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Intercalation Reactions of the Neptunyl(VI) Dication with Hydrogen Uranyl Phosphate and Hydrogen Neptunyl Phosphate Host Lattices

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The hydrated layered solids hydrogen uranyl phosphate, HUO_2PO_4, HUP, and its isostructural neptunyl analogue, $HNpO_2PO_4$, HNpP, can be intercalated with UO_2^{2+} and NpO_2^{2+} ions to yield a family of layered, hydrated solids that have been characterized by X-ray powder diffraction and by infrared, Raman, and electronic spectroscopy. Aqueous reactions of HUP with UO_2^{2+} and of HNpP with NpO_2^{2+} lead to hydrated layered solids $(UO_2)_3(PO_4)_2$, UP, and $(NpO_2)_3(PO_4)_2$, NpP; preparation of UP from HUP and of NpP from HNpP can also be effected by thermal decomposition of the parent solids, thus affording a set of "self-intercalation" reactions that are reversible. "Cross-intercalation" reactions (UO_2^{2+} into HNpP; NpO_2^{2+} into HUP) also proceed under stoichiometric conditions. Conducting the cross-intercalation reactions with high concentrations of intercalating ion leads to substantial substitution of actinyl ions in the host lattice sheets. The intercalation reactions of HUP and HNpP are shown to be selective by the marked preference found for intercalating Np(VI) over Np(V), as evidenced by the lack of reactivity of NpO_2^+ toward either host. Characterization by X-ray powder diffraction revealed that all of the solids could be indexed on the basis of tetragonal unit cells; the a lattice constant is ~6.95 Å in all samples, but intercalation of actinyl ions increases the interlamellar spacing, $c/2$, from ~8.7 Å in HUP and HNpP to ~11.2 Å. Vibrational and optical properties of the intercalated solids are derived from transitions characteristic of the actinyl ions comprising the solids.

Introduction

We and others have recently demonstrated that the luminescent, layered hydrate hydrogen uranyl phosphate, $HUO_2PO_4{\cdot}4H_2O$, HUP, is a versatile host lattice for intercalation chemistry.[1-3] Among the intercalating species we have employed is the uranyl ion itself.[4,5] In these earlier studies we showed that HUP can intercalate UO_2^{2+} ions from aqueous solution or undergo thermal decomposition in an aqueous slurry to yield a common product, a lamellar hydrate of uranyl phosphate, $(UO_2)_3(PO_4)_2{\cdot}8H_2O$, UP. The latter reaction can be described as a "self-intercalation" reaction, since the intercalating UO_2^{2+} ions were originally part of the host lattice.

The existence of the hydrated, isostructural neptunyl analogue of HUP, $HNpO_2PO_4$, HNpP,[6] prompted us to investigate the intercalative ion-exchange chemistry of the neptunyl dication, NpO_2^{2+}. We report in this paper that strong parallels exist between neptunyl and uranyl intercalation chemistry. In particular, we demonstrate that HNpP can be converted to a lamellar hydrate of neptunyl phosphate, $(NpO_2)_3(PO_4)_2$, NpP (isostructural with UP), either by intercalation with NpO_2^{2+} from aqueous solution or via a self-intercalation thermal decomposition reaction. We show, too, that "cross-intercalation" reactions (UO_2^{2+} into HNpP; NpO_2^{2+} into HUP) proceed under stoichiometric conditions to yield lamellar solids. When these cross-intercalation reactions are conducted at high concentrations of intercalating ion, host ion lability is evident from exchange of actinyl ions from the lattice sheets. The intercalation reactions of HUP and HNpP are shown to be selective by the marked preference found for intercalating Np(VI) over Np(V), as evidenced by the lack of reactivity of NpO_2^+ toward either host.

Experimental Section

Materials and Analyses. Due to the high α activity of ^{237}Np, 1.6×10^3 dpm/μg, all manipulations with Np, with the exception of the weighings for elemental and TGA analyses (vide infra), were performed in an air atmosphere inside a glovebox train designed for transuranics. Solutions containing the NpO_2^{2+} ion were prepared by dissolving NpO_2 in HNO_3/HF solution and treating the dark green solution with hot concentrated $HClO_4$ (Mallinckrodt Chemicals); at this point, the dark burgundy solution was determined to have a ~3:2 $NpO_2^{2+}{:}NpO_2^+$ composition by its visible spectrum.[7] This solution was heated to fuming and the solvent evaporated to near dryness. The residue was then dissolved in enough water to yield a nearly pure 0.1 M NpO_2^{2+} solution. *Warning: Many perchlorate salts detonate when heated.* Solutions of NpO_2^+ (0.3 M) were prepared by electrolytic reduction of NpO_2^{2+} solutions.[8]

Phosphoric acid (85%) was obtained from Mallinckrodt Chemicals, and $UO_2(NO_3)_2{\cdot}6H_2O$ (99.3%), from Aldrich Chemicals. Samples of $HUO_2PO_4{\cdot}4H_2O$ (HUP) were prepared as previously described.[9]

Samples used for elemental and TGA analyses were weighed out in an inert-atmosphere box (drybox) during which time they can lose H_2O; hydration values should thus be regarded as approximate. Analyses for Np were performed with a quantitative α-counting system using a 2π ionization chamber. Thermogravimetric analyses (TGA) were collected on a Perkin-Elmer TGA 7 thermogravimetric analyzer by using a ramp of 5 °C/min from 50 to 550 °C and an argon purge.

