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Der Pharma Chemica, 2015, 7(1):184-190
(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X
CODEN (USA): PCHHAX

Synthesis and characterization of oxomolybdenum (V) and dioxomolybdenum (VI) complexes with ONO donor hydrazone derived from 2-benzimidazolyl mercaptoaceto hydrazide and *o*-hydroxy aromatic aldehyde

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ABSTRACT

A few monomeric novel oxomolybdenum (V) and *cis*-dioxomolybdenum (VI) complexes with 2-benzimidazolyl mercaptoaceto hydrazone ligand (LH₂) of the general formula [MoO(LH)Cl₂] and [MoO₂(L).H₂O] respectively have been synthesized and characterized by elemental analyses, molar conductance, magnetic susceptibilities, UV-Visible, Infrared, ¹H NMR and ESR spectral studies. The interpretation of analytical data revealed that the complexes have 1:1 metal to ligand ratio and the ligands exhibit two different types of coordination patterns. The spectral data suggest that, the hydrazone ligands act as monobasic terdentate and exist in keto form in oxomolybdenum (V) complexes whereas in dioxomolybdenum (VI) complexes they act as dibasic terdentate and exist in enol form. ESR spectral data suggest that monomeric nature of oxomolybdenum (V) complexes with distorted octahedral geometry. The thermal stabilities of the complexes have been studied by TG and DTG techniques. The kinetic parameters were calculated from the thermal decompositions of dioxomolybdenum (VI) complexes using Coats–Redfern and MKN methods. The antibacterial activity studies have been under taken and results are discussed.

Keywords: Oxomolybdenum (V), Terdentate hydrazone, monomeric, Thermal stabilities, Antibacterial activity

INTRODUCTION

Coordination chemistry of molybdenum still engages the attention, due to the chemistry of its oxidation state, coordination number, their impact on structure, reactivity and because of the potential applications of molybdenum compounds [1-6]. In second series of transition metals, only molybdenum represents a biometal, important for microorganisms, plants and animals. Interest in the chemistry of metallacyclic oxomolybdenum (V) and (VI) complexes grows continuously particularly due to their potential relevance as model systems for molybdenum enzymes [7-11]. In a number of enzymatic systems, it is observed that, the oxidation state of molybdenum is generally high usually +5 or +6. These high oxidation states may confer properties upon the molybdenum protein complexes (enzymes) which may not have been apparent, either from the study of the simple molybdenum complexes or of other metalloenzymes. Among the molybdenum complexes, *cis*-dioxomolybdenum (VI) complexes have been extensively studied, particularly as models for the active sites of oxo-transfer molybdoenzymes such as sulfite and aldehyde oxidase, xanthine oxidase, xanthine dehydrogenase and nitrate reductase [12-14]. In addition to these the variety of chemical reactions has been reported to be catalysed by coordination compounds of molybdenum [15,16]. Again, coordination chemistry of molybdenum (VI) assumed special importance because it is relatively harmless to the environment [17] and the complexes are of significant interest and attention because of their biological activity including anticancer, antibacterial and antitumor properties [18-24]. In this context, the coordination environment around the molybdenum ion by the hydrazones and the increasing in biological

applications of the complexes has intensified an interest in this field. In continuation of our earlier work [25,26], this paper describes the synthesis and characterization of oxomolybdenum (V) and dioxomolybdenum (VI) complexes with tridentate ONO donor hydrazones derived from the condensation of 2-benzimidazolyl mercaptoaceto hydrazide and o-hydroxy aromatic aldehyde, LH₂ (Structure I).

