



SYNTHESIS, CHARACTERIZATION AND COMPARATIVE STUDY OF SOME DIOXOMOLYBDENUM(VI) SCHIFF BASES COMPLEXES DERIVED FROM AROYL HYDRAZONE

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ABSTRACT

Synthesis and characterization and comparative study of some novel dioxomolybdenum (VI) complexes having the general formula $cis-[MoO_2(L)(solv)]$ (where LH_2 = Schiff base derived from nicotinic acid hydrazide (NAH), benzoic acid hydrazide (BAH), salicylic acid hydrazide (SAH) and o-hydroxyacetophenone (hap) and salicylaldehyde (sal) and $solv=ethanol/H_2O$) are reported. The various Schiff base ligands are prepared by condensation of nicotinic acid hydrazide (NAH), benzoic acid hydrazide (BAH), salicylic acid hydrazide (SAH) with salicylaldehyde and substituted salicylaldehyde. The $cis-[MoO_2(L)(solv)]$ complexes are synthesized by reacting $cis-[MoO_2(acac)_2]$ and the ligands in ethanol according to the reaction,

Δ , 6hrs



Where S= Solvent.

These Schiff base ligands and their MoO_2 complexes are characterized by elemental analysis, IR, NMR, UV-Vis and conductivity measurements, thermo gravimetric and powder X-ray diffraction analysis. The spectral studies suggest that 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, six-coordinated, and crystalline and adopt triclinic crystal system with P type lattice. The sixth coordination site is occupied by a labile solvent molecule.

KEYWORDS: Schiff bases, hydrazones, Dioxomolybdenum complexes.

INTRODUCTION

Molybdenum complexes with Schiff base ligands have gained considerable importance due to their potential for biological and



physiological activity and industrial use [1-6]. Studies on complexes of oxomolybdenum(V) and dioxomolybdenum(VI) have opened up a new vista of research and analysis of biochemical significance. A great deal of work has been carried out in the synthesis and characterization of oxo-, dioxo-molybdenum complexes with one vacant site which might allow binding and displacement of various substrates [7]. 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 co-ordinated 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, structural characterization and comparative study of some *cis*-dioxomolybdenum(VI) complexes with Schiff bases derived from salicylaldehyde(sal) and *o*-hydroxybenzophenone with nicotinic acid hydrazide(NAH), benzoic acid hydrazide(BAH) and salicylic acid hydrazide(SAH). These Schiff bases form mononuclear dioxomolybdenum(VI) complexes having the general formula MoO₂(L)(S) (where LH₂= Schiff base represented as ,H₂sal-NAH, H₂sal -BAH, H₂sal -SAH, H₂hbp-NAH, H₂ hbp -BAH, H₂ hbp -SAH). 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.

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. MoO₂(acac)₂ was prepared according to reported method.[8]



PHYSICAL MEASUREMENTS

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 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 $2\theta/\text{min}$. Radiation used was Cu-k wavelength 1.54056 A° 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 (2θ) were obtained and indexing and calculation of unit cell parameters were performed with the help of Powder-X Software.[9-11]

SYNTHESIS OF SCHIFF BASE LIGANDS (1a-6a)

An ethanolic solution of ketone/aldehyde such as salicyladehyde(sal); o-hydroxybenzophenone (hbp) was mixed with an amine such as nicotinic acid hydrazide(NAH); benzoic acid hydrazide (BAH) and salicylic acid hydrazide (SAH) in 1: 1 molar ratio. The mixture was heated under reflux for 2-4 h and then cooled in an ice bath. The yellow crystals that

separated out were filtered, washed several times with ethanol and then dried in vacuo. The ligands obtained are N'[(1Z)-1-(2-hydroxyphenyl)phenylethylidene] nicotinoylhydrazine (H₂hbp-NAH) (**1a**), N'Salicylidene nicotinoylhydrazine(H₂sal-NAH) (**2a**), N'[(1Z)-1-(2-hydroxyphenyl) phenylethylidene] benzoylhydrazine (H₂hbp-BAH) (**3a**), N'Salicylidene benzoyllhydrazine (H₂sal-BAH) (**4a**), N'[(1Z)-1-(2-hydroxyphenylphenyl)ethylidene] salicyloylhydrazine (H₂hbp-SAH) (**5a**), N'Salicylidene salicyloylhydrazine (H₂sal-SAH) (**6a**).

SYNTHESIS OF MOLYBDENUM COMPLEXES (1b-6b)

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 :



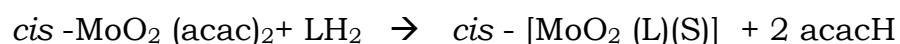
EtOH

Where, 'S' is solvent

The *cis*-[MoO₂(L)(solv)] complexes synthesized by reacting *cis*-[MoO₂(acac)₂] and the ligands (**1a-6a**) in ethanol are *cis*-[MoO₂(H₂hbp-NAH)(EtOH)] (**1b**), *cis*-[MoO₂(sal-NAH)(EtOH)] (**2b**), *cis*-[MoO₂(H₂hbp-BAH)(EtOH)] (**3b**), *cis*-[MoO₂(sal-BAH)(EtOH)] (**4b**), *cis*-[MoO₂(H₂hbp-SAH)(EtOH)] (**5b**) and *cis*-[MoO₂(sal-SAH)(H₂O)] (**6b**).

RESULTS AND DISCUSSION

Bis(acetylacetonato) dioxomolybdenum(VI) [*cis*-MoO₂(acac)₂], undergoes ligand exchange reaction with the Schiff bases (**1a-6a**) and complexes of the type [MoO₂ (L)(S)] (where LH₂= 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 acetylactone 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 for ligands (**1a-6a**) and for complexes (**1b-6b**) are shown in Figure 1 and 2. The molar conductance of the complexes in DMF is found to be in the range 1.97-6.53 ohm⁻¹cm⁻¹mol⁻¹ which indicates that they are all non-electrolytes. The ligands were tested separately for conductance and none of them indicated any measurable conductance.

