Some Oxygen-donor Complexes of Cyclopentadienyluranium(IV) *N*-Thiocyanate; Steric Considerations and Stability

Kenneth W. Bagnall* and **Li Xing-fu**
Chemistry Department, The University of Manchester, Manchester M13 9PL

The oxygen-donor complexes $[U(cp)(NCS)_3L_2]$ [cp = η-C_5H_5, L = $Me_3CCONMe_2$ (dmpva), $Me_2CHCONMe_2$ (dmiba), PPh_3O, and $P(NMe_2)_3O$ (tdpo)] have been prepared and i.r. and u.v.–visible (solution and solid reflectance) spectra are reported for them. Analogous complexes with L = $MeCONMe_2$ (dma), $EtCONMe_2$ (dmpa), $EtCONEt_2$ (depa), pyridine, and 2,2′-bipyridyl could not be isolated and disproportionation to $[U(cp)_3(NCS)]$ and $[U(NCS)_4L_x]$ occurred. The observations are discussed in terms of the steric crowding about the uranium atom using a cone-packing model.

Complexes of composition $[U(cp)X_3L_x]$ [cp = η-C_5H_5; X = Cl, $x = 1$, L = 1,2-dimethoxyethane (dme);[1] $x = 2$, L = $MeCONMe_2$ (dma),[2] tetrahydrofuran (thf),[3] $P(NMe_2)_3O$ (tdpo);[4] X = Cl or Br, $x = 1$, L = $Ph_2(O)PCH_2CH_2P(O)Ph_2$ (dppoe);[2] $x = 2$, L = $Me_3CCONMe_2$ (dmpva) or PPh_3O [2]] have been reported and *X*-ray crystallography has shown that in the structures of $[U(cp)Cl_3(tdpo)_2]$[4] and $[U(cp)Cl_3(PPh_3O)_2]\cdot$thf[5] the oxygen-donor ligands occupy *cis* positions on an octahedrally co-ordinated uranium atom if the C_5H_5 ring is considered as occupying one apex of the octahedron. This result led to the suggestion[6] that the η^5-bonded C_5H_5 ring may exert a *trans* directing influence on the oxygen-donor ligand, that is, that one of the latter has to be *trans* to the ring for either electronic or steric reasons in order to avoid the weakening of the metal–ring bond which would be expected if the ring were *trans* to an electron-withdrawing group or ion such as a halogen. Because of the decreased steric requirements and electron-withdrawing capacity of the thiocyanate anion as compared with halide anions, it was of interest to attempt to isolate complexes of the type $[U(cp)(NCS)_3L_2]$ and the results are described in this paper.

Results and Discussion

Complexes of $U(cp)(NCS)_3$.—The green amide and phosphine oxide complexes $[U(cp)(NCS)_3L_2]$, where L = $Me_2CHCONMe_2$ (dmiba), dmpva, PPh_3O, and tdpo, were obtained from the filtrate of the reaction of UCl_4 with the stoicheiometric quantities of Tl(cp), K(NCS), and the ligand in thf [equation (i)]. The compounds are soluble in thf, MeCN,

$$UCl_4 + Tl(cp) + 3\,K(NCS) + 2\,L \longrightarrow [U(cp)(NCS)_3L_2] + 3\,KCl\downarrow + TlCl\downarrow \quad (i)$$

and CH_2Cl_2, and are slightly soluble in benzene and toluene, but are insoluble in other hydrocarbons. $[U(cp)(NCS)_3(thf)_2]$ was not obtained from thf solution, and the products from the reaction were found to contain variable amounts of KCl. In one instance the analytical results were close to the values expected for $K[U(cp)(NCS)_3Cl(thf)_2]$, but this was not reproducible. With dma, dmpa, $EtCONEt_2$ (depa), pyridine (py), or 2,2′-bipyridyl (bipy) as the added ligand, disproportionation to $[U(cp)_3(NCS)]$ and a complex of $U(NCS)_4$ occurred. With dma the known[7] complex $[U(NCS)_4(dma)_4]$ was isolated, while with bipy a product of composition close to $[U(NCS)_4(bipy)_3]$ was obtained. Disproportionation also occurred in the attempted preparation of the dmpa and depa complexes from the known[8] UCl_4 analogues by reaction with the stoicheiometric quantities of K(NCS) and Tl(cp) in thf. No identifiable products could be obtained when 2,6-dimethylpyridine was used as the ligand.

