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SYNTHESIS, SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES ON MOLYBDENUM (IV), (V) and (VI) COMPLEXES WITH SCHIFF BASE LIGAND

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ABSTRACT

A terdentate ligand (Ambtn) was obtained by condensing 2-aminobenzaldehyde with 1,3-diaminopropane which reacts with MoO_2 $(acac)_2$ in methanol medium to form a series of mononuclear oxomolybdenum(VI), dinuclear molybdenum(V) and mononuclear molybdenum(IV) complexes. These oxomolybdenum(VI) and molybdenum(V) complexes are diamagnetic, whereas oxomolybdenum(IV) complex is paramagnetic, all these complexes are non-electrolyte and the complexes contain MoO^{2+}, $Mo_2O_3^{4+}$ and MoO^{2+} species respectively. These complexes are characterized on the basis of elemental analysis, IR, UV-Visible, ESR spectras, conductivity, magnetic measurements and cyclic voltammogram studies.

Keywords: Molybdenumacetylacetone, triphenylphosphine, 1,3-bis(2-aminobenzylideneamino)propane(Amptn), oxomolybdenum.

INTRODUCTION

The coordination chemistry of molybdenum in the oxidation states +4, +5 and +6 has received much attention recently due to the realization that molybdenum in these oxidation states is an essential trace element in a variety of redox enzymes[1]. For example aldehyde sulphite, xanthine oxidase, nitrate reductase and nitrogenase.

The oxidation state of molybdenum in the oxocomplexes are determined by the number of oxo-groups attached to molybdenum. It has been shown that oxomolybdenum(VI) and oxomolybdenum(V) complexes are stable. Whereas oxomolybdenum(IV) complex is unstable. It is stable at vaccum condition. Similar observation have been made by Kumar and Chaudhry[2]. In order to study the physical properties of diamine schiff base complexes of oxomolylbdenum(VI). (V) and (IV). We have prepared these complexes[1-3].

EXPERIMENTAL

All the chemicals were used of reagent grade. Methanol and acetylacetone were purified by standard methods. Molybdenumacetylacetonate and 2-Cyanopridiniumoxotetrachloromolybdate(V) were prepared by literature methods[3,4].

SYNTHESIS OF LIGAND

Into a solution of 2-aminobenzaldehyde[5] (3.8g) in methanol (50ml) and 1,3-diaminopropane(1.3ml) was added slowly with constant stirring at 50°C for about one hour. The reaction mixture was poured into a beaker containing crushed ice. The schiff base ligand was separated out. The product was collected by filtration, washed with methanol and recrystallised from boiling methanol, dried in air, yield ≈80.

Synthesis of Complexes

Preparation of oxomolybdenum(VI)complex: [MoO_2(L)] (1)

Into a stirred suspension of $MoO_2(acac)_2$ (1.3g) in absolute methanol (25ml) and a methanolic solution (15ml) of 1,3-bis(2-aminobenzylideneamino)propane (1.12g) was added slowly with constant stirring and refluxed for about one hour. The product was separated out, filtrated, washed with methanol and dried in air, yield ≈ 90%.

Preparation of oxomolybdenum(V)complex: [Mo_2O_3(L)] (2)
A methanolic solution (25ml) of 2-cyanopyridiniumoxotetrachloromolybdate(V) (1.4g) and 1,3-bis(2-aminobenzylideneamino)propane (2.25g) in distilled methanol (20ml) was added with constant stirring and refluxed for about 30minutes. The reaction mixture was immediately turned deep red colour. The reddish-brown microcrystalline solid was separated out. The product was filtred, washed with absolute methanol and dried in vaccum over potassium hydroxide pellets. Yield~75%.

Preparation of oxomolybdenum(IV) complex: (MoO(L)] (3)
Methanolic solutions of $MoO_2(acac)_2$ (1.3g), 1,3-bis(2-aminobenzylideneamino)propane (1.12g) and triphenylphosphine (0.39g) were added slowly with constant stirring and refluxed for about 30minutes. A greenish-yellow coloured product was separated out. The product was filtered and washed with methanol. Since the complex was hygroscopic, it was dried in vaccum, over potassium hydroxide pellets. Yield~80%.

RESULTS AND DISCUSSION

All these Oxomolybdenum(IV), (V) and (VI) schiff's base complexes have poor solubility in common organic solvents except dimethylsulphoxide. The analytical date for the various oxomolybdenum schiff's base complexes are given in Table –1.

Table – 1: Elemental and IR data for oxomolybdenum(VI), (V) and (IV) complexes

Complex No.	Ligand /complex	Composition(%)			ν(Mo=O) cm^{-1}	ν(C=N) cm^{-1}	ν(N-H) cm^{-1}
		C	H	N			
	Ambtn	--	--	--	--	1633	3431
1	[MoO_2(L)]	49.98 (50.25)	4.10 (4.43)	14.01 (13.79)	920, 929	1680	3400
2	[Mo_2O_3(L)]	51.20 (51.26)	4.10 (4.52)	13.99 (14.07)	908	1610	3370
3	[MoO(L)]	52.04 (52.30)	4.72 (4.61)	14.39 (14.35)	927	1680	3425

Some of the characteristic IR absorption frequencies of complexes(1-3) and the ligand are also listed in Table-1. In the ligand the ν(N-H) and ν(C=N) stretching frequencies appear at 3431cm^{-1} and 1633cm^{-1} region respectively. In general in the complexes(1-3) the above absorptions are broad and shifted considerably.

