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Metallurgical and Biological Activity of Peroxo Complexes of Molybdenum (VI) Containing Organic Acid and Amine Bases

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Abstract: This study describes with the preparation, characterization and bioactivity of peroxo complexes [A: $MoO(O_2)$(gly)(Q); B: $MoO(O_2)$(ala)(2-pic)]of Mo(VI)] containing organic acid and amine bases. Both the complexes A and B were characterized by a variety of physicochemical techniques, viz., elemental analyses, molar conductivity, IR, NMR and electronic spectral studies. The analytical data were in good agreement with the proposed emperical formulae of both the complexes. The molar conductance values indicated both the complexes are non-electrolytes in DMF revealing that the anions are covalently bonded in all the cases. The magnetic moment values indicated that both the complexes were dimagnetic in nature suggesting that there were no changes in the oxidation states of the metal ions upon complexation. The electronic spectral data of the complexes A and B showed bands at 315-355 nm region due to the charge transfers band only. The antimicrobial properties of the peroxo complexes of Mo(VI) indicated that both the complexes were stronger antibacterial and antifungal agents. However, the highest antifungal activity was shown in the complex B against *A. niger* (16 mm) while the complex A of Mo(VI) showed lowest activity (10 mm). The MIC experiment showed that the complex B of Mo(VI) were more potent against all the bacteria tested than the complex A. Results showed that the complex A of Mo(VI) exhibits more toxic to brine shrimp compared to complex B of Mo(VI) indicating the lower values of LC_{50} for both the exposure 16 and 36 h.

Key words: Peroxo complexes, Mo(VI), metallurgical and biological activity, toxicity

INTRODUCTION

Peroxo heteroligand transition metal complexes are an important class of reactive intermediates in catalytic oxidations and they very likely play a substantial role as active centers in biological processes involving dioxygen species (Falbe, 1975; Rebsdat and Mayer, 1987; Swarup *et al*., 2004). Some more recent review articles on the dioxygen and the peroxo metal complexes (Zarza *et al*., 1994) and on the molybdenum complexes summarized the current research and existing knowledge in these areas (Citeau, 2005).

Peroxo complexes of Mo(VI) have been known for a long time (Preet *et al*., 2004) and their catalytic activity has been a topic of considerable interest (Bartzatt, 2003; Wu *et al*., 2002). Since dioxygen, hydrogen peroxide or alkyl hydroperoxides do not undergo a spontaneous oxygen transfer to olefins to yield the corresponding epoxides, efforts have been made during the last decades for a selective activation of these oxidizing agents. Only in the case of ethylene, a direct epoxidation using dioxygen has successfully been applied in a technical scale process. Higher epoxides, which can not be synthesized this way owing to unselective oxidation, are usually obtained by the reaction of an olefin with an activated peroxidic compound. The mechanistic details of the activation steps involved herein have been subject of experimental and theoretical studies since Prileshajew investigated the reaction between olefins and per-carboxylic acids. Starting with the work of Milas, transition metal compounds like V_2O_5, MoO_3, WO_3 or OsO_4 have been used as catalysts for olefin epoxidation with hydrogen peroxide, leading to the first technical processes for olefin epoxidation with transition metal catalysts about 30 years later. In these processes, alkyl hydroperoxides are activated by high valent transition metal catalysts. A heterogeneous titanium/silica support catalyzes the epoxidation of propylene with *tert*.-butyl hydroperoxide (from O_2 and isobutene by autoxidation) in the SHELL process, while a homogeneous system based on soluble molybdenum (VI) compounds is used in the ARCO/HALCON process in combination with *tert*.-butyl hydroperoxide or ethylbenzene hydro peroxide (from ethylbenzene and O_2). The by-products *tert*.-BuOH and 1-phenylethanol are converted into *tert*.-$BuOCH_3$ and styrene for economical reasons.

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Around the same time as the start of development of prodrugs, transition metal complexes were found to have physiological properties (Aquino *et al*., 2001; Bryliakov *et al*., 2001). In all cases where transition metal complexes are used as drugs, the systems are designed so that upon ligand dissociation, cleavage or elimination, the metal is delivered as the cytotoxic species. The cytotoxicity of the metal raises the possibility of using transition metal complexes as potential prodrugs in conjunction with known anti cancer compounds. More specifically, by binding a known anti tumor agent as the dissociating ligand, we may have the capability of using a transition metal as a delivery system for anti tumor agents. Another incentive for the development of these types of systems is that upon cleavage of the pharmacologically active ligand, delivery of a cytotoxic metal species also occurs (Talati and Gandhi, 1983; Ronconi *et al*., 2003). This report deals the synthesis, spectral data and properties of the peroxo complexes of Molybdenum (VI) with organic acids and amine bases. It also describes the antimicrobial and toxicological activity of the complexes.

