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In-situ synthesis and antibacterial activity of novel macrocyclic complexes of *cis*-dioxomolybdenum (VI)

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ABSTRACT

Synthesis of several novel dioxomolybdenum(VI) complexes with formula [MoO2(mac)](acac)2, (where mac = tetraazamacrocyclic ligands derived from condensation of thenil with 1,2-diaminobenzene or 2,3-diaminopyridine and their reactions with β-diketones), using dioxometal ion as kinetic template are reported. The complexes were characterized by molar conductance, elemental analyses, infrared and UV-Vis spectral studies. The spectral data indicate that ligands act as tetradentate chelating agent. All the complexes were found to have octahedral geometry with six coordination. The antibacterial activities of the synthesized complexes were tested against six different bacterial strains. Almost all the complexes showed low to moderate activity against Staphylococcus aureus, Escherichia coli, Salmonella typhi and Pseudomonas aeruginosa.

Keywords: *dioxomolybdenum(VI), thenil, macrocyclic complexes.*

1. INTRODUCTION

Schiff bases play an important role in chemistry as they easily form stable complexes with most transition metal ion. Schiff base complexes may severe as models for biologically important species. Intensive research efforts have been directed to study the transition metal complexes of high denticity ligands with a view to obtain the metal complexes of unusual configuration and coordination number [1]. Molybdenum is versatile in nature due to its multiple oxidation state ranging from –2 to +6 as well as coordination numbers which vary from four to eight [2]. The dioxomolybdenum (VI) complexes with denticity ligands have great importance in theoretical and practical areas, especially for biological processes. Mo(VI) is present as a simple molybdate $[MoO_4]^{2-}$ ion in aqueous solution depending on the concentration and pH of the solution. The $[MoO_4]^{2-}$ ion can serve as oxygen atom transfer agents [3]. Their oxygen atom transfer properties play an important role in the functioning mechanism of molybdenum oxotransferase [4, 5]. It is important in the fully oxidized states of a number of redox enzymes, in which their active sites consists of a *cis*-dioxomolybdenum moiety [6-8].

In the second series of transition metals, only molybdenum is considered as a biometal which is important for human, animal and plants pathogenic microorganisms [9, 10]. The coordination chemistry of Mo(VI) is of actively interest in the current research because of their catalytic properties and biological activities [11-14]. Physiological functions of oxomolybdoenzymes have

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been established by molybdenum [15-17]. Thenil is a versatile chelating agent. It has two reactive carbonyl groups capable of undergoing Schiff base condensation with a variety of di- and polyamines. Thus, thenil has played an important role in the design of macrocyclic ligands.

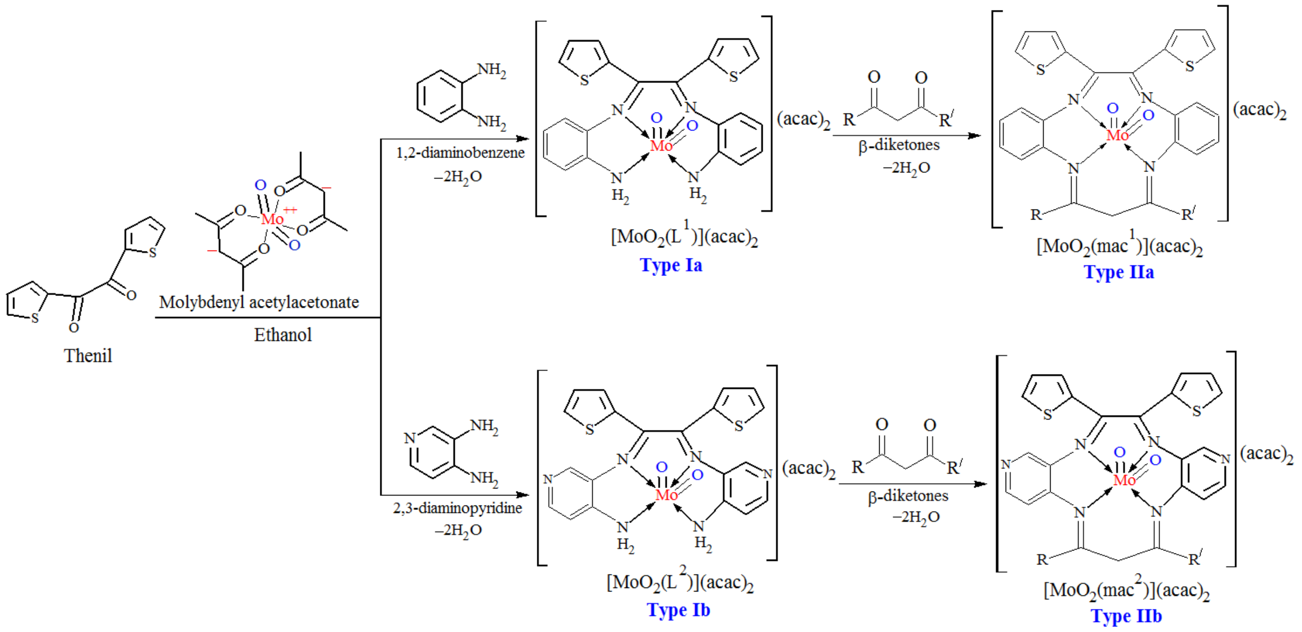
Within this context, some dioxomolybdenum(VI) complexes with high denticity ligands derived from condensation of thenil with 1,2-diaminobenzene or 2,3-diaminopyridine, capable of undergoing cyclization with β-diketones via the metal template effect have been prepared, characterized and their tentative structures are ascertained based on molar conductivity, elemental analysis, electronic and IR spectroscopy.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. All the chemicals and the solvents employed were of AR grade. The β-diketones viz. acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane were Sisco Research Laboratory products. The diamines used were of AR grade products. Thenil used was Aldrich product. Dioxomolybdenum(VI) acetylacetonate was prepared by standard method using sodium molybdate and acetylacetone [18].

