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SYNTHESIS, CHARACTERISATION AND BIOLOGICAL ACTIVITY OF DIOXOMOLYBDENUM(VI) COMPLEXES WITH UNSYMMETRICAL BIDENTATE SCHIFF BASES

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ABSTRACT

Imines derived from sulpha drugs and amino phenyl thiazole with different aldehydes and ketones and their molybdenum(VI) complexes have been synthesized and characterized by their elemental analyses, magnetic moments, IR, electronic spectra molar conductance, ^{1}H NMR, ^{13}C NMR spectra and thermal analysis. Spectral studies reveal that sulpha drug Schiff bases and benzothiazolines react with dioxobis (2,4–pentanedionato) molybdenum (VI) as chelating agents coordinating through N⌒NH and N⌒SH functional groups, having N⌒N and N⌒S donor systems, respectively in 1:1:1 ratio resulting in the isolation of complexes having general formula $MoO_2(L^1)$ (L^{2-9}). Studies also indicate octahedral geometry for diamagnetic molybdenum (VI) mononuclear complexes. All the ligands along with their complexes have been tested in *vitro* against a number of pathogenic fungi and bacteria to assess their growth inhibiting potential.

Key words : Dioxomolybdenum (VI) Complex, Schiff base, Biological Activity

INTRODUCTION

Molybdenum is an important transition element, which has a major role as trace element[1] and is an indispensable constituent of enzymes that are involved in the function of nitrogen fixing nitrogenase[2]. Complexes containing the molybdenum –oxogroup, dominate the higher oxidation states of molybdenum. Most simple Mo (VI) coordination complexes contain the cis–$MoO_2$2+ cation[3], and participate in many oxygen atom transfer reactions[4]. Schiff bases are an important class of ligands in coordination chemistry and have many applications[5] in various fields. The chemistry of Schiff base complexes continues to attract many researchers[6,7] because of their wide applications in food industry, dye industry analytical chemistry, catalysis, antimicrobial activity, agrochemical activity[8] and pharmacological applications[9]. Sulpha drugs have long been used as life saving drugs against various diseases[11–13]. The Schiff bases have been found to be active against different types of bacteria and viruses. It has now been observed that some of these show increased activity when administered in the form of metal complexes. Literature survey reveals that there is enormous growth of the study of the metal complexes of

Schiff bases. However, there is no systematic study of the unsymmetrical coordination complexes of transition metals with Schiff bases and particularly of molybdenum (VI) from sulpha drugs and aminobenzothiazole with different carbonyl compounds. The present paper therefore deals with the study of unsymmetrical dioxomolybdenum(VI) complexes of these bidentate Schiff bases of biological importance.

EXPERIMENTAL

All the chemicals used were of AR grade. Adequate precautions were taken to exclude moisture from the system. The chemicals and solvents used were dried and purified by standard methods before use. Dioxobis(2,4–pentanedionato) molybdenum (VI) was prepared according to the literature method[14].

Preparation of ligands

2–Acetylnaphthalenebenzothiazoline (L^1H) was prepared by the condensation of 2–acetylnaphthalene with 2–mercaptoaniline and sulpha drug. Schiff bases were prepared by condensation of various sulpha drugs with different aldehydes and ketones. The ligands used were L^2H (2–Acetylnaphthalenesulphapyridine), L^3H (2–Acetylthiophenesulphapyridine), L^4H (Thiophene–2–carbaldehydesulphapyridine), L^5H (2–Fluorobenzaldehydesulphapyridine), L^6H (2–Acetylthiophene sulphaguanidine) L^7H (2–Acetylnaphthanlenesulphaguanidine). L^8H (3,4,5, Trimethoxybenzaldehydesulphadiazine) and L^9H (Furfuraldehydesulphamethazine). Reactants were taken in 1:1 molar ratio in ethanolic medium and were refluxed or stirred for 7–8 hrs. On cooling, the crystals were formed, which were filtered, recrystallized in the same solvent and finally dried *in vacuo*.

Preparation of the complexes

The bimolar reactions of dioxobis(2,4–pentanedionoto)molybdenum (VI) with unsymmetrical monofunctional bidentate ligands 2–acetylnaphthalenebenzothiazoline L^1H) and various sulpha drug Schiff bases ($L^{2-9}H$) in 1:1:1 molar ratio were carried out in 50 mL dry methanol. The reaction mixture was refluxed for 12–14h on a fractionating column. After the completion of the reaction the excess of the solvent was distilled off and the product was dried in *vacuo*. The complexes were washed with cyclohexane and recrystallized from methanol to obtain the pure product.

