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Preparation and Crystallographic and Spectral Properties of the Octahedral Hexafluoroprotactinate(IV) $(NEt_4)_2PaF_6$

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Bis(tetraethylammonium) hexafluoroprotactinate(IV) has been prepared in both cubic and tetragonal crystal modifications by reactions in oxygen-free propylene carbonate. The tetragonal (β) phase is isostructural with the uranium(IV) analog which appears to exist in only one modification. Solid-state transmission spectra indicate that both α- and β-$(NEt_4)_2PaF_6$ exhibit octahedral stereochemistry and the results are interpreted in terms of two ligand field parameters and the spin-orbit coupling constant. The values obtained are compared with those available for other octahedral $5f^1$ compounds. Infrared data are reported for both crystal modifications of $(NEt_4)_2PaF_6$ and for β-$(NEt_4)_2UF_6$.

As part of a detailed study[1] of the trends in bonding of $5f^1$ compounds we recently reported optical spectral data for the octahedral compounds $(NEt_4)_2PaCl_6$ and $(NEt_4)_2PaBr_6$, together with an analysis of data available for certain six-coordinate hexahalogenouranates(V) and neptunium hexafluoride. 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 ion was varied with a fixed metal ion oxidation state. At that time the only protactinium(IV) fluoro complexes known were[2] $(NH_4)_4PaF_8$, a series of the type $M^I{}_7Pa_6F_{31}$ (M^I = Na, K, Rb), all of which contain eight-coordinate Pa(IV) ions, and $LiPaF_5$, in which the Pa(IV) ion is nine-coordinate. Indeed, although a variety of actinide(IV) fluoro complexes of the types $M^I{}_2M^{IV}F_6$ and $M^{II}M^{IV}F_6$ (M^I = univalent cation, M^{II} = divalent cation, and M^{IV} = an actinide element) were known,[2] the available structural information indicated that the actinide(IV) ions were either eight- or nine-coordinate. Thus, no six-coordinate actinide fluoro complexes had been identified although structural and/or optical spectral data were not available for all the compounds (*e.g.*, δ-Na_2UF_6, β- and δ-$(NH_4)_2UF_6$, and Cs_2UF_6).

As a preliminary to the attempted preparation of octahedral protactinium(IV)-fluoro complexes we had studied the reaction between UF_4 and an excess of NEt_4F in water, which yields only NEt_4UF_5, when Dr. J. L. Ryan (Batelle Northwest) informed us[3] that he had prepared octahedral complexes of the type $(NEt_4)_2M^{IV}F_6$ (M^{IV} = U, Np, Pu) by reactions in propylene carbonate. Using a slightly modified procedure with the same solvent we have now prepared $(NEt_4)_2PaF_6$ in two crystal modifications and report here the spectral and crystallographic properties of both modifications together with some of their chemical properties. The optical spectra indicate that both forms contain octahedrally coordinated Pa(IV) ions and are interpreted in terms of two ligand field parameters, θ and Δ, and the spin-orbit coupling constant,[3] and the resulting values are compared with those available for other octahedral $5f^1$ compounds. X-Ray diffraction and infrared results are also provided for $(NEt_4)_2UF_6$ which has only been obtained in one crystal form, that being isostructural with β-$(NEt_4)_2PaF_6$.

Experimental Section

Reagents. PaF_4 was available as part of a batch of material prepared several years ago;[4] UF_4 was provided by Mr. E. W. Hooper (Chemistry Division, AERE, Harwell). Commercial tetraethylammonium fluoride (Eastman Kodak) was vacuum dried for *ca.* 4 hr (10^{-3} Torr) after which time no bands due to water were present in its infrared spectrum. Propylene carbonate ($CH_3CHOCOOCH_2$) and acetone were flushed with argon (99.999% purity) immediately before use to remove oxygen and stored over freshly dried molecular sieves in an inert-atmosphere box. Methyl cyanide was purified as described previously.[5] The hexafluorouranate(IV) and -protactinate(IV) were prepared in an inert-atmosphere glove box (oxygen <20 ppm; H_2O <20 ppm) in which samples were dispensed for X-ray powdered diffraction and spectral studies and for analysis.

