



Antibacterial Effects of Mo(VI) Macrocyclic Compounds

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<http://dx.doi.org/10.13005/ojc/400518>

(Received: June 24, 2024; Accepted: October 08, 2024)

ABSTRACT

Preparing a monomeric [MoO₂(SL)] containing a Schiff base was achieved by condensing furil with 3-bromo-5-(trifluoromethyl) benzene-1,2-diamine, along with preparing 4 different compounds containing [MoO₂(MSL)]. A study of the interaction between 1,3-diketones and [MoO₂(SL)] is presented in this paper. As part of the study, UV-Vis, magnetic, IR, NMR, and thermal characterization were carried out on five MoO₂(VI) compounds. The coordination number of Mo will be six. The molybdenum octahedral geometry in these compounds consists of 4 N- and 2 O-atoms. When tested against *S. aureus* and *S. typhi*, there was moderate activity in all compounds synthesized. It is based on the chelation hypothesis that antibacterial tasks progress.

Keywords: Molybdenum(VI), Furil, β-diketones, macrocyclic compounds,
Schiff base, Chelation presumption, Antibacterial activity.

INTRODUCTION

A macrocyclic compound must contain at least nine atoms, including all heteroatoms. Three donor atoms must be present in this type of compound. The progress of macrocyclic compounds has accelerated over the past decades¹⁻⁵. A significant role is played in coordination chemistry by ligands containing N-atoms and their compounds. The physicochemical and biochemical properties of metal compounds are explored in various research papers⁶⁻¹¹. The transamination reactions of transitional Schiff bases with vitamin B6 can be

catalyzed by a formulation containing transitional Schiff bases with vitamin B6^{12,13}. Additionally, Schiff base compounds have antitumor, antifungal, and antiviral properties as well as anti-inflammatory properties¹⁴⁻²⁰.

In the bioinorganic field, Schiff base compounds can be used to model metal positions in metalloproteins and enzymes²¹. It has been shown that various Schiff bases have greater anticancer activity than isolated ligands²²⁻²⁹. Additionally, consumer electronics memory storage devices and chemistry reactions continue to fascinate them.



Different configurations and coordination numbers are found in ligands with extreme density in transition metal compounds^{30,31}. It is possible to adapt molybdenum in this aspect because of its multiple oxidation states. There is also a range of coordination numbers from 4 to 8³². Molybdenum compounds can be combined with ligands containing heteroatoms to form Schiff base structures, which can be utilized in both homogeneous and heterogeneous reactions. Moreover, MoO₂ compounds possess multiidentate ligands, enabling them to be applied in a range of biological applications³³⁻³⁹. Aqueous solutions of Mo(VI) can readily deliver [MoO₄]²⁻. [MoO₄]²⁻ ion concentration can be determined by pH and solution concentration. Oxygen transfer can be accomplished through the [MoO₄]²⁻ ion, which has been shown to exist as a template. Molybdenum oxotransferase is negatively affected by their oxygen transfer properties⁴⁰⁻⁴³. A number of redox enzymes have been shown to be fully oxidized. These active sites contain cis-dioxomolybdenum moiety.

Human pathogenic microorganisms, animal pathogens, and vegetation pathogens require molybdenum as a biometal⁴⁴⁻⁴⁸. A lot of research is currently being conducted on Mo(VI) coordinate chemistry because of its biological properties and catalytic properties⁴⁹⁻⁵². Oxomolybdoenzymes are set up by molybdenum molecules⁵³⁻⁵⁵. Furil may be useful as a chelating agent since it can be used in a variety of ways. Due to its reactive carbonyl groups, diamines and furils may undergo Schiff base condensation. It is essential for the synthesizing of macrocyclic ligands to use furil.

Under certain conditions, the reactions of diamine with furil can synthesize furil's denticity ligands. 1,3-Diketones are formed by the impact of metal templates on synthesized compounds. The proposed structures have been corroborated by various analytical techniques, including TG, molar conductivity, NMR, IR, and UV-Visible spectroscopy.

