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New insights into the chemistry of *cis*-dioxomolybdenum (VI) complexes with symmetrical tetradentate Schiff bases and their antibacterial activity

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ABSTRACT

Synthesis of five new dioxomolybdenum(VI) complexes having formula [MoO2(mac)](acac)2, with a Schiff base , derived from condensation of furil with 2,3 - diamino - 5 - bromopyridine and their cyclization with β - diketones are reported. The dioxomolybdenum(VI) complexes have been characterized by elemental analyses, molar conductance, UV - Vis, IR and thermal studies. The probable coordination number of molybdenum is six. All complexes of dioxomolybdenum(VI) have octahedral geometry. Almost all the complexes showed low to moderate activity against S. aureus and S. typhi, the enhancement in the antibacterial activity being explained on the basis of chelation theory.

Keywords: *Dioxomolybdenum(VI), furil, macrocyclic complexes.*

1. INTRODUCTION

The *cis*-dioxomolybdenum(VI) complexes with Schiff bases dominate coordination chemistry of molybdenum(VI) [1]. The molybdenum complexes have played the important role as molybdoenzymes due to their preparative accessibility [2-4]. The coordination chemistry of molybdenum has received great attention from researchers due to the chemistry of its coordination number, oxidation state, ligating atom, their structure, reactivity and potential applications of molybdenum complexes [5-7]. A number of planner tetradentate ligands are capable of giving six coordinated complexes [8]. In the second transition series, only molybdenum is important as micronutrients for plants, animals and microorganisms. There are many reports on the use of *cis* - dioxomolybdenum(VI) complexes-, which act as catalysts in some biological processes [9,10]. The biological importance of molybdenum is due to its ability to provide facile electron-transfer pathways. Molybdenum-catalyzed oxygen-transfer reactions have attracted considerable interest. Furil is a versatile chelating ligand having two reactive carbonyl groups capable of undergoing Schiff base condensation with di - and polyamines. Thus, furil has played an important role in the designing of macrocyclic ligands and such ligands form macrocyclic complexes with molybdenum [11]. With the importance of dioxomolybdenum(VI) cations in oxygen transfer reactions, a new series of dioxomolybdenum(VI) macrocyclic complexes with new denticity ligands derived from condensation of furil with 2,3 - diamino - 5 - bromopyridine capable of undergoing cyclization with β-diketones via the metal template effect have been prepared.

Herein, the synthesis of these complexes and their tentative structures, based on molar conductivity, elemental analyses, UV - VIS, IR and TGA/DTA are reported.

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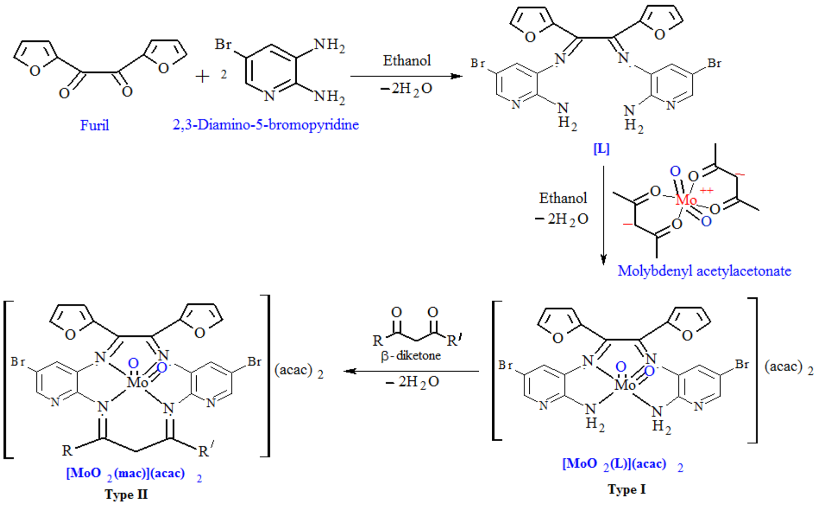
2. EXPERIMENTAL SECTION

2.1 Materials and methods: All chemicals used were of reagent grade. Molybdenyl acetylacetonate, diamine, furil and β - diketones, namely acetylacetone, benzoylacetone, thenoyltrifluoroacetone, and dibenzoylmethane were purchased from Aldrich.

