

Synthesis and properties of neptunium(VI,V) and plutonium(VI) pertechnetates

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(Received March 13, 2002; accepted in revised form September 17, 2002)

Neptunium / Plutonium / Pertechnetates / Crystal structure / IR and visible Spectroscopy

Summary. Preparation, crystal structure and properties revealed through IR and visible absorption spectroscopy study of Np(V,VI), Pu(VI) compounds formed with pertechnetate anions are reported. Spectrophotometric study of Np(V) and Pu(VI) in NH_4TcO_4 aqueous solutions (TcO_4^- concentration ranging between 0.2–0.5 M) shows only a slight interaction of NpO_2^+ and PuO_2^{2+} -ions with pertechnetate oxoanions in solution. On the contrary, for Np(V), Np(VI) and Pu(VI) pertechnetates in solid state, changes in the spectra clearly evidence the coordination of the actinides(V,VI) with TcO_4^- -anions. That is in agreement with Np(VI) pertechnetate X-ray structural analysis performed on a single crystal.

1. Introduction

The main chemical forms of technetium in nuclear fuel reprocessing solutions are considered to be $\text{UO}_2(\text{TcO}_4)_2 \cdot n\text{H}_2\text{O}$, $\text{Pu}(\text{TcO}_4)_4 \cdot n\text{H}_2\text{O}$ and $\text{ZrO}(\text{TcO}_4)_2 \cdot n\text{H}_2\text{O}$, or similar mixed complexes with additional nitrate ligands [1]. But till now, there is no clear evidence for the existence of such compounds and their properties are rather poorly studied. Numerous attempts were undertaken to study complexation of actinides with single charge tetraoxoanions of different heptavalent elements. From IR studies, one can learn that the pertechnetate oxoanion is acting in the solid state as a strong bidentate ligand and is able to complex to some extent uranyl cation in dilute solution [2]. Upon crystallization from aqueous solutions, uranyl pertechnetate forms a dihydrate salt, $\text{UO}_2(\text{TcO}_4)_2 \cdot 2\text{H}_2\text{O}$ whereas uranyl perchlorate forms higher hydrates. In [3] it was shown that uranyl pertechnetate dihydrate, is dehydrated in steps to form $\text{UO}_2(\text{TcO}_4)_2 \cdot 1.5\text{H}_2\text{O}$, $\text{UO}_2(\text{TcO}_4)_2 \cdot \text{H}_2\text{O}$ and finally the anhydrous $\text{UO}_2(\text{TcO}_4)_2$. The synthesis and properties of thorium pertechnetate have also been reported [4].

Concerning the perchlorates, it was first shown that uranyl perchlorate exists only as a hexahydrate [2] but later Alcock and Esperas [5] showed unambiguously that a heptahydrate $\text{UO}_2(\text{ClO}_4)_2(\text{H}_2\text{O})_7$ can also be formed depending on crystallization conditions. Neptunium(V) perchlorate

exists as a tetrahydrate $\text{NpO}_2\text{ClO}_4 \cdot 4\text{H}_2\text{O}$, whose crystal structure and electronic absorption spectrum were already reported in the literature [6]. Both perchlorate compounds are structurally well-characterized and indicate clearly that perchlorate anions do not enter the first coordination sphere of the actinide ion.

According to this literature survey, a question remains still open: do the pertechnetate ions enter the first coordination sphere in actinide complexes? In an attempt to remove this uncertainty, neptunium and plutonium complexes in aqueous solutions as well as in solid phase crystallized from solutions were spectroscopically investigated in this work.

2. Experimental

2.1 Synthesis of actinide pertechnetate complexes

Amounts of 10 g of technetium-99 metal of analytical grade [7] were oxidized in air stream at 500 °C to form Tc_2O_7 and then transformed into pertechnic acid following the Boyd's procedure [8]. In the second step, hydroxides $\text{Np}(\text{VI})\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{Pu}(\text{VI})\text{O}_3 \cdot \text{H}_2\text{O}$ were dissolved in these pertechnic acid solutions up to pH 4–5.

