Synthesis, Chemical Behaviour, and Structure (Crystal and Solution) of a Fluorouranocene(ιv) Tetrafluoroborate; X-Ray Crystal Structure of [{Ucp″$_2$(μ-BF$_4$)(μ-F)}$_2$] [cp″ = η-C$_5$H$_3$(SiMe$_3$)$_2$]†

Peter B. Hitchcock, Michael F. Lappert, and Richard G. Taylor

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

Reaction of Ag[BF$_4$] in OEt$_2$ with either [Ucp″$_2$Cl$_2$] or [Ucp″$_2$(CH$_2$R)$_2$] [cp″ = η-C$_5$H$_3$(SiMe$_3$)$_2$, R= SiMe$_3$ or Ph] affords the monofluoro(tetrafluoroborato)uranocene(ιv), which in the crystal is a dimer (1) with a pair of bridging bidentate BF$_4^-$ ligands and a (μ-F)$_2^-$ arrangement, with mean U–FB, U–F, and B–FU bond lengths of 2.41, 2.31, and 1.34 Å respectively, and B–F (terminal) of 1.38(4) and 1.23(2) Å; in CDCl$_3$ or CD$_3$C$_6$D$_5$ (1) is in equilibrium with the monomer (2), with ΔH = 54.2 kJ mol^{-1} and ΔS *ca.* 200 J mol^{-1} K^{-1} for the dissociation, and for each of (1) and (2) there is a temperature-dependent dynamic process, with ΔG$^{\ddagger}_{263 \text{ or } 288 \text{ K}}$ = *ca.* 50 kJ mol^{-1}, which may relate to U–cp″ rotations.

We have recently shown that various uranocene(ιv) complexes [Ucp″$_2$(X)Y] are accessible from the corresponding dichloride (X = Cl = Y) when the cyclopentadienyl ligand is η-C$_5$H$_3$(SiMe$_3$)$_2$ (abbreviated as c̄p″).[1] We now report (i) an interesting crystalline derivative [{U cp″$_2$(μ-BF$_4$)(μ-F)}$_2$], (1); (ii) the X-ray structure of (1); (iii) its equilibrium in CDCl$_3$ or CD$_3$C$_6$D$_5$ solution with the monomer [Ucp″$_2$(BF$_4$)F], (2); (iv) the synthesis (Scheme 1) of (1) and (2) from [Ucp″$_2$Cl$_2$],[1] (3), or [Ucp″$_2$(CH$_2$R)$_2$], (4);[1] (v) the thermodynamic parameters for the equilibrium (1) ⇌ 2(2); (vi) ΔG‡ for a variable temperature phenomenon (probably U–cp″ rotations) associated with each of (1) and (2); and (vii) the reaction (v or vi in Scheme 1) of (1) with base L [L = NMe$_3$ or OC$_4$H$_8$ (≡ thf)] to yield BF$_3$(L) and the as yet incompletely characterised fluoride [{Ucp″$_2$F$_2$(thf)$_m$}$_n$], (5).

Although a non-co-ordinating anion is essentially unattainable, [BF$_4$]$^-$ is generally held to come close to such a goal. The

isolation and X-ray characterisation of the hydrocarbon-soluble (tetrafluoroborato)uranium(ιv) complex (1) is therefore surprising, not least because it is binuclear in the crystal, and moreover it has the [BF$_4$]$^-$ as a bidentate bridging ligand (Figure 1). The only precedent of which we are aware is that of [{Cu(μ-BF$_4$)(bipy)}$_n$][BF$_4$]$_n$ (bipy = α,α′-bispyridine), which comprises an infinite chain of [Cu(BF$_4$)(bipy)]$^+$ ions with successive copper centres bridged by bidentate [BF$_4$]$^-$ ions.[2] Interestingly a (μ-F)$_2^-$ binuclear metal complex also occurs in Cu^{II} chemistry. Thus, [{Cu(μ-F)(mppz)}$_2$][BF$_4$]$_2$ (mppzH = 3-Me-5-Ph-pyrazole) contains dimeric co-square planar cations, with mean Cu–F 1.94 Å.[3] The [BF$_4$]$^-$ ions are only weakly co-ordinated to Cu, with mean Cu–FBF$_3$ 2.61 Å, although the overall Cu^{II} co-ordination environment is similar to that found for U^{IV} in complex (1) (if each c̄p″ ligand is taken as providing merely a single co-ordination site). The co-ordination number of uranium in complex (1) is greater than that of any previously known organoactinoid compound.[4]

