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Reactions of Strontium, Lanthanum, and Europium Iodides. Direct Preparation of Phosphorus Triiodide from Phosphates

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Received July 28, 1975 AIC50694E

Phosphorus triiodide has been prepared in high yields by the high-temperature reaction of metal iodide, metal phosphate, and silicon dioxide. Mixtures with europium, lanthanum, and strontium as the metallic element react under vacuum at 800–1000 °C to produce large quantities of hexagonal ($a = 7.133$ (2), $c = 7.414$ (2) Å) phosphorus triiodide and smaller quantities of diphosphorus tetraiodide and a polymorphic form of phosphorus. Products of the europium system have been characterized and include europium(II) silicate, $EuSiO_3$, and europium(II) tetraeuropium(III) oxide trisilicate, $Eu_5O(SiO_4)_3$. Europium(II) diiodide, EuI_2, europium(II) diiodide hydrate, $EuI_2{\cdot}H_2O$, and silicon tetraiodide have also been identified as side products. X-ray data are reported for the products and the mass spectrum of PI_3 has been obtained. The preparative reactions are presented, and thermodynamic calculations for the processes are described.

Introduction

During the course of an attempt to purify europium diiodide by vacuum distillation in a vitreous silica tube at 1000 °C, a substantial quantity of a red-orange crystalline product formed in the room-temperature region of the transport tube. This moderately volatile material was subsequently identified as a mixture of phosphorus triiodide and diphosphorus tetraiodide. The origin of the phosphorus was traced to hypophosphorous acid stabilizer in the commercial hydriodic acid used for preparation of the europium diiodide by the ammonium halide matrix method.[1,2] The hypophosphite was presumably oxidized to phosphate[3] under the conditions of the matrix procedure.

The process was obviously a new method for preparing the phosphorus iodides, which have only been synthesized from the elements or from other trihalides.[3] The reaction seemed interesting because of its novelty and because of its potential as a direct synthetic route to the iodides of phosphorus and possibly other semimetallic elements. The present investigation was initiated in an effort to define the reaction and to identify the parameters which affect it.

Experimental Section

Preparative Methods. The preparative methods involved the high-temperature reaction of mixtures containing anhydrous metal iodide, metal phosphate, and silicon dioxide. The iodides and phosphates were prepared from commercially available metal oxides (La_2O_3 and Eu_2O_3, 99.99% purity, American Potash and Chemical Corp.) and carbonates ($SrCO_3$, reagent grade, J. T. Baker Chemical Co.). The anhydrous halides were obtained by dissolution of the oxide or carbonate in minimal hydriodic acid (50.8% HI, 0.8% H_2PO_3, J. T. Baker Chemical Co.) and dehydration under vacuum in a matrix[2] of ammonium iodide (NH_4I, reagent grade, J. T. Baker Chemical Co.). The metal iodides were purified by distillation from graphite containers in an externally heated Vycor vacuum system. The phosphates were prepared by dissolution of the oxide or carbonate in minimal nitric acid, precipitation with phosphate ion (85% H_3PO_4, analytical grade, Mallinckrodt Chemical Works), and dehydration of the filtered product in air at 200 °C. Vitreous silicon dioxide (SiO_2, 99.9% minimum purity, General Electric Lamp Glass Department) was ground to 325 mesh or finer. Mixtures (1–2 g) of the reactants in 1:1:10 molar ratios of MI_x–M_yPO_4–SiO_2 (M = Sr, La, Eu) were prepared in a nitrogen-filled glovebox and placed in vitreous silica reaction tubes (1.0- or 2.5-cm i.d. × 30-cm length) which were sealed at one end and had a ground-glass connection and a stopcock closure at the other end. After connection of the reaction vessel to a liquid nitrogen trapped vacuum system (residual pressure $<10^{-5}$ Torr), the reaction mixture was positioned in an external resistance furnace and heated slowly (1–2 h) to 300 °C to degas the sample and then rapidly (0.5 h) to the reaction temperature (900–950 °C). Progress of the reaction was followed by visual means and by temperture measurements on the reaction vessel in the cooler region outside the furnace. The migration of hot gaseous products produced a noticeable (10–20 °C) increase in the temperature, which decreased to a constant value during the 1–2 h required for completion of the reaction. After cooling, the evacuated reaction tubes were removed to a glove box for product examination. The triiodide was purified by sublimation in evacuated Pyrex tubes subjected to temperature gradients with maxima of 50 °C and minima of 20 °C. The thermal stability of gaseous triiodide was examined by extended (4 weeks) heating of the equilibrium vapor in an evacuated silica ampule with a 40–800 °C temperature gradient.

