

metals and this is in agreement with the observations in substituted ferrocenes and, more important, with the $\text{Cr}(h^6\text{-C}_6\text{H}_6)(\text{CO})_3$ structure.

A test of these hypotheses would be found in the molecular structure of a ring-substituted lanthanide complex. Here, the 4f orbital involvement is not nearly as important as in the actinides and inward tilting of the $p\pi$ orbitals on the ligands should not be as important. Since the charge on the central lanthanide ions is $3+$, the orbital contraction effect should be intermediate between that observed in the transition metals and the actinides. We plan to pursue this by carrying out a detailed structure analysis of a TMCOT complex of zirconium, hafnium, or a lanthanide.

Registry No. $\text{U}(\text{TMCOT})_2$, 12715-87-6.

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Studies with Heptavalent Neptunium. Identification and Crystal Structure Analysis of $\text{LiCo}(\text{NH}_3)_6\text{Np}_2\text{O}_8(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ ¹

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The compound $\text{LiCo}(\text{NH}_3)_6\text{Np}_2\text{O}_8(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ was precipitated from a LiOH solution of Np(VII) by slowly diffusing in a solution of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$. It was identified by combining elemental chemical analyses and single-crystal X-ray diffraction. The analog containing Na was produced from a NaOH solution of Np(VII), but no similar product was obtained from KOH solutions. The crystals are monoclinic (space group $C2/c$) with $a = 10.739$ (4), $b = 10.450$ (4), $c = 15.013$ (5) Å, and $\beta = 116^\circ 38$ (5)'; $Z = 4$. There are two independent Np atoms in the asymmetric unit, and each is coordinated by an octahedron of O atoms which make four short and two long bonds. These octahedra are linked through two of their O atoms into chains along c with the long axes of the octahedra alternately parallel and perpendicular to the chain. Lithium ions share four O atoms with three octahedra and are also linked to two H_2O molecules, while the $\text{Co}(\text{NH}_3)_6^{3+}$ octahedra lie between chains and cross-link them. The presence of OH^- ions and H_2O molecules is deduced from structural chemical considerations and chemical analyses. The existence of the $[\text{NpO}_4(\text{OH})_2]^{3-}$ ion in solution is proposed and an explanation is offered for the manner in which the crystalline precipitates are formed.

Introduction

The heptavalent state of the transuranic elements neptunium and plutonium was reported by Spitsyn and co-workers² in 1969. They found Np(VII) and Pu(VII) to be rather stable in alkaline solution but unstable in acid. By choosing cations sufficiently soluble in alkali, they were able to make several solid compounds of Np(VII) and Pu(VII). The only one characterized by chemical analysis was formulated as $\text{Co}(\text{NH}_3)_6\text{NpO}_5 \cdot 3\text{H}_2\text{O}$, I. Following this discovery, a number of workers³⁻⁵ prepared compounds of Np(VII) by solid-state reactions between alkali peroxides and dioxides or hydroxides of Np(V) and Np(VI). The compounds were produced as fine powders; hence little or nothing was learned of their structures.

Because NpO_2^+ and NpO_2^{2+} are well-known ionic species, as is the uranyl ion, UO_2^{2+} , in which U(VI) is isoelectronic with Np(VII), Spitsyn, *et al.*,² reasoned that NpO_2^{3+} may also exist and exhibit the same linear, double-bonded configuration as these three ions. Thus, when they prepared

the compound above, they suggested that the NpO_5^{3-} ion is present and has a linear $\text{O}=\text{Np}=\text{O}$ group within it. Independently, Jorgensen⁶ proposed that in solution the ion is hexagonal-bipyramidal *trans*- $[\text{NpO}_2(\text{OH})_6]^{3-}$.

It was primarily to establish experimentally the configuration of the ion containing heptavalent Np that we undertook our study.

