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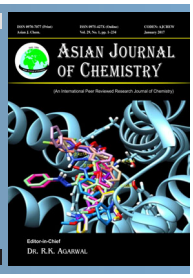

Synthesis, Characterization and Antibacterial Studies of Heterobinuclear Cadmium-Tungsten Complexes of Dithiocarbamates

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The heterobinuclear complexes $[CdWO_2(L)_3(H_2O)_2]$ (L = dithiocarbamates) 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 FT-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 FT-IR and thermal decomposition studies confirmed the presence of a coordinated water molecule. 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. The antimicrobial activity of the complexes were determined by disc diffusion and well diffusion method.

Keywords: Heterobinuclear complexes, Dithiocarbamates, Antibacterial studies.

INTRODUCTION

Dori [1] studied the complexes of tungsten(V) are monomeric $[W_2O_4(EDTA)]^{2-}$, $WCl_3(OR)_2]$ (R = Me, Et), $M[WCl_4(OR)_2]$ and $M[WCl_5(OR)$ (M = tetra alkyl ammonium; R = Me, Et). Yamamoto *et al.* [2] studied the purification of first naturally occurring tungstoenzymes, from one of the acetogens. Sung and Holm [3] studied the tungstoenzymes 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 *et al.* [4]. The possibility emerges that active N-formylmethanofuran dehydrogenases enzymes resemble rhodobacter sphaeroides DMSO reductase (DMSOR) by having two pterin dithiolenes and one endogenous protein ligand in the W(IV) oxidation state. Johnson *et al.* [5] studied that tungsten plays a key role in the biological activity of enzymes like *Pyrococcus furiosus*, *Thermococcus litoralis*, *Clostridium thermoautotrophicum* and *Pelobacter acetylencicus*. Chirila *et al.* [6] studied several Fe-W-S and Cu-W-S heterobimetallic complexes and the binuclear oxo bridges in iron-tungsten and manganese-tungsten complexes. Morrow *et al.* [7] studied some mixed olefin-alkyne complexes of molybdenum and tungsten dithiocarbamate. We hereby present the preparation, characterization and antibacterial studies 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 ligands of 4-morpholinyldithiocarbamate and 1-piperidinyldithiocarbamate were prepared by the solution route procedures.

$CdWO_4$ was prepared by mixing cadmium nitrate (1.5 g) in water (20 cm^3) with sodium tungstate (1.65 g) in water (20 cm^3). Cadmium tungstate was filtered and dried. $CdWO_4{\cdot}H_2O$ (0.5 g) was dissolved in DMF (20 cm^3) and conc. HCl (2.0 cm^3) 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 cm^3) was added with constant stirring under ice-cold conditions. The brown coloured complex was filtered, washed with water and MeOH and dried.

The CHN analyses were carried out on a Heraeus CHN-O-Rapid analyzer. Cadmium and tungsten were determined 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 6 °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, which were developed in an iodine chamber. The conductivity measurements of the complexes in DMF were carried out on a METZER 440 digital conductivity bridge. The redox titrimetric 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 are 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 spectra-photometer. The cyclicvoltammetric measurements for the complex were conducted in DMF using tetraethylammonium perchlorate (0.1 M) as the supporting electrolyte.

Antibacterial activity was assayed using the agar well diffusion test and disc diffusion method. Antibacterial activity was assayed using the agar well diffusion test technique. Muller Hinton Agar Medium (MHA) was prepared and then sterilized by autoclaving at 121 °C and 15 lbs pressure for 15 min. 20 mL of the sterilized media was poured into sterilized Petri dish and allowed to solidify at room temperature. A sterile cotton swab was used for spreading the test microorganism from the 24 h inoculated broth evenly on the MHA plates. Similarly swabbing was done separately for each test microorganism on the MHA plates and left for few minutes to allow complete absorption of the inoculum. In each of these plates 7 mm diameter wells were made using an appropriate size sterilized cork borer. Each complex extract was added to the respective wells on the MHA plates. The extract loaded plates were kept for incubation at 37 °C for 24 h. After incubation, a clear zone was observed around the well, which was evidence of the presence of antibacterial active compounds in the complexes. Diameters of the zone of inhibition were measured in millimeters (including the diameter of the well).

