Contribution from the Inorganic Chemistry Laboratory, University of Oxford, Oxford, United Kingdom

Octahedral Complexes of Uranium(IV). II.[1]
Magnetic and Spectral Effects of Tetragonal Distortion

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Received March 3, 1969

The electronic spectra and magnetic susceptibilities of the complexes $[UCl_4L_2]$ *and* $[UBr_4L_2]$ *(*$L = Et_3PO$*,* Ph_3AsO*,* Et_3AsO*) have been measured. Relative values of the nephelauxetic and ligand field effects for these and similar complexes have been derived and used to explain the magnetic behaviour. Infrared data is reported in support of the proposed structures.*

Introduction

The factors determining the energy levels in the $5f^2$ configuration of uranium(IV) in octahedral complexes have been discussed by Pappalardo and Jørgensen.[3] For the hexahalouranate(IV) anions, Satten *et al.*[4] have calculated the energy parameters from the absorption spectra, and have confirmed the earlier interpretation of the magnetic moment.[5] We have used these results to interpret absorption spectra and magnetic susceptibilities of a series of six-coordinate complexes of uranium(IV) using a two parameter model.

Experimental Section

Preparation of the starting materials: Uranium tetrachloride was prepared by the method of Hermann and Suttle,[6] and uranium tetrabromide by reacting bromine and uranium metal at 700°C in an evacuated silica tube for four days (the product contains a little uranium pentabromide).[7] Commercial tetraphenylphosphonium chloride was recrystallised from methyl cyanide before use. The corresponding bromide was prepared from the chloride on an ion exchange column in dilute aqueous solution. Triphenylphosphineoxide was recrystallised from ethyl acetate. Triethylphosphineoxide was prepared by peroxide oxidation of triethylphosphine and purified by fractional distillation. Triphenylarsineoxide was prepared by the method of Shriner and Wolf.[8] Triethylarsineoxide was prepared by the method of Merijanian and Zingaro.[9] The physical properties of all the above compounds were checked against literature values. Methyl cyanide was dried over phosphorus pentoxide and distilled under nitrogen before use.

Preparation of the complexes: The complexes were prepared by adding the stoichiometric amount of phosphonium halide, phosphineoxide or arsineoxide in methyl cyanide to a suspension of the uranium tetrahalide in methyl cyanide, and shaking the mixture for a short time. The products separated out and were recrystallised from methyl cyanide. Exceptions to the general procedure are (1) the complexes of the triphenylphosphineoxide and triphenylarsineoxide ligands and $[UBr_4(Et_3AsO)_2]$ which were too insoluble for recrystallisation, and were purified by washing with methyl cyanide and (2) the complex $[UCl_4(Et_3PO)_2]$ where crystallisation was induced after evaporation of the solvent by adding a few drops of dichloromethane and then carbon tetrachloride. The crude product was recrystallised from dichloromethane-carbon tetrachloride. In the preparation of many of these complexes, cooling in the initial stage is necessary, since the reaction is very exothermic and at room temperature considerable oxidation of uranium(IV) occurs.

Analysis: Phosphorus,[10] arsenic,[10] and uranium[11] were determined spectrophotometrically and halogen by potentiometric titration.[12]

Conductivity measurements: The conductivities of solutions of the complexes in nitromethane and nitrobenzene were measured on an ac bridge using a cell with fixed black platinum electrodes. The conductivity of the solvent was subtracted from the readings on solutions.

Infrared spectra: These were recorded on a Beckmann IR II spectrophotometer (600-33 cm^{-1}) and on a Perkin-Elmer model 337 (4000-600 cm^{-1}). The complexes were mulled in liquid paraffin B.P. and pressed into potassium chloride discs.

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Table I. General physical data, yields, and analyses of complexes of uranium(IV)

Compound	Colour[a]	mp[b] °C	Λ_m[c]	Λ_m[d]	Yield %	C% Found	C% Calc.	H% Found	H% Calc.	P or As% Found	P or As% Calc.	U% Found	U% Calc.	Cl or Br% Found	Cl or Br% Calc.
$(Ph_4P)_2[UCl_6]$	Blue-green	298-299	163	—	90	50.6	51.0	3.7	3.6	5.5	5.5	21.0	21.1	18.9	18.8
$(Ph_4P)_2[UBr_6]$	Green	288-292	165	—	80	42.3	41.3	3.2	2.9	4.6	4.4			33.8	34.3
$(Ph_4P)_2[UCl_4Br_2]$	Green	288-291	165	—	80	48.5	47.3	3.8	3.5	5.1	5.1			11.7 13.2	11.6Cl 13.1Br
$[UCl_4(Ph_3PO)_2]$	Blue-green	300-305[f]	14.5	—	90	46.0	46.2	3.2	3.2	6.7	6.6	25.7	25.4		
$[UBr_4(Ph_3PO)_2$	Blue-green	300-305[g]	28.5	—	75	38.5	38.8	2.7	2.7	5.6	5.6	21.3	21.4		
$[UCl_4(Et_3PO)_2]$	Green crystals Blue powder	191-193[h]	7.4	—	30	22.2	22.2	4.7	4.7	9.6	9.6	36.7	36.6		
$[UBr_4(Et_3PO)_2]$	Blue-green	188-191	12.7	—	25	17.3	17.4	3.7	3.7	7.5	7.5			38.3	38.8
$[UCl_4(Ph_3AsO)_2]$	Blue	302-305	10.7	—	75	42.0	42.2	3.0	3.0	14.6	14.6			13.3	13.8
$[UBr_4(Ph_3AsO)_2]$	Blue	306-310	45.8[e]	0.9	90	34.7	36.0	2.6	2.5	12.5	12.5			26.6	26.6
$[UCl_4(Et_3AsO)_2]$	Yellow-green	202-205	0.6	—	75	19.2	19.6	4.4	4.1	20.5	20.4			18.7	19.3
$[UBr_4(Et_3AsO)_2]$	Blue-green	181-185	30.0[e]	0.85	80	15.5	15.8	3.2	3.3	16.3	16.4			34.1	35.0

