Anionic Tris(cyclopentadienyl)actinide(IV) Complexes

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Anionic complex salts, $A^+[M(cp)_3(NCS)_2]^-$ (cp = η-C_5H_5), where A = [K(Crypt)] (Crypt = Cryptofix-222) or NMe_4 and M = U, and A = $AsPh_4$ with M = U, Np, or Pu, have been prepared. Spectrophotometric and other evidence indicates trigonal-bipyramidal co-ordination for the metal atoms in the uranium complex anions, as in the known structure of the neutral complex $[U(cp)_3(NCS)(NCMe)]$. The η-methylcyclopentadienyl analogue of the last complex is more difficult to obtain and dissociates more readily than the cp compound. Although evidence for the formation of uncharged $[Np(cp)_3(NCS)(NCMe)]$ in solution was obtained, the neutral neptunium complex could not be isolated and $[Pu(cp)_3(NCS)]$ reacts even less readily with methyl cyanide. A systematic investigation of the effects of the additional anion Y^- in various solvents for the systems $[U(cp)_3XY]^-$, where X and/or Y = F^-, OH^-, CN^-, $NCBH_3^-$, NCS^-, and NCO^-, shows that, in addition to steric factors, the specific distribution of the excess negative charge plays an important role. The first mixed anionic complex $K[U(cp)_3(OCN)(NCS)]$ was also obtained. Infrared, ^1H n.m.r. (U compounds only), and near-i.r.–visible spectra are reported.

The common co-ordination geometry of neutral, four-co-ordinate tris(η-cyclopentadienyl)actinide(IV) complexes, $[M(cp)_3X]$, is trigonal pyramidal or pseudo-tetrahedral. A neutral five-co-ordinate complex, $[U(cp)_3(NCS)(NCMe)]$, has recently been shown to exhibit trigonal-bipyramidal co-ordination geometry,[1] and evidence is available [2,3] for the formation of five-co-ordinate uranium(IV) in solution as well as in some, possibly metastable, solid salts of the diaqua-cation $[U(cp)_3(OH_2)_2]^+$. However, the existence of mononuclear, negatively charged five-co-ordinate actinide analogues has not been reported hitherto.

Anionic mixed-ligand *d* transition-metal–cyclopentadienyl complexes are usually unstable with respect to decomposition unless π-acceptor ligands, such as CO, are present.[4] However, in *f* transition-metal systems the metal ion cannot participate in π back-bonding, and complexes with uncharged π-acceptor ligands have not been recorded, but a number of stable anionic cyclopentadienyl complexes which do not involve π-acceptor ligands have recently been reported for some early *d* transition elements [5] and for various lanthanides.[6]

It was therefore of interest to investigate the effects of varying the anions X^- and/or Y^- in systems of the type $[U(cp)_3XY]^-$, and also the steric and/or electronic effects, if any, of replacing cp by η-methylcyclopentadienyl (mcp) and of replacing U by Np or Pu.

Results and Discussion

$[U(cp)_3X_2]^-$(X = *Small, Nucleophilic Ligand*).—Because of the somewhat restricted space available for the two axial ligands in a trigonal-bipyramidal complex anion, $[U(cp)_3X_2]^-$, it might be expected that very small ligands, such as F^- and OH^-, would form complexes of this type. However, reaction of an aqueous solution of the ion $[U(cp)_3(OH_2)_2]^+$, or an aqueous suspension of $[U(cp)_3F]$, with aqueous alkali fluoride yields a green precipitate of what appears to be hydrated $UF_2(OH)_2$ (atomic ratio, by analysis, U : F *ca.* 1 : 2) and cyclopentadiene is liberated. Similarly, treatment of an aqueous solution of $[U(cp)_3Cl]$ with aqueous hydroxide ion at pH ⩾ 7 yields a bright green precipitate of uranium(IV) hydroxide or hydrated oxide. Both this and the hydroxo-difluoride are extremely air-sensitive and become black on exposure to atmospheres containing even traces of oxygen.

The majority of the known neutral $[U(cp)_3X]$ complexes are either insoluble in weakly acid aqueous media or dissolve with dissociation of the U–X bond but without rupture of the U–cp bonds. The reactions with excess fluoride or hydroxide ion leading to the elimination of cyclopentadiene probably take place by way of the formation of the short-lived intermediate anion, $[U(cp)_3X_2]^-$. Support for this comes from the atomic ratio U : F *ca.* 1 : 2 in all of the products of the reactions with alkali fluoride except that obtained using the acid salt, $NH_4F\cdot HF$, where the product was identified by *X*-ray powder photography as [7] α-$UF_4\cdot NH_4F$. The decreased stability of the U–cp bonds in such intermediate anions may be due to an increase in the net negative charge on the cp ligands owing to the concentration of negative charge on, and close to, the central metal ion. Alternatively, the high electronegativity of F^- and OH^- may lead to electron withdrawal from the U–cp bonds to such an extent that the bonds rupture.

$[U(cp)_3X_2]^-$ [X = *Cyanide and Cyanotrihydroborate* ($NCBH_3^-$)].—The small CN^- anion should satisfy the steric requirements in a potential anionic complex $[U(cp)_3(CN)_2]^-$ and should also be capable of delocalising the excess negative charge arising in such an anion over the axial N≡C–U–C≡N fragment. In addition, the CN^- group is less electronegative than F^- or OH^-. The parent complex, $[U(cp)_3(CN)]$ (1), was first prepared [8] by reaction of $[U(cp)_4]$ with anhydrous HCN, but we have obtained (1), and the analogous $[U(mcp)_3(CN)]$ (2), more simply by treating aqueous solutions of $[U(cp)_3Cl]$ or $[U(mcp)_3Cl]$ with aqueous alkali cyanide, when (1) and (2) form as green precipitates. Similarly, water can be replaced by MeCN as solvent, an indication that the formation of (1) is preferred to that of either $[U(cp)_3(CN)(NCMe)]$ or $[U(cp)_3(CN)_2]^-$. In agreement with the original report,[8] both com-

Table 1. Comparison of the properties of various $[U(cp)_3X]$ and $[U(mcp)_3X]$ complexes with the corresponding $SnMe_3X$ systems

Compound	ν(CN)/cm^{-1}	M.p./°C	Sublimation temp./°C	Comments
$[U(cp)_3(CN)]$	2 110 2 112[a]	$\geqslant$200 (decomp.)		assumed to be oligomeric
$[U(mcp)_3(CN)]$	2 096	$\geqslant$200 (decomp.)		
$[U(cp)_3(NCS)]$	2 017	decomp. >180 (vacuum)		
$[U(cp)_3(NCS)(NCMe)]$	2 030, 2 054 (sh)			
$[U(cp)_3F]$		321 (decomp.)	170	
$[U(mcp)_3F]$[b]		300 (decomp.)	150	
$[U(cp)_3Cl]$		260	210	not oligomeric
$[U(mcp)_3Cl]$		223	140	
$SnMe_3(CN)$[c]	2 163			
$SnMe_3F$[d]		375 (decomp.)		oligomeric[d,e]
$SnMe_3Cl$		38		

[a] Ref. 8. [b] Ref. 13. [c] Ref. 32. [d] Ref. 33. [e] Ref. 9.

