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Short communication

SHORT COMMUNICATION

Synthesis and characterization of *cis*-dioxomolybdenum(VI) complexes having furil as a precursor molecule

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Abstract: The syntheses of some new dioxomolybdenum(VI) complexes having the general formula $[\text{MoO}_2(\text{mac})](\text{acac})_2$, (where mac = tetraazamacrocyclic ligands derived from the condensation of furil with 1,2-diaminobenzene or 2,3-diaminopyridine and their reaction with β -diketones) using the dioxometal ion as a kinetic template are reported. The prepared complexes were characterized by molar conductance, elemental analyses, infrared and electronic data. The spectral data indicate that the ligands act as tetradentate chelating agents. Due to their biological relevance, molybdenum catalyzed oxygen transfer reactions are of great interest. All the dioxomolybdenum(VI) complexes had octahedral geometry with six coordination.

Keywords: dioxomolybdenum(VI); condensation; amines; macrocyclic complexes.

INTRODUCTION

The versatile nature of molybdenum is due to its multiple oxidation states, which range from -2 to $+6$, and coordination numbers, which vary from four to eight.¹ In the second transition series, only molybdenum is considered as a bio-metal that is important for animals, plants and microorganisms. There are many reports on the use of dioxomolybdenum(VI) complexes, which act as catalysts in some biological processes^{2,3} and in some industrial processes.^{4–6} Due to their relevance in biological processes, molybdenum-catalyzed oxygen-transfer reactions have attracted considerable interest. Mo(VI) is present as a simple molybdate (MoO_4^{2-}) ion in aqueous solution depending on its concentration and the pH

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of the solution. The coordination chemistry of Mo(VI) is an actively pursued area of current research because of its catalytic properties and biological activities.^{7–10} Furil is a versatile chelating ligand having two reactive carbonyl groups capable of undergoing Schiff base condensation with a variety of di- and polyamines. Thus, furil has played an important role in the design of macrocyclic ligands. In this context, some dioxomolybdenum(VI) complexes with new high denticity ligands derived from the condensation of furil with 1,2-diaminobenzene or 2,3-diaminopyridine, capable of undergoing cyclization with β -diketones *via* the metal template effect, were prepared, characterized and their tentative structures ascertained.

Herein, the synthesis of these complexes and their tentative structures, based on molar conductivity, elemental analysis, and electronic and IR spectroscopy, are reported.

EXPERIMENTAL

Materials and methods

All the employed chemicals and solvents were of reagent grade. The β -diketones *viz.* acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane were SRL products and the diamines used were reagent grade products. Furil was obtained from Aldrich. Dioxomolybdenum(VI) acetylacetonate was prepared by the standard method using sodium molybdate and acetylacetone.

Analytical methods and physical measurements

The microanalysis of carbon, hydrogen and nitrogen for the complexes were realized at the Central Research Facility, NERIST, Nirjuli-791109, Itanagar, Arunachal Pradesh, India. Molybdenum was estimated gravimetrically after decomposing the complex with concentrated nitric acid by the standard method.¹¹ Sulphur was estimated as barium sulphate.¹² The standard technique of melting point (uncorrected) determination using a sulphuric acid bath was employed. The electronic spectra of the complexes were recorded on a Beckmann DU-2 spectrophotometer and a Φ 10 Russian spectrophotometer in the ranges 2000–185 nm and 700–400 nm. The infrared spectra of the complexes were recorded in the region 4000–200 cm^{-1} in pressed KBr pellets on a Perkin-Elmer 621 and a Beckmann Acculab-9 spectrophotometers.

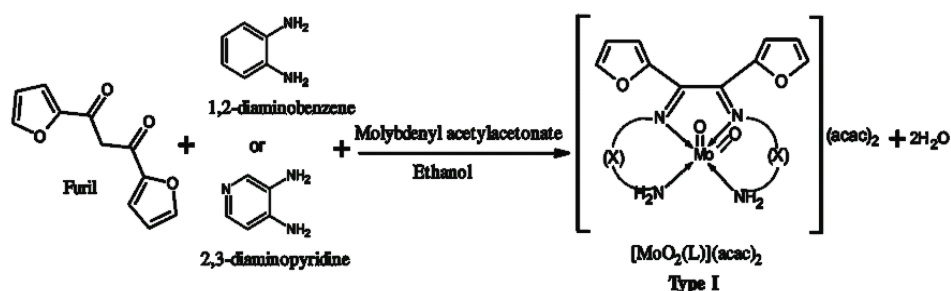
In-situ preparation of dioxomolybdenum(VI) complexes with ligands derived by condensation of furil with 1,2-diaminobenzene or 2,3-diaminopyridine