In the solid state, Np(VI) and Pu(VI) and Np(V) pertechnetates have been isolated in form of finely powdered samples. In all cases, it was impossible to exclude a priori, the simultaneous presence of differently hydrated compounds.

Crystals were grown by slow evaporation. Crystallization was difficult because of the high solubility of the compounds. Different evaporation rates and temperatures ranging from 0 to 100 °C usually resulted in the formation of pseudo glassy compounds. The crystalline compounds were only obtained for a very slow evaporation rate at 10 to 20 °C. Even under these conditions, Np(V) pertechnetate was obtained as a mixture of different polycrystalline compounds. However, it was possible to isolate a very small quantity of a pure compound that was large enough for spectroscopic studies.

For Np(VI) and Pu(VI) salts of TcO_4^- , crystallization was easier than for Np(V), but the crystals obtained were hygroscopic and not stable in air. Large amounts of pure Np(VI) and Pu(VI) phases were obtained for accurate chemical analysis.

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2.2 Measurements

Depending upon their volume and quality, the crystals obtained were characterized by: 1) X-ray structural analysis carried out on crystals sealed into glass capillaries (CAD4 diffractometer, graphite monochromator, $\lambda_{\text{MoK}\alpha}$, $\omega/2\theta$ -scanning). 2) UV-VIS-NIR-IR spectroscopic studies performed on Specord M80 for IR spectra and Shimadzu-3100 for UV-VIS-NIR spectra.

3. Results and discussion

3.1 Crystal structure of $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]$

An X-ray diffraction experiment was performed on a single crystal of $0.20 \times 0.15 \times 0.10$ mm in dimensions. Based on 16 reflections of $2\theta > 26^\circ$ the parameters of a triclinic cell were determined: $a = 5.322(5)$ Å, $b = 13.034(7)$ Å, $c = 15.460(9)$ Å; $\alpha = 107.08(5)^\circ$, $\beta = 98.05(7)^\circ$, $\gamma = 93.86(6)^\circ$; space group $P-1$, $Z = 2$; $d_{\text{calc}} = 4.084$ g/cm³; $\mu_{\text{MoK}\alpha} = 12.98$ mm⁻¹. The intensities of 5133 reflections were measured at $2\theta < 56^\circ$, 3481 of them being independent with $I > 2\sigma(I)$. The structure was solved by the direct method. All non-hydrogen atoms were first refined in isotropic approximation, then absorption correction using DIFABS method [9] was applied. The H atoms were not localised and omitted in the calculation of structure factors. The refinement of non-hydrogen atoms in anisotropic approximation by full-matrix least-squares on F^2 (4600 reflections, 262 parameters, SHELXL93 [10]) has provided $R(F) = 0.0285$ and $R_w(F^2) = 0.0686$ (for reflections with $I > 2\theta(I)$).

Atomic coordinates and temperature factors for $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]$ are given in Table 1, the bond lengths and bond angles in Table 2. The structure of neptunyl dipertechetate sesquihydrate is built from electroneutral ribbons whose composition is in agreement with the formula $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]_n$ (Fig. 1). The coordination polyhedra (CP) of both crystallographically independent Np atoms are distorted pentagonal bipyramids with the 'yl' O atoms occupying the apical positions. The equatorial positions of Np(1) CP are occupied by five oxygen atoms from the coordinated TcO_4 groups. Four of these TcO_4 groups are bidentate-bridging (*i.e.* two groups of $\text{Tc}(1)\text{O}_4$, one $\text{Tc}(2)\text{O}_4$ and one $\text{Tc}(3)\text{O}_4$), the fifth group is monodentate ($\text{Tc}(4)\text{O}_4$). The equatorial environment of Np(2) is formed by two O atoms of bidentate-bridging $\text{Tc}(2)\text{O}_4$ and $\text{Tc}(3)\text{O}_4$ groups and three O atoms of coordinated water molecules.

