

Preparation and Characterization of Mo(VI) and Mo(IV) Complexes with Schiff Base Ligands Bidetentate Derived from Salicylic Acid Hydrazide and The Study of Their Biological Activity



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ABSTRACT

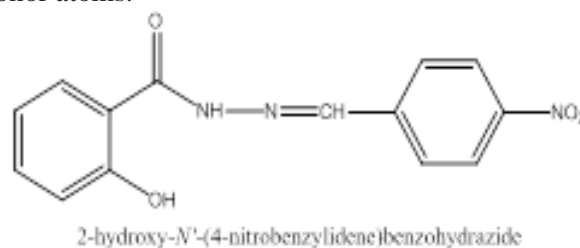
Mo(VI), and Mo(IV) complexes with two Schiff base ligands derived from salicylic acid hydrazide with 4-dimethylaminobenzaldehyde and 4-Nitrobenzaldehyde have been prepared and characterized by several techniques: infrared and electronic spectra, magnetic susceptibility, molar conductance measurements, and the metal content in complexes are estimated by gravimetric analysis. Based on this study square pyramidal structure for Mo(IV) complexes and octahedral structure for the Mo(VI) complexes are proposed. The biological activity of these are studied against two strain gram +ve bacteria (*Staphalococcus auras*, *P.aeruginosa*) and two strain gram -ve bacteria (*E.coli*, *Enterococcus*) and yeast *Candida albicans* to assess their inhibiting potential. The results show the two ligands are inactive against *Staphalococcus auras* and they have moderate activity against the rest microbacterial organisms, the antimicrobial screening show that complex [MoO (Lb)₂] exhibit the most activity against the two types of bacteria and the complex [MoO (La)₂] exhibit the most activity against the yeast *Candida albicans*.

Introduction

Transition metal complexes of Schiff bases have been the most widely studied coordination compounds in the past few years due to their unusual magnetic properties, novel structural features and relevance to biological systems.(1) Metal complexes play an essential role in many fields such as oxidation catalysis, electrochemistry, agriculture, pharmaceutical, and industrial chemistry.(2) The coordination chemistry of molybdenum in the oxidation states +4, +5, and +6 has received much attention recently due to the realization that molybdenum in these oxidation states is an essential trace element in a variety of redox enzymes.(3) The oxidation state of molybdenum in the oxocomplexes is determined by the number of oxo-groups attached to molybdenum.(4) Mo(IV) complexes with ligand hydrazine carboxamide and hydrazine carbothioamide showed antibacterial activity against *Staphalococcus auras* and *xanthomonas compestris*.(2).

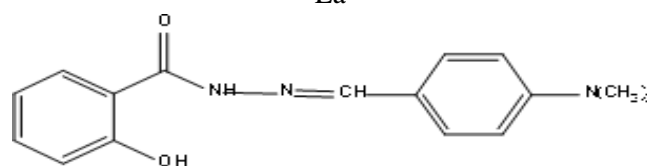
In order to study the physical, and antimicrobial properties of Schiff base with (O,N) donor atoms complexes of oxomolybdenum(VI) and (IV), two Schiff base ligand derived from salicylic acid hydrazide with 4-dimethylaminobenzaldehyde and 4-Nitrobenzaldehyde have been taken as potential (N,O) bidetentate ligand containing two donor atoms.

The aim of the present study is to prepare, characterize, and determine the antimicrobial activity of Mo(VI), Mo(IV) complexes with two Schiff base ligands derived from aroyl hydrazide containing (O,N) donor atoms.



2-hydroxy-N'-(4-nitrobenzylidene)benzohydrazide

La



N'-(4-dimethylaminobenzylidene)-2-hydroxybenzohydrazide

Lb

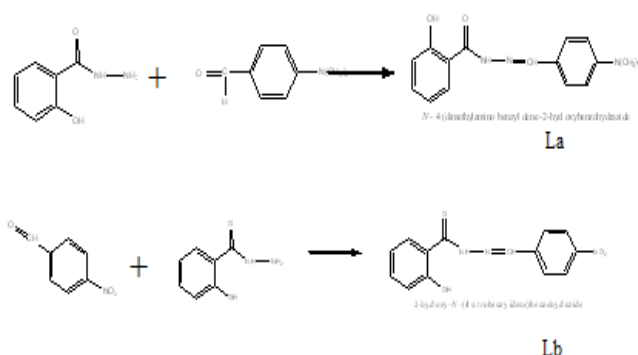
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Material and Methods