In the i.r. spectra of the complexes $[U(cp)(NCS)_3L_2]$ (Table 1) the characteristic C_5H_5 ring modes appeared at 1 015—1 020 and 790—798 cm^{-1}. The splitting of the C=O stretching feature in the i.r. spectrum of $[U(cp)(NCS)_3(dmpva)_2]$ implies the presence of both strongly [ν(CO), 1 555 cm^{-1}] and weakly bonded [ν(CO), 1 615 cm^{-1}] dmpva. Dissolution of the compound in thf and reprecipitation of the complex with 2-methylbutane, which is miscible with dmpva, did not change the i.r. spectrum in any way, and the split feature was also observed when the complex was prepared from $[UCl_4(dmpva)_2]$ instead of UCl_4. The ^1H n.m.r. spectrum of the complex in CD_2Cl_2 did not provide any evidence for free dmpva, but this would not be conclusive if the exchange between free and bonded ligand was fast on the n.m.r. time-scale. The shifts observed for ν(PO) (L = PPh_3O or tdpo) and ν(CO) (L = dmpva) in the i.r. spectra were appreciably greater than those observed for the corresponding complexes of $U(NCS)_4$ with the phosphine oxides[9] or dmpva,[10] whereas the shift in ν(CO) for the dmiba complex is of the same order as that reported for $[U(NCS)_4(dmiba)_4]$.[10] The C–N stretching mode appears at 2 000—2 020 cm^{-1} in the i.r. spectra of the complexes, which is on the borderline for distinguishing between sulphur and nitrogen bonding in thiocyanates;[11] however, this feature is of relatively high intensity in each case, which suggests that the thiocyanate groups are nitrogen bonded.[12,13] The C–S feature in the i.r. spectra of *N*-bonded thiocyanates usually appears between 760 and 880 cm^{-1}, as against 700 cm^{-1} for *S*-bonded thiocyanates,[14,15] but this feature could not be identified owing to interference from features arising from the organic ligands.

Table 1. Infrared spectral data (cm^{-1}) for the complexes

Complex	ν(X=O)^{a}	Δν(X=O)^{a}	ν(CN)	ν(U–C_5H_5)^{b}
$[U(cp)(NCS)_3(dmiba)_2]$	1 590	40	2 000	250
$[U(cp)(NCS)_3(dmpva)_2]$	1 615,^{c} 1 555	15,^{c} 75	2 010	250
$[U(cp)(NCS)_3(PPh_3O)_2]$	1 050	133	2 020, 2 000	250
$[U(cp)(NCS)_3(tdpo)_2]$	1 046	154	2 020, 2 000	265—240

^{a} X = C (amide) or P (phosphine oxide). ^{b} Metal–ring mode. ^{c} Very weak feature.

Table 2. Principal features (1 000—1 300 nm) of the u.v.–visible spectra of the complexes $[U(cp)X_3L_2]$

Complex	Solution in thf	Solid reflectance
$[U(cp)(NCS)_3(tdpo)_2]$	1 090, 1 125, 1 190	1 060, 1 100, 1 160
$[U(cp)(NCS)_3(PPh_3O)_2]$	1 100, 1 180	1010, 1 170
$[U(cp)Cl_3(PPh_3O)_2]$ *	1 111, 1 178	1 104
$[U(cp)(NCS)_3(dmpva)_2]$	1 165, 1 200	1 115, 1 185
$[U(cp)Cl_3(dmpva)_2]$ *	1 158, 1 195	1 115, 1 185
$[U(cp)(NCS)_3(dmiba)_2]$	1 140, 1 200	1 115, 1 185

* Data from ref. 2.

