OPEN ACCESS IOURNAL

BIOINTERFACE RESEARCH IN APPLIED CHEMISTRY

ORIGINAL ARTICLE www.BiointerfaceResearch.com ISSN 2069-5837

Volume 4, Issue 1, 2014, 671-677

Received: 18.10.2013 / Accepted: 14.01.2014 / Published on-line: 15.02.2014

New insights into the chemistry of dioxomolybdenum(VI) complexes with Schiff base

Devendra P. Rao[1,*]

ABSTRACT

New five dioxomolybdenum(VI) complexes with tetradentate Schiff base ligand, derived from condensation of furil with 2,3-diaminophenazine and their cyclization with β – diketones are reported. Synthesized complexes by elemental analyses, molar conductivity, UV-Vis and IR spectral studies. The coordination number of molybdenum in synthesized complexes is six. The geometry of dioxomolybdenum(VI) complexes are distorted octahedral.

Keywords: *cis-Dioxomolybdenum(VI) complexes, Schiff base, tetradentate ligand.*

1. INTRODUCTION

Molybdenum is a versatile in nature with large number of stable oxidation states, among which +4, +5 and +6 have received great attention recently, and coordination numbers varying from four to eight [1]. Only molybdenum in the second row of transition metals represents a biometal important for microorganisms, plants and animals. A number of dioxomolybdenum(VI) complexes with Schiff bases have been reported for synthesis, characterization and reactivity studies [2-5]. Molybdenum is an essential element of the nitrogenase enzyme, and cofactor for a great number of enzymes involved in protein synthesis. Many chemical reactions have been reported to be catalyzed by molybdenum complexes [6-8]. Dioxomolybdenum(VI) complexes have been reported as oxidation catalysts for epoxidation of olefins [9-12]. Some of the dioxomolybdenum complexes posses oxygen atom transfer properties like oxidizing thiols, polyketones and tertiary phosphines [13,14].

Furil is versatile in nature having two reactive carbonyl groups capable of undergoing Schiff base condensation with di- and polyamines. Thus, furil has played significant role in the design of macrocyclic ligands and such ligands form macrocyclic complexes with molybdenum [15]. Molybdenum-catalyzed oxygen-transfer reactions have attracted great interest. With this aspect, a new series of dioxomolybdenum(VI) macrocyclic complexes with new macrocyclic ligands derived from condensation of furil with 2,3-diaminophenazine capable of undergoing cyclization with β-diketones *via* the metal template effect have been prepared.

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

2. EXPERIMENTAL SECTION

2.1 Materials and methods. All the chemicals used were of reagent grade. Molybdenyl acetylacetonate, diamine, furil and β - diketones, namely acetylacetone, benzoylacetone,

