

Mononuclear Dioxomolybdenum(VI) and Dioxotungsten(VI) Complexes with Di(1-Phenyl Tetrazoline)-5, 5'-Disulphide

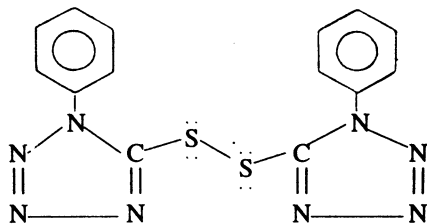
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Di (1-phenyl tetrazoline) -5, 5'-disulphide (TDS) forms very stable complexes with MO_2^{2+} species ($M = \text{Mo}$ or W) having general formula $[\text{MO}_2(\text{TDS})_2\text{Cl}_2]$ and $[\text{MO}_2(\text{TDS})_4\text{Cl}_2]$. The disulphide ligand interacts with MO_2^{2+} species through one of the disulphide sulphur atoms. All the complexes are distorted octahedral structure in which two oxygen atoms are *cis* in MO_2 group and two bulky ligands are at *trans* dispositions.

INTRODUCTION

Molybdenum is thought to be one of the essential trace element in the biological system¹⁻³. Several aspects of molybdenum chemistry have been widely studied to gain a better understanding of its biological relevance but the precise nature of many of the species is hard to ascertain⁴. In the oxo-complexes of hexavalent molybdenum, MoO^{4+} , MoO_2^{2+} & MoO_3 structural units are usually encountered. Although, MoO^{4+} ⁵ and MoO_3 ⁶ are known only in a relatively small number of molybdenum(VI) complexes, complexes containing the MoO_2^{2+} core are by far the most common in molybdenum(VI) Chemistry⁷⁻¹⁰. Moreover, this group is present in certain enzymes.^{11, 12} In view of these significances the present work is under taken at the synthesis and characterisation of some complexes of MoO_2^{2+} and its analogue WO_2^{2+} with solid and stable physiologically active di-(1-phenyl tetrazoline)-5, 5'-disulphide(I)



EXPERIMENTAL

All chemical used were chemically pure grade. Phenyl isothiocyanate was prepared by the method of Gilman and Blatt¹³ and 1-phenyl tetrazoline-5-thiol

was prepared by the method of Lieber *et al.*¹⁴. The ligand was prepared by the method described earlier¹⁵. Complexes were prepared using a general method. An alcoholic solution of metal salt was mixed with ligand solution in ethyl acetate using an appropriate molar ratio. The reaction mixture was then refluxed and the volume of the mixture reduced to *ca.* 40 mL by evaporation. The pH of the mixture adjusted to 6 using the corresponding acid or the base. The complexes formed were digested on water bath for 1/2 h, centrifuged, washed with ice-cold ethanol and dried over anhydrous CaCl₂ in a vacuum desiccator.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Compound	Colour/ (m.p., °C)	Molar conductance ($\Omega^{-1} \text{ cm}^2 \text{ Mole}^{-1}$)	% Analysis Found/(Calcd)			
			C	H	N	M
[MoO ₂ (TDS) ₂ Cl ₂]	greenish yellow (250)	13.2	37.32 (37.08)	2.10 (2.22)	24.89 (24.72)	10.96 (10.60)
[MoO ₂ (TDS) ₄ Cl ₂]	blue (250)	160	41.30 (41.60)	2.40 (2.47)	27.62 (27.73)	6.01 (5.94)
[WO ₂ (TDS) ₂ Cl ₂]	greenish yellow (250)	10.4	33.56 (33.78)	2.11 (2.01)	22.32 (22.52)	18.32 (18.48)
[WO ₂ (TDS) ₄ Cl ₂]	yellow (250)	155	39.50 (39.47)	2.21 (2.34)	26.46 (26.31)	10.52 (10.79)

RESULTS AND DISCUSSION

Di(1-phenyl tetrazoline) -5, 5'-disulphide (TDS) forms nonhygroscopic and stable yellow or yellowish green coloured, solid with MO₂²⁺ species (M = Mo or W). Analytical data (Table-1) indicate 1:2 and 1:4 metal ligand stoichiometry having empirical formula MO₂(TDS)₂Cl₂ and MO₂(TDS)₄Cl₂. All the complexes are diamagnetic as expected for *d*-configuration¹⁶ and fairly soluble in DMF. The molar conductance of 10⁻³M solution of MO₂(TDS)₂Cl₂ and MO₂(TDS)₄Cl₂ are found in the range of 9–10 and 150–170 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively suggesting their formula as [MO₂(TDS)₂Cl₂] and [MO₂(TDS)₄Cl₂].

