Formation and Crystal Structure of *trans*-Bis(acetonitrile)tris-(η^5-cyclopentadienyl)uranium(IV) Tetrachloro-*trans*-dioxouranate(VI): † a Novel Species involving the First Cationic Organo-*f*-metal Complex and Uranium in Two Different Oxidation States

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Treatment of a solution of $[U^{IV}(cp)_3Cl]$ (cp = η^5-C_5H_5) in CH_3CN with gaseous butadiene containing traces of O_2 initiates the formation of a crystalline green product composed of the novel cationic complex $[U^{IV}(cp)_3(NCMe)_2]^+$, the anion $[U^{VI}O_2Cl_4]^{2-}$, and two non-co-ordinated butadiene molecules. This salt contains the first example of a well defined cationic organo-*f*-element complex, and provides at the same time a new example of a crystallographically confirmed $[U(cp)_3XY]$ (X, Y = neutral and/or anionic ligand) system of trigonal bipyramidal co-ordination. The results are discussed in relation to the as yet unsubstantiated access to organometallic compounds of U^V and U^{VI} with the cp ligand.

The pesudotetrahedral tris(cyclopentadienyl)uranium(IV) complexes $[U(cp)_3X]$ (cp = η^5-C_5H_5),[1] and apparently to an even greater extent their numerous trigonal bipyramidal derivatives, $[U(cp)_3XY]^q$ (q = 0 or −1),[2-5] undergo a wide range of reactions. Apart from controlled photochemical [6,‡] and thermal [7,§] reduction to $U^{III}(cp)_3$ derivatives, and thermolytic elimination of RH from $[U(cp)_3R]$ (R = alkyl) systems,[8] ready oxidation (albeit almost exclusively to so far unspecified products) [5] as well as substitution and replacement reactions, respectively, of any of the ligands X, Y, and cp, or combinations of them, have been observed. Thus reactions of types (a), (b), (e), and (f) in the Scheme exemplify clean substitutions of the uncharged ligand Y, of anionic X, of both X and Y, and of all initial ligands, respectively. Details of reaction (d) where two cp ligands and Y, but not X (= NCS), are displaced simply by the solvent thf, are still unknown; however, the electronic spectra in the near-i.r.–visible range, the vibrational spectra, and the elemental analysis of the product resulting from *e.g.* $[U(cp)_3(NCS)(NCMe)]$ in MeCN–thf are consistent with the assumption of a monocyclopentadienyluranium(IV) species.[5]

Likewise, no well defined products have so far been obtained, even by controlled admission of dioxygen, from various $[U(cp)_3X]$ and $[U(cp)_3XY]$ systems. Nevertheless, many virtually unchanged samples exhibit in their i.r. spectra, after exposure to traces of O_2, pronounced absorptions typical of ν_{UO} in uranyl systems [9,10] and of 'non-aromatic' ν_{CH} around *ca.* 2 900 cm^{-1} in addition to the usually weakened spectrum of the initial organouranium species. In view of various unsuccessful attempts to prepare cyclopentadienyl derivatives of the $[U^{VI}O_2]^{2+}$ cation from U^{VI} compounds,[11,¶] any formation of such systems by direct oxygenation of $U^{IV}(cp)_3$ species seems unlikely too. The major aspect of the present contribution is to demonstrate that $[U(cp)_3XY]$ systems, under carefully chosen conditions, may undergo various combinations of the different reactions depicted in the Scheme; nevertheless, the unique and still organometallic, uranyl-containing species $[U^{IV}(cp)_3(NCMe)_2]_2[U^{VI}O_2Cl_4]$ has been obtained.

Results

Chemical and Spectroscopic Results.—From concentrated and cooled (*ca.* −18 °C) solutions of $[U(cp)_3Cl]$ in strictly O_2- and H_2O-free MeCN, well-shaped green crystals exclusively of $[U(cp)_3Cl(NCMe)]$ (1) are obtained [2] after *ca.* 10 h. However, application of less purified MeCN leads after 3—4 months to a greenish brown, amorphous precipitate (2) the i.r. spectrum of which shows uranyl ν_{UO} absorptions. Bubbling (<1 min) of *ca.* 20—50 cm^3 of gaseous standard grade butadiene [‖] through an initially green solution of $[U(cp)_3Cl]$ in pure MeCN even after 1 min causes a significant darkening of the solution towards red-brown, and after 1—2 days at *ca.* −18 °C light green, crystalline needles are deposited on the glass walls above the solution. After storage under N_2 the isolated crystals turn almost black, retaining a shiny surface and still exhibiting their green colour under intense light irradiation. The vibrational spectrum of this crystalline product, $[U(cp)_3(NCMe)_2]_2[UO_2Cl_4]\cdot 2C_4H_6$ (3) (Figure 1) is identical to that of '$[U(cp)_3(NCMe)_2]_2[UO_2Cl_4]\cdot C_5H_6$' (2), and in view of the limited amount of material various suitable crystals of (3) were subjected only to an *X*-ray analysis (see later).

