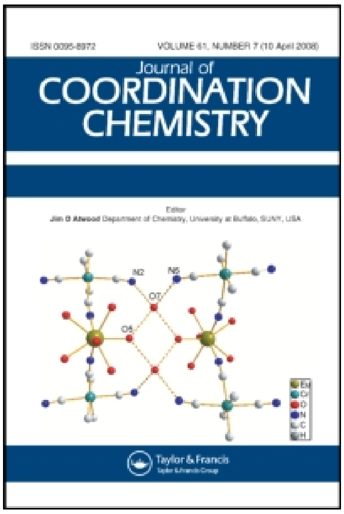

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In-situ preparation of macrocyclic complexes of dioxomolybdenum(VI) involving a heterocyclic precursor

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In-situ preparation of macrocyclic complexes of dioxomolybdenum(VI) involving a heterocyclic precursor

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Dioxomolybdenum(VI) complexes $[MoO_2(mac)](acac)_2$ (where mac = tetraazamacrocyclic ligands derived from condensation of thenil with 1,2-diaminobenzene or 2,3-diaminopyridine and their reaction with β-diketones) have been prepared using dioxometal ion as kinetic template. Tentative structures of the complexes have been proposed on the basis of elemental analysis, infrared, and electronic data. All the dioxomolybdenum(VI) complexes are six-coordinate octahedral ones.

Keywords: Dioxomolybdenum(VI); Kinetic template; Macrocyclic complexes

1. Introduction

Thenil is a versatile chelating agent having two reactive carbonyl groups capable of undergoing Schiff-base condensation with a variety of di- and polyamines. The use of metals as templates in such reactions has led to the synthesis of metal complexes of macrocyclic ligands. Thus, thenil has played an important role in the development of macrocyclic complexes. Such complexes show unusual structures and stability and are known to have relevance to biological systems [1–5]. This provides an opportunity to design and study biological model systems to understand the chemical changes taking place. However, in most cases, the template effect of metal ions of the first transition series has been studied and complexes of macrocyclic ligands with dioxomolybdenum(VI) incorporating four nitrogen donors has received less attention [6, 7]. The important role of molybdenum in physiological functions of oxomolybdoenzymes has been established [8–11]. This class of enzymes catalyzes conversion of xanthine to uric acid, sulfite to sulfate, and nitrite to nitrate, involving molybdenum centers undergoing redox reactions by transfer of oxygen. Mo-K-EXAFS [8] studies

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have established that the metal is coordinated to one or more terminal oxo-groups in each enzyme.

Some dioxomolybdenum(VI) complexes with new high denticity ligands derived by 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 and characterized, and their tentative structures ascertained.

2. Experimental

2.1. *Materials and methods*

All chemicals and the solvents used were of reagent grade. Dioxomolybdenum(VI) sulfate was procured from Aldrich; β-diketones, namely acetylacetone, benzoylacetone, thenoyltrifluoroacetone, and dibenzoylmethane were SRL products and the diamines used were of reagent grade. Thenil was obtained from Aldrich.

2.2. *Analytical methods and physical measurements*

Molybdenum was estimated gravimetrically after decomposing the complex with concentrated nitric acid by standard method [12]. Carbon and hydrogen microanalyses for the complexes were done at Central Research Facility, NERIST, Nirjuli 791109, Itanagar, Arunachal Pradesh, India. Standard method was employed to estimate nitrogen. Sulfur was estimated as barium sulfate [13]. The standard technique of melting point (uncorrected) determination using sulfuric acid bath was employed.

Electronic spectra of the complexes were recorded on a Beckmann DU-2 spectrophotometer and c Φ10 Russian spectrophotometer instrument from 2000 to 185 nm and 700 to 400 nm. Infrared spectra of the complexes (4000–200 cm^{-1}) were recorded in KBr on Perkin-Elmer 621 and Beckmann Acculab-9 spectrophotometers.

