# Behavior of Pu(VI) and Np(VI) in Malonate Solutions

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Abstract—Complexation of  $PuO_2^{2+}$  in solutions containing malonate anions  $C_3H_2O_4^{2-}$  (L<sup>2-</sup>) is studied by spectrophotometry. Mono- and bimalonate complexes are formed. The monomalonate complex was isolated as  $PuO_2L \cdot 3H_2O$ . It is isostructural to  $UO_2L \cdot 3H_2O$  and forms rhombic crystals with the unit cell parameters a = 9.078(2), b = 7.526(2), and c = 6.2005(15) Å, space group  $Pmn2_1$ . The electronic absorption spectrum of the monomalonate complex is characterized by a strong band at 843 nm. In malonate solutions, Pu(VI) is slowly reduced to the pentavalent state even in the cold. The reduction of Np(VI) is considerably faster and more sensitive to increasing temperature. Some kinetic features of the reduction are discussed.

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Synthesis of Pu(VI) solid compounds from aqueous solutions and their characterization require data on the behavior of Pu(VI) and Pu(V) in the presence of complexing agents [1-3]. There is very limiting information on this topic for both Pu and Np. Choppin et al. reported on complexation of the neptunyl ion with aromatic polycarboxylates, particularly, phthalate [4]. More recently we published new data on Np(VI) and Pu(VI) complexation with phthalate in neutral aqueous solutions [5]. Nikol'skii et al. [6] studied the reduction of Pu(VI) with hydrogen peroxide in buffer solutions of organic acids, particularly, malonic acid. In this study we have gained additional information on the complexation and reduction of Pu(VI) and also on the disproportionation of Pu(V) in malonate solutions. For comparison, the behavior of Np(VI) was also examined.

#### EXPERIMENTAL

In the experiments we used the  $^{239}$ Pu stock solution prepared by the following procedure. Pu(IV) was sorbed on an anion exchanger, eluted, precipitated as Pu(IV) oxalate hexahydrate, and dissolved in the equimolar mixture of concentrated HClO<sub>4</sub> and HNO<sub>3</sub>. An aliquot of the resulting solution was concentrated to wet salts by evaporation with concentrated HClO<sub>4</sub>, avoiding decomposition of PuO<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (for this purpose, in the final stage, we combined heating with air flushing to remove HClO<sub>4</sub> vapor). The resulting salt was dissolved in a fixed volume of water. In this working solution we determined pH and Pu concentrate

tion (spectrophotometrically by the absorption band of  $PuO_2^{2+}$  at 831 nm). The Pu concentration in the stock and working solutions was 0.376 and 0.208 M, respectively. If necessary, the Pu(VI) solutions were neutralized to pH 3–5 by adding 1 M NH<sub>4</sub>OH. The working solutions were used for no more than 5 days. The solutions of Np(VI) were prepared as in [7].

Malonic acid  $[H_2L, L = CH_2(COO)_2]$  (analytically pure grade) was recrystallized prior to use. Then 1– 3 M H<sub>2</sub>L stock solutions were prepared, whose exact concentration was determined by titration with an alkali in the presence of phenolphthalein. The working solutions of Li<sub>2</sub>L and LiHL were prepared from the stock H<sub>2</sub>L solutions by adding estimated amounts of LiOH.

All the solutions were prepared with double-distilled water. All other chemicals were of chemically pure or ultrapure grade and were used without additional purification. The instruments and measuring procedures were the same as described in [1].

#### **RESULTS AND DISCUSSION**

#### Plutonyl Complexation in Malonate Solutions

Complexation of  $PuO_2^{2+}$  with  $L^{2-}$  was studied spectrophotometrically by successive addition of fixed volumes of 0.05 M (NH<sub>4</sub>)<sub>2</sub>L to the neutral perchlorate solution of Pu(VI) (pH ~5). It is known that sharp strong bands of *f*-*f* transitions in the spectra of plutonyl solutions are very sensitive to the ligand sur-