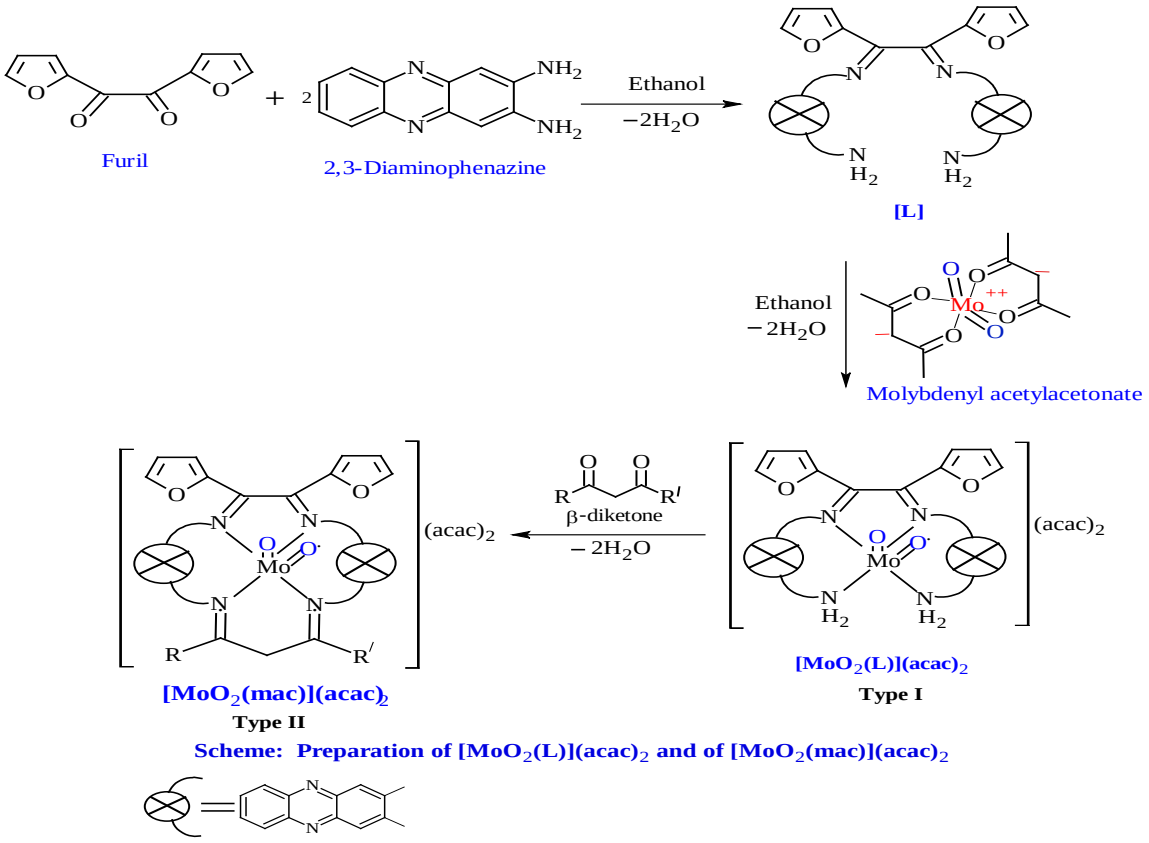
[1] Coordination Chemistry Laboratory, Department of Chemistry, D.A-V. P.G. College, Kanpur-208001, Uttar Pradesh, India

*Corresponding author e-mail address: ***devendrapratapprao@yahoo.com***

thenoyltrifluoroacetone, and dibenzoylmethane were purchased from Aldrich and used without further purification.

2.2 Analytical Methods and Physical Measurements. IR and TG/DTA were done at SAIF, IIT Bombay, India. Microanalysis of carbon, hydrogen and nitrogen for the complexes were carried out with Flash EA 1112 Series elemental analyzer. Kjeldahl's method was used to estimate nitrogen for the synthesized complexes. After decomposition of the complex, molybdenum was estimated gravimetrically by standard method [16]. Estimation of sulfur was carried out as barium sulfate [17]. Uncorrected melting points were determined by standard technique using sulfuric acid bath. The UV-visible spectra 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 (4000 - 50 cm^{-1}) were recorded on Nicolet Instruments Corporation, USA model no. Magna 550 spectrophotometer with CsI pellets. Thermograph of the $[MoO_2(L)](acac)_2$ complex were carried out under flowing 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* preparation of dioxomolybdenum(VI) complexes with ligands derived by condensation of furil with 2,3-diaminophenazine and their reactions with β-diketones. Figure 1 shows the preparation method of $[MoO_2(mac)](acac)_2$.



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

Where, L = furil + 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: *In-situ* preparation of macrocyclic complexes of *cis*-dioxomolybdenum(VI)

An ethanolic solution of molybdenyl acetylacetonate (5 mmol, 1.6307 g) was added dropwise to a refluxing solution of furil (5 mmol, 0.9507 g) and 2,3-diaminophenazine (10 mmol, 2.1023 g) in ethanol (50 mL) in RB flask. The resulting mixture was mild refluxed for 3h. The color of the reaction mixture turned into dirty yellow. The obtained precipitate was filtered off, washed with cold

ethanol for several times and isolated under in vacuum desicator over silica gel. Purity of the synthesized complex was checked by TLC. The yield was 40 % (type I). The reaction mixture of type I mixed 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 prepared macrocyclic complexes was checked by TLC (yield 55 %). 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)
$[MoO_2(L)](acac)_2$	$C_{44}H_{36}N_8MoO_8$	900.75	40	130	58.67 (57.05)	4.02 (3.10)	12.43 (11.0)	10.65 (9.75)	
$[MoO_2(mac^1)](acac)_2$	$C_{49}H_{40}N_8MoO_8$	964.84	55	145	60.99 (59.90)	4.17 (3.32)	11.61 (10.86)	9.94 (8.80)	
$[MoO_2(mac^2)](acac)_2$	$C_{54}H_{42}N_8MoO_8$	1026.92	60	125	63.15 (62.0)	4.12 (3.35)	10.91 (9.85)	9.34 (8.45)	
$[MoO_2(mac^3)](acac)_2$	$C_{52}H_{37}N_8MoO_8SF_3$	1086.92	55	128	57.46 (56.70)	3.43 (2.70)	10.30 (9.60)	8.82 (8.05)	2.95 (2.35)
$[MoO_2(mac^4)](acac)_2$	$C_{54}H_{44}N_8MoO_8$	1028.93	45	115	63.03 (62.15)	4.31 (3.85)	10.89 (10.05)	9.32 (8.75)	