The solution behaviour of complex (1) is interesting, and was explored by use of variable temperature ¹H, ¹¹B, and ¹⁹F

---

† No reprints available.
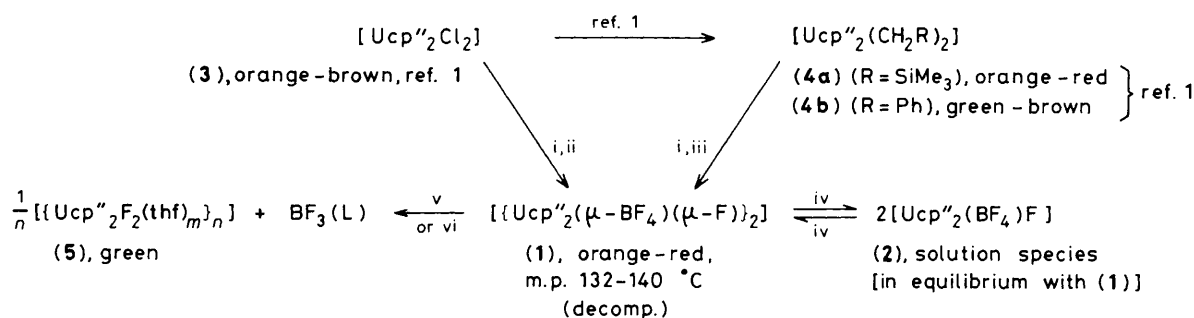
Scheme 1. *Abbreviations:* cp″ = η-C₅H₃(SiMe₃)₂, L = thf = tetrahydrofuran or L = NMe₃. *Reagents and conditions:* i, 2Ag[BF₄], OEt₂, *ca.* 20 °C; ii, 30 min; iii, *ca.* 12 h; iv, CDCl₃ (¹H n.m.r. expts.) or CD₃C₆D₅ (¹¹B n.m.r. expts.); v, NMe₃, *ca.* 20 °C; vi, [²H₈]-thf, *ca.* 20 °C. *Identification procedures:* compound (**1**) was obtained as red cubes from n-C₆H₁₄ at −30 °C, and was characterised by microanalysis, i.r. (Nujol) [absorptions (other than from cp″): 1232m, 1056s, 740s, and 410w cm⁻¹] and ¹H and ¹¹B n.m.r. spectroscopy (see text), and X-ray diffraction (Figure 1); compound (**5**) was identified in solution in a mixture with BF₃(L), using ¹H, ¹¹B, and ¹⁹F n.m.r. spectroscopy.

(6)
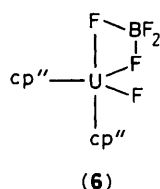
n.m.r. spectroscopy. At 305 K, the ¹¹B experiments showed two signals, at δ −120.7 and −131.9 p.p.m. [rel. to BF₃(OEt₂)], which gradually, as well as reversibly, changed in relative intensity, so that on warming, the former, attributed to the monomer (**2**) (see Scheme 1), grew in intensity at the expense of the latter, assigned to (**1**). This sequence was independent of concentration or solvent (CDCl₃ or CD₃C₆D₅). Likewise, a similar phenomenon was observed relating to the ¹H signals of the SiMe₃ groups, with that at δ 1.26 (rel. to SiMe₄), assigned to (**2**), growing in intensity on warming while that at δ −6.75, due to (**1**), was progressively diminished. Integrations allowed equilibrium constants for (**1**) ⇌ 2(**2**) to be evaluated and van't Hoff plots gave values for ΔH (kJ mol⁻¹) [54.2 (¹H n.m.r., CDCl₃ or CD₃C₆D₅) or 49.1 (¹¹B n.m.r., CD₃C₆H₅)] and ΔS (J mol⁻¹ K⁻¹) [209 (¹H n.m.r., CDCl₃), 195 (¹H n.m.r., CD₃C₆D₅), or 206 (¹¹B n.m.r., CD₃C₆H₅)].

