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The Synthesis and Characterization of Neptunium Hydroxysulfate, $Np(OH)_2SO_4$*

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Neptunium (IV) hydroxysulfate, $Np(OH)_2SO_4$, was synthesized using hydrothermal techniques. The X-ray powder diffraction pattern indicates that the compound is isomorphous with the Th(IV) and U(IV) analogs. Cell constants for the three compounds clearly show the effcts of the actinide contraction. Visible and near-ir spectra are consistent with the presence of Np(IV) and are compared to spectra of Np(IV) in acidic solution. The ir spectrum contains bands which are assigned to the hydroxy and sulfate groups.

Introduction

Neptunium is one of several actinides which in the quadrivalent state exists in strongly acidic solutions as the aquo ion. As the acidity is lowered, hydrolysis reactions become an important aspect of the chemistry of such highly charged species. The similarity of the first hydrolysis constants for U(IV), Np(IV), and Pu(IV) (*1*) suggests that these cations may form an isomorphous series of compounds based on their hydrolytic behavior. Previous investigation with U(IV) (*2*, *3*) revealed the existence of at least two compounds which contain bridging hydroxy groups, one of which is isomorphous with Th(IV) hydroxysulfate (*4*).

Both hydrated and anhydrous hydroxysulfates of a number of quadrivalent metal ions have been synthesized and their structures characterized. Since the compounds $Th(OH)_2SO_4$ (*4*), $U(OH)_2SO_4$ (*2*), and $Hf(OH)_2SO_4$ (*5*) are isostructural, it is apparent that a wide range of metal–oxygen bond lengths, ~2.42 to 2.17 Å, can be accommodated in a common structural type. We reasoned that given the appropriate conditions, it should be possible to prepare compounds with intermediate bond lengths such as $Np(OH)_2SO_4$ and $Pu(OH)_2SO_4$. Consequently, we investigated the behavior of Np(IV) and Pu(IV) under the hydrothermal conditions which lead to formation of the Th(IV) and U(IV) hydroxysulfates. In this paper we report the synthesis and characterization of the Np(IV) hydroxysulfate. Results for the Pu(IV) system will be reported elsewhere.

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Experimental

A solution of Np(IV) (8.0×10^{-2} *M*, 20 ml) in 0.5 *M* sulfuric acid was prepared by electrochemical oxidation (platinum anode) at −0.150 V vs saturated calomel electrode (SCE) of a solution of Np(III) which was prepared by electrochemical reduction (mercury pool cathode at −0.700 V vs SCE) of a solution of Np(V) in 0.5 *M* sulfuric acid. Using Schlenk techniques, a portion (17 ml) of the green Np(IV) solution was sealed under slight vacuum in a thick-walled Pyrex tube (0.75 in. o.d., 0.50 in. i.d., ~6 in. length). This tube was placed in an appropriate secondary and heated in an oven at 140°C. The maximum pressure under these conditions was 3.6 atm. Examination upon removal from the oven after 168 hr revealed the presence of clusters of dark-green crystals and a very pale-green solution. The tube then was submerged in a water bath at room temperature to quench any further reaction or structural change. The crystals were separated from the solution by filtration, washed with 95% EtOH, and air-dried.

X-Ray powder diffraction patterns were recorded using standard Debye–Scherrer techniques. Infrared spectra were taken on a Beckmann IR10 infrared spectrophotometer. Visible and near-ir spectra were recorded on a Cary 17 spectrophotometer.

Results and Discussion

In addition to an analysis of the crystals identified as $Np(OH)_2SO_4$ by X-ray methods, both the infrared and optical spectra were recorded to gain further insight into the electronic structure and to explore features of the bonding not previously reported in this type of compound.

The crystals of $Np(OH)_2SO_4$ obtained in the hydrothermal reaction were found to be stable in air for a period of at least 1 year. The observed X-ray powder diffraction lines, those calculated on the basis of the refined cell constants, the corresponding *hkl* values, and qualitative estimates of intensity are listed in Table I. The powder pattern initially was indexed by analogy with the $U(OH)_2SO_4$ structure (*2*). The cell constants then were refined on the basis of the *hkl* values as obtained. Table II lists the cell constants for the isomorphous series of compounds $An(OH)_2SO_4$, where *An* = Th, U, Np.