The elemental analysis of (2) differs markedly from that of (1) [2] and is, in accordance with the *X*-ray crystallographically determined composition of (3), $[U(cp)_3(NCMe)_2]_2[UO_2Cl_4]\cdot 2C_4H_6$, best correlated with the composition '$[U(cp)_3$-

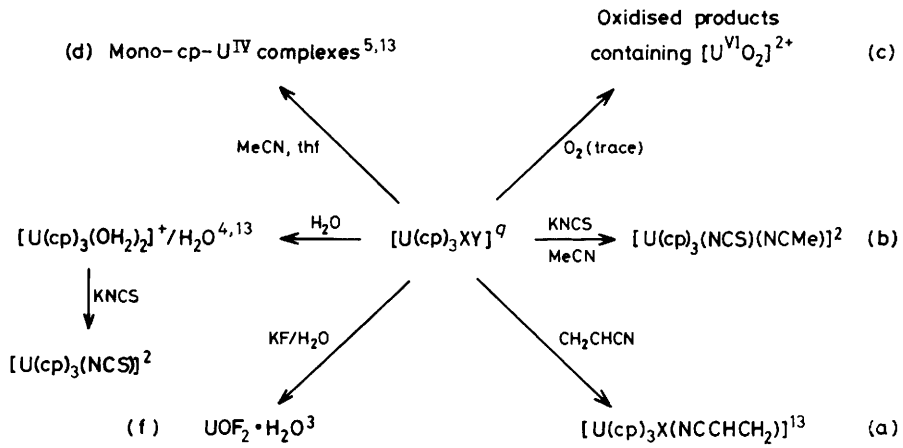
† *Supplementary data available* (No. SUP 23553, 12 pp.): thermal parameters, structure factors. See Notice to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

‡ Possibly *via* intermediate adducts like $[U(cp)_3R]\cdot thf$ *cf.* ref. 6.

§ A complete list of refs. up to 1980 is given in ref. 6; in a more recent contribution the involvement of intermediates like $[U(cp)_3RR']$ (RR' = alkyl) has been suggested.[7] Further reports of thermal reduction of $[U(cp)_3X]$ systems are noted in ref. 6.

¶ Uranyl compounds are generally reduced to U^{IV} organometallics by $Na(C_5H_5)$. For the most recent attempts to arrive at $[U^{VI}O_2R_2]$ (R = alkyl) systems see A. M. Seyman, *Inorg. Chim. Acta*, 1982, **58**, 71.

‖ Originally, butadiene was used to test $[U(cp)_3Cl(NCMe)]$, or decomposition products thereof, as potential catalysts for olefin polymerization.



Scheme. Representative ligand substitution and oxidation processes of $[U(cp)_3XY]^q$ systems. Unless otherwise stated, X = Cl, Y = CH_3CN $q = 0$; (d) if X = Y = NCS and $q = -1$, reaction with [KL(NCS)] leads to $[KL]_2[U(cp)(NCS)_5]$ [5] (L = 4,7,13,16,21,24-hexa-oxa-1,10-diazabicyclo[8.8.8]hexacosane)

