IR FREQUENCIES (cm^{-1}) OF CADMIUM-TUNGSTEN DITHIOCARBAMATES

1	2	3	Assignments
3430 (m)	3440 (m)	3420 (m)	$\nu(OH)$
1650 s	1665 s	1600 s	$\delta(H_2O)$
1500 s	1485 s	1500 s	$\nu(CN)$
1000 s	1000 s	1020 s	$\nu(CS)$
908 s, 916 s	885 s, 892 s	894 s, 908 s	$\nu(W{=}O_t)$
780 s	785 s	786 s	$\nu(Cd—O—W)_{asym}$
560 s	560 s	550 s	$\nu(Cd—O—W)_{sym}$
500 s	500 s	500 s	$\nu(Cd—OH_2)$

s = strong, m = medium.

The fast atom bombardment mass spectrum (FABMS) of $[CdWO_2(Et_2dtc)_3 \cdot (H_2O)_2]$ showed 16 lines at m/z 808–824 in Fig. 2. The 16 peaks in the range m/z 660–676 are attributed to the successive loss of the diethyldithiocarbamate. The peaks at 400 and 391 are attributed to the successive loss of cadmium diethyldithiocarbamate. The isotopic cluster peaks are characteristic[20, 21] of the fragments containing metal ions. The spectrum showed a cluster of individual peaks for a given ion radical. It is due to the presence of isotopes of different atomic weights. The probable number of peaks has been calculated in a cluster taking into account the various isotopes (W, 182, 183, 184, 186; Cd, 106, 110, 111, 112, 113, 114; S, 32, 34) and their abundance taken from literature[22]. The number of peaks in the original compound coincides with expected theoretical numbers. $[CdWO_2(Et_2dtc)_3(H_2O)_2]$ should have 16 peaks cluster with varying intensities depending upon the abundance. When one Et_2dtc is removed the number of peaks falls as expected. When $Cd(Et_2dtc)$ gets eliminated the number of peaks is found (Table-4) to be in the range of m/z 660–675. The cyclic voltamogram of $[CdWO_2(Et_2dtc)_3(H_2O)_2]$ has an irreversible cathodic wave at 0.31 V *vs.* SCE, which is assigned as one electron reduction step due to formation of the W(IV) and thus characteristic of the W(V) centre. Cadmium(II) and tungsten(V) are bridged (Fig. 3) by oxo group forming octahedral geometry around tungsten(V) and tetrahedral geometry around cadmium(II) and are completed by the oxo, aqua and bidentate ligands.

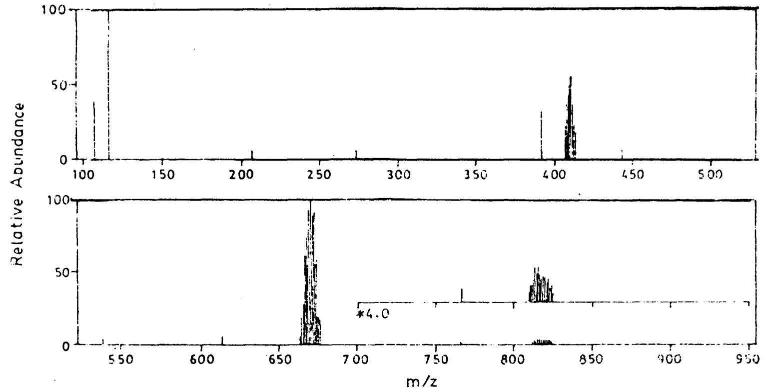

Fig. 2. FAB Mass spectrum of $[CdWO_2(Et_2dtc)_3(H_2O)_2]$ in *m*-nitrobenzyl alcohol.

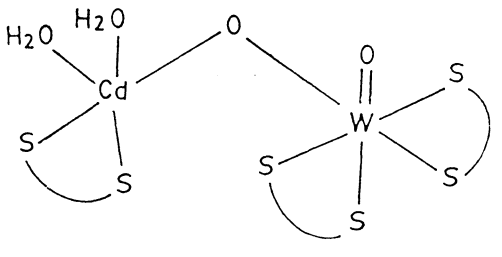

Fig. 3. Proposed structure of $[CdWO_2(L)_3(H_2O)_2]$ (L = dithiocarbamate).

TABLE-4

MASS SPECTRA DATA OF $[CdWO_2(Et_2dtc)_3(H_2O)_2]$

Molecular ion	Peak values			
	Experimental		Calculated	
	No. of peaks	m/z	No. of peaks	m/z
$[CdWO_2(Et_2dtc)_3(H_2O_2)]^+$	16	809, 810, 811, 812; 813, 814, 815, 816 817, 818, 819, 820 821, 822, 823, 824	16	809, 810, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 826
$[CdWO_2(Et_2dtc)_2(H_2O)_2]^+$	15	664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678	14	658, 659, 660, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672
$[WO_2(Et_2dtc)(H_2O)_2]^+$	8	406, 407, 408, 409 410, 411, 412, 413	6	400, 402, 403, 404, 406, 408

Isotopes Cd 110 (13%), 111 (13%), 112 (24%), 113 (12%), 114 (29%) and 116 (8%).
S 32 (95%) and 34 (5%).
W 182 (26%), 183 (15%), 184 (31%) and 186 (28%).

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