Table 1 — Electronic Spectral Data and Relevant Ligand Field Parameters†

<table>
<thead>
<tr>
<th>Complex</th>
<th>(v_1) (cm(^{-1}))</th>
<th>(v_2) (cm(^{-1}))</th>
<th>(v_3) (cm(^{-1}))</th>
<th>(B)</th>
<th>(\beta_{3g})</th>
<th>L.F.S.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni(DEAPG)}]_{2}\text{Cl}_4)</td>
<td>9800</td>
<td>16000</td>
<td>27200</td>
<td>24500</td>
<td>26705</td>
<td>27950</td>
</tr>
<tr>
<td>([\text{Ni(DEAPG)}]<em>{2}(\text{CN})</em>{2}\text{Cl}_4)</td>
<td>9840</td>
<td>15550</td>
<td>27250</td>
<td>24715</td>
<td>26733</td>
<td>27949</td>
</tr>
<tr>
<td>([\text{Ni(DEAPG)}]<em>{2}(\text{NCS})</em>{2})</td>
<td>10000</td>
<td>15630</td>
<td>24753</td>
<td>24750</td>
<td>26727</td>
<td>28320</td>
</tr>
</tbody>
</table>

* (a), (b), (c) and (d) refer to methods of calculations for \(B\) using equations (3), (4), (5) and (6) respectively.
† Fitted values of \(v_1\), \(v_2\) and \(v_3\) refer to calculating the value of a band by putting the value of \(B^*\) (calculated from the observed bands \(v_1\), \(v_2\) and \(v_3\) using Eq. (5) and 10 \(Dq\) (from Eq. 1) in Eq. 2. In method (c) both the bands, \(v_2\) and \(v_3\) are calculated from Eq. 2.

The IR spectrum of the ligand indicates the characteristics of these complexes have been studied. The electronic spectral data indicate that the complexes possess octahedral geometry. The calculated values of \(B\) and particularly the value of the nephelauxetic ratio, \(\beta_{3g}\), depend significantly on the method adopted for their calculations (see Table 1). The results indicate that the best fit for the transitions \(v_2\) and \(v_3\) can be obtained by using Eq. (5).

The IR spectrum of the ligand indicates the presence of keto, azomethine and 1,4-disubstituted groups. On complexation, \(v>C=O\) and \(v-C=N-\) are shifted to lower values indicating coordination through the keto and azomethine group. The presence of \(\text{NH}_3\) in the complex \([\text{Ni(DEAPG)}]_{2}(\text{NH}_3)_2\text{Cl}_4\) is indicated by the appearance of a band at 3370 cm\(^{-1}\). The \(v-C=N\) frequency in the complex \([\text{Ni(DEAPG)}]_{2}(\text{CN})_{2}\) is observed at 2036 cm\(^{-1}\) and this lower value, compared to that of the free ion, also indicates coordination.

The complex \([\text{Ni(DEAPG)}]_{2}(\text{NCS})_{2}\) exhibits \(v-C=N-\) and \(v=C=S\) frequencies at 2070 and 820 cm\(^{-1}\), respectively, indicating bonding through sulphur atom of NCS group. \(vM-Cl\) frequency in \([\text{Ni(DEAPG)}]_{2}\text{Cl}_4\) was observed at 350 cm\(^{-1}\). Bands occurring in the range 580-570, 510-500 cm\(^{-1}\) in the spectra of the complexes have been assigned to \(vM-O\) and \(vM-N\) modes respectively.

References

Reactions of (dicyclopentadienyl)(dichloro)(oxy)molybdenum(VI) with sodium salts of various thiocarboxylic acids in tetrahydrofuran medium, yield the complexes of the formula \((\text{CSH}_3)_2\text{MoO(SOCR)}_2\), where \(R = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5\) or \(\text{C}_6\text{H}_5\). The foul smelling complexes are monomeric and non-ionic in nature. The IR spectra, thermal stabilities and some physical characteristics of these complexes have been studied.

In continuation of our work on pseudohalide\(^4\), isomeric nitro, phenolic and thioldisubstituted derivatives of (dicyclopentadienyl)[dichloro](oxy)molybdenum(VI), we report here the preparation and characterization of thio-carboxylato derivatives of (dicyclopentadienyl)[dichloro](oxy)molybdenum(VI).

Thiocarboxylato derivatives of (dicyclopentadienyl)[dichloro](oxy)molybdenum(VI) have been prepared by reacting the latter\(^5\) with sodium salts of various thiocarboxylic acids in tetrahydrofuran (Eq. 1). The compounds are brownish-black to violet-black in colour and have characteristic disagreeable odour.
of (oxy)(tetrachloro)molybdenum(VI) with sodium over lithium aluminium hydride. (Oxy)(tetrachloro)conventional methods. THF, refluxed over potassium molybdenum(VI) was prepared from molybdenum in benzene and conductance measurements in nitrobenzene respectively. Thioacids are commercially available.

Preparation of (dicyclopentadienyl)(oxy)(dithioformato)molybdenum(VI) — Sodium thioformate (0·33 g 0·004 mole) was added to (dicyclopentadienyl)(oxy)-(dichloro)molybdenum(VI) (0·62 g, 0·002 mole) in tetrahydrofuran (100 ml). The reaction mixture was refluxed and stirred for 5-6 hr at 70-75°. The resulting solution was filtered through a G sintered glass disc and the filtrate, on evaporation under reduced pressure and repeated washings with petroleum ether (40°-60°C), yielded brownish-black crystals corresponding to the formula (C₅H₅)₂MoO(SOCR)₂.

Other compounds were prepared analogously.

References

Nitro, Nitrito & Nitrato Derivatives of Dicyclopentadienyl- & Bisindenyl-titanium(IV) Dichlorides
R. S. Arora, M. S. Bhalla & R. K. Multani
Department of Chemistry, University of Delhi
Delhi 110007

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Six new nitro, nitrito and nitrato complexes of titanium(IV) of the general formula (π-D)₂TL₄
(where D = cyclopentadienyl or indenyl group and L = nitro, nitrito or nitrato group) have been isolated and characterized. The non-ionic and monomeric nature of these complexes has been inferred on the basis of conductance, molecular weight and analytical data. These compounds have been further characterized on the basis of IR studies.