Preparation & Characterization of Tris(methylcyclopentadienyl)-uranium(IV) Compounds

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The synthesis and characterization of tris(methylcyclopentadienyl)uranium compounds; (CH₃C₅H₅)₃UX where X = Cl, Br, BH₄ and n - OC₄H₉ are reported. Some properties of these compounds are described and compared with those of tris(cyclopentadienyl)uranium(IV) complexes. Infrared (4000 - 200 cm⁻¹), mass spectra and X-ray powder patterns of the compounds are discussed. Evidence is given for the presence of centrally π-bonded methylcyclopentadienyl groups.

Several tris(cyclopentadienyl)uranium(IV) derivatives have been reported since the synthesis of tris (cyclopentadienyl) uranium(IV) chloride by Reynold and Wilkinson. In addition, some ring substituted cyclopentadienyluranium(IV) complexes have also been described. The monomethylcyclopentadienyl (Mcp) compounds of transition metals and lanthanides show pronounced change in their properties as compared to the corresponding cyclopentadienyl complexes due to increased electron density on the rings and metal atom. This paper describes the synthesis, characterization and some physical properties of (Mcp)₃UX (X = Cl, Br, BH₄ and OC₄H₉) complexes. A brief communication on the photoelectron spectra of chloride, bromide and borohydride derivatives has been recently reported, but no synthetic and physical data were given.

Materials and Methods

Infrared spectra were recorded in mull on a Perkin-Elmer grating spectrophotometer model 577. Mass spectra were recorded on a Micromass 7070 F double focusing mass spectrometer equipped with direct probe inlet. The X-ray diffraction powder patterns were taken on a Debye-Scherrer 114.83 mm camera using CuKα radiation. The samples were filled in 0.3 mm quartz capillaries inside a dry box.

All the operations were carried out under an atmosphere of oxygen-free nitrogen gas. Tetrahydrofuran (THF) and hexane were first distilled over LiAlH₄ and then over sodium benzophenone ketyl under nitrogen. They were further degassed in vacuo prior to use.

Uranium(IV) chloride was prepared by the reported procedure. UBr₄ was prepared by the bromination of uranium metal and vacuum sublimed. Thallous methylcyclopentadienide (TIMcp) was prepared as reported and purified by vacuum sublimation. The mass spectrum showed parent ion peak at m/e 284 due to ⁶⁸⁸UCl₂H₂.

Uranium in the complexes was determined by the reported procedure after destroying the organic matter. C and H microanalyses were carried out at the Bio-organic Division of this Centre.

Tris (methylcyclopentadienyl)uranium(IV) chloride — In a 100 ml two-necked reaction vessel with a side arm having a break seal, 3.07 g (8.08 mmol) UCl₃ and 6.97 g (24.60 mmol) of TIMcp were placed. To this, THF (~50 ml) was vacuum-transferred at 77 K. The two arms were then sealed under oxygen-free nitrogen. The contents were allowed to attain room temperature and stirred for 24 hr. The dark-brown solution obtained was filtered through a sintered glass to separate TiCl₄. THF was vacuum-distilled and the dark-brown solid obtained was vacuum-dried for 5-6 hr. It was purified by vacuum-sublimation at 418 K (10⁻⁴ torr) to get 1.64 g (~40 %) of dark-brown crystals [Found : C, 42.6; H, 4.6; Cl, 5.6. Calc. : C, 42.3; H, 4.1; Cl, 6.94 %]. The IR spectrum showed peaks at (cm⁻¹): 3050 w, 2920 s, 2820 m, 1400 m, 1100 m, 1070 m, 1046 w, 1025 w, 925 m, 840 m, 805 s, 786 s, 718 w, 605 w, 338 w, 252 sh, 245 m and 220 w.