2.4 Antibacterial activity assay. The antibacterial activity of the prepared complexes was evaluated *in vitro* against four bacterial strains i.e. *Staphylococcus aureus, Enterobacter aerogenes, Salmonella typhi* and *Bacillus subtilis* using cup and agar-well diffusion method [18-20]. Doxycycline was used as the standard antibacterial agent and wells having size of 6 mm in diameter were dug in the agar media with the help of metallic borer. The density of microbial inoculum in each well was adjusted to 3×10^5 colony-forming units (CFU) mL^{-1} were spread on the surface of the agar. The synthesized dioxomolybdenum(VI) complexes were dissolved in 1 % DMSO and concentration of the test sample (was 300 µg mL^{-1} in DMSO). The test samples were distributed in separate wells. Other wells were filled with DMSO and the antibacterial agent doxycycline. Growth inhibition was determined after 28 h incubation at 35 ^{0}C.

3. RESULTS SECTION

The dioxomolybdeum(VI) complexes with Schiff base were synthesized 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 resulted in macrocyclic complexes according to Figure 1.

3.1 Infrared spectra. The IR spectra of all the complexes and their tentative assignments are given in table 2. The linkage 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 [20-24]. The region 1657 - 1648 cm^{-1} is associated with >C=N absorption, which normally present at 1675 cm^{-1} in isolated ligands [20-23]. Absorption band at around 485 cm^{-1} may be assigned to ν_{Mo-N} vibration [25], which is absent in free ligands. The coordination of two keto groups of furil through carbonyl oxygen with diamines was evidenced by the appearance of >C=N band and the absence of the > C=O band around 1710 cm^{-1} [26,27]. The asymmetrical and symmetrical N-H stretching vibrations of the coordinated terminal amino group observed at 3365 and 3202 cm^{-1} [26]. The dioxomolybdenum(VI) complexes to synthesize preferentially a cis-dioxo group due to the maximum utilization of the d-orbital for bonding. The *cis*-dioxomolybdenum(VI) complexes showed

two Mo=O stretching bands at 900 - 907 cm^{-1} and 936 - 956 cm^{-1} due to asymmetric and symmetric stretching modes of the cis-$[MoO_2]^{2+}$ core in C_{2V} symmetry [28]. These two IR spectral bands are assigned to $\nu_{asym(O=Mo=O)}$ and $\nu_{sym(O=Mo=O)}$ vibrations respectively [29-32]. Generally, the frequencies of $\nu_{sym(O=Mo=O)}$ vibrations are higher than those of $\nu_{asym(O=Mo=O)}$ [33,34]. The presence of acetylacetonate group present at outer coordination sphere is confirmed by the bands appearing around 1528 - 1550 cm^{-1} and 1452 - 1470 cm^{-1} are assigned to $\nu_{C=O}$ and $\nu_{C=C}$ vibrations [35]. Infrared spectral bands of the synthesized 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 processes [35,36].

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)	$\nu_{asym\ (N-H)}$	$\nu_{sym(N-H)}$
$[MoO_2(L)](acac)_2$	1645s	485m	1528s	1455m	900s	936m	3365s	3202m
$[MoO_2(mac^1)](acac)_2$	1657m	486s	1545m	1470m	902w	940s		
$[MoO_2(mac^2)](acac)_2$	1648m	484m	1550s	1452m	902s	950m		
$[MoO_2(mac^3)](acac)_2$	1650s	485m	1548s	1465m	900m	948m		
$[MoO_2(mac^4)](acac)_2$	1656m	478m	1545m	1455m	907m	956s		

3.2 UV-Visible spectra. The UV-Vis spectra of the dioxomolybdenum(VI) complexes were measured in 10^{-3} mol L^{-1} DMF solution and these spectral bands are interpreted according to reported energy level scheme [37,38]. The UV-Vis spectra are similar to other *cis*-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 ligand - to-metal charge – transfer (LMCT) and intraligand n→ π* / π → π* transitions. The bathochromic shift about 20 nm proved that coordination of the azomethine nitrogen to the molybdenum.

