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Synthesis, spectral and antibacterial studies of oxomolybdenum (V) and dioxomolybdenum (VI) complexes with 2-imidazolyl mercaptoaceto hydrazone

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ABSTRACT

Synthesis of new oxomolybdenum (V) and dioxomolybdenum (VI) complexes with 2-imidazolyl mercapto aceto hydrazone (LH_2; structure I) derived from 2-imidazolyl mercaptoaceto hydrazide and o-hydroxy aromatic aldehyde are reported. The complexes have been characterised by elemental analysis, molar conductance, magnetic susceptibility, IR, UV-vis, EPR and ^1H NMR spectral studies. The physicochemical studies and spectral data indicate that LH_2 acts as monovalent ONO donor containing chelating agent, thus exists in keto form. From analytical data the stoichiometry of the oxomolybdenum (V) and dioxomolybdenum (VI) complexes have been found to be 1:1 (metal: ligand) ratio with the general formula $[MoO(LH)Cl_2]$ and $[MoO_2(LH)Cl]$ respectively. Dioxomolybdenum (VI) complexes are diamagnetic, contain MoO_2^{2+} species, where as oxomolybdenum (V) complexes are paramagnetic and all the complexes are non-electrolytic nature. 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 thermogravimetric techniques. The hydrazones and oxomolybdenum (V) and dioxomolybdenum (VI) complexes were screened for their in vitro antibacterial activities against Salmonella paratyphi and Bacillus cirroflagellosus. Antibacterial studies of the present complexes show that the oxomolybdenum (V) complexes were more potent bactericides than the ligand and the dioxomolybdenum (VI) complexes.

Keywords: Dioxomolybdenum (VI), Spectral studies, Thermal stabilities, Distorted octahedral, Antibacterial activities.

INTRODUCTION

Molybdenum is a versatile transition metal with a large number of stable and accessible oxidation states, the oxidation states +4, +5 and +6 has received much attention recently. It has been shown that dioxomolybdenum (VI) and oxomolybdenum (V) complexes are stable, whereas oxomolybdenum (IV) complex is unstable, but stable at vacuum condition. The higher oxidation states of molybdenum are dominated by complexes contain the oxo and dioxomolybdenum groups [1-3]. The coordination chemistry of hexavalent molybdenum is dominated [4] by complexes of coordination number 6. A substantial number of complexes with MoO_2^{2+} core with six coordinated octahedral structures are reported. Within the second series of transition metals only molybdenum represents a biometal important for microorganisms, plants and animals.

Molybdenum is an essential component of the enzyme nitrogenase, vitamin, mineral supplements, and cofactor for a lot of enzymes involved in protein synthesis. A variety of chemical reactions has been reported to be catalysed by coordination compounds of molybdenum [5-7]. The complexes of molybdenum have also been studied as a model

for molybdenum containing enzymes [8]. Studies on complexes of oxomolybdenum (V) and dioxomolybdenum (VI) have opened up a new vista of research and analysis of uncharted biochemical significance.

The increasing biological applications namely antimicrobial, antifungal, antitubercular, antitumor activities [9-10] etc., of the complexes of transition metal with hydrazones have intensified interest in research and analytical studies on the metallic complexes [11-13]. We report here in the synthesis and characterisation of some new complexes of oxomolybdenum (V) and dioxomolybdenum (VI) with a tridentate hydrazone derived from the condensation of 2-imidazolyl mercaptoaceto hydrazide and o-hydroxy aromatic aldehyde abbreviated as LH_2. During our investigation various spectral (IR, UV-vis, ^{1}HNMR and EPR) methods have been used. The thermal behaviour and antibacterial activities of the complexes have also been studied.

