

Synthesis, characterization and antifungal studies of oxomolybdenum (V) complexes of Schiff bases derived from hydrazine carboxamide and thiosemicarbazide

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(Received: September 20, 2008; Accepted: October 26, 2008)

ABSTRACT

A few oxomolybdenum (V) complexes of Schiff bases derived from Pyridine-2-carboxaldehyde, 2, 5-dihydroxy acetophenone, 5-nitrobenzaldehyde and 2,5-dihydroxynaphthaldehyde with Hydrazine carboxamide [PyCHC], [DHAPHC], [NBALHC] and [DHNALHC], respectively, and thiosemicarbazide [PyCTSC], [DHAPTSC], [NBALTSC] and [DHNALTSC], respectively, were prepared and characterized by elemental analyses, IR, electronic spectra, molar conductance and magnetic susceptibility. These studies indicated octahedral geometry around the metal ion. The complexes were also screened for biological activities.

Key words : Schiff base, antifungal studies, octahedral.

INTRODUCTION

Schiff base complexes with transition metals are known from the middle of nineteenth century. These complexes play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures.¹⁻³ Imines are an important class of ligands in coordination chemistry and have various applications in analytical chemistry and in catalysis.^{4,5} Schiff bases and their transition metal complexes have been used as antioxidative⁶, antitumour⁷, antiviral⁸, antineoplastic⁹, antimicrobial¹⁰, hypotensive and hypothermic reagents^{11,12}. Schiff base can also be used as an analytical reagent for epoxydation of olefins¹³.

Molybdenum is a versatile transition element¹⁴ due to the fact that it possesses a large number of stable and accessible oxidation states ranging from +2 to +6. Oxomolybdenum (V) species

dominate the higher oxidation states¹⁵. A number of chemical reactions are catalyzed by complexes of molybdenum. It is one of the most biologically active transition elements and is an essential micronutrient for microorganisms, plants and animals¹⁶. Certain metalloenzymes also contain molybdenum (V) species.

In view of the importance of oxomolybdenum (V) complexes, we have isolated and characterized some new complexes and results of study are reported here.

MATERIAL AND METHODS

All chemicals used were of AR grade or equivalent purity. Materials used for the preparation of ligands (Schiff bases) were different aldehydes and amino compounds. These were collected from different pharmaceuticals such as Aldrich, Lancaster, Sisco and E. Merck etc.

The ligands form complexes with oxomolybdenum (V) used in term of MoCl_5 (Aldrich chemicals, USA). Elemental analyses were carried out at RSIC CDRI, Lucknow. Conductivity measurements were carried out at Philips conductivity Bridge model PR9500 with a dip type conductivity cell at Department of Chemistry, Bareilly College, Bareilly. The conductance of the complexes was measured in methanol, DMF and DMSO at 25°C. Magnetic susceptibility of the complexes were determined by Gouy method at Department of Chemistry, Bareilly College, Bareilly. The sample tube was calibrated with CuSO_4 . The IR spectra of complexes were recorded with Perkin Elmer Spectrometer model 651 in KBr or in nujol phase at RSIC CDRI, Lucknow. The visible spectra were recorded with Beckmann DU-2-spectrophotometer in the range of 750 cm^{-1} to 300 cm^{-1} at Department of Chemistry, Bareilly College, Bareilly.

Preparation of ligands

The Schiff bases were prepared by the condensation of carbonyl and amino compounds. The amino compound was dissolved in ethanol and refluxed for about half an hour. Now the requisite amount of carbonyl compound was added to the flask and this mixture was refluxed for about 6 hours and kept for 24 hours. The crystals of ligand were obtained and purified by recrystallization. The purity of ligand was checked by elemental analyses and M.P.

Preparation of metal complexes

A methanolic solution of MoCl_5 (2 mmol) was added to a hot solution of the ligand (2 mmol) in the same solvent. The solution which formed was heated over a water bath for few minutes. The precipitated complexes were filtered, washed with aqueous methanol and dried over P_4O_{10} in vacuum.

RESULTS AND DISCUSSION

Elemental analyses indicate that oxomolybdenum (V) complexes have the composition $[\text{MoO}(\text{PyCHC})\text{Cl}_2]$, $[\text{MoO}(\text{DHAPHC})\text{Cl}_2]$, $[\text{MoO}(\text{NBALHC})\text{H}_2\text{OCl}_2]$, $[\text{MoO}(\text{DHNALHC})\text{Cl}_2]$, $[\text{MoO}(\text{PyCTSC})\text{Cl}_2]$, $[\text{MoO}(\text{DHAPTSC})\text{Cl}_2]$, $[\text{MoO}(\text{NBALTSC})\text{H}_2\text{OCl}_2]$ and $[\text{MoO}(\text{DHNALTSC})\text{Cl}_2]$. The formation of these complexes was indicated by the vast difference

between the melting points of the ligands and their respective complexes.

