



*J. Serb. Chem. Soc.* 76 (2) 221–233 (2011)  
JSCS–4114

## Synthesis and characterization of oxomolybdenum(V) and dioxomolybdenum(VI) complexes derived from *N'*-(2-hydroxy-3-methoxybenzylidene)isonicotinohydrazide

MADHAVAN NAIR LEKSHMY HARIKUMARAN NAIR\*  
and DEVAKIAMMA THANKAMANI

*Department of Chemistry, University College, Thiruvananthapuram-695 034, India*

(Received 8 February, revised 23 August 2010)

**Abstract:** Several novel complexes of oxomolybdenum(V) and dioxomolybdenum(VI) were synthesized with the Schiff base, *N'*-(2-hydroxy-3-methoxybenzylidene)isonicotinohydrazide (HL) derived from 3-methoxysalicylaldehyde and isonicotinohydrazide. The complexes were characterized by elemental analyses, molar conductance and magnetic susceptibility, as well as IR, <sup>1</sup>H-NMR, FAB mass and UV–Vis spectral studies. The complexes have the general formulae [MoO(L)XCl] and [MoO<sub>2</sub>(L)X], where X=NO<sub>3</sub> or ClO<sub>4</sub>. The IR spectra of these complexes indicate that the ligand HL acts as a monoanionic tridentate chelating agent. The spectra indicate the monodentate mode of coordination for the nitrate and perchlorate groups. The X-ray diffraction studies of [MoO(L)NO<sub>3</sub>Cl] correspond to an orthorhombic crystal lattice with unit cell dimensions *a* = 15.49 Å, *b* = 12.44 Å and *c* = 10.11 Å. All the complexes were found to have distorted octahedral geometry. Thermal studies of the complex [MoO<sub>2</sub>(L)NO<sub>3</sub>] showed that it was stable up to 240 °C, above which it started to decompose. The optimized geometry of ligand and one of its complexes, [MoO(L)NO<sub>3</sub>Cl], have been obtained by a molecular mechanics method. Antibacterial studies of the present complexes show that the oxomolybdenum(V) complexes were more potent bactericides than the ligand and the dioxomolybdenum(VI) complexes.

**Keywords:** oxomolybdenum(V); dioxomolybdenum(VI); 3-methoxysalicylaldehyde isonicotinoylhydrazide; thermal analysis; 3D modelling.

### INTRODUCTION

Coordination chemistry of molybdenum still engages the attention of researchers due to the chemistry of its oxidation state, coordination number, ligating atom, their impact on structure, reactivity and because of the potential

\* Corresponding author. E-mail: drmlhnair@gmail.com  
doi: 10.2298/JSC100208009N

applications of molybdenum compounds.<sup>1-8</sup> Molybdenum is a biologically important trace metal that occurs in the redox-active sites of molybdo-enzymes involved in nitrogen, carbon or sulphur metabolism. Molybdenum is a micronutrient for microorganisms, plants and animals. The biochemical importance of molybdenum is due to its ability a) to provide facile electron-transfer pathways, a consequence of the easy inter-convertibility of the different oxidation states and b) to form bonds with nitrogen-, oxygen-, and sulphur-donors, which are sufficiently strong to permit the existence of stable complexes but also sufficiently labile to permit facile ligand exchange reactions or changes in the molybdenum co-ordination number. Hydrazones derived from isonicotinohydrazide and their complexes have applications in various fields, such as biological, analytical and pharmacological areas and are reported to have lower toxicity than the hydrazide.<sup>9,10</sup>

In view of the versatile importance of hydrazones and molybdenum, the synthesis, characterization, thermal behaviour, and biological and 3D molecular modelling studies of some nitrate and perchlorate complexes of oxomolybdenum(V) and dioxomolybdenum(VI) species with a Schiff base (HL), derived from 3-methoxysalicylaldehyde and isonicotinohydrazide are reported herein.

#### EXPERIMENTAL

##### *Materials and methods*

Molybdenum pentachloride (Alfa Aesar, Lancaster) and molybdenum trioxide (Loba Chemie, Mumbai, India) were used. All other chemicals were of A R grade.

##### *Synthesis of the ligand (HL)*

The Schiff base (C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>) (Fig. 1) was prepared<sup>1</sup> by mixing methanolic solutions of 3-methoxysalicylaldehyde (0.05 mol, 50 mL) and isonicotinohydrazide (0.05 mol, 50 mL) and refluxing the mixture for ≈30 min. The pale yellow solid which separated was filtered, washed with methanol and dried. The purity of the ligand was monitored by TLC. It was characterized by elemental analysis, IR, UV and <sup>1</sup>H-NMR spectroscopy. Yield: 70 %; m.p. 260 °C; Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>: C, 61.99; H, 4.83; N, 15.49 %. Found: C, 61.50; H, 4.95; N, 15.24 %. <sup>1</sup>H-NMR (300 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 12.27 (1H, s, -OH), 10.74 (1H, s, -NH), 8.70 (1H, s, CH=N), 3.97 (3H, s, -OCH<sub>3</sub>), 6.85-8.9 (7H, m, aromatic H).

