Adducts of Uranium Tetrahalides and Organic Nitriles

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The compounds UX_4,4RCN with X = Cl, Br, R = Me, Et, Pr^n, Pr^i, Bu^n, and Ph and UX_4,3Bu^tCN have been prepared. The visible spectra and magnetic properties of the 4 : 1 adducts are consistent with an eight-co-ordinate configuration at the uranium atom.

THE compounds UCl_4,4MeCN and UBr_4,4MeCN have been prepared by the reaction of the appropriate tetrahalide with methyl cyanide, and their magnetic susceptibilities have been measured between 100 and 300 K,[1] following an earlier (erroneous) report of the preparation of the compound UCl_4,2MeCN.[2] We now extend these observations to include adducts with other aliphatic and aromatic nitriles.

EXPERIMENTAL

All the compounds described are hygroscopic and were handled in an atmosphere of dry, oxygen-free nitrogen. Uranium tetrachloride[3] was purified by sublimation at 500 °C at *ca.* 10^{-4} mmHg. Uranium tetrabromide was prepared by allowing uranium turnings to react with bromine in a glass tube at 500 °C under the vapour pressure of bromine at −25 °C. Under these conditions the pure tetrabromide, when formed, sublimes directly out of the reaction zone. The nitriles were carefully dried and purified by conventional methods and stored over molecular sieve. The adducts were prepared as follows.

TABLE 1

Analytical and magnetic data

	Found (%)		Reqd. (%)				
	U	Halide	U	Halide	μ_{eff}^{298}/B.M.	$-\theta$/K[a]	S[a,b]
UCl_4,4MeCN	43·7	26·0	43·7	26·1	2·89	158(4)	0·619(8)
UBr_4,4MeCN	32·9	44·2	33·0	44·3	2·78	148(2)	0·685(4)
UCl_4,4EtCN	39·6	23·7	39·7	23·6	2·88	204(9)	0·560(10)[c,d]
UBr_4,4EtCN	30·6	41·1	30·6	41·1	2·89	196(2)	0·567(4)[c,e]
UCl_4,4Pr^nCN	36·1	21·4	36·3	21·6	2·90	150(2)	0·623(3)
UBr_4,4Pr^nCN	28·4	38·5	28·5	38·4	2·92	146(3)	0·619(5)
UCl_4,4Pr^iCN	36·3	21·8	36·3	21·6	2·81	152(3)	0·614(5)
UBr_4,4Pr^iCN	28·6	38·5	28·5	38·4			
UCl_4,4Bu^nCN	33·5	19·8	33·4	19·9	2·81	163(3)	0·646(6)
UBr_4,4Bu^nCN	26·5	36·0	26·7	35·9	2·81	91(3)	0·710(8)
UCl_4,3Bu^tCN	38·2	22·5	37·9	22·5	2·63	277(4)	0·598(6)[c,f]
UBr_4,3Bu^tCN	29·7	39·3	29·5	39·6			
UCl_4,4PhCN	30·0	17·8	30·0	17·9	2·87	122(2)	0·681(4)
UBr_4,4PhCN	24·4	32·7	24·7	32·9	2·91	151(2)	0·621(4)

[a] Figures in brackets are the standard deviations and refer to the last digits of the number. [b] $1/\chi_A = S(T - \theta)$, c.g.s. units. [c] Based on susceptibilities at high temperatures only. [d] χ_A Increased from 3540 × 10^{-6} at 294 K to 5832 × 10^{-6} at 98 K. [e] χ_A Increased from 3567 × 10^{-6} at 294 K to 5945 × 10^{-6} at 98 K. [f] χ_A Increased from 2938 × 10^{-6} at 294 K to 4745 × 10^{-6} at 98 K.

The liquid ligand (*ca.* 10 ml) was added to the uranium tetrahalide (*ca.* 4 g). The mixture was cooled if the reaction was strongly exothermic or warmed if the reaction was slow and was then allowed to stand at room temperature for *ca.* 1 h with occasional stirring. The sparingly soluble product was washed by decantation with pure ligand, and dried at *ca.* −5 °C under reduced pressure. Analyses are in Table 1. Uranium was determined by titration against cerium(IV) and halide gravimetrically.