IR SPECTRA

The IR spectra of the Schiff base ligands reveal the presence of νNH and νC=O groups which are found to be absent in their corresponding MoO₂ complexes and a new C-O stretch was found, giving >C=N-N=C< framework. This suggests occurrence of keto-imino tautomerisation of the ligand during complexation. The presence of two prominent bands in the complexes (**1b-6b**) in the regions 874-948 cm⁻¹ and 848-913 cm⁻¹ due to the ν_{sym}(O=Mo=O) and ν_{asym}(O=Mo=O) respectively, confirms the presence of *cis*-MoO₂²⁺ centre.[12-15] It has been reported before that the MoO₂²⁺ moiety prefers to form *cis* configuration due to the maximum utilization of the d-orbitals for the chemical bonding.[16-18] Further, the complexes (**1b- 4b**) exhibit an additional band in the region 3066-3453 cm⁻¹ which is attributed to ν_{OH} of C₂H₅OH molecule coordinated to the sixth site[19]. The complexes (**5b and 6b**) exhibit a band in the range 1604-1624 cm⁻¹ due to ν_{OH} of coordinated H₂O molecule to the sixth site.

Thus, the Schiff bases are found to be dibasic tridentate ligands having -N, O, O donor sites and their MoO₂ complexes show octahedral geometry, having general formula [MoO₂(L)(S)], the sixth site being occupied by the solvent molecule.



The IR spectra of complexes (Table 2) also reveal that both symmetric and asymmetric stretching of *cis*-MoO₂ in the complex formed with (H₂hbp-NAH) (**1b**) occur at a relatively higher energy (904 and 948cm⁻¹) than the corresponding (H₂sal-NAH) (**2b**), (913 and 920 cm⁻¹). Similarly, both symmetric and asymmetric stretching of *cis*-MoO₂ in the complex formed with (H₂hbp-BAH) (**3b**); (H₂hbp-SAH) (**5b**) occur at a relatively higher energy (899 and 923 cm⁻¹); (893 and 943 cm⁻¹) respectively, than the corresponding (H₂sal-BAH) (**4b**), (914 and 895 cm⁻¹) and (H₂sal-SAH) (**6b**), (891 and 910 cm⁻¹) respectively. Moreover, the difference between symmetric and asymmetric frequencies of O=Mo=O is also less ($\Delta\nu = 10-25$ cm⁻¹) for complexes (**2b**, **4b**, **6b**) whereas this difference is more ($\Delta\nu = 30-50$ cm⁻¹) for complex (**1b**; **3b**; **5b**). The differences in stretching frequencies of O=Mo=O of the *cis*-MoO₂ moiety may be attributed to the progressively decreasing steric and electron withdrawing character of benzyl and -H on azomethine carbon in the complexes (**1b**; **3b** ; **5b**)and (**2b**, **4b**, **6b**), respectively.

Further, appearance of $\nu(\text{Mo}=\text{O})$ symmetric and asymmetric peaks in complexes (**1b and 2b**) occur at relatively high energy as compared to (**3b-6b**). This may be due to the presence of heterocyclic ring of nicotinic acid hydrazide (NAH) which is probably exerting distant effect on O=Mo=O bonds.

ELECTRONIC SPECTRA

In their electronic spectra, the ligands (**1a-6a**) showed peaks in the region 295-390 nm which can be attributed to intra ligand transitions. (Table-1) Similarly, the *cis*- MoO₂ complexes displayed a broad band in the range 390-410nm which could be assigned to the ligand metal charge transfer transition (LMCT), between the lowest empty d⁰orbital (d π) of molybdenum and the highest occupied ligand molecular orbital (p π) i.e. Mo (d π) \leftarrow O (p π) transition. Several of the MoO₂ complexes showed

LMCT band in this range [20, 21]. As obvious for $4d^0$ system, no d-d transitions were expected in all the above complexes.

It has been observed that there is no significant effect on $Mo(d\pi) \leftarrow O(p\pi)$ transition due to substitutional changes on hydrazide moiety (NAH, BAH and SAH). On the other hand, the substituent present on azomethine carbon is found to exert a certain influence on the LMCT energy. In case of $-C_6H_5$ on azomethine carbon, an average increase of energy by 15-20 nm was observed in comparison to unsubstituted azomethine carbon (**2b,4b,6b**).

It appears that the energy of $Mo(d\pi)$ level is progressively moved away from $O(p\pi)$ orbital as the electron donating character of the substituent ($-H$, $-C_6H_5$) increases as shown below in the **figure 3**.

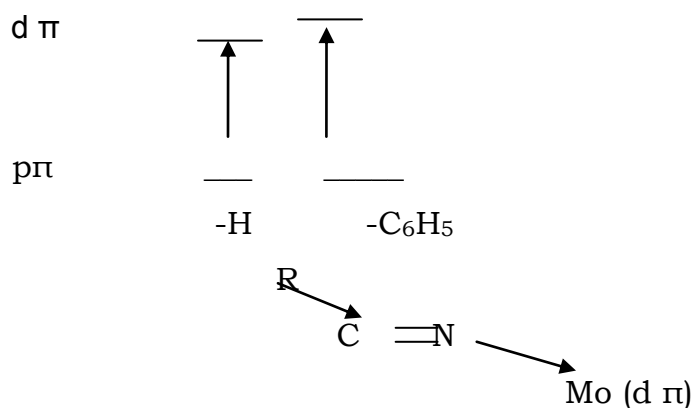


Figure:3 Predicted Influence of substituent's on energy level of $Mo(d\pi)$ orbital

1H NMR SPECTRA

The IR data is further supported by the 1H NMR spectral data (Table2). The 1H NMR spectral data for the ligands (**1a-6a**) exhibit signals due to the phenolic OH protons and NH protons. The absence of these signals in the spectra of the complexes indicate coordination through the phenolic oxygen and enolization of the $-C=O$ of the aroyl keto group and consequent deprotonation. The ethanol coordination to molybdenum in



complexes (**1b- 4b**) is supported by the presence of the singlet, triplet and quartet of OH, CH₃ and CH₂ at 11.1-12.93, 1.06-1.42 and 2.69-3.70 ppm respectively. The H₂O coordination to molybdenum centre in complexes (**5b - 6b**) is supported by the absence of the singlet, triplet and quartet of OH, CH₃ and CH₂, respectively. Due to rapid exchange of protons in the coordinated H₂O, the signal corresponding to H₂O could not be observed.