The principal features of the u.v.–visible spectra (solid reflectance and solution in thf) of the complexes are summarised in Table 2. These spectra are similar to those reported[2] for the complexes $[U(cp)X_3L_2]$ (X = Cl or Br), with strong features in the range 1 100—1 200 nm, consistent with a low-symmetry, high-co-ordination number ($\geqslant 8$) environment for the uranium(IV) centre.

Steric Considerations in Uranium(IV) *Complexes*.—The disproportionation of complexes of the type $[U(cp)(NCS)_3L_2]$, where L is small (thf, dma, *etc.*), as described above, and of complexes of $U(cp_2)Cl_2$,[2,16,17] as compared with the stability with respect to disproportionation of $[U(cp)(NCS)_3L_2]$, where L is relatively large (*e.g.* L = PPh_3O, tdpo, *etc.*), and of complexes of the type $[U(cp)_2Cl\{HB(pz)_3\}]$ or $[U(cp)_2\{HB(pz)_3\}_2]$[18] (pz = pyrazolyl), suggests that steric effects may play a predominant role in determining the structure, stability, and stoicheiometry of *f*-transition-metal complexes. We have found that a cone-packing model provides a useful basis for the rationalisation of the behaviour of such complexes, and the model, which will be discussed in detail in a later paper, is briefly described here.

In any discussion of steric crowding, it is essential to distinguish between *first-* and *second-order* steric crowding. The former refers to the crowding caused by the atom, or group of atoms, directly co-ordinated to the metal centre, while the latter refers to crowding caused by the remaining atoms of a co-ordinating group which are not themselves directly bonded to the metal centre. It is also necessary to distinguish between the *overall* steric effects which may lead to the instability of a given compound and the *local* steric effects which affect the arrangement of ligands around the metal centre.

Two terms are used to describe these steric effects. Firstly, the cone angle factor (c.a.f.), which is the solid angle of the cone comprising the metal centre at the apex and the primary co-ordinating atom or the complete ligand [Figure 1(*a*)], divided by 4π. Secondly, there is the fan angle which describes the crowding in the plane; this is the angle subtended by the primary co-ordinating atom (f.a.) or the whole ligand (f.a.s.) in the various symmetry planes [Figure 1(*b*)]. The term f.a.s. is the same as 'cone angle' as defined by Tolman[19] and others.[20,21]

The basis for the calculation of c.a.f. and f.a. for the η-C_5H_5 group is shown in Figure 2. The fan angle, $\theta = \tan^{-1}(R_0/b)$ and

$$\text{the cone angle factor} = \frac{1}{4\pi}\int_0^{\theta}\int_0^{2\pi}\sin\theta\cdot d\theta d\varphi = \tfrac{1}{2}(1-\cos\theta).$$

The results for 19 organometallic compounds of uranium and thorium are given in Table 3, and the average contributions for a number of co-ordinating atoms or groups are given in Table 4. From these calculations Σ c.a.f. for the 17 uranium(IV) compounds averages 0.80 (σ = 0.03). The values of Σ c.a.f. are expressed graphically in Figure 3 for the complexes of $U(cp)_nCl_{4-n}$ (n = 0—4). In this graph the lines AA′ and BB′ represent the requirements for noble-gas electron formulations equivalent to 18 and 32 electrons respectively. As one would expect, the noble-gas formalism has no relation to the stability of these compounds and it can be seen that the known compounds fall into a fairly broad belt distributed around a value Σ c.a.f = 0.80 (σ *ca.* 0.08). This is a clear indication that steric crowding is an essential factor in actinide co-ordination and organometallic chemistry.

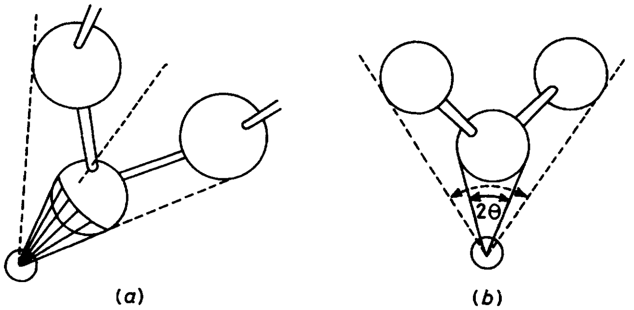

Figure 1. First- and second-order cone angles (*a*) and fan angles (*b*). When the ligand is irregular in shape, the fan angles in different planes will not be the same

