Synthesis, magnetic and spectral studies of some novel binuclear dioxomolybdenum(VI) chelates involving Schiff bases derived from sulpha drugs and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one

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Received 23 October 2002; revised 24 September 2003

This paper reports the synthesis of six new binuclear dioxomolybdenum(VI) complexes of the composition [Mo₂O₂(OH)₂]₄(L₂), where L = N-(4'-benzoylidenec-3'-methyl-1'-phenyl-2'-pyrazoline-5'-one)sulphadimidine (HL₁), N-(4'-benzoylidenec-3'-methyl-1'-phenyl-2'-pyrazoline-5'-one)sulphadiazine (HL₂), N-(4'-benzoylidenec-3'-methyl-1'-phenyl-2'-pyrazoline-5'-one)sulphanilamide (HL₃), N-(4'-benzoylidenec-3'-methyl-1'-phenyl-2'-pyrazoline-5'-one)sulphamidin (HL₄), N-(4'-benzoylidenec-3'-methyl-1'-phenyl-2'-pyrazoline-5'-one)sulphamethoxazine (HL₅) or N-(4'-benzoylidenec-3'-methyl-1'-phenyl-2'-pyrazoline-5'-one)sulphadimethoxine (HL₆). These complexes have been obtained by the interaction of bis(acetylacetonato)dioxomolybdenum(VI) with the said ligands in ethanol. All these complexes have been characterized by elemental analysis, molar conductance, decomposition temperature and magnetic measurements, ¹H NMR, IR and electronic spectral studies.

IPC Code: Int. Cl. 7 C01G 39/2

Molybdenum is a versatile transition element because it possesses a large number of stable and accessible oxidation states as well as coordination numbers, which vary from four to eight. A large number of important chemical reactions are catalyzed by molybdenum compounds. Industrial processes such as hydrodesulphurization and olefin epoxidation are carried out over molybdenum catalysts. Nature has also incorporated molybdenum into a number of important redox enzymes.

Complexes containing the molybdenum-oxo group dominate the higher oxidation state of molybdenum. Most simple Mo(VI) coordination complexes contain the cis-MoO₂²⁺ cation. Recent Extended X-ray Absorption Fine structure (EXAFS) studies have shown the presence of this group as well as sulphur in the vicinity of molybdenum in the oxidized forms of xanthine oxidase and sulphite oxidase. Syama and Maurya have reviewed the coordination chemistry of molybdenum Schiff base complexes.

The pronounced biological activity of the metal complexes of Schiff bases derived from sulpha drugs has led to considerable interest in their coordination chemistry. The Schiff bases derived by the condensation of sulphonamides with salicylaldehyde are not only good complexing agents, but bacteriocides as well.

Previous reports from our laboratory describe the synthesis and characterization of two series of mononuclear metal chelates with some Schiff base derived from ligands of sulpha drugs and o-vanilline or 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one.

A literature survey on Schiff base complexes of dioxomolybdenum(VI) reveals that there is no report on such complexes involving Schiff bases derived from 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one and sulpha drugs. Owing to the lack of work on coordination compounds of dioxomolybdenum(VI) involving pyrazolone based Schiff bases of sulpha drugs, it was thought of interest to synthesize and characterize some dioxomolybdenum(VI) complexes with Schiff bases derived from 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one and sulpha drugs, viz., = N-(4'-benzoylidenec-3'-methyl-1'-phenyl-2'-pyrazoline-5'-one)sulphadimidine (HL₁), N-(4'-benzoylidenec-3'-methyl-1'-phenyl-2'-pyrazoline-5'-one)sulphanilamide (HL₃), N-(4'-benzoylidenec-3'-methyl-1'-phenyl-2'-pyrazoline-5'-one)sulphadiazine (HL₂), N-(4'-benzoylidenec-3'-methyl-1'-phenyl-2'-pyrazoline-5'-one)sulphamidin (HL₄), N-(4'-benzoylidenec-3'-methyl-1'-phenyl-2'-pyrazoline-5'-one)sulphamethoxazine (HL₅) or N-(4'-benzoylidenec-3'-methyl-1'-phenyl-2'-pyrazoline-5'-one)sulphadimethoxine (HL₆). The structures of the Schiff base ligands are shown in Structure 1.