2.3. In-situ *preparation of dioxomolybdenum(VI) complexes with ligands derived by condensation of thenil with 1,2-diaminobenzene or 2,3-diaminopyridine*

Molybdenylacetylacetonate (2 mmol) dissolved in methanol (25 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 (25 mL). The mixture was refluxed for 6 h, when the color of the solution turned yellow. The solvent was removed under vacuum at room temperature and the dark yellow product isolated. The complex was thoroughly washed with methanol/ethanol mixture. Yield 70%.

2.4. In-situ *preparation of macrocyclic complexes of dioxomolybdenum(VI)*

Molybdenylacetylacetonate (2 mmol) dissolved in methanol (25 mL) was added to a refluxing solution of thenil (2 mmol) and 1,2-diaminobenzene or 2,3-diaminopyridine (4 mmol) in ethanol (25 mL). The mixture was refluxed for 5 h, when the color of the solution intensified and turned yellow. To this reaction mixture, an ethanolic solution (10 mL) of acetylacetone (2 mmol) and glacial acetic acid (5 mL) were added. The reaction mixture was refluxed for 5 h and yellow precipitate was obtained. The complex was purified by washing with 10 mL of methanol/ethanol (1 : 1). Yield 60%. The same procedure was adopted for the synthesis of other dioxomolybdenum(VI) macrocyclic complexes using benzoylacetone, thenoyltrifluoroacetone, and dibenzoylmethane. The physical and analytical data of the complexes are presented in table 1.

3. Results and discussion

The dioxomolybdenum(VI) complexes were synthesized using *in-situ* method by refluxing thenil, diamines, and molybdenylacetylacetonate in 1 : 2 : 1 molar ratio in aqueous ethanol. The reaction proceeds according to the following equation:

$$\text{Thenil} + 1,2\text{-diaminobenzene} + \text{Molybdenylacetylacetonate}$$

or

2,3-diaminopyridine

$$\Big\downarrow \text{Ethanol}$$

$$[\mathrm{MoO_2(L)}](\mathrm{acac})_2 + 2\mathrm{H_2O}, \textbf{(I)}$$

where L^1 = Thenil + 1,2-diaminobenzene and L^2 = Thenil + 2,3-diaminopyridine.

The parent complexes $[\mathrm{MoO_2(L)}](\mathrm{acac})_2$ react with β-diketones to yield $[\mathrm{MoO_2(mac)}](\mathrm{acac})_2$ as given below:

$$[\mathrm{MoO_2(L)}](\mathrm{acac})_2 + \beta\text{-diketones} \rightarrow [\mathrm{MoO_2(mac)}](\mathrm{acac})_2 + 2\mathrm{H_2O}, \textbf{(II)}$$

where mac = tetraazamacrocyclic ligands derived from condensation of L^1 or L^2 with β-diketones in the presence of dioxomolybdenum(VI) cation.

The elemental analyses (table 1) of complexes show 1 : 1 metal to ligand stoichiometry. The molar conductivity of dioxomolybdenum(VI) complexes in DMF showed Λ_M values between 120 and 138 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$, which indicate their electrolytic nature.

3.1. *Infrared spectra*

The important bands of the infrared spectra for complexes are listed in table 2. The macrocyclic complexes of dioxomolybdenum(VI) exhibit >C=N absorption around 1625–1610 $\mathrm{cm^{-1}}$, which normally appears at 1660 $\mathrm{cm^{-1}}$ in free ligands [14–16]. The lowering of this band (type-**I**) indicates coordination of nitrogen of azomethine to molybdenum [14–17]. A band at 300 $\mathrm{cm^{-1}}$ may be assigned to ν(Mo–N) [18]. The appearance of >C=N band and the absence of >C=O band around 1700 $\mathrm{cm^{-1}}$ are conclusive evidence for condensation of the diamines with the two keto groups of thenil [19]. Bands at 3350 and 3180 $\mathrm{cm^{-1}}$ may be assigned to the asymmetrical and symmetrical N–H stretching modes of coordinated terminal amino group [19]. The dioxomolybdenum(VI) complexes prefer to form a *cis*-dioxo due to the maximum utilization of the d-orbital for bonding. The *cis*-dioxo configuration in $\mathrm{MoO_2}$(VI) [20–22] is characterized by two infrared bands, ν_{asym}(O=Mo=O) and ν_{sym}(O=Mo=O),

Table 1. Physical and analytical data of the complexes.