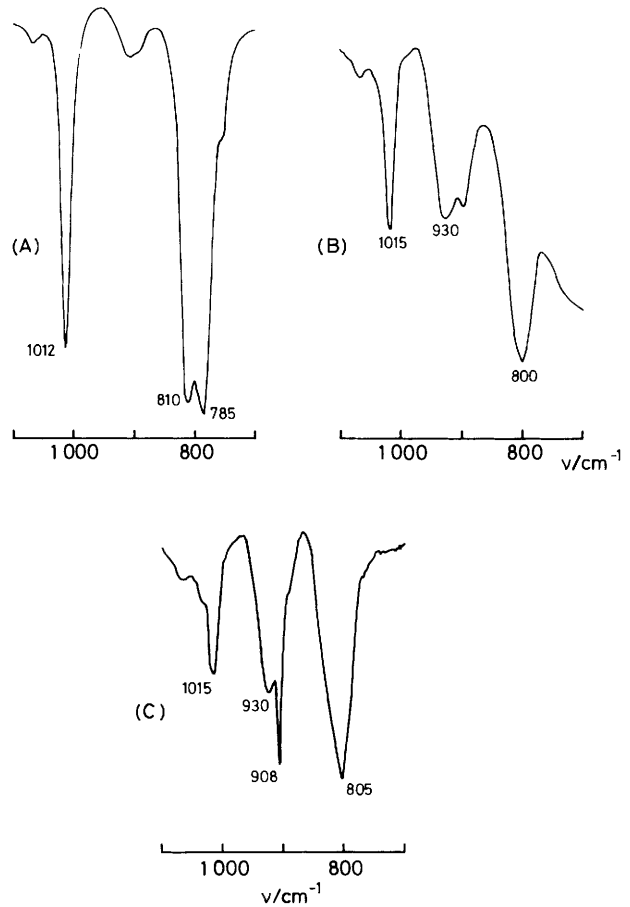


Figure 1. Infrared spectra in the ν_{UO} region (KBr pellets) of two samples after partial exposure to oxygen {A = $[U(cp)_3(CN)]$,[3] B = $[U(cp)_3Cl(NCMe)]$} and (C) of pure (3); this spectrum is identical with that of (2)

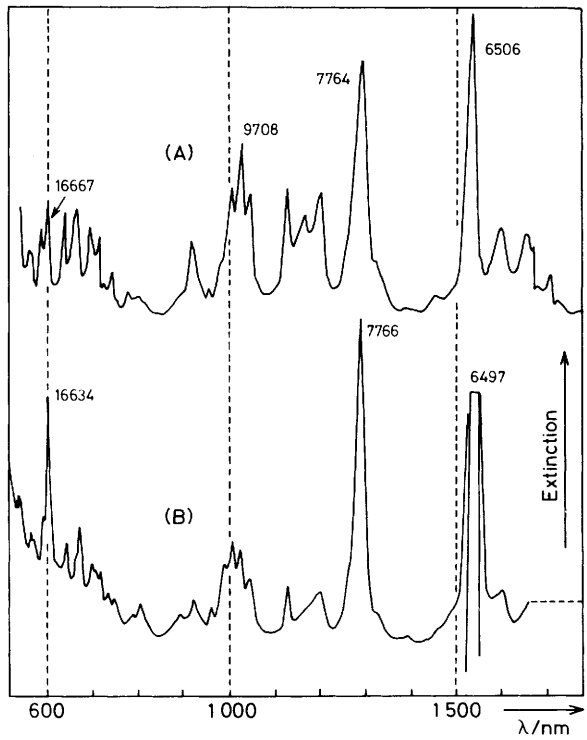


Figure 2. Near-i.r.–visible spectra of $[U(cp)_3Cl(NCMe)]$ (A) and product (2) (B) in MeCN

$(NCMe)_2]_2[UO_2Cl_4]\cdot C_5H_6$'. While the i.r. spectrum of (3) is devoid of absorptions typical of butadiene, the corresponding spectrum of (2) shows at least one sharp extra band at 2 850 cm^{-1}, probably due to the methylene group of cyclopentadiene. Unlike most monoacetonitrile adducts $[U(cp)_3X(NCMe)]$, both (2) and (3) exhibit in the ν_{CN} region, apart from the 'Fermi-resonance peak' (at 2 301 cm^{-1}), two genuine ν_{CN} absorptions (2 274 and 2 250 cm^{-1}) which might reflect some deviation from the centrosymmetric local symmetry of the $[U(cp)_3(NCMe)_2]^+$ cation. It is also noteworthy that (2) and (3) give rise, unlike many other uranyl complexes,[12] to two intense absorptions in the ν_{UO} region which differ in their appearance from the corresponding bands of other partially oxygenated $[U(cp)_3X]$ systems (Figure 1). When (2) is dissolved in thf and the solution evaporated, the i.r. spectrum of the residue is devoid of all characteristic MeCN absorptions and of the sharp band of (2) at 908 cm^{-1}. Possibly $[U(cp)_3Cl]$ has been formed here, along with another, non-ionic uranyl compound.

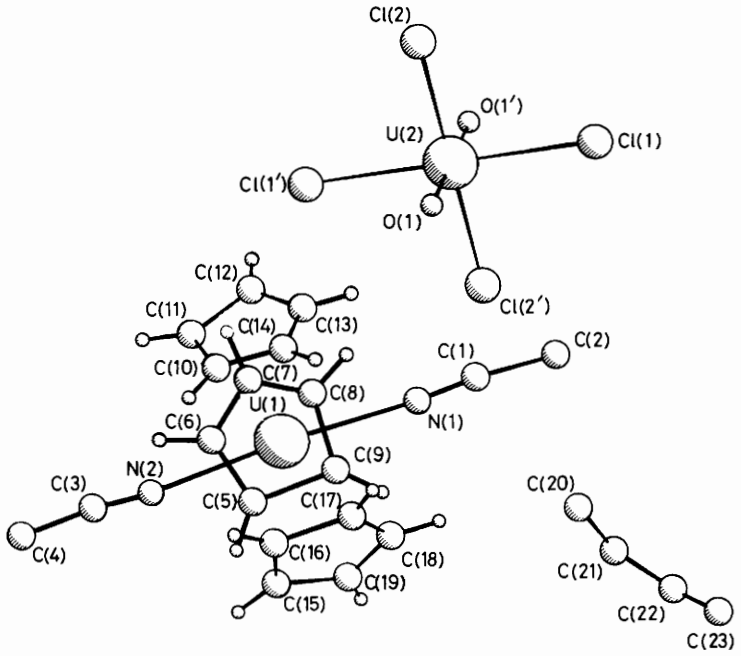


Figure 3. The three components of (3), the $[U(cp)_3(NCMe)_2]^+$ cation, the $[UO_2Cl_4]^{2-}$ anion, and molecular C_4H_6, with the atom numbering system