EXPERIMENTAL

Materials

A reagent grade chemical was used by chemists to prepare Schiff bases (ligands) and compounds from business resources. Additionally, we obtained molybdenyl acetylacetonate, trifluoromethyl

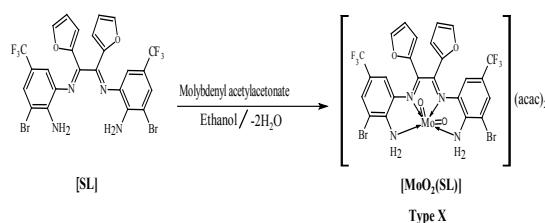
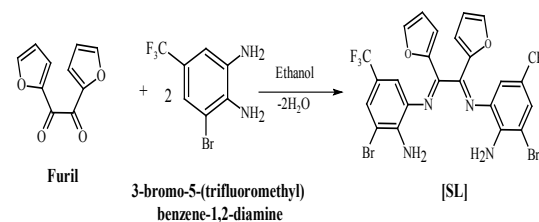
benzene-1,2-diamine, furil, and 1,3-diketones without further refinement from Aldrich.

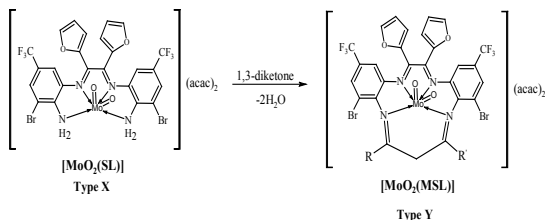
Physical Measurements and Analytical Methods

For synthesized compounds, Kjeldahl's method is used to determine nitrogen content. After decaying the compound, molybdenum was measured using a gravimetric method⁵⁶. A method of estimating sulfur was developed for barium sulfate⁵⁷. Sulfuric acid baths were used in addition to general methods for calculating uncorrected melting points. UV spectra were computed using a Labinda-UV 3000+UV/Vis spectrophotometer in ethanol. The Infrared spectra of compounds MoO₂(VI) were recorded using ATR at UPTTI Kanpur. Spectrometer PLN 2-II JMM ECS-400 (JEOL) was employed for ¹H NMR spectrum of MoO₂(VI) compounds. Thermal Analyser USA, SDT Q600 V 20.9 Built 20 was employed to investigate the temperature distributions of MoO₂(SL) in nitrogen gas atmosphere from 50-900°C with a heating rate of 10°C minute⁻¹.

Mo(VI) compounds synthesis

Here are three schemes for synthesizing [MoO₂(MSL)]. After dropping 5 mmol of molybdenyl acetylacetonate into ethanol drop-wise, furil (5 mmol) and 3-bromo-5-(trifluoromethyl) benzene-1,2-diamine (10 mmol) into ethanol were added. Two hours after the reaction mixture has been refluxed slightly, the solution has turned brown color. The product was then washed in ethanol and vacuum-isolated using silica gel after filtering. An analysis of the compound's purity was conducted using TLC. Therefore, the yield (Type X) increased to 55%. In Fig. 1 and 2, MoO₂(SL) and Schiff base ligand (SL) are shown as 3D structures.





