



## NOTE

### Synthesis and Characterization of Dioxomolybdenum(VI) Complexes with 1,10-Phenanthroline and 2,2'-Bipyridyl

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Two new dioxomolybdenum(VI) complexes  $[\text{MoO}_2\text{L}_2]^{2+}$  [ $\text{L} = \text{phen}(\text{I}), \text{bipy}(\text{II})$ ] with heterocyclic amines 1,10-phenanthroline and 2,2'-bipyridyl ligands have been synthesized and characterized. Compounds **I** (93 % yield) and compound **II** (92 % yield) were obtained from the reactions of  $\text{MoO}_2(\text{acac})_2$  [acac = acetylacetonato] with 1 equivalent of phen and bipy. Elemental analysis and  $^1\text{H}$ ,  $^{13}\text{C}$ NMR, IR spectral data indicated that both structures compounds were six-coordinate and suggest that they have nearly octahedral symmetry.

**Key Words:** 2,2'-Bipyridyl, Dioxomolybdenum(VI), 1,10-Phenanthroline, Structures.

Organometallic derivatives of transition metal oxides have been established as important species in many catalytic transformations, the most important of which are oxidation catalysis and olefin metathesis<sup>1</sup>. Dioxomolybdenum complexes are important catalysts or catalyst precursors for oxygen-atom transfer reactions in chemical and biological systems<sup>2</sup>. In addition to, in the research of olefin epoxidation, molybdenum(VI) complexes are considered to be versatile and effective catalysts with alkyl hydroperoxides as oxidants<sup>3,4</sup>. The useful role of molybdenum is not restricted to artificial catalysis alone, since it is an essential element in diverse biological systems, as nature has made use of molybdenum centre in various redox enzymes<sup>5-7</sup>.

Homo and hetro complexes of dioxomolybdenum(VI) with bidentate nitrogen donors have received considerable attention in recent years<sup>8-11</sup>. It has been shown<sup>12</sup> that 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen) fails to form trischelated complexes with  $\text{Mo}(\text{CO})_6$  and instead of complex,  $\text{Mo}(\text{CO})_4(\text{phen})$  and  $\text{Mo}(\text{CO})_4(\text{bipy})$  are formed. Steele<sup>13</sup> reported trischelated 2,2'-bipyridyl and 1,10-phenanthroline complexes  $[\text{Mo}(\text{bipy})_3]\text{X}_3$  and  $[\text{Mo}(\text{phen})_3]\text{X}_3$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{I}^-$ ) by the reaction of ammonium hexahalogenomolybdate (**III**) with bipy or phen in water-ethanol-hydrochloric acid mixture. Similarly, Carmichael *et al.*<sup>14</sup> obtained a 2,2'-bipyridyl complex,  $\text{Mo}_2\text{Cl}_6(\text{bipy})_3$  for which they proposed the ionic formula  $[\text{Mo}(\text{bipy})_2\text{Cl}_2]^+[\text{Mo}(\text{bipy})\text{Cl}_4]^-$ . Furlani and coworkers<sup>15</sup> were also unable to isolate *tris*(bipyridyl) complexes and obtained compounds of the type  $\text{LH}[\text{MoCl}_4\text{L}]$  ( $\text{L} = \text{bipy}$  or  $\text{phen}$ ). The variety of possible molybdenum complexes with wide choice

of 2,2'-bipyridyl and 1,10-phenanthroline ligands and coordination environments, has prompted us to undertake research in this area<sup>16</sup>. Compounds of dioxomolybdenum(VI) with 2,2'-bipyridyl and 1,10-phenanthroline are synthesized and characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR and elemental analysis.

Ammonium heptamolybdate tetrahydrate, acetyl acetone (acacH), 2,2'-bipyridyl, 1,10-phenanthroline, were used as received from commercial (Merck). Solvent ethanol was dried and distilled before use by standard methods. Ethanol was used without any further purification as received.

#### Preparation of complexes

**Preparation of  $\text{MoO}_2(\text{acac})_2$ :** This was prepared from ammonium heptamolybdate tetrahydrate and acetyl acetone following the published procedure<sup>9</sup>.

**General method for the preparation of complexes  $[\text{MoO}_2\text{L}_2](\text{OH})_2$  ( $\text{L} = \text{phen}, \text{bipy}$ ):**  $\text{L}$  (5 mmol) were dissolved in 50 mL ethanol by refluxing on a water bath and 5 mmol of solid  $\text{MoO}_2(\text{acac})_2$  was added to the ligands solution and the mixture was refluxed for 2 h and the precipitate filtered, which was washed successively with ice-cold water and dried *in vacuo* over silica gel.

IR spectra (as KBr discs) were recorded with a Perkin-Elmer spectrum GX.  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra were recorded with a Bruker Specto Spin 500MHz spectrometer in  $\text{DMSO}-d_6$  as solvent and carbon, hydrogen and nitrogen analysis were carried out by CHN-O-Rapid Heraeus elemental analyzer.