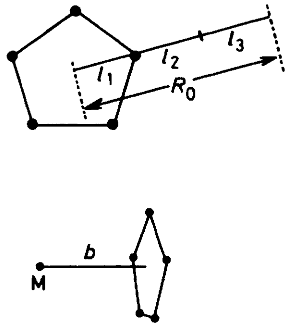

Figure 2. The basis for calculation of c.a.f. and f.a. for the η-C_5H_5 group: l_1 = distance from the centre of the ring to each carbon atom, l_2 = carbon–hydrogen bond length, and l_3 = Van der Waals radius of the hydrogen atom ($l_1 + l_2 + l_3 = R_0$); b is the distance between the ring centre and the metal atom

In the case of the complexes $[U(cp)(NCS)_3L_2]$ described earlier in this paper, the value of c.a.f. for the NCS group is much smaller than that of the Cl atom in the $[U(cp)Cl_3L_2]$ analogues, so that the isolation of the thiocyanato-complexes will be more critically dependent on the c.a.f. of the ligand L than is the case for the chloride complexes. An assessment of Σ c.a.f. for the thiocyanate complexes is illustrated in Figure 4. When L = tdpo and PPh_3O, Σ c.a.f. is 0.76 and, as described earlier, the complexes with these two ligands were isolated. However, for the amide complexes Σ c.a.f. is 0.74, so that only those amide ligands which provide secondary steric crowding owing to their bulk (dmiba and dmpva) provide isolable complexes. Similarly, with the ligands thf, py, and bipy, Σ c.a.f. is close to 0.72 and complexes with these ligands could not be isolated, in conformity with the observations on crowding and stability discussed above.

Table 3. Calculated values of c.a.f. and f.a. for some thorium(IV) and uranium(IV) organometallic compounds

Compound[a]	Co-ordination number and geometry[b]	Co-ordinating atom or group[c]	Bond length/Å	c.a.f.	f.a./°	Σ c.a.f.	Ref.
[U(cp)$_3$Cl]	10, tet.	U–cp	2.74	0.213	55	0.783	*d*
		U–Cl	2.56	0.144	45		
[U(cp)$_3$F]	10, tet.	U–cp	2.74	0.213	55	0.732	*e*
		U–F	2.32	0.093	36		
[U(cp)$_3$(C≡CH)]	10, tet.	U–cp	2.68	0.220	56	0.818	*f*
		U–C	2.33	0.158	46.5		
[U(cp)$_3$(C$_8$H$_9$)]	10, tet.	U–cp	2.73	0.213	55	0.771	*g*
		U–C	2.55	0.132	41.5		
[U(cp)$_3$(Bu^n)]	10, tet.	U–cp	2.72	0.215	55.5	0.781	*g*
		U–C	2.48	0.136	43.3		
[U(cp)$_4$]	12, tet.	U–cp	2.81	0.210	54.5	0.840	*h*
[U(η-C$_5$H$_4$Me)Cl$_3$(thf)$_2$]	8, oct.	U–cp	2.72	0.217	55.5	0.829	17
		U–Cl	2.56	0.144	45.3		
		U–O	2.45	0.090	34.8		
[U(cp)Cl$_3$(PPh$_3$O)$_2$]	8, oct.	U–cp	2.78	0.211	54.8	0.814	
		U–Cl	2.648	0.133	43		
		U–O	2.31	0.102	38		
Li$_2$[U(C$_2$B$_9$H$_{11}$)$_2$Cl$_2$]	—, tet.	U–ring (C$_2$B$_2$)	2.72	0.248	59.7	0.782	*j*
		U–Cl	2.599	0.143	44.5		
[U(cp)$_3${MeC(CH$_2$)$_2$}]	10, tet.	U–cp	2.74	0.213	55	0.775	*k*
		U–C	2.48	0.136	43.5		
[U(cp)$_3$(NCS)(NCMe)]	11, C_{3v}	U–cp	2.764	0.208	54.2	0.819	*l*
		U–N(CS)	2.407	0.109	38.5		
		U–N(CMe)	2.678	0.086	34.1		
Li[U$_2$Cl$_5${(η-C$_5$H$_4$)$_2$CH$_2$}$_2$].2thf	10, —	U–Cl	2.706	0.127	42.5	0.832	*m*
		U–Cl	2.68	0.086	39.7		
		U–ring		0.364	—		
[U{(η-C$_5$H$_4$)$_2$CH$_2$}Cl$_2$(bipy)]	10, —	U–Cl	2.706	0.127	41.7	0.788	*n*
		U–N	2.68	0.086	34.0		
		U–ring		0.364	—		
[U(BH$_4$)$_4$(thf)$_2$]	14, —	U–H	2.44	0.0537	—	0.821	*o*
		U–O	2.47	0.0881	—		
[U(BH$_4$)$_4$(OPr$^n{}_2$)]	13, —	U–H	2.41	0.055	—	0.787	*p*
		U–O	2.48	0.088			
[{U(cp)$_2$(μ-CHPPh$_2$CH$_2$)}$_2$]	9, —	U–cp	2.78	0.211	54.8	0.791	*q*
		U–C	2.537	0.129	42		
[U(cp)$_3$(pz)]	11, —	U–cp	2.762	0.212	55	0.796	*r*
		U–N (average)	2.383	0.112	39		
[{(η-Me$_5$C$_5$)$_2$Th(μ-OCMeCMeO)}$_2$]	8(9), —	Th–ring	2.845	0.261	60	0.762	*s*
		Th–O	2.154	0.120	41.4		
[(η-Me$_5$C$_5$)$_2$ThCl(OCCH$_2$CMe$_3$)]	9, —	Th–ring	2.526	0.264	60	0.809	*t*
		Th–Cl	2.672	0.131	44		
		Th–O	2.37	0.097	36		
		Th–C	2.44	0.141	45		

