

bridging dithiooxalate ligands and the dimers are linked in infinite chains of dimers through the potassium. The bond distances and angles of the Sn-SS and Sn-OO chelated ligands are profoundly different but are comparable to those reported for other dithiooxalate complexes. The bond distances in the Sn-OO-C₂-SS-Cu bonded ligand indicates delocalization of charge from the sulfur to the oxygen.

A band at 1627 cm⁻¹ in the infrared spectrum of the complex is assigned to the C=O bond in the Sn-S₂-C₂-O₂-K bonded ligand. The band at 1371 cm⁻¹ is assigned to the longer C-O bond in the Sn-O₂-C₂-S₂Cu bonded ligand.

The infrared absorptions near ca. 1400 cm⁻¹, in the spectra of similar polynuclear complexes,¹ are considered indicative of Sn-O₂-C₂-S₂-Cu bonded ligands.

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Registry No. KSn[(S₂C₂O₂)₃Cu(P(tol)₃)₂]·2CH₃COCH₃, 62476-47-5.

Supplementary Material Available: A compilation of observed structure factor amplitudes, their estimated standard deviations, and the difference |F_o| - |F_c| and tables of the derived carbon atom positions of the phenyl rings and the calculated hydrogen atom positions (9

pages). Ordering information is given on any current masthead page.

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Crystal Structure of Barium Neptunyl(V) Triacetate Dihydrate¹

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Barium neptunyl(V) triacetate dihydrate was prepared from Np(V) in a concentrated acetate solution, and its crystal structure determined by x-ray diffraction methods. The body-centered tetragonal unit cell, with dimensions $a = 19.167$ (5) and $c = 9.476$ (3) Å, contains eight formula units of BaNpO₂(CH₃CO₂)₃·2H₂O. The space group is $I4_2d$. Positions and anisotropic thermal parameters of the 11 independent atoms were refined by the least-squares method using 964 diffractometer-measured intensities, at the conclusion of which the agreement index, R_F , was 0.046. Linear NpO₂⁺ entities are present in the crystal and have six oxygen atoms from three acetate ions in a planar hexagon around their equators. These hexagonal bipyramids are cross-linked by sharing their acetate oxygen atoms with Ba²⁺ ions, each of which has six different oxygen atoms from acetate ions plus two water molecules in its coordination polyhedron. The neptunyl O atoms are bonded solely to the Np atom at bond lengths of 1.85 (2) Å, and the bonds between acetate O atoms and the Np atom range in length from 2.52 (2) to 2.56 (2) Å. These lengths are correlated with bond strengths and valence, and the geometries of actinyl(V) ions are put on a quantitative experimental basis.

Introduction

The existence of ions of dioxygenated pentavalent and hexavalent actinides is well established, and their presence in the solid state is known for Np(V), Pu(V), Am(V), U(VI), Np(VI), Pu(VI), and Am(VI). Although the geometry of the UO₂²⁺ ion has been studied in scores of crystalline compounds, little attention has been given to the structure of various species containing transuranic elements, because their radioactivity causes some handling difficulty. Recently the structures of two compounds containing the NpO₂²⁺ ion were determined by single-crystal x-ray diffraction;³ they are Na₄NpO₂(O₂)₃·9H₂O and K₄NpO₂(CO₃)₃. Also, before the present study, one structure containing the NpO₂⁺ ion had been determined by similar methods;⁴ it is that of Cs₃NpO₂Cl₄. A number of powder x-ray diffraction studies of pentavalent actinide-dioxo compounds have been done (see Table I), but precise bond lengths are not available from these.

Infrared studies have been used by Vodovatov, Mashirov, Suglobov, and co-workers^{4,9-11} as a means of comparing bond strengths among the transuranic actinyl species. They have evaluated the effect on the primary O=M=O bond strengths¹² (M = Np, Pu, Am) of several factors which include

