Adducts of Uranium Tetrahalides with *N*-Donor Ligands and Properties of the Octathiocyanatouranate(IV) Anion in a Cubical Configuration

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Electronic spectra and magnetic measurements are reported for some new adducts of uranium tetrachloride and uranium tetrabromide with aromatic, alicyclic, and aliphatic amines; and for some previously reported amine adducts of uranium tetrachloride and also for the compound $[(Et_4N)_4][U(NCS)_8]$ in which the anion has a cubical configuration. The data suggest that the adducts with pyridine and piperidine may have an unusual configuration.

APART from the thiocyanate complexes [1-3] $[U(NCS)_8]^{4-}$ and $U(NCS)_4,4dma$,[†] reported complexes of uranium(IV) which contain *N*-donor ligands are adducts of uranium tetrachloride or its solvolysis product uranium trichloride ethoxide.[4] Reported adducts fall mainly into two categories: those of the type UCl_4N_2 with N provided by Me_3N,[5] py,[5,6] RNH_2 ($R = Me, Et, Pr^n$),[7] $PhNH_2$,[8] and those of the type UCl_4N_4 with N from Pr^nNH_2,[7] Bu^nNH_2,[6] pip,[6] en,[6] phen,[4] MeCN,[9] RCN ($R = Et, Pr^n, Pr^i, Ph$).[10] The complexes $UCl_4,EtNH_2$,[7] UCl_4,quin,[11] and $UX_4,3Bu^tCN$ [10] have been reported, but the compound $UCl_4,1{\cdot}5$ py [8] could not be re-prepared.[6] Also, a variety of ammonia adducts have been reported.[6,12]

We have repeated the preparation of some of these compounds and have prepared some new adducts including some with secondary amines and some of uranium tetrabromide, in order to study their spectral and magnetic properties.

EXPERIMENTAL

All the compounds described [except $T_4U(NCS)_8$] are hygroscopic and were handled in an atmosphere of dry, oxygen-free nitrogen. Uranium tetrahalides were prepared and purified as before,[10] and the ligands were carefully dried and purified by conventional methods. The complexes were typically prepared as pale green precipitates when an ethyl acetate solution of the ligand was added slowly to an ethyl acetate solution of the uranium tetrahalide. The products were dried under reduced pressure at room temperature. Analyses are in the Table.

The piperidine adducts were prepared without solvent, but reaction of uranium tetrachloride with other liquid amines in the absence of solvent was strongly exothermic, and tended to give black tars or oils. 1,8-Diaminonaphthalene and *o*-phenylenediamine also gave adducts but these could not be isolated in a state of analytical purity.[13] The preparation of the aniline adduct [8] could not be repeated [13] in ethyl acetate though when a solution of uranium tetrachloride was added to a solution of aniline a precipitate was initially formed which dissolved on further addition of uranium tetrachloride solution. Pyrrole does not appear to interact with uranium tetrachloride.

Analytical and magnetic data

	Found		Calc.				
	U	Hal	U	Hal	$\mu_{eff.}^{298}$	S [a]	$-\theta$ [a]
$UCl_4,3Me_2NH$	46·3	27·7	46·2	27·5	2·65	0·864(2)	92(1)
$UCl_4,2Et_2NH$	45·3	26·8	45·2	26·9	2·53		253 [b]
$UBr_4,2Et_2NH$	33·6	45·4	33·8	45·4	2·72		127 [b]
$UCl_4,3Pr^i_2NH$	34·6	20·6	34·8	20·7	2·71	0·79(2)	100(6)
$UCl_4,3Bu^tNH_2$	39·5	23·7	39·7	23·7	[c]		
UCl_4,2py	44·2	26·4	44·3	26·3	2·61	0·780(4)	148(2)
UBr_4,2py	44·8	33·1	44·7	33·3	2·61	0·779(3)	148(1)
UCl_4,4pip	32·8	19·8	33·1	19·7	2·89	0·818(5)	49(1)
UBr_4,4pip	26·3	35·4	26·5	35·6	2·79	0·950(5)	25(1)
UCl_4,3pyd	40·3	24·2	40·7	23·9	2·72	0·809(3)	96(1)
UBr_4,4pyd	28·1	38·1	28·3	38·0	2·85	0·758(2)	86(1)
UCl_4,2phen	32·5	19·4	32·2	19·2	2·71	0·792(8)	112(4)
UBr_4,2phen	25·9	34·6	25·9	34·8	2·60	0·82(2)	139(6)
UCl_4,2bipy	34·0	20·3	34·4	20·5	2·60	0·71(9)	180(10)
UBr_4,2bipy	27·7	36·7	27·4	36·4	2·67	0·869(5)	89(1)

[a] C.g.s. units, obtained from $1/\chi = S(T - \theta)$ by linear regression. Figures in parentheses are standard deviations in last digits. [b] Approximate values. [c] Turned mauve on standing under nitrogen.