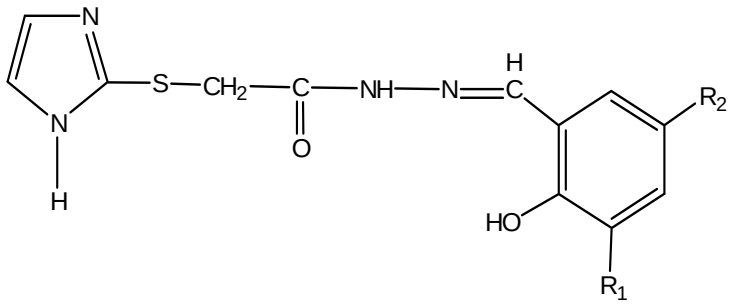
MATERIALS AND METHODS

All the chemicals used for the synthesis of ligand and complexes were of reagent grade. Methanol and acetyl acetonate were purified by standard methods. Molybdenum pentachloride (Aldrich chemicals) is used and molybdenum acetyl acetonate is prepared by literature method [14].

The metal content and chlorine in all the complexes were determined by using standard procedures [15]. Carbon, Hydrogen and Nitrogen were determined on Carlo Erba CHN analyser. 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 were recorded on a Nicolet 170 SX FT-IR spectrophotometer in KBr pellets in the range 4000-400 cm^{-1}. Magnetic moments of the complexes were measured with a Faraday balance using mercury (II) tetrathiocyanatocobaltate (II) as calibrant. The EPR spectra of oxomolybdenum (V) complexes at room temperature were recorded on Varian E-4X band EPR spectrophotometer using TCNE as the g marker. ^{1}H NMR spectra of dioxomolybdenum (VI) complexes were recorded on a Bruker Avance 300 MHz spectrometer operating at 300.13 MHz. Thermograms were recorded on a Perkin Elmer analyser in N_2 atmosphere at a heating rate of 10 ^{0}C. Antibacterial activities of the ligands (LH_2) and their oxomolybdenum (V) and dioxomolybdenum (VI) complexes along with the standard were carried out against the pathogenic bacteria *Salmonella paratyphi* and *Bacillus cirroflagellosus* by cup plate method.

Synthesis of 2-imidazolyl mercaptoaceto hydrazone (LH_2)

To an absolute ethanolic solution (100 ml) containing sodium metal (2.8 g) was added with stirring 2-mercapto imidazole (10 g) and the resulting mercaptide was slowly treated with ethyl chloroacetate (30-40 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 concentrated to about 50% of its original volume and hydrazine hydrate was added. 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 (yield 72-74%). Further to an ethanolic solution of 2-imidazolyl mercaptoaceto hydrazide (0.1mol), salicylaldehyde / substituted salicylaldehyde (0.1mol) were added and the mixture was refluxed on a steam bath for about 3h. 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 structure of the ligand is represented as follows.



Ligand	R_1	R_2
L^1H_2	H	H
L^2H_2	OCH_3	H
L^3H_2	H	CH_3

I. Structure of ligand (LH_2)

Synthesis of oxomolybdenum (V) complexes

The chloride complex was prepared by adding a methanolic solution of $MoCl_5$ (2mmol) in small quantities with stirring to a hot methanolic solution of the ligand (2mmol) in methanol. The pH of the mixture was adjusted to 4 with NaOAc / HOAc buffer and stirring was continued for 10-15 min. The solid complex which separated out was suction filtered, washed first with aqueous methanol and finally with ether and dried over P_4O_{10} in vacuum.

Synthesis of dioxomolybdenum (VI) complexes

Molybdenum acetyl acetonate (0.01 mol) was dissolved in ethanol (30-40 ml) was added. The mixture was stirred on magnetic stirrer for about three hours at room temperature and refluxed on a water bath for about an hour. The orange red coloured complex thus obtained was filtered, washed several times with ethanol and dried under vacuum over anhydrous $CaCl_2$.

RESULTS AND DISCUSSION

All the metal complexes are coloured stable towards air and moisture at room temperature. They are partially soluble in common organic solvents such as acetone, chloroform and soluble in DMF and DMSO. The molar conductivity of all the complexes in 10^{-3}M DMF solution lies in the range 2.9-6.2 mho.cm^2 mol^{-1} indicating the non electrolytic nature [16]. Magnetic moment of oxomolybdenum (V) complexes (1.72-1.79BM) corresponds to the spin only value (1.73BM) expected for oxomolybdenum (V) complexes indicating the absence of any Mo-Mo interactions [17]. All the dioxomolybdenum (VI) complexes are diamagnetic as expected for a d^o system. The analytical data (Table.1) shows that all the complexes are mononuclear and the ligand coordinates to the metal ion in 1:1 ratio thus proposed formulae for oxomolybdenum (V) and dioxomolybdenum (VI) are $[MoO(LH)Cl_2]$ and $[MoO_2(LH)Cl_2]$ respectively.

