

# Synthesis and Characterization of Dioxomolybdenum (VI) complexes with Schiff base

V. K. Ojha<sup>1</sup>, Arpita Arya<sup>2</sup> and Rajesh Kumar<sup>3</sup>

Department of Chemistry

<sup>1</sup> Associate Professor, D. S. College, Katihar (Bihar),

<sup>2</sup> Research scholar, B. N. Mandal University, Madhepura(Bihar),

<sup>3</sup> Assistant Professor, B. P. S. College, Desari (Vaishali).

**ABSTRACT:** Molybdenum is a versatile transition metal with a large number of stable and accessible oxidation states, within the second series of transition metals only molybdenum represents a biometal, important for microorganisms, plants and animals. The increasing biological applications, namely antibacterial, antifungal, antitubercular, antitumour activities etc. of the complexes of transition metals with hydrazones have intensified interest in research and analytical studies on these metallic complexes. Higher biological activity compared to the parental hydrazone has frequently been thought to be due to their ability to chelate trace metals. This enables their application as antitumor, antifungal, antibacterial and antitubercular drugs.

Studies on complexes of dioxomolybdenum(VI) have opened up a new vista of research and analysis of uncharted biochemical significance. We report herein the synthesis and characterization of some new complexes of dioxomolybdenum(VI) with a tridentate Schiff base, 3-methoxysalicylaldehyde isonicotinoylhydrazone (MSINH) derived from 3-methoxysalicylaldehyde and isonicotinoylhydrazide. During our investigation, various spectral (IR, UV-vis, NMR, FAB mass EPR) methods have been used. The x-ray diffraction patterns, thermal behaviour, anticancer and antibacterial activities of some selected complexes have also been studied.

**Keywords:** Antifungal, Antitubercular, Anticancer and Antibacterial activities.

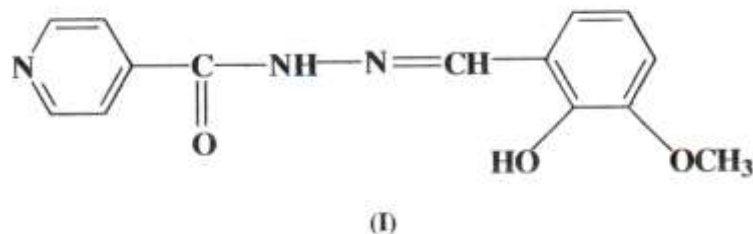
## I. Materials and Methods

Molybdenum pentachloride (Alfa Aesar, Lancaster) and molybdenum trioxide (Loba Chemie, Mumbai, India) were used. All other chemicals were of AR grade.

Metal and chloride were estimated by standard methods. The elemental analyses (C, H, N and S) were carried out at the Sophisticated Test and Instrumentation Center (STIC), Kochi. The IR spectra of ligand and complexes were recorded in the region 4000-400 cm<sup>-1</sup> on a Perkin-Elmer 397 spectro-photometer. Room temperature molar conductance of the complexes in DMF was recorded on an Elico direct reading conductivity meter at a concentration of ~10<sup>-3</sup> M. Electronic absorption spectral measurements of the complexes in methanol were measured using Jasco- V – 550 – UV – vis spectrophotometer. <sup>1</sup>H NMR spectra of the ligand and the complexes were recorded on a 300 MHz FT NMR instrument using TMS as reference. Thermal analysis of one of the complex [MoO(MSINH)Cl<sub>2</sub>] was carried out by heating in air at a rate of 10°C per minute on a Mettler TG-50 thermo balance. X-ray powder diffraction pattern was recorded using a Philips X-ray PW1710 diffractometer. The FAB mass spectrum of [MoO(MSINH)Cl<sub>2</sub>] was recorded on a Jeol JMS600H mass spectrometer. The X-Q band EPR spectrum was recorded at room temperature on a Varian E-112 spectrophotometer with DPPH as the standard, at RSIC, Chennai. The magnetic susceptibilities were recorded at room temperature by Gouy method. Diamagnetic corrections for various atoms and structural units were computed using Pascal's constants.

## 1. Synthesis of 3-methoxysalicylaldehyde isomnicotinoylhydrazone (MSINH)

The Schiff base, MSINH ( $C_{14}H_{13}N_3O_3$ ) (I) was prepared by mixing equimolar solutions of 3-methoxysalicylaldehyde and isonicotinoylhydrazide in methanol and refluxing the mixture for ~30 min. The pale yellow solid separated was filtered, washed with methanol and dried. Purity of the ligand was monitored by TLC. It was characterized by elemental analysis, IR, UV and NMR spectra.



## 2. Synthesis of dioxomolybdenum(VI) complexes

$MoO_3$  (1 mmol) was dissolved in minimum amount of hot conc HCl (2 ml). It was then added to the ligand (1 mmol) solution in methanol with constant stirring. The solid which separated out immediately was suction filtered, washed with aqueous methanol, then with ether and dried over  $P_4O_{10}$  *in vacuo*. The method adopted for the preparation of the thiocyanate complex was the same as that adopted for the preparation of oxomolybdenum (V) complexes.