Table 2. Analytical data[a] (%)

	M	C	H	N	S	NCS
$K[U(cp)_3(OCN)(NCS)]$[b,c]	41.2 (41.6)	35.0 (35.7)	2.75 (2.60)	4.95 (4.90)	5.40 (5.60)	
$[AsPh_4][U(cp)_3(NCS)_2]$[d]	26.5 (25.5)	52.1 (52.8)	3.7 (3.75)	2.6 (3.0)	7.3 (6.9)	
$[NMe_4][U(cp)_3(NCS)_2]$	39.1 (38.2)	38.6 (40.4)	4.3 (4.4)	6.2 (6.7)	8.6 (10.3)	
$[AsPh_4][Np(cp)_3(NCS)_2]$	25.9 (25.4)					11.7 (12.4)
$[AsPh_4][Pu(cp)_3(NCS)_2]$	25.3 (25.6)					12.0 (12.4)
$[Np(cp)_3(NCS)]$	48.0 (48.3)					11.4 (11.8)
$[U(mcp)_3(NCS)]$[c]	44.3 (44.65)	42.8 (42.9)	3.95 (3.95)	2.7 (2.7)	6.05 (6.00)	
$K[U(mcp)_3(NCS)_2]$[c,e]		30.5 (32.0)	3.10 (2.55)	7.20 (6.65)	13.15 (15.5)	
$[U(cp)_3(CN)]$[f]	53.4 (51.9)	25.2 (41.9)	2.20 (3.30)	1.75 (3.05)		
$[U(cp)_3(CN)$[g]	51.5 (51.9)	32.6 (41.9)	2.80 (3.30)	2.15 (3.05)		
$[U(cp)_3(CN)]$[h]		26.0 (41.9)	2.50 (3.30)	2.00 (3.05)		
$[U(cp)_3(NCBH_3)(NCMe)]$	34.6 (46.3)	37.5 (42.0)	4.15 (4.10)	6.15 (5.45)		
$[U(cp)_3(OCN)]$		39.8 (40.4)	3.10 (3.15)	2.55 (2.95)		
$[U(cp)_3(OCN)(NCMe)]$[c]	43.7 (46.1)	34.2 (41.9)	3.35 (3.50)	4.00 (5.45)		
$UF_2(OH_2)=UOF_2\cdot H_2O$[i]	76.7 (76.8)					
$UF_4\cdot NH_4F$	68.3 (67.8)		1.10 (1.15)	4.00 (4.00)		

[a] Calculated values are given in parentheses. [b] K, 7.05 (6.80)%. [c] Analyses by Dornis and Kolbe, Mikroanalytisches Laboratorium. [d] As, 7.95 8.05)%. [e] Probably contaminated with starting material; calculated data are for $K[U(mcp)_3(NCS)_2]$: KNCS = 1 : 2. [f] From reaction of $[U(cp)_3Cl]$ with CN^-. [g] From reaction of $[U(cp)_3Cl]$ with $NCBH_3^-$. [h] From reaction of $[U(cp)_3Cl]$ with $K_2[Zn(CN)_4]$ (ref. 23). [i] U : F = 1 : 2.

Table 3. Infrared spectra (cm^{-1}) of $[M(cp)_3(NCS)_2]^-$ and of $[M(cp)_3(NCS)]$ with the corresponding $Sn^{IV}Me_3$ systems for comparison

		M		
Compound	Assignment	U	Np	Pu
$[NMe_4][M(cp)_3(NCS)_2]$	ν(CN)	2 065, 2 057		
$[AsPh_4][M(cp)_3(NCS)_2]$	ν(CN)	2 065, 2 050	2 068, 2 053	2 070, 2 055
$[K(Crypt)][M(cp)_3(NCS)_2]$	ν(CN)	2 050[a]		
$[AsPh_4][M(cp)_3(NCS)_2]$	ν(M-cp)	236	229	227
$[K(thf)_n][M(mcp)_3(NCS)_2]$	ν(CN)	2 055		
$[M(cp)_3(NCS)]$	ν(M-cp)	246	246	248
$[M(cp)_3(NCS)]$	ν(CN)	2 020	2 030	2 035
$[M(mcp)_3(NCS)]$	ν(CN)	2 030		
$[\{M(cp)_3(CN)\}_n]$	ν(M-cp)	245		
$[NMe_4][SnMe_3(NCS)_2]$[b]	ν(CN)	2 070[c]		
$SnMe_3(NCS)$[d]	ν(CN)	2 045[c]		
$SnMe_3(NCS)$[e]	ν(CN)	2 098 (sh), 2 079vs, 2 046 (sh)[c]		
$[NMe_4]NCS$	ν(CN)	2 062		

[a] Single, highly symmetric ν(CN) absorption. [b] Ref. 15(*a*). [c] M = Sn. [d] In CCl_4 solution. [e] Solid sample; structure involves NCS bridges [ref. 15(*b*)].

pounds are extremely air-sensitive (pyrophoric in air), insoluble in water and in all common organic solvents, including dimethylformamide, and are involatile even under high vacuum, although we have been able to obtain a relatively simple mass spectrum of $[U(cp)_3(CN)]$ at temperatures above 150 °C [most prominent values of *m/e* 459, 394, 329, and 264 for the fragments $U(cp)_n(CN)^+$ with n = 3—0]. Both (1) and (2) decompose above *ca.* 200 °C with the evolution of unidentified gases, leaving a black, pyrophoric residue.

The insolubility and involatility (see Table 1) of the two complexes suggest that (1) and (2) are oligomeric and are probably composed of linear chains, $-U-CN-U-CN-$, linked by strong CN bridges, as in the known oligomer $[\{Sn(CH_3)_3(CN)\}_n]$,[9] unlike the case of $[U(cp)_3F]$ in which, in spite of a linear $-U-F\cdots U-F\cdots$ arrangement, the three cp ring normals remain non-planar.[10] In addition, the near-i.r.–visible spectra of the corresponding cyanides are typical of $[U(cp)_3XY]$ systems with trigonal-bipyramidal co-ordination. The most prominent features in such spectra are the absorptions at 605 ± 5 (sharp) and 1 530 ± 20 nm; the latter, consisting of 2—3 bands, depending on the sample preparation, gives rise to the most intense feature in the near-i.r.–visible spectrum. Absorptions at 1 000—1 050 and 1 100—1 250 nm, which are apparently characteristic of $[U(cp)_3X]$ systems,[1,3,11] are usually absent (1 100—1 250 nm) or modified (1 000—1 050 nm).

The attempted preparation of the anionic species $[U(cp)_3(CN)_2]^-$ or $[U(mcp)_3(CN)_2]^-$ by reaction of $[U(cp)_3(CN)]$ or $[U(mcp)_3(CN)]$ with an excess of alkali cyanide in water, tetrahydrofuran (thf), or MeCN was unsuccessful, from which it appears that the chemical stability of the oligomeric $[\{U(cp)_3(CN)\}_n]$ species, involving alternating U–C and U–N bonds, is much greater than that of species which involve only U–C bonds. It should also be noted that $[U(mcp)_3(CN)]$ does not show any substantial increase in solubility and volatility relative to $[U(cp)_3(CN)]$ as is usually observed on methylation of the cp ring. This feature is illustrated by the comparison in Table 1 of data for $[U(cp)_3(CN)]$ and $[U(cp)_3(NCS)]$ with those for $[U(cp)_3Cl]$ and $[U(cp)_3F]$.

