

Oxo-molybdenum(V) Complexes

Part I. Molybdenum(V) Complexes with N-Oxides

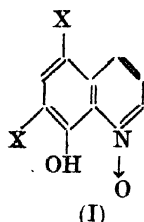
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Several types of co-ordination compounds with oxine N-oxide of the composition $[\text{MoOCl}(\text{AB})_2]$ (where ABH = a molecule of oxine N-oxide/5,7-dibromo oxine N-oxide (DBO N-oxide), $[\text{MoO}_2(\text{oxine N-oxide})\text{py}]$ and $[\text{Mo}_2\text{O}_2\text{Cl}_4(\text{AB})_2(o\text{-phen})]$ have been synthesized and characterised by IR, reflectance spectra and elemental analysis. The complexes are all diamagnetic except oxo-chloro-bis(oxine N-oxide) Mo(V) which is feebly paramagnetic.

N-OXIDES, though much weaker donors than the parent reagents, form stable complexes with many metals particularly with the transition metals¹⁻⁷ and rare earths⁸. But there is to date, only one report of such an oxo-molybdenum(V) complex². This communication deals with a few complexes of oxo-molybdenum(V) with oxine-N-oxide ($X = \text{H}$) and its 5,7-dibromo derivative ($X = \text{Br}$) (Structure I).



A filtered alcoholic (anhydrous) solution of $(\text{NH}_4)_2[\text{MoOCl}_2]$ reacts with excess oxine N-oxide to yield a snuff coloured solid of composition $[\text{MoOCl}(\text{oxine N-oxide})_2]$. The complex is feebly paramagnetic possibly due to polymerization. It has been suggested that Mo(V) complexes containing single oxygen bridge have the higher magnetic moment⁹. The 5,7-dibromo derivative yields deep-brown diamagnetic compound of similar composition.

Instead of using oxine N-oxide or its dibromo derivative in excess, if molybdenum and the reagents are used in (1 : 1) ratio in anhydrous alcohol and then one mole of *o*-phenanthroline is added, crystalline complexes of general composition $\text{Mo}_2\text{O}_2\text{Cl}_4(\text{AB})_2(o\text{-phen})$ (where ABH = a molecule of oxine N-oxide/5,7-dibromo oxine N-oxide) are obtained which are diamagnetic. The diamagnetism of the Mo(V) compounds are suggestive of Mo-Mo bonding in the solid complexes. That the complex is not a mixture of $[\text{MoOCl}(\text{AB})_2]$ and $[\text{MoOCl}_3(o\text{-phen})]$ has been proved by an examination of the properties of these two complexes. $[\text{MoOCl}_3(o\text{-phen})]$ ¹⁰ is green, para-

magnetic complex, whereas $[\text{MoOCl}(\text{oxine N-oxide})_2]$ and $[\text{MoOCl}(\text{BDO oxine N-oxide})_2]$ are snuff-coloured, feebly paramagnetic ($\mu_{\text{eff}} = 0.70 \text{ B.M.}$), and brown, and diamagnetic, respectively.

Earlier studies of compounds with quinoline carboxylic acids¹¹ namely MoO_2QX (where QH = a molecule of quinoline carboxylic acid and X = a heterocyclic base) inspired similar studies with oxine-N-oxide and the compound $[\text{MoO}_2(\text{oxine N-oxide})(\text{py})]$ (where py = pyridine) has been isolated and characterised. This is also diamagnetic.

The complexes are insoluble in common organic solvents and so reflectance spectra were recorded (see Fig. 1).

The spectral bands for the complexes are not well defined. From Fig. 1, the only band assignments which can be made reasonably are for the 370 nm band for oxo-chlorobis(dibromooxine N-oxide) (I) and 550 nm band for μ -*o*-phenanthroline dioxo-tetrachlorobis(dibromooxine N-oxide) (III). The bands for oxo-chlorobis(oxine N-oxide) (II) are not resolved at all. The approximate peak positions for the above complexes are given purely on the basis of visual observation. IR spectra have been shown to be used to detect metal-oxygen bond in oxo-metal complexes with extreme reliance. The complexes have strong absorption bands at 909, 917, 971, 1042 and 1053 cm^{-1} respectively. The bands corresponding to 909 and 917 cm^{-1} have been assigned to symmetric $\text{Mo}=\text{O}$ stretching frequency^{5,9,12}. Absorption around 649, 725 and 847 cm^{-1} are characteristic of co-ordinated *o*-phenanthroline¹³. The band around 704 and 714 cm^{-1} may be assigned to $\text{Mo}-\text{O}-\text{Mo}-\text{O}$ ^{5,9}. However in the case of $[\text{Mo}_2\text{O}_2\text{Cl}_4(\text{DBO oxine N-oxide})_2(o\text{-phen})]$, this band is masked by that of co-ordinated *o*-phenanthroline.