Analytical methods and physical measurements

Analyses for carbon, hydrogen and nitrogen in the complexes were carried out at CDRI Lucknow. The molybdenum content in the synthesized complexes was determined gravimetrically as bis(8–hydroxyquinolato)dioxomolybdenum (VI) [$(MoO_2(C_9H_6OH)_2]$ by the standard method.[15] Conductance measurements were performed at room temperature in dry DMF using a Systronics conductivity bridge Type 305 and molecular weights were determined by the Rast

Camphor Method. Electronic spectra of the complexes were recorded in chloroform on a UV–160A Shimadzu spectrophotometer in the range 200–600 nm. ^{1}H NMR spectra were recorded on a JEOL FX–90Q spectrometer in DMSO–d_6 using TMS as the internal standard. ^{13}C NMR spectra were recorded in MeOH at 22.49 MHz at CDRI Lucknow. IR spectra were recorded on a Perkin Elmer 577 grating spectrophotometer. The analytical data of the synthesized complexes are given in Table 1.

Table 1. Physical properties and analytical data of molybdenum (VI) complexes

Complex	Colour	M.p. (°C)	Mol.Wt. Found (Calcd.)	Elemental Analysis Found (Calcd.) %		
				Mo	N	S
$MoO_2(L^1)(L^2)$	Black	103	826 (804.26)	11.75 (11.87)	6.80 (6.96)	7.58 (7.97)
$MoO_2(L^1)(L^3)$	Black	75	785 (760.22)	12.10. (12.56)	7.21 (7.36)	12.56 (12.64)
$MoO_2(L^1)(L^4)$	Black	115	779 (746.19)	12.24 (12.79)	7.28 (7.50)	12.64 (12.88)
$MoO_2(L^1)(L^5)$	Black	83	782 (758.15)	12.48 (12.60)	7.21 (7.38)	8.42 (8.45)
$MoO_2(L^1)(L^6)$	Black	110	756 (725.17)	12.84 (13.17)	9.24 (9.65)	13.01 (13.25)
$MoO_2(L^1)(L^7)$	Black	70	788 (769.21)	12.12 (12.41)	8.76 (9.10)	8.06 (8.33)
$MoO_2(L^1)(L^8)$	Black	130	857 (81.21)	11.12 (11.50)	8.14 (8.41)	7.24 (7.70)
$MoO_2(L^1)(L^9)$	Black	103	774 (759.16)	12.48 (12.60)	8.86 (9.23)	8.10 (8.44)

Antimicrobial Screening

Bioeffeciency of the parent ligands and their complexes was tested in *vitro* for the growth inhibiting potential against various fungal and bacterial strains using radial growth method and paper disc technique, respectively. Fungal strains *Alternaria alternata, Helminthosporeum gramineum* and Bacterial strains *Staphylococcus aureus* (+) and *Xanthomonas compestris*(–) were used. The biocidal activity have been compared with the conventional fungicide, *Bavistin* and the conventional bactericide, *Streptomycin*, taken as standard in either case. Data are given in Tables 2 and 3.

Table 2. Antifungal screening data of ligands and their metal complexes

Compound	Antifungal (% inhibition after 96 h)					
	Alternaria alternata conc. (ppm)			*Helminthosporeum gramineum* conc. (ppm)		
	50	100	200	50	100	200
L^1H	42	49	57	41	46	49
L^2H	48	52	62	45	56	63
$MoO_2(L^1)(L^2)$	69	77	84	66	72	80
L^3H	46	50	58	52	57	64
$MoO_2(L^1)(L^3)$	72	81	89	77	82	88
L^4H	32	45	51	48	53	67
$MoO_2(L^1)(L^4)$	68	74	82	67	71	84
L^5H	36	46	52	46	54	68
$MoO_2(L^1)(L^5)$	70	74	76	82	85	87
L^6H	45	47	51	40	42	48
$MoO_2(L^1)(L^6)$	69	72	76	70	74	77
L^7H	50	57	61	53	57	66
$MoO_2(L^1)(L^7)$	78	81	85	80	82	89
L^8H	51	58	64	60	68	72
$MoO_2(L^1)(L^8)$	77	79	83	76	82	87
L^9H	34	38	45	40	49	54
$MoO_2(L^1)(L^9)$	62	76	84	70	75	83
Standard	90	100	100	89	100	100

RESULTS AND DISCUSSION

The reactions of dioxobis(2,4–pentanedionato)molybdenum (VI) with monofunctional bidentate unsymmetrical ligands in 1:1:1 molar ratio have been carried out with the liberation of two molecules of 2,4–pentanedione. These are soluble in MeOH, DMF and DMSO. The complexes were found to be diamagnetic as expected for $4d^0$ configuration. The general equation may be represented as follows :

$$MoO_2(C_5H_7O_2)_2 + L^1H + L^{2\text{-}9}H \xrightarrow[1:1:1]{MeOH} [MoO_2(L^1)(L^{2\text{-}9})] + 2\,C_5H_8O_2$$

UV spectra of the ligands and their complexes show bands at ~274 and 300 nm assignable to π–π* electronic transitions within the benzene ring. An other band observed at *ca.* 370 nm in the spectra of the said ligands is due to n–π* transitions of the azomethine (>C=N) group. However, in the spectra of complexes, this band shifts to lower wavelength due to the coordination of azomethine nitrogen to the metal atom, indicating the delocalisation of the electronic charge within the chelate ring and thereby stabilizing the resulting complexes. The complexes also exhibit a strong band at 390–400 nm due to L→M charge transfer transitions between the lowest empty molybdenum 'd' orbital and the highest occupied ligand molecular orbital, as reported earlier[16].

