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Synthesis and Characterization of Oxomolybdenum(V) and Dioxomolybdenum(VI) Complexes of 2,3-Dimethyl-1-phenyl 4-(2-Hydroxy-5-bromobenzylideneamino)pyrazol-5-one

M.L. HARIKUMARAN NAIR* and M.S. PRAMILA GLADIS
Department of Chemistry, University College, Thiruvananthapuram-695 034, India
E-mail: drmlhnair@gmail.com

A few oxomolybdenum(V) and dioxomolybdenum(VI) complexes of the ligand 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-bromobenzylideneamino)pyrazol-5-one (BSAP) with the composition [MoO(BSAP)XCl_2] and [MoO_2(BSAP)XCl] (where X = Cl, NCS, NO_3, ClO_4) have been prepared. The complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements and IR, UV, ^{1}H NMR and ESR spectroscopic studies. The thermal behaviour of some of the complexes were also examined. The ligand and some of the complexes were screened for their possible antibacterial activities against gram positive and gram negative bacteria. All the oxomolybdenum(V) complexes showed normal magnetic behaviour. The molar conductance values of the complexes indicate that they are non-electrolytes. The X-ray diffraction patterns of the complex [MoO(BSAP)Cl_3] have been examined and was indexed. The results show that the complex belongs to the orthorhombic crystal system with unit cell dimensions a = 13.6167 Å, b = 10.3163 Å and c = 7.8616 Å. The ligand behaves as a neutral bidentate one. The complexes are found to be monomeric and neutral with distorted octahedral geometry.

Key Words: Oxomolybdenum(V), Dioxomolybdenum(VI), Complexes, Pyrazol-5-one, Octahedral.

INTRODUCTION

Molybdenum is a versatile transition element[1] due to the fact that it possesses a large number of stable and accessible oxidation states ranging from -2 to + 6. Oxomolybdenum(V) and *cis*-dioxomolybdenum(VI) species dominate the higher oxidation states[2]. A number of chemical reactions are catalyzed by complexes of molybdenum. It is one of the most biologically active transition elements and is an essential micronutrient for microorganisms, plants and animals[3]. Certain metalloenzymes contain molybdenum(V) and dioxomolybdenum(VI) species.

In view of the importance of oxomolybdenum(V) and dioxomolybdenum(VI) complexes, we have isolated and characterized some new complexes of the potential multidentate ligand 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-bromobenzylideneamino)pyrazole-5-one (BSAP, Fig. 1) derived from biologically active molecule, 4-aminoantipyrine.

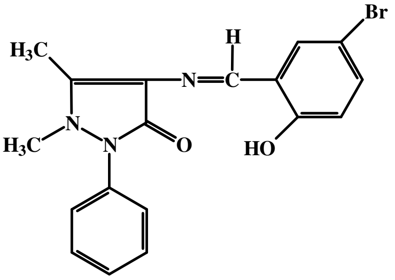


Fig.1. Structure of 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-bromobenzylideneamino)pyrazol-5-one

EXPERIMENTAL

4-Aminoantipyrine (Fluka, Switzerland) molybdenum pentachloride (Aldrich chemicals Co, Milwaukee, USA), 5-bromosalicylaldehyde (Lancaster, AlfaAesar, USA) molybdenumtrioxide (Lobochemie, Bombay, India) were used as such. All other chemicals were of AR grade.

Synthesis of the ligand: The ligand was synthesised from 4-aminoantipyrine and 5-bromosalicylaldehyde by mixing equimolar solutions in methanol and refluxing the reaction mixture on a water bath for *ca.* 0.5 h. The solid product separated on cooling was filtered, washed with methanol and dried over P_4O_{10} in vacuum.

Synthesis of Mo(V) complexes: [MoO(BSAP)Cl_3]: A methanolic solution of $MoCl_5$ (2 mmol) was added to a hot solution of the ligand (2 mmol) in the same solvent and refluxed for 2-3 h. The solid separated on concentrating the solution was suction filtered, washed with aqeous methanol and dried over P_4O_{10} in vacuum.

Synthesis of [MoO(BSAP)(ClO_4)Cl_2], [MoO(BSAP)(NO_3)Cl_2], [MoO(BSAP)(NCS)Cl_2]: The following general method was adopted for the preparation of these oxomolybdenum(V) complexes.