The bromide derivative was prepared by a similar procedure using UBr₄. The tetrahydroborate and n-butoxy compounds were obtained by reacting purified (Mcp)₃UCl and NaBH₄ or n-NaOC₄H₉ in THF at room temperature for 5-7 days. The yields of the compounds were generally low since they were purified by slow sublimation in vacuo. The compound (Mcp)₃UOC₄H₉ was obtained as a sticky green solid at room temperature when THF was vacuum-distilled from the solution. Its mass spectrum showed parent ion peak at m/e 548 corresponding to C₂₂H₂₃O₃U, and there was no peak higher than the molecular weight. The IR spectrum did not show any evidence of oxidation. Efforts to sublime the...
compound in vacuo using 195K cold finger were not successful.

Results and Discussion

The reported complexes were characterized on the basis of chemical analysis and mass spectrometry (Table 1).

These compounds are highly oxygen-sensitive and decompose rapidly even on slight exposure. They were always stored under oxygen-free nitrogen in sealed ampoules. (Mcp)3UCI is highly soluble in THF giving deep-brown solution; it is slightly soluble in benzene and chloroform but insoluble in carbon tetrachloride and hexane. The compound is not wetted by degassed water, but on keeping a green solution is obtained probably due to the same type of dissociation as that observed for (C5H5)3UCI1.

The reaction between (Mcp)3UCI and freshly prepared ferrous chloride in THF12 did not give any 1,1-dimethyI-ferrocene even after keeping for several hours at room temperature, thus showing that there is no ionic dissociation leading to (CH2C5H5)~ ion, and metal to ring bonds are not electrostatic in nature3. Compared to tris(cyclopentadienyl)uranium (IV) compounds, these complexes melt at ~40° lower temperatures, and are more volatile than the former.

The partial mass spectra of all the compounds are listed in Table 2. The fragmentation patterns of the complexes clearly confirm the compositions of these compounds.

The relatively high intensity of parent ion peak in all the compounds, which is not the case with tris(cyclopentadienyl)uranium(IV)14 and trisindenyluranium(IV) compounds15, would suggest a greater degree of stability for these complexes. The most intense peak in all the spectra was found to be of (Mcp)2UR+ ion (R = Cl, Br, OC2H5) except in the case of borohydride derivative where it was of (Mcp)2U+. This is in conformity with the behaviour of other reported complexes of uranium14. In contrast to the highest peak of CpUO+ reported in a recent work on Cp3UOC2H516, the ion (Mcp)2- UOC2H5+ appears as the strongest mass peak.

Although care was taken to load the samples in the mass spectrometer under nitrogen cover after monitoring the purity by IR spectrum18, the borohydride derivative showed peaks due to impurity at m/z 523, 444 and 429 corresponding to the oxidation product (Mcp)3U(O2)BH4 and its fragments. This is indicative of high chemical reactivity of this compound.

The X-ray diffraction powder patterns of these compounds are poor, making it difficult to interpret the data. However, the chloride and bromide complexes have somewhat similar patterns and hence are iso-structural. The borohydride derivative shows some similarity with the halides but the present data do not establish the structure to be identical.

The infrared spectra of these compounds in the rock salt region closely resemble those reported for (Mcp)2MCl4 (M=Ti, Zr and Hf) and (Mcp)2Fe319. No spectral data for lanthanide complexes containing Mcp ligands have been reported.

The IR bands at (cm-1) 3078-90(w) due to v(CH); 1018-30(m) due to δ(CH); 775-805 (s-sh) due to v(CH); and 752-790 (vs) due to v(CH), characteristic of π-bonded cyclopentadienyl groups, are present in all the complexes11,18. In the cases of π-bonded complexes containing Mcp ligands, the (CH) out-of-plane vibration was observed at ~859 cm-1 for (Mcp)2TiCl4, 850 cm-1 for (Mcp)2ZrCl4 and 860 cm-1 for (Mcp)2HfCl4. A strong absorption is reported at 730 cm-1 in (Mcp)Ti, which is a compound with significant σ-character18; when this is compared with the above results it is apparent that some degree of σ-character is present in the complexes under study.