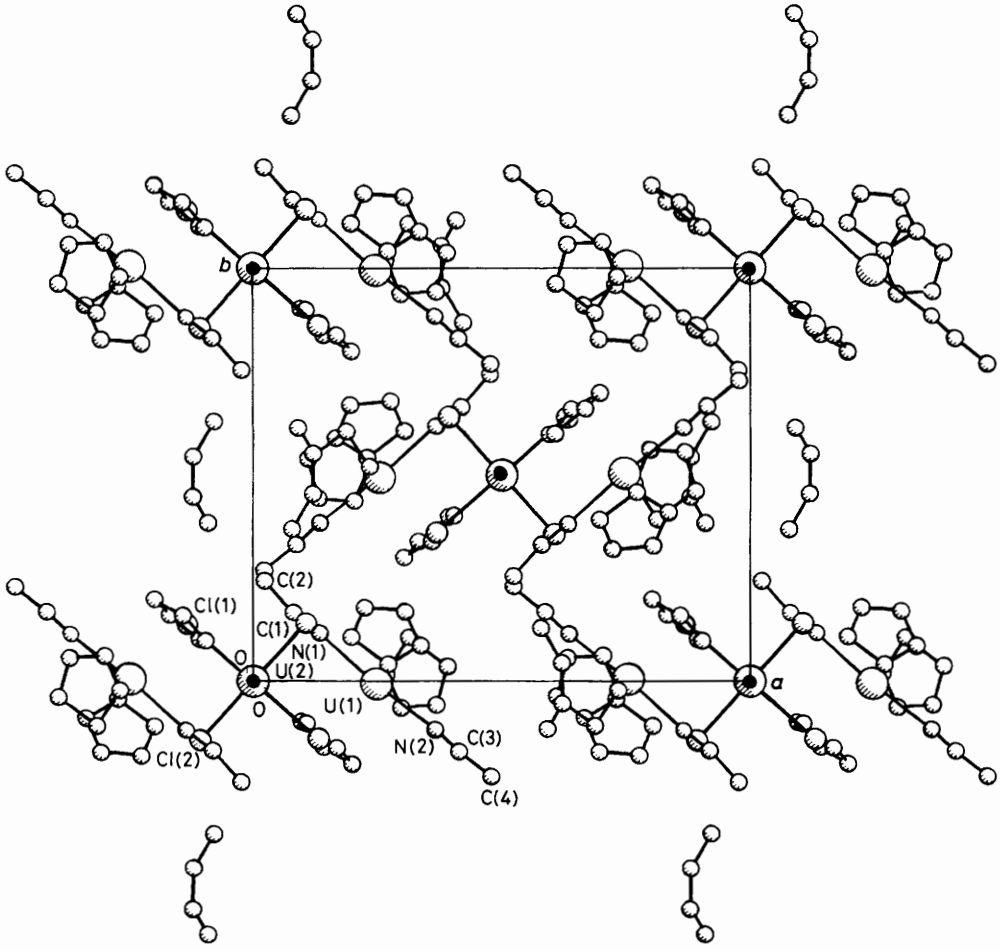


Figure 4. A view of the unit cell contents of (3) down *c*

Table 1. Interatomic distances (Å) with e.s.d.s in parentheses

U(1)–N(1)	2.61(2)	N(1)–C(1)	1.15(4)	C(1)–C(2)	1.57(5)
U(1)–N(2)	2.58(2)	N(2)–C(3)	1.09(4)	C(3)–C(4)	1.41(4)
U(2)–Cl(1)	2.77(1)	U(2)–Cl(2)	2.53(1)	U(2)–O(1)	1.75(2)
Ring A		Ring B		Ring C	
U(1)–C(5)	2.74(4)	U(1)–C(10)	2.68(4)	U(1)–C(15)	2.77(4)
U(1)–C(6)	2.77(5)	U(1)–C(11)	2.68(4)	U(1)–C(16)	2.68(5)
U(1)–C(7)	2.78(4)	U(1)–C(12)	2.87(6)	U(1)–C(17)	2.76(5)
U(1)–C(8)	2.67(5)	U(1)–C(13)	2.70(4)	U(1)–C(18)	2.78(5)
U(1)–C(9)	2.71(4)	U(1)–C(14)	2.70(4)	U(1)–C(19)	2.79(4)
U–C	2.73	U–C	2.73	U–C	2.76
U(1)–M_A [a]	2.46	U(1)–M_B	2.47	U(1)–M_C	2.49

Averages

U(1)–C	2.74	C_C–C_C	1.39
C_A–C_A	1.40	C–C	1.39
C_B–C_B	1.37	U(1)–M	2.47

[a] M = centre of a C_5H_5 ring.