α-$(NEt_4)_2PaF_6$. PaF_4 (0.06 g) was heated for 10–15 min at 70–80° with NEt_4F (0.07 g, equivalent to a PaF_4:NEt_4F mole ratio of *ca.* 1:2.5) dissolved in propylene carbonate (1 ml). A small amount of insoluble residue was removed by centrifugation and acetone (4 ml) was added to the pale green propylene carbonate solution to precipitate the product, which was allowed to crystallize overnight (yield 65%). The product was washed with acetone and vacuum dried (10^{-4} Torr). *Anal.* Calcd for $(NEt_4)_2PaF_6$: Pa, 38.18; F, 18.84. Found: Pa, 38.0; F, 18.3. The same crystal modification was obtained at ice temperature as a second crop of crystals from the reactions which yielded β-$(NEt_4)_2PaF_6$, the propylene carbonate:acetone ratio again being *ca.* 1:4 when α-$(NEt_4)_2PaF_6$ formed.

β-$(NEt_4)_2PaF_6$. PaF_4 (0.05–0.140 g) was heated with NEt_4F in propylene carbonate (0.25–0.5 ml) as described above following which only an equal volume of acetone was added to the green solution after removal of a small quantity of insoluble residue by centrifugation. This mixture was cooled in ice (packed around a cold finger which is an integral part of the inert-atmosphere box) for several hours following which a further 0.25 ml of acetone was added and the mixture cooled again. The off-white (extremely pale green) crystalline product was isolated by centrifugation, washed with acetone (three 0.5-ml portions), and vacuum dried at room temperature (10^{-4} Torr). The yield was 55%. *Anal.* Found: Pa 37.9; F 18.5.

β-$(NEt_4)_2UF_6$. UF_4 (300–500 mg) was treated with tetraethylammonium fluoride in propylene carbonate (1 ml) as described above for β-$(NEt_4)_2PaF_6$. The addition of acetone (2 ml) resulted in the formation of virtually colorless (extremely pale green) crystals which were isolated by centrifugation, washed with acetone, and vacuum dried at room temperature (10^{-4} Torr). The initial yield (50–60%) was increased appreciably by the addition of further portions of acetone to the initial supernatant. Successive batches of the product from individual reactions gave virtually identical X-ray powder diffraction patterns and analyses. *Anal.* Calcd for $(NEt_4)_2UF_6$: U, 38.88; F, 18.63. Found: U, 38.8; F, 18.3.

Physical Measurements. Solid-state transmission spectra (0.2–2.0 μ) were recorded using the technique described earlier.[6] Infrared spectra were obtained for mulls in Nujol mounted between KBr plates (4000–700 cm^{-1}) or polythene plates (700–32 cm^{-1}) using a Hilger-Watts Infrascan and a Perkin-Elmer 180, respectively. Raman spectra were obtained using a Cary 83 instrument (argon ion line, 4881 Å).

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[1] N. Edelstein, D. Brown, and B. Whittaker, *Inorg. Chem.*, **13**, 563 (1974).

[2] R. A. Penneman, R. B. Ryan, and A. Rosenzweig, *Struct. Bonding*, 13, 1 (1973).

[3] J. L. Ryan, personal communication, 1973; J. L. Ryan, J. M. Cleveland, and G. H. Bryan, *Inorg. Chem.*, **13**, 214 (1974).

[4] D. Brown and P. J. Jones, *J. Chem. Soc. A*, 719 (1967).

[5] D. Brown and P. J. Jones, *J. Chem. Soc. A*, 247 (1967).

[6] D. Brown, B. Whittaker, and J. Edwards, Report AERE-R 7480, Atomic Energy Research Establishment, Harwell, England, 1973.

X-Ray powder diffraction samples were mounted in 0.2- or 0.3-mm diameter Lindemann glass capillaries, which were sealed and coated with Bostik[7] to prevent accidental breakage. Films were recorded using a 19-cm Debye–Scherrer camera with nickel-filtered copper radiation (λ_{α_m} 1.5418 Å) and exposure times of 12–16 hr (35 kV, 15 mA). The indexed reflections were refined by a least squares method using the program COHEN.[8] The agreement limit was set to 0.0004 for values of $\sin^2\theta$.