Experimental Section

Preparation of Compounds. The oxidation of Np to the heptavalent state was done essentially as described by Spitsyn, *et al.*,² and refined by Zielen and Cohen.⁷ High-purity $^{237}\text{NpO}_2$, with less than 10 ppm of other actinides present, was obtained from the Isotopes Division of Oak Ridge National Laboratory. In a typical preparation of a Np(VII) solution, 200 mg of NpO_2 was dissolved in HNO_3 , evaporated to dryness, and taken up in 5 ml of 1 *N* HClO_4 . Addition of solid NaNO_2 reduced this to a blue-green solution of Np(V). To this was added an excess of 2.5 *N* LiOH to precipitate out gray Np(V) hydroxide. The solid was centrifuged off, washed with 1 *N* LiOH, and then suspended in 50 ml of 1 *N* LiOH in a bubbler flask. Ozone produced by a semimicro ozonizer described by Bonner⁸ was bubbled through this suspension for 1 hr, causing dissolution of the hydroxide and producing a clear, pink solution of Np(VI). With continued ozone flow, the solution soon darkened and after another hour was very dark green. This solution was ~0.015 *N* in Np(VII) and served as stock for compound preparation.

Simultaneous dropwise addition of solutions of 0.02 *N* $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ and 0.015 *N* Np(VII) to a stirred solution of 1 *N* LiOH yielded brilliant green platelets of I whose largest dimension was less than

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) V. I. Spitsyn, A. D. Gelman, N. N. Krot, M. P. Mefodiyeva, F. A. Zakharova, Yu. A. Komkov, V. P. Shilov, and I. V. Smirnova, *J. Inorg. Nucl. Chem.*, **31**, 2733 (1969).

(3) C. Keller and H. Seiffert, *Inorg. Nucl. Chem. Lett.*, **5**, 51 (1969).

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(5) M. Pages, F. Nectoux, and W. Freundlich, *Radiochem. Radioanal. Lett.*, **7**, 155 (1971).

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(7) A. J. Zielen and D. Cohen, *J. Phys. Chem.*, **74**, 394 (1970).

(8) W. A. Bonner, *J. Chem. Educ.*, **30**, 452 (1953).

20 μ . Anal. Calcd: Np, 44.5. Found: Np, 44.3. Since these crystals were too small for single-crystal X-ray diffraction analysis, another method was devised with the intention of growing larger specimens. Three layers consisting of the above-mentioned components (Np on bottom) were carefully placed in a 1-cm diameter glass tube and allowed to mix by diffusion over a 1-2-week period. During this time there grew on the walls dark green, pyramidal crystals up to 150 μ in length. These were subsequently determined to be $\text{LiCo}(\text{NH}_3)_6\text{Np}_2\text{O}_8(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, IIA. There was also formed in the tube a considerable amount of finely powdered $\text{Co}(\text{OH})_3$ and possibly some reduction products of Np(VII). After completion of the diffusion, the reactants were removed, the crystals were washed with ethanol, air-dried, and then mechanically removed from the walls.

The identification of these crystals involved complementary tasks of X-ray diffraction and elemental analyses. Although the accuracy of the latter was limited by the small quantities of compound available (a few milligrams per run), they provided good corroboration of the results indicated by the crystal structure analysis. Analysis for Np was by coulometric titration,⁹ for Li by flame spectrophotometry, and for H and N by use of a Perkin-Elmer Model 240 elemental analyzer in a glove box. Anal. Calcd for $\text{LiCo}(\text{NH}_3)_6\text{Np}_2\text{O}_8(\text{OH})_2 \cdot 2\text{H}_2\text{O}$: Li, 0.83; Np, 56.4; N, 10.0; H, 2.88. Found: Li, 0.70 ± 0.07 ; Np, 54.6 ± 0.6 ; N, 10.6 ± 0.7 ; H, 2.74 ± 0.10 (uncertainties are standard deviations).

Stock solutions of Np(VII) were made by ozonization in LiOH, NaOH, and KOH. In each, rapid precipitation produced the small crystals of I; slow diffusion yielded large crystals of IIA and IIB (containing Na instead of Li) in LiOH and NaOH, respectively, but none in KOH.