$HNpO_2PO_4{\cdot}4.5H_2O$, HNpP. A modification of the published procedure was employed.[6] Solid HNpP was prepared by addition of 20 mL of 0.1 M H_3PO_4 solution to 20 mL of a 0.1 M NpO_2^{2+} solution whose pH had been adjusted to 1 with NaOH. After the solution was stirred for 20 min at room temperature, a pale purple solid formed. The solid was isolated by centrifugation, washed several times with distilled water, and allowed to air dry in the glovebox overnight. Anal. Calcd for $H_{10}O_{10.5}PNp$: Np, 53.1. Found: Np, 54.4. TGA indicates 4.5 ± 0.6 waters of hydration. Calcd for 4.5 H_2O: 18.2. Found: 18.1. Although the solid will be referred to as hydrated $HNpO_2PO_4$, a small quantity of Na^+ ion may have substituted for H^+ in the solid.

$(NpO_2)_3(PO_4)_2{\cdot}5H_2O$, NpP. A room-temperature preparation of this salt was accomplished by mixing 10 mL of 0.1 M NpO_2^{2+} solution (an ~20-fold excess) with 20 mg of HNpP and stirring the slurry for 48 h. The pale purple-green solid was isolated by centrifugation, washed with distilled water, and allowed to dry in the glovebox atmosphere overnight. Thermal decomposition of HNpP provided a second route to NpP: a slurry of HNpP in distilled water was heated at 70 °C for 24 h and then isolated from the warm solution as described above. This latter sample was analyzed. Anal. Calcd for $H_{10}O_{19}P_2Np_3$, NpP: Np, 65.4. Found: Np, 65.7. TGA indicates 5.0 ± 0.2 waters of hydration. Calcd for 5.0 H_2O: 8.3. Found: 8.2.

$(NpO_2)(UO_2PO_4)_2{\cdot}4H_2O$, NpUP. Intercalation of NpO_2^{2+} into HUP was accomplished by combining 20 mg of HUP with a solution of 250 μL of 0.1M NpO_2^{2+} in 10 mL of distilled water and stirring for 48 h. This led to the isolation (vide supra, NpP) of a yellow-green powder. Anal. Calcd for $H_8O_{18}P_2NpU_2$, NpUP: Np, 22.2. Found: Np, 23.3. TGA indicates 4.0 ± 0.2 waters of hydration. Calcd for 4.0 H_2O: 6.7. Found: 6.6.

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(1) Rosenthal, G. L.; Ellis, A. B. *J. Less-Common Met.* **1988**, *139*, 299.
(2) Olken, M. M.; Verschoor, C. M.; Ellis, A. B. *Inorg. Chem.* **1986**, *25*, 80.
(3) Pozas-Tormo, R.; Moreno-Real, L.; Martínez-Lara, M.; Bruque-Gamez, S. *Inorg. Chem.* **1987**, *26*, 1442.
(4) Rosenthal, G. L.; Ellis, A. B. *J. Am. Chem. Soc.* **1987**, *109*, 3157.
(5) Dorhout, P. K.; Rosenthal, G. L.; Ellis, A. B. *Solid State Ionics* **1989**, *32/33*, 50.
(6) Weigel, F.; Hoffman, G. *J. Less-Common. Met.* **1976**, *44*, 125.
(7) Hagen, P. G.; Cleveland, J. M. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2905.
(8) Newton, T. W.; Hobart, D. E.; Palmer, P. D. NNWSI Report LA-UR-86-967.
(9) Olken, M. M.; Biagioni, R. N.; Ellis, A. B. *Inorg. Chem.* **1983**, *22*, 4128.

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$(UO_2)_{1.5}(NpO_2)_{1.5}(PO_4)_2 \cdot 4H_2O$, UNpP. Intercalation of UO_2^{2+} into HNpP was accomplished by combining 20 mg of HNpP with a solution of 50 μL of 1.0 M UO_2^{2+} in 10 mL of distilled water and stirring for 48 h. This led to the isolation (vide supra, NpP) of a yellow-green powder. Anal. Calcd for $H_8O_{18}P_2Np_{1.5}U_{1.5}$, UNpP: Np, 33.2. Found: Np, 33.0. TGA indicates 4.0 ± 0.2 waters of hydration. Calcd for 4.0 H_2O: 6.7. Found: 6.0.

Structural and Optical Measurements. Powder X-ray diffraction data for the presumed fully hydrated materials were collected by the Debye–Scherrer technique on an Enraf Nonius 601 generator using Cu Kα radiation and a 114.6-mm-diameter camera. These samples were prepared for data collection by introducing the powders into quartz capillaries inside the air-filled glovebox. Diffraction patterns were indexed on the basis of tetragonal unit cells for all the solids, and the cell constants were refined by using least-squares analysis. Values of $1/d^2$ and *hkl* assignments are available as supplementary material.