2.2.Analytical Methods and Physical Measurements. Carbon, hydrogen and nitrogen microanalyses of the complexes were estimated by using MLW-CHN microanalyser were done at CRF, NERIST, Nirjuli-791109, Itanagar, Arunachal Pradesh, India. Molybdenum was estimated gravimetrically standard method [19]. Sulfur was estimated as barium sulfate in the laboratory [20]. Melting point (uncorrected) determination of the complexes was done by the standard technique using sulfuric acid bath. The infrared spectra of the complexes were recorded in the region 4000-50 cm^{-1} in pressed KBr pellets on a Nicolet Instruments Corporation, USA model no. Magna 550. The electronic spectra of the complexes were recorded by using ethanol as solvent by Varian, Cary-5000 spectrophotometer instrument in the ranges 3300-175 nm.

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



2.3. *In-situ* preparation of dioxomolybdenum(VI) complexes with ligands derived by condensation of thenil with 1,2-diaminobenzene or 2,3-diaminopyridine and their reactions with β-diketones. Molybdenyl acetylacetonate (2 mmol) dissolved in ethanol (20 mL) was added to a refluxing solution of thenil (2 mmol) and 1,2-diaminobenzene (4 mmol) or 2,3-diaminopyridine (4 mmol) in ethanol (20 mL). The color of the solution turned yellow when the mixture was allowed to react under mild reflux for 6 h. The solvent was evaporated under vacuo at room temperature and the dirty yellow color product (70 %, type Ia and Ib) was obtained. The complex was thoroughly washed with ethanol. The reaction mixture of Ia and Ib suspended in ethanol was further reacted for 5h with β-diketones such as acetylacetone or benzoylacetone or thenoyltrifluoroacetone or dibenzolylmethane (1:1) to get macrocyclic products (Type IIa and IIb), which were isolated under vacuo and their purity was checked by TLC. The yield was found to be 60%.

In scheme: X = 1,2-diaminobenzene or 2,3-diaminopyridine; L^1 = thenil + 1,2 diaminobenzene; L^2 = thenil + 2,3-diaminopyridine; mac = tetraazamacrocyclic ligands carried out from condensation of L^1 or L^2 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 = (A) acetylacetone, (B) benzoylacetone, (C) thenoyltrifluroacetone, (D) dibenzoylmethane.

2.4. Physical and Analytical data of the molybdenum complexes.

[MoO₂(L¹)](acac)₂: Yield: 65 %; m.p.. 306 ^{0}C; Anal. Calcd. for $C_{32}H_{32}N_4MoO_6S_2$ (FW 728.70): C, 52.8; H, 4.4; N, 7.7; Mo, 13.2; S, 8.8 %. Found: C, 52.4; H, 4.1; N, 7.5; Mo, 13.0; S, 8.6 %.