Experimental

3-Methyl-1-phenyl-2-pyrazolin-5-one was obtained from Johnson Chemical Co., Bombay. The sulpha drugs, viz., sulphadiazine, sulphadimidine, sulphamidin, sulphamethoxazine and sulphadimethoxine were procured from Sigma Chemical Co., U.S.A. Ammonium molybdate, acetylacetone and benzoyl chloride were purchased from B.D.H. Chemicals Bombay. All other chemicals used were of
analytical reagent grade. The parent compound, bis(acetylacetonato)dioxomolybdenum(VI),[MoO$_2$(acac)$_2$] was prepared by the method of Chen et al.$^{18}$ while 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (BMHP) was prepared by the method reported elsewhere.$^{19}$

**Synthesis of Schiff bases**

An ethanolic solution (~15 mL) of BMHP (0.01 mol), was added to the solution 0.01 mol of sulphamethoxazole, sulphadiazine or sulphamerazine in ethanol (25 mL) or sulphamethoxine in ethanol along with two drops of HCl (25 mL, 3.10 g, 0.01 mol) or 0.01 mol of sulfanilamide in acetone (20 mL). The resulting solution was refluxed with stirring for 4-5 hours, and then filtered to remove insoluble sulpha drug if any. The filtrate so obtained was concentrated on a water bath and left overnight at room temperature when yellow crystals of Schiff bases separated out from their respective solution. The crystals thus obtained were washed with ethanol and dried in vacuo.

The Schiff base with sulphadimidine was prepared by refluxing a 1:1 mixture of BMHP (0.01 mol) and sulphadimidine (0.01 mol) in ethanol (~15 mL) for 4-5 hours in the presence of anhydrous sodium acetate (~0.40 g) and few drops of glacial acetic acid. The reaction mixture was poured into distilled water (~100 mL) when a yellow precipitate was obtained. It was filtered, washed with ethanol and recrystallized from acetone to obtain the desired Schiff base. The characterization data of Schiff bases are given in Table 1.

**Synthesis of complexes**

The respective Schiff base (0.001 mol) was dissolved by heating in 30 mL ethanol. To this resulting solution, an ethanolic solution (10 mL) of bis(acetylacetonato)dioxomolybdenum(VI) (0.001 mol) was added. The resulting solution was refluxed for 8-10 h and then concentrated to half of its volume. The resulting precipitate was filtered and washed several times with ethanol to remove unreacted ligand and parent compound. The product was dried in vacuo. The analytical data of the complexes are given in Table 2.

Carbon, hydrogen and nitrogen were determined micro-analytically at Central Drug Research Institute, Lucknow. The metal content in each chelate was determined$^{20}$ as MoO$_5$. Electronic spectra of complexes were recorded on ATI Unicam UV-2-100 UV/Visible spectrophotometer in our department. Magnetic measurements were performed using a vibrating sample magnetometer (VSM) method at Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai. Solid state infrared spectra were recorded in KBr at Central Drug Research Institute, Lucknow. Conductance measurements were performed at room temperature in dimethylformamide using a Toshniwal Conductivity bridge and dip type cell with a smooth platinum electrode of cell constant 1.02. The $^1$H NMR spectra of two representative compounds were recorded in DMSO-d$_6$ at Indian Institute of Technology, Chennai. The decomposition temperatures of the Schiff bases and complexes were recorded using an electrically operated melting point apparatus (Kumar Industries, Bombay).