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 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 are pure and discrete in nature. Thermal decomposition data (Table-2) of the complexes **1-3** in the first step indicated the loss of one coordination water molecule in the temperature range 90-130 °C.

The powder EPR spectra of the complexes **1-3** were recorded at room temperature. The spectra showed trace level impurities of Cu^{2+} and Fe^{3+}. The μ_{eff} values 1.6-1.7 BM indicated the presence of one unpaired electron. The lower value of the magnetic moment in compound **2** may be due to the magnetic interactions between the adjacent paramagnetic centers 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) indicated the presence of coordinated water molecules. The bands at 3440 and 1650 cm^{-1} are attributed to ν(OH) and δ(H_2O) respectively. The bands at 1500 and 1020 $cm^{-1}$are attributed to ν(CN) and ν(CS) of the bidentate dithiocarbamate ligand. The band at 900 cm^{-1} is assigned to ν(W=O_t) which is characteristic [8] of mono nuclear tungsten(V) complexes. The splitting of these bands and the shift to higher frequency (about 10 cm^{-1}) suggest that WO_2^{2+}

TABLE-1
ELEMENTAL ANALYSES DATA OF CADMIUM-TUNGSTEN DITHIOCARBAMATES

Complex code	Elemental analysis (%): Found (calcd.)						μ_{eff} (B.M.)	g_{av}
	C	H	N	S	W	Cd		
1. $[CdWO_2(Et_2dtc)_3(H_2O)_2]$	22.06 (22.78)	4.52 (4.05)	5.88 (5.31)	23.20 (22.78)	22.98 (23.64)	14.41 (14.22)	1.65	1.9978
2. $[CdWO_2(1\text{-}Pipdtc)_3(H_2O)_2]$	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. $[CdWO_2(4\text{-}Morphdtc)_3(H_2O)_2]$	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

TABLE-2
TG-DTA DATA OF CADMIUM-TUNGSTEN DITHIOCARBAMATE COMPLEXES

Complex code	Temperature range (°C)	Weight loss (%)		DTA peaks (°C)	Probable phase formed
		Found	Calcd.		
1. $[CdWO_2(Et_2dtc)_3(H_2O)_2]$	90-130	3.53	3.48	80 (-)	$CdWO_2(Et_2dtc)_3$
	200-290	51.91	51.06	240 (+)	$CdO + WS_3$
	300-600	55.62	54.94	525 (+)	$CdWO_4$
2. $[CdWO_2(1\text{-}Pipdtc)_3(H_2O)_2]$	30-100	2.86	2.18	60 (-)	$CdWO_2(1\text{-}pipdtc)_3$
	110-200	20.83	21.54	165 (+)	$CdWO_2(1\text{-}pipdtc)_2$
	210-290	51.85	52.53	240 (+)	$CdS + WO_3$
	300-510	57.43	56.40	420 (+)	$CdWO_4$
3. $[CdWO_2(4\text{-}Morphdtc)_3(H_2O)_2]$	30-100	5.40	5.24	66 (-)	$CdWO_2(4\text{-}morphdtc)_3$
	110-200	47.04	47.49	160 (+)	$CdO + WS_3$
	210-290	57.77	56.23	235 (+)	$CdS + WO_3$
	300-510	59.62	58.19	426 (+)	$CdWO_4$

TABLE-3
PRINCIPLE FT-IR FREQUENCIES (cm^{-1}) OF
CADMIUM-TUNGSTEN DITHIOCARBAMATES

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

species. The band at 785 cm^{-1} is attributed to ν(Cd-O-W) bridged vibration. The band at 500 cm^{-1} may be assigned Nakamoto *et al.* [8] to ν(Cd-OH_2). The IR spectral data indicated the presence of coordinated water molecules, (W=O_t) (terminal) and Cd-O_b-W (bridge) and the bidenticity of the ligands. The ^{1}H NMR spectra of **1** were recorded in $CDCl_3$ using TMS as a reference. The spectrum of compound **1** has a quartet peak due to –N-CH_2 having d 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. Given the geometry of the molecule, due to restriction in free rotation, the environment 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 and there by bringing difference in the chemical environments of the protons.