[MoO₂(L²)](acac)₂: Yield: 62 %; m.p.. 304 ^{0}C; Anal. Calcd. for $C_{30}H_{30}N_6MoO_6S_2$ (FW 730.8): C, 49.3; H, 4.1; N, 11.5; Mo, 13.1; S, 8.8 %. Found: C, 49.1; H, 4.0; N, 11.3; Mo, 13.0; S, 8.5 %.

[MoO₂(mac¹ᴬ)](acac)₂: Yield 65 %; m.p.. 308 ^{0}C; Anal. Calcd. for $C_{37}H_{36}N_4MoO_6S_2$ (FW 792.79): C, 56.1; H, 4.6; N, 7.1; Mo, 12.1; S, 8.1 % . Found: C, 59.9; H, 4.4; N, 7.0; Mo, 11.9; S, 7.9 %.

[MoO₂(mac¹ᴮ)](acac)₂: Yield 64 %; m.p.. 305 ^{0}C; Anal. Calcd. for $C_{42}H_{38}N_4MoO_6S_2$ (FW 854.86): C, 59.0; H, 4.5; N, 6.6; Mo, 11.2; S, 7.5 % . Found: C, 58.9; H, 4.2; N, 6.4; Mo, 11.1; S, 7.4 %.

[MoO₂(mac¹ᶜ)](acac)₂ : Yield: 64 %; m.p.. 304 ^{0}C; Anal. Calcd. for $C_{40}H_{33}N_4MoO_6S_2F_3$ (FW 882.80): C, 52.5; H, 3.8; N, 6.4; Mo, 10.5; S, 7.3 %. Found: C, 52.2; H, 3.7; N, 6.2; Mo, 10.8; S, 7.1 %.

[MoO₂(mac¹ᴰ)](acac)₂: Yield 65 %; m.p.. 306 ^{0}C; Anal. Calcd. for $C_{47}H_{40}N_4MoO_6S_2$ (FW 916.93): C, 61.6; H, 4.4; N, 6.1; Mo, 10.5; S, 7.0 %. Found: C, 61.3; H, 4.1; N, 6.0; Mo, 10.2; S, 6.8 %.

[MoO₂(mac²ᴬ)](acac)₂: Yield: 62 %; m.p.. 305 ^{0}C; Anal. Calcd. for $C_{35}H_{34}N_6MoO_6S_2$ (FW 794.76): C, 52.9; H, 4.3; N, 10.6; Mo, 12.1; S, 8.1 %. Found: C, 52.7; H, 4.1; N, 10.5; Mo, 11.8; S, 8.0 %.

[MoO₂(mac²ᴮ)](acac)₂: Yield: 64 %; m.p.. 308 ^{0}C; Anal. Calcd. for $C_{40}H_{36}N_6MoO_6S_2$ (FW 856.84): C, 56.0; H, 4.2; N, 9.8; Mo, 11.2; S, 7.5 %. Found: C, 55.8; H, 4.0; N, 9.6; Mo, 11.1; S, 7.2 %.

[MoO₂(mac²ᶜ)](acac)₂: Yield: 62 %; m.p.. 304 ^{0}C; Anal. Calcd. for $C_{38}H_{31}N_6MoO_6S_2F_3$ (FW 884.77): C, 51.6; H, 3.5; N, 9.5; Mo, 10.8; S, 7.3 %. Found: C, 51.3; H, 3.1; N, 9.3; Mo, 10.6; S, 7.0 %.

[MoO₂(mac²ᴰ)](acac)₂: Yield: 64 %; m.p.. 305 ^{0}C; Anal. Calcd. for $C_{45}H_{38}N_6MoO_6S_2$ (FW 918.91): C, 58.8; H, 4.1; N, 9.2; Mo, 10.5; S, 7.0 %. Found: C, 58.5; H, 4.0, N, 9.1; Mo, 10.3; S, 6.8 %.

Where, L^1 = Ligand procured by condensation of thenil with 1,2-diaminobenzene (1:2); L^2 = Ligand procured by condensation of thenil with 2,3-diaminopyridine(1:2); Mac^{1A} = macrocyclic ligand procured by condensation of L^1 with acetylacetone; Mac^{2B} = macrocyclic ligand procured by condensation of L^1 with benzoylacetone; Mac^{3C} = macrocyclic ligand procured by condensation of L^1 with thenoyltrifluoroacetone; Mac^{4D} = macrocyclic ligand procured by condensation of L^1 with dibenzoylmethane; Mac^{2A} = macrocyclic ligand procured by condensation of L^2 with acetylacetone;

Mac^{2B} = macrocyclic ligand procured by condensation of L^2 with benzoylacetone; Mac^{2C} = macrocyclic ligand procured by condensation of L^2 with thenoyltrifluoroacetone; Mac^{2D} = macrocyclic ligand procured by condensation of L^2 with dibenzoylmethane. 1:1 metal to ligand stoichiometry showed by elemental analyses of the complexes.

