Inorg. Chem. **2008**, *47*, 2943−2945

Inorganic Chemistry
Communication

First Structural Evidence of Actinide−Nitrite Coordination

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Received January 25, 2008

The first nitrite complex of actinide metal, $\{C(NH_2)_3\}_2[NpO_2(NO_2)(Pic)_2]$, was synthesized, and its crystal structure was determined using X-ray diffractometry and confirmed by NIR and IR spectroscopies. Main crystallographic data: space group $P\bar{1}$, triclinic, $a = 8.9329(1)$ Å, $b = 11.6669(2)$ Å, $c = 11.6698(2)$ Å, $\alpha = 68.080(1)°$, $\beta = 88.213(1)°$, $\gamma = 73.254(1)°$, $V = 1076.45(3)$ Å^3, and $Z = 2$.

Nitrous acid is a weak monobasic acid existing only in solutions or in the form of nitrite salts. It can be prepared by adding mineral acid to nitrite of sodium and rapidly decomposes into nitrogen oxides and nitric acid. Nitrous acid is widely used in nuclear chemistry as an oxidizing−reducing reagent.[1] For example, sodium nitrite is one of the most convenient reagents for reduction of Np(VI) to Np(V) used in laboratory practice. Another reason for interest in the interaction of actinides with a nitrite anion is the high concentration of this anion (up to 1 M) in high-level radioactive wastes.

While the oxidation–reduction reactions of neptunium in the presence of nitrite ion have been studied,[2] there is relatively little known about $Np-NO_2^-$ complexation. The only data available on neptunium nitrite complexes are the stability constants for Np(V). The stability constant for the $[NpO_2NO_2]$ complex equal to $\log \beta = -(0.05 \pm 0.05)$ ($I = 2$ M) was obtained from a solvent extraction experiment.[3] The slightly higher value of $\log \beta = 0.14$ ($I = 2$ M) was determined using spectrophotometry.[4] There are no data on complexation with other actinides in solution and on solid compounds.

In addition to pure radiochemical interest in the interaction of actinides with a nitrite ion, the biochemical importance of the process must not be underestimated. The concentration of nitrite in living organisms is closely related to the reactions of other nitrogen oxides. The two major sources of nitrite ion are oxidation of NO produced by NO synthase and nitrate reduction by bacteria.[5] The nitrite concentrations in the organisms range from 0.1 to 10 μM, values comparable with the concentrations of lactate and oxalate.[6]

In this work, we present the synthesis,[7] X-ray structure determination,[8] and vis/NIR and IR spectroscopic study[9] of the first nitrite complex of actinide, $\{C(NH_2)_3\}_2[NpO_2(NO_2)(Pic)_2]$.

The structure of $\{C(NH_2)_3\}_2[NpO_2(NO_2)(Pic)_2]$ consists of complex anions $[NpO_2(NO_2)(Pic)_2]^{2-}$ (Figure 1) and guanidinium cations. The coordination polyhedron of a Np

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(7) A hexavalent neptunium-237 stock solution was prepared by a technique that included anion-exchange purification from possible inorganic admixtures followed by precipitation of the oxalate of tetravalent Np in order to avoid any organics. Dissolution and destruction of the oxalate complex were carried out in concentrated nitric acid, and then the solution was evaporated up to wet salts and dissolved in distilled water. The reduction of hexavalent to pentavalent neptunium was performed by adding a $NaNO_2$ solution (2 M). Then an excess of concentrated NH_4OH was added to precipitate NpO_2OH, which was used as a neptunium precursor. The precipitate was centrifuged and washed by distilled water five times. For synthesis, NpO_2OH was dissolved in 0.1 M picolinic acid. Then diguanidinium carbonate neutralized by picolinic acid and $NaNO_2$ was added. A compound was obtained during isothermal evaporation at 22 °C of the mixture with a molar ratio of Np/guanidinium/Pic/Na equal to 1:1:2:5.

(8) The data were collected on a Bruker KAPPA APEX II diffractometer with a CCD area detector using graphite monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation. A single crystal was mounted on a glass fiber and transferred to the goniometer for data collection. The crystal was cooled to 100 K under a cold nitrogen gas stream. The structure was solved using the *SHELXTL* software package, and absorption corrections were made with *SADABS*. The structure was refined by full-matrix least squares on F^2. All of the non-H atoms were readily located, and their positions were refined anisotropically. H atoms were refined isotropically. Main crystallographic data: $M = 679.39$, space group $P\bar{1}$, $a = 8.9329(1)$ Å, $b = 11.6669(2)$ Å, $c = 11.6698(2)$ Å, $\alpha = 68.080(1)°$, $\beta = 88.213(1)°$, $\gamma = 73.254(1)°$, $V = 1076.45(3)$ Å^3, $Z = 2$, number of reflections = 21 939, number of unique reflections = 11 992, $2\theta_{max} = 80°$, R1 = 0.019, wR2(F^2) = 0.045.

