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

**A. A. Bessonov, N. N. Krot, M. S. Grigor'ev, and V. I. Makarenkov**

*Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia*

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**Abstract**—Heteroligand compounds $AnO_2(bipy)OOCC_6H_5$ (An = Np, Pu; bipy = α,α-bipyridine, $C_{10}H_8N_2$) 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), $c$ = 17.370(3) Å, and β = 96.51(1)° for Pu. The compounds crystallize in the monoclinic system, space group $P2_1/n$, $Z$ = 4. The electronic absorption spectra of crystalline compounds suggest pentagonal-bipyramidal surrounding of the central atom and the presence of cation–cation bonds with $AnO_2^+$ 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 $AnO_2^+$ ion. The principal difference is that in the structure of $AnO_2^+$ 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 $AnO_2^+$ 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 ammonia solutions. Preliminarily, 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 $N_2H_4$ solutions, whose concentration was determined iodometrically, 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 $NpO_2NO_3$ 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 $NpO_2OOCC_6H_5(bipy)_n \cdot mH_2O$. For more precise

Unit cell parameters of Np(V) and Pu(V) benzoate complexes with bipyridine, $AnO_2(bipy)OOCC_6H_5$, An = Np, Pu

| Compound | $a$, Å | $b$, Å | $c$, Å | β, deg | $V$, Å$^3$ |
|---|---|---|---|---|---|
| $NpO_2(bipy)OOCC_6H_5$ (**I**), powder (295 K) | 9.2162(7) | 10.2339(8) | 17.4083(17) | 96.48(1) | 1631.4(2) |
| $PuO_2(bipy)OOCC_6H_5$ (**II**), powder (295 K) | 9.1983(18) | 10.2052(18) | 17.370(3) | 96.51(1) | 1620.0(5) |

determination of the composition, the compound was analyzed gravimetrically (calcination to $NpO_2$). The results of the analysis correspond to the formula $NpO_2(bipy)OOCC_6H_5$ (**I**). Samples of **I**, mg: 3.764; 12.412. Found $NpO_2$, %: 49.8; 48.4. $NpO_2(bipy) \cdot OOCC_6H_5$. Calculated $NpO_2$, %: 49.27.

Hence, as in the case of compounds described in [1–3, 5], each $NpO_2^+$ 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 $PuO_2(ClO_4)_2$ solution with pH ~4 was diluted with water to $(5–8) \times 10^{-3}$ M, and a 3–4-fold excess of 0.5 M lithium benzoate and an equimolar amount of $N_2H_4$ 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(V), 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 $PuO_2(bipy)OOCC_6H_5$ (**II**). This conclusion was confirmed by the analysis of the compound for plutonium by calcination at 800°C to $PuO_2$. Samples of **II**, mg: 2.394; 15.668. Found $PuO_2$, %: 50.17; 49.34. $PuO_2(bipy)OOCC_6H_5$. Calculated $PuO_2$, %: 49.45.

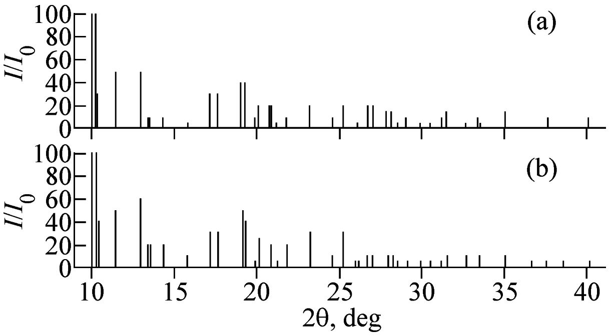

**Fig. 1.** X-ray powder patterns: (a) $NpO_2(bipy)OOCC_6H_5$ (**I**) and (b) $PuO_2(bipy)OOCC_6H_5$ (**II**).

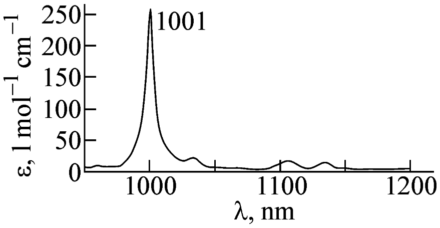

**Fig. 2.** Electronic absorption spectrum of $NpO_2(bipy) \cdot OOCC_6H_5$ (**I**) [1.945 mg/163 mg KBr (melted)].

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 $5 \times 10^{-5}$ 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 $NpO_2^+$ 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 $NpO_2^+$ 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 $PuO_2^+$ ions and crystalline Pu(V) compounds with pentagonal-bipyramidal oxygen surrounding of the

