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Synthesis of neptunyl(VI) hydroxides and their ^{237}Np Mössbauer spectra

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Four types of neptunyl(VI) hydroxides have been synthesized by chemical oxidation of Np(IV) instead of ozone oxidation of Np(V) which caused the partial oxidation to the heptavalent state. $NpO_2(OH)_2$ (I) and $NpO_2(OH)_2 \cdot H_2O$ (orthorhombic type) (II) have been obtained by adding pyridine to the solution at 373K and 343K, respectively. $NpO_2(OH)_2 \cdot H_2O$ (hexagonal type) (III) and $NpO_2(OH)_2 \cdot xH_2O \cdot yNH_3$ ($x+y=1$) (IV) have been prepared by using LiOH and NH_4OH , respectively. The four materials have been characterized by X-ray powder diffraction patterns, thermogravimetric analysis and ^{237}Np Mössbauer spectra. The ^{237}Np Mössbauer spectrum of (I) measured first time as anhydrous neptunyl(VI) hydroxide ($\delta = -46.2$ mm/s, $e^2qQ = 193$ mm/s and $\eta = 0.16$ at 4.8K) has more distinct five-line Mössbauer pattern than those of (II), (III) and (IV). The Mössbauer spectra for (II), (III) and (IV) are slightly different from each other. The structural information has been obtained from these data.

Introduction

There is a wide interest in neptunium chemistry associated with reprocessing of nuclear fuels and treatment of actinide wastes; a number of groups have been investigating the neptunyl(VI) hydroxides.[1–8] ^{237}Np Mössbauer spectroscopy is a powerful tool for structural studies, since the hyperfine parameters are much influenced by the oxidation state of Np and the environment around the Np site.[2,9–13] The hydroxide compounds should be formulated as $NpO_2(OH)_2 \cdot nH_2O$ rather than $NpO_3 \cdot (n+1)H_2O$ often described in literature, because the Mössbauer parameters support the existence of the cationic moiety $(NpO_2)^{2+}$.[2] Infra-red spectral evidence also suggests that $NpO_3 \cdot 2H_2O$ is represented by $NpO_2(OH)_2 \cdot H_2O$.[3] BAGNALL and LAIDLER prepared $NpO_3 \cdot 2H_2O$ and $NpO_3 \cdot H_2O$ by ozone oxidation of aqueous neptunium(V) hydroxide at 18 and 90 °C, respectively.[5] KALVIUS reported that the material obtained by ozone oxidation contained heptavalent neptunium species as an impurity.[2] Although the neptunyl(VI) hydroxides with $n=0$, 1 and 3 were reported,[1–8] there remain some ambiguities in the preparative methods associated with the partial oxidation, water contents, the crystallinity and the thermal behavior.

We have undertaken various preparations of neptunyl(VI) hydroxides by chemical oxidation to avoid the formation of Np(VII) species. We have carried out the characterization and the ^{237}Np Mössbauer measurements of them.

Experimental

Synthesis and characterization

The $^{237}NpO_2$ powder used as the starting material was dissolved in concentrated HNO_3 by heating to a slight boil. The solution obtained was evaporated to wet salts. The dry residue was dissolved in distilled water. The hydroxides were obtained as described below, from the aqueous $Np(VI)O_2\ (NO_3)_2 \cdot xH_2O$ solution (hereafter called as the starting solution) thus obtained. All precipitates were separated by vacuum filtration and washed by distilled water. The pH was measured using a pH-test paper. The precipitate was examined by powder X-ray diffraction patterns using a diffractometer, model RAD-3C (Rigaku Co., Cu Kα radiation). The thermal behavior of the compounds was investigated in a dry atmosphere on a Sartorius MP8 electric microbalance by recording the thermogravimetric (TG) curve. The formula was determined based on the TG and the XRD data.

$NpO_2(OH)_2$ (I)

Into the starting neptunium(VI) solution, a small amount of pyridine was added at 373 K. The reddish brown precipitate was formed at pH 3.5. $NpO_2(OH)_2 \cdot H_2O$ (orthorhombic type) (II).

Into the starting solution, a small amount of pyridine was added at 343 K. A chocolate-brown precipitate was obtained at pH 3.5. Attempts to prepare NpO_2CO_3 [14] by adding Li_2CO_3 to the starting solution led to the formation of $NpO_2(OH_2) \cdot H_2O$ (orthorhombic type) at about pH 4.

