



Synthesis and Antibacterial Activity of Novel Molybdenum Complexes with Macrocylic Schiff Base Derived from Furanylethanedione

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A new MoO₂(VI) complex of formulation [MoO₂(L)](acac)₂ prepared by a Schiff base, synthesized *via* reaction of di-2-furanylethanedione with 5-chloropyridine-2,3-diamine and four new MoO₂(VI) complexes having formulæ [MoO₂(ML)](acac)₂, derived from cyclization of [MoO₂(L)](acac)₂ with β-diketones are reported in this work. The synthesized MoO₂(VI) complexes were characterized on the basis of various analyses like thermal studies, UV-Vis, elemental analyses, NMR, IR and molar conductance. The coordination number of molybdenum metal is six. All the MoO₂(VI) complexes have distorted octahedral structure in which Mo atom is coordinated with two O-atoms and four N-atoms. All the complexes show moderate activity against *S. typhi* and *S. aureus*. Advancement in the antibacterial task is thought to be of chelation speculation.

Keywords: MoO₂(VI), β-Diketones, Thermal study, Macrocylic Schiff base.

INTRODUCTION

A macrocyclic complex is a cyclic complex which contains nine or more than nine (involving all hetero atoms) as well as three or more donor atoms. The coordination chemistry area of macrocyclic compounds has experienced amazing growth during the last 25 years [1-4]. A number of transition metals form stable complexes with Schiff bases. The complexes with Schiff base may models for organically important species. Complexes of transition metal with multidentated ligands of unexpected structure and coordination number have been evaluated [5]. Oxidation numbers of Mo varying from -2 to +6. This is why molybdenum is flexible in nature [6]. The ability to arrangement of molybdenum complexes with N, O and S-atom containing ligands prompted advancement of molybdenum complexes which are proficient catalysts in homogeneous and additionally in heterogeneous reactions [7-12].

Mo(VI) is present in aqueous medium as a straight forward [MoO₄]²⁻ ion depends upon on the pH, concentration and of the medium. Oxygen transfer behaviour can show by molybdate ion agents [13]. Oxygen transfer activity of molybdate ion play

a great role in the mechanism of molybdenum oxotransferase [14,15]. Molybdate ion is paramount in the quite oxidized conditions of many redox catalysts. In this case their dynamic sites comprise of a *cis*-MoO₂ moiety [16-18].

Inside the second row of transition elements, only Mo is advised as bio-metal. Molybdenum is valuable for plants pathogenic, animal and human organisms [19,20]. Mo(VI) coordination chemistry is an important in research because of their enzymatic and organic interest [21-24]. Molybdenum established the physiologic actions of oxomolybdoenzymes [25-27]. Di-2-furanylethanedione is an adaptable chelating agent and consist of two reactive -CO groups. Consequently, di-2-furanylethanedione has performed a mandatory aspect for the synthesis in macrocyclic ligands.

With above subject, few MoO₂(VI) compounds with poly-denticity ligands will synthesize from reaction of di-2-furanylethanedione with diamine. The synthesized complex has capability of cyclization reaction with β-diketones through the template of metal. Keeping in view of the value of MoO₂(VI) ions in O-atom exchange reactions and antibacterial routines, a fresh number of MoO₂(VI) macrocyclic complexes are actually

synthesized. These complexes along with ligands have new denticity extracted from condensation of di-2-furanylethanedione with 5-chloropyridine-2,3-diamine effective at undergoing reaction with 1,3-diketones *via* the template effect of metal design have been formed.

EXPERIMENTAL

Reagent grade chemicals are used for the synthesis of Schiff base and their complexes. All the reagents and solvents were purchased from Aldrich and utilized without similarly purging, such as MoO₂(acac)₂, 5-chloropyridine-2,3-diamine, di-2-furanylethanedione and 1,3-diketones (2,4-pentanedione, 1-phenyl-1,3-butanedione, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, and 1,3-diphenyl-1,3-propanedione).