Physical Measurements. An X-ray powder pattern of I was made with a 114.6-mm diameter camera using Ni-filtered Cu K α radiation. The film was measured on a reader with a steel scale accurate to ± 0.05 mm. No correction was made for film shrinkage. For use in identification the eight largest interplanar spacings (in Å) and the intensity associated with each are as follows: 6.66 (s), 5.90 (m), 5.65 (w), 5.45 (m), 5.27 (vs), 4.22 (ms), 3.86 (s), 3.69 (s). Electronic spectra of Np solutions taken during the ozonization process were obtained at room temperature using a Cary Model 14 spectrophotometer and a cell of 1-cm path length. First, the Np(VI) solution gave absorptions near 6320, 6020, and 5300 Å as described by Cohen and Fried;¹⁰ then the solution, after the appearance of a small amount of Np(VII), gave the very strong, characteristic absorptions near 4100 and 6200 Å .^{2,10} The latter maxima rapidly increased with Np(VII) concentration to mask soon the absorptions of Np(VI). The electronic spectrum of a single crystal of IIA was then recorded with a special microspectrophotometer;¹¹ it began to absorb strongly at about 8000 Å and was opaque at about 7000 Å and below. This was taken as additional evidence that the neptunium in the crystal is heptavalent.

Single-Crystal X-ray Diffraction. The crystal used for the initial X-ray diffraction studies was one grown by diffusion in NaOH solution and was expected to be compound I. Thus, when its lattice parameters did not correspond to the powder pattern for I, it was considered to be a polymorph of this compound. In the course of the structure determination most of the atoms present were identified, but one atom which caused difficulties was suspected of being Na. It was then that additional crystals were grown, this time from LiOH solution, and indeed Li was eventually found to be present in the site formerly suspected to be occupied by Na. The difficulty with the original crystal arose from a small amount of twinning across a pseudo mirror plane at $y = 1/2$, causing some apparent mixing of Np and Na atoms at certain sites. The structure determination to be detailed below is based on crystals grown from LiOH solution.

Precession photographs were used to determine the crystal system (monoclinic), the pattern of systematic absences (hkl for $h + k$ odd; $h0l$, l odd), and preliminary values for the unit-cell dimensions. A computer-controlled Picker four-circle diffractometer was used to obtain improved lattice measurements and to evaluate intensities. To obtain these data, a wedge-shaped crystal of 0.11 mm in largest dimension was sealed in glass to confine the radioactive ²³⁷Np and mounted with the crystal c^* axis perpendicular to the ϕ axis of the goniometer. Mo K α (Nb-filtered) X-rays at a takeoff angle of 2° were employed, and the detector was a scintillation counter behind a 6 mm² receiving aperture at a distance of 22 cm from the crystal.

(9) R. W. Stromatt, *Anal. Chem.*, **32**, 134 (1960).

(10) D. Cohen and S. Fried, *Inorg. Nucl. Chem. Lett.*, **5**, 653 (1969).

(11) L. J. Nugent, P. G. Laubereau, G. K. Werner, and K. L. Vander Sluis, *J. Phys. Chem.*, submitted for publication.

Step scans of about 2° in the θ - 2θ mode were made for each reflection, and the backgrounds were measured at the ends and averaged. All 2715 independent reflections out to $2\theta = 65^\circ$ were recorded. A reference reflection was measured hourly, and its intensity changed less than 5% during the data collection period. Twelve reflections in the 2θ range of 51 - 54° were carefully centered and the angles were used to obtain the best values of the unit-cell dimensions by least-squares refinement.

Data Reduction and Structure Determination. Corrections for absorption of X-rays were calculated by use of the program ORABS.¹² For this calculation the crystal was described by six bounding planes whose equations were derived from microscopic measurements of the crystal corners. A mass absorption coefficient of $50 \text{ cm}^2 \text{ g}^{-1}$ for Np was obtained by interpolation between values given by Roof,¹³ and the calculated linear absorption coefficient, μ , for the compound was 135 cm^{-1} . Calculated transmission factors ranged from 0.40 to 0.59. It should be noted that, in the case of Np irradiated with Mo K α , there is more than the usual uncertainty in the effect of absorption caused by inaccuracies in describing the specimen shape when μ is large. That is, the proximity of the Np L absorption edge to the Mo K α emission wavelength causes an abrupt change in μ for the sample as the 2θ scan is made. This effect is less important at higher angles because of dispersion, and we have partially compensated for it by omitting the low-angle reflections from the refinement.

