

Syntheses, Spectral, Surface Morphological and Gamma Ray Irradiation Studies of Some Oxomolybdenum(V) and Dioxomolybdenum(VI) Complexes of an Azo Dye Derived from 4-aminoantipyrine

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ABSTRACT. Syntheses of some novel oxomolybdenum(V) and dioxomolybdenum(VI) complexes with an azo dye methoxyphenolazoantipyrine (HL) derived from 4-aminoantipyrine and 2-methoxyphenol are reported. The complexes have been characterized by elemental analyses, molar conductance, magnetic susceptibility data, IR, UV-Vis, ¹H NMR, EPR and FAB mass spectral studies. The physicochemical studies and spectral data indicate that HL acts as a bidentate chelating ligand. The complexes have the general formulae [MoO(HL)XCl₂] and [MoO₂(HL)XCl], where X=Cl, NCS or NO₃. All the complexes are found to have distorted octahedral geometry. Structural and morphological characterization of the complexes [MoO(HL)Cl₃](1) and [MoO₂(HL)Cl₂](4) before and after gamma ray irradiation, was performed by X-ray diffraction and scanning electron microscopy (SEM). The ligand and the complexes were screened for their possible antimicrobial activities.

Key words: Oxomolybdenum(V), Dioxomolybdenum(VI), 4-Aminoantipyrine, Spectral studies, γ -Irradiation

INTRODUCTION

Molybdenum is a biologically important trace element that occurs in the redox active sites of molybdoenzymes involved in nitrogen, sulfur or carbon metabolism.¹ Recent years have witnessed a phenomenal growth in the coordination chemistry of high valent oxomolybdenum complexes owing to their potential applications.²⁻⁶ The 'oxo-type' molybdoenzymes, which possess a common molybdenum cofactor and catalyze biological two electron reactions that involve a change in the number of oxygen atoms in the substrate.⁷ Molybdenum is a versatile transition element because it possesses a large number of stable and accessible oxidation states as well as coordination numbers. The formal oxidation state of molybdenum fluctuates between +6 and +4 via a +5 intermediate during turnover.⁸ A variety of chemical reactions are catalyzed by the molybdenum coordination complexes.⁹

Herein, we report the synthesis, spectral characterization, thermal and antibacterial studies of complexes of oxomolybdenum(V) and dioxomolybdenum(VI) species with a potentially bidentate ligand derived from 4-aminoantipyrine and 2-methoxyphenol. The irradiation may induce changes in textural, structural, electric, thermal and magnetic properties of a large variety of solids.^{10,11} Literature survey revealed that spectral and X-ray diffraction studies of irradiated salts as well as metal complexes

are limited.¹² Knowledge regarding the radiation effect benefit the development of advanced material in various fields. Moreover, since studies concerning the effect of γ -radiation on transition metal complexes are rare, the effect of γ -radiation on X-ray diffraction and surface morphology of two of the complexes have also been incorporated in the present investigation.

EXPERIMENTAL

Materials and Physical Measurements

Molybdenum pentachloride (Alfa Aesar, Lancaster, UK) and molybdenum trioxide (Loba Chemie, Mumbai, India) were used. All other chemicals were of AR grade.

Metal and chloride were estimated by standard methods.¹³ The elemental analyses (C, H, N and S) were carried out at the Sophisticated Test and Instrumentation Center (STIC), Kochi. Room temperature molar conductance of the complexes in methanol was recorded on Elico direct reading conductivity meter at a concentration of $\sim 10^{-3}$ M. The magnetic susceptibilities were recorded at room temperature by Gouy method. Diamagnetic corrections for various atoms and structural units were computed using Pascal's constants.¹⁴ The IR spectra (KBr, cm⁻¹) of ligand and complexes were recorded in the region 4000-400 cm⁻¹ on Perkin-Elmer 397 Spectrophotometer. Electronic absorption spectral measurements of the com-

plexes in methanol were conducted using Jasco-V-550-UV-Vis spectrophotometer. ^1H NMR spectra of the ligand, HL and the complex **4** were recorded on a 300 MHz FT NMR instrument using TMS as reference. The FAB mass spectrum of ligand HL, $[\text{MoO}(\text{HL})\text{Cl}_3](1)$ and $[\text{MoO}_2(\text{HL})\text{Cl}_2](4)$ were recorded in a JEOL JMS600H mass spectrometer at NIIST, Thiruvananthapuram, India. EPR spectra of the complex **1** in solid state at LNT was recorded on a Varian E-112 Spectrometer at X-band, using TCNE as marker with 100 kHz modulation frequency and 9.1 GHz microwave frequency at the SAIF, IIT, Mumbai, India. Thermal studies were carried out by heating in air at a rate of $10\text{ }^\circ\text{C}/\text{min}$ on a Perkin Elmer, Diamond TG/DTA Analyser. X-ray powder diffraction patterns of unirradiated and irradiated samples were recorded using Philips X-ray PW1710 diffractometer using nickel filter (Cu-K_α radiation $\lambda=1.5406$). Surface morphological study of unirradiated and irradiated samples were recorded using JEOL Model JSM-6390LV. The samples were subjected to gamma irradiation to a dose of 800 kGy using ^{60}Co γ -ray in Gamma chamber 5000cc self shielded at constant intensity under room temperature at a dose rate of 1.85 kGy h^{-1} .