3. Synthetic route to [MoO₂(MSL)]

MSL¹: R = CH₃, R' = CH₃; MSL²: R = C₆H₅, R' = CH₃; MSL³: R = C₄H₃S, R' = CF₃; MSL⁴: R = C₆H₅, R' = C₆H₅

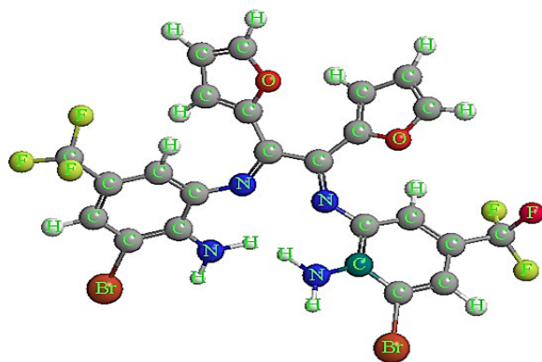


Fig. 1. 3D structure of ligand

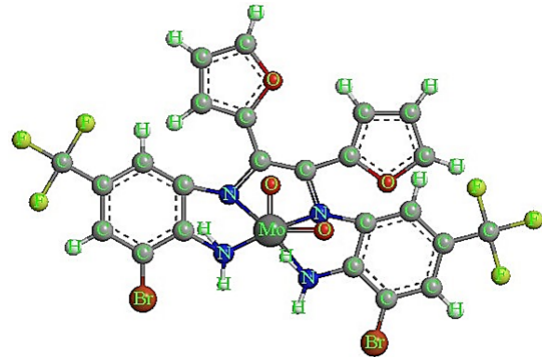


Fig. 2. 3D structure of [MoO₂(SL)]

After 3 h the 1,3-diketones were added to Kind X ethyl alcohol solution and a solid product was formed. Pigments of Type Y were isolated as yellow solid macrocyclic stable products from the reaction with 1,3-diketones (0.5 mmol : 0.5 mmol). Macrocyclic compounds are tested for purity by TLC.

Where,

Abbreviations: SL = Schiff base ligand; MSL¹ = compound with ligand and 2,4-pentanedione; MSL² = compound with ligand and Benzoylacetone; MSL³ = compound with ligand and 2-Thenoyltrifluoroacetone; MSL⁴ = compound with ligand and Dibenzoylmethane.

Elemental analysis (Table 1) data further supports the fact that they are 1:1 metal: ligand complex.

Antibacterial activity assay

An agar-well diffusion process was used to test resistance to antibacterial agents in several strains of bacteria. Diffusion in agar-wells was conducted⁵⁸⁻⁶⁰. A similar level of antibacterial activity was obtained by Doxycycline as well as other antibiotics. A metallic borer was used to drill 6 mm-diameter holes in agar media. We adjusted the density of all bacterial suspensions to 3x10⁵ CFU per mL. Standardized suspensions were used to expand agar. A 1% DMSO solution of 300 g per liter of the produced compounds was used in the investigation. The examined samples were poured into each well. A remainder of the wells contained DMSO (0.05%) and Doxycycline (0.5%). Growth inhibition is determined after 35 h of incubation at 355°C.

Table 1: CHN data of ligand and its compounds

Compound	Yield%	E.F.	F.W.	m.p.(°C)	(%). Calcd./.(found)				
					C	S	N	Mo	H
SL	46	C ₂₄ H ₁₄ Br ₂ F ₆ N ₄ O ₂	664.2	130	43.40 (42.5)	--	8.43 (8.35)	--	2.12 (2.10)
[MoO ₂ (SL)]	50	C ₃₄ H ₂₈ Br ₂ F ₆ MoN ₄ O ₈	990.35	135	41.23 (41.15)	--	5.65 (5.60)	9.68 (9.61)	2.84 (2.80)
[MoO ₂ (MSL ¹)]	55	C ₃₉ H ₃₂ Br ₂ F ₆ MoN ₄ O ₈	1054.44	128	44.42 (44.35)	--	5.31 (5.24)	9.09 (9.00)	43.05 (42.90)
[MoO ₂ (MSL ²)]	50	C ₄₄ H ₃₄ Br ₂ F ₆ MoN ₄ O ₈	1116.51	140	47.33 (47.27)	--	5.01 (4.95)	8.59 (8.53)	3.06 (3.02)
[MoO ₂ (MSL ³)]	48	C ₄₂ H ₃₂ Br ₂ F ₆ MoN ₄ O ₈ S	1122.54	135	44.93 (44.85)	2.85 (2.82)	4.99 (4.93)	8.54 (8.50)	2.87 (2.85)
[MoO ₂ (MSL ⁴)]	52	C ₄₉ H ₃₆ Br ₂ F ₆ MoN ₄ O ₈	1178.59	130	49.93 (48.90)	--	4.75 (4.71)	8.14 (8.10)	3.07 (3.00)