Methanolic solutions of $MoCl_5$ (2 mmol) containing 2-3 drops of $HClO_4$/0.5 g of $LiNO_3$/0.5 g of NH_4NCS as the case may be were mixed with the ligand (2 mmol) solution in methanol and refluxed for *ca.* 2 h. The solid separated on concentrating the solution was suction filtered, washed with aqeous methanol and dried over P_4O_{10} in vacuum.

Synthesis of dioxomolybbdenum(VI) complexes: [$MoO_2(BSAP)Cl_2$] MoO_3 (1 mmol) was dissolved in conc. HCl (2 mL) and added to a hot solution of the ligand (1 mmol) in methanol. The reaction mixture was refluxed for *ca.* 2 h. The solid which separated on concentrating the solution was filtered, washed with aqeous methanol and dried over P_4O_{10} in vacuum.

Synthesis of [$MoO_2(BSAP)(ClO_4)Cl$], [$MoO_2(BSAP)(NO_3)Cl$], [$MoO_2(BSAP)(NCS)Cl$]: The following general method was adopted for the preparation of these dioxomolybdenum(VI) complexes.

MoO_3 (1 mmol) was dissolved in conc. HCl and to this 2-3 drops of $HClO_4$/0.5 g $LiNO_3$/0.5 g of NH_4NCS as the case may be were added. This was then added to a hot solution of the ligand (1 mmol) in methanol. This reaction mixture was refluxed for *ca.* 2 h. The solid separated on concentrating the solution was suction filtered, washed with aqueous methanol and dried over P_4O_{10} in vacuum.

All the complexes are dark brown coloured and are non-hygroscopic. They are soluble in methanol, ethanol, acetonitrile and acetone. Carbon, hydrogen and nitrogen of the complexes were estimated by microanalytical methods at Sophisticated Test and Instrumentation Centre (STIC), Kochi, Kerala. Metal, halide and sulphur in the complexes were estimated by standard methods[4]. Perchlorates in the complexes were determined by Kurz's method[5]. The IR spectra were recorded as KBr pellets in the 4000-400 cm^{-1} region on a Jasco FTIR 430 spectrophotometer. Electronic spectra were recorded in methanol solution with Jasco V-550 UV-Vis spectrophotometer in the range 1000-300 nm. ESR spectrum of Mo(V) complex in polycrystalline form at room temperature was run on a Varian E-112 X-Q band spectrometer with DPPH as reference material. ^1H NMR spectrum was recorded in $CDCl_3$ on 300 MHz (Bruker Advance dpx-300) FT-NMR spectrometer using TMS as reference material. The molar conductances of the complexes in $C_6H_5NO_2$, CH_3OH and CH_3CN (10^{-3} M) were measured at 300 ± 2 K using an Elico conductivity bridge type CM 82T with a dip type cell (ec-0.03) fitted with platinum electrodes (cell constant is 0.94 cm^{-1}). Magnetic susceptibilities at room temperature (300 ± 2 K) were measured 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[6]. The X-ray powder diffraction patterns were obtained on Philips X-ray diffractometer (PW 1710) using CuK_α radiation with $\lambda = 1.5405$ Å. Thermogravimetric curves of complexes were recorded on a Mettler TG-50 thermobalance with 10 ºC/min in air. The antibacterial activity of the ligand and the complexes at different concentrations were tested by agar diffusion method using two bacteria *viz.*, *Staphylococcus aureus* and *Escherichia coli*. Here the positive control was gentamycin and the negative control was methanol.

RESULTS AND DISCUSSION

The analytical data of oxomolybdenum(V) complexes (Table-1) corresponds to the composition [$MoOLXCl_2$] and dioxomolybdenum(VI) complexes (Table-2) corresponds to the composition [MoO_2LXCl], where X = Cl, ClO_4, NO_3 or NCS and L = BSAP. Molar conductance values (Tables 1 and 2) show that all the complexes behave as non-electrolytes. The oxomolybdenum(V) complexes have magnetic moments in the range 1.70-1.75 BM at 298 ± 2 K (Table-1) indicating the absence of any metal-metal interaction. The dioxomolybdenum(VI) complexes are found to be diamagnetic as expected for a do system.

Infrared spectrum of the ligand BSAP exhibits a broad medium intensity band *ca.* 3410 cm^{-1}, which may be assigned to intramolecular hydrogen bonding of hydroxyl group[7] (Tables 3 and 4). In the spectra of all the oxomolybdenum(V) and dioxomolybdenum(VI) complexes, this band appears *ca.* 3430 cm^{-1}, indicating the non-participation of -OH group in the coordination to the metal ion. The ν(C=O) and ν(C=N) (azomethine) observed at 1637 and 1597 cm^{-1} in the ligand spectrum shows a downward shift to *ca.* 1600 and 1565 cm^{-1} in all the complexes, confirming the involvement of the pyrazolone carbonyl and azomethine group in coordination to the metal ion[8-10]. Thus the ligand BSAP behaves as neutral bidentate chelating agent in these complexes.