MATERIALS AND METHODS

The chemicals used for the synthesis of ligands and complexes were of reagent grade. Molybdenum acetyl acetonate is prepared using standard method. The molybdenum and chlorine contents in the complexes were determined by using standard procedures [27]. Carbon, Hydrogen and Nitrogen were determined on Carlo Erba CHN analyzer. Conductance measurements were made using 10⁻³ M solutions of complexes in DMF using Elico conductivity bridge type CM-82 provided with a cell having cell constant 0.52 cm⁻¹. The electronic spectra of complexes in DMF were recorded on Hitachi 2001 spectrophotometer and IR spectra of the ligand and the complexes were recorded in KBr matrix using Perkin Elmer 783 model IR spectrometer in the range of 4000-200 cm⁻¹. Magnetic moments of oxomolybdenum (V) complexes were measured with a Faraday balance using mercury tetrathiocyanatocobaltate (II) as calibrant. The EPR spectra of oxomolybdenum (V) complexes at room temperature were recorded in the polycrystalline form on Varian E-4X band EPR spectrophotometer using TCNE as the g-marker. ¹H NMR spectra were recorded in DMSO-d₆ on a Bruker Avance-300 spectrometer using TMS as an internal standard. TG and DTG were carried out for the representative complexes on a Perkin Elmer analyzer in the range of room temperature to about 800°C in N₂ atmosphere at a heating rate of 10°C. The kinetic parameters were computed from the thermal decomposition of dioxomolybdenum (VI) complexes by using Coat's-Redfern and MKN methods. The ligands and their complexes were screened for their in-vitro antibacterial activity against the pathogenic bacteria *Salmonella Paratyphi* and *Bacillus Cirroflagellosus* by cup plate method.

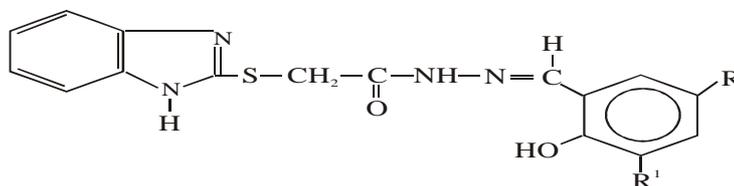
Synthesis of ligands: a) Synthesis of 2-benzimidazolyl mercaptoaceto hydrazide:

2-mercapto benzimidazole (18.7 g) was added with stirring to an absolute ethanolic solution (100 ml) containing sodium metal (2.8 g) and the resulting mercaptide was slowly treated with ethyl chloroacetate (35-40 ml). The mixture was refluxed on a steam bath for about an hour and filtered hot in a dry Buckner funnel. The alcoholic solution was further concentrated to half of its original volume and added hydrazine hydrochloride (15 ml). The solution was refluxed for about 20 h on a steam bath and cooled in ice. The separated solid was filtered, washed with water and crystallized from alcohol.

b) Synthesis of 2-benzimidazolyl mercaptoaceto hydrazone (LH₂):

To an ethanolic solution of 2-benzimidazolyl mercaptoaceto hydrazide (0.1mol) was added o-hydroxy aromatic aldehyde (0.1mol) and the mixture was refluxed on a steam bath for about 3 hours. The solution was filtered hot from the suspended impurities, concentrated and cooled. The separated solid was filtered, washed with water and crystallized from alcohol. The purity of the ligand was checked by TLC (Yield 68-72%).

Synthesis of oxomolybdenum (V) complexes: The complex was prepared by adding a methanolic solution of MoCl₅ (0.01 mol) in small quantities with stirring to a hot methanolic solution of the hydrazone ligand (0.01 mol). The pH of the mixture was adjusted to 4 with NaOAc / HOAc buffer and stirring was continued for 10-15 min. The complex which separated out was suction filtered, washed first with aqueous methanol and finally with ether and dried over P₄O₁₀ in vacuum (Yield 68-72%).



L¹H₂ - L⁵H₂

Ligand	R	R ¹
L ¹ H ₂	H	H
L ² H ₂	Cl	H
L ³ H ₂	Br	H
L ⁴ H ₂	CH ₃	H
L ⁵ H ₂	H	OCH ₃

I. Structure of ONO donor hydrazone ligands (LH₂)

Synthesis of dioxomolybdenum (V) complexes: Molybdenum acetyl acetonate (0.01mol) was dissolved in ethanol (~ 30 ml) in a beaker, to this hydrazone ligand (0.01mol) was added. The mixture was stirred on magnetic stirrer for ~ 3 hours at room temperature and refluxed on a water bath for about an hour. The colored complex thus obtained was filtered, washed with ethanol and dried under vacuum over anhydrous calcium chloride (Yield 68-70%).

