H$_2$baen·2B, 63832-98-4; H$_2$baen·2C, 63848-88-4; Ni(baen), 36802-27-4; Cu(baen), 36885-37-7; A, 4083-64-1; B, 1972-28-7; C, 762-42-5; ^{13}C, 14762-74-4.

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Mössbauer Spectra of Np(V)–Cr(III) and Np(V)–Rh(III) Complexes[1]

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The aqueous Np(V) ion forms weak complexes with a number of trivalent cations;[2] however, the Np(V) ion forms particularly stable complexes with Cr(III)[3a] and Rh(III)[3b] ions. The Np(V)–Cr(III) and Np(V)–Rh(III) complexes can be separated from the remaining uncomplexed ions by ion exchange.[3a] The suggested structure for these complexes involves substituting the NpO$_2^+$ ion for a water molecule in the first coordination sphere of the hexaaquochromium(III) and hexaaquorhodium(III) ions. The Np(V) ion is believed to enter the coordination sphere axially and is coordinated through an oxygen atom to the Cr(III) or Rh(III) ion. Normally, the linear NpO$_2^+$ ion coordinates around its equator, so the axial coordination of these complexes presents an unusual environment for the Np(V) ion. This paper reports a study of the Np(V) in the Cr(III) and Rh(III) complexes by Mössbauer spectroscopy. Because Cr(III) is paramagnetic (3d^3, high spin) and Rh(III) diamagnetic (4d^6, spin = 0), a contrast in magnetic effects is also expected.

Experimental Section

NpO$_2$ was dissolved in hot 6 M HNO$_3$, and the resulting ^{237}Np concentration was assayed radiometrically. The Np(V):Np(VI) ratio was then determined spectrophotometrically. Np(VI) was reduced to Np(V) by adding the calculated amount of KI, and the solution was filtered to remove precipitated iodine. Neptunium(V) hydroxide was then precipitated by adding aqueous ammonia. The hydroxide
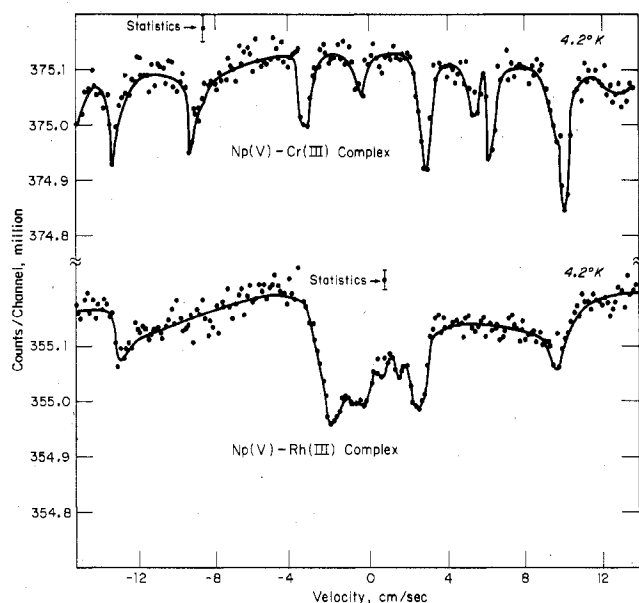

Figure 1. Mössbauer spectra of Np(V)–Cr(III) and Np(V)–Rh(III) complexes.

was filtered and washed until free of ammonia and dissolved in 1 M HClO$_4$ to yield the Np(V) stock solution.

Solid Rh(H$_2$O)$_6$(ClO$_4$)$_3$ was prepared for the Np(V)–Rh(III) complex by fuming rhodium trichloride (Research Organic/Inorganic Chemical Corp.) in concentrated perchloric acid.[4] Chromium chloride (Fisher Chemical Co.) was dissolved in water, and the solution was allowed to stand at room temperature for 1 week. The mixture of chromium(III) hydroxides was then precipitated with NaOH, and the hydroxides were washed with water and dissolved in a minimum volume of 3 M HClO$_4$ to produce a perchlorate solution of mixed Cr(H$_2$O)$_6^{3+}$, Cr(H$_2$O)$_5$Cl^{2+}, and Cr(H$_2$O)$_4$Cl$_2^+$ ions.

