Registry No. SiO_2, 7631-86-9; EuI_2, 22015-35-6; $EuPO_4$, 13537-10-5; LaI_3, 13813-22-4; $LaPO_4$, 13778-59-1; SrI_2, 10476-86-5; $Sr_3(PO_4)_2$, 7446-28-8; PI_3, 13455-01-1; $EuSiO_3$, 15060-38-5; $Eu_5O(SiO_4)_3$, 58023-80-6; P_2I_4, 13455-00-0; SiI_4, 13465-84-4.

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Preparation and Spectral Properties of Actinide(IV)–Hexaiodo Complexes

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Hexaiodo complexes of the type $R_2M^{IV}I_6$ (R = NEt_4, NMe_3Ph; M^{IV} = Th, Pa, U) have been prepared by reactions in oxygen-free, anhydrous methyl cyanide. Ir and Raman data are reported together with electronic spectral results for the protactinium(IV) and uranium(IV) complexes. Ligand field and spin–orbit coupling constants derived for the hexaiodoprotactinates(IV) are discussed in relationship to values obtained earlier for other hexahalogenoprotactinates(IV), $(NEt_4)_2PaX_6$ (X = F, Cl, Br).

As part of a detailed investigation of the trends in bonding of $5f^1$ compounds we have previously reported[1,2] optical spectral data for octahedral compounds of the type $(NEt_4)_2PaX_6$ (X = F, Cl, Br). The trends in the ligand field parameters θ and Δ were explained qualitatively in terms of molecular orbital theory with large variations in σ bonding dominating the total ligand field splitting as the halide was varied, a feature which was also observed for certain hexahalogenouranates(V). Hexaiodo complexes of tetravalent actinide elements have not been extensively studied[3,4] and the single protactinium(IV) complex reported,[4] $(Ph_3MeAs)_2PaI_6$, was only prepared on a very small scale and its physical properties were not examined.

We report now the preparation of new hexaiodo complexes, $(NEt_4)_2M^{IV}I_6$ (M^{IV} = Th, Pa, U) and $(NMe_3Ph)_2M^{IV}I_6$ (M^{IV} = Pa, U), together with details of their ir, Raman, and (Pa and U only) solid-state electronic spectra and x-ray powder diffraction results. The ligand field and spin–orbit coupling constants derived from the electronic spectra of the hexaiodoprotactinates(IV) are compared with those available for other octahedral $5f^1$ compounds.

Experimental Section

All reactions and sample preparation were performed in inert-atmosphere dryboxes (oxygen <20 ppm; H_2O <20 ppm) on account of the ready hydrolysis and oxidation (Pa) of the complexes and to afford protection against the radioactivity associated with ^{231}Pa.

Reagents. Thorium,[3] protactinium,[4] and uranium[3] tetraiodides were prepared according to the methods in the references cited. Commercially available NEt_4I and NMe_3PhI (B.D.H. Ltd.) were vacuum dried at room temperature (10^{-4} Torr) for several hours after which time no bands due to water were present in their ir spectra. Methyl cyanide was purified as described previously,[5] flushed with argon (99.999% purity), and stored in the inert-atmosphere glove boxes over freshly dried molecular sieves. It was passed down a column of new sieves immediately prior to use.

Hexaiodo Complexes $R_2M^{IV}I_6$ (R = NEt_4, NMe_3Ph; M^{IV} = Th, Pa, U). The appropriate tetraiodide (0.05–0.5 g) was heated with the stoichiometric quantity (1:2 mole ratio) of tetraalkyl(aryl)ammonium iodide in anhydrous, oxygen-free methyl cyanide (0.2–1.0 ml). The reaction mixture was cooled in ice, and the crystalline product was isolated by centrifugation, washed with ice-cold methyl cyanide, and vacuum dried at room temperature. Yields were in the range 70–90%. Anal. Calcd for $(NEt_4)_2ThI_6$: Th, 18.51; I, 60.74. Found: Th, 18.60; I, 59.85. Calcd for $(NEt_4)_2UI_6$: U, 18.89; I, 60.43. Found: U, 18.84; I, 60.24. Calcd for $(NMe_3Ph)_2UI_6$: U, 18.72; I, 59.86. Found: U, 18.75; I, 59.92. The hexaiodoprotactinates(IV), which are isostructural with their thorium and uranium analogues, were identified by x-ray powder diffraction analysis.

