Synthesis and X-Ray Diffraction Studies of cis MoO$_2$ (VI) Complexes Derived from Benzoyl Hydrazones

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ABSTRACT
Some novel dioxo-molybdenum (VI) hydrazone complexes of Schiff base ligands having the general formula cis-[MoO$_2$(L)(solv)] (where LH$_2$ = Schiff base ligand and solv=ethanol/H$_2$O) are synthesized, characterized by elemental, spectral analysis and structure and symmetry properties is determined using XRD. X-ray powder diffractionometry deals exclusively with crystalline materials, the diffraction pattern being used to determine the degree of crystallinity, (e.g. the dimensions of the crystalline region in otherwise amorphous substance). X-ray powder diffractions of the dioxo-molybdenum (VI) complexes of Schiff base derived from salicylaldehyde (sal) and substituted salicylaldehydes such as o-hydroxyacetophenone (hap); o-hydroxypropiophenone (hpp) with benzoic acid hydrazide (BAH) have been studied and all were found crystalline. The lattice parameters and Miller’s indices were computed. The indexing and calculation of unit cell parameters were performed with the help of Powder-X Software. The 2θ values, the relative intensity, the interplanar distance along with Miller’s indices for corresponding angles are calculated for the complexes. After indexing the X-ray powder patterns and unit cell refinements, it is found that the complexes (1-3) are crystalline and adopt triclinic crystal system with P type lattice. This is expected for distorted octahedral complexes.

Keywords— Dioxo-molybdenum(VI)Hydrazone complexes, Schiff base ligands, XRD, Triclinic.

I. INTRODUCTION
Coordination chemistry of molybdenum(VI) has attracted considerable attention due to its biochemical significance[1] as well as for the catalytic properties in several organic synthesis procedures.[2] Schiff bases are a kind of interesting ligands in coordination chemistry.[3] In recent years, a number of molybdenum(VI) complexes with Schiff bases derived from salicylaldehyde and primary amines have been reported.[4] Hydrazones, bearing -C(O)=NH=N=CH- groups, are a kind of special Schiff bases, which are of particular interest in coordination chemistry and biological applications. Schiff base complexes of molybdenum have been used in applications related to catalytic, enzymological and oxygen transfer reactions [5]. Tridentate dibasic Schiff base complexes such as cis-MoO$_2$L(S) (S = solvent) are good substrates for redox reactions because of the ability of S replacement with other solvent[6]. The availability of such a labile site imparts catalytic property to these complexes. Dibasic tridentate Schiff base ligands around octahedral molybdenum(VI) provide suitable geometry with one vacant site for substrate binding. We have been interested in five coordinated octahedral cis-MoO$_2$ complexes with non-symmetrical Schiff base having mixed sets of donor atoms in which the sixth co-ordination site is occupied by a solvent molecule. In view of this, we report the synthesis and X-ray diffraction analysis of some cis-dioxomolybdenum(VI) complexes with Schiff bases derived from salicylaldehyde(sal), o-hydroxyacetophenone(hap) and o-hydroxypropiophenone (hpp) with benzoic acid hydrazide (B-AH). These Schiff bases forms mononuclear dioxomolybdenum(VI) complexes having the general formula MoO$_2$L(S) (where LH$_2$= Schiff base represented as H$_2$sal-BAH, H$_2$hap-BAH and H$_2$hpp-BAH). The ligands and the complexes are characterized by elemental analysis, molar conductance and spectroscopic (IR, $^1$HNMR and UV-Vis) , thermogravimetric (TGA) and X-ray diffraction analysis.