After correction for absorption, the data were normalized by interpolation between measurements of the reference reflection, corrected for Lorentz and polarization factors and reduced to squared structure factors.

The refined values of the monoclinic unit-cell dimensions of $\text{LiCo}(\text{NH}_3)_6\text{Np}_2\text{O}_8(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ at 23° are $a = 10.739$ (4), $b = 10.450$ (4), $c = 15.013$ (5) Å , and $\beta = 116^\circ 38$ (5)'. While the systematic absences indicated the probable space group to be either Cc or $C2/c$, a satisfactory structure was found only with the latter choice. There are four formula units in the cell; the calculated density is 4.26 g cm^{-3} . For the isomorphous compound containing Na, the corresponding crystal data are $a = 10.865$ (3), $b = 10.597$ (3), $c = 14.867$ (4) Å , $\beta = 115^\circ 13$ (5)', and $d_{\text{calcd}} = 4.23 \text{ g cm}^{-3}$.

Determination of atomic positions was begun with limited knowledge of the composition of the crystals based on the mode of preparation and on a neutron-activation analysis, which showed the presence of Np and Co. A Patterson map was calculated and interpreted to yield the positions of Np in 4(a) and 4(e) and Co in 4(b) of space group $C2/c$. Using phases calculated from these atoms, an electron density map was prepared. It contained (in addition to Np and Co) nine independent maxima, of approximately equal size, in general positions 8(f). Three of these were readily identified as N atoms by their association with and distance from Co; the rest were assumed to be O atoms. Additionally, in the crystal grown from NaOH solution there was a maximum of height intermediate between O and Co also in 4(e) but related to the Np in 4(e) by reflection in a pseudo mirror plane through the origin. Neither Co nor Na in this site would refine satisfactorily and the Np in 4(e) had an unusually large temperature factor. Subsequently, with a crystal grown from LiOH solution, it was shown that Li occupies the site in question. Thus it appears that the original specimen from NaOH solution was partially twinned, yielding an apparent mixing of Na and Np in the two kinds of 4(e) sites. This possibility has not been investigated further.

Structure Refinement. Variable positional parameters and anisotropic thermal parameters for all nonhydrogen atoms (except that the temperature factor of Li was kept isotropic) were refined by the method of least squares.¹⁴ The quantity minimized was $\Sigma(1/\sigma^2)(F_o^2 - F_c^2)^2$, in which F_o and F_c are observed and calculated structure factors and the variance, σ^2 , is based on counting statistics and an allowance of 5% of the intensity to account for unknown, systematic errors. For the computation of F_c , the scattering factors of Cromer and Waber¹⁵ for Np(VI), Co(III), O, N, and Li were used, with Np and Co corrected for anomalous dispersion

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(14) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Report No. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(15) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

Table I. Positional and Thermal^a Parameters for $\text{LiCo}(\text{NH}_3)_6\text{Np}_2\text{O}_8(\text{OH})_2 \cdot 2\text{H}_2\text{O}$

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Np(1)	0	0	0	21.3 (8)	13.0 (6)	12.7 (4)	0	7.0 (4)	0
Np(2)	0	0.13251 (9)	$\frac{1}{4}$	32.1 (9)	28.0 (7)	16.1 (5)	0	2.8 (5)	0
Co	0	$\frac{1}{2}$	0	16 (2)	14 (2)	10 (1)	0	0 (1)	0
N(1)	0.1449 (13)	0.3722 (13)	0.0178 (11)	22 (11)	25 (10)	35 (8)	14 (11)	14 (8)	7 (8)
N(2)	0.3638 (12)	0.1375 (13)	0.4790 (10)	21 (11)	26 (9)	27 (7)	-1 (10)	10 (7)	-3 (8)
N(3)	0.0537 (17)	0.4930 (13)	0.1436 (11)	65 (16)	43 (12)	16 (6)	0 (12)	11 (8)	3 (8)
O(1)	0.3403 (15)	0.2178 (13)	0.2152 (11)	72 (16)	51 (13)	45 (9)	-11 (12)	23 (10)	5 (9)
O(2)	0.1363 (12)	0.0038 (12)	0.2852 (9)	34 (11)	35 (9)	20 (6)	16 (11)	7 (6)	7 (8)
O(3)	0.1370 (12)	0.2619 (12)	0.2854 (9)	45 (12)	31 (10)	31 (7)	-13 (11)	9 (7)	-3 (8)
O(4)	0.4787 (12)	0.3696 (12)	0.0754 (8)	41 (11)	39 (9)	18 (6)	-10 (11)	6 (6)	-11 (7)
O(5)	0.0222 (11)	0.1291 (11)	0.4134 (7)	46 (11)	27 (8)	12 (5)	-13 (10)	8 (6)	1 (6)
O(6)	0.2373 (11)	0.0002 (11)	0.1010 (8)	22 (9)	50 (10)	11 (5)	7 (9)	4 (6)	-3 (6)
Li ^b	0	0.8549 (34)	$\frac{1}{4}$						