Table I. Compounds Containing the MO₂⁺ Ion, M = Np, Pu, Am

Structure type	Compd	Ref
KPuO ₂ CO ₃ (hexagonal)	KNpO ₂ CO ₃	5
	KPuO ₂ CO ₃	6
	KAmO ₂ CO ₃	5
	NH ₄ PuO ₂ CO ₃	6
	RbAmO ₂ CO ₃	6
CaUO ₂ O ₂ (rhombohedral)	CsAmO ₂ CO ₃	7
	KAmO ₂ F ₂	8
	RbNpO ₂ F ₂	7
	RbPuO ₂ F ₂	7
	RbAmO ₂ F ₂	7
	NH ₄ PuO ₂ F ₂	7
Cs ₃ NpO ₂ Cl ₄ (monoclinic)	Cs ₃ NpO ₂ Cl ₄	4
	Cs ₃ PuO ₂ Cl ₄	4
	Cs ₃ AmO ₂ Cl ₄	4

the valence of M, the atomic number, and the nature of the secondary ligands which bond to the linear ion around its equator. In making these comparisons they included the idea of Zachariasen¹³⁻¹⁵ that the strengths of the primary and secondary bonds in these species are interdependent because of the need that the sum of bond strengths around a particular

Table II. Refined Positional and Thermal^a Parameters for BaNpO₂(CH₃CO₂)₃·2H₂O

Atom	x	y	z	10 ⁴ β ₁₁	10 ⁴ β ₂₂	10 ⁴ β ₃₃	10 ⁴ β ₁₂	10 ⁴ β ₁₃	10 ⁴ β ₂₃
Np	0.36674 (4)	1/4	1/8	11.6 (3)	13.3 (3)	65 (1)	0 ^b	0	9.8 (6)
Ba	0.59569 (6)	1/4	1/8	7.8 (3)	12.3 (3)	61 (2)	0	0	9.8 (8)
O(1)	0.3655 (8)	0.3126 (7)	0.2736 (19)	29 (4)	20 (4)	97 (22)	9 (3)	7 (9)	-1 (9)
O(2)	0.2486 (9)	0.2066 (6)	0.2005 (18)	20 (3)	20 (3)	130 (24)	5 (4)	1 (9)	27 (8)
O(3)	0.4753 (7)	0.3110 (8)	0.0274 (18)	17 (3)	32 (5)	112 (22)	6 (3)	5 (8)	30 (9)
O(4)	0.3766 (6)	0.1478 (6)	0.2972 (15)	16 (3)	17 (3)	99 (21)	-3 (3)	10 (7)	0 (7)
O(w)	0.1848 (11)	0.0560 (11)	0.1072 (28)	46 (7)	58 (7)	89 (28)	4 (6)	-9 (14)	26 (14)
C(1)	0.2146 (10)	1/4	1/8	9 (5)	13 (5)	92 (33)	0	0	-6 (16)
C(2)	0.1394 (13)	1/4	1/8	4 (6)	119 (25)	211 (72)	0	0	-151 (41)
C(3)	0.4424 (10)	0.1481 (10)	0.2952 (28)	13 (4)	19 (5)	121 (33)	3 (4)	10 (10)	-5 (11)
C(4)	0.4714 (14)	0.1066 (14)	0.4243 (34)	33 (8)	46 (10)	135 (41)	23 (7)	-12 (15)	49 (17)

^a The coefficients given are for the temperature factor $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2hkb_{12} - 2hlb_{13} - 2klb_{23})$. ^b Atoms on twofold axes have the following constraints on thermal parameters: $\beta_{12} = \beta_{13} = 0$.

atom be equal to its formal valence.

There is a need for direct measurement of bond lengths by crystallographic methods in order to corroborate these conclusions and to relate bond lengths to bond strengths. The preparation and structure analysis of BaNpO₂(CH₃CO₂)₃·2H₂O which we describe here was done to provide further precise bond lengths to aid in quantitatively establishing these relationships among actinyl compounds.

Experimental Section

Preparation of the Compound. Pentavalent Np was obtained by dissolving ²³⁷NpO₂ in concentrated HNO₃ and then reducing the Np(VI) with a small quantity of H₂O₂. Pale blue crystals of BaNpO₂(CH₃CO₂)₃·2H₂O were grown from a solution that was 6 M in NaCH₃CO₂, 0.1 M in Mg(NO₃)₂, 0.1 M in BaCl₂, and 0.01 M in NpO₂⁺. (It is not known whether the Mg²⁺ ions played any role; they were present, as were the Ba²⁺ ions, in an attempt to provide suitable cations for growing large crystals.) The crystals grew slowly, over about 1 week, and were mostly rectangular parallelepipeds of dimensions up to 0.05 cm on an edge. Conventional elemental analysis of the compound was not done because of the small quantity prepared, but the chemical formula was established by means of the crystal structure analysis.

