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# CHEMICAL ASPECTS OF $^{237}Np$ MÖSSBAUER SPECTROSCOPY

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# CHEMICAL ASPECTS OF $^{237}$Np MÖSSBAUER SPECTROSCOPY

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## INTRODUCTION

The $^{237}$Np Mössbauer effect has been especially useful in studies of neptunium chemistry, by virtue of its excellent resolution and straightforward experimental techniques. Neptunium can have valences from +3 to +7, and a broad range of compounds can be prepared that are analogous to those of other actinide elements. Studies on neptunium compounds, for example, have a ready application to the analogous compounds of uranium and plutonium. The emphasis in this paper will be on the application of the $^{237}$Np Mössbauer effect to problems in neptunium chemistry.

### Description of $^{237}$Np Mössbauer Effect

The Mössbauer effect of $^{237}$Np was discovered by Stone and Pillinger[1] at the Savannah River Laboratory, and the experimental techniques were further developed by G. M. Kalvius and co-workers at the Argonne National Laboratory.[2] The fundamentals of $^{237}$Np Mössbauer spectroscopy have been discussed in three excellent reviews[3-5] and will be reviewed very briefly here.

The gamma ray used for the $^{237}$Np Mössbauer effect results from the 59.5 keV, $5/2^- \rightarrow 5/2^+$ E1 transition in $^{237}$Np, and has a $t_{1/2}$ of 63 ns. The 59.5 keV level is accessible from the α-decay of $^{241}$Am, β-decay of $^{237}$U or the electron-capture decay of $^{237}$Pu. The 433-y $^{241}$Am is the most convenient source, and the minimum line-width is obtained with 5% Am metal alloyed with a cubic thorium metal.[6]

The transitions between the $5/2^-$ excited state and $5/2^+$ ground state of $^{237}Np$ are illustrated in Fig. 1. Both the excited and ground state are split by electric and magnetic fields. Fig. 1 shows the appearance of the spectra for (bottom Fig. 1, left to right) for a quadrupole-split spectrum, an unsplit spectrum, a magnetically-split spectrum, and a spectrum that has a combination of quadrupole and magnetic splitting. Pillinger and Stone[3] have discussed the analysis of $^{237}Np$ Mössbauer spectra.

For chemical effects, the isomer shift is the most useful hyperfine interaction. The isomer shift is determined by the Coulomb interaction of the electrons with the nucleus. The central field interactions that cause the isomer shift are spherically symmetric and result primarily from s orbitals. For neptunium ions, the 6s orbitals are shielded from the nucleus by the inner 5f orbitals (Fig. 2). An increase in the number of 5f electrons increases the shielding and decreases the isomer shift.

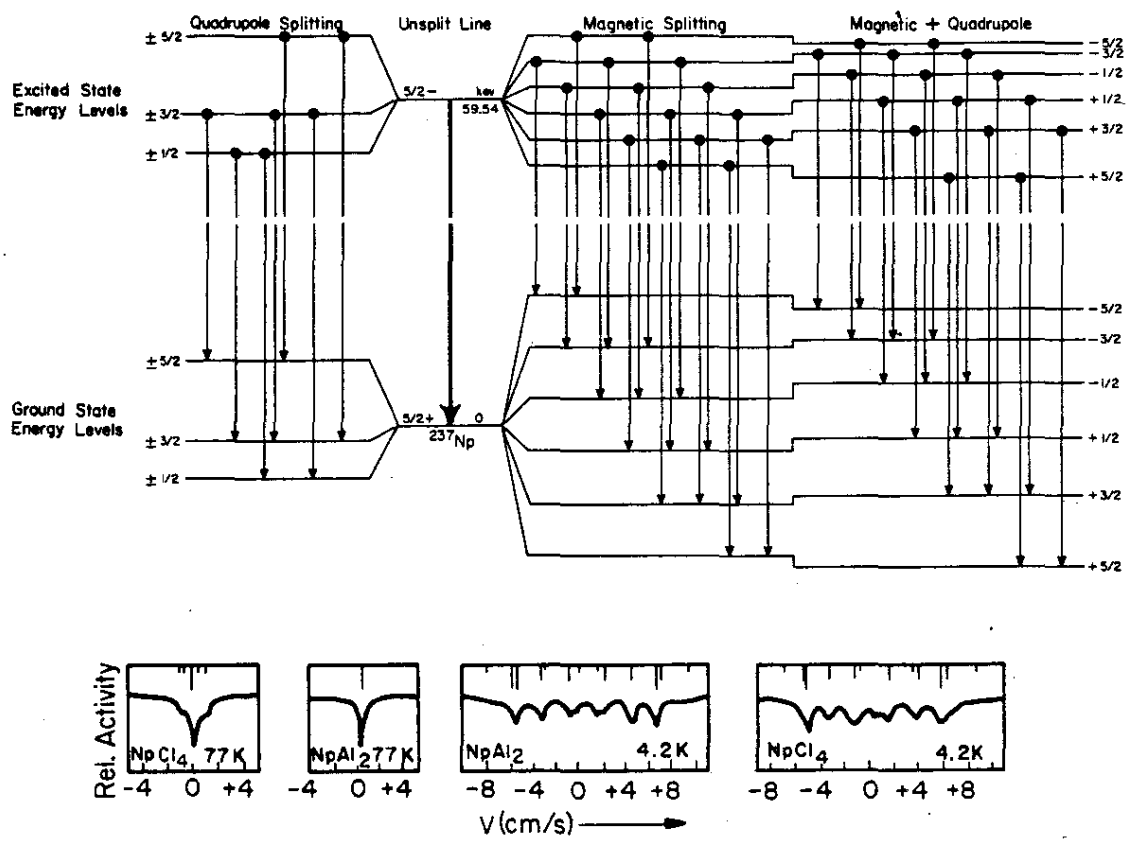


Fig. 1. Splitting of the ground state and 59.5 keV level of $^{237}Np$ in magnetic and electric fields