The molar conductance values of these complexes at 10^{-3} M dilution were recorded in MeOH, DMF and DMSO. All complexes of oxomolybdenum (V) have the values of molar conductance which are very low as compared to the values for 1:1 electrolytes. These complexes are, therefore, non-electrolytic in nature^{17,18}.

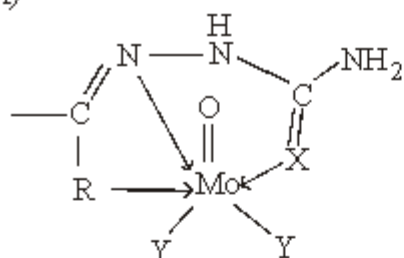
Vibrational spectra of ligand as well as complexes in the region $4000\text{--}2000\text{ cm}^{-1}$ has been recorded and structurally significant vibrational bands are reported in Table 1.

In the IR spectra the bands at 1590 and 1690 cm^{-1} , 1580 and 1685 cm^{-1} , 1595 and 1688 cm^{-1} , and 1585 and 1686 cm^{-1} , in (PyCHC), (DHAPHC), (NBALHC) and (DHNALHC), respectively, due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{O})$ have shifted to a higher wave-number, indicating coordination through the azomethine nitrogen and carbonyl oxygen to the central metal atom, respectively. While the bands at 1620 and 785 cm^{-1} , 1600 and 774 cm^{-1} , 1630 and 770 cm^{-1} and 1615 and 760 cm^{-1} in (PyCTSC), (DHAPTSC), (NBALTSC) and (DHNALTSC), respectively due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ have shifted towards higher wave number in their respective complexes indicating coordination of azomethine nitrogen and thionyl sulfur to the central metal atom respectively. The free ligands display two sharp bands at 3448 and 3321 cm^{-1} , assignable to asymmetric and symmetric NH_2 groups, respectively, which remain at almost the same positions in all the metal complexes, suggesting that the amino group is not involved in chelation. The pyridine ring vibrations are observed at higher frequencies ($1020\text{--}1025$ and 670 cm^{-1}) in (PyCHC) and (PyCTSC) indicating an additional bonding through pyridine nitrogen¹⁹ in the complex. The bands at 1510 cm^{-1} in (DHAPHC) and (DHNALHC), and 1495 cm^{-1} in (DHAPTSC) and (DHNALTSC) due to $\nu(\text{C}-\text{O})$ phenolic oxygen have shifted to 1540 cm^{-1} and 1525 cm^{-1} respectively in the metal complexes, suggesting deprotonation and complexation of phenolic oxygen during complex formation. The bands at ($660\text{--}520$), and ($421\text{--}430$) can be assigned to $\nu(\text{Mo}-\text{N})$ and $\nu(\text{Mo}-\text{O})$ ²⁰, respectively, the appearance of which further

Table 1: Analytical and physical data of the molybdenum complexes

Compound/Colour	M.P. °C	Elemental analyses found (Calcd), %						Important IR spectral bands				μ_{eff} , BM
		C	H	N	S	Cl	M	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{S})$	$\nu(\text{Mo}=\text{O})$	
1. [MoO(PyCHC)Cl ₂] (Brown)	265	24.19 (24.27)	2.42 (2.31)	16.00 (16.18)	-	20.09 (20.23)	27.53 (27.74)	1590	1690	-	950	1.70
2. [MoO(DHAPHC)Cl ₂] (Light brown)	247	27.51 (27.69)	2.49 (2.46)	10.60 (10.76)	-	17.70 (17.94)	24.53 (24.61)	1580	1685	-	960	1.63
3. [MoO(NBALHC)H ₂ OCl ₂] (Deep brown)	213	23.40 (23.52)	2.56 (2.45)	13.53 (13.72)	-	17.29 (17.15)	23.70 (23.52)	1595	1688	-	962	1.75
4. [MoO(DHNALHC)Cl ₂] (Yellow)	278	33.65 (33.80)	2.26 (2.34)	9.80 (9.85)	-	16.36 (16.43)	22.40 (22.53)	1585	1686	-	950	1.78
5. [MoO(PyCTSC)Cl ₂] (Green)	268	23.10 (23.20)	2.14 (2.20)	15.30 (15.46)	8.71 (8.83)	19.25 (19.33)	26.25 (26.51)	1620	-	785	955	1.73
6. [MoO(DHAPTSC)Cl ₂] (Light yellow)	239	26.40 (26.60)	2.30 (2.46)	10.15 (10.34)	7.79 (7.88)	17.19 (17.24)	23.70 (23.64)	1600	-	774	963	1.68
7. [MoO(NBALTSC)H ₂ OCl ₂] (Yellow red)	209	22.80 (22.64)	2.26 (2.35)	13.11 (13.20)	7.66 (7.54)	16.41 (16.50)	22.59 (22.64)	1630	-	770	965	1.79
8. [MoO(DHNALTSC)Cl ₂] (Brown red)	250	32.49 (32.57)	2.15 (2.26)	10.70 (10.85)	7.15 (7.23)	15.76 (15.83)	21.66 (21.71)	1615	-	760	955	1.80

