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Studies of Some Molybdenum Complexes with Bidentate Monobasic Ligand

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ABSTRACT

In pursuance of present research work on the Molybdenum complexes. We intent to synthesize some Molybdenum complexes through condensation between Dioxo(2,4-pentanedionato) molybdenum(VI) and sulfapyridine with 2-acetylnaphthalene, 2-acetylthiophene, thiophene-2-carbaldehyde. The ligands thiophene thiosemicarbazone(LH) was prepared by the condensation of thiophene-2-carbaldehyde and thiosemicarbazide and other was prepared by the condensation of different sulfadrugs with various aldehydes and ketones. Due to the wide range of medicinal properties of sulfadrugs and thiosemicarbazones and their ability to form chelates with the metal ions, we under took the synthesis of symmetrical dioxomolybdenum (VI) complexes with neutral bidentate monobasic chelating ligands and screened them for their antifungal and antibacterial activities. The monoanionic form of the ligands for the group of macrocycles appears to be one of the important factors for electrostatic interaction of the metal ion with the macrocyclic ligands which improve the extra stability of the complexes. The synthesized Molybdenum complexes and ligands have been characterized by various spectral data as IR, NMR, UV, X-Ray and molar conductance, magnetic susceptibility with elemental analysis. Higher biological activity due to their ability to chelate trace with metals and enable their application as antitumor, antifungal, antibacterial, and antitubercular drugs. The ligand behave as a neutral bidentate and the complexes are found to be monomeric and diamagnetic distorted octahedral structure.

KEYWORD-: Molybdenum (VI) complexes, spectroscopic properties, Thiophene-2-carbaldehyde, Thiosemicarbazide, Biological activity and sulfadrugs.

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INTRODUCTION

Molybdenum is a versatile transition metal with a large number of stable and accessible oxidation states ranging from -2 to +6. Dioxomolybdenum (VI) species dominate the higher oxidation states. Its most important oxidation state is +6.Which it exists in the form of dipositive Dioxomolybdyl cation MoO_2^{2+}. A number of chemical reactions are catalyzed by complexes of molybdenum. It is one of the most biologically active element inessential micronutrients, plants and animals.[1-3] Within the second series of transition metals only molybdenum ·increasing biological application, namely antibacterial, antifungal, ant-tubercular, antitumor's, 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 hydrazones has frequently been thought to be due to their ability to chelating trace metals. This enables their application as antitumor's, antifungal, antibacterial, and ant-tubercular drugs. Molybdenum atoms bonded through O, N, and S atoms. These Mo sites supposed to be active centres for the catalytic activity of the enzymes[4-6].EXAFS studies have indicated the presence of an oxo group attached to Molybdenum[7-9]. Studies on complexes of Dioxomolybdenum (VI) have opened up a new vista of research and analysis of uncharged biochemical significance. The chemistry of Dioxomolybdenum (VI) complexes has received considerable attention in recent years. The various ligands with different donor properties into Dioxomolybdenum give complexes which exhibit intriguing lability differences. There is extensive literature on the use of Dioxomolybdenum (VI) complexes as catalysts in some important industrial processes, as well as their role in some biological process. Heterocyclic thiosemicarbazones as well as their metal complexes possess various biological activities[10-12].These compounds are emerging as a new class of experimental anticancer chemotherapeutic agents[13-15].Sulfadrugs have been used against the treatment of various diseases[16-20].With these advantages, we have extended our study to two new dioxo complexes of molybdenum(VI) with O-phenylenediamine (OPDA) and 4-Methyl-O-phenylenediamine (4-Me-OPDA) ligands.

Materials and Methods

All the chemicals used were of analytical reagent grade purified by standard method and dry before use. The solvent were dried prior to use. Precautions were taken to exclude moisture from the system.

Ligands Synthesis

1.Thiophene thiosemicarbazone, LH.