Analyses. Thorium, uranium, and iodide were determined as described previously.[3]

Physical Measurements. The f–f and vibronic transitions of octahedral complexes have low extinction coefficients and it is necessary to use small crystals of the compound without grinding rather than rapidly precipitated material which results in very weak spectra due to extensive light scattering. Samples were prepared by mixing a few small crystals (ca. 10 mg of material) with a very small quantity of grease (Voltalef-901, from Plastimer, 92 Clichy, France) in the center of a silica plate (3-cm diameter), placing an aluminum foil mask with a central hole of 6.0-mm diameter around the mixture, and pressing a second silica plate onto this to spread the mixture in the cavity. Alternatively, a rubber mask, 0.8 mm thick, with a central hole of 3.5-mm diameter was placed on a silica plate and the resulting cavity was filled with grease. A few small crystals, 10–20 mg of material, were pressed into the grease and the mixture was compressed to give a matrix of crystals bonded together with a trace of grease by covering the cavity with the second silica plate and clamping the assembly in the sample holder, which was part of a commercial cryostat unit (solid-state sample holder, Type LT-SH, and variable-temperature

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Table I. Partial X-Ray Powder Diffraction Data for $(NEt_4)_2PaI_6$

$\sin^2 \theta_{obsd}$	I_{estd}[a]	$\sin^2 \theta_{obsd}$	I_{estd}[a]
0.0108	m+	0.0716	s
0.0115	m–	0.0772	m–
0.0293	w–	0.0788	m–
0.0331	w––	0.0826	m
0.0426	m	0.0853	m
0.0451	m	0.0959	m+
0.0464	w–	0.0974	w–
0.0501	w	0.0996	w
0.0511	w	0.1045	m+
0.0521	w–	0.1080	w
0.0545	w–	0.1122	w+
0.0563	w–	0.1143	w–
0.0571	w–	0.1171	w–
0.0604	w	0.1261	m+
0.0622	w–	0.1327	m+
0.0644	w	0.1386	w
0.0666	w–	0.1421	w
0.0689	w–	0.1471	w
		0.1542	w–

[a] Key: s, strong; m, medium; w, weak.

unit, Type VLT-2, from Research and Industrial Instrument Co., Croydon, England). The sample holder was transferred to a fume cupboard and decontaminated by cleaning with ethanol. It was then fixed in the cryostat unit which has been modified by the addition of bolts and wing nuts to secure the lid to provide safe containment for radioactive samples. Liquid nitrogen was used as coolant to obtain the low-temperature spectra. A Cary 14 spectrophotometer was employed in the transmission mode to record spectra. A combination of suitable grease blanks and perforated metal foil attenuators was inserted in the reference beam to compensate for scatter and give a reasonably flat base line. The problems associated with recording solid-state transmission spectra and the experimental techniques employed are discussed in more detail elswhere.[6]

Ir and Raman spectra were recorded on a Perkin-Elmer 180 instrument and a Cary Model 83 (488-nm argon ion laser excitation) instrument, respectively. Nujol mulls of the compounds were employed for ir studies while solid samples were mounted in stoppered, thin-walled, 2–3-mm i.d. silica or glass tubes for Raman work. The sample holders were mounted in Perspex boxes with either polythene film or silica windows, the boxes then being sealed to prevent accidental release of radioactive contamination.[7]

X-ray powder diffraction samples were mounted in 0.3-mm diameter Lindemann glass capillaries which were sealed and coated with Bostikot[8] to prevent accidental breakage. Films were recorded using a 19-cm Debye–Sherrer camera with nickel-filtered Cu Kα radiation ($\lambda(\alpha_m)$ 1.5418 Å).

Results and Discussion

The hexaiodo complexes crystallize when the appropriate tetraiodide and alkyl(aryl)ammonium iodide are mixed in anhydrous, oxygen-free methyl cyanide. The products are extemely sensitive toward moisture, and for small-scale preparations (e.g., 50 mg of PaI_4) it is essential to pass previously purified methyl cyanide down a column of fresh molecular sieves in order to ensure complete absence of water. They are moderately soluble in methyl cyanide and insoluble in isopentane. The addition of aqueous ammonia results in the formation of hydrous oxides, the characteristic black protactinium(IV) hydroxide turning white within a few minutes in the presence of oxygen.