[a] The colour is very dependent on the state of division of the complex. [b] Compounds decompose at the melting point. [c] Molar conductivity (cm^2/ohm. mol) of 10^{-3} *M* solutions in nitromethane at 20°C. [d] Molar conductivity (cm^2/ohm. mol) of 10^{-3} *M* solutions in nitrobenzene at 20°C. [e] The high values are likely to be due to solvation effects resulting from the high ionizing power of nitromethane. The values in nitrobenzene are normal for non-electrolytes. [f] P. Gans and B. C. Smith, *J. Chem. Soc.*, 4172 (1964), give mp 300°C; J. P. Day, and L. M. Venanzi, *J. Chem. Soc. A.*, 197 (1966) gives mp 318-322°C. [g] J. P. Day, *ibid.*, gives mp 208-210°C. [h] J. P. Day, *ibid.*, gives mp 323-327°C; P. Gans and B. C. Smith, *J. Chem. Soc.*, 4172 (1964), give mp 202-206°C.

Table II. Far infrared bands.[a]

O_h assignments	ν_3[b] (cm^{-1}) $\nu(UX_6)$	ν_4[c] (cm^{-1}) $\delta(UX_6)$
$[UCl_6]^{2-}$	257	111
$[UBr_6]^{2-}$	181	73

D_{4h} assignments	$\nu_3(A_{2u})$ (cm^{-1}) $\nu(UO'_2)$	$\nu_9(E_u)$ (cm^{-1}) $\nu(UX_4)$	$\nu_4(A_{2u})$ and $\nu_{10}(E_u)$ (cm^{-1}) $\delta(UX_4)$		Band A (cm^{-1})[d]	
$[UCl_4(Ph_3PO)_2]$	418	265[d] 260	117	154	265 260	202
$[UBr_4(Ph_3PO)_2]$	426	185	74	74	253	205
$[UCl_4(Et_3PO)_2]$	428	263[d] 252	105	126	263 252	
$[UBr_4(Et_3PO)_2]$	432	184	70	77	260	
$[UCl_4(Ph_3AsO)_2]$	346[e]	263[d] 240	101	122	263 240	203[f]
$[UBr_4(Ph_3AsO)_2]$	348[e]	172	75	75	267	201[f]
$[UCl_4(Et_3AsO)_2]$	311	263[d] 240	101	122	263 240	
$[UBr_4(Et_3AsO)_2]$	309	172	75	75	253	
$[UCl_4Br_2]^{2-}$	253[g] 258	253[g] 258	113	113	74[h]	

[a] Bands in the spectra of the complexes which appear in the free ligand spectra have not been included. The numbering of bands is that given in Ref. 18(a). [b] Previously assigned by D. Brown, *J. Chem. Soc., A*, 766 (1966). [c] Assigned to the T_{1u} halogen bending mode in agreement with Satten[3] and Jørgensen.[2] [d] It is uncertain which of the two bands is ν_9. For the origin of the other band, band A, see text. [e] The complexes have a band at 390 cm^{-1}. The ligand spectrum is poorly resolved in this region. [f] The ligand band at 185 cm^{-1} is absent from the spectra of the complexes. [g] The mixed halogen formulation is supported by the absence of bands due to $[UX_6]^{2-}$ (X=Cl and Br) particularly ν_3 of $[UBr_6]^{2-}$. The UBr_2 group asymmetric stretch, $\nu_3(A_{2u})$ is not observed. [h] Assigned to the UBr_2 group bending vibration, $\nu_{11}(E_u)$.

Visible and ultraviolet spectra: Diffuse reflectance spectra were recorded on a Unicam S.P. 700 recording spectrophotometer, fitted with an S.P. 735 diffuse reflectance attachment. Potassium chloride was used as a reflectance comparison.

Magnetic susceptibility measurements: These were measured on two Faraday type balances, one covering the temperature range 100°K to 400°K and the other 14°K to 90°K. Fields up to 8000 oersteds were used.

