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Structural Characterization of Neptunyl(VI) Trinitrato Complexes: $M[NpO_2(NO_3)_3]$ ($M = NH_4^+$ and K^+)

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^{237}Np Mössbauer spectra of two neptunyl(VI) trinitrato complexes, $M[NpO_2(NO_3)_3]$ ($M = NH_4^+$ **1** and K^+ **2**) were measured at 4.5 K, 10 K and 30 K, respectively. The spectra show magnetic hyperfine splittings similar to the spectrum of $Rb[NpO_2(NO_3)_3]$ **3** already reported. Since the SQUID data of **1** indicate that **1** is paramagnetic from 2 K to room temperature, the magnetic hyperfine splittings are due to slow paramagnetic relaxation. The crystal structures of **1** and **2** were refined by the Rietveld analysis, and the mean Np–O bond distances of **1** and **2** have been obtained. Almost the same Np–O bond distances of **1**, **2** and **3** exhibit about the same δ values. This is consistent with the linear relationship between the δ values and the mean Np–O bond distances established for the neptunyl(VI) compounds.

^{237}Np Mössbauer spectroscopy is a powerful tool for investigating the structures and chemical properties of neptunium compounds, because the ^{237}Np Mössbauer parameters, such as the isomer shift (δ) and the quadrupole coupling constant (e^2qQ), are very sensitive to the environment around the Np atoms.[1–6] It also often gives an effective internal magnetic field (H_{eff}) at the Np atoms.

We carried out a systematic investigation of neptunyl(VI) compounds by ^{237}Np Mössbauer spectroscopy, in combination with their powder X-ray diffraction (XRD) and magnetic susceptibility measurements. We previously reported that four kinds of neptunyl(VI) hydroxides were characterized by XRD, and were able to be structurally classified from the results of their ^{237}Np Mössbauer spectroscopy.[7] It is well known that all of neptunyl(VI) trinitrato complexes, $M[NpO_2(NO_3)_3]$ ($M = NH_4^+$, K^+, Rb^+ and Cs^+), are isostructural.[8] The crystal structure of $Rb[NpO_2(NO_3)_3]$ **3** has been determined by a single-crystal X-ray structure determination.[9] The structure of the $[NpO_2(NO_3)_3]^-$ anion has a hexagonal-bipyramidal coordination around the Np(VI) ion with three bidentate nitrate groups. The ^{237}Np Mössbauer spectrum of **3** at 4.2 K was also reported by Stone and Pillinger.[10] Its magnetic hyperfine structures in the ^{237}Np Mössbauer spectrum were discussed by Dunlap and Kalvius.[1,11]

In this present paper, we report on new results of neptunyl(VI) trinitrato complexes, $M[NpO_2(NO_3)_3]$ ($M = NH_4^+$ **1**, K^+ **2**), investigated by ^{237}Np Mössbauer spectroscopy, the Rietveld analysis and magnetic measurements. These new data indicate that the structural and electronic properties of **1** and **2** are almost identical to those of **3**.

Experimental

Synthesis. Material **1** was synthesized according to Alcock's method.[9] The neptunyl(VI) nitrate salt, $NpO_2(NO_3)_2{\cdot}xH_2O$, was prepared by adding concentrated nitric acid into a 0.1 M Np(V and VI) stock solution and then evaporating it. Then **1** (brown precipitation) was obtained by the addition of a slight excess NH_4NO_3 to the neptunyl(VI) nitrate solution, and evaporating it at about 333 K. Subsequently, **2** and freshly prepared **3** were also obtained according to the same method by using KNO_3 and $RbNO_3$, respectively.

X-ray Diffraction Analysis. Freshly prepared **1**, **2** and **3** were identified by powder XRD. A conventional Rigaku-3C diffractometer with Cu $K\alpha$-radiation was used for measuring the powder XRD patterns. Powder XRD data of **1** and **2** for the Rietveld analysis were collected as follows: the sample was completely ground in order to obtain a homogeneous powder. The step-scan mode was used and the fixed time was adjusted in order to obtain 5000 counts for the strongest peak. The crystal structures of **1** and **2** were refined by software, RIETAN-97β,[12] which is based on the Rietveld method.

