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Synthesis, characterization and antibacterial evaluation of five dioxomolybdenum(VI) complexes coordinated by Schiff derivatives

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ABSTRACT

The synthesis of new five dioxomolybdenum(VI) complexes with tetradentate Schiff base ligand, derived from condensation of thenil with 2,3-diaminophenazine and their cyclization with β – diketones described in this paper. The compounds were characterized by elemental analyses, molar conductivity, UV-Vis and IR spectral studies. The octahedral coordination of molybdenum in synthesized complexes is completed by two oxo oxygens, four nitrogens from derived ligand. Synthesized dioxomolybdenum(VI) complexes have distorted octahedral geometry.

Keywords: *cis-dioxomolybdenum(VI), thenil, Schiff base, tetradentate ligand.*

1. INTRODUCTION

Molybdenum complexes have been widely used with large number of stable oxidation states, among which +4, +5 and +6 have received considerable attention and coordination numbers varying from four to eight [1]. Molybdenum complexes with Schiff base have great importance due to their potential for biological and physiological activity [2,3]. A large variety of dioxomolybdenum(VI) complexes with Schiff bases have been reported for synthesis, characterization and reactivity studies [4,5]. Molybdenum is essential for the nitrogenase enzyme and many chemical reactions have been catalyzed by molybdenum complexes [6-8]. Dioxomolybdenum(VI) complexes have been stated as oxidation catalysts for epoxidation of olefins [9-12]. Some of the molybdenum complexes posses oxygen atom transfer properties like oxidizing thiols, polyketones and tertiary phosphines [13,14]. Thenil have versatile nature due to their two reactive carbonyl groups which undergo Schiff base condensation with di- and polyamines. Thus, thenil has played important role in the synthesis of macrocyclic ligands and such ligands form macrocyclic complexes with molybdenum [15]. In recent years, their antimicrobial potency has gained special attention against both human and plant pathogenic microorganisms [16,17]. The aim of the present study was to synthesize a new series of dioxomolybdenum(VI) macrocyclic complexes with macrocyclic ligands derived from condensation of thenil with 2,3-diaminophenazine capable of undergoing cyclization with β-diketones via the metal template effect have been prepared.

The author reports herein the synthesis and tentative structures of these complexes based on molar conductance, elemental analyses, TGA/DTA, electronic and- IR spectra.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods

All chemicals used for the synthesis of ligands and complexes were of reagent grade and employed as purchased from commercial sources. Molybdenyl acetylacetonate, 2,3-diaminophenazine, thenil and β - diketones, namely acetylacetone, benzoylacetone, thenoyltrifluoroacetone, and dibenzoylmethane were purchased from Aldrich and employed without further purification.

