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Biologically potent dioxomolybdenum(VI) complexes with nitrogen-sulfur and nitrogen-oxygen donar ligands : Synthesis, characterisation and antimicrobial activity

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ABSTRACT

Molybdenum(VI) complexes of 3,4,5-trimethoxybenzaldehydethio semicarbazone (TBTSCZH), 3,4,5-trimethoxybenzaldehydesemicarbazone (TBSCZH), 3,4,5-trimethoxy-benzaldehydebenzothiazoline (TBBZTH) and 3,4,5-trimethoxybenzaldehyde- S-benzyldithiocarbazate (TBDTCZH) have been synthesized and characterized by physico-chemical and spectroscopic studies. The complexes $MoO_2(L)_2$ (where L represented the deprotonated form of the ligands), were formed by the reactions between dioxobis(2,4-pentanedionato-O,O')molybdenum(VI) and the ligands TBTSCZH, TBSCZH, TBBZTH and TBDTCZH by using both techniques (thermal and microwave). The structural features of these molybdenum complexes were explored by IR, ^{1}H NMR, ^{13}C NMR and molecular weight determinations. An octahedral arrangement of ligands around the central molybdenum atom is proposed. All the four ligands and their complexes have been screened for their biological activity on several pathogenic fungi and bacteria and the data show good activity of these complexes and ligands.

KEYWORDS

Dioxomolybdenum(VI) complexes;
Spectral studies;
Schiff base;
Antimicrobial studies.

INTRODUCTION

Molybdenum is an important transition element, which has a major role as trace elements and is an indispensable constituent of enzymes that are involved in the function of nitrogen fixing nitrogenase[1]. A large number of stable and accessible oxidation states and coordination number render molybdenum to be a versatile transition element. Molybdenum is the only element in the second and third transition series which plays major role as trace element in enzymes. The presence of cis-dioxymolybdenum cation $[MoO_2]^{+2}$ in the oxidized form of certain molybdoenzymes has recently generated tremendous interest[2]. The cis-$[MoO_2]^{+2}$ centre dominates the chemistry of d^o molybdenum(VI) complexes[3] and participates in many oxygen atom transfer reactions[4-6].

Schiff bases are an important class of ligands in coordination chemistry and have many applications[7] in various fields. The chemistry of Schiff base complexes continues to attract many researchers[8,9] because of their wide applications in food industry, dye industry, analytical chemistry, catalysis, antimicrobial activity, agro chemical activity[10] and pharmacological applications[11].

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 azomethine metal complexes[12]. In view of the importance of the dioxomolybdenum(VI) complexes, we have synthesized and characterized some new complexes of the said potential bidentate ligands.

EXPERIMENTAL

All the chemicals and solvents used were dried and purified by the standard methods. Dioxobis(2,4-pentanedionato)molybdenum(VI) was prepared according to the literature method[13].

Preparation of the Ligands

The different routes were employed for the synthesis of the ligands.

These are-

1. Microwave assisted synthesis

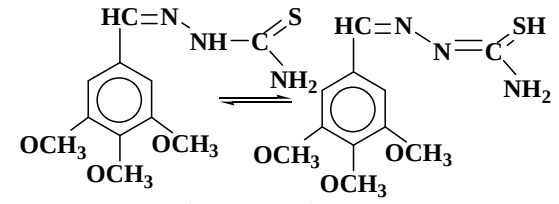
For microwave assisted synthesis of the ligands TBTSCZH, TBSCZH, TBBZTH and TBDTCZH the thiosemicarbazide, semicarbazidehydrochloride, 2-aminothiophenol and S-benzyldihiocarbazate were reacted with 3,4,5-trimethoxybenzaldehyde in ethanolic media, using a conventional microwave oven, where the consumption of ethanol as solvent is very little (2-3 ml). The reactions were completed in a short period (4-8 minutes). The completion of the reaction is checked by TLC.