RESULTS AND DISCUSSION

Infrared spectra

The scheme shows the synthesis of dioxomolybdenum(VI) through an in-situ reaction of furil, molybdenum salt, and diamine in a 1:1:2 aqueous ethanol solution. The IR spectra of ligands and compounds exhibit several bands, detailed in Table 2. A macrocyclic species with azomethine N-atoms coordinated to molybdenum shows decreased C=N absorption frequencies⁶¹⁻⁶⁴. The band positions for isolated ligand >C=N absorbances are 1645-1670 cm⁻¹^{61,62}, and a Mo-N non-ligand vibration at 510-570 cm⁻¹ might cause this⁶⁵. Furil shows >C=N bands around 1660 cm⁻¹, making it a strong chelate ligand for diamines^{66,67}. Various ring and C-H vibrations are noted in the IR of MoO₂(VI) compounds

and isolated ligands, with asymmetrical and symmetrical (N-H) wide bands at 3435 and 3080 cm⁻¹, respectively. The absence of the NH group indicates that [MoO₂(SL)] and [MoO₂(MSL)] are identical. Mo(VI) compounds are mainly bonded via d-orbitals, typically forming cis-dioxo groups. The C_{2v} symmetry of dioxomolybdenum(VI) compounds reveals both $\nu_{\text{asymmetric O=Mo=O}}$ and symmetric $\nu_{\text{O=Mo=O}}$ vibrations in the IR spectrum⁶⁸⁻⁷⁶. The $\nu_{\text{asym(O=Mo=O)}}$ vibration is at a lower energy than the $\nu_{\text{sym(O=Mo=O)}}$ ^{77,78}. Bands around 1555-1572 cm⁻¹ and 1465-1480 cm⁻¹ in the outer coordination sphere correspond to C=O and C=C frequencies⁷⁹. A similar spectral pattern can be observed for macrocyclic compounds in the infrared region. The presence of amino groups attached to the carbonyl group in 1,3-diketones eliminates the asymmetric and symmetric stretching vibrations of these functional groups^{79,80}.

Table 2: IR bands of free ligand and its molybdenum compounds (ν/cm^{-1}) KBr, 4000-400 cm⁻¹

Compound	C=N	Mo-N	C=O (acac)	ν of		$\nu_{\text{asym(O=Mo=O)}}$	$\nu_{\text{sym(O=Mo=O)}}$	$\nu_{\text{asym(N-H)}}$	$\nu_{\text{sym(N-H)}}$
				C=C (acac)					
SL	1670	---	---	---	---	---	---	3330	3085
[MoO ₂ (SL)]	1645	510	1565	1465	910	975	3435	3080	
[MoO ₂ (MSL ¹)]	1664	570	1572	1480	890	968			
[MoO ₂ (MSL ²)]	1660	535	1560	1472	915	972			
[MoO ₂ (MSL ³)]	1650	565	1555	1470	904	960			
[MoO ₂ (MSL ⁴)]	1655	545	1564	1470	894	972			

¹H NMR spectra

In DMSO-D₆, all MoO₂(VI) compounds and their ligands were analyzed by ¹H NMR. SL should present a signal because of NH₂ at δ (5.30) as in [MoO₂(SL)] at δ (7.22) but not for other macrocyclic compounds, indicating the presence of 1,3-diketones from which cyclization results^{81,82}. All ten protons of the ligand are found in δ (7.43-6.53) multiplets in isolated ligands and molybdenum compounds. Protons on aromatic rings show $\sim \delta$ 7.30 peaks. The reason for these shifts was attributed to two types of azomethine used during the preparation of the macrocyclic compound.

