

## Oxotransition metal complexes of O,O-diethylphosphonyldithiocarbamate

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**Abstract.** O,O-Diethylphosphonyldithiocarbamate complexes of oxovanadium(IV), oxoniobium(V), oxomolybdenum(V), oxotungsten(V, VI) and oxouranium(VI), formulated as  $\text{VO}(\text{DPD})_2$ ,  $\text{NbO}(\text{DPD})_2$ ,  $\text{Mo}_2\text{O}_5(\text{DPD})_4$ ,  $\text{W}_2\text{O}_7(\text{DPD})_4$ ,  $\text{WO}_3(\text{DPD})_2$  and  $\text{UO}_2(\text{DPD})_2$  [ $\text{DPD} = (\text{EtO})_2\text{P}(\text{O})\text{NHCS}_2^-$ ] have been prepared. These have been characterised on the basis of elemental analyses, electrical conductance, magnetic susceptibility and spectral studies. IR spectral data indicate bidentate nature of the ligand. These complexes are fairly stable in inert atmosphere but decompose on standing in air.

**Keywords.** O,O-Diethylphosphonyldithiocarbamate; oxovanadium(IV); oxoniobium(V); oxomolybdenum(V); oxotungsten(V, VI); oxouranium(VI).

### 1. Introduction

The dithiocarbamate derivatives find their use as fungicides and pesticides (Thorn and Ludwig 1962). Besides their biological significance, the dithiocarbamate ligands possess structural importance too. Dithiocarbamate derivatives often exhibit unusual coordination phenomena because in some complexes, the dithiocarbamate ligand behaves as a monodentate group (Johnson *et al* 1969; Domenicano *et al* 1966), while in others it acts as a bidentate group (Kaushik *et al* 1978, 1979).

In an earlier communication, we reported (Sodhi and Kaushik 1981) a number of O,O-diethylphosphonyldithiocarbamate complexes of the type  $[(\text{EtO})_2\text{P}(\text{O})\text{NHCS}_2]_n\text{M}$  {M = Cu(I), ( $n=1$ ); Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Ni(II), ( $n=2$ ); Co(III), Fe(III), Mn(III), As(III), Sb(III) and Bi(III), ( $n=3$ )}. Our interest in the investigation of bonding mode of O,O-diethylphosphonyldithiocarbamate moiety prompted us to synthesise and characterise some oxotransition metal dithiocarbamates.

### 2. Experimental

#### 2.1 Materials and methods

Potassium O,O-diethylphosphonyldithiocarbamate was prepared by the method described by Addor (1970). Nitrobenzene for conductance measurements was purified as given in the literature (Fay *et al* 1967). The metal contents in these compounds were determined by standard methods (Vogel 1978). Nitrogen was estimated by Kjeldahl's method and sulphur as barium sulphate.

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Conductance measurements were made in nitrobenzene at  $30 \pm 0.1$  using an Elico Conductivity Bridge (Model CM-82). Infrared spectra were recorded (KBr pellets) in the  $4000\text{--}200\text{ cm}^{-1}$  region with a Perkin-Elmer 621 spectrophotometer. Magnetic moment studies were made by the Gouy's method using mercury tetrathiocyanato cobaltate(II) as calibrant.

## 2.2 Preparation of the complexes

2.2a *Oxobis(diethylphosphonyldithiocarbamato)vanadium(IV)*,  $VO(DPD)_2$ : To an aqueous solution of  $VOSO_4 \cdot 2H_2O$  was added an aqueous solution of the ligand in 1:2 molar ratio at  $0\text{--}5^\circ\text{C}$  and the contents stirred for about 15 min at this temperature when yellowish precipitate appeared. It was washed with ice cold water followed by an aqueous ethanol. It was then reprecipitated from an acetone solution by adding petroleum ether ( $60\text{--}80^\circ$ ), dried and stored *in vacuo* over  $P_4O_{10}$ .

2.2b *Oxotris(diethylphosphonyldithiocarbamato)niobium(V)*,  $NbO(DPD)_3$ : It was prepared by mixing an aqueous solution of the ligand to an aqueous solution of niobium pentachloride in 1:3 metal to ligand molar ratio, followed by stirring for 10 min. The white precipitate obtained was washed with ice-cold water and aqueous ethanol. These were recrystallised from an acetone solution by adding petroleum ether ( $60\text{--}80^\circ$ ) and dried *in vacuo* over  $P_4O_{10}$ .