A very strong band observed *ca.* 960 cm^{-1} in the vibrational spectra of oxomolybdenum(V) complexes can be assigned to Mo=O *str.* frequency[11,12]. Strong bands exhibited by the dioxomolybdenum(VI) complexes in the region 960-930 and 920-890 cm^{-1} are attributed to ν_{sym}(O=Mo=O) and ν_{asym}(O=Mo=O), respectively of *cis*-MoO_2 moiety[13,14]. MoO_2 prefers to form a *cis*-configuration due to maximum utilization of the dπ orbitals of the metal for bonding. Bands observed around 590 and 530 cm^{-1} are assigned to ν(M-N) and ν(M-O) modes, respectively[15].

An examination of the IR spectra of the complexes reveal that the anions are also coordinated to the metal ions. The IR spectra of the thiocynate complexes show a very strong band *ca.* 2041 cm^{-1} ν(C-N) along with medium intensity bands *ca.* 745 cm^{-1} ν(C-S) and another medium intensity band *ca.* 505 cm^{-1} δ(N-C-S), showing N-coordinated thiocyanate in these complexes[16].

The perchlorate complex of oxomolybdenum(V) shows strong bands at 1184, 1079, 937, 683 and 647 cm^{-1} and dioxomolybdenum(VI) in the region 1187, 1050, 934, 684 and 637 cm^{-1}. These bands are assignable to ν_4, ν_1, ν_2, ν_3 and ν_5 vibrational modes of unidentately coordinated perchlorate group[17].

The nitrate complex of oxomolybdenum(V) exhibits three additional bands at 1472, 1322 and 1010 cm^{-1} and dioxomolybdenum(VI) have three

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF OXOMOLYBDENUM(V) COMPLEXES OF BSAP

Complex	Elemental analysis (%): Found (Calcd.)					μ_{eff} (BM)	Molar conductance (ohm^{-1} cm^2 mol^{-1}) × 10^{-3}			λ_{max} (cm^{-1})		
	C	H	N	S	Mo		Nitrobenzene	Acetonitrile	Methanol	Charge transfer	$b_2 \rightarrow b_1$	$b_2 \rightarrow e$
$[MoO(BSAP)Cl_3]$	38.07 (35.76)	2.52 (2.65)	7.04 (6.95)	-	16.89 (17.20)	1.72	1.5	10.2	6.3	26100	21745	13915
$[MoO(BSAP)(ClO_4)Cl_2]$	32.85 (32.33)	2.53 (2.40)	6.57 (6.29)	-	14.01 (14.36)	1.74	2.5	11.1	9.1	26765	19750	14588
$[MoO(BSAP)(NO_3)Cl_2]$	34.85 (34.24)	2.39 (2.54)	8.30 (8.88)	-	15.12 (15.21)	1.75	1.4	3.2	4.5	25945	20950	13587
$[MoO(BSAP)(NCS)Cl_2]$	38.00 (36.38)	2.63 (2.55)	8.44 8.75)	5.02 (5.11)	16.35 (15.30)	1.70	1.5	12.1	5.3	25930	20450	15100

TABLE-2
PHYSICAL AND ANALYTICAL DATA OF DIOXOMOLYBDENUM(VI) COMPLEXEXS OF BSAP

Complex	Elemental analysis (%): Found (Calcd.)					Molar conductance (ohm^{-1} cm^2 mol^{-1}) × 10^{-3}		
	C	H	N	S	Mo	Nitrobenzene	Acetonitrile	Methanol
$[MoO_2(BSAP)Cl_2]$	37.02 (36.94)	2.94 (2.74)	7.02 (7.18)	-	17.74 (16.41)	1.6	15.1	7.3
$[MoO_2(BSAP)(ClO_4)Cl]$	33.02 (33.3)	2.28 (2.46)	5.93 (6.48)	-	15.01 (14.79)	1.5	9.3	5.0
$[MoO_2(BSAP)(NO_3)Cl]$	34.93 (35.34)	2.31 (2.62)	8.95 (9.16)	-	14.85 (15.69)	1.1	8.0	7.1
$[MoO_2(BSAP)(NCS)Cl]$	38.71 (37.54)	2.11 (2.63)	9.44 (9.22)	5.72 (5.30)	16.05 (15.85)	3.0	14.5	13.0