C,H,N-Elemental analyses for the synthesized complexes were done at CRF, NERIST, Itanagar, India by using CHN analyzer. Nitrogen estimation for the prepared complexes was done by Kjeldahl's method. Molybdenum element estimated gravimetrically by regular method after decomposition of the molybdenum complex [28]. Estimation of S-element was done as BaSO₄ [29]. Standard technique was used for determining uncorrected melting points with the help of sulfuric acid bath. The electronic absorption spectral measurements (ultraviolet-visible spectra) for the formed MoO₂ complexes were performed on Labinda-UV3000+ UV/VIS spectrophotometer in 1100 - 220 nm range by using ethanol as solvent. IR absorption spectra of the synthesized MoO₂(VI) complexes over the 4000-400 cm⁻¹ range were recorded in KBr on Perkin-Elmer Spectrum version 10.03.06 spectrophotometer. ¹H NMR spectra were acquired on JMM ECS-400 (JEOL) spectrometer with 400 MHz. Thermograph of parent complex [MoO₂(L)](acac)₂ was recorded under N₂ atmosphere between 50-600 °C at the 10 °C min⁻¹ heating rate through TG/DTA-Perkin Elmer, USA heat analyzers.

Synthesis of MoO₂(VI) complexes with Schiff base (L):

The solution of molybdenyl acetylacetonate (2.5 mmol, 0.81537 g) in ethyl alcohol was added drop by drop to solution of di-2-furanylethanedione (2.5 mmol, 0.4753 g) and 5-chloropyridine-2,3-diamine (5 mmol, 0.71785 g) in ethyl alcohol (50 mL). The mixture was gently refluxed for 2 h. The reaction mixture turned dirty yellow. The produced result filtered off and washed with ethyl alcohol. The solid product was isolated in vacuum in presence of silica gel. The progress of the reaction was followed by TLC until the reaction was completed. The yield of [MoO₂(L)](acac)₂ was 55 % (type I).

Equimolar concentrations of different 1,3-diketones *viz.* 2,4-pentanedione, 1-phenyl-1,3-butanedione, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione or 1,3-diphenyl-1,3-propanedione and the obtained product (type I) in ethyl alcohol refluxed for 2 h. TLC was used for checking the purity of type (II) macrocyclic complexes.

The solution of type I poured in ethyl alcohol and again reacted with 1,3-β-diketones in a ratio of 1:1 for 2 h to form macrocyclic products (type II). TLC was also used for checking the purity of type (II) macrocyclic complexes.

Physical and analytical data

Ligand (1): Yield: 72 %; m.p.: 90 °C; Anal. calcd. (found) % for C₂₀H₁₄N₆O₂Cl₂ (m.w. 441.27): C, 54.43 (54.40); H, 3.19

(3.22); N, 19.04 (19.02); where L = ligand prepared by reaction of di-2-furanylethanedione with 5-chloropyridine-2,3-diamine (1:2).

[MoO₂(L)](acac)₂ (2): Yield: 55 %; m.p.: 140 °C; Anal. calcd. (found) % for C₃₀H₂₈N₆O₈Cl₂Mo (m.w. 767.43): C, 46.95 (46.92); H, 3.67 (3.65); N, 10.95 (10.97); Mo, 12.50 (12.49).

[MoO₂(ML¹)](acac)₂ (3): Yield: 55 %; m.p.: 102 °C; Anal. calcd. (found) % for C₃₅H₃₂N₆O₈Cl₂Mo (m.w. 831.52): C, 50.55 (50.54); H, 3.87 (3.86); N, 10.10 (10.08); Mo, 11.53 (11.52); where ML¹ = macrocyclic ligand prepared by the reaction of ligand (L) with 1,3-diketone-2,4-pentanedione.

[MoO₂(ML²)](acac)₂ (4): Yield: 65 %; m.p.: 128 °C; Anal. calcd. (found) % for C₄₀H₃₄N₆O₈Cl₂Mo (m.w. 893.59): C, 53.76 (53.75); H, 3.83 (3.83); N, 9.40 (9.41); Mo, 10.73 (10.72); where ML² = macrocyclic ligand prepared by the reaction of ligand (L) with 1,3-diketone-1-phenyl-1,3-butanedione.