THERMOGRAVIMETRIC ANALYSIS

Thermal behavior of the complexes (**1b-6b**) was studied in the temperature range 30-800°C, with increase of 10°C/min. The TG curves exhibit weight loss in four steps corresponding to the release of solvent molecule, two stage decomposition of Schiff base ligands and finally the formation of molybdenum trioxide (Table 3). Complexes (1b, 2b, 3b and 4b) undergo a rapid weight loss from 80-102°C due to release of coordinated C₂H₅OH molecule and in the complexes (5b and 6b) the release of the coordinated H₂O occurs in the temperature range 80-100°C.

The Schiff base ligands decompose in two steps in the temperature range 210-770°C, the first step corresponding to significant weight loss and the second showing a gradual weight loss. The % weight loss value of the final residues was in accordance with that of molybdenum trioxide for all the complexes.

X-RAY POWDER DIFFRACTION ANALYSIS

The XRD data was obtained using Powder-X Software. 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 inter-planar distance along with Miller's indices for corresponding angles are tabulated for the complexes.

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 hkl indexing and space identification was carried out and complexes **(1b-6b)** adopt distorted octahedral geometry with triclinic space grouping. The lattice constants were calculated, complex **(1b)** - $a = 7.9 \text{ \AA}$; $b = 10.1 \text{ \AA}$; $c = 10.35 \text{ \AA}$ and $\alpha = 80^\circ$, $\beta = 79^\circ$ $\gamma = 76^\circ$; **(2b)** - $a = 7.99 \text{ \AA}$; $b = 10.1 \text{ \AA}$; $c = 10.42 \text{ \AA}$ and $\alpha = 81^\circ$; $\beta = 80^\circ$; $\gamma = 79.2^\circ$; **(4b)** - $a = 8 \text{ \AA}$ $b = 10.2 \text{ \AA}$; $c = 10.35 \text{ \AA}$ and $\alpha = 80.9^\circ$, $\beta = 79.7^\circ$, $\gamma = 78.1^\circ$ **(6b)** - $a = 7.88 \text{ \AA}$ $b = 10.45 \text{ \AA}$; $c = 10.1 \text{ \AA}$ and $\alpha = 81.5^\circ$, $\beta = 78.6^\circ$, $\gamma = 78^\circ$. We have earlier reported the single crystal structure of *cis*-MoO₂(L) (Solv), where L = salicylaldehyde salicyloyl hydrazide) which was found to be triclinic with P type space group[22].

Thus, on the basis of elemental analysis, IR and TGA, all the complexes have their sixth coordinating site occupied by a solvent molecule either C₂H₅OH or H₂O. The Schiff base ligands coordinate through azomethine nitrogen, phenolic and enolic oxygen atoms (-N, O, O) confirming to distorted octahedral geometry.

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 complexes adopt triclinic crystal system with P type lattice space group. 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 [23].

REFERENCES

- Shailendra N.B, Gonzalez Garza M.T., Cruz-Vega D.E., Castro Garza J.C., Saleem K., Naqui F., Maurya M.R. and Azam A., (2002), Bio-org. & Medicinal Chem. Lett., 12 , (6) , 869-871.
- Rana A., Dinda R., Sengupta P., Ghosh S. and Falvello L.R., Synthesis , (2002), Polyhedron, 21, 1023-1030 .
- Owaik T.G., Jerzykiewicz L., Sofczak J. aw.M and Kowski Zio J.J., (2003), Inorg. Chim. Acta, 356, 387-391.
- Ambrazaik K., Pelech R., Milchert E., Dziemobowska T. and Rozwadowski Z., (2004), J. Mol. Catal. A- Chemical, 211, 9-16.
- Valente A.A., Petrovski E., Branco L.C., Afonso C., Pillinger M., Lopes Romao A.D., Nunes C.D. and Goncalves I.S. ,(2004), J. Mol. Catal. A- Chemical, 218 , 5-11.
- Nunes C.D., Pillinger M., Valente A.A., Lopes A.D. and Goncalves I.S., (2003), Inorg. Chem. Comm., 6, 1228-1233.
- Rao S. N., Mishra D. D., Maurya R.C., and Rao N. N., (1995), Bull. Chem. Soc. Jpn., 68, 1589-1592.
- Chen G.J.J., McDonald J-W and Neuton W.E., (1976), Inorg.Chem., 15 ,pp.2612-2615.
- Syed L.E. and Iskander M.F., (1971),J. Inorg. Nucl. Chem., 33 , 435-443.
- W.H. Bragg and W.L. Bragg, (1933) "*The Crystalline State*", Bell, London.
- Bunn, (1945) "*Chemical Crystallography*", Oxford University Press.
- Azaroff and Buerger, (1958) , "*The powder Method*", McGraw Hill, London.



- Rao S.N., Munshi K.N., and Rao N.N., (1999), J.Mol.Catal. A- Chem.,145 , 203-210.
- Rao S.N., Munshi K.N., Rao N.N., (2000), J Mol. Catal. A- Chem.,156, 205-211
- Rao S.N., Kathale N., Munshi K.N., Rao N.N.,(2007), Inorg. Chim Acta., 360 , 4010-4016 .
- N. Kathale, Rao S.N., Munshi K.N., Rao N.N., (2001), 31 , 859-871.
- Rao S.N., Jaiswal M.N., Mishra D.D., Maurya R.C. and Rao N.N., (1993),Polyhedron, 12, 2045-2050.
- Pickett C., Kumar S., Vella P.A. and Zubieta J., (1982).Inorg. Chem., 21, , 908-916.
- Syamal A., Maurya M.R., (1986), Transition Met. Chem., 11, 255-258.
- S.N. Rao, D. D. Mishra, R.C. Maurya, and N. N. Rao, (1995), Synth. React. Inorg. Met.-Org. Chem., 25, 437-449.
- Maurya R. C., Mishra D. D., Rao S. N., Verma R. and Rao N. N.,(1997) ,Indian J. Chem., 36A, , 599-601.
- Rao S.N., Munshi K.N. ,Rao N.N., Badbhade M.M. and Suresh E., (1999), Polyhedron , 18 ,pp.2491-2497.
- M. A. Katkar, S. N. Rao and H. D. Juneja, RSC Advances, 2, 8071–8078, 2012.