RESULTS AND DISCUSSION

Oxomolybdenum (V) and dioxomolybdenum (VI) complexes are coloured, insoluble in common organic solvents but soluble in DMF and DMSO and are stable towards air and moisture at room temperature. The molar conductivity of the complexes in 10^{-3} M DMF solution lies in the range of 2.9-9.4 $\text{mho.cm}^2 \text{mol}^{-1}$, these values are much less than those expected for 1:1 electrolytes and hence all the complexes are treated as non-electrolytes [28]. Magnetic moments of the oxomolybdenum (V) complexes (1.71-1.78 BM) correspond to the spin only value (1.73 BM) expected for oxomolybdenum (V) complexes indicating the absence of any Mo-Mo interactions [29]. The interpretation of the analytical data (Table.1) reveal that the mononuclear complexes and the ligand coordinates to the molybdenum ion in 1:1 ratio, thus proposed formulae for oxomolybdenum (V) and dioxomolybdenum (VI) complexes are $[\text{MoO}(\text{LH})\text{Cl}_2]$ and $[\text{MoO}_2(\text{L})\cdot\text{H}_2\text{O}]$ respectively.

Electronic spectra: The ligands show bands at 328-370, 301-332 and 278-296 nm. The spectra of oxomolybdenum (V) complexes show moderately intense band in the region 365-390 nm which may be attributed to $\text{O}(\pi) \rightarrow \text{d}(\text{Mo})$ transitions. The band due to the transition ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ ($\text{d}_{xy} \rightarrow \text{d}_{z^2}$) is probably masked by the above band. The complexes also exhibit two more bands, a medium intensity band at ~ 490nm and 705-740 nm assigned to ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ ($\text{d}_{xy} \rightarrow \text{d}_{x^2-y^2}$) and ${}^2\text{B}_2 \rightarrow {}^2\text{E}_1$ ($\text{d}_{xy} \rightarrow \text{d}_{xz}, \text{d}_{yz}$) transitions respectively indicate the presence of an unpaired electron in the d_{xy} orbital. No bands are observed above 980 nm and hence the possibility of tetrahedral structure can be ruled out. From the electronic spectra the complexes can be at best considered as octahedral [30] with strong tetragonal distortion resulting from the Mo=O multiple bond. In dioxomolybdenum (VI) complexes the ligand bands are shifted due metal charge transfer transition. The absence of any bands in the visible beyond 425 nm suggest that the oxidation state of molybdenum there in is +6, which is further supported by the diamagnetic behaviour of the complexes.

Table-1: Analytical and physical data of oxomolybdenum (V) and dioxomolybdenum (VI) complexes with hydrazone ligands