^a Anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. ^b Isotropic $B = 1.1 (5) \text{ \AA}^2$.

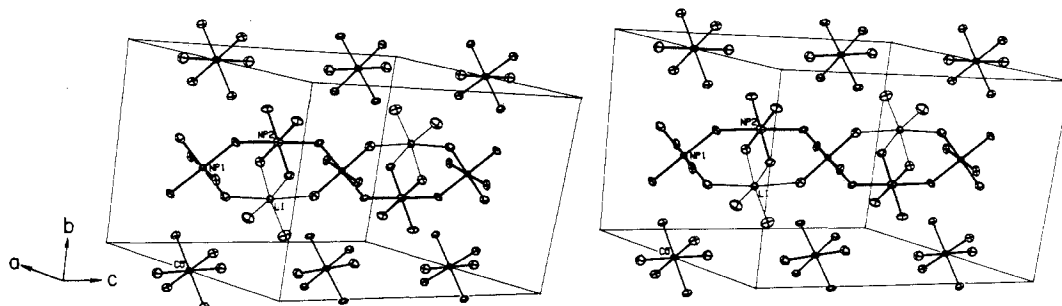


Figure 1. A stereoscopic view of a portion of the structure of $\text{LiCo}(\text{NH}_3)_6\text{Np}_2\text{O}_8(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ in relation to the unit cell.

components.¹⁶ The 1728 reflections having $F_o^2 > 3\sigma(F_o^2)$ were considered observable and used in the refinement. The structure factors of the 24 reflections having $2\theta < 12.5^\circ$ were calculated but were not included in the refinement because of difficulty caused by the closeness of Mo $K\alpha$ and Np L-edge wavelengths. The agreement index, $R = \sum |F_o| - |F_c| / \sum |F_o|$, was 0.057 for the final parameters, and the standard deviation of an observation of unit weight was 1.55. The values of the refined parameters and their standard deviations are given in Table I, and a list of observed and calculated structure amplitudes is available elsewhere.¹⁷

Results and Discussion

The crystal structure of IIA is illustrated by Figure 1, which shows the basic structural units in the unit cell, and by Figure 2, which gives more detail, including bond lengths for a portion of the structure and a representation of the thermal ellipsoids. Each Np atom is surrounded by six O atoms, and the resulting octahedra share corners to form a chain along the c direction. The Li^+ ions are attached periodically along the chains by sharing O atoms, and the $\text{Co}(\text{NH}_3)_6^{3+}$ ions are located between chains and cross-link them. The positions of H atoms in this structure have not been determined directly but have been deduced qualitatively from chemical and structural reasoning as follows. First, it is obvious that the N atoms symmetrically distributed around the Co ions must belong to ammonia molecules and carry three H atoms each. Then the two O(1) atoms which appear to be attached only to the Li^+ ions must belong to water molecules because of their isolated positions. And finally, the O(6) atoms which have long bond distances to Np(1) are probably in OH^- ions because of the length of the bonds and the fact that O^{2-} or H_2O would not satisfy the requirements of electroneutrality. Assignment of H atoms in