Synthesis of Ligand (HL)

Synthesis of ligand, HL ($\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_3$) in Fig. 1 was carried out by 4-aminoantipyrine and 2-methoxyphenol by diazotization and coupling as reported earlier.¹⁵ Purity of the ligand was tested by TLC. It was characterized by IR, UV and ^1H NMR spectroscopy. m.p. $231\text{ }^\circ\text{C}$.

Synthesis of Oxomolybdenum(V) Complexes

The chloride complex was prepared by adding a methanolic solution of MoCl_5 (2 mmol, 20 mL) in small quantities with stirring to a hot methanolic solution of the ligand (2 mmol, 20 mL). The solution formed was refluxed for 2-3 h. The precipitated complexes were filtered, washed with aqueous methanol and dried over P_4O_{10} *in vacuo*.

The following general method was adopted for the preparation of thiocyanate and nitrate complexes.¹² A methanolic solution of MoCl_5 (2 mmol, 20 mL) containing 2 mmol of

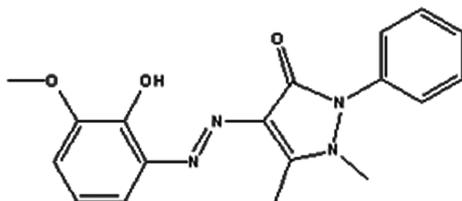


Fig. 1. Tentative structure of Ligand HL.

$\text{NH}_4\text{CNS}/2\text{ mmol LiNO}_3$, was added to a hot methanolic solution of the ligand (2 mmol, 20 mL). The thiocyanate complex was precipitated on heating the mixture at $40\text{ }^\circ\text{C}$ for ~ 30 min, while the nitrate complex was precipitated on refluxing the solution for 2-3 h. The precipitated complexes were suction filtered, washed with aqueous methanol (1:1) followed by dry ether and then dried over P_4O_{10} *in vacuo*.

Synthesis of Dioxomolybdenum (VI) Complexes

MoO_3 (2 mmol) was dissolved in minimum amount of hot conc. HCl (4 mL). Methanolic solution of this was added dropwise with stirring to a methanolic solution of the ligand (2 mmol, 20 mL). The solution formed was refluxed for 2-3 h. The solid separated was suction filtered, washed first with aqueous methanol, then with ether and dried over P_4O_{10} *in vacuo*. The thiocyanate and nitrate complexes were prepared in the same manner as the oxomolybdenum(V) complexes.

Antimicrobial Study

Antitubercular activity of HL and complexes against *M. tuberculosis* H37Rv and antibacterial activity against *Escherichia coli* and *Lactobacillus leichmannii* were done by the Resazurin assay method at the Rajeev Gandhi Centre for Biotechnology (Thiruvananthapuram).

RESULTS AND DISCUSSIONS

Analytical Measurements

All the complexes are deeply coloured and fairly stable at room temperature. They are non hygroscopic solids and soluble in common organic solvents, like acetone, chloroform, methanol, acetonitrile, DMF and DMSO. Formulation of these complexes have been done on the basis of their elemental analytical data, molar conductance and magnetic susceptibility measurements. The analytical data show that all the complexes are mononuclear with the general formulae $[\text{MoO}(\text{HL})\text{Cl}_2\text{X}]$ and $[\text{MoO}_2(\text{HL})\text{ClX}]$, where $\text{X}=\text{Cl}, \text{NCS}, \text{NO}_3$. The molar conductances of the complexes in methanol is in the range of $3.6\text{--}14.8\text{ ohm}^{-1}\text{cm}^2$, adequately confirming the non electrolytic nature of the complexes.¹⁶

Magnetic Susceptibilities

The magnetic susceptibility values of all the oxomolybdenum (V) complexes at room temperature are near the spin-only value (1.73 B.M.) as expected of a d^1 system. This shows the absence of Mo-Mo interaction in these com-

Table 1. Analytical data of the ligand and complexes

Ligand/Complexes	Yield (%)	Composition % found (calc)						λ_m^a	μ_{eff}^b (B.M.)
		Mo	Carbon	Hydrogen	Nitrogen	Chlorine	Sulphur		
HL	75	-	68.56(68.35)	5.89(6.02)	11.64(11.95)	-	-	-	-
[MoO(HL)Cl ₃] (1)	82	17.08(17.23)	38.50(38.84)	3.18(3.26)	10.01(10.06)	18.96(19.11)	-	11.2	1.67
[MoO(HL)Cl ₂ (NCS)] (2)	78	16.28(16.56)	39.24(39.39)	3.04(3.13)	11.82(12.08)	12.08(12.24)	5.21(5.53)	5.6	1.63
[MoO(HL)Cl ₂ (NO ₃)] (3)	74	16.34(16.45)	36.84(37.06)	2.98(3.11)	11.78(12.01)	11.98(12.16)	-	13.4	1.68
[MoO ₂ (HL)Cl ₂] (4)	84	17.46(17.85)	40.01(40.24)	3.18(3.38)	10.17(10.43)	12.96(13.20)	-	7.4	diamagnetic
[MoO ₂ (HL)(NCS) ₂] (5)	80	16.24(16.47)	39.68(41.24)	2.82(3.11)	14.26(14.43)	-	10.95(11.01)	6.6	diamagnetic
[MoO ₂ (HL)Cl(NO ₃)] (6)	77	16.82(17.02)	37.87(38.36)	3.06(3.22)	11.98(12.43)	6.12 (6.29)	-	5.8	diamagnetic

^aMolar conductivity, 10⁻³ M Methanol at 298 K.