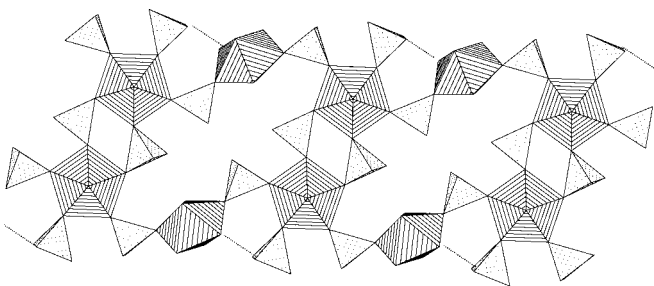


Fig. 1. Electroneutral ribbon $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]_n$ in the structure of $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]$.

Table 1. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) in the structure of $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]$.

Atom	x	y	z	U_{eq}
Np(1)	7526 (1)	3552 (1)	3311 (1)	16 (1)
Np(2)	7488 (1)	7973 (1)	1870 (1)	18 (1)
Tc(1)	4864 (2)	3607 (1)	5635 (1)	25 (1)
Tc(2)	9967 (1)	5025 (1)	1526 (1)	21 (1)
Tc(3)	6018 (2)	638 (1)	3726 (1)	28 (1)
Tc(4)	10 168 (1)	1420 (1)	1271 (1)	24 (1)
O(1)	10 544 (12)	3832 (5)	3963 (4)	36 (1)
O(2)	4490 (12)	3304 (5)	2655 (4)	37 (2)
O(3)	10 122 (11)	8489 (5)	1524 (4)	31 (1)
O(4)	4782 (12)	7460 (5)	2180 (5)	35 (1)
O(11)	5927 (12)	3904 (4)	4727 (4)	30 (1)
O(12)	3052 (14)	4570 (4)	6185 (5)	38 (2)
O(13)	7454 (19)	3536 (8)	6374 (6)	77 (3)
O(14)	3140 (20)	2394 (5)	5265 (7)	75 (3)
O(21)	9080 (14)	4377 (5)	2271 (4)	40 (2)
O(22)	9289 (12)	6344 (4)	1864 (4)	31 (1)
O(23)	8324 (14)	4385 (5)	464 (4)	40 (2)
O(24)	13 112 (12)	4994 (5)	1499 (5)	37 (2)
O(31)	6739 (16)	1914 (5)	3659 (5)	46 (2)
O(32)	7062 (15)	-322 (5)	2847 (5)	50 (2)
O(33)	7426 (18)	577 (6)	4747 (5)	63 (2)
O(34)	2854 (16)	372 (6)	3642 (6)	58 (2)
O(41)	8881 (14)	2179 (5)	2196 (5)	39 (2)
O(42)	7865 (13)	442 (5)	572 (5)	41 (2)
O(43)	12 642 (16)	824 (6)	1645 (5)	55 (2)
O(44)	11 138 (17)	2237 (6)	683 (5)	56 (2)
O _w (1)	4918 (12)	8859 (5)	960 (5)	37 (2)
O _w (2)	6412 (12)	6735 (5)	336 (4)	33 (1)
O _w (3)	9958 (15)	8184 (5)	3362 (4)	43 (2)

The Np–O distances in the nearly linear and symmetric NpO_2 groups equal 1.727(7)–1.738(7) Å while the Np–O_{equat} distances vary within the interval 2.325(7)–2.419(7) Å, the largest values being found for coordinated water molecules. The average Tc–O distance in the TcO_4 groups is 1.703(6) Å. The shortest Tc–O distance in TcO_4 groups, 1.672(7) Å, was found for Tc(1) while the largest one, 1.740(7) Å, was found for Tc(3).

