were prepared by dissolving a calculated amount of each in 0·01 M HNO₃.

Spectrophotometric measurements were made on Zeiss-Specol. All measurements were carried out at 30 ± 1°C in a 50% methanol-50% water (by volume) medium adjusted to 0·005 M with respect to nitric acid.

The nature of complexes in iron(III)-3 CIOHB system was determined by the method of Vosburgh and Cooper⁶. The observations showed that only one complex with λmax of 550 nm is formed. The 1 : 1 composition of the complex was determined by Job’s⁷ and slope-ratio⁸ methods. The apparent stability constant of the complex log K = 2·18 was calculated from absorbance data by the method of Mukherji and Dey⁹.

![Fig. 1. Job’s Curve for Iron(III)-3 CIOHB-EDTA complex. Curve A, Iron(III)-3 CIOHB; Curve B, Iron (III)-3 CIOHB EDTA; Curve C, Difference of Curves A and B.](image)

The method used to determine the composition of colourless complexes has been described earlier⁵. A solution containing Fe(2 CIOHB)₂ (1 × 10⁻³ M) was prepared by mixing equal volumes of iron(III) (2 × 10⁻³ M) and 3 CIOHB (1 × 10⁻²) solutions. The continuous variation⁷ studies were carried out using 1 × 10⁻³ M Fe (3 CIOHB)₂ and 1 × 10⁻³ M carboxylic acid solutions. The absorbances were measured at 530 nm. Two sets of solutions for each equilibrium, one with and the other without the carboxylic acid, were prepared. The difference in the absorbances of the pair of corresponding solutions for the two sets corresponds to the Y function in Job’s curve. Maximum in Y indicates 1:1 composition for the colourless complexes of iron(III) with citric, oxalic, EDTA and malonic acids. Typical results are shown in Fig. 1 for Fe(III)-3 CIOHB-EDTA system. It can be seen from Fig. 1 that the maximum decolourisation was observed at a ratio of iron(III) : EDTA = 1 : 1. This indicates the formation of a complex corresponding to the formula Fe(EDTA)⁻³ under the experimental conditions used. Results obtained with citric acid, oxalic acid and malonic acid also indicated that iron(III) forms 1:1 complexes with these acids under the conditions of the present study.


2. — and —, Ibid., 1971, 48, 1177.

**TETRAFLUORENYL OXY MOLYBDENUM(VI) AND TUNGSTEN(VI)**

The present communication deals with the preparation and characterization of tetrafluorenyl oxy molybdenum (VI) and tungsten (VI) by the reactions of molybdenum and tungsten oxo tetra-chloride with sodium salts of fluorene in tetrahydrofuran.

**EXPERIMENTAL**

Operations were carried out under anhydrous conditions. A good grade of tetrahydrofuran was further purified by distillation over lithium aluminium hydride. Tungsten oxy tetrachloride was prepared by refluxing tungsten trioxide with thionyl chloride and the excess of thionyl chloride was removed by evaporation under reduced pressure. The bright reddish mass so formed was sublimed at 120–135°C and yielded scarlet red needles. Molybdenum oxy tetrachloride was prepared by the method reported by Colten et al.⁵. Infrared spectra (KBr) were recorded on Perkin Elmer Infracord Model-137 spectrophotometer. Tungsten...
or molybdenum was estimated as 8-hydroxy quinolate while carbon and hydrogen were determined by microanalytical methods.

Preparation of tetrafluorenol oxy molybdenum. — Small pieces of sodium (0·5 g; 0·022 mole) were added to fluorene (3·65 g; 0·022 mole) in tetrahydrofuran (90 ml). The mixture was stirred vigorously for 10–12 hrs under nitrogen at room temperature. The mixture was gradually added with constant stirring to a suspension of molybdenum oxy tetrachloride (1·26 g; 0·005 mole) in tetrahydrofuran (100 ml). Stirring was continued for 7–8 hrs at room temperature. The solution was filtered through a G-4 sintered glass disc and the residue was washed with tetrahydrofuran. The filtrate along with the washings was evaporated under reduced pressure (30–35 mm) and the orange crystalline compound thus obtained was found to have the composition (C₁₅H₉)₄MoO, yield 80% (Found: C, 80·3; H, 4·5; Mo, 12·2; calc. for C₂₉H₂₃MoO: C, 80·81; H, 4·69; Mo, 12·41%).