rounding of the central atom, and, therefore, they are convenient for studying the complexation. The optical spectra were recorded in the range of strong plutonyl absorption at 820-860 nm. Figure 1 shows that, for  $[L^{2-}]$ :  $[PuO_2^{2+}] < 1$ , as the ligand concentration increases, the intensity of the band at 831 nm regularly decreases, and that of the new band at 840 nm increases (curves 1-3). By analogy with the Pu(VI) oxalate complexes [8–10], it may be suggested that, in this case, the monomalonate complex is formed. The maximal intensity of this band is observed at  $[PuO_2^{2+}]:[L^{2-}] \sim 1:1.3$  (curve 4), i.e., at a small excess of the ligand against the 1:1 stoichiometric ratio, suggesting relatively high stability of the complex. The presence of an isobestic point at 835 nm reflects the preferential formation of the single complex under the indicated conditions. With further increasing  $[L^{2-}]$ :  $[PuO_2^{2+}]$  ratio, the intensity of the band at 840 nm decreases, and the intensity of a new band at 846 nm increases, as a result of the addition of the second ligand molecule to the 1:1 complex (curves 5– 8). The presence of the second isobestic point at 843 nm suggests that a single complex dominates at  $[L^{2-}]$ :  $[PuO_2^{2+}] = 1.5-5.6$ , presumably,  $PuO_2L_2^{2-}$ . The molar extinction coefficients of the Pu(VI)mono- and bimalonate complexes are about 330 and  $420 \text{ 1 mol}^{-1} \text{ cm}^{-1}$  at 840 and 846 nm, respectively. The latter value reasonably agrees with that reported in [6].

### Isolation of Pu Complexes from Malonate Solutions

We attempted to isolate the solid plutonyl monomalonate complex from the solution, to compare its properties with those of the corresponding uranyl complex  $UO_2L \cdot 3H_2O$  [11]. Initially we obtained a solid compound simply by gradual evaporation of the solution containing the stoichiometric amounts of  $PuO_2^{2+}$  and  $(NH_4)_2L$ . The X-ray diffraction pattern of this solid showed that the main phase is isostructural to UO<sub>2</sub>L 3H<sub>2</sub>O. Also some minor phases in noticeable amounts were found. To obtain the pure complex, 0.065 ml of 0.5 M  $(NH_4)_2L$  was added to 0.2 ml of  $1.25 \times 10^{-3}$  M PuO<sub>2</sub><sup>2+</sup> in a test tube. Then we introduced as a seed a small crystal obtained in the preceding experiment. Upon grinding this crystal with a glass rod, a voluminous heavy precipitate started to form under the supernatant layer, and the mother liquor became practically colorless. To recrystallize the resulting compound, the test tube was tightly sealed and allowed to stand at  $\sim 0-3^{\circ}C$  for 20 h. The X-ray diffraction analysis showed that the resulting single-phase crystalline product is isostructural to



**Fig. 1.** Electronic spectra of the plutonyl solutions at various Pu(VI):L ratios: (*1*)  $[Pu(VI)] = 1.164 \times 10^{-3}$ ,  $[(NH_4)_2L] = 0$  M; (2)  $[Pu(VI)] = 1.152 \times 10^{-3}$ ,  $[(NH_4)_2L] = 0.50 \times 10^{-3}$  M; (3)  $[Pu(VI)] = 1.129 \times 10^{-3}$ ,  $[(NH_4)_2L] = 0.82 \times 10^{-3}$  M; (4)  $[Pu(VI)] = 1.129 \times 10^{-3}$ ,  $[(NH_4)_2L] = 1.46 \times 10^{-3}$  M; (5)  $[Pu(VI)] = 1.124 \times 10^{-3}$ ,  $[(NH_4)_2L] = 1.69 \times 10^{-3}$  M; (6)  $[Pu(VI)] = 1.119 \times 10^{-3}$ ,  $[(NH_4)_2L] = 1.92 \times 10^{-3}$  M; (7)  $[Pu(VI)] = 1.097 \times 10^{-3}$ ,  $[(NH_4)_2L] = 2.83 \times 10^{-3}$  M; and (8)  $[Pu(VI)] = 1.029 \times 10^{-3}$ ,  $[(NH_4)_2L] = 5.75 \times 10^{-3}$  M.



**Fig. 2.** X-ray diffraction diagrams of (1)  $UO_2(OOC)_2CH_2$ ·  $3H_2O$  [11] and (2)  $PuO_2(OOC)_2CH_2$ ·  $3H_2O$ .