All chemicals used in this work are of analytical reagent grade and used as received from supply, salicylic acid hydrazide and Schiff base ligands are prepared according to literature methods.(5 ,6) The starting complex [MoO₂(acac)] is prepared as described in the literature(7) Melting points are recorded with Stuart melting points apparatus SMP30 and are uncorrected. IR spectra are recorded on SHIMADZU FTIR-8400 spectrophotometer in the frequency range 4000-400 Cm⁻¹ the measurements are carried out with samples in KBr disc, magnetic susceptibility measurements for Mo(IV) complexes are measured by using the equation $\mu_{\text{eff}}=2.82(\text{XMT})^{1/2}$ B.M., and carried out on Magnetic Susceptibility Bruker B.M at room temperature , UV-Visible spectra are recorded by using JENAY 6405 UV/VIS. Spectrophotometer in range 1200-200 nm in DMF , molybdenum is analytically determined according to the literature,(8). The molar conductivities of complexes measured by using Martin instrument Mi 805 and the antimicrobial activity of the prepared complexes are evaluated by the agar well diffusion. The organisms used are local (Staphalococcus auras, Enterococcus, E.coli, P.aeruginosa and yeast Candida albicans) .

Preparation of Schiff base ligands

To solution of 0.005 mole (0.76) g of salicylic acid hydrazide in 25 ml of absolute ethanol, 0.005 mole (0.746) g of 4- dimethylaminobenzaldehyde, or 0.005 mole (0.755) g of 4-nitrobenzaldehyde in 25 ml of absolute ethanol are added separately and the mixtures were refluxed for 4 hours where by yellow solids are precipitated. The solids are filtered, washed with ethanol several times, dried in vacuum in presence of CaCl₂, and recrystalized in ethanol.(6) Scheme(1).



Scheme (1). The preparation of two Schiff base ligands.

Preparation of Mo(VI) complexes: [MoO₂La₂] and [MoO₂Lb₂]

Into a stirred suspension of MoO₂(acac)₂ (0.001 mole (0.3) g in absolute methanol (20) ml, methanolic solutions(15) ml of the two Schiff base ligands (0.002 mole (0.56) g of La and (0.57)g of Lb are added separately and slowly with constant stirring and refluxed for two hours. The colored products are separated out, filtered, and washed with methanol dried in air.

Preparation of Mo(IV) complexes: [MoOLa₂] and [MoOLb₂]

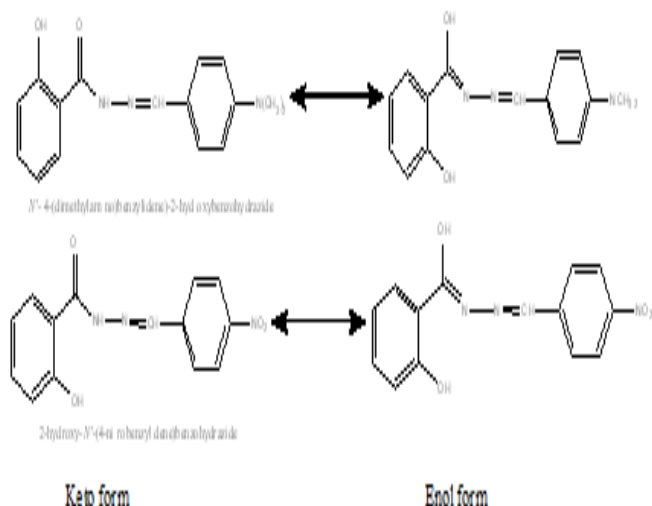
Methanolic solutions (20) ml of MoO₂(acac)₂ (0.001) mole (0.3) g, each Schiff base ligands (0.002) mole, and (0.001) mole (0.262) g of triphenylphosphine were added separately and slowly with constant stirring and refluxed for 30 minutes. Greenish yellow colored products were separated out. The products were filtered and washed with methanol and dried over CaCl₂.

