

# THE SYNTHESIS, CRYSTAL STRUCTURE AND SOME PROPERTIES OF



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The pentavalent neptunium perhenates  $\text{NpO}_2\text{ReO}_4$  and  $\text{NpO}_2\text{ReO}_4 \cdot 6\text{H}_2\text{O}$  are discussed in [1], but their crystal structure is not determined to the present day. Although structural investigations of Np(V) compound with various inorganic anions are rather extensive, the currently available data are not sufficient to predict the possibility of  $\text{ReO}_4$  ion coordination to the Np atom. It is known that  $\text{ClO}_4^-$  ion, which is isoelectronic and isostructural to  $\text{ReO}_4$  ion, is not enter the coordination sphere of central atom in the solid compounds of uranium and neptunium  $\text{UO}_2(\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}$  [2]  $[\text{NpO}_2(\text{H}_2\text{O})_4]\text{ClO}_4$  [3],  $[\text{NpO}_2(\text{Urea})_5]\text{ClO}_4 \cdot \text{H}_2\text{O}$  [4],  $(\text{NpO}_2)_2(\text{DMSO})_7(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  [5]. This raises the question of whether the formation of solid Np(V) perhenate is possible. The resolution of the issue can also be useful for prediction of Np(V) interaction with  $\text{TcO}_4^-$ .

The crystals of  $[\text{NpO}_2(\text{ReO}_4)(\text{Phen})(\text{H}_2\text{O})_2]$  (**I**) for X-ray analysis were chosen from a solid phase obtained by mixing solutions of  $\text{NpO}_2\text{ReO}_4$  ( $10^{-2}$  mol/l) and  $\text{Phen} \cdot \text{H}_2\text{O}$  (0.1 mol/l) in ethanol followed by the evaporation at a temperature lower than  $20^\circ\text{C}$ .  $\text{NpO}_2\text{ReO}_4$  was prepared by the dissolution of  $\text{NpO}_2\text{OH}$  in  $\text{HReO}_4$  and the evaporation at a temperature lower than  $40^\circ\text{C}$ .

Crystallographic data were obtained at low temperature (110K) on Bruker SMART single-crystal diffractometer using graphite monochromated  $\text{MoK}\alpha$  radiation. The collection of data was carried out up to  $2\theta_{\text{max}}=60^\circ$  measured for  $-10 \leq h \leq 10$ ,  $-15 \leq k \leq 15$ ,  $-29 \leq l \leq 29$ . The structure was solved by direct method. All non-hydrogen atoms were refined with anisotropic thermal parameters by a full-matrix least-squares procedure on  $F^2$ . Hydrogen atoms of the 1,10-phenanthroline were fixed in the ideal positions, while hydrogen atoms of water molecules were not localized. All calculations were performed using the SHELXTL PLUS program package. Crystallographic data for compound **I** are given in Table 1.

Table 1. Crystallographic data.

a, Å	7.288(1)
b, Å	10.513(2)
c, Å	20.936(4)
<b>b</b> , deg	96.939(5)
Space group	$P2_1/c$
V, Å <sup>3</sup> ; Z	1592.2(5); 4
$d_{\text{calc}}$ , g/cm <sup>3</sup>	3.052
Number of reflections	5132
Number of unique reflections ( $I > 2\sigma(I)$ )	3018
Number of parameters refined	217
R, wR( $F^2$ )	0.058, 0.126

The crystal structure **I** consists of complex  $[\text{NpO}_2(\text{ReO}_4)(\text{Phen})(\text{H}_2\text{O})_2]$  molecules (Figure 1). The coordination polyhedron of the Np atom is pentagonal bipyramid which equatorial positions occupied by two nitrogen atoms of 1,10-phenanthroline and oxygen atoms of monodentate  $\text{ReO}_4^-$  anion and two water molecules.