TABLE-3
KEY IR BANDS (cm^{-1}) OF OXOMOLYBDENUM(V) COMPLEXES OF BSAP

BSAP	AA	BB	CC	DD	Assignments
–	3420	3470	3465	3430	ν(O-H) free
3414	–	–	–	–	ν(O-H) hydrogen bonded
–	–	–	–	2034	ν(C-N) of NCS^-
1637	1601	1596	1599	1590	ν(C=O) of Pyrazolone
1597	1576	1577	1567	1568	ν(C=N) of azomethine
–	–	–	1472	–	ν_4 of NO_3 coordinated
–	–	–	1322	–	ν_1 of NO_3 coordinated
–	–	1184	–	–	ν_4 of perchlorate
–	–	1079	–	–	ν_1 of perchlorate
–	–	–	1010	–	ν_2 of NO_3 coordinated
–	960	966	968	966	ν(Mo=O)
–	–	937	–	–	ν_2 of perchlorate
–	–	–	–	745	ν(C-S) of thiocyanate
–	–	683	–	–	ν_3 of perchlorate
–	–	647	–	–	ν_5 of perchlorate
–	–	–	–	505	ν(N-C-S)

AA = $[MoO(BSAP)Cl_3]$; BB = $[MoO(BSAP)(ClO_4)Cl_2]$;
CC = $[MoO(BSAP)(NO_3)Cl_2]$; DD = $[MoO(BSAP)(NCS)Cl_2]$

TABLE-4
KEY IR BANDS (cm^{-1}) OF DIOXOMOLYBDENUM(VI) COMPLEXES OF BSAP

BSAP	AA	BB	CC	DD	Assignments
–	3432	3430	3440	3465	ν(O-H) free
3414	–	–	–	–	ν(O-H) hydrogen bonded
–	–	–	–	2034	ν(C-N) of NCS^-
1637	1601	1595	1601	1600	ν(C=O)of Pyrazolone
1597	1576	1567	1560	1569	ν(C=N) of azomethine
–	–	–	1495	–	ν_4 of NO_3 coordinated
–	–	–	1347	–	ν_1 of NO_3
–	–	1187	–	–	ν_4 of perchlorate
–	–	1050	–	–	ν_1 of perchlorate
–	–	–	1023	–	ν_2 of NO_3
–	937	966	955	939	ν_{sym} of (O=Mo=O)
–	–	934	–	–	ν_2 of perchlorate
–	893	909	906	911	ν_{asym} of (O=Mo=O)
–	–	–	–	746	ν(C-S) of thiocyanate
–	–	684	–	–	ν_3 of perchlorate
–	–	647	–	–	ν_5 of perchlorate
–	–	–	–	505	ν(N-C-S)

AA = $[MoO_2(BSAP)Cl_2]$; BB = $[MoO_2(BSAP)(ClO_4)Cl]$;
CC = $[MoO_2(BSAP)(NO_3)Cl]$; CC = $[MoO_2(BSAP)(NCS)Cl]$

bands at 1495, 1347 and 1023 cm^{-1} assignable to ν_4, ν_1 and ν_2, respectively of coordinated nitrate group. Separation between the two bands ν_4 and ν_1 (*ca.* 150 cm^{-1}) indicates the monodentate nature of the nitrate group[18].

In the ^{1}H NMR spectra of the ligand and dioxomolybdenum(VI) complexes sharp multiple signals of the aromatic protons are noticed in the region 6.81-7.52 ppm. The signals due to the protons of >C-CH$_3$ group and -N-CH$_3$ group are observed in the region 2.42 and 3.21 ppm, respectively. The signal due to -OH proton is present in the region 13.28 ppm[19]. The presence of -OH signal both in the ligand and complex indicates its non-involvement in coordination.

The electronic spectral bands of oxomolybdenum(V) complexes (Table- 1) showed a moderately intense band in the region of 27000-25100 cm^{-1}, attributed to $O\pi \rightarrow d(Mo)$. The band due to the transition $^2B_2 \rightarrow {}^2A_1$ ($d_{xy} \rightarrow d_{z^2}$) is masked by this band. The complexes exhibited two more bands, a medium intensity band in the region 22212-19234 and 15384-13172 cm^{-1} assigned to $^2B_2 \rightarrow {}^2B_1$ ($d_{xy} \rightarrow d_{x^2-y^2}$) and $^2B_2 \rightarrow {}^2E$ ($d_{xy} \rightarrow d_{xz}, d_{yz}$), respectively[20]. The electronic spectra indicate octahedral environment for all the complexes[21].