II. RESULT AND DISCUSSION
Bis(acetylacetonato)ioxomolybdenum(VI) [cis-MoO$_2$(acac)$_2$], undergoes ligand exchange reaction with the Schiff bases (1a-3a) and...
complexes of the type [MoO₂(L)(S)] (where LH₂= Schiff base) are formed as follows:

\[
cis\text{-MoO}_2(\text{acac})_2 + \text{LH}_2 \rightarrow cis\text{-}[\text{MoO}_2(\text{L})(\text{S})] + 2\text{acacH}
\]

The analytical data presented in Table 1 show that the Schiff bases behave as dibasic, tridentate ligands, hence complete replacement of the bidentate acetylacetonate occurs under the reaction conditions and the solvent molecule occupies the sixth coordination position. The analytical data further support the formulation of the complexes as cis-[MoO₂(L)(S)]. The structures 1a-3a for ligands and 1b-3b for complexes are shown in Figure 1.

X-RAY POWDER DIFFRACTION ANALYSIS

The single crystals of complexes in DMF could not be obtained; hence, XRD patterns of the same are studied and reported. All the complexes were found to be crystalline and their X-ray powder diffractograms were collected. The lattice parameters and Miller’s indices were computed. The indexing and calculation of unit cell parameters were performed with the help of Powder-X Software. The calculated and observed 20 value, the relative intensity, the interplanar distance along with Miller’s indices for corresponding angles are tabulated for the complexes (Table 2-4). On the basis of X-ray powder patterns and unit cell refinements, it is found that all the complexes adopt triclinic crystal system with P type lattice space group. The lattice constants were calculated, complex (1b) - a = 8 Å ; b = 10.2 Å ; c = 10.35 Å and α = 80.9°, β = 79.7°, γ = 78.1° ; (2b) - a = 8 Å ; b = 10.2 Å ; c = 10.35 Å and α = 80.9°, β = 79.7°, γ = 78.2°. (3b) - a = 7.75 Å, b = 10.4 Å, c = 10.25 Å and α = 80°, β = 78.65°, γ = 78.15°.

We have earlier reported the single crystal structure of cis-MoO₂(L) (Solv), where L = salicylaldehyde salicyloyl hydrazone) which was found to be triclinic with P type space group[10].

### III. EXPERIMENTAL

#### MATERIALS

Ammonium molybdate(VI) tetrahydrate was obtained from Sisco Research Laboratory, Mumbai, India. Salicylaldehyde, o-hydroxyacetophenone, o-hydroxypropiophenone, o-hydroxy benzophenone and benzoic acid hydrazide were procured from Lancaster synthesis Ltd, UK. Ethanol and acetone used as solvent for synthesis were of high purity. MoO₂(acac)₂ was prepared according to reported method[11].

### PHYSICAL MEASUREMENT

Microanalysis of the Schiff base ligands and complexes were performed on a Perkin-Elmer(USA) 2400 Series II, elemental analyzer. The solutions of both ligands and complexes were prepared in HPLC grade DMF and electrical conductance measurements were performed using a Toshiwai Conductivity Bridge and a dip type cell calibrated with potassium chloride solutions. IR spectra for ligands and complexes were recorded in the range 400-4000 cm⁻¹ on a Nicolet Magna IR 550 series II spectrophotometer using KBr pellets. H NMR spectra were recorded in DMSO-d₆ on a Bruker DRX-300 instrument, using TMS as an internal standard. Electronic spectra were recorded for solutions of ligands and complexes in DMF on a Shimadzu UV 3101 PC spectrophotometer. The thermogravimetric analysis is done on Mettler Toledo (Star Switzerland SDTA/TGA 851) Instrument, to determine the decomposition temperature of complexes. The X ray diffraction patterns have been recorded in 20 range from 13 to 64° on Philips (Holland) automated X-ray powder diffractometer. The operating target voltage was 35 kV, and the tube current was 20 mA. The scanning speed was 0.5 20/min. Radiation used was Cu-K wavelength 1.54056 Å using monochromater for filtering β – radiations and reducing noise due to white radiations and also to increase resolution. The values of interplaner spacing (d) corresponding to Bragg reflections (20) were obtained and indexing and calculation of unit cell parameters were performed with the help of Powder-X Software [11-14].