Complex	Empirical formula	Decomposing temperature (°C)	C% Calcd (found)	H% Calcd (found)	N% Calcd (found)	Mo% Calcd (found)	S% Calcd (found)
$[MoO_2(L^1)](acac)_2$	$C_{32}H_{32}N_4MoO_6S_2$	306	52.8 (52.6)	4.4 (4.3)	7.7 (7.6)	13.2 (13.1)	8.8 (8.7)
$[MoO_2(L^2)](acac)_2$	$C_{30}H_{30}N_6MoO_6S_2$	304	49.3 (49.2)	4.1 (4.0)	11.5 (11.5)	13.1 (13.1)	8.8 (8.7)
$[MoO_2(mac^1)](acac)_2$	$C_{37}H_{36}N_4MoO_6S_2$	308	56.1 (56.0)	4.5 (4.5)	7.1 (7.0)	12.1 (12.0)	8.1 (8.0)
$[MoO_2(mac^2)](acac)_2$	$C_{42}H_{38}N_4MoO_6S_2$	305	59.0 (58.9)	4.4 (4.3)	6.6 (6.6)	11.2 (11.2)	7.5 (7.4)
$[MoO_2(mac^3)](acac)_2$	$C_{40}H_{33}N_4MoO_6S_3F_3$	304	52.5 (52.4)	3.6 (3.5)	6.1 (6.0)	10.5 (10.4)	10.5 (10.4)
$[MoO_2(mac^4)](acac)_2$	$C_{47}H_{40}N_4MoO_6S_2$	306	61.6 (61.5)	4.4 (4.3	6.1 (6.1)	10.5 (10.5)	7.0 (6.9)
$[MoO_2(mac^5)](acac)_2$	$C_{35}H_{34}N_6MoO_6S_2$	305	52.9 (52.8)	4.3 (4.3)	10.6 (10.5)	12.1 (12.0)	8.1 (8.0)
$[MoO_2(mac^6)](acac)_2$	$C_{36}H_{36}N_6MoO_6S_2$	308	56.0 (55.9)	4.2 (4.1)	9.8 (9.7)	11.2 (11.2)	7.5 (7.4)
$[MoO_2(mac^7)](acac)_2$	$C_{38}H_{31}N_6MoO_6S_2F_3$	304	49.8 (49.7)	3.4 (3.3)	9.2 (9.1)	10.5 (10.4)	10.5 (10.4)
$[MoO_2(mac^8)](acac)_2$	$C_{45}H_{38}N_6MoO_6S_2$	305	58.8 (58.7)	4.1 (4.0)	9.2 (9.1)	10.5 (10.4)	7.0 (6.9)

L^1 = ligand derived by condensation of thenil with 1,2-diaminobenzene (1 : 2); L^2 = ligand derived by condensation of thenil with 2,3-diaminopyridine (1 : 2); Mac^1 = macrocyclic ligand derived by condensation of L^1 with acetylacetone; Mac^2 = macrocyclic ligand derived by condensation of L^1 with benzoylacetone; Mac^3 = macrocyclic ligand derived by condensation of L^1 with thenoyltrifluoroacetone; Mac^4 = macrocyclic ligand derived by condensation of L^1 with dibenzoylmethane; Mac^5 = macrocyclic ligand derived by condensation of L^2 with acetylacetone; Mac^6 = macrocyclic ligand derived by condensation of L^2 with benzoylacetone; Mac^7 = macrocyclic ligand derived by condensation of L^2 with thenoyltrifluoroacetone; Mac^8 = macrocyclic ligand derived by condensation of L^2 with dibenzoylmethane.

Table 2. Infrared spectral bands of complexes.