Table 2. Bond angles (°) with e.s.d.s in parentheses

U(1)–N(1)–C(1)	175(3)	O(1)–U(2)–Cl(1)	92(1)
N(1)–C(1)–C(2)	170(4)	O(1)–U(2)–Cl(2)	91(1)
N(1)–U–N(2)	175.4(8)	Cl(1)–U(2)–Cl(2)	89.8(4)
U(1)–N(2)–C(3)	173(3)	O(1)–U–Cl(1)	88(1)
N(2)–C(3)–C(4)	173(4)	Cl(1)–U(2)–Cl(2′)	90.2(4)
		O(1)–U–Cl(2′)	89(1)
M_A–U(1)–M_B	115.9(1)	M_A–U(1)–M_C	121.2(1)
M_B–U(1)–M_C	122.7(1)		
N(1)–U(1)–M_A	89.3(6)	N(2)–U(1)–M_A	90.2(6)
N(1)–U(1)–M_B	91.2(6)	N(2)–U(1)–M_B	93.2(6)
N(1)–U(1)–M_C	87.1(6)	N(2)–U(1)–M_C	89.2(6)

Averages

C–C–C	107.9	M–U(1)–M′	119.9
N(1)–U(1)–M	89.2	N(2)–U(1)–M	90.9

Table 3. Least-squares planes with deviations (Å) of the relevant atoms in square brackets. The equation of a plane in the direct space is given by $PX + QY + RZ = S$ and angles (°) between the planes

	P	*Q*	*R*	*S*
Plane 1: C(5)—C(9)	10.2601	2.0029	−9.7720	−0.0638
[C(5) −0.005, C(6) 0.003, C(7) 0.002, C(8) −0.006, C(9) 0.006]				
Plane 2: C(10)—C(14)	10.5345	9.9841	−1.1939	−0.5366
[C(10) −0.013, C(11) 0.032, C(12) −0.043, C(13) 0.040, C(14) −0.015]				
Plane 3: C(15)—C(19)	−0.3372	8.1649	8.9301	6.9635
[C(15) 0.026, C(16) −0.044, C(17) 0.046, C(18) −0.033, C(19) 0.005]				
Plane 4: M_A,M_B,M_C	10.0431	−7.8907	4.4442	4.7761
[U(1) 0.036, N(1) −2.569, N(2) 2.618, C(1) −3.722, C(2) −5.266, C(3) 3.707, C(4) 5.120]				

Angles (°) between the planes

1–2	58.2
1–3	59.1
2–3	62.7

Unlike thf, MeCN and H_2O readily dissolve compound (2) with retention of the green colour. The electronic absorption spectrum of a MeCN solution is, apart from some variation in relative intensities, very similar to that of $[U(cp)_3Cl(NCMe)]$ in MeCN (Figure 2); this observation underlines the usefulness of the empirically introduced near-i.r.–visible spectroscopic criterion [13] to differentiate $U^{IV}(cp)_3$ derivatives of trigonal bipyramidal and pseudotetrahedral co-ordination.[4,14,15] The ^1H n.m.r. spectrum of $[U(cp)_3Cl]$ in CH_3CN shows for the cp ring proton resonance one singlet at 8.89 p.p.m. (upfield, relative to $[Th(cp)_3Cl]$). This signal experiences a weak low-field shift to 8.32 p.p.m. immediately after treatment of the solution with butadiene, and has migrated after 2 h downfield to 8.10 p.p.m. These shift values are more similar to that of the cation $[U(cp)_3(OH_2)_2]^+$ (8.30 p.p.m.), which is assumed to predominate in solutions of $[U(cp)_3Cl]$ in H_2O,[13,15] than to the shift of 9.56 p.p.m. of definitely pseudotetrahedral $[U(cp)_3Cl]$ in C_6D_6 solution.[16]

X-Ray Crystallographic Results.—A perspective drawing of the three components of (3) {the ions $[U(cp)_3(NCMe)_2]^+$ and $[UO_2Cl_4]^{2-}$, and C_4H_6} is shown in Figure 3 along with the atom-numbering scheme. Relevant interatomic distances and bond angles are given in Tables 1 and 2, and significant best mean planes, and angles between them, in Table 3. Figure 4 represents a view down the *c* axis of the unit cell, confirming that the three components (cations, anions, and neutral molecules) are present in the ratio 2 : 1 : 2.