Several short contacts O_{water}...O(TcO_4) in the structure are obviously due to the formation of H-bonds (Table 3). One of these bonds O_w(1)...O(42) connects atoms inside the ribbon while the rest is linking different ribbons into a three-dimensional network. In the crystal structure of $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]$, the ribbons extend in the [010] direction and the ribbon plane is very close to the (101) one. The dihedral angle between the least-squares plane based on the Np atoms of a single $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]_n$ ribbon and the (101) plane is only 0.4°. The equatorial plane of Np(1) CP almost coincides with the least-square ribbon plane (dihedral angle 5.3°), while the Np(2) CP is strongly rotated relatively to the ribbon plane (dihedral angle 48.8°). Such a strong rotation of CP is obviously caused by H-bond formation between different ribbons.

The data presented in Table 2 show that the average Np–O distance in $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]$ is similar to those found in other Np(VI) compounds and the average Tc–O distance is close to analogous distances in coordinating pertechnetate oxoanions [11]. It worth noting

Table 2. Selected inter-atomic distances (d) and bond angles (ω) in the structure of $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]$.

Distance	d , Å	Angle	ω , deg.
Np(1)–O(1)	1.727 (7)	O(1)–Np(1)–O(2)	178.6 (3)
Np(1)–O(2)	1.738 (7)		
Np(1)–O(11)	2.390 (6)	O(11)–Np(1)–O(31)	70.0 (2)
Np(1)–O(21)	2.385 (6)	O(21)–Np(1)–O(41)	73.8 (2)
Np(1)–O(31)	2.376 (6)	O(31)–Np(1)–O(41)	72.2 (2)
Np(1)–O(41)	2.325 (6)	O(11)–Np(1)–O(12) ^a	72.2 (2)
Np(1)–O(12) ^a	2.396 (6)	O(21)–Np(1)–O(12) ^a	72.1 (2)
Np(2)–O(3)	1.731 (6)	O(3)–Np(2)–O(4)	177.9 (3)
Np(2)–O(4)	1.733 (6)		
Np(2)–O(22)	2.386 (5)	O(22)–Np(2)–O _w (2)	72.2 (2)
Np(2)–O _w (1)	2.411 (6)	O _w (1)–Np(2)–O _w (2)	72.7 (2)
Np(2)–O _w (2)	2.409 (6)	O(22)–Np(2)–O _w (3)	70.2 (2)
Np(2)–O _w (3)	2.419 (7)	O _w (1)–Np(2)–O(32) ^b	73.3 (3)
Np(2)–O(32) ^b	2.337 (6)	O _w (3)–Np(2)–O(32) ^b	71.8 (3)
Tc(1)–O(11)	1.713 (6)	O(11)–Tc(1)–O(12)	111.9 (3)
Tc(1)–O(12)	1.731 (6)	O(11)–Tc(1)–O(13)	107.6 (4)
Tc(1)–O(13)	1.689 (9)	O(11)–Tc(1)–O(14)	109.6 (4)
Tc(1)–O(14)	1.672 (7)	O(12)–Tc(1)–O(13)	110.0 (4)
		O(12)–Tc(1)–O(14)	109.6 (4)
		O(13)–Tc(1)–O(14)	107.8 (5)
Tc(2)–O(21)	1.713 (6)	O(21)–Tc(2)–O(22)	109.9 (3)
Tc(2)–O(22)	1.723 (5)	O(21)–Tc(2)–O(23)	109.1 (3)
Tc(2)–O(23)	1.688 (7)	O(21)–Tc(2)–O(24)	109.9 (3)
Tc(2)–O(24)	1.683 (7)	O(22)–Tc(2)–O(23)	109.2 (3)
		O(22)–Tc(2)–O(24)	109.9 (3)
		O(23)–Tc(2)–O(24)	108.9 (3)
Tc(3)–O(31)	1.718 (6)	O(31)–Tc(3)–O(32)	110.6 (3)
Tc(3)–O(32)	1.740 (7)	O(31)–Tc(3)–O(33)	109.0 (4)
Tc(3)–O(33)	1.677 (8)	O(31)–Tc(3)–O(34)	109.8 (4)
Tc(3)–O(34)	1.675 (8)	O(32)–Tc(3)–O(33)	110.0 (4)
		O(32)–Tc(3)–O(34)	109.1 (4)
		O(33)–Tc(3)–O(34)	108.4 (5)
Tc(4)–O(41)	1.740 (6)	O(41)–Tc(4)–O(42)	108.7 (3)
Tc(4)–O(42)	1.704 (7)	O(41)–Tc(4)–O(43)	110.2 (4)
Tc(4)–O(43)	1.691 (7)	O(41)–Tc(4)–O(44)	109.1 (3)
Tc(4)–O(44)	1.690 (7)	O(42)–Tc(4)–O(43)	108.8 (4)
		O(42)–Tc(4)–O(44)	109.4 (4)
		O(43)–Tc(4)–O(44)	110.6 (4)

