Behavior of Np(V) Malonates under Hydrothermal Conditions

N. N. Krot, M. S. Grigor'ev, and I. A. Charushnikova

Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, Russia

Received February 20, 2003

Abstract—Two new Np(V) malonates, LiNpO₂L · 2H₂O and KNpO₂L, where L = CH₂(COO)₂, were synthesized, and their characteristics were studied. Similar to their chemical analogs with Na⁺, NH₄⁺, and Cs⁺ ions in the outer sphere, these compounds transform into well crystallized neptunyl(V) compounds of the MNpO₂CO₃ · nH₂O type on heating in sealed ampules beneath the layer of the corresponding alkali metal or ammonium malonate solution at a temperature higher than 140°C. Under hydrothermal conditions (NpO₂)₂L · 4H₂O is not converted to lower hydrates, and above 135°C it decomposes to form a dark gray amorphous product.

We reported previously [1] on the synthesis and some characteristics of Np(V) malonates $(NpO_2)_2L \cdot nH_2O$ (n = 4, 3, 1), MNpO₂L (M = NH₄ and Cs), and NaNpO₂L · 2H₂O, where L = CH₂(COO)₂. Single crystals of tetra- and trihydrate of simple neptunyl(V) malonate were prepared, and their structures were studied by X-ray diffraction [2, 3]. In both cases, interesting systems of mutual coordination of the NpO₂⁺ ions through the "yl" oxygen atoms (cation–cation bonds) were found. The remaining Np(V) malonates were synthesized only in the finely crystalline state, and their structure was not elucidated.

All neptunium(V) malonates were synthesized at room temperature or under heating on a boiling water bath. The aim of this work was to study the behavior of the above compounds under hydrothermal conditions with the aim to prepare some of these in the crystalline form suitable for X-ray studies. In parallel, two new compounds of the MNpO₂L $\cdot n$ H₂O type with M = Li and K were synthesized and studied.

EXPERIMENTAL

We used practically neutral (pH ~5) working solutions with the Np(V) nitrate concentration of 0.08– 0.15 M, which were prepared by dissolving NpO₂OH in the stoichiometric amount of dilute HNO₃. Neptunium was purified by anion exchange and precipitation of Np(C₂O₄)₂ · 6H₂O. The solution concentration was determined gravimetrically after evaporation of the samples to wet salts and calcination of the dry residues to NpO₂. The solutions of analytically pure grade malonic acid were analyzed by titration with a reference NaOH solution. Alkali metal and ammonium malonates were prepared by neutralization of accurately measured volumes of malonic acid solutions with stoichiometric amounts of the corresponding alkali or NH_4OH . The final solutions had pH 6–7, and their concentrations were in the range 0.2–0.9 M. All working solutions were prepared in distilled water.

The spectrophotometric measurements were carried out with a Shimadzu UV-3100 spectrometer (Japan). The electronic absorption spectra (EAS) of crystalline compounds were recorded from pellets pressed with calcined NaCl as described in [4]. The X-ray powder patterns were registered in a focusing Guinier camera (Cu K_{α_1} radiation, internal reference Si). The samples were weighed with a Sartorius microbalance (sensitivity 1 µg).

RESULTS AND DISCUSSION

The hydrothermal behavior of simple neptunyl(V)malonates was studied by an example of $(NpO_2)_2L$. H₂O prepared as described in [1], i.e., by crystallization from an NpO₂OH solution in a small excess of malonic acid at room temperature. Compounds $MNpO_2L \cdot nH_2O$ were synthesized considering our previous results [1]. For this purpose, to samples of 0.08-0.15 M NpO₂NO₃, the corresponding alkali metal or ammonium malonate was added to the concentration excess of 0.1–0.2 M, and the mixture was heated on a boiling water bath for 1–3 h. Then, after cooling to room temperature, the light bluish crystalline precipitates were filtered off on a glass filter in a vacuum, thoroughly washed with water, and dried in an air flow for 2-3 h. The final products with M = Cs, NH_4 , and Na were identified by X-ray phase analysis as CsNpO₂L, NH₄NpO₂L, and NaNpO₂L. 2H₂O, respectively. The composition of the new compounds with M = Li and K, corresponding to the formulas LiNpO₂L · 2H₂O and KNpO₂L, was determined