Table 1: Analytical Data and Electronic Spectral Data of Ligands (1a-6a) and Complexes (1b-6b)

Sr. no.	Ligands/ complexes	Color	F.W.	Yield (%)	m.p (°C)	Elemental Analysis(%):			UV-Vis λ nm(ϵ M ⁻¹ cm ⁻¹)
						Calculated	(found)		
						C	H	N	
1a	H ₂ hbp-NAH; C ₁₉ H ₁₅ N ₃ O ₂	Yellow	317	87	190	71.92 (71.90)	4.73 (4.75)	13.24 (13.25)	295 (1.7x10 ⁴) 330 (1.7x10 ⁴)
1b	MoO ₂ (hbp-NAH); MoC ₂₁ H ₁₉ N ₃ O ₅	Green	488.94	89	285	51.54 (51.24)	3.88 (4.02)	8.89 (8.79)	405 (7.5x10 ³)
2a	H ₂ sal-NAH; C ₁₃ H ₁₁ N ₃ O ₂	Yellow	241	85	160	64.73 (65.83)	4.56 (4.32)	17.42 (17.46)	295 (2.1x10 ⁴) 330 (2.0x10 ⁴)
2b	MoO ₂ (sal-NAH); MoC ₁₅ H ₁₅ N ₃ O ₅	Green	412.94	84	210	43.58 (43.97)	3.63 (3.65)	10.17 (10.2)	410(0.3x10 ⁴)
3a	H ₂ hbp-BAH; C ₂₀ H ₁₆ N ₂ O ₂	Cream	316	82.87	220	75.94 (75.76)	5.97 (5.66)	10.44 (9.47)	300 (1.9x10 ⁴) 350 (1.9x10 ⁴)
3b	MoO ₂ (hbp-BAH); MoC ₂₂ H ₂₀ N ₂ O ₅	Green	487.94	86	255	45.08 (45.82)	4.09 (4.12)	5.73 (5.8)	405 (1.9x10 ⁴)
4a	H ₂ sal-BAH; C ₁₄ H ₁₂ N ₂ O ₂	Cream	240	82.48	184	70.0 (69.82)	5.00 (4.78)	11.66 (10.79)	280 (1.6x10 ⁴) 330 (2.9x10 ⁴)
4b	MoO ₂ (sal-BAH); MoC ₁₆ H ₁₆ N ₂ O ₅	Green	411.94	89	289	46.60 (46.12)	3.88 (3.87)	6.79 (6.95)	410 (0.3x10 ⁴)
5a	H ₂ hbp-SAH; C ₂₀ H ₁₆ N ₂ O ₃	Cream	332	83.16	189	71.28 (71.66)	4.81 (4.44)	8.43 (8.55)	300 (1.0x10 ⁴) 360 (1.0x10 ⁴)
5b	MoO ₂ (hbp-SAH); MoC ₂₀ H ₁₆ N ₂ O ₆	Green	475.94	86	300	50.42 (50.35)	3.36 (3.51)	5.88 (5.98)	405(1.0x10 ⁴)
6a	H ₂ sal-SAH; C ₁₄ H ₁₂ N ₂ O ₃	Yellow	256	89	182	65.6 (65.83)	4.68 (4.32)	5.46 (5.11)	297 (1.7x10 ⁴) 335 (2.2x10 ⁴)
6b	MoO ₂ (sal-SAH); MoC ₁₄ H ₁₂ N ₂ O ₆	Orange	399.94	86	254	42.00 (41.90)	3.00 (2.65)	7.00 (6.95)	410 (1.95x10 ⁴)

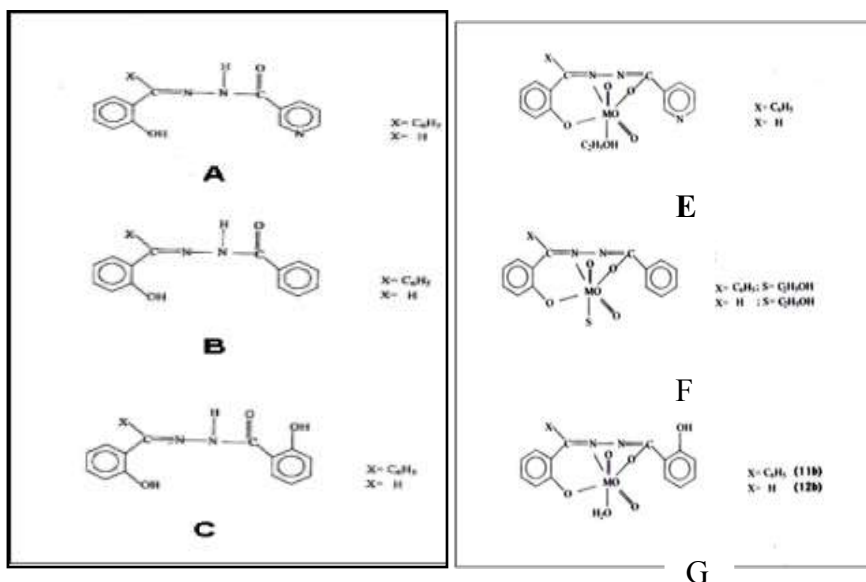
Table 2: IR and ¹H NMR Spectral Data of Ligands (1a-6a) and Complexes (1b-6b)