^bMagnetic susceptibility per metal atom.

plexes. The presence of Mo=O bond in oxomolybdenum (V) complexes produce strong tetragonal distortion and this may cause reduction in magnetic moment values. The high spin orbit coupling constant¹⁷ of Mo ($\lambda=1000 \text{ cm}^{-1}$) also lowers the μ_{eff} value. All the dioxomolybdenum (VI) complexes are found to be diamagnetic as expected for a d⁰ system. The analytical data are presented in Table 1.

Infraed Spectra

Important infrared spectral bands of the ligand and complexes and their tentative assignments are given in Table 2. In all the complexes ligand coordinates through carbonyl oxygen and one of the nitrogens of the diazo group as evidenced by the shift of $\nu_{\text{C=O}}$ and $\nu_{\text{N=N}}$ to lower frequencies.¹⁸ The spectrum of the ligand HL exhibits a broad medium band at 2925 cm⁻¹ is assigned to hydrogen bonded OH group. This band disappears in the spectra of all the complexes and a broad medium intensity band observed at ~3450 cm⁻¹, confirming the presence of free OH group and their non participation in coordination with the metal ion.¹⁵

Dioxomolybdenum (VI) complexes display two Mo=O stretches at ~936-942 cm⁻¹ and at ~906-910 cm⁻¹ due to symmetric and antisymmetric stretching of *cis*-MoO₂²⁺ core. The MoO₂²⁺ prefers to form a *cis* configuration due

to maximum utilization of the d π groups. A very strong band observed at ~960 cm⁻¹ in the spectra of oxomolybdenum complexes corresponds to Mo=O stretching frequency.³ New weak bands at ~590 cm⁻¹ and at ~440 cm⁻¹ in the metal complexes have been assigned to $\mu_{\text{Mo-O}}$ and $\mu_{\text{Mo-N}}$ modes respectively.¹⁹ The N-coordinated nature of the thiocyanate group is indicated by the bands at ~2060 cm⁻¹ ($\mu_{\text{C-N}}$), ~840 cm⁻¹ ($\nu_{\text{C-S}}$) and ~490 cm⁻¹ (δ_{NCS}). The IR spectra of the nitrate complexes suggest²⁰ monocoordination of the nitrate group ν_4 at ~1490 cm⁻¹, ν_1 at ~1380 cm⁻¹ and ν_2 at ~1034 cm⁻¹.

Electronic Spectra

The electronic absorption bands of bidentate azo dye ligand (HL) and the oxomolybdenum (V) complexes were recorded in methanol. The electronic spectrum of the ligand shows an intense band at 249 nm and a band of less intensity at 322 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively. These bands suffer marginal shifts on complexation. The electronic spectra of the complexes showed a red shift to ~256 nm and ~334 nm.²¹

The electronic spectra of octahedral oxomolybdenum (V) complexes usually exhibit three distinct bands in the region 690-740 nm, 450-520 nm and 380-440 nm, assignable to ²B₂→²E ($d_{xy} \rightarrow d_{xz}$, d_{yz}), ²B₂→²B₁ ($d_{xy} \rightarrow d_{x^2-y^2}$)

Table 2. Important IR data of ligand and its metal complexes

Ligand/Complexes	IR data (cm ⁻¹)				
	$\nu_{\text{O-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{N=N}}$	$\nu_s \text{Mo=O}$	$\nu_a \text{Mo=O}$
HL	2925	1634	1465	-	-
[MoO(HL)Cl ₃] (1)	3436	1585	1452	958	-
[MoO(HL)Cl ₂ (NCS)] (2)	3392	1592	1450	960	-
[MoO(HL)Cl ₂ (NO ₃)] (3)	3462	1587	1454	956	-
[MoO ₂ (HL)Cl ₂] (4)	3429	1584	1454	942	908
[MoO ₂ (HL)(NCS) ₂] (5)	3436	1590	1448	936	910
[MoO ₂ (HL)Cl(NO ₃)] (6)	3444	1582	1450	938	906

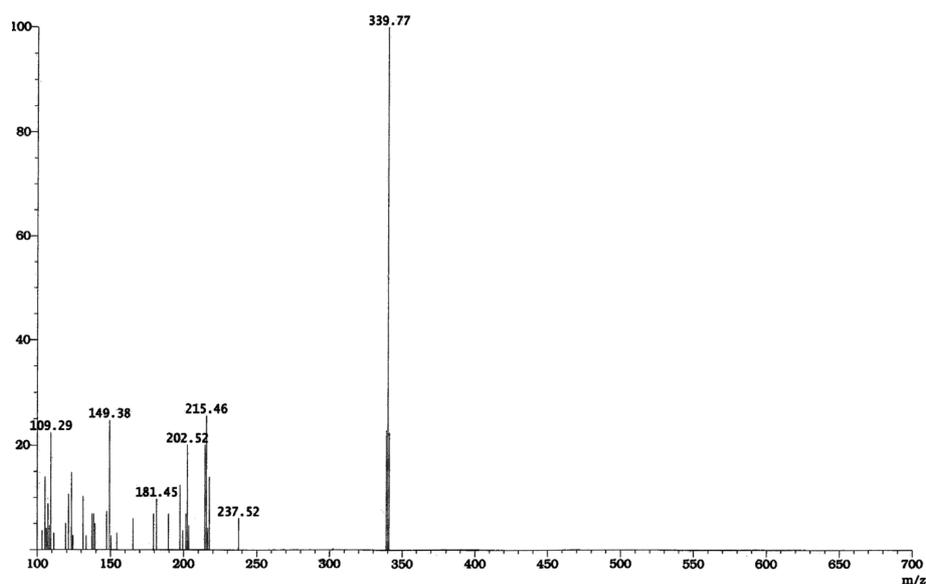


Fig. 4. FAB mass spectrum of HL.

not be seen if there is signal broadening due to spin lattice relaxation and spin-spin interaction.¹⁴ In the present case the isotropic nature of the spectrum is attributable to enhanced spin lattice relaxation and spin-spin interaction, moreover the spectrum is recorded in a magnetically concentrated medium.²⁶ Absence of half field signal in the EPR spectrum rules out any metal-metal interaction in the complex.

