IR spectra of acetamide complexes were recorded on Specord 75 in nujol phase whereas those of other compounds were recorded on a Perkin-Elmer grating infrared spectrophotometer model 577 in KBr.

The imido and imidooxoproxy derivatives of zirconium(IV) were obtained by heating Zr(OPr)i4, Pr(OH) with amide in benzene under reflux. Typically, acetamide (0.249 g) was added to Zr(OPr)i4, Pr(OH) (1.37 g) in dry benzene (70 ml). The mixture was refluxed for 12 hr, during which time liberated isopropanol was collected in the form of a benzene-isopropanol azoetorpe at 72°. The excess of benzene was removed from the insoluble product by fractionation at 80°. The white insoluble product obtained was washed first with ethanol (3 x 1.5 ml) to remove traces of unreacted acetamide, if any, present and finally washed with dry benzene (3 x 2 ml). The complex was dried to constant weight under reduced pressure (10−2 torr) at room temperature. (PriO)2Zr(NHCOCH3)2, yield 90%. [Found: Zr, 27.84; N, 4.25. Calc. Zr, 27.87; N, 4.97%]. Iso- propanol was estimated by oxidation with normal sulphuric acid and back titration of the excess dichromate iodometrically.

Thanks are due to Prof. R. N. Kapoor, Chemistry Department, University of Delhi, for helpful discussions. Thanks are also due to Prof. R. C. Kapoor, Head, Department of Chemistry, University of Jodhpur, for providing laboratory facilities and the UGC, New Delhi for a research fellowship to one of us (KRN).

References

Synthesis & Characterisation of New Molybdenum(VI) Complexes

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Some new molybdenum (VI) complexes of triazole 1-oxides of composition \( MoO_2L_2 \) are reported. Evidences suggest cis-dioxo structure for them.

The recognition of molybdenum as an active site in many biosystems has given a new impetus to the synthesis and study of new molybdenum compounds in different oxidation states. During the course of our study of the transition metal complexes of triazole 1-oxides (I, \( X = H, OC_2H_5, OC_6H_4 \)), new molybdenum compounds were synthesised and studied using these ligands, since very little work is reported on molybdenum complexes. For convenience the ligand system (I) has been abbreviated as \( (R-C_6H_4)X \) and the complex as \( (R-C_6H_4)X \) \( MoO_2 \).

The ligands used here were synthesised by a general method. The molybdenum complexes were prepared as follows: one mol equivalent of molybdenum (ammonium molybdate) was dissolved in minimum quantity of water by adding a few drops of ammonia solution. This was added to a clear solution of 2 mol equivalent of ligand in methanol with stirring. The solution was acidified with conc. \( HNO_3 \) to pH 3–4. An orange coloured solution was formed which on cooling gave yellow-orange crystals. The crude product was recrystallised from methanol and dried \emph{in vacuo}. Characterisation data of the complexes are presented in Table 1.

All the molybdenum complexes are stable in air and soluble in many organic solvents. These complexes are diamagnetic and monomeric in methanol...
Table 1 — Characterisation Data and IR Frequencies for the Molybdenum Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>C (%)</th>
<th>H (%)</th>
<th>Mo (%)</th>
<th>IR vmax (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc.</td>
<td>Found</td>
<td>Calc.</td>
<td>Found</td>
</tr>
<tr>
<td>(C₆H₅-C₆H₅)₂MoO₂</td>
<td>52.18</td>
<td>52.30</td>
<td>3.62</td>
<td>3.60</td>
</tr>
<tr>
<td>(C₆H₅-C₆H₅OCH₃)₂MoO₂</td>
<td>50.98</td>
<td>51.24</td>
<td>3.92</td>
<td>3.90</td>
</tr>
<tr>
<td>(CH₃-C₆H₅)₂MoO₂</td>
<td>39.26</td>
<td>39.05</td>
<td>3.74</td>
<td>3.62</td>
</tr>
<tr>
<td>(C₂H₅-C₂H₅OCH₃)₂MoO₂</td>
<td>39.34</td>
<td>39.62</td>
<td>4.10</td>
<td>4.08</td>
</tr>
<tr>
<td>(C₆H₅-C₆H₅OCH₃)₂MoO₂</td>
<td>41.86</td>
<td>41.05</td>
<td>4.65</td>
<td>4.51</td>
</tr>
<tr>
<td>(CH₃-C₆H₅)₂MoO₂ •</td>
<td>44.12</td>
<td>44.81</td>
<td>5.14</td>
<td>5.04</td>
</tr>
</tbody>
</table>