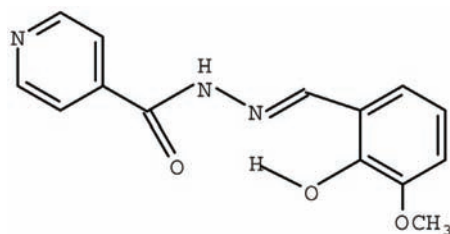


Fig. 1. Structural formula of the ligand (HL).

#### *Synthesis of the oxomolybdenum(V) complexes*

The following general method was adopted for the preparation of the complexes.<sup>11</sup> A methanolic solution of  $\text{MoCl}_5$  (2 mmol, 20 mL) containing  $\approx 0.3$  g  $\text{LiNO}_3$ /2–3 drops of perchloric acid as the case may be, was added to a hot methanolic solution of the ligand (2 mmol, 20 mL). The pH of the mixture was adjusted to  $\approx 4$  with  $\text{NaOAc}/\text{HOAc}$  buffer. The complexes precipitated on refluxing the solution for 20–30 min. The precipitated complexes were suction filtered, washed with aqueous methanol (1:1) followed by dry diethyl ether and dried over  $\text{P}_4\text{O}_{10}$  *in vacuo*.

#### *Synthesis of the dioxomolybdenum(VI) complexes*

The dioxomolybdenum(VI) complexes were prepared by adding, dropwise a solution of  $\text{MoO}_3$  (2 mmol, 20 mL) in hot conc.  $\text{HCl}$  (2 mL) containing  $\approx 0.3$  g  $\text{LiNO}_3$ /2–3 drops of perchloric acid to a methanolic solution of the ligand (2 mmol, 20 mL) under constant stirring. The complexes precipitated on refluxing the solution for 0–30 min. The separated solid was suction filtered, washed with aqueous methanol, then with diethyl ether and dried over  $\text{P}_4\text{O}_{10}$  *in vacuo*.

Metal, chloride and perchlorate were estimated by standard methods.<sup>12</sup> The elemental analyses (C, H and N) were realised at the Sophisticated Test and Instrumentation Centre (STIC), Kochi, India. The IR spectra ( $\text{KBr}$ ,  $\text{cm}^{-1}$ ) of the ligand and the complexes were recorded in the region 4000–400  $\text{cm}^{-1}$  on a Perkin-Elmer 397 spectrophotometer. The room temperature molar conductances of the complexes in DMF were recorded on an Elico direct reading conductivity meter at a concentration of  $\approx 10^{-3}$  M. The electronic absorption spectral measurements of the complexes in methanol were measured using a Jasco-V-550-UV-Vis spectrophotometer. The  $^1\text{H-NMR}$  spectra of the ligand and the complexes were recorded on a 300 MHz FT-NMR instrument using TMS as the reference. The FAB mass spectrum of  $[\text{MoO}_2(\text{L})\text{NO}_3]$  was recorded in a JEOL JMS600H mass spectrometer. Thermal analysis of the complex  $[\text{MoO}_2(\text{L})\text{NO}_3]$  was performed by heating in air at a rate of 10  $^\circ\text{C}/\text{min}$  on a Mettler TG-50 thermobalance. The X-ray powder diffraction patterns were recorded using a Philips X-ray PW1710 diffractometer. The magnetic susceptibilities were recorded at room temperature by the Gouy method. Diamagnetic corrections for various atoms and structural units were computed using Pascal's constants.<sup>13</sup>

#### *Antibacterial activity*

The ligand, HL, and the complexes were screened *in vitro* for their possible antibacterial activities against *Salmonella typhi* MTCC734, *Pseudomonas aeruginosa* MTCC 2642, *Escherichia coli* 585, *Proteus vulgaris* 177, *Bacillus subtilis* 2248 and *Streptococcus thermophilus* 1938 using the disc diffusion method (Kirby Bauer Method).<sup>14</sup>

All the plates were allowed to air dry under sterile conditions and swabbed with the pure culture of the bacteria on the Mueller Hinton Agar (MHA) plates (100 mm). The already prepared sterile discs (6 mm) impregnated with the studied compounds were aseptically placed above the seeded plates using sterile forceps. A disc was also used in pure chloroform to provide a control. The plates were incubated for 24 h at 37  $^\circ\text{C}$  and the zones of inhibition caused by the antibiotic compounds against the bacteria were measured in millimetres.

### RESULTS AND DISCUSSION

All the four complexes were coloured, non-hygroscopic solids, which were stable in air. They were sparingly soluble in common organic solvents, such as acetone and chloroform, and completely soluble in methanol, DMF and DMSO.