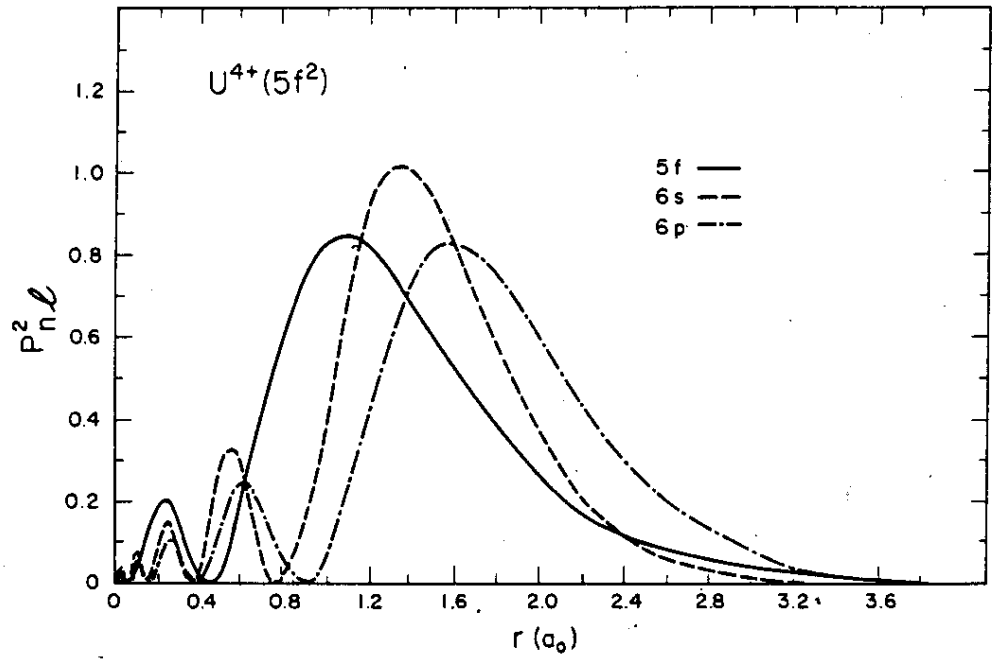


Fig. 2. Radial charge density for $U^{4+}$ ((——) 5f; (---) 6s; (— • —) 6p) (courtesy of N. M. Edelstein, Lawrence Berkeley Laboratory, Berkeley, CA)

The isomer shifts of $^{237}Np$ in its different valences (+3 to +7) cover a range from -6.9 to +3.5 cm/s, and provide an easy identification of the neptunium valence in a neptunium compound. The isomer shifts of the neptunium valence states are shown in Fig. 3 for fluorides and oxides. The Np(VI) and Np(V) isomer shifts for the oxides are more positive than the isomer shifts of the fluoride, because the covalent bonding of the oxygen atoms in the $NpO_2^{2+}$ and $NpO_2^{+}$ contributes electron density to the shielding 5f orbitals.

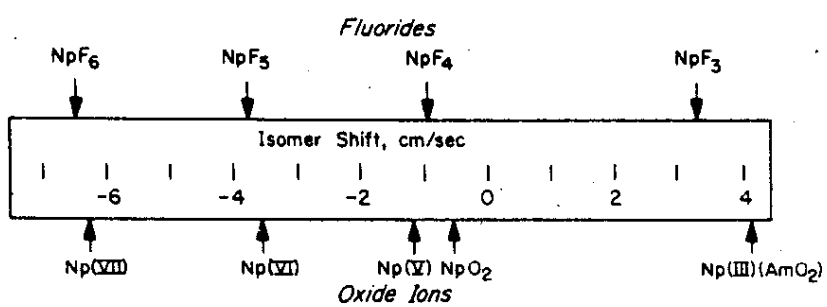


Fig. 3. Isomer shifts of Np fluorides and Np oxide ions

Neptunium(VII)

Russian workers reported the discovery of neptunium (VII) in 1967.[7,8] Solutions containing Np(VII) were prepared by bubbling ozone through a slurry of Np(VI) hydroxide in 3M NaOH. A compound with the hexaminecobalt (III) cation was isolated and analyzed to be $Co(NH_3)_6NpO_5 \cdot xH_2O$. The determination of the valence of neptunium in this compound and in the solutions depended on the stoichiometry of some chemical reactions that were not straightforward, so there was doubt about the existence of Np(VII). To resolve this doubt, Np(VII) solutions and the $Co(NH_3)_6NpO_5 \cdot xH_2O$ were prepared and their Mössbauer spectra measured.[9]

The isomer shift for neptunium in these compounds was in the range -6.5 to -6.8 cm/s, and established beyond question that the Russian workers had discovered Np(VII). (All isomer shifts are relative to $NpAl_2$ = 0. Isomer shifts reported relative to $NpO_2$ have been converted by subtracting 0.53 cm/s from their values.) The Mössbauer spectrum of $Co(NH_3)_6NpO_5 \cdot xH_2O$, shown in Fig. 4, was analyzed as having two nonequivalent Np(VII) ions with the same isomer shift -6.81 cm/s, but different quadrupole splittings (eqQ/4), 2.1 cm/s for the A site, and 3.1 cm/s for the B site.[9] Later studies by Frohlich, et. al.,[10] reported isomer shifts of -6.64 cm/s for Np(VII) in $Co(en)_3NpO_5 \cdot xH_2O$ (eqQ/4 = 2.45 cm/s) and -7.42 cm/s for Np(VII) in $Li_5NpO_6$ (eqQ/4 = 0.85 cm/s).