The reaction of *bis*(acetyl acetonato) dioxomolybdenum(VI) with 2,2'-bipyridyl and 1,10-phenanthroline ligands in pure, absolute ethanol leads to the isolation of bischelated complexes

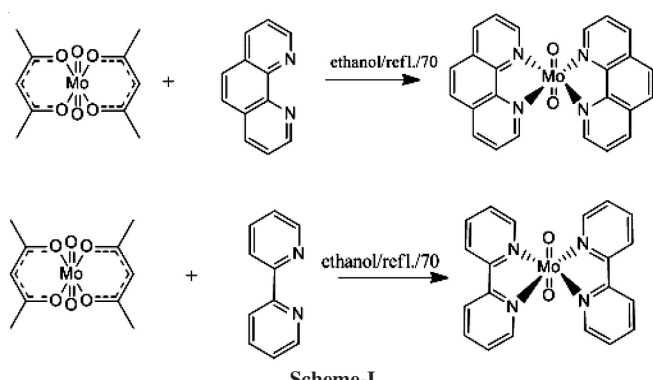
TABLE-2  
 IR FREQUENCIES OF THE BISCHELATED COMPLEXES (cm<sup>-1</sup>)

Complexes	v(Mo=O)	v(C-N)	v(O-H)	v(C=C)	v(C=O)	v(C-H)
MoO <sub>2</sub> (acac) <sub>2</sub>	904, 933	–	–	1502	1586	2920
[MoO <sub>2</sub> (phen) <sub>2</sub> ] <sup>2+</sup>	882, 909	1146	3406	1427, 1579	–	3059
[MoO <sub>2</sub> (bipy) <sub>2</sub> ] <sup>2+</sup>	880, 912	1110	3400	1442, 1517	–	3080

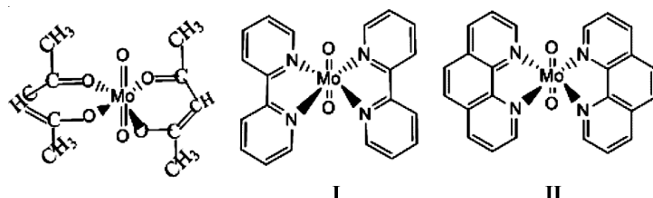
 TABLE-3  
<sup>1</sup>H, <sup>13</sup>C NMR SPECTRAL DATA FOR THE BISCHELATED COMPLEXES δ (ppm)

Compound	<sup>1</sup> H NMR	<sup>13</sup> C NMR
[MoO <sub>2</sub> (acac) <sub>2</sub> ]	6.02 (s,2H), 2.11 (s,2H)	24.8, 139.5, 119.1
[MoO <sub>2</sub> (phen) <sub>2</sub> ] <sup>2+</sup>	7.78 (S, 4H), 7.99 (S, 4H), 8.49 (S, 4H), 9.10 (S, 4H), 3.3 (S, 2H)	124.1, 127.5, 129.3, 137.0, 146.4, 150.8
[MoO <sub>2</sub> (bipy) <sub>2</sub> ] <sup>2+</sup>	7.25 (s, 4H), 7.7 (s, 8H), 8.3 (s, 4H), 3.5 (S, 2H)	121.302, 124.988, 138.049, 150.101

[MoO<sub>2</sub>(phen)<sub>2</sub>]<sup>2+</sup> sky-blue and [MoO<sub>2</sub>(bipy)<sub>2</sub>]<sup>2+</sup> emerald precipitate, which are fairly stable in air. The scheme of reaction is **Scheme-I**.



Scheme-I


 Scheme-II: Structure [MoO<sub>2</sub>(acac)<sub>2</sub>] and proposed structures for compounds I and II

In moisture, bischelated phen and bipy complexes are more stable than the bischelated acetylacetonato complex. In aqueous suspension also the acetylacetonato complex is more susceptible to hydrolysis than bischelated phen and bipy complexes. This difference of stability is attributed to the delocalized π-electron system present in the ring of phen and bipy complexes.

The physical properties and elemental analysis of the complexes are presented in Table-1. The IR spectra of the complexes are summarized in Table-2.

The C-O band at 1262-1022 cm<sup>-1</sup> in the [MoO<sub>2</sub>(acac)<sub>2</sub>] complex and absence of other complexes indicates bidentate phen and bipy bonding. A comparison of v(Mo=O) stretching frequency in the spectrum of [MoO<sub>2</sub>(acac)<sub>2</sub>] with bischelated phen and bipy complexes indicates a little change in the frequencies. This may be due to the presence of the aromatic

 TABLE-1  
 ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE BISCHELATED COMPLEXES

Compounds	Colour	Elemental analysis (%): Calcd. (Found)		
		C	H	N
MoO <sub>2</sub> (acac) <sub>2</sub>	Yellow	36.69 (36.59)	4.8 (4.6)	–
MoO <sub>2</sub> (phen) <sub>2</sub>	Sky blue	24.64 (24.86)	3.28 (3.18)	11.49 (11.37)
MoO <sub>2</sub> (bipy) <sub>2</sub>	Emerald	23.12 (23.11)	3.08 (3.05)	10.78 (10.65)

rings in these compounds, which in greater coupling and conjugation. The <sup>1</sup>H, <sup>13</sup>C NMR spectra of the complexes (Table-3) are in accordance with the above observations.

[MoO<sub>2</sub>(acac)<sub>2</sub>] complex has octahedral geometry, therefore we resulted these reactions must exist with retention configuration and coordination number. These data are consistent with six fold coordination of bischelated molybdenum(VI) complexes and exhibit octahedral geometry. Although our inability in obtaining a single crystal but to account for the NMR and IR results, two structures **I** and **II** are proposed in **Scheme-I**.

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