It is an orange crystalline compound, stable in dry and inert atmosphere but decomposes without melting at 94°C. It is immiscible with water but soluble in common organic solvents like dichloromethane, chloroform, carbon tetrachloride, benzene, acetone, dioxane, dimethylformamide and methanol. The infrared spectrum (in KBr) shows the following absorption peaks:

<table>
<thead>
<tr>
<th>3050</th>
<th>1705</th>
<th>1640</th>
<th>1530</th>
<th>1510</th>
<th>1460</th>
<th>1400</th>
<th>1340</th>
<th>m</th>
<th>1170</th>
<th>1050</th>
<th>955</th>
<th>820</th>
<th>735</th>
<th>695 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>w</td>
<td>w</td>
<td>w</td>
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<td>m</td>
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</tbody>
</table>

Preparation of tetrafluorenol oxy tungsten. — To tungsten oxy tetrachloride (1·35 g; 0·004 mole) in tetrahydrofuran (120 ml) was added sodium salt of fluorene (0·016 mole). The mixture was stirred and refluxed at 70–75°C for 2–3 hrs and filtered. Its volatile constituents were removed by distillation under reduced pressure and the pink crystalline compound thus obtained was found to have the formula (C₁₅H₉)₄WO, yield 55% (Found: C, 71·9; H, 4·0; W, 21·2; calc. for C₂₉H₂₃WO: C, 72·56; H, 4·21; W, 21·36%).

It is a pink crystalline compound, stable thermally as well as chemically. It is non-volatile and does not sublime in vacuum. It is fairly soluble in common organic solvents, viz., acetone, benzene, tetrahydrofuran, carbon disulphide, dichloromethane, chloroform, carbon tetrachloride, ethanol and insoluble in water. The infrared spectrum (KBr) shows the following absorption peaks:

<table>
<thead>
<tr>
<th>3070</th>
<th>1720</th>
<th>1650</th>
<th>1520</th>
<th>1450</th>
<th>1405</th>
<th>1345</th>
<th>1170</th>
<th>m</th>
<th>1050</th>
<th>950</th>
<th>830</th>
<th>740</th>
<th>695 cm⁻¹</th>
</tr>
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<tbody>
<tr>
<td>w</td>
<td>m</td>
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</tr>
</tbody>
</table>

The preparation of tetrafluorenol oxy molybdenum (VI) and tungsten (VI) may be regarded as analogous to the preparation of fluorenol derivatives of various metal atoms¹⁻⁷ as well as tetrapentadienyl oxy tungsten⁸.

\[ \text{MoOCl}_4 + 4 \text{C}_{15} \text{H}_9 \text{Na} \rightarrow (\text{C}_{15} \text{H}_9)_4 \text{MoO} + 4 \text{NaCl} \]
\[ \text{WOCl}_4 + 4 \text{C}_{15} \text{H}_9 \text{Na} \rightarrow (\text{C}_{15} \text{H}_9)_4 \text{WO} + 4 \text{NaCl} \]

The infrared spectrum of tetrafluorenol oxy molybdenum or tungsten shows the usual peaks of the C=C group¹⁰, viz., the C-H stretching frequencies at ~ 3050 cm⁻¹, the perpendicular hydrogen wagging mode at ~ 820 cm⁻¹, the parallel hydrogen wagging vibration at ~ 1050 cm⁻¹, the bands due to the C-C stretching mode and the ring breathing mode of the cyclopentadienyl rings at ~ 1450 cm⁻¹ and ~ 1170 cm⁻¹ respectively; in addition to these it also shows the peaks of the phenyl groups, the C-H stretching frequencies at ~ 1400 cm⁻¹, the C=C stretching vibration at ~ 1640 cm⁻¹, C-H out of plane bending at ~ 735 cm⁻¹ and the absorption bands at 695 cm⁻¹ may be due to methylene rocking vibration¹¹. Furthermore the bands at ~ 950 cm⁻¹ may result from the presence of M=O linkage as observed in the case of MoOCl₄ and WOCl₄¹².

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and

Dept. of Chemistry, B. L. Kalstostra, University of Jammu, Jammu-1, December 27, 1972.