$LiNpO_2L \cdot 2H_2O$									
d _{exp}	d _{calc}	hkl	Ι	d _{exp}	d _{calc}	hkl	Ι		
7.59	7.60	100	vs	2.383	2.383	022	W		
6.10	6.08	$\overline{1}01$	vs	2.366	2.365	112	W		
6.01	6.04	001	vs	2.246	2.246	221	VW		
5.43	5.43	110	vs	2.178	2.179	231	m		
4.76	4.77	011	m	2.139	2.139	230	m		
3.876	3.882	020	S	2.122	2.122	320	W		
3.587	3.583	211	S	2.090	2.092	122	W		
3.547	3.559	111	S	2.060	2.059	301	VW		
3.458	3.458	120	vs	1.9701	1.9702	232	VW		
3.406	3.415	210	vs	1.9429	1.9410	040	W		
3.294	3.302	102	m	1.8993	1.8982	123	m		
3.263	3.266	021	S	1.8783	1.8807	140			
3.023	3.019	002	VW	1.8478	1.8490	141	m		
2.811	2.814	012	VW	1.8212	1.8187	321	W		
2.792	2.787	121	W	1.8135	1.8109	330	W		
2.717	2.716	220	VW	1.7954	1.7959	323	m		
2.597	2.595	211	m	1.7861	1.7870	023	W		
2.534	2.535	300	W	1.7516	1.7494	241	W		
2.507	2.504	302	VW	1.7323	1.7314	113	W		
2.449	2.450	130	S	1.7059	1.7073	420	W		
2.404	2.210	310	m	<u> </u>	L	L	L		
KNpO ₂ L**									
d_{\exp}	Ι	d _{exp}	Ι	d_{\exp}	Ι	d_{\exp}	Ι		
9.44	S	3.316	S	2.337	m	1.9608	m		
7.60	W	3.249	m	2.277	m	1.9462	m		
6.45	m	3.197	w	2.221	VW	1.9373	m		
5.67	vs	3.020	VW	2.206	S	1.8490	W		
5.09	m	2.973	m	2.194	S	1.8157	m		
5.02	W	2.859	vw	2.180	VW	1.7967	W		
4.79	VS	2.800	W	2.157	VW	1.7787	m		
4.39	W	2.711	m	2.123	W	1.7204	S		
4.03	VS	2.673	VS	2.096	VW	1.6487	m		
3.960	W	2.548	S	2.076	m	1.6085	m		
3.826	VS	2.524	m	2.057	W	1.5870	VW		
3.663	m	2.456	vs	2.039	m	1.5555	m		
3.613	W	2.432	S	2.027	W	1.5300	W		
3.553	m	2.376	S	1.9903	m	1.5086	W		

Table 1. Interplanar spacings (d_{exp}, \dot{A}) and relative intensities* (I) of lines in the X-ray powder patternes of double Np(V) malonates

* (vs) very strong, (s) strong, (m) medium, (w) weak, and (vw) very weak. ** Plus 14 lines down to $d_{\exp} = 1.1533$ Å.

by chemical analysis for neptunium and malonate ion by procedures described in [1]. For LiNpO₂L·2H₂O, found, %: Np 57.2, 57.6; $CH_2(COO)_2^{2^-}$ 24.9, 24.3. Calculated, %: Np 57.25; $CH_2(COO)_2^{2^-}$ 24.64.

For KNpO₂L, found, %: Np 58.1, 57.9; CH₂. $(COO)_2^{2-}$ 24.3, 25.1. Calculated, %: Np 57.81; CH₂(COO)₂²⁻ 24.88.

The X-ray powder patterns of LiNpO₂L · 2H₂O and KNpO₂L are given in Table 1. The X-ray powder pattern of LiNpO₂L·2H₂O was indexed in monoclinic system with the unit cell parameters a = 8.3167(8), b = 7.7641(5), c = 6.6045(6) Å, $\beta = 113.89(1)^{\circ}, V =$ 390(1) Å³, space group $P2_1$ or $P2_1/m$.

Comparison of data listed in Table 1 with published

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data [1] showed that LiNpO₂L \cdot 2H₂O is not isostructural with NaNpO₂L \cdot 2H₂O. The same is true for the pair NH₄NpO₂L and KNpO₂L. At the same time, it should be noted that LiNpO₂L \cdot 2H₂O and KNpO₂L are similar to the previously studied compounds of the MNpO₂L \cdot *n*H₂O type in their color, EAS, and features of crystallization from a solution. In all the cases, the precipitation from a solution proceeds fairly slowly, which is typical for compounds with a polymeric structure. The rate of crystallization grows with increasing Np(V) concentration and temperature and somewhat decreases with increasing concentration of malonate ions. The latter fact is apparently caused by formation of the fairly stable Np(V) bimalonate complex in the solution [5, 6].

It is seen from the figure that, in the EAS of $LiNpO_2L \cdot 2H_2O$ and $KNpO_2L$, similar to the spectra of related compounds [1], the absorption band at approximately 980 nm, characteristic of the hydrated NpO_2^+ ions, is considerably weakened. This fact suggests centrosymmetrical oxygen surrounding of the neptunium atom in these salts [7]. The most probable coordination polyhedron (CP) of the central atom is a hexagonal bipyramid, apparently somewhat distorted. Unfortunately, with this symmetry of CP we cannot judge from EAS the presence or absence of cation–cation bonding in the structure of the compounds.

KNpO₂L and especially LiNpO₂L \cdot 2H₂O are appreciably soluble in water. For example, after stirring for 6 h excess LiNpO₂L \cdot 2H₂O with 0.06 M Li₂L the Np concentration in the liquid phase was 8.5 × 10⁻³ M (15°C). After precipitation of KNpO₂L by the above procedure, 1.3×10^{-3} M Np(V) was found in the mother liquor with [L^{2–}] = 0.14 M.