Molybdenyl acetylacetonate (2 mmol) dissolved in methanol (20 mL) was added to a refluxing solution of furil (2 mmol) and 1,2-diaminobenzene (4 mmol) or 2,3-diaminopyridine (4 mmol) in ethanol (20 mL). The mixture was allowed to react under mild reflux for 6 h, when the colour of the solution turned yellow (Scheme 1). The solvent was removed under *vacuo* at room temperature and the dirty yellow colour product was isolated. The complex was thoroughly washed with methanol/ethanol mixture. The yield was 70 %.

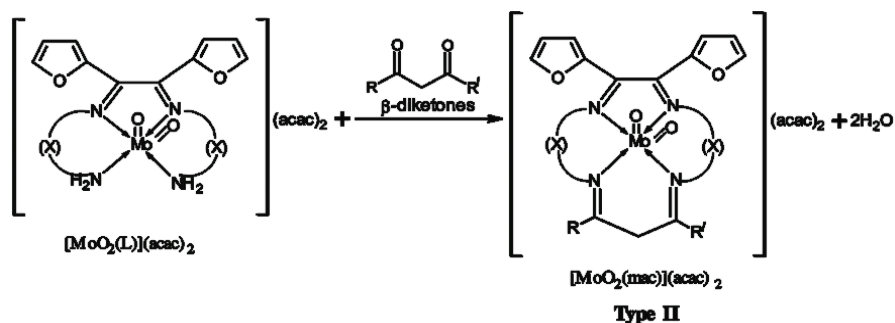
In situ preparation of macrocyclic complexes of dioxomolybdenum(VI)

Molybdenyl acetylacetonate (2 mmol) dissolved in methanol (20 mL) was added to a refluxing solution of furil (2 mmol) and 1,2-diaminobenzene or 2,3-diaminopyridine (4 mmol) in ethanol (25 mL). The mixture was subjected to mild reflux for 6 h, when the colour of the solution intensified and turned yellow (Scheme 2). To this reaction mixture, an ethanolic

solution (10 mL) of acetylacetonate (2 mmol) and glacial acetic acid (5 mL) were added. The reaction mixture was refluxed for about 6 h whereby a yellow precipitate was obtained. The filtered precipitate of the complex was purified by washing with 10 mL of a mixture of methanol/ethanol (1:1). The yield was 60 %. The same procedure was adopted for the synthesis of other dioxomolybdenum(VI) macrocyclic complexes using benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane.



Scheme 1. Preparation of dioxomolybdenum(VI) complexes; X = 1,2-diaminobenzene or 2,3-diaminopyridine; L¹ = furil + 1,2-diaminobenzene; L² = furil + 2,3-diaminopyridine.



Scheme 2. Preparation of macrocyclic complexes of dioxomolybdenum(VI); mac = tetraazamacrocyclic ligands derived from the condensation of L¹ or L² with β -diketones in presence of the dioxomolybdenum(VI) cation; R = CH₃, C₆H₅, C₄H₃S, C₆H₅; R' = CH₃, CH₃, CF₃ or C₆H₅; β -diketone = acetylacetone, benzoylacetone, thenoyltrifluoroacetone or dibenzoylmethane.

RESULTS AND DISCUSSION

The dioxomolybdenum(VI) complexes 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, as shown in Scheme 1, which resulted in the macrocyclic complexes according to Scheme 2.

Physical and analytical data of the molybdenum complexes

The physical and analytical data of the complexes are given in the Supplementary material to this paper. The elemental analyses of the complexes agreed

with the theoretical values and showed 1:1 metal to ligand stoichiometry. The molar conductivity of dioxomolybdenum(VI) complexes in dimethylformamide showed values of Λ_M between 125–140 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, which indicate their electrolytic nature.