The X-ray powder pattern of $Np(OH)_2SO_4$ clearly shows the isomorphous nature of Th, U, and Np compounds. Several low-order reflections which were not observed in the thorium or uranium structures were observed in the case of neptunium. The *d* spacings of these additional reflections coincide with those calculated on the basis of the refined cell parameters. The intensities of the observed lines also are in full agreement with the expected relative intensities.

The cell constants of the $An(OH)_2SO_4$

TABLE I

X-RAY POWDER DATA FOR $Np(OH)_2SO_4$[a]

d_{obs}	d_{calc}	*hkl*	*I*
5.90	5.93	101	W
5.72	5.75	200	S
4.48	4.49	011	S
4.42	4.43	201	S
4.18	4.18	111	S
4.10	4.12	210	S
3.53	3.54	211	M
3.34	3.36	301	W
	3.32	102	
2.95	2.97	202	M
	2.94	020	
	2.92	311	
2.88	2.89	112	S
	2.88	400	
2.66	2.66	401	M
	2.65	212	
2.63	2.64	121	W
	2.62	220	
2.58	2.58	410	S
	2.57	302	

TABLE I—(*Continued*)

d_{obs}	d_{calc}	*hkl*	*I*
2.45	2.45	221	M
	2.42	411	
2.27	2.26	103	M
2.21	2.21	402	M
	2.21	321	
2.18	2.18	501	W
2.15	2.15	013	W
	2.14	203	
2.12	2.11	113	W
2.04	2.06	420	M
	2.05	411	
1.975	1.978	303	S
	1.972	421	
1.940	1.936	322	S
1.915	1.918	600	S
	1.917	502	
1.895	1.888	031	M
1.870	1.875	313	M
	1.863	131	
1.843	1.848	601	W
1.823	1.824	610	M
	1.823	512	
1.800	1.801	403	S
1.765	1.769	422	M
	1.764	611	
1.735	1.732	223	M
	1.732	004	
1.693	1.694	331	S
	1.689	132	
1.660	1.658	204	W
1.642	1.644	114	W
	1.642	323	
	1.637	232	
1.625	1.630	503	W
	1.621	430	
1.610	1.614	612	M
	1.607	620	
1.600	1.600	701	M
	1.596	214	
1.543	1.544	711	W
1.495	1.495	033	W
	1.493	024	
1.480	1.483	133	W
	1.480	124	
	1.475	603	
1.463	1.460	531	W
1.440	1.440	712	M
	1.439	414	
	1.438	800	

[a] Intensities, judged visually, are strong = S, medium = M, weak = W.

TABLE II

CELL CONSTANTS[a] FOR *An*$(OH)_2SO_4$ (*An* = Th, U, Np)

An	*a*	*b*	*c*
Th	11.733(5)	6.040(5)	7.059(5)
U	11.572(5)	5.926(5)	6.969(5)
Np	11.508(14)	5.888(7)	6.927(9)

[a] The cell constants in angstroms are followed by the estimated standard deviations of the last digits in parentheses.

compounds gradually decrease on going from thorium to neptunium (Table II). The decrease is more pronounced on going from thorium to uranium than from uranium to neptunium. Such a decrease in the cell constants is expected when the effective ionic radii (*6*) of the An^{4+} ions are considered. The values for the ionic radii of Th^{4+} (1.06 Å), U^{4+} (1.00 Å), and Np^{4+} (0.98 Å), as derived from oxides and fluorides, also display a relatively large decrease from thorium to uranium and a small decrease from uranium to neptunium. In analogy to the lanthanides, the *An*$(OH)_2SO_4$ family of compounds demonstrates the effect of the actinide contraction on the cell constants of an isomorphous series, i.e., as the atomic number of the actinide becomes larger, the cell constants become smaller.

The infrared spectrum of $Np(OH)_2SO_4$ is shown in Fig. 1. The spectrum was obtained from a pressed KBr pellet of the powdered sample. Features due to hydroxide and sulfate are especially prominent.

