Synthesis and Study of Np(V) and Pu(V) Benzoate Complexes with Bipyridine

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Abstract—Heteroligand compounds AnO₃(bipy)OOCC₆H₅ (An = Np, Pu; bipy = α,α-bipyridine, C₁₀H₈N₂) were synthesized and studied. It follows from powder X-ray patterns that these compounds are isostructural. Their unit cell parameters, determined by indexing of the powder X-ray patterns, are as follows: a = 9.2162 (7), b = 10.2339(8), c = 17.4083(17) Å, and β = 96.48(1)° for Np and a = 9.1983(18), b = 10.2052(18), c = 17.3703(3) Å, and β = 96.51(1)° for Pu. The compounds crystallize in the monoclinic system, space group P2₁/n, Z = 4. The electronic absorption spectra of crystalline compounds suggest pentagonal-bipyramidal surrounding of the central atom and the presence of cation–cation bonds with AnO₃⁺ ions acting as monodentate ligands with respect to each other. The IR spectra of the compounds were recorded, and their thermal behavior in air was studied.

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The bipy complexes of Np(V) nitrate [1], thiocyanate [2], formate [3], acetate [3], and propionate [4] and similar complexes of Pu(V) formate [3] and propionate [4] have been reported. All of them are characterized by bidentate coordination of one bipy molecule in the equatorial plane of the AnO₃⁺ ion. The principal difference is that in the structure of AnO₃⁺ nitrate, thiocyanate, and propionate complexes there are no cation–cation (CC) bonds, whereas in formate and acetate complexes, according to spectrophotometric data, these bonds exist. Hence, the kind of the anion in AnO₃⁺ bipy complexes essentially affects the structure. In this study, we additionally examined this phenomenon, using as example the bipy complexes of An(V) benzoates, which contain phenyl substituents.

EXPERIMENTAL

The experiments were performed with 0.1–0.2 M solutions of Np(V) nitrate and Pu(V) perchlorate, which were prepared by the method described in [5]. 0.5–1.0 M solutions of lithium, sodium, and ammonium benzoates were prepared by dissolving benzoic acid samples in equimolar amounts of the corresponding alkali or ammonium solutions. Preliminary, pure grade benzoic acid was purified by dissolution in aqueous ammonia, filtration, and precipitation with a small excess of HCl. The precipitate was separated on a glass frit and dried at 90°C. The 0.5 M working solutions of pure grade bipy were prepared by dissolving its analytical samples in ethanol. To reduce Pu(VI), freshly prepared 0.5–1.0 N₂H₄ solutions, whose concentration was determined photometrically, were used. The apparatus and methods were the same as in [5].

RESULTS AND DISCUSSION

Preliminary experiments showed that Np(V) and Pu(V) benzoate complexes with bipy are fairly completely precipitated in well-crystallized form at room temperature from dilute (0.01–0.002 M) actinide(V) solutions. The following procedure was used to synthesize the neptunyl(V) compound.

An aliquot of a neutral 0.145 M NpO₂NO₃ solution was diluted with water by a factor of ~30, and a 0.5 M solution of sodium or potassium nitrate and a 0.5 M solution of bipy were added to obtain 0.02 and 0.01 M concentrations, respectively. Within a few minutes after mixing, a crystalline precipitate started to separate, and within 2–4 h the process was complete. The precipitate was filtered off in a vacuum on a glass frit, thoroughly washed with water, and dried by passing air through the frit for 3–4 h. Qualitative tests showed that the compound synthesized contained no alkali metal ions. Hence, its composition can be described by the general formula NpO₂OOCC₆H₅(bipy)ₙ·mH₂O. For more precise
Unit cell parameters of Np(V) and Pu(V) benzoate complexes with bipyridine, AnO₂(bipy)OCC₆H₅, An = Np, Pu

<table>
<thead>
<tr>
<th>Compound</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>β, deg</th>
<th>V, Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>NpO₂(bipy)OCC₆H₅ (I), powder (295 K)</td>
<td>9.2162(7)</td>
<td>10.2339(8)</td>
<td>17.4083(17)</td>
<td>96.48(1)</td>
<td>1631.4(2)</td>
</tr>
<tr>
<td>PuO₂(bipy)OCC₆H₅ (II), powder (295 K)</td>
<td>9.1983(18)</td>
<td>10.2052(18)</td>
<td>17.370(3)</td>
<td>96.51(1)</td>
<td>1620.0(5)</td>
</tr>
</tbody>
</table>

Hence, as in the case of compounds described in [1–3, 5], each NpO₂⁺ ion in I coordinates one bipy molecule, and the compound contains no water of crystallization. The X-ray powder pattern of I (Fig. 1a) was indexed in the monoclinic system with the unit cell parameters listed in the table.

The procedure for the synthesis of the Pu(V) benzoate complex with bipy consisted of the following stages. The measured volume of freshly prepared 0.15 M PuO₂Cl₂ solution with pH ~4 was diluted with water to (5–8)×10⁻³ M, and a 3–4-fold excess of 0.5 M lithium benzoate and an equimolar amount of N₂H₄ with respect to plutonyl(V) were added. The initially formed precipitate of Pu(VI) benzoate dissolved in 1–2 min under stirring due to its transformation into Pu(IV), and then a 0.5 M bipy solution was added to a concentration of ~0.01 M. Within a few minutes, a finely crystalline gray precipitate started to form. Its formation was complete in 1–2 h. Then the precipitate was worked up as described above for Np. The powder pattern of the crystalline product obtained showed (Fig. 1b; see table) that it was isostructural to I. Thus, its composition is described by the formula PuO₂(bipy)OCC₆H₅ (II).

Both I and II are very poorly soluble in water. In the mother liquor over the precipitate of I, the spectrophotometrically determined content of Np(V) was no more than 5×10⁻³ M. At the same time, precipitation of I and II from solutions proceeds very slowly, especially from dilute solutions.

As seen from Fig. 2, the electronic absorption spectrum (EAS) of crystalline I contains a strong band with a maximum at 1001 nm typical for NpO₂⁺ compounds with five O atoms in the equatorial plane. Hence, pentagonal bipyramids are the coordination polyhedra of I and II. The above band in the spectrum of I is substantially shifted to the long-wave region as compared to hydrated neptunyl(V) ion. This shift can be only partially (to 4–6 nm) attributed to coordination of bipy and benzoate ions. This was confirmed by EAS of aqueous Np(V) solutions containing excess of the above ligands. The major fraction of the shift (14–16 nm) is undoubtedly caused by CC interaction. In accordance with the previously found relationships [6–8], in this case NpO₂⁺ ions behave with respect to each other as monodentate ligands. As compounds I and II are isostructural, the plutonyl(V) compound should have the same structure.

In the number of bands and their intensity, EAS of II (Fig. 3) is very similar to the spectra of hydrated PuO₂⁺ ions and crystalline Pu(V) compounds with pentagonal-bipyramidal oxygen surrounding of the...