Thiophene thiosemicarbazone ($LH=C_6H_7N_3S_2$) was prepared by the condensation of thiophene-2-carbaldehyde(C_4H_3SCHO) and thiosemicarbazide (CH_5N_3S).Reaction were taken in 1:1 molar ratio in ethanol medium and the solution was fluxed or stirred for 7 to 8 hours. On cooling the crystals formed were crystallized in the ethanol solvent and then dried in vacuum.

$$C_4H_3SCHO + CH_5N_3S \rightarrow C_6H_7N_3S_2\ (LH) + H_2O$$

2. Sulfadrugs azomethines,

Sulfadrugs azomethines were prepared by the condensations of different sulfadrugs with various aldehydes or ketones. The sulfadrugs azomethines used (L^1H, L^2H, L^3H) were synthesized by the condensation of sulfapyridine with 2-acetylnaphthalene, 2-acetylthiophene, thiophene-2-carbaldehyde respectively. Reactants were taken in 1:1 molar ratio in ethanol medium and the solution was refluxed or stirred for 7 to 8 hours. On cooling the crystals obtained were crystallized in the ethanol solvent and then dried in vacuum.

$$C_{11}H_{11}N_3SO_2 + C_{12}H_{10}O \rightarrow C_{23}H_{19}N_3SO_2\ (LH^1) + H_2O$$

$$C_{11}H_{11}N_3SO_2 + C_6H_6SO \rightarrow C_{17}H_{15}N_3S_2O_2\ (LH^2) + H_2O$$

$$C_{11}H_{11}N_3SO_2 + C_5H_4SO \rightarrow C_{16}H_{13}N_3S_2O_2\ (LH^3) + H_2O$$

Preparation of complexes-

1.Preparation of $MoO_2(L)(L^1)$

A methanolic solution (500 ml) of Dixobis(2,4-pentanedionato) molybdenum (VI) and the ligands thiophenethiosemicarbazone($LH=C_6H_7N_3S_2$) and 2-acetylnapthalene sulfapyridine ($L^1H= C_{13}H_{19}N_3SO_2$) was refluxed for 12-14 hours. A brown colour of crystalline solid is separated out. After the completion of the reaction, the excess solvent was distilled off and the product was dried in vacuum and melt at 75^0C. They are soluble in methanol, ethanol, acetone and ethanenitrile solvent but do not soluble in polar solvent.

$$MoO_2(C_5H_7O_2)_2 + LH + L^1H - MoO_2(L)\ (L^1) + 2C_5H_7O_2$$

2.Preparation of $MoO_2(L)(L^2)$

A methanolic solution (50 ml) of Dioxobis(2,4-pentanedionato) molybdenum(VI) and the ligands thiophenethiosemicarbazone ($LH=C_6H_7N_3S_2$) and 2-acetylthiophene ($L^2H=C_{17}H_{15}N_3S_2O_2$) was refluxed for 12-14 hours. A light brown colour of crystalline solid is separated out. After the completion the excess solvent was distilled off and the product was dried in vacuum and melt at.120°C.The complexes are also soluble in organic solvent as methanol, ethanol, acetone and ethanenitrile,but does not soluble in polar solvent as like water.

$$MoO_2(C_5H_7O_2)_2 + LH + L^2H \rightarrow MoO_2(L)(L^2) + 2C_5H_7O_2$$

3.Preparation of $MnO_2(L)(L^3)$.

A methanolic solution (50ml) of thiobis(2,4-pentanedionato)molybdenum(VI) and the ligands thiophene thiosemicarbazone($LH=C_6H_7N_3S_2$) and thiophene-2-carbaldehyde sulfapyridine($L^3H=C_{16}H_{13}N_3S_2O_2$) was refluxed for 12-14 hours. A light brown colour of crystalline solid is separated out. After the completion of the reaction, the excess solvent was distilled off and the product dried in vacuum and melt at 117°C.They are soluble in organic solvent as methanol, ethanol, propanone and ethanenitrile but not soluble in polar solvent

