

Oxohalobis(oxinato)molybdenum(V) Complexes

D JOSHUA ANTHONY RAJ & K S NAGARAJA

Department of Chemistry, Loyola College
(Autonomous), Madras 600 034

and

M R UDUPA*

Department of Chemistry, Indian Institute
of Technology, Madras 600 036

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Molybdenum complexes of the type, $\text{MoOX}(\text{oxine})_2$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I) have been prepared and characterized. The conductivity values indicate that the complexes are non-electrolytes. The magnetic and EPR spectral data suggest that the complexes are monomeric with molybdenum in pentavalent state. The electronic spectral bands at 640, 540 and 370 nm are assigned to $b_2 \rightarrow e$, $b_2 \rightarrow b_1$ and $\text{O}(\pi) \rightarrow d(\text{Mo})$ transitions respectively. The IR frequency at 930 cm^{-1} due to $\nu_{\text{Mo}=\text{O}}$ confirms the presence of MoO^{3+} moiety. Based on these data an octahedral structure, with oxo, halo and bidentate oxinato ligands completing six coordination around molybdenum, has been proposed. The complexes are stable upto 200°C and undergo oxidative decomposition in air to MoO_3 around 650°C .

Enzymes such as nitrogenase, nitrate reductase, xanthine dehydrogenase, xanthine oxidase, sulphite oxidase and aldehyde oxidase contain molybdenum atoms bonded through O, N and/or S atoms. These Mo sites are supposed to be the active centres for the catalytic activity of the enzymes¹. Except nitrogenase, other molybdo-enzymes are found² to be EPR-active during electron transfer, which is attributed to the presence of Mo(V) centres; EXAFS studies have indicated³ the presence of an oxo group attached to molybdenum. This has aroused considerable interest in the study of oxomolybdenum(V) complexes. The reported synthetic procedures⁴⁻⁷ for the oxohalomolybdenum(V) complexes involve the use of $(\text{NH}_4)_2\text{MoOX}_5$ or atom transfer reactions. We report in this note an elegant method^{8,9} of preparation of oxohalomolybdenum(V) complexes of oxine. The ligand oxine was selected because it is similar to flavin unit which is generally associated with the molybdo-enzymes.

Molybdenum trioxide, hydrazine and oxine were of LR grade. Hydrazinium halides were prepared by following the method reported⁸ elsewhere.

Preparation of oxochlorobis(oxinato)- molybdenum(V), $\text{MoOX}(\text{oxine})_2$

To suspension of MoO_3 (0.5 g) in 20 ml N,N-dimethylformamide, was added 1 ml of conc. HCl

followed by hydrazinium chloride (2 g). The reaction mixture was stirred. To the resultant clear green solution was added an ethanolic solution of oxine (2 g in 60 ml). After stirring for 15 min, the precipitated product was filtered, washed with ethanol and dried; yield 70%. The other halo complexes were prepared by similar procedures employing the respective hydrazinium halides and hydrohalic acids. Polyethylene containers were employed for the preparation of fluoro complex.

The conductivities of the complexes were measured in N,N-dimethylformamide using a Wyne Kerr autobalance B 642 conductivity bridge. Magnetic susceptibility measurements were carried out on a Gouy balance and the magnetic moment values were calculated after applying¹⁰ diamagnetic and temperature independent paramagnetic corrections. The electronic, IR and far IR spectra were recorded on Carl Zeiss DMR 21, Perkin-Elmer 257, Polytech IR 12 spectrophotometers respectively and EPR spectra were recorded on a Varian E-4 x-band spectrometer. The thermal decomposition study was made using a Stanton recording thermobalance in air at a continuous heating rate of 6°C min^{-1} .

The analytical, conductivity, magnetic and spectral data are given in Tables 1 and 2. The molar conductivity values are in the range $14\text{--}22 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ which suggest that the complexes are non-electrolytes.

The magnetic moment values of $\sim 1.7 \text{ B.M.}$ correspond to the presence of one electron indicating that Mo is in d^1 configuration. The EPR spectra of powder samples exhibited a single line. However, the spectra in dichloromethane showed a six-line pattern due to the interaction of electron spin with the nuclear spin ($I = 5/2$) of ^{95}Mo and ^{97}Mo . The calculated g_{av} values of 1.9-2.0 indicate that the complexes are monomeric with molybdenum in the pentavalent state.