The coordinates of the atoms marked with additional 'a' and 'b' are referred to those given in Table 1 by symmetry transformations $(1-x, 1-y, 1-z)$ and $(x, 1+y, z)$ respectively.

Table 3. Possible H-bonds in the structure of $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]$.

Distance	d , Å	Symmetry transformation for the second atom
O _w (1)...O(3)	2.866 (9)	$-1+x, y, z$
O _w (1)...O(42)	2.762 (9)	$x, 1+y, z$
O _w (1)...O(43)	2.887 (9)	$-1+x, 1+y, z$
O _w (2)...O(23)	2.755 (10)	$1-x, 1-y, -z$
O _w (2)...O(44)	2.748 (9)	$2-x, 1-y, -z$
O _w (3)...O(13)	2.807 (11)	$2-x, 1-y, 1-z$
O _w (3)...O(33)	2.979 (10)	$2-x, 1-y, 1-z$

that $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]$ is the first compound where the bidentate-bridging pertechnetate ions have a symmetry C_{2v} .

3.2 Spectroscopic study of neptunium and plutonium pertechnetates

3.2.1 Optical spectroscopy

Aqueous solution of pertechnetate complexes

The optical spectra recorded on Np(V) and Pu(VI) in 0.2–0.5 M ammonium pertechnetate aqueous solutions slowly acidified with the corresponding acid were identical to the spectra obtained for Np(V) and Pu(VI) in perchlorate solutions. The concentrations were close to the solubility limit of the salts investigated. Consequently, we exclude complexation of neptunyl(V) or plutonyl(VI) cations with pertechnetate oxoanions in solution.

Solid Np(V) and Pu(VI) pertechnetates

The optical spectrum of the Np(V) ($5f^2$) compound formed with TcO_4^- anion is presented in Fig. 2. Compared to the spectrum of the hydrated NpO_2^{2+} -ion in solution, the main absorption band corresponding to the spin allowed transition $^3H_4 \rightarrow ^3F_4$ is red-shifted from 984.6 nm ($10\,149\text{ cm}^{-1}$) in solution to 1016 nm (9840 cm^{-1}) in the solid and forms a doublet with maxima at 1016 and 1026 nm ($9840\text{--}9743\text{ cm}^{-1}$). The shift indicates that the pertechnetate acts as a ligand and the doublet that the crystal lattice of the compound formed offers two slightly different surroundings for the Np(V) cations. Moreover, the very large shift (309 cm^{-1}) of this $5f\text{--}5f$ electronic transition, suggests a neptunyl(V) cation-cation interaction in this lattice or a strong interaction between Np(V) and Tc(VII) *via* an oxygen atom analogous to that assumed in CrO_4^{2-} , VO_3^- [12] and MoO_4^{2-} [13] salts. It worth recalling that the structure of Np(V) perchlorate tetrahydrate displays mutual coordination of mono-dentate neptunyl(V) groupings but no ClO_4^- coordination.