[MoO₂(ML³)](acac)₂ (5): Yield: 60 %; m.p.: 105 °C; Anal. calcd. (found) % for C₃₈H₂₉N₆O₈SCl₂F₃Mo (m.w. 953.59); ; Anal. calcd. (found) % for C, 47.86 (47.85); H, 3.06 (3.05); N, 8.81 (8.81); S, 3.36 (3.36); Mo, 10.06 (10.05); where ML³ = macrocyclic ligand prepared by the reaction of ligand (L) with 1,3-diketone-4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione.

[MoO₂(ML⁴)](acac)₂ (6): Yield: 55 %; m.p.: 120 °C; Anal. calcd. (found) % for C₄₅H₃₆N₆O₈Cl₂Mo (m.w. 955.66): C, 56.55 (56.53); H, 3.79 (3.78); N, 8.79 (8.78); Mo, 10.03 (10.01); where ML⁴ = macrocyclic ligand prepared by the reaction of ligand (L) with 1,3-diketone-1,3-diphenyl-1,3-propanedione.

Antibacterial assay: The synthesized MoO₂(VI) complexes were evaluated for antibacterial properties *in vitro* across four bacterial stresses *i.e.* *S. typhi*, *S. aureus*, *E. aerogene* and *B. subtilis* making use of cup and diffusion method of agar-well [20-22]. Herein, doxycycline drug was taken as standard antibacterial agent. Bore holes of 6 mm in diameter had been burrow in the agar by making use of metallic trencher. The denseness of solution of all bacteria in every pit has been adjusted in order to 3 × 10⁵ CFU/mL. The standardized solution were developed upon the top of agar medium. The formed MoO₂(VI) complexes were mixed in 1 % DMSO. Trial sample was contained 300 μg mL⁻¹ concentration. The trial samples have been placed in the analogous wells. Rest wells had been engaged with doxycycline (0.05 %) antibacterial agent and DMSO. Growth restriction has been check out after 28 h incubation at 35 °C.

RESULTS AND DISCUSSION

Infrared analysis: The MoO₂(VI) complexes with Schiff base were prepared by the reaction of molybdenyl acetylacetonate, 5-chloropyridine-2,3-diamine and di-2-furanylethanedione in 1:2:1 ratio in ethyl alcohol. Essential infrared spectral bands of ligand. MoO₂(VI) complexes and their uncertain modes were showed in Table-1. N-atoms of azomethine groups coordinated to Mo in all synthesized cyclic complex. It was evidenced by the lowering of ν(C=N) frequencies [30-33]. The frequencies 1653-1651 cm⁻¹ is assigned to stretching vibration of with >C=N group absorption. These frequencies normally origins at 1680 cm⁻¹ in ligands [30-32]. New infrared band about 468-466 cm⁻¹ might be represented to ν(Mo-N) vibration [28,34], which is lacking in isolated ligands. Bonding of two

TABLE-1
 INFRARED SPECTRAL BANDS (cm⁻¹) OF LIGAND AND MoO₂(VI) COMPLEXES

Complex	$\nu(\text{C}=\text{N})$	$\nu(\text{Mo}-\text{N})$	$\nu(\text{C}=\text{O})$ of acetylacetonate	$\nu(\text{C}=\text{C})$ of acetylacetonate	$\nu_{\text{asym}}(\text{O}=\text{Mo}=\text{O})$	$\nu_{\text{sym}}(\text{O}=\text{Mo}=\text{O})$	$\nu_{\text{asym}}(\text{N}-\text{H})$	$\nu_{\text{sym}}(\text{N}-\text{H})$
L	1646s	–	–	–	–	–	3356s	3180s
[MoO ₂ (L)](acac) ₂	1653s	468m	1564s	1459m	903s	930s	3344s	3175s
[MoO ₂ (ML ¹)](acac) ₂	1645s	465s	1558m	1470m	901s	935s	–	–
[MoO ₂ (ML ²)](acac) ₂	1651s	466m	1564s	1483m	903s	931s	–	–
[MoO ₂ (ML ³)](acac) ₂	1655s	474m	1565s	1465m	905m	935m	–	–
[MoO ₂ (ML ⁴)](acac) ₂	1650m	469m	1542m	1470m	900m	944s	–	–

ketonic groups of di-2-furanylethanedione *via* >C=O oxygen with diamines was evidenced through the presence of >C=N band and the missing of >C=O band near to 1710 cm⁻¹ [35,36].