In the octahedral complexes of molybdenum (V), the single electron located in d_{xy} orbital. This orbital is related to other four d orbitals by rotations about one or other of the cartesian axes. If the rotation moves the electron into a vacant orbital, then the current resulting from the circulation leads to a magnetic field that opposes the applied field. Consequently the larger laboratory field is required to meet the Zeeman conditions and the calculated g value will be smaller than the free electron.²⁷

FAB Mass Spectra

Mass spectroscopy, which is mainly applied in the analysis of biomolecules, has been increasingly used as a powerful structural characterization technique in coordination chemistry. The FAB mass spectra of the ligand HL (Fig. 4) and its complexes **1** and **4** were recorded and their stoichiometric compositions were compared. The molecular ion peak $[M+H]^+$ for ligand ($C_{18}H_{18}N_4O_3$), is at 339.77. The complexes **1** and **4** show molecular ion peaks at m/z 556.16 and 537.21 respectively, suggesting the complexes to be monomeric.

Thermal Studies

Thermal behavior of the complexes **1** and **5** were studied by TGA and DTG techniques by heating in air at a rate of 10 °C per min. TG and DTG curves of complexes **1** and **4** were shown in Figs. 5 and 6, respectively.

The decomposition of the complex **1** takes place in three stages as indicated by the DTG peaks at 204 °C, 336 °C and 639 °C. The stability range was extended from ambient temperature to 170 °C. The initial mass loss 1-2% may be due to the desorption of moisture. First decomposition stage starts at 170 °C and ended at 230 °C. The mass loss of 6.37% (calc.6.43%) is assigned to the loss of one mole of chlorine atom. The second stage decomposition ranged from 270 °C to 410 °C. The weight loss at this stage was 43.8% and this stage could not be assigned to any specific decomposition. After this stage, weight loss takes place

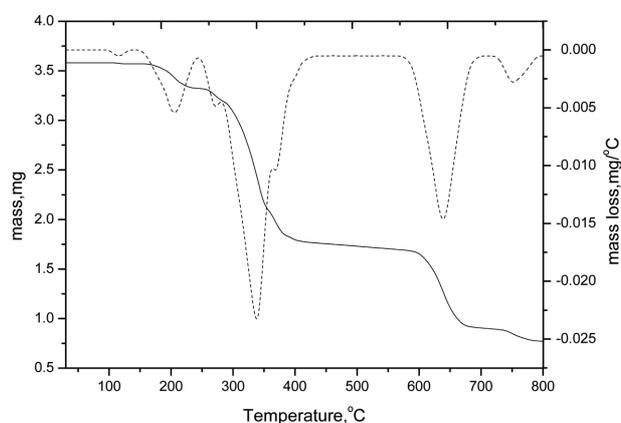


Fig. 5. TG and DTG curves of $[MoO(HL)Cl_3]$.

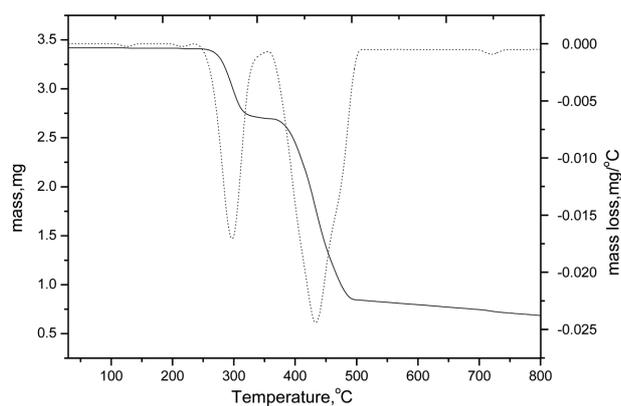


Fig. 6. TG and DTG curves of $[\text{MoO}_2(\text{HL})(\text{NCS})_2]$.

slowly and continuously. The sample showed another weight loss in the region 590–680 °C. The weight loss in this stage was 24.07% (calc. 24.52%) ascribed to the oxidative decomposition of the remaining part of the complex to give MoO_3 as the ultimate residue. The weight of the sample at 680 °C was consistent with the formation of MoO_3 . The sample showed another weight loss in the region 740–790 °C. This may be due to the volatilization of MoO_3 above 740 °C.^{28,29}

The thermal decomposition of the complex **5** occurred in two stages as denoted by the DTG peaks at 297 and 434 °C. The complex is stable up to 260 °C. The first stage decomposition starts at 260 °C and is completed at 330 °C.