In one set of experiments, the reaction mixture was systematically changed to determine the effects of known and possible system components on the reaction. In addition to the variation of the metal (M), the reaction was attempted in the presence and the absence of ammonium iodide and silicon dioxide. Exclusion of SiO_2 was achieved by containment of the reaction mixture in a graphite cup. Misch metal iodide, which was prepared from misch metal oxide (Code 330, American Potash and Chemical Corp.), was also substituted for the pure iodides.

A detailed investigation of the reaction was conducted with the europium system. Reaction mixtures were prepared by a modified matrix procedure.[1,2] After dissolution of europium oxide in hydriodic acid, a known fraction of the metal ion was precipitated by addition of standard phosphoric acid. In addition to ammonium iodide, the desired quantity of silicon dioxide was added before vacuum dehydration of the matrix at 200 °C and sublimation of the ammonium iodide at 400 °C. The ratios of EuI_2:$EuPO_4$ and EuI_2:SiO_2 were varied in the ranges 1:3 to 1:10 and 1:5 to 1:10, respectively. These mixtures were allowed to react according to the procedure described previously; however, in some experiments the heating times were increased up to 15 h. Identification of reaction residues was facilitated by leaching experiments which employed water and nitric acid solutions for successive dissolution of components from the product mixture.

Characterization Procedures. Reaction products were characterized by a combination of x-ray diffraction, x-ray fluorescence, mass spectrometry, and optical microscopy. Powder x-ray diffraction data were obtained with an evacuated 114.6-mm diameter Guinier-Haegg camera using Cu Kα_1 radiation and silicon ($a = 5.43062$ Å) as an internal standard. Diffraction samples were routinely coated with paraffin oil to minimize reaction with the atmosphere during transfer and exposure. For extremely air-sensitive materials, the plastic tape which was used for a sample mount was lined with a glass sheet from a thinly blown Pyrex bubble, and the oil-coated sample was then covered with a second piece of glass-lined tape. Weissenberg and precession methods were employed for single-crystal investigations. Crystals were selected under paraffin oil and sealed in glass capillaries. Qualitative analyses for the metals and iodine were effected with a Siemens Model 4b x-ray fluorescence spectrometer using tungsten radiation, a LiF analyzer, and scintillation detection. Mass spectra of the volatile solids were obtained with an AEI Model 902 spectrometer. The sample probe for solids was heated at 45 °C, and spectra were obtained at ionizing voltages of 20 and 70 eV. All manipulations and sample preparations were performed in the glovebox, which was purged of both water and oxygen; all air-sensitive samples were transported to the various instruments in nitrogen-filled containers.

Results and Discussion

The General Reaction. The reactions of all mixtures of metal iodide, metal phosphate, and silicon dioxide proceed with similar results. Reaction products are found in five tem-

Table I. Collection Temperatures and Crystallographic Data for Reaction Products

Product	Collection temp, °C	Crystal system	Lattice parameters[a]					
			a, Å	*b*, Å	*c*, Å	α, deg	β, deg	γ, deg
PI_3	25-50	Hex	7.133 (2)		7.414 (2)			
P_2I_4	25-50	Tricl	4.558 (2)	7.071 (4)	7.392 (3)	80.17 (5)	106.92 (3)	98.07 (3)
SiI_4[b]	25-50	Cub	12.019 (6)					
P	200-400	Monocl[c]	7.29 (7)					
EuI_2	500-700	Monocl	7.63 (1)	8.23 (1)	7.91 (1)		97.5 (1)	
$EuSiO_3$	800-1000	Tetr	5.044 (5)		10.14 (1)			
$Eu_5O(SiO_4)_3$	800-1000	Hex	9.47 (1)		7.016 (7)			
SiO_2[d]	800-1000	Tetr	4.978 (3)		6.936 (6)			
$EuI_2 \cdot H_2O$	*e*	Orth	9.67 (2)	12.37 (4)	4.482 (7)			

[a] Uncertainties in the last digit appear in parentheses. [b] Isolated only for the lanthanum system. [c] Indexed on a pseudocubic system; cf. ref 9. [d] α-Crystobalite modification. [e] An indirect product obtained by atmospheric hydration of EuI_2.