IR spectral bands of tetradentate ligand and as well as its dioxomolybdenum(VI) complexes are quite complicated due to the presence of various ring vibrations and C-H vibrations. A wide band centered at 3356 cm⁻¹ for $\nu_{\text{asym}}(\text{N}-\text{H})$ and 3180 for $\nu_{\text{sym}}(\text{N}-\text{H})$. In the complex [MoO₂(L)](acac)₂ the two bands of primary amine appeared, but the second band is absent in complex [MoO₂(ML)](acac)₂, which confirm the coordination of NH-with the metal [37]. This is because of high application of *d*-orbital for coordination. The MoO₂(VI) complexes offer two Mo=O stretching bands at 903 and 931-930 cm⁻¹. These bands occur due to two stretching vibrations. These bands include one asymmetric stretching vibration and other symmetric stretching vibration of *cis*-[MoO₂]²⁺ moiety in C_{2v} symmetry [38]. These bands are assigned to $\nu_{\text{asym}}(\text{O}=\text{M}=\text{O})$ and $\nu_{\text{sym}}(\text{O}=\text{M}=\text{O})$ vibrations, respectively [38-44]. The $\nu_{\text{asym}}(\text{O}=\text{M}=\text{O})$ vibrations are less than those of $\nu_{\text{sym}}(\text{O}=\text{M}=\text{O})$ [45,46]. The absorption bands present around 1483-1459 and 1564-1540 cm⁻¹ are assigned to $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$ vibrations. These absorption bands confirmed the occurrence of (acac)₂ group present in outer sphere [47]. IR bands of the rest MoO₂(VI) complexes exhibited the matching pattern of absorption bands. Both N-H stretching (asymmetrical and symmetrical) modes of terminal -NH₂ groups disappear. This is because of bonding of these -NH₂ groups with CO group of 1,3-diketones in cyclization mechanism [47,48].

¹H NMR analysis: ¹H NMR spectra of ligand (L) and all the synthesized molybdenum complexes have been documented in DMSO-*d*₆. ¹H NMR spectrum of synthesized free ligand shows signal due to NH₂ at δ 5.72, which is also present in [MoO₂(L)](acac)₂ at δ 4.96 but absent in other four macrocyclic complexes [MoO₂(ML)](acac)₂ which suggest the cyclization by β -diketones (Table-2). The ten protons appear as multiplets within the range δ 6.80-7.24 for the ligand and molybdenum complexes. The peaks around δ 7.24 are assigned to protons of aromatic ring. ¹H NMR spectrum around δ 3.7-4.8 assigned to CH₂N fragment. The appearance of these chemical shifts may be due to the formation of two types of azomethine that is involved in the formation of macrocyclic complex. The sharp signal found as a singlet at δ 2.98 may be due to the water present in DMSO-*d*₆ sample used (Table-2).

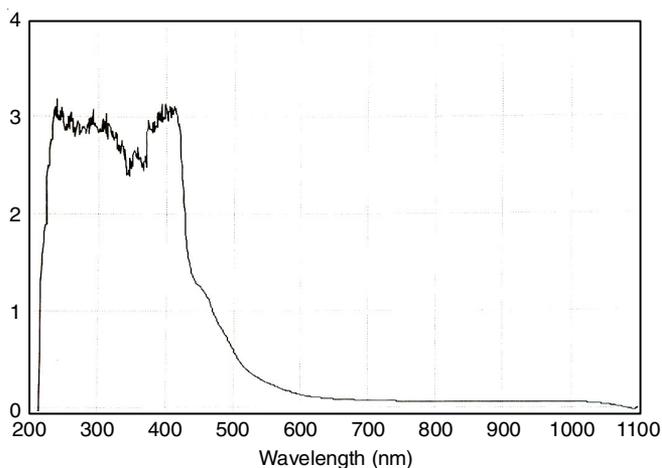
UV-visible spectra: The ultraviolet-visible spectra of tetradentate tetraaza ligand and dioxomolybdenum(VI) complexes were noted in ethanol. These electronic bands are construed according to reported vitality plan [49,50]. The spectra in the dioxomolybdenum(VI) complexes with tetradentate ligand are similar to be able to the other thereby suggesting a new uniform