^{237}Np Mössbauer Spectroscopy. A metallic ^{241}Am source ($\sim$600 MBq) and a sample containing 120 mg Np cm^{-2} were kept at a lower temperature in a cryostat. The ^{237}Np Mössbauer spectra were measured by the transmission method.[13] The 60 keV γ-rays were counted with a pure germanium detector. The Doppler velocities were measured with a laser Mössbauer velocity calibrator (WissEl MVC-450). The source was moved in a sinusoidal drive mode using a Mössbauer drive unit (WissEl MDU-1200). The ^{237}Np Mössbauer spectra were computer-fitted using the Lorentz approximation. The δ values were referred to $NpAl_2$ at 4.2 K. The values of the magnetic moments for the ground and excited states related to the ^{237}Np Mössbauer transition, used for the fitting procedure, were $\mu_g = 2.8$ n.m. and $\mu_e = 1.5$ n.m., respectively.[14]

Measurement of 1's Magnetization. A magnetization measurement of **1** was performed for a polycrystalline sample using a

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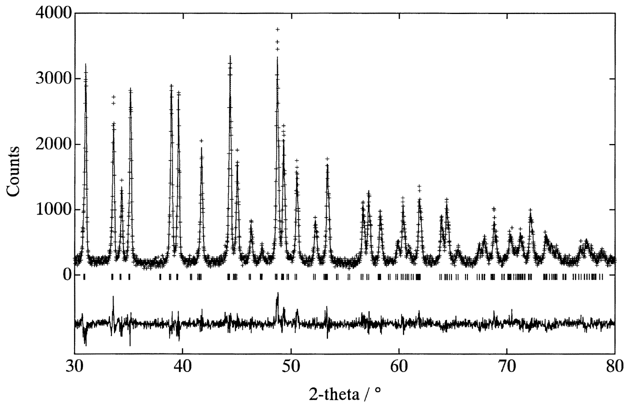

Fig. 1. Result of the Rietveld refinement for the neptunyl(VI) trinitrato complex, $NH_4[NpO_2(NO_3)_3]$ **1**. (Plus marks: observed, solid line: calculated. $R_{wp} = 12.67\%$, $R_p = 9.78\%$, $R_e = 10.66\%$, $S = 1.19$).

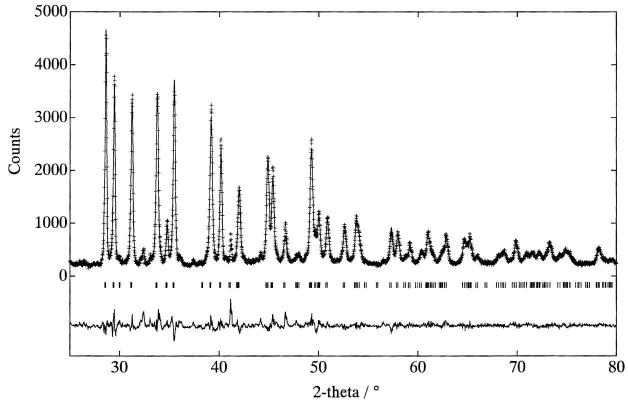

Fig. 2. Result of the Rietveld refinement for the neptunyl(VI) trinitrato complex, $K[NpO_2(NO_3)_3]$ **2**. (Plus marks: observed, solid line: calculated. $R_{wp} = 9.21\%$, $R_p = 6.38\%$, $R_e = 4.38\%$, $S = 2.10$).

SQUID magnetometer (MPMS, QD). The magnetic susceptibility measurement was made from 2 K to room temperature. Revision of the diamagnetism was not performed.

Results and Discussion

The Rietveld Analysis. The results of the Rietveld refinement of **1** and **2** with space group R-3C (No.167) are shown in Figs. 1 and 2, respectively. The Rietveld refinement of **1** was performed from 2-theta = 30° to 80°, good results were obtained ($R_{wp} = 12.67\%$, $R_p = 9.78\%$, $R_e = 10.66\%$, $S = 1.19$). The Rietveld refinement of **2** was made from 2-theta = 25° to 80°, good results were also obtained ($R_{wp} = 9.21\%$, $R_p = 6.38\%$, $R_e = 4.38\%$, $S = 2.10$).

