Synthesis of New Crystalline Pu(V) Compounds from Solutions: VII. Synthesis and Study of MPuO$_2$C$_2$O$_4$·nH$_2$O with M = NH$_4$ and Cs

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

Received July 22, 2004

Abstract—Double monooxalates MPuO$_2$C$_2$O$_4$·nH$_2$O with NH$_4^+$ and Cs$^+$ ions in the outer sphere were isolated from weakly acidic aqueous solutions of Pu(V). The unit cell parameters of these compounds were determined. The ammonium salt is isostructural to its neptunyl(V) analog; its structure is characterized by the monodentate cation–cation interaction of plutonyl(V) ions. Cesium plutonyl(V) salt isolated from a solution is not isostructural to the neptunyl(V) compound and is easily dehydrated at room temperature to form tetrahydrate, which transforms to dihydrate at 110°C. The latter compound, according to the IR spectra, can have a network system of cation-cation bonds involving PuO$_2^+$. As shown previously [1], Pu(V) compounds with the general composition NaPu$_2$C$_2$O$_4$·nH$_2$O with n = 3, 1, and 0 can be readily prepared in the pure form. They are the salts of the monooxalate complex PuO$_2$C$_2$O$_4$ and are isostructural to the corresponding Np(V) compounds. This fact suggests that the mutual coordination of PuO$_2^+$ ions through the “yl” oxygen atoms, unknown previously, is manifested at least in the structure of NaPuO$_2$C$_2$O$_4$·H$_2$O, i.e., cation–cation (CC) bonds are formed, since, according to the spectrophotometric data, they are present in NaNpO$_2$C$_2$O$_4$·H$_2$O [1, 2]. The CC interaction of the “yl” cations was also found in the structure of MNpO$_2$C$_2$O$_4$·nH$_2$O with M = K, NH$_4$, and Cs [2], and in the case of NH$_4$NpO$_2$C$_2$O$_4$·2.67H$_2$O the CC interaction was confirmed by X-ray diffraction analysis [3]. Therefore, it was interesting to prepare new plutonyl(V) compounds of the MPuO$_2$C$_2$O$_4$·nH$_2$O type and to examine the extent of their structural analogy with the corresponding Np(V) salts. Here we present data on the synthesis, characteristics, and structure of double Pu(V) monooxalates with NH$_4^+$ and Cs$^+$ ions in the outer sphere.

EXPERIMENTAL

We used freshly prepared weakly acidic (pH 4–5) 0.1–0.2 M PuO$_2$ClO$_4$, 0.2 M NpO$_2$NO$_3$ solutions prepared according to the procedure described in [1]. In the synthesis, Pu(VI) was converted into the pentavalent state by addition of equimolar amounts of 0.8 M N$_2$H$_4$. For binding of Np(V) and Pu(V) into monooxalate complexes, a small excess of 0.5 M (NH$_4$)$_2$C$_2$O$_4$ or 0.5 M Cs$_2$C$_2$O$_4$ (approximately 30% above equimolar ratio) was added to the working solutions. The cesium oxalate solution was prepared by mixing the calculated amounts of titrated H$_2$C$_2$O$_4$ and CsOH solutions. The other solutions were prepared by common procedures using distilled water and chemically pure grade chemicals.

RESULTS AND DISCUSSION

Preliminary experiments showed that synthesis of NH$_4$PuO$_2$C$_2$O$_4$·nH$_2$O (I) is complicated by relatively high solubility of the compound and extremely slow crystallization in the cold. Heating of plutonyl(V) solutions is impossible because of the tendency of Pu(V) to disproportionate in hot oxalate solutions [4]. On the other hand, an increase in the initial concentration of Pu(V) promotes its autoxidation–autoreduction. In addition, at a small excess of oxalate ions, the disproportionation products, especially Pu(IV), can form precipitates. A large excess of C$_2$O$_4^{2-}$ ions is inadmissible, since it results in conversion of PuO$_2$(C$_2$O$_4$)$_3^{3-}$ complexes to PuO$_2$(C$_2$O$_4$)$_2^{2-}$, which prevents precipitation of I.