Optical measurements were performed on samples that were presumed to be fully hydrated. Samples containing Np were placed in a sealed Plexiglass box fitted with quartz windows (for UV–vis spectra) or AgCl windows (for IR spectra) for secondary containment. For photoluminescence (PL) and Raman spectra, secondary containment was achieved by placing the samples in a capillary tube surrounded by a quartz tube.

Infrared spectra were recorded as Nujol mulls on NaCl plates by using a Bio-Rad Digilab FTS-40 FTIR spectrometer. Raman spectra were recorded by using a Nicolet 1180 E Raman data system, a Spex Industries Ramalog 0.85-m double monochromator with holographic gratings, and an RCA PMT 31034 A detection system. The 647.1-nm line of a Spectra-Physics 171 Kr^+ laser was used as the scattering source, and multiscanning was employed.

Electronic absorption spectra were recorded on a Perkin-Elmer 330 UV–vis–near-IR spectrophotometer using silicone grease mulls, as previously described.[9] For PL spectra, a Spex Fluorolog spectrophotometer equipped with a Xe arc lamp was employed.

Results and Discussion

In sections below we discuss the intercalative reaction chemistry of NpO_2^{2+} and the composition of the resulting solids, structural properties of the materials on the basis of X-ray diffraction, infrared, and Raman spectroscopy, and their electronic absorption spectra.

Syntheses and Composition. All samples were weighed in an inert-atmosphere (dry)box prior to elemental and TGA analyses. Since this process may result in a loss of waters of hydration from the solids, the reported values should be considered as approximate.

$HNpO_2PO_4 \cdot 4.5H_2O$, HNpP. Powdered, hydrated samples of HNpP are prepared by a general aqueous precipitation route used for synthesizing hydrogen actinyl phosphates (eq 1);[6] hydrate

$$AnO_2^{2+} + H_3PO_4 \rightarrow HAnO_2PO_4 + 2H^+ \qquad (1)$$

$$An = U, Np, Pu, Am$$

waters are omitted for simplicity. Samples of HNpP gave a satisfactory Np analysis. The TGA data shown in Figure 1 indicate that about 3 of the 4.5 ± 0.6 waters of hydration are lost below 150 °C, with the remaining water lost between 150 and 500 °C.

$(NpO_2)_3(PO_4)_2 \cdot 5H_2O$, NpP. On the basis of the conversion of HUP to UP, the two independent routes given in eq 2 and 3 were used to convert HNpP to NpP. The intercalative ion-exchange

$$AnO_2^{2+} + 2HAnO_2PO_4 \rightleftarrows (AnO_2)_3(PO_4)_2 + 2H^+ \qquad (2)$$

$$3HAnO_2PO_4 \rightleftarrows H_3PO_4 + (AnO_2)_3(PO_4)_2 \qquad (3)$$

$$An = U, Np$$

reaction (eq 2) proceeded readily with HNpP and NpO_2^{2+} to yield NpP. The TGA data of Figure 1 show a loss of roughly five waters of hydration between 50 and 500 °C. Though isostructural with UP (vide infra), NpP has fewer waters of hydration on the basis of TGA data, possibly due to the loss of water to the glovebox atmosphere during sample preparation. We again stress that the hydration value should be considered as approximate.

Heating an aqueous slurry of HNpP at 70 °C for 24 h converted the solid to NpP (eq 3); this reaction can be regarded as the sum of eq 2 and a reaction that solubilizes HNpP as HPO_4^{2-} and NpO_2^{2+}. Besides a satisfactory Np analysis, isolated samples had X-ray and spectral features (vibrational and electronic) identical with those of samples synthesized by eq 2. As was found for UP, the self-intercalation reaction is reversible:[4] samples of NpP revert to HNpP over 48 h on standing in the mother liquor at room temperature. On the basis of this reversibility, we have written eq 2 and 3 as equilibria. With shorter reaction times or lower temperatures, reaction 3 is incomplete, as evidenced by the presence of both HNpP and NpP in the X-ray powder diffraction pattern. Similar observations were made for the uranyl analogues.[4,5]

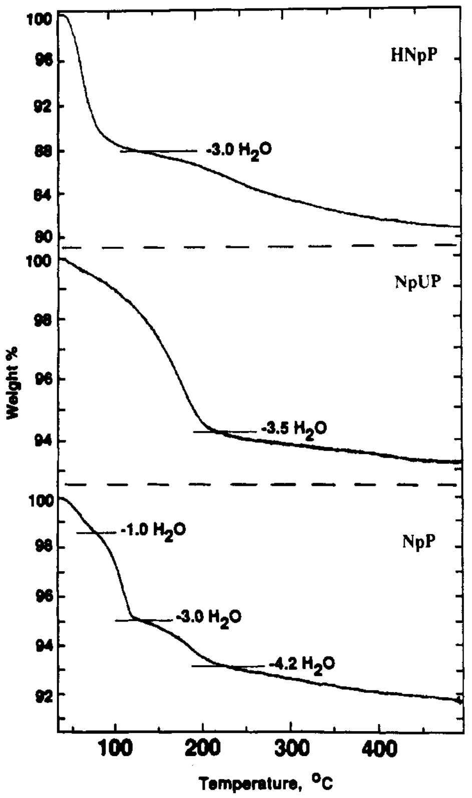

Figure 1. Thermogravimetric curves for HNpP, NpUP, and NpP. Horizontal lines indicate the calculated number of waters lost. The curve for UNpP is similar in character to that for NpUP.

