SYNTHESIS AND CHARACTERISATION OF SOME MOLYBDENUM COMPLEXES WITH BIDENTATE LIGANDS.

Dr RAMAN KUMAR [1]Dr. MANAN SHARMA
Department of chemistry, P.N.College Parsa,Saran.
Jai Prakash University Chapra, Bihar Pin – 841301
[1]Manjhi Inter college Manjhi, Post + PS- Manjhi Dist- Chapra

ABSTRACT

Molybdenum is a versatile transition metal and a number of chemical reaction as well as physiological reactions are catalysed by its complexes. Its most important oxidation state is +6 in which it exists in the form of dipositive dioxo molybdyl cation MoO_2^{2+} 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 thiosemicarbazone and other was prepared by the condensation of different sulfadrugs with various aldehydes and ketones. The synthesized Molybdenum complexes and ligands have been characterized by various spectral as IR, NMR, UV, X-Ray Spectral and elemental analysis. Higher biological activity due to their ability to chelate trace with metals and enables their application as antitumor, antifungal, antibacterial, and antitubercular drugs. The complexes are monomeric and diamagnetic octahedral structure. Within the second series of transition metals only molybdenum increasing biological application, namely antibacterial, antifungal, antitubercular, anti-tumour, activities etc, of the complexes of transition metals. The increased potency of metal complexes may be assigned to their increased lipophilic nature due to their chelation. These Mo sites supposed to be active centres for the catalytic activity of the enzymes. Mo is one of the most biologically active elements is an essential micronutrients for microorganisms, plants and animals. 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 processes

Introduction

Molybdenum is a versatile transition metal with a large number of stable and accessible oxidation states. Its most important oxidation state is +6 which it exists in the form of

dipositive Dioxomolybdyl cation MoO_2^{2+}.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, antitubercular, anti-tumour, 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 antitumrous, antifungal, antibacterial, and antitubercular 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) has opened up a new vesta of research and analysis of un charged 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[13-16].Sulfadrugs have long been used against various diseases[17-20].With these advantages, we have extended our study to two new dioxo complexes of molybdenum(VI)with O-phenylenediamine(OPDA) and4-Methyl-O-phenylenediamine (4-Me-OPDA) ligands.

Materials and Methods

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

Ligands Synthesis

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).

$$C_4H_3SCHO + CH_5N_3S \rightarrow C_6H_7N_3S_2 + H_2O$$

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 and the solution was refluxed or stirred for 7 to 8 hours. On cooling the crystals formed were crystallized in the same solvent and dried in vacuum.

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 solid is separated out. After the completion of the reaction, the excess solvent was distilled off and the product was dried in vacuum and m.p75^{0}C.

$MoO_2(C_5H_7O_2)_2 + LH + L^1H - MoO_2(L)(L^1) + 2C_5H_8O_2$

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 solid is separated out. After the completion the excess solvent was distilled off and the product was dried in vacuum and m.p.120^{o}C.

$MoO_2(C_5H_7O_2)_2 + LH + L^2H \rightarrow MoO_2(L)(L^2) + 2C_5H_8O_2$

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

A methanolic solution (50 ml) of thiobis (2,4-pentanedionato) molybdenum (VI) and the ligands thiophenethiosemicarbazone($LH=C_6H_7N_3S_2$)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 solid is separated out. After the completion of the reaction, the excess solvent was distilled off and the product dried in vacuum and m.p117^o C.

$MoO_2(C_5H_7O_2)_2 + LH + L^3H \rightarrow Mo0_2(L)(L^3) + 2C_5H_8O_2$

RESULTS AND DISCUTION

The reaction of Dioxobis(2,4-pentanedionate)molybdenum(VI) with unsymmetrical ligands thiophenethiosemicarbazone (LH) on one hand and 2-acetylnaphthalenesulfapyridine(L^1H) 2-acetylthiophenesulfapyridine(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 brown coloured solids (Table-1) are soluble in methanol, DMF and DMSO. The complexes are monomeric and diamagnetic as expected for their 4d configuration.

Table -1

Analytical and physical data of molybdenum 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 (Table-2) of the sulfadrugs ligands show medium intensity bands at 3300-3100 cm^{-1} (NH). In thiophenethiosemicarbazone 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 coordinaton 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 thiol sulphour respectively. Sharp band due to azomethine moiety shifts slightly towards lower frequently(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[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 vacant 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.

Complexs	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

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.

