

Synthesis and Spectral Studies of Some Oxomolybdenum(V) and Dioxomolybdenum(VI) Complexes of the Azo Dye Derived from 4-Amino-2,3-dimethyl-1-phenyl Pyrazol-5-one

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Some novel oxomolybdenum(V) complexes of the type MoOLXCl₂ (L = BPAAP, X = Cl, NCS, ClO₄ or NO₃) and dioxomolybdenum(VI) complexes of the type MoO₂LX₂ (L = BPAAP, X = Cl, ClO₄ or ½SO₄) and MoO₂LXCl (L = BPAAP, X = NCS or NO₃) with the azo dye, 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-bromophenyl azo) pyrazol-5-one (bromophenolazoantipyrine-BPAAP) derived from 4-aminoantipyrine, have been synthesized and characterized by elemental analysis, magnetic and conductance measurements, IR, electronic, ESR and X-ray diffraction spectral studies. Magnetic and ESR spectral data suggest that the Mo(V) complexes are monomeric with molybdenum in the pentavalent state. The electronic spectral bands of these complexes at 650, 500 and 390nm are assigned to b₂→e, b₂→b₁ and O(π)→d(Mo) transitions respectively. The IR data confirms the neutral bidentate behaviour of the ligand and the presence of MoO³⁺ moiety in Mo(V) complexes and *cis*-MoO₂ moiety in Mo(VI) complexes. The XRD pattern of one of the complexes studied suggest orthorhombic structure with unit cell dimensions a = 10.485 Å, b = 13.829 Å and c = 17.89 Å.

Key Words: Synthesis, Bromophenolazoantipyrine, Dioxomolybdenum(VI), Oxomolybdenum(V), Complexes.

INTRODUCTION

Molybdenum is a versatile transition metal and a number of chemical reactions are catalyzed by its complexes. It is one of the most biologically active elements and is an essential micronutrient for microorganisms, plants and animals^{1,2}. Nature has incorporated molybdenum into a number of redox enzymes. Enzymes such as nitrogenase, nitrate reductase, xanthine dehydrogenase, xanthine oxidase, sulphite oxidase and aldehyde oxidase

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contain molybdenum atoms bonded through O, N and/or S atoms. These Mo sites are supposed to be active centres for the catalytic activity of the enzymes³. EXAFS studies have indicated the presence of an oxo group attached to molybdenum⁴. This has aroused considerable interest in the study of oxomolybdenum complexes. Hence we have isolated and characterized some new oxomolybdenum(V) and dioxomolybdenum(VI) complexes of a potentially tridentate ligand, 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-bromophenylazo) pyrazol-5-one (bromophenolazo antipyrine-BPAAP) (Fig. 1), an azodye derived from the biologically active molecule 4-aminoantipyrine (4-amino-2,3-dimethyl-1-phenyl pyrazol-5-one).

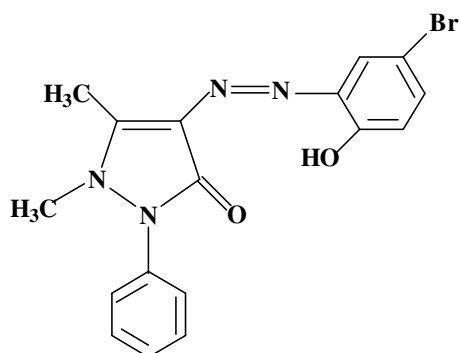


Fig. 1. Bromophenolazoantipyrine (BPAAP)

EXPERIMENTAL

MoCl₅ (Aldrich Chemicals, USA), MoO₃ (Lobochemie, Mumbai), 4-aminoantipyrine (Fluka, Switzerland), *p*-bromophenol (Spectrochem, Mumbai) were used as supplied. All other chemicals used were of BDH AR grade.

The ligand BPAAP was synthesized from 4-aminoantipyrine and *p*-bromophenol by diazotisation and coupling as described in the literature⁵.

The oxomolybdenum(V) complexes were prepared by adding dropwise a methanolic solution of MoCl₅ (2 mmol) or MoCl₅ containing 4-5 drops of HClO₄/0.5 g NH₄CNS/LiNO₃ as the case may be, to a methanolic solution of the ligand (2 mmol) with stirring for 15 min. The precipitated complex was suction filtered, washed with aqueous methanol and dried over P₄O₁₀ *in vacuo*.

The dioxomolybdenum(VI) complexes were prepared by adding dropwise a solution of MoO₃ (2 mmol) in hot con. HCl or MoO₃ (2 mmol) in hot con. HCl containing 0.5 g NH₄CNS/LiNO₃/Li₂SO₄ or a methanolic

solution of MoO₂(acac)₂ (2 mmol) containing 3-4 drops of HClO₄, to a methanolic solution of the ligand (2 mmol) with stirring. The reddish brown solution obtained in each case was refluxed for 1-2 h. The solid complex separated on cooling was suction filtered, washed with aqueous methanol and dried over P₄O₁₀ *in vacuo*.