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$NpO_2(OH)_2 \cdot H_2O$ *(hexagonal type) (III)*

Into the starting solution, a 4M LiOH solution was added at 343 K until a dark brown precipitate was formed. The precipitation occured above pH 7.

$NpO_2(OH)_2 \cdot xH_2O \cdot yNH_3$ $(x+y = 1)$ *(IV)*

Into the starting solution, an excess amount of NH_4OH at 343 K was added until a dark brown precipitate was obtained above pH 7. Uptake of NH_3 into the material was confirmed by using Nessler's reagent.

^{237}*Np Mössbauer measurements*

Mössbauer spectra were measured using a cryostat equipped with a driving system (WissEl GmbH, System MS II).[15] An assembled ^{241}Am metal source was used.[16] About 120 mg (100 mg Np/cm^2) of the sample was used as an absorber for the Mössbauer measurement. The data obtained were least square fitted to Lorentzian lines by a personal computer using an "IGOR" (Wave Metrics, Lake Oswego, Oregon) software.

Results and discussion

Synthesis

Various treatments of the starting solution gave various kinds of neptunyl(VI) hydroxides. Water contents and qualities of crystallinity depend on the treatments. The freshly prepared neptunyl(VI) hydroxides by chemical oxidation do not contain Np(VII) species (see Mössbauer spectra), whereas those obtained by ozone oxidation were contaminated by Np(VII) species.[2]

$NpO_2(OH)_2$ (I) was prepared by a method similar to $UO_2(OH)_2 \cdot H_2O$.[17] The similar conditions provide $NpO_2(OH)_2$ and $UO_2(OH)_2 \cdot H_2O$. This is an example that properties of Np(VI) ion are slightly different from those of U(VI) ions while the resemblances between U and Np are useful in a study on the neptunium compounds.

$NpO_2(OH)_2$ (I) and $NpO_2(OH)_2 \cdot H_2O$ (II) were obtained by adding pyridine at 343 K and 373 K, respectively . The water contents are associated with the reaction temperatures.

The use of NH_4OH provided $NpO_2(OH)_2 \cdot xH_2O \cdot yNH_3$ $(x+y=1)$ (IV) since partial replacement of H_2O by NH_3 happens in the structure. LOGVIS and KROT reported that the $NpO_3 \cdot xH_2O \cdot yNH_3$ $(=NpO_2(OH)_2 \cdot (x-1)H_2O \cdot yNH_3)$ was obtained by using hexamethylene- tetramine in heated solution.[1]

Powder X-ray diffraction patterns

Figure 1 shows the powder X-ray diffraction patterns for (I), (II), (III) and (IV). The X-ray diffraction data of $NpO_2(OH)_2$ (I) are identical with those reported for $NpO_3 \cdot H_2O$ obtained by ozone oxidation.[5] Since the powder X-ray pattern of $NpO_2(OH)_2$ at RT is similar to that of β-$UO_2(OH)_2$ whose structure is known,[18] the structure of $NpO_2(OH)_2$ probably consists of parallel infinite $NpO_2(OH)_2$ layers. When temperature is lowered, β-$UO_2(OH)_2$ where the U atom coordinates to six O atoms is known to transform irreversibly to α-$UO_2(OH)_2$ where the U atom coordinates to eight O atoms.[19] $NpO_2(OH)_2$ with similar structure to α-$UO_2(OH)_2$ has not been obtained.[24] The powder X-ray pattern of (I) at RT did not change before and after cooling in order to measure the Mössbauer spectra. This suggests that the irreversible change corresponding to that of the uranyl compounds to α-$UO_2(OH)_2$ does not happen. The powder X-ray diffraction method under low temperature range will be helpful to obtain further details about possible existence of $NpO_2(OH)_2$ form similar to α-$UO_2(OH)_2$.