2.5. Antibacterial Activity Test. The synthesized dioxomolybdenum(VI) complexes were evaluated *in vitro* for their antibacterial activity against six bacterial strain viz. *Staphylococcus aureus, Bacillus subtilis Enterobacter aerogenes, Escherichia coli, Salmonella typhi,* and *Pseudomonas aeruginosa* using cup and agar-well diffusion method [21]. The doxycycline was used as a reference antibiotic drug. Wells having size of 6 mm in diameter were cut in the agar medium. The density of each bacterial strain in each well was adjusted to $3x10^5$ colony-forming units (CFU) mL^{-1} and the obtained inoculums was spread on the surface of the agar using a cotton stick. The dioxomolybdenum(VI) complexes were dissolved in 1 % DMSO and the concentration of the test sample was 300 µg/mL in DMSO. The test samples were introduced in the respective wells. Negative and positive control wells were filled with DMSO and respectively, doxycycline. Growth inhibition was calculated after 25 h incubation at 37 ^{0}C.

3. RESULTS SECTION

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

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

Complex	$\nu_{C=N}$	$\nu_{Mo\text{-}N}$	$\nu_{C=O}$ of acetylacetonate	$\nu_{C=C}$ of acetylacetonate	ν_{asym} (O=Mo=O)	ν_{sym} (O=Mo=O)	$\nu_{asym\,(N\text{-}H)}$	$\nu_{sym(N\text{-}H)}$
$[MoO_2(L^1)](acac)_2$	1618	301	1562	1515	908	944	3348	3180
$[MoO_2(L^2)](acac)_2$	1620	302	1560	1513	902	938	3352	3178
$[MoO_2(mac^{1A})](acac)_2$	1622	303	1564	1515	906	942		
$[MoO_2(mac^{1B})](acac)_2$	1620	304	1562	1515	904	946		
$[MoO_2(mac^{1C})](acac)_2$	1618	303	1560	1517	910	938		
$[MoO_2(mac^{1D})](acac)_2$	1620	302	1562	1513	906	944		
$[MoO_2(mac^{2A})](acac)_2$	1616	303	1564	1517	910	942		
$[MoO_2(mac^{2B})](acac)_2$	1620	304	1560	1513	903	943		
$[MoO_2(mac^{2C})](acac)_2$	1624	303	1562	1517	902	938		
$[MoO_2(mac^{2D})](acac)_2$	1618	302	1560	1515	902	940		

3.1. Infrared spectra. Important infrared spectral bands of the complexes and their tentative assignments are given in table 1. In all macrocyclic complexes of dioxomolybdenum(VI), the coordination of nitrogen atoms of azomethine groups to the molybdenum was evidenced by the shift of $\nu_{C=N}$ to lower frequencies [22-25]. Here >C=N absorption around 1624- 1616 cm^{-1}, which normally appears at 1650 cm^{-1} in free ligands [22-24]. New weak band at around 306 cm^{-1} may be assigned to $\nu_{Mo\text{-}N}$ vibration [26]. The two keto groups of thenil coordinate through carbonyl oxygen with diamines was supported by the appearance of >C=N band and the absence of the >C=O band around 1700 cm^{-1} [27,28]. Asymmetrical and symmetrical N-H stretching modes of the coordinated terminal amino group observed at 3352 and 3180 cm^{-1} [27]. Due to the maximum utilization of the d-orbital for bonding, the dioxomolybdenum(VI) complexes form preferentially a cis-dioxo group. The dioxomolybdenum(VI) complexes displayed two Mo=O stretching bands at 902-910 cm^{-1} and 938-946 cm^{-1} due to asymmetric and symmetric stretching of the cis-MoO_2^{2+} core in C_{2V} symmetry. These two infrared bands are assigned to $\nu_{asym(O=Mo=O)}$ and $\nu_{sym(O=Mo=O)}$ vibrations respectively [29-32]. The bands appearing at 1562 cm^{-1} and 1515 cm^{-1} are assigned to $\nu_{C=O}$ and $\nu_{C=C}$ vibrations of acetylacetonate group present in outer coordination sphere [33]. IR spectra of the macrocyclic complexes of type-IIa and IIb show the same pattern of spectral bands. But the asymmetrical and symmetrical N-H stretching modes of terminal amino groups disappear due to condensation of these amino groups with carbonyl group of β-diketones in cyclization reactions [34,35].