Molybdenum, chloride, perchlorate and sulphur in the complexes were estimated by standard methods⁶. IR (KBr) and electronic (methanol) spectra were recorded on a Jasco FTIR 430 and Jasco V-550 UV-Vis spectrophotometers respectively. The ESR spectra of the complexes in the polycrystalline form were recorded at room temperature on a varian E-112 X-Q band spectrometer with DPPH as reference. Magnetic susceptibilities of the complexes were measured at room temperature on a Gouy balance using Hg[Co(NCS)₄] as the calibrant. Diamagnetic corrections for various atoms and structural units were computed using Pascal's constants.

Molar conductances of the complexes in C₆H₅NO₂, CH₃OH and CH₃CN (*ca.* 10⁻³ M) were measured at room temperature using an Elico digital conductivity meter with a dip type cell (cell constant 1 cm⁻¹). The X-ray powder diffraction pattern of one of the complexes were obtained on a Philips X-ray diffractometer (PW 1710) employing CuK_α radiation (λ = 1.54056 Å).

RESULTS AND DISCUSSION

All the complexes are stable, crystalline, non-hygroscopic solids partially soluble in common organic solvents and insoluble in ether. The analytical data are in agreement with the compositions proposed for the complexes in Table-1. The molar conductance values of the complexes (Table-1) indicate their non-electrolytic nature.

The magnetic moment values (1.73 B.M.) of the oxomolybdenum(V) complexes confirm the presence of Mo(V) in these complexes with *d*¹ configuration of molybdenum. All the dioxomolybdenum(VI) complexes are diamagnetic as expected.

In the IR spectrum, the free ligand exhibits a broad medium intensity band *ca.* 3100 cm⁻¹, assignable to hydrogen bonded-OH group⁷. This band disappears on complexation in all the cases and a new band appears at *ca.* 3400 cm⁻¹ indicating the presence of free-OH group and its non-participation in coordination. The ν(C=O) observed at 1650 cm⁻¹ and ν(N=N) observed at 1450 cm⁻¹ in the ligand spectrum are red shifted to 1590 and 1420 cm⁻¹, respectively in the spectra of the complexes suggesting their

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF MOLYBDENUM COMPLEXES

Complex (Colour)	Found (Calculated) %					Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) $\times 10^{-3}$			μ_{eff} (B.M.)	g_{av}
	Mo	C	H	N	S	C ₆ H ₅ NO ₂	CH ₃ CN	CH ₃ OH		
[MoO(BPAAP)Cl ₃] (Brown)	16.02 (15.85)	33.77 (33.70)	2.50 (2.48)	9.31 (9.25)	– –	1.5	9.1	6.1	1.74	1.97
[MoO(BPAAP)(NCS) Cl ₂] (Reddish brown)	15.41 (15.28)	34.48 (34.40)	2.41 (2.39)	11.19 (11.15)	5.14 (5.10)	2.3	10.9	8.1	1.73	1.98
[MoO(BPAAP)(ClO ₄)Cl ₂] (Chocolate brown)	14.48 (14.33)	30.56 (30.48)	2.26 (2.24)	8.41 (8.37)	– –	1.2	12.4	5.9	1.72	–
[MoO(BPAAP)(NO ₃)Cl ₂] (Reddish brown)	15.29 (15.18)	32.36 (32.29)	2.39 (2.37)	11.12 (11.08)	– –	1.1	11.3	6.3	1.76	–
[MoO ₂ (BPAAP) Cl ₂] (Brown)	16.53 (16.38)	35.91 (34.82)	2.58 (2.56)	9.59 (9.56)	– –	1.6	14.2	6.2	–	–
[MoO ₂ (BPAAP)(NCS)(Cl)] (Brown)	15.91 (15.77)	35.58 (35.51)	2.49 (2.47)	11.55 (11.51)	5.31 (5.26)	2.8	14.6	12.8	–	–
[MoO ₂ (BPAAP)(ClO ₄) ₂] (Brown)	13.33 (13.44)	28.51 (28.58)	2.08 (2.10)	7.80 (7.84)	– –	1.3	9.2	4.9	–	–
[MoO ₂ (BPAAP)(SO ₄)] (Reddish brown)	15.86 (15.71)	33.47 (33.40)	2.48 (2.46)	9.22 (9.17)	5.29 (5.24)	1.2	11.1	6.1	–	–
[MoO ₂ (BPAAP)(NO ₃)Cl] (Reddish brown)	– –	– –	– –	11.47 (11.43)	– –	0.8	7.9	5.6	–	–

participation in the coordination. The non-ligand bands at 560 cm⁻¹ ν (Mo-N) and 440 cm⁻¹ ν (Mo-O) further supports the coordination through the azo group nitrogen and carbonyl oxygen atoms⁸. Thus BPAAP behaves as a neutral bidentate ligand in all these complexes.