Analysis. Protactinium and uranium were precipitated as hydrous oxides by the addition of aqueous ammonia to the solid complexes and weighed as Pa_2O_5 and U_3O_8, respectively, following ignition at 800°. Fluorine was determined by the recommended SAC method involving titration with thorium.[9]

Results and Discussion

Crystallographic and Chemical Properties. β-$(NEt_4)_2PaF_6$ crystallizes from reasonably concentrated solutions in oxygen-free propylene carbonate, *e.g.*, 0.14–0.2 g of ^{231}Pa ml^{-1}, on the addition of an equal volume of acetone. The second crop of crystals, obtained following the addition of a second, larger volume of acetone, is invariably α-$(NEt_4)_2PaF_6$. The β modification has also been obtained as the product of a single reaction in oxygen-free methyl cyanide. This product, however, was not pure and the use of this solvent was not pursued in view of the decomposition of $(NEt_4)_2UF_6$ in methyl cyanide noted by Ryan, *et al.*[3] On standing at room temperature (25°) for a period of 3 weeks β-$(NEt_4)_2PaF_6$ transforms completely to α-$(NEt_4)_2PaF_6$, which is apparently the most stable phase of the hexafluoroprotactinate(IV), whereas only the β phase has so far been obtained for the uranium(IV) analog. It has not been possible to reverse the β- → α-$(NEt_4)_2PaF_6$ transformation by cooling the α phase in liquid nitrogen, nor has the $\beta \rightarrow \alpha$ change been observed under similar conditions using freshly prepared β-$(NEt_4)_2PaF_6$ or β-$(NEt_4)_2UF_6$ (*cf.* the β- → α-$(NEt_4)_2ThCl_6$ transformation which occurs on cooling in liquid nitrogen[10]). Attempts to obtain α-$(NEt_4)_2UF_6$ by heating the β phase in a sealed X-ray capillary at *ca.* 90° resulted in decomposition of the material, while crystallization from large volumes of propylene carbonate–acetone mixtures (*cf.* the preparation of α-$(NEt_4)_2PaF_6$) again yielded only the β phase. Our observations indicate that β-$(NEt_4)_2PaF_6$ is only obtained by crystallization from concentrated solution, behavior which is similar to that recently found[11] for α-U(acac)$_4$ (acac = acetylacetone). It is possible, although not established, that the ready transformation β- → α-$(NEt_4)_2PaF_6$ is associated with radiation damage since no similar change occurs with β-$(NEt_4)_2UF_6$ and the sample of PaF_4 available contained approximately a 7-year growth of the intensely radioactive protactinium-231 decay chain.

α-$(NEt_4)_2PaF_6$ possesses face-centered cubic symmetry with a_0 = 13.22 ± 0.01 Å. A partial list of indexed $\sin^2\theta$ values is shown in Table I together with visually estimated intensities. It is interesting to note that orthorhombic $(NEt_4)_2UCl_6$ is reported[12] to undergo a reversible phase change at 94° to become face-centered cubic and, indeed, the X-ray powder pattern of β-$(NEt_4)_2UF_6$ can be indexed on the basis of a slightly smaller orthorhombic cell than that of $(NEt_4)_2UCl_6$ (a_0 = 14.23 Å, b_0 = 14.73 Å, c_0 = 13.33 Å, space group $D_{2h}{}^{23}$-*Fmmm*) with the same space group.

Table I. Partial X-Ray Powder Diffraction of α-$(NEt_4)_2PaF_6$

$\sin^2\theta_{obsd}$	$\sin^2\theta_{calcd}$	*hkl*	I^a	$\sin^2\theta_{obsd}$	$\sin^2\theta_{calcd}$	*hkl*	I^a
0.0104	0.0102	111	s	0.1463	0.1462	533	w+
0.0136	0.0136	200	m	0.1502	0.1496	622	w+
0.0272	0.0272	220	s–	0.1738	0.1734	551	m–
0.0376	0.0374	311	s–		0.1734	711	
0.0413	0.0408	222	m–	0.1773	0.1768	640	m–
0.0538	0.0543	400	w+	0.1908	0.1904	642	m–
0.0640	0.0646	331	m	0.2008	0.2006	553	m–
0.0673	0.0681	420	m+		0.2006	713	
0.0820	0.0816	422	m	0.2278	0.2278	733	w–
0.0921	0.0918	511	m+	0.2313	0.2312	820	w
	0.0918	333			0.2312	644	
0.1086	0.1088	440	w+	0.2442	0.2448	822	w–
0.1189	0.1190	531	m+	0.2543	0.2550	555	vw–
0.1222	0.1224	442	m–		0.2550	751	
	0.1224	600		0.2827	0.2822	753	vw–
0.1361	0.1360	620	m–		0.2822	911	

[a] Visually estimated: s, strong; m, medium; w, weak; vw, very weak.