¹H NMR in DMSO-D₆: SL: N-H (δ = 5.30, 4H), HC-Ar (δ = 7.43, 2H; 7.17, 2H), HC-furan (δ = 6.53, 4H; 7.84, 2H); [MoO₂(SL)]: N-H (δ = 7.22, 4H), HC-Ar (δ = 7.30, 2H; 7.40, 2H), HC-furan (δ = 6.53, 4H; 7.84, 2H); [MoO₂(MSL¹)]: HC-Ar (δ = 7.46, H; 7.63, 2H), HC-furan (δ = 6.53, 4H; 7.84, 2H), =C-CH₃ (δ = 0.87, 6H), -CH₂ (δ = 1.05, 2H); [MoO₂(MSL²)]: HC-Ar (δ = 7.46, 2H; 7.63, 2H), HC-furan (δ = 6.50, 4H; 7.45, 2H), -CH₂ (δ = 1.05, 2H); [MoO₂(MSL³):

HC-Ar (δ = 7.46, 2H; 7.63, 2H), HC-furan (δ = 6.50, 4H; 7.75, 2H), =C-CH₃ (δ = 0.87, 3H), -CH₂ (δ = 1.05, 2H), HC-thienyl (δ = 7.50, 1H; 7.25, 1H; 7.36, 1H); [MoO₂(MSL₄)]: HC-Ar (δ = 7.46, 2H; 7.63, 2H), HC-furan (δ = 6.45, 4H; 7.65, 2H), -CH₂ (δ = 1.05, 2H).

UV-Visible spectra

Ligand and dioxomolybdenum(VI) compounds suggest a strength energy level scheme that is consistent with these spectra in ethanol^{83,84}. Dioxomolybdenum(VI) compound spectra are similar to those of tetradentate ligands. It is no longer expected that the Mo(VI) ion will exhibit pure d-d absorption bands due to its lack of d- electron. There is a charge transfer between Molybdenum d-orbitals and nitrogen d-orbitals in all molybdenum compounds [N(π) \rightarrow d(Mo)]. It exhibits homogeneous UV-Vis spectra when nitrogen donor atoms are present in dioxomolybdenum(VI). These compounds show intense UV-Vis absorption bands at 290 and 315nm attributed to intraligand transitions and $n\rightarrow\pi^*/\pi\rightarrow\pi^*$ transitions. It seems to have N(π) \rightarrow d(Mo) in the region of 380–395nm for the band.

Other bands can also accommodate transitions ${}^2B_2 \rightarrow {}^2A_1$ ($d_{xy} \rightarrow d_{x^2-y^2}$) which are well-suited for mediating charge transfer between LUMO and HOMO. Diagrams of Ballhausen-Gray energy levels have been provided for these compounds. Almost all compounds have octahedral distortions in their electronic spectrums⁸⁵⁻⁸⁷.

Magnetic properties

Regarding dioxomolybdenum(VI) compounds, diamagnetism does not need to be mentioned when referring to d0 configuration. These electrons are missing in the d-orbitals, so no d-d transitions can be calculated for these compounds. Λ_M of these Mo compounds in DMF at approximately 10^{-3} M show a 1:1 sort electrolyte. These compounds exhibit Λ_M values of 97–115 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Molar conductance values suggested tentative shapes for both Type X and Type Y compounds, as predicted by the schemes.

Thermogravimetric analyses

The TG curve of a compound decomposed in one step is illustrated in Fig. 3. Approximately 83.1% of the weight is lost at 279°C due to the decomposition of the Schiff ligands and acetylacetonates, with the calculated weight being around 83%. A residue of 16.3% of MoO_3 remains after heating to 281°C. This weight percent is attributed to MoO_2 at 324°C and is 14.48.