UV Spectra

The ligand bands at 230 and 270 nm are due to π-π* transitions within the benzene ring and that around 320nm 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.

^{13}C NMR Spectra

The considerable shift in the position of carbon atoms adjacent to azomethine nitrogen (155.20-161.62ppm) and thiolic sulphour (164.15-177.86ppm) 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 $MoO_2(L)(L^1)$ complexes

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

Biological activity.

On the basis of evident from antimicrobial screening data that the of Dioxomolybdenum(VI) chelating ligand complexes are highly effective with respect to 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 depends upon the concentration of the complexes. Higher the concentration of complexes higher is the antimicrobial activity. The increased potency of metal complexes may be assigned to their increased surface area with lipophilic nature arising due to their chelation.[23] Which enhance the antimicrobial activity on chelate then the

probability of the metal ion nature 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 equatorial mode of 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]

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 axial mode of layer lattice structure. The unianionic 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 with overlapping of atomic orbitals which improve the extra stability and concentration 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 as a single entity, while symmetrical axial oxo group 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.

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.

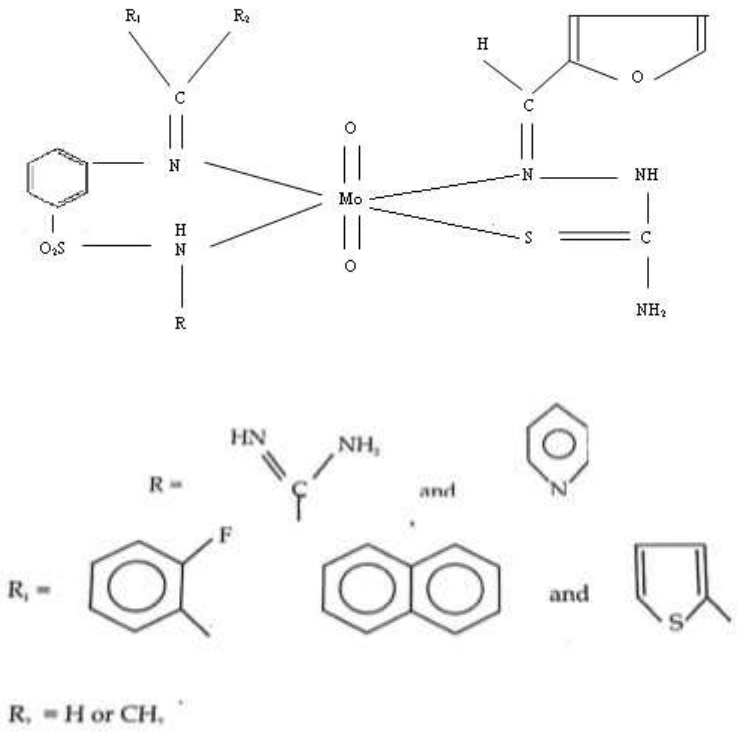

Figure-1

REFERENCES

1. Pedro oliver dunstan. Thermochemistry of adducts of some transition metals (II) bromides with pyridine N-oxide. *Thermochimica acta.* 2004**,** *409* (1) 19-24.
2. Raman kumar,Synthesis and Spectral studies of macrocyclic Ni (II) complexes with multidentate ligands. Research Journal of Chemistry and Environment Vol. 23 (9) September 2019.68-70
3. Yong-Hui Tian, Aaron W. Pierpont, and Enrique R. Batista. How Does Nishibayashi's Molybdenum Complex Catalyze Dinitrogen Reduction to Ammonia, *Inorganic Chemistry* **2014,***53,*(8),4177-4183.
4. D.J.A. Raj, K.S. Nagaraja and M.R. Udupa, The synergistic effect of metallic molybdenum dioxide nanoparticle decorated graphene as an active electrocatalyst for an enhanced hydrogen evolution reaction. Indian. J. Chem. 1985, 24. 869.
5. Russ Hille, James Hall, And Partha Basu, the mononuclear molybdenum enzymes**,** chem rev. 2014 apr 9,114(7), 3963-4038.
6. SALI THOMAS† and M.L. HARIKUMARAN NAIR. Synthesis and Spectral Studies of Some Oxomolybdenum(V) and Dioxomolybdenum(VI) Complexes of the Azo Dye Derived from 4-Amino2,3-dimethyl-1-phenyl Pyrazol-5-one. Asian Journal of Chemistry. 2007, Vol. 19, No. 5, 3461-3467.
7. A.K. Elsawaf, D.X. West, F.A.Elsaied and R.M. Elbahnasaway, synthesis and characterization of the complexes of Mn(II), Fe(II), Co(II), Ni(H), Cu(II), Zn(II) AND Cd(II) With N-Benzoyl-N -2-Thiophenethiocarbohydrazide.Transition Met. Chem. 1997, 22, 360.