Refinement of the orthorhombic unit cell dimensions showed a_0 and b_0 to be equal within experimental error, *viz.*, a_0 = 12.81 Å, b_0 = 12.80 Å, and c_0 = 13.54 Å. We have been able unable to obtain crystals suitable for single-crystal studies which are essential to prove unambiguously whether the β phase is orthorhombic with a_0 accidentally equal to b_0 or is actually tetragonal. However, assuming tetragonal symmetry and converting the resulting face-centered cell (not a Bravaris lattice) to the corresponding body-centered tetragonal cell by rotation of the axes 45° around c_0 yields, after refinement, a cell with dimensions a_0 = 9.05 ± 0.01 Å and c_0 = 13.54 ± 0.01 Å. A partial list of $\sin^2\theta$ values indexed on the basis of this unit cell is shown in Table II. Relatively poor powder patterns were obtained for β-$(NEt_4)_2PaF_6$ and an insufficient number of lines could be measured accurately enough to allow a reliable calculation of the unit cell.

Both $(NEt_4)_2PaF_6$ and $(NEt_4)_2UF_6$ are air-sensitive compounds, the former undergoing oxidation to unidentified protactinium(V) species and the latter rapidly deliquescing to form a green solution. The addition of aqueous ammonia to $(NEt_4)_2PaF_6$ results in the formation of the characteristic black protactinium(IV) hydroxide which, in the presence of air, turns white within minutes. Both compounds are appreciably soluble in propylene carbonate and methyl cyanide but fail to dissolve in acetone, isopentane, carbon tetrachloride, and ether. Shortly after dissolution of $(NEt_4)_2PaF_6$ in commercial methyl cyanide (water content 0.3%) containing oxygen, a gelatinous precipitate, presumably hydrous protactinium(V) oxide, is formed. The thermal instability of β-$(NEt_4)_2UF_6$ has been mentioned above; during attempts to obtain solid-state spectral data above room temperature α-$(NEt_4)_2PaF_6$ was observed to decompose rapidly at *ca.* 420 K.

Infrared and Raman Spectra. Two infrared- and three Raman-active fundamental modes of vibration are predicted by group theory for regular octahedral molecules of the type MX_6 belonging to the point group O_h. Thus, the three *gerade* modes ν_1 (a_{1g}), ν_2 (e_g), and ν_5 (t_{2g}) give rise to Raman-active fundamentals while the two t_{1u} modes, ν_3 and ν_4, are permitted as fundamentals in the infrared spectra. The t_{2u} mode, ν_6, is totally forbidden. Two infrared modes are in fact observed for both α- and β-$(NEt_4)_2PaF_6$ and for β-$(NEt_4)_2UF_6$. These occur at 404 (vs) and 148 (m) cm^{-1} for both modifications of $(NEt_4)_2PaF_6$ and at 406 (vs) and 155 (m) cm^{-1} for β-$(NEt_4)_2UF_6$. A weak shoulder at 378 cm^{-1} in the spectrum of β-$(NEt_4)_2UF_6$ may indicate slight

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(7) Bostik is a registered trade name. This material and the appropriate thinner were purchased from Bostik Ltd., Leicester, England.

(8) J. A. C. Marples, and J. L. Shaw, Report AERE-R 5210, Atomic Energy Research Establishment, Harwell, England, 1966.

(9) We thank Mr. A. Wood and Mr. M. Preston (Applied Chemistry Division, AERE, Harwell, England) for fluorine determinations.

(10) D. Brown, *J. Chem. Soc. A*, 766 (1966).

(11) D. Brown and B. Whittaker, unpublished observations, 1973.

(12) E. Staritzky and J. Singer, *Acta Crystallogr.*, 5, 536 (1956).