2. Conventional heating synthesis

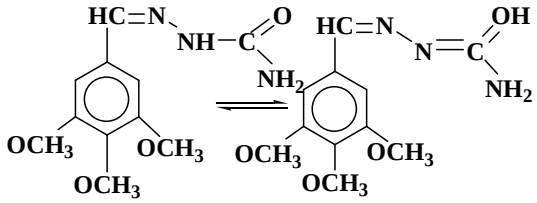
For the comparison purpose, above ligands were also synthesized by the thermal method. For this the weighed amounts of 3,4,5-trimethoxybenzaldehyde and thiosemicarbazide, semicarbazide hydrochloride and 2-aminothiophenol and S-benzyldihiocarbazate were mixed together in 100 ml ethanol in 250 ml beaker. The contents were refluxed for 4-16 hrs. on an oil bath. The solid products were precipitated. These were dried in vacuum and recrystallized from the same solvent. A comparison between thermal method and microwave method has been given in TABLE 1. The ligands used are :

Preparation of the complexes

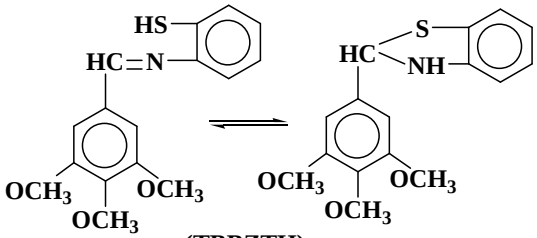
1. Microwave Assisted Method : In microwave assisted synthesis the reactions of dioxobis(2,4-pentanedionato-O,O')molybdenum(VI) with the ligands (TBTSCZH, TBSCZH, TBBZTH and TBDTCZH) were carried out in 1:2 molar ratios, using 2-3 ml of dry methanol as a solvent using microwave oven. The products were recovered from the microwave oven and dried under reduced pressure. The resulting products were repeatedly washed with dry cyclohexane and then finally dried at 40-60° / 0.5 mm for 3-4 hours.
2. Conventional Heating Method : These molybdenum (VI) complexes were also synthesized by the thermal method. In the thermal method instead of 4-7 minutes reactions were completed in 14-16 hours and yield of products were also lesser than obtained by the microwave assisted synthesis (TABLE 1).



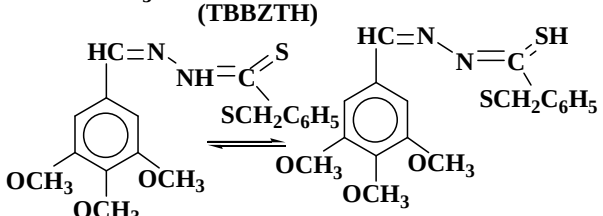
(TBTSCZH)



(TBSCZH)



(TBBZTH)



(TBDTCZH)

RESUTLS AND DISCUSSION

The reactions of the dioxobis (2,4-pentanedionato-O,O') molybdenum(VI) with the said monofunctional

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TABLE 1 : Comparison between microwave and thermal method

Compound	Yield (%)		Solvent (ml)		Time	
	Thermal Method	Microwave Method	Thermal Method	Microwave Method	Thermal Method Hr.	Microwave Method Minute
TBTSCZH	86	92	90	4	3.5	4
TBSCZH	80	90	100	3	4.0	5
TBBZTH	82	90	90	3	3.5	5
TBDTCZH	75	89	95	4	3.5	7
$MoO_2(TBTSCZ)_2$	73	88	40	2	13	4
$MoO_2(TBSCZ)_2$	72	80	40	3	14	6
$MoO_2(TBBZT)_2$	74	85	30	3	16	5
$MoO_2(TBDTCZ)_2$	74	86	30	3	15	6

TABLE 2 : Physical properties of ligands and their dioxomoly bdenum complexes

Compound	Colour	M.P. (°C)	Mol. Wt. found (Calcd.)	Elemental analysis found (Calcd.) %		
				N	S	Mo
TBTSCZH	White	100	238 (269.31)	15.04 (15.60)	11.21 (11.91)	-
TBSCZH	Off white	210	234 (253.25)	16.34 (16.59)	-	-
TBBZTH	Mustard yellow	108	288 (303.37)	14.20 (14.61)	10.22 (10.56)	-
TBDTCZH	Turmeric yellow	122	356 (376.48)	7.18 (7.44)	17.25 (17.02)	-
$MoO_2(TBTSCZ)_2$	Army Green	120	630 (664.55)	12.32 (12.64)	9.75 (9.64)	14.20 (14.43)
$MoO_2(TBSCZ)_2$	Dark Green	135	608 (632.43)	13.12 (13.28)	-	15.02 (15.17)
$MoO_2(TBBZT)_2$	Dark Green	160	750 (733.66)	3.95 (3.81)	8.55 (8.73)	12.95 (13.07)
$MoO_2(TBDTCZ)_2$	Green	140	850 (878.88)	6.45 (6.37)	14.39 (14.59)	10.76 (10.91)

bidentate ligands were carried out in a 1:2 molar ratio in dry methanol. The reaction proceeds with the liberation of two molecules of 2,4-pentanedione. The resulting coloured solids are soluble in methanol, chloroform, DMF, DMSO and THF. They are monomeric and dimagnetic which expected for their 4 d^o configurations. The physical and analytical data of these complexes are listed in TABLE 2.