2.2c  $\mu$ -*Oxodioxobis(diethylphosphonyldithiocarbamato)dimolybdenum(V)*,  $[MoO(DPD)_2]_2O$ : Addition of a fresh aqueous solution of sodium dithionite to a stirred solution of the ligand (0.02 mol) and sodium molybdate (0.01 mol) in water resulted in the formation of a brownish-green precipitate. It was washed with cold water and ethanol. It was finally recrystallised from an acetone solution by adding petroleum ether ( $60\text{--}80^\circ$ ) dried and kept in vacuum over  $P_4O_{10}$ .

2.2d  $\mu$ -*Oxodioxobis(diethylphosphonyldithiocarbamato)ditungsten(V)*,  $[WO(DPD)_2]_2O$ : It was prepared by adding an aqueous solution of ligand in excess of an aqueous solution of sodium tungstate at  $0\text{--}5^\circ\text{C}$  and the contents stirred for about 15 min at this temperature. The metal complex thus precipitated was washed with ice cold water followed by aqueous ethanol. It was then recrystallised from an acetone solution by adding petroleum ether ( $60\text{--}80^\circ$ ), dried and kept *in vacuo* over  $P_4O_{10}$ .

2.2e *Dioxobis(diethylphosphonyldithiocarbamato)tungsten(VI)*,  $WO_2(DPD)_2$ : It was prepared by adding dilute hydrochloric acid to a cold aqueous solution of the ligand (0.02 mol) and sodium tungstate (0.01 mol). The light green precipitate thus obtained was washed with cold water followed by aqueous ethanol. It was reprecipitated from an acetone solution by adding petroleum ether ( $60\text{--}80^\circ$ ) and dried under vacuum.

2.2f *Dioxobis(diethylphosphonyldithiocarbamato)uranium(VI)*,  $UO_2(DPD)_2$ : It was prepared by mixing an aqueous solution of ligand to an aqueous solution of uranyl acetate in 1:2 molar ratio and the contents stirred for about 15 min at  $0\text{--}5^\circ\text{C}$ . The orange-coloured complex thus precipitated was washed with ice cold water followed by aqueous ethanol. It was reprecipitated from an acetone solution by the addition of petroleum ether ( $60\text{--}80^\circ$ ), dried and stored *in vacuo* over  $P_4O_{10}$ .

### 3. Results and discussion

The analytical data and some physical characteristics of the complexes are listed in table 1. All the complexes are soluble in common organic solvents. Conductance measurements show that all the complexes are nonelectrolytes in nitrobenzene. All the complexes are fairly stable in inert atmosphere and decompose on standing in air.

#### 3.1 Magnetic moments

All the complexes except those of oxovanadium (IV) are diamagnetic. The magnetic moments of oxovanadium (IV) complexes lie in the range 1.70-1.72 BM at room temperature. These values lie within the range reported for oxovanadium (IV) complexes having one unpaired electron.

#### 3.2 Infrared spectra

Table 2 lists the important infrared frequencies of the complexes. All the complexes exhibit only one strong band at  $\sim 1000 \text{ cm}^{-1}$  supporting the bidentate nature of the dithiocarbamates and also suggesting the chelating nature of the ligand (Johnson *et al*

Table 1. Analytical data and physical characteristics of the complexes

Complex	Melting point ( $^{\circ}\text{C}$ )	Colour	% of elements Calc. (Found)		
			M	S	N
$\text{VO}(\text{DPD})_2$	107 (d)	Yellow	9.75(9.92)	12.23(12.01)	2.67(2.88)
$\text{NbO}(\text{DPD})_3$	200 (d)	White	11.72(11.81)	8.07(8.19)	1.76(1.93)
$\text{Mo}_2\text{O}_3(\text{DPD})_4$	208 (d)	Brownish green	16.66(16.80)	5.55(5.62)	1.21(1.09)
$\text{W}_2\text{O}_3(\text{DPD})_4$	> 250 (d)	White	27.71(27.83)	4.81(4.89)	1.05(1.16)
$\text{WO}_2(\text{DPD})_2$	125 (d)	Light green	27.38(27.12)	9.52(9.77)	2.08(2.32)
$\text{UO}_2(\text{DPD})_2$	120 (d)	Orange	32.78(32.93)	8.81(9.02)	1.92(2.14)

DPD = O,O-diethylphosphonyldithiocarbamate  
(d) with decomposition

Table 2. Characteristic infrared bands ( $\text{cm}^{-1}$ ) of the complexes.