The remarkable chemical stability of $[\{U(cp)_3(CN)\}_n]$ is also brought out by some of the chemical properties of the cyanoborate complex, $[U(cp)_3(NCBH_3)]$. This compound was first prepared by reaction of $[U(cp)_3Cl]$ with $K[NCBH_3]$ in thf and is thought to be oligomeric *via* B–H–U bonds.[12] Two alternative preparative routes are by reaction of $[U(cp)_3Cl]$ with $Na[NCBH_3]$ in either MeCN or H_2O, which yield the trigonal-bipyramidal species $[U(cp)_3(NCBH_3)(NCMe)]$ and, presumably, $[U(cp)_3(NCBH_3)(OH_2)]$; vacuum drying of the hydrate or of the MeCN adduct after treatment with thf then yields $[U(cp)_3(NCBH_3)]$. In the above cases the final step represents the removal of a weakly bonded ligand (L = MeCN, thf, or water) from a trigonal-bipyramidal type system, $[U(cp)_3(NCBH_3)L]$.

As the second σ lone electron pair of the CN group in $[U(cp)_3(NCBH_3)]$ is bonded to the BH_3 group, the formation of the anionic complex $[U(cp)_3(NCBH_3)_2]^-$ should not be prevented by association of the type observed in $[\{U(cp)_3(CN)\}_n]$. However, if a saturated aqueous solution of $[U(cp)_3(NCBH_3)]$ is treated with an excess of $Na[NCBH_3]$, a green precipitate of $[U(cp)_3(CN)]$ is obtained after a few hours. This reaction also occurs in the absence of an excess of $Na[NCBH_3]$ over a longer period. The i.r. and near-i.r.–visible spectra of this product are identical with the corresponding spectra of authentic $[\{U(cp)_3(CN)\}_n]$, but the latter is extremely air-sensitive whereas the products obtained in this work were stable in air for several days. However, one feature common to all the different samples of $[\{U(cp)_3(CN)\}_n]$ obtained in this work and in other studies in our laboratory [13] is that the C and N analyses are always unrealistically low (see Table 2). This probably [14] results from the lower combustion temperatures used in modern C,H,N analysers as compared with that used in the original work.

$[U(cp)_3X_2]^-$ (X = *Thiocyanate*).—The first recorded trigonal-bipyramidal complex of the type $[U(cp)_3XY]$ was the neutral compound, $[U(cp)_3(NCS)(NCMe)]$, the structure of which confirms that the thiocyanate group is *N*-bonded.[1] Replacement of the neutral ligand by another NCS^- ion, or addition of the latter to $[U(cp)_3(NCS)]$, should yield the anionic trigonal-bipyramidal complex, $[U(cp)_3(NCS)_2]^-$, in a suitable solvent. Water turns out to be unsatisfactory for this purpose, probably because the solubilities of $[U(cp)_3(NCS)]$ and $[U(cp)_3(NCS)(OH_2)]$ [1] are low, and although a pale green solution is usually obtained on filtration after reaction of aqueous $[U(cp)_3Cl]$ with potassium thiocyanate (molar ratios 1 : 1 or 1 : 2), the near-i.r.–visible spectrum of which indicates the presence of uranium(IV), the dissolved species is free of organic ligands which suggests that it is a decomposition product. However, the electronic near-i.r.–visible spectra of $[U(cp)_3(NCS)]$ in thf and MeCN in the presence of an excess of KNCS clearly indicate that the formation of a trigonal-bipyramidal species takes place (see Table 6).

The attempted isolation of the new thiocyanate species from thf solution yielded mixtures of the product and starting materials in varying proportions. Reaction of $[U(cp)_3(NCS)(NCMe)]$ with the calculated quantity of KNCS in methyl cyanide also gave a similar result, although with a 3—5 molar excess of KNCS the final product consisted, according to its i.r. spectrum, of $K[U(cp)_3(NCS)_2]$ and KNCS. {A rather confusing feature of the i.r. spectrum is that the modes ν(CN) for the thiocyanate group in KNCS, $[U(cp)_3(NCS)(NCMe)]$, and $[U(cp)_3(NCS)_2]^-$ are almost coincident at 2 045 cm^{-1}}. Addition of the cryptand 'Cryptofix-222'* (Crypt) to the methyl cyanide solution, removal of the solvent, and subsequent extraction of the expected $[K(Crypt)][U(cp)_3(NCS)_2]$/$[K(Crypt)]NCS$ mixture with benzene, followed by evaporation of the extract, finally yields an air-sensitive green solid, the i.r. spectrum of which exhibits only one, remarkably symmetrical ν(CN) feature at 2 050 cm^{-1}. The i.r. spectrum of this product in the ν(CN) region indicates that the insoluble salts KNCS and $[K(Crypt)]NCS$, as well as $[U(cp)_3(NCS)]$, are absent, but further assessment of the i.r. spectrum is hampered by the presence of a number of intense features due to the $[K(Crypt)]^+$ ion. Although the analyses of the compound suggest that it is $[K(Crypt)][U(cp)_3(NCS)_2]$, we have been unable to prepare pure samples of the compound. With a preparative ratio $[U(cp)_3(NCS)]$: KNCS of $\lesssim 2:1$, the final yield is extremely low, while for the ratio $>2:1$ elimination of cp appears to take place, an interesting new reaction pattern of a $[U(cp)_3X_2]^-$ system which is being further investigated. The attempted preparation of $Cs[U(cp)_3(NCS)_2]$ from stoicheiometric quantities of $[U(cp)_3(NCS)]$, KNCS, and CsCl in MeCN yielded a green solution, the near-i.r.–visible spectrum of which was typical of the $[U(cp)_3(NCS)_2]^-$ anion, but evaporation of the supernatant to dryness *in vacuo* yielded a solid which, from its *X*-ray powder diffraction pattern, was identified as $[U(cp)_3(NCS)(NCMe)]$.

Because the anion $[U(cp)_3(NCS)_2]^-$ is rather large, the formation of salts with other bulky cations was investigated. $[NMe_4][U(cp)_3(NCS)_2]$ and $[AsPh_4][U(cp)_3(NCS)_2]$ were obtained as green solids by evaporating to dryness the filtrate resulting from the reaction of stoicheiometric quantities of KNCS, $[U(cp)_3(NCS)]$, and NMe_4Cl or $AsPh_4Cl$ in thf (both) or MeCN ($AsPh_4Cl$ only). $[AsPh_4][U(cp)_3(NCS)_2]$ was found

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* 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

Table 4. Room temperature $\Delta_{iso.}$ values * (p.p.m.)

Sample	C_5H_4 protons	C_5H_5 protons	$\Delta_{iso.}$ (average)	CH_3 protons	Solvent
$[U(mcp)_3Cl]$	−6.2, 25.4		9.6	2.7	$[^2H_8]$thf
$[U(cp)_3(NCS)]$		9.2			$[^2H_8]$toluene
$[U(mcp)_3(NCS)]$	−8.7, 23.1		7.2	5.8	$[^2H_8]$toluene
$[U(cp)_3(NCS)_2]^-$		16.3			$[^2H_8]$thf
$[U(mcp)_3(NCS)_2]^-$	16.4, 17.0		16.7	−0.1	$[^2H_8]$thf
$[U(cp)_3(OCN)(NCS)]^-$		14.1			CD_3CN

* External references for ^1H n.m.r. data were $[Th(mcp)_3Cl]$ or $[Th(cp)_3Cl]$; positive values refer to upfield shifts.