Table 1: Results of chemical analysis, magnetic susceptibility and molar conductance data of the ligands and their oxomolybdenum (V) and dioxomolybdenum (VI) complexes.

Ligand&Complex	Elemental analysis Found (Calcd%)					Magnetic Moment (BM)	Molar conductance ($\Omega^{-1}cm^2mol^{-1}$)
	C	H	N	Cl	Mo		
L^1H_2	51.80 (52.17)	4.19 (4.35)	19.68 (20.29)	–	–	–	–
$[MoO(L^1H)Cl_2]$	32.09 (31.44)	2.33 (2.40)	12.86 (12.22)	14.94 (15.50)	20.09 (20.95)	1.72	5.4
$[MoO_2(L^1H)Cl]$	33.14 (32.84)	2.62 (2.50)	12.24 (12.77)	8.03 (8.09)	21.34 (21.88)	–	6.2
L^2H_2	50.02 (50.98)	4.51 (4.57)	18.92 (18.30)	–	–	–	–
$[MoO(L^2H)Cl_2]$	31.12 (31.97)	2.63 (2.66)	11.23 (11.47)	14.15 (14.55)	19.12 (19.66)	1.79	2.9
$[MoO_2(L^2H)Cl]$	32.96 (33.30)	273 (2.77)	11.74 (11.95)	7.41 (7.58)	19.86 (20.48)	–	4.7
L^3H_2	53.06 (53.79)	4.70 (4.83)	18.91 (19.31)	–	–	–	–
$[MoO(L^3H)Cl_2]$	32.64 (33.05)	2.61 (2.75)	11.43 (11.86)	14.86 (15.04)	19.82 (20.32)	1.74	3.3
$[MoO_2(L^3H)Cl]$	33.92 (34.47)	2.76 (2.87)	12.02 (12.37)	7.79 (7.84)	20.91 (21.20)	–	5.1

The important IR frequencies of ligand LH_2 and its complexes are given in Table. 2 the IR spectra of ligands show a broad band around 3380–3345cm^{-1} due to the intramolecular hydrogen bonded –OH. The ligands show bands in the regions 3200–3185, 3050–3030 and 1690–1665cm^{-1} assigned to υ(N-H) of hydrazide, υ(N-H) of imidazole moiety and υ(C=O) respectively. The bands due to υ(C–O) and υ(C=N) are located in the regions 1520–1490 and 1640–1625cm^{-1} respectively. In oxomolybdenum (V) and dioxomolybdenum (VI) complexes the band due to υ(OH) disappears indicating clearly the involvement of oxygen of the phenolic group in coordination after deprotonation. The band due to υ(NH) of hydrazide remain unaltered this suggest that coordination of the ligand in keto form. The intense ligand band in the region 1520-1495cm^{-1} shift to higher region ~15-20cm^{-1} this supports the deprotonation of phenolic –OH on coordination with metal ion. The υ(C=O) and υ(C=N) bands in the spectrum of the ligand show a down field shift by 22-30cm^{-1} in the spectra of the complexes indicating coordination through carbonyl oxygen and azomethine nitrogen respectively [18,19]. The coordination of azomethine nitrogen atom is further supported by the shift of υ(N-N) vibration observed in the region 996-985cm^{-1} in the ligands to higher frequency by ~ 16-20cm^{-1} in the complexes this is due to the reduction of lone pair repulsion forces in the adjacent nitrogen atoms [20]. A very strong band observed in the region of 948-942cm^{-1} in the spectra of oxomolybdenum(V) complexes corresponds to Mo=O stretching frequency [18], dioxomolybdenum(VI) complexes displays two Mo=O stretching bands at 945-935cm^{-1} and 916-900cm^{-1} due to symmetric and antisymmetric stretching of the cis-MoO_2^{2+} core [21]. The MoO_2^{2+}

prefers to form the cis configuration due to maximum utilisation of the dπ groups. The new weak bands at 585-560cm^{-1} and 474-465cm^{-1} in the metal complexes have been assigned to the υ(Mo-O) and υ(Mo-N) modes respectively.