perature regions of the vacuum system. Large quantities of iodine condense in the liquid nitrogen trap and other products appear in the four temperature zones listed in Table I. Red-orange phosphorus iodide products collected in the room-temperature region are partially separated by differences in their vapor pressures. The triiodide migrates rapidly down the tube with the formation of hexagonal-shaped crystals; a mixed product containing acicular crystals of the tetraiodide remains in the region of the initial condensation. Single-crystal x-ray diffraction data for the triiodide show hexagonal symmetry and systematic absences consistent with space groups *P*63 and *P*63/*m*. The lattice parameters for the iodides (Table I) were obtained from powder data; reflection indices were assigned using single-crystal results for both PI_3 and P_2I_4.[4] Identification of the triiodide was hindered by a literature error in the value for the *c* parameter. The value (7.42 Å) is correct in the original report[5] but is in error in the abstract (7.24 Å)[5] and in a subsequent compilation (7.27 Å).[6]

The purified triiodide was further characterized by its melting point and by mass spectrometric analysis. The triiodide appears to melt reproducibly at 60.5 (5) °C but turns dark brown above 62 °C. The color change is reversible on heating at 57–59 °C, but the resultant products are amorphous to x-rays. Although this behavior suggests decomposition of the solid, the gas phase shows no evidence for disproportionation at temperatures up to 800 °C. The mass spectra are independent of the applied ionizing voltages and clearly identify the triiodide. The fragmentation pattern with the relative ion intensities in parentheses follows: P^+ (5), P_2^+ (6), I^{2+} (2), P_3^+ (1), P_4^+ (9), I^+ (80), PI^+ (51), I_2^+ (87), PI_2^+ (94), PI_3^+ (100). These data are consistent with the fragmentation pattern of PCl_3 and PBr_3.[7] The PX_3^+:PX_2^+ ratio increases reguarly from 0.6 for the chloride to 0.8 for the bromide to 1.1 for the iodide. An ion current with a relative intensity of approximately 5 is assignable to HI^+, which apparently results from hydrolysis of the sample during handling. The previous report that PI_3 is thermally unstable with the formation of I^+, HI^+, and I_2^+ on mass spectrometric analysis[7] is not confirmed by the present results. The mass spectrum of P_2I_4 has not been obtained because attempts to separate P_2I_4 from PI_3 by sublimation resulted only in transport of PI_3 and in formation of a black residue in the region of the initial charge. This result is indicative of P_2I_4 disproportionation, is inconsistent with the effusion study of Finch et al.,[8] who observed a congruent sublimation reaction for P_2I_4, and cannot be explained.

A brown-black product condensing in the 200–400 °C zone of the reaction tube has been identified as elemental phosphorus. X-ray data in Table I agree with that of Olshausen[9] for the monoclinic (pseudocubic) form of red phosphorus. Fluorescence data for these products show the presence of both the metallic elements and iodine. It appears that trace quantities of the metal iodides are transported to the cooler zone, but the presence of polymeric phosphorus iodides cannot be excluded.

The results of systematic changes in the reaction mixture show that metal iodide, phosphate, and silicon dioxide are necessary for preparation of the phosphorus iodides. Traces of orange product were observed in the absence of silicon dioxide but were of insufficient quantity for characterization. The use of misch metal oxide as a starting material resulted in only small quantities of triiodide. Cerium oxide, which is not converted to the iodide by the matrix method, was present in high concentration and resulted in a sharp reduction in yield. The reaction is unaffected by either the exclusion or the addition of ammonium iodide.