[a] C$_8$H$_9$ = *p*-xylyl; C$_2$B$_9$H$_{11}$ = η^5-(1,2-dicarbaundecaboranediyl. [b] tet. = tetrahedral, oct. = octahedral; a dash (—) indicates that the geometry is not definable. [c] U–cp, U–ring, and Th–ring represent bond distances to the centroid of the ring. [d] C. Wong, T. Yen, and T. Lee, *Acta Crystallogr.*, 1965, **18**, 340. [e] R. R. Ryan, R. A. Penneman, and B. Kanellakopulos, *J. Am. Chem. Soc.*, 1975, **97**, 4258. [f] J. L. Atwood, M. Tsutsui, N. Ely, and A. E. Gebala, *J. Coord. Chem.*, 1976, **5**, 209. [g] G. Perego, M. Cesari, F. Farina, and G. Lugli, *Acta Crystallogr., Sect. B*, 1976, **32**, 3034. [h] J. H. Burns, *J. Organomet. Chem.*, 1974, **76**, 2365. [i] G. Bombieri, G. de Paoli, and K. W. Bagnall, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 359. [j] J. R. Fronczek, G. W. Halstead, and K. N. Raymond, *J. Am. Chem. Soc.*, 1977, **99**, 1769. [k] G. W. Halstead, E. C. Baker, and K. N. Raymond, *J. Am. Chem. Soc.*, 1975, **97**, 3049. [l] R. D. Fischer, E. Klahne, and J. Kopf, *Z. Naturforsch., Teil B*, 1978, **33**, 1393. [m] C. A. Secaur, V. W. Day, R. D. Ernst, W. J. Kennelly, and T. J. Marks, *J. Am. Chem. Soc.*, 1976, **98**, 3713. [n] T. J. Marks, *J. Organomet. Chem.*, 1977, **138**, 157. [o] R. R. Rietz, A. Zalkin, D. H. Templeton, N. M. Edelstein, and L. K. Templeton, *Inorg. Chem.*, 1978, **17**, 658. [p] A. Zalkin, R. R. Rietz, D. H. Templeton, and N. M. Edelstein, *Inorg. Chem.*, 1978, **17**, 661. [q] R. E. Cramer, R. B. Maynard, and J. W. Gilje, *J. Am. Chem. Soc.*, 1978, **100**, 5562. [r] C. W. Eigenbrot, jun., and K. N. Raymond, *Inorg. Chem.*, 1981, **20**, 1553. [s] J. M. Manriquez, P. J. Fagan, T. J. Marks, C. S. Day, and V. W. Day, *J. Am. Chem. Soc.*, 1978, **100**, 7112. [t] T. J. Marks, J. M. Manriquez, P. J. Fagan, V. W. Day, C. S. Day, and S. H. Vollmer, in ' Lanthanide and Actinide Chemistry and Spectroscopy,' ed. N. M. Edelstein, *A.C.S. Symp. Ser.*, No. 131, 1980, p. 11.