The IR spectra of oxomolybdenum(VI) complex shows a strong band in the region at 920 and 929cm^{-1}. These two band patterns are characteristic of a cis-dioxomolybdenum(VI) centre(7-9) (O=M=O). The oxomolybdenum(V) is shows a single band present in the region at 908cm^{-1}.Which indicates only one υ(Mo----O-----Mo) bond[10]. Finally oxomolybdenum(IV) reacts with triphenylphosphine where the MoO_2^{2+} unit transfers one oxygen atom to PPh_3 converting it in to $OPPh_3$[11]. Obviously the complexes are polymeric, but afford only one band in the υ(Mo=O) region at 927cm^{-1} indicates absence of oxobridge group.

The electronic spectra of the oxomolybdenum(VI) and (V) complexes display two low-energy absorption band (Table-2). These bands are assignable to a S(pπ)→Mo(dπ) ligand to metal charge transfer (lmct) transitions[12]. The molybdenum(IV) complex exhibit only one absorption band above 400nm. Thus the maximum at 520nm may represent one of the d-d transitions in the d^2 system. Similar observations have been made by kumar and chaudhury in their works on synthesis, spectroscopy and electrochemical properties of molybdenum complexes with dithioacid ligands[2]. All these molybdenum shciff's base complexes in dimethylsulphoxide solutions are within the range reported[3] 1:1 (metal:ligand) ratio suggesting non-electrolytic behaviour.

The magnetic susceptibility measurement of the oxomolybdenum(VI) and (V) complexes are diamagnetic. However the μeff=0 for oxomolybdenum (IV) complex is within a value μeff=2.16BM. The observed μeff value is slightly lower than the expected value for a d^2(S=1) spin-triplet ground state due to strong spin-orbit coupling (Table 2).

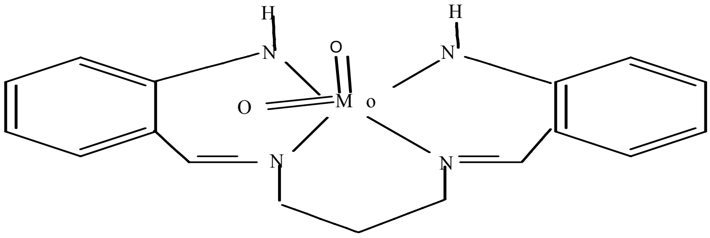
Oxomolybdenum(VI) and (V) Schiff base complexes are ESR inactive[13]. Whereas the oxomolybdenum (IV) complex is ESR active and the g value is 2.274 (Fig-2), this indicates that the unpaired electrons is located in a molybdenum centred orbital. This g value is fairly low which indicates a high-degree of nitrogen coordination in the complex. Cyclic voltammogram of all these oxomolybdenum(VI), (V) and (IV) complexes are irreversible. The molybdenum(VI) complex consumes a two-electron transfer at the metal-centre[14,15] thus the electro-reduced solution [Mo$^{(VI)}$ →Mo$^{(IV)}$] containing molybdenum (IV) and there is no oxidation peak observed. The molybdenum(V) dimeric complex observed only one-electron reduction and also there is no oxidation peak observed.

The oxomolybdnum(IV) complex has also been studied. The electrontransfer behaviour of [MoO(L)] shows an irreversible one-electron oxidation to +0.27V (Vs. SCE) and a two-electron reductive[12] response at -1.00V and -0.33V. This indicates that the two-electron reduction is [Mo$^{(IV)}$→Mo$^{(II)}$] and one-electron oxidation is [Mo$^{(IV)}$→Mo$^{(V)}$]

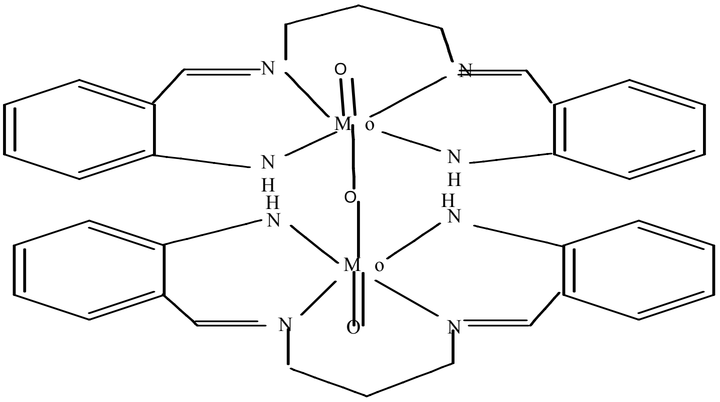
Table– 2:UV, ESR, Magnetic and Cyclic voltametric data for oxomolybdenum(VI), (V) AND (IV) complexes

Complex No.	**complexes**	**Absorption (nm)**	**μeff (BM)**	**g**	**Epc (V)**	**Epa (V)**
1	[MoO_2(L)]	285,385,445,465	--	--	-0.53, -0.87	--
2	[Mo_2O_3(L)]	290,380,440,470	--	--	-1.10	--
3	[MoO(L)]	285,360,520	2.158	2.278	-1.00 -0.33	+0.17

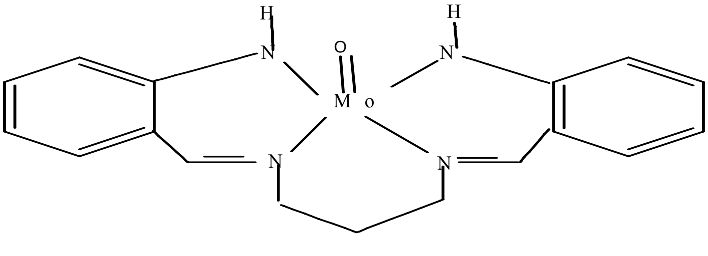
The structure of oxomolybdenum (VI) complex as shown in fig.1



The structure of oxomolybdenum (V) complex as shown in fig.2



The structure of oxomolybdenum (IV) complex as shown in fig.3



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