 TABLE-2
¹H NMR SPECTRAL DATA OF LIGAND AND DIOXOMOLYBDENUM COMPLEXES (δ)

Complex	HC-Ar	N-H	C-H ₃	C-H
L	7.24 10H	5.72 4H	–	–
[MoO ₂ (L)](acac) ₂	6.95 10H	4.72 4H	2.47 12H	5.69 2H
[MoO ₂ (ML ¹)](acac) ₂	7.12 10H	–	2.45 12H	5.66 2H
[MoO ₂ (ML ²)](acac) ₂	7.05 10H	–	2.51 12H	5.71 2H
[MoO ₂ (ML ³)](acac) ₂	6.80 10H	–	2.69 12H	5.65 2H
[MoO ₂ (ML ⁴)](acac) ₂	6.89 10H	–	2.60 12H	5.71 2H

structure for all. The absorption bands of genuine *d-d* transition aren't expected to show up because Mo(VI) ion has no electron in *d*-orbital. Charge transfer transition was existed from atomic orbital of nitrogen to a molybdenum element *d*-orbital [N(π) \rightarrow *d*(Mo)]. The bands for such transition can be assigned. The recorded ultraviolet-visible spectra are comparable of rest MoO₂(VI) complexes that contain nitrogen atoms as donor sites.

Intra-ligand transition and $n \rightarrow \pi^*/\pi \rightarrow \pi^*$ transitions may occur in synthesized complexes. These transitions can be identified by powerful absorption bands in the ultraviolet region at \sim 293 nm and at \sim 330 nm. A reasonably intensive band appeared in the area \sim 380-390 nm is caused by [N(π) \rightarrow *d*(Mo)]. The transition ²B₂ \rightarrow ²A₁ (*d*_{xy} \rightarrow *d*_{x²-y²}) is probably masked by the above bands. It may be designated for charge-transfer transition from ligand (highest occupied ligand molecular orbital) to metal (the lowest unoccupied molybdenum *d*-orbital) [51,52]. Energy level diagram for synthesized Mo(VI) complexes was applied given by Ballhausen-Gray. UV-visible spectra (Fig. 1) show an octahedral arrangement (distorted) for all Mo(VI) complexes [53].


 Fig. 1. UV spectrum of [MoO₂(L)](acac)₂

Conductivity and magnetic susceptibility: The complexes of $\text{MoO}_2(\text{VI})$ have d^0 configuration. Therefore, they are diamagnetic. The absence of electron in d -orbital of $\text{MoO}_2(\text{VI})$ results in no $d-d$ transitions. The 1:1 type electrolytes were proven by the molar conductance (Λ_M) merit for each of $\text{MoO}_2(\text{VI})$ complexes in DMF at about 10^{-3} . The values of molar conductivity of these $\text{MoO}_2(\text{VI})$ complexes exist in the range $100\text{--}110 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Thus, the conductance values suggest the uncertain structures of type (I) $\text{MoO}_2(\text{VI})$ complexes and type (II) macrocyclic $\text{MoO}_2(\text{VI})$ complexes as presented in **Schemes I and II**.

Thermogravimetric analysis: Thermogravimetric analysis of $[\text{MoO}_2(\text{L})](\text{acac})_2$ complex was conducted in the heat range $50\text{--}600 \text{ }^\circ\text{C}$ with a $10 \text{ }^\circ\text{C min}^{-1}$ temperature interval. No decomposition observed below $140 \text{ }^\circ\text{C}$ (Fig. 2). The complex $[\text{MoO}_2(\text{L})](\text{acac})_2$ undergoes decomposition in two actions: (a) in first step, decomposition ($140\text{--}265 \text{ }^\circ\text{C}$) is due to the loss of ligand (obs. mass loss 55.50 %, calcd. 59.50 %) (b) in second step, the second gradual weight loss of at high temperature