Sr . No .	Ligands/ Complexes	Infrared Data (cm ⁻¹)						δ, ppm
		ν(O H)	ν(NH)	ν(C=N)	ν(C=O)	ν(C- O)	ν(Mo=O)	
1a	H ₂ hbp- NAH; C ₁₉ H ₁₅ N ₃ O ₂	332 2	3021	1660	1672	-----	-----	11.70(s,OH,1H); 12.09(s,NH,1H); 6.97- 8.02m,ArH,13H).
1b	MoO ₂ (hbp- NAH); MoC ₂₁ H ₁₉ N 3O ₅	321 1	----- -	1625 1594	----- -	1156	948 904	11.70(s,OH,1H);1.28-1.42(q,- CH ₃ ,3H); 2.12- 2.19(t,CH ₂ ,2H); 6.97- 8.02m,ArH,13H).
2a	H ₂ sal-NAH; C ₁₃ H ₁₁ N ₃ O ₂	325 0	3100	1580	1608	-----	-----	11.43(s,OH, 1H); 12.20(s,NH,1H); 8.3(s,CH,1H);6.87- 8.75(m,ArH,8H).
2b	MoO ₂ (sal- NAH) MoC ₁₅ H ₁₅ N 3O ₅	331 5	----- -	1560 1535	----- -	1151	920 913	12.91(s, OH,1H); 8.34(s,CH,1H)1.06-1.17 (q,- CH ₃ , 3H); 3.16-3.31(t,CH ₂ ,2H); 6.87-8.75(m,ArH,8H).
3a	H ₂ hbp- BAH ; C ₂₀ H ₁₆ N ₂ O ₂	354 0	3063	1608	1652	----- --	-----	10.92(s,OH,1H);13.1(s,NH,1 H);7.08-8.03(m,ArH,14H).
3b	MoO ₂ (hbp- BAH); MoC ₂₂ H ₂₀ N 2O ₅	306 6	----- -	1595 1553	----- --	1177	923 899	11.1(s,OH,1H); 1.21-1.29(q,- CH ₃ ,3H); 2.56-2.57(t,- CH ₂ ,3H); 7.01- 8.05(m,ArH,14H).
4a	H ₂ sal-BAH; C ₁₄ H ₁₂ N ₂ O ₂	363 1	3260	1622	1672	----- -	-----	11.58(s,OH,1H);11.82(s,NH,1 H); 8.53(s,CH,1H); 6.86- 8.5(m,ArH,9H).
4b	MoO ₂ (sal- BAH) ; MoC ₁₆ H ₁₆ N 2O ₅	320 0	----- --	1612 1556	----- --	1153	914 895	11.58(s,OH,1H); 8.53(s,CH,1H);1.37-1.41(q,- CH ₃ ,3H);3.38-3.44(t,- CH ₂ ,3H); 6.94- 8.12(m,ArH,9H).
5a	H ₂ hbp-SAH ; C ₂₀ H ₁₆ N ₂ O ₃	334 3 332 0	3060	1600	1648	-----	-----	11.52(s,OH,2H); 10.4(s,NH,1H); 7.54-8.28 (m ,ArH,13H).
5b	MoO ₂ (hbp- SAH); MoC ₂₀ H ₁₆ N 2O ₆	334 3 162 4	-----	1595. 01 1604. 45	-----	1248	943;8 93	11.5(s,OH,1H); 1.4- 1.64(q,CH ₃ ,3H);2,81- 2.98(t,CH ₂ , 2H) ; 7.4-7.81 (m ,ArH,13H).
6a	H ₂ sal-SAH; C ₁₄ H ₁₂ N ₂ O ₃	329 0 320 0	3050	1618	1655	-----	-----	11.97(s,OH,2H) ; 11.40(s,NH,1H) ;8.6 (s,CH,1H) 6.8-7.93(m,ArH ,8H)
6b	MoO ₂ (sal- SAH) ; MoC ₁₄ H ₁₂ N 2O ₆	329 0 162 4	----- -	1601 1552	----- --	1246	891 910	11.31(s,OH,1H); 8.68(s,CH,1H) ; 6.90-8.68 (m,ArH,8H)

Table 3: Thermal Decomposition Data of complexes (1b-6b)

Sr . n o.	T _d (°C)	% Weight Loss											
		1b MoO ₂ (hbp- NAH) MoC ₂₁ H ₁₉ N ₃ O ₅		2b MoO ₂ (Sal- NAH) MoC ₁₅ H ₁₅ N ₃ O ₅		3b MoO ₂ (hbp- BAH) MoC ₂₂ H ₂₀ N ₂ O ₅		4b MoO ₂ (sal- BAH) MoC ₁₆ H ₁₆ N ₂ O ₅		5b MoO ₂ (hbp- SAH) MoC ₂₀ H ₁₆ N ₂ O ₆		6b MoO ₂ (sal- SAH) MoC ₁₄ H ₁₂ N ₂ O ₆	
		Cal c.	Obs .	Cal c.	Obs .	Cal c.	Obs .	Cal c.	Obs .	Cal c.	Obs .	Cal c.	Obs .
1	80- 102 °C	9.4 0	9.2 5	9.40	9.25	9.42	8.73	11.1 6	10.8 8	3.70	3.52	4.5 0	4.20
2	296 - 420 °C	44. 02	43. 82	44.0 2	43.8 2	44.1 2	44.4 5	32.5 0	33.2 1	42.5 8	42	31. 15	32.1 5
3	420 - 770 °C	48. 39	47. 71	48.3 9	47.6 2	48.1 8	48.7 2	48.1 8	47.4 7	51.3 4	50.5 0	51. 34	52.1 0

T_d - Decomposition temperature



**Fig1: A- Proposed structure for 1a and 2a
1b and 2b**

**B- Proposed structure for 3a and 4a
3b and 4b**

**C- Proposed structure for 5a and 6a
5b and 6b**

Fig 2: E- Proposed structure for

F- Proposed structure for

G- Proposed structure for

Table 1 : Analytical Data of Ligands (1a-6a) and Complexes (1b-6b)

Sr no	Ligands/ complexes	Color	F.W.	Yield (%)	m.p (°C)	Elemental Analysis(%): Calculated (found)		
						C	H	N
1a	H ₂ hbp- NAH;C ₁₉ H ₁₅ N ₃ O ₂	Yellow	317	87	190	71.92;(71.90)	4.73;(4.75)	13.24;(13.25)
1b	MoO ₂ (hbp- NAH);MoC ₂₁ H ₁₉ N ₃ O ₅	Green	488.94	89	285	51.54;(51.24)	3.88;(4.02)	8.89;(8.79)
2a	H ₂ sal- NAH;C ₁₃ H ₁₁ N ₃ O ₂	Yellow	241	85	160	64.73;(65.83)	4.56;(4.32)	17.42;(17.46)
2b	MoO ₂ (sal- NAH);MoC ₁₅ H ₁₅ N ₃ O ₅	Green	412.94	84	210	43.58;(43.97)	3.63;(3.65)	10.17;(10.2)
3a	H ₂ hbp-BAH; C ₂₀ H ₁₆ N ₂ O ₂	Cream	316	82.87	220	75.94(75.76)	5.97(5.66)	10.44(9.47)
3b	MoO ₂ (hbp- BAH);MoC ₂₂ H ₂₀ N ₂ O ₅	Green	487.94	86	255	45.08(45.82)	4.09(4.12)	5.73(5.8)
4a	H ₂ sal- BAH;C ₁₄ H ₁₂ N ₂ O ₂	Cream	240	82.48	184	70.0(69.82)	5.00(4.78)	11.66(10.79)
4b	MoO ₂ (sal- BAH);MoC ₁₆ H ₁₆ N ₂ O ₅	Green	411.94	89	289	46.60(46.12)	3.88(3.87)	6.79(6.95)
5a	H ₂ hbp- SAH;C ₂₀ H ₁₆ N ₂ O ₃	Cream	332	83.16	189	71.28(71.66)	4.81(4.44)	8.43(8.55)
5b	MoO ₂ (hbp- SAH);MoC ₂₀ H ₁₆ N 2O ₆	Green	475.94	86	300	50.42(50.35)	3.36(3.51)	5.88(5.98)
6a	H ₂ sal- SAH;C ₁₄ H ₁₂ N ₂ O ₃	Yellow	256	89	182	65.6(65.83)	4.68(4.32)	5.46(5.11)
6b	MoO ₂ (sal-SAH); MoC ₁₄ H ₁₂ N ₂ O ₆	Orange	399.94	86	254	42.00(41.90)	3.00(2.65)	7.00(6.95)

