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Coordination chemistry of neptunyl(V) compounds by means of Mössbauer spectroscopy

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Abstract

Five neptunyl(V) compounds were synthesized and studied by ^{237}Np Mössbauer spectroscopy. The isomer shifts (δ) of the Mössbauer spectra ranged from -18.6 to -19.0 mm s^{-1} for the compounds with Np atoms surrounded by seven oxygen atoms. Interlaced two sets of hyperfine splitting were observed in the spectra for the acetate and the benzoate, δ's of one set with larger magnetic splitting were -19.4 and -19.5 mm s^{-1}, respectively, but those of the other set with smaller magnetic splitting were -13.2 and -10.8 mm s^{-1}, respectively. From the comparison of the present results with those reported on neptunyl(V) and (VI) compounds, it is concluded that there are two neptunium sites in the acetate and the benzoate in their structure, one is the site with the coordination number (CN) of 7 and the other is that with CN of 8. © 1998 Elsevier Science S.A.

Keywords: Mössbauer spectroscopy; Neptunyl(V) compounds; Isomer shift; Coordination number; Two Np sites; Carboxylates

1. Introduction

Neptunium exhibits five oxidation states from III to VII both in aqueous solution and in the solid state. Among the oxidation states, the pentavalent state is the most stable in aqueous solution under the atmospheric condition. The chemical form is NpO_2^+ and it behaves apparently as +1 state in an aqueous solution. As a result, its salt is usually difficult to precipitate from the solution. On the other hand, the specific interaction of neptunyl(V) ions with highly charged cation including actinyl ions, such as UO_2^{2+}, has been well known since 1961 [1]. This is called 'cation–cation interaction'. The interaction is now popular but is known only in aqueous solutions till recently. Cousson et al. firstly found the evidence of such interaction in the solid state, that is, neptunyl(V) ion dimers in the lattice of neptunyl(V) benzenehexacarboxylate (mellitate) [2]. After their study, the synthesis of many kinds of neptunyl(V) compounds have been investigated [3–10]. Some of their structure have been analyzed by single crystal X-ray crystallography [4,5,8]. But little studies were published on the pentavalent compounds by Mössbauer spectroscopy [11]. In this report, we synthesized five neptunyl(V) compounds and studied by Mössbauer spectroscopy in order to discuss the coordination of oxygen atoms in the equatorial plane of the neptunyl(V) ion.

2. Experimental

For the preparation of neptunium(V) stock solution, NpO_2 was dissolved in concentrated nitric acid under slightly boiling condition. The obtained neptunium(VI) solutions were evaporated to wet salt, which was dissolved in water. From the solution after adding of excess $NaNO_2$, neptunyl(V) hydroxide was precipitated using NH_4OH. The NpO_2OH precipitate was separated from the mother solution by vacuum filtration, washed by water and dissolved in 0.5 M HNO_3 without excess acid. The obtained practically neutral neptunyl(V) nitrate solutions were used as the stock solution.

The compounds were prepared by literature methods as following. The malonate, $(NpO_2)_2C_3H_2O_4{\cdot}4H_2O$ [3,4]: This compound was crystallized at room temperature from a solution formed by dissolving freshly precipitated neptunyl(V) hydroxide into a small excess malonic acid solution. The formate, $NpO_2OOCH{\cdot}H_2O$ [5,6]: The solutions of 0.4 ml 4 M NH_4OOCH and 0.3 ml 2 M HCOOH were added to 5 ml of about 0.12 M neptunyl(V) nitrate solution. The mixture stood for 3 hours on a boiling water

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bath, until precipitates appeared. The glycolate, $NpO_2OOCCH_2OH{\cdot}H_2O$ [7,8]: This compound was synthesized by dissolving freshly precipitated neptunyl(V) hydroxide into a small excess glycolic acid solution followed by evaporation of the solution until green crystals formed. The acetate, $NpO_2OOCCH_3{\cdot}H_2O$ [9]: This compound was prepared by two ways. Method-1 was that freshly precipitated neptunyl(V) hydroxide was dissolved into an excess amount of glacial acetic acid, and slowly formed precipitates were filtered from the mother liquor. Method-2 was that a small excess quantity of $NaOOCH_3$ was added to a solution of neptunium(V) after the pH was adjusted to 4–5 with NH_4OH, and formed crystalline was filtered. The benzoate, $NpO_2OOCC_6H_5{\cdot}4H_2O$ [10]: It was prepared that a small excess quantity of $NH_4OOCC_6H_5$ was added to a solution of neptunium(V) after the pH was adjusted to 4–5 with NH_4OH, formed precipitates were filtered.