Table.2: Important IR spectral data of ligands and their oxomolybdenum (V) and dioxomolybdenum (VI) complexes

Ligand/Complex	ν(N-H) imidazole	ν(N-H) Hydrazine	ν(C=O)	ν(C=N) azomethine	ν(C-O) Phenolic	ν(N-N)	ν(M=O)	ν (M-O)	ν(M-N)
L^1H_2	3032	3192	1686	1638	1508	987	-	-	-
$[MoO(L^1H)Cl_2]$	3031	3196	1658	1613	1526	1004	944	576	473
$[MoO_2(L^1H)Cl]$	3035	3194	1662	1617	1524	1007	942 906	582	468
L^2H_2	3048	3180	1679	1627	1503	996	-	-	-
$[MoO(L^2H)Cl_2]$	3051	3185	1654	1605	1520	1014	946	569	472
$[MoO_2(L^2H)Cl]$	3047	3182	1651	1603	1522	1017	937 904	571	466
L^3H_2	3034	3185	1672	1631	1494	992	-	-	-
$[MoO(L^3H)Cl_2]$	3031	3188	1652	1613	1509	1009	942	581	470
$[MoO_2(L^3H)Cl]$	3036	3190	1648	1618	1512	1012	993 911	575	473

Electronic spectra of the tridentate ONO donor hydrazone ligand and the oxomolybdenum (V) complexes were recorded in DMF. All the oxomolybdenum (V) complexes show moderately intense band in the region 350-385nm which may be attributed to O(π) → d(Mo) transitions. The band due to the transition $^2B_2 \rightarrow {}^2A_1$ ($d_{xy} \rightarrow d_{z2}$) is probably masked by the above bands. The complexes exhibit two more bands, a medium intensity band at ~485nm and 715-750nm assigned to $^2B_2 \rightarrow {}^2B_1$ ($d_{xy} \rightarrow d_{x2-y2}$) and $^2B_2 \rightarrow {}^2E_1$ ($d_{xy} \rightarrow d_{xz}, d_{yz}$) transitions respectively (an unpaired electron is in the d_{xy} orbital). The electronic spectra thus indicate octahedral environment for all the complexes [22]. No bands are observed above 1000nm and hence the possibility of tetrahedral structure can be ruled out. The complexes can be at best considered as octahedral with strong tetragonal distortion resulting from the Mo=O multiple bond.

In electronic spectra of dioxomolybdenum(VI) complexes three bands observed in the region 290-425nm are due to metal charge transfer transition the absence of any bands in the visible region beyond 430nm suggest that the oxidation state of molybdenum there in is +6 which is also supported by the diamagnetic behaviour of the complexes.

The X-band ESR spectrum of $[Mo(L^1H)Cl_2]$ has been recorded in the polycrystalline form at room temperature using DPPH free radical as the g marker. The spectrum (Fig.1) is characterised only a single line with unresolved parallel and perpendicular components. The absorption at ~3350 G is characteristic of Mo^{+5} species and the absence of any half field signal at ~1500 G rules out any metal-metal interaction in the complex. The ESR parameters (Table 3) were found to be $g_{\parallel}$ =1.9428 $g_{\perp}$=1.9072 and g_{av}=1.9191. The calculated g_{av} value indicates that the complex is monomeric with molybdenum in the pentavalent state [23].