The sharp absorption at 3510 cm^{-1} is assigned to the O–H stretch of the coordinated hydroxide group. This peak is particularly sharp when compared to aquo groups, lattice water, or hydrogen-bonded O–H groups. This sharpness is consistent with the lack of significant hydrogen bonding. The frequency of this O–H stretch is at the lower end of the range observed for alkali metal hydroxides (*7*), and indicates

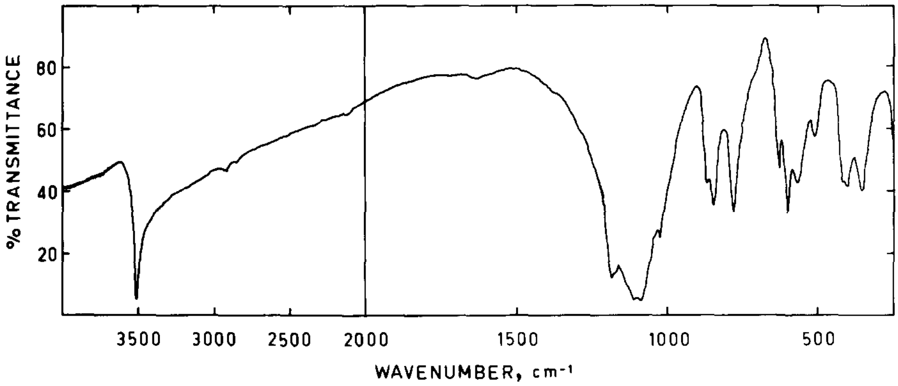

FIG. 1. Infrared spectrum of $Np(OH)_2SO_4$.

substantial Np–O bonding. Absorptions for Cu(II) hydroxy-bridged species also show absorptions in this region (*8*). Absorptions at 850 and 782 cm^{-1} are assigned to the *M*–O–H bending mode, in analogy to absorptions observed near these frequencies in $U(OH)_2SO_4$ (*9*). Deuteration of the uranium compound clearly indicates the OH-bending absorptions since the absorptions in $U(OD)_2SO_4$ shift from 825 and 760 to 663 and 629 cm^{-1}, respectively. Again, the frequencies of these *M*–O–H bending modes are near the lower end of the range in which such modes normally occur and substantial *M*–O bonding is indicated. The higher energy of these vibrations in $Np(OH)_2SO_4$ could be due to stronger *M*–O bonding for $U(OH)_2SO_4$.

Sulfate bands are observed from 1250–1000 cm^{-1}. Although splitting of the broad ν_3 absorption band is indicated, the magnitude of the splitting is small. The ν_4 absorption, which is expected to occur from 580–640 cm^{-1}, is not readily distinguished from several Np–O absorptions in the same region. Based on the relatively unperturbed ν_3 band, weakly complexed sulfate groups are indicated.

The absorption spectra of samples of $Np(OH)_2SO_4$ crystals which had been pulverized and pressed into pellets with KBr exhibited the expected characteristics of a $5f^3$ configuration subject to a large crystal-field splitting. Results are shown in Fig. 2 for the near-infrared and visible regions at ~298° compared to the spectrum of Np^{4+} (aquo) in a similar range. It is apparent that while the detailed character of the two spectra are dissimilar, the energies at which the structural features occur is comparable.

The structure of $Np(OH)_2SO_4$ can be described by analogy to the uranium analog as built up of $Np(OH)_2$ chains linked together by sulfate ions. Although the site symmetry is C_s, the eight nearest-neighbor oxygen atoms form an approximate square archimedian antiprism, one layer of oxygens from –OH groups and one layer from sulfate groups.

The low site symmetry is of interest from the standpoint of optical spectroscopy. Practically all of the more detailed investigations of the spectra 4+ actinides deal with compounds in which the central ion is at a site of relatively high, frequently inversion, symmetry. As a consequence, the spectra are almost entirely vibronic in character and the energies of the electronic $f \rightarrow f$ transitions must be deduced from a band structure analysis (*10*). In odd *f*-electron spectra such as the present case, $Np^{4+}(5f^3)$, any symmetry lower than cubic