The identification of the formed compounds was made by comparison of the X-ray diffraction pattern with the reported one. The X-ray powder diffraction patterns were obtained using a diffractometer, model RAD-3C (Rigaku Co., Cu K_α radiation). Mössbauer spectra were measured in a cryostat equipped with a driving system (WissEl GmbH, System MS II) [12]. An assembled ^{241}Am metal source was used [13]. The Doppler motion of the source was sinusoidal.

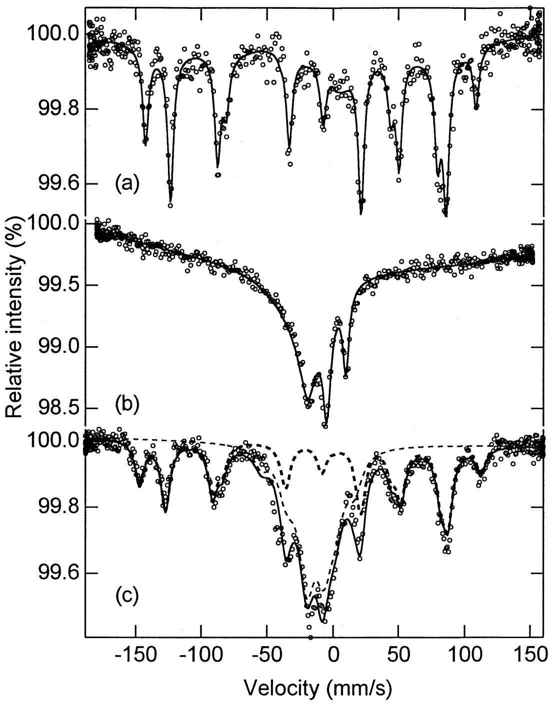

Fig. 1. Representative Mössbauer spectra of neptunyl(V) compounds. (a) $(NpO_2)_2C_3H_2O_4{\cdot}4H_2O$ (the malonate), (b) $NpO_2OOCCH_2OH{\cdot}H_2O$ (the glycolate), (c) $NpO_2OOCCH_3{\cdot}H_2O$ (the acetate). The solid lines through data points in (a) and (b) show the least-squares fitting. In (c), thick and thin broken lines and solid line show the least-squares fitted site-1 and site-2 and sum of them, respectively.

3. Results and discussion

The Mössbauer spectra were measured at various temperatures for all compounds synthesized. In Fig. 1, representative spectra are shown for some compounds, which are obtained at the lowest temperature studied for the compounds. The parameters of the Mössbauer spectra for all compounds are summarized in Table 1.

For the malonate at 4.6 K, the spectrum displayed only one set of large magnetic splitting as seen in Fig. 1 a. The spectra were changed gradually with the temperature. It is identified that this alternation of the spectra was due to the paramagnetic relaxation effects. For the formate, the spectra obtained in the range of temperature studied consisted of only one set of large hyperfine splitting. The details will be reported elsewhere [14]. For the glycolate, the spectrum even at 5.3 K (the lowest temperature studied) showed a magnetic relaxation, which is shown in Fig. 1 b. The spectra were analyzed by a newly developed method, which will be published separately [15].

The structure of the malonate, the formate and the glycolate is known by X-ray crystallography. In neptunyl(V) compounds, pentagonal bipyramid is the most common structure and these three compounds are the cases. That is, each Np atom exists as a linear $(O\text{–}Np\text{–}O)^+$ ion with five secondary oxygen atoms coordinating to it in a perpendicular plane. As shown in Table 1, their isomer shifts were spread in a short range from -18.6 to -19.0 mm s^{-1}.

It has been reported that two nonequivalent types of neptunyl(V) ions exist in a 1 to 1 ratio in the structure of the malonate [4]. However, from a viewpoint of Np itself, it is always surrounded by two nearest oxygen neighbors and by five second oxygen neighbors in the equatorial plane. This means that Np atom exists in similar situation of coordination number 7 in this compound. Thus, this small difference from the environment of Np atom was undetected by Mössbauer spectroscopy.