(9) NIR and IR spectra were measured using Shimadzu UV3100 and Specord M80 spectrometers, respectively. Samples of ~2 wt % of the solids were prepared in NaCl pellets. Selected frequencies (cm^{-1}) of the IR spectrum and their assignments: 3460s, 3412s, $\nu(NH_2)$; 3236s, 3216s, ν(CH); 1660sh, 1652m, ν(C=O); 1582vs, $\nu_{as}(NO_2)$; 1560vs, ν_{as} (COO$^-$); 1476m, $\nu(CN)_{Pyr}$; 1408 vs, 1396sh, ν_s(COO$^-$); 1376sh, $\nu_{as}(NO_2)$; 1262–1120m, $\rho(CH)_{Pyr}$; 812vs, $\gamma(CH)_{Pyr} + \nu(NpO_2^+)$; 674m, 636m, δ(COO$^-$); 544m, $\delta(NO_2^-)$; 464w, $\rho(NO_2^-)$.

10.1021/ic800158f CCC: $40.75

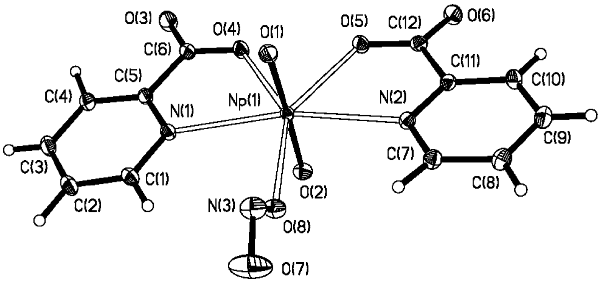

Figure 1. Ellipsoid representation (50% probability) of a $[NpO_2(NO_2)(Pic)_2]^{2-}$ anion in the structure of $\{C(NH_2)_3\}_2[NpO_2(NO_2)(Pic)_2]$.

atom is a pentagonal bipyramid. The axial positions are occupied by O atoms of the neptunyl group. The Np−O distances are equal to 1.8324(10) and 1.8314(10) Å. The O−Np−O angle is equal to 177.01(4)°. The equatorial positions of the pentagonal bipyramid are occupied by two N and two O atoms of picolinate ions and an O atom of a nitrite anion. The Np−N distances are equal to 2.6244(11) and 2.6209(11) Å. The distances between Np and O atoms of picolinate anions are equal to 2.4239(10) and 2.4475(10) Å, and the distance between Np and O atoms of a nitrite anion is slightly longer, 2.4598(10) Å. The mean deviation of atoms from the least-squares equatorial plane is 0.039 Å.

The nitrite anion acts as a monodentate ligand with N−O distances equal to 1.2887(16) and 1.2204(19) Å for bridging and terminating O atoms, respectively; the O−N−O angle is equal to 114.57(13)°. The plane of the nitrite ion is inclined to the equatorial plane of the Np atom by an angle of 96.2°.

The picolinate anions play the role of chelating bidentate ligands and form five-membered metallorings with the Np atom. The coordination of carboxylic groups leads to differentiation of the C−O bond lengths for bridging and terminating O atoms, which are equal to 1.2740(17), 1.2686(17) Å and 1.2401(16), 1.2439(16) Å, respectively. The C−C distances are equal to 1.5091(18)−1.5135(17) and 1.3833(19)−1.393(2) Å for single and aromatic bonds. The N−C distances lie in the region from 1.3391(17) to 1.3467(17) Å. The rings are almost planar; the mean deviations of atoms are equal to 0.006 and 0.004 Å. The angles between the rings and equatorial plane of the Np atom are equal to 2.9° and 6.6°. The angle between the pyridine rings is equal to 6.6°.