Table 2: IR Spectral Data of Ligands (1a-6a) and Complexes (1b-6b)

Sr. No.	Ligands/ Complexes	Infrared Data (cm ⁻¹)					
		v(OH)	v(NH)	v(C=N)	v(C=O)	v(C-O)	v(Mo=O)
1a	H ₂ hbp-NAH;C ₁₉ H ₁₅ N ₃ O ₂	3322	3021	1660	1672	-----	-----
1b	MoO ₂ (hbp-NAH);MoC ₂₁ H ₁₉ N ₃ O ₅	3211	-----	1625;1594	-----	1156	948;904
2a	H ₂ sal-NAH;C ₁₃ H ₁₁ N ₃ O ₂	3250	3100	1580	1608	-----	-----
2b	MoO ₂ (sal-NAH);MoC ₁₅ H ₁₅ N ₃ O ₅	3315	-----	1560;1535	-----	1151	920;913
3a	H ₂ hbp-BAH;C ₂₀ H ₁₆ N ₂ O ₂	3540	3063	1608	1652	-----	-----
3b	MoO ₂ (hbp-BAH);MoC ₂₂ H ₂₀ N ₂ O ₅	3066	-----	1595;1553	-----	1177	923;899
4a	H ₂ sal-BAH;C ₁₄ H ₁₂ N ₂ O ₂	3631	3260	1622	1672	-----	-----
4b	MoO ₂ (sal-BAH);MoC ₁₆ H ₁₆ N ₂ O ₅	3200	-----	1612;1556	-----	1153	914;895
5a	H ₂ hbp-SAH;C ₂₀ H ₁₆ N ₂ O ₃	3343;3320	3060	1600	1648	-----	-----
5b	MoO ₂ (hbp-SAH);MoC ₂₀ H ₁₆ N ₂ O ₆	3343;1624	-----	1595.01;1604.45	-----	1248	943;893
6a	H ₂ sal-SAH;C ₁₄ H ₁₂ N ₂ O ₃	3290;3200	3050	1618	1655	-----	-----
6b	MoO ₂ (sal-SAH);MoC ₁₄ H ₁₂ N ₂ O ₆	3290;1624	-----	1601;1552	-----	1246	891;910

Table 3 : Electronic Spectral Data of Ligands (1a-6a) and their Dioxomolybdenum Complexes (1b-6b)

Sr. No.	Ligands/ Complexes	UV-Vis λ nm(εM ⁻¹ cm ⁻¹)	Sr. No.	Ligands/ Complexes	UV-Vis λ nm(εM ⁻¹ cm ⁻¹)	Sr. No.	Ligands/ Complexes	UV-Vis λ nm(εM ⁻¹ cm ⁻¹)
1a	H ₂ hbp-NAH C ₁₉ H ₁₅ N ₃ O ₂	295 (1.7x10 ⁴) 330 (1.7x10 ⁴)	3a	H ₂ hbp-BAH C ₂₀ H ₁₆ N ₂ O ₂	300 (1.9x10 ⁴) 350 (1.9x10 ⁴)	5a	H ₂ hbp-SAH C ₂₀ H ₁₆ N ₂ O ₃	300 (1.0x10 ⁴) 360 (1.0x10 ⁴)
1b	MoO ₂ (hbp-NAH) MoC ₂₁ H ₁₉ N ₃ O ₅	405 (7.5x10 ³)	3b	MoO ₂ (hbp-BAH) MoC ₂₂ H ₂₀ N ₂ O ₅	405 (1.9x10 ⁴)	5b	MoO ₂ (hbp-SAH) MoC ₂₀ H ₁₆ N ₂ O ₆	405(1.0x10 ⁴)
2a	H ₂ sal-NAH C ₁₃ H ₁₁ N ₃ O ₂	295 (2.1x10 ⁴) 330 (2.0x10 ⁴)	4a	H ₂ sal-BAH C ₁₄ H ₁₂ N ₂ O ₂	280 (1.6x10 ⁴) 330 (2.9x10 ⁴)	6a	H ₂ sal-SAH C ₁₄ H ₁₂ N ₂ O ₃	297 (1.7x10 ⁴) 335 (2.2x10 ⁴)
2b	MoO ₂ (sal-NAH) MoC ₁₅ H ₁₅ N ₃ O ₅	410(0.3x10 ⁴)	4b	MoO ₂ (sal-BAH) MoC ₁₆ H ₁₆ N ₂ O ₅	410 (0.3x10 ⁴)	6b	MoO ₂ (sal-SAH) MoC ₁₄ H ₁₂ N ₂ O ₆	410 (1.95x10 ⁴)

Table 4 : ¹H NMR Spectral Data of Ligands (1a-6a) and Complexes (1b-6b)

