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Studies on Metal-ligand Vibrations in the Complexes of Dioxomolybdenum(VI) and Zirconium(IV) with Dibenzyl Sulphide and Dibenzyl Selenide

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The octahedral complexes of Zr(IV) and MoO_2(VI) with dibenzyl sulphide (DBS) and dibenzyl selenide (DBSe) having general formula $[Zr(NH_3)_5L]\cdot nH_2O$ and $NH_4[MoO_2(OH)_3L]$ (where L = DBS or DBSe) have been prepared and investigated. IR data indicate that ligands co-ordinate through sulphur or selenium atoms of the C–S or C–Se group respectively. νZr–N, νZr–S, νZr–Se, νMo–S, νMo–Se and νMo=O mode of vibrations have also been reasonably assigned in the far infrared region of the spectra of the complexes.

INTRODUCTION

Dibenzyl sulphide (DBS) has been used as a ligand by Haake *et al.*[1–2] James *et al.*[3] have used $[RhCl_3\text{–}\{(PhCH_2)_2S\}_3]$ as a catalyst for the hydrogenation of maleic acid and *trans*-cinnamic acid. Some complexes of this ligand and its selenium analogue have also been reported by Singh and coworkers[4,5]. However, no attention has been paid to study the complexes of second row transition metals in higher oxidation states, specially Mo(VI) which is thought to be one of the essential elements in biological system[6,7]. Moreover, well defined stable dioxomolybdenum(VI) complexes are relatively sparse[8]. In view of this, the present work has been undertaken on the synthesis and characterization of complexes of dibenzyl sulphide and benzyl selenide, and the results on MoO_2(VI) and Zr(IV) complexes are reported here.

EXPERIMENTAL

All chemicals used were of chemically pure grade. Dibenzyl sulphide and dibenzyl selenide were prepared by the method of Singh *et al.*[4] and the products were analysed and their purity spectroscopically confirmed. The MoO_2(VI) and Zr(IV) complexes were prepared by mixing 0.03 mole of corresponding metal salt solution and 0.08 mole solution of ligands in 100 ml ethanol. The mixture was digested on water bath to about 50 ml and the pH of mixture was adjusted to *ca.* 7 using NH_4OH and mineral acid of corresponding salt. The volume of working mixture was further reduced to *ca.* 20 ml by evaporation and cooled. Solid crystals separated out were filtered, washed with ethanol and dried over anhydrous $CaCl_2$ in a vacuum desiccator.

RESULTS AND DISCUSSION

MoO_2(VI) and Zr(IV) form stable complexes with DBS and DBSe. The analytical data indicate the empirical formula of these complexes to be $NH_4MoO_2(OH)_3L$ and $Zr(NH_3)_5L{\cdot}(NO_3)_4{\cdot}nH_2O$ where L = DBS/DBSe and n = 2 or 4 for sulphur and selenium complexes of Zr(IV). The complexes are either insoluble or partially soluble in common organic solvents such as chloroform, ethanol, methanol, benzene, carbon tetrachloride etc. Thus their conductance and molecular weights could not be measured. However, the Na_2CO_3 extract of Zr(IV) complexes responded to the positive *ring test* of nitrate group indicating the presence of ionic nitrate. Zr(IV) complexes are more thermally stable than MoO_2(VI) complexes. All Zr(IV) complexes have m.pt. beyond 350°C. Their insolubility and very high melting points suggest their polymeric nature.

ANALYTICAL DATA OF COMPLEXES

Compounds	Colour	% Analysis (Found/Cal.)			
		C	H	N	M (Mo/Zr)
$NH_4[MoO_2(OH)_3(DBS)]$	Violet	41.01 (40.87)	5.22 (5.10)	3.50 (3.40)	23.30 (23.35)
$NH_4[MoO_2(OH)_3(DBSe)]$	Black	37.01 (36.68)	4.58 (4.80)	3.11 (3.05)	21.22 (20.96)
$[Zr(NH_3)_5(DBS)](NO_3)_4{\cdot}2H_2O$	White	26.32 (26.33)	4.52 (4.54)	19.73 (19.60)	14.06 (14.26)
$[Zr(NH_3)_5(DBSe)](NO_3)_4{\cdot}4H_2O$	Light Yellow	24.64 (24.52)	4.22 (4.23)	18.32 (18.30)	13.01 (13.28)