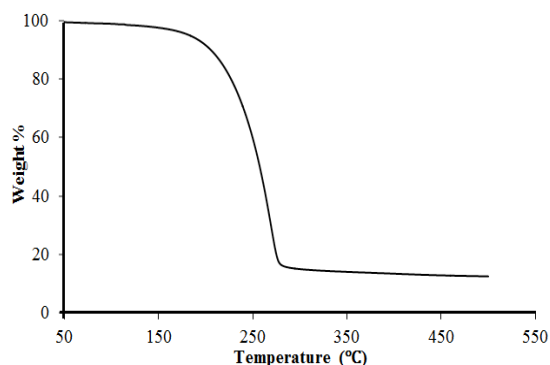


Fig. 3. $[\text{MoO}_2(\text{SL})]$ TG thermograph

Antibacterial activity

The dioxomolybdenum(VI) compounds in Table 3 possess antimicrobial properties. The results of the formed compounds on various bacteria such as *S. aureus*, *B. subtilis*, *E. aerogenes* and *S. typhi* were compared. An explanation for the improved antibacterial properties of Mo(VI) compounds can be found in the chelation presumption^{79,80}. In most cases, the compounds had a modest or low impact on *B. subtilis*, and *S. typhi*.

By using the positive control, we calculate the percentage inhibition effect using Eq 1.

$$\% \text{ inhibition effect} = \frac{\text{extract inhibition halo diameter}}{\text{positive control inhibition halo diameter}} \times 100 \quad (1)$$

Table 3: Data for antibacterial activities exhibited by various bacterial species^a

Compound	<i>S. aureus</i>	<i>E. aerogenes</i>	<i>S. typhi</i>	<i>B. subtilis</i>	Doxycycline
$[\text{MoO}_2(\text{SL})]$	19	20	15	17	25
$[\text{MoO}_2(\text{MSL}^1)]$	17	21	16	16	24
$[\text{MoO}_2(\text{MSL}^2)]$	18	20	19	17	24
$[\text{MoO}_2(\text{MSL}^3)]$	18	19	16	17	26
$[\text{MoO}_2(\text{MSL}^4)]$	17	19	16	15	24

^aDMSO is used to dissolve 300 $\mu\text{g mL}^{-1}$ of material per well in cups and wells. The inhibition zones range from 23-26, 15-18, and 19-22 for strong, moderate, good activity respectively. The antibiotic drug doxycycline is used as a reference drug for the measurement of inhibition zones (mm).

InChI

InChI=1S/C24H14Br2F6N4O2.Mo.2O/c25-13-7-11(23(27,28)29)9-15(19(13)33)35-21(17-3-1-5-37-17)22(18-4-2-6-38-18)36-16-10-12(24(30,31)32)8-14(26)20(16)3

InChI key of parent compound

BVPYRZUCCWATKB-UHFFFAOYSA-N

Smiles notation

FC(F)(F)c1cc(Br)c2[NH2][Mo]34(=O)(=O)[NH2]c5c(Br)cc(cc5[N]3=C(c6occc6)C(=[N]4c2c1)c7occc7)C(F)(F)F

LogP

5.50 +/- 0.67

CONCLUSION

As the crystal structures of the respective

compounds have not been isolated, crystal structures cannot be provided. Based on the above elemental and spectral studies, $[\text{MoO}_2(\text{SL})]$ or $[\text{MoO}_2(\text{MSL})]$ can be used to represent all compounds synthesized. These compounds have been tested for their antibacterial activity. This paper presents an analysis of dioxin derivatives derived from molybdenum Schiff bases. Two carbonyl groups, found in furil, proved this by using a flexible chelator. The geometric shape of $\text{MoO}_2(\text{VI})$ centers is controlled by macrocyclic products formed by their reaction with 1,3-diketones. Mo is surrounded by a distorted octahedron. Using furil and diamines, Schiff bases are condensed using dioxomolybdenum(VI) cation in an ethanol medium. Nitrogen atoms in azomethine form tetradentate bonds with molybdenum ions in synthesized Schiff bases. An ion of Mo is present in each ligand, based on analytical data.

Funding

This work was supported by the CSJM University, Kanpur, Uttar Pradesh, India under the C.V. Raman Minor Research Project Scheme (letter number CSJMU/P&C/CVR/316/2024, dated 07 March 2021).

ACKNOWLEDGMENT

It would be appreciated if the authors could thank the BoM-Secretary, D.A-V. Post-Graduate College, Kapur for the opportunity to look at the work in a laboratory setting. Fortuitously, UPTTI Kanpur India supplies analytical facilities.

Conflict of Interest

The financial interests of the authors are not in conflict.

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