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Study of molybdenum complex in isomeric aspect

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Abstract

Molybdenum is an important metal in living organisms and occurs in at least four enzymes, Xanthine oxidase, Aldehyde oxidase, Nitrate reductase and Nitrogenase. The important role of molybdenum has been established in physiological functions of oxomolybdenoenzymes. This class of enzymes catalyse conversion of Xanthine of Uric acid, sulphite to sulphate and nitrate to nitrite, which involve the molybdenum centers undergoing redox reactions by transfer of oxygen atoms. It possesses a large number of stable and variable oxidation states as well as coordination numbers, which can vary from four to eight. Although only a minor constituent of the earth's crust, molybdenum is readily available to biological systems because of the solubility of molybdate salts in water. Molybdenum is found in the active sites of enzymes¹ such as nitrogenase, aldehyde oxidase, xanthine oxidase, sulfite oxidase, nitrate reductase and xanthine dehydrogenase.

Keywords: Molybdenum complex, isomeric aspect, oxomolybdenoenzymes

Introduction

In contrast to the multinuclear iron- and molybdenum-containing centers in bacterial nitrogenases (responsible for fixing atmospheric nitrogen into the biosphere), the active sites of all other well-characterized molybdenum-containing enzymes and mononuclear. The vast majority of these enzymes possess at least one Mo=O unit in their active sites and are often referred to as oxo-molybdenum enzymes^[1]. The fact that molybdenum-oxygen bonds are present in molybdo enzymes has stimulated research in molybdenum complexes with oxygen environments. In order to mimic the biological systems, a number of oxomolybdenum compounds have been synthesized and studied.

Several industrial processes such as ammoxidation of olefins,^{2a} olefin epoxidation^{2b} and olefin metathesis^{2c} are performed over molybdenum catalysts. The reactivity of selected *cis*-dioxomolybdenum (VI) compounds is recently reviewed by Jeyakumar and Chand^[3], also by Sand and Perdosa^[4]. We have surveyed the literature on synthesis and reactivity of Mo(VI)-ONO type complexes. In the year 1989 syamal and Maurya published a review on Schiff base complexes of molybdenum^[6] which also accounted *cis*-dioxomolybdenum (VI)- tridentate Schiff base ligands. This document covers the chemistry of several *cis*-dioxomolybdenum complexes of dianionic tridentate ONO ligands, mostly Schiff bases, with particular emphasis on the recent progress.

Present scenario in molybdenum chemistry has attracted world-wide attention. Consequently, we are also attached to carry out research in this fascinating field and as a result the present program of synthesizing and characterizing a series of Mo(VI) complexes with a series of macrocyclic ligand is undertaken. Before presenting the outcome of present work, it will be appropriate to present earlier work done in the field.

Geometrical Polymerization

The coordination geometry around the Mo center in a mononuclear complex can be best described as a distorted octahedron in which the ONO-tridentate ligand occupies meridional position with who anionic oxygen donors mutually trans and are cis to the oxygen centers of the *cis*-dioxo group (figure-1).

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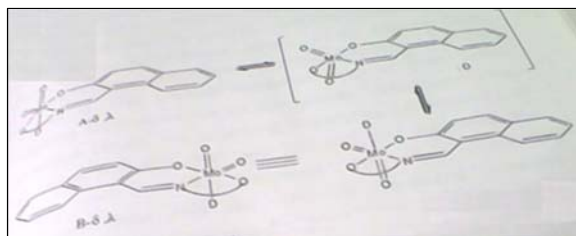
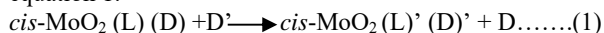


Fig 1: Proposed pathway showing inter-conversion of the isomers A and B.

Scheme 3.

The usual octahedral geometry of a molybdenum center is additionally completed by a coordinated solvent molecule or monodentate neutral ligand (D). The labile coordination site of molybdenum occupied by D allows favorable uptake and activation of substrates during the Lewis acid catalyzed transformations. However, this site can also be responsible for dimerization and oligomerization/polymerization of mononuclear complexes. The coordination polymer of a polynuclear Dioxomolybdenum (VI) complexes generally exhibits a linear Mo=O...Mo=O... chain where the axial oxo-ligand participates in bridging. The arrangement gives rise to a structure where one (MoO(μ-O)(L)) unit coordinates to the sixth site of the molybdenum atom of an adjacent unit. Tri/tetranuclear cyclic structures having three/four such units cyclised to give six/eight-membered rings or even higher nuclearity cyclic structures are also known [29]. The mononuclear complexes exhibit two stretching frequencies [ν(O)=Mo=O] in the region 910-950 cm⁻¹ and 890-925 cm⁻¹ indicating the presence of cis-MoO₂ fragment. However, oligomeric compounds show one ν(Mo=O) vibrational stretching frequency in the region 930 cm⁻¹ and a strong characteristic band around 800 cm⁻¹ due to Mo=O...Mo=O... interaction. Thus, IR spectroscopy can be used to distinguish an oligomeric complex from a monomeric complex. [9] The oligomers react with wide variety of unidentate neutral ligands, (D) such as aldehydes, amides, amines, sulfoxides, phosphine oxides, water, alcohol and phosphines to form mononuclear complexes. Further, the mononuclear molybdenum complexes can undergo ligand substitution reactions where (D) can be substituted by (D₂) as shown in equation 1.



On the basis of ligand displacement reactions, the binding of some D (or D₂) increases in the order of cetaldehyde < benzaldehyde < ethanol < anisaldehyde < dimethylformamide < picoline < dimethyl

sulfoxide < imidazole < pyridine-N-oxide [9]. The complexes are found to be non-electrolyte and diamagnetic as expected for a 4d⁰ system, however, ligand to metal charge transfer (LMCT) band can be seen in the electronic spectrum. [7, 10] Nkajima *et al.* have discussed structural properties of a monomeric complex in the solid and solution states [16]. The cis-dioxomolybdenum (VI) complex of the chiral Schiff base ligand, 2b derived from 2-hydroxy-1-naphthaldehyde and (R)-2-aminobutanol can potentially give four possible isomeric structures i.e., A-δ, -λ, B-δ and B-λ due to the conformational changes of the non-planar five-member ring as shown in scheme 2.

Observation of only one set of signals in the proton NMR spectrum of the complex, even at low temperature, suggests rapid exchange of the isomers in NMR time scale. However, the X-Ray crystal structure revealed the existence of the A-δ

isomer, in solid state. Fast puckering of the conformation of the chelate.

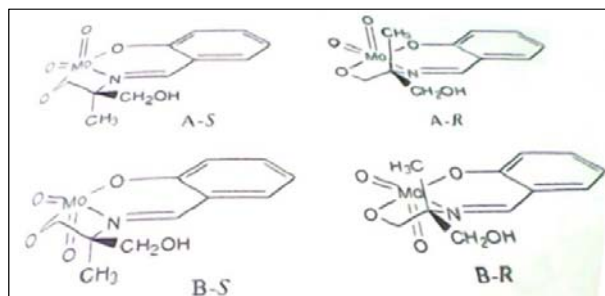


Fig 2: Four isomers of the monomeric complex generated from a prochiral ligand. The complex B-R is the mirror image of A-S, and B-S is the mirror of A-R

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