MATERIALS AND METHODS

General methods for the preparation of the complexes of the type $[Mo(O)(O_2)_2.amH.L_2]$; where, M = Mo(VI), amH = amino acids, such as glycine, alaline ; L_2 = ligands such as quinoline, 2-picoline.

The molybdic acid (1.5 g, 0.01 mol) in H_2O_2 (30%, 30-50 mL) was heated and filtered to obtain a clear solution. Solution of the ligands such as 2-picoline, quinoline were dissolved in ethanol (30-50 mL). The solution of other ligands of amino acids such as glycine, alaline dissolved in water with slowly constant stirring. These above three solutions were mixed carefully with slowly constant stirring and reduced the volume to 20 mL. The yellow precipitate of the complex was observed immediately. The product was isolated and washed with water and ethanol. The complex was dried *in vaccuo* over P_2O_5 in a vaccum desiccator.

Reaction of the complexes with allyl alcohol (Reaction A): A stoichiometric amount of allyl alcohol was added to a suspension of complex A (1.03 g and 0.003 mol) or complex B (1.23 g and 0.003 mol) in THF (30 mL). The mixture was stirred under reflux at 70°C for 40 h. Microdistillation under 19 mm Hg pressure yielded glycidol (0.14 g, 77% yield) at 142-150°C. The glycidol was identified by means of its phenylurethan derivative, mp. 58-60°C[35] (60°C) (Heinish *et al*., 1980).

Catalytic reaction with allyl alcohol (Reaction B): Allyl alcohol (16.04 g, 0.30 mol) was dissolved in dioxane (20 mL) and 0.9 g of complex A or B was added followed by 30% H_2O_2 (20 mL). The mixture was kept under reflux at 90°C for 24 h. The reaction mixture was filtered and the filtrate distilled at 19 mm Hg pressure. The product collected at 178-180°C was glycerol (53% yield). The glycerol as identified as its tribenzoyl ester derivative, m.p. 68-70°C[37] (m.p. 69°C) (Baranyi and Feher, 1979).

Reaction with triphenylphosphine (Reaction C): A solution of triphenylphosphine (1.642 g, 0.006 mol) in THF (20 mL) was added to a suspension of complex A (1.04 g, 0.003 mol) or B (1.32 g, 0.003 mol) in THF (40 mL). The mixture was stirred under reflux for 48 h. TLC indicated that the reaction was complete. The reaction mixture was filtered and the residue was collected. A yellowish white powder was recovered from the filtrate which was identified by melting point as triphenylphosphine oxide, m. p. 156-157°C(m.p. 157°C) (Szente *et al*., 1984).

Reaction with triphenylarsine (Reaction D): A solution of triphenylarsine (1.12 g, 0.003 mol) in THF (30 mL) was added to a suspension of complex A (1.93 g, 0.003 mol) or complex B (1.53 g, 0.003 mol) in THF (4-5 mL). The mixture was refluxed for 48 h at 60°C. TLC indicated the triphenylarsine was converted completely into triphenylarsine oxide. The reaction mixture was filtered and the residue was collected. Evaporation of the filtrate yielded the product, m.p.(190-192°C), (Meyer-Rohn and Puschmann, 1981).

The present complexes were characterized by IR, UV, magnetic moment, melting point, conductivity measurement and NMR studies.

Antimicrobial assay: *In vitro* antimicrobial screening is generally performed by disc diffusion method for primary selection of the compounds as therapeutic agent (Nakazawa and Yamauchi, 1980; Kulieve, 1979a). Disc diffusion method is highly effective for rapidly growing microorganisms and the activities of the test compounds are expressed by measuring the diameter of the zone on inhibition. Generally the more susceptible the organism the bigger is the zone of inhibition. The method is essentially a qualitative or semi quantitative test indicating sensitivity or resistance of microorganisms to the test materials as well as bacteriostatic or bactericidal activity of a compound (Kulieve, 1979b). The standard test microorganisms were collected from the Molecular Genetics Laboratory, Department of Pharmacy, Rajshahi University. The complexes A and B were tested against the pathogenic bacteria viz., *Streptococcus*-β-