Table 5. *X*-Ray powder diffraction data ($\sin^2\theta$ values)

$[AsPh_4]$-$[U(cp)_3(NCS)_2]$	$[AsPh_4]$-$[Np(cp)_3(NCS)_2]$	$[AsPh_4]$-$[Pu(cp)_3(NCS)_2]$
0.0080w	0.0081w	
0.0099w	0.0100w−	0.0099w
0.0111m	0.0112m	0.0111m−
0.0126m−	0.0127m−	0.0126w+
0.0134w+	0.0134w+	0.0135w+
0.0138m	0.0141m−	0.0138m−
0.0161m	0.0162m−	0.0161m−
0.0182m	0.0184w+	0.0183m−
0.0194m−	0.0197w+	0.0195m
0.0238w−	0.0239w−	
0.0248w−	0.0251w−	
0.0290m+	0.0292m+	0.0291m+
0.0297w	0.0300w	
0.0311w−	0.0312w	
0.0338w	0.0340w	
0.0481w		

to be stable to air and to water, in which it is insoluble, over a period of several weeks, whereas the tetramethylammonium salt was slightly less stable in these respects. The corresponding neptunium(IV) and plutonium(IV) compounds, $[AsPh_4]$-$[M(cp)_3(NCS)_2]$, were obtained in a somewhat similar manner as red-brown and dark brown solids respectively, both of which are also stable to air for several weeks. *X*-Ray powder photography (Table 5) shows that these two compounds are isostructural with $[AsPh_4][U(cp)_3(NCS)_2]$.

The CN-stretching and metal-ring features in the i.r. spectra are summarised in Table 3, from which it can be seen that $\nu(CN)$, a split feature for the cations NMe_4^+ and $AsPh_4^+$, increases very slightly in frequency from uranium to plutonium. The frequencies assignable to $\nu(CN)$ in the i.r. spectra of the complex anions are, as for the adduct $[U(cp)_3(NCS)(NCMe)]$,[1] noticeably higher than those for the corresponding uncharged (and pseudo-tetrahedral) parent compounds $[M(cp)_3(NCS)]$, suggesting a somewhat weaker electron donation by the NCS groups, perhaps for steric reasons. This behaviour parallels that of the organotin complexes $[SnMe_3(NCS)_2]^-$ and $SnMe_3(NCS)$.[15] The organoactinide compounds $[M(cp)_3(NCS)]$ (M = U, Np, or Pu) and the $SnR_3(NCS)$ systems * are unusual examples of metal thiocyanate complexes for which the $\nu(CN)$ frequencies are lower than the value for the 'free' NCS anion. Another interesting feature (Table 3) is that the i.r.-active metal-ring stretching mode of the complex anions appears at appreciably lower frequencies than that in the uncharged $[M(cp)_3(NCS)]$ compounds, including $[U(cp)_3(CN)]$. A corresponding frequency shift has not been observed in the case of the $SnMe_3$ complexes.[15] The near-i.r.–visible spectra of the neptunium and plutonium compounds, like that of the uranium compound, differ markedly from those of $[M(cp)_3(NCS)]$ for the two elements (Table 6, Figures 1—3), and demonstrate that for all three actinides the transition from pseudo-tetrahedral to trigonal-bipyramidal co-ordination is accompanied by marked changes in the electronic spectra. Although the spectrum of $[Np(cp)_3(NCS)]$ in MeCN (Figure 2) shows some features characteristic of that of $[AsPh_4][Np(cp)_3(NCS)_2]$ in thf, as well as features due to $[Np(cp)_3(NCS)]$, all attempts to isolate $[Np(cp)_3(NCS)(NCMe)]$ from the solution yielded only $[Np(cp)_3(NCS)]$. The spectrum of $[Pu(cp)_3(NCS)]$ in MeCN (Figure 3) shows only slight differences from that in thf at ambient temperature, indicating that the MeCN adduct is

Table 6. The most prominent electronic transitions of the uranium(IV) complexes assumed to involve trigonal-bipyramidal co-ordination

		Spectral range (cm^{-1})	
Complex	Sample preparation	16 500 ±200	6 450 ±150
$[U(cp)_3(NCS)(NCMe)]$ [a]	solid [b]	16 442	6 518, 6 454
$[U(cp)_3(NCS)(NCMe)]$	MeCN	16 475	6 515, 6 239
$K[U(cp)_3(NCS)_2]$	MeCN	16 393	6 515, 6 330
$K[U(cp)_3(NCS)_2]$	thf	16 367	6 579, 6 305
$K[U(mcp)_3(NCS)_2]$	thf	16 260	6 570, 6 257
$[K(Crypt)][U(cp)_3(NCS)_2]$	MeCN	16 393	6 579, 6 337
$[AsPh_4][U(cp)_3(NCS)_2]$	thf	16 420	6 568, 6 310
$[AsPh_4][U(cp)_3(NCS)_2]$	MeCN	16 420	6 575, 6 333
$[AsPh_4][U(cp)_3(NCS)_2]$	solid [c]	16 400	6 546, 6 338
$[AsPh_4][U(cp)_3(NCS)_2]$	solid [d]	16 400	6 546, 6 503, 6 313
$[NMe_4][U(cp)_3(NCS)_2]$	thf	16 370	
$[U(cp)_3(OCN)(NCMe)]$	MeCN	16 505	6 584, 6 484
$K[U(cp)_3(OCN)(NCS)]$	solid [b]	16 405	6 503, 6 340
$[U(cp)_3Cl]$ [e]	thf	(16 545) [f]	
$[U(cp)_3(NCS)]$ [e]	thf	(16 441) [f]	
$[\{U(cp)_3(CN)\}_n]$	solid [b]	16 441	6 494, 6 343
$K[U(mcp)_3\{C(CN)_3\}Cl]$ [g,h]	thf	16 528	6 493
$[U(mcp)_3\{C(CN)_3\}]$ [h]	emission	16 722	6 493

[a] Structure determined by *X*-ray analysis (ref. 1). [b] Teflon discs (ref. 28). [c] At 298 K. [d] At 77 K. [e] Pseudo-tetrahedral co-ordination. [f] Comparatively weak absorptions. [g] Assumed composition. [h] Ref. 11.

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* Formal parallels between $[U(cp)_3X]$ and SnR_3X systems extend to the formation of both pseudo-tetrahedral and trigonal-bipyramidal complexes as well as MR_3XX' (M = U or Sn) systems in which X and X′ occupy *cis* positions (*cf.* J. A. Zubieta and J. J. Zuckerman, *Prog. Inorg. Chem.*, 1978, **24**, 251).

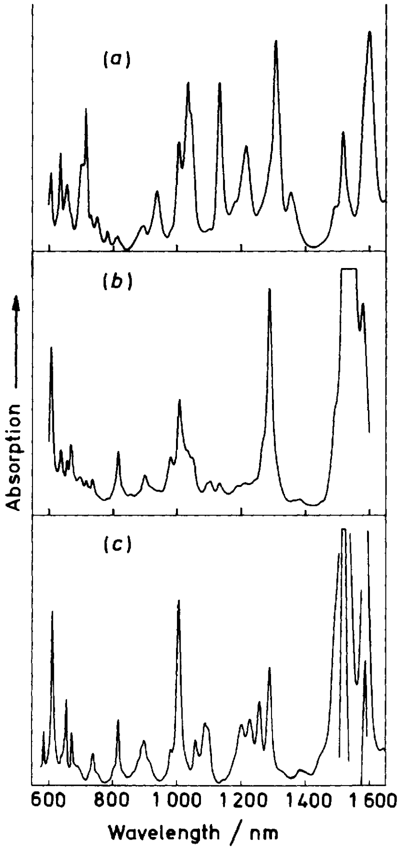

Figure 1. Near-i.r.-visible spectra of [U(cp)$_3$(NCS)] in (*a*) thf and (*b*) MeCN, and (*c*) of [AsPh$_4$][U(cp)$_3$(NCS)$_2$] in thf