A comparison of the infrared spectral bands of the ligand and complexes indicate the following:

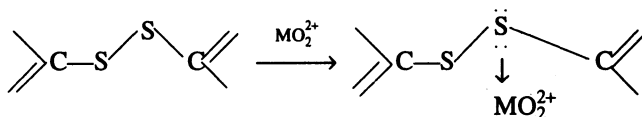
- (I) The spectra of the ligand (TDS) and the complexes are quite similar from 4000 cm⁻¹ to 1595 cm⁻¹.
- (II) The band at 1495 cm⁻¹ in the spectrum of the ligand remains almost at the same place with the same intensity in the spectra of the complexes. As this a mixed band having contribution from $\nu(\text{C}=\text{N})$ and δCH , there appears to be no involvement of these groups in coordination.
- (III) Another change is observed in 1335 cm⁻¹ region where there is a weak band in the spectrum of the ligand but this band disappears from the spectra of the complexes. This indicates bonding of the ligand through sulphur. This is also supported by the splitting of the $\nu(\text{C}-\text{S})$ band of the ligand (690 cm⁻¹) into two new bands of complexation. of the

$\nu(\text{C—S})$ band of the ligand remains at about the same position but $\nu(\text{C—S})$ (M) mode shifts to lower region ($675\text{--}662\text{ cm}^{-1}$). This indicates that out of the C—S—S—C skeleton of the ligand, one of the two sulphur atoms has coordinated with MO_2^{2+} ion while the other sulphur atom remains uncoordinated (C—S—S—C). This generates two $\nu(\text{C—S})$



bands νCS and $\nu\text{CS(M)}$ as indicated above.

- (IV) The medium bands at 570 cm^{-1} ($\nu_{\text{asym}}\text{C—S—S—C}$) and at 555 cm^{-1} ($\nu_{\text{sym}}\text{C—S—S—C}$) in the spectrum of the ligand much more affected on coordination to MO_2^{2+} species. The 555 cm^{-1} band disappears and only one medium band is observed at $560 \pm 5\text{ cm}^{-1}$. This may be taken as proof of coordination of one of the S-atoms of the disulphide group (S—S) to all dioxo metal ions as below:



However, the 555 cm^{-1} band is considerably reduced in intensity and it is observed as weak shoulder only in $\text{WO}_2(\text{TDS})_2\text{Cl}_2$.

- (V) The $\nu(\text{S—S})$ mode¹⁷⁻²⁰ observed at 500 cm^{-1} in the form of a medium band in the spectrum of the ligand red shifts (*ca.* 20 cm^{-1}) to lower frequencies and its intensity is considerably reduced on coordination of the ligand to MO_2^{2+} ion. This further supports coordination of the ligand to the dioxo metal ion through disulphide sulphur.
- (VI) Two non-ligand bands at 960 cm^{-1} and 900 cm^{-1} in dioxomolybdenum (VI) complexes and at 970 cm^{-1} and 910 cm^{-1} in dioxotungsten (VI) complexes are consistent with *cis*-dioxo structure of the MO_2^{2+} species. Generally *trans*-dioxo group exhibit only one $\nu(\text{M=O})$ band.²⁴ Thus, these six coordinate complexes have most probably distorted octahedral structure with the oxygens mutually *cis*, thereby maximising the $\text{O}(\text{p}\pi) \rightarrow \text{M}(\text{d}\pi)$ bonding and the bulky ligands take up *trans* disposition.
- (VII) New bands at 370 cm^{-1} and 320 cm^{-1} in $[\text{MoO}_2(\text{TDS})_2\text{Cl}_2]$ and at 410 cm^{-1} and 360 cm^{-1} in $[\text{WO}_2(\text{TDS})_2\text{Cl}_2]$ are assigned due to metal-chlorine and metal-sulphur stretching mods.²⁵⁻²⁷

Thus, on the basis of aforesaid observations, distorted octahedral structure may be assigned to all these complexes. The two oxygen atoms in MO_2 moiety are *cis* and two bulky disulphide ligands are *trans* disposition in octahedral structure considering steric bulk of disulphide ligand.

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