**Results and discussion**

The dioxomolybdenum(VI) complexes of Schiff bases (Table 3) were prepared according to the following reaction. Their physical properties are listed in Table 2.

$$2[MoO_2(acac)_2] + 2HL + 4H_2O \xrightarrow{\text{Reflux}} \left[MoO_2(OH)_2(L)H_2\right] + 4acacH$$

where HL = HL$^1$, HL$^2$, HL$^3$, HL$^4$, HL$^5$ or HL$^6$. 
The driving force of the reaction for the formation of these complexes along with the elimination of acacH is the better donating capability of the sulpha drug Schiff bases compared to acetylacetonate anion. The presence of water in the ethanol is responsible for the inclusion of OH group within coordination sphere and the formation of acacH. Such a result has already been reported by us in the synthesis of dioxomolybdenum(VI) complexes with hydrazones derived from acid hydrazides and furfural or thiophene-2-aldehyde using [MoO$_2$(acac)$_2$] as a precursor. The synthesized complexes are coloured, non-hygrosopic and air stable solids. They are soluble in dimethylformamide, dimethylsulphoxide and insoluble in all other common organic solvents.

The important infrared spectral bands and their tentative assignments are given Table 3. The MoO$_2^{2+}$ moiety prefers to form a cis-dioxo grouping due to the maximum utilization of the $d$-orbital for bonding. The dioxo-configuration is characterized by two infrared active modes of $v_{as}(O=Mo=O)$ and $v_{s}(O=Mo=O)$ in C$_{2v}$ symmetry. The trans-MoO$_2^{2+}$ moiety would exhibit a single infrared active stretching band of $v_{as}(O=Mo=O)$. The presence of two infrared bands in the 899-910 and 940-949 cm$^{-1}$ regions due to $v_{as}(O=Mo=O)$ and $v_{s}(O=Mo=O)$, respectively, in the present complexes is strong indicative of the cis-MoO$_2^{2+}$ structure.

The IR spectra of ligands HL$_1$ to HL$_6$ show $v(C=O)$ (cyclic) in the region 1624-1653 cm$^{-1}$, suggesting their existence in the keto-form in the solid state. Thus, the ligands HL$_1$ to HL$_6$, contain six potential donor sites: (i) the ketonic oxygen, (ii) the cyclic nitrogen $N_1$, (iii) the cyclic nitrogen $N_2$, (iv) the azomethine nitrogen, (v) the sulphonamide (SO$_2$NH) oxygen or nitrogen and (vi) the ring nitrogen of sulpha drug. The MoO$_2$(acac)$_2$ reacts with each of the Schiff base ligands in ethanol to form stable dioxomolybdenum(VI)

| Table 1—Characterization data of synthesized sulpha drug Schiff bases |
|--------------------------|--------------------------|--------------------------|--------------------------|
| S. No. | Schiff base (Empirical Formula) (Mol.Wt.) | $\begin{array}{ccc} \text{Found (Calcd., \%)} \\ \text{C} & \text{H} & \text{N} \end{array}$ | Colour | Dec. Temp. ($^\circ$C) |
|----------|-----------------------------------|--------------------------|--------------------------|
| 1. | HL$_1$ (C$_{29}$H$_{36}$N$_6$O$_5$S$_2$Mo$_2$) | $\begin{array}{ccc} 63.21 & 4.53 & 13.59 \end{array}$ | Daffodil | 192 |
| 2. | HL$_2$ (C$_{29}$H$_{36}$N$_6$O$_5$S$_2$Mo$_2$) | $\begin{array}{ccc} 64.72 & 4.75 & 15.69 \end{array}$ | Yellow | 185 |
| 3. | HL$_3$ (C$_{29}$H$_{36}$N$_6$O$_5$S$_2$Mo$_2$) | $\begin{array}{ccc} 63.95 & 4.82 & 12.69 \end{array}$ | Daffodil | 215 |
| 4. | HL$_4$ (C$_{29}$H$_{36}$N$_6$O$_5$S$_2$Mo$_2$) | $\begin{array}{ccc} 66.39 & 4.70 & 13.72 \end{array}$ | Green | 173 |
| 5. | HL$_5$ (C$_{29}$H$_{36}$N$_6$O$_5$S$_2$Mo$_2$) | $\begin{array}{ccc} 60.98 & 4.60 & 14.89 \end{array}$ | Pale | 173 |
| 6. | HL$_6$ (C$_{29}$H$_{36}$N$_6$O$_5$S$_2$Mo$_2$) | $\begin{array}{ccc} 61.04 & 4.76 & 14.73 \end{array}$ | Buff | 217 |