Table 4. Average contributions of some co-ordinating atoms or groups

Co-ordinating atom or group	Bonding	Ligand–metal bond length/ Å	c.a.f.	f.a./°
C_5H_5	η^5	2.73	0.21	55
C_5Me_5	η^5	2.76	0.27	63
C	σ-Alkyl	2.48	0.136	43
C	σ-Alkyne	2.33	0.158	46
O	$(\gtrdot\mathrm{P}){=}\mathrm{O}$	2.24	0.11	39
O	$(>\mathrm{C}){=}\mathrm{O}$ (Amide)	2.31	0.10	36
O	$\gtrdot\mathrm{C{-}O{-}C}\lessdot$ (Et_2O,thf)	2.48	0.09	33
N	Anion (NCS^-)	2.41	0.11	39
N	Neutral (NCMe, py, bipy)	2.68	0.085	33
Cl	Terminal	2.60	0.14	44
Cl	Bridging	2.86	0.11	40
F	Terminal	2.32	0.093	36

Table 5. Analytical results (%) *

Complex	U	C	H	N	S
$[U(cp)(NCS)_3(dmiba)_2]$	32.3 (33.6)	33.9 (33.9)	4.7 (4.4)	10.1 (9.9)	14.6 (13.6)
$[U(cp)(NCS)_3(dmpva)_2]$	32.5 (32.4)	36.2 (35.9)	5.4 (4.8)	9.8 (9.5)	12.8 (13.1)
$[U(cp)(NCS)_3(PPh_3O)_2]$	22.1 (23.0)	50.3 (51.2)	3.7 (3.4)	3.6 (4.0)	9.2 (9.3)
$[U(cp)(NCS)_3(tdpo)_2]$	27.5 (28.5)	29.2 (28.9)	5.3 (4.9)	14.7 (15.1)	12.0 (11.5)

* Calculated values are given in parentheses.

Experimental

All of the experimental work, including the drying of solvents and the handling of air- and moisture-sensitive products, was carried out as described previously.[22] UCl_4,[23] Tl(cp),[24] and the amides used as ligands [25] were prepared by published methods. PPh_3O (B.D.H., Ltd.) was used as supplied and tdpo (Koch-Light, Ltd.) was distilled under reduced pressure before use.