$T_4U(NCS)_8$ is conveniently prepared in the open laboratory as follows: dissolve uranium metal in a mixture of ethanol and conc. hydrochloric acid, and add TBr to the filtered solution to give a precipitate of T_2UCl_6. T_2UCl_6 (1 mol) is mixed with KNCS (8 mol) and TBr (2 mol) in dry methyl cyanide. The precipitate of potassium halides is removed by filtration, and washed with hot methyl cyanide. The *product* is recovered by evaporating the solvent and is recrystallised from methyl cyanide, m.p. 242° (Found: C, 39·3; H, 6·6; N, 13·8. $C_{40}H_{80}N_{12}S_8U$ requires C, 39·2; H, 6·6; N, 13·7%). The compound is air-stable in the solid state, slowly oxidised by air in hot methyl cyanide and rapidly oxidised by air in hot nitromethane to give *tetraethylammonium dioxopentathiocyanatouranate*(VI) *monohydrate*, m.p. 195—196° (Found: C, 36·0; H, 6·45; N, 11·5. $C_{29}H_{62}N_8O_3S_5U$ requires C, 36·3; H, 6·45; N, 11·5%).

Magnetic data and electronic spectra were obtained as before.[10] The magnetic susceptibility measured at 5800,

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[†] Abbreviations used: dma, *NN*-dimethylacetamide; bipy, 2,2′-bipyridyl; phen, 1,10-phenanthroline; py, pyridine; pip, piperidine; en, ethylenediamine; quin, quinoline; pyd, pyrrolidine; T, tetraethylammonium (Et_4N); thf, tetrahydrofuran.

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[13] Similar observations are reported in ref. 6.

6700, and 7000 G was independent of field strength in all cases and could be fitted to the Curie–Weiss expression $1/\chi = S(T - \theta)$ over the temperature range studied (100—300 K) with the exception of $T_4U(NCS)_8$. The susceptibility is therefore defined by the parameters S and θ given in the Table.

RESULTS AND DISCUSSION

Previous preparations of amine complexes of uranium tetrachloride were achieved in butyl acetate as solvent [8] or by reaction of the tetrachloride with pure amines at low temperatures. Ethyl acetate was found to be a suitable solvent for these preparations as it forms solvates from which the solvent is easily displaced by amines to give, for the most part, insoluble products. The adducts $UCl_4,2EtNH_2$ and $UCl_4,2Et_2NH$ have also been prepared in a similar manner elsewhere, though the latter compound appeared to be ferromagnetic.[14] Our diethylamine adduct had a field-independent moment.

If the amine solution was added too rapidly to the tetrahalide solution oily products were obtained but these could often be converted into microcrystalline solids by repeated washings with ethyl acetate. Addition of the uranium tetrahalide solution to the amine solution tends to give black products of indefinite composition, but which appear to be ammonolysed. It therefore appears that the uranium tetrahalides are easily ammonolysed in the presence of excess of amine. Similarly solvolysed products are obtained when uranium tetrachloride reacts with the higher alcohols.[15] Presumably the extent of solvolysis is greater with the amines because of their higher basicity.

The stoicheiometry of the complexes formed can be rationalised in terms of the electroneutrality principle. Thus, if the metal–donor bond is considered to be predominantly electrostatic, the number of donors is limited by the extent to which the electric charge on the uranium atom is neutralised by contributions from the donor atoms. This contribution depends upon the ' donor power ' of the ligand, *i.e.* its Lewis basicity. A useful measure of the ' donor power ' of a ligand is its donor number DN_A, a number directly derived from the enthalpy of the reaction of the ligand with an acceptor molecule A.[16] The fact that there is a good correlation between stoicheiometry and donor number for a variety of ligands, as shown first by du Preez *et al.*,[17] is evidence that the foregoing assumptions are valid for complexes of uranium tetrahalides.