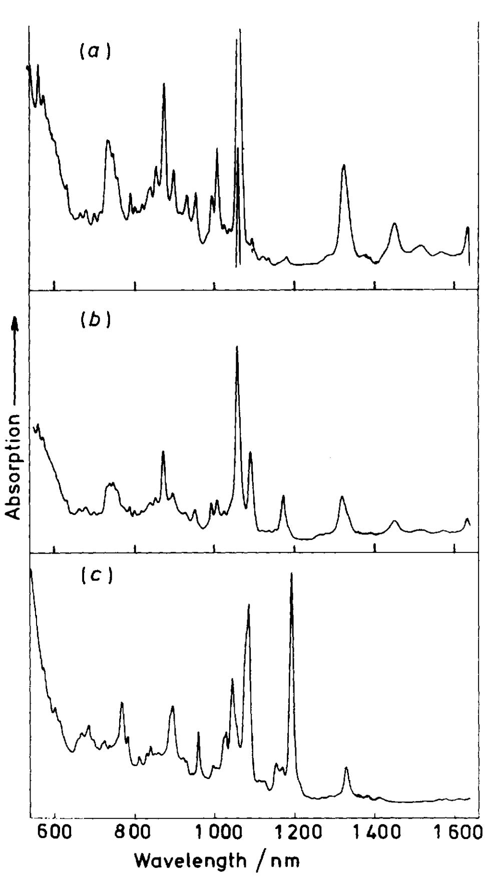

Figure 2. Near-i.r.-visible spectra of [Np(cp)$_3$(NCS)] in (*a*) thf and (*b*) MeCN, and (*c*) [AsPh$_4$][Np(cp)$_3$(NCS)$_2$] in thf

formed only to a minor extent, and the latter could not, in fact, be isolated. These observations suggest that steric problems arising from the actinide contraction hinder the formation of the trigonal bipyramidal MeCN adduct of [M(cp)$_3$(NCS)] (M = Np and Pu).

The mcp analogue, [U(mcp)$_3$(NCS)(NCMe)], also appears to be less stable than the corresponding cp complex, a result which may be due to competition between electron donation from MeCN and from mcp, the latter being a potentially better donor than cp itself. Thus the green product obtained by reaction of [U(mcp)$_3$Cl] with KNCS in MeCN was found to be [U(mcp)$_3$(NCS)] mixed with a small amount of its MeCN adduct, from which pure [U(mcp)$_3$(NCS)] was obtained as a brown solid by sublimation under high vacuum. This result may provide a more effective route to the preparation of [U(mcp)$_3$(NCS)] which, unlike [U(cp)$_3$(NCS)], cannot be obtained by precipitation from aqueous media and is only obtained in $\leqslant 50\%$ yield from thf solutions of [U(mcp)$_3$Cl] and KNCS. Similarly, in the analogous reaction of [U(mcp)$_3$(NCS)] with an excess of KNCS in thf, the formation of the [U(mcp)$_3$(NCS)$_2$]$^-$ anion proceeds much more slowly than is the case with [U(cp)$_3$(NCS)] (hours instead of 2—3 min), a result which may again be due to steric effects, owing to the much larger spatial requirement of three rapidly rotating mcp ligands. (This is also probably the reason why the temperature dependence of the ^{1}H n.m.r. spectrum of [U(mcp)$_3$F] does not exhibit [13] any anomalies corresponding to those observed in the spectrum of [U(cp)$_3$F],[16] which are most likely to arise from dimerisation of the latter in [^{2}H$_8$]toluene and the formation of the adduct [U(cp)$_3$F·thf] in [^{2}H$_8$]thf.) The green product isolated from thf solution by evaporation appears, from its i.r. spectrum and elemental analyses, to be a mixture of K[U(mcp)$_3$(NCS)$_2$] and KNCS (*ca.* 3 : 1) and, possibly, small amounts of [U(mcp)$_3$(NCS)]. Addition of n-pentane to the thf solution precipitates KNCS and an unidentified organic product, and evaporation of the resulting solution leads to a brown solid, evidently [U(mcp)$_3$(NCS)], which again yields a green solution containing the [U(mcp)$_3$(NCS)$_2$]$^-$ ion on treatment with a solution of KNCS in thf (identification by u.v.-visible and ^{1}H n.m.r. spectroscopy).

The ^{1}H n.m.r. spectra of the anions [U(cp)$_3$(NCS)$_2$]$^-$ and [U(mcp)$_3$(NCS)$_2$]$^-$ in [^{2}H$_8$]thf are quite unusual in that the temperature dependence of the (average) isotropic cp ring proton shift, $\Delta_{iso.}$, passes through a maximum at about 250 K (Figure 4) instead of increasing regularly with decreasing temperature. The measured $\Delta_{iso.}$ values for the two pairs of complexes, [U(cp)$_3$(NCS)]/[U(cp)$_3$(NCS)$_2$]$^-$ and [U(mcp)$_3$(NCS)]/[U(mcp)$_3$(NCS)$_2$]$^-$, are also compared in Table 4. Surprisingly, the two very widely separated signals of the ring protons in the α- and β-positions relative to the ring methyl group of [U(mcp)$_3$(NCS)] become very closely spaced in the anionic derivative. Moreover, the averaged values of $\Delta_{iso.}$ for the two anionic complexes are about twice as large (at *ca.* 250 K) as the corresponding averaged values for the uncharged parent complexes.

Apart from those for the anionic complex [U(cp)$_3$(OCN)(NCS)]$^-$ (see below), data for other charged and uncharged tris(cyclopentadienyl)uranium(IV) complexes of potential trigonal-bipyramidal co-ordination geometry are also included in Figure 4. Not only do the two adducts [U(cp)$_3$(NCS)(NCMe)] and [U(cp)$_3$(OCN)(NCMe)] also give rise to $\Delta_{iso.}$ *versus* temperature (*T*) plots which exhibit a maximum, but

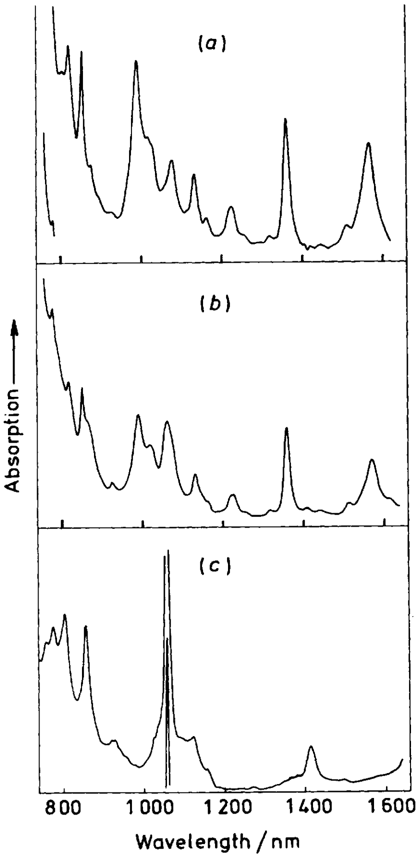

Figure 3. Near-i.r.–visible spectra of $[Pu(cp)_3(NCS)]$ in (*a*) thf and (*b*) MeCN, and (*c*) of $[AsPh_4][Pu(cp)_3(NCS)_2]$ in thf