All chemical manipulations were carried out in a glovebox because of the α radioactivity of the ²³⁷Np, and the crystals were sealed in thin-walled glass capillary tubes before removal from the box for x-ray study.

X-Ray Diffraction. X-ray precession photographs were used to determine that the crystal lattice is body-centered tetragonal and to obtain provisional values for the unit cell dimensions. Systematic absences ($h + k + l \neq 2n$ for the general hkl reflections and $2h + l \neq 4n$ for the hhl reflections) indicated the probable space group to be either $I4_1md$ or $I4_2d$. The latter was subsequently shown to be correct by the successful structure refinement.

For the collection of intensity data a long, thin crystal of dimensions 0.005 × 0.012 × 0.104 cm was mounted on a Picker four-circle goniometer with the long dimension along the ϕ axis. Using the angular settings of 12 carefully centered reflections (with $2\theta = 49$ – 56° using Mo K α , λ 0.709 26 Å) the best estimates of the unit cell dimensions were obtained by the method of least squares. At 25 °C, they are $a = 19.167$ (5) and $c = 9.476$ (3) Å. From these values and the chemical formula obtained later, a crystal density of 2.36 g cm⁻³ ($Z = 8$) is calculated. A rough experimental estimate of 2.6 g cm⁻³ was made by flotation in heavy liquids; this enabled us to choose the correct number of formula units in the cell.

Diffraction intensities were measured automatically under computer control. The x radiation used was Mo K α (Nb filtered) at a 2° takeoff angle; the scintillation detector was located behind a 0.6 cm square aperture at 21 cm from the crystal. The θ - 2θ scanning technique was used and the background determined by averaging measurements made at the ends of each scan. The scan ranges varied from 1.3° at low angles up to 1.6° at 60° which was the maximum 2θ used. A single reference reflection was measured hourly and remained constant to better than 1% over 10 days of data collection; thus no detectable damage to the crystal was done by the α activity during this time. More than 2000 reflections were measured but many equivalent by symmetry, and an appreciable number were affected adversely by the presence of a small misoriented portion of the sample (satellite crystal).

Structure Determination and Refinement

Data Reduction. A correction for the effect of absorption was made by measurement of boundary planes and calculation¹⁶ of transmission factors using a linear absorption coefficient of 59.8 cm⁻¹. These factors ranged from 0.50 to 0.73 and their reciprocals were multiplied by the measured intensities as were the Lorentz and polarization corrections and a normalization factor, based on interpolation between measurements of the reference reflection. This yielded a set of relative squared structure factors, F_o^2 , whose variances were taken to be $\sigma^2(F_o^2) = \sigma_c^2 + (0.04F_o^2)^2$, where σ_c^2 is the variance attributable to counting statistics.

Structure Determination. A Patterson map was calculated from the F_o^2 values, and its prominent peaks were interpreted as vectors among the Np and Ba atoms. Each of these atoms lies on a twofold axis of space group $I4_2d$ in a set of equipoints 8(d). Subsequent Fourier syntheses, phased with just these two independent atoms, easily revealed the location of the remaining atoms. At this point it was ascertained that the compound includes no Mg and is a dihydrate. There are two crystallographically independent acetate groups in the structure; one has its C atoms on the twofold axes along with the Np and Ba atoms, and the other is in the general position 16(e).

Refinement. Atomic coordinates and anisotropic thermal parameters for all of these atoms were refined by the method of least squares. The function minimized was $\sum w(F_o^2 - F_c^2)^2$, in which $w = 1/\sigma^2(F_o^2)$ and F_c is the calculated structure factor. In calculating F_c , scattering factors¹⁸ for neutral atoms were used, and the real and imaginary components of anomalous dispersion¹⁹ for Ba and Np were included. Only those observations were included in the refinement for which $F_o^2 > 3\sigma(F_o^2)$. Also omitted were those reflections which were judged to be questionable because their strip-chart traces suggested the presence of a satellite crystal. This still left some 964 observations for adjusting the 76 structural parameters. The refinement converged after a few cycles, and the agreement index, $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$, reached 0.046 with $\sigma_f = 1.75$. Hydrogen atoms were not included in the calculations.

Refined positional and thermal parameters are listed in Table II, and a table of observed and calculated structure factors is available.²⁰ Bond lengths and angles are given in Table III.