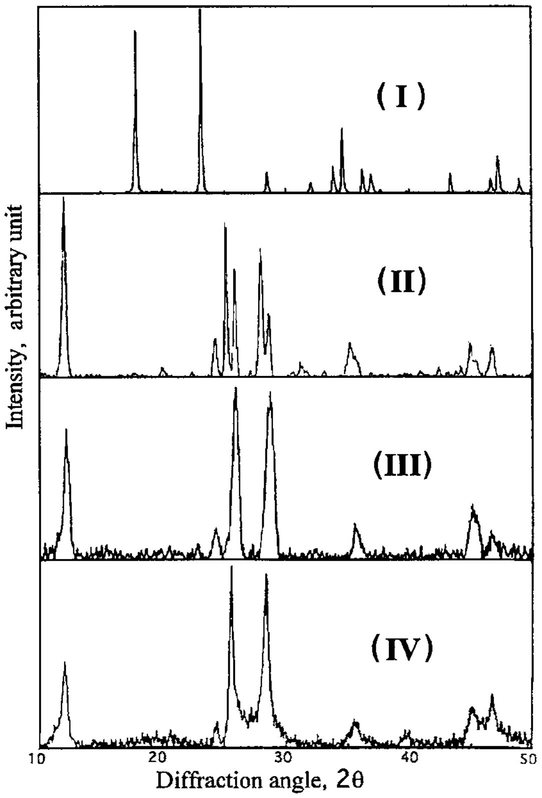

Fig. 1. The powder X-ray diffraction patterns for $NpO_2(OH)_2$ (I), $NpO_2(OH_2) \cdot H_2O$ (orthorhombic type) (II), $NpO_2(OH_2) \cdot H_2O$ (hexagonal type) (III), and $NpO_2(OH)_2 \cdot xH_2O \cdot yNH_3$ $(x+y=1)$ (IV)

The powder X-ray diffraction patterns indicate that monohydrates are classified into three types: orthorhombic type (II), hexagonal type (III) and amorphous type which will be reported elsewhere. Considering the X-ray studies on the analogous uranium compounds,[20] the pattern of (II) can be indexed on the basis of an orthorhombic cell with $a = 1384(1)$, $b = 1655(2)$, $c = 1471.3(7)$ pm. The analogous pattern of (II) with that of $NpO_3 \cdot 2H_2O$ prepared from molten salts by COHEN[6] shows that these are the same compounds. The patterns of (III) and (IV) can be indexed on the basis of a hexagonal cell with $a = 398.5(9)$, $c = 1461(2)$ pm and $a = 402.3(4)$, $c = 1458.9(9)$ pm, respectively. Comparing the structures of (II), (III) and (IV), we consider the subcell in the unit cell according to Reference 20. The subcell paremeters are ; (II): $a = 403.2(3)$, $b = 413.7(4)$, $c = 735.7(3)$ pm, $\gamma = 120.9(1)°$, $V = 1.053(1) \cdot 10^8$ pm^3; (III): $a = 398.5(9)$, $b = 398.5(9)$, $c = 730(1)$ pm, $\gamma = 120°$, $V = 1.004(5) \cdot 10^8$ pm^3; (IV): $a = 402.3(4)$, $b = 402.3(4)$, $c = 729.5(4)$ pm, $\gamma = 120°$, $V = 1.023(2) \cdot 10^8$ pm^3. The subcell of (II) is similar to that of (III) and (IV). The slight distortion of the hexagonal cell of (III) gives the orthorhombic cell of (II). Although KIMURA et al. reported $NpO_3 \cdot H_2O$ ($= NpO_2(OH)_2$) with $a = 401.8$, $b = 695.9$ and $c = 741.0$ pm in the orthorhombic crystal system,[7,8] these cell parameters can approximately transform to those of (III) and are close to those of the subcell in $UO_3 \cdot 2H_2O$ and related compounds.[21] Thus we consider the $NpO_3 \cdot H_2O$ ($= NpO_2(OH)_2$) reported by KIMURA et al. should be $NpO_3 \cdot 2H_2O$ ($= NpO_2(OH)_2 \cdot H_2O$). The TG data of (III) also support the formula is $NpO_2(OH)_2 \cdot H_2O$.

The powder X-ray data suggests that each uranium atom of $UO_2(OH)_2 \cdot H_2O$ is surrounded by eight oxygen atoms.[20] The powder X-ray data indicate that the subcell of $NpO_2(OH)_2 \cdot H_2O$ compounds is similar to that of $UO_2(OH)_2 \cdot H_2O$. So we assume that Np atom coordinates to eight oxygen in (II) and (III).

Interestingly, it was found that the powder X-ray diffraction pattern of (III) is almost identical with that of (IV) though that of uranium(VI) anologous compounds containing NH_3 are different from that of $UO_3 \cdot 2H_2O$ ($= UO_2(OH)_2 \cdot H_2O$).[20]

The $NpO_2(OH)_2 \cdot H_2O$ compounds can be considered as intercalation compounds consisting of infinite two-dimensional $NpO_2(OH)_2$ layers and guest H_2O molecules between the layers. The $NpO_2(OH)_2 \cdot 3H_2O$[3] reported may result from the larger extent of intercalation of H_2O into the interlayer space. It is considered that guest H_2O molecules can be exchanged for NH_3 molecules in the space. The coincidence of powder X-ray data between (III) and (IV) does not necessarily support an idea that the ammonia molecule is directly linked to the Np atoms in (IV).