(A)

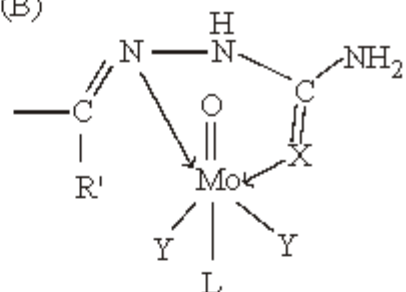


Structure for complexes 1, 2, 4, 5, 6 and 8

Where X = O or S

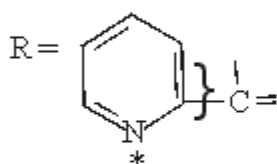
Y = Cl⁻

(B)

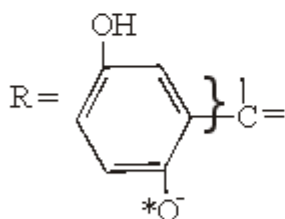


Structure for complexes 3 and 7

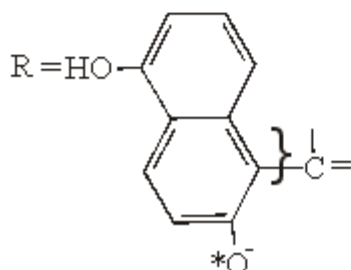
Where X = O or S

Y = Cl⁻L = H₂O*

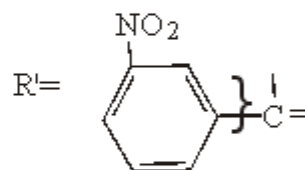
in complexes (1) and (5)



in complexes (2) and (6)



in complexes (4) and (8)



in complexes (3) and (7)

* = Donor atom.

Scheme 1

supports bonding of the ligand to the metal through nitrogen and oxygen.

The appearance of a new band at 3300 and 3350 cm^{-1} in the complexes of (NBALHC) and (NBALTSC), respectively, indicated the presence of water molecules. The -OH rocking and wagging bands between 800-720 cm^{-1} indicated their coordinated nature in the complex. This is further supported by thermogravimetric analysis in which the percent weight loss of two water molecules occurs above 160°C²¹. In all complexes of oxomolybdenum (V) a sharp peak appeared at 290-370 cm^{-1} showed the coordination occurred through chlorine atom²². A very strong band occurring at 950 cm^{-1} in oxomolybdenum (V) complexes can be attributed to $\nu(\text{Mo}=\text{O})$ ²³.

The oxomolybdenum (V) complexes are paramagnetic in nature. The values of magnetic moment are in the range of 1.62-1.80 BM which corresponds to the spin-only value (1.73 BM) expected for these complexes showing the absence of any Mo-Mo interaction. The oxomolybdenum (V) complexes appear to have octahedral geometry.

The electronic spectral bands of the present oxomolybdenum (V) complexes show similar absorption peaks²⁴. A moderately intense band observed in the region of 27027-25000 cm^{-1}

attributed to $\text{O}(\pi) \rightarrow \text{d}(\text{Mo})$. The band due to the transition ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ ($\text{d}_{xy} \rightarrow \text{d}_z^2$) is probably masked by the above bands. The complexes exhibit two more bands, a medium intensity band at 20833-19230 cm^{-1} and a weak broad band, spread over the region 15151-12820 cm^{-1} assigned to ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ ($\text{d}_{xy} \rightarrow \text{d}_{x^2-y^2}$) and ${}^2\text{B}_2 \rightarrow {}^2\text{E}_1$ ($\text{d}_{xy} \rightarrow \text{d}_{yz}, \text{d}_{xz}$), respectively (the unpaired electron is in the d_{xy} orbital). The spectral bands at 15151-12820 cm^{-1} indicate octahedral environment for the complexes²⁵.

On the basis of available evidences a distorted octahedral geometry (due to Mo=O bond) has been suggested for all the oxomolybdenum (V) complexes.

Antifungal activity

Biocidal activity of a potentially active molecule is altered on its complexation with a suitable metal ion²⁶. The ligands and their oxomolybdenum(V) complexes were evaluated for their antifungal activities. *A. niger* and *C. albicans* at concentrations of 1mgmL^{-1} employing the disc method²⁷. The results of minimum inhibitory concentration (MIC) values showed that the Schiff bases and their metal complexes are active against the said fungus. The fungal activity of the metallic complexes was found higher than the corresponding Schiff bases.

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