

Synthesis and X-Ray Diffraction Studies of *cis* MoO₂ (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*-[MoO₂(L)(solv)] (where LH₂ = Schiff base ligand and solv=ethanol/H₂O) are synthesized, characterized by elemental, spectral analysis and structure and symmetry properties is determined using XRD. X-ray powder diffractometry 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 diffractograms of the dioxo-molybdenum (VI) complexes of Schiff base derived from salicylaldehyde (sal) and substituted salicylaldehydes such as *o*-hydroxyacetophenone (hap); *o*-hydroxypropionophenone (hpp) with benzoic acid Hydrazone (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

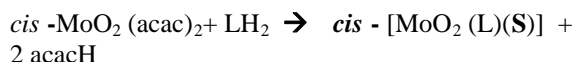
Coordination chemistry of molybdenum(VI) has attracted considerable attention due to its biochemical significance [1] as well as for the efficient catalytic properties in several organic synthesis procedures [2]. Schiff bases are a kind of interesting ligands in coordination chemistry [3]. In recent 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*-MoO₂L(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*-MoO₂ 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*-hydroxypropionophenone (hpp) with benzoic acid hydrazone (BAH). These Schiff bases form mononuclear dioxomolybdenum(VI) complexes having the general formula MoO₂(L)(S) (where LH₂= Schiff base represented as H₂sal-BAH, H₂hap-BAH and H₂hpp-BAH). The ligands and the complexes are characterized by elemental analysis, molar conductance and spectroscopic (IR, ¹HNMR and UV-Vis), thermogravimetric (TGA) and X-ray diffraction analysis.

II. RESULT AND DISCUSSION

Bis(acetylacetonato) molybdenum(VI) [*cis*-MoO₂(acac)₂], undergoes ligand exchange reaction with the Schiff bases (1a- 3a) and

complexes of the type $[\text{MoO}_2(\text{L})(\text{S})]$ (where $\text{LH}_2 =$ Schiff base) are formed as follows:



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 $\text{cis} - [\text{MoO}_2(\text{L})(\text{S})]$. 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 are performed with the help of Powder-X Software. The calculated and the observed 2θ 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**) - $a = 8 \text{ \AA}$; $b = 10.2 \text{ \AA}$; $c = 10.35 \text{ \AA}$ and $\alpha = 80.9^\circ$, $\beta = 79.7^\circ$, $\gamma = 78.1^\circ$; (**2b**) - $a = 8 \text{ \AA}$; $b = 10.2 \text{ \AA}$; $c = 10.35 \text{ \AA}$ and $\alpha = 80.8^\circ$; $\beta = 79.7^\circ$; $\gamma = 78.2^\circ$; (**3b**) - $a = 7.75 \text{ \AA}$, $b = 10.4 \text{ \AA}$; $c = 10.25 \text{ \AA}$ and $\alpha = 80^\circ$, $\beta = 78.65^\circ$, $\gamma = 78.15^\circ$.

We have earlier reported the single crystal structure of $\text{cis-MoO}_2(\text{L})$ (Solv), where L = salicylaldehyde salicyloyl hydrazide) 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-hydroxybenzophenone and benzoic acid hydrazide were procured from Lancaster synthesis Ltd. (UK). Ethanol and acetone used as solvent for synthesis were of high purity. $\text{MoO}_2(\text{acac})_2$ 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 Toshniwal Conductivity Bridge and a dip type cell calibrated with potassium chloride solutions. IR spectra for ligands and complexes were recorded in the range $400-4000 \text{ cm}^{-1}$ on a Nicolet Magna IR 550 series II spectrophotometer using KBr pellets. ^1H NMR spectra were recorded in DMSO-d_6 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 2θ 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 $0.5 \text{ } 2\theta/\text{min}$. Radiation used was Cu-k wavelength 1.54056 \AA using monochromator for filtering β - radiations and reducing noise due to white radiations and also to increase resolution. The values of interplanar spacing (d) corresponding to Bragg reflections (2θ) were obtained and indexing and calculation of unit cell parameters were performed with the help of Powder-X Software [11-14].