Results and Discussion

The compounds investigated are listed in Table I. Their properties are similar to those of the corresponding compounds described earlier.[1] The structural formulation of the complexes is based on their stoichiometric formulae, the solution conductivity data, and the infrared spectra. Complexes $[UX_4L_2]$ (X = Cl, Br; L = Ph_3PO, Et_3PO, Ph_3AsO, Et_3AsO) have been assigned *trans*-configurations on the basis of their infrared spectra. This assignment is supported by the visible and ultraviolet spectra, which consist of a series of sharp weak bands characteristic of vibronic spectra, which are only found in centrosymmetric environments where the u↔g selection rule is applicable.

Infrared spectra: The relevant frequencies observed in the far infrared region and their assignments are given in Table II.

The following points are worthy of comment: (1) the vibration ν_4 of the O_h point group is degraded into $\nu_4(A_{2u})$ and $\nu_{10}(E_u)$ in the D_{4h} point group and bands in the region 100-150 cm^{-1} (in the chloro-complexes) and 75 cm^{-1} (in the bromo-complexes) have been assigned to the latter vibrations. (2) assignments of U–O′ asymmetric stretching vibrations were made using published results for M–O stretching frequencies.[13] (3) the origin of bands at about 260 cm^{-1} (Band A), not attributable to ν_9, is uncertain. Their origin could be due to the U–O′ bending mode, $\nu_{11}(E_u)$ in D_{4h}. As this mode also involves changes in the P–O–U or As–O–U angles, it might be better described as a P–O–U or As–O–U angle deformation mode.

This analysis accounts for all the additional bands in the complexes, with the exception of a medium, sharp band around 200 cm^{-1} in the complexes of the triaryl ligands. Triphenylarsineoxide shows a band at 185 cm^{-1} which disappears on complexation, and as this band is of similar intensity to the band at 200 cm^{-1} shown by the complexes it is probable that the latter band is a modified ligand vibration.

The number of additional bands found in the infrared spectra of these complexes clearly indicates a *trans*-substituted octahedral configuration. For a *cis*-substituted configuration, all the modes are infrared active, and 12 additional bands would be expected in the complexes.

Wilkins *et al.*[14] have assigned bands at 300-325 cm^{-1} in complexes $[SnX_4(Ph_3PO)_2]$ and $[Me_2SnX_2(Ph_3PO)_2]$ to Sn–O stretching frequencies. Bands at 390-425 cm^{-1} in the complexes have been assigned to modifications of the 403 cm^{-1} phenyl band. In the analogous arsineoxide complexes, they find Sn–O stretching frequencies at 370-425 cm^{-1}. The different direction of the shift in M–O stretching frequencies between phosphineoxide and arsineoxide complexes of uranium(IV) and tin(IV) is surprising. Our assignment is based on the presence of a band at 428 cm^{-1} in $[UCl_4(Et_3PO)_2]$ which cannot be assigned to a modified ligand vibration, and the absence of bands in the 290-330 cm^{-1} region in the spectra of the complexes of the triphenylphosphineoxide ligands. In a further paper, however, Wilkins *et all.*[15] report Sn–O stretching frequencies at 400-470 cm^{-1} in complexes $[SnX_4(Me_3PO)_2]$.

Near infrared spectra have been studied in the region 4000-700 cm^{-1}. The spectra are identical with those of the ligands they contain, except for the region 1200-1000 cm^{-1} for the phosphineoxide complexes, and the region 900-750 cm^{-1} for the arsineoxide complexes. These changes can be attributed to shifts in the P–O or As–O stretching frequency on complexation, and the values obtained are given in Table III. In the phosphineoxide ligands, the P–O stretch of the free ligand disappears on complexation and a series of weak ligand bands (1096-998 cm^{-1} for Ph_3PO, 1045-985 cm^{-1} for Et_3PO), appear in the complexes with greately increased intensity. The analogous arsineoxide ligands show the same weak band structure, which is however unchanged in intensity on complexation. The increase in intensity is therefore attributed to the P–O stretch being shifted to these regions on complex-formation, and the position of the P–O stretch in the complexes is recorded as the centre of this region of greatly increased intensity.

Table III. Phosphineoxide and arsineoxide bond stretching vibrations

	P–O or As–O stretching frequency in cm^{-1}				
Ligand(L)	Free Ligand	$[UCl_4L_2]$	Change	$[UBr_4L_2]$	Change
Ph_3PO	1195	1045	−150	1030	−165
Et_3PO	1155	1025	−130	1010	−145
Ph_3AsO	880	840	−40	827	−53
Et_3AsO	865	825 (810)	−45	797	−68

The downfield shifts are greater than those normally observed for the first transition series of −50 cm^{-1} for Ph_3PO and 0 cm^{-1} for Ph_3AsO complexes, but smaller than those observed for the uranium(V) complexes, $[UCl_5(Ph_3PO)]$ of −217 cm^{-1} and $[UCl_5(C_8H_{17})_3PO]$ of −160 cm^{-1}.[16] The results show a larger shift in the bromo- than in the chloro-complexes, which may be indicative of a stronger interaction between the ligand and uranium in the former. Cotton has discussed the factors affecting the shift,[17] and the model he proposes adequately explains our results.