The ESR spectrum of oxomolybdenum (V) complexes which were recorded in polycrystalline form at room temperature exhibited a single line only. The ESR parameters are found to be $g_{11} = 1.974$, $g_{\perp r} = 1.956$ and $g_{av} = 1.9669$. The g_{av} value indicates that the pentavalent Mo in the complex is monomeric[22].

Thermogravimetric curves of complexes [MoO(BSAP)Cl$_3$] and [MoO$_2$(BSAP)Cl$_2$] were recorded in the temperature range from room temperature to 1000 °C. The complex [MoO(BSAP)Cl$_3$] shows a weight loss of 80.35 % at 491 ºC corresponding to the oxidative decomposition to give MoO$_3$ as the ultimate residue. The complex [MoO$_2$(BSAP)Cl$_2$] decomposes in two well defined stages. A final weight loss of 75.51 % at 464 ºC has been ascribed to the oxidative decomposition to give MoO$_3$.

The X-ray diffraction study of the complex [MoO(BSAP)Cl$_3$] has been carried out and was indexed (Fig. 2 and Table-5) using Hesse and Lipson's procedure[23,24]. The results show that the complex belongs to the orthorhombic crystal system, having unit cell dimensions a = 13.6167 Å, b = 10.3163 Å and c = 7.8616 Å.

The ligand BASP and the complexes [MoO(BSAP)Cl$_3$] and [MoO$_2$(BSAP)Cl$_2$] were screened for their possible antibacterial activities against the gram positive bacteria *Staphylococcus aureus* ATCC 25923 and gram negative bacteria *Escherichia coli* ATCC 25922 at concentrations 50, 100, 200 and 400 µg/disc by agar diffusion method (Table-6).

The ligand BSAP and [MoO(BSAP)Cl$_3$] exhibited antimicrobial property against gram positive *S. aureus* and the activity was concentration dependent. There was an increase in zone of inhibition with the increase in concentration.

TABLE-5
X-RAY DIFFRACTION DATA OF [MoO(BSAP)Cl_3]

Line	hkl	$Sin^2\theta$ (obs.)	$Sin^2\theta$ (calcd.)	Relative intensity (%)
1	100	0.00320	0.00320	42.97
2	010	0.00507	0.00557	16.57
3	110	0.00877	0.00877	100.0
4	001	0.00964	0.009606	51.18
5	200	0.01280	0.01280	11.31
6	011	0.01577	0.01518	66.91
7	210	0.01728	0.01837	32.30
8	111	0.019665	0.01838	50.08
9	020	0.02119	0.02228	62.51
10	201	0.02245	0.02240	46.36
11	120	0.02486	0.02550	19.68
12	300	0.02864	0.02880	94.17
13	021	0.03079	0.03190	41.48
14	310	0.03407	0.03430	66.05
15	220	0.03680	0.03510	11.68
16	002	0.03870	0.03840	25.90
17	221	0.04640	0.04470	23.56
18	030	0.05010	0.05010	26.30
19	400	0.05280	0.05120	57.80
20	410	0.05570	0.05680	17.77
21	031	0.05870	0.05970	32.95
22	321	0.06080	0.06070	10.76
23	411	0.06510	0.06640	43.99
24	420	0.07480	0.07350	19.37
25	500	0.08090	0.08000	06.42
26	421	0.08450	0.08310	17.38
27	003	0.08750	0.08650	10.52
28	511	0.09519	0.09520	20.47
29	213	0.10500	0.10490	15.02
30	422	0.11160	0.11190	15.61
31	341	0.12610	0.12750	16.78
32	233	0.14650	0.14940	08.81
33	503	0.16540	0.16650	09.37
34	350	0.18970	0.18880	05.96
35	234	0.21670	0.21660	02.65

TABLE-6
ANTIBACTERIAL ACTIVITY OF BSAP, [MoO(BSAP)Cl_3] AND [MoO_2(BSAP)Cl_2]