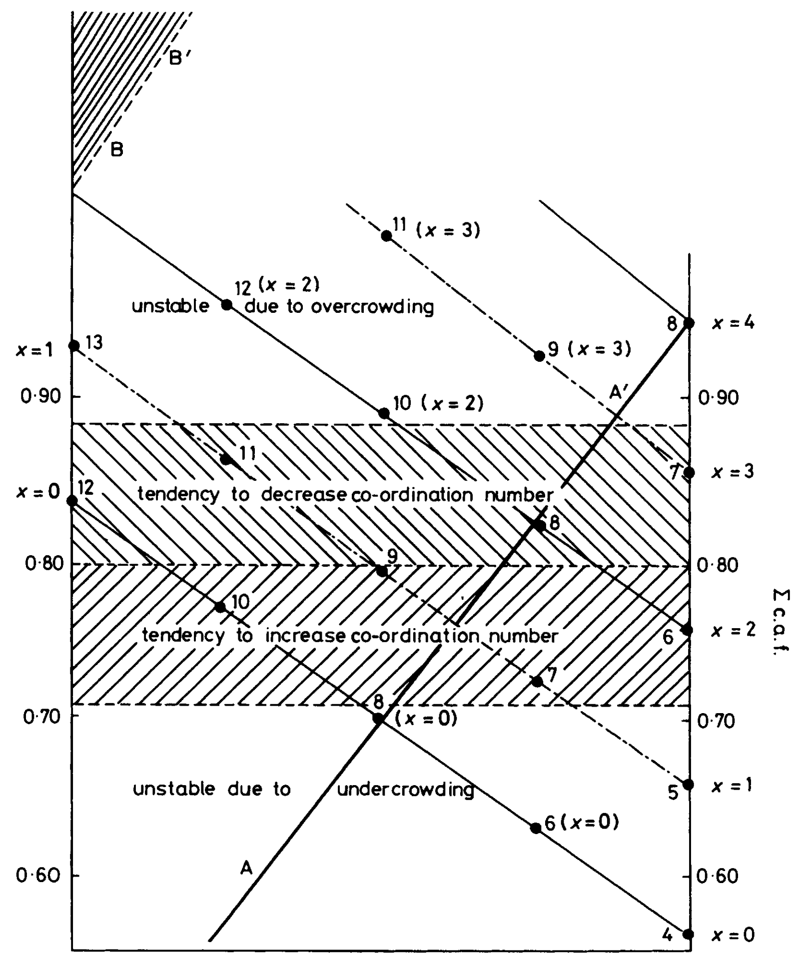

Figure 3. Steric effects in cyclopentadienyl chloro-uranium(IV) complexes with oxygen-donor ligands. The numbers within the diagram refer to the co-ordination numbers of the uranium atoms in the complexes

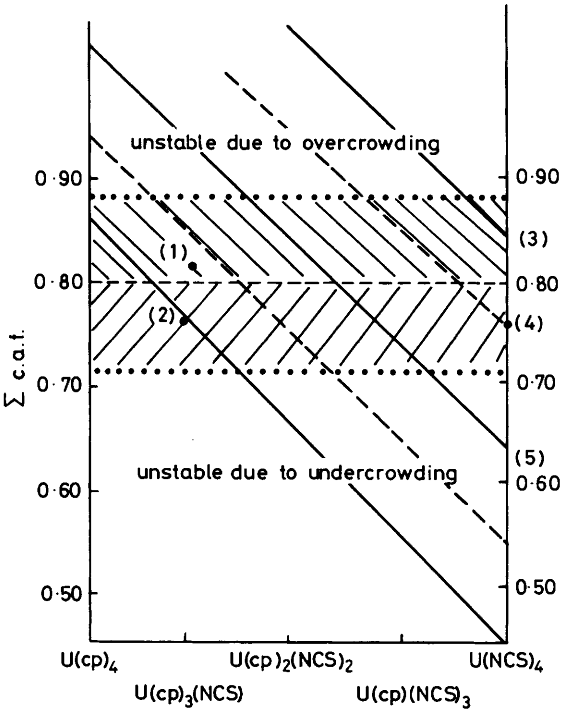

Figure 4. Values of c.a.f. for cyclopentadienyl thiocyanato-uranium(IV) complexes with neutral ligands (L = PPh_3O, tdpo, thf, py, bipy, dma, dmpa, depa, dmpva, and dmiba): (1) $[U(cp)_3(NCS)(NCMe)]$, (2) $[U(cp)_3(NCS)]$, (3) $[U(NCS)_4L_4]$ or $[U(NCS)_8]^{4-}$, (4) $[U(NCS)_4L_3]$ or $[U(NCS)_7]^{3-}$, (5) $[U(cp)_n(NCS)_{4-n}L_2]$ (n = 0—4)

Hydrogen-1 n.m.r. spectra and other physical measurements were carried out as described previously.[22,25]

Preparations.—(η-*Cyclopentadienyl*)*tri-iso-thiocyanatobis*(*triphenylphosphine oxide*)*uranium*(IV). Uranium tetrachloride (2.6744 g, 7.04 mmol) was dissolved in thf (50 cm³) and K(NCS) (2.0529 g, 21.12 mmol) and Tl(cp) (1.8963 g, 7.04 mmol) were added to the solution. After stirring for 0.5 h, PPh_3O (3.9192 g, 14.08 mmol) was added, and the mixture was stirred for 72 h. After centrifugation, the supernatant was evaporated to dryness *in vacuo*, and the residue was triturated with n-pentane and dried *in vacuo* to yield the green *product* (yield, 50%).