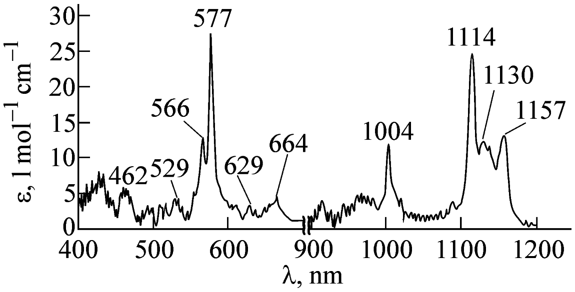

**Fig. 3.** Electronic absorption spectrum of $PuO_2(bipy)\cdot OOCC_6H_5$ (**II**) [5.932 mg/135 mg KBr (melted)].

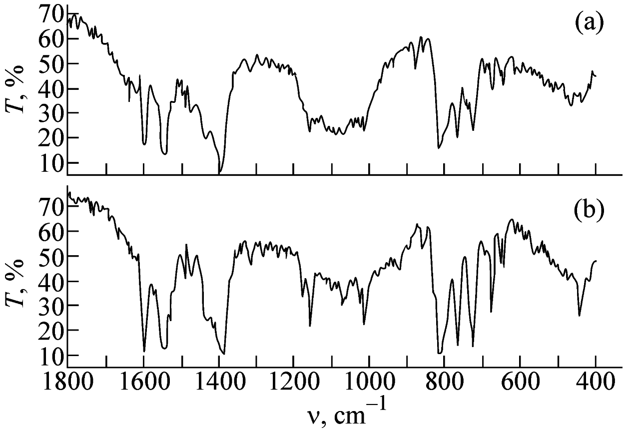

**Fig. 4.** Fragments of IR spectra (melted KBr): (a) $NpO_2\cdot(bipy)OOCC_6H_5$ (**I**) and (b) $PuO_2(bipy)OOCC_6H_5$ (**II**).

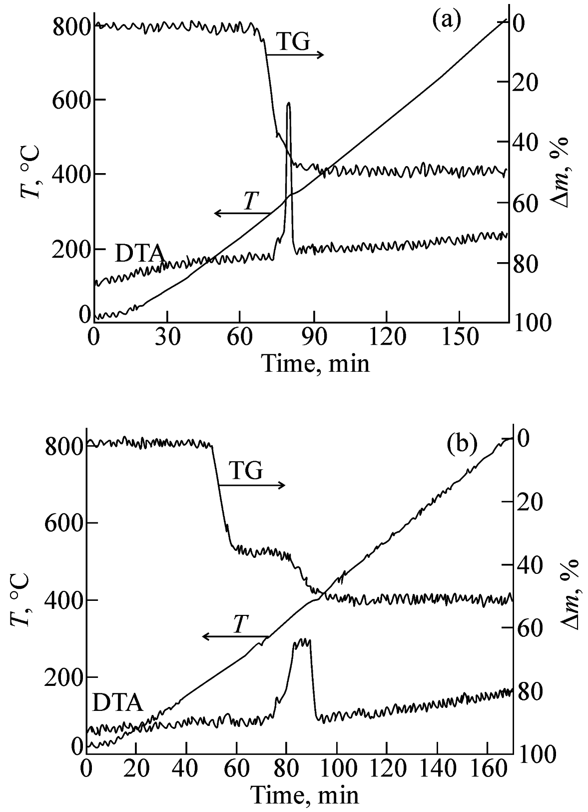

**Fig. 5.** Thermal behavior in air: (a) $NpO_2(bipy)OOCC_6H_5$ (**I**), sample 12.412 mg, $\Delta m$ = 51.6%; (b) $PuO_2(bipy)\cdot OOCC_6H_5$ (**II**), sample 15.668 mg, $\Delta m$ = 50.66%.

central atom [9]. This fact confirms the above conclusion that the equatorial plane of $AnO_2^+$ ions consists of five oxygen atoms.

Along with similarity of X-ray powder patterns, the practical identity of the IR spectra also confirms the structural similarity of **I** and **II**. The bands at 816–812, 740, and 724 cm$^{-1}$ should be probably assigned to antisymmetric stretching vibrations of neptunyl(V) and plutonyl(V) ions. Noticeable broadening and splitting of the antisymmetric stretching vibrations were repeatedly mentioned for $AnO_2^+$ compounds with CC interaction [8]. Thus, the data of IR spectrophotometry confirm CC interaction in the compounds studied. Absorption at 676–672 cm$^{-1}$ can belong to symmetrical stretching vibrations of $AnO_2^+$ ions. In turn, from this assignment follows pronounced nonequivalence of An–O bonds in neptunyl(V) and plutonyl(V) dioxocations. In other words, monodentate CC interaction in the compounds is realized so that the lengths of An–O bonds in $AnO_2^+$ noticeably differ, which makes IR-active the symmetric vibrations. Manifestation of $\nu_s(NpO_2^+)$ at 688 cm$^{-1}$ was observed in the spectrum of $NH_4NpO_2C_2O_4\cdot 2.67H_2O$ [10, 11], whose structure is built of cyclic trimers composed of $AnO_2^+$ ions coordinated to each other in the monodentate fashion, with noticeably differing lengths of terminal and bridging Np–O bonds. Similar coordination of actinyl(V) ions can be expected in **I** and **II**. However, the final conclusion can be derived after X-ray structural analysis of these compounds.

Derivatograms of **I** and **II** (Fig. 5) confirm the absence of water molecules and demonstrate high thermal stability of these compounds. Compound **I** is stable to ~300°C and then decomposes with an exothermic effect and formation of $NpO_2$ at a temperature higher than 400°C. Decomposition of **II** starts at 190°C and occurs in two stages. In the first stage, Pu(V) probably transforms into Pu(IV) and then, above 325°C, the compound completely decomposes with exothermic combustion of the organic products. At 450°C, decomposition is complete with the formation of $PuO_2$.

Thus, in contrast to Np(V) nitrate [1], thiocyanate [2], and propionate [4], neptunyl(V) and plutonyl(V) benzoates form bipy complexes whose structure contains CC bonds with monodentate mutual coordination of $AnO_2^+$ ions. More detailed data on the character of CC interactions in **I** and **II** can be obtained by X-ray structural analysis of these compounds.

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