### Biological activity of the compounds

Anticancer screening was done at the regional cancer Center, Thiruvananthapuram by MTT assay and antibacterial screening by disc diffusion method. Cytotoxicity was measured on human cervical cancer cell lines (HeLa) using the assay MTT.

The ligand (MSINH) and the complexes  $[MoO(MSINH)Cl_2]$  and  $[MoO(MSINH)Cl]$  were screened *in vitro* for their possible antibacterial activities using the disc diffusion method (Kirby Baure method) For the pathogenic bacteria, viz., *salmonella typhi* MTCC 734, *Pseudomonas aeruginosa* MTCC 2642, *Escherichia coli* 585, *Proteus vulgaris* 177, *Bacillus subtilis* 2248 and *streptococcus thermophilus* 1938.

## II. Result and Discussion

The chemical analyses data and physical properties of the ligand and their complexes are given in Table -1). All the complexes are coloured, not-hygroscopic solids and stable in air. They are sparingly soluble in common organic solvents like acetone, chloroform, acetonitrile and completely soluble in ethanol, methanol, DMF and DMSO.

The molar conductance values of  $10^{-3}$  M solutions of complexes lie in the range  $45-46 \Omega^{-1} cm^2 mol^{-1}$  in dry DMF indicate their non electrolyte behaviour. All the oxocomplexes show magnetic moment values in the range of 1.66-1.78 BM, which corresponds to spin-only value (1.73 BM) expected for oxomolybdenum(V) complexes showing the absence of Mo-Mo interaction. All the dioxomolybdenum(VI) complexes are found to be diamagnetic as expected for a  $d^0$  system. The results show that the ligand coordinates to the metal ion in 1:1 ratio and suggest that the proposed formulas are  $[MoO(MSINH)X]$  and  $[MoO(MSINH)ClX]$ , where X=Cl, NCS.

Important infrared spectral bands of the ligand and complexes and their tentative assignments are given in Table-2. IR spectra of the ligand and its complexes are quite complex due to the presence of various ring vibrations and C-H absorptions. A broad band centered at  $3201 cm^{-1}$  in the free ligand can be

assigned to the  $\nu_{N-H}$  stretching. In the complexes this band remains unaltered. This suggests non-participation of the NH group in bonding. The infrared spectrum of the free ligand exhibits bands at 3438  $\text{cm}^{-1}$  and 1353  $\text{cm}^{-1}$  due to phenolic OH.

Ligand/Complexes	Found(Cal.)(%)						$\mu_{\text{eff}}$ (BM)
	Mo	C	H	N	Cl	S	
MSINH	--	61.5 (61.99)	4.95 (4.83)	15.24 (15.49)	--	--	--
[MoO(MSINH)Cl <sub>2</sub> ]	21.43 (21.17)	37.83 (37.11)	2.80 (2.67)	9.5 (9.27)	16.02 (15.65)	--	1.78
[MoO(MSINH)CINCS]	20.89 (20.17)	38.01 (37.87)	2.34 (2.54)	11.65 (11.78)	7.81 (7.45)	6.42 (6.74)	1.66
[MoO(MSINH)Cl]	22.35 (22.12)	39.01 (38.78)	2.91 (2.79)	9.55 (9.69)	8.67 (8.17)	--	--
[MoO(MSINH)CINCS]	21.61 (21.03)	39.92 (39.48)	2.45 (2.65)	12.38 (12.28)	--	6.86 (7.03)	--

These bands are absent in the spectra of the complexes, indicating the deprotonation of phenolic OH on coordination with metal ions. This is further supported by the shifting of the intense ligand band at 1317  $\text{cm}^{-1}$  due to phenolic C-O to 1340  $\text{cm}^{-1}$ . The  $\nu_{C=O}$  observed at 1670  $\text{cm}^{-1}$  in the spectrum of the ligand shows a downward shift by -30  $\text{cm}^{-1}$  in all the complexes indicating coordination through the carbonyl oxygen. The vibration band at 1626  $\text{cm}^{-1}$  assigned to  $\nu_{C=N}$  in the spectrum of ligand shows downward shift by ~30  $\text{cm}^{-1}$  in the spectra of the complexes confirming coordination through azomethine. The coordination through the azomethine nitrogen atom is further supported by the shift of  $\nu_{N-N}$  vibration observed at 998  $\text{cm}^{-1}$  in the ligand to higher frequency by ~20  $\text{cm}^{-1}$  in the complexes. It is due to the reduction of lone pair repulsive forces in the adjacent nitrogen atoms.