even the cation $[U(cp)_3(OH_2)_2]^+$ and the soluble precursor of the oligomeric $[\{U(cp)_3[C(CN)_3]\}_n]$,[11] which is presumably $[U(cp)_3\{C(CN)_3\}Cl]^-$, give rise below *ca.* 350 K to $\Delta_{iso.}$ *versus* *T* plots with an inverse temperature dependence, which is also unlike the behaviour of normal paramagnetic samples. This suggests that a maximum will be reached at a still higher temperature. After replacement of cp by mcp, the tricyanomethide complexes again exhibit two extremely close-lying α- and β-ring-proton shifts.[11] Only the $\Delta_{iso.}$ *versus* *T* plot of '$U(cp)_3Cl(NCMe)$' {*i.e.* $[U(cp)_3Cl]$ dissolved in CD_3CN} remains almost unchanged relative to the corresponding plot of $[U(cp)_3Cl]$ in $[^2H_8]$thf, in apparent contradiction to the near-i.r.–visible spectrum of the solution which suggests the formation of an adduct with MeCN.[1] However, both ^1H and ^{13}C n.m.r. studies of the system (in CD_3CN) indicate that exchange of MeCN is rapid on the n.m.r. time-scale, whereas such exchange is probably slow on the near-i.r.–visible time-scale.

$[U(cp)_3XY]^-$ (X = *Thiocyanate*, Y = *Cyanate*).—When a solution of $[U(cp)_3(NCS)(NCMe)]$ in MeCN was stirred for several hours at room temperature in the presence of KOCN, which is almost insoluble in MeCN, the i.r. spectrum of the green product isolated from the supernatant by vacuum evaporation indicated that it was mainly the starting material. Weaker, additional features at 2 185, 2 220, and 2 170 [ν(CN) of OCN], 1 304 [ν(CO) of OCN], 660 and 620 cm^{-1} [δ(NCO)], and the absence of features characteristic of KNCS, indicated that addition of the NCO anion had occurred to a minor extent. However, when an equimolar amount of solid KNCS was added to an olive-green solution of $[U(cp)_3(OCN)(NCMe)]$ in MeCN, the colour darkened immediately and after removal of the solvent a very air-sensitive, greenish brown solid formed as a glassy layer on the walls of the reaction vessel. Elemental analyses (Table 2) are consistent with the formulation $K[U(cp)_3(ONC)(NCS)]$ and this is supported by the absence of ν(CN) for co-ordinated MeCN (2 250—2 300 cm^{-1}) [1] or for $[U(cp)_3(NCS)]$, and by the near-i.r.–visible spectrum of the product, which is not the same as

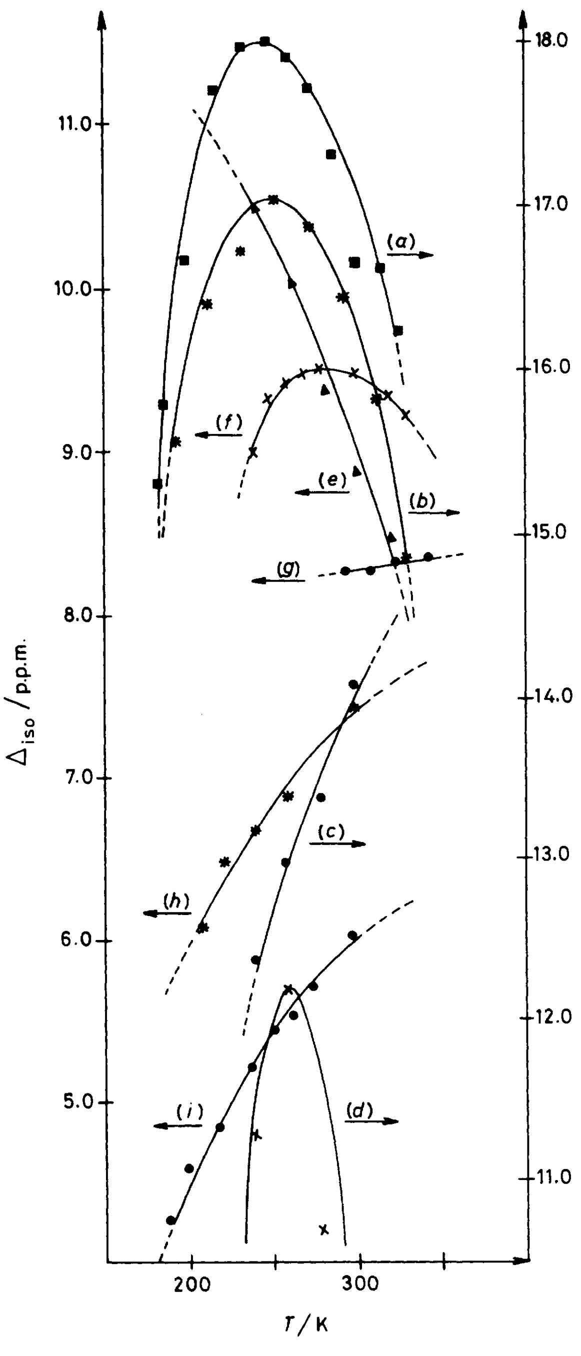

Figure 4. Temperature dependence of $\Delta_{iso.}$ in the ^1H n.m.r. spectra of (*a*) $[U(mcp)_3(NCS)_2]^-$, (*b*) $[U(cp)_3(NCS)_2]^-$, (*c*) $[U(cp)_3(OCN)(NCS)]^-$, (*d*) $[U(cp)_3(OCN)(NCMe)]$, (*e*) $[U(cp)_3Cl(NCMe)]$, (*f*) $[U(cp)_3(NCS)(NCMe)]$, (*g*) $[U(cp)_3(D_2O)_2]^+$, (*h*) $[U(cp)_3\{C(CN)_3\}Cl]^-$, and (*i*) $[U(mcp)_3\{C(CN)_3\}Cl]^-$; arrows indicate vertical axis referred to; positive values of $\Delta_{iso.}$ correspond to high-field shifts. Solvents: (*a*) and (*b*) $[^2H_8]$thf, (*c*)—(*f*) CD_3CN, (*g*) D_2O, (*h*) and (*i*) $[^2H_6]$acetone

that of $K[U(cp)_3(NCS)_2]$, although it is undoubtedly typical of trigonal-bipyramidal co-ordination. Moreover, the absence of features typical of $[U(cp)_3(NCS)]$ or $[U(cp)_3(OCN)]$ indicates that the product is not a mixture such as $[U(cp)_3(OCN)(NCMe)]/KNCS$, $[U(cp)_3(OCN)]/KNCS$, or $[U(cp)_3(OCN)]/[U(cp)_3(NCS)]/KNCS/KOCN$. In addition, although KOCN, unlike KNCS, is almost insoluble in MeCN, the precipitation of KOCN was not observed at any stage of the reaction, so that simple replacement of NCO^- by NCS^- does not occur.

The temperature dependence of the ^1H n.m.r. spectrum of the product in CD_3CN solution (Figure 4) differs markedly from the behaviour ($\Delta_{iso.}$ *versus T*) found for complexes of the type $[U(cp)_3(NCS)_2]^-$, $[U(cp)_3(NCS)(NCMe)]$, and $[U(cp)_3(OCN)(NCMe)]$. The inverse temperature dependence up to at least 300 K, as well as the relatively large values (>12 p.p.m.) for $\Delta_{iso.}$, are, however, compatible with the presence of another negatively charged complex of trigonal-bipyramidal co-ordination geometry. Formation of a polynuclear trigonal-bipyramidal type anion, involving linear ^-OCN bridges, such as $[SCN{-}U(cp)_3{-}NCO{-}U(cp)_3{-}NCS]^-$, can be ruled out on the basis of the elemental analyses and in view of the appearance of only a single cp ring proton resonance.