$(NpO_2)(UO_2PO_4)_2 \cdot 4H_2O$, NpUP. The "cross-intercalation" reaction shown in eq 4 proceeds essentially to completion when

$$NpO_2^{2+} + 2HUO_2PO_4 \rightarrow (NpO_2)(UO_2PO_4)_2 + 2H^+ \qquad (4)$$

conducted with a stoichiometric amount of NpO_2^{2+} solution; a Np analysis is in accord with the indicated composition. Formulation of NpUP as a tetrahydrate is based on the TGA data of Figure 1, which also shows that most of the water has been lost by ~200 °C. NpUP appears to be isostructural with the UP octahydrate, but the smaller degree of hydration in NpUP, indicated by TGA, may again reflect loss of water to the inert glovebox atmosphere.

$(UO_2)_{1.5}(NpO_2)_{1.5}(PO_4)_2 \cdot 4H_2O$, UNpP. With equal moles of UO_2^{2+} ions and HNpP, the other cross-intercalation reaction (eq 5) did not proceed as written: the reaction appeared to go beyond

$$UO_2^{2+} + 2HNpO_2PO_4 \rightarrow (UO_2)(NpO_2PO_4)_2 + 2H^+ \qquad (5)$$

a simple cation exchange of the protons, on the basis of Np analysis, leading presumably to partial substitution of UO_2^{2+} for NpO_2^{2+} in the host lattice. The solid that was isolated appeared to be a tetrahydrate from TGA data.

Cross-Intercalation Reactions at High Intercalant Concentration. When concentrated solutions of the intercalant (0.5–1.0 M; a several hundred-fold excess) were used for the cross-intercalation reactions, X-ray diffraction patterns and visible absorption spectra of the solid products along with absorption spectra of the solutions indicated that the host actinyl cation was exchanging with the guest actinyl ion. Thus, when a slurry of HUP was prepared in concentrated NpO_2^{2+} solution, we observed a substantial concentration of UO_2^{2+} in solution after 6 h of reaction at room temperature and a concurrent change in color of the solid from bright yellow to purple. We also observed several phases (the major products being isostructural with HUP and/or HNpP and with NpP and/or UP) in the X-ray pattern of the solid. Likewise, after preparation of a slurry of HNpP in concentrated UO_2^{2+} solution, the recovered yellow solid was largely the HUP and/or HNpP with NpP and/or UP phases from X-ray data, although no NpO_2^{2+} could be detected in the visible electronic spectrum of the solid; correspondingly, the solution contained a large NpO_2^{2+} concentration. Equation 6 summarizes these reactions, where $An'O_2^{2+}$ represents the exchanging ion.

$$H(AnO_2)PO_4 + An'O_2^{2+} \rightarrow H(An'O_2)PO_4 + AnO_2^{2+} \qquad (6)$$

These observations demonstrate that the HUP and HNpP host lattice AnO_2^{2+} ions are labile under certain experimental conditions. This lability would, of course, be masked in reactions of UO_2^{2+} with HUP and of NpO_2^{2+} with HNpP but is clearly evident in the cross-intercalation reaction run at high concentration, wherein the intercalating actinyl ion serves as a label. Host lattice actinyl ion exchange could also have occurred in the preparation of NpUP and UNpP from dilute actinyl solutions, leading to a structural ambiguity: at this point we do not know how the intercalating actinyl ion is distributed among host and guest lattice sites. The origin of the observed lattice AnO_2^{2+} ion lability may simply be acidity, since the parent compounds HUP and HNpP are acid soluble, and solutions of UO_2^{2+} and NpO_2^{2+} hydrolyze extensively to yield strongly acidic solutions.[10]

Given the evidence for host lattice reactivity, our use of the term "intercalation" merits some discussion. Mechanistically, any of the reactions investigated may involve dissolution and reprecipitation of the host lattice, although we only have evidence for this under a limited set of experimental conditions. The term intercalation is thus loosely defined: the observed exchanges of guest ions may be accompanied by host lattice reconstruction. If they are, the product host lattice may or may not be chemically identical with the original host lattice.