To overcome the above difficulties, compound I was initially synthesized at the initial concentration of Pu(V) not exceeding 0.045 M at a temperature...
of approximately 0°C with addition of NH₄NO₃ as a salting-out agent. As seen from Fig. 1, the main reflections in the powder X-ray pattern of the resulting product unambiguously belong to a crystalline phase isostructural to NH₄NpO₂C₂O₄·2.67H₂O (II) [3], i.e., under the above conditions NH₄PuO₂C₂O₄·2.67H₂O (I) is precipitated. However, the measures taken did not provide synthesis of I in the form of an individual phase, and we failed to avoid the presence of impurities manifested as weak lines in the powder X-ray patterns of the final products. The compound was prepared in the purest state as follows.

A 0.7-ml sample of freshly prepared 0.15 M PuO₂(ClO₄)₂ solution with pH approximately 5 was diluted with 1 ml of 8 M NH₄NO₃, then 0.4 ml of 0.3 M (NH₄)₂C₂O₄ and 0.16 ml of 0.7 M N₂H₄ were added. After stirring, the solution was kept at room temperature (approximately 20°C) for 1 h. In so doing, within several minutes after mixing the reactants, the solution got turbid, and within half an hour a heavier finely crystalline gradually settling precipitate started to form. After an additional 30 min, the precipitate was filtered off with a dense glass frit, washed with cold (0°C) water, and dried in an air flow on the filter for 3 h. The yield of the final product was 7.2 mg (approximately 25%). A comparison of the results of indexing of the X-ray powder pattern of I (see table) with the unit cell parameters of the similar neptunyl(V) compound II (space group P6₃/m) [3] unambiguously shows that these compounds are structurally similar. The IR spectra of I and II, particularly, the shapes and positions of the bands of antisymmetric stretching vibrations νₐs(AnO₂⁻) are similar (Fig. 2): both bands are split in two components with maxima at 804 and 792 cm⁻¹ in the case of Np and 804 and 796 cm⁻¹ in the case of Pu. This fact once again confirms the similarity in the crystal structure of NH₄PuO₂C₂O₄·2.67H₂O and its neptunyl(V) analog and, hence, the presence of monodentate CC interaction of the PuO₂²⁺ groups in I as shown in Fig. 3.

### Unit cell parameters of MAnO₂C₂O₄·nH₂O, M = NH₄ and Cs, An = Np and Pu

<table>
<thead>
<tr>
<th>Compound</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>α, deg</th>
<th>β, deg</th>
<th>γ, deg</th>
<th>Z</th>
<th>V, Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄PuO₂C₂O₄·2.67H₂O (I)</td>
<td>11.309(8)</td>
<td>11.309(8)</td>
<td>11.666(2)</td>
<td>90</td>
<td>90</td>
<td>120</td>
<td>6</td>
<td>1292.1(13)</td>
</tr>
<tr>
<td>NH₄NpO₂C₂O₄·2.67H₂O (II)</td>
<td>11.367(3)</td>
<td>11.367(3)</td>
<td>11.8204(11)</td>
<td>90</td>
<td>90</td>
<td>120</td>
<td>6</td>
<td>1322.6(5)</td>
</tr>
</tbody>
</table>
| Crystalline oxalate CsPuO₂C₂O₄·nH₂O (III) less soluble than I, was prepared pure without complications. In the first run, to 0.3 ml of 0.12 M PuO₂(ClO₄)₂ we added an equal volume of 5 M CsCl, and after cooling the CsClO₄ precipitate was separated by centrifugation. To the mother liquor transferred to a separate test tube, we added 0.05 ml of 0.8 M N₂H₄ and then, immediately, 0.03 ml of 1.5 M K₂C₂O₄. The tube was kept at 0°C for approximately 20 h. As a result, flesh-colored prismatic crystals were formed on the tube walls, and a weakly colored voluminous precipitate was formed on the bottom. The crystals were removed from the ampule walls, and the powder pattern of these crystals was recorded without drying. This powder pattern was of high quality and was indexed in the rhombic system (see table), possible space group P2₁₁₂₁. A part of crystals was dissolved in 0.4 M HClO₄ for spectrophotometric monitoring of Pu(VI) accumulation in the solution due to disproportionation of plutonyl(V). Pu(VI) was accumulated in the solution at a rate expected for the given condi-

**Fig. 1.** Powder diffraction patterns of (1) NH₄NpO₂C₂O₄·2.67H₂O and (2) the product obtained in the synthesis of complex plutonyl(V) monooxalate. The asterisks denote the reflections of an impurity phase.