After keeping at 115° C for 1 h and cooling in a desiccator over granulated KOH, the weight loss of LiNpO₂L·2H₂O corresponded to one H₂O molecule. However, the monohydrate formed gradually absorbs water at storage in air and within approximately 4 days transforms into the initial compound.

To study the hydrothermal behavior of Np(V) malonates, glass ampules (D = 6 mm) were charged with weighed portions of the compounds and a small volume (0.3–1 ml) of water or solution of the corresponding M₂L with addition of H₂L to a concentration of approximately 0.02 M with the aim to decrease pH of the liquid phase and suppress hydrolysis of neptunyl(V). The ampules were hermetically sealed and kept in an oven with automatic temperature control for several hours or days. The temperature variation during heating was in the limits of $\pm 2^{\circ}$ C.



Electronic absorption spectra of crystalline (1) $LiNpO_2L \cdot 2H_2O$ and (2) $KNpO_2L$.

The experiments showed that heating of $(NpO_2)_2L \cdot 4H_2O$ in a hermetically sealed ampule to $125^{\circ}C$ under a layer of 0.02 M H₂L does not result in decomposition of the compound. Heating to $135^{\circ}C$ results in slow transformation of the compound into a dark gray flocculent product. The similar pattern is observed in the case of addition of $(NH_4)_2L$ to the liquid phase up to the concentration of 0.01-0.05 M, though the rate of decomposition of the compound somewhat decreases. Thermal instability of simple Np(V) malonates under hydrothermal conditions excludes the possibility of preparation by this procedure of single crystals of $(NpO_2)_2L \cdot 2H_2O$ or anhydrous salt, formed under heating of the tetra- and trihydrate to 140 and $200^{\circ}C$, respectively [1].

The behavior of double malonates under hydrothermal conditions strongly depends on the kind of the outer-sphere cation, excess of L^{2-} , and the presence of malonic acid. At $[L^{2-}] < 0.3$ M, in the absence of H₂L, above 135°C the compounds MNpO₂L·2H₂O with M = Li and Na transform into dark gray products, as in the case of simple malonates. When H₂L is added to the liquid phase to a concentration of 0.05– 0.1 M, LiNpO₂L·2H₂O under the layer of 0.25 M Li₂L at a temperature of approximately 150°C slowly transforms into a dense bluish precipitate consisting of hexagonal plate-like prisms. At 165°C, this process is complete in 3 h. Further heating to 180°C does not affect the precipitate. In the case of NaNpO₂·2H₂O,

 Table 2. Parameters of hexagonal unit cells of anhydrous double Np(V) carbonates

Compound	a, Å	<i>c</i> , Å	<i>V</i> , Å ³	Refer- ences	
KNpO ₂ CO ₃ KNpO ₂ CO ₃	5.120 5.104(1)	9.971 10.104(1)	226.4 227.95(7)	[9, 10] This work	
NH ₄ PuO ₂ CO ₃ CsNpO ₂ CO ₃	5.090 5.118(1)	10.390 12.079(1)	233.1 274.01(8)	[11] This work	

on heating for 3 h in 0.3 M $Na_2L + 0.05$ M H_2L , druses of crystals in the form of grayish-green elongated tetrahedral prisms are formed. An increase in the Na_2L concentration to 0.25 M results in formation of a mixture of the above crystals and a gray amorphous decomposition product.

The compounds $MNpO_2L$ with $M = NH_4$, K, and Cs gradually transform into dense bluish crystalline products even at $[L^{2-}] = 0.03$ M in the presence of 0.05 M H₂L at a temperature of approximately 140°C. This pattern is retained with increasing concentration of malonate ions to 0.3 M and temperature to 180°C. In all cases, the solutions over precipitate in ampules are transparent and colorless.

The crystalline products formed from $MNpO_2L \cdot nH_2O$ under hydrothermal conditions were studied by X-ray phase analysis. The X-ray powder patterns showed that, under these conditions, double carbonates of the general formula $MNpO_2CO_3 \cdot nH_2O$ were formed, with the K and Cs salts being anhydrous. Their X-ray powder patterns were indexed [7] and refined [8] in the hexagonal system (Table 2). They are similar to those published for isostructural monocarbonates $KNpO_2CO_3$ and $NH_4PuO_2CO_3$ [9–11].

The analysis of X-ray powder patterns of double Np(V) carbonates with Li and Na showed that, under hydrothermal conditions, mixtures of products consisting of anhydrous salts and hydrates were formed. The single crystals of LiNpO₂CO₃ · 2H₂O were obtained, and its crystal structure was solved. The monoclinic unit cell parameters are a = 8.775(1), b = 5.058(1), c = 6.643(1) Å, $\beta = 90.04(1)^\circ$, V = 294.8 Å³, space group *Cm*.

The X-ray powder pattern of the ammonium salt

was indexed in the monoclinic system: a = 12.540(1), b = 6.242(1), c = 6.248(1) Å, $\beta = 91.05(1)^{\circ}$, V = 488.98(12) Å³. Based on the unit cell volume, the compound was identified as NH₄NpO₂CO₃ · 0.5H₂O (Z = 4). The results of studying carbonates will be described in more detail in a separate paper.

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