The analytical and spectroscopic data (Tables I and II, respectively) showed that all the complexes were mononuclear with the general formulae  $[\text{MoO}(\text{L})\text{ClX}]$  and  $[\text{MoO}_2(\text{L})\text{X}]$ , where  $\text{X} = \text{ClO}_4$  or  $\text{NO}_3$ . The low conductance values<sup>15</sup> of the chelates support the non-electrolytic nature of the complexes. The magnetic susceptibility values of the oxomolybdenum(V) complexes at room temperature were close to the spin-only value ( $1.73 \mu_{\text{B}}$ ) of oxomolybdenum(V) species. This shows the absence of Mo–Mo interaction<sup>16</sup> in these complexes. Due to Mo=O in oxomolybdenum(V) complexes, strong tetragonal distortion may occur and this causes a slight reduction in the magnetic moment values. All the dioxomolybdenum(VI) complexes were found to be diamagnetic, as expected for  $d^0$  systems.

TABLE I. Analytical data of the complexes

Complex <sup>a</sup>	Yield %	Found (Calc.), %					$\Lambda_{\text{M}}$ S $\text{cm}^2 \text{mol}^{-1}$	$\mu_{\text{eff}}$ $\mu_{\text{B}}$
		Mo	C	H	N	Cl		
$[\text{MoO}(\text{L})\text{NO}_3\text{Cl}]$	72	20.35 (20.00)	35.64 (35.06)	2.64 (2.52)	11.82 (11.68)	7.94 (7.39)	42	1.70
$[\text{MoO}(\text{L})\text{ClO}_4\text{Cl}]$	65	18.36 (18.55)	32.86 (32.52)	2.43 (2.3)	8.42 (8.13)	13.98 (13.7)	54	1.69
$[\text{MoO}_2(\text{L})\text{NO}_3]$	78	20.58 (20.85)	36.79 (36.54)	2.72 (2.63)	12.41 (12.17)	–	45	–
$[\text{MoO}_2(\text{L})\text{ClO}_4]$	67	19.47 (19.28)	34.11 (33.79)	2.21 (2.43)	8.32 (8.44)	7.34 (7.12)	56	–

<sup>a</sup>L =  $\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_3$

TABLE II. IR spectral data in  $\text{cm}^{-1}$  of the ligand and the complexes (abbreviations as in Table I)

Complexes	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-O}}$	$\nu_{\text{N-N}}$	$\nu_{\text{M=O}}(\text{sym})$	$\nu_{\text{M=O}}(\text{asym})$
HL	3201	1670	1626	1317	998	–	–
$[\text{MoO}(\text{L})\text{NO}_3\text{Cl}]$	3205	1640	1600	1337	1026	945	–
$[\text{MoO}(\text{L})\text{ClO}_4\text{Cl}]$	3205	1650	1601	1341	1018	945	–
$[\text{MoO}_2(\text{L})\text{NO}_3]$	3205	1637	1604	1338	1022	945	902
$[\text{MoO}_2(\text{L})\text{ClO}_4]$	3202	1636	1604	1339	1024	955	920

### IR spectra

In order to study the binding mode of the Schiff base to the metal in the complexes, the IR spectrum of the free ligand was compared with the spectra of the complexes. Important infrared spectral bands of the ligand and complexes and their tentative assignments are given in Table II. In all complexes, the keto-form of the ligand coordinates through the carbonyl oxygen and the azomethine nitrogen as evidenced by the shift of  $\nu_{\text{C=O}}$  and  $\nu_{\text{C=N}}$  to lower frequencies.<sup>17,18</sup> The coordination through the azomethine nitrogen atom was further supported by the shift of the  $\nu_{\text{N-N}}$  vibration observed at  $998 \text{ cm}^{-1}$  in the ligand to a higher frequency in the complexes by  $\approx 20 \text{ cm}^{-1}$ .<sup>17</sup> This is due to a reduction of lone pair repulsive forces in the adjacent nitrogen atoms.<sup>19</sup> The deprotonated OH group

was also involved in the coordination. This is supported by the disappearance of the free ligand bands at 3438 and 1353  $\text{cm}^{-1}$  due to the phenolic OH groups. The intense ligand band at 1317  $\text{cm}^{-1}$ , due to phenolic C–O, was also shifted to  $\approx 1340\text{cm}^{-1}$ , which further supports the same conclusion.<sup>1</sup>