2.2 Analytical Methods and Physical Measurements: The elemental analyses, IR and TG/DTA were performed at SAIF, IIT Bombay, India. Microanalysis of carbon, hydrogen and nitrogen for the complexes were done by using Flash EA 1112 Series. Kjeldahl's method was employed to estimate nitrogen for the complexes. Molybdenum was estimated gravimetrically after decomposing the complex with concentrated nitric acid by standard method [12]. Sulfur was estimated as barium sulfate [13]. The standard technique of melting point (uncorrected) determination using sulfuric acid bath was employed. The electronic spectra of the complexes were recorded by using methanol as solvent by UV - 1800, Shimadzu instrument in the ranges 1100 - 220 nm at D.A-V. P.G. College, Kanpur, India. The infrared spectra of the complexes (4000 - 50 cm^{-1}) were recorded in CsI pellets on Nicolet Instruments Corporation, USA model no. Magna 550 spectrophotometer. Thermograph of the $[MoO_2(L)](acac)_2$ complex was done under N_2 atmosphere in the temperature range 50 - 600 ^0C at the heating rate 10 ^0C min^{-1} using TG/DTA - Perkin Elmer, USA thermal analyzer.

2.3 *In-situ* preparation of dioxomolybdenum(VI) complexes with ligands derived by condensation of furil with 2,3-diamino-5-bromopyridine and their reactions with β-diketones: Scheme shows the preparation procedure of $[MoO_2(mac)](acac)_2$. An ethanolic solution of molybdenyl acetylacetonate (5 mmol, 0.8153g) was added dropwise to a refluxing solution of furil (5 mmol, 0.4753g) and 2,3 - diamino - 5 - bromopyridine (10 mmol, 0.9401g) in ethanol (25 mL) in RB flask. The resulting reaction mixture was mild refluxed for 2h. The color of the mixture turned into dirty yellow. The solid product was filtered off, washed with cold ethanol, and isolated under *in vacuo* over silica gel. Purity of the complex was checked by TLC. The yield was 55 % (type I). The reaction mixture of type I suspended in ethanol further reacted for 2h with β-diketones such as acetylacetone or benzoylacetone or thenoyltrifluoroacetone or dibenzolylmethane (1:1) to get macrocyclic products (type II). The purity of the macrocyclic complexes was checked by TLC (yield 60 %).



Scheme: Preparation of $[MoO_2(L)](acac)_2$ and of $[MoO_2(mac)](acac)_2$

Where, L = furil + 2,3-diamino-5-bromopyridine; mac = macrocyclic ligands carried out from condensation of L with β-diketones in presence of dioxmolybdenum(VI) cation; R = CH_3, C_6H_5, C_4H_3S, C_6H_5; R' = CH_3, CH_3, CF_3, C_6H_5; respective β-diketone = (i) acetylacetone, (ii) benzoylacetone, (iii) thenoyltrifluoroacetone, (iv) dibenzoylmethane.

Figure 1: *In-situ* preparation of macrocyclic complexes of *cis*-dioxomolybdenum(VI)

Elemental analyses (table 1) of the complexes showed 1:1 metal to ligand stoichiometry.

Table 1: Physical and analytical data of the complexes.