The lattice parameters obtained in the Rietveld refinement are **1**: $a = 9.26(5)$ Å and $c = 18.92(7)$ Å; **2**: $a = 9.22(5)$ Å and $c = 18.76(7)$ Å. These agree with the reported data[8] and are associated with the size and shape of the NH_4^+, K^+ and Rb^+ ions. The lattice parameters of **1** are nearer to those of **3** than **2**.[8–9]

Table 1. Fractional Atomic Coordinates with Standard Deviations in Parentheses for the Neptunyl(VI) Trinitrato Complex, $NH_4[NpO_2(NO_3)_3]$ **1** Obtained by the Rietveld Method

Atom	x	y	z	B_{eq}(Å^2)*
Np	0	0	0.25	3.44
N (NH_4)	0	0	0	2.60
O1	0	0	0.3417(12)	3.55
N(NO_3)	−0.3125(40)	0	0.25	3.43
O2	−0.4430(32)	0	0.25	4.55
O3	−0.1742(17)	0.1322(8)	0.2563(6)	3.66

*The thermal parameters (B_{eq}) were fixed to the values corresponding to the atoms of uranyl(VI) trinitrato complex, $Rb[UO_2(NO_3)_3]$[15] which is isostructural with the neptunyl(VI) trinitrato complex, $NH_4[NpO_2(NO_3)_3]$ **1**.

Table 2. Fractional Atomic Coordinates and Thermal Parameters with Standard Deviations in Parentheses for the Neptunyl(VI) Trinitrato Complex, $K[NpO_2(NO_3)_3]$ **2** Obtained by the Rietveld Method

Atom	x	y	z	B_{eq}(Å^2)
Np	0	0	0.25	2.06(9)
K	0	0	0	5.83(26)
O1	0	0	0.3426(6)	1.10(32)
N	−0.3060(27)	0	0.25	1.05(56)
O2	−0.4432(17)	0	0.25	2.49(46)
O3	−0.1757(30)	0.1301(29)	0.2542(4)	4.88(42)

Table 3. Selected Bond Distances (Å) and Bond Angles (°) for the Neptunyl(VI) Trinitrato Complex, $NH_4[NpO_2(NO_3)_3]$ **1** and $K[NpO_2(NO_3)_3]$ **2** with Standard Deviations in Parentheses Obtained by the Rietveld Method

	NH_4-$[NpO_2(NO_3)_3]$ **1**	K-$[NpO_2(NO_3)_3]$ **2**	Rb-$[NpO_2(NO_3)_3]$[9] **3**
Np–O1	1.735(5)	1.737(13)	1.731(4)
Np–O3	2.468(4)	2.452(16)	2.469(6)
Mean Np–O	2.285	2.283	2.284
N–O3	1.259(6)	1.265(20)	1.276(3)
N–O2	1.208(5)	1.203(25)	1.199(6)
M–O1	2.995(5)	2.954(14)	3.027(3)
M–O2	3.148(13)	3.131(13)	3.159(5)
M–O3	3.242(5)	3.249(16)	3.262(6)
O1–Np–O3	87.2(3) 92.8(7)	88.1(6) 91.8(7)	87.7(3) 92.3(3)
O3–Np–O3	69.9(2) 51.2(3)	69.9(6) 50.3(5)	68.7(6) 51.6(6)
O1–Np–O1	180.0	180.0	180.0
O2–N–O3	122.1(6)	120.0(5)	122.5(3)
O3–N–O3	115.8(5)	120.0(8)	114.9(6)

The final atomic coordinates of **1** and **2** are listed in Table 1 and 2, respectively. The selected bond distances and bond angles are listed in Table 3 along with the reported data of **3**. As shown in Fig. 3, the structure of the $[NpO_2(NO_3)_3]^-$ anion in **1** and **2** adopts a hexagonal-bipyramidal geometry consisting of the Np(VI) ion coordinated with three bidentate nitrate ions and two oxide ions. The mean Np–O bond-distances of **1** and **2** are 2.285 Å and 2.283 Å, respectively. They are very close to that of **3** (2.284 Å) within the experimental error.