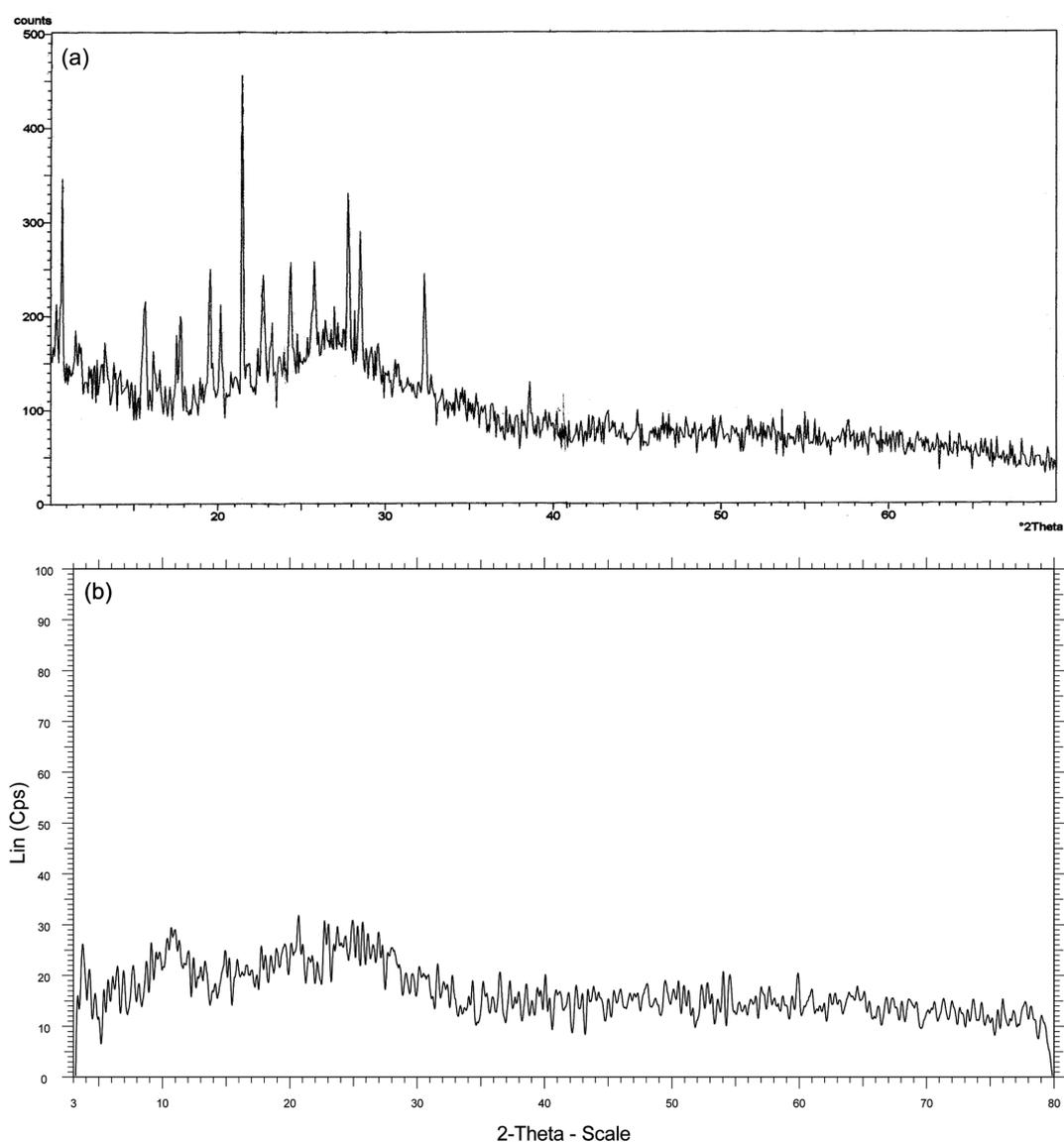


Fig. 7. (a) X-ray powder diffraction pattern of $[\text{MoO}(\text{HL})\text{Cl}_3]$ before irradiation, (b) X-ray powder diffraction pattern of $[\text{MoO}(\text{HL})\text{Cl}_3]$ after irradiation.

The mass loss of 20.47% (calc. 19.95%) corresponded to the loss of anionic part of the complex. The second stage decomposition ranges from 380 °C to 490 °C. The weight loss at this stage was 54.68% (calc. 55.86%). The weight of the sample at 490 °C was consistent with the formation of MoO₃ formed by the oxidative decomposition of the complex.

Irradiation Studies

X-ray diffraction and surface morphology of the complexes [MoO(HL)Cl₃] and [MoO₂(HL)Cl₂] were studied before and after gamma irradiation.

Colour

No colour change occurred upon irradiation indicating the absence of colour centers in the sample.

X-ray Diffraction Studies

X-ray diffractograms for the unirradiated and irradiated samples of [MoO(HL)Cl₃] and [MoO₂(HL)Cl₂] are given in Figs. 7a, 7b, 8a & 8b, respectively. XRD patterns are indexed using Hesse and Lipson's procedure.³⁰ Lattice constants and lattice parameters are listed in Table 3 and the X-ray diffraction data are presented in Tables 4 & 5.