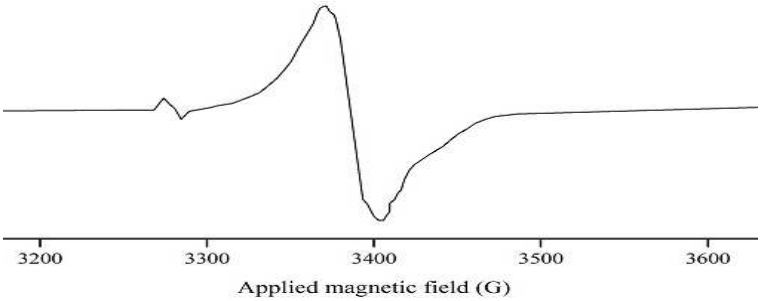


Fig.1: ESR spectrum of $[Mo(L^1H)Cl_2]$

^{1}H NMR spectral data of the ligand L^1H_2 and its dioxomolybdenum (VI) complex is presented in Table 3. ^{1}H NMR spectrum of the ligand L^1H_2 shows a multiplet between 7.32-8.02ppm due to aromatic protons. Singlet at 3.68ppm due to $–CH_2–$ protons, singlet at 8.36ppm due to azomethine proton. The singlets at 12.04, 11.02 and 12.76ppm are assigned to phenolic –OH, –NH (hydrazine) and –NH (imidazole) respectively. But in the case of dioxomolybdenum (VI) complexes the signal of phenolic –OH has been disappeared indicating the involvement phenolic oxygen in the coordination via deprotonation. The singlet at δ8.36 observed in the spectrum of ligand shows down field shift indicating nitrogen of azomethine group in complexes. Signal due to –NH(hydrazine) at δ11.02 in the free ligand,

appears almost same region in the complexes. Presence of this signal in the complex indicates that ligand exists in the keto form.

Table 3: ESR and ^{1}H NMR spectral data

ESR spectral data of $[MoO(L^1H)Cl_2]$		^{1}H NMR spectral data		
		L^1H_2	$[MoO_2(L^1H)Cl]$	Assignment
$g_{\parallel}$	1.9428	7.32-8.02m	7.26-8.01m	Aromatic protons
		3.68s	4.22s	$-CH_2$-protons
$g_{\perp}$	1.9072	8.36s	8.62s	-N=CH azomethine proton
		11.02s	11.01s	-NH hydrazine proton
g_{av}	1.9191	12.04s	_	-OH proton(phenolic)
		12.76s	12.75s	-NH imidazole proton

Thermal decomposition behaviour of the complexes $[MoO(L^1H)Cl_2]$ and $[MoO_2(L^2H)Cl]$ were studied using TG and DTG techniques by heating in air at a rate of 10 ^oC per min. The TG and DTG curves of the complexes (Fig. 2 & 3) exhibit a plateau up to 210 ^oC indicating the absence of coordinated water or other solvent molecules and also that the complexes are stable up to this temperature. The complex $[MoO(L^1H)Cl_2]$ is stable still 210 ^oC with total decomposition of the complex at 560 ^oC in three stages as denoted by the DTG peaks at 235 ^oC, 308 ^oC and 472 ^oC. First mass loss of 7.68% (Calcd 7.73%) 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 [24]. The second mass of 35.98% (Calcd 36.81%) corresponds to the loss of a part of the ligand $C_5H_6N_3OS$, 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.

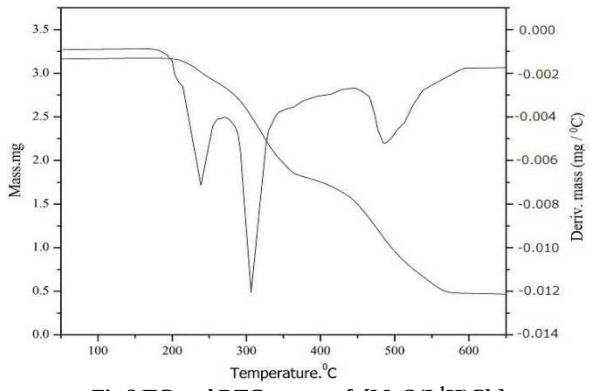


Fig.2 TG and DTG curves of $[MoO(L^1H)Cl_2]$

The decomposition of the complex $[MoO_2(L^2H)Cl]$ occured in three stages as indicated by the DTG peaks at 295 ^oC and 424 ^oC and 752 ^oC. The first decomposition starts at ~230 ^oC and ended at 340 ^oC. The mass loss of 32.68% (Calcd 33.23%) corresponds to the loss of ≈ 0.5mole of the ligand. The second stage was more complicated it ranged from 340-535 ^oC. The weight loss in this stage was 58.27% (Calcd 59.18%). The weight of the sample at 535 ^oC was consistent with the formation of MoO_3. The sample shows another weight loss in the region 685-770 ^oC. The weight loss of the sample at 770 ^oC was less then that expected if MoO_2 was formed this may be due to the volatilisation of MoO_3 above 685 ^oC[25].