Description and Discussion of the Structure

The Np(V) atoms are found, as expected, to be involved in triatomic NpO₂⁺ ions. These are linear within experimental error (178.5 (9)°) and the Np=O distance is 1.85 (2) Å. Six oxygen atoms belonging to three acetate ions fill the equatorial region of the neptunyl ion, giving the Np atom a hexagonal-bipyramidal coordination overall, as shown in Figure 1. The six equatorial O atoms lie very nearly in a plane; none deviates from the best least-squares plane by more than 0.032 Å. The linear NpO₂⁺ portion is perpendicular to this plane within experimental error. While the point symmetry at the Np atom in the crystal is actually C₂, the entire [NpO₂(CH₃CO₂)₃]²⁻ bipyramid has nearly D_{3h} symmetry.

There are two independent acetate ions in the asymmetric unit of structure. One has its C atoms on a twofold axis and is thus strictly planar while the other is nearly planar with the methyl C atom a little out of the plane of the carboxyl atoms. The C-O bond lengths are normal within experimental error

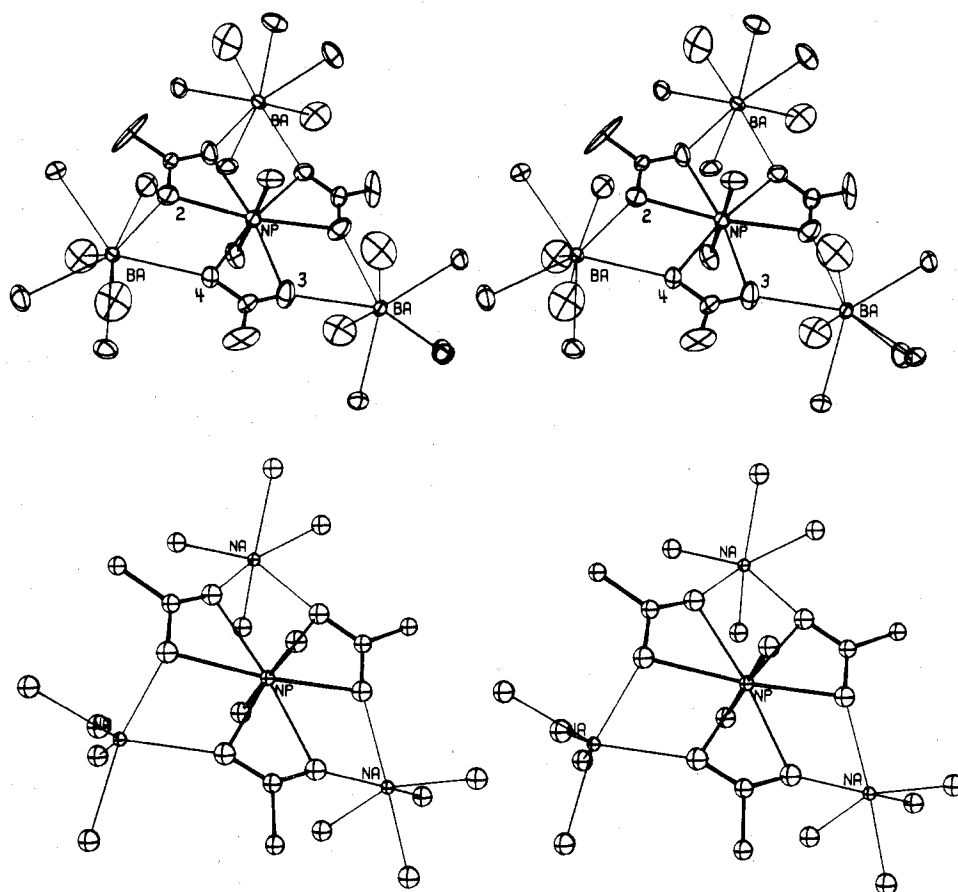


Figure 1. Stereoscopic drawing to show the environment of the NpO_2^+ ion in $\text{BaNpO}_2(\text{CH}_3\text{CO}_2)_3 \cdot 2\text{H}_2\text{O}$ (above) and the NpO_2^{2+} ion in $\text{NaNpO}_2(\text{CH}_3\text{CO}_2)_3$ (below). Thermal ellipsoids of 50% probability are used to represent atoms in the upper drawing; spheres of arbitrary size are used below.