In the last years, picolinates of Np(V) with different Np to Pic ratios were synthesized.[10,11] The crystal structure of $[NpO_2(Pic)(H_2O)]$ consists of infinite chains. The equatorial plane of the Np atom is formed by one N atom, two O atoms of two different picolinate ions, and two water molecules. By this means, picolinate ions function as tridentate bridging ligands connecting adjacent Np atoms through carboxylic groups. The structure of $\{C(NH_2)_3\}[NpO_2(Pic)_2(H_2O)] \cdot {}^{11}/_{3}H_2O$ contains $[NpO_2(Pic)_2(H_2O)]^-$ anions, where picolinate ions are bidentate chelating ligands coordinating to Np by N and one of the carboxylic O atoms. Similar surroundings of the Np atom are observed in $Cs[NpO_2(Pic)_2(HPic)] \cdot 3H_2O$, with the only difference that a molecule of picolinic acid (HPic) is monodentately coordinated to a Np atom instead of a water molecule.

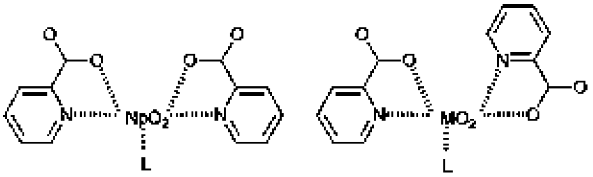

Figure 2. Relative arrangement of two bidentate picolinate ions in $\{C(NH_2)_3\}_2[NpO_2(NO_2)(Pic)_2]$ (left) and other structurally characterized picolinates of NpO_2 and UO_2 (right).

IR spectrum of $\{C(NH_2)_3\}_2[NpO_2(NO_2)(Pic)_2]$ shows several groups of highly resolved bands in intervals 3600–2600, 1780–960, and 900–480 cm^{-1}. The assignments of selected frequencies[9] are based on literature data.[12] Coordination of O atoms of nitrite and picolinate ions leads to the low-energy shift of stretching vibrations as compared to free ligands. In contrast, coordination of the N atom of the picolinate ion is manifested by an increase in the frequency of the pyridine ring stretching vibration. In addition, the increase of the frequency of CH deformation vibrations likely results in the intersection of the corresponding band with the band of the neptunyl stretching vibration. A similar complication of this region of the spectrum was observed for $[(NpO_2)(Pic)(H_2O)_2]$.[10] The NIR spectrum of $\{C(NH_2)_3\}_2[NpO_2(NO_2)(Pic)_2]$ contains the absorption band with a maximum of 988 nm corresponding to the f−f electron transition.

An interesting feature of the complex $\{C(NH_2)_3\}_2[NpO_2(NO_2)(Pic)_2]$ is the presence of two different coordinated acido ligands in its structure, which is not typical for neptunium complexes. The fact that a nitrite ion coordinates to the Np atom concurrently with a picolinate ion is even more surprising taking into account the significantly higher values of the stability constants for Np(V) complexes with picolinic acid ($\log \beta_1 = 3.69 \pm 0.04$ and $\log \beta_2 = 6.98 \pm 0.04$)[10] as compared to the Np(V) complex with nitrous acid and the possibility of the formation of a 1:3 complex with picolinic acid (like $Cs[NpO_2(Pic)_2(HPic)] \cdot 3H_2O$) or a 1:2 complex with a water molecule acting as the ligand (like $\{C(NH_2)_3\}[NpO_2(Pic)_2(H_2O)] \cdot {}^{11}/_{3}H_2O$). Another distinctive structural feature of $\{C(NH_2)_3\}_2[NpO_2(NO_2)(Pic)_2]$ is the relative arrangement of bidentate picolinate ions as compared to other structurally characterized neptunium(V) or uranium(VI) picolinates (Figure 2).

In conclusion, the solid complex of actinide metal with a nitrite ion, $\{C(NH_2)_3\}_2[NpO_2(NO_2)(Pic)_2]$, was synthesized for the first time. Its crystal structure was determined by X-ray diffractometry and confirmed using spectrophotometry. By this means, the possibility of coordination of a nitrite anion to a Np(V) group was proven. Taking into account that actinides in other oxidation states usually exhibit a stronger complexing ability than Np(V), we can expect that the formation of other nitrites is possible.

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Acknowledgment. This research was supported by the Russian Foundation for Basic Research (Project No. 08-03-00525a). The X-ray structural research was conducted at the Department of the Structural Chemistry of Radioactive Elements of the Center of Physical Methods of Studies (Institute of Physical Chemistry and Electrochemistry).

Supporting Information Available: Complete tables of crystal and structure refinement data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for compound **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC800158F