| Table 2—Analytical data and some physical properties of the synthesized complexes |
|--------------------------|--------------------------|--------------------------|--------------------------|
| S. No. | Complex (Empirical Formula) (Mol.Wt.) | $\begin{array}{ccc} \text{Found (Calcd., \%)} \\ \text{C} & \text{H} & \text{N} & \text{Mo} \end{array}$ | Colour | Dec. Temp. ($^\circ$C) | Yield ($\%$) | $\lambda_{mt}$ (Ohm$^{-1}$ cm$^{-1}$-mole$^{-1}$) |
|----------|-----------------------------------|--------------------------|--------------------------|
| 1. | $\left[\text{MoO}_2(\text{OH})_2\right]_2\text{HL}_2$ (C$_{45}$H$_{56}$N$_6$O$_4$S$_2$Mo$_4$) (1313.88) | $\begin{array}{ccc} 49.39 & 3.42 & 10.72 & 14.51 \end{array}$ | Daffodil | 235 | 35 | 10 |
| 2. | $\left[\text{MoO}_2(\text{OH})_2\right]_2\text{HL}_2$ (C$_{45}$H$_{56}$N$_6$O$_4$S$_2$Mo$_4$) (1363.88) | $\begin{array}{ccc} 51.09 & 3.88 & 12.37 & 14.12 \end{array}$ | Yellow | 220 | 40 | 10 |
| 3. | $\left[\text{MoO}_2(\text{OH})_2\right]_2\text{HL}_2$ (C$_{45}$H$_{56}$N$_6$O$_4$S$_2$Mo$_4$) (1370.88) | $\begin{array}{ccc} 49.58 & 3.42 & 12.91 & 14.72 \end{array}$ | Olive | 289 | 50 | 20 |
| 4. | $\left[\text{MoO}_2(\text{OH})_2\right]_2\text{HL}_2$ (C$_{45}$H$_{56}$N$_6$O$_4$S$_2$Mo$_4$) (1315.88) | $\begin{array}{ccc} 47.89 & 3.52 & 9.78 & 16.69 \end{array}$ | Daffodil | 280 | 55 | 10 |
| 5. | $\left[\text{MoO}_2(\text{OH})_2\right]_2\text{HL}_2$ (C$_{45}$H$_{56}$N$_6$O$_4$S$_2$Mo$_4$) (1307.88) | $\begin{array}{ccc} 51.32 & 3.72 & 10.78 & 14.72 \end{array}$ | Pale yellow | 295 | 50 | 10 |
| 6. | $\left[\text{MoO}_2(\text{OH})_2\right]_2\text{HL}_2$ (C$_{45}$H$_{56}$N$_6$O$_4$S$_2$Mo$_4$) (1427.88) | $\begin{array}{ccc} 48.79 & 3.69 & 11.81 & 13.48 \end{array}$ | Daffodil | 280 | 50 | 10 |
ligand bridged binuclear complexes. That both the (acac) ligand were displaced by these ligands was supported by the absence of characteristic peaks of $\nu(C=O)$ (1562 cm$^{-1}$) and $\nu(C=C)$ (1515 cm$^{-1}$) of coordinated acetylacetone$^{23}$ groups in the infrared spectra, and the analytical data of the synthesized derivatives.