The general equation may be represented as follows :

$$MoO_2(C_5H_7O_2)_2 + LH \xrightarrow{1:2} [MoO_2(L)_2] + 2C_5H_8O_2$$

U.V. spectra

The electronic spectra of the ligands TBTSCZH, TBSCZH and TBDTCZH exhibit three intense maxima at *ca.* 245, 340 and 420 nm, respectively. The band at *ca.* 245 nm assignable to π-π^* (benzenoid) electronic transitions. The band at *ca.* 340 and 420 nm in the spectra of the ligands are due to π-π^* and n-π^* transitions, respectively, within the >C=N- chromophores. The hypsochromic shifting of the third band in the spectra of the complexes may be attributed to the coordination of the azomethine nitrogen to the molybdenum atom. The electronic spectrum of the ligand TBBZTH consists of two bands around 250 and 320 nm, characteristics of benzothiazolines. These may be attributed to the ϕ-ϕ^* and π-π^* (benzenoid) transitions, respectively. A new band around 400 nm due to n-π^* electronic transitions of the azomethine group is observed in the spectra of the complexes, which remains absent in the free ligand and thus proves the benzothiazoline nature of the TBBZTH ligand.

I.R. spectra

The infrared spectra of the ligands TBTSCZH, TBSCZH and TBDTZH exhibit medium intensity bands in the region 3250-3100 cm^{-1} due to the νNH vibrations. These bands disappear in the spectra of the complexes, indicating deprotonation of this group on complexation. The spectra of the ligands do not show bands in the region 2565 cm^{-1} due to νSH, indicating ketonic form in the solid state. However, the solution spectra show bands due to νSH as well as νNH[14], indicating the presence of an enolic tautomeric form. The characteristics azomethine (>C=N) stretching vibration appears in the region, 1620-1590 cm^{-1} and thus gets shifted towards the higher frequency in the spectra of the molybdenum complexes suggesting the coordination of the azomethine nitrogen to the molybdenum atom. Strong bands in the ligands at 1050 cm^{-1} are assigned to ν(C=S)[15]. In the metal complexes these bands disappear, indicating the coordination of the ligands through the thiolosulfur. Simiarly, a strong band in the ligands around 1650 cm^{-1} due to ν(C=O) also disappears in the spectra of the metal complexes, which indicate the formation of C-O-M type of bonding. The bands ob-

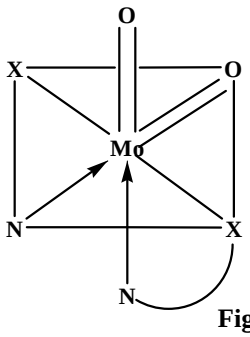
served in the region 3430-3350 cm^{-1} in the ligands attributed to asymmetric and symmetric modes of the NH_2 group remain at nearly the same position in the complexes, indicating the non-involvement of this group in chelation. In addition to this the spectrum of the ligand TBDTCZH shows doublet at 2900 and 2950 cm^{-1}, which can be attributed to symmetric and asymmetric vibrations of S-CH_2-C_6H_5 grouping[16] and reduced to a weak doublet in the spectra of the complexes.

In the spectrum of the ligand TBBZTH the absence of ν(SH) at 2600-2530 cm^{-1} and ν(C=N) at 1620-1590 cm^{-1} is a strong evidence for the ring structure. On complexation, the band at 3240-3150 cm^{-1} due to NH stretching vibrations of the benzothiazoline, disappears and a band at 1600 cm^{-1} is observed due to ν(C=N) vibrations. The chelation of this benzothiazoline and the said ligands through the azomethine nitrogen and thiolic sulphur further gets support by the appearance of the new bands at ca. 650 cm^{-1}, 435 cm^{-1} and 360 cm^{-1}, in the spectra of the complexes due to ν(Mo-O), ν(Mo←N) and ν(Mo-S), respectively. A doublet in the spectra of the complexes at *ca.* 910cm^{-1}, which may be assigned to ν_{sym} (O=Mo=O) and $\nu_{asy.}$ (O=Mo=O), respectively, indicates the cis MoO_2 structure.