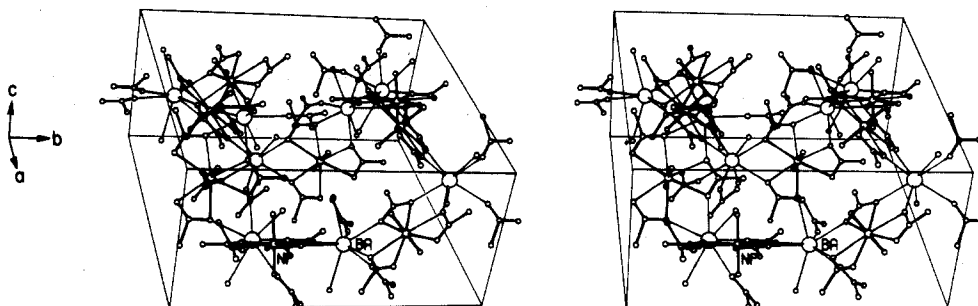


Figure 2. Stereoscopic representation of approximately one unit cell of the structure. The Ba and Np atoms are labeled. All other atoms belong to acetate ions except for the lone atoms attached to the Ba atoms; these are O atoms of H_2O molecules.

(Table III). The apparent C-C bond lengths listed in Table III are shortened by the large thermal motions of the methyl groups, and corrections assuming the riding model yielded more reasonable values of 1.53 (4) Å for C(1)-C(2) and 1.60 (4) Å for C(3)-C(4). The bonds from the Np atoms to the ligand O atoms range in length from 2.52 to 2.56 Å.

The Ba^{2+} ion is coordinated by eight O atoms: one each from six different acetate ions and two from water molecules, designated O(w). This polyhedron has a twofold axis and is best described as intermediate between a dodecahedron and a square antiprism when the criteria of Lippard and Russ²¹ are applied. The Ba-O distances to acetate O atoms range from 2.69 to 2.75 Å and average 2.72 Å; these are close to the Ba-O distance of 2.76 Å in BaO (NaCl type). The Ba-O(w) distance is 2.93 Å. The water molecule does not appear to form any hydrogen bonds; the nearest O...O contact, outside of neighbors within the coordination polyhedron, is 3.82 Å, which is too long.

The crystal structure, as illustrated in Figure 2, is a continuous three-dimensional network in which the NpO_2^+ and Ba^{2+} ions are linked by sharing of CH_3CO_2^- ions. Although there are two crystallographically independent acetate ions, they play the same role in linking cations together. The two O atoms of each carboxyl group form a bidentate linkage to an Np atom and in addition each forms a bond to a different Ba atom; thus each acetate is shared by two Ba^{2+} ions and one NpO_2^+ .

There is considerable evidence from infrared studies^{9,11,22} of the stretching frequencies of NpO_2^{2+} and NpO_2^+ ions that the Np=O bonds are weaker in the latter. This has been explained⁹ in terms of the molecular orbital picture²³ of bonding in neptunyl ions. The electrons of highest energy are in two nonbonding orbitals. These have quite different spatial distributions; the one of higher energy is oriented along the neptunyl axis and the next higher one between this axis and the equator. The NpO_2^{2+} ion then has its one nonbonding

Table III. Selected Bond Distances and Angles

Distances, Å			
Np-O(1)	1.85 (2)	O(2)-C(1)	1.28 (2)
-O(2)	2.52 (2)	-O(2)	2.19 (3)
-O(3)	2.56 (2)	-O(4)	2.85 (2)
-O(4)	2.56 (2)	-O(w)	3.26 (3)
Ba-O(2)	2.69 (2)	O(3)-C(3)	1.22 (3)
-O(3)	2.75 (2)	-O'(3)	2.98 (3)
O(4)	2.73 (2)	-O(4)	2.17 (2)
-O(w)	2.93 (3)	-O(w)	3.29 (3)
O(1)-O(2)	3.10 (2)	O(4)-C(3)	1.26 (3)
-O'(2)	3.11 (2)	C(1)-C(2)	1.44 (3)
-O(3)	3.14 (3)	C(3)-C(4)	1.56 (3)
-O'(3)	3.21 (2)		
-O'(4)	3.14 (3)		
-O(4)	3.17 (2)		
-O(w)	3.82 (3)		
Angles, Deg			
O(1)-Np-O'(1)	178.5 (9)	C(4)-C(3)-O(3)	126 (2)
O(1)-Np-O(2)	89.2 (6)	C(4)-C(3)-O(4)	110 (2)
O(1)-Np-O'(2)	89.4 (6)	O(3)-C(3)-O(4)	122 (2)
O(1)-Np-O(3)	89.4 (6)		
O(1)-Np-O'(3)	91.8 (6)	O(2)-Ba-O'(2)	75.8 (7)
O(1)-Np-O(4)	90.7 (6)	O(2)-Ba-O(4)	63.5 (5)
O(1)-Np-O'(4)	89.4 (6)	O(2)-Ba-O'(4)	82.4 (5)
O(2)-Np-O'(2)	51.7 (6)	O(2)-Ba-O(w)	70.6 (6)
O(2)-Np-O(4)	68.4 (4)	O(4)-Ba-O(3)	80.7 (4)
O(3)-Np-O'(4)	50.2 (4)	O(4)-Ba-O'(w)	87.1 (5)
O(3)-Np-O(3)	71.2 (6)	O(3)-Ba-O(w)	83.8 (5)
		O(3)-Ba-O'(w)	70.9 (6)
C(2)-C(1)-O(2)	121 (1)		
O(2)-C(1)-O'(2)	119 (2)		