The new weak bands at ~500  $\text{cm}^{-1}$  and ~430  $\text{cm}^{-1}$  in the metal complexes have been assigned to  $\nu_{Mo-N}$  and  $\nu_{Mo-O}$  modes respectively. Dioxomolybdenum(VI) complex displays two Mo=O stretches at ~940-960  $\text{cm}^{-1}$  and ~898-920  $\text{cm}^{-1}$  due to symmetric and antisymmetric stretching of *cis*-MoO<sub>2</sub><sup>+2</sup> core. The MoO<sub>2</sub> prefers to form a *cis* configuration due to maximum utilization of the *dπ* groups. A very strong band observed at ~940  $\text{cm}^{-1}$  in the spectra of oxomolybdenum(V) complexes corresponds to Mo=O stretching frequency. The N-coordinated nature of the thiocyanate group is indicated by the  $\nu_{C-N}$  (~2060  $\text{cm}^{-1}$ ),  $\nu_{C-S}$  (~860  $\text{cm}^{-1}$ ) and  $\delta_{NCS}$  (~490  $\text{cm}^{-1}$ ) bands.

Ligand/Complexes	$\nu_{O-H}$	$\nu_{N-H}$	$\nu_{C=O}$	$\nu_{C=N}$	$\delta_{O-H}$	$\nu_{C-O}$	$\nu_{N-N}$	$\nu_{M=O}$
MSINH	3438	3201	1670	1626	1353	1317	998	--
[MoO(MSINH)Cl <sub>2</sub> ]	--	3205	1633	1597	--	1342	1022	941
[MoO(MSINH)CINCS]	--	3200	1633	1599	--	1343	1025	939
[MoO(MSINH)Cl]	--	3203	1636	1607	--	1340	1022	944
[MoO(MSINH)CINCS]	--	3202	1635	1604	--	1342	1033	904

The  $^1\text{H}$  NMR spectra of (MSINH) and  $[\text{MoO}(\text{MSINH})\text{Cl}]$  were recorded in  $\text{DMSO-}d_6$ .  $^1\text{H}$  NMR spectrum of the free ligand shows signal due to OH at  $\delta$  (10.74) in the free ligand appears at 10.5 in the complex. Presence of NH proton in the complex indicates that the ligand exists in the keto form. A singlet at  $\delta$ (8.7) observed in the spectrum for the free ligand shows downfield shift to  $\delta$ (9.05) indicating coordination of azomethine nitrogen in the complexes, due to the reduction of electron density at azomethine C-H. The methoxy protons of the ligand and the complex appear at  $\delta$  (3.97). The seven aromatic protons appear as multiplets within the range  $\delta$  (8.8-8.96) (isonicotinic 4H and  $\delta$  (7.04 – 6.83) (phenyl 3H) for the ligand and dioxomolybdenum complexes. The sharp signal found as a singlet at  $\delta$  (2.49) be due to the water present in  $\text{DMSO-}d_6$  sample used.

The X-band EPR spectrum (Fig-1) of  $[\text{MoO}(\text{MSINH})\text{Cl}_2]$  recorded in the polycrystalline form at room temperature is characterized by only a single line with unresolved parallel and perpendicular components. The EPR parameters were found to be  $g_{\parallel} = 1.9355$ ,  $g_{\perp} = 1.9049$  and  $g_{\text{av}} = 1.9151$ . The calculated  $g_{\text{av}}$  values indicate that the complex is monomeric with molybdenum in the pentavalent state.

## REFERENCES:

- [1] Dutta R L & Syamal A, *Elements of Magnetochemistry*, 200 Edn, (East West Press, New Delhi) 1992, p. 8.
- [2] Singh N, Hingorani S, Srivastava J, Puri V & Agarwala B V, *Synth React Inorg Met-Org Chem*, 22 (1992) 1283
- [3] Harikumar Nair M L & Prabhakaran C P, *Indian J. Chem*, 35A (1996) 771.
- [4] Bower J J, Leonard S S & Shil X, *Mol Cell Bio Chem*, 279 (2005) 3.
- [5] *Hyperchem 7.5 Professional Version for Windows Molecular Modeling System*, (Hypercube Inc, Canada) 2005.
- [6] Mandlik P R, More M B & Aswar , *Indian J Chem*, 42 A (2003) 1064; Sharma V K, Shipra Srivastava & Ankita Srivastava, *J Coord Chem*, 59(12) (2006) 1321.
- [7] Sekhon B S & Gandhi L, *Resonance*, 1 (2006) 75.
- [8] Harikumar Nair M L & Nisha Kumari K R, *Asian J Chem*, 19 (2007) 468.
- [9] Sheela A, Pramila Gladis M S & Harikumar Nair M L, *J Indian Chem Soc*, 84 (2007) 329.
- [10] Kilic A & Tas E, *Synth React Inorg Metal-Org Nano-Metal Chem*, 37 (2007) 583.
- [11] Harikumar Nair M L & Siji V L, *J Indian Chem Soc*, 85 (2008) 589.
- [12] Mishra A P & Mrnika Soni, *Metal-Besed Drugs*, (2008) doc: 10.1155/2008/875410.
- [13] Harikumar Nair M L & Pramila Gladis M S, *Asian J Chem*, 20 (2008) 2504.