Complex	Empirical Formula	F.W.	Yield (%)	m.p. (^{0}C)	C % Calcd. (found)	H % Calcd. (found)	N % Calcd. (found)	Mo % Calcd. (found)	S % Calcd. (found)
$[MoO_2(L)](acac)_2$	$C_{30}H_{28}N_6MoO_8Br_2$	856.33	75	131.5	42.07 (41.05)	3.29 (3.10)	9.81 (9.75)	11.20 (10.10)	
$[MoO_2(mac^1)](acac)_2$	$C_{35}H_{32}N_6MoO_8Br_2$	920.42	68	125	45.67 (45.55)	3.50 (3.32)	9.13 (9.00)	10.42 (9.25)	
$[MoO_2(mac^2)](acac)_2$	$C_{40}H_{34}N_6MoO_8Br_2$	982.49	65	128	48.90 (48.80)	3.48 (3.35)	8.55 (8.50)	9.76 (7.62)	
$[MoO_2(mac^3)](acac)_2$	$C_{38}H_{29}N_6MoO_8SBr_2F_3$	1042.49	72	120	43.78 (43.65)	2.80 (2.70)	8.06 (8.00)	9.20 (8.15)	3.07 (2.98)
$[MoO_2(mac^4)](acac)_2$	$C_{45}H_{36}N_6MoO_8Br_2$	1044.56	70	107	51.74 (51.65)	3.47 (3.40)	8.05 (7.90)	9.18 (8.05)	

2.4 Antibacterial activity assay: The antibacterial activity of the synthesized dioxomolybdenum(VI) complexes were evaluated *in vitro* against four bacterial strains i.e. *Staphylococcus aureus, Bacillus subtilis, Enterobacter aerogenes*-, and *Salmonella typhi* using cup and agar-well diffusion method [14-16]. Doxycycline was used as the standard antibacterial agent. Wells having size of 6 mm in diameter were dug in the agar media with the help of metallic borer. The density of each bacterial suspension in each well was adjusted to 3×10^5 colony-forming units (CFU) mL^{-1}. The standardized suspensions-were spread on the surface of the agar. The synthesized complexes were dissolved in 1 % DMSO and concentration of the test sample was 300 µg mL^{-1}. The test samples were introduced in the corresponding wells. Other wells were filled with DMSO and antibacterial agent doxycycline (0.05 %). Growth inhibition was evaluated after 28 h incubation at 35 ^{0}C.

3. RESULTS SECTION

The complexes of dioxomolybdeum(VI) with Schiff base were prepared using an *in-situ* method by refluxing the reaction mixture of furil, diamines and molybdenyl acetylacetonate in 1:2:1 molar ratio in aqueous ethanol which result in macrocyclic complexes according to scheme.

3.1 Infrared spectra: The IR spectral bands of all the complexes and their tentative assignments are given in table 2. The coordination of nitrogen atoms of azomethine groups to the molybdenum in all macrocyclic complexes were evidenced by the shift of $\nu_{C=N}$ to lower frequencies [17-20]. The region 1652 - 1645 cm^{-1} is associated with >C=N absorption, which normally appears at 1680 cm^{-1} in isolated ligands [17-19]. New absorption band at around 306 cm^{-1} may be assigned to ν_{Mo-N} vibration [21], which is absent in free ligands. The coordination of two keto groups of furil through carbonyl oxygen with diamines was supported by the appearance of >C=N band and the absence of the > C=O band around 1710 cm^{-1} [22,23]. The asymmetrical and symmetrical N-H stretching modes of the coordinated terminal amino group observed at 3348 and 3201 cm^{-1} [22]. The dioxomolybdenum(VI) complexes to form preferentially a cis-dioxo group due to the maximum utilization of the d-orbital for bonding. The dioxomolybdenum(VI) complexes showed two Mo=O stretching bands at 899 - 903 cm^{-1} and 942 - 1011 cm^{-1} due to asymmetric and symmetric stretching of the cis-$[MoO_2]^{2+}$ core in C_{2V} symmetry [24]. These two infrared spectral bands are assigned to $\nu_{asym(O=Mo=O)}$ and $\nu_{sym(O=Mo=O)}$ vibrations respectively [25-28]. Generally, the frequencies of

$\nu_{asym(O=Mo=O)}$ vibrations are lower than those of $\nu_{sym(O=Mo=O)}$ [29,30]. The presence of acetylacetonate group present in outer coordination sphere is confirmed by the bands appearing around 1540 - 1561 cm^{-1} and 1458 - 1479 cm^{-1} are assigned to $\nu_{C=O}$ and $\nu_{C=C}$ vibrations [31]. Infrared spectral bands of the macrocyclic complexes of type - IIa and IIb show the same pattern of spectral bands. The asymmetrical and symmetrical N-H stretching modes of terminal amino groups disappear due to coordination of these amino groups with carbonyl group of β-diketones in cyclization reactions [31,32].