The dioxomolybdenum(VI) complexes displayed two Mo=O stretching bands at 945–955  $\text{cm}^{-1}$  and 900–920  $\text{cm}^{-1}$  due to the symmetric and antisymmetric stretching of the *cis*-MoO<sub>2</sub><sup>2+</sup> core.<sup>20</sup> The MoO<sub>2</sub><sup>2+</sup> prefers to form the *cis* configuration due to the maximum utilization of the  $d\pi$  groups. A very strong band observed at  $\approx 940\text{ cm}^{-1}$  in the spectra of oxidomolybdenum(V) complexes corresponds to the Mo=O stretching frequency.<sup>21</sup> New weak bands at  $\approx 550\text{ cm}^{-1}$  and at  $\approx 460\text{ cm}^{-1}$  in the metal complexes are assigned to the  $\nu_{\text{Mo-O}}$  and  $\nu_{\text{Mo-N}}$  modes, respectively.<sup>22</sup>

The IR spectra of the nitrate complexes suggest monocoordination of the nitrate group ( $\nu_4$ , 1530  $\text{cm}^{-1}$ ;  $\nu_1 \approx 1380\text{ cm}^{-1}$  and  $\nu_2 \approx 1034\text{ cm}^{-1}$ ). For the perchlorate complexes, two bands (split bands), observed at  $\approx 1114$  and  $\approx 1060\text{ cm}^{-1}$ , are assigned to  $\nu_4$  and  $\nu_1$ . The bands at  $\approx 640$  and  $\approx 620\text{ cm}^{-1}$  can be assigned, respectively, to  $\nu_3$  and  $\nu_5$  of monodentately coordinated perchlorate group. The medium intensity absorption band expected at  $\approx 925\text{ cm}^{-1}$  in the spectra of the complexes cannot be located because of ligand vibrations in this region.<sup>23</sup>

#### <sup>1</sup>H-NMR spectra

The <sup>1</sup>H-NMR spectra of HL and [MoO<sub>2</sub>(L)NO<sub>3</sub>] were recorded in DMSO-*d*<sub>6</sub>. The signal at  $\delta$  12.27 ppm in the spectrum of the ligand disappeared because of complexation, suggesting coordination through the deprotonated phenolic oxygen. Presence of a sharp singlet at  $\delta$  10.8 ppm in the complex indicates that the ligand exists in the keto-form. The signal at  $\delta$  8.7 ppm of the ligand was shifted to 9.1 ppm, indicating coordination of azomethine nitrogen in the complexes. The methoxy protons and the seven aromatic protons of the ligand and complex appeared at nearly the same positions.<sup>1</sup>

#### Electronic spectra

The electronic spectra of the tridentate ONO donor hydrazone ligand and the oxomolybdenum(V) complexes were recorded in methanol. The electronic spectrum of the ligand showed intense bands at 246 and 298 nm. Similar bands of lower intensity were observed at 362 and 377 nm. These bands are assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively.<sup>24</sup> They suffered considerable shifts in intensity and wavelength on coordination.

The electronic spectra of the [MoO(L)NO<sub>3</sub>Cl] and [MoO(L)ClO<sub>4</sub>Cl] complexes are characterized by strong absorption bands in the UV region at  $\approx 230\text{ nm}$  and at  $\approx 270\text{ nm}$  and less intense bands at  $\approx 320\text{ nm}$  and at  $\approx 370\text{ nm}$ . The latter bands may be assigned to metal–ligand charge transfer, possibly superposed by ligand  $n \rightarrow \pi^*$  transitions.<sup>25</sup>

The electronic spectra of octahedral oxomolybdenum (V) complexes usually exhibit three distinct bands in the regions 690–740 nm, 520–450 nm and 380–440 nm, assignable to  ${}^2B_2 \rightarrow {}^2E$  ( $d_{xy} \rightarrow d_{xz}$ ,  $d_{yz}$ ),  ${}^2B_2 \rightarrow {}^2B_1$  ( $d_{xy} \rightarrow d_{x^2-y^2}$ ) and  ${}^2B_2 \rightarrow {}^2A_1$  ( $d_{xy} \rightarrow d_{z^2}$ ) transitions, respectively.<sup>26</sup> In the present study,  $[\text{MoO}(\text{L})\text{NO}_3\text{Cl}]$  showed a medium intensity band at  $\approx 459$  nm and a weak broad band at  $\approx 660$  nm. The corresponding bands for  $[\text{MoO}(\text{L})\text{ClO}_4\text{Cl}]$  were at  $\approx 468$  nm and at  $\approx 665$  nm. However, the third band was not observed in these complexes, probably due to masking by the low energy tail of the much more intense charge-transfer transitions  $\text{O}(\pi) \rightarrow d(\text{Mo})$ , involving the excitation of an electron from the highest filled MO associated with oxygen to the d-orbital of Mo. The electronic spectra indicate an octahedral environment for all the complexes and are in conformity with the Ballhausen-Gray scheme for octahedral geometry.<sup>27</sup>

#### FAB mass spectra

The FAB mass spectrum of the complex  $[\text{MoO}_2(\text{L})\text{NO}_3]$  showed the characteristic molecular ion peak at  $m/z = 459.91$  ( $\text{M}^+$ ), which corresponds to the molecular weight of the complex. The other important peaks are due to the formation of various fragments,<sup>28</sup> such as  $(\text{M}-\text{OCH}_3)^+$ ,  $(\text{M}-\text{NO}_3)^+$ ,  $(\text{C}_6\text{H}_5\text{N}_2\text{O})^+$ ,  $(\text{C}_8\text{H}_7\text{NO}_2)^+$ ,  $(\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_3)^+$ , etc.