The Np(V)–Rh(III) complex was prepared[3b] by dissolving an approximately equimolar amount of solid Rh(H$_2$O)$_6$(ClO$_4$)$_3$ in a solution of Np(V) and by allowing the resulting solution to stand at room temperature for 2 weeks.[3b] The Np(V)–Cr(III) complex was prepared by adding the solution of mixed Cr(III) cations to an Np(V) solution, and the mixture was allowed to stand 2 weeks.

Absorption spectra of these solutions with a Cary 14 spectrophotometer showed the Np(V)–Rh(III) solution had about 50% of the Np(V) as the Np(V)–Rh(III) complex. The Np(V)–Cr(III) solution showed about 30% of the Np as the Np(V)–Cr(III) complex. No Np(IV) or Np(VI) species were detected in the spectra.

Mössbauer spectra of the complexes were then determined from the complexes absorbed on Dowex[5] 50 cation-exchange resin. Dowex 50 resin, either 2 or 4% cross-linked, 100–200 mesh, was graded to remove fines and was then washed with concentrated HCl, water, and 2 M HClO$_4$. After the resin was washed with 2 M HClO$_4$, it was again washed with water and then packed in a 6-mm-diameter × 3-cm glass column. A solution containing either the Np(V)–Rh(III) or Np(V)–Cr(III) complex was passed through the column and eluted with 2 M HClO$_4$ to remove Np(V) and Rh(III) or Cr(III) from the resin. More of the solution of the complexes was then passed through the column and Np(V) and Rh(III) were again eluted until the resin was saturated with the Np(V)–Rh(III) or Np(V)–Cr(III) complex. The resin was forced from the column mechanically, and excess solution was removed by a vacuum on a Büchner funnel. The resin was then packed tightly in a plastic holder which was sealed for Mössbauer measurements, as previously performed.[6]

Results and Discussion

The Mössbauer spectra measured at 4.2 K of the Np(V)–Cr(III) and Np(V)–Rh(III) complexes absorbed on Dowex 50 cation-exchange resin are shown in Figure 1. (The curves in these spectra were not computer fits.) The spectrum of the Np(V)–Cr(III) complex has the major features of a spectrum combining large magnetic and small quadrupole splitting, similar to that of neptunium(V) oxalate,[7] with some weak satellite lines. These weak satellite lines suggest a minor

fraction of the Np(V) ions are in a different site. The hyperfine splitting is quite large—one line at the negative extreme of the spectrum is beyond the range of the Mössbauer drive. The Mössbauer parameters of the major resonances are the magnetic hyperfine constant ($g_0\mu_N H_{eff}$ = 9.91 ± 0.29 cm/s), the quadrupole coupling constant ($^1/_4 eqQ$ = 2.9 ± 0.9 cm/s), and the isomer shift (relative to NpAl$_2$) (1.69 ± 0.21 cm/s). These values are consistent with other Np(V) compounds with magnetic hyperfine splitting at 4.2 K, such as neptunium(V) hydroxide[6] and neptunium(V) oxalate,[7] and indicate nothing unusual for the Mössbauer spectrum of the Np(V)–Cr(III) complex.

The spectrum of the Np(V)–Rh(III) complex does not correspond to any simple pattern. The resonances at −13 and +9.7 cm/s correspond to the strongest lines of magnetic hyperfine structure. From the intensity of these resonances, they represent only a minor fraction of the total neptunium. The Mössbauer parameters derived from these resonances are $g_0\mu_N H_{eff}$ = 9.9 ± 0.2 cm/s and δ = 1.7 ± 0.2 cm/s. The isomer shift value is in the proper range for a Np(V) species.

The strong resonance in the center of the spectrum of the Np(V)–Rh(III) complex represents the major fraction of the Np(V) present. This resonance is interpreted as being dominated by quadrupole splitting and is complicated by intermediate relaxation effects. In the fast relaxation limit, a spectrum collapses to a single resonance or a quadrupole-split resonance; at long relaxation times, the spectrum is magnetically split. Intermediate relaxation times produced broadened resonances,[7] and since the relaxation processes often have different rates in different directions along the lattice of a solid, an extremely strange spectrum can result. An important difference occurs between the spectra of the Np(V)–Cr(III) complex and the Np(V)–Rh(III) complex: the spectrum of the Np(V) ion in the Cr(III) complex is magnetically split; the spectrum of the Np(V) ion in the Rh(III) complex is not split.