Since Mo(VI) has a d^0 configuration, in some complexes, a medium intense bands appearing in the region at ≈ 360 nm and at ≈ 410 nm may be assigned for LMCT transition between the lowest unoccupied molybdenum d-orbital and highest occupied ligand molecular orbital [39,40]. Ballhausen - Gray scheme have provided energy level scheme for these complexes and the electronic spectra indicate a distorted octahedral geometry for all the complexes [41].

3.3 Magnetic and molar conductance measurements: The Mo(VI) complexes are diamagnetic, as expected for d^0 configuration. There is no d-d transitions are observed for these complexes because is no electron present in d-orbital. The molar conductivity (Λ_M) values for all synthesized dioxomolybdenum(VI) complexes in DMF at *ca.* 10^{-3} M suggest 1:1 type electrolytes. The molar conductance values of complexes lie between 105 - 110 Ω^{-1} cm^2 mol^{-1}.

The above results 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 was recorded in the temperature range 50 - 600 ^{0}C at the heating rate of 10 ^{0}C min^{-1} of $[MoO_2(L)](acac)_2$ complex. The complex was stable up to 145 ^{0}C. For $[MoO_2(L)](acac)_2$ complex two quite steep decomposition steps were observed (a) first step of decomposition is due to partial removal of ligand (145 - 250 ^{0}C; mass loss obs. 56 %, calcd. 60 %). (b) the second step is the left residue of first step decomposed gradually at elevated temperature (300 - 465 ^{0}C) giving a mass loss about 25 % against calculated mass loss of 21 %. A residue roughly corresponds to MoO_3 (obs. residual mass = 10 %, calcd. = 16.8 %) have been left after 450 ^{0}C. Two peaks were appeared in DTA thermogram. One peak is endothermic which is due to melting of the complex (128 ^{0}C). Second peak is exothermic. Closer to exothermic peak an exothermic hump was also observed at 448.5 ^{0}C which may due to exothermic decomposition of the residual mass in the second step.

3.5 Antibacterial activity: The results of the antimicrobial activities of synthesized dioxomolybdenum(VI) complexes are given in table 3. Almost all the synthesized complexes showed low to moderate activity against the tested strains. It is to be noticed the increased 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), which can be explained on the basis of chelation theory [42,43].

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

Complex	*Staphylococcus aureus*	*Enterobacter aerogenes*	*Salmonella typhi*	*Bacillus subtilis*	*Doxycycline*
$[MoO_2(L)](acac)_2$	16	15	15	19	26
$[MoO_2(mac^1)](acac)_2$	15	22	16	--	23
$[MoO_2(mac^2)](acac)_2$	18	18	--	20	23
$[MoO_2(mac^3)](acac)_2$	16	20	16	19	24
$[MoO_2(mac^4)](acac)_2$	18	22	15	21	25

4. CONCLUSIONS

The present research work demonstrate simple synthetic paths to new dioxomolybdenum(VI) with Schiff base. Used 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 MoO2(VI) centre. The geometry around Mo is distorted octahedral in synthesized complexes. Template effect of dioxomolybdenum(VI) cation plays an important role in the synthesis of Schiff base using furil and diamines in ethanol medium. Prepared Schiff bases behave as tetradentate ligands by coordinating to the metal ion through the azomethine nitrogen atoms. The presence of one metal ion in ratio to one 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 synthesized complexes. X - ray crystallographic data of the complexes, which might confirm the tentative structures, could not be possible, as suitable crystals were not isolated. All complexes exhibited low to moderate antibacterial activity, but generally improved as compared with the ligand.

5. ACKNOWLEDGMENT

This research work was financially supported by the UGC, New Delhi, India [project F. No. 39 - 740/2010 (SR)]. I am thankful to the Secretary, Board of Management, D.A-V. P.G. College,

Kanpur, U.P., India for providing laboratory facilities for research work. Author is grateful to SAIF, IIT, Bombay, India and STIC, Kochi, India for providing analytical facilities.

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