The Europium System. The extensive investigation of the europium system has permitted the identification of the additional reaction products in Table I and the definition of an overall reaction. Europium diiodide[10] is transported out of the reaction zone and, if not rigorously isolated from the atmosphere, reacts with moisture to produce the orthorhombic diiodide monohydrate. Formation of the $BaCl_2 \cdot H_2O$-type[11] phase is indicated by the diffraction data which show systematic extinctions consistent with space group *Pbnm*. Nonvolatile reaction products remain in the 800–1000 °C reaction zone and are amorphous to x-rays after normal reaction periods. After extended (12–15 h) heating, these products give complex diffraction patterns and are composed of unreacted vitreous silica, thin cream-colored platelets, and a yellowish green material. Fluorescence analysis shows that these residues contain both europium and iodine. Since water leaching eliminates the iodine fluorescence but does not alter the diffraction patterns, it appears that the residues contain trace quantities of EuI_2. The acid-insoluble cream-colored platelets are the α-crystobalite modification of SiO_2. The yellowish green material is a mixture of europium(II) silicate, $EuSiO_3$ ($EuO \cdot SiO_2$),[12] and europium(II) tetraeuropium(III) oxide trisilicate, $Eu_5O(SiO_4)_3$ ($EuO \cdot 2Eu_2O_3 \cdot 3SiO_2$).[13] Diffraction data for $EuSiO_3$ are similar to those of $SrSiO_3$ [14] and have been tentatively indexed on the tetragonal system indicated in Table I. The *c* parameter of the apatite-type $Eu_5O(SiO_4)_3$ phase is substantially larger than that reported previously (6.99 Å)[13] and suggests that the composition of that product lies within the region of variable composition bounded by $Eu^{II}Eu_4^{III}O(SiO_4)_3$ and $Eu^{III}_{4.67}O(SiO_4)_3$.[13] Formation of the most silica-rich silicates is expected because of the high SiO_2 contents of the reaction mixtures. It is not known whether the observed silicates are formed initially or whether they are only the final equilibrium products. The formation of crystabolite is rather surprising but probably results from mineralization processes accompanying silicate formation.

Characterization of the products for europium permits definition of the preparative reaction for phosphorus triiodide

$$2.5EuI_2(l) + EuPO_4(s) + 3SiO_2(s) \rightarrow PI_3(g) + I_2(g) + 2.25EuSiO_3(s) + 0.25Eu_5O(SiO_4)_3(s) \qquad (1)$$

Formation of the triiodide is detected at a reaction temperature of approximately 850 °C and occurs at temperatures as high as 1000 °C. It is obvious that the iodide acts both as a reducing agent and as an iodinating agent. The presence of strong reducing conditions is indicated by the large *c* parameter for $Eu_5O(SiO_4)_3$. The observed $EuSiO_3$ to $Eu_5O(SiO_4)_3$ ratios are consistent with the quantities predicted by eq 1 and indicate that the Eu(II)–Eu(III) redox couple is not involved in the reaction.

The effectiveness of eq 1 under various conditions has been determined with data from the modified matrix procedures. The yield of triiodide varies markedly with the EuI_2:$EuPO_4$ ratio. At 10:1 EuI_2:$EuPO_4$, the phosphorus iodide product is 60–75% of the theoretical yield and, within the limits of x-ray and mass spectrometric analyses is pure PI_3. At 3:1 EuI_2:$EuPO_4$, the yield of phosphorus iodide is approximately 45% of the theoretical value, and the product contains substantial quantities of P_2I_4. The amount of phosphorus formed in the 200–400 °C zone appears to increase with the phosphate concentration, but the inability to isolate the product quantitatively has prevented verification of this observation. Likewise, the inability to separate PI_3 and P_2I_4 has prevented quantification of their ratios.

The Strontium and Lanthanum Systems. Reactions of the strontium and lanthanum iodides are similar to that observed for europium. The formation of PI_3 in these systems clearly demonstrates that the redox process does not involve metal couples. The lowest temperatures at which PI_3 forms, 750 °C for strontium and 800 °C for lanthanum, are substantially below that for europium.

The reactions for the lanthanum and strontium systems have been proposed by analogy to the europium data. The nonvolatile products in these systems are amorphous and have not been identified; however, annealing experiments would most certainly result in the formation of the highest silicates, $La_2Si_2O_7$ ($La_2O_3{\cdot}2SiO_2$) and $SrSiO_3$ ($SrO{\cdot}SiO_2$), in the respective systems. The probable reactions are given by eq 2 and 3.

$$1.67LaI_3(l) + LaPO_4(s) + 2.67SiO_2(s) \rightarrow PI_3(g) + I_2(g) + 1.33La_2Si_2O_7(s) \qquad (2)$$

$$2.5SrI_2(l) + 0.5Sr_3(PO_4)_2(s) + 4SiO_2(s) \rightarrow PI_3(g) + I_2(g) + 4SrSiO_3(s) \qquad (3)$$