Antimicrobial activity

The overnight cultures (0.2 ml) of each bacterium are dispensed into 20 ml sterile nutrient broth and incubated for about 3-5 h to standardize the culture. A loopful of the local cultures is used for the antibacterial assay. Muller Hilton agar is prepared and 20 ml of sterilized media is poured in to petriplates and allowed for solidification. The bacterial lawn culture is made using sterile cotton swab and labelled. The plates are incubated immediately at 37 °C for 24 h. Activity is determined by measuring the diameter of zones showing complete inhibition (mm).⁽⁹⁾

Results and discussion

Aroylhydrazide are N and O donor atoms which potentate the formation of polydentate Schiff base ligands. The lactam (keto) or lactim (enol) tautomeric forms scheme (2) give variation to the donating properties of the ligands.



Scheme(2): keto and enol forms of Schiff base ligands

All the complexes are colored, solids and are stable in air. All complexes melt over 350 °C and they are soluble in DMSO and DMF as shown in the table(1).

Table (1) the analytical and physical data of Schiff base ligands and its complexes

Compound	Formula	Color	Solubility	m.p °C	% Of metal (cal) obs.
[La]	C ₁₆ H ₁₇ N ₃ O ₂	yellow	ethanol	255	-
[Lb]	C ₁₄ H ₁₁ N ₃ O ₄	yellow	ethanol	268	-
[MoO ₂ (La) ₂]	C ₃₂ H ₃₂ Mo ₂ N ₆ O ₆	yellow	DMSO,DMF	>350	(13.85) 12.44
[MoO(La) ₂]	C ₃₂ H ₃₂ Mo ₂ N ₆ O ₅	Greenish-yellow	DMSO,DMF	>350	(14.18) 13.87
[MoO ₂ (Lb) ₂]	C ₂₈ H ₂₀ Mo ₂ N ₄ O ₁₀	yellow	DMSO,DMF	>350	(13.78) 13.32
[MoO(Lb) ₂]	C ₂₈ H ₂₀ Mo ₂ N ₄ O ₉	Greenish-yellow	DMSO,DMF	>350	(14.10) 12.8

Infrared Spectra

In order to study the bonding mode of ligands to metal ions in the complexes, IR spectrum of the free ligands are compared with the spectra of metal complexes. The most characteristic IR spectral bands of the ligands and their complexes are discussed in Table (2). The IR spectra of the two free ligands contain characteristic bands at around 3110 Cm⁻¹, 1650 Cm⁻¹, and 1620 Cm⁻¹ due to ν(OH), ν(C=O) and ν(CH=N) respectively. In the IR spectra of the molybdenum complexes the bands at around 1650 Cm⁻¹ and 3250 Cm⁻¹ due to ν(C=O), and ν(N-H) disappeared as the ligands coordinate from the oxime oxygen and the band around 1615 Cm⁻¹ due to ν(CH=N) shifted to around (1590-1595) Cm⁻¹ for the four complexes as the N of (CH=N) coordinate to the molybdenum, There are additional new vibrations between 1140-1150 Cm⁻¹ due to ν(C-O) of enol form of ligands and there are characteristic bands for ν(Mo=O) cis at around 841-920 Cm⁻¹, for Mo(VI) complexes, and ν(Mo=O) at around 920 Cm⁻¹ for Mo(IV) complexes⁽⁴⁾, and there are additional bands observed at around 1610 and 1615 Cm⁻¹ are attributed to the > C=N-N=C< ⁽⁹⁾, 480-530 Cm⁻¹ and 418-454 Cm⁻¹ due to ν(Mo-O) and ν(Mo-N) respectively.

Table (2) characteristic IR bands spectral bands of ligands and its complexes in Cm⁻¹

Compound	ν(OH)	ν(N-H)	ν(C=N)	ν(C-O)	ν(C=O)	ν(Mo-O)	ν(Mo-N)
La	3100	3250	1620	-----	1650	-----	-----
Lb	3010	3225	1620	-----	1650	-----	-----
[MoO ₂ (La) ₂]	3099	-----	1585	1142	-----	480	440
[MoO(La) ₂]	3100	-----	1581	1148	-----	505	418
[MoO ₂ (Lb) ₂]	3010	-----	1582	1140	-----	510	450
[MoO(Lb) ₂]	3012	-----	1585	1150	-----	530	454