Complex	Bands (cm^{-1}) (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
$[MoO_2(L^1)](acac)_2$	1618	301	1562	1515	908	944	3348	3180
$[MoO_2(L^2)](acac)_2$	1620	302	1560	1513	902	938	3352	3178
$[MoO_2(mac^1)](acac)_2$	1622	303	1564	1515	906	942		
$[MoO_2(mac^2)](acac)_2$	1620	304	1562	1515	904	946		
$[MoO_2(mac^3)](acac)_2$	1618	303	1560	1517	910	938		
$[MoO_2(mac^4)](acac)_2$	1620	302	1562	1513	906	944		
$[MoO_2(mac^5)](acac)_2$	1616	303	1564	1517	910	942		
$[MoO_2(mac^6)](acac)_2$	1620	304	1560	1513	903	943		
$[MoO_2(mac^7)](acac)_2$	1624	303	1562	1515	902	938		
$[MoO_2(mac^8)](acac)_2$	1618	302	1560	1517	902	940		

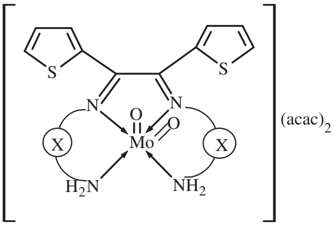
(1) ν(>C=N); (2) ν(Mo–N); (3) ν(C=0) of acetylacetonate group; (4) ν(>C=C<) of acetylacetonate group; (5) ν_{asym}(O=Mo=O); (6) ν_{sym}(O=Mo=O); (7) ν_{asym}(N–H) and (8) ν_{sym}(N–H).

in C_{2v} symmetry. The two infrared bands at 898–910 cm^{-1} and 935–945 cm^{-1} are assigned to ν_{asym}(O=Mo=O) and ν_{sym}(O=Mo=O), respectively. Bands at 1562 and 1515 cm^{-1} are assigned to ν(C=O) and ν(C=C) of acetylacetonate present in the outer coordination sphere [23]. The infrared spectra of macrocyclic complexes of type-**II** show the same pattern of bands but the asymmetric and symmetric N–H stretching modes of terminal amino groups disappear due to condensation of these amino groups with carbonyl of β-diketones in cyclization reactions [24, 25].

3.2. *Electronic spectra*

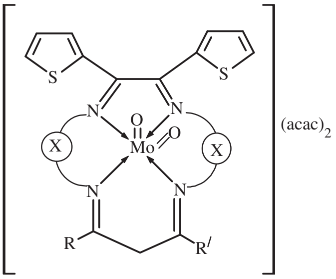
The patterns of the electronic spectra of the dioxomolybdenum(VI) complexes are similar and interpreted according to an energy level scheme [26, 27]. Electronic spectra of the complexes were recorded in 10^{-3} mol L^{-1} DMF. High intensity peaks at 295–360 nm of the dioxomolybdenum(VI) complexes appear due to intraligand $n \rightarrow \pi^*/\pi \rightarrow \pi^*$ transitions. A medium intensity peak at 343 and 394 nm may be assigned for ligand-to-metal charge transfer between the lowest empty molybdenum d-orbital and the highest occupied ligand molecular orbital [21].

On the basis of the above studies, the following tentative structures may be proposed for dioxomolybdenum(VI) complexes of type-**I**:



where X = 1,2-diaminobenzene or 2,3-diaminopyridine.

The tentative structures for macrocyclic complexes of type-**II** are shown below:



where

R	R′	*β*-Diketone
CH_3	CH_3	Acetylacetone
C_6H_5	CH_3	Benzoylacetone
C_4H_3S	CF_3	Thenoyltrifluroacetone
C_6H_5	C_6H_5	Dibenzoylmethane

4. Conclusions

The spectral data show that thenil is a versatile chelating agent having two reactive carbonyl groups capable of undergoing Schiff-base condensation with a variety of diamines. Schiff bases are tetradentate ligands by bonding to the metal ion through the azomethine and amine nitrogens. The analytical data show the presence of one metal ion per ligand and suggest a mononuclear structure. The analytical and electronic data are in the favor of octahedral structure for MoO_2(VI) complexes.

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