Silicon tetraiodide has also been observed as a lower temperature (500–600 °C) product of the lanthanum system. A 10–20-mg sample of a light yellow air-sensitive product was collected, recrystallized by sublimation, and identified by powder and single-crystal x-ray diffraction data for the colorless octahedral crystals. The SiI_4 is probably produced by a high-temperature reaction similar to that which has been reported for the reaction of lanthanide halides with silica.[15]

Conclusions

The direct preparation of phosphorus triiodide from phosphates at 800–1000 °C is certainly an unexpected process. The redox reactions described by eq 1–3 are, however, very similar to eq 4, which describes the commercial process for

$$Ca_3(PO_4)_2(s) + 3SiO_2(s) + 5C(s) \rightarrow P_2(g) + 5CO(g) + 3CaSiO_3(s,l) \qquad (4)$$

phosphorus production.[3] The essential difference between the two processes is the reducing agent, which in the iodide case results in halogenation of the phosphorus.

Although the calculations of Schaefer and Trinkel[16] indicate that the partial pressures of both PI_3 and P_2I_2 in equilibrium with red phosphorus are high at 250–400 °C, the apparent stability of the triiodide at temperatures up to 1000 °C is surprising. The reaction mechanism is not known, but the direct effect of phosphate concentration on the relative amounts of PI_3, P_2I_4, and P suggests that iodination occurs in the high-temperature reaction zone. Formation of the phosphorus iodides by combination of the elements in the cooler zones cannot be excluded although reaction of the elements in the gas phase seems improbable because of the low partial pressures. Mass spectrometric examination of the effusate species from a high-temperature Knudsen source would clarify the mechanism.

Table II. Estimated Free Energy Changes and Equilibrium Partial Pressures of PI_3 for the Reaction of Metal Iodides and Phosphates with Silicon Dioxide at 1200 K

Metal system (temp for PI_3, °C)[a]	Reaction	Estd ΔG°_{1200},[b] kcal/mol	Estd equil *P* of PI_3(g), Torr
Eu (850)	1	45	0.06
La (800)	2	35	0.5
Sr (750)	3	30	1.3

[a] The temperature for PI_3 appears in parentheses and is the lowest temperature at which deposition of PI_3 is observed. [b] The estimated uncertainties are ±10 kcal/mol in the free energy or a factor of 10 in the PI_3 pressure.

It is instructive to examine the thermodynamics of the preparative reactions and to correlate the data with experimental observations. The free energy changes for eq 1–3 at 1200 K have been calculated using published and estimated free energies of formation[17–21] and are presented in Table II. Estimated free energies have been derived from published values for model systems. For example, $\Delta G_f^\circ{}_{298}$ of $EuSiO_3$(s) has been calculated from the ΔG°_{1200} for the general reaction

$$MO(s) + SiO_2(s) \xrightarrow{1200\ K} MSiO_3(s)$$

The free energy change employed for this reaction is the constant value obtained for the manganese and lead systems using $\Delta G_f^\circ{}_{1200}$ data for $MnSiO_3$ and $PbSiO_3$ in combination with $\Delta G_f^\circ{}_{1200}$ data for silicon dioxide and the respective metal oxides. The free energy changes and the corresponding equilibrium pressures of PI_3 are consistent with the temperature trend observed for the appearance of the triiodide. The free energies estimated for the corresponding reactions of the metal iodides with their phosphates to produce the metal oxides instead of the silicates are more positive than the values in Table II by approximately 75 kcal. This result clearly demonstrates that silicon dioxide is essential because of thermodynamic factors.

Reactions of the type described in this investigation are expected to occur for a variety of active metal systems and are potential starting points for the industrial synthesis of phosphorous acid and other compounds which might be derived from the triiodide. A possible advantage of the direct synthesis lies in eliminating the inefficiency of first preparing elemental phosphorus and then oxidizing it back to the trivalent state. The effects of impurities and contaminants are not known, but the potential of the process seems sufficient to merit further investigation.

The present investigation has demonstrated that the iodide systems of the lanthanide and alkaline earths are reactive media which might be employed for preparing iodides of other semimetals. This work has also shown that the available crystallographic and structural data for phosphorus triiodide are substantially inaccurate. Single-crystal x-ray data have been collected for PI_3, and a communication of the complete structure is anticipated.[22] Hopefully, the present results will stimulate additional efforts to find new synthetic routes for well-known molecules.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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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Received August 15, 1975		AIC50611U

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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