The frequency of the ν(CN) feature of the NCO ligand in the i.r. spectrum of $[U(cp)_3(OCN)(NCS)]^-$ (2 190 cm^{-1}) is the same as in the i.r. spectra of $[U(cp)_3(OCN)]$ and $[U(mcp)_3(OCN)]$, and the ν(CN) feature of the NCS ligand is almost the same as that for the $[U(cp)_3(NCS)_2]^-$ anion. The i.r. spectra do not provide evidence for the co-ordination mode of the OCN ligand, but in view of the preference for oxygen normally exhibited by uranium ions, one cannot rule out the relatively rare case of U–OCN co-ordination, and the formula of the complex anion is so written.

On exposure to air the colour of the new complex darkens within 10—20 s; it decomposes above 140 °C, appearing to melt at about 190 °C, and gas evolution occurs above 200 °C. On washing the solid with deoxygenated water, the features in the i.r. spectrum which are characteristic of the cyanate ligand decrease in intensity relative to those of the NCS ligand, indicating that the latter is the more strongly bonded to the central uranium atom.

$[U(cp)_3XY]^-$ (X *and* Y = *Alkynyls and Alkyls*).—According to an earlier report,[17] the reaction of $[U(cp)_3(CCH)]$ with $LiBu^n$ in thf at −78 °C yields $[U(cp)_3(Bu^n)]$ and not the anionic complex $[U(cp)_3(CCH)(Bu^n)]^-$. We have found that the reaction of $[U(cp)_3Cl]$ with lithium alkynyls in MeCN instead of thf does not yield either the known $[U(cp)_3(CCR)]$ (R = alkyl) systems nor the expected adducts $[U(cp)_3(CCR)(NCMe)]$, but only the still unsatisfactorily characterised complexes $U^{IV}(cp)_n$ ($n \leqslant 3$) with an extra ligand, the i.r. absorptions of which above 2 000 cm^{-1} appear, unlike those for the known $[U(cp)_3(CCR)]$, at higher frequencies than for the alkynes HCCR and at lower frequencies than for MeCN.

Complexes of the type $[U(cp)_3R]$ (R = alkyl) have recently been shown to react with LiMe to yield the novel, and surprisingly stable, anionic uranium(III) complex,[18] $[U(cp)_3Me]^-$. It therefore appears that complexes of the type $[U(cp)_3RR']^-$ (R and R′ = alkyl) will only exist as unstable intermediates because of a tendency to undergo redox reactions spontaneously.

Conclusions

From the results reported in this paper, it is apparent that anionic actinide(IV) organometallic compounds of the general type $[M(cp)_3XY]^-$ (M = U, Np, and Pu) are easily accessible, and surprisingly stable, provided that the counter cation is sufficiently large and the ligands X and Y are ' hard bases,' sterically well suited and able to contribute to the delocalisation of the negative charge without being too reductive. No information is available for the corresponding $Th^{IV}(cp)_3$ systems, and the preparation of $[Th(cp)_3(NCS)]$ does not appear to have been reported. The chloride, $[Th(cp)_3Cl]$, unlike $[U(cp)_3Cl]$, is known to be rapidly and completely hydrolysed by water,[2,19] a result which may be due to the less crowded environment of the thorium atom, so that an investigation of the systems $[Th(cp)_3XY]^-$ might well prove to be interesting.

There is evidence that the M–cp ring bonding is weaker in the anionic complexes relative to that in the neutral and cationic $[U(cp)_3XY]$ systems, which would be expected from the increased electron density on the anionic species. This weakening of the M–cp bonds facilitates reactions leading to the replacement of cp ligands, an aspect which will be considered in a subsequent communication. The change from the pseudo-tetrahedral geometry of the $[M(cp)_3X]$ complexes to the trigonal bipyramidal $[M(cp)_3XY]^q$ ($q = +1, 0,$ and -1) systems is always accompanied by marked changes in the electronic spectra and (for M = U) by unexpected changes in the temperature behaviour of the ^1H n.m.r. spectra. Because q can, in principle, take the values +1, 0, or −1, and X may be the same as Y, or a different ligand, a much wider range of variations can be expected within the new group of trigonal-bipyramidal systems relative to the well known family of pseudo-tetrahedral parent complexes.

However, it must be emphasised that not all $[M(cp)_3XY]^q$ systems will necessarily adopt trigonal-bipyramidal co-ordination geometry. There are a number of examples of compounds of the type $[U(cp)_3X]$ in which the ligand X makes use of more than one co-ordination site (*e.g.* X = cp, η^3-BH_4,[20] or η^2-pyrazolyl[21]); η^2-co-ordination has also been assumed for the dimer $[\{U(cp)_3F\}_2]$ observed in non-co-ordinating solvents[13,16] as well as for the intermediates $U(cp)_3R{\cdot}AlR'_3$[22a] and $U(cp)_3R{\cdot}AlClR'_2$[22b] to explain the observed exchange of R and Cl respectively. The existence of isomers of $[M(cp)_3XY]^q$, where X and Y occupy either *cis* or *trans* positions, and where the favoured form might well depend on the nature of X and Y and the reaction medium, cannot therefore be ignored.

It is interesting to note that some compounds of the type $[U(cp)_3X]$ react with, for example, H_2O, ROH, and NH_4Y by simultaneous replacement of both X and cp (*e.g.* if X = BH_4, OR, alkyl, or cp) whereas in other cases [*e.g.* if X = halogen, pseudohalogen, NO_3,[3] or $C(CN)_3$[11]] products which leave the $U(cp)_3$ moiety intact are preferred. If we assume that the *cis* isomers of the complexes $[U(cp)_3XY]^q$ would undergo protolytic cp ring abstraction as readily as do most of the $[U(cp)_3X]$ systems with a multihapto-co-ordinated ligand X (and X = σ-allyl[20]), then the observation of substantial quantities of non-organometallic, green uranium(IV) by-products formed in the precipitation of some ultimately very water-stable $[U(cp)_3X]$ compounds in water (*e.g.* X = NCS or OCN, see above) might be the result of the simultaneous formation of intermediates which adopt *both* isomeric forms. Furthermore, the quite surprising instability of the assumed intermediates $[U(cp)_3X_2]^-$ (X = F or OH, see above) in water is in marked contrast to the well established stability of $[U(cp)_3Cl]$ even in very acid aqueous media,[2] to the resistance of $[AsPh_4][U(cp)_3(NCS)_2]$ towards water (see above), and to the stability of some new polymeric $[\{U(cp)_3X\}_n]$ systems to reaction with NH_4Cl,[23] observations which do not preclude the possibility of energetically favoured *cis*-$[U(cp)_3X_2]^-$ species.