Table II. Partial X-Ray Powder Diffraction Pattern of β-$(NEt_4)_2UF_6$

$\sin^2 \theta_{obsd}$	$\sin^2 \theta_{calcd}$	*hkl*	I^a	$\sin^2 \theta_{obsd}$	$\sin^2 \theta_{calcd}$	*hkl*	I^a
0.0104	0.0104	101	s	0.1306	0.1302	330	m−
0.0128	0.0128	002	m−		0.1308	116	
0.0143	0.0143	110	m−	0.1444	0.1447	420	m−
0.0274	0.0273	112	s−	0.1523	0.1521	413	w
0.0289	0.0288	200	m+	0.1572	0.1567	422	w
0.0363	0.0363	103	m+	0.1747	0.1743	226	w+
0.0391	0.0393	211	s−		0.1749	324	
0.0418	0.0418	202	m−	0.1838	0.1842	431	w
0.0517	0.0516	004	w		0.1842	501	
0.0574	0.0579	220	w+	0.1883	0.1882	510	w
0.0650	0.0650	213	m+	0.1950	0.1947	217	w
0.0682	0.0683	301	w+	0.2010	0.2011	512	w−
0.0707	0.0707	222	m	0.2097	0.2101	433	w
0.0722	0.0722	310	m	0.2129	0.2131	521	w−
0.0805	0.0806	204	m−	0.2217	0.2215	118	vw−
0.0853	0.0852	312	m	0.2319	0.2317	800	w−
0.0875	0.0880	105	m	0.2388	0.2391	523	w−
0.0943	0.0941	303	w−	0.2465	0.2462	530	vw−
0.0971	0.0972	321	m+		0.2468	336	
0.1095	0.1096	224	w	0.2529	0.2527	327	vw−
0.1165	0.1164	006	m−	0.2600	0.2593	532	w−
0.1232	0.1231	323	m−		0.2605	600	
0.1260	0.1262	411	m−				

[a] Visually estimated: s, strong; m, medium; w, weak; vw, very weak.

Table III. Spectral Results for α-$(NEt_4)_2PaF_6{}^a$

	At 300 K			At 85 K		
	Band position, cm^{-1}	Intens	Freq, cm^{-1}	Band position, cm^{-1}	Intens	Freq, cm^{-1}
	12,048	w, sh		12,084	w	+638
	11,600	m		11,593	s	+147
Γ_7-Γ_6				(11,446)		0
				11,299	s	−147
	11,111	s, b		11,111	sh	−335
				10,504	w	
	9,881	m, b		10,060	m	
Γ_7-$\Gamma_8{}'$				9,862	m	
	9,276	m, b		9,515	m	
	6,094	s, sp	+404	6,105	s, sp	+407
	5,838	s, sp	+148	5,843	s, sp	+145
Γ_7-$\Gamma_7{}'$	5,690	s, sp	0	5,698	s, sp	0
	5,543	m	−147	5,552	w	−146
	5,280	w	−410			

[a] Key: sp, sharp; s, strong; sh, shoulder; m, medium; w, weak; b, broad. Values in parentheses are estimated.

distortion from perfect octahedral symmetry. Our value of ν_3 is in excellent agreement with that reported by Ryan, *et al.*,[3] for $(NEt_4)_2UF_6$. As discussed below vibronic bands associated with both ν_3 and ν_4 are observed in the electronic spectra of the hexafluoroprotactinates(IV).

Attempts to obtain Raman data for β-$(NEt_4)_2UF_6$ have unfortunately been unsuccessful. Both the solid compound and solutions in propylene carbonate exhibit strong, broad-band fluorescence. This is apparently due to impurities in tetraethylammonium fluoride since this material exhibits the same fluorescence. Repeated recrystallization of NEt_4-F from ethanol-acetone mixtures and treatment of propylene carbonate solutions with either activated charcoal or alumina failed to remove the fluorescence. Although it can be partially "burned-out" by prolonged exposure to the Raman beam, we were still unable reliably to identify bands which could be assigned to ν_1, ν_2, or ν_5.

Electronic Spectra. The solid-state transmission spectra obtained for α-$(NEt_4)_2PaF_6$ (0.4-2.0 μ) are illustrated in Figures 1 and 2, and the measured peak positions and assignments for this compound are shown in Table III. The estimated accuracy of measurement is ±10 Å. The peaks shown at *ca.* 1.17, 1.37, and 1.68 μ are present in the spectra of NEt_4F and NEt_4Cl and are attributed to transitions within the tetraethylammonium cation. The rest of the spectrum is similar to those we reported earlier[1] for the octahedral