With some nitriles adducts with variable ligand : uranium ratios of less than 4 : 1 were obtained, but conditions for the preparation of pure compounds of this type could not be reproduced, as all the adducts tend to lose ligand under reduced pressure, particularly at elevated temperatures. However, *tetrachlorobis(isopropyl cyanide)uranium*(IV) was consistently formed when the 4 : 1 adduct was warmed to 40 °C at *ca.* 15 mmHg pressure, for *ca.* 1 h (Found: Cl, 27·0; U, 45·95. $C_8H_{14}Cl_4N_2U$ requires Cl, 27·4; U, 45·95%).

Reflectance spectra 4000—25,000 cm^{-1} were obtained on a Unicam SP 700 spectrophotometer, using the SP 735 diffuse reflectance attachment and magnesium oxide as standard. Observed band frequencies are given in Table 2 and some typical spectra in the Figure.

Magnetic susceptibilities were measured between 98 and 300 K on a Stanton SM12 Gouy balance calibrated with HgCo$(NCS)_4$.† The susceptibilities were corrected for diamagnetism and were independent of field strength in all cases. The slope, S, of the plot of inverse atomic susceptibility, $1/\chi_A$ against absolute temperature, T, where $1/\chi_A = S(T - \theta)$, was determined by a standard least-squares program, and the value of the Weiss constant, θ, and its standard error were obtained by extrapolation to $1/\chi_A = 0$ using S and the intercept (on the $1/\chi_A$ axis) and their standard errors. Effective magnetic moments, calculated as $\mu_{eff}^{293} = 2{\cdot}83\sqrt{293\chi_A}$, S, and θ are included in Table 1.

The susceptibilities of UCl_4,4EtCN, UCl_4,4EtCN, and UCl_4,3Bu^tCN deviate significantly from Curie–Weiss behaviour, as shown in Table 1. Because of the large value of θ, μ_{eff} decreases to *ca.* 1·75 B.M. at 80 K for most compounds.

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† We thank Dr. A. Earnshaw for the calibration and use of this instrument.

[1] K. W. Bagnall, D. Brown, and P. J. Jones, *J. Chem. Soc.* (*A*), 1966, 1763.

[2] P. Gans, Ph.D. Thesis, University of London, 1964.

[3] J. A. Herman and J. F. Suttle, *Inorg. Synth.*, 1957, **5**, 143.

TABLE 2

Spectral band positions (10^{-3} × frequency/cm^{-1}) and intensities (0—1 on arbitrary scale)

