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MÖSSBAUER SPECTRA OF Np(V)-Cr(III) AND
Np(V)-Rh(III) COMPLEXES

by

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MÖSSBAUER SPECTRA OF Np(V)-Cr(III) AND
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ABSTRACT

The Mössbauer spectra of complexes between Np(V) and Cr(III) or Rh(III) ions absorbed on cation exchange resin were measured at 4.2°K with a constant acceleration Mössbauer spectrometer. The spectrum of the Np(V)-Cr(III) complex showed a strong magnetic splitting with Mössbauer parameters of $g_o \mu_N H_{eff} = 9.91$ cm/sec, $1/4 eqQ = -2.9$ cm/sec, and $\delta = 1.69$ cm/sec. The spectrum of the Np(V)-Rh(III) complex was dominated by quadrupole splitting with a minor fraction showing magnetic hyperfine structure. The results of these measurements are consistent with the suggested structure of the complexes - substituting NpO_2^+ in the transition metal ion coordination sphere - and the magnetic properties of paramagnetic Cr(III) ion ($3d^3$, high spin) and diamagnetic Rh(III) ion ($4d^6$, spin = 0).

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Introduction

The aqueous Np(V) ion forms weak complexes with a number of trivalent cations;¹ however, the Np(V) ion forms particularly stable complexes with Cr(III)² and Rh(III)³ ions. The Np(V)-Cr(III) and Np(V)-Rh(III) complexes can be separated from the remaining uncomplexed ions by ion exchange.^{2,3} The suggested structure for these complexes involves substituting the NpO_2^+ ion for a water molecule in the first coordination sphere of the hexaaquo Cr(III) and Rh(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 present 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 6M 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. Np(V) hydroxide was then precipitated by adding aqueous ammonia. The hydroxide was filtered and washed until free of ammonia and dissolved in 1M HClO_4 to yield the Np(V) stock solution.

Solid $\text{Rh}(\text{H}_2\text{O})_6(\text{ClO}_4)_3$ was prepared for the $\text{Np}(\text{V})$ - $\text{Rh}(\text{III})$ 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 a week. The mixture of $\text{Cr}(\text{III})$ hydroxides were then precipitated with NaOH , and the hydroxides were washed with water and dissolved in a minimum volume of 3M HClO_4 to produce a perchlorate solution of mixed $\text{Cr}(\text{H}_2\text{O})_6^{+3}$, $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{+2}$, and $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^{+1}$ ions.

The $\text{Np}(\text{V})$ - $\text{Rh}(\text{III})$ complex was prepared³ by dissolving an approximately equimolar amount of solid $\text{Rh}(\text{H}_2\text{O})_6(\text{ClO}_4)_3$ in a solution of $\text{Np}(\text{V})$ and by allowing the resulting solution to stand at room temperature for two weeks.³ The $\text{Np}(\text{V})$ - $\text{Cr}(\text{III})$ complex was prepared by adding the solution of mixed $\text{Cr}(\text{III})$ cations to an $\text{Np}(\text{V})$ solution, and the mixture was allowed to stand two weeks.

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

Mössbauer spectra of the complexes were then determined from the complexes absorbed on *Dowex** 50 cation exchange resin. *Dowex* 50 resin, either 2 or 4% cross-linked, 100 to 200 mesh, was graded to remove fines and was then washed with concentrated HCl , water, and 2M HClO_4 .

* Trademark of Dow Chemical Company.

After the resin was washed with 2M HClO_4 , it was again washed with water and then packed in a 6-mm-diameter \times 3-cm glass column. A solution containing either the $\text{Np(V)}\text{-Rh(III)}$ or $\text{Np(V)}\text{-Cr(III)}$ complex was passed through the column and eluted with 2M 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 $\text{Np(V)}\text{-Rh(III)}$ or $\text{Np(V)}\text{-Cr(III)}$ 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 and sealed for Mössbauer measurements, as previously performed.⁵

Results and Discussion

The Mössbauer spectra measured at 4.2°K of the $\text{Np(V)}\text{-Cr(III)}$ and $\text{Np(V)}\text{-Rh(III)}$ complexes absorbed on *Dowex* 50 cation exchange resin are shown in Figure 1. The spectrum of the $\text{Np(V)}\text{-Cr(III)}$ complex has the major features of a spectrum combining large magnetic and small quadrupole splitting, similar to Np(V) oxalate,⁶ 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 magnetic hyperfine constant $g_{\text{O}}\mu_{\text{N}}H_{\text{eff}} = 9.91 \pm 0.29$ cm/sec; quadrupole coupling constant $1/4 \text{ eqQ} = 2.9 \pm 0.9$ cm/sec; the isomer shift (relative to

NpAl_2) = 1.69 ± 0.21 cm/sec. These values are consistent with other Np(V) compounds with magnetic hyperfine splitting at 4.2°K, such as Np(V) hydroxide⁵ and Np(V) oxalate,⁶ 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/sec 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 $g_{\text{eff}} \mu_{\text{N}}^{\text{H}} = 9.9 \pm 0.2$ cm/sec and $\delta = 1.7 \pm 0.2$ cm/sec. 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 Np(V) ion in the Cr(III) complex is magnetically split; 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 is consistent with the suggested structure^{1,2,3} 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).