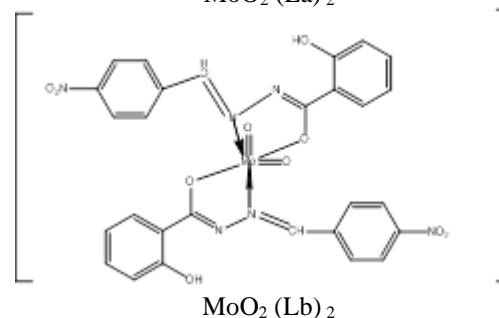
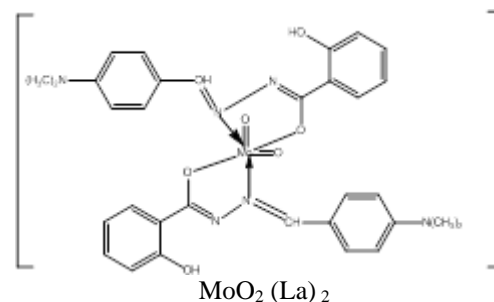
Electronic Spectral and Magnetic Moment Data

The electronic spectra and magnetic moments of the ligands and their metal complexes are disused in Table (3).

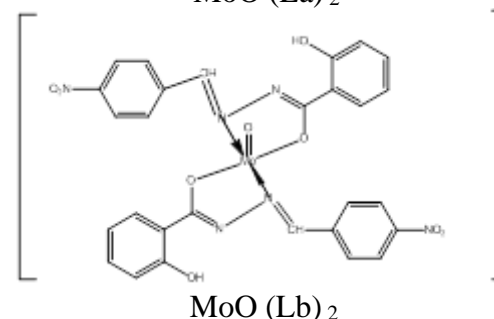
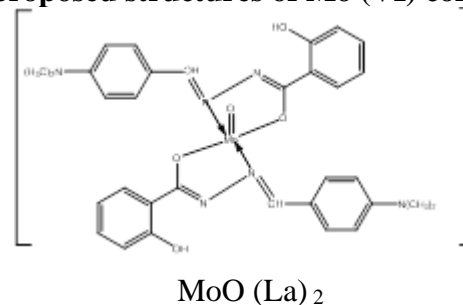
The absorption bands of the complexes will help to give an idea of their structure. The electronic spectra of the two ligands and all complexes in DMF are at room temperature Table (3). The aromatic band of the ligands at 258 nm is attributed to $\pi \rightarrow \pi^*$ transition of benzene ring. The band at 395 nm is attributed to $n \rightarrow \pi^*$ transition of the non-bonding electrons ⁽¹⁰⁾. The electronic spectra of molybdenum (VI) complexes display shoulder in 380,485 nm region and two strong absorption are located in the 250,262 nm region due to L-Mo(d π) LMCT and interligand transition respectively.⁽¹¹⁾ The Mo(IV) complexes showed strong bands at 495 nm represent one of the d-d transition in the d^2 system. The magnetic susceptibility measurements of the Mo (IV) complexes show $\mu_{\text{eff}}=2.3$ B.M, where as Mo (VI) complexes are diamagnetic. From this octahedral structure of Mo (VI) complexes are proposed and square pyramidal for Mo (IV) complexes are proposed.

Table (3). the electronic spectra, magnetic moments, and molar conductivity of ligands and its complexes in $1 \times 10^{-3} \text{M}$ in DMSO.

Compound	Abs. bands (nm)	Assignment	μ_{eff} B.M	Mho $\text{Cm}^2 \cdot \text{mol}^{-1}$ DMF DMSO		Structure
La	258, 395	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$	-	-	-	
Lb	258, 395	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$	-	-	-	
[MoO ₂ (La) ₂] [MoO ₂ (Lb) ₂]	380,485 250,262	LMCT INLT	0	5.33 5.2	6.1 5.7	Octahedral
[MoO(La) ₂] [MoO(Lb) ₂]	385,490 255,260	LMCT INLT	2.3	6.87 7.66	6.54 7.45	Square pyramidal



The proposed structures of Mo (VI) complexes



The proposed structures of Mo (IV) complexes

Conductivity Measurement

The molar conductance of the prepared complexes is determined at concentrations of $1 \times 10^{-3} \text{M}$ at room temperature in DMSO and DMF solvents, Table (3). Show values in range (5.4-8.49) Mho $\text{Cm}^2 \cdot \text{mol}^{-1}$ for all complexes indicating that the complexes are non electrolyte ⁽¹²⁾.