$$MoO_2(C_5H_7O_2)_2 + LH + L^3H \rightarrow Mo0_2(L)(L^3) + 2C_5H_7O_2$$

RESULTS AND DISCUTION

The reaction of Dioxobis (2,4-pentanedionate)molybdenum(VI) with unsymmetrical ligands thiophene thiosemicarbazone (LH) on one hand and 2-acetylnaphthalene sulfapyridine(L^1H) 2-acetylthiophene sulfapyridine(L^2H) thiophene-2-carbaldehyde sulfapyridine (L^3H), on the other hand have been carried out in 1:1:1 molar ratio in dry methanol. The reaction proceeds with the liberation of two molecules of 2,4-pentanedione. The resulting complexes are brown coloured and non-hygroscopic solids but soluble in organic solvent as methanol, ethanol, acetone, acetonitrile, DMF and DMSO. The complexes are monomeric and diamagnetic as expected for their maximum utilization of the available vacent inner d- orbitals of central metal ion for bonding of dπ-pπ configuration. The related data having given below in Table-1

Table- 1 Analytical and physical data of Dioxomolybdenum (VI) Complexes.

Complex	**colour**	**M.P**	**Found (Calculated)**			**Molar conductance (W^{-1}cm^{-2}mol^{-1}) x 10^{-3}**		
						$C_6H_5NO_2$	**CH_3CN**	**CH_3OH**
$MoO_2(L)(L^1)$	Brown	75	11.67 (11.80)	13.38 (13.50)	13.31 (13.40)	1.6	14.2	6.2
$MoO_2(L)(L^2)$	Light Brown	120	12.42 (12.58)	19.08 (19.19)	14.11 (14.28)	1.9	14.4	8.2
$MoO_2(L)(L^3)$	Brawn	117	12.62 (12.85)	19.54 (19.60)	14.28 (14.59)	2.8	14.6	12.8

IR Spectra

IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer. IR spectra (Table-2) of the sulfadrugs ligands show medium intensity bands at 3300-3100 cm^{-1} (NH). In thiophene thiosemicarbazone strong band appears at 1050-1040 cm^{-1} (C=S).A sharp band at 1620 cm^{-1} (C=N) azomethine is observed in both types of the ligands. On complexation, the band use to ν_{NH} disappears, indicating deprotonation of hydrogen followed by coordination through nitrogen and the band due to $\nu_{C=S}$ also disappears suggesting thioenolisation of the ligand and its chelation with the metal ion through thiolsulphour respectively. Sharp band due to azomethine moiety shifts slightly towards lower frequency (10-20cm^{-1}) in the complexes indicating the coordination of azomethine nitrogen to the metal atom. The bands observed at 3430-3350 cm^{-1} attributed to asymmetric and symmetric modes of $-NH_2$ group remain nearly at the same position in the spectra of the complexes. Some new bands are observed in the complexes at 480(Mo-N) and 360 cm^{-1}(Mo-S). The strong bands exhibited to the Dioxomolybdenum (VI) complexes at 930-950 and 900-915 cm^{-1} are attributed to terminal ν_{sym} O=Mo=O and ν_{asym} O=Mo=O respectively, in symmetrical arrangement of MoO_2^{2+}moiety[21-22].The symmetrical arrangement of MnO_2^{2+} is prefers than unsymmetrical arrangement because symmetrical arrangement provide extra stability with maximum utilization of the available vacent inner d- orbitals of central metal ion for bonding of dπ-pπ with the oxo group in complexes in which both oxygen are in equatorial mode to one another around the central metal ion .

Table-2 IR spectral data of Dioxomolybdenum (VI) complexes.