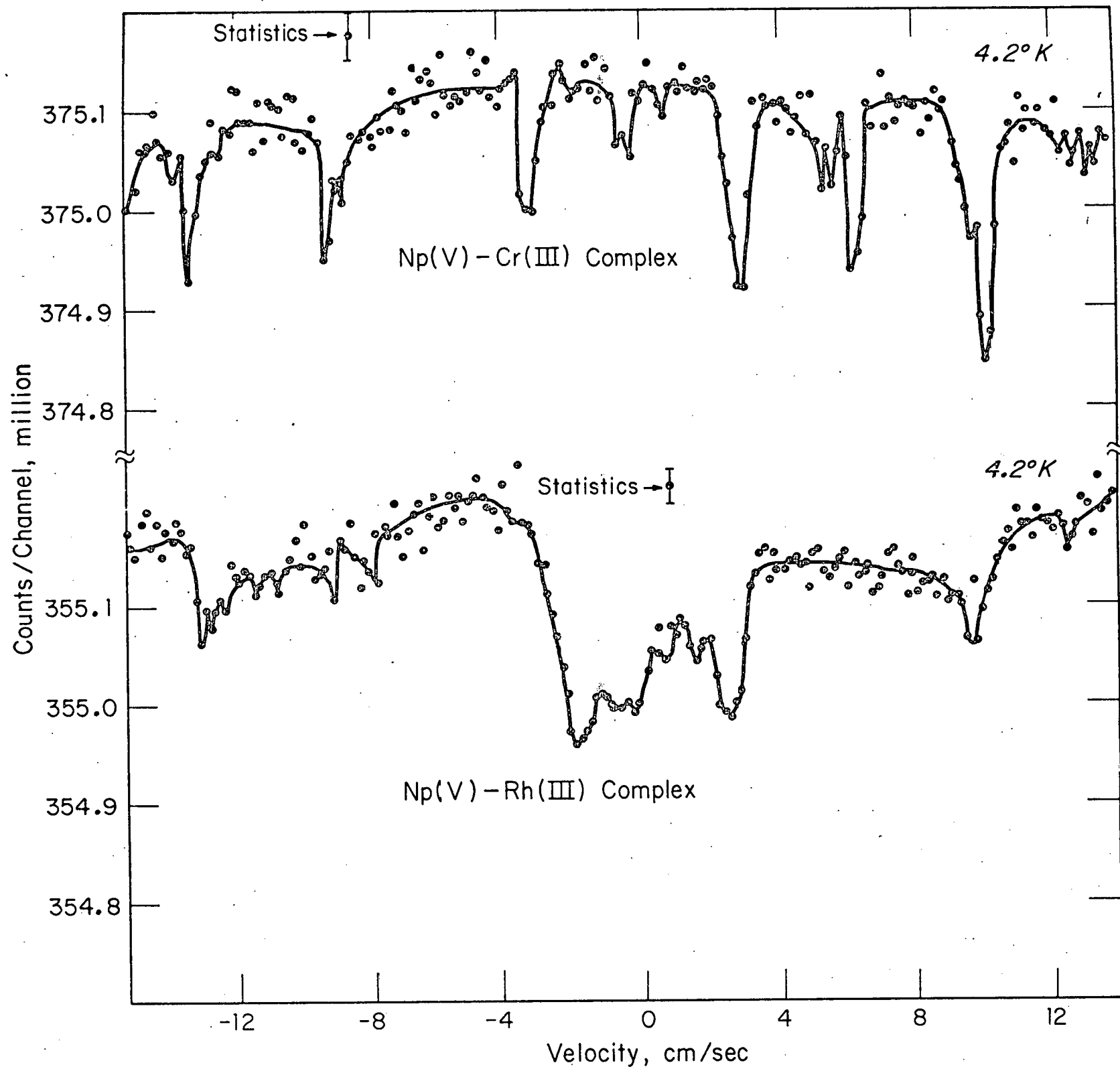
The cation exchange resin was assumed to have little influence on the environment of the complexes, or the complex ions held on the resin primarily by an ion-pair association. However, this assumption probably underestimates the possibilities that some resin sites may enter the coordination sphere of 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.

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

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



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