haemolyticus, *Bacillus subtilis*, *Sarcina lutea*, *Pseudomonas aeruginosa*, *Bacillus megaterium*, *Escherichia coli*, *Salmonella typhi*, *Shigella sonnei*, *S. flexneri*, *S. dysenteriae*, *S aurus*, *S. shiga* and the pathogenic fungi viz., *Aspergillus niger*, *A. fumigatus* and *A. flarus* as a concentration of 200 μg disc $^{-1}$ for each. The antimicrobial activity was determined after 72 h of incubation at room temperature (30°C). The media used in these respects were nutrient agar (DIFCO) for antibacterial assay and potato dextrose agar for antifungal assay. The experiment was performed in duplicate to minimize errors.

Minimum Inhibitory Concentration (MIC) of a compound is defined as the lower concentration of that compound in a medium without visible growth of the test organisms. The basic principle is the dilution tests which comprises the serial dilution of the antimicrobial agent inoculated with the organism. For the test, standard serial dilution technique was employed (Jaura and Sharma, 1979). The media used in this respect was nutrient broth (DIFCO). The MIC of the complexes A and B was determined against pathogenic bacteria viz., *Pseudomonas aeruginosa*, *Streptococcus-β-haemolyticus*, *Escherichia coli*, *Bacillus subtilis*.

Cytotoxicity bioassay: Brine shrimp lethality bioassay is a recent development in the assay procedure for the bioactive compounds (Doadrio, 1980), which indicates cytotoxicity as well as a wide range of pharmacological activities e.g., anticancer, antiviral, pesticidal etc. of the compounds Here, *in vivo* lethality test were carried out using brine shrimp nauplii eggs (*Ariemia salina* L.). Eggs were placed on one side of a small tank divided by a net containing 3.8% NaCl solution for hatching. In other side of the tank, a light source was placed in order to attract the nauplii. After two days of hatching period the nauplii were ready for the experiment as described previously. Three mg of the complexes were accurately measured and dissolved in 0.6 mL of DMSO to get a concentration of 5 mg mL $^{-1}$. From the stock solutions, 10, 20, 40, 80 and 160 μL were placed in 5 different vials making the volume up to 5 mL.

The brine shrimp nauplii 10 in number were then placed in each vial. For the control test of each vial, one vial containing the same volume of DMSO plus water up to 5 mL was used. After 24 h of incubation, the vials were observed using a magnifying glass and the number of survivors in each vial were counted and noted. From this data, the percentage of mortality of the nauplii was calculated for each concentration and LC_{50} and LC_{99} values were determined using probit analysis.

RESULTS AND DISCUSSION

The formation of the complexes can be shown by the following reaction:

$$MoO_3 + H_2O_2 + amH + L \rightarrow [MoO(O_2)(amH)^2] + H_2O$$

Where, M = Mo(VI)
L = glycine, 2-picoline, quinoline, amH, alanine.

The analytical data and their physical properties of the complexes are given in Table 1 and 2. The analytical data are in good agreement with the proposed emperical formulae of the present complexes. Their structures have been proposed on the basis of conductivity and magnetic measurements and electronic spectral data (Table 2).

The molar conductance of 10^{-3} M solutions of the complexes in DMSO were measured at 30°C. The molar conductance values (Table 2) indicate all the complexes are non-electrolytes in DMF revealing that the anions are covalently bonded in all the cases.

Salient features of the IR spectra of the complexes are summarized in Table 3. The complexes A and B display

Table 1: Analytical data and physical properties of the Mo complexes

No.	Complexes	Y%	M%	C%	H%	N%	Melting point (±0.5°C)
A	$[MoO(O_2)(gly)(Q)]$	67	22.57	36.90	3.41	9.77	205
			(22.78)	(37.05)	(3.56)	(9.97)	
B	$[MoO(O_2)(ala)(2\text{-pic})]$	68	23.02	34.69	4.41	10.03	175
			(23.23)	(34.86)	(4.60)	(10.17)	

Figure in parenthesis indicates the calculated values

Table 2: Physical properties and electronic spectral data of the Mo complexes

No.	Complexes	Colour	Molar conductance $\Omega^{-1}cm^2Mole^{-1}$	Magnetic moment μ_{eff} (BM)	λ max (nm)
A	$[MoO(O_2)(gly)(Q)]$	Light yellow	4.5	0.702	315
B	$[MoO(O_2)(ala)(2\text{-pic})]$	Yellowish green	3.7	0.419	355