Sr.No.	Ligands/ Complexes	δ , ppm
1a	H ₂ hbp-NAH; C ₁₉ H ₁₅ N ₃ O ₂	11.70(s,OH,1H); 12.09(s,NH,1H); 6.97-8.02m,ArH,13H).
1b	MoO ₂ (hbp-NAH); MoC ₂₁ H ₁₉ N ₃ O ₅	11.70(s,OH,1H); 1.28-1.42(q,-CH ₃ ,3H); 2.12-2.19(t,CH ₂ ,2H); 6.97-8.02m,ArH,13H).
2a	H ₂ sal-NAH; C ₁₃ H ₁₁ N ₃ O ₂	11.43(s,OH, 1H); 12.20(s,NH,1H); 8.3(s,CH,1H); 6.87-8.75(m,ArH,8H).
2b	MoO ₂ (sal-NAH); MoC ₁₅ H ₁₅ N ₃ O ₅	12.91(s, OH, 1H); 8.34(s,CH,1H) 1.06-1.17 (q,-CH ₃ , 3H); 3.16-3.31(t,CH ₂ , 2H); 6.87-8.75(m,ArH,8H).
3a	H ₂ hbp-BAH; C ₂₀ H ₁₆ N ₂ O ₂	10.92(s,OH,1H); 13.1(s,NH,1H); 7.08-8.03(m,ArH,14H).
3b	MoO ₂ (hbp-BAH); MoC ₂₂ H ₂₀ N ₂ O ₅	11.1(s,OH,1H); 1.21-1.29(q,-CH ₃ ,3H); 2.56-2.57(t,-CH ₂ ,3H); 7.01-8.05(m,ArH,14H).
4a	H ₂ sal-BAH; C ₁₄ H ₁₂ N ₂ O ₂	11.58(s,OH,1H); 11.82(s,NH,1H); 8.53(s,CH,1H); 6.86-8.5(m,ArH,9H).
4b	MoO ₂ (sal-BAH); MoC ₁₆ H ₁₆ N ₂ O ₅	11.58(s,OH,1H); 8.53(s,CH,1H); 1.37-1.41(q,-CH ₃ ,3H); 3.38-3.44(t,-CH ₂ ,3H); 6.94-8.12(m,ArH,9H).
5a	H ₂ hbp-SAH; C ₂₀ H ₁₆ N ₂ O ₃	11.52(s,OH,2H); 10.4(s,NH,1H); 7.54-8.28 (m ,ArH,13H).
5b	MoO ₂ (hbp-SAH); MoC ₂₀ H ₁₆ N ₂ O ₆	11.5(s,OH,1H); 1.4-1.64(q,CH ₃ ,3H); 2.81-2.98(t,CH ₂ , 2H) ; 7.4-7.81 (m ,ArH,13H).
6a	H ₂ sal-SAH; C ₁₄ H ₁₂ N ₂ O ₃	11.97(s,OH,2H) ; 11.40(s,NH,1H) ; 8.6 (s,CH,1H) 6.8-7.93(m,ArH ,8H)
6b	MoO ₂ (sal-SAH) MoC ₁₄ H ₁₂ N ₂ O ₆	11.31(s,OH,1H); 8.68(s,CH,1H) ; 6.90-8.68 (m,ArH,8H)

Table 5: Thermal Decomposition Data of complexes (1b-6b)

Sr . n o.	T _d (°C)	% Weight Loss											
		1b MoO ₂ (hbp-NAH) MoC ₂₁ H ₁₉ N ₃ O ₅		2b MoO ₂ (Sal-NAH) MoC ₁₅ H ₁₅ N ₃ O ₅		3b MoO ₂ (hbp-BAH) MoC ₂₂ H ₂₀ N ₂ O ₅		4b MoO ₂ (sal-BAH) MoC ₁₆ H ₁₆ N ₂ O ₅		5b MoO ₂ (hbp-SAH) MoC ₂₀ H ₁₆ N ₂ O ₆		6b MoO ₂ (sal-SAH) MoC ₁₄ H ₁₂ N ₂ O ₆	
		Cal c.	Obs .	Cal c.	Obs .	Cal c.	Obs .	Cal c.	Obs .	Cal c.	Obs .	Cal c.	Obs .
1	80-102 °C	9.40	9.25	9.40	9.25	9.42	8.73	11.16	10.88	3.70	3.52	4.50	4.20
2	296-420 °C	44.02	43.82	44.02	43.82	44.12	44.45	32.50	33.21	42.58	42	31.15	32.15
3	420-770 °C	48.39	47.71	48.39	47.62	48.18	48.72	48.18	47.47	51.34	50.50	51.34	52.10

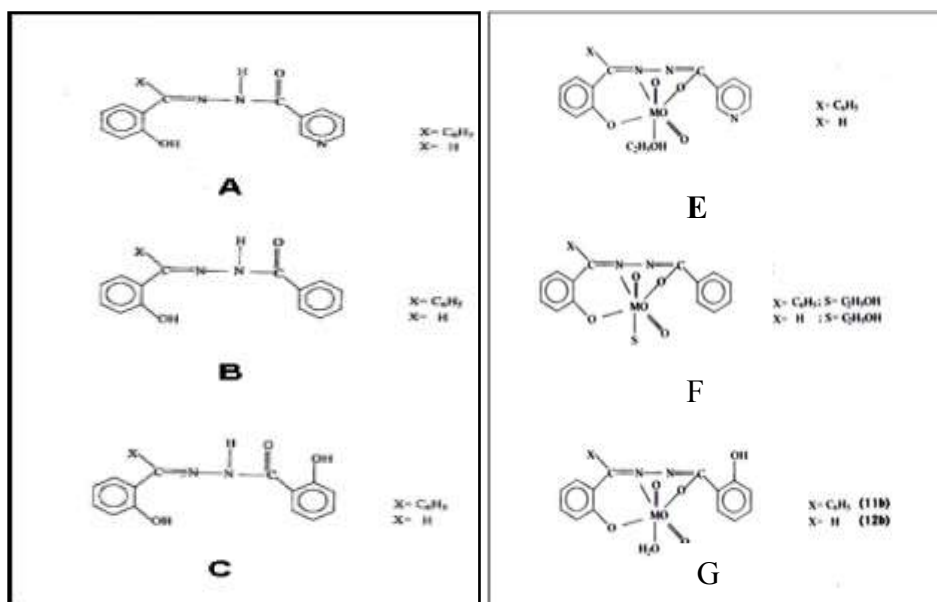
T_d - Decomposition temperature
Table 6: X-ray Diffraction Data of representative Complex MoO₂(hbp-NAH) (C₂H₅OH) (1b)

