Molybdenum(VI) Complexes with Schiff Base Containing N-Hetero Atom

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Abstract: Parent dioxomolybdenum(VI) complex formation by the reaction of MoO2(acac)2 with Schiff base tetradentate ligand, described in this paper. Schiff base tetradentate ligand [H2NCH2CH2N=C(C(R)CH=O)CH2] obtained from the condensation of di-2-thienylethanedione with 1,2-diaminoethane. Macrocyclic molybdenum complexes were obtained from the cyclization of a synthesized complex with different 1,3 – diketones. The general formula of parent molybdenum complex is given as [MoO2(H2NCH2CH2N=C(C(R)CH=O)CH2)](acac)2 and for macrocyclic molybdenum complex is [MoO2{(CH2CH2N=C(C(R)CH=O)CH2)2N=C(R)CH2C(R’)=N}](acac)2. Ligand and all molybdenum complexes were characterized by elemental analyses(EA), molar conductivity(ΛM), ultraviolet(UV-Vis), and infrared (IR) spectral studies. The distorted octahedral geometry of element Mo in the parent as well as in macrocyclic molybdenum complexes is completed by two oxo O-atoms, four N-atoms from derived Schiff ligand.

Keywords: molybdenum complexes; di-2-thienylethanedione; macrocyclic ligand; cyclization.

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1. Introduction

Molybdenum is a valuable metal, with its ability to form complexes with several Schiff bases [1-5]. It is a necessary unit of defined enzymes, which catalyze the reduction of molecular nitrogen into ammonia (nitrogen fixation) in plants. It is also a significant unit of that enzymes which catalyze oxidation from aldehyde to carboxylic acid, sulfite to sulfate, olefin epoxidation as well as xanthene to uric acid in animals [6-9]. Oxo- and dioxomolybdenum was studied widely as catalysts for a number of transformation reactions, generally for sulfoxidation [5], O- atom transfer reactions (OAT) [10-18], antioxidant activity [19], and neutral esterification agents [20] as well. Some transition metal complexes with a large selection of oximes and Schiff base and coordination sphere have facilitated us to carry out our work in this area [21,22]. Schiff base transition complexes have demonstrated important implications in many transformations as homogeneous as well as heterogeneous catalysts [23], for example, ketones reduction in alcohol medium [24] and alkylation of allylic compounds [25-27]. Metal chelates of oxime present relatively markedly higher biological properties that relative free ligands [28]. Different complexes of oximes showed cytotoxicity in murine and human tissue cultured cells [29]. The purpose of the current research was to prepare a unique molybdenum complex with Schiff base macrocyclic ligands synthesized from the reaction of di-2-thienylethanedione with...
1,2-diaminoethane. This complex was suitable for undergoing cyclization with 1,3-diketones through the metal template effect.

The authors reported the synthesis and formal structures of these parents and cyclized molybdenum complexes based on different characterization viz. molar conductance, EA, infrared, and electronic spectra.

2. Materials and Methods

2.1. Materials.

All chemicals used for the synthesis of Schiff base, parent, and macrocyclic complexes were of reagent grade. Molybdenyl acetylacetonate, 1,2-diaminoethane, di-2-thienylethanedione, and 1,3-diketones, namely dibenzoylethene acetylacetone, thenoyltrifluoroacetone, and benzoylaceton were purchased from Aldrich. These were used as such i.e., without further purification.

2.2. Analytical Methods.

Elemental microanalysis of the ligand and complexes were carried out at CRF, NERIST, Nirjuli-791109, Itanagar, Arunachal Pradesh, India. The standard method (Kjeldahl) was availed for nitrogen estimation. Metal and sulfur were estimated after the decomposition of the complex by standard methods [30,31]. Undisciplined melting points were evaluated by the standard method using a sulphuric acid bath. The electronic spectra measurements of the ligand and complexes were recorded on a Φ10 Russian spectrophotometer and Beckmann DU-2 spectrophotometer, the ranges 700-400 nm and 2000-185 nm, and by using methanol as solvent. The infrared spectra (4000 - 50 cm⁻¹) of the complexes were observed KBr. The models of IR spectrophotometers were Perkin-Elmer 621 and Beckmann Acculab-9.