All the ligands show a sharp and strong band due to $\nu(C=N)$ of the azomethine group at 1585-1600 cm$^{-1}$. The observed low energy shift of this band in the spectra of the complexes indicates the coordination of azomethine nitrogen$^{24}$.

The $\nu(C=N)$ (cyclic) arising from pyrazolone and sulpha drug skeletons in the ligands appear at ~1590 cm$^{-1}$ and at 1620-1630 cm$^{-1}$, respectively, do not show any change in their position in the IR spectra of the complexes. The $\nu(C=N)^{25}$ appears to be merged with $\nu(C=N)$ (azomethine group). These observations indicate the non-participation of the respective cyclic nitrogen in the coordination. The coordination of ring nitrogen$^{26}$ ($N_1$) is unlikely due to the steric demand of the bulky phenyl group attached with it. All the ligands show a very strong band at 1624-1653 cm$^{-1}$ due to $\nu(C=O)^{26}$ in a cyclic environment of the pyrazolone skeleton. This band is observed at the same frequency in the chelates, indicating the non-involvement of the carbonyl oxygen towards coordination to MoO$_2^{2+}$ moiety.

The IR spectra of all the six ligands exhibit two strong bands at 1325-1360 and 1105-1153 cm$^{-1}$, which are attributed to asymmetric and symmetric stretching vibration of SO$_2$ group. In the spectra of complexes both the bands are split into two bands. The band observed at 1325-1360 in the spectra of respective ligands is split into two bands appearing at 1352-1379 and 1250-1332 cm$^{-1}$, while the band at 1105-1153 is split into two bands at 1116-1164 and 1064-1099 cm$^{-1}$ in the spectra of complexes. Splitting of these bands indicates that one of the sulphonyl oxygens is coordinated to the metal centre in the present complexes. The slightly higher shifted bands (1352-1379 and 1116-1164 cm$^{-1}$) correspond to the vibrations of uncoordinated S=O band and the lower bands (1250-1332 and 1064-1099 cm$^{-1}$) correspond to the vibration of coordinated S=O. Hence, the present ligands are coordinated to the MoO$_2^{2+}$ moiety through one of the oxygen atoms of the sulphonyl group as shown below.

$$O = S= O: \rightarrow MoO_2^{2+}$$

The IR spectra of all the complexes exhibit two bands at 3540-3580 and 3137-3400 cm$^{-1}$ which are attributed to stretching modes of coordinated hydroxyl group. The $\nu(NH)$ modes in the sulphonamide group of the uncoordinated Schiff bases, which are observed at 3396-3425 and 3300-3355 cm$^{-1}$, remain unaltered or merged with $\nu(OH)$ modes in the spectra of their complexes. This suggests that sulphonamide nitrogen is not involved in coordination. The above observation suggests that all the ligands behave as neutral bidentate ligand.

The molar conductances of the complexes ($10^{-3} M$ solutions) in dimethylformamide are in the range (10-20 ohm$^{-1}$ cm$^{-1}$ mol$^{-1}$), as expected for non-electrolytes$^{27}$. Such a non-zero molar conductance value for each of the complexes in the present study is most probably due to the strong donor capacity of dimethylformamide which may lead to the displacement of anionic ligand and change of electrolyte$^{27}$ type. All the complexes, as expected for complexes of dioxygenylbdenum(VI), are diamagnetic$^{28}$.