Cooling the solution resulted, not only in bringing about these relative intensity changes of the two ¹H n.m.r. signals, but also the progressive splitting of each into a doublet; the processes associated with these splitting phenomena must be due to magnetic inequivalence of the two c̄p″ ligands at low temperature. For the dimer (**1**), this is most plausibly attributed to a hindered (on the n.m.r. time scale) rotation about U–cp″. In the monomer it is either ascribable to the same mechanism or, alternatively, to the loss of stereochemical non-rigidity upon cooling to give a limiting spectrum due to the quasi-five-co-ordinate structure (**6**). However, ΔG‡(Tc), the activation free energy change at the coalescence temperature Tc, for dimer and monomer was found to be very similar, being 49.6 (Tc = 263 K) and 51.1 (Tc = 288 K) kJ mol⁻¹, respectively. Hence, it is likely that the kinetic phenomenon being observed in the two complexes is the same, and this points to rotations about U–cp″. {The ΔG‡ (Tc) values were calculated using the expression ΔG(Tc) = −R(Tc)ln[πΔνh|2k(Tc)], where Δν is the peak separation (Hz) at slow exchange.}

The ¹⁹F n.m.r. spectrum in [²H₈]toluene showed a singlet broad (w₁, *ca.* 150 Hz) signal at δ −154.8 p.p.m. (rel. to CFCl₃), which was temperature invariant for the range
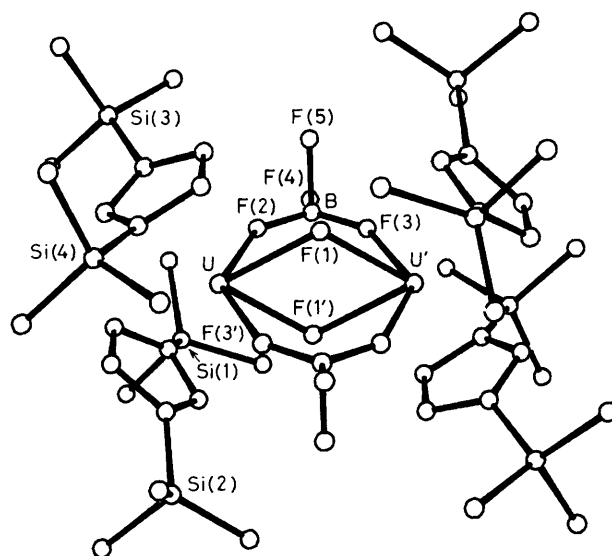
Figure 1. The molecular structure for [{Ucp″₂(μ-BF₄)(μ-F)}₂], (**1**), and atom numbering scheme. Relevant dimensions are: U–F(1) 2.354(5), U–F(2) 2.402(5), U–F(3′) 2.420(5), U–F(1′) 2.260(5), B–F(2) 1.33(2), B–F(3) 1.36(2), B–F(4) 1.23(2), B–F(5) 1.38(4), U–cen1 2.473, U–cen2 2.466 Å; F(2)–B–F(3) 118(1), U–F(1)–U′ 118.0(2), U–F(2)–B 141.4(7), U′–F(3)–B 141.2(7)°. (cen1 and cen2 are the centroids of the cyclopentadienyl rings.)

233—340 K, and this is attributed to a fast F⁻ exchange mechanism not only within the [BF₄]⁻ ligand, but also between F⁻ and [BF₄]⁻, with the time-averaged ¹⁹F chemical shifts for complexes (**1**) and (**2**) being indistinguishable.

The lability of the fluorides in complexes (**1**) and (**2**) is consistent with the chemical observation (v or vi in Scheme 1) that abstraction of BF₃ is exceedingly facile. At this time the uranocene(ɪv) fluoride (**5**) has not been isolated as crystalline material.

Crystal data for (**1**):‡ C₄₄H₈₄B₂F₁₀Si₈U₂, M = 1525.5, monoclinic, space group P2₁/c, a = 13.392(2), b = 17.960(3), c = 13.926(1) Å, β = 106.85(2)°, U = 3205.68 Å³, Z = 2, Dc = 1.58 g cm⁻³. The structure of [{Ucp″₂(μ-BF₄)(μ-F)}₂], (**1**),

Figure 1, was solved by routine heavy atom methods and refined to $R = 0.036$, $R' = 0.044$ for 2270 reflections [with $I > 3\sigma(I)$] measured on a CAD 4 diffractometer with Mo-K_α radiation.

References

1 P. B. Hitchcock, M. F. Lappert, A. Singh, R. G. Taylor, and D. Brown, *J. Chem. Soc., Chem. Commun.*, 1983, 561.
2 H. Nakai, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1637.
3 W. C. Velthuizen, J. G. Haasnoot, A. J. Kinneging, F. J. Rietmeijer, and J. Reeding, *J. Chem. Soc., Chem. Commun.*, 1983, 1366.
4 *Cf.*, T. J. Marks and R. D. Ernst, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 3, Ch. 21.