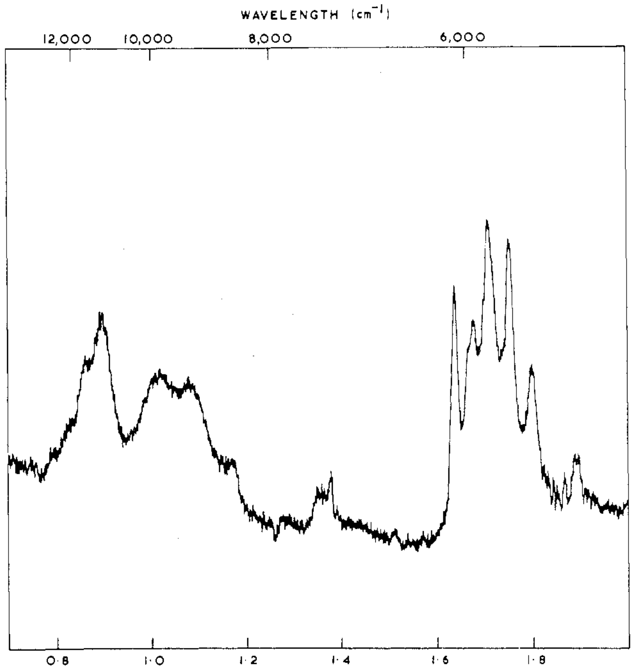

Figure 1. Spectrum of $(NEt_4)_2PaF_6$ at 300 K.

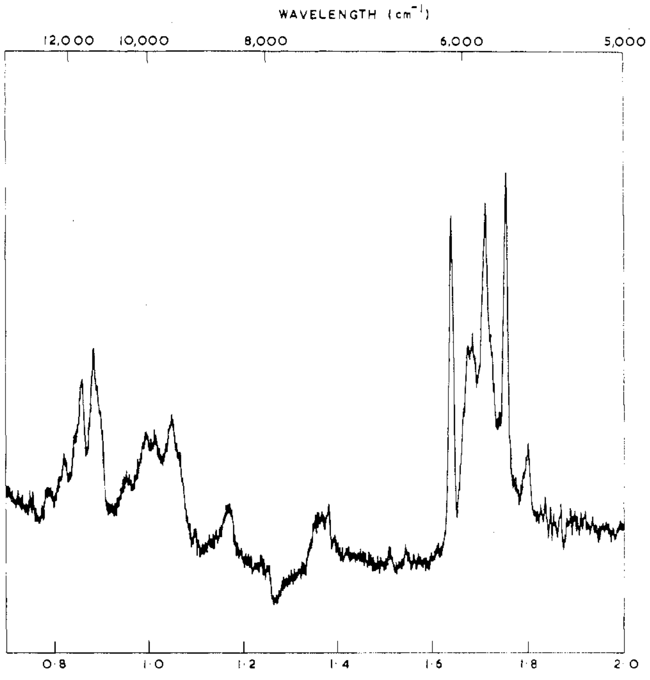

Figure 2. Spectrum of $(NEt_4)_2PaF_6$ at 85 K.

Table IV. Comparison of Calculated and Experimental Transition Energies for $(NEt_4)_2PaF_6$

	Energy, cm^{-1}			
	Γ_7-Γ_6	Γ_7-$\Gamma_8{}'$	Γ_7-$\Gamma_7{}'$	*g*
Calcd[a]	11,537	9586	5717	−0.704
Exptl	11,446	9708	5698	(−0.75)[b]

[a] Parameters used to obtain these results are given in Table V.
[b] Estimated value.

Table V. Values of the Ligand Field Parameters θ and Δ and the Spin-Orbit Coupling Constant ζ for 5f Octahedral Compounds

	Parameters, cm^{-1}				Parameters, cm^{-1}				Parameters, cm^{-1}		
Compd	θ	Δ	ζ	Compd	θ	Δ	ζ	Compd	θ	Δ	ζ
α-$(NEt_4)_2PaF_6$	4502	3074	1508	$(Ph_4As)UF_6$	6882	4479	1885	NpF_6	17498	5619	2433
$(NEt_4)_2PaCl_6$	1873	1634	1523	$(NEt_4)UCl_6$	3371	2936	1913				
$(NEt_4)_2PaBr_6$	1268	1707	1535	$(NEt_4)UBr_6$	2375	2935	1925				

complexes $(NEt_4)_2PaCl_6$ and $(NEt_4)_2PaBr_6$, and the optical absorption bands are again assigned to transitions from the ground Γ_7 level to the Γ_7', Γ_8', and Γ_6 states (Table IV). Not unexpectedly, however, the observed bands have shifted appreciably to lower wavelengths. β-$(NEt_4)_2PaF_6$ exhibits an identical spectrum.