Term [a]	UCl_4,4MeCN	UCl_4,4EtCN	UCl_4,4Pr^{i}CN	UCl,4Bu^{n}CN	UBr_4,4EtCN	UBr_4,4Pr^{n}CN	UBr_4,4PhCN
					4·04 (0·54)	4·06 (0·64)	4·08 (0·89)
$^3F_2$	4·18 (0·60)	4·25 (0·82)	4·29 (0·92)	4·18 (0·75)	4·29sh (0·38)	4·29sh (0·51)	4·58 (0·84)
	4·35 (0·58)	4·36 (0·82)		4·36 (0·73)			
	4·62 (0·50)	4·59 (0·79)					4·65sh (0·77)
	4·73 (0·52)	4·76 (0·74)	4·75 (0·82)	4·75 (0·71)			4·82sh (0·55)
	4·93 (0·30)	5·00 (0·51)	5·00sh (0·53)	5·22 (0·72)			
$^3H_5$	5·88sh (0·53)	5·82sh (0·74)	5·88sh (0·86)	5·83sh (0·72)		5·91 (0·47)	5·89 (0·87)
	5·97 (0·62)	5·94 (0·80)	5·95 (0·90)	5·96 (0·77)	5·92 (0·44)	5·98 (0·92)	
	6·69 (0·79)	6·71 (0·92)	6·71 (0·96)	6·73 (0·97)	6·58 (0·81)	6·58 (0·60)	6·58 (0·93)
$^3F_3$	8·40sh (0·73)	8·45sh (0·89)	8·48sh (0·95)	8·44sh (0·86)	8·46sh (0·81)	8·46sh (0·80)	8·33sh (0·94)
	8·76 (0·85)	8·79 (0·96)	8·77 (0·97)	8·77 (0·92)		8·66 (0·85)	8·62sh (0·97)
$^3F_4$	9·35sh (0·73)	9·35sh (0·91)	9·39sh (0·95)	9·39sh (0·88)	9·11sh (0·80)	9·11sh (6·78)	9·26sh (0·94)
$^3H_6$	11·11 (0·57)	11·11 (0·79)	11·14 (0·86)	11·05 (0·71)	11·07 (0·35)	11·09 (0·33)	10·93 (0·87)
	14·60 (0·78)	14·64 (0·93)	14·66 (6·98)	14·71sh (0·91)	14·77 (0·88)	14·75 (0·87)	14·71 (0·99)
	14·97 (0·90)	14·99 (0·99)	14·97 (1·00)	14·93 (0·94)	14·99 (0·87)	14·97 (0·87)	14·97 (0·99)
$^3P_0$, $^1G_4$	15·38 (0·88)	15·38 (0·97)		15·36 (0·94)	15·38 (0·67)	15·38 (0·64)	15·38 (0·96)
	15·58 (0·84)	15·58 (0·96)		15·55 (0·92)	15·67 (0·56)	15·67 (0·53)	15·63 (0·93)
	15·75 (0·77)	15·75 (0·95)	15·75 (0·98)	15·70sh (0·90)			
$^1D_2$	16·26 (0·59)	16·39 (0·80)	16·45 (0·88)	16·37 (0·80)	16·13 (0·32)	16·10 (0·27)	16·13 (0·87)
$^3P_1$	17·86 (0·69)	17·89 (0·89)	17·89 (0·89)	17·86 (0·82)	17·48 (0·69)	17·48 (0·71)	17·45 (0·95)
$^1I_6$	19·69 (0·69)	19·47 (0·89)	19·53 (0·95)	19·61 (0·84)	19·65 (0·71)	19·49 (0·69)	19·42 (0·95)
	20·41 (0·78)	20·53 (0·92)	20·49 (0·97)	20·53 (0·84)	20·20 (0·77)	20·12 (0·73)	20·12 (0·96)
$^3P_2$	22·73 (0·78)	22·83 (0·93)	22·73 (0·97)	22·83 (0·93)	22·32 (0·77)	22·32 (0·73)	22·32 (0·96)

[a] Assignments as in P. Gans, B. J. Hathaway, and B. C. Smith, *Spectrochim. Acta*, 1965, **21**, 1589.

The i.r.-active vibration frequency ν(C–N), measured on a Perkin-Elmer 457 spectrophotometer, rose by *ca.* 25 cm^{-1} from the value for the free ligand for all nitrile adducts.

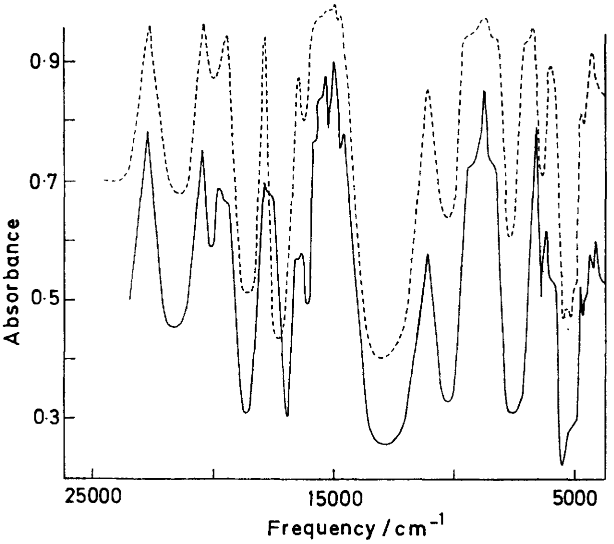

FIGURE 1 Diffuse reflectance spectra of some typical 4 : 1 adducts; solid line, UCl_4,4MeCN; broken line, UCl_4,4Pr^{i}CN

DISCUSSION

The complexes of uranium tetrachloride and tetrabromide with organic nitriles are weak: they can easily be dissociated into tetrahalide and free nitrile by the action of heat. Bagnall *et al.*[1] obtained no evidence for thermally stable complexes between MX_4,4MeCN and MX_4. Our results show that adducts with other nitriles probably behave similarly with respect to dissociation, with the possible exception of the Pr^{i}CN adduct. With Bu^{t}CN, however, the 4 : 1 adducts cannot be formed, presumably because this ligand is so bulky that a 4 : 1 complex is sterically impossible.