Table 2: Infrared spectral bands (ν / cm^{-1}) of molybdenum complexes. All spectra were recorded using CsI in the range 4000 - 50 cm^{-1}.

Complex	$\nu_{C=N}$	ν_{Mo-N}	$\nu_{C=O}$ of acetylacetonate	$\nu_{C=C}$ of acetylacetonate	ν_{asym} (O=Mo=O)	ν_{sym} (O=Mo=O)	$\nu_{asym (N-H)}$	$\nu_{sym(N-H)}$
$[MoO_2(L)](acac)_2$	1652s	481m	1561s	1479m	899s	1011m	3348s	3201m
$[MoO_2(mac^1)](acac)_2$	1650m	480s	1560m	1475m	903w	942s		
$[MoO_2(mac^2)](acac)_2$	1650m	482m	1555s	1458m	902s	955m		
$[MoO_2(mac^3)](acac)_2$	1645s	485m	1558s	1472m	900m	958m		
$[MoO_2(mac^4)](acac)_2$	1647m	485m	1540mS	1472m	905m	964s		

3.2 UV - Visible spectra: The absorptions appearing in UV-Vis spectra of the dioxomolybdenum(VI) complexes were carried out in 10^{-3} mol L^{-1} DMF solution and these spectral bands are interpreted according to reported energy level scheme [33,34]. The UV - Vis spectra are similar to other dioxomolybdenum(VI) complexes having nitrogen donor atoms. The UV - Vis spectra of these complexes are characterized by strong absorption bands in the UV region at≈ 275 nm and at≈ 390 nm seem to be due to charge transfer and intraligand n→ π* / π → π* transitions.

In some complexes, a medium intense bands appearing in the region at≈ 360 nm and at≈ 410 nm may be assigned for L→M charge - transfer transition between the lowest unoccupied molybdenum d-orbital and highest occupied ligand molecular orbital [35,36]. Ballhausen - Gray scheme have provided energy level scheme for these complexes. The electronic spectra indicate a distorted octahedral geometry for all the complexes [37].

3.3 Magnetic and molar conductance measurements: The dioxomolybdenum(VI) complexes are diamagnetic, as expected for d^0 configuration. Since there is no electron present in d-orbital, no d-d transitions are observed for these complexes. The molar conductivity (Λ_M) values for all dioxomolybdenum(VI) complexes in DMF at *ca.* 10^{-3} M suggest 1:1 type electrolytes. The molar conductance values of these complexes lie between 100 - 110 Ω^{-1} cm^2 mol^{-1}.

In conclusion, the above details support the tentative structures of dioxomolybdenum(VI) complexes of the type (I) and macrocyclic complexes of the type (II) as shown in the scheme.

3.4 Thermogravimetric analyses: The thermogram of $[MoO_2(L)](acac)_2$ complex was recorded in the temperature range 50 - 600 ^{0}C at the heating rate of 10 ^{0}C min^{-1}. The complex is stable upto 151 ^{0}C (Fig. 1). The $[MoO_2(L)](acac)_2$ complex decomposed in two steps: (a) first step of decomposition (151 - 270 ^{0}C) is due to partial removal of ligand (mass loss obs. 58.5 %, calcd. 61.91 %) (b) in the second step, the left residue of first step decomposed gradually at elevated temperature (300 - 470

^{0}C) giving a mass loss about 30 % against calculated mass loss of 23 %. Finally, a residue roughly corresponds to MoO_3 (obs. residual mass = 12.5 %, calcd. = 16.8 %) have been left after 470 ^{0}C. In DTA thermogram, two peaks were obtained. First peak is endothermic which is due to melting of the complex (131.5 ^{0}C). Second peak is exothermic. Near this exothermic peak an exothermic hump was also observed at 457.39 ^{0}C which may due to exothermic decomposition of the residual mass in the second step.