Code	Complex formula [Abbreviation]	Found (Calcd) %					Molar conductance $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	μ_{eff} B.M
		C	H	N	Mo	Cl		
C ₁	$[\text{MoO}(\text{C}_{16}\text{H}_{13}\text{N}_4\text{O}_2\text{S})\text{Cl}_2]$ $[\text{MoO}(\text{L}^1\text{H})\text{Cl}_2]$	38.68 (39.02)	2.61 (2.64)	11.32 (11.38)	16.23 (16.26)	14.39 (14.43)	8.2	1.74
C ₂	$[\text{MoO}(\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_2\text{S})\text{Cl}_2]$ $[\text{MoO}(\text{L}^2\text{H})\text{Cl}_2]$	36.36 (36.47)	2.24 (2.28)	10.60 (10.64)	15.16 (15.19)	20.18 (20.23)	5.7	1.72
C ₃	$[\text{MoO}(\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_2\text{SBr})\text{Cl}_2]$ $[\text{MoO}(\text{L}^3\text{H})\text{Cl}_2]$	33.54 (33.63)	2.07 (2.10)	9.78 (9.81)	13.89 (14.01)	12.36 (12.43)	9.4	1.77
C ₄	$[\text{MoO}(\text{C}_{17}\text{H}_{15}\text{N}_4\text{O}_2\text{S})\text{Cl}_2]$ $[\text{MoO}(\text{L}^4\text{H})\text{Cl}_2]$	40.16 (40.32)	2.94 (2.96)	10.98 (11.07)	15.66 (15.81)	13.98 (14.03)	7.3	1.76
C ₅	$[\text{MoO}(\text{C}_{17}\text{H}_{15}\text{N}_4\text{O}_3\text{S})\text{Cl}_2]$ $[\text{MoO}(\text{L}^5\text{H})\text{Cl}_2]$	38.69 (39.08)	2.82 (2.87)	10.64 (10.73)	15.25 (15.33)	13.51 (13.60)	8.6	1.74
C ₆	$[\text{MoO}_2(\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_2\text{S})\text{H}_2\text{O}]$ $[\text{MoO}_2(\text{L}^1)\text{H}_2\text{O}]$	41.06 (40.44)	2.97 (3.01)	12.02 (11.94)	19.95 (20.37)	-	3.4	Diamag.
C ₇	$[\text{MoO}_2(\text{C}_{16}\text{H}_{11}\text{N}_4\text{O}_2\text{S})\text{H}_2\text{O}]$ $[\text{MoO}_2(\text{L}^2)\text{H}_2\text{O}]$	37.86 (38.06)	2.54 (2.58)	11.06 (11.10)	17.93 (18.02)	-	4.2	Diamag.
C ₈	$[\text{MoO}_2(\text{C}_{16}\text{H}_{11}\text{N}_4\text{O}_2\text{SBr})\text{H}_2\text{O}]$ $[\text{MoO}_2(\text{L}^3)\text{H}_2\text{O}]$	35.32 (34.97)	2.35 (2.38)	10.08 (10.20)	17.18 (17.47)	-	2.9	Diamag.
C ₉	$[\text{MoO}_2(\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}_2\text{S})\text{H}_2\text{O}]$ $[\text{MoO}_2(\text{L}^4)\text{H}_2\text{O}]$	41.97 (42.15)	3.29 (3.31)	11.46 (11.57)	19.72 (19.82)	-	2.4	Diamag.
C ₁₀	$[\text{MoO}_2(\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}_3\text{S})\text{H}_2\text{O}]$ $[\text{MoO}_2(\text{L}^5)\text{H}_2\text{O}]$	40.96 (40.82)	3.18 (3.22)	11.21 (11.19)	19.64 (19.18)	-	3.5	Diamag.

IR spectra: The important infrared frequencies exhibited by the free ligands and their complexes are listed in Table 2. The infrared spectra of hydrazones (LH_2) show bands in the regions 3215-3190, 3062-3025 and 1700-1678 cm^{-1} assigned to $\nu(\text{N-H})$ of hydrazide, $\nu(\text{N-H})$ of imidazole moiety and $\nu(\text{C=O})$ respectively. The bands due to $\nu(\text{C-O})$ and $\nu(\text{C=N})$ are located in the regions 1510-1485 and 1650-1622 cm^{-1} respectively. These ligands show a broad band around 3410-3365 cm^{-1} due to the intramolecular hydrogen bonded -OH. The ligands exhibit two different types of coordination pattern. In all the complexes the band due to $\nu(\text{OH})$ disappears indicating clearly the involvement of oxygen of the phenolic group in coordination after deprotonation. The shift of the $\nu(\text{C-O})$ to higher frequency by 18-22 cm^{-1} indicates the coordination of phenolic oxygen to the molybdenum ion. In oxomolybdenum (V) complexes the band due to $\nu(\text{NH})$ of hydrazide remain unaltered this suggest that coordination of the ligand in keto form. The intense ligand band in the region 1510-1485 cm^{-1} shift to higher region ~18-22 cm^{-1} this supports the

deprotonation of phenolic –OH on coordination with metal ion. The $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ bands in the spectrum of the ligand show a down field shift by 14-20 cm^{-1} in the spectra of the complexes indicating coordination through carbonyl oxygen and azomethine nitrogen respectively [31]. The coordination of azomethine nitrogen atom is further supported by the shift of $\nu(\text{N}-\text{N})$ vibration observed in the region 989-975 cm^{-1} in the ligands to higher frequency by ~15-18 cm^{-1} in the complexes this is due to the reduction of lone pair repulsion forces in the adjacent nitrogen atoms. A very strong band observed in the region of 954-940 cm^{-1} in the spectra of oxomolybdenum (V) complexes corresponds to Mo=O stretching frequency [31].

