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Structural and spectral investigation of a neptunium(V) complex with 2,2′-bipyridine

Grigorii B. Andreev,[a] Alexander M. Fedosseev,*[a] Nina A. Budantseva[a] and Mikhail Yu. Antipin[b]

[a] *Institute of Physical Chemistry, Russian Academy of Sciences, 117915 Moscow, Russian Federation.*
Fax: +7 095 335 2005; e-mail: fedosseev@ipc.rssi.ru
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow, Russian Federation.*
Fax: +7 095 135 5085; e-mail: xray@xray.ineos.ac.ru

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The new neptunium(V) complex $[NpO_2(bipy)(H_2O)_3](NO_3)$ was synthesised, and its structure was determined by X-ray diffraction analysis and IR spectroscopy.

The coordination of nitrogen atoms to the neptunyl ion NpO_2^+ is of interest because only two complexes with 2,6-pyridinedicarboxylate anions acting as chelate ligands are known.[1] The nitrogen atoms of pyridine and 2,2′-bipyridine easily enter into the coordination sphere of uranyl.[2–6] Although the coordination interactions of neptunyl and uranyl are similar, the coordination behaviours of these ions are different, for instance, in the tendency of the neptunyl ion to so-called cation–cation interactions. In this respect, the capability of neptunyl to coordinate nitrogen atoms is not predictable. To clarify this uncertainty, we studied the structure of a neptunyl complex with 2,2′-bipyridine.

The blue prismatic crystals for X-ray analysis were chosen from a solid phase obtained by mixing $NpO_2ClO_4 \cdot nH_2O$ and 2,2′-bipyridinium nitrate solutions in ethanol followed by evaporation to dryness and repeated recrystallisation from ethanol–toluene at ambient temperature. $NpO_2ClO_4 \cdot nH_2O$ was prepared by the dissolution of neptunyl hydroxide in a stoichiometric amount of an aqueous 0.5 M perchloric acid solution and the evaporation at a temperature lower than 120 °C.

The crystal structure of **1** consists of $[NpO_2(bipy)(H_2O)_3]^+$ cations (Figure 1) and NO_3^- anions.† The coordination polyhedron of the Np atom is a pentagonal bipyramid which equatorial positions occupied by two nitrogen atoms of a 2,2'-bipyridine molecule acting as a bidentate ligand and three water molecules. The Np–O distances lie in the range 2.45(1)–2.49(1) Å. The Np–N bonds are significantly longer, and the bond lengths are equal to 2.66(1) and 2.62(1) Å. The maximum deviation of atoms from the mean equatorial plane is equal to 0.298 Å. The shortest distance between neptunium atoms is 5.560 Å.

The O–Np–O bond angle in the NpO_2 group is close to 180°, and it is equal to 178.5(4)° while the Np–O bond lengths differ and are equal to 1.86(1) and 1.77(1) Å.

The N–C and C–C distances in the 2,2′-bipyridine molecule lie in the range 1.35(2)–1.41(2) and 1.31(2)–1.41(2) Å for rings containing the N(1) and N(2) atoms, respectively. The angle between these rings is equal to 2.9°. The maximum deviations of atoms from mean planes are 0.038 and 0.022 Å.

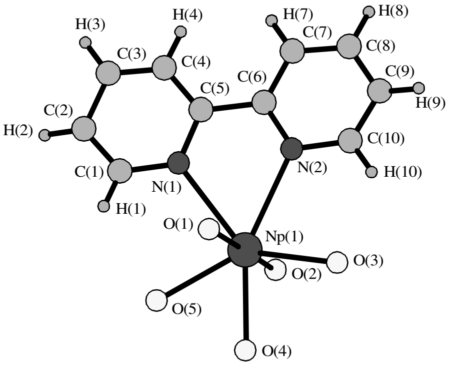

Figure 1 Structure of the cation $[NpO_2(bipy)(H_2O)_3]^+$. Selected bond lengths (Å): Np–N(2) 2.62(1), Np–N(1) 2.66(1), Np–O(2) 1.86(1), Np–O(1) 1.77(1), Np–O(5) 2.46(1), Np–O(3) 2.46(1), Np–O(4) 2.49(1); principal bond angle: O(1)–Np–O(2) 178.5(4)°.

The nitrate group acts as the second sphere anion, which is not typical for neptunium complexes. In addition, there is a short contact [1.72(2) Å] between one oxygen atom of the nitrate group and the water molecule entering the first coordination sphere of the neptunyl group. The N–O distances of the NO_3 group lie in the range 1.23(2)–1.29(2) Å.