Optical spectra recorded on crystalline Pu(VI) ($5f^2$) compounds formed with pertechnetate anions have shown that the pertechnetate ion enters the coordination sphere of

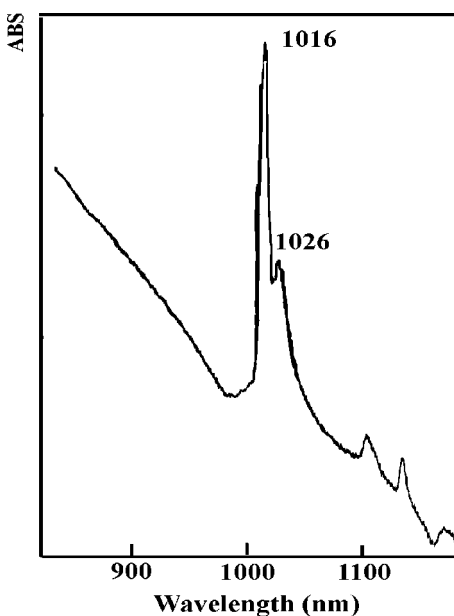


Fig. 2. Absorption spectrum of the solid Np(V) complex formed with TcO_4^- -ion in NaCl-matrix.

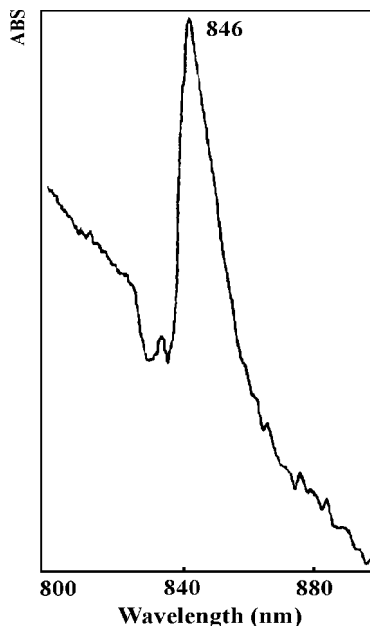


Fig. 3. Absorption spectrum of the solid Pu(VI) complex formed with TcO_4^- -ion in NaCl-matrix.

the plutonyl-ion. Indeed, the main Pu(VI) absorption band is strongly (228 cm^{-1}) red-shifted from 830 nm ($12\,045\text{ cm}^{-1}$) for plutonyl perchlorate to 846 nm ($11\,817\text{ cm}^{-1}$) for plutonyl pertechnetate (Fig. 3), indicating that the nephelauxetic effect operates on the Slater parameters describing the electronic repulsion between $5f$ -electrons. Therefore, pertechnetate ion is an inner sphere ligand in Pu(VI) coordination contrary to perchlorate.

3.2.2 Far-IR spectroscopy

Neptunium(VI) pertechnetate

In $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]$ spectrum (Fig. 4), several intense absorption bands appear in the $966\text{--}846\text{ cm}^{-1}$ energy region. The narrow bands at 966 and 934 cm^{-1} are assigned to stretching vibrations (ν_3) of the two crystallographically independent NpO_2^{2+} -groupings. The broader

band at $894\text{--}882\text{ cm}^{-1}$ is assigned to asymmetric and symmetric stretching vibrations of the mono- and bidentate TcO_4^- -groupings. The free TcO_4^- -ion exhibits one absorption band at 912 cm^{-1} [14], which upon Np(VI) complex formation, is split and shifted towards lower frequencies.

The coordinated water molecule absorbs at $3496\text{--}3172\text{ cm}^{-1}$ (asymmetric and symmetric OH stretching modes), at 1658 and 1644 cm^{-1} (HOH bending modes) and at $672\text{--}552\text{ cm}^{-1}$ (rotational modes). The intensity of the OH stretching vibrations is close to that of the absorption bands of the main groups, NpO_2^{2+} and TcO_4^- . The high intensity of $\nu(\text{OH})$ band can not be explained by the formation of very strong H-bonds since the band maximum and the satellites fall into the region characteristic of medium strength H-bonds [15]. Most likely, the peculiarity of this vibration band is resulting from a reduced number of degrees of freedom for the water molecule in the crystal lattice of $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]$.