Electronic spectra: Absorption spectra from 27000-4000 cm^{-1} have been obtained for all the solid complexes by diffuse reflectance techniques. In all cases intense absorption occurs above 27000 cm^{-1} and a few broad bands appear; these are discussed elsewhere.[18] The principal bands in all the spectra are given in Table IV. In this table, the ligand bands (usually 3 or 4 in number, between 4000 cm^{-1} and 6000 cm^{-1}) have been omitted. The spectra consist of series of weak sharp bands; each band in one spectrum corresponds approximately in shape, relative intensity, and position, to one in each of the other spectra. In some cases a splitting of bands is observed, and Table IV records the mean value of the corresponding bands. Band assignments in complexes $[UX_4L_2]$ were based on the close analogy of their spectra with those of $[UX_6]^{2-}$ which have been previously assigned.[4]

Ligand changes may have two effects on the spectra: (1) ligands with nephelauxetic effects larger than chloride will decrease the separations of the individual multiplets (J-levels) as such ligands reduce F_2, F_4, F_6 and ζ_{5f} and (2) ligands with ligand field strengths larger than chloride will tend to increase the spread of the ligand field group of levels from each J-level as this is dependant on ligand field strength. Following Jørgensen[19] the nephelauxetic ratio, β, for

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Table IV. Visible and near infrared spectra: band heads in wave numbers.

J level			L = Ph_3PO		L = Et_3PO		L = Ph_3AsO		L = Et_3AsO			
		$[UCl_6]^{2-}$	$[UCl_4L_2]$	$[UBr_4L_2]$	$[UCl_4L_2]$	$[UBr_4L_2]$	$[UCl_4L_2]$	$[UBr_4L_2]$	$[UCl_4L_2$	$[UBr_4L_2]$	$[UCl_4Br_2]^{2-}$	$[UBr_6]^{2-}$
	$^3P_2$	24,580	25,200	24,720	26,200	—	—	—	—	—	24,500	23,870
		23,480	23,750	23,610	25,350	25,200	—	25,450	—	—	23,300	23,000
		22,080	22,550	22,200	22,900	23,750	24,200	—	24,850	—	22,050	21,680
		21,900	22,250	22,020	22,530	22,550	23,050	22,650	23,550	23,000	21,800	21,550
	$^1I_6$	20,650	21,700	20,800	21,980	22,370	22,950	22,400	22,700	22,180	20,700	20,400
		20,450	21,250	20,350	21,100	21,100	21,800	21,000	21,530	21,470	20,580	20,300
		20,300	21,000	20,170	20,900	20,750	21,380	20,800	21,530	21,050	20,200	20,200
		19,850	20,320	19,800	20,300	20,000	20,300	20,020	20,420	20,100	19,600	—
	$^3P_1$	18,910	19,320	19,060	19,430	19,080	19,320	20,000	20,180	19,950	18,900	18,450
		18,200	18,500	18,200	—	18,900	—	19,400	—	—	18,200	17,270
		17,000	17,500	17,500	17,820	17,700	17,950	17,940	18,520	18,750	16,900	16,400
	$^3P_0$	16,760	17,300	17,000	17,380	16,950	17,220	17,020	17,560	17,200	16,820	16,280
$^1G_4$	$^1D_2$	15,810	16,650	16,150	16,400	16,350	16,400	16,300	17,380	17,200	15,750	15,700
		15,810	16,150	15,700	16,280	16,120	16,400	16,200	16,700	16,650	15,750	15,580
		15,260	15,550	15,300	15,650	15,580	16,400	15,900	16,180	16,250	15,070	15,150
		14,400	14,200	14,200	15,080	15,000	15,800	15,380	16,180	15,700	14,500	14,200
		13,200	13,300	13,300	14,280	14,100	15,300	14,300	15,580	14,850	12,900	12,750
	$^3H_6$	12,900	13,300	13,100	13,370	13,450	14,150	13,690	14,330	14,550	12,900	12,600
		12,120	12,450	12,350	12,600	12,500	13,450	13,000	13,710	13,700	12,120	12,000
		11,300	11,550	11,600	11,600	11,820	12,720	12,060	12,700	12,500	11,300	11,200
		10,700	10,600	10,750	11,050	11,250	11,800	11,300	12,040	12,120	10,700	10,400
		10,100	10,300	10,000	10,620	10,700	10,720	10,700	11,200	11,180	10,120	10,000
		9,720	9,900	9,750	9,900	10,200	10,200	10,000	10,410	10,500	9,500	9,700
$^3F_4$	$^3F_3$	9,500	9,600	9,600	9,650	9,720	10,000	10,000	10,410	10,000	9,250	9,150
		9,300	9,450	9,250	9,450	9,300	9,370	9,420	9,600	9,750	9,250	9,150
		8,150	8,400	8,450	8,500	8,470	8,700	8,600	8,800	8,950	8,120	8,000
		7,350	7,400	7,500	7,820	7,800	8,100	8,150	8,600	8,525	7,400	7,420
	$^3H_5$	7,100	7,150	7,150	7,400	7,300	7,950	7,560	7,400	7,800	7,100	7,100
		6,350	6,480	6,270	6,350	6,600	6,300	6,740	6,800	7,050	6,360	6,250
	$^3F_2$	5,005	5,200	5,125	5,240	5,250	5,440	5,400	5,600	5,700	4,950	4,860