The NIR and IR spectra of $[NpO_2(bipy)(H_2O)_3](NO_3)$ were obtained using Shimadzu UV3100 and Specord M80 spectrophotometers, respectively. Samples were prepared by pressing a triturated mixture of the compound with molten NaCl.

The IR spectrum contains many overlapped absorption bands. These bands are difficult to assign. For instance, some intense bands in the region 3500–3100 cm^{-1} are associated with the stretching vibrations ν(C–H) and ν(O–H); however, not all of these groups take part in the H-bond formation. The vibrations δ(C–N) and $\nu(NO_3^-)$ and the skeleton vibrations of pyridine rings arise in the region 1600–1250 cm^{-1}.

The asymmetry of NpO_2^+ induced by a significant distinction between the interatomic distances Np(1)–O(1) and Np(1)–O(2) leads to the low frequency shift of $\nu_{as}(NpO_2^+)$ to 762 cm^{-1} (in comparison with ν_{as} 824 cm^{-1} in the IR spectrum of a NpO_2ClO_4 solution[7]) and the appearance of the symmetric mode $\nu_s(NpO_2^+)$ 740 cm^{-1}.

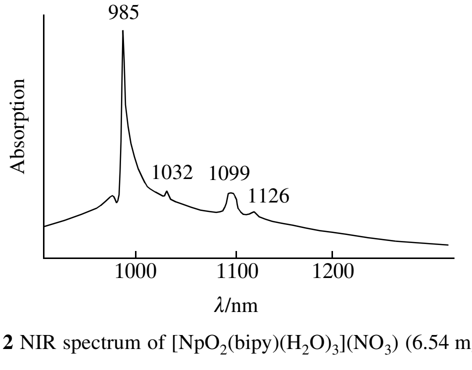

Figure 2 NIR spectrum of $[NpO_2(bipy)(H_2O)_3](NO_3)$ (6.54 mg in a NaCl matrix).

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† All crystallographic data were obtained on a Siemens P3/PC single-crystal X-ray diffractometer using graphite monochromated MoKα radiation. The collection of data was carried out up to $2\theta_{max} = 62°$ measured for $0 \leqslant h \leqslant 30$, $0 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 12$ using a $\theta/2\theta$ scan technique. The structure was solved by a 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 2,2′-bipyridine molecule were fixed in the ideal positions, while hydrogen atoms of water molecules were not localised. All calculations were performed using the SHELXTL PLUS program package.

Crystallographic data for $[NpO_2(bipy)(H_2O)_3](NO_3)$: space group $Pca2_1$ (no. 29), $a = 21.023(6)$, $b = 7.872(2)$, $c = 8.870(3)$ Å, $V = 1467.9(7)$ Å^3, $Z = 4$, $d_{calc} = 2.929$ g cm^{-3}, $R = 0.042$, $R_W = 0.108$, Flack parameter 0.06(5). Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/82.

In the NIR spectrum of solid $[NpO_2(bipy)(H_2O)_3](NO_3)$, a set of bands of various intensities is observed (Figure 2). The most intense narrow band of Np^V corresponding to the *f–f* electron transition has a maximum at 985 nm, which insignificantly differs from the position in the spectrum of a hydrated ion (981 nm).[8] This fact is unexpected because it was demonstrated that the increasing of $Np–O_{oxo}$ distances during O-donor coordination (including cation–cation interactions), as a rule, is accompanied by a considerable low frequency shift of the *f–f* absorption band.[9,10] It may be assumed that the participation of 5*f*-electrons in the coordination of a bipyridine molecule by NpO_2^+ is not dominant. Probably, the formation of a coordination bond is due to the 6*d*-electrons of Np^V and the electrons of a ligand.

Compound **1** represents the first example of a pentavalent neptunium complex with 2,2′-bipyridine. Only two such compounds of hexavalent neptunium are known at present. These are the complexes $NpO_2(bipy)(NO_3)_2$ and $NpO_2(bipy)(OAc)_2$,[2] which are isomorphous and isostructural to U^{VI} analogues. In their structures, the neptunium atom has a hexagonal bipyramidal coordination; the equatorial plane consists of two N atoms of 2,2′-bipyridine with Np–N distances ranging from 2.564 to 2.630 Å and four O atoms of two nitrate or acetate groups, which act as bidentate ligands.

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