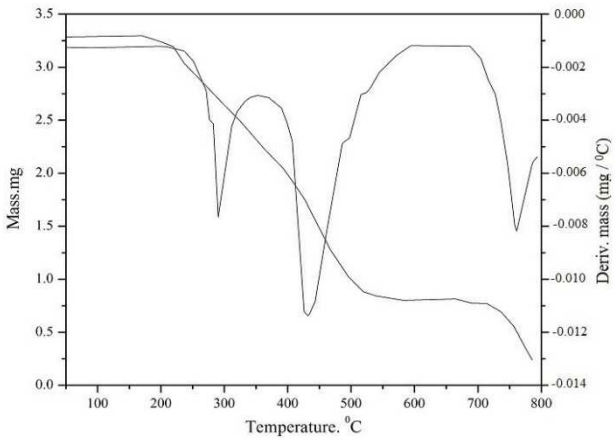


Fig.3 TG and DTG curves of $[MoO_2(L^2H)Cl]$

Antibacterial activity:

The ligands and their complexes were screened for antibacterial activity against *Salmonella paratyphi* and *Bacillus cirroflagellosus* and the results obtained are presented in Table 4. 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. The antibacterial studies reveal that oxomolybdenum (V) complexes show higher activity than the dioxomolybdenum (VI) complexes (Fig. 4). The antibacterial activity of the complexes may result from various modes by which these antibacterials act on bacteria. It may be due to factors such as inhibition of cell wall formation leading to lysis, damage of the cell wall leading to loss of cell contents and hence to a cell death, inhibition of protein production and there by arresting bacterial growth and inhibition of the production of nucleic acids, thereby preventing bacterial production. Metal chelates have simultaneously polar and non-polar properties; this makes them suitable for permeation in to cells and tissues. Changing hydrophilicity and lipophilicity probably leads to a reduction of the solubility and permeability barriers of cells, which in turn enhances the bioavailability of chemotherapeutics on the one hand and their potentiality on the other[26]. 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.

Table 4: Antimicrobial activity of the ligands and their oxomolybdenum (V) and dioxomolybdenum (VI) complexes (Zone of inhibition in mm)

Sl No	Compound	Antibacterial activity	
		S.p	B.c
1	L^1H_2	12	11
2	$[MoO(L^1H)Cl_2]$	20	21
3	$[MoO_2(L^1H)Cl]$	16	15
4	L^2H_2	13	12
5	$[MoO(L^2H)Cl_2]$	23	22
6	$[MoO_2(L^2H)Cl]$	15	17
7	L^3H_2	11	14
8	$[MoO(L^3H)Cl_2]$	23	24
9	$[MoO_2(L^3H)Cl]$	18	16
10	Contrimoxazole	30	28