Lattice imperfections caused by irradiation influence

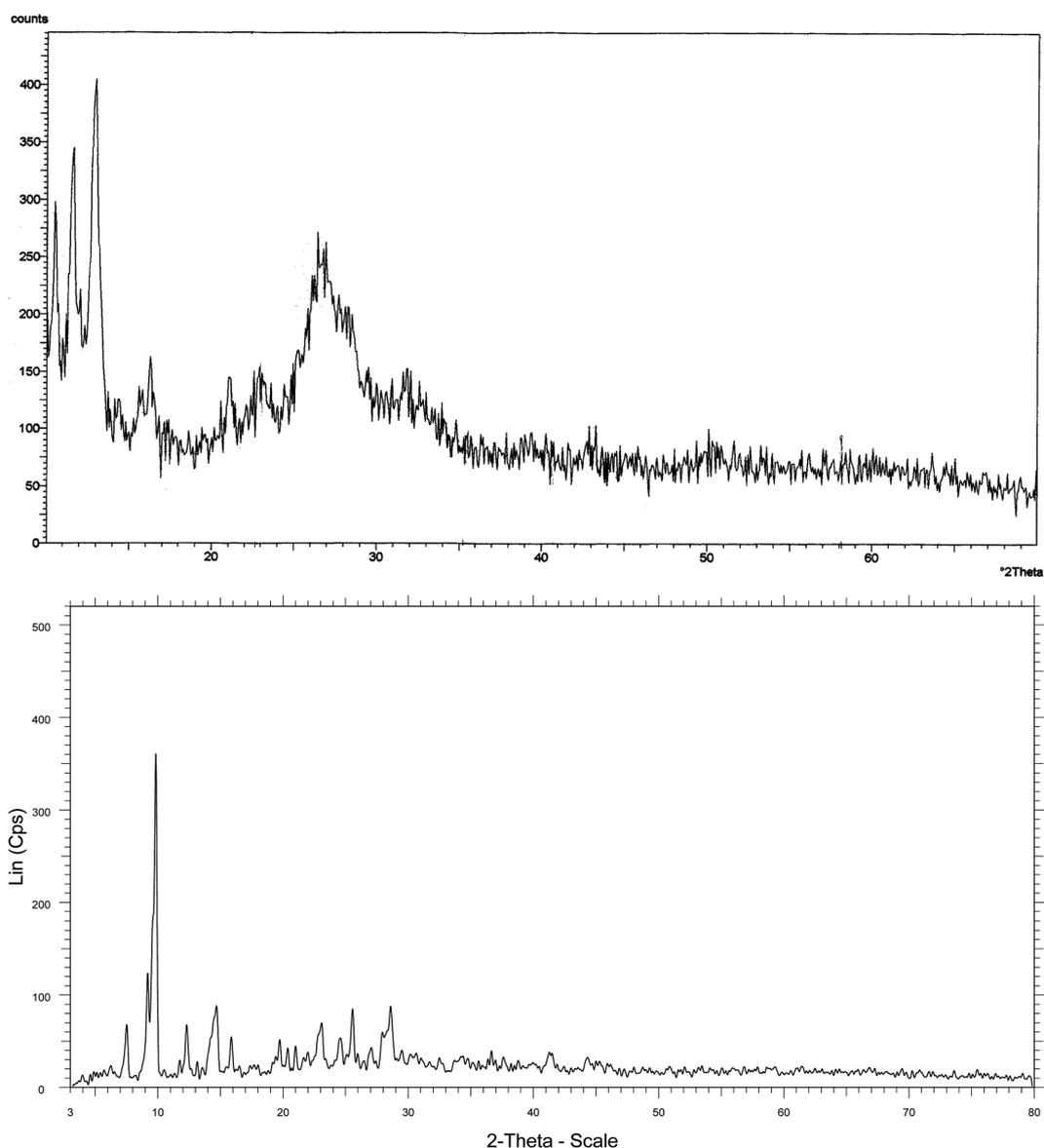


Fig. 8. (a) X-ray powder diffraction pattern of [MoO₂(HL)Cl₂] before irradiation, (b) X-ray powder diffraction pattern of [MoO₂(HL)Cl₂] after irradiation.

Table 3. Lattice constants and lattice parameters

Complexes	Lattice Constants (Å)			Lattice parameters (Å)			Particle size (nm)
	A	B	C	a	b	c	
[MoO(HL)Cl ₃] Unirradiated	0.009	0.020	0.016	8.12	5.44	6.08	40.33
[MoO ₂ (HL)Cl ₂] Unirradiated	0.0198	0.0133	0.009	5.47	6.67	8.11	23.9
[MoO ₂ (HL)Cl ₂] Irradiated to 800 kGy	0.0044	0.00653	0.00715	11.60	9.52	9.10	24.1

Table 4. XRD data of [MoO(HL)Cl₃]

Unirradiated MoO(HL)Cl ₃			
Sin ² θ (obs)	Sin ² θ (calc)	hkl	Intensity %
0.0086	0.009	100	68.14
0.0238	0.025	101	33.40
0.0287	0.029	110	46.85
0.0345	0.036	011	100
0.0442	0.045	111	46.74
0.0495	0.052	201	46.06
0.0576	0.056	210	60.10
0.0605	0.064	002	55.03
0.0774	0.073	102	42.95
0.1091	0.105	121	14.12

the X-ray diffraction pattern of a substance. In the present study it is observed that unit cell parameters changed upon irradiation. The intensities of powder lines and the cor-

responding 2θ values are found to be different for the irradiated sample. The unirradiated [MoO(HL)Cl₃] was found to have orthorhombic lattice but the irradiated [MoO(HL)Cl₃] recorded only very few reflections and hence could not be indexed. This may be an indication of the amorphous nature of the complex. Both unirradiated and irradiated [MoO₂(HL)Cl₂] complexes are found to have orthorhombic lattice.