Antimicrobial Activity

The Schiff base ligands and its molybdenum complexes are evaluated for antimicrobial activity in concentration of 100 ppm. against two strain gram +ve bacteria (Staphalococcus auras, P.aeruginosa) and two strain gram -ve bacteria (E.oli, Enterococcus) and yeast Candida albicans. The antimicrobial results are

given in Table (4). These observations show that the two Schiff base are inactive against staphalococcus auras, whereas the prepared complexes are active. The metal complexes show higher activity than the ligands against all the bacteria and the yeast. Chelation may enhance the biochemical potential of bioactive organic species⁽¹³⁾. The antimicrobial screening show that complex [MoO (Lb)₂] exhibits the most activity against the two types of bacteria and the complex [MoO (La)₂] exhibit the most activity against the yeast. It has been suggested that the ligands with the N and O donor system might have inhibited enzymes production, since enzymes that require free hydroxyl groups for their activity appear especially susceptible to deactivation by the ions of the complexes.⁽¹⁴⁾ Such increased activity of the metal chelates can be explained based on chelation theory. On chelation, the polarity of metal ion will be reduced to greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π electrons over the whole chelate ring and enhances the penetration of the complexes into lipid membranes blocking of the metal binding sites in the enzymes of microorganisms.⁽¹⁵⁾

Table (4) Antimicrobial activity of ligands and its complexes in (mm) (concentration of 100 ppm in DMSO solvent:

Compound	Staphalococcus	E.coli	P.aeruginosa	Enterococcus	C.albicans
La	-----	4.7	4.2	3.7	3.33
Lb	-----	4.1	4.3	4.1	4.2
[MoO ₂ (La) ₂]	12.6	8.2	9.43	8.81	11.2
[MoO (La) ₂]	10.2	11.3	14.8	12.6	14.7
[MoO ₂ (Lb) ₂]	15.3	8.8	11.2	10.5	9.4
[MoO (Lb) ₂]	17.5	13.7	12.5	13.3	12.8

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تحضير وتشخيص معقدات الموليبدنوم(VI) و الموليبدنوم(IV) مع قواعد شيف ثنائية المنح المشتقة من السالسليك أسيد هيدرازيد ودراسة فعاليتها البايولوجيه

عثمان إبراهيم حمادي

الخلاصة

تم تحضير معقدات للموليبدنوم بحالات تاكسدية (VI) و(IV) مع اثنين من قواعد شيف المشتقة من السالسليك أسيد هيدرازيد مع 4-داي مثل امينوبنزالديهيد و 4-ناتروبنزالديهيد وتم تشخيصها بعدة تقنيات: طيف الأشعة تحت الحمراء والأطياف الالكترونية فوق البنفسجية والمرئية، التوصيلية المولارية، قياسات الحساسية المغناطيسية وتم تقدير نسبة الفلز في المعقدات باستخدام التحليل الكرافامتري 0 اعتمادا على نتائج هذه الدراسات تم اقتراح شكل فراغي ثماني السطوح لمعقدات الموليبدنوم (VI) وشكل هر م رباعي لمعقدات الموليبدنوم (IV). تم دراسة الفعالية البايولوجيه لقواعد شيف ومعقداتها ضد نوعين من البكتريا الموجبة والسالبة (*Staphalococcus auras*, *P.aeruginosa* *E.coli*, *Enterococcus*) وضد الخميرة *Candida albicans* أظهرت النتائج انه كلا الليكاندين غير فعالة ضد *Staphalococcus auras* ومتوسطه الفعالية تجاه بقيه الأحياء المجهرية كما وبينت أن المعقد [MoO(Lb)₂] له أعلى فعالية من بقيه المعقدات المحضرة تجاه جميع البكتريا المستخدمة وبينت أيضا أن المعقد [MoO (La)₂] له أعلى فعالية تجاه الخميرة *Candida albicans* .