#### X-Ray diffraction studies

The complex  $[\text{MoO}(\text{L})\text{NO}_3\text{Cl}]$  was found to be orthorhombic by the X-ray powder diffraction method and was indexed (Fig. 2 and Table III) using the Hesse and Lipson procedure.<sup>29</sup> The lattice constants were found to be:  $A =$

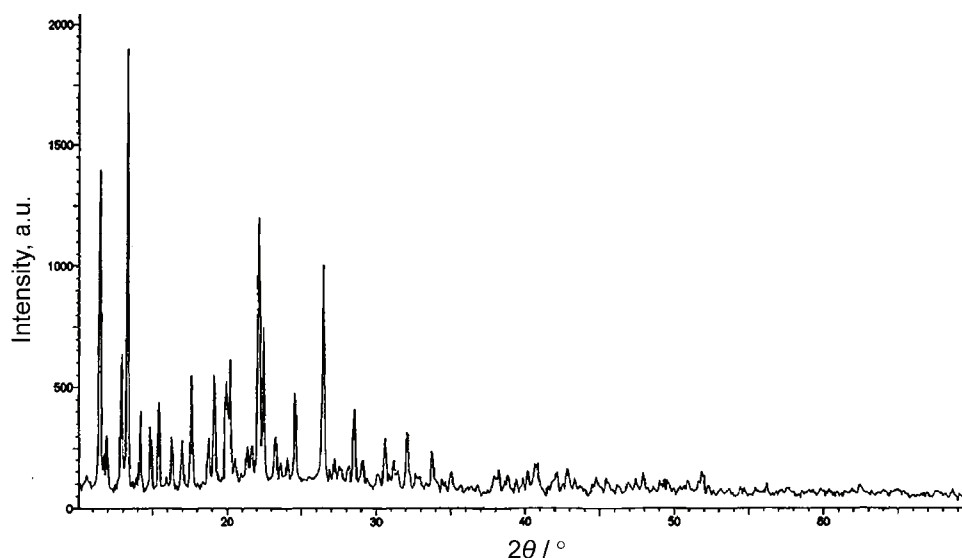


Fig. 2. X-ray diffractions pattern of  $[\text{MoO}(\text{L})\text{NO}_3\text{Cl}]$ .

= 0.0024742,  $B = 0.003831$  and  $C = 0.0058091$ , and the unit cell dimensions were  $a = 15.49 \text{ \AA}$ ,  $b = 12.44 \text{ \AA}$  and  $c = 10.11 \text{ \AA}$ .

TABLE III. X-Ray diffraction data of  $[\text{MoO}(\text{L})\text{NO}_3\text{Cl}]$  (abbreviations as in Table I)

Line	$\sin^2\theta$ (obs)	$\sin^2\theta$ (Calcd.)	Intensity
1	0.008556	0.008274	3.89
2	0.009895	0.009897	61.85
3	0.012502	0.012114	22.19
4	0.013376	0.013728	100.00
5	0.01517	0.015324	18.27
6	0.01786	0.017798	21.21
7	0.020004	0.019537	13.51
8	0.021666	0.021133	10.48
9	0.023298	0.023236	26.69
10	0.027576	0.027067	26.04
11	0.030131	0.029541	19.05
12	0.036596	0.036953	59.2
13	0.040336	0.040288	13.01
14	0.045135	0.045505	24.45
15	0.052209	0.052282	51.19
16	0.060592	0.607210	19.27
17	0.062755	0.062823	7.64
18	0.067307	0.067606	5.03
19	0.069485	0.069579	13.21
20	0.072426	0.071193	5.53
21	0.076238	0.077002	15.16
22	0.079404	0.079876	4.06
23	0.084189	0.084532	9.77
24	0.090387	0.089387	5.54
25	0.105813	0.105672	4.23
26	0.109906	0.109029	3.02
27	0.120846	0.121486	6.20
28	0.128667	0.129894	4.98
29	0.133522	0.137322	4.08
30	0.144992	0.145228	3.33
31	0.149316	0.149059	3.06
32	0.164578	0.167796	5.30
33	0.174162	0.175434	2.56
34	0.184266	0.182820	3.53
35	0.191142	0.191195	4.54
36	0.221449	0.228308	2.89
37	0.267035	0.263271	1.55
38	0.308593	0.302859	1.08