The uranium ion in the cationic unit may be considered as formally 11-co-ordinate if each η^5-cp ligand is assumed to occupy three co-ordination sites (total ligand hapticity, $\Sigma\eta$ = 17). Alternatively, as the centres M_A—M_C of the three cp ligands constitute an equatorial plane with the two equivalent MeCN ligands in the corresponding axial positions, the co-ordination of the central uranium ion can be considered as trigonal bipyramidal (pseudo-D_{3h} symmetry). In fact, the average of the M–U–M′ angles is 120°, while the M–U–N angles average 90°, the two axial MeCN ligands lying practically collinear with an N(1)–U(1)–N(2) angle of 175.4(8)°. The average of all the U–C distances is 2.74(1) Å. These features differ only slightly from the average U–C distance (2.73 Å) and the average M–U–X angle (*ca.* 100°) reported for pseudo-tetrahedral $[U(cp)_3X]$ systems (X = halide or alkyl ligands).[17] Hence the addition of a fifth ligand of little steric congestion does not noticeably influence the $U(cp)_3X$ moiety. Conversely, the U–C distances are known to increase considerably if a fourth cp ligand is added to the $U(cp)_3^+$ nucleus (average value 2.81 Å).[18]

For the cp ligands of (3), an average C–C distance of 1.39 Å is observed; the individual bond distances range between 1.21 and 1.61 Å. These findings correlate with the large individual standard deviation of the C–C distances (0.06 Å), mainly due to the thermal librational motion of the rings as well as to the predominance of scattering by the uranium atom for all types of reflection. This feature has also been found for the complex $[U(cp)_3(\sigma^1\text{-}CH_2CMeCH_2)]$.[19]

Comparisons of the different U–N(MeCN) distances in the trigonal bipyramidal complexes $[U(cp)_3(NCS)(MeCN)]$ and (3), as well as of the U–N(NCS) distances in $[U(cp)_3(NCS)(MeCN)]$ [2] and $[AsPh_4][U(cp)_3(NCS)_2]$ have been discussed elsewhere.[20] In view of some evidence of a mutual '*trans*-

effect ' of the two axial ligands, both from structural and from spectroscopic results,[2,3] knowledge of the structural features of the quasi-tetrahedral complex [U(cp)$_3$(NCS)] would be highly desirable.

The anion $[UO_2Cl_4]^{2-}$ lies on a crystallographic inversion centre and its symmetry is approximately D_{4h}. The U–O uranyl distance [1.75(2) Å] is usual, whereas the two U–Cl distances are less so (see discussion in the Experimental section); however, the average U–Cl distance of 2.65 Å is in agreement with the covalent radii sum.[21]

Discussion and Conclusions

The results demonstrate for the first time that by exposure of a [U(cp)$_3$X] and a [U(cp)$_3$XY] system to traces of dioxygen (as present in commercial butadiene, or as being accumulated over several months in a closed vessel), a well defined organometallic product containing a uranyl complex as one component is obtained. The uranyl moiety is, however, devoid of any organic ligand; this observation correlates well with the previously reported failure to obtain cp complexes of the UO_2^{2+} cation.[11] Our findings are also in accord with general experience, according to which U^V systems tend to occur only as intermediates during the reduction of U^{VI} and the oxidation of U^{VI} species. Molecular U^{III} complexes have, on the other hand, been oxidised by O_2 to well defined U^{IV} [22] and U^V systems.[23]

Our experimental results suggest that the two products (2) and (3) are very closely related species containing the same cationic and anionic components; however, their tendency to crystallize seems to be influenced by the presence of other inert molecules of suitable dimensions such as butadiene or cyclopentadiene. The organometallic component of (2) and (3), $[U(cp)_3(NCMe)_2]^+$, is the third crystallographically confirmed example of a U(cp)$_3$ derivative of trigonal bipyramidal co-ordination;[2,20] it also appears to be the first reported strictly cationic organometallic complex of an *f*-element. Although it has so far been impossible to procure single crystals suitable for an *X*-ray analysis of salts of the assumed composition [U(cp)$_3$(OH$_2$)$_2$]X, the existence of non-hydrated $[U(cp)_3(OH_2)_2]^+$ cations of trigonal bipyramidal co-ordination seems likewise justified.[4] However, even in the pure salt $[U(cp)_3(OH_2)_2]NO_3$,[4] hydrogen bonds between the oxygen atoms of co-ordinated H_2O and free NO_3^- ions are likely to stabilize the solid (relative to [U(cp)$_3$(ONO$_2$)]·2H$_2$O), whereas the organometallic cation of (3) appears to be an ideally isolated ionic species within its crystal lattice.