^{237}Np Mössbauer spectra

The ^{237}Np Mössbauer spectra of (I–IV) showed the absorption lines due to the hexavalent state without any lines assignable to the heptavalent species, indicating the materials prepared by chemical oxidation do not have heptavalent neptunium species as an impurity which were the by-product in the material obtained by ozone oxidation.[2,4]

We have found that the spectra of anhydrous hydroxide (I) are clearly different from those of monohydrate and NH_3-containing hydroxides (II–IV), which showed similar spectra. As shown in Fig. 2, the ^{237}Np Mössbauer spectrum of (I) at 4.8 K has well-splitted five line Mössbauer pattern due to smaller η value, compared to that of (II) at 11 K.

As seen in Table 1, the isomer shift, $\delta = -46.2$ mm/s and asymmetry parameter, $\eta = 0.16$ of (I) are smaller than those of (II), (III) and (IV), and the quadrupole coupling constant, $e^2qQ = 193$ mm/s is larger than those of (II), (III) and (IV), suggesting the shorter neptunyl Np-O bond length of (I) than those of (II), (III) and (IV). The Mössbauer parameters, especially, e^2qQ, of (II), (III) and (IV) are also different from those of $NpO_2(OH)_2 \cdot H_2O$ quoted by Tabuteau in the review[9] ($\delta = -41(1)$ mm/s, $e^2qQ = 201(3)$ mm/s, $\eta = 0.7$). We consider that the e^2qQ value of 201 mm/s may not have been accurately determined due to the co-existing peaks of the heptavalent neptunium species as an impurity (see Fig. 10 in page 366 of Ref. 2), although the original paper[22] does not report the e^2qQ value.

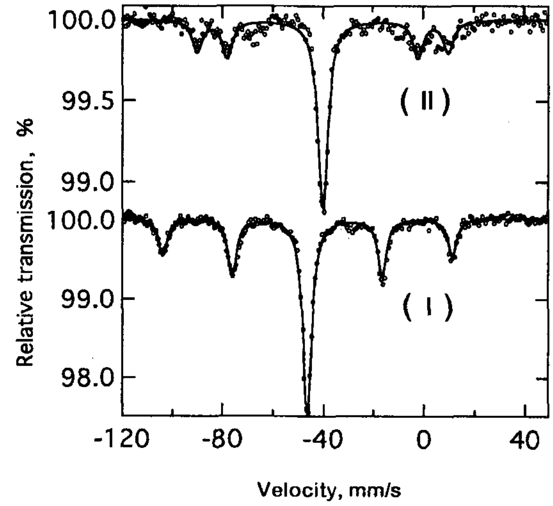

Fig. 2. ^{237}Np Mössbauer spectra for $NpO_2(OH)_2$ (I) at 4.8 K and $NpO_2(OH_2) \cdot H_2O$ (orthorhombic type) (II) at 11 K

Table 1. ^{237}Np Mössbauer parameters of neptunyl(VI) hydroxides at various temperatures

Compound		T, K	δ (NpAl$_2$), mm/s	e^2qQ, mm/s	η
$NpO_2(OH)_2$	(I)	4.8	–46.2(1)	193(1)	0.16(1)
		25	–46.4(1)	193(1)	0.16(1)
		41	–46.3(1)	194(1)	0.14(1)
		86	–46.5(3)	193*	0.15*
$NpO_2(OH)_2 \cdot H_2O$	(II)	11	–39.9(1)	179(1)	0.69(1)
$NpO_2(OH)_2 \cdot H_2O$	(III)	11	–43.4(1)	149(1)	0.59(1)
$NpO_2(OH)_2 \cdot xH_2O \cdot yNH_3$	(IV)	4.6	–44.6(1)	168(1)	0.65(1)

* These parameters were fixed to the average of those obtained at 4.8–41 K.

There are differences in the Mössbauer spectra between (II) and (III), suggesting different environments around Np(VI) atoms. These results agree with the different powder X-ray diffraction patterns. Since (III) was obtained above pH 7, it may exist in the form $H_2NpO_4 \cdot H_2O$ and Li_2NpO_4 besides NpO_2 $(OH)_2 \cdot H_2O$. In spite of the similarities of powder X-ray diffraction patterns between (III) and (IV), the Mössbauer spectrum of (IV) is slightly different from that of (III). The replacement of H_2O with NH_3 affects the environment around the Np atoms.