3.2. UV-Visible spectra: The UV-Vis spectra of the dioxomolybdenum(VI) complexes were carried out in 10^{-3} mol L^{-1} dimethylformamide solution and these spectral bands are interpreted according to reported energy level scheme [36,37]. The UV-Vis spectra are similar to other dioxomolybdenum(VI) complexes involving nitrogen donor atoms. The UV-Vis spectra of the complexes are characterized by strong absorption bands in the UV region at ≈290 nm and at ≈360 nm seem to be due to intra ligand n → π* / π → π* transitions.

A medium intense bands appearing in the region at ≈345 nm and at ≈395 nm may be assigned for ligand to metal charge – transfer transition between the lowest unoccupied molybdenum d-orbital and highest occupied ligand molecular orbital [38,39]. The electronic spectra indicate an octahedral geometry for all the complexes and are confirmed with the help of Ballhausen-Gray scheme for octahedral geometry [40].

Table 2: Antibacterial activities of macrocyclic complexes of dioxomolybdenum(VI)[a]

Complex	*Staphylococcus aureus*	*Bacillus subtilis*	*Enterobacter aerogenes*	*Escherichia coli*	*Salmonella typhi*	*Pseudomonas aeruginosa*	*Doxycycline*
$[MoO_2(L^1)](acac)_2$	18	--	19	19	15	20	24
$[MoO_2(L^2)](acac)_2$	16	21	--	22	18	--	23
$[MoO_2(mac^{1A})](acac)_2$	--	20	22	22	16	20	26
$[MoO_2(mac^{1B})](acac)_2$	18	22	22	22	15	19	24
$[MoO_2(mac^{1C})](acac)_2$	16	19	19	19	16	21	24
$[MoO_2(mac^{1D})](acac)_2$	17	20	--	21	--	18	23
$[MoO_2(mac^{2A})](acac)_2$	16	22	19	19	16	18	25
$[MoO_2(mac^{2B})](acac)_2$	18	19	22	22	18	20	26
$[MoO_2(mac^{2C})](acac)_2$	15	20	21	21	--	15	24
$[MoO_2(mac^{2D})](acac)_2$	15	19	--	21	17	15	24

[a] *In vitro*, cup and well diffusion method, conc. 300 µg/mL in DMSO; Zone of inhibition (mm): dash indicate inactivity; 15-18 = moderate activity; 19-22 = good activity; 23-26 = strong activity; Doxycycline as reference antibiotic drug.

3.3. Magnetic and molar conductance measurements: As expected, these d^0 metal ion complexes are diamagnetic in nature. No d-d transitions are observed for these complexes consistent with d^0 configuration. The molar conductivity (Λ_M) values for all dioxomolybdenum(VI) complexes in dimethylformamide at *ca.* 10^{-3} M were close to those of 1:1 type electrolytes. The molar conductance values for these complexes lie between 120-130 ohm^{-1} cm^2 mol^{-1}.

The above details support the tentative structures of dioxomolybdenum(VI) complexes of the type (Ia and Ib) and macrocyclic complexes of the type (IIa and IIb) as shown in the scheme.

3.4. Antibacterial Activity: The synthesized dioxomolybdenum(VI) complexes were tested against *Staphylococcus aureus, Bacillus subtilis Enterobacter aerogenes, Escherichia coli, Salmonella typhi* and *Pseudomonas aeruginosa* using cup and well diffusion method and data are given in table 2. Doxycycline was used as a reference antibiotic drug. Almost all the complexes showed low to moderate activity against *S. aureus, E. coli, S. typhi* and *P. aeruginosa*.

4. CONCLUSIONS

The spectral data have confirmed the Schiff base condensation of thenil, which is a versatile chelating agent having two reactive carbonyl groups with diamines and their cyclizations with β-diketones leading to 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 formation of Schiff base using thenil and diamines in aqueous 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 proved by analytical data. The analytical data also suggest a mononuclear structure for the complexes. The analytical and electronic data support the six coordinate structure for cis- dioxomolybdenum(VI) complexes. All complexes have been found biologically active.

5. ACKNOWLEDGMENTS

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