The magnetic splitting in the Mössbauer spectrum of the Np(V)–Cr(III) complex and the lack of magnetic splitting for the major fraction of the Np(V)–Rh(III) complex are consistent with the suggested structure[3] of these complexes and the magnetic properties of the Cr(III) and Rh(III) ions. The complexes are formed by slowly replacing a water molecule in the first coordination sphere of Cr(III) or Rh(III) with the neptunyl ion NpO$_2$$^+$. The Cr(III) or Rh(III) coordinates to the Np(V) ion through one of the Np(V) oxygen atoms. Thus, the NpO$_2$$^+$ ion presumably retains its axial symmetry, but the electrostatic field on the Np(V) ion is distorted by the Cr(III) or Rh(III) ion. The field from the strongly paramagnetic Cr(III) ion (3d^3, high spin) induces magnetic splitting in the Mössbauer spectrum of the Np(V)–Cr(III) complex, but no splitting is induced by the diamagnetic Rh(III) ion (4d^6, spin = 0).

The cation-exchange resin was assumed to have little influence on the environment of the complexes or the complex ions held on the resin primarily by an ion-pair association. However, this assumption probably underestimates the possibilities that some resin sites may enter the coordination sphere of the transition metal ion or that the protons held on resin sites near the complex may influence the field on the Np(V) ion. Presumably, the magnetically split structure in the Np(V)–Rh(III) spectrum may arise through an effect of this nature.

Registry No. NpO$_2$$^+$, 21057-99-8; Rh(H$_2$O)$_6$$^{3+}$, 16920-31-3; Cr(H$_2$O)$_6$$^{3+}$, 14873-01-9.

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Conversion of Hydrous Germanium(II) Oxide to Germynyl Sesquioxide, (HGe)$_2$O$_3$

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Germanium(II) hydroxide (hydrous germanium(II) oxide) is a white, yellow, or brown noncrystalline material, only slightly soluble in water and alkaline solutions, having no definite stoichiometry, and represented by formulas such as GeO·xH$_2$O, Ge(OH)$_2$·xH$_2$O, and, loosely, Ge(OH)$_2$.[1-4] We have found that digestion of a suspension of either yellow or brown germanium(II) hydroxide in aqueous sodium hydroxide solutions yields a dark brown insoluble compound which has properties distinctly different from those of the starting hydroxide. The compound, after being thoroughly washed and dried in vacuo at room temperature, is a dark brown pyrophoric powder with a composition close to (HGe)$_2$O$_3$. The empirical formula and properties of the compound suggest that it is a polymer consisting of Ge–H groups linked by oxygen atoms, i.e., "germynyl sesquioxide."[5-7]

Vibrational Spectra. Infrared spectra indicate that (HGe)$_2$O$_3$ is structurally different from various forms of germanium(II) hydroxide which have not been treated with hydroxide solutions. Figure 1 shows the pertinent regions of Nujol and halocarbon mull spectra of germanium(II) hydroxide samples that were subjected to the various treatments outlined in Table I. The bands near 3300 and 1650 cm^{-1} which appear in some spectra (especially those of samples B and C) are undoubtedly due to water.[8] These bands were very prominent in the spectrum (not shown) of a sample which had been purposely dried less thoroughly than the other samples. Samples B and C (which had not been treated with hydroxide) showed broad absorptions in the regions of 800 and 540 cm^{-1}, in agreement with a spectrum earlier reported for Ge(OH)$_2$.[3]

The bands near 2000, 835, and 760 cm^{-1}, which appear in the spectra of the samples treated with hydroxide (D, E, and F), are characteristic of Ge–H stretching,[9] vibrations of a germanium–oxygen network of the type[7]

$$
\begin{array}{c}
\diagup O- \\
-Ge-O- \\
\diagdown O-
\end{array}
$$

and Ge–H deformation,[9] respectively. It is significant that sample E (which was briefly washed with acid after the hydroxide treatment) had an infrared spectrum essentially the same as those of samples D and F. This result shows that (HGe)$_2$O$_3$ is not rapidly reconverted to Ge(OH)$_2$ by treatment with acid. Samples B and C, which were not treated with hydroxide, were brown and yet showed none of the distinctive absorptions characteristic of (HGe)$_2$O$_3$. This result shows that