Complex	$\nu(\text{C}\dots\text{N})$	$\nu(\text{C}\dots\text{S})$	$\nu(\text{C-O})$	$\nu(\text{P=O})$	$\nu(\text{M-S})$	$\nu(\text{M=O})$	
$\text{VO}(\text{DPD})_2$	1355s	1005s	1120s	1260m	345m	945m	
$\text{NbO}(\text{DPD})_3$	1340s	1000s	1105s	1275m	360m	925w	
$\text{Mo}_2\text{O}_3(\text{DPD})_4$	1350s	1005s	1105s	1272m	350m	955w	$\nu(\text{Mo-O-Mo})$ 430w 750m
$\text{W}_2\text{O}_3(\text{DPD})_4$	1360s	1010s	1110s	1265m	355m	900w	
$\text{WO}_2(\text{DPD})_2$	1355s	1000s	1100s	1270m	348m	910w	
$\text{UO}_2(\text{DPD})_2$	1365s	1000s	1115s	1275m	355m		$\nu(\text{U-O})$ 915s, 800w

s = strong, m = medium, w = weak.

1969; Brown and Smith 1972; Bonati and Ugo 1967). A doublet is expected in the region  $1000 \pm 50 \text{ cm}^{-1}$  if the ligand is to behave as monodentate. The ligand band at  $\sim 1350 \text{ cm}^{-1}$  is assigned to the  $\nu(\text{C}=\text{N})$ . The occurrence of this band at lower energy in the complexes compared with those of corresponding dialkyl dithiocarbamate complexes, indicates considerably less double bond character of the  $(\text{C}=\text{N})$  bond in these complexes. A strong band at  $\sim 1100 \text{ cm}^{-1}$  is assigned to  $\nu(\text{C}-\text{O})$  in the  $\text{C}_2\text{H}_5\text{OP}$  group, while that at  $\sim 1260 \text{ cm}^{-1}$  is due to  $\nu(\text{P}=\text{O})$ . The  $\nu(\text{N}-\text{H})$  occurs at  $\sim 3075 \text{ cm}^{-1}$ . The bands in the range  $360\text{--}345 \text{ cm}^{-1}$  are assigned to  $\nu(\text{M}-\text{S})$  vibrations (Bradley and Gitlitz 1969).

The new bands in the infrared spectra at *ca* 945 and  $925 \text{ cm}^{-1}$  in the oxovanadium (IV) and oxoniobium (V) complexes, respectively may be assigned to  $\nu(\text{M}=\text{O})$  vibrations (Selbin 1966; Sabatini and Bertini 1966). Complexes of the type  $\text{Mo}_2\text{O}_3(\text{DPD})_4$  have a single  $\text{Mo}=\text{O}$  stretching mode at  $955 \text{ cm}^{-1}$ . In addition, two bands are observed at *ca* 430 and  $750 \text{ cm}^{-1}$  which may be assigned to a symmetrical and antisymmetrical  $\text{Mo}-\text{O}-\text{Mo}$  stretching modes (Cotton and Wing 1965) respectively. In the oxotungsten (V, VI) complexes, the absorption due to  $\nu(\text{W}=\text{O})$  was observed at  $\sim 900 \text{ cm}^{-1}$ . In the oxouranium (VI) complex, two bands at *ca* 915 and  $800 \text{ cm}^{-1}$  may be assigned (Cattalini *et al* 1971) to  $\nu(\text{U}-\text{O})_{\text{asymm}}$  and  $\nu(\text{U}-\text{O})_{\text{symm}}$  modes. These observations indicate that the  $\text{UO}_2$  moiety is virtually linear (Cattalini *et al* 1971).

A comparison of  $\nu(\text{M}-\text{O})$  stretching vibrations in the present complexes with other compounds of similar composition (Kumar and Kaushik 1981), reveals that these frequencies are not sensitive to any unusual geometry.

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