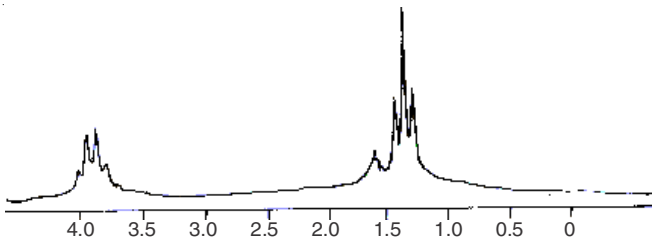

Fig. 1. ^{1}H NMR spectrum of [$CdWO_2(Et_2dtc)_3(H_2O)_2$] in $CDCl_3$

The fast atom bombardment mass spectrum (FABMS) of [$CdWO_2(Et_2dtc)_3(H_2O)_2$] 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 cadmium diethyldithiocarbamate. The peaks at 400 and 391 are attributed to the successive loss of dithiocarbamates and water molecules. Udupa *et al.* [9,10] studied that the isotopic cluster peaks are characteristics of the fragments containing metal ions. The spectrum shows 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 a account the various isotopes (^{182}W, ^{183}W, ^{184}W, ^{186}W, ^{106}Cd, ^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, ^{114}Cd, ^{32}S and ^{34}S) and their abundance. The number of peaks in the original compound coincides with expected theoretical numbers. For example [$CdWO_2(Et_2dtc)_3(H_2O)_2$] should have 16 peaks in the cluster with varying intensities depending upon the abundance.

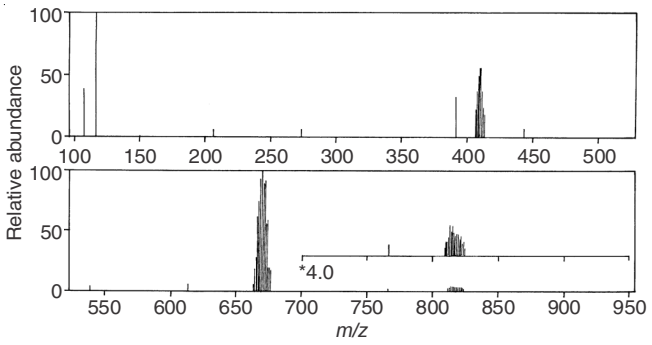

Fig. 2. FAB mass spectrum of [$CdWO_2(Et_2dtc)_3(H_2O)_2$] in *m*-nitrobenzyl alcohol

When one Et_2dtc is removed the number of peaks fall as expected. $Cd(Et_2dtc)_2$ get eliminated and the number of peaks has been found to be in the range of *m/z* 660-675. The cyclic voltammogram of [$CdWO_2(Et_2dtc)_3(H_2O)_2$] has an irreversible cathodic wave at 0.31 V *vs.* SCE, which is assigned one electron reduction step due to formation of the W(IV) and is characteristic of the W(V) centre. Tungsten(V) and cadmium(II) are bridged by μ-oxo group and the octahedral geometry around tungsten(V) and the tetrahedral geometry around cadmium(II) are completed (Fig. 3) by the oxo, aqua and bidentate ligands. Among all the complex the methanol showed highest zone of inhibition for *Bacillus subtilis* (14 mm) followed by *Staphylococcus aureus* (10 mm), while the Gram-negative bacterias showed no activity. The ethanolic extract of *Ulva reticulate* showed the highest activity for *Bacillu subtilis* (12 mm).

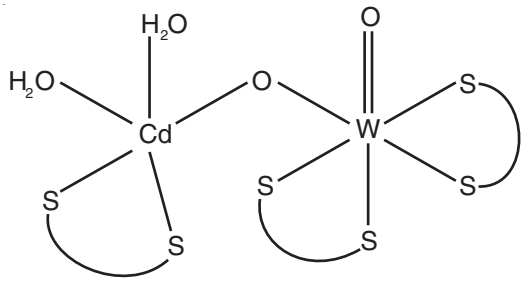

Fig. 3. Proposed structure of [$CdWO_2(L)_3(H_2O)_2$] (L = dithiocarbamate)

Conclusion

The heterobinuclear complexes were prepared and characterized by antibacterial studies. The ^{1}H 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. The present study concluded that heterobinuclear complex prepared by using dithiocarbamates are having potential sources of bioactive compounds and can be used as source for antibacterial agent.

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