2 : 1 Complexes are formed with the most basic amines, pyridine and diethylamine. Dimethylamine, which is presumably less basic than the ethyl homologue because the methyl group is a weaker electron donor than the ethyl group, gives a 3 : 1 complex. This behaviour is similar to the case of the phosphine oxides, where octahedral 2 : 1 complexes are always formed with the single exception of trimethylphosphine oxide which also forms a 3 : 1 adduct.[18-21] Primary amines appear to give 4 : 1 adducts.[7]

Exceptions to the simple rule occur when factors such as steric hindrance or the chelate effect become important. Thus, the chelating ligands bipyridyl and *o*-phenanthroline presumably form complexes of the 4 : 1 type though the basicity of the ligands is not very different from that of pyridine. It is possible that di-isopropylamine and di-*tert*-butylamine are sterically hindered from forming 4 : 1 complexes.

With pyrrolidine the tetrachloride forms a 3 : 1 adduct and the tetrabromide forms a 4 : 1 adduct. This difference, which has been noted with other types of ligand such as sulphoxides,[22] implies that the tetrabromide is a better acceptor than the tetrachloride, contrary to what one expects on steric grounds. However, since the bromide ion is a poorer donor than the chloride ion,[16] the tetrabromide should be a better acceptor than the tetrachloride on the basis of the electroneutrality principle, as the electric charge on its uranium atom should be larger.

The donor number of ethyl acetate ($DN_{SbCl_5} = 17{\cdot}1$) is similar to that of acetone ($DN_{SbCl_5} = 17{\cdot}0$) and tetrahydrofuran ($DN_{SbCl_5} = 20{\cdot}0$). As the latter two ligands form 3 : 1 complexes the ethyl acetate complex UX_42L is unlikely to be octahedral. However, ethyl acetate is displaced easily by amines to form the complexes reported here, because the amines have a much higher donor number (*e.g.* for pyridine $DN_{SbCl_5} = 33{\cdot}1$). In general the solvent should have as low a donor number as possible so that solubility effects being favourable, acetonitrile ($DN_{SbCl_5} = 14{\cdot}1$) might be a better general purpose solvent for preparing adducts of the actinide halides.

The salt $T_4U(NCS)_8$ is particularly interesting since the uranium atom is surrounded by an almost regular cube of nitrogen atoms in the crystalline state, with the uranium atoms at sites of D_{4h} crystallographic symmetry.[23] It has been suggested [23] that a specific interaction between anion and cations causes this unusual configuration to be adopted, since i.r. evidence suggests that other salts of the $U(NCS)_8^{4-}$ anion do not have this structure.[2] The properties of the tetraethylammonium salt may therefore help to identify cubical co-ordination in other uranium(IV) compounds.

The reflectance spectrum of $T_4U(NCS)_8$ is of the ' medium ' type [20] but in methyl cyanide the molar extinction coefficients are comparable with those of octahedral complexes,[21] Figure 1. This suggests that the electronic transitions are Laporte-forbidden and that a centrosymmetric configuration persists in solution in

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which, perhaps, each anion is associated with four cations arranged ' equatorially ' as in the crystal.

The plot of the inverse of the magnetic susceptibility of $T_4U(NCS)_8$ against temperature is distinctly curved, Figure 2, and the curvature cannot be eliminated by supposing that it originates from a simple temperature independent susceptibility contribution (second-order Zeeman effect).[24] Crude extrapolation to $1/\chi = 0$ gives a Weiss constant θ *ca.* $-35°$ and consequently μ_{eff} varies little with temperature. However, a theoretical study[25] has shown that an f^2 electronic configuration in a cubical ligand field should give a first-order effective magnetic moment (accidently) equal to the spin-only value of 2·83 B.M., independent of temperature. The nitrogen ligand atoms in $T_4U(NCS)_8$ are disposed at the vertices of a cube, within the precision of the X-ray structure determination.[23] It is therefore clear that second order Zeeman effects are important in cubical uranium(IV) compounds, thought not as important as in octahedral compounds which show (only) a larger temperature-independent susceptibility.[25] These results on $T_4U(NCS)_8$ are closely similar to results obtained for UO_2 dissolved in ThO_2 in which the co-ordination at uranium is strictly cubical.[26] Extrapolation to zero uranium content gave $\mu_{eff} = 2{\cdot}9$ B.M. at 238 K and $\mu_{eff} = 2{\cdot}7$ B.M. at 83 K.