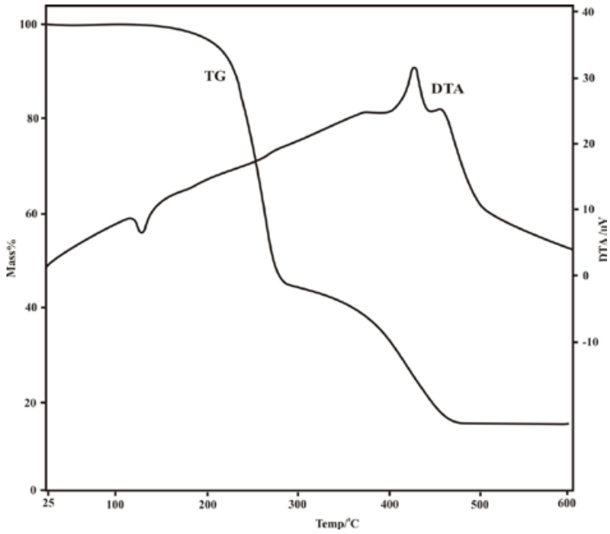


Figure 2: TG and DTA curves of $[MoO_2(L)](acac)_2$

3.5 Antibacterial activity: The results of the antimicrobial activities of the synthesized dioxomolybdenum(VI) complexes are given in table 3. The synthesized dioxomolybdenum(VI) complexes were tested against *Staphylococcus aureus, Bacillus subtilis, Enterobacter aerogenes,* and-, *Salmonella typhi.* The enhancement in the antibacterial activity of dioxomolybdenum(VI) complexes can be explained on the basis of chelation theory [38,39]. The reference material is doxycycline drug. Almost all the complexes showed low to moderate activity against *S. aureus* and *S. typhi.*

Table 3: Antibacterial activities of macrocyclic complexes of dioxomolybdenum(VI)[a]

Complex	*Staphylococcus aureus*	*Enterobacter aerogenes*	*Salmonella typhi*	*Bacillus subtilis*	*Doxycycline*
$[MoO_2(L)](acac)_2$	15	16	16	20	23
$[MoO_2(mac^1)](acac)_2$	17	18	15	--	26
$[MoO_2(mac^2)](acac)_2$	16	20	--	19	24
$[MoO_2(mac^3)](acac)_2$	18	22	18	19	23
$[MoO_2(mac^4)](acac)_2$	18	16	17	22	25

4. CONCLUSIONS

The present study demonstrate simple synthetic paths to obtain new dioxomolybdenum(VI) with Schiff base. The employed spectroscopic techniques have confirmed the Schiff base condensation of furil which is a versatile chelating agent having two reactive carbonyl groups with diamines and their cyclizations with β-diketones undergoing formation of macrocyclic products to ensure controlled geometry around MoO_2(VI) centre. The geometry around Mo is distorted octahedral. The kinetic template effect of dioxomolybdenum(VI) cation plays an important role in the synthesis of Schiff base using furil and diamines in ethanol medium. Synthesized Schiff bases behave as tetradentate ligands by coordinating to the metal ion through the azomethine nitrogen atoms. The presence of one metal ion per ligand molecule is confirmed by analytical data. The mononuclear six coordination of all the *cis*- dioxomolybdenum(VI) complexes, and the six coordinate distorted octahedral structure have been proposed for these complexes. X - ray crystallographic data, which might confirm the tentative structures, could not be possible, as suitable crystals were not isolated. All complexes were capable of inhibiting bacterial growth to a certain extent.

5. ACKNOWLEDGMENT

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