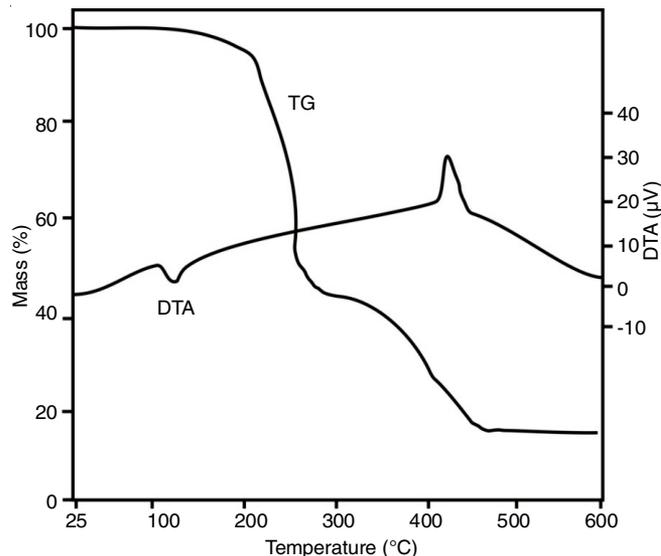
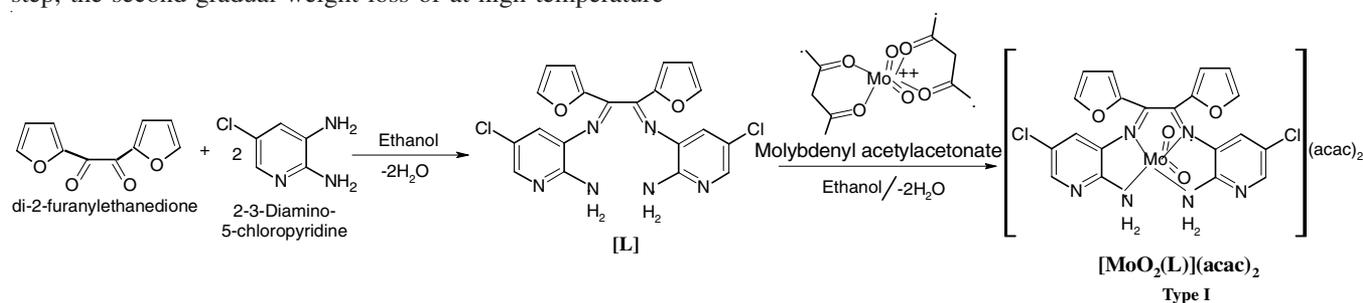
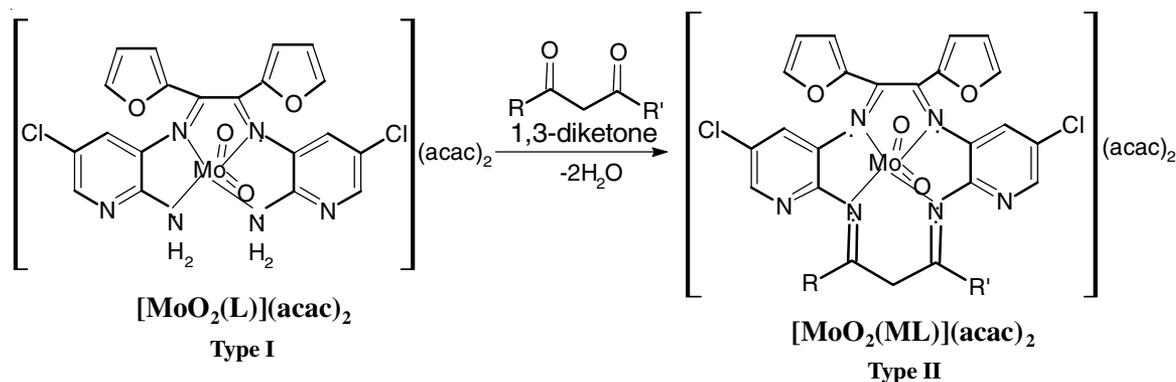
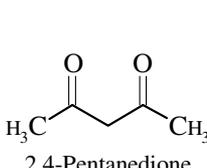
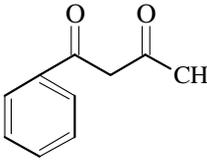
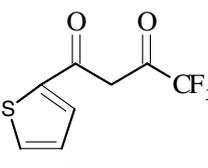
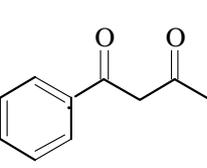