In IR spectra of the dioxomolybdenum (VI) complexes the bands due to $\nu(\text{N}-\text{H})$ hydrazide and $\nu(\text{C}=\text{O})$ disappear due to enolization of the ligands followed by coordination of carboxyl oxygen to the metal ion via deprotonation, it is further supported by the appearance of a new band around 1616-1602 cm^{-1} due to $>\text{C}=\text{N}-\text{N}=\text{C}<$. The band due to $\nu(\text{C}=\text{N})$ also suffers a negative shift by 16-20 cm^{-1} indicating the involvement of azomethine nitrogen in the coordination. The complexes contain a medium intense broad band around 3530-3475 cm^{-1} have been assigned $\nu(-\text{OH})$ of coordinated water, further confirmed by thermal studies. In the present dioxomolybdenum (VI) complexes the acetyl acetonate groups are totally exchange by hydrazone ligands that act as dibasic terdentates. The complexes with cis MoO₂ moiety exhibit two strong bands at 980-935 and 904-865 cm^{-1} assignable to symmetry and asymmetric $\nu(\text{O}=\text{Mo}=\text{O})$ respectively [32,33].

In the far IR region the complexes show bands around 552-538 and 432-414 cm^{-1} are assigned to $\nu(\text{Mo}-\text{O})$ and $\nu(\text{Mo}-\text{N})$ modes respectively. The $\nu(\text{Mo}-\text{N})$ band is usually sharp and strong and the $\nu(\text{Mo}-\text{O})$ band is broad and strong. Since a large dipole moment change is involved in the vibrations of the Mo-O bond comparison to that of the Mo-N bond. Hence it is expected that the $\nu(\text{Mo}-\text{O})$ band should appear at a higher energy in comparison to that of the $\nu(\text{Mo}-\text{N})$ band. The Mo-O bond length is usually shorter than the Mo-N bond length and this also supports the occur of the $\nu(\text{Mo}-\text{O})$ band at a higher energy in comparison to that of the $\nu(\text{Mo}-\text{N})$ band. In oxomolybdenum (V) complexes the band around 328-315 cm^{-1} is assigned to the $\nu(\text{Mo}-\text{Cl})$ mode [33].

Table-2: Important IR frequencies of the hydrazone ligands and their complexes

Ligand / Complex	$\nu(\text{OH})$ phenolic	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$ azometh	$\nu(\text{Mo}-\text{O})$	$\nu(\text{Mo}-\text{N})$	$\nu(\text{Mo}=\text{O})$
C ₁₆ H ₁₄ N ₄ O ₂ S L ¹ H ₂	3398	1684	1648	-	-	-
[MoO(C ₁₆ H ₁₃ N ₄ O ₂ S)Cl ₂] [MoO(L ¹ H)Cl ₂]	-	1663	1630	541	426	948
[MoO ₂ (C ₁₆ H ₁₂ N ₄ O ₂ S)H ₂ O] [MoO ₂ (L ¹)H ₂ O]	-	-	1628	539	432	972 868
C ₁₆ H ₁₃ N ₄ O ₂ SCl L ² H ₂	3409	1678	1624	-	-	-
[MoO(C ₁₆ H ₁₂ N ₄ O ₂ SCl)Cl ₂] [MoO(L ² H)Cl ₂]	-	1658	1608	533	419	954
[MoO ₂ (C ₁₆ H ₁₁ N ₄ O ₂ SCl)H ₂ O] [MoO ₂ (L ²)H ₂ O]	-	-	1610	542	427	965 873
C ₁₆ H ₁₃ N ₄ O ₂ SBr L ³ H ₂	3375	1697	1635	-	-	-
[MoO(C ₁₆ H ₁₂ N ₄ O ₂ SBr)Cl ₂] [MoO(L ³ H)Cl ₂]	-	1674	1618	552	430	945
[MoO ₂ (C ₁₆ H ₁₁ N ₄ O ₂ SBr)H ₂ O] [MoO ₂ (L ³)H ₂ O]	-	-	1616	547	422	978 892
C ₁₇ H ₁₆ N ₄ O ₂ S L ⁴ H ₂	3368	1689	1628	-	-	-
[MoO(C ₁₇ H ₁₅ N ₄ O ₂ S)Cl ₂] [MoO(L ⁴ H)Cl ₂]	-	1666	1612	546	426	942
[MoO ₂ (C ₁₇ H ₁₄ N ₄ O ₂ S)H ₂ O] [MoO ₂ (L ⁴)H ₂ O]	-	-	1612	538	418	938 879
C ₁₇ H ₁₆ N ₄ O ₃ S L ⁵ H ₂	3402	1672	1645	-	-	-
[MoO(C ₁₇ H ₁₅ N ₄ O ₃ S)Cl ₂] [MoO(L ⁵ H)Cl ₂]	-	1656	1620	551	422	951
[MoO ₂ (C ₁₇ H ₁₄ N ₄ O ₃ S)H ₂ O] [MoO ₂ (L ⁵)H ₂ O]	-	-	1622	540	428	966 864