A close examination of infrared spectra of DBS, DBSe and their analogous compound, $C_6H_5CH_2{\cdot}CH_2C_6H_5$,[9] reveals a close similarity. However, the medium band at 1242 cm^{-1} is present in the spectrum of DBS but is absent in the spectrum of $C_6H_5CH_2{\cdot}CH_2C_6H_5$ as well as $C_6H_5CH_2{\cdot}SeCH_2{\cdot}C_6H_5$. So, it may be assumed that this band has major contribution from νCS. A doublet at 770, 760 cm^{-1} and a very broad band in the range 720–700 cm^{-1} (multiplet) are present in the spectrum of $C_6H_5CH_2{\cdot}SeCH_2{\cdot}C_6H_5$ corresponding to monosubstituted benzene ring and νCS mode of vibration. There are significant changes in the positions and intensites of the bands in the spectrum of the complexes due to coordination. The νCS and νCSe bands of the DBS and DBSe ligands respectively shift from 720 to 670 ± 10 and 615 to 580 ± 10 cm^{-1} on complexation with Zr(IV) and

$MoO_2(VI)$ ions[4-5]. These changes, especially the red shifting, indicate bonding through sulphur and selenium atoms. A strong band observed at 825 cm^{-1} in the spectrum of DBSe is absent in the spectra of DBS and $C_6H_5CH_2 \cdot CH_2C_6H_5$. Hence it may be assigned to νC–Se. The νCSe band of the free DBSe ligand almost disappears in the IR spectra of complexes indicating coordination of DBSe through selenium. The new bands at 1337 ± 5 cm^{-1}, 830–750 cm^{-1} in all Zr(IV) complexes supported the presence of ionic nitrate[10-11] and no such bands are present in DBS, DBSe and other $MoO_2(VI)$ complexes. The two new bands having medium intensity observed at 930 and 880 cm^{-1} in $NH_4[MoO_2(OH)_3L]$ are assigned due to presence of cis-dioxo group in $MoO_2(VI)$ complexes[12-14]. Akira Nakamura *et al.*[13] have suggested similar observation for complexes having general formula $MoO_2((L-L)_2$ where L = diethylthiocarbamate. These authors have observed ν_{sym} Mo=O at 878 cm^{-1} and ν_{asym} Mo=O at 910 cm^{-1} for $MoO_2(dtc)_2$ complexes. Thus, following Stiefel[6], Wentworth[14] and Moore *et al.*[15] the presence of *cis*-dioxo groups are suggested in MoO_2^{2+} moiety. Moreover, preferably *trans* disposition of DBS/DBSe reasonably suggested keeping the bulky nature of these organic ligands.

The bands observed at 3440 sb, 3180 w, 1620 m, 1360 sb and 880 w *cm*$^{-1}$ in $[Zr(NH_3)_5(DBS)](NO_3)_4 \cdot 2H_2O$ and at 3430 sb, 3240 s, 1650 mb, 1460–1290 sb and 835 w *cm*$^{-1}$ in $[Zr(NH_3)_5(DBSe)](NO_3)_4 \cdot 2H_2O$ are assigned to ($\nu H_2O + \nu_a NH_3$), $\nu_s NH_3$, ($\delta_a HNH + \delta H_2O$) $\delta_s(NH_3)$ and $\delta(NH_3)$ mode of vibrations[16,17] respectively. New bands at 3560 ± 10 and 1115 ± 5 cm^{-1} in $MoO_2(VI)$ complexes are assigned to νOH and δMo–O modes[18] and at 3150 ± 10, 1405 ± 5 cm^{-1} are due to characteristic absorption band of NH_4^+-ion[19]. Moreover, there is not any band near 1600 cm^{-1}, clearly indicating the presence of hydroxo group in all $MoO_2(VI)$ complexes[20].

The far infrared spectra of complexes show new bands at 520, 430, 420, 370, 360, 340 and 310 cm^{-1} are assigned due to νZr–N, νZr–S, νZr–Se aMo–Se, ν_aMo–S, ν_sMo–Se and ν_sMo–S mode of vibrations respectively. The low value of νMo–S compared to νZr–S may be explained on the basis of mass effect of heavy molybdenum atom. Thus, on the basis of aforesaid discussion, the octahedral configuration may be suggested to all complexes. However, in dioxomolybdenum(VI) complexes at equatorial position dioxo groups are at *cis* and most probably OH is *trans* to OH, DBS or DBSe is *trans* to one of the dioxogroups, and one OH group is *trans* to other oxygen of *cis* dioxo group.

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