The electronic spectral bands observed around 640 and 540 nm are assigned⁶ to $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$ transitions respectively. The high energy and high intensity band around 370 nm is most likely due to $\text{O}(\pi) \rightarrow d(\text{Mo})$ charge-transfer transition rather than the halogen to molybdenum charge-transfer as explained by Sabat *et al*¹¹. This transition is probably obscured by the more intense $\text{S} \rightarrow \text{Mo}$ charge-transfer band in the complexes^{8,9} of type $\text{MoOX}(\text{Et}_2\text{dtc})_2$ and hence is not located.

The IR spectra of the complexes show a strong band around 930 cm^{-1} corresponding⁹ to $\text{Mo}=\text{O}$ stretching frequency. The principal bands of oxine moiety are

Table 1—Analytical, Conductivity and Magnetic Moment Data of the Molybdenum Complexes

Complex	Found (calc.), %					Λ_M (ohm ⁻¹ cm ² mol ⁻¹)	$\mu_{\text{eff.}}$	g_{av}
	C	H	N	X	Mo			
MoOF(oxine) ₂	51.41 (51.54)	2.84 (2.89)	6.57 (6.68)	—	22.60 (22.88)	13.6	1.69	1.93
MoOCl(oxine) ₂	49.58 (49.62)	2.80 (2.78)	6.33 (6.43)	8.07 (8.14)	21.70 (22.02)	22.0	1.67	1.97
MoOBr(oxine) ₂	44.92 (45.02)	2.55 (2.52)	5.79 (5.83)	16.85 (16.84)	19.60 (19.98)	15.9	1.70	1.98
MoOI(oxine) ₂	41.03 (41.01)	2.32 (2.30)	5.31 (5.31)	23.95 (24.07)	17.60 (18.20)	14.8	1.70	2.06

Table 2—Electronic and Infrared Spectral Data of the Molybdenum Complexes

Complex	λ_{max} (nm) (ϵ)			ν (cm ⁻¹)			
				Mo=O	Mo—O	Mo—N	Mo—X
MoOF(oxine) ₂	610 (480)	530 (110)	370 (910)	935	540	310	555
MoOCl(oxine) ₂	640 (610)	520 (130)	365 (3740)	935	535	310	295
MoOBr(oxine) ₂	645 (665)	530 (140)	365 (4400)	940	540	310	210
MoOI(oxine) ₂	645 (630)	525 (145)	365 (4200)	925	540	315	—

observed at 1500 [νCN], 1100 [νCO] and 640 and 430 cm⁻¹ (quinoline ring) which show slight shifts in their positions from those observed in the spectrum of the free ligand suggesting the deprotonation and chelation of oxine to molybdenum^{12,13}. In the far IR region, the spectra exhibit bands around 540 and 310 cm⁻¹ due to Mo—O and Mo—N stretching frequencies respectively. The bands at 555, 295 and 210 cm⁻¹ are assigned^{8,9} to $\nu\text{Mo—F}$, $\nu\text{Mo—Cl}$ and $\nu\text{Mo—Br}$ respectively. The Mo—I stretching frequency appears below 200 cm⁻¹ and could not be recorded by the instrument used in the present study.

The thermogravimetric study in air suggests that the complexes decompose in two stages in the temperature ranges (in °C) 280-480 and 500-620 (fluoro), 200-380 and 580-660 (chloro), 200-400 and 580-640 (bromo) and 190-410 and 585-640 (iodo). The mass losses observed at the first stage for the fluoro, chloro, bromo and iodo complexes are 34, 8, 17 and 22% respectively. Though the intermediate phases have not been isolated and identified by chemical analyses, the observed mass losses suggest the removal of an oxine, and a chlorine, bromine or iodine moiety. The respective calculated mass losses are 34.4, 8.1, 16.6 and 22.3%. The final product of decomposition, obtained around 650°C, in all the cases is analyzed to be MoO₃ which is confirmed by the observed and calculated mass losses. The results suggest that the fluoro complex is thermally most stable and the iodo complex is the least. Further, Mo

—X (X = Cl, Br, I) bond is less stable towards heat than the Mo-oxine bonds whereas the latter seem to be comparatively less stable than the Mo—F bond.

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