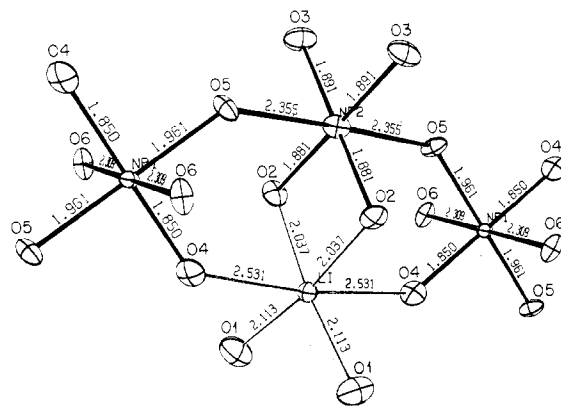


Figure 2. Part of the chain structure showing bond lengths and atom identification.

this manner yields the formula for the compound as written above; and the elemental analysis, while not accurate to better than 4%, is in agreement with this formulation.

In Table II are listed bond lengths and angles of interest. From the values of the Co-N bond lengths and N-Co-N angles it is seen that the $\text{Co}(\text{NH}_3)_6^{3+}$ ions are nearly regular octahedra, little perturbed by their attachments to the rest of the structure. The Co-N distances are comparable to those found in $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.¹⁸ In the case of Np(2) there are four quite short bonds to O atoms in a nearly square arrangement and, perpendicular to this square, two other long bonds to O atoms. A similar configuration is arrayed around Np(1), except that the long bonds are at approximately right angles to those for Np(2) and the square is somewhat distorted because two of its corner O atoms are shared with Np(2) atoms. The other two corner atoms are weakly attracted to Li^+ ions. The Li-O distances of 2.04 Å to O(2) and 2.11 Å to H_2O are in agreement with known values, e.g., in $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ¹⁹ and in lithium glycolate mono-

(16) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(17) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-466.

(18) Y. Shigeta, Y. Komiyama, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **36**, 1159 (1963).

Table II. Distances and Angles

Atoms	Dist, Å	No.	Atoms	Dist, Å	No.
Np(1)-O(4)	1.85 (1)	2	Co-N(3)	1.97 (1)	2
-O(5)	1.96 (1)	2	-N(2)	1.97 (1)	2
-O(6)	2.31 (1)	2	-N(1)	1.98 (1)	2
Np(2)-O(2)	1.88 (1)	2	Li-O(2)	2.04 (3)	2
-O(3)	1.89 (1)	2	-O(1)	2.11 (3)	2
-O(5)	2.36 (1)	2	-O(4)	2.53 (1)	2
			-Np(2)	2.90 (4)	1

Atoms	Angle, deg	Atoms	Angle, deg
N(1)-Co-N(2)	90.7 (6)	O(2)-Np(2)-O'(3)	180.0 (6)
N(1)-Co-N(3)	90.0 (6)	O(2)-Np(2)-O(5)	89.7 (5)
N(2)-Co-N(3)	91.1 (6)	O(2)-Np(2)-O'(5)	89.1 (5)
O(4)-Np(1)-O(5)	90.9 (5)	O(3)-Np(2)-O'(3)	88.7 (8)
O(4)-Np(1)-O(6)	90.1 (5)	O(3)-Np(2)-O(5)	90.9 (5)
O(5)-Np(1)-O(6)	90.6 (4)	O(3)-Np(2)-O'(5)	90.4 (5)
O(2)-Np(2)-O'(2) ^a	88.7 (8)	O(5)-Np(2)-O'(5)	178.3 (6)
O(2)-Np(2)-O(3)	91.3 (5)		

^a The primed atom is related to its unprimed equivalent by rotation about a twofold axis through Np(2).

hydrate,²⁰ and provide additional evidence that the occupant of the Li site has been correctly identified.

There is likely to be a considerable number of hydrogen bonds in this structure because of the numerous N-H and O-H groups which are present. In Table III are listed the short contacts between atoms which may involve N-H...O or O-H...O bonds, but is not possible, in general, to place definitely the H atoms with the present data. One exception seems to be that the water molecule, with O(1) at its apex, can be said to be H bonded to O(3) and O(6) because of the closeness of these two atoms and the O(3)...O(1)...O(6) angle of 101.6°.