The results of the Rietveld refinement suggest that different M cations can influence the lattice parameter and the unit-cell

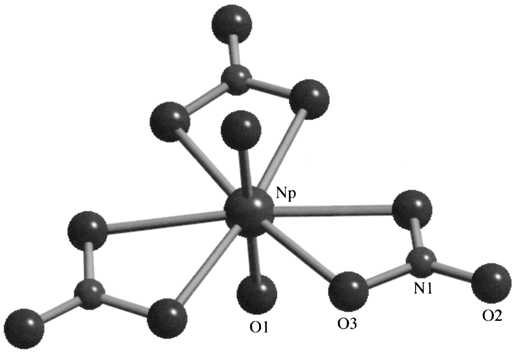

Fig. 3. Structure of the $[NpO_2(NO_3)_3]^-$ anion in the neptunyl(VI) trinitrato complexes of **1** and **2** obtained by the Rietveld analysis.

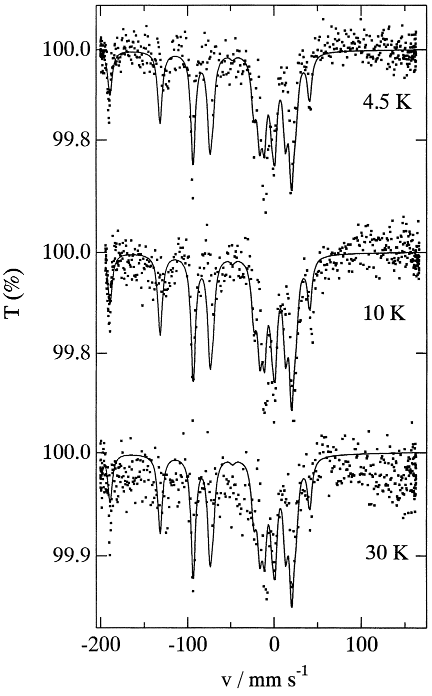

Fig. 4. ^{237}Np Mössbauer spectra for the neptunyl(VI) trinitrato complex, $NH_4[NpO_2(NO_3)_3]$ **1** at 4.5 K, 10 K and 30 K.

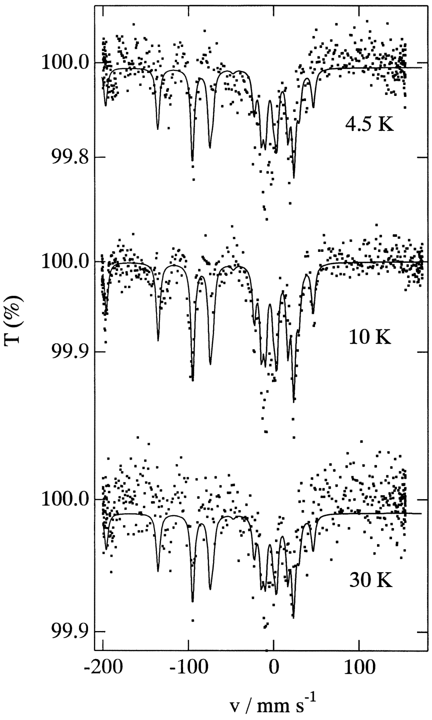

Fig. 5. ^{237}Np Mössbauer spectra for the neptunyl(VI) trinitrato complex, $K[NpO_2(NO_3)_3]$ **2** at 4.5 K, 10 K and 30 K.