Infrared spectra

The characteristic infrared spectral bands for the complexes are listed in the Table given in the Supplementary material to this paper. The macrocyclic complexes of dioxomolybdenum(VI) exhibit $>\text{C}=\text{N}$ absorption around 1625–1610 cm^{-1} , which normally appears at 1660 cm^{-1} in free ligands.^{13–15} The lowering of this band in the complexes (Type-I) indicates coordination of the nitrogen atoms of the azomethine groups to the molybdenum.^{13–16} The presence of a band at around 300 cm^{-1} may be assigned to $\nu(\text{Mo}-\text{N})$ vibrations.¹⁷ The appearance of $>\text{C}=\text{N}$ band and the absence of the $>\text{C}=\text{O}$ band around 1700 cm^{-1} is conclusive evidence for the condensation of the diamines with the two keto groups of furil.^{18,19} The bands appearing at 3350 and 3180 cm^{-1} may be assigned to asymmetrical and symmetrical N–H stretching modes of the coordinated terminal amino group.¹⁸ The dioxomolybdenum(VI) complexes prefer to form a *cis*-dioxo group due to the maximum utilization of the d-orbital for bonding. The *cis*-dioxo configuration in the dioxomolybdenum(VI) moiety^{20–22} is characterized by two infra-red bands, $\nu_{\text{asym}}(\text{O}=\text{Mo}=\text{O})$ and $\nu_{\text{sym}}(\text{O}=\text{Mo}=\text{O})$ in C_{2v} symmetry. The presence of two infra-red bands in the 898–910 cm^{-1} and 935–945 cm^{-1} regions are assigned to $\nu_{\text{asym}}(\text{O}=\text{Mo}=\text{O})$ and $\nu_{\text{sym}}(\text{O}=\text{Mo}=\text{O})$ vibrations, respectively. The bands appearing at 1562 and 1515 cm^{-1} are assigned to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ vibrations of the acetylacetonate group present in the outer coordination sphere.²³ The infrared spectra of macrocyclic complexes of Type-II show the same pattern of bands but the asymmetrical and symmetrical N–H stretching modes of the terminal amino groups are absent due to condensation of these amino groups with the carbonyl group of the β -diketones in cyclization reactions.^{24,25}

Electronic spectra

These spectra are similar to other dioxomolybdenum(VI) complexes involving nitrogen donor atoms. The electronic spectra of the complexes were recorded in $10^{-3} \text{mol L}^{-1}$ solution in DMF and these spectral bands are interpreted according to earlier reported energy level scheme.^{26,27} The high intensity peaks observed in the region 295–360 nm of the dioxomolybdenum(VI) complexes seem to appear due to intra-ligand $n \rightarrow \pi^*/\pi \rightarrow \pi^*$ transitions. A medium intensity peak appearing in the region 343 and 394 nm may be assigned as a ligand to metal charge-transfer transition between the lowest empty molybdenum d-orbital and highest occupied ligand molecular orbital.²⁸

The above details support the tentative structures of dioxomolybdenum(VI) complexes of Type (I) and macrocyclic complexes of type (II), as shown in the Schemes 1 and 2.

CONCLUSIONS

The spectral data show that the Schiff base condensation of furil, a versatile chelating agent, with diamines and their cyclization reaction with β -diketones were achieved by virtue of the kinetic template effect of the dioxomolybdenum(VI) cation in aqueous ethanol medium. The Schiff bases behave as tetradentate ligands by bonding to the metal ion through the azomethine nitrogen atoms. The analytical data show the presence of one metal ion per ligand molecule and suggest a mononuclear structure for the complexes. The analytical and electronic data support the octahedral structure for the dioxomolybdenum(VI) complexes.

SUPPLEMENTARY MATERIAL

Physical and analytical data of the synthesized molybdenum complexes are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА *cis*-ДИОКСОМОЛИБДЕН(VI) КОМПЛЕКСА КОЈИ САДРЖЕ ФУРИЛ КАО ПРЕКУРСОРСКИ МОЛЕКУЛ

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Полазећи од диоксомолибден(VI) јона темплатном методом синтетисани су нови комплекси опште формуле $[\text{MoO}_2(\text{mac})](\text{acac})_2$ (mac = тетраазамакроциклични лиганди добивени кондензацијом фурила са 1,2-диаминобензеном или 2,3-диаминопиридином и њиховом реакцијом са β -дикетонима). Синтетисани комплекси су окарактерисани на основу кондуктометријских мерења, резултата елементалне анализе, инфрацрвених и електронских апсорпционих спектра. На основу спектроскопских мерења нађено је да координациони број диоксомолибдена(VI) износи шест и да комплекси имају октаедарску геометрију са тетрадентатном координацијом испитиваних лиганата.

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