2.3. In-situ preparation of [MoO₂(H₂NCH₂CH₂N=CC₄H₃S–CC₄H₃S=NCH₂CH₂)₂(acac)] and [MoO₂{(CH₂CH₂N=CC₄H₃S–CC₄H₃S=NCH₂CH₂)N=C(R)CH₂C(R')=N}](acac)₂.

Firstly, refluxed the solution of di-2-thienylethanedione (2.5 mmol, 0.5570 g) and 1,2-diaminoethane (5 mmol) in 50 mL ethanol in an RB flask. For the preparation of [MoO₂(mac)](acac)₂, the ethanolic solution of molybdenyl acetylacetonate (2.5 mmol, 0.8154 g) was added slowly to the above-refluxed solution. The obtained solution was mildly refluxed for 3h and got a dirty yellow color reaction mixture. The precipitate was collected by filtration, washed with cold ethanol, and dried in a vacuum desiccator over silica gel to obtain a solid product. TLC technique was used for checking the purity of the prepared complex (yield: 65%, type ‘A’). Ethanolic mixture of type ‘A’ complex again reacted for 2h with 1,3-diketones like 2,4-pentanedione or 1-phenyl-1,3-butanedione or 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione or 1,3-diphenyl-1,3-propanedione (1:1) to get macrocyclic complex (type ‘B’). The purity of the prepared complex was checked by TLC (yield 50 %) (scheme 1,2 & 3). The above method was also used to synthesize rest complexes.

The in-situ syntheses of [MoO₂(H₂NCH₂CH₂N=CC₄H₃S–CC₄H₃S=NCH₂CH₂NH₂)](acac)₂ and [MoO₂{(CH₂CH₂N=CC₄H₃S–CC₄H₃S=NCH₂CH₂)N=C(R)CH₂C(R')=N}](acac)₂ are shown in the following schemes.
Scheme 1. Synthesis of Ligand (L).

Scheme 2. Synthesis of [MoO$_2$(L)](acac)$_2$.

Scheme 3. Synthesis of [MoO$_2$(M)](acac)$_2$.

Where, Ligand (L) obtained from the reaction of Thenil and 1,2-diaminoethane; Macrocyclic ligands (ML) obtained from the reaction of L with 1,3-diketones in presence of MoO$_2$(VI) cation.

The metal to ligand stoichiometry (1:1 molar ratio) was proved by the elemental analyses (table 1) of the complexes.
These bands are assigned to ν_{\text{C=O}} which is absent in isolated ligands [37]. Asymmetric stretching vibrations of the coordinated terminal –NH₂ were observed at 3352 and 3178 cm⁻¹ [38,39]. This resulted in parent complexes according to scheme 1 and 2. Further cyclization of this parent complexes was done by the reaction of parent complex with 1,3-diketones according to scheme 3.

3.1. Infrared spectra.

The IR spectra of complexes are given in table 2. The shifting of ν_{\text{C=O}} to lower frequencies proved the bonding of N-atoms of azomethine groups to the Mo-atom in all macrocyclic complexes [32-36].ν_{\text{C=O}} absorption proved by the IR bands near 1624 - 1618 cm⁻¹. Generally, this type of band normally appears at 1645 cm⁻¹ in ligands [32-35]. IR band present around 303 cm⁻¹ may represent ν_{\text{Mo-N}} mode, which is absent in isolated ligands [37]. The coordination of two keto groups of di-2-thienylethanedione through carbonyl oxygen with N-atom of 1,2-diaminoethane has been proved by the presence of ν_{\text{C=O}} band and the missing of the ν_{\text{C=O}} band around 1710 cm⁻¹ [38,39]. Asymmetric and symmetric, the N-H stretching vibrations of the coordinated terminal –NH₂ were observed at 3352 and 3178 cm⁻¹ [38]. The formation of the cis-dioxo group is due to the maximum utilization of d-orbital for bonding. Infrared active vibrations viz. the symmetric Mo=O stretch at 936 - 942 cm⁻¹ and asymmetric Mo=O stretch at 904 - 910 cm⁻¹ of complexes of the cis-[MoO₂]²⁺ core has C₂v symmetry [40]. These bands are assigned to ν_{\text{sym}}(O=Mo=O) and ν_{\text{asym}}(O=Mo=O) vibrations respectively [41-44].