Experimental

Ammonium oxopentachloromolybdate was prepared by following standard procedure¹⁴. Oxine

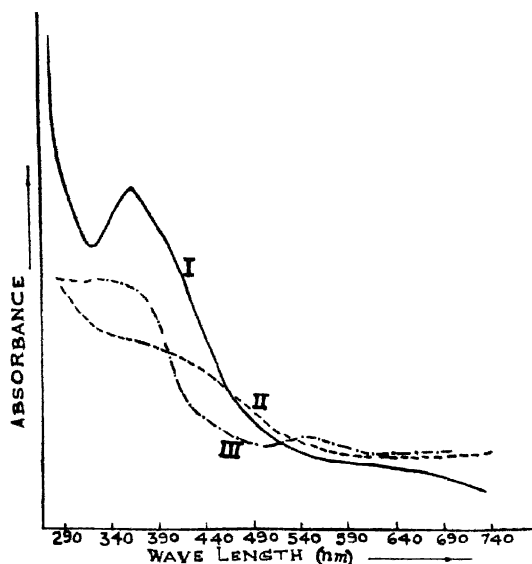


Fig. 1. Reflectance spectra of the complexes (Absorbance is arbitrary) :

- I. Oxo-chloro-bis(dibromo oxine N-oxide)-molybdenum(V)
- II. Oxo-chloro-bis(oxine N-oxide)-molybdenum(V)
- III. μ -o-phenanthroline-dioxo-tetrachloro-bis (dibromo oxine N-oxide)-dimolybdenum(V).

N-oxide and its dibromo derivative were prepared following Bhat and Jain¹⁵, and Ramiah¹⁶. No precaution to exclude air or moisture was taken during the preparation of complexes.

I. *Oxo-chloro-bis(oxine N-oxide) molybdenum (V)* (Snuff coloured) :

To one mole of filtered anhydrous alcoholic solution of ammonium oxo-pentachloromolybdate, three moles of alcoholic solution of oxine N-oxide was added. A snuff colour precipitate appeared immediately which when refluxed on sand bath provides snuff colour crystalline compound. The precipitate was washed with anhydrous alcohol and dried over CaCl_2 . (Found : Mo, 20.2; Cl, 7.25; N, 2.8; $[\text{MoOCl}(\text{oxide N-oxide})_2]$ requires Mo, 20.5; Cl, 7.6; N, 2.9%).

II. *Oxo-chloro-bis(5,7-dibromooxine N-oxide) molybdenum (V)* (Brown coloured) :

The brown crystalline compound was prepared by following the above procedure except the mixed solvent; alcohol-chloroform, was used instead of anhydrous alcohol (Found : Mo, 20.0; Cl, 7.0; N, 6.0; $[\text{MoOCl}(\text{DBO N-oxide})_2]$ requires : Mo, 20.3; Cl, 7.4; N, 5.8%. $\mu_{\text{eff}} = 0.70$ B.M.)

III. *Pyridine-dioxo-mono (oxine N-oxide) molybdenum (V)* (Dull orange) :

One mole of ammoniumoxopentachloromolybdate was dissolved in minimum quantity of rectified spirit.

Two moles of reagent with five moles of pyridine was refluxed when a clear solution was obtained. To this clear solution, the brown solution of ammonium-oxochloromolybdate in rectified spirit was added. Immediately a dull-orange coloured crystalline precipitate was obtained. It was refluxed for half an hour on sand bath, cooled, filtered, washed with rectified spirit and dried over CaCl_2 . (Found : Mo, 27.2; N, 7.3; $[\text{MoO}_2(\text{oxine N-oxide})(\text{py})]$ requires : Mo, 26.8; N, 7.5%).

IV. μ -o-phenanthroline-dioxo-tetrachloro-bis(oxine N-oxide) di-molybdenum (V) (Snuff coloured) :

To one mole of filtered anhydrous alcoholic solution of ammoniumoxopentachloromolybdate, a mixture of two moles of anhydrous alcoholic solution of oxine N-oxide and one mole of alcoholic solution of o-phenanthroline was added. Immediately a snuff coloured solid separated. This was refluxed for one hour on sand bath and filtered. It was washed repeatedly with alcohol and dried over CaCl_2 . (Found : Mo, 21.8; Cl, 16.2; N, 6.2; $[\text{Mo}_2\text{O}_2\text{Cl}_4(\text{oxine N-oxide})_2(\text{o-phen})]$ requires : Mo, 22.1; Cl, 16.4; N, 6.3%).

V. μ -o-phenanthroline-dioxo-tetrachloro-bis (dibromo oxine-N-oxide) (di-molybdenum (V) :

This was prepared as above using dibromo oxine N-oxide in place of oxine N-oxide. The solvent used was a mixture of anhydrous alcohol and chloroform. (Found : Mo, 16.1; Cl, 11.8; N, 4.5; $[\text{Mo}_2\text{O}_2\text{Cl}_4(\text{DBO oxine N-oxide})_2(\text{o-phen})]$ requires : Mo, 16.4; Cl, 12.0; N, 4.6%).

Analytical procedures : Molybdenum was estimated gravimetrically as MoO_2 (oxinate) after decomposing the complex by fuming with concentrated H_2SO_4 and HNO_3 .

Chlorine was estimated after decomposing the complex with alkaline hydrogen peroxide and precipitating Cl^- as AgCl after acidification with HNO_3 . This was dissolved in NH_4OH , reprecipitated with dil. HNO_3 and weighed as AgCl as usual. Nitrogen was estimated by semi-micro combustion technique. The magnetic susceptibility was measured in a Gouy balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as calibrant. IR spectra were scanned on Perkin-Elmer Spectrophotometer using KBr disc. technique.

Reflectance spectra were recorded using a Cary Spectrophotometer (model 14).

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