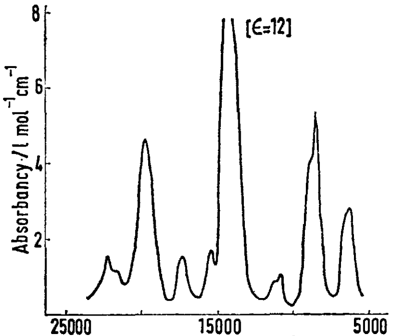

FIGURE 1 Electronic absorption spectrum of $(Et_4N)_4\,[U(NCS)_8]$ in MeCN solution. The diffuse reflectance spectrum of the solid is very similar

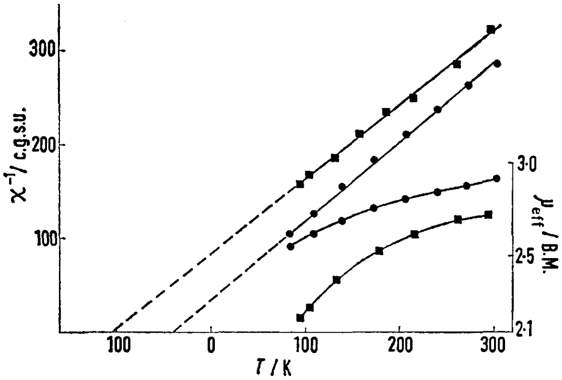

FIGURE 2 Magnetic susceptibility and effective moments for $(Et_4N)_4[U(NCS)_8]$, ●; and $K_4[U(NCS)_8]$, ■ (ref. 1)

In the second order Zeeman effect the ground term is mixed in with higher electronic terms of the same symmetry, and the exact result depends on the term separation relative to kT.[24] In a cubical field of O_h symmetry the $\Gamma_5(T_{2u})$ component of the $^3H_4$ term probably lies lowest,[25] and this can mix with both $\Gamma_3(E_u)$ and $\Gamma_4(T_{1u})$ terms which also originate from $^3H_4$, under the influence of magnetic field. In fields of lower symmetry the degeneracy of the T_{1u} and T_{2u} terms must be lifted so the number of possible second-order interactions increases. The susceptibility of the potassium salt $K_4U(NCS)_8$ is lower than that of the tetraethylammonium salt at a given temperature, Figure 2, and the moment varies more with temperature.[1] The difference in magnetic behaviour between the two isomeric forms of the anion must thus be due largely to second order effects. A small Weiss constant may be an indication of a cubical crystal field, but small Weiss constants are sometimes observed in compounds whose configuration cannot be cubical, *e.g.* UBr_4, $\theta = -35$ K,[27] $UCl_4 2Pr^iCN$, $\theta = -37$ K,[10,22] or UBr_4,3thf, $\theta = -20$ K.[22] The low θ value for the piperidine adducts (Table) may well signify an unusual configuration. In fact the α-hydrogen atoms are so placed as to perhaps exert a significant influence on the stereochemistry of the complexes.

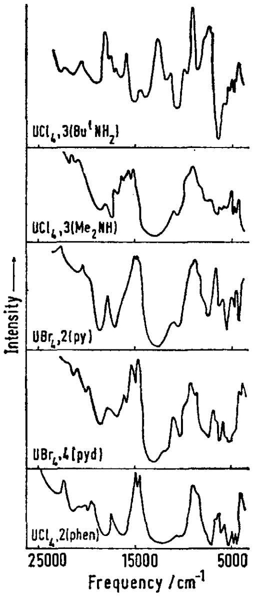

FIGURE 3 Some typical diffuse reflectance spectra of N-adducts of UCl_4 and UBr_4

Octahedral complexes exhibit ' weak ' electronic spectra with a distinctive and characteristic pattern of bands, while most also show a temperature-independent

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magnetic susceptibility.[19-21] The bispyridine adducts do not exhibit electronic spectra characteristic of an octahedral complex, Figure 3, and their susceptibility obeys the Curie–Weiss law. It is therefore unlikely that the pyridine adducts are octahedral, though no alternative structure can be proposed on the basis of the present evidence.

The diffuse reflectance spectra shown in Figure 3 are typical for amine adducts and belong to the ' medium ' category,[20] but do not show any regularities in the fine structure of the bands. The amine adducts are therefore different from sulphoxide [20,22] and nitrile [10] adducts which show ' strong ' spectra, and this probably arises from the fact that the amines are the most strongly basic of these ligands, and therefore cause the greatest crystal field splitting of the J levels. The wide variety of magnetic behaviour amongst the UX_4N_4 type of complex further suggests that crystal field splitting is significant in these compounds and that both first and second order Zeeman effects may be important. More detailed interpretation of the spectral and magnetic data must clearly await further structural determinations by X-ray methods.

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