#### Thermal studies

Thermal behaviour of the  $[\text{MoO}_2(\text{L})\text{NO}_3]$  complex was studied by non-isothermal thermogravimetric, TG, and differential TG, DTG, analyses by heating

the sample in air at a rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  (Fig. 3). The stability range extended from ambient temperature to  $240\text{ }^{\circ}\text{C}$ . The decomposition of the complex occurred in three stages as indicated by the DTG peaks at  $302$ ,  $439$  and  $760\text{ }^{\circ}\text{C}$ . First decomposition stage started at  $250\text{ }^{\circ}\text{C}$  and ended at  $350\text{ }^{\circ}\text{C}$ . The mass loss of  $25.9\%$  (Calcd.  $26.3\%$ ) corresponded to the loss of  $\approx 0.5$  mol of the ligand. The second stage was more complicated and it ranged from  $350$  to  $560\text{ }^{\circ}\text{C}$ . The weight loss in this stage was  $57.7\%$  (Calcd.  $57.5\%$ ). The weight of the sample at  $560\text{ }^{\circ}\text{C}$  was consistent with the formation of  $\text{MoO}_3$ . The sample showed another weight loss in the region  $700$ – $790\text{ }^{\circ}\text{C}$ . The weight of the sample,  $15.8\%$  (Calcd.  $27.8\%$ ), at  $790\text{ }^{\circ}\text{C}$  was less than that expected if  $\text{MoO}_2$  was formed. This may be due to the volatilization of  $\text{MoO}_3$  above  $700\text{ }^{\circ}\text{C}$ .<sup>30</sup>

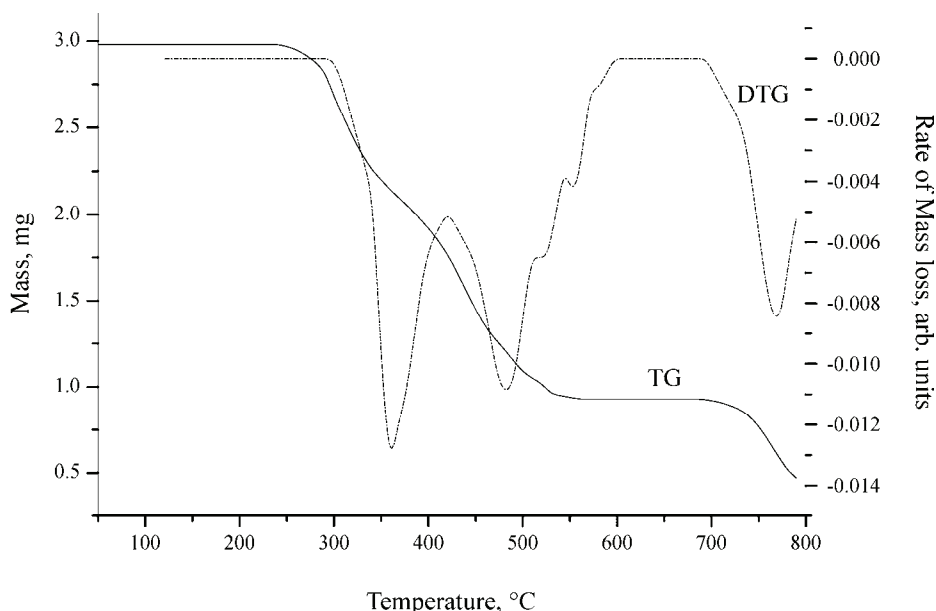


Fig. 3. TG and DTG curves of  $[\text{MoO}_2(\text{L})\text{NO}_3]$ .

#### Antibacterial studies

The ligand and the complexes were screened for their antibacterial activity and the results obtained are presented in Table IV. A comparative study of the ligand and the complexes revealed that the oxo-complexes showed higher activity than the dioxo-complexes. The ligand was inactive against all the applied pathogenic bacteria *P. aeruginosa*. appeared to be resistant to all the tested compounds.

The antibacterial activity of the complexes may result from various modes by which these antibacterials act on bacteria. It may be due to factors such as inhibition of cell wall formation leading to lysis, damage of the cell wall leading to



loss of cell contents and hence to cell death, inhibition of protein production and thereby arresting bacterial growth and inhibition of the production of nucleic acids, thereby preventing bacterial reproduction. Metal chelates have simultaneously polar and non-polar properties; this makes them suitable for permeation into cells and tissues. Changing hydrophilicity and lipophilicity probably leads to a reduction of the solubility and permeability barriers of cells, which in turn enhances the bioavailability of chemotherapeutics on the one hand and their potentiality on the other.<sup>31</sup> The low activity of dioxo-complexes may be due to low lipid solubility, steric and pharmacokinetic factors which play vital roles in deciding the potency of an antibacterial agent.