Partial x-ray powder diffraction data for $(NEt_4)_2PaI_6$ are listed in Table I together with visually estimated intensities; the thorium and uranium analogues are isostructural. The complexes appear to possess low symmetry and unit cells dimensions have not been obtained.

Ir and Raman Spectra. Two infrared-active fundamentals, ν_3 (t_{1u}) and ν_4(t_{1u}), and three Raman-active fundamentals, ν_1(a_{1g}), ν_2(e_g) and ν_5(t_{2g}), are predicted by group theory for regular octahedral molecules of the type MX_6 belonging to the point group O_h. The t_{2u} mode, ν_6, is totally forbidden. Comparison of our spectra for the hexaiodo complexes with those for hexafluoro, hexachloro, and hexabromo complexes of a variety of tetravalent actinide elements[7] results in the assignments shown in Table II. As indicated, Raman data could not be obtained for either $(NEt_4)_2PaI_6$, which exhibited strong fluorescence, or $(NEt_4)_2UI_6$, which decomposed in the laser beam. A definite assignment of ν_4 was not possible: a relatively weak, split absorption was observed around 60 cm^{-1} but this coincided with the probable position of the lattice mode and with a band observed in the spectra of thick mulls of NEt_4I. However, there is probably a contribution to this absorption from ν_4 since, on a mass basis (e.g., $\nu_4(I) = [M(Cl)/M(I)]^{1/2}\nu_4(Cl)$ and $\nu_4(I) = [M(Br)/M(I)]^{1/2}\nu_4(Br)$ with[7] $\nu_4(Cl)$ = ca. 110 cm^{-1} and $\nu_4(Br)$ = ca. 81 cm^{-1}), this mode would be expected between 55 and 65 cm^{-1}. The ν_2 mode was not observed in the Raman spectrum of $(NEt_4)_2ThI_6$. Although this mode was recently reported[9] as a medium-intensity band at 230 cm^{-1} for solid hexachlorouranates(IV), we have been unable to reproduce this and believe that the observation was incorrect. Thus as discussed elsewhere[7] numerous samples of Cs_2UCl_6 have been examined at Harwell and other laboratories using exciting wavelengths of 488, 514, and 613 nm and in all instances no evidence was found for a band around 230 cm^{-1}. Our results confirmed those of Beringer et al.,[10] who observed only ν_1 and ν_5 in the spectra of hexachloroneptunates (IV).

Table II. Ir and Raman Data for Hexaiodo Complexes

Compd	Color	Obsd vibrational modes, cm^{-1} ν_1	ν_3	ν_4	ν_5
$(NEt_4)_2ThI_6$	White	131	143	*c*	68, 50[c]
$(NEt_4)_2PaI_6$	Blue	*a*	143	*c*	*a*
$(NEt_4)_2UI_6$	Red	*b*	143	*c*	*b*

[a] Not observed owing to fluorescence. [b] Not observed owing to rapid decomposition of compound in laser beam. [c] Discussed in the text.

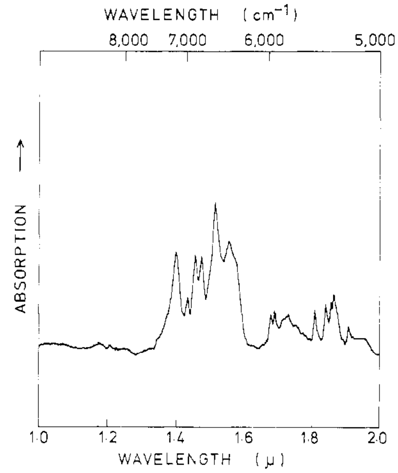

Figure 1. Spectrum of $(NEt_4)_2PaI_6$ at 300 K.