Selectivity of Intercalation. Interestingly, attempts to intercalate the NpO_2^+ ion into HUP and HNpP were unsuccessful, even in the presence of 0.3 M NpO_2^+ solutions. Likewise, competition experiments with HUP or HNpP, using an equimolar NpO_2^+/NpO_2^{2+} mixture, only yielded NpUP and NpP, respectively, as gauged by electronic spectra. Thus, a band at 1200 nm characteristic of the NpO_2^{2+} species was present in the solids, while the sharp, intense 960-nm band characteristic of NpO_2^+ was absent.[11a] The marked preference of the HUP and HNpP hosts for NpO_2^{2+} over NpO_2^+ is striking. We have considered both redox and complexation properties of the two neptunyl ions as sources of this selectivity. There is no evidence from spectroscopic data that redox chemistry occurs: neptunyl and uranyl ions appear to retain their oxidation state during the ion-exchange reactions. On the other hand, complexation properties of the NpO_2^{2+} and NpO_2^+ ions are quite different,[11b,12] and those of the dication more closely resemble those of UO_2^{2+}, where data are available. For example, NpO_2^{2+} and UO_2^{2+} have virtually identical formation constants for complexation with chloride, but NpO_2^+ shows no evidence of complexation with this anion.[13] The complexation properties presumably reflect charge/size ratios of the ions (M–O bond length of 1.85 Å in NpO_2^+, 1.77 Å in UO_2^{2+}, and 1.71 Å in NpO_2^{2+}).[14]

Structural Properties. X-ray Data. Characterization by X-ray powder diffraction reveals that all of the compositionally characterized compounds appear to be single phase. They are layered solids that can be indexed on the basis of tetragonal unit cells. The powder X-ray diffraction patterns demonstrate that HNpP is isostructural with HUP[6] and that NpP, NpUP, and UNpP are isostructural with UP.[4,5] Whether these Np/U structural similarities correspond to identical hydration compositions cannot be determined accurately from our data.

Table I. Lattice Constants[a]

sample[b]	a, Å	$c/2$, Å[c]	sample[b]	a, Å	$c/2$, Å[c]
HUP[d]	6.973 (3)	8.707 (5)	NpP	6.99 (4)	11.1 (6)
HNpP[e]	6.92 (4)	8.75 (5)	UNpP	6.99 (3)	11.2 (6)
UP[f]	6.93 (5)	11.1 (4)	NpUP	6.97 (4)	11.1 (7)

[a] All samples were single phase that could be indexed to tetragonal unit cells. Errors in table entries are estimated standard deviations based on least-squares refinement. [b] Sample abbreviations are given in the text and Experimental Section. [c] The $c/2$ lattice parameter represents the interlamellar spacing, viz., the interplanar spacing between adjacent actinyl phosphate layers.[23] [d] Reference 24. [e] Original synthesis reported a = 6.96 (2) Å and c = 8.76 (6) Å, where c is equivalent to the interlamellar spacing.[6] [f] Reference 4.

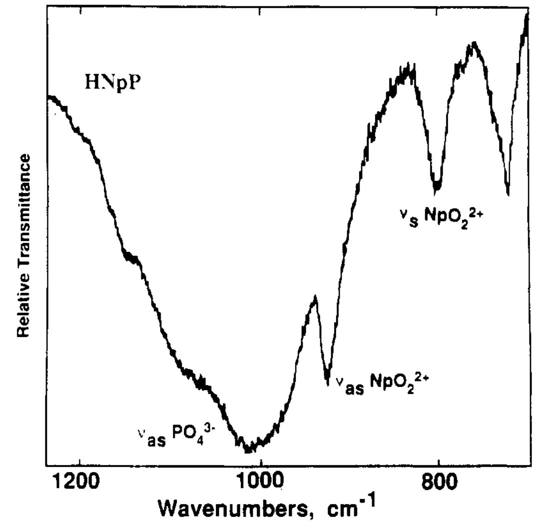

Figure 2. Infrared absorption spectrum of HNpP in Nujol oil. The labeled assignments are discussed in the text. The peak at ~720 cm^{-1} is from Nujol oil.

As shown in Table I, the samples have an a lattice constant of ~6.95 Å. The interlamellar spacing, $c/2$, is about 8.7 Å for the parent solids HUP and HNpP but increases to ~11.2 Å upon intercalation of actinyl ions, suggesting that the ions have their principal rotation axes parallel to the actinyl phosphate sheets.[4,15] It is noteworthy that both UP and NpP, prepared by either intercalation or thermal decomposition from HUP and HNpP, respectively, exhibit X-ray diffraction patterns with fewer and more diffuse lines than their precursors, indicative of a lower degree of crystallinity. The same is true of the X-ray diffraction patterns for the products of the cross-intercalation reactions.