^{1}H NMR spectra

The bonding pattern discussed above gets further support by the proton magnetic resonance spectral studies of the ligands and their complexes. The ^{1}H NMR spectra of the ligands TBTSCZH, TBSCZH and TBDTH show signals due to –NH group (δ 10.65-10.98 ppm) and –SH group (δ 7.88-7.96 ppm). In case of the 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. All the said free ligands and their molybdenum complexes show multiplets in the region δ 6.25-8.80 ppm attributable to aromatic protons, which appear almost at the same position in the respective ligands. The NH_2 protons give singlet at δ 3.48-4.20 in the ligands TBTSCZH and TBSCZH as well as their corresponding molybdenum (VI) complexes. It shows that the NH_2 group is not taking part in the complexation.

The ^{1}H NMR spectrum of the ligand TBBZTH shows the signal of –NH proton at δ 5.40 ppm which found absent in the spectra of the molybdenum(VI) complexes confirming the deprotonation of –NH group and coordination of molybdenum with nitrogen atom. The H-C=N signal is found in upfield or shielded region in benzothiazoline ligand and its molybdenum(VI) complexes as compared to the thiosemicarbazone, semicarbazone and dithiocarbazate and their molybdenum(VI) complexes.



Where, X = S and O and N∩X is the donor system of the ligands

Figure 1

The spectrum of the ligand TBDTCZH also shows an additional peak at δ 1.78 ppm due to S-CH_2-Ph protons and this peak appears in deshield region in its corresponding metal complex.

^{13}C-NMR spectra

The ^{13}C NMR spectra of one of the ligand and its corresponding metal complexes have been recorded in $CDCl_3$. The chemical shift values of the carbon atom attached to the azomethine nitrogen, thiolic sulfur or amido oxygen, show considerable shift which further support the proposed coordination in the complexes.

On the basis of the above studies the coordination pattern shown in figure 1 is concluded.

Antimicrobial studies

Bioefficiency 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 *M.phaseolina, F.oxysporum* and Bacterial strains *S.aureus* and *K.aerogenous*, were used. The biocidal activity have been compared with the conventional fungicide. *Bavistin* and the conventional bactericide, *Streptomycin*. All the screening data are given in TABLES 3 and 4.

It is apparent that sulfur containing compounds are more toxic than the oxygen containing compounds. It

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TABLE 3 : Antifungal activity of the ligands and their dioxomolybdenum complexes (Average % inhibition after 96 hours)

Compound	*Fusarium oxysporum*			*M phaseolina*		
	50	100	200	50	100	200
TBTSCZH	25	38	53	26	39	46
TBSCZH	20	35	45	18	35	42
TBBZTH	27	40	49	26	40	46
TBDTCZH	29	45	56	29	47	52
$MoO_2(TBTSCZ)_2$	39	50	65	41	47	68
$MoO_2(TBSCZ)_2$	37	45	59	35	46	65
$MoO_2(TBBZT)_2$	41	51	65	45	49	68
$MoO_2(TBDTCZ)_2$	43	64	71	49	52	73
Standard (Bavistin)	86	100	100	82	100	100

TABLE 4 : Antibacterial activity of the ligands and their dioxomoly bdenum complexes diameter of inhibition zone (mm)

Compound	*S aureus*		*K.aerogenous*	
	500	1000	500	1000
TBTSCZH	6	8	2	3
TBSCZH	4	5	1	3
TBBZTH	7	10	2	4
TBDTCZH	8	12	3	5
$MoO_2(TBTSCZ)_2$	8	10	4	6
$MoO_2(TBSCZ)_2$	7	9	2	5
$MoO_2(TBBZT)_2$	9	11	4	7
$MoO_2(TBDTCZ)_2$	9	14	5	8
Standard (Streptomycin)	15	17	3	5

has been suggested that the ligands with the N and S donor system might have inhibited the enzyme production, since the enzymes which require free sulfhydryl group for their activity appear to inactivation by the ions of the complexes. The complexes facilitate their diffusion through the lipid layer of spore membranes to the site of action ultimately killing them by combining with –SH groups of certain cell enzymes. The toxicity of the dioxomolybdenum(VI) complexes can be well understood by considering the chelation theory. Chelation reduces the polarity of the central metal ion mainly because of the partial sharing of its positive charges with the donor groups and possible π-electron delocalisation within the whole chelate ring. This chelation increases the lipophilic nature of the central atom which favours its permeation through the lipid layer of the membrane. Complexes inhibit the growth of the fungi and bacteria to a greater extent as the concentration is increased[17].

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