A band observed at 100 cm^{-1} in the Raman spectra of certain samples of $(NEt_4)_2ThI_6$ is believed to be due to hydrolysis products since it increases relative to other bands on exposure of the compound to moisture and is the only band present in the spectrum of an aqueous solution of $(NEt_4)_2ThI_6$. This band is therefore valuable in assessing the purity of a sample of this material. It is not possible at present to decide which of the two remaining bands (Table II) should be assigned to ν_5 and which to a lattice mode.

Electronic Spectra. The solid-state spectra obtained for $(NEt_4)_2PaI_6$ are shown in Figures 1 and 2 and that for $(NEt_4)_2UI_6$ at 85 K is shown in Figure 3. The last has not been interpreted and will not be discussed in detail.

The measured band positions for $(NEt_4)_2PaI_6$ and

Table III. Spectral Results for the Hexaiodoprotactinates(IV)[a]

	$(NEt_4)_2PaI_6$						$(NMe_3Ph)_2PaI_6$					
	At 85 K			At 300 K			At 85 K			At 300 K		
	Band position, cm^{-1}	Intens	Freq, cm^{-1}	Band position, cm^{-1}	Intens	Freq, cm^{-1}	Band position, cm^{-1}	Intens	Freq, cm^{-1}	Band position, cm^{-1}	Intens	Freq, cm^{-1}
Γ_7–Γ_6							7413	w	+420			
	7262	w	+298	7262	sh	+298	7315	m	+322			
	7138	s	+174	7143	s	+179	7143	s	+150	7143	s, br	+145
	7102	sh	+138									
	6964	m	0	6964	w	0	6993	m	0	6998	vw	0
	6868	m	−96	6859	s	−105	6887	sh	−106			
	6770	m	−194	6780	s	−184	6840	s	−153	6840	s, br	−158
	6729	sh	−235				6752	w	−241			
Γ_7–Γ_8'	6601	s		6605	s		6627	s		6614	s, br	
	6502	s		6431	s		6494	s		6398	s, br	
Γ_7–Γ_7'	5534	w	+152	5525	m	+140	5540	w	+155	5540	m	+149
	5432	w	+50	5429	m	+44	5423	w	+38	5429	m	+38
	5382	sh	0	5385	m	0	5385	m	0	5391	m	0
	5359	m	−23	5362	m	−23	5362	m	−23	5371	m	−20
				5350	sh	−35	5333	sh	−107	5330	sh	−61
	5241	w, br	−141	5244	w	−141	5236	w, br	−149	5241	w	−150

[a] Key: s, strong; m, medium; w, weak; br, broad; sh, shoulder.

Table IV. Calculated and Experimental Transition Energies, Ligand Field Parameters, and Spin–Orbit Coupling Constants for Hexahalogenoprotactinates(IV)

Compd		Energy, cm^{-1}			g	Parameters, cm^{-1}		
		Γ_7–Γ_6	Γ_7–Γ_8'	Γ_7–Γ_7'		θ	Δ	ζ
α-$(NEt_4)_2PaF_6$[a]	Calcd	11 537	9586	5717	−0.704	4502	3074	1508
	Exptl	11 446	9708	5698	−0.75[d]			
$(NEt_4)_2PaCl_6$[b]	Calcd	8 029	6988	5347	−1.115	1873	1634	1523
	Exptl	8 011	7022	5330	−1.141			
$(NEt_4)_2PaBr_6$[b]	Calcd	7 509	6767	5401	−1.100	1268	1707	1535
	Exptl	7 480	6828	5365	−1.150[d]			
$(NEt_4)_2PaI_6$[c]	Calcd	7 002	6497	5397	−1.142	832	1546	1542
	Exptl	6 998	6506	5391	−1.150[d]			
$(NMe_3Ph)_2PaI_6$[c]	Calcd	6 973	6497	5399	−1.130	782	1592	1540
	Exptl	6 964	6518	5385	−1.150[d]			

[a] Reference 2. [b] Reference 1. [c] This work. [d] Estimated value.

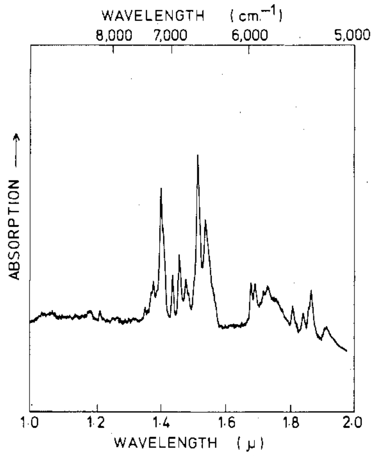

Figure 2. Spectrum of $(NEt_4)_2PaI_6$ at 85 K.