Infrared and Raman Spectra. Figure 2 presents the infrared spectrum of HNpP. The spectrum of HNpP is quite similar to that of HUP and leads to analogous assignments: the spectrum is dominated by a phosphate stretching band at ~1000 cm^{-1} and by asymmetric and symmetric NpO_2^{2+} stretching modes that appear at 930 and 810 cm^{-1}, respectively; the assignments are based on those reported for UP.[16,17]

Figure 3 illustrates the variations observed in the infrared actinyl and phosphate stretching regions for UNpP and NpUP, for which two different actinyl ions are present, and for NpP, possessing inter- and intralamellar NpO_2^{2+} ions. Like HNpP, the three compounds of Figure 3 all contain the NpO_2^{2+}/UO_2^{2+} bands at ~930 and 810 cm^{-1}, although the neptunyl and uranyl stretches are not resolvable. In contrast to the case of the actinyl region

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(10) Allard, B.; Kipatsi, H.; Liljenzen, J. O. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1015.
(11) (a) Katz, J. J.; Seaborg, G. T.; Morss, L. R. *The Chemistry of the Actinide Elements*, 2nd ed.; Chapman and Hall: New York, 1986; Vol. 1, p 466. (b) *Ibid.*, p 483. (c) *Ibid.*, p 469.
(12) Maya, L. *Inorg. Chem.* **1984**, *23*, 3926.
(13) (a) Day, R. A.; Powers, R. M. *J. Am. Chem. Soc.* **1954**, *76*, 3895. (b) Danesi, P. R.; Chiarizia, R.; Scibona, G.; D'Alessandro, G. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2396.
(14) Burns, J. H.; Musikas, C. *Inorg. Chem.* **1977**, *16*, 1619.
(15) Pavković, N.; Marković, M. *Radiochim. Acta* **1983**, *34*, 127.
(16) Pekárek, V.; Veselý, V. *J. Inorg. Nucl. Chem.* **1965**, *27*, 1151.
(17) Pham-Thi, M.; Colomban, Ph. *J. Less-Common. Met.* **1985**, *108*, 189.

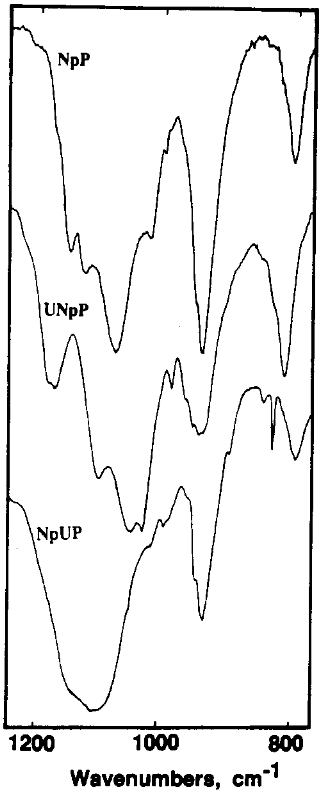

Figure 3. Infrared absorption spectra of NpP, UNpP, and NpUP in Nujol oil.

of the spectra, a dramatic change in the phosphate stretching region from ~1000 to 1200 cm^{-1} is seen in comparing HNpP, Figure 2, with the intercalated derivatives, NpP, NpUP, and UNpP. These changes are reminiscent of those observed for HUP and UP tetrahydrate and have been attributed to the presence of an asymmetric arrangement of actinyl ions around the phosphates that distort the tetrahedral symmetry.[16,17] Such distortions, as well as differences in hydration and sample preparation, could also account for the individual differences in the phosphate regions of the spectra in Figure 3.

Attempts to record Raman spectra for HNpP, NpP, and UNpP were unsuccessful due to their rapid photodegradation in the laser beam to green solids that presumably contain Np(IV) or Np(V);[11a] such a reduction could conceivably be coupled with the oxidation of lattice water to oxygen, on the basis of ground-state aqueous, acid redox couples (NpO_2^{2+}/NpO_2^{+} is 1.24 V; NpO_2^{2+}/Np^{4+} is 0.94 V vs NHE[11c]) and by assuming an increase in these potentials of about 1 V, if the absorption band at ~1200 nm (vide infra) represents the redox-active excited state. Raman spectra of these materials were collected but did not yield any assignable peaks. Figure 4 presents Raman spectra for HUP and NpUP. For the latter compound, we assign the two bands at 827 and 803 cm^{-1} to the UO_2^{2+} and NpO_2^{2+} symmetric stretching modes, respectively.[18] There appears to be a ~15-cm^{-1} red shift in the uranyl ion frequency in NpUP relative to HUP, where it occurs at 843 cm^{-1}. This is not surprising given the sensitivity of the uranyl stretching frequency to its coordination environment.[19,20] The ν_s phosphate stretching band for NpUP occurs at ~1000 cm^{-1} and is split, perhaps reflecting an asymmetric environment at the phosphate site.[17,18] The bands at ~190 cm^{-1} represent the uranyl and, presumably, neptunyl symmetric bending modes.

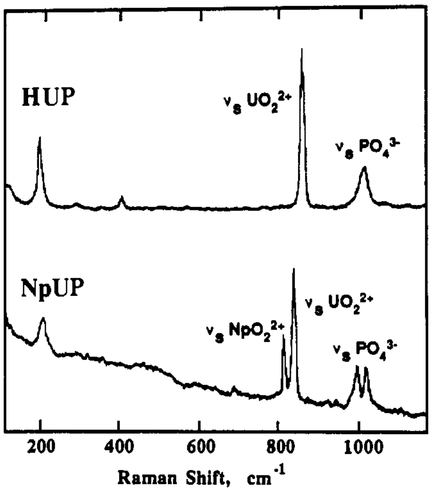

Figure 4. Raman spectra of HUP and NpUP solids at 298 K. The labeled assignments are discussed in the text.