Fig. 2. TG and DTA thermographs of $[\text{MoO}_2(\text{L})](\text{acac})_2$



Scheme-I: Synthesis of $[\text{MoO}_2(\text{L})](\text{acac})_2$



Macrocyclic complexes	ML^1	ML^2	ML^3	ML^4
R & R'	R=CH ₃ R'=CH ₃	R=C ₆ H ₅ R'=CH ₃	R=C ₄ H ₃ S R'=CF ₃	R=C ₆ H ₅ R'=C ₆ H ₅
1,3-Diketones	 2,4-Pentanedione	 1-Phenyl-1,3-butanedione	 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione	 1,3-Diphenyl-1,3-propanedione

where, L = di-2-furanylethanedione + 5-chloropyridine-2,3-diamine; ML = Macrocyclic ligands carried out from condensation of L with 1,3-diketones in presence of dioxmolybdenum(VI) cation

Scheme-II: Synthesis of $[\text{MoO}_2(\text{ML})](\text{acac})_2$

TABLE-3
ANTIBACTERIAL PROPERTIES OF MACROCYCLIC COMPLEXES OF MoO₂(VI)

Complex	<i>S. aureus</i>	<i>E. aerogenes</i>	<i>S. typhi</i>	<i>B. subtilis</i>	Doxycycline
[MoO ₂ (L)](acac) ₂	14	16	16	20	26
[MoO ₂ (ML ¹)](acac) ₂	16	19	17	18	25
[MoO ₂ (ML ²)](acac) ₂	15	19	16	--	25
[MoO ₂ (ML ³)](acac) ₂	16	20	18	21	26
[MoO ₂ (ML ⁴)](acac) ₂	17	16	17	22	23

(300–460 °C) resulting in mass loss about 33 % versus computed mass loss of 29 %. Finally, a precipitate obtained approximately be in agreement with MoO₃ (obs. residual mass = 10.30 %, calcd. = 15.2 %) have already been kept after 460 °C. Two peaks had been obtained in DTA curve. Endothermic decomposition as a result of melting of the complex (140 °C) can be seen by the first peak. The second peak is due to the exothermic effect. Near this exothermic peak in DTA curve, an exothermic bump had been also observed at 451.50 °C. Residual mass obtained from exothermic decomposition in second step was proved by exothermic bump.

Antibacterial activity: The synthesized complexes of MoO₂(VI) had been analyzed against *S. typhi*, *B. subtilis*, *S. aureus* and *E. aerogenes*. Chelation principle was applied to explain the improvement in the antibacterial property of MoO₂(VI) complexes [47,48]. The growth inhibition showed in only two out of four bacteria namely *Staphylococcus aureus* and *Salmonella typhi* by all the MoO₂(VI) complexes (Table-3).

Conclusion

In this study, a basic pathways to form new MoO₂(VI) complexes with Schiff base is described. The spectroscopic methods have established the formation of Schiff base via reaction of di-2-furanylethanedione which is a flexible denticity ligand having two responsive >C=O groups with diamines. Macrocyclic MoO₂(VI) complexes formed by cyclizations of parent complex with β-diketones. The geometry about molybdenum metal is octahedral (distorted). Dioxomolybdenum(VI) cation act as kinetic template. A significant action was created by kinetic template in the formation of Schiff base using di-2-furanylethanedione and diamines in ethyl alcohol. Tetradentate tetraaza ligands behaviours were showed by formed Schiff bases. These Schiff bases coordinated towards molybdenum ion from the nitrogen atoms of azomethine. The analytical data confirmed the occurrence of one metal ion per ligand. Synthesized *cis*-MoO₂(VI) complexes have mononuclear six coordination sphere. Distort octahedral geometry happen to be recommended for these *cis*-MoO₂(VI) complexes.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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