Table 3: IR spectral data of the Mo complexes

No.	ν (N-H) cm^{-1}	ν (C = O) cm^{-1}	ν (C-O) cm^{-1}	ν (M = O) cm^{-1}	ν (M-N) cm^{-1}	Y_1 (O-O) cm^{-1}	ν_3 (M<O) cm^{-1}	ν_2 (M<O) cm^{-1}
A	3386 br	1606 vs	1550	971 vs	439 w	903 s	623 br	523 w
B	3421 br	1627 s	1505 m	894 s	-	844 m	636 w	559 w

Related band intensities are denoted by vs, s, m, w and br representing very strong, strong, medium, weak and broad band, respectively

band 1606-1627 and 1505-1550 cm^{-1} due to v(C = O) and v(C-O), respectively, significantly lower man that of free ligand v(C = O) = 1700 cm^{-1} and v(C-O) = 1600 cm^{-1}; indicating the coordination of amino acid through its carboxylate anions. The disappearance of the v(O-H) mode observed in the free amino acid molecule clearly indicate the loss of protons from O-H group upon coordination, revealing that acids are dinegative bidentate ligand coordinating through the carboxylate anion.

The complexes A and B show eleven v(N-H) bands from 3386 to 3421 cm^{-1}, which are significantly lower than the free ligand (amino base) bands (3300-3500 cm^{-1}). It clearly suggests the coordination of amino groups through nitrogen atoms of amino base. Further more, the metal peroxo grouping gives rise to three IR active vibrational modes. These are mainly O-O stretching (v_1), the symmetric M-O stretch (v_2) and the anti-symmetric M-O stretch (v_3). The characteristic v_1(O-O) mode of the complexes appeared at 844-903 cm^{-1}, indicating that the dioxygen moieties are bonded on side-on fashion with the Mo(VI). In the present complexes, the v_3 and v_2 modes appeared at 623 to 636 and 523-559 cm^{-1}, respectively. The v(M = O) (M = Mo) bands in the complexes A and B appeared at 894-971 cm^{-1}.

The in-plane and out-of-plane ring deformation modes of heterocyclic amines observed at 500 and 700 cm^{-1}, respectively undergo a positive shifts in mixed ligand complexes confirming their coordination through nitrogen. The presence of metal nitrogen bonding in the complex A is evident from the appearance of v(M-N) modes at 439 cm^{-1} in the spectra of the complexes (Doadrio *et al*., 1980; Yang and Chang, 1982).

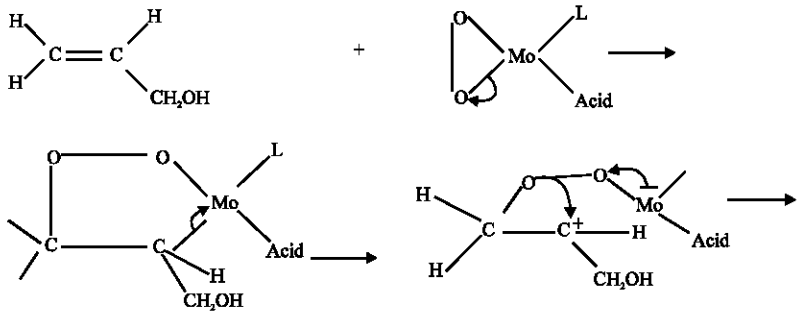
The observed values of effective magnetic moment (μ_{eff}) of the complexes of room temperature are given in Table 2. The magnetic moment values of dioxomolybdenum (VI) complexes (0.419 to 0.702 BM) indicated that these complexes were dimagnetic in nature suggesting that there were no changes in the oxidation states of the metal ions upon complexation. The electronic spectral data (Table 2) of the complexes A and B showed bands at 315-355 nm region due to the charge transfers band only (Bruce *et al*., 1984).

Reactivity: Various peroxo complexes of transitional metals containing monodentate and bidentate organic moieties were found to be reactive towards oxidation reaction.