TABLE IV. Antibacterial activity of the ligand and its complexes against pathogenic bacteria (abbreviations as in Table I)

Compound	Zone of inhibition, mm					
	<i>S. typhi</i> MTCC 734	<i>P. aeruginosa</i> MTCC 2642	<i>E. coli</i> MTCC 585	<i>P. vulga-</i> <i>ris</i> 1771	<i>B. subtilis</i> 2248	<i>S. thermo-</i> <i>philus</i> 1938
HL	–	–	–	–	–	–
[MoO(L)NO <sub>3</sub> Cl]	T	–	T	14	11	14
[MoO(L)ClO <sub>4</sub> Cl]	T	–	10	15	12	15
[MoO <sub>2</sub> (L)NO <sub>3</sub> ]	–	–	–	11	–	–
[MoO <sub>2</sub> (L)ClO <sub>4</sub> ]	–	–	–	12	–	–
Control (chloroform at 10 µl/disc)	–	–	–	–	–	–

### 3D molecular modelling

The molecular modelling was constructed using modelling and analysis software<sup>32</sup> CHEM Bio3D Ultra 11.0. The possible 3D structures of the ligand and one of the complexes, [MoO(L)NO<sub>3</sub>Cl], as a representative, were optimized by molecular mechanics calculations, MM<sub>2</sub> giving the lowest energy CHEM 3D models. The CHEM 3D model of the ligand HL is shown in Fig. 4, while that of [MoO(L)NO<sub>3</sub>Cl] is shown in Fig. 5. Selected bond angles and the bond angle

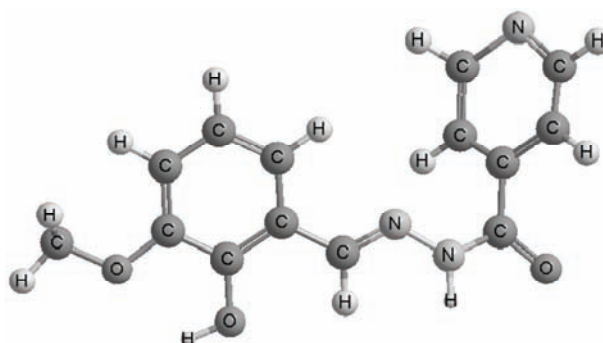


Fig. 4. Proposed 3D structure of the ligand (HL).

around the octahedral surrounding, given in Table V, are calculated values after energy minimization<sup>33,34</sup> in CHEM 3D.

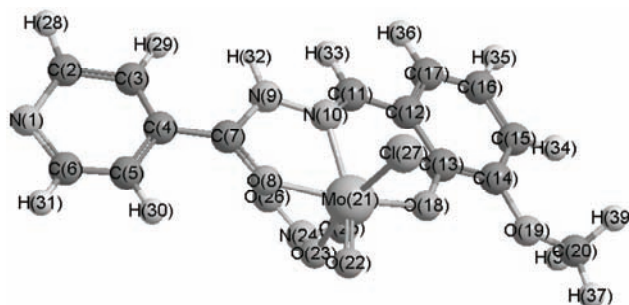


Fig. 5. Proposed 3D structure of the complex [MoO(L)NO<sub>3</sub>Cl].

TABLE V. Selected bond lengths/bond angles of the complex [MoO(L)NO<sub>3</sub>Cl] (abbreviations as in Table I)

Bond	Bond length, Å	Bond	Bond angle, deg.
Mo(21)–Cl(27)	2.2973	Cl(27)–Mo(21)–O(23)	169.1658
Mo(21)–O(23)	1.9534	Cl(27)–Mo(21)–O(22)	87.3513
O(22)–Mo(21)	1.6773	Cl(27)–Mo(21)–O(18)	88.7829
Mo(21)–O(18)	1.9432	Cl(27)–Mo(21)–N(10)	85.8183
N(10)–Mo(21)	2.0074	Cl(27)–Mo(21)–O(8)	103.5166
O(8)–Mo(21)	1.9352	O(23)–Mo(21)–O(22)	84.4090
		O(23)–Mo(21)–O(18)	86.6129
		O(23)–Mo(21)–N(10)	104.5423
		O(23)–Mo(21)–O(8)	83.8798
		O(22)–Mo(21)–O(18)	105.2278
		O(22)–Mo(21)–N(10)	155.3596
		O(22)–Mo(21)–O(8)	92.3625
		O(18)–Mo(21)–N(10)	98.2704
		O(18)–Mo(21)–O(8)	159.0781
		N(10)–Mo(21)–O(8)	66.4086

Based on all the above spectral data and physicochemical studies, a distorted octahedral geometry (Figs. 6 and 7) are tentatively proposed for all the complexes.