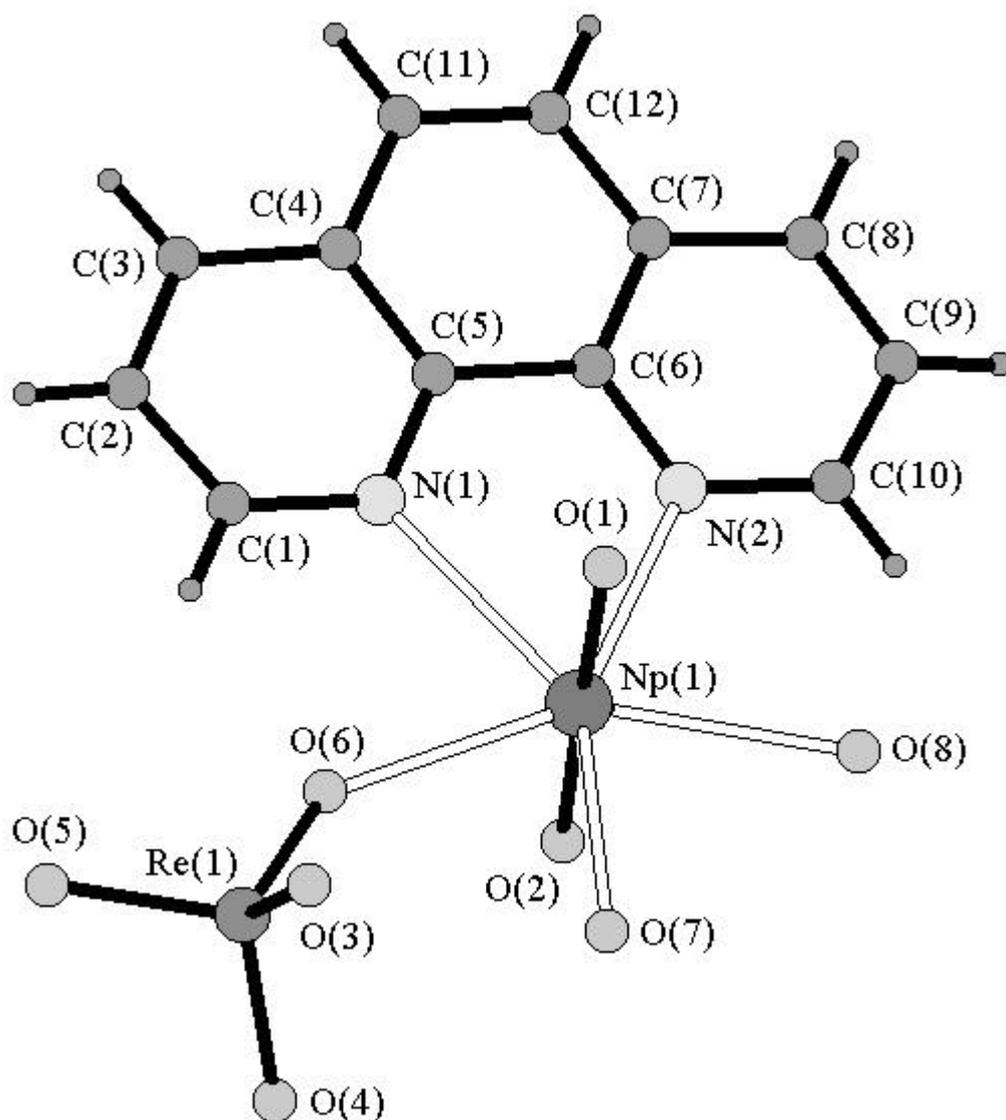


Figure 1. The crystal structure of **I**.

The distances between neptunium atom and oxygen atoms of water molecules are equal to 2.445(8) and 2.532(8) Å, the Np-O ( $\text{ReO}_4$ ) bond length is 2.457(8) Å. The Np-N distances are significantly longer and equal to 2.641(9) and 2.59(1) Å. The maximum deviation of atoms from mean equatorial plane is equal to 0.135 Å. The  $\text{NpO}_2$  group is nearly linear and symmetric. The O-Np-O angle is equal to 178.0(3)°, the Np-O distances have unusual large values (1.902(9) and 1.907(10) Å).

The  $\text{ReO}_4^-$  anion acts as monodentate ligand. The coordination polyhedron of Re atom is the tetrahedron. The O-Re-O angles lie in the range 108.2(5)-112.1(4)°. The Re-O distances are equal to 1.695(9)-1.711(10) Å for the terminal atoms, and the length of bridging Re-O bond is 1.729(8) Å.

The phenanthroline molecule acts as bidentate chelate ligand and form pentagonal ring with Np atom. The N-C and C-C bonds lie in the ranges 1.34(2)-1.36(2) Å and 1.36(4)-1.45(4) Å, respectively.

The NIR and IR spectra of **I** were obtained using Shimadzu UV3100 and Specord M80 spectrophotometers, respectively. Samples were prepared by pressing triturated mixture of the compound with molten NaCl.

In the NIR spectrum of **I** the intense absorption band of Np(V) at 985 nm corresponds to the f-f electron transition.

The IR spectrum contains a large number of absorption bands, some of which are overlapped. In the Table 2 the probable spectral band assignments are presented.

Table 2. IR spectral band assignments ( $\text{cm}^{-1}$ ).

$\nu(\text{HOH})$	3448, 3340, 3260
$\delta(\text{H}_2\text{O})$	1670, 1664, 1640
$\nu(\text{CC}), \nu(\text{CN})$	1715, 1692, 1586, 1574, 1558, 1536, 1520, 1488, 1466, 1446, 1434
$\nu(\text{CH})$	2970
$\gamma(\text{CH})$	1148, 1100, 870, 864, 728, 720, 668, 624
$\nu_s(\text{ReO}_4)$	948
$\nu_{as}(\text{ReO}_4)$	920, 900
$\nu_{as}(\text{NpO}_2)$	816, 804

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