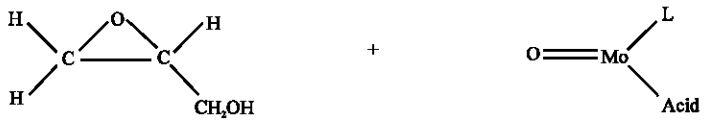
To explore the reactivity of the present peroxo complexes, complexes A and B were allowed to react with triphenylphosphine. The reaction produced triphenylphosphine oxide (Reaction A). The product showed IR band at 1193 cm^{-1}, attributed to the v(P = O) mode. The IR spectrum of the metal residue of reaction showed the disappearance of v_1(O-O) bands which indicate the transfer of peroxo oxygen to the substrate.

The present peroxo complexes were found to liberate iodine on treatment with aqueous potassium iodide. Base on this observation, the possible reactivity of complexes towards olefinic compounds could be explored.

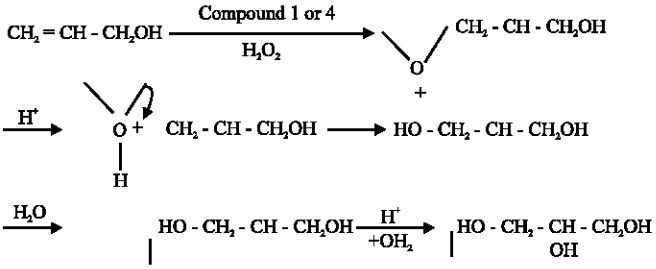
However, the compounds A and B reacts stoichiometrically with allyl alcohol (Reaction A) producing glycidol as identified by an IR band 1057 cm^{-1} due to the C-O-C stretching mode (Ramadan and Hamza, 1999). A possible reaction path is given in Scheme 1 and 2.



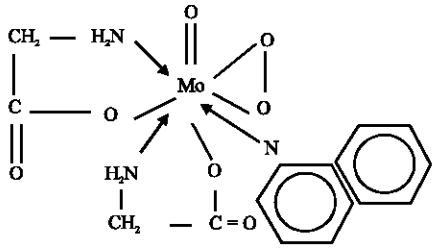
Scheme 1



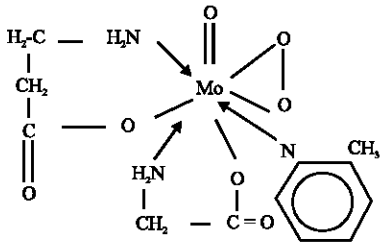
Scheme 2



Scheme 3



Complex A: $[MoO(O_2)(Gly)_2Q]$



Complex B: $[MoO(O_2)(ala)_2(2\text{-pic})]$

Fig. 1: Possible structure of the complexes A and B

In reaction B, compound A or B was used to catalyze the oxidation of allyl alcohol by H_2O_2 and in this case the product isolated was glycerol. The IR spectrum of this product was identical with that of an authentic sample. A possible reaction path is shown in Scheme 2. Reaction C and D produced triphenylphosphine oxide and triphenylarsine oxide, respectively. The products display IR bands at 1195 and 880 cm^{-1} due to v(P = O) and v(As = O) modes, respectively. The IR spectra of the residue of reaction C and D showed the disappearance of v_1(O-O) bands which indicate the transfer of the peroxo oxygen to the substrates. A possible reaction path is shown in Scheme 3.

Reaction B produced triphenylarsine. The product displays IR band 880 cm^{-1} due to v(As = O) mode (Bortolini *et al*., 1986; Sabastiyan and Venkappayya, 1992). The IR spectra of the residue of reaction showed the disappearance of v_1(O-O) band which indicates the transfer of peroxo oxygen to the substrate. A possible reaction path is given in Scheme 3.

On the basis of the above assessment the possible structure of the A and B of Mo(VI) are given in the Fig. 1.

Table 4: Antibacterial activity of the complexes of Mo(VI)

	Diameter of zone inhibition (mm) 200 μg $disc^{-1}$	
Bacteria	Complex A	Complex B
S. dysenteriae	22	26
E. coli	30	18
S. bodyii	29	15
S.-β-haemolyticus	26	17
S. sonnei	27	16
P. auriginosa	32	20
S. aureus	25	17
B. subtilis	25	17
S. typhi	26	26
S. flexneri	27	27
B. megatrium	34	34
S. lutea	33	33
S. shiga	29	29

Table 5: Antifungal activity of the complexes of Mo(VI) against

Sample No.	Complexes	Diameter of zone inhibition (mm) 200 μg $disc^{-1}$ *A. niger*	*A. fumigatus*	*A. flavus*
A	$[MoO(O_2)(gly)(Q)]$	10	12	14
B	$[MoO(O_2)(ala)(2\text{-pic})]$	16	13	15

Antimicrobial activity: Antimicrobial activities of the test samples are expressed by measuring the zone of inhibition observed around the area.