### SYNTHESIS OF SCHIFF BASE LIGAND (1a-3a)

An ethanolic solution of salicylaldehyde (1.06 ml, 10 mmol), o-hydroxyacetophenone (1.36 g, 10 mmol) and o-hydroxypropiophenone (1.50 g, 10 mmol) was added to a hot ethanolic solution of benzoic acid hydrazide (1.36 g, 10 mmol). The mixture was heated under reflux for 4-6 h and then cooled in an ice bath. The cream coloured crystals that separated out were filtered, washed several times with ethanol and then dried in vacuo. Yield: (1a) 2.26 g, 82.5%; (2a) 2.31 g, 80.0%; (3a) 2.64 g, 85.6%.

### IV. SYNTHESIS OF MOLYBDENUM COMPLEXES (1b-3b)

Bis(acetylacetonato)dioxomolybdenum (VI) [cis- MoO₂(acac)₂] undergoes ligand exchange with the Schiff bases in a suitable solvent and complexes of the type MoO₂(L)(S) (where LH₂ = Schiff base) are formed as follows:

\[\Delta,6h\]
MoO$_2$(acac)$_2$ + LH → cis-MoO$_2$(L)(S) + 2 acacH ----(1)

EtOH

Where, ‘S’ is solvent

The hot ethanolic solution of the appropriate Schiff base ligand (1 mmol, 1a 0.240 g) was added to an ethanolic solution of [cis-MoO$_2$(acac)$_2$] (1 mmol, 0.326 g) under vigorous stirring. Similarly, a 1:1 mixture of the appropriate Schiff base ligand (1 mmol, 2a 0.254 g; 3a 0.268 g) and [cis-MoO$_2$(acac)$_2$] (1 mmol , 0.326 g.) was dissolved in 10 ml acetone. The reaction mixtures were then refluxed for 6h. The reaction mixture was then poured into excess of distilled water (~100-150 ml) and the wall of the container was gently scratched using a glass rod to facilitate formation of precipitate. The precipitate that separated out from water was filtered, washed several times with water and ethanol and then dried in vacuo. Yield : (1b) 0.5 g, 89.0%. (2b) 0.49 g, 84.5%; (3b) 0.53 g, 86.0%

TABLE I Analytical Data of Ligands (1a-3a) and Complexes (1b-3b)

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**Fig.1: Predicted structures 1a-3a for ligands and 1b-3b for complexes**

TABLE II: X-Ray Diffraction Data of Complex MoO$_2$(Sal-BAH) (C$_2$H$_8$OH) (1b)

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TABLE II: X-Ray Diffraction Data of Complex MoO$_2$(Sal-BAH) (H$_2$O) (1b)

Crystal system: Triclinic  Lattice Type: P  
Lattice Parameters: a = 8.0 Å; b = 10.2 Å; c = 10.35 Å  
Lattice Parameter: Alpha =80.9°; Beta = 79.7°; Gamma = 78.1°
### TABLE III: X-Ray Diffraction Data of Complex MoO$_2$(Hap-BAH) (H$_2$O) (2b)

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### TABLE IV: X-Ray Diffraction Data of Complex MoO$_2$(Hpp-BAH) (H$_2$O) (3b)

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### V. CONCLUSIONS

It is evident from the above data, the Schiff base ligands behave as dibasic tridentate ligands and co-ordinate through phenolic oxygen, azomethine nitrogen and enolic oxygen atoms. The complexes are found to be monomers, non-electrolytes, diamagnetic and six co-ordinated. The sixth site in the complex is occupied by an ethanol/water group, which allows the binding and displacement of several substrate molecules during their use as a catalyst in the oxidation reactions. The use of the complexes of this type as catalyst for epoxidation of olefins is studied and reported elsewhere [7-9]. After indexing the X-ray powder patterns and unit cell refinements, it is found that the complexes (1-3) are crystalline and adopt triclinic crystal system with P type lattice. This is expected for distorted octahedral complexes.

### REFERENCES