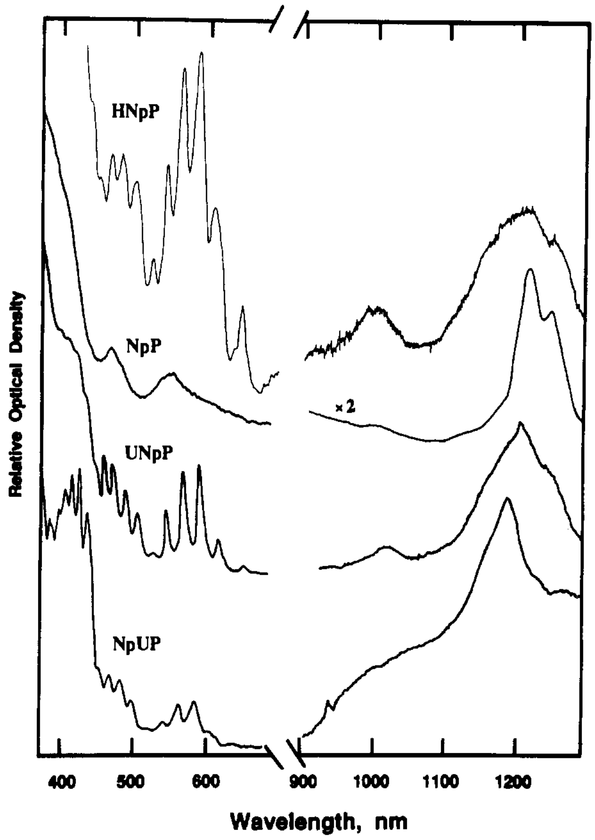

Figure 5. Visible–near-IR absorption spectra of HNpP, NpP, UNpP, and NpUP solids in silicone grease at 298 K. The discontinuities in the base lines are due to a detector change near 800 nm.

Optical Properties. Absorption spectra of several of the solids are shown in Figure 5. The pale purple solid, HNpP, displays the characteristic vibronic structure of the NpO_2^{2+} absorption near 500 and 600 nm reported for aqueous perchlorate solutions.[21] The spacings in the vibronic progression average ~704 cm^{-1} (715 cm^{-1} was observed in solution), corresponding to the excited-state symmetric stretching mode of NpO_2^{2+}. A similar assignment is made for UO_2^{2+} in HUP for which a separation of ~708 cm^{-1} is found (718 cm^{-1} reported for perchlorate solutions[22]). Bands at ~1200 and ~960 nm are also seen in this spectrum. Interestingly, the 960-nm band's intensity is much greater relative to the 1200-nm band's intensity than is observed in aqueous perchloric acid.[11a]

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(18) Madic, C.; Begun, G. M.; Hobart, D. E.; Hahn, R. L. *Inorg. Chem.* **1984**, *23*, 1914.

(19) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978; p 115.

(20) Ohwada, K. *Spectrochim. Acta, Part A* **1968**, *24A*, 595.

(21) Sjoblom, R.; Hindeman, J. C. *J. Am. Chem. Soc.* **1951**, *73*, 1744.

(22) Bell, J. T.; Biggers, R. E. *J. Mol. Spectrosc.* **1968**, *25*, 312.

(23) Morosin, B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3732.

(24) Dorhout, P. K.; Rosenthal, G. L.; Ellis, A. B. *Inorg. Chem.* **1988**, *27*, 1159.

Samples of HNpP did not exhibit photoluminescence at room temperature between 400 and 900 nm. As noted above, we did observe what appears to be photoreduction of HNpP to a green solid upon excitation with 418- and 647-nm Kr^+ laser lines. Introduction of NpO_2^{2+} into the HUP host lattice effectively quenches the characteristic uranyl emission of HUP, analogous to the quenching found by intercalating UO_2^{2+} into HUP.[4]

Samples of NpUP and UNpP have absorption spectra that are a composite of NpO_2^{2+} (450–700 nm and near-IR region) and UO_2^{2+} (400–500 nm) electronic transitions. The electronic spectrum of NpP exhibits two broad, weak absorptions between 400 and 700 nm as well as the characteristic near-infrared Np(VI) absorption. The variations in peak shape in the 900–1200-nm region are noteworthy but have not been further investigated. For none of these species were we able to detect emission from 500 to 900 nm.

Conclusion

Both the HUP and HNpP host lattices intercalate NpO_2^{2+} and UO_2^{2+} ions to yield a family of hydrated, lamellar host lattices. "Cross-intercalation" reactions of UO_2^{2+} into HNpP and of NpO_2^{2+} into HUP demonstrate that host lattice substitution can occur. Both host lattices show a remarkable selectivity for intercalating NpO_2^{2+} over NpO_2^+ under ambient conditions. Vibrational and optical properties of the intercalated solids are derived from the actinyl transitions.

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Supplementary Material Available: A table of $1/d^2$ and *hkl* values from powder X-ray diffraction (2 pages). Ordering information is given on any current masthead page.