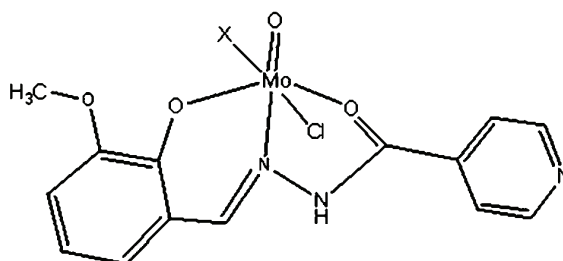


Fig. 6. Proposed 2D structure of [MoO(L)XCl], X = NO<sub>3</sub>, ClO<sub>4</sub>.

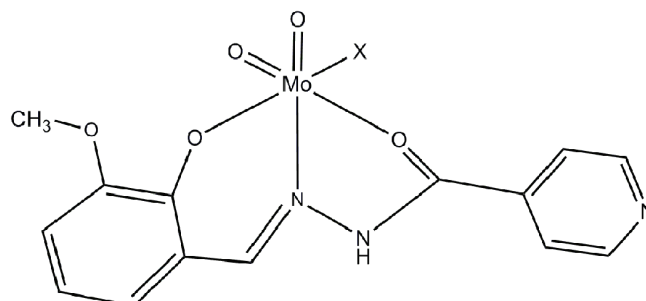


Fig. 7. Proposed 2D structure of  $[\text{MoO}_2(\text{L})\text{X}]$ ,  $\text{X} = \text{NO}_3, \text{ClO}_4$ .

### CONCLUSIONS

From the spectroscopic, analytical and thermal analyses data, it can be concluded that the molybdenum existed in a distorted octahedral environment with the ligand as a monoanionic tridentate chelating agent. The FAB mass spectral data suggest the monomeric nature of the complexes. The results of antibacterial studies revealed that the oxomolybdenum complexes exhibited much higher activity than the ligand and the dioxomolybdenum complexes.

*Acknowledgement.* The authors are thankful to NIIST, Thiruvananthapuram, STIC, Kochi and the Department of Chemistry, University of Kerala, Thiruvananthapuram for the facilities. One of us (DT) expresses her gratitude to the UGC for the award of a Teacher fellowship under FDP.

### ИЗВОД

#### СИНТЕЗА И КАРАКТЕРИЗАЦИЈА ОКСОМОЛИБДЕН(V) И ДИОКСОМОЛИБДЕН(VI) КОМПЛЕКСА СА *N'*-(2-ХИДРОКСИ-3-МЕТОКСИБЕНЗИЛИДЕН)-ИЗОНИКОТИНОХИДРАЗИДОМ

M. L. HARIKUMARAN NAIR и D. THANKAMANI

*Department of Chemistry, University College, Thiruvananthapuram-695 034, India*

Синтетизовано је неколико нових оксомолибден(V)- и диоксомолибден(VI)-комплекса који као лиганд садрже Шифову базу *N'*-(2-хидрокси-3-метоксибензилиден)изоникотинохидразид (HL), који је изолован у реакцији између 3-метокси-салицилалдехида и изоникотинохидразида. Поред елементарне микроанализе, моларне проводљивости, магнетних мерења, за карактеризацију комплекса употребљене су IR,  $^1\text{H-NMR}$ , FAB масена и UV-Vis спектроскопске методе. Нађено је да комплекси имају општу формулу  $[\text{MoO}(\text{L})\text{XCl}]$  и  $[\text{MoO}_2(\text{L})\text{X}]$  ( $\text{X} = \text{NO}_3$  или  $\text{ClO}_4$ ). На основу IR спектроскопије закључено да је лиганд HL у овим комплексима моноанјонског типа и да је тридентатно координован, док су нитратни и перхлоратни ањони у овим комплексима монодентатно координовани. На основу рендгенске дифракционе анализе нађено је да  $[\text{MoO}(\text{L})\text{NO}_3\text{Cl}]$  комплекс има орторомбичну кристалну решетку са јединичном ћелијом димензија  $a = 15,49 \text{ \AA}$ ,  $b = 12,44 \text{ \AA}$  и  $c = 10,11 \text{ \AA}$ , као и да је дисторговане октаедарске геометрије. Термална анализа  $[\text{MoO}_2(\text{L})\text{NO}_3]$  комплекса је показала да су сви комплекси стабилни до температуре од  $240 \text{ }^\circ\text{C}$ , а да изнад ове температуре долази до њиховог разлагања. Методом молекулске механике оптимизована је геометрија лиганда и комплекса формуле  $[\text{MoO}(\text{L})\text{NO}_3\text{Cl}]$ . Антибактеријска испитивања су показала да

комплекси оксомолибдена(V) имају већу активност од комплекса диоксомолибдена(VI), као и од самог лиганда.

(Примљено 8. фебруара, ревидирано 23. августа 2010)

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