¹H NMR spectra: The ¹H NMR spectrum the ligand (L²H₂) shows a multiplet between 7.28-8.08 ppm due to aromatic protons, singlet at 3.72 ppm due to –CH₂– protons, singlet at 8.32 ppm is due to azomethine proton. The singlets at 12.03, 11.02 and 12.67 ppm are assigned to phenolic –OH, –NH (hydrazine) and –NH (imidazole) respectively. In the dioxomolybdenum (VI) complex [MoO₂(L²).H₂O] the signal of phenolic –OH has been disappeared indicating the involvement of phenolic oxygen in the coordination *via* deprotonation. Further the proton

singlet signal at 11.02 ppm due to -NH (hydrazine) is also disappears confirms that ligand acts as dibasic terdentate and exist in an enol form in the complex, which is also supported by IR. The azomethine proton peak is shifted to downfield to 8.64 ppm suggests that the involvement of azomethine nitrogen to the metal ion. The multiplet signals are observed between 7.26-8.02 ppm due to aromatic protons.

ESR spectra: The ESR spectrum of polycrystalline form of $[\text{MoO}(\text{L}^3\text{H})\text{Cl}_2]$ complex is characterized by only a single line with unresolved parallel and perpendicular components. The ESR parameters were found to be $g_{\parallel} = 1.9402$, $g_{\perp} = 1.9052$ and $g_{\text{av}} = 1.9197$. The calculated g_{av} value indicates that the complex is monomeric with molybdenum in the pentavalent state [34-36].

Thermal studies: Thermal stabilities of the representative complexes $[\text{MoO}(\text{L}^1\text{H})\text{Cl}_2]$, $[\text{MoO}_2(\text{L}^1)\text{H}_2\text{O}]$ and $[\text{MoO}_2(\text{L}^5)\text{H}_2\text{O}]$ were studied using TG in air at a heating rate of 10°C per min in conjugation with DTG. The TG and DTG curves of the complexes exhibit a plateau $\sim 195^\circ\text{C}$ indicating the absence of coordinated water or other solvent molecule. The complex $[\text{MoO}(\text{L}^1\text{H})\text{Cl}_2]$ undergoes decompositions in three steps in between temperature range of $195\text{-}570^\circ\text{C}$ as denoted by the DTG peaks at 242°C , 310°C and 466°C . First mass loss of 7.07 (Calcd 7.12%) corresponds to the elimination of one chlorine atom. Monodentate ligand trans to oxo oxygen is weakly bound to molybdenum and are known to undergo cleavage on heating [37]. The second mass of 41.05% (41.87%) corresponds to the loss of a part of the ligand $\text{C}_9\text{H}_8\text{N}_3\text{OS}$, finally a mass loss has been ascribed to the oxidative decomposition of the remaining part of the complex to give MoO_3 as the ultimate residue.

The dioxomolybdenum (VI) complexes undergo decomposition in two steps (Table 3). The complexes were stable upto $\sim 125^\circ\text{C}$, they registered the first decomposition between the temperature range $\sim 130\text{-}185^\circ\text{C}$, the weight loss in the step corresponds to the loss of one mole of coordinated water molecule. The second step of decomposition occur between the temperature range $\sim 185\text{-}590^\circ\text{C}$, the weight loss in this step corresponds to the loss of one mole of ligand. Beyond 600°C a plateau is obtained which indicates the formation of stable molybdenum oxide (MoO_3) product.