Table 1. Elemental analysis of the synthesized complexes.

| Complex      | Formula Weight | Empirical Formula | Mo % (Calcd.) | C % (Calcd.) | S % (Calcd.) | H % (Calcd.) | N % (Calcd.) | Decomp. temp. (°C) | Yield (%) |
|--------------|----------------|-------------------|---------------|-------------|-------------|-------------|-------------|---------------------|-----------|
| Macroyclic complex [A] | 696.70 | C₂₂H₃₀N₄S₂O₆Mo | (13.80) | (50.00) | (9.20) | (5.20) | (8.00) | 304 | 65 |
| Macroyclic complex [B] | 758.77 | C₃₄H₃₄N₄S₂O₆Mo | (12.60) | (53.80) | (8.50) | (5.04) | (7.40) | 306 | 60 |
| Macroyclic complex [C] | 818.77 | C₂₂H₃₀N₄S₂O₆Mo | (11.70) | (47.00) | (7.00) | (4.10) | (6.80) | 305 | 55 |
| Macroyclic complex [D] | 820.84 | C₂₂H₃₀N₄S₂O₆Mo | (11.70) | (57.10) | (7.80) | (5.00) | (6.80) | 304 | 50 |
| Parent complex | 632.61 | C₂₂H₃₀N₄S₂O₆Mo | (15.20) | (45.60) | (10.10) | (5.10) | (8.90) | 305 | 50 |

Parent complex:

\[ \text{[MoO}_2\text{(H}_2\text{NCH}_2\text{CH}_2\text{N=C(C=C(\text{NH})=N})\text{(acac)}\text{] (acac)}_2 \]

Macroyclic complex:

[A] \rightarrow \text{[MoO}_2\{\text{(CH}_2\text{CH}_2\text{N=C(C=C(\text{NH})=N})\text{H}_2\text{CH}_2\text{N=C(C=C(\text{NH})=N})\text{N=C(C=C(\text{NH})=N})\text{(acac)}\text{] (acac)}_2 \]

[B] \rightarrow \text{[MoO}_2\{\text{(CH}_2\text{CH}_2\text{N=C(C=C(\text{NH})=N})\text{H}_2\text{CH}_2\text{N=C(C=C(\text{NH})=N})\text{N=C(C=C(\text{NH})=N})\text{N=C(C=C(\text{NH})=N})\text{(acac)}\text{] (acac)}_2 \]

[C] \rightarrow \text{[MoO}_2\{\text{(CH}_2\text{CH}_2\text{N=C(C=C(\text{NH})=N})\text{H}_2\text{CH}_2\text{N=C(C=C(\text{NH})=N})\text{N=C(C=C(\text{NH})=N})\text{N=C(C=C(\text{NH})=N})\text{(acac)}\text{] (acac)}_2 \]

[D] \rightarrow \text{[MoO}_2\{\text{(CH}_2\text{CH}_2\text{N=C(C=C(\text{NH})=N})\text{H}_2\text{CH}_2\text{N=C(C=C(\text{NH})=N})\text{N=C(C=C(\text{NH})=N})\text{N=C(C=C(\text{NH})=N})\text{(acac)}\text{] (acac)}_2 \]
general, the vibrational frequencies of $\nu_{\text{asym}(O=Mo=O)}$ vibrations are lower than the ones $\nu_{\text{sym}(O=Mo=O)}$ vibrations [45,46].