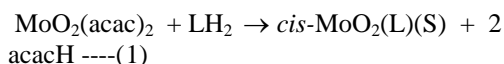
SYNTHESIS OF SCHIFF BASE LIGAND(1a-3a)

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) $[\text{cis} - (\text{MoO}_2(\text{acac})_2)]$ undergoes ligand exchange with the Schiff bases in a suitable solvent and complexes of the type $\text{MoO}_2(\text{L})(\text{S})$ (where $\text{LH}_2 =$ Schiff base) are formed as follows :

$\Delta, 6\text{h}$



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*-MoO₂(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*-MoO₂(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)

Sr. no.	Ligands/ complexes	Elemental Analysis(%):		
		Calculated	found	
		C	H	N
1a	H ₂ sal-BAH C ₁₄ H ₁₂ N ₂ O ₂	64.73 (65.83)	4.56 (4.32)	17.42 (17.46)
1b	MoO ₂ (sal-BAH) MoC ₁₆ H ₁₆ N ₂ O ₅	43.58 (43.97)	3.63 (3.65)	10.17 (10.2)
2a	H ₂ hap-BAH C ₁₅ H ₁₄ N ₂ O ₂	65.88 (65.61)	5.09 (5.08)	16.47 (16.17)
2b	MoO ₂ (hap-BAH) MoC ₁₅ H ₁₄ N ₂ O ₅	44.97 (45.10)	3.98 (3.74)	9.83 (9.70)
3a	H ₂ hpp-BAH C ₁₆ H ₁₆ N ₂ O ₂	66.90 (66.40)	5.57 (5.60)	15.61 (15.36)
3b	MoO ₂ (hpp-BAH) MoC ₁₆ H ₁₆ N ₂ O ₅	42.76 (42.26)	2.37 (2.30)	9.60 (9.52)

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

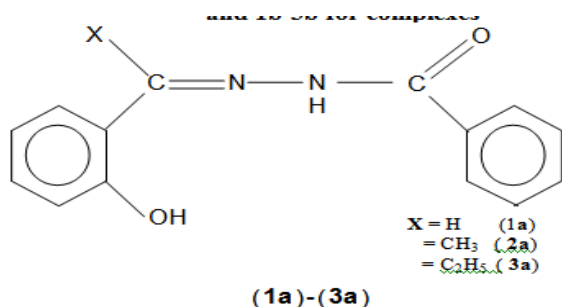


TABLE II: X-Ray Diffraction Data of Complex MoO₂(Sal-BAH) (C₂H₅OH) (1b)

h	k	l	2θ	2θ	2θ	d	d	Inten sity (Exp.)
			(Exp.)	(Calc.)	(Diff.)	(Exp.)	(Calc.)	
-1	0	0	11.057	11.426	-0.369	7.99542	7.737	118.9
0	1	1	11.699	11.691	0.008	7.55851	7.563	66.84
-1	-1	0	12.958	13.157	-0.199	6.82642	6.723	41.50
1	1	1	14.109	14.140	-0.030	6.27199	6.258	832.5
-1	0	1	15.147	15.430	-0.283	5.84465	5.738	38.71
-1	1	0	15.704	15.761	-0.058	5.63862	5.618	53.75
-1	1	1	18.438	18.347	0.092	4.80801	4.831	63.29
-1	1	1	18.438	18.347	0.092	4.80801	4.831	63.29
0	2	1	18.836	18.927	-0.092	4.70744	4.684	75.79
-1	-2	0	19.282	19.420	-0.138	4.59949	4.567	145.6
0	-2	1	21.175	20.937	0.238	4.19242	4.239	91.33
-1	0	2	21.933	22.410	-0.477	4.04923	3.964	50.06
-1	0	2	22.228	22.410	-0.182	3.99611	3.940	111.4
-1	-2	1	22.894	22.941	-0.047	3.88128	3.873	49.00
0	2	2	23.573	23.505	0.068	3.77104	3.781	112.4
2	1	2	26.144	26.129	0.015	3.40573	3.407	206.6
2	2	0	26.516	26.492	0.024	3.35880	3.361	75.93
0	-1	3	29.121	29.041	0.080	3.06398	3.072	39.80
2	0	3	32.381	32.475	-0.094	2.76259	2.754	39.86
2	-2	1	32.874	32.734	0.139	2.72231	2.733	38.38
2	-3	1	40.109	39.975	0.134	2.24636	2.253	41.59

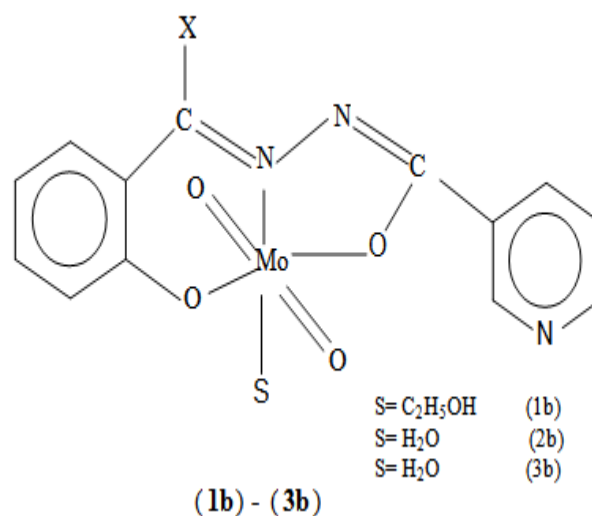


TABLE II: X-Ray Diffraction Data of Complex MoO₂(Sal-BAH) (H₂O) (1b)