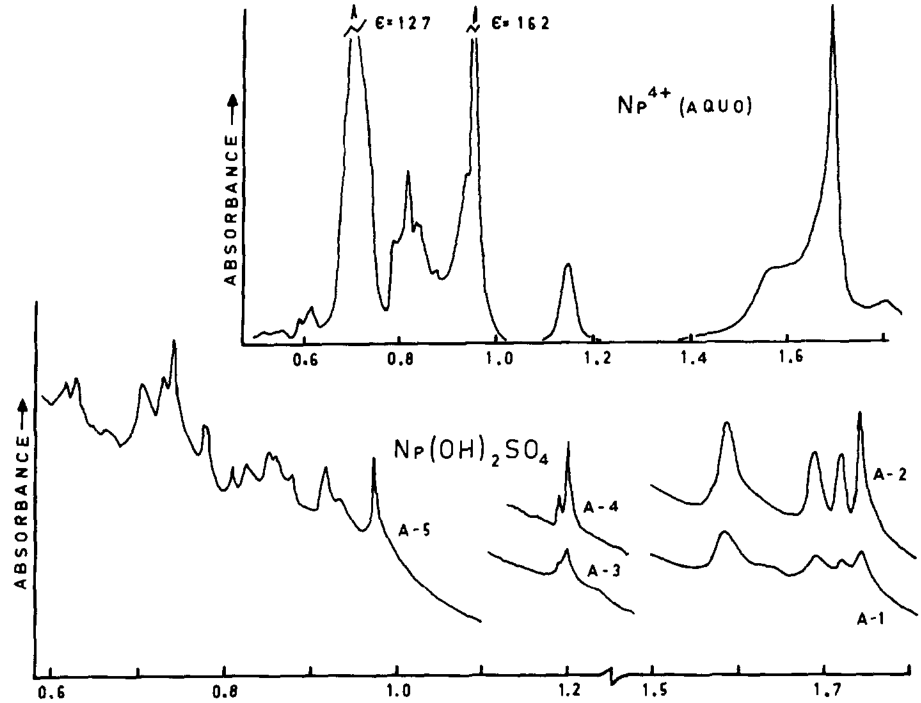

FIG. 2. Comparison of absorption spectra of $Np(OH)_2SO_4$ (lower) with that of aqueous Np^{4+} (upper). The absorption coefficients and spectrum of aqueous Np^{4-} are taken from P. G. Hagan and J. M. Cleveland, *J. Inorg. Nucl. Chem.* **28**, 2905 (1966). The spectra for $Np(OH)_2SO_4$ are: (A-1) $^4H_{11/2}$ transition at ambient temperature; (A-2) same at 77°K; (A-3) $^2F_{3/2}$ transition at ambient temperature; (A-4) same at 77°K; (A-5) ambient temperature.

will split each free-ion state into $J + \frac{1}{2}$ crystal-field components, and the $f \rightarrow f$ transition intensities are expected, in general, to be large compared to any accompanying vibronic transitions.

An extensive analysis of the spectra will be discussed in a subsequent communication. Nevertheless, we note the correspondence between the structure observed for $Np(OH)_2SO_4$ on the ~1000- to 1800-nm range and that for a comparable range in the related $5f^3$ configuration of $U^{3+}:LaCl_3$ (*12*). The isolated $^4I_{11/2}$ and $^4F_{3/2}$ states observed in U^{3+} near 2200 and 1400 nm, respectively, can be observed near 1675 and 1200 nm in Np^{4+}. Cooling the Np^{4+} sample to liquid nitrogen temperatures clearly reveals spectral features which can be interpreted as identifying four of the six crystal-field components of $^4I_{11/2}$ and both components of $^4F_{3/2}$, the latter with a very small energy separation. The spectra in Fig. 2 show no evidence of vibronic superstructure nor do spectra taken at ~4°K. It is of interest to point out that while the total splitting of the $^4I_{11/2}$ state of $U^{3+}:LaCl_3$ was computed to be only ~154 cm^{-1}, the apparent observed splitting in Np^{4+} is nearer 700 cm^{-1}, indicative of the much larger crystal-field interaction.

In a recent investigation of the spectra of frozen solutions of Gd^{3+}, a correlation between the latter spectra and that of a single-crystal $GdCl_3 \cdot 6H_2O$ was pointed out (*13*), suggesting that an approximate square antiprismatic arrangement of the eight nearest-neighbor oxygens could be common to both species. The approximate D_{4d} symmetry of the square antiprism gives rise to a crystal-field potential containing only three parameters for the odd f^n configurations. The observed crystal-field structure in $ErCl_3 \cdot 6H_2O$ can be satisfactorily reproduced on the basis of this approximation (*11*). The eightfold coordination of Np^{4+} in $Np(OH)_2SO_4$ and a probable similar coordination of the aquo ion may be amenable to the same approximation which could result in a considerable simplification of the crystal-field analysis. One of the features of the spectra shown in Fig. 2 that we might hope to begin to explore based on further detailed knowledge of the crystal field is the mechanism whereby certain components of the solution spectrum of Np^{4+} gain an extraordinary intensity compared to the features observed in the crystal, and apparently relative to the other more "normal" band intensities.

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