The existence of (acac)$_2$ group present at outside coordination circle is demonstrated by the bands appearing around 1513 - 1517 cm$^{-1}$ and 1560 - 1564 cm$^{-1}$ are relegated to $\nu_{\text{C=C}}$ and $\nu_{\text{C=O}}$ vibrations [47]. Infrared frequencies of the complexes of type - B show the same pattern of spectral frequencies. The N-H stretching vibrations ($\nu_{\text{asym}(N-H)}$ and $\nu_{\text{sym}(N-H)}$) of the terminal –NH$_2$ groups disappear. This is because of the bonding of these –NH$_2$ groups with > C=O group of 1,3-diketones in the cyclization processes [47-48].

| Table 2. IR spectral bands (ν / cm$^{-1}$) of synthesized complexes. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Complex          | $\nu_{\text{C=N}}$ | $\nu_{\text{Mo-N}}$ | $\nu_{\text{C=O}}$ of acetylacetonate | $\nu_{\text{asym}}(O=Mo=O)$ | $\nu_{\text{sym}}(O=Mo=O)$ | $\nu_{\text{asym}}(N=H)$ | $\nu_{\text{sym}}(N=H)$ |
| Macroyclic complex [A] | 1624m | 303s | 1560s | 1515m | 910s | 938s | |
| Macroyclic complex [B] | 1618s | 301m | 1564m | 1517s | 908s | 942s | |
| Macroyclic complex [C] | 1622s | 302s | 1560s | 1513m | 906m | 936m | |
| Macroyclic complex [D] | 1620s | 303m | 1562m | 1517m | 904m | 942s | |
| Parent complex | 1620s | 304m | 1564s | 1513m | 904s | 940m | 3352s | 3178m |

3.2. UV - Visible spectra.

The UV spectra of the MoO$_2$(VI) complexes had been recorded in a solution of DMF of 10$^{-3}$ mol L$^{-1}$ concentration. These signals are interpreted in step with the energy level scheme [47-50]. The UV spectra are similar to those MoO$_2$(VI) complexes having hetero donor atoms like N-atom. The electronic spectra of these MoO$_2$(VI) complexes are via a means of strong absorption bands within the UV region at $\approx$ 295 nm, and $\approx$ 360 nm appears to be because of LMCT (ligand-to-metal charge – transfer) and intraligand $n \rightarrow \pi^*$ / $\pi \rightarrow \pi^*$ transitions. The bathochromic shift approximately 20 nm showed that linkage of the azomethine nitrogen to the molybdenum.

Since Mo(VI) has d$^0$ configuration, some complexes showed intense medium bands in the area at $\approx$ 343 nm and $\approx$ 394 nm. These bands may be due to LMCT transition between the lowest unoccupied (LUMO) d-orbital of Mo-metal and highest occupied molecular orbital (HOMO) ligands [51-53]. Energy level scheme (Ballhausen-Gray scheme) applied for parent and macrocyclic complexes. The UV spectra show a distorted octahedral configuration for macrocyclic complexes [54].

3.3. Magnetic and molar conductance measurements.

Practically, the Mo(VI) complexes are diamagnetic. Because it has a d$^0$ configuration, and no d-d transitions are possible. 1:1 type electrolytes suggested by the molar conductivity ($\Lambda$M) for all formed complexes in DMF at ca. 10$^{-3}$ M. $\Lambda$M values of synthesized complexes lie between 95 - 105 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

All the above data proved the uncertain structures of the complexes of the type A and macrocyclic complexes of type B as shown in schemes 2 and 3.
4. Conclusions

All MoO$_2$(VI) complexes are ready and structurally characterized. Used spectroscopic spectra have confirmed the formation of complexes to confirm geometry around the MoO$_2$(VI) center. The distorted octahedral geometry found around Mo in synthesized MoO$_2$(VI) complexes. Formed Schiff bases have tetradentate ligands properties. It is bonding to the metal ion through the azomethine N-atoms. Analytical data demonstrated the existence of 1:1 of metal ion and ligand molecule. X-ray crystal data of the synthesized complexes, which could ensure the tentative structures, could not be attainable as a result of appropriate crystals, were not isolated.

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Conflicts of Interest

The authors declare no conflict of interest.

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