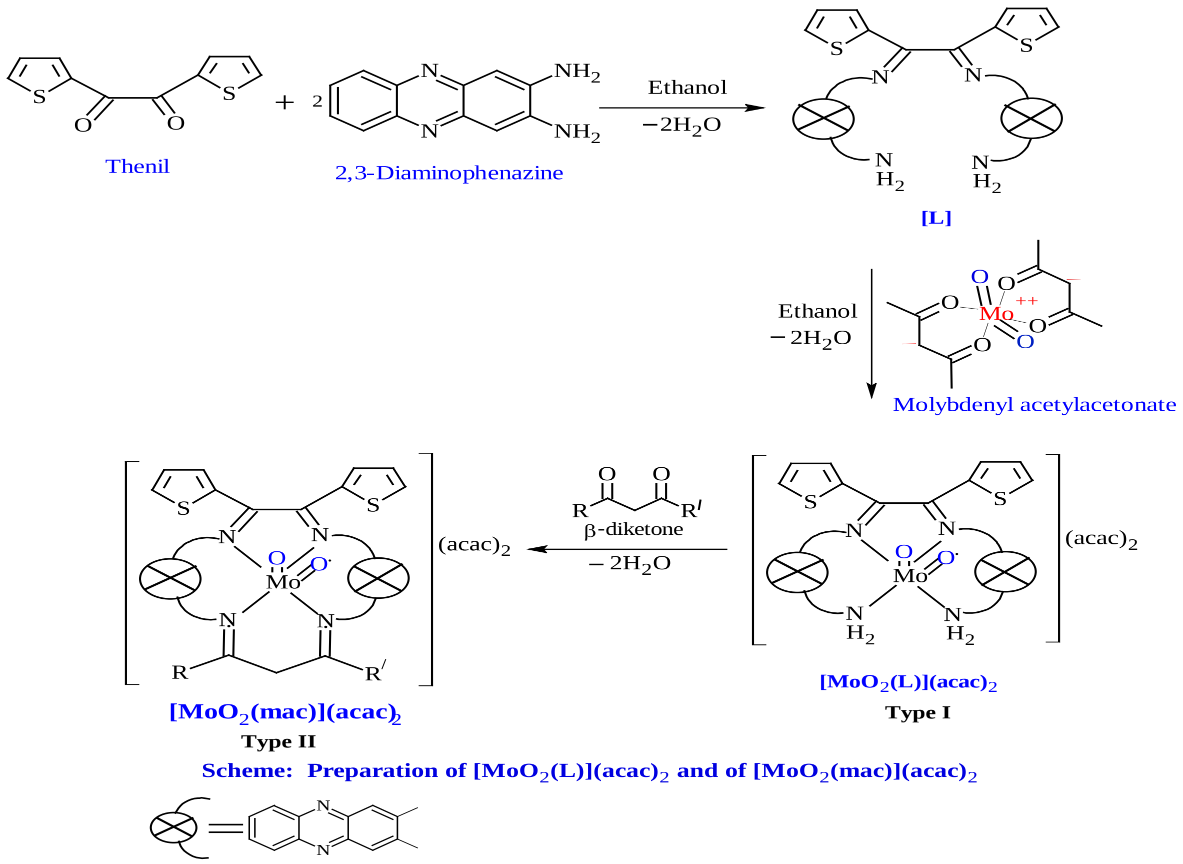
2.2. Analytical Methods

IR and TG/DTA were done at Sophisticated Analytical Instrumental Facility, IIT Bombay, India. Microanalysis (C, H, N and S) of the complexes were carried out with Flash EA 1112 Series elemental analyzer. Kjeldahl's method was used for nitrogen estimation of the synthesized complexes. After decomposition of the complex, metal and sulfur were estimated by standard methods [18,19]. Uncorrected melting points were determined by standard technique. The electronic absorption spectral measurements of the complexes were recorded on UV - 1800, Shimadzu instrument in the ranges 1100 - 220 nm by using methanol as solvent at D.A-V. P.G. College, Kanpur, U.P., India. The infrared spectra of the complexes were recorded in the region 4000 - 50 cm^{-1} on Nicolet Instruments Corporation, USA model no. Magna 550 spectrophotometer with CsI pellets. Thermograph of the $[MoO_2(L)](acac)_2$ complex were recorded under the flow of nitrogen gas 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 synthesis of dioxomolybdenum(VI) complexes with ligands derived by condensation of thenil with 2,3-diaminophenazine and their reactions with β-diketones

In order to prepare $[MoO_2(mac)](acac)_2$, an ethanolic solution of molybdenyl acetylacetonate (5 mmol, 1.6307 g) was added gradually to a refluxing solution of thenil (5 mmol, 1.1114 g) and 2,3-diaminophenazine (10 mmol, 2.1023 g) in ethanol (50 mL) in RB flask (figure 1). The color of the reaction mixture turned into dirty yellow after mild refluxed for 2h. Precipitate was filtered off, washed with cold ethanol and isolated under in vacuum desicator over silica gel. Purity of the prepared complex was checked by TLC (yield: 60 %, type I). Ethanolic mixture of type I complex further reacted for 2h with β-diketones such as acetylacetone or benzoylacetone or thenoyltrifluoroacetone or dibenzolylmethane (1:1) to get macrocyclic complex (type II). The purity of the synthesized macrocyclic product was checked by TLC (yield 45 %).

Elemental analyses (table 1) of the complexes proved 1:1 molar ratio of metal to ligand stoichiometry.



Where, L = thenil + 2,3-diaminophenazine; 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. Scheme for *in-situ* preparation of macrocyclic complexes of *cis*-dioxomolybdenum(VI).

Table 1. Elemental analysis of the dioxomolybdenum(VI) complexes.

Complex	Empirical Formula	F.W.	Yield (%)	Decomp. temp. (^{0}C)	C % Calcd. (found)	H % Calcd. (found)	N % Calcd. (found)	Mo % Calcd. (found)	S % Calcd. (found)
$[MoO_2(L)](acac)_2$	$C_{44}H_{36}N_8MoO_6S_2$	932.89	50	135	56.65 (56.05)	3.88 (3.25)	12.01 (11.55)	10.28 (9.70)	6.87 (6.04)
$[MoO_2(mac^1)](acac)_2$	$C_{49}H_{40}N_8MoO_6S_2$	996.97	65	140	59.03 (58.65)	4.04 (3.96)	11.23 (9.64)	9.62 (9.15)	6.43 (5.59)
$[MoO_2(mac^2)](acac)_2$	$C_{54}H_{42}N_8MoO_6S_2$	1059.05	65	130	61.24 (61.00)	3.99 (3.75)	10.58 (9.15)	9.05 (8.65)	6.05 (5.90)
$[MoO_2(mac^3)](acac)_2$	$C_{52}H_{37}N_8MoO_6S_3F_3$	1119.05	50	132	55.81 (54.45)	3.33 (2.86)	10.01 (9.55)	8.57 (8.15)	8.59 (8.00)
$[MoO_2(mac^4)](acac)_2$	$C_{54}H_{44}N_8MoO_6S_2$	1061.07	55	125	61.12 (60.58)	4.17 (3.65)	10.56 (10.00)	9.04 (8.95)	6.04 (5.74)