### Table 1 — Physical Properties of the Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>m.p. (K)</th>
<th>Sublimation</th>
<th>Uranium, Mol. wt</th>
<th>% wt</th>
<th>Temp. Found</th>
<th>Found</th>
<th>(K)</th>
<th>(Calc.)</th>
<th>(Calc.)</th>
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<tbody>
<tr>
<td>(Mcp)3UCI</td>
<td>Dark-brown</td>
<td>485-87</td>
<td>418-33</td>
<td>46.21</td>
<td>510</td>
<td>510</td>
<td>(46.63)</td>
<td>(510.82)</td>
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<tr>
<td>(Mcp)2UBH4</td>
<td>Reddish-brown</td>
<td>473(d)</td>
<td>393-403</td>
<td>49.40</td>
<td>490</td>
<td>490</td>
<td>(48.57)</td>
<td>(490.19)</td>
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<tr>
<td>(Mcp)2UOC2H5</td>
<td>Green</td>
<td>--</td>
<td>--</td>
<td>45.13</td>
<td>548</td>
<td>548</td>
<td>(43.43)</td>
<td>(548.49)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mcp)2UBr</td>
<td>Brown</td>
<td>530</td>
<td>413-33</td>
<td>42.26</td>
<td>556</td>
<td>556</td>
<td>(42.71)</td>
<td>(555.28)</td>
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</tr>
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</table>

*by mass spectrometry

### Table 2 — Partial Mass Spectra of the Compounds

| m/e | ion | r.i. | m/e | ion | r.i. | m/e | ion | r.i. | m/e | ion | r.i. | m/e | ion | r.i. |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 510 | (Mcp)3UCI+ | 22 | 490 | (Mcp)2UBH4+ | 33 | 548 | (Mcp)2UOC2H5+ | 22 | 556 | (Mcp)2UBr+ | 30 | 254 | UO+ | 3 |
| 475 | (Mcp)2U+ | 4 | 475 | (Mcp)2UBH4+ | 25 | 536 | (Mcp)2UOC2H5+ | 3 | 554 | (Mcp)2UBr+ | 34 | 398 | (Mcp)2UBH4+ | 23 |
| 431 | (Mcp)2UCl+ | 100 | 411 | (Mcp)2UBH4+ | 80 | 468 | (Mcp)2UOC2H5+ | 100 | 316 | (Mcp)2UBr+ | 10 | 396 | (Mcp)2UBH4+ | 23 |
| 396 | (Mcp)2UCI+ | 10 | 396 | (Mcp)2UBH4+ | 100 | 454 | (Mcp)2UOC2H5+ | 14 | 475 | (Mcp)2UBr+ | 100 | 254 | UO+ | 3 |
| 352 | (Mcp)2UCI+ | 30 | 316 | (Mcp)2U+ | 40 | 412 | (Mcp)2UBH4+ | 26 | 398 | (Mcp)2UBH4+ | 23 | 316 | (Mcp)2UBr+ | 10 |
| 317 | (Mcp)2U+ | 17 | 238 | U+ | 238 | U+ | 238 | U+ | 238 | U+ | 1 |
The spectrum of (Mcp)$_2$UCl when compared with that of (C$_5$H$_5$)$_2$UCl (prepared as reported in reference 14b) contained three additional bands at 1490, 1205 and 840 cm$^{-1}$ which are attributed to the substituted methyl group in the ring. The absorption band at 1500 cm$^{-1}$ in (Mcp)$_2$ZrCl$_2$ and [(Mcp)$_2$ZrCl]$_2$ and at 845 cm$^{-1}$ in the spectra of [(Mcp)UCl$_4$(THF)] and [(Mcp)$_2$(Cp)UCl] have previously been assigned to CH$_3$ group.

A single, medium intensity band due to ν(B-Ht) at 2450 cm$^{-1}$ together with two bands due to ν(B-Hb) mode at 2250 and 2210 cm$^{-1}$ and a bridge deformation mode at 1500 cm$^{-1}$ in the spectrum of (Mcp) UCI can be tentatively assigned to νU-Cl vibration.ν

The far IR spectra of the present complexes show bands around 600, 340 and 245 cm$^{-1}$ which may be attributed to metal-ring vibrations respectively.νν

References