$[U(cp)(NCS)_3(tdpo)_2]$, $[U(cp)(NCS)_3(dmiba)_2]$, and $[U(cp)(NCS)_3(dmpva)_2]$ were prepared in the same way (yields of the green *products*, 50, 55, and 55% respectively). Analyses (Table 5) were obtained as described previously.[22]

Acknowledgements

We thank Mr. M. A. Hart for the microanalyses (C, H, N, S, and U) and the Government of the People's Republic of China for support (to L. X-f.).

References

1 L. Doretti, P. Zanella, G. Faraglia, and S. Faleschini, *J. Organomet. Chem.*, 1972, **43**, 339.
2 K. W. Bagnall, J. Edwards, and A. C. Tempest, *J. Chem. Soc., Dalton Trans.*, 1978, 295.
3 K. W. Bagnall and J. Edwards, *J. Organomet. Chem.*, 1974, **80**, C14.
4 F. Benetollo, G. Bombieri, G. de Paoli, P. Zanella, and K. W. Bagnall, 9th International Conference on Organometallic Chemistry, Dijon, France, 1979.
5 G. Bombieri, G. de Paoli, A. Del Pra, and K. W. Bagnall, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 359.
6 K. W. Bagnall, *Proc. 11éme Journées des Actinides, Jesolo*, 1981, 14.
7 K. W. Bagnall, D. Brown, and R. Colton, *J. Chem. Soc.*, 1964, 2527.
8 K. W. Bagnall, R. L. Beddoes, O. S. Mills, and Li Xing-fu, preceding paper.
9 Z. M. S. Al-Kazzaz, K. W. Bagnall, and D. Brown, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1501.
10 K. W. Bagnall, Li Xing-fu, G. Bombieri, and F. Benetollo, *J. Chem. Soc., Dalton Trans.*, 1982, 19.
11 A. Sabatini and I. Bertini, *Inorg. Chem.*, 1965, **4**, 1665; 1966, **5**, 1025.
12 S. Fronaeus and R. Larsson, *Acta Chem. Scand.*, 1962, **16**, 1447.
13 C. Pecile, *Inorg. Chem.*, 1966, **5**, 210.
14 J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 1961, 4590.
15 A. Turco and C. Pecile, *Nature* (*London*), 1961, **191**, 66.
16 B. Kanellakopulos, C. Aderhold, and E. Dornberger, *J. Organomet. Chem.*, 1974, **66**, 447.
17 R. D. Ernst, W. J. Kennelly, C. S. Day, V. W. Day, and T. J. Marks, *J. Am. Chem. Soc.*, 1979, **101**, 2656.
18 K. W. Bagnall, A. Beheshti, J. Edwards, F. Heatley, and A. C. Tempest, *J. Chem. Soc., Dalton Trans.*, 1979, 1241.
19 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
20 J. D. Smith and J. D. Oliver, *Inorg. Chem.*, 1978, **17**, 2585.
21 G. Ferguson, P. J. Roberts, E. C. Alyea, and M. Khan, *Inorg. Chem.*, 1978, **17**, 2965.
22 K. W. Bagnall, J. Edwards, J. G. H. du Preez, and R. F. Warren, *J. Chem. Soc., Dalton Trans.*, 1975, 140.
23 J. A. Herman and J. F. Suttle, *Inorg. Synth.*, 1957, **5**, 143.
24 E. O. Fischer, *Angew. Chem.*, 1957, **69**, 207.
25 K. W. Bagnall, J. G. H. du Preez, J. Bajorek, L. Bonner, H. Cooper, and G. Segal, *J. Chem. Soc., Dalton Trans.*, 1973, 2682.

Received 25*th January* 1982; *Paper* 2/143