Table-3: Thermal data for thermal decomposition of dioxomolybdenum (VI) complexes

Complex	Decomposition temp. range (K)	Peak temp (K)	Decomposition product	Weight loss (%)		Residue (%) MoO_3	
				Obs	Calcd	Obs	Calcd
$[\text{MoO}_2(\text{L}^1)\text{H}_2\text{O}]$	395-460	416	1 mole H_2O	3.74	3.83	29.92	30.60
	460-856	538	1 mole ligand	65.38	65.13		
$[\text{MoO}_2(\text{L}^5)\text{H}_2\text{O}]$	408-466	423	1 mole H_2O	3.66	3.60	27.62	28.76
	466-868	554	1 mole ligand	68.05	67.23		

The kinetic parameters such as activation energy, entropy of activation and Arrhenius factor were calculated from the thermal decomposition stages of dioxomolybdenum (VI) complexes (Table 4) using Coat's-Redfern and MKN equations by graphical as well as least square method. In each complex, the energy of activation value for the second stage decomposition was found to be higher than those for the first stage decomposition but the entropy of activation values are in reverse manner, which indicates that the rate of decomposition decreases in stepwise reactions [38].

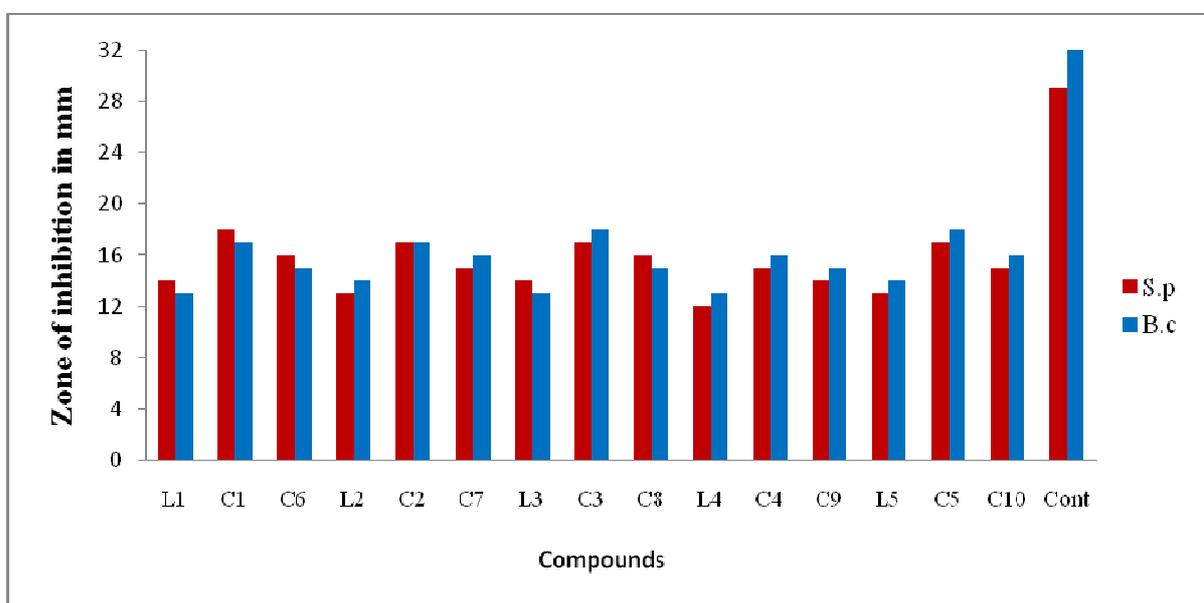
Table-4: Kinetic parameters for the two stages of thermal decomposition of dioxomolybdenum (VI) complexes using Coat's-Redfern (MKN) equation

Complex	Decomposition stage	Energy of activation, E_a (kJ mol^{-1})	Arrhenius factor, A (S^{-1})	Entropy of activation, ΔS^\ddagger ($\text{JK}^{-1} \text{mol}^{-1}$)
$[\text{MoO}_2(\text{L}^1)\text{H}_2\text{O}]$	I	22.6374 (22.6412)	117.7479 (67.3484)	-208 (-212)
	II	47.9465 (49.1466)	22.61×10^4 (17.66×10^4)	-147 (-152)
$[\text{MoO}_2(\text{L}^5)\text{H}_2\text{O}]$	I	18.9033 (19.0375)	36.4553 (22.7664)	-216 (-222)
	II	49.5861 (50.8878)	31.74×10^4 (24.41×10^4)	-143 (-147)

Antimicrobial activity: The ligands and their complexes were screened for antibacterial activity against *Salmonella Paratyphi* and *Bacillus Cirroflagellosus* by cup-plate method and the results obtained are presented in Table 5. It evident from the bacterial screening data that, hydrazones are weakly active than complexes, overall, the ligands and the complexes are less active as compared to the standard *Contrimoxazole* used in the present study (fig.1). The comparative study of the ligands and their complexes revealed that the oxo- complexes showed higher activity than the dioxo-complexes. The low activity of dioxo-complexes may be due to low lipid solubility, steric and pharmacokinetic factors which play vital roles in deciding the potency of an antibacterial agent [39].