The square-planar NpO₄⁻ atomic grouping with four short bonds has not been reported before, although the linear triatomic NpO₂⁺ and NpO₂²⁺ ions are well known.^{21,22} There is, however, one report of a similar bonding arrangement for U(VI), *i.e.*, in the compounds Li₄UO₅ and Na₄UO₅.²³ In both these compounds the four short U-O distances are 1.99 Å, and there are two additional O atoms at 2.23 and 2.32 Å for Li₄UO₅ and Na₄UO₅, respectively. More commonly, U(VI) appears as the UO₂²⁺ ion; and uranyl bond lengths have been determined in numerous compounds. Zachariasen^{21,24} has presented a table corre-

(19) A. C. Larson, *Acta Crystallogr.*, **18**, 717 (1965).

(20) R. H. Colton and D. E. Henn, *Acta Crystallogr.*, **18**, 820 (1965).

(21) W. H. Zachariasen, *Acta Crystallogr.*, **7**, 795 (1954).

(22) L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, **21**, 542 (1953).

(23) H. Hoekstra and S. Siegel, *J. Inorg. Nucl. Chem.*, **26**, 693 (1964).

Table III. Possible Hydrogen-Bond Distances (Å)

N(1)...O(4)	2.90 (2)	N(3)...O(2)	3.01 (2)
O(6)	2.93 (2)	O(1)	3.02 (2)
O(2)	3.15 (2)	O(3)	3.08 (2)
O(1)	3.19 (2)	O(6)	3.16 (2)
N(2)...O(5)	2.88 (2)	O(1)...O(6)	2.76 (2)
O(6)	3.08 (2)	O(3)	2.86 (2)
O(3)	3.12 (2)	O(6)...O(3)	2.98 (2)
O(2)	3.16 (2)		

lating U-O bond lengths with bond strengths: 2.08 Å for a single bond, decreasing to 1.70 Å for a double bond. Many workers have used this table with their observed bond lengths to obtain values of the bond order. For example, in Li₄UO₅ the four short bonds were deduced to be of order 1.17, and in UO₂(OH)₂²⁵ the uranyl bond length is 1.82 Å corresponding to a bond order of 1.5. Thus we conclude qualitatively, taking into account the actinide contraction (~0.01 Å) and the higher charge on Np(VII), that the bonds in the square NpO₄⁻ group are of some multiplicity greater than 1. By analogy with the highly stable [O=U=O]²⁺, it seems probable that the heptavalent state of Np is stabilized by the formation of these multiple bonds.

As for the Np-O long bonds perpendicular to the squares, the Np(1)-OH distance of 2.31 Å agrees closely with the average U-OH distance of 2.33 Å in UO₂(OH)₂.²⁵ The Np(2)-O distance of 2.36 Å is somewhat longer because of the O atom being shared with Np(1).

The observation that atoms Np(1) and Np(2) have such similar environments in this crystal leads us to suggest that Np(VII) in alkaline solution exists as the [NpO₄(OH)₂]³⁻ ion. If this is correct, an explanation can be offered for the fact that I is obtained by rapid precipitation from the solution with Co(NH₃)₆³⁺ ion and that IIA and IIB result from the slow diffusion reaction. For this purpose the formula of I is rewritten as Co(NH₃)₆NpO₄(OH)₂·2H₂O (without changing its elemental composition). This compound could result from rapid reaction of Co(NH₃)₆³⁺ and [NpO₄(OH)₂]³⁻ ions. Slow diffusion could allow polymerization of the [NpO₄(OH)₂]³⁻ ions by splitting out one hydroxide ion each, substitution of Li⁺ ions for Co(NH₃)₆³⁺, and production of IIA which has the structure reported here.

Registry No. Neptunium, 7439-99-8; Co(NH₃)₆Cl₃, 10534-89-1; Co(NH₃)₆NpO₄(OH)₂·2H₂O, 37541-34-7; LiCo(NH₃)₆Np₂O₈(OH)₂·2H₂O, 37200-28-5.

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