 $UO_2L \cdot 3H_2O$  (Fig. 2), so that its composition could be written as  $PuO_2L \cdot 3H_2O$ . Additional information on the structure and composition of this complex can be extracted from its optical spectrum (Fig. 3): the presence of a characteristic absorption band at 843 nm, corresponding to the *f*-*f* transition, suggests that, like in the uranyl analog, the coordination polyhedron of Pu is a distorted pentagonal bipyramid. The X-ray diffraction pattern of the compound was indexed in the rhombic system (space group  $Pmn2_1$ ). The unit cell parameters are given in Table 1. For comparison, we included the unit cell parameters for  $UO_2L \cdot 3H_2O$ , determined by single-crystal X-ray diffraction [11].

We failed in attempts to isolate the bimalonate

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Compound	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	<i>V</i> , Å <sup>3</sup>
$UO_2L \cdot 3H_2O$ [11], single crystal	9.0780(18)	7.5261(18)	6.2005(16)	423.63(17)
$PuO_2L \cdot 3H_2O$	9.052(2)	7.523(2)	6.1946(15)	421.84(18)

**Table 1.** Unit cell parameters of  $AnO_2L \cdot 3H_2O$ , An = U, Pu (space group  $Pmn2_1$ , Z = 2)

complex  $PuO_2L_2^{2-}$ . The solutions containing from two- to fivefold excess of the ligand remained transparent when allowed to stand at  $0-3^{\circ}C$  for several days, although their volume was reduced by half through evaporation. However, it is worth noting that with time (7 days after), in the tightly sealed test tube, a solid phase started to form slowly. The amount of the precipitate obtained in ten days was sufficient for X-ray diffraction analysis. The analysis of the solid phase revealed that it was  $NH_4PuO_2L$  described previously [3]. This compound was formed also as a minor phase in the first of the experiments on the synthesis of  $PuO_2L \cdot 3H_2O$ . Therefore, even in the cold, Pu(VI) is slowly reduced in the malonate solutions to Pu(V) with formation of poorly soluble  $NH_4PuO_2 \cdot$ (OOC)<sub>2</sub>CH<sub>2</sub>.

Reduction of  $PuO_2^{2+}$  in Malonate Solutions

When preparing both Pu(VI) and Pu(V) compounds from malonate solutions, it is important to know the effect of the temperature on the reduction rate of



**Fig. 3.** Electronic absorption spectrum of  $PuO_2(OOC)_2CH_2$  ·  $3H_2O$  (KBr).



**Fig. 4.** Kinetics of Pu(VI) reduction to Pu(V) with malonate at various temperatures [degree of reduction is given as the percent of the initial Pu(VI) concentration].

Pu(VI) in these solutions. To perform the experiments at a constant ionic strength, we prepared three stock solutions: (A) 1 M LiNO<sub>3</sub>, (B) 0.2 M Li<sub>2</sub>L + 0.4 M  $LiNO_3$ , and (C) 0.2 M LiHL + 0.8 M  $LiNO_3$ . These solutions were used to prepare an isomolar series. The reduction of Pu(IV) was studied at 20, 30, 50, and 70°C in the solution prepared by mixing 1.5, 0.75, and 0.75 ml of solutions A, B, and C, respectively. The procedure was as follows. A spectrophotometric cell with the solution was placed into a temperature-controlled cell holder arranged in a cell compartment and held for 15 min at the desired temperature. Then an estimated volume of the neutral Pu(VI) perchlorate solution of a known concentration was introduced into the cell. The solution was quickly mixed with a glass capillary. Then the cell was covered with a Teflon lid, and the spectrum was measured. The reduction of Pu(VI) was monitored by the decrease in the intensity of the plutonyl absorption band at 846 nm. The results are given in Fig. 4. At room temperature (20°C), we observed no noticeable reduction of Pu(VI) in 2 h. At 30°C, about 9% of Pu was reduced in 2 h. With increasing temperature to 50 and 70°C, the degree of Pu reduction increased to about 16 and 45%, respectively. We did not perform a detailed study of this process, since our goal was to ascertain the possibility of obtaining Pu(V) compounds through reduction of  $PuO_2^{2+}$  in malonate solutions. Even though this possibility was demonstrated by the example of formation of NH<sub>4</sub>PuO<sub>2</sub>L, the low rate of Pu(VI) reduction makes such a method unsuitable. Therefore, to convert the plutonyl ion into  $PuO_2^+$ , stronger reducing agents should be used.

