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ORGANOMETALLIC CHEMISTRY OF URANIUM

II. THE PREPARATION AND PROPERTIES OF $CpUCl_3 \cdot DME$

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SUMMARY

Cyclopentadienyluranium(IV) chloride has been prepared as the dimethoxyethane adduct of formula $CpUCl_3 \cdot DME$ by treatment of uranium tetrachloride with cyclopentadienylthallium in dimethoxyethane. It has been characterized by IR and electronic spectra.

Knowledge of the chemistry of organometallic uranium(IV) compounds, containing both cyclopentadienyl and halide groups, has previously been confined to compounds of the type Cp_3UX ($Cp = C_5H_5$, $X = F$, Cl, Br, I)[1,2] and Cp_2UCl_2[3]. We describe below the preparation of a new compound, $CpUCl_3 \cdot DME$ (DME = dimethoxyethane), the first uranium compound containing only one organic group bonded to the metal.

EXPERIMENTAL

Products and manipulations were as in ref. 3. A typical synthesis was as follows: a mixture of uranium tetrachloride (1.45 g, 3.81 mmole) and cyclopentadienylthallium (1.03 g, 3.81 mmole) in DME was stirred for about 7 h at room temperature; the green solution was filtered to remove the TlCl, and the solvent was evaporated *in vacuo*. The green solid obtained was soluble in tetrahydrofuran but insoluble in hydrocarbons. The compound is more soluble than uranium tetrachloride in DME; in DME uranium tetrachloride is known to form a slightly soluble adduct $UCl_4 \cdot 2DME$[4].

Attempts at sublimation led to decomposition of $CpUCl_3 \cdot DME$. The adduct also decomposes in the presence of air, especially in solution, and so all operations were performed under nitrogen (dried over Na/K alloy). (Found: C, 21.2; H, 3.0; Cl, 21.1; U, 46.8. $C_9H_{15}O_2UCl_3$ calcd.: C, 21.6; H, 3.1; Cl, 21.3; U, 47.6%.)

Spectra

The IR spectra of $CpUCl_3 \cdot DME$ were measured in Nujol mulls (CsI discs) on a Perkin–Elmer 621 Spectrophotometer. In the 1300–400 cm^{-1} region the compound shows the following peaks: 1290 m, 1261 w, 1249 m, 1187 m, 1152 vw, 1115 m, 1084 s, 1065 (sh), 1024 s, 855 s, 847 s, 832 m, 800 mw, 582 vw, 464 (br)m, 394 m. The complex

$UCl_4 \cdot 2DME$, prepared as reported in ref. 4, gave: 1292 (sh), 1287 w, 1251 m, 1245 m, 1187 m, 1152 vw, 1117 (sh), 1114 m, 1082 s, 1065 (sh), 1022 s, 960 vw, 854 s, 847 (sh), 831 m, 800 vw, 586 vw, 533 vw, 393 m.

The visible spectra of cyclopentadienyluranium(IV) chloride and uranium tetrachloride in DME (taken with a Beckman DK2A Spectrophotometer) are shown in Fig. 1.

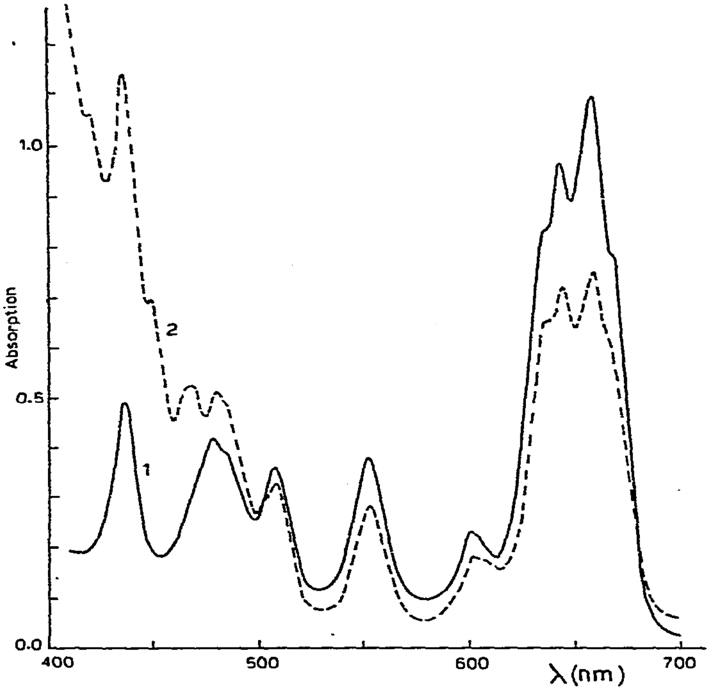

Fig. 1. Electronic spectra in dimethoxyethane. Solid line: UCl_4, conc. $2.5 \cdot 10^{-2}$ *M*. Dotted line: $CpUCl_3$, conc. $3 \cdot 10^{-2}$ *M*.

Magnetic measurements

The magnetic susceptibility of $CpUCl_3 \cdot DME$, measured in the solid phase at 25° by the Gouy method, and corrected for diamagnetism of the ligands (−155 cgs u), was $2796 \cdot 10^{-6}$ cgs u.

DISCUSSION

The IR spectrum of $CpUCl_3 \cdot DME$ in the region examined and at about 3000 and 1500 cm^{-1} is very similar to that of $UCl_4 \cdot 2DME$. Most of the bands are due to the DME, which shields the peaks due to the cyclopentadienyl group[3].

The visible spectra of both the compounds are shown in Fig. 1. They differ below 500 nm, where the organometallic compound shows a higher extinction coefficient. This type of behaviour has been observed for the spectra of Cp_3UCl in THF[1] and Cp_2UCl_2 in DME (our unpublished data). In the region 700–1200 nm the two examined compounds show identical bands.

The μ_{eff} of the prepared compound, calculated using the spin only formula, is 2.59 BM, which is very close to the value found for Cp_2UCl_2[3], suggesting a similar spin multiplicity.

The behaviour of cyclopentadienyluranium(IV) chlorides towards DME indicates that the ability to coordinate neutral ligands increases in the series $Cp_2UCl_2 < CpUCl_3 < UCl_4$, and suggests a preference for coordination number eight in these types of uranium compounds. Our work continues with the aim to prepare adducts of $CpUCl_3$ with various ligands containing oxygen and nitrogen as donor atoms. We have so far obtained good evidence for complex formation with neutral chelating ligands, such as 2,2′-bipyridine and *o*-phenanthroline, and with ionic chelating ligands such as acetylacetone.

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