The observed rise in ν(C–N) upon co-ordination indicates that all the ligands are co-ordinated, but this rise cannot be interpreted unambiguously in terms of changes in the C–N bond strength, since it could result mainly from kinematic coupling.

It is striking that almost all the nitrile adducts have a 4 : 1 stoicheiometry. With neutral monodentate ligands this stoicheiometry has been reported in UCl_4,4piperidine,[4] UCl_4,4Bu^nNH_2,[4] UCl_4,4ROH (R = Me, Et, Pr),[5] UCl_4,4$POCl_3$,[6] but with phosphine oxides and arsine oxides octahedral 2 : 1 adducts are formed [7-9] whereas with organic sulphoxides 3 : 1, 5 : 1, and 7 : 1 adducts may be prepared.[10] Although in many cases the relationship between stoicheiometry and co-ordination number is uncertain, uranium(IV) shows a marked tendency toward eight-co-ordination. There does not appear to be a rational explanation for the variation of stoicheiometry (or co-ordination number) amongst the various adducts.*

The diffuse reflectance spectra of the 4 : 1 nitrile adducts conform to the 'strong' type of spectrum

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* It has recently been suggested (J. G. H. du Preez and C. P. J. van Vuuren, *J. S. African Chem. Inst.*, 1971, **24**, 149) that the number of ligands attached to an uranium tetrahalide moiety can be directly correlated with the base strength of the ligand, as measured by the enthalpy of reaction of the ligand with antimony pentachloride of phenol. This correlation could be rationalized in terms of the electroneutrality principle: the number of attached ligands is limited by the extent to which negative charge builds up on the uranium atom.

[4] J. Selbin, M. Schober, and J. D. Ortego, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1385.

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[7] P. Gans and B. C. Smith, *J. Chem. Soc.*, 1964, 4172.

[8] J. P. Day and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 197.

[9] B. C. Lane and L. M. Venanzi, *Inorg. Chim. Acta*, 1969, **3**, 239.

[10] K. W. Bagnall, D. Brown, D. H. Holah, and F. Lux, *J. Chem. Soc.* (*A*), 1968, 465.

previously described.[11] This type of spectrum is observed in many compounds in which the uranium atom is known to be eight-co-ordinated and it is, therefore, very likely that this is so in the nitrile adducts. While a square antiprism is the most likely configuration of the ligand atoms on electrostatic grounds, solid UCl_4 which does not have this configuration has a ' strong ' spectrum.

The magnetic susceptibility data for the 4 : 1 nitrile adducts are similar to each other, and in agreement with previous observations.[1] Indeed, since the (systematic) packing error amounts to *ca.* 4% the data are more similar than the raw figures indicate. This shows that the compounds are probably magnetically dilute, and that there are only small differences in the fields generated by the ligands. The main effect of ligand fields upon the energy levels in uranium(IV) compounds is on the Russel–Saunders terms and their *J* components. It is becoming clear that the spatial arrangement of the ligands is more important in this respect than the exact nature of the ligands except in the case of octahedral compounds such as UCl_6^{2-} where clear evidence for crystal field splitting of *J* levels has been found.[12] The compound $UCl_4,2Pr^iCN$ does not appear to be of this symmetrical type because its spectrum is not ' weak '.[11] The magnetic susceptibility is certainly not independent of temperature, as it would be for a regular octahedral complex,[12] but $UBr_4,2Et_3AsO$ which does have a ' weak ' spectrum shows a similar magnetic behaviour.[9]

The fact that the susceptibilities of the EtCN and Bu^tCN adducts deviate from the Curie–Weiss behaviour is unusual but hardly significant in view of the fact that this law is without theoretical meaning in the present circumstances. It does however suggest that further deviations from this law might be expected if the susceptibilities are measured at temperatures below that of boiling nitrogen.

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[11] P. Gans, B. J. Hathaway, and B. C. Smith, *Spectrochim. Acta*, 1965, **21**, 1589.

[12] R. A. Satten, C. L. Schreiber, and E. Y. Wong, *J. Chem. Phys.*, 1965, **42**, 162.