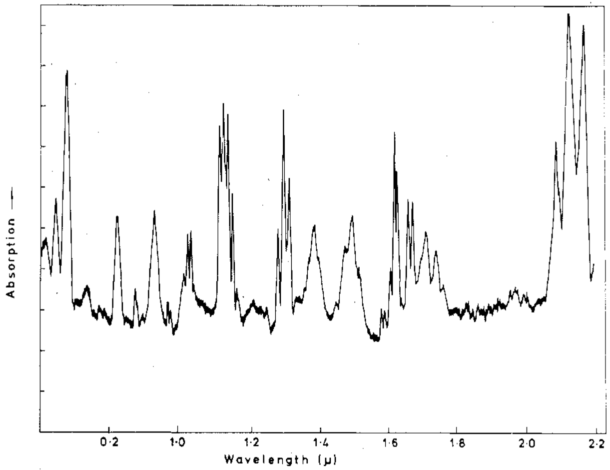

Figure 3. Spectrum of $(NEt_4)_2UI_6$ at 85 K.

$(NPhMe_3)_2PaI_6$ are provided in Table III together with assignments. The estimated accuracy of measurement is ±10 Å. Bands present in the spectra (Figures 1 and 2) at ca. 1.68 μ are associated with transitions within the tetraethylammonium cation. No other bands were observed at higher wavenumbers. The spectra are similar to those we reported earlier[1,2] for the octahedral hexahalogenoprotactinates(IV) [$(NEt_4)_2PaX_6$; X = F, Cl, Br] and the optical absorption bands are similarly assigned to transitions from the Γ_7 ground level to the Γ_6, Γ_7', and Γ_8' states as indicated in Table III.

The spectra are dominated by vibronic transitions which arise from the coupling of the vibrational modes with the pure electronic transitions. The strongest vibronic bands are those which are caused by motions which destroy the center of symmetry of the complex during vibration [i.e., $\nu_3(T_{1u})$, $\nu_4(T_{1u})$, and $\nu_6(T_{2u})$]. In the PaI_6^{2-} electronic spectra it appears possible to correlate the vibronic band occurring at ca. ±145 cm^{-1} from the Γ_7–Γ_7' transition with the $\nu_3(T_{1u})$ normal mode (Table II). Other vibronic bands are probably due to other normal modes or combinations of normal modes including those of the cation.[11] Higher resolution spectra are necessary to resolve these bands further. The Γ_8' level is again observed

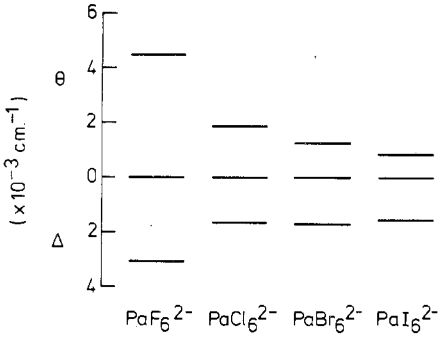

Figure 4. Ligand field splittings θ and Δ for octahedral complexes of the type $(NEt_4)_2PaX_6$ (X = F, Cl, Br, I).

to be split as in the spectra of other octahedral protactinium(IV) complexes[1,2] and a range of uranium(V) complexes.[12,13]

The assignments at 85 K shown in Table III were used to fit the ligand field splittings, θ and Δ, and the spin–orbit coupling constant, ζ, and in order to have a check on these parameters the *g* value for PaI_6^{2-} was estimated at −1.15 (cf. ref 1 and 2). The experimental and calculated values are compared in Table IV, and the θ and Δ values are compared with those for other hexahalogenoprotactinates(IV) in Figure 4. The apparent increase in the spin–orbit coupling constant ζ through the series from the fluoride to the iodide complex should be treated with caution since the values obtained are strongly dependent on the *g* values estimated. Magnetic measurements are necessary on these compounds in order to determine accurate values of ζ.