In the spectra of the thiocyanate complexes the bands at 2044 cm⁻¹ ν (C-N), 820 cm⁻¹ ν (C-S) and 490 cm⁻¹ δ (N-C-S) indicate the N-coordinated nature of the thiocyanate group⁹. The bands at 1150 (ν_4), 1050 (ν_1), 920 (ν_2), 640 (ν_3) and 610 cm⁻¹ (ν_5) in the spectra of the perchlorate complexes are suggestive of unidentate coordination¹⁰. The IR spectra of the nitrate complexes show three non-ligand bands at 1470 (ν_4), 1350 (ν_1) and 1008 cm⁻¹ (ν_2), confirming monodentate coordination¹¹. The chelating bidentate coordination of the sulphate group¹² is indicated by the bands at 1240, 1170 and 1075 cm⁻¹ (split components of ν_3), 995 cm⁻¹ (ν_1), 645, 620 and 595 cm⁻¹ (split components of ν_4) and 465 cm⁻¹ (ν_2).

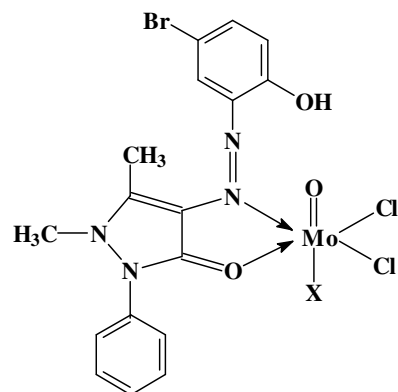
The IR spectra of all the oxomolybdenum(V) complexes show a very strong band at *ca.* 960 cm⁻¹ assignable to Mo=O stretching frequency¹³. Two strong bands in the region 940-950 cm⁻¹ ν_s (O=Mo=O) and 900-910 cm⁻¹ ν_{as} (O=Mo=O) exhibited by the spectra of dioxomolybdenum complexes are indicative of *cis*-MoO₂ moiety¹⁴.

The electronic spectra of Mo(V) complexes usually exhibit three distinct absorption bands in the region 13500-14500, 19000-22000 and 22500-26000 cm⁻¹ assignable to $b_2 \rightarrow e$, $b_2 \rightarrow b_1$ and $b_2 \rightarrow a_1$ transitions respectively. Usually the third band may be obscured by the more intense charge-transfer transition $O(\pi) \rightarrow d(\text{Mo})$ involving the excitation of an electron from the highest filled π -bonding M.O. associated with oxygen to the *d*-orbital of Mo. All the Mo(V) complexes show bands in the region 14700-15400 cm⁻¹ (680-650 nm), 2000 cm⁻¹ (500 nm) and 25000-26000 cm⁻¹ (400-380 nm). The electronic spectra indicate octahedral environment for all the complexes and are in conformity with the Ballhausen-Gray scheme for an octahedral geometry¹⁵.

The ESR spectra of the complexes [MoO(BPAAP)Cl₃] and [MoO(BPAAP)(NCS)Cl₂] recorded in the polycrystalline form at room temperature exhibited a single line only. The calculated g_{av} values of 1.97 and 1.98 indicate that the complexes are monomeric with molybdenum in the pentavalent state¹⁶.

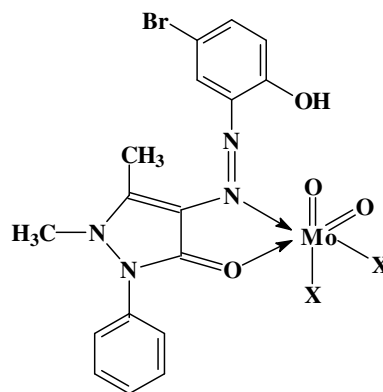
The X-ray powder diffraction lines of the complex [MoO₂(BPAAP)Cl₂] have been successfully indexed using Hesse and Lipson's procedure^{17,18} and was found to be orthorhombic. The lattice parameters computed are $a = 10.485 \text{ \AA}$, $b = 13.829 \text{ \AA}$ and $c = 17.89 \text{ \AA}$.

On the basis of the above evidences a distorted octahedral geometry is suggested for these complexes (Figs. 2-4).



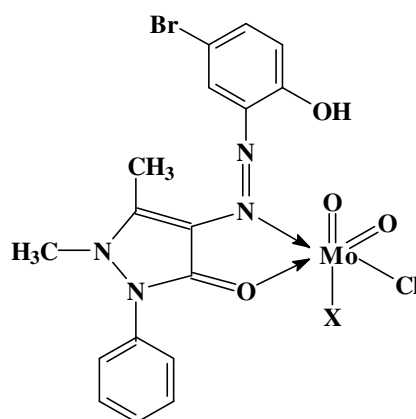
X = Cl, NCS, ClO₄ or NO₃

Fig. 2



X = Cl, ClO₄ or 1/2SO₄

Fig. 3.



X = NCS or NO₃

Fig. 4.

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