8. D.S.West, M.A.Lockwood, M.D.Owens and A.E. Liberta, Structural and physical correlations in the biological properties of transition metal heterocyclic thiosemicarbazone and *S*-alkyldithiocarbazate complexes. Transition Met. Cham. 1997, 22, 366.
9. A.K. Elsawaf, D.X. West, F.A.Elsaied and R.M. Elbahnasaway, Transition Met. Chem. 1997, 22, 360.
10. H. Beraldo, I.P. Boyd and D.X. West, Cobalt(II) and nickel(II) complexes of *N*(4′) substituted 3- and 4-acetylpyridine thiosemicarbazones**.** *Transition Metal Chemistry*, 2002, vol. 27, 85–88.
11. A.Murugkar, B.Unnikrishnan, S.B.Padhye,R.Bhonde,S.Teat, E.Triantafallau and E. Sinn, Metal Based Drugs, 1999, 6, 177.
12. A. Murukgar, S.B. Padhye, S. Guha Roy and U. Wagh, Annual Reports Section "A" (Inorganic Chemistry) Inorg. Chem. Commun, 1999, 2, 545.
13. C.G.Tang and A.G.Wadd in Encyclopedia of Inorganic Chemistry, ed.R.B.King, Wiley, Diphenylthallium (III) thiosemicarbazonates: flexibility of coordination in the solid state and polymorphism in chloroform solution. - Inorganica chimica, 2003, 16, 256- 262.
14. J.H.Enemark and C.G.Young, Bioinorganic Chemistry of Pterin-Containing Molybdenum and Tungsten Enzymes. Advances in Inorganic Chemistry, 1993, Vol.40, 1- 8.
15. R.V.Singh Rakhi Dwivedi and Sanjay Sharma, Molybdenum, molybdenum oxides and their electrochemistry, J. Indian Chem. Soc, 2004, 81,454.
16. D.Kiriya, M.Tosum, P.Zhao, J.S.Kang, and A. Javey, Air-Stable Surface Charge Transfer Doping of MoS_2 by Benzyl Viologen. *J. Am. Chem. Soc.* 2014, 136, 22, 7853–7856.

17. J.W. Jiang, and H.S. Park, Mechanical properties of MoS_2/graphene heterostructures Applied. Physics. 2014, Lett. 105, 033108.

18. A.Murugkar, B.Unnikrishnan, S.B.Padhye,R.Bhonde,S.Teat, E.Triantafallau and E. Sinn, Recent advances in delivery of photosensitive metal-based drugs.Metal Based Drugs, 1999, 6, 177.

19. .J.Kang, W.Liu, and K.Banerjee,High-performance MoS_2 transistors with low-resistance molybdenum contacts, Appl. Phys.2014, Lett. **104**,093106.

20. B. K. BURGESS, D. J. LOWE. Mechanism of Molybdenum Nitrogenase. *ChemInform* **1997,** *28,* 10.

21. H. Sloan. Chromium, molybdenum and tungsten. *Annual Reports Section "A" (Inorganic Chemistry)* **1997,***93*,165.

22. Jing Zhang, Xiaoyin Tian, Mingjie Liu, Hua Guo, Jiadong Zhou, Qiyi Fang, Zheng Liu, Qin Wu, Jun Lou. Cobalt-Modulated Molybdenum–Dinitrogen Interaction in MoS2 for Catalyzing Ammonia Synthesis. *Journal of the American Chemical Society* **2019,** *141* (49),19269-19275.

23. Singh Devendra Kumar and Kumar Raman Synthesis and spectral Studies of Cobalt (II) and Nickel (II) complexes with 18-membered macrocyclic ligand derived from malonodihydrazide. Oriental Journal of Chemistry. 2011,Vol. 27, No. (1). 277-281.

24. Fahmi n, singh rv, synthesis, structural characterization and biological screening of manganese (II) complexes of s o and n donor agents, Indian. J. Chem, Sect. A. Inorganic, physical, theoretical & analytical, 1997, 36 (9), 805-808.