electron in the latter orbital while both orbitals are filled in the NpO_2^+ ion and the $\text{Np}=\text{O}$ bond is consequently weaker.

If, however, these f electrons are involved in bonding with the equatorial ligands, in cases where the latter are strong complexers, then the weakening of the primary bond is not so great. Earlier, we demonstrated³ that the NpO_2^{2+} primary bonds are weakened on changing the ligand from carbonate to peroxide, as evidenced by an increase in the $\text{Np}=\text{O}$ bond length from 1.776 Å in the former to 1.838 Å in the latter. Thus, to examine only the effect of changing Np(VI) to Np(V) we need to keep the equatorial ligands fixed. This is achieved by comparing the $\text{BaNpO}_2(\text{CH}_3\text{CO}_2)_3 \cdot 2\text{H}_2\text{O}$ structure with that of $\text{NaNpO}_2(\text{CH}_3\text{CO}_2)_3$ ²⁴ which has the same ligand and a very similar configuration (Figure 1). The axial O atoms of the NpO_2^+ and NpO_2^{2+} ions are bonded only to the Np atoms and the equatorial regions are occupied by a planar array of acetate ions. Each acetate ion is shared with two other cations: Ba^{2+} in the first instance and Na^+ in the second. These cations are linked also to four other O atoms from different acetate ions and the (larger) Ba^{2+} ion has two additional H_2O molecules in its coordination polyhedron. The $\text{Np}=\text{O}$ bond lengths are 1.85 (2) and 1.71 (4) Å in NpO_2^+ and NpO_2^{2+} , respectively; this clearly shows the weakening of the bond.

A similar comparison can be made between the $\text{Np}=\text{O}$ length of 1.86 (6) Å in $\text{Cs}_3\text{NpO}_2\text{Cl}_4$ and that in $\text{Cs}_2\text{NpO}_2\text{Cl}_4$

of 1.72 (7) Å (estimated by subtracting 0.01 Å from the $\text{U}=\text{O}$ value²⁵ in $\text{Cs}_2\text{UO}_2\text{Cl}_4$). The bond lengths differ by about the same amount as in the acetates, but here the uncertainties are much larger.

Finally, it is noted that the procedure offered by Zachariasen¹⁵ for predicting bond lengths is not satisfactory in the case of $\text{BaNpO}_2(\text{CH}_3\text{CO}_2)_3 \cdot 2\text{H}_2\text{O}$. By use of his method the actinyl $\text{M}=\text{O}$ bond length is established by starting with a valence of 2 for the O atom and then counting the bonds it makes to other atoms. In cases such as $\text{NaNpO}_2(\text{CH}_3\text{CO}_2)_3$ the O atom is bonded only to the Np atom, leading to an $\text{Np}=\text{O}$ bond strength of 2.0. Likewise a value of 2.0 would be deduced for the bond strength in $\text{BaNpO}_2(\text{CH}_3\text{CO}_2)_3 \cdot 2\text{H}_2\text{O}$, and the predicted $\text{Np}=\text{O}$ bond length would be 1.74 Å. In order to predict the observed bond length of 1.85 Å, a bond strength of 1.7 has to be assumed. Such a value seems more reasonable in view of the earlier discussion of the role of nonbonding electrons.

Registry No. $\text{BaNpO}_2(\text{CH}_3\text{CO}_2)_3 \cdot 2\text{H}_2\text{O}$, 60064-06-4.

Supplementary Material Available: Listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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