In view of the recent description of salts involving similar anionic $[U(cp)_3XY]^-$ moieties,[3] trigonal bipyramidal actinide complexes $[M(cp)_3XY]^q$ (M = *f* metal; $q = 0$ or ± 1) have been shown to exist, the diversity of which suggests an even richer variety of trigonal bipyramidal complexes, as compared with the ' parent ' group of pseudotetrahedral co-ordination.

The complexes (2) and (3) represent, furthermore, new examples of the few organometallic and related uranium compounds that involve uranium in two different oxidation states. One U^{III}/U^{IV} species, $U^{IV}(cp)_3F{\cdot}U^{III}(cp)_3$,[24] and a non-isolated related adduct, $U^{IV}(cp)_3Cl{\cdot}U^{III}(cp)_3$,[6] have so far been described. Our oxidation product (3) can be best compared with the U^{IV}/U^{VI} species $[U^{IV}Cl_3L']_2[U^{VI}O_2Cl_3(OH)(OH_2)]{\cdot}CH_3NO_2$ (L′ = 1,4,7,10,13,16-hexa-oxacyclooctadecane) obtained by partial oxidation of UCl_4 in nitromethane solution in the presence of L′, and probably traces of O_2 and H_2O.[25] UCl_4 is well known to be completely oxidized to uranyl compounds in the presence of suitable extra ligands and O_2 and under mild conditions;[26] however, the access to well defined mixed-valence systems is still very limited.

Experimental

The basic procedures adopted for the preparation of the products (2) and (3) were the same as described in ref. 2. MeCN was dried first with P_2O_5, then treated with $NaHCO_3$, and finally distilled under N_2. Consequently, none of the products exhibited noticeable absorptions typical of ν_{OH} in the i.r. spectrum. I.r. spectra were taken with a Perkin-Elmer 577 instrument, near-i.r.–visible spectra with a Cary 17 spectrophotometer, and ^{1}H n.m.r. spectra with a Varian NV 14 CW spectrometer (60 MHz) allowing the use of non-deuteriated solvents. The source of butadiene was a small commercial demonstration bomb. Elemental analyses of (2) were carried out by Dornis and Kolbe, Microanalytical Laboratory, Mülheim/Ruhr (Found: C, 33.45; H, 3.25; Cl, 9.25; U, 46.1. Calc. for $C_{43}H_{48}Cl_4N_4O_2U_3$ {[U(cp)$_3$(NCMe)$_2$]$_2$[UO$_2$Cl$_4$]·C$_5$H$_6$}: C, 33.95; H, 3.15; Cl, 9.3; U, 46.95%).

Crystal Data of (3).—$C_{23}H_{24}Cl_2N_2OU_{\frac{3}{2}}$, $M = 775.4$, Monoclinic, space group $P2_1/n$, $a = 16.038(5)$, $b = 13.242(4)$, $c = 11.465(4)$ Å, $\beta = 99.9(1)°$, $Z = 4$, $D_c = 2.15$ g cm^{-3}, $U = 2\,398.6$ Å^{-3}, $F(000) = 1\,313$, μ(Mo-K_α) = 99.2 cm^{-1}, $\lambda = 0.710\,69$ Å. A dark green, prismatic single crystal of approximate dimensions 0.04 × 0.02 × 0.15 mm, mounted in a glass capillary, was used for data collection.

Data Collection and Structure Refinement.—*X*-Ray intensity data were collected with a four-circle Philips PW 1100 automated diffractometer with graphite-monochromated Mo-K_α radiation. The unit cell was determined on the basis of 25 strong reflections found by mounting the crystal at random and varying the orientation angles φ and χ around 120°, with the detector position varying between $\theta = 6°$ and $\theta = 10°$. For the determination of precise lattice parameters 20 strong reflections with $8 \leqslant \theta \leqslant 12°$ were considered. Integrated intensities of *hkl* reflections with k, $l \geqslant 0$ and $6 \leqslant 2\theta \leqslant 50°$ were measured using the $\theta/2\theta$ scan method with a scanning speed of 0.03° s^{-1}, a scan width of 1.2° and two background counts of 20 s at each end of the scans. Of the 4 663 reflections thus considered, 1 627 having a net intensity greater than 3σ (σ = standard error based on counting statistics) were used for the structure determination and refinement.