Table 3. Antibacterial screening data of ligands and their metal complexes

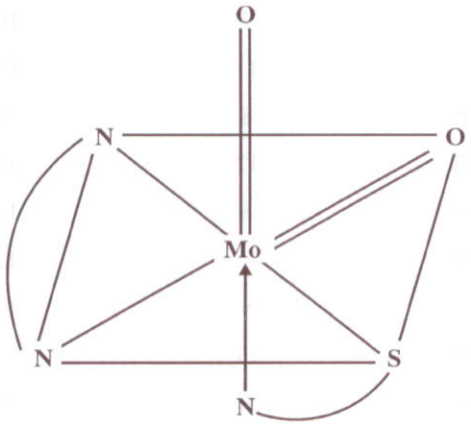
Compound	Antibacterial – Diameter of Inhibition Zone (mm)			
	Staphylococcus aureus (+) conc. (ppm)		*Xanthomonas compestris* (–) conc. (ppm)	
	500	1000	500	1000
L^1H	5	7	8	10
L^2H	4	6	7	11
$MoO_2(L^1)(L^2)$	8	11	10	14
L^3H	5	9	7	10
$MoO_2(L^1)(L^3)$	7	10	8	14
L^4H	4	7	6	9
$MoO_2(L^1)(L^4)$	7	10	9	12
L^5H	5	7	10	12
$MoO_2(L^1)(L^5)$	9	11	12	15
L^6H	6	8	7	11
$MoO_2(L^1)(L^6)$	9	12	11	14
L^7H	6	8	11	13
$MoO_2(L^1)(L^7)$	9	12	12	14
L^8H	7	9	12	15
$MoO_2(L^1)(L^8)$	9	11	13	17
L^9H	4	6	7	11
$MoO_2(L^1)(L^9)$	8	11	11	14
Standard	15	17	17	18

The IR spectra of sulpha drug ligands show medium intensity bands at 3300–3100 cm^{-1} due to ν_{NH} vibrations. IR spectra of benzothiazoline ligand shows band at 2600–2500 cm^{-1} due to ν_{SH} vibrations. The sulpha drug ligands show a sharp band at ~1620 cm^{-1} due to $\nu_{C=N}$ vibrations. However, after complexation, band due to $\nu_{C=N}$ shifts slightly towards lower frequency (10–20 cm^{-1}) indicating the coordination of azomethine nitrogen to the metal atom. The bands due to ν_{NH} and ν_{SH} disappear indicating deprotonation followed by coordination through nitrogen and thiolic sulphur, respectively and some new bands in the complexes appear at ~430, ~380 and ~360 cm^{-1} attributed to ν(Mo–S) and ν(Mo–N) vibrations, respectively. The bands in the spectra of the complexes in the regions, 920–910 and 900–890 cm^{-1} may be assigned to $\nu_{sym.}$ (O=Mo=O) and $\nu_{asym.}$ (O=Mo=O) indicating a cis–MoO_2 structure.

The bonding pattern discussed above gets further support by the proton magnetic resonance spectral studies of the ligands and their complexes in deuterated DMSO–d_6. The ^1H NMR spectra of free ligands show signals due to –NH group (δ10.60–10.96 ppm) and –SH group (δ7.88–7.97 ppm). In case of corresponding complex the signals due to –NH and –SH protons of the ligand unit disappear indicating deprotonation and simultaneous covalent bond formation through nitrogen and sulphur.

^{13}C NMR spectral data show considerable shits in the position of carbon atoms adjacent to azomethine nitrogen (δ155.20–161.62 ppm) and further support to the proposed coordination in the complexes.

Thermogravimetric analysis of $MoO_2(L^1)(L^8)$ has also been carried out to evaluate its thermal stability. The TGA curve for the complex shows first mass loss around 183.6^{0}C. The subsequent step show mass loss upto 500.5^{0}C. Almost 55% mass loss occur in the procedure. At this temperature MoO_3 is presumed to be the end product (calculated mass loss 55.25% found 55%). DTA curve for particular complex shows one endothermic peak at 178.5^{0}C, which



(where NN and NS represent the donor systems of different ligands)

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is due to melting transition, second endothermic peak at 295.5^{0}C and an exothermic peak at 351.6^{0}C due to decomposition are observed. An exothermic peak at T_{max}=515^{0}C corresponds to crystalline phase. On the basis of these studies, the structure (I) has been proposed for the resulting complexes.

It is evident from the antimicrobiol screening data (Tables 2 and 3) that the metal chelates are more potent than the parent ligands. The increased potency of metal complexes may be assigned to their increased lipophilic nature arising due to chelation[17]. Mode of action of antimicrobial activity may involve various targets in microorganisms e.g., interference with the cell wall synthesis and damage to cytoplasmic membrane leading to cell death.

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