Test sample			Zone of inhibition (mm)	
			E. coli ATCC 25922	*S. aureus* ATCC 25923
BSAP	50 µg	Unit 1,2,3	Nil	Nil
	100 µg	Unit 1	Nil	1
		Unit 2	Nil	I
		Unit 3	Nil	< 1
	200 µg	Unit 1	Nil	2
		Unit 2	Nil	2
		Unit 3	Nil	2
	400 µg	Unit 1	Nil	3
		Unit 2	Nil	3
		Unit 3	Nil	2
	800 µg	Unit 1	Nil	4
		Unit 2	Nil	4
		Unit 3	Nil	4
[MoO(BSAP)Cl_3]	50 µg	Unit 1	Nil	1
		Unit 2	Nil	1
		Unit 3	Nil	1
	100 µg	Unit 1	Nil	3
		Unit 2	Nil	3
		Unit 3	Nil	2
	200 µg	Unit 1	Nil	4
		Unit 2	Nil	5
		Unit 3	Nil	4
	400 µg	Unit 1	Nil	5
		Unit 2	Nil	5
		Unit 3	Nil	6
	800 µg	Unit 1	Nil	7
		Unit 2	Nil	6
		Unit 3	Nil	7
[MoO_2(BSAP)Cl_2]	50 µg	Unit 1,2,3	Nil	Nil
	100 µg	Unit 1,2,3	Nil	Nil
	200 µg	Unit 1,2,3	Nil	Nil
	400 µg	Unit 1,2,3	Nil	Nil
	800 µg	Unit 1	Nil	1
		Unit 2	Nil	< 1
		Unit 3	Nil	1
Negative control			Nil	Nil
Gentamycin 10 mcg			19	24

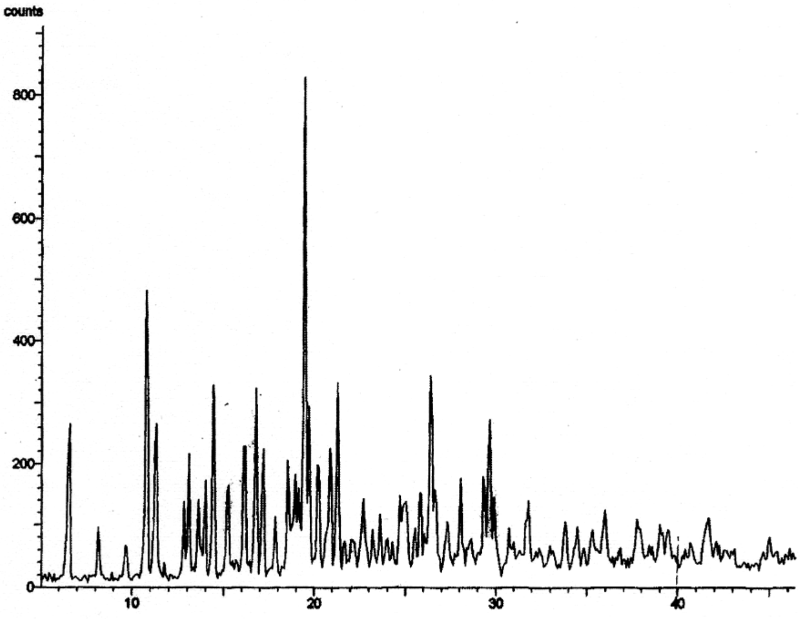
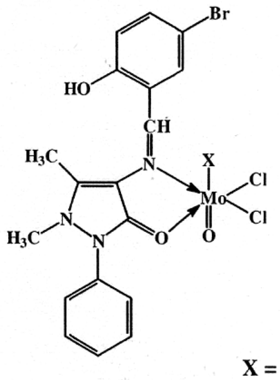
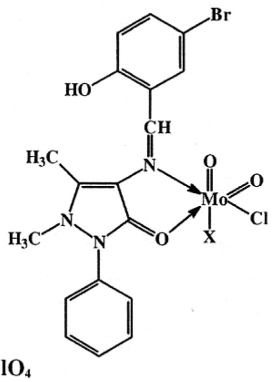


Fig. 2. X-Ray diffraction patterns of $[MoO(BSAP)Cl_3]$

On the basis of these available evidences, a distorted octahedral (distorted due to Mo=O bond) geometry is suggested for all the oxomolybdenum(V) and dioxomolybdenum(VI) complexes. The suggested structures of the complexes are given in Figs. 3 and 4 where X = Cl, NO_3, NCS or ClO_4.





X = Cl, NCS, NO_3 or ClO_4

Fig. 3. Structure of MoO(V) complexes of BSAP

Fig. 4. Structure of MoO_2(VI) complexes of BSAP

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