The intensities of three standard reflections, monitored at 100 reflection intervals, showed no greater fluctuations than those expected from Poisson statistics. The intensity data were corrected for Lorentz and polarization effects, and for absorption following the method of North *et al.*[27]

The uranium atom positions were determined from a three-dimensional Patterson function. One uranium atom U(2) has a general position, the second U(2) occupies an inversion centre. The subsequent Fourier-difference synthesis phased on the heavy-atom positions allowed the location of the majority of the non-hydrogen atoms. Their position and thermal parameters were obtained by full-matrix least-squares refinements minimizing $\Sigma w[|F_o| - |F_c|]^2$ using unitary weight factors as, with $w = 1$, there was a reasonable consistency in a test of $w\Delta^2$ for data sectioned with respect to both $|F_o|$ and $(\sin\theta)/\lambda$. Anisotropic temperature factors were introduced for all the non-hydrogen atoms except those belonging to the cyclopentadienyl rings because of the limited number of data. The hydrogen atom contributions of the latter groups were calculated assuming planar pentagons and fixed atoms ($d_{C-H} = 0.95$ Å and $B_{iso} = 7$ Å^2). This model converged with an *R* value of 0.06. A difference Fourier map calculated at this stage revealed residual maxima of about 2—3 e Å^{-3}. These were interpreted as carbon atoms of disordered butadiene molecules. The introduction of the four carbon atoms at the

Table 4. Atomic co-ordinates (× 10^4) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
U(1)	2 466(1)	−55(2)	5 157(1)
U(2)	0	0	0
Cl(1)	−1 308(9)	1 386(10)	−375(17)
Cl(2)	−1 063(8)	−1 424(11)	−420(12)
O	−37(13)	−66(30)	1 512(17)
N(1)	1 336(16)	1 180(20)	4 042(22)
C(1)	809(21)	1 668(33)	3 505(26)
C(2)	233(22)	2 441(26)	2 705(37)
N(2)	3 656(16)	−1 153(19)	6 329(24)
C(3)	4 137(18)	−1 689(21)	6 741(26)
C(4)	4 778(22)	−2 297(28)	7 393(32)
C(5)	3 902(21)	375(22)	4 244(31)
C(6)	3 681(27)	−568(34)	3 811(36)
C(7)	2 968(22)	−629(32)	3 050(35)
C(8)	2 667(30)	207(38)	2 914(39)
C(9)	3 131(22)	1 065(31)	3 565(33)
C(10)	1 683(23)	−1 607(28)	6 019(35)
C(11)	1 974(28)	−1 994(34)	4 967(39)
C(12)	1 408(39)	−1 598(45)	3 918(66)
C(13)	961(27)	−981(33)	4 436(40)
C(14)	1 065(23)	−1 005(29)	5 617(35)
C(15)	3 353(27)	886(32)	7 144(37)
C(16)	2 711(27)	419(36)	7 468(42)
C(17)	1 970(34)	1 078(38)	6 938(42)
C(18)	2 237(30)	1 799(37)	6 200(41)
C(19)	3 047(24)	1 713(30)	6 352(33)
C(20)	763(26)	3 650(34)	5 182(38)
C(21)	1 153(37)	4 514(42)	4 681(49)
C(22)	1 613(47)	5 510(54)	4 582(61)
C(23)	984(42)	5 666(55)	5 072(59)
H(1)	439	57	479
H(2)	400	−116	407
H(3)	275	−122	264
H(4)	213	29	243
H(5)	301	177	356
H(6)	190	−175	683
H(7)	243	−246	501
H(8)	14	−173	311
H(9)	57	−52	401
H(10)	72	−65	608
H(11)	393	71	735
H(12)	272	−16	796
H(13)	140	102	708
H(14)	188	226	571
H(15)	340	213	597

indicated positions into an isotropic refinement gave rise to an *R* value of 0.047, which was considered as final.

In this model, however, the U–X distances within the $[UO_2Cl_4]^{2-}$ anion did not emerge quite satisfactorily, the calculated U–Cl bond lengths being U(2)–Cl(1) = 2.8 Å and U(2)–Cl(2) = 2.5 Å. The values usually found for such U–Cl bonds lie, in close agreement with the sum of the covalent radii (2.68 Å),[21] between 2.66 and 2.70 Å.

However, all attempted improvements either by replacing Cl(2) with an OH group or by distributing different ratios for the two positions of O and Cl turned out to be unsatisfactory, and it was concluded that the best possible model with reasonable thermal values is $[UO_2Cl_4]^{2-}$, although we cannot exclude a system with irregular distribution of Cl and OH. At least in view of both the average U–Cl distances and the various valence angles, the present assumption of a $[UO_2Cl_4]^{2-}$ anion appears acceptable. It is of some interest that from $U^{III}Cl_3$, 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine (L), and traces of O_2 another salt involving the $[U^{VI}O_2Cl_4]^{2-}$ anion, $[NaL]_2[UO_2Cl_4]$, is formed.[28]

The anomalous dispersions terms for U (ref. 29) were taken into account in the refinement. Atomic scattering factors for U were taken from ref. 30, for the other non-hydrogen atoms from ref. 31, and for hydrogen from ref. 32. Data processing and computation were carried out using the SHELX 76 programs package.[33] Final positional parameters are presented in Table 4.

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