Crystal system: Triclinic Lattice Type: P
Lattice Parameters: a = 8 °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 MoO₂(Hap-BAH) (H₂O) (2b)

Crystal system: Triclinic Lattice Type: P
Lattice Parameters: a = 8 °A (unit cell dimensions);
b = 10.2 °A ; c = 10.35 °A and Lattice Parameter:
Alpha =80.8°; Beta= 79.7° ; Gamma= 78.2°

h	k	l	2θ	2θ	2θ	d	d	Intensity
			(Exp.)	(Calc.)	(Diff.)	(Exp.)	(Calc.)	
0	1	1	11.520	11.586	-0.066	7.6753	7.63150	77.21
-1	0	0	12.072	11.825	0.248	7.3252	7.47807	44.60
1	0	1	13.865	13.559	0.306	6.3818	6.52530	115.07
-1	1	0	15.481	15.947	-0.466	5.7192	5.55312	34.10
-1	0	1	16.425	15.958	0.467	5.3926	5.54944	30.46
0	2	0	17.611	17.583	0.028	5.0320	5.03988	144.30
1	0	2	20.133	19.692	0.441	4.4069	4.50462	24.81
0	-1	2	20.910	20.961	-0.051	4.2448	4.23470	24.85
0	-1	2	21.278	20.961	0.317	4.1722	4.23470	24.75
-1	2	0	22.533	22.943	-0.410	3.9427	3.87319	26.22
0	2	2	23.302	23.293	0.009	3.8142	3.81575	28.08
2	0	0	23.675	23.778	-0.103	3.7550	3.73904	31.43
1	-2	1	24.721	24.814	-0.094	3.5985	3.58519	178.21
1	3	1	26.632	26.670	-0.038	3.3444	3.33983	24.62
1	0	3	27.958	27.509	0.450	3.1887	3.23983	36.23
2	2	2	28.369	28.686	-0.317	3.1434	3.10951	32.75
-1	2	2	28.820	28.902	-0.082	3.0953	3.08669	31.08
-1	-3	1	30.390	30.318	.072	2.9388	2.94569	32.13
0	4	1	35.477	35.484	-0.007	2.5283	2.52779	22.00
3	1	2	36.389	36.418	-0.029	2.4670	2.46511	30.91
2	0	4	39.960	39.998	-0.038	2.2543	2.25231	22.00

TABLE IV: X-Ray Diffraction Data of Complex MoO₂(Hpp-BAH) (H₂O) (3b)

h	k	l	2θ	2θ	2θ	d	d	Intensity
			(Exp.)	(Calc.)	(Diff.)	(Exp.)	(Calc.)	
-1	-1	0	12.735	13.169	-0.434	6.945	6.71744	29.78
1	1	1	14.187	14.141	0.046	6.237	6.25778	400.38
-1	0	1	15.543	15.427	0.116	5.696	5.73909	129.28
0	2	1	18.892	18.909	-0.018	4.693	4.68929	308.18
1	2	1	19.779	19.604	0.175	4.484	4.52470	59.62
1	2	2	23.421	23.394	0.027	3.795	3.79956	112.39
1	-2	1	24.877	24.845	0.032	3.576	3.58079	144.85
-2	0	1	25.492	25.846	-0.354	3.491	3.44429	72.02
-2	0	1	25.882	25.846	0.035	3.439	3.44429	31.92
0	3	0	26.971	26.991	-0.021	3.303	3.30075	34.80
-2	1	1	28.078	28.396	-0.317	3.175	3.14062	80.16
-1	1	3	31.448	31.448	0.000	2.842	2.84242	29.18
-2	2	0	31.814	31.795	0.019	2.810	2.81216	34.02
1	-3	1	33.126	33.040	0.086	2.702	2.70895	66.08
0	-3	2	34.300	34.279	0.021	2.612	2.61384	48.43
0	0	4	35.533	35.527	0.006	2.524	2.52485	38.55
3	-1	0	37.563	37.549	0.013	2.392	2.39338	39.70

Crystal system: Triclinic Lattice Type: P
Lattice Parameters: a = 7.75 °A (unit cell dimensions); b = 10.4 °A; c =10.25 °A
Lattice Parameter : Alpha = 80° ; Beta = 78.65°; Gamma = 78.15°

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.

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