High energy of radiation may change the physical properties of materials. The changes are strongly dependent on the internal structure of the absorbed substance, the radiation energy and dose.³¹ The radiation may cause ionization or excitation of the electrons and possibly, displacement of atoms from their sites in the lattice of the solid. The size of the crystal may change due to the stress caused by irradiation. If the crystals are under uniform stress, a contraction of the unit cell occurs. The stress factor and structure fac-

Table 5. XRD data of [MoO₂(HL)Cl₂]

Unirradiated MoO ₂ (HL)Cl ₂				Irradiated MoO ₂ (HL)Cl ₂			
Sin ² θ (obs)	Sin ² θ (calc)	hkl	Intensity %	Sin ² θ (obs)	Sin ² θ (calc.)	hkl	Intensity %
0.00845	0.009	001	67.74	0.00419	0.0044	100	18.4
0.01265	0.0133	010	100	0.00630	0.00653	010	33.9
0.01991	0.0198	100	24.7	0.00723	0.00715	001	100
0.03327	0.033	110	20.62	0.01134	0.01155	101	18.4
0.04198	0.042	111	51.78	0.015	0.01368	011	13
0.0397	0.036	002	17.11	0.01619	0.0176	200	24.1
0.0766	0.073	120	13.55	0.01889	0.01808	111	14.8
0.10172	0.1015	211	82.77	0.02921	0.0305	120	13.9
0.18085	0.1782	300	4.08	0.03115	0.03128	211	11.4
				0.03618	0.03513	012	10.1
				0.03304	0.033	102	12
				0.0388	0.03767	122	15.2
				0.03920	0.03953	112	16
				0.03957	0.0396	300	17.7
				0.04517	0.04613	310	14.4
				0.05457	0.05328	311	11.5
				0.05815	0.05877	030	16.1
				0.059183	0.05912	122	15.5
				0.06468	0.06435	003	10.7
				0.09882	0.09837	330	10.5
				0.12419	0.12312	033	10.1

tor are responsible for the overall change in the intensity of diffraction lines, crystallite size and unit cell parameters.³²

The particle sizes calculated using Scherer equation, $d = \frac{B \lambda}{\beta \cos \theta}$, (where d , B , λ , β and θ are the particle diameter, in Å, of the crystalline phase, Scherer constant (0.9), wavelength of X-ray beam (1.5439 Å), FWHM (Full Width Half Maximum) of the main diffraction line of XRD and its diffraction angle, respectively).

Surface Morphology

SEM micrographs of the ligand, unirradiated and irradiated samples of $[\text{MoO}(\text{HL})\text{Cl}_3]$ and $[\text{MoO}_2(\text{HL})\text{Cl}_2]$ are given in Fig. 9. Changes in the scanning electron micrographs indicate that the applied dose can cause changes in the surface morphology of crystals.

The SEM micrograph of the ligand as shown in Fig. 9(a) reveal an amorphous nature for the ligand. The SEM

images of the unirradiated $[\text{MoO}(\text{HL})\text{Cl}_3]$ and $[\text{MoO}_2(\text{HL})\text{Cl}_2]$ complexes of the ligand given in Figs. 9(b), (c), (e) and (f), respectively exhibit significant change in morphology upon complex formation. The SEM image of the unirradiated $[\text{MoO}(\text{HL})\text{Cl}_3]$ (Figs. 9b & 9c) shows the presence of micro rods and micro spheres, the diameter of which is less than 2 μm . The SEM image at lower resolutions of the unirradiated $[\text{MoO}_2(\text{HL})\text{Cl}_2]$ complex (Fig. 9e) distinctly reveal the formation of micro rods with an average diameter of approximately 2 μm . Higher resolutions of this complex show the presence of nano spheres on the surface of the microrods.

Figs. 9(d) and (g) depict the SEM images of the $[\text{MoO}(\text{HL})\text{Cl}_3]$ and $[\text{MoO}_2(\text{HL})\text{Cl}_2]$ complexes after γ irradiation. Irradiation of the complexes with γ rays have brought about noticeable changes in the particle size and morphology of the samples. The oxomolybdenum (V) complex have crystals with well defined edges and exhibits