Table 4. ^{237}Np Mössbauer Parameters for the Neptunyl(VI) Trinitrato Complexes, $M[NpO_2(NO_3)_3]$ ($M = NH_4^+$ **1**, K^+ **2** and Rb^+ **3**) at Various Temperature

Complex	δ*/mm s^{-1}	e^2qQ/mm s^{-1}	H_{eff}/T	T/K
$NH_4[NpO_2(NO_3)_3]$ **1**	−36.2(3)	244(2)	291(2)	4.5
	−36.5(1)	243(1)	288(1)	10
	−36.7(2)	245(1)	288(3)	30
$K[NpO_2(NO_3)_3]$ **2**	−36.1(3)	241(2)	289(2)	4.5
	−36.0(1)	243(1)	288(1)	10
	−36.3(2)	244(1)	288(3)	30
$Rb[NpO_2(NO_3)_3]$** **3**	−36.5(2)	243(2)	291(2)	4.5
	−36.3(2)	245(2)	288(1)	10
	−36.1(3)	247(3)	288(2)	30

*Relative to $NpAl_2$ at 4.2 K. **Stone and Pillinger reported ^{237}Np Mössbauer parameters at 4.2 K: $\delta = -38(3)$ mm s^{-1}, $e^2qQ = 248(6)$ mm s^{-1}, $H_{eff} = 52.9(5)$ mm s^{-1} (1 mm s^{-1} = 5.62×10^2 T, assuming $\mu_g = 2.8$ n.m. for ^{237}Np) in Reference 10. The H_{eff} value 333(3) T calculated from the data of Ref. 10 was reported in the review of Ref. 1. This value may be obtained by using the different magnetic moment for the ground state of ^{237}Np Mössbauer transition (μ_g = 3.14 n.m.).[18] Our recalculation of the H_{eff} for **3** by using $\mu_g = 2.8$ n.m. gave the value of 297 T.

volume, but can hardly influence the bond distance and the bond angle between the neptunium atom and the coordinated oxygen atom.

^{237}Np Mössbauer Spectra and SQUID Data. The ^{237}Np Mössbauer spectra of **1** and **2** at 4.5 K, 10 K, and 30 K are shown in Figs. 4 and 5, respectively. The obtained ^{237}Np Mössbauer parameters are listed in Table 4. The spectra of **1** and **2** are similar to the reported spectrum of **3**, and similar magnetic hyperfine splitting patterns can be clearly observed from 4.5 K to 30 K.

Although neptunyl (V and VI) complexes are thought to be paramagnetic, Nakamoto et al have recently discovered a ferromagnetic neptunyl(V) formate complex, $NpO_2(OOCH)\cdot H_2O$, below 12 K.[16] The spectra of **1** and **2** with magnetic hyperfine splittings may arise from two possibilities: firstly, slow paramagnetic relaxation; secondly, the presence of a magnetically ordered state in the measured temperature range. It is not easy to distinguish the two possibilities using only the results of their ^{237}Np Mössbauer spectroscopy.

The magnetization of **1** measured by SQUID gives useful information about distinguishing the two possibilities. A plot of the reciprocal molar susceptibility of **1** against the temperature is shown in Fig. 6. The reciprocal molar susceptibility nearly follows the Curie–Weiss law from 2 K to room temper-

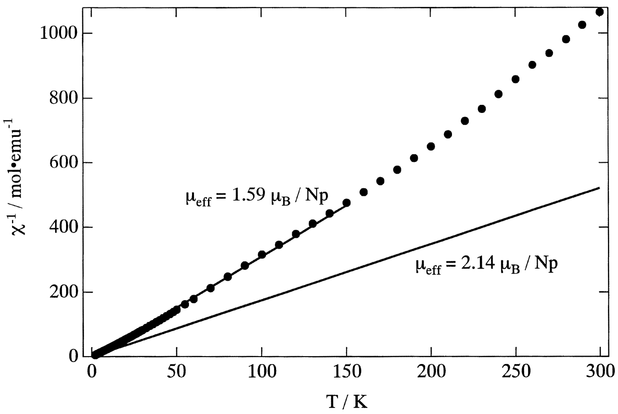

Fig. 6. Plot of the reciprocal molar susceptibility against temperature for the neptunyl(VI) trinitrato complex, $NH_4[NpO_2(NO_3)_3]$ **1** (Experimental: μ_{eff} = 1.59 μ_B/Np, theoretical: μ_{eff} = 2.14 μ_B/Np.).