The very marked decrease in θ and the relatively constant value of Δ across the series $PaF_6^{2-} \rightarrow PaI_6^{2-}$ (Figure 4) reflect the progressive lowering in energy of the Γ_6 state relative to the Γ_8' and Γ_7' states shown in Table IV. The Γ_7' state in fact increases very slightly in energy from $PaCl_6^{2-}$ to PaI_6^{2-}. As discussed previously, it can be shown for $5f^1$ compounds in octahedral symmetry that

$$\theta \simeq (\alpha_\pi^2 + \alpha_\sigma^2 - \alpha_\pi'^2)(E_f - E_p) \qquad (1a)$$

and

$$\Delta \simeq (\alpha_\pi'^2)(E_f - E_p) \qquad (1b)$$

where α_π and α_σ are ligand admixture coefficients for the t_{1u} state, α_π' is that for the t_{2u} state, and E_f and E_p are the binding energies of the outer f metal ion electrons and the outer p shell ligand electrons, respectively. Thus, since θ changes much more rapidly than Δ for the hexahalogenoprotactinates(IV) (Figure 4) and α_π and α_π' involve the same ligand orbital, changes in π bonding will have relatively little effect on θ but (eq 1) will directly affect Δ. It appears therefore that as the halide ion is changed from fluoride to iodide in the hexahalogenoprotactinates(IV) $(NEt_4)_2PaX_6$ (X = F–I), large changes in σ bonding occur while the π bonding is relatively unaffected.

Summary

The preparation of actinide(IV)–hexaiodo complexes $R_2M^{IV}I_6$ (R = NEt_4, NMe_3Ph; M^{IV} = Th, Pa, U) is described. Ir, Raman, and electronic spectral data are reported for the protactinium(IV) and uranium(IV) complexes. Ligand field parameters and spin–orbit coupling constants derived for the hexaiodoprotactinates(IV) are discussed in relationship to earlier values obtained for other octahedral hexahalogenoprotactinates(IV), $(NEt_4)_2PaX_6$ (X = F, Cl, Br), and shown to fit the trends previously identified for these compounds.

Registry No. $(NEt_4)_2ThI_6$, 56848-01-2; $(NEt_4)_2PaI_6$, 56930-81-5; $(NEt_4)_2UI_6$, 56848-06-7; $(NMe_3Ph)_2PaI_6$, 51268-19-0; $(NMe_3Ph)_2UI_6$, 58002-46-3.

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Anionic Linear Chain Iridium Carbonyl Halides

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The compounds $K_{0.60}Ir(CO)_2Cl_2{\cdot}0.5H_2O$, $(TTF)_{0.61}Ir(CO)_2Cl_2$ (TTF = tetrathiafulvalenium), $K_{0.57}Ir(CO)_2Br_2{\cdot}0.2CH_3COCH_3$, and $Cs_{0.60}Ir(CO)_2Br_2$ have been investigated by chemical analysis, infrared and ^{193}Ir Mössbauer spectroscopy, electrical conductivity, and magnetic susceptibility measurements. Conducting linear chains of *cis*-$[Ir(CO)_2X_2]^{0.60-}$ (X = Cl, Br) units are shown to be present in these compounds. The apparently well-defined compounds $K_{0.98}Ir(CO)_2Cl_{2.42}{\cdot}0.2CH_3COCH_3$ and $Na_{0.93}Ir(CO)_2Cl_{2.32}{\cdot}0.3CH_3COCH_3$ are reformulated as $K_{0.60}Ir(CO)_2Cl_2{\cdot}0.4KCl{\cdot}0.2CH_3COCH_3$ and $Na_{0.61}Ir(CO)_2Cl_2{\cdot}0.32NaCl{\cdot}0.3CH_3COCH_3$, in which the KCl and NaCl are present interstitially in the lattice of linear chains.

Square-planar coordinated transition metal atoms often stack along the axis perpendicular to the ligand planes to form linear chains of metal–metal bonded atoms. A compound made up of parallel chains of this type, with only weak interaction between adjacent chains, is a potential one-dimensional conductor. In order for such a compound to be highly conducting, the d-band arising from the metal–metal interaction must not be completely filled. The known