2.4. Antibacterial activity assay

The complexes were evaluated *in vitro* for their antibacterial activities against four bacterial strains i.e. *Staphylococcus aureus*, *Enterobacter aerogenes*, *Salmonella typhi* and *Bacillus subtilis* using cup and agar-well diffusion method [20,22]. Here, doxycycline was taken as the standard antibacterial agent. In this method, nutrient agar was used for bacteria. Wells having size of 6 mm in diameter were dug in the agar media. The density of microbial inoculum in each well was adjusted to 3 × 10^5 colony-forming units (CFU) mL^{-1} were spread over the surface of the agar. The synthesized dioxomolybdenum(VI) complexes dissolved in 1 % DMSO were added to the test sample. The concentration of test sample was 300 µg mL^{-1} in DMSO. Prepared test samples were distributed in separate wells. Left wells were filled with DMSO and the antibacterial agent doxycycline. Finally, growth inhibition was evaluated as millimeters (mm) diameter after 24 h incubation at 35 ^{0}C.

3. RESULTS SECTION

The five complexes with Schiff base were synthesized 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, which resulted in macrocyclic dioxomolybdenum(VI) complexes according to Figure 1.

3.1. Infrared spectra

The IR spectra of all the complexes and their tentative assignments are summarized in table 2. The bonding of nitrogen atoms of azomethine groups to the molybdenum in all macrocyclic complexes were proved by the shift of νC=N to lower frequencies [22-26]. The IR bands around 1655 - 1644 cm^{-1} is associated with >C=N absorption, which normally appear at 1665 cm^{-1} in isolated ligands [22-25]. IR band at around 485 cm-1 may be assigned to νMo-N vibrational mode which is absent in free ligands [27]. The coordination of two keto groups of thenil through carbonyl oxygen with nitrogen atom diamines was evidenced by the appearance of >C=N band and the absence of the > C=O band around 1710 cm^{-1} [28,29]. The N-H stretching vibrations (asymmetrical and symmetrical) of the coordinated terminal amino group observed at 3360 and 3200 cm^{-1} [28]. Maximum utilization of d-orbital for bonding is responsible for the synthesis of cis-dioxo group. The complexes exhibit their IR active modes namely, the asymmetric Mo=O stretch at 900 - 905 cm^{-1} and the symmetric Mo=O stretch at 935 - 955 cm^{-1} of the cis-$[MoO_2]^{2+}$ core in C2V symmetry [30]. These two bands are assigned to νasym(O=Mo=O) and νsym(O=Mo=O) vibrations respectively [31-34]. Generally, the vibrational frequencies of νsym(O=Mo=O) vibrations are higher than those of νasym(O=Mo=O) [35,36].

The existence of acetylacetonate group present at outer coordination sphere is proved by the bands appearing around 1525 - 1550 cm^{-1} and 1450 - 1465 cm^{-1} are assigned to νC=O and νC=C vibrations [37]. IR bands of the macrocyclic complexes of type - II show the same pattern of spectral bands. The νasym(N-H) and νsym(N-H) N-H stretching modes of terminal amino groups disappear due to bonding of these amino groups with carbonyl group of β-diketones in cyclization processes [37-38].

Table 2. IR spectral bands (ν / cm^{-1}) of molybdenum complexes 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)	$\nu_{asym\,(N-H)}$	$\nu_{sym(N-H)}$
$[MoO_2(L)](acac)_2$	1655s	475m	1525s	1458m	905s	935m	3360s	3200m
$[MoO_2(mac^1)](acac)_2$	1644m	478s	1548s	1465m	904s	945s		
$[MoO_2(mac^2)](acac)_2$	1650s	480m	1545m	1450s	900s	952s		
$[MoO_2(mac^3)](acac)_2$	1652s	482s	1550s	1465m	903m	946m		
$[MoO_2(mac^4)](acac)_2$	1655m	482m	1545m	1462m	905m	955s		