Table V. Summary of the visible and ultraviolet spectral analysis

Hypothetical ion	% change in spherical parameters (β values)[a]				% change in non-spherical parameters (δ values)[a]			
	From % shifts	mean	From least squares	mean	From least squares	mean	From splitting ratios	mean
$[UCl_6]^{2-}$	0		0		0		0	
$[UBr_6]^{2-}$	−1.6		−1.25		−8.6		−15	
$[U(Ph_3PO)_6]^{4+}$ [b]	8.7	7.2	11.4	9.4	26	22.5	60	61.5
[c]	5.7		7.5		19		63	
$[U(Et_3PO)_6]^{4+}$ [b]	12.0	13.5	21.3	21.8	101	102	114	112
[c]	15.1		22.4		104		111	
$[U(Ph_3AsO)_6]^{4+}$ [b]	20.4	19.6	30.0	31.3	113	119	150	148
[c]	18.9		32.6		124		147	
$[U(Et_3AsO)_6]^{4+}$ [b]	27	28.1	39.6	42.5	131	137	210	196
[c]	29.3		45.4		142		183	

[a] Two values are given for each complex. The first from the difference between the value of the parameters for complexes $[UCl_4L_2]$ and $[UCl_6]^{2-}$. The second was obtained from complexes $[UBr_4L_2]$ in a similar way using our values of the parameters for $[UBr_6]^{2-}$. [b] From $[UCl_4L_2]$. [c] From $[UBr_4L_2]$.

each complex is defined as the ratio of the F parameters in each complex to the values of the parameters in $[UCl_6]^{2-}$. The ligand field ratio, δ, has been similarly defined.

The two parameters β and δ have been obtained by analysis of the spectra, and used to evaluate quantitative differences between the nephelauxetic and ligand field effects of the various ligands and those of chloride. The values obtained are given in Table V. The nephelauxetic parameter β was obtained as given elsewhere.[1] Values of δ were obtained from the ratios of the separations between pairs of bands arising from the same J-level in the complex and in $[UCl_6]^{2-}$. Approximately twelve values of δ were obtained in this manner for each complex and a mean value calculated.

The parameters β and δ were also evaluated by a two parameter treatment based on the relationship:

$$E_{ML_n}(j,k) = A_j + B_j(\beta - 1) + C_k \cdot \delta$$

where

$E_{ML_n}(j,k)$ = energy of an absorption band in the complex ML_n; A_j = value of the energy of the j^{th} J-level in $[UCl_6]^{2-}$; B_j = mean gradient of the dependence of the energy of the j^{th} J-level on F_2, F_4, and F_6 at the values in $[UCl_6]^{2-}$; C_k = energy difference $E_{[UCl_6]^{2-}}(j,k)$ and A_j.

The values of A_j were obtained from the calculations on $[UCl_6]^{2-}$ by Satten[4] as the baricentre of the crystal field levels arising from the j^{th} J-level. The value of B_j for each J-level was obtained from the difference in the calculated energy of the j^th^ J-level in $[UBr_6]^{2-}$ from that in $[UCl_6]^{2-}$ and the ratios of F_2, F_4, and F_6 found for these two complexes.[4] (The ratios of the F_2, F_4, and F_6 values are 0.9720, 0.9720, and 9722 respectively). A least squares fit for the parameters was made for the ten strongest bands for each complex. In all cases, two values for the change in nephelauxetic and ligand field effects relative to those for $[UCl_6]^{2-}$ were calculated for the hypothetical $[UL_6]^{4+}$ ions, one from the parameters for $[UCl_4L_2]$ and the other from the parameters for $[UBr_4L_2]$. This procedure is supported by the observation that the parameters for $[UCl_4Br_2]^{2-}$ are approximately one third of the way between those of $[UCl_6]^{2-}$ and those of $[UBr_6]^{2-}$. The results are given in Table V.

Nephelauxetic effects: The four values obtained for β for each hypothetical $[UL_6]^{4+}$ complex are in fair agreement. The sequence of ligands remains the same for the two methods and corresponds to that found for complexes of nickel(II)[20] and differ only in the relative positions of Ph_3PO and Ph_3AsO for complexes of cobalt(II).[20] It is worth noting that the alkyl derivatives of the phosphineoxides and arsineoxides exert a considerably smaller nephelauxetic effect than the corresponding aryl derivatives.

Ligand field effects: The observed spectrochemical order of ligands in uranium(IV) complexes is:

$$Br^- < Cl^- < Ph_3PO < Et_3PO < Ph_3AsO < Et_3AsO$$

which is analogous to that found for nickel(II) and cobalt(II) complexes.[20] The ligand field effects of ligands R_3PO and R_3AsO are considerably larger than those of Ph_3PO and Ph_3AsO respectively.