Correlations of isomer shift (δ) with coordination number(CN), of δ with Np-O mean distance and of δ with e^2qQ have been reported for the Np(VI) compounds.[2,9–13] It is found approximately in Fig. 3 that correlations between δ and e^2qQ exist for (I), (II), (III) and (IV), including other reported oxygen-coordinated NpO_2^{2+} compounds. The ^{237}Np isomer shift values of (II), (III) and (IV) are in the characteristic range for CN = 8, while that of (I) does not fall in the range for CN = 6. There are three possible explanations about δ value of (I): First, the phase transformation of (I) as reported in β-$UO_2(OH)_2$ from CN = 6 to 8 occurs on cooling. However, the temperature independent Mössbauer parameters of (I) (Table 1) do not suggest such phase transformation in the temperature range, 4.8–86 K. Secondly, in case of no such phase transformation, longer Np-O mean distance of six-coordinated (I) (212 pm) makes its δ value less negative than those for six-coordinated other compounds with the distances of 205–210 pm. The larger e^2qQ of 193 mm/s for (I) compared to 100 mm/s for the six-coordinated compounds may be ascribed to smaller neptunyl Np-O length of 180 pm (I) than 189 pm (K_2NpO_4), 190 pm (β-Na_2NpO_4) and 186 pm ($BaNpO_4$). Thirdly, without phase transformation, the smaller ligand electronegativity of OH group than oxygen in six-coordinated compound allows the less negative δ value.

It should be noted that the correlation of δ with Np-O mean distance are observed here also for eight-coordinated (II), (III) and (IV): the smaller subcell volume of (III) and (IV) than (II) (probably corresponding to the smaller mean bond length), results in the more negative δ values of (III) and (IV) than (II).

We demonstrate that the ^{237}Np Mössbauer parameters of the anhydrous hydroxide are clearly different from those of monohydrates. These parameters are explained through insight into the structural chemistry of the hydroxides studied. Single crystal X-ray structure determination will be helpful for obtaining further details.

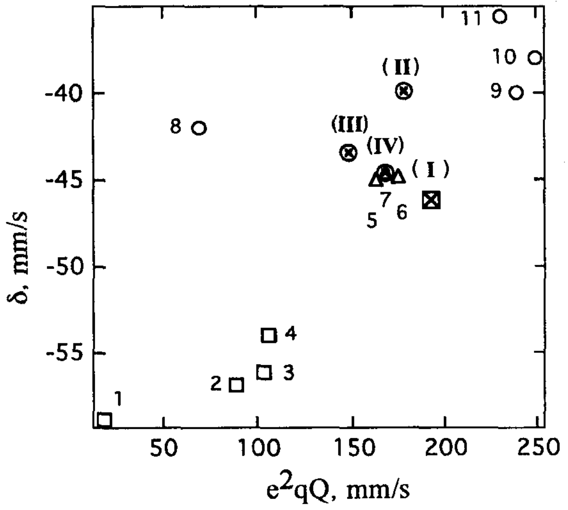

Fig. 3. Plot of isomer shifts against quadrupole coupling constants for oxygen-coordinated Np(VI) compounds. (I) $NpO_2(OH)_2$, (II) $NpO_2(OH_2) \cdot H_2O$ (orthorhombic type), (III) $NpO_2(OH_2) \cdot H_2O$ (hexagonal type), (IV) $NpO_2(OH)_2 \cdot xH_2O \cdot yNH_3$ ($x+y = 1$); six-coordinated with elongation (□), 1) Li_4NpO_5; six-coordinated with contraction (⊠), 2) K_2NpO_4, 3) β-Na_2NpO_4, 4) $BaNpO_4$; seven-coordinated (Δ) 5) $(NH_4)_2Np_2O_7 \cdot H_2O$, 6) $K_2(NpO_2)_2V_2O_8$, 7) $Tl_2(NpO_2)_2V_2O_8$; eight-coordinated (○) 8) $NpO_2(NO_3)_2 \cdot 6H_2O$, 9) $NaNpO_2(CH_3COO)_3$, 10) $RbNpO_2(NO_3)_3 \cdot 6H_2O$, 11) NpO_2CO_3. The data for compounds 1)–11) are taken from Ref. 9

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