The spectrum of α-$(NEt_4)_2PaF_6$ is dominated by vibronic bands as were those recorded[1] for the hexachloro- and hexabromoprotactinate(IV), and the mean values obtained for the vibrational transitions, 147 and 407 cm^{-1}, compare favorably with those observed directly for ν_4 and ν_3, respectively, in the infrared spectra of both α- and β-$(NEt_4)_2PaF_6$. A further similarity with the spectra of $(NEt_4)_2PaCl_6$ and $(NEt_4)_2PaBr_6$ is the splitting observed for the Γ_8' level in octahedral symmetry. Data available on similar splittings observed for a range of uranium(V) complexes are summarized and discussed elsewhere.[13] The shifts to lower wavelength observed with decreasing temperature for the bands associated with the Γ_8' and Γ_6 levels are associated with the smaller contribution from vibronic transitions to the low-energy side of the bands at lower temperatures.

The 300 K spectrum shows broad unresolved features for the higher energy transitions which makes their assignment difficult. Therefore, the assignment at 85 K shown in Table III was used to fit the ligand field splittings, θ and Δ, and the spin-orbit coupling constant, ζ. In order to have a check on these parameters the *g* value for PaF_6^{2-} was estimated as -0.75 (*cf.* the values available for the UF_6^- ion and NpF_6,[1] -0.700 and -0.604, respectively). The experimental and calculated values are compared in Table IV. The values obtained for θ, Δ, and ζ are compared in Table V with those for other $5f^1$ octahedral compounds. It can readily be seen that the PaF_6^{2-} parameters fit the trends observed in the other $5f^1$ compounds. The parameter Δ changes less with increasing oxidation state or increasing electronegativity of the halide ion for a fixed oxidation state than does θ. Qualitatively this trend has been correlated with changes in σ bonding dominating the total ligand field splittings.

Further magnetic and optical measurements in progress on the $5f^1$ compounds will enable more quantitative conclusions to be drawn.

Summary

The syntheses of two crystallographic forms of $(NEt_4)_2PaF_6$ are described and X-ray powder diffraction data for these compounds and $(NEt_4)_2UF_6$ are reported. $(NEt_4)_2PaF_6$ exhibits face-centered cubic symmetry and the powder pattern from β-$(NEt_4)_2UF_6$ was indexed on the basis of an orthorhombic unit cell. Infrared and optical data are reported for α- and β-$(NEt_4)_2PaF_6$. The spectral data are consistent with an octahedral (or a very slightly distorted octahedral) array of F^- ions surrounding the tetrapositive metal ion. The ligand field and spin-orbit parameters obtained fit the trends reported earlier for other octahedral $5f^1$ halide compounds.

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Registry No. $(NEt_4)_2PaF_6$, 49772-07-8; $(NEt_4)_2UF_6$, 42294-80-4; NEt_4F, 665-46-3; PaF_4, 13842-89-2; UF_4, 10049-14-6.

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(13) D. Brown, B. Whittaker, and N. Edelstein, Report AERE-R 7481, Atomic Energy Research Establishment, Harwell, England, 1973.

Contribution from Ames Laboratory–USAEC and the Department of Chemistry,
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The Detection of Praseodymium, Europium, Gadolinium and Holmium Carbonyls Using Matrix Isolation

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Carbonyl compounds of the rare earth metals praseodymium, gadolinium, and holmium were prepared by codeposition of the metal atoms with carbon monoxide in argon matrices. Infrared absorptions attributable to the species $M(CO)_x$, x = 1–6, were observed. The final product upon controlled annealing of the matrix was assigned to the hexacarbonyl. The variation of the carbonyl stretching frequency with coordination number is similar to that observed in other carbonyl complexes, namely, the frequency increases with increasing coordination number; however, the variation of the CO stretching frequency for different metals is very small. The spectra of the carbonyl compounds of europium were measured but the assignments were less certain.

Introduction

On the basis of their chemical and physical properties, the lanthanide metals can be classified as "typical" or "atypical."[1] A "typical" lanthanide shows a characteristic oxidation number of +3 and possesses a high melting and

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(1) K. A. Gschneidner, *J. Less-Common Metals*, 25, 405 (1971).