* Determined gravimetrically as oxinide
† Recorded in KBr on a Perkin-Elmer spectrophotometer, model 297.

(mol. wts determined with Knauer vapour pressure osmometer). These experimental results suggest that these molybdenum complexes can be represented as MoO₂L₂. This is in agreement with the fact that majority of Mo(VI) complexes of organic ligands have the composition Mo₆O₆L₂ while Mo(V) complexes are dinuclear with oxo-bridges, though some monomeric species are reported recently.

In complexes of this type the dioxo groups can be either cis or trans. The cis-dioxo grouping is characterised by two IR and Raman active stretching modes while trans-dioxo by a single IR active and a single Raman active stretch at different frequencies. The presence of two MoO₂ bands in the region 900-960 cm⁻¹ in six-coordinate MoO₂⁺ compounds is strongly indicative of the cis dioxo structure. The IR frequencies observed for our compounds, presented in Table 1, correspond with the bands observed for other six-coordinate cis-MoO₂⁺ species.

Mo(VI) octahedral complexes do not show any electronic transition in the IR and visible regions but exhibit some high intensity transitions in the UV region. The presence of bands in the 27,000 30,000 cm⁻¹ region has been taken to be characteristic of the molybdenyl group. In β-diketonates an intense band assignable to O→Mo charge transfer transition at 25,000 cm⁻¹ has been located near 52,000 cm⁻¹. The molybdenum complexes reported here exhibit an intense transition at 25,000 cm⁻¹. No other transition is observed in the IR or visible region. We could not go below 26,000 cm⁻¹ in the UV region due to instrument limitation. The transition at 25,000 cm⁻¹ is a ligand transition since the same transition is observed in other triazene 1-oxides. The absence of any other transition in the visible or IR region is an indirect evidence to show that molybdenum is not in the V oxidation state in these complexes.

References

Di-2-pyridyl ketone & Benzotriazole Complexes of Zinc(II)

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Zinc(II) pseudohalides (cyanate, thiocyanate and azide) have been reacted with di-2-pyridyl ketone (dpk) and benzotriazole(bzt) in ethanolic medium and six compounds have been isolated and characterised on the basis of analytical, conductance and infrared spectral data. The compound Zn(dpk)(N₃)₂ is four coordinated; Zn(bzt)(NCS)₂ and Zn(bzt)(N₃)₂ are five coordinated; and Zn(dpk)(NCS)₂, Zn(dpk)(NCS)₂ and Zn(bzt)(NCS)₂ are six coordinated.

The ligands, di-2-pyridyl ketone (dpk) and benzotriazole(bzt), are interesting ligands as they exhibit different modes of coordination. Di-2-pyridyl ketone may function as a neutral bidentate ligand coordinating either through N, O or N, N and a number of its complexes with different metal ions, viz. Cu(II), Mn(II), Fe(II), Co(II), Ni(II), have been reported. Benzotriazole may function as a neutral monodentate or acicid bidentate ligand and its complexes with Pd(II), Cu(II), Ni(II), Co(II & III), Rh(II), Os(III), Mn(II)⁶⁻¹³ have been already reported. The pseudohalides, thiocyanate, cyanate and azide, are interesting for their different modes of coordination. In the present note an attempt has been made to...