The results revealed that the complexes are more microbial toxic than the free metal ions or ligands. Both the complexes of metals under investigations showed more or less activities against the thirteen pathogenic bacteria tested. From the zone of inhibition, it is observed that the complexes A and B of Mo(VI) exhibited greater susceptibilities towards all the bacteria used. The results also revealed that the complex A of Mo(VI) showed strong activity against both the Gram positive and Gram negative bacteria than the complex B indicating the higher zone of inhibition (Table 4).

From the zone of inhibition, it is observed that both the complexes A and B of Mo(VI) showed significant activity towards all the fungi used. The highest antifungal activity was shown in the complex B against *A. niger* (16 mm) while the complex A of Mo(VI) showed lowest activity (10 mm) (Table 5).

The present findings of MIC experiment showed that the complex B of Mo(VI) were more potent against all the bacteria tested than the complex A. The bacteria

Table 6: The MIC values of the complexes of Mo(VI) against bacteria *P. auriginosa*, *S.-β-haemolyticus*, *E. coli*, *B. subtilis*

		Minimum inhibition concentration (μg mL^{-1})			
No.	Complexes	*P. auriginosa* (-ve)	*S.-β-haemolyticus* (+ ve)	*E. coli* (-ve)	*B. subtilis* (- ve)
A	[MoO(O_2)(gly)(Q)]	32	32	16	32
B	[MoO(O_2)(ala)(2-pic)]	64	64	32	64

Table 7: Brine shrimp lethality bioassay for Mo(VI) complexes

		Exposure 16 h		Exposure 36 h	
Sample No.	Complex	LC_{50}	LC_{99}	LC_{50}	LC_{99}
		(μg mL^{-1})			
A	[MoO(O_2)(gly)(Q)]	14.31	137.13	7.89	100.99
B	[MoO(O_2)(ala)(2-pic)]	14.98	195.51	9.92	85.93

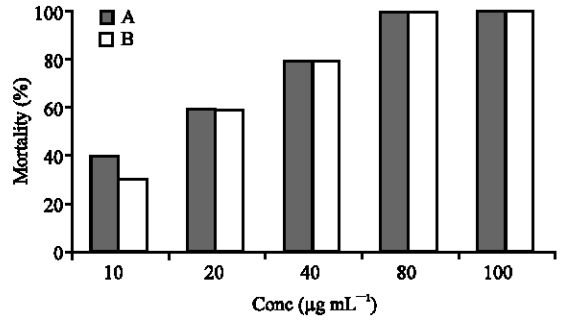


Fig. 2: Toxicidal effect peroxo complexes of Mo(VI) ions after 16 h exposure against brine shrimp nauplii [A: MoO(O_2)(gly)(Q), B: MoO(O_2)(ala)(2-pic)]

P. auriginosa, *S.-β-haemolyticus* and *B. subtilis* were more resistant to the complex B having the higher values of MIC, while the bacteria *E. coli* was least resistant (Table 6). These findings also clearly support the results of earlier antibacterial and antifungal investigations.

Cytotoxicity activity: The mortality rate of brine shrimp nauplii was found to be increased with the increase of concentration for all the complexes (Fig. 2). Figure 2 showed that the concentration 160 μL mL^{-1} caused 100% mortality in brine shrimp for both the complexes of Mo(VI) at the exposures of 16 and 36 h.

Results showed that the complex A of Mo (VI) exhibits more toxic to brine shrimp compared to complex B of Mo(VI) indicating the lower values of LC_{50} for both the exposure 16 and 36 h (Table 7).

CONCLUSIONS

It is concluded that the analytical data were in good agreement with the proposed emperical formulae of both the complexes. The molar conductance values indicated both the complexes are non-electrolytes in DMF revealing that the anions are covalently bonded in all the cases. The complex A of Mo(VI) showed strong activity against both the gram positive and gram negative bacteria than the complex B indicating the higher zone of inhibition. The present findings of MIC experiment showed that the complex B of Mo(VI) were more potent against all the bacteria tested than the complex A. Results showed that the complex A of Mo (VI) exhibits more toxic to brine shrimp compared to complex B of Mo(VI) indicating the lower values of LC_{50} for both the exposure 16 and 36 h.

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