## Reduction of $NpO_2^{2+}$ in Malonate Solutions

It was demonstrated in the preliminary experiments that, in contrast to Pu(VI), Np(VI) is noticeably reduced by the malonate ions even at room temperature, making it possible to examine the kinetic features of the reaction An(VI)  $\rightarrow$  An(V). We performed a series of experiments to examine the effect of the temperature, Np concentration, and solution composition on the reaction kinetics. In the experiments we used the above-specified solutions A, B, and C. The

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Run no.	[L <sup>2-</sup> ] : [HL <sup>-</sup> ]	$[L^{2-}] + [HL^{-}], M$	T, °C	$[Np] \times 10^3$ , M	$k_{\rm in} \times 10^2$ , min <sup>-1</sup>
1	1	0.1	308.3	0.85	3.70
2	1	0.1	308.3	1.7	3.58
3	1	0.1	308.3	3.4	3.75
4	1	0.1	312.3	1.7	6.77
5	1	0.1	317.3	1.7	11.46
6	1	0.1	322.3	1.7	26.04
7	0.15	0.1	312.3	1.7	7.8
8	0.36	0.1	312.3	1.7	7.8
9	0.67	0.1	312.3	1.7	8.1
10	6.5	0.1	312.3	1.7	8.53
11	1	0.2	312.3	1.7	8.49
12	1	0.033	312.3	1.7	7.27

Table 2. Influence of solution composition and temperature on Np(VI) reduction in malonate solutions

procedure was the same as for Pu, but the reaction was monitored by the accumulation of Np(V), i.e., by the increase in the intensity of the NpO<sub>2</sub><sup>+</sup> band. The kinetic curves obtained at various temperatures are presented in Fig. 5. As seen, in the case of Np, the temperature has a stronger effect on the reduction as compared to Pu. Even at 35°C, 75% of Np(VI) was reduced in 2 h, and at 50°C, Np(VI) was completely reduced in this time.

The kinetic curves obtained for the reduction of Np(VI) cannot be fitted exclusively by a first- or second-order equation, suggesting a complex mechanism of the reduction. We proposed the following scheme for this process. In the first stage, the bimalonate complex is formed fast with a 100% yield because of a large excess of the free ligand:

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$$NpO_2^{2^+} + 2C_3H_2O_4^{2^-} \xrightarrow{\rightarrow} NpO_2(C_3H_2O_4)_2^{2^-}.$$
(1)

The rate-determining stage of the reaction is the intramolecular reduction of Np(VI) with formation of the Np(V) monomalonate complex and the radical ion  $C_3H_2O_4^{\bullet}$ 

$$NpO_2(C_3H_2O_4)_2^{2-} \xrightarrow{slow} NpO_2C_3H_2O_4^{-} + C_3H_2O_4^{\bullet} (2)$$

The accumulation of Np(V) can shift the reaction to the left:

$$NpO_2C_3H_2O_4^- + C_3H_2O_4^- \xrightarrow{\text{fast}} NpO_2(C_3H_2O_4)_2^{2-}. (3)$$

However, the radical formed is also involved in irreversible reduction of Np(VI) with formation of glycolic acid and carbon dioxide:

$$NpO_{2}(C_{3}H_{2}O_{4})^{2^{-}} + C_{3}H_{2}O_{4}^{\bullet} \xrightarrow{\text{tast}} NpO_{2}(C_{3}H_{2}O_{4})^{3^{-}} + C_{2}H_{3}O_{3}^{-} + CO_{2} + H^{+}.$$
(4)

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To check the mechanism suggested for the reduction of Np(VI) in malonate solutions, the reaction was performed in a temperature controlled bubbler at 70°C with bubbling Ar successively through the reaction mixture and 0.1 M Ba(OH)<sub>2</sub>. Indeed, CO<sub>2</sub> appeared to be among the reaction products  $[Ba(OH)_2$  solution became turbid in short time because of the formation of BaCO<sub>3</sub>], which is consistent with the suggested scheme.