On the other hand, the acetate and the benzoate showed completely different feature in the spectra. The spectrum of the acetate is shown in Fig. 1 c. Interlaced two sets of hyperfine splitting were observed in the spectrum of this compound. As mentioned in experimental section, the compound was prepared by completely different two methods. However, we had very similar spectra from two products. Thus, it seems that these compounds have two sites of neptunyl(V) ions from these spectra. Both isomer shifts of site-1 and site-2 stay constant within experimental error at -19.4 (site-1) and -13.2 mm s^{-1} (site-2), respectively, for the span of temperature studied. The internal magnetic fields of two sites had no temperature dependence, and the magnitude were about 525 T for site-1 and about 50 T for site-2. The results are shown in Fig. 2. The intensity ratio of two sites [site-1/(site-1+site-2)] stayed

Table 1
Mössbauer parameters of neptunyl(V) compounds measured at the lowest temperature in the present experiments

Compound	Isomer shift[a] mm s^{-1}	B_{eff} T	e^2qQ mm s^{-1}	Temperature K
Malonate	−18.6±0.1	506±0.4	85.5±0.5	4.6
Formate	−18.9±0.1	555±0.5	88.5±0.6	4.3
Glycolate	−19.0±0.2	(550)[b]	96.0±0.8	5.3
Acetate, Site-1	−19.4±0.2	525±2	83.7±1.2	5.3
Acetate, Site-2	−13.2±0.4	50±3	83.7±1.2	5.3
Benzoate, Site-1	−19.5±0.4	481±2	78.9±2.4	4.5
Benzoate, Site-2	−10.8±0.8	110±2	78.1±3.0	4.5

[a] Isomer shift with respect to $NpAl_2$.
[b] See reference [15].

constant for full range studied, as shown in Fig. 3. All observation as a whole showed that two sites were independent in the compound.

The recoilless fraction of the benzoate was small even at the lowest temperature studied. We obtained poor quality spectra for this compound. However, careful analysis showed similar results to those from the acetate. There were two sites in the spectrum, and the isomer shifts were −19.5 for site-1 and −10.8 mm s^{-1} for site-2, respectively. The internal magnetic fields were greatly separated each other as also shown in Fig. 2. The magnitude was about 480 T for site-1 and about 110 T for site-2. The intensity ratio of two sites was slightly different from the case of the acetate, that was not 1 to 1 ratio but probably 3 to 2 ratio as also shown in Fig. 3.

Unfortunately, the single-crystal X-ray structure of the acetate and the benzoate has been unknown. From extensive studies by electronic absorption spectra (EAS), it has been confirmed that all neptunyl(V) compounds with pentagonal bipyramidal oxygen environment of Np atom show a narrow intensive peaks in wavelength interval between 950 and 1050 nm like hydrated NpO_2^+ ions in solutions [16]. It was reported that EAS of the acetate and the benzoate showed the peaks [10,17]. Thus, pentagonal bipyramidal structure must exist in the compounds. However, in those reports it was reported that anomalously high shift of the band for the benzoate compared with that in aqueous solutions was not unambiguously explained and the absorption coefficients were comparatively small. This shows a possibility to exist another kind crystallographical site.

Fig. 4 shows the summary of isomer shifts in neptunyl(V) compounds. The isomer shifts of site-1 in the acetate and the benzoate are very close to those of the compounds with CN 7. The values of isomer shifts of site-2 in the compounds are close to each other but are far apart from site-1. We synthesized $NH_4NpO_2(CHOO)_2$ and measured the Mössbauer spectrum. The Np atom is surrounded by eight oxygen atoms in the form of a hexagonal bipyramid. The isomer shift was −15.8±0.6