Magnetic susceptibilities: The paramagnetic susceptibility of uranium(IV) in the various complexes is given in Table VI and shown as a function of temperature in the figure. For $[UCl_6]^{2-}$, $[UBr_6]^{2-}$, $[UCl_4Br_2]^{2-}$, and $[UCl_4(Ph_3PO)_2]$, the paramagnetic susceptibilities are virtually independent of temperature, but for the other complexes an increasing dependence on temperature is observed as the difference in ligand field strength between axial and equatorial ligands increases. The paramagnetic susceptibility of uranium(IV) complexes with regular octahedral structure has been attributed to a large high frequency term, arising from interaction of the $A_1(^3H_4)$ ground state with the $T_1(^3H_4)$ excited state.[4,5] The magnetic susceptibility arising from the high frequency term, when the separation of the interacting levels is comparable with kT, is given by Figgis[21] and can be usefully expressed either as:

$$\chi'_M = \left[\frac{1-e^{-\Delta E/kT}}{n+m\,.\,e^{-\Delta E/kT}}\right]\cdot\frac{2N\beta^2I^2}{\Delta E} \qquad (1)$$

$$\chi'_M = \left[\frac{1-e^{-\Delta E/kT}}{n+m\,.\,e^{-\Delta E/kT}}\right]\cdot n\,.\,\chi'_{max} \qquad (2)$$

or as

$$\frac{\Delta E}{kT} = 2.303\,\log_{10}\left[\frac{m+n\,.\,\chi'_{max}}{n(\chi'_{max}-\chi'_M)}\right] \qquad (3)$$

where n is the degeneracy of the ground state; m is the degeneracy of the excited state; ΔE is the energy separation between them; χ'_{max} is the maximum value of the susceptibility as kT→0 and χ'_M is the value at temperature T°K; and $I = <\Gamma_{Excited}|L_z+2S_z|\Gamma_{Ground}>$.

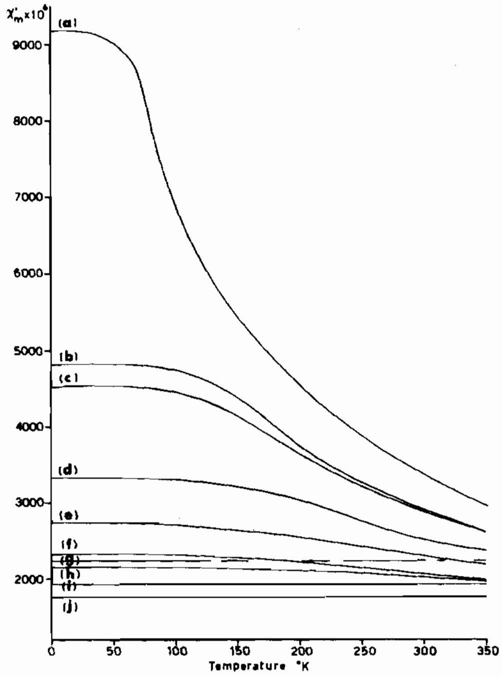

Figure 1. *Temperature dependence of the magnetic susceptibility of complexes of uranium(IV).* (a) $[UBr_4(Et_3AsO)_2]$, (b) $[UBr_4(Ph_3AsO)_2]$, (c) $[UCl_4(Et_3AsO)_2]$, (d) $[UBr_4(Et_3PO)_2]$, (e) $[UCl_4(Ph_3AsO)_2]$, (f) $[UBr_4(Ph_3PO)_2]$, (g) $[UBr_6]^{2-}$, (h) $[UCl_4(Et_3PO)_2]$, (i) $[UCl_6]^{2-}$, (j) $[UCl_4(Ph_3PO)_2]$.

Calculations for the octahedral complexes $[UCl_6]^{2-}$ and $[UBr_6]^{2-}$ using equation 2 with n = 1 and m = 3 and with the ΔE values calculated by Satten[4] show that at the highest temperature measured, the calculated susceptibility is 10-20% less than the value observed. We attribute the difference to the orbital contribution to the susceptibility of the electrons that are thermally occupying the $T_1(^3H_4)$ excited state. Their contributions can be calculated as:

$$\chi'_{additional} = \left[\frac{3e^{-\Delta E/kT}}{1+3e^{-\Delta F/kT}}\right]\cdot\frac{2}{(2.84)^2\,.\,T}$$

The sum of the two contributions with the ΔE values quoted in Table VII reproduces the observed temperature independence, including the very broad maximum consistently observed between 200-250°C. A similar calculation has been made for $[UCl_4(Ph_3PO)_2]$ assuming a negligible splitting of the T_1 state, and a value for ΔE derived.

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(20) F. A. Cotton, D. M.L. Goodgame, and M. Goodgame, *Inorg. Chem.*, *1*, 239 (1962) and references quoted therein.
(21) B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, 6, 42 (1964).