Complex	**ν_{N-H} cm^{-1}**	**$\nu_{C=N}$ cm^{-1}**	**ν_{Mo-N} cm^{-1}**	**ν_{Mo-S} cm^{-1}**
$MoO_2(L)(L^1)$	3430	1600	480	360
$MoO_2(L)(L^2)$	3410	1595	485	365
$MoO_2(L)(L^3)$	3380	1585	475	355

^{1}H NMR Spectra

^{1}H NMR spectra (DMSO-d6) were recorded on a JEOL FX90Q spectrometer using TMS as an internal standard. Sulfapyridine and sulfaguanidine ligands show signals at δ 11.75 and 11.80 respectively, due to -NH proton which disappear in the complexes showing the deprotonation and the coordination through nitrogen of this group. The presence of two new signals at δ 10.32 and 3.20 in sulfaguanidine ligand show the presence of -NH and $-NH_2$ protons, respectively. These signals also appear in the complexes indicating that these are not participating in the coordination. In thiosemicarbazone ligand, the signal at δ 3.60(SH) disappears in the complexes, indicating deprotonation and coordination through thiol sulphour with central metal ion in complexes.

UV Spectra

The electronic spectra ($CHCl_3$) were recorded on a Shimadzu UV-160 spectrophotometer. The ligand bands at 230 and 270 nm are due to π-π* transitions within the benzene ring and that around 320 nm is due to π-π* transitions of the azomethine group. However in the metal complexes the first two bands remains unaltered whereas the third undergoes a blue-shift due to coordination of nitrogen to the central metal atom. The electronic spectra indicate octahedral environment for all the complexes. Magnetic susceptibilities at room temperature were measured by Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. During the course of present investigation of magnetic properties of the complexes at room temperature is diamagnetic corrections for various atoms and structural units were computed using Pascal's constants. which suggests diamagnetic octahedral arrangement of ligands around the central metal ion.

^{13}C NMR Spectra

^{13}C NMR spectra were (MeOH) at 22.49 MHZ, N and S were estimated by Kjeldahl's and Messenger's methods. The considerable shift in the position of carbon atoms adjacent to azomethine nitrogen (155.20-161.62 ppm) and thiolic sulphour(164.15-177.86 ppm) in the ^{13}CNMR spectra further support the proposed coordination in the complexes.

X-Ray Spectral analysis

The X-ray powder diffraction study of the compound $MoO_2(L)(L^1)$ was carried out (Table-3). The results show that the compound belongs to the orthorhombic crystal system having unit cell parameters, a = 30.205Å, c =21.8496Å and $\alpha = \beta = \Upsilon = 90^0$

Table- 3 X-ray powder diffraction data of $MoO_2(L)(L^1)$

Peak No	20^0 Obs	h	k	I	d.spacing.Obs (Å)
1	11.5	0	2	2	7.5570
2	12.7	0	0	4	6.8567
3	16.0	0	3	2	5.5350
4	16.7	0	1	5	5.2420
5	23.2	2	3	0	3.8310
6	23.5	2	3	1	3.7830
7	26.8	2	4	1	3.3240
8	28.1	1	1	8	3.1730
9	30.2	3	0	4	2.9500
10	33.7	3	3	4	2.6570

Conductivity measurement.

The molar conductance of the complexes in CH_3OH, CH_3CN and $C_6H_5NO_2$ (1.0 x 10^{-3}mol dm^{-3}) solvent were measured at approx 300 k using an Elico conductivity bridge CM 82T with a dip type cell adjusted with platinum electrodes. Molar conductance values of the complexes were found to be lie in the range of 2.1-15.7 $ohm^{-1}cm^2$ mol^{-1} and indicate their non-electolytic nature.Which clearly indicates that anionic part of ligands are coordinated with metal atom / ions. The molar conductance values also supported the structure assigned on the basis of physicochemical and spectroscopic measurements.The conductivity measurement data have been presented below in Table-4

Table-4 Molar conductance data ($ohm^{-1}cm^2$ mol^{-1}) of Dioxomolybdenum (VI) Complexes of ligands.

Complexes	CH_3OH	CH_3CN	$C_6H_5NO_2$
$MoO_2(L)(L^1)$	7.5	15.7	1.8
$MoO_2(L)(L^2)$	5.3	9.6	1.6
$MoO_2(L)(L^3)$	7.4	8.4	1.3

Biological activity.