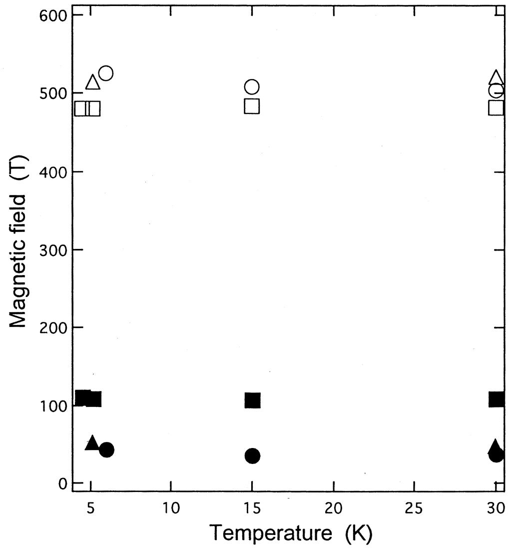

Fig. 2. Internal magnetic field of two Np atom sites in the acetate and the benzoate. Site-1: Acetate, Method-1: ○, Method-2: △; Benzoate:□. Site-2: Acetate, Method-1: ●, Method-2: ▲; Benzoate: ■.

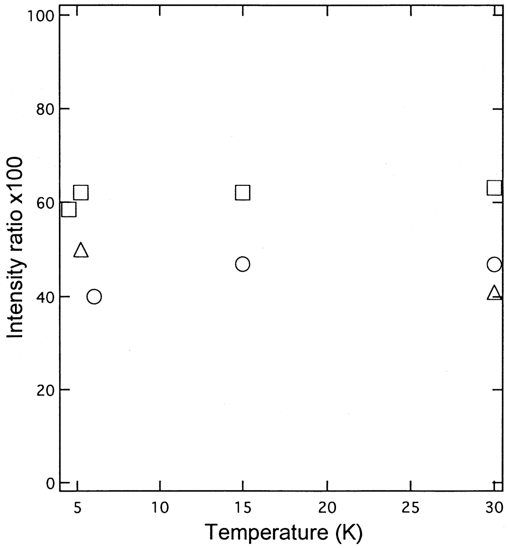

Fig. 3. Intensity ratio of two sites [site-1/(site-1+site-2)] in the acetate and the benzoate. Acetate, Method-1: ○, Method-2: △; Benzoate: □.

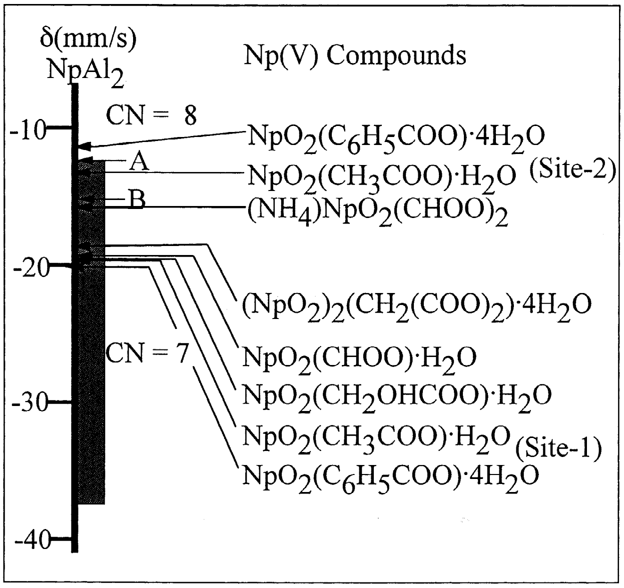

Fig. 4. Summary of isomer shifts in neptunyl(V) and (VI) compounds.

$\mathrm{mm\,s^{-1}}$ and also shown in Fig. 4 [14]. In the figure, reported isomer shifts were shown for neptunyl(V) compounds which have eightfold coordination, that is, -15 $\mathrm{mm\,s^{-1}}$ for $NH_4(NpO_2)F_2$ (Fig. 4 B) and -12 $\mathrm{mm\,s^{-1}}$ for $K(NpO_2)CO_3$ (Fig. 4 A) [18]. These values are close to those of site-2.

Thus, it can be concluded that the CN of site-2 is 8 similar to the case of the complex neptunyl(V) acetate [19] or the neptunyl(V) nitrate [20], and there are two crystallographically independent neptunium atoms exist in the acetate and the benzoate. This conclusion is further supported by one experimental evidence, which in neptunyl(VI) compounds the isomer shift increases with CN of Np atoms as reported in the reference [11].

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