Table VI. Magnetic susceptibility data.

						L=Ph$_3$PO				L=Et$_3$PO				L=Ph$_3$AsO				L=Et$_3$AsO			
[UCl$_6$]$^{2-}$		[UCl$_4$Br$_2$]$^{2-}$		[UBr$_6$]$^{2-}$		[UCl$_4$L$_2$]		[UBr$_4$L$_2$]		[UCl$_4$L$_2$]		[UBr$_4$L$_2$]		[UCl$_4$L$_2$]		[UBr$_4$L$_2$]		[UCl$_4$L$_2$]		[UBr$_4$L$_2$]	
T°K	$10^6\chi'_m$ [a,b]	T°K	$10^6\chi'_m$	T°K	$10^6\chi'_m$	T°K	$10^6\chi'_m$	T°K	$10^6\chi'_m$	T°K	$10^6\chi'_m$	T°K	$10^6\chi'_m$	T°K	$10^6\chi'_m$	T°K	$10^6\chi'_m$	T°K	$10^6\chi'_m$	T°K	$10^6\chi'_m$
341	1988	364	2204	353	2245	336	1748	349	1957	341	1973	349	2383	352	2159	353	2591	367	2566	292	3425
290	2000	318	2263	305	2267	298	1759	318	2037	319	2012	327	2446	345	2201	326	2731	297	2901	227	4130
246	2010	276	2274	270	2271	227	1760	295	2077	274	2033	287	2583	304	2296	294	2926	293	2891	147	5540
173	1965	220	2274	268	2283	147	1761	268	2148	246	2078	281	2618	246	2431	290	2951	245	3251	111	6745
135	1940	136	2254	219	2283	123	1766	245	2145	223	2113	248	2764	181	2566	244	3301	191	3691	92	6975
117	1935	103	2234	135	2254	103	1772	182	2227	188	2101	180	3143	137	2656	187	3811	139	4261	90	7620
103	1930			103	2245			136	2259	137	2153	137	3213	101	2691	157	4366	107	4431	77	7880
								104	2274	103	2138	102	3288	77	2720	103	4681	77	4540	63	8865
								77	2310	77	2210	77	3325	20	2740	77	4810	20	4540	54	9000
								20	2340	20	2130	20	3325			20	4810			20	9145
																				14	9145

[a] emu mole^{-1}. The observed molar susceptibility has been corrected for the diamagnetism of all the atoms and ions according to the values given by P. W. Selwood, « Magnetochemistry », Interscience, New York, 2nd edition, 1956. [b] All the measurements refer to the mean value of measurements at 8000 and 4500 oersteds. The two values showed no significant difference.

Table VII. Summary of the analysis of the magnetic susceptibility data

			From equation 2		From equation 3		Conclusions drawn from 2 and 3			
Symmetry	Compound	χ'_{max} $\times 10^{-6}$ cgs	Possible n and m values	ΔE values cm^{-1}	Possible n and m values	ΔE values cm^{-1}	ΔE cm^{-1}	Ground State	Excited State	I^2
O$_h$	(Ph$_4$P)$_2$[UCl$_6$]	1970					870	A	T	3.24
	(Ph$_4$P)$_2$[UBr$_6$]	2240					760	A	T	3.22
D$_{4h}$	[UCl$_4$(Ph$_3$PO)$_2$]	1770					960	A	T	3.22
	[UBr$_4$(Ph$_3$PO)$_2$]	2320	n=1, m=3	740			740	A	T	3.29
			n=1, m=2	630			or 630	A	E	2.80
	[UCl$_4$(Et$_3$PO)$_2$]	2130	n=1, m=3	840			840	A	T	3.43
			n=1, m=2	768			or 768	A	E	3.13
	[UBr$_4$(Et$_3$PO)$_2$]	3325	n=1, m=2	450			450	A	E	2.87
	[UCl$_4$(Ph$_3$AsO)$_2$]	2730	n=1, m=2	538			538	A	E	2.81
	[UBr$_4$(Ph$_3$AsO)$_2$]	4810	n=1, m=2	320	n=1, m=2	320	320	A	E	2.95
	[UCl$_4$(Et$_3$AsO)$_2$]	4540	n=1, m=2	332	n=1, m=2	325	328	A	E	2.85
	[UBr$_4$(Et$_3$AsO)$_2$]	9140	n=1, m=2	163	n=2, m=1	117	116	E	A	4.06
			n=2, m=1	115						

Table VIII. Correlation of magnetic susceptibility and electronic spectra.