S.p=*Salmonella paratyphi* B.c=*Bacillus cirroflagellosus*

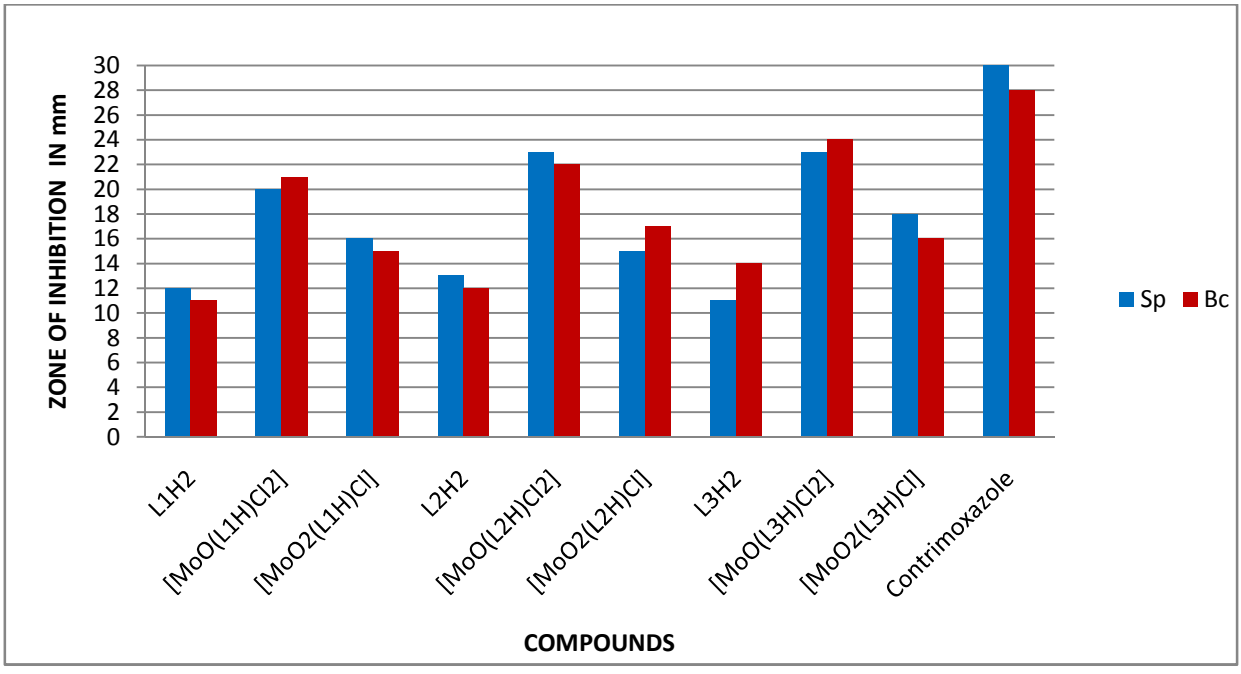
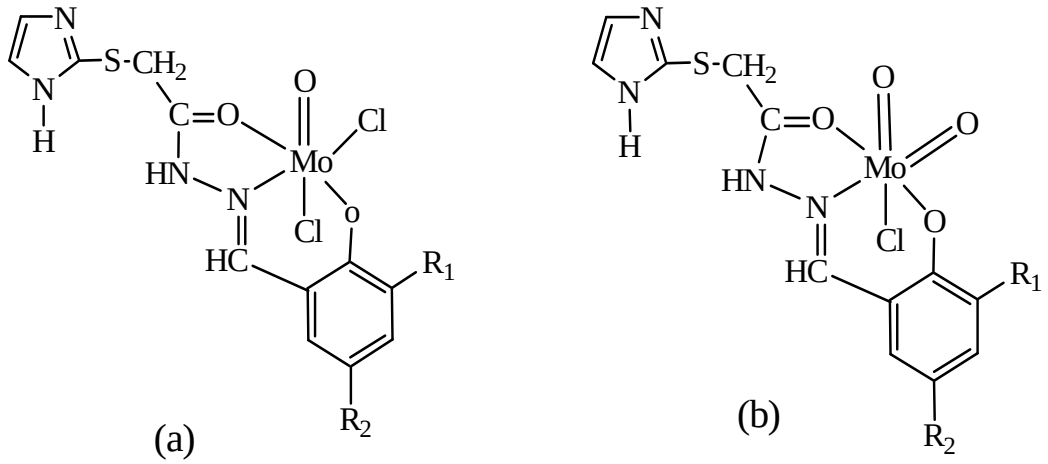


Fig.4 Antibacterial activity of ligands and their complexes

CONCLUSION

The spectroscopic, analytical and thermal data, indicates that the molybdenum exist in a distorted octahedral environment with the ligand as a monovalent tridentate chelating agent (Structure II). The results of antibacterial studies revealed that the oxomolybdenum complexes show higher activity than the ligand and the dioxomolybdenum complexes.



II. Proposed structures of (a) oxomolybdenum (V) (b) dioxomolybdenum (VI) complexes.

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