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Ferromagnetic Behavior in Linear Charge-Transfer Complexes. Structural and Magnetic Characterization of Octamethylferrocene Salts: $[Fe(C_5Me_4H)_2]^{\bullet+}[A]^{\bullet-}$ (A = TCNE, TCNQ)

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The reaction of $Fe^{II}(\eta^5\text{-}C_5Me_4H)_2$ with cyano acceptors A {A = TCNE (tetracyanoethylene), TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane), *n*-$C_4(CN)_6$ (*n*-hexacyanobutadiene), $C_6(CN)_6$ [tris(dicyanomethylene)cyclopropane], DDQ (2,3-dichloro-5,6-dicyanobenzoquinone), $TCNQF_4$ (perfluoro-7,7,8,8-tetracyano-*p*-quinodimethane)} results in formation of 1:1 charge-transfer salts of $[Fe^{III}(C_5Me_4H)_2]^{\bullet+}[A]^{\bullet-}$ composition. The TCNE and TCNQ complexes have been structurally characterized. The $[Fe^{III}(C_5Me_4H)_2]^{\bullet+}[TCNE]^{\bullet-}$ salt belongs to the centrosymmetric *Cmca* space group [a = 14.990 (3) Å, b = 11.580 (7) Å, c = 12.503 (4) Å, Z = 4, T = 23 °C, V = 2170 (3) Å^3, R_u = 0.037, R_w = 0.040]. The anion exists as isolated planar $[TCNE]^{\bullet-}$ radicals. The C—C, C—CN, and C≡N bonds are 1.385 (6), 1.426 (4), and 1.135 (5) Å, respectively, and the NC—C—CN, NC—C—C, and N≡C—C angles are 118.7 (4), 120.6 (4), and 179.6 (4)°, respectively. The $[Fe^{III}(C_5Me_4H)_2]^{\bullet+}[TCNQ]^{\bullet-}$ salt belongs to the centrosymmetric $P\bar{1}$ space group [a = 8.636 (1) Å, b = 9.574 (3) Å, c = 10.025 (4) Å, α = 63.77 (3)°, β = 70.22 (2)°, γ = 162.79 (2)°, Z = 1, T = 23 °C, V = 651.6 (3), R_u = 0.052, R_w = 0.054]. The anion exists as isolated planar $[TCNQ]^{\bullet-}$ radicals. The HC—CH, HC—C, C—C(CN)$_2$, C—CN, and C≡N bonds are 1.358, 1.419, 1.405, 1.417, and 1.148 Å, respectively, and the HC—C(H)—C, HC—C—CH, NC—C—CN, NC—C—C, and N≡C—C angles average 121.6, 116.7, 115.6, 122.1, and 178.9°, respectively. The solid-state structure for both salts consists of linear chains of $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}D^{\bullet+}\cdots$. The cation for both salts has a staggered conformation with the Fe asymmetrically bonded to the C_5 ring; i.e., the average Fe–CH and Fe–CMe separations are 2.057 and 2.099 Å, respectively. The Fe–C_5 ring centroid distance is 1.694 Å for the $[TCNE]^{\bullet-}$ salt and is 1.710 Å for the $[TCNQ]^{\bullet-}$ salt. The high-temperature magnetic susceptibility for polycrystalline samples of these complexes can be fit by the Curie–Weiss law, $\chi = C(T - \Theta)^{-1}$, with $\Theta = +0.5 \pm 2.2$ K, and μ_{eff} ranges from 2.71 to 3.97 μ_B, suggesting that the polycrystalline samples measured had varying degrees of orientation. The 7.0 K EPR spectrum of the radical cation exhibits an axially symmetric powder pattern with $g_\parallel = 4.11$ and $g_\perp = 1.42$, and the EPR parameters are essentially identical with those reported for ferrocenium and decamethylferrocenium. No EPR spectrum is observed at 78 K. Akin to the $[Fe(C_5Me_5)_2]^{\bullet+}$ salts, these salts have ^{57}Fe Mössbauer spectra consistent with complete charge transfer; however, unlike the case for the former complexes, quadrupole splittings of 0.30 and 0.22 mm/s are observed at 4.8 and 298 K, respectively. The absence of strong interionic magnetic coupling for the $[Fe(C_5Me_4H)_2]^{\bullet+}$ salts contrasts with the behavior of the $[Fe(C_5Me_5)_2]^{\bullet+}$ salts.

Introduction

One-dimensional, 1-D, charge-transfer complexes frequently exhibit unusual optical, electrical,[2-4] and, recently, unusual cooperative magnetic properties.[5] For example, the reaction of decamethylferrocene, $Fe(C_5Me_5)_2$, and 7,7,8,8-tetracyano-*p*-quinodimethane, TCNQ, gives three major products of varying stoichiometry, conductivity, and magnetism. Two 1:1 charge-

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(2) See for example: *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Publisher Corp.: New York, 1982, 1983; Vols. 1-3. Simon, J.; Andre, J. J. *Molecular Semiconductors*; Springer Verlag: New York, 1985.

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