Plutonyl(VI) pertechnetate

The IR spectrum of plutonium(VI) pertechnetate $[(\text{PuO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]$ differs notably from that of $[(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}]$. The intense absorption band in the $948\text{--}864\text{ cm}^{-1}$ region (Fig. 5) results evidently from overlapping of the vibration bands belonging to pertechnetate and plutonyl groupings. The number of shoulders indicates the degree of distortion of both groups. Two broad absorption bands are observed in the region $3550\text{--}3300\text{ cm}^{-1}$ and $3280\text{--}3150\text{ cm}^{-1}$. The former might be assigned either to lattice water molecule vibration $\nu(\text{OH})$, or to coordinated H_2O -molecule vibration. The band at 620 cm^{-1} , which can be attributed to rotational vibrations $\rho_1(\text{H}_2\text{O})$, shows very low intensity.

Np(V) pertechnetate

The spectrum in Fig. 6 presents the three main far-IR absorption regions. The band in the $780\text{--}730\text{ cm}^{-1}$ energy region corresponds to the stretching modes of the NpO_2^+ group. It contains an intense doublet and a number of very poorly resolved bands appearing as shoulders. Such a rich

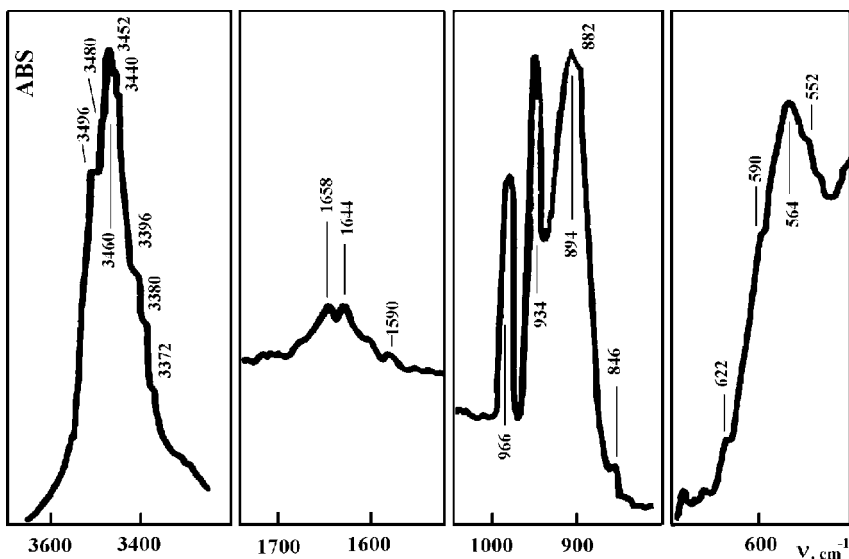


Fig. 4. IR spectrum of the solid Np(VI) complex formed with TcO_4^- -ion in NaCl-matrix.

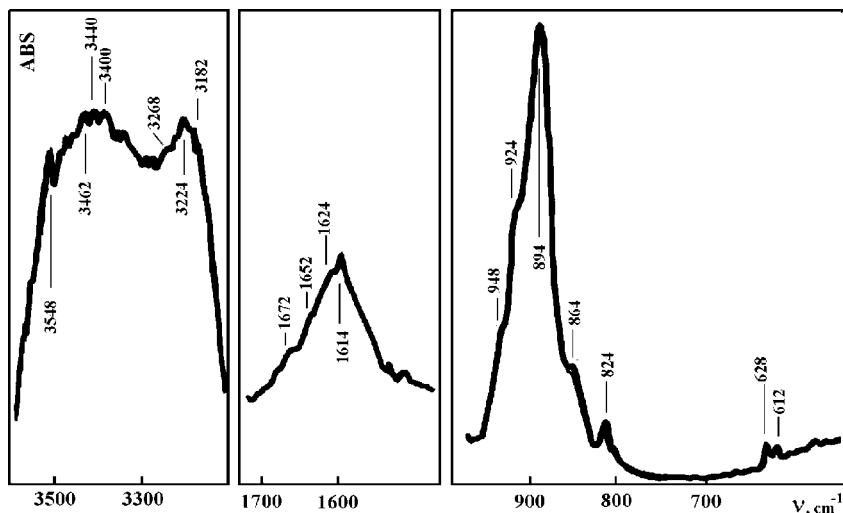


Fig. 5. IR spectrum of the solid Pu(VI) complex with TcO_4^- -ion in NaCl-matrix.