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Table 3---Important IR spectral bands (cm$^{-1}$) of the synthesized complexes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compounds</th>
<th>$\nu(C=N)$</th>
<th>$\nu_{as}(SO_2)$</th>
<th>$\nu_{s}(SO_2)$</th>
<th>$\nu(OH)$</th>
<th>$\nu_{s}(O=Mo=O)$</th>
<th>$\nu_{as}(O=Mo=O)$</th>
<th>$\nu(C=O)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$[\text{MoO}_2(\text{OH})_2(\text{HL})_2]_2$</td>
<td>1581</td>
<td>1352</td>
<td>1120</td>
<td>3575</td>
<td>947</td>
<td>902</td>
<td>1647</td>
</tr>
<tr>
<td>2.</td>
<td>$[\text{MoO}_2(\text{OH})_2(\text{HL})_2]_2$</td>
<td>1581</td>
<td>1379</td>
<td>1290</td>
<td>1074</td>
<td>3137</td>
<td>943</td>
<td>899</td>
</tr>
<tr>
<td>3.</td>
<td>$[\text{MoO}_2(\text{OH})_2(\text{HL})_2]_2$</td>
<td>1572</td>
<td>1379</td>
<td>1327</td>
<td>1094</td>
<td>3356</td>
<td>949</td>
<td>910</td>
</tr>
<tr>
<td>4.</td>
<td>$[\text{MoO}_2(\text{OH})_2(\text{HL})_2]_2$</td>
<td>1574</td>
<td>1379</td>
<td>1250</td>
<td>1064</td>
<td>3200</td>
<td>950</td>
<td>901</td>
</tr>
<tr>
<td>5.</td>
<td>$[\text{MoO}_2(\text{OH})_2(\text{HL})_2]_2$</td>
<td>1580</td>
<td>1370</td>
<td>1332</td>
<td>1099</td>
<td>3362</td>
<td>908</td>
<td>908</td>
</tr>
<tr>
<td>6.</td>
<td>$[\text{MoO}_2(\text{OH})_2(\text{HL})_2]_2$</td>
<td>1580</td>
<td>1377</td>
<td>1320</td>
<td>1095</td>
<td>3400</td>
<td>1605</td>
<td>1653</td>
</tr>
</tbody>
</table>
Electronic spectra of a few complexes were recorded in 10^{-3} M dimethylformamide solutions. In view of the high intensity (ε = 4800-6500 L mol^{-1} cm^{-1}) peaks observed at 295-360 nm in complexes (1), (3) and (4), they seem to be appeared due to intraligand n-π* π-π* transitions. In case of complexes (2) and (4), a medium intensity (ε = 2461-2716 L mol^{-1} cm^{-1}) peak appearing in the region 341 and 394 nm may be due to the ligand to metal charge transfer transition between the lowest empty molybdenum d orbital and the highest occupied ligand molecular orbital. This result is comparable with the results reported elsewhere for dioxomolybdenum(VI) complexes.

The ^1H NMR spectra of two representative compounds, [{MoO_2(OH)_2} _2(HL^6)_2] and [{MoO_2(OH)_2} _2(HL^5)_2] were recorded in DMSO-d_6. Both compounds exhibit proton signals due to -CH_3 (pyrazolone skeleton), -NH (sulphonamide), aromatic group (pyrazolone and sulpha drug) and -OH protons at 2.5, 6.0, 6.5-6.8 and 11.3-11.4 ppm, respectively. One additional proton signal at 2.3 ppm due to -CH_3 group of sulphamerazine was observed in the ^1H NMR spectrum of compound [{MoO_2(OH)_2} _2(HL^5)_2]. These data support the infrared results already concluded for these complexes.

After recapitulating our experimental data from all the studies presented above indicate that the complexes may be formulated as [{MoO_2(OH)_2} _2(HL^5)_2], where HL = HL^1, HL^2, HL^3, HL^4, HL^5 or HL^6. A ligand bridged binuclear structure has been tentatively proposed for these complexes as shown in the structure II.

**Acknowledgement**

The authors are thankful to Hon. Justice Gulab Gupta, Vice-chancellor of this University, for encouragement, and Professor K. K. Mishra, Head, Department of Chemistry, for laboratory facilities. RCM is grateful to the University Grants Commission, New Delhi, for financial assistance in the form of research project. Analytical facilities provided by the Central Drug Research Institute, Lucknow, India, and the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai, India, are gratefully acknowledged. Thanks are also due to Hon. Reviewer for constructive comments and suggestions in order to improve the manuscript.

**References**