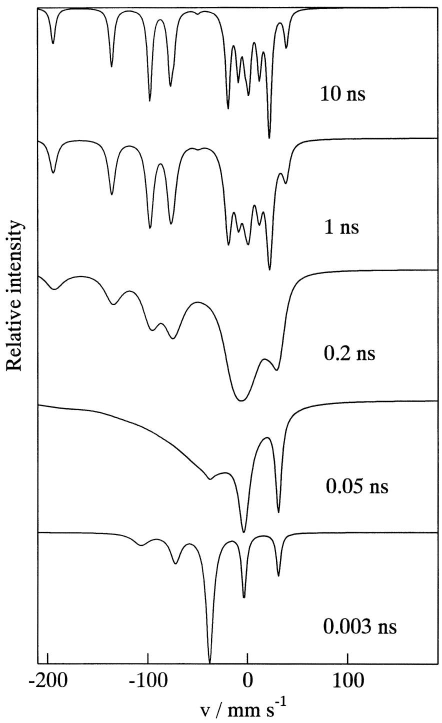

Fig. 7. Simulated ^{237}Np Mössbauer spectra for several relaxation times (τ) with H_{eff} = 290 T, 2Γ = 5 mm s^{-1}, δ = -38 mm s^{-1} and e^2qQ = 230 mm s^{-1}. (H_{eff} // V_{zz}).

ature. The value of the effective magnetic moment (μ_{eff}) was estimated to be $\sim$1.59 μ_B/Np, which is smaller than the theoretical value (2.14 μ_B/Np) of $Np^{6+}(5f^1)$.

These SQUID data and the ^{237}Np Mössbauer spectra indicate that **1** is paramagnetic down to 2 K. The magnetic hyperfine splittings observed in **1** and **2**'s Mössbauer spectra are due to slow paramagnetic relaxation, as reported by Dunlap et al.[1,11]

As shown in Fig. 7, we have simulated the ^{237}Np Mössbauer spectra for several relaxation times (τ) with H_{eff} = 290 T, 2Γ = 5 mm s^{-1}, δ = -38 mm s^{-1} and e^2qQ = 230 mm s^{-1}, being based on the paramagnetic relaxation model[17]; 2Γ represents the line-width. According to a simulation of the relaxation spectra, the ^{237}Np Mössbauer spectra of **1** and **2** are similar to the modulation that the τ are longer than about 1 ns. The simulation also insists that the magnetic hyperfine splittings of **1** and **2** are due to slow paramagnetic relaxation. It should be noted that Dunlap has discussed a hyperfine interaction which contains H_x, H_y and H_z in the Hamiltonian.[1,11]

The ^{237}Np Mössbauer spectra of freshly prepared **3** at 4.5 K, 10 K and 30 K have also shown magnetic hyperfine splittings, as reported by Stone and Pillinger, who might not consider relaxation.[10] The spectra of **1**, **2** and **3** suggest that the relaxation times of **1**, **2** and **3** are of the same order.

As listed in Table 4, the δ and e^2qQ values of **1** and **2** are the same as that of **3** within the experimental error, respectively. The δ values are typical for Np(VI) compounds. It is well known that there is a linear relationship between the δ values and the mean Np–O bond distances for the Np(VI) compounds.[2] In the present study, almost the same Np–O bond distances of **1**, **2** and **3** exhibit almost the same δ values. This is consistent with the linear relationship between the δ values and the mean Np–O bond distances established for the neptunyl(VI) compounds.

Conclusion

The results of ^{237}Np Mössbauer spectroscopy and a magnetization measurement indicate that the magnetic hyperfine splittings of **1** and **2** observed in their ^{237}Np Mössbauer spectra are due to slow paramagnetic relaxation. The δ values and e^2qQ values of **1** and **2** are the same as those of **3** within the experimental error, respectively. The Rietveld analyses of **1** and **2** indicate that the mean bond distances, Np–O, of **1**, **2** and **3** are very close to one another. As for **1**, **2** and **3**, the relationship between the mean Np–O bond distances and the ^{237}Np Mössbauer δ values has been reconfirmed. The ^{237}Np Mössbauer parameters suggest that the environments around Np(VI) of **1** and **2** are similar to those of **3**. The influences of the different M cations to the environments around Np(VI) are relatively small for the neptunyl(VI) trinitrato complexes.

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