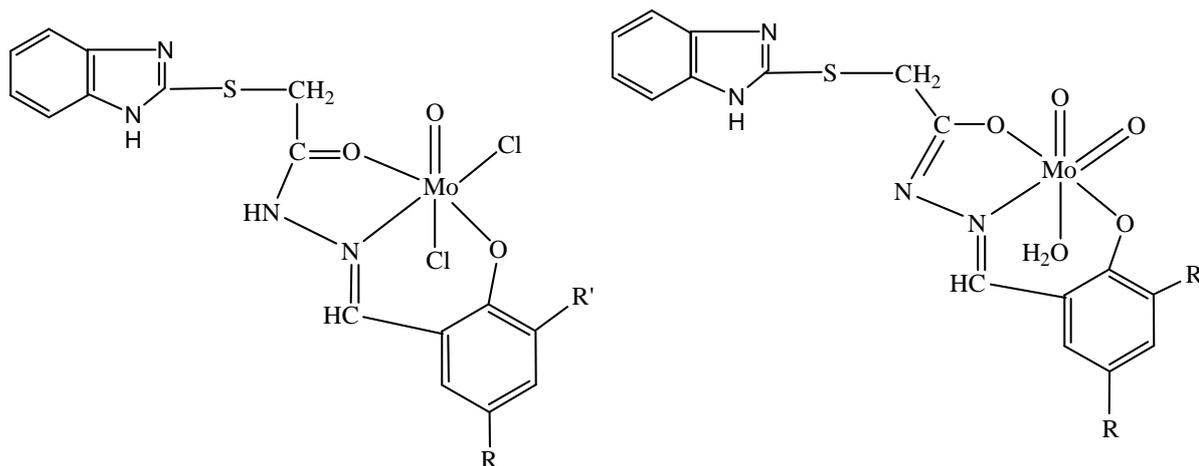
Table -5: Antibacterial activity of the hydrazones and their complexes (zone of inhibition in mm)

Code	Compound	Antibacterial activity	
		S.p	B.c
L ₁	L ¹ H ₂	14	13
C ₁	[MoO(L ¹ H)Cl ₂]	18	17
C ₆	[MoO ₂ (L ¹).H ₂ O]	16	15
L ₂	L ² H ₂	13	14
C ₂	[MoO(L ² H)Cl ₂]	17	17
C ₇	[MoO ₂ (L ²).H ₂ O]	15	16
L ₃	L ³ H ₂	14	13
C ₃	[MoO(L ³ H)Cl ₂]	17	18
C ₈	[MoO ₂ (L ³).H ₂ O]	16	15
L ₄	L ⁴ H ₂	12	13
C ₄	[MoO(L ⁴ H)Cl ₂]	15	16
C ₉	[MoO ₂ (L ⁴).H ₂ O]	14	15
L ₅	L ⁵ H ₂	13	14
C ₅	[MoO(L ⁵ H)Cl ₂]	17	18
C ₁₀	[MoO ₂ (L ⁵).H ₂ O]	15	16
Cont	Contrimoxazole	29	32

**Fig.1. Antibacterial activity of hydrazones and their complexes**

CONCLUSION

On the basis of all the above analytical, spectral and thermal studies, a distorted octahedral geometry (Structure II) has been tentatively proposed for all the complexes. The hydrazone ligand acts as monobasic tridentate in a keto form in oxomolybdenum complexes whereas in dioxomolybdenum complexes it acts as dibasic tridentate in an enol form. The results of antibacterial data show that the antibacterial activities of the ligands were enhanced on complexation, but less active than the standard used. It is observed that, oxo-complexes showed higher activity than the dioxo-complexes.



II. Proposed structures of oxomolybdenum (V) complexes

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