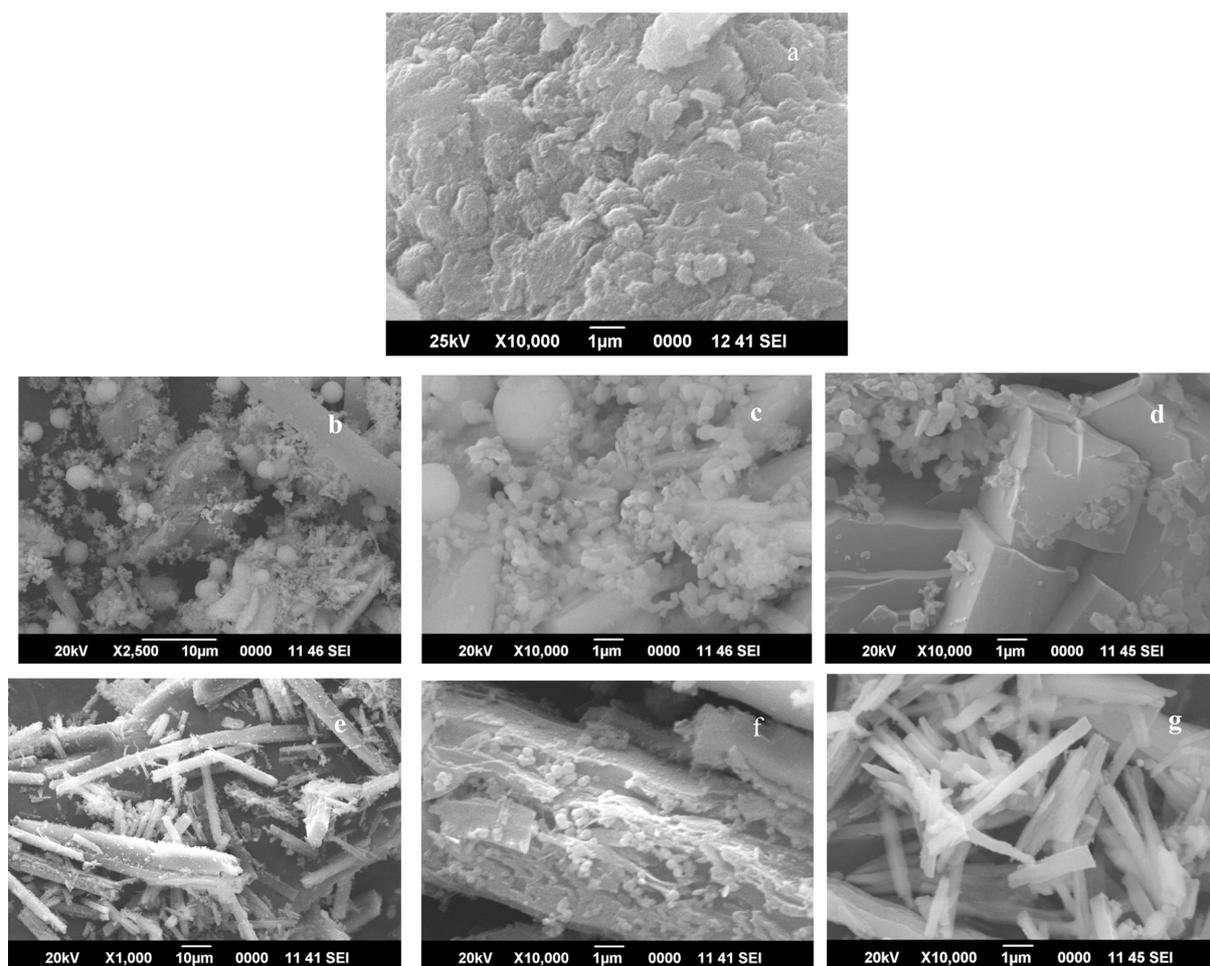


Fig. 9. SEM Micrographs of ligand and complexes. 9a Ligand, 9b & c $[\text{MoO}(\text{HL})\text{Cl}_3]$ before irradiation, 9d $[\text{MoO}(\text{HL})\text{Cl}_3]$ after irradiation, 9e & f $[\text{MoO}_2(\text{HL})\text{Cl}_2]$ before irradiation, 9g $[\text{MoO}_2(\text{HL})\text{Cl}_2]$ after irradiation.

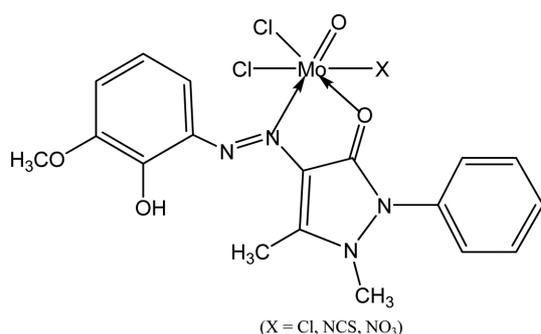


Fig. 10. Proposed 2D structure of [MoO(HL)XCl₂].

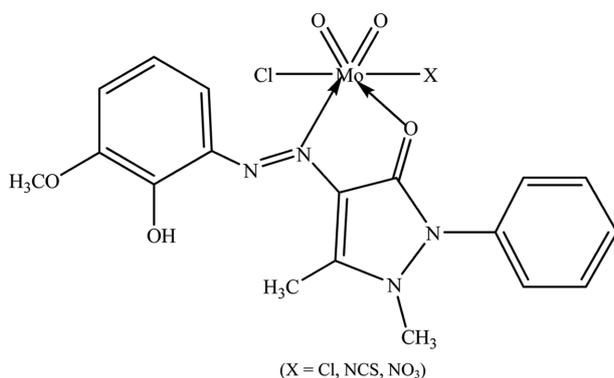


Fig. 11. Proposed 2D structure of MoO₂(HL)XCl].

some degree of aggregation. On the other hand, the nano spheres seen on the surface of the micro rods of dioxomolybdenum (VI) complex have completely vanished and the complex achieve a rod or stick shape with prismatic geometry. Moreover the length of the rods has been brought down to less than that before irradiation. The diameter or thickness of the rods has been reduced to less than 300 nm after γ irradiations. The results clearly indicate that γ irradiation has a vital effect in tuning the size and morphology of the synthesized complexes.

Antimicrobial Study

The ligand and complexes were not active against *M. tuberculosis* H37Rv, *E. coli* and *Lactobacillus leichmannii*.

Thus on the basis of the spectral data and physicochemical studies, a distorted octahedral geometry (Figs. 10 and 11) has been tentatively proposed for all the complexes.

CONCLUSION

The synthesis and characterization of octahedral oxomolybdenum (V) and dioxomolybdenum (VI) complexes with bidentate chelating ligand are reported. From the

spectroscopic, analytical and thermal analysis data, it can be concluded that the molybdenum existed in a distorted octahedral environment with the ligand. The FAB mass and EPR spectral data suggest monomeric nature of the complexes. X-ray diffraction study revealed that unit cell parameters have changed upon irradiation. SEM study showed that γ irradiation have impact on the size and morphology of the synthesized complexes.

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