It is evident from the antimicrobial screening data that the molybdenum chelating ligand complexes are more effective than the parent free ligands. The ligands have many donor atoms (N, O and S) and are analogous to biological environment to some extent. The activity of the complexes increases as their concentration increases. The increased potency of metal complexes may be assigned to their increased lipophilic nature arising due to their chelation.[23] Which enhance the antimicrobial activity on chelate then the probability of the metal ion will be reduced to greater extent and increase the lipophilic and absorbing nature of complexes due to the equatorial overlapping of ligand filled orbital with vacant outer d- orbital of the metal ion. Further it increasing the delocalization of electrons of metal ion with absorbing power over the whole chelating ring then the mode of action of antimicrobials may involve various targets in microorganism e.g. interference with cell wall synthesis, damage to the cyoplasmic membrane as a result of which cell permeability may be attached or they may disorganise the lipoproteins leading to cell death.[24]

The electronic, and NMR spectra with physical and analytical data, suggested octahedral geometry for the complexes which is justified by other physic-chemical as well as IR spectral data. On the basis of above results the complexes have been suggested to have the structure as Figer-1.

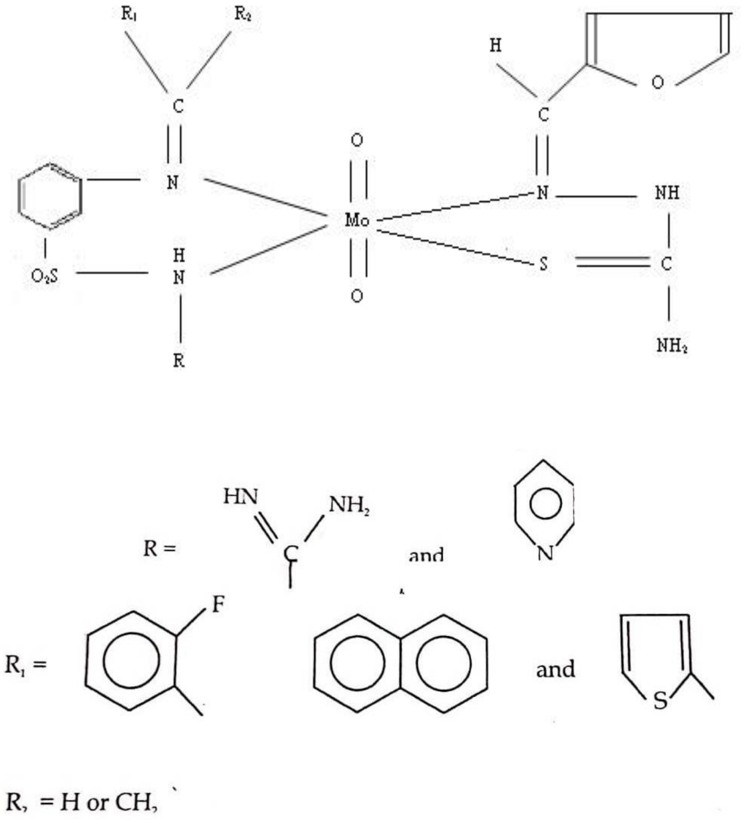

Figure-1Octahedral geometry of the Dioxomolybdenum (VI) complexes

CONCLUSION

Thus on the basis of above studies it is concluded that the ligand acts in a bidentate manner and coordination as proposed through the equatorial mode of three donor nitrogen and one S atoms of the macrocyclic ligand shifts 4-coordinations in planar frame work. The remaining centres of central metal ions coordination are satisfied by symmetrical configuration of two O-atoms of the oxo groups above and below in a layer lattice structure. The monoanionic form of the ligands for the group of macrocycles appears to be one of the important factors for electrostatic interaction of the metal ion with the macrocyclic ligands which improve the extra stability of the complexes. The metal ion in complexes enclosing by macrocyclic cavity in which both are forming 5-membered chelating ring with the thiosemicarbazone moieties and sulfapyridine which enhance their extra stability of the complexes. On the basis of physicochemical and spectroscopic observations it is proposed that the geometry of the complexes are monomeric diamagnetic octahedral in geometry.

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