Thus, the decrease in the Np(VI) concentration is controlled by reactions (2) and (4) and can be described by a rather complex rate equation. However, in the initial stage, the process rate is controlled essentially by reaction (2), since the Np(V) concentration is still low and reverse reaction (3) may be neglected. In this case, the rate of Np(V) accumulation is controlled by the first-order kinetics of dissociation of the Np(VI) bimalonate complex, and the corresponding rate constant can be estimated from the tangent to the initial portion of the kinetic curve.

The reaction rate constant in the initial stage is given in Table 2, as influenced by the experimental



Fig. 5. Kinetics of Np(VI) reduction to Np(V) with malonate at various temperatures [degree of reduction is given as the percent of the initial Np(VI) concentration].



Fig. 6. Logarithm of the rate constant of Np(VI) reduction to Np(V) with malonate as a function of the reciprocal temperature.

conditions. As expected, increase in the initial Np(VI) concentration has no effect on the rate constant (run nos. 1–3). As noted above, the temperature is an important factor of the process: its increase by every 5°C over the range 35–50°C nearly doubles the rate constant (run nos. 2, 4–6). Also we examined the effect of the solution composition. Neither the  $[L^{2-}]$ :  $[HL^{-}]$  ratio (run nos. 4, 7–10) nor the change in the total malonate concentration by about an order of magnitude (run nos. 11, 12) considerably influenced the reaction kinetics, confirming our suggestion that the reduction rate is controlled primarily by the kinetics of dissociation of the Np(VI) bimalonate complex, which proceeds at about 100% yield, regardless of the composition of the malonate solutions.

The activation energy of the Np(VI) reduction was estimated from the Arrhenius curves (Fig. 6) to be about  $113 \text{ kJ mol}^{-1}$ .

Thus, we demonstrated a relatively high stability of Pu(V) in malonate solutions, which, keeping in mind that Pu(VI) is readily reduced with hydrogen peroxide, gives a good way to isolation of crystalline Pu(V) compounds from such solutions. On the contrary, it appeared impossible to synthesize  $NpO_2L$ .  $3H_2O$  as an analog of the uranyl and plutonyl complexes, because of high reduction rate of Np(VI) with the malonate ion even in the cold. The results obtained in this study are helpful for synthesis of crystalline compounds of penta- and hexavalent Pu and Np.

#### REFERENCES

- Krot, N.N., Bessonov, A.A., Grigor'ev, M.S., and Charushnikova, I.A., *Radiokhimiya*, 2004, vol. 46, no. 6, pp. 516–520.
- Krot, N.N., Bessonov, A.A., Charushnikova, I.A., et al., Radiokhimiya, 2005, vol. 47, no. 3, pp. 224– 227.
- Krot, N.N., Bessonov, A.A., Grigor'ev, M.S., and Makarenkov, V.I., *Radiokhimiya*, 2005, vol. 47, no. 5, pp. 431–433.
- Choppin, G.R., Stout, B.E., and Pages, M., J. Alloys Comp., 1998, vols. 271–273, pp. 774–777.
- Krot, N.N., Bessonov, A.A., Grigor'ev, M.S., et al., Radiokhimiya, 2004, vol. 46, no. 5, pp. 389–395.
- Nikol'skii, B.P., Posvol'skii, M.V., and Krylov, L.I., *Radiokhimiya*, 1965, vol. 7, no. 3, pp. 298–305.
- Bessonov, A.A., Afonas'eva, T.V., and Krot, N.N., *Radiokhimiya*, 1990, vol. 32, no. 5, pp. 31–35.
- Gel'man, A.D. and Drabkina, L.E., *Zh. Neorg. Khim.*, 1958, vol. 3, no. 5, pp. 1105–1108.
- Mefod'eva, M.P., Krot, N.N., Smirnova, T.V., and Gel'man, A.D., *Radiokhimiya*, 1969, vol. 11, no. 2, pp. 193–200.
- Mefod'eva, M.P., Grigor'ev, M.S., Afonas'eva, T.V., and Kryukov, E.B., *Radiokhimiya*, 1981, vol. 23, no. 5, pp. 697–703.
- 11. Grigor'ev, M.S., Antipin, M.Yu., and Krot, N.N., *Radiokhimiya*, 2005, vol. 47, no. 2, pp. 97–99.
- 12. Ermolaev, N.P., Krot, N.N., and Gel'man, A.D., *Ra-diokhimiya*, 1967, vol. 9, no. 2, pp. 171–178.