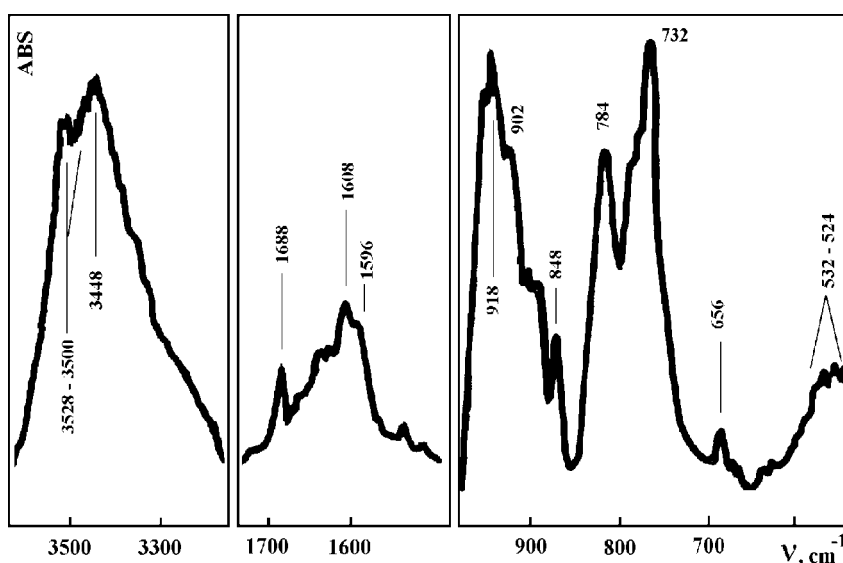


Fig. 6. IR spectrum of the solid Np(V) complex formed with TcO_4^- -ion in the NaCl-matrix.

set of vibration frequencies may originate in the bidentate coordination of NpO_2^+ groupings. The $950\text{--}850\text{ cm}^{-1}$ band results from vibrations of differently distorted pertechnetate ions. By analogy with Np(V) perchlorates [10], we expect one or more water molecules to enter the coordination sphere of neptunyl(V) ion in the structure. Indeed, the observed H_2O libration band (at 530 cm^{-1}) provides evidence for such coordinated water molecules. Moreover, the splitting of the vibration bands ($1690\text{--}1596\text{ cm}^{-1}$) shows that water molecules participate in the formation of a set of hydrogen bonds, some of them being rather strong such as the one corresponding to the satellite line at 1690 cm^{-1} . The $\nu(\text{OH})$ stretching vibration band in the region $3550\text{--}3300\text{ cm}^{-1}$ is broad and intense and splits into some components. This feature is common for crystallohydrates in which a large number of energetically different water molecules are present [16].

4. Conclusion

The optical spectra recorded on Np(V) and Pu(VI) in $0.2\text{--}0.5\text{ M}$ ammonium pertechnetate aqueous solutions have

shown almost no complexation of neptunyl or plutonyl cations with pertechnetate oxoanions in solution. Spectroscopic data obtained for crystalline Np(V), Np(VI) and Pu(VI) compounds show that pertechnetate anions enter the coordination sphere of the actinide ion. X-ray diffraction analysis and far-IR spectroscopy have confirmed the complex formation.

Acknowledgment. The help of the Centre of X-Ray Structural Researches of the Department of General and Technical Chemistry of Russian Academy of Sciences (headed by RAS corresponding member M.Yu. Antipin) where the X-ray diffraction experiments were carried out is highly acknowledged.

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