h	k	l	2θ	2θ	2θ	d	d	Intensity
			(Exp.)	(Calc.)	(Diff.)	(Exp.)	(Calc.)	(Exp.)
-1	0	0	11.357	11.678	-0.321	7.78530	7.57183	101.42
0	1	1	11.796	11.774	0.022	7.49612	7.51027	99.76
0	-1	1	13.426	13.477	-0.051	6.58947	6.56468	327.81
1	1	1	13.835	14.051	-0.216	6.39554	6.29791	161.00
1	1	1	14.456	14.051	0.405	6.12245	6.29791	87.27
-1	0	1	15.520	15.688	-0.168	5.70475	5.64406	115.84
-1	0	1	15.930	15.688	0.242	5.55902	5.64406	121.18
0	0	2	17.767	17.603	0.164	4.98823	5.03421	163.40
0	2	0	18.087	18.255	-0.168	4.90053	4.85590	176.50
0	1	2	18.629	18.722	-0.093	4.75936	4.73593	113.65
1	0	2	19.548	19.581	-0.033	4.53756	4.53004	185.45
1	0	2	19.936	19.581	0.356	4.45005	4.53004	170.05
0	-1	2	20.763	20.918	-0.154	4.27456	4.24339	286.22
0	-2	1	21.225	21.335	-0.110	4.18263	4.16128	238.64
-1	0	2	22.251	22.664	-0.413	3.99196	3.92019	189.83
1	2	2	23.235	23.252	-0.016	3.82513	3.82247	110.25
-1	-1	2	24.305	24.402	-0.097	3.65917	3.64482	115.68
-1	2	1	25.013	25.180	-0.167	3.55713	3.53390	196.93
2	2	1	25.844	25.941	-0.097	3.44459	3.43199	134.99
2	2	0	26.482	26.522	-0.041	3.36307	3.35802	111.12
0	3	0	27.520	27.531	-0.010	3.23847	3.23727	140.91
2	2	2	28.120	28.319	-0.199	3.17075	3.14895	113.76
2	2	2	28.492	28.319	0.173	3.13019	3.14895	122.16
-1	-2	2	28.818	29.144	-0.326	3.09553	3.06163	107.83
1	3	2	29.557	29.618	-0.061	3.01976	3.01371	135.30
-2	-2	1	29.856	29.904	-0.048	2.99025	2.98552	123.59
-1	-3	1	30.641	30.608	0.033	2.91543	2.91850	91.81
2	1	3	31.575	31.566	0.009	2.83124	2.83206	105.09
-2	-1	2	32.229	32.237	-0.008	2.77523	2.77460	81.91
2	0	3	32.800	32.761	0.039	2.72823	2.73140	95.55
2	3	2	33.403	33.086	0.317	2.68036	2.70531	95.70
3	1	1	34.118	34.093	0.025	2.62582	2.62767	94.95
3	1	0	34.764	34.710	0.054	2.57849	2.58234	108.33
3	2	1	35.496	35.458	0.038	2.52698	2.52960	80.00
-3	-1	1	37.714	37.576	0.138	2.38328	2.39171	101.91
2	1	4	38.380	38.460	-0.080	2.34346	2.33875	90.36
-1	1	4	40.296	40.000	0.297	2.23632	2.25222	79.43



Table7: X-ray Diffraction Data of representative Complex MoO₂ (sal-NAH)(C₂H₅OH) (2b)

H	k	l	2 θ	2 θ	2 θ	d	d	Intensity
			(Exp.)	(Calc.)	(Diff.)	(Exp.)	(Calc.)	(Exp.)
0	1	1	11.522	11.679	-0.157	7.67403	7.57091	61.00
0	-1	1	12.799	13.283	-0.484	6.91080	6.66017	259.21
1	0	1	13.762	13.741	0.021	6.42940	6.43920	126.15
1	1	1	14.893	14.615	0.278	5.94369	6.05599	78.91
1	1	1	15.105	14.615	0.490	5.86055	6.05599	61.47
-1	1	0	16.280	16.187	0.093	5.44021	5.47132	154.08
0	2	0	17.972	18.027	-0.055	4.93158	4.91673	72.10
0	2	1	19.017	19.003	0.014	4.66307	4.66647	177.85
-1	-2	0	19.877	19.936	-0.059	4.46306	4.45003	128.66
-1	0	2	22.251	22.642	-0.391	3.99201	3.92399	89.54
-1	2	0	23.218	23.361	-0.142	3.82786	3.80489	28.93
-1	-1	2	24.498	24.478	0.020	3.63072	3.63360	53.75
1	-2	1	25.012	25.147	-0.135	3.55724	3.53841	71.07
1	-2	1	25.617	25.147	0.470	3.47455	3.53841	116.41
0	0	3	26.039	26.247	-0.208	3.41923	3.39263	24.37
2	0	2	27.728	27.685	0.043	3.21468	3.21960	45.38
2	-1	1	28.319	27.850	0.469	3.14895	3.20092	34.50
1	-1	3	30.284	30.429	-0.145	2.94897	2.93526	29.45
2	-1	2	31.196	31.111	0.085	2.86481	2.87245	23.25
-1	3	1	32.471	32.427	0.044	2.75518	2.75880	23.01
-2	-1	2	32.896	32.790	0.106	2.72051	2.72908	45.17
1	-3	1	33.271	33.351	-0.080	2.69068	2.68443	56.75
-1	2	3	34.900	35.016	-0.116	2.56872	2.56049	20.86
-2	0	3	38.630	38.621	0.010	2.32884	2.32940	24.00
2	2	4	40.290	40.184	0.105	2.23667	2.24229	24.32
0	-3	3	40.585	40.605	-0.019	2.22107	2.22006	22.07
-1	2	4	42.259	42.256	0.004	2.13688	2.13705	24.72
0	-4	2	42.765	42.810	-0.045	2.11279	2.11067	25.66
-1	4	2	43.210	43.221	-0.011	2.09205	2.09154	20.23
1	5	1	45.461	44.989	0.472	1.99355	2.01336	22.04



**Fig1: A- Proposed structure for 1a and 2a
1b and 2b**

**B- Proposed structure for 3a and 4a
structure for 3b and 4b**

**C- Proposed structure for 5a and 6a
5b and 6b**

Fig 2: E- Proposed structure for

F- Proposed

G- Proposed structure for