3.2. UV - Visible spectra

The electronic spectra of the dioxomolybdenum(VI) complexes were observed in 10^{-3} mol L^{-1} DMF solution and these bands are interpreted according to reported energy level scheme [37,38]. The electronic spectra are similar to other *cis*-dioxomolybdenum(VI) complexes having nitrogen as donor atoms. The electronic spectra of these dioxomolybdenum(VI) complexes are characterized by strong absorption bands in the UV region at ≈ 285 nm and at ≈ 390 nm seem to be due to ligand-to-metal charge – transfer (LMCT) and intraligand n→ π* / π → π* transitions. The bathochromic shift about 20 nm confirmed that linkage of the azomethine nitrogen to the molybdenum. Since Mo(VI) has a none d-electron, in some complexes, a medium intense bands shown in the region at ≈ 365 nm and at ≈ 405 nm may be assigned for LMCT transition between the lowest unoccupied d-orbital of molybdenum and highest occupied molecular orbital ligands [41,42]. Ballhausen-Gray scheme energy level scheme applied for these complexes and the electronic spectra show a distorted octahedral structure for all the complexes [43].

3.3. Magnetic and molar conductance measurements

Experimentally, the Mo(VI) complexes are diamagnetic, as expected for d^0 configuration and no d-d transitions are observed. The molar conductivity (Λ_M) for all synthesized complexes in DMF at ca. 10^{-3} M suggests 1:1 type electrolytes. The molar conductance values of dioxomolybdenum(VI) complexes lie between 95 - 110 Ω^{-1} cm^2 mol^{-1}.

The above data support the tentative structures of the complexes of the type (I) and macrocyclic complexes of the type (II) as shown in the Figure 1.

3.4. Thermogravimetric analyses

The thermogram of $[MoO_2(L)](acac)_2$ complex was captured in the temperature range 50 - 600 0C at the heating rate of 10 ^{0}C min-1. This complex was stable up to 135 ^{0}C. For $[MoO_2(L)](acac)_2$ complex two quite fast decomposition steps were observed (a) first step of decomposition is due to partial isolation of ligand (135 - 230 ^{0}C; mass loss obs. 55 %, calcd. 65 %). (b) the second step is the left residue of first step decomposed gradually at elevated temperature (290 - 460 ^{0}C) giving a mass loss about 25 % (cald. 20 %). A residue nearly corresponds to MoO_3 (obs. residual mass = 10 %, calcd. = 16.8 %) have been left after 435 ^{0}C. Two peaks were appeared in DTA curve. First peak is endothermic which is due to decomposition of the complex (120 ^{0}C) and second peak is exothermic. Neighbour to exothermic peak an exothermic hump was observed at 430 ^{0}C which may due to exothermic decomposition of the residual mass in the second step.

3.5. Antibacterial activity

The data of the antibacterial activities of synthesized complexes are given in table 3. Almost all the synthesized dioxomolybdenum(VI) complexes showed low to moderate activity against the tested strains. The enhancement in the antibacterial activity of dioxomolybdenum(VI) complexes, as compared with their ligand against *S. aureus* (complexes $[MoO_2(mac^2)](acac)_2$ and $[MoO_2(mac^4)](acac)_2$) and *E. aerogenes* (all complexes) can be explained on the basis of chelation theory [44-45].

Table 3. Antibacterial activities of macrocyclic complexes of dioxomolybdenum(VI)^a.

Complex	*Staphylococcus aureus*	*Enterobacter aerogenes*	*Salmonella typhi*	*Bacillus subtilis*	*Doxycycline*
$[MoO_2(L)](acac)_2$	18	22	16	20	25
$[MoO_2(mac^1)](acac)_2$	15	20	16	--	24
$[MoO_2(mac^2)](acac)_2$	18	20	--	20	23
$[MoO_2(mac^3)](acac)_2$	17	22	16	19	24
$[MoO_2(mac^4)](acac)_2$	18	18	15	21	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.

4. CONCLUSIONS

Five new dioxomolybdenum(VI) complexes with Schiff base have been prepared and structurally characterized - using elemental analysis, electronic spectra, IR spectra and molar conductance. Used spectroscopic techniques have confirmed the formation of macrocyclic products to ensure controlled geometry around MoO_2(VI) centre. The geometry around Mo is distorted octahedral in synthesized dioxomolybdenum(VI) complexes. Prepared Schiff bases behave as tetradentate ligands by bonding to the metal ion through the nitrogen atoms of azomethine. Analytical data proved the presence of one metal ion in ratio to one ligand molecule. X - ray crystallographic data of the synthesized dioxomolybdenum(VI) complexes, which might confirm the tentative structures, could not be possible because suitable crystals were not isolated. Low to moderate antibacterial activity exhibited by all complexes, but improved as compared with the Schiff base ligand.

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