Experimental

All preparative work involving non-aqueous solvents was carried out in dry-atmosphere, nitrogen-filled glove-boxes (water $\leqslant$20 p.p.m., oxygen $\leqslant$20 p.p.m.) to afford protection against the α-radiation emitted by ^{237}Np and ^{239}Pu, and to protect samples against atmospheric oxygen and moisture. For preparative reaction in aqueous media, laboratory distilled water was redistilled twice under a nitrogen atmosphere. Commercially available Cryptofix-222, $Na[NCBH_3]$, $NH_4F \cdot NH$ (Merck, Darmstadt), $AsPh_4Cl$ (Aldrich), and NMe_4Cl (B.D.H., Ltd.) were used as supplied; UCl_4,[24] $[U(cp)_3Cl]$,[11,25] $[U(mcp)_3Cl]$,[11] $[Np(cp)_3Cl]$[26] (using thf), and $[Pu(cp)_3(NCS)]$[27] were prepared by published methods. $[U(cp)_3(NCS)]$ was prepared in a similar manner to $[Np(cp)_3(NCS)]$ (see below), but omitting the dichloromethane extraction, and by a previously published method.[1] $[AsPh_4]NCS$ was prepared by treating a solution of $AsPh_4Cl$ with the stoicheiometric quantity of KNCS in MeCN and evaporating the supernatant to dryness *in vacuo*. Solvents and KNCS were dried as previously described.[27]

Vibrational spectra were obtained using Perkin-Elmer PE 577 or PE 325, Beckman IR-7 (with NaCl and CsI prisms), Beckman IR-12, or Polytec FIR 30A spectrometers. Electronic spectra in the near-i.r.–visible region of solutions, Teflon discs,[28] or finely ground powders were recorded using Cary 17 or Beckman DK 2A spectrometers, the latter adapted for diffuse reflectance. Mass spectra were obtained using a Varian CH 112 instrument, and ^1H n.m.r. spectra either with a 90 MHz Bruker WH 90 instrument with the Bruker Data System model B.NC12 or with a Jeol JNH-C-60 HL instrument. *X*-Ray powder diffraction photographs were obtained using a Debye-Scherrer 19-cm camera with Cu-K_α radiation ($\lambda = 1.5418$ Å) or (in the case of α-$UF_4 \cdot NH_4F$) by the Guinier method, using a Guinier–de Wolff camera No. II. Precipitates involving '$UOF_2 \cdot H_2O$' and UO_2 were found to be amorphous to *X*-rays.

Preparations.—(*a*) $[AsPh_4][U(cp)_3(NCS)_2]$. The compound $[U(cp)_3(NCS)]$ (0.4144 g, 0.843 mmol), KNCS (0.0838 g, 0.862 mmol), and $AsPh_4Cl$ (0.3553 g, 0.849 mmol) were stirred together overnight in thf or MeCN (*ca.* 10 cm^3) and the bright green supernatant was evaporated to dryness *in vacuo* (yield 84%). $[NMe_4][U(cp)_3(NCS)_2]$ was prepared in the same way from thf solution.

(*b*) $[Np(cp)_3(NCS)]$. The compound $[Np(cp)_3Cl]$ (0.303 45 g, 0.649 mmol) and KNCS (0.063 25 g, 0.651 mmol) were stirred together in thf (10 cm^3) overnight (16 h). After centrifugation the supernatant was evaporated to dryness *in vacuo*; the residue was extracted into dichloromethane, and the *product* was isolated from the extract by evaporation *in vacuo*. The rusty brown solid was finally washed with n-pentane (2 × 2 cm^3), in which it is very slightly soluble, and then dried *in vacuo* (yield *ca.* 60%). The complex $[U(mcp)_3(NCS)]$ was prepared in essentially the same manner from $[U(mcp)_3Cl]$ and KNCS. Pure, deep brown $[U(mcp)_3(NCS)]$ was obtained from the olive-coloured crude product by extraction with n-pentane (*ca.* 20 h, yield 46%).

(*c*) $[AsPh_4][Np(cp)_3(NCS)_2]$. The compound $[Np(cp)_3(NCS)]$ (0.090 25 g, 0.184 mmol) and $[AsPh_4]NCS$ (0.0812 g, 0.184 mmol) were stirred together overnight in thf (3—5 cm^3). After centrifugation, the deep cherry-red supernatant was evaporated to dryness *in vacuo* and the red-brown residue was washed with n-pentane (2 × 2 cm^3) and dried *in vacuo* (yield 73%). The plutonium analogue $[AsPh_4][Pu(cp)_3(NCS)_2]$ was prepared in the same way (yield *ca.* 80%). Both salts are completely soluble in thf, MeCN, and CH_2Cl_2.

(*d*) *Reactions in aqueous solution*. The compounds $[U(cp)_3(CN)]$, $[U(mcp)_3(CN)]$, $[U(cp)_3(OCN)]$, and $[U(cp)_3(NCBH_3)]$, and the non-organometallic products $UOF_2 \cdot xH_2O$, $UO_2 \cdot xH_2O$, and $UF_4 \cdot NH_4F$, were obtained from aqueous solutions of $[U(cp)_3Cl]$ or $[U(mcp)_3Cl]$ and the respective alkali-metal salt in almost quantitative yields following published procedures.[11,29]

(*e*) $[U(cp)_3(OCN)(NCMe)]$ *and* $[U(cp)_3(NCBH_3)(NCMe)]$. These compounds were prepared by a similar method to that for $[U(cp)_3(NCS)(NCMe)]$.[1]

(*f*) $K[U(cp)_3(OCN)(NCS)]$. Greenish brown $[U(cp)_3(OCN)(NCMe)]$ (0.3430 g, 0.60 mmol) was dissolved in MeCN (10 cm^3). After addition of an equimolar quantity of KNCS and stirring (1—2 min), a clear green solution resulted (no KOCN was precipitated). Stirring (*ca.* 1 h), filtration, and removal of the solvent under reduced pressure left an amorphous, glassy solid layer on the walls of the tube. The *product* was 'shock-cooled' in liquid nitrogen and vacuum dried (yield 92%).

(*g*) $[K(Crypt)][U(cp)_3(NCS)_2]$. The complex $[U(cp)_3(NCS)(NCMe)]$ was added to an equimolar quantity of KNCS dissolved in MeCN (*ca.* 20 cm^3) containing Cryptofix-222 (KNCS : Crypt *ca.* 1 : 2.5). The resulting dark green solution was stirred (*ca.* 2 h), filtered and, after removal of the solvent, the residue was extracted into benzene. The *product* was obtained from the extract as a light green solid on evaporation *in vacuo* (yield *ca.* 10%).

Analyses.—Neptunium-237 and plutonium-239 were determined as described previously[27] for ^{239}Pu; thiocyanate was determined by published methods.[30] The analytical results are given in Table 2. Combustion analyses (C,H,N) were carried out using either the Heraeus automatic CHN-Mikro instrument or the Erber Elemental Analyser model 1140. Uranium was determined by treating the sample several times with concentrated HNO_3 and ultimately weighing as U_3O_8 after ignition or by titration with $K_2Cr_2O_7$.[31] The amount of fluoride anion consumed during the reaction of $[U(cp)_3Cl]$ and NaF or KF in water was determined indirectly by titration of the residual fluoride anion with 0.1 N $Th(NO_3)_4$ solution using Alizarin S as indicator. Complete analyses of some compounds, which are indicated in Table 2, were also made by Dornis and Kolbe, Mikrochemisches Laboratorium, Mülheim-Ruhr, W. Germany.

Acknowledgements

We thank Mr. M. A. Hart for the microanalyses (C,H,N,S,U) and Mr. G. Jahn for some of the ^1H n.m.r. spectra; one of us (M. J. P.) is indebted to the S.R.C. and to the U.K.A.E.A. for the award of a C.A.S.E. research studentship and to the latter for subsequent support. The work was also supported in part by the Deutsche Forschungsgemeinschaft (D. F. G.) and the Fonds der Chemischen Industrie.

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Received 17*th February* 1982; *Paper* 2/296