Complex	Mean δ [a]	Position of hypothetical T$_1$(^{3}H$_4$) (cm^{-1}) ΔE$_{A_1-T_1}$	Observed separation (cm^{-1}) ΔE$_{A_1-T_1}$	ΔE$_{A_1-T_1}$−ΔE$_{obs}$ (cm^{-1})	Tetragonal distortion [b]
[UCl$_6$]$^{2-}$	1.000		870 (T$_1$)		0
[UBr$_6$]$^{2-}$	0.914		760 (T$_1$)		0
[UCl$_4$(Ph$_3$PO)$_2$]	1.075	966	960 (T$_1$)		0.225
[UBr$_4$(Ph$_3$PO)$_2$]	1.018	893	630 (E)	263	0.311
[UCl$_4$(Et$_3$PO)$_2$]	1.34	1305	768 (E)	537	1.02
[UBr$_4$(Et$_3$PO)$_2$]	1.28	1232	450 (E)	782	1.11
[UCl$_4$(Ph$_3$AsO)$_2$]	1.40	1378	538 (E)	840	1.19
[UBr$_4$(Ph$_3$AsO)$_2$]	1.32	1280	320 (E)	960	1.28
[UCl$_4$(Et$_3$AsO)$_2$]	1.44	1437	328 (E)	1109	1.37
[UBr$_4$(Et$_3$AsO)$_2$]	1.39	1364	−116 (E)	1480	1.46

[a] Calculated from the least square parameters for [UL$_6$]$^{4+}$ and [UX$_6$]$^{2-}$. [b] The difference in δ value between [UL$_6$]$^{4+}$ and [UX$_6$]$^{2-}$.

In complexes with D$_{4h}$ symmetry, the ground state interacts with the E and A$_1$ states derived from T$_1$(^{3}H$_4$). The observed values have been analysed in terms of equations 2 and 3. Of the values of n and m considered (n = 1, m = 1, 2, 3 and n = 2, m = 1), only those given in Table VII give a fit, using equation 2, with the experimental data to within experimental error. Complexes where the difference between χ'_{max} and χ'_M is large in the temperature range measured give linear plots of 1/T against the log function of equation 3 for different values of n and m. In each case, only one of these lines corresponding to particular values of n and m has the zero intercept required by equation 3, defining the values of n, m, and ΔE quoted in Table VII. These results show that (1) in the complexes with O$_h$ symmetry, [UCl$_6$]$^{2-}$ and [UBr$_6$]$^{2-}$, the susceptibility arises from interaction of a T$_1$ excited state with the A$_1$ ground state; (2) as the tetragonality increases interaction occurs between an A$_1$ ground state and an E excited state; and (3) for strongly tetragonal complexes *e.g.* [$UBr_4(Et_3AsO)_2$] the E state has crossed the A_1 state and one observes an A_1 excited state interacting with an E ground state.

The ligand field produced by the ligands in the D_{4h} complexes can be considered as being the sum of two contributions: (1) the average field of the ligands operating on a complex of O_h symmetry and (2) a tetragonal component which is defined as the difference between the strength of the ligand field of the axial ligands and the equatorial ligands. This procedure allows one to define a hypothetical $T_1(^3H_4)$ state corresponding to the average field defined above, which can be compared with the $T_1(^3H_4)$ state observed in the complexes of O_h symmetry. Thus, effect (1) alters the separation between the $A_1(^3H_4)$ ground state and the first T_1 level of $[UBr_6]^{2-}$ producing a decrease of 110 cm^{-1} as compared with $[UCl_6]^{2-}$, corresponding to a 8.6% decrease in ligand field strength. A_1–T_1 separations have been calculated for D_{4h} complexes using the average field approximation (see Table VIII). Effect (2) has been considered as a a tetragonal perturbation on this situation, whose principal effect is to split the T_1 state into an E state and an A state. The extent of this splitting is expected to be a function of the tetragonal distortion which has been evaluated from the parameters obtained from the visible and uv spectra. The analysis of the magnetic susceptibility data suggests that this distortion lowers the energy of the E state derived from T_1 and raises the energy of the A state. The observed separation should be given by:

$$\Delta E_{obs} = \Delta E_{A-E} = \Delta E_{A-T_1} - f(\text{Tetragonal distortion})$$

Table VIII shows that ($\Delta E_{A-T_1} - \Delta E_{obs}$) and the tetragonal distortion are indeed related.

In complexes with small tetragonal distortions, *i.e.* [$UBr_4(Ph_3PO)_2$] and [$UCl_4(Et_3PO)_2$], the A state arising from the splitting of $T_1(^3H_4)$ still interacts appreciably with the ground state. Analysis of the observed χ'_{max} values for the above complexes, taking into account interaction with both A and E states, (using I^2 values derived from the other complexes) give the following values:

	ΔE_{A-E} cm^{-1}	ΔE_{A-A} cm^{-1}	$\chi'_{max\ A-E}$ $\times 10^{-6}$cgs	$\chi'_{max\ A-A}$ $\times 10^{-6}$cgs	$\chi'_{max\ obs}$ $\times 10^{-6}$cgs
[$UBr_4(Ph_3PO)_2$]	668	1293	2,246	89	2,320
[$UCl_4(Et_3PO)_2$]	732	2451	2,050	82	2,130

These calculations show that the contribution to the susceptibility of the interaction with the A excited state is (1) less than 3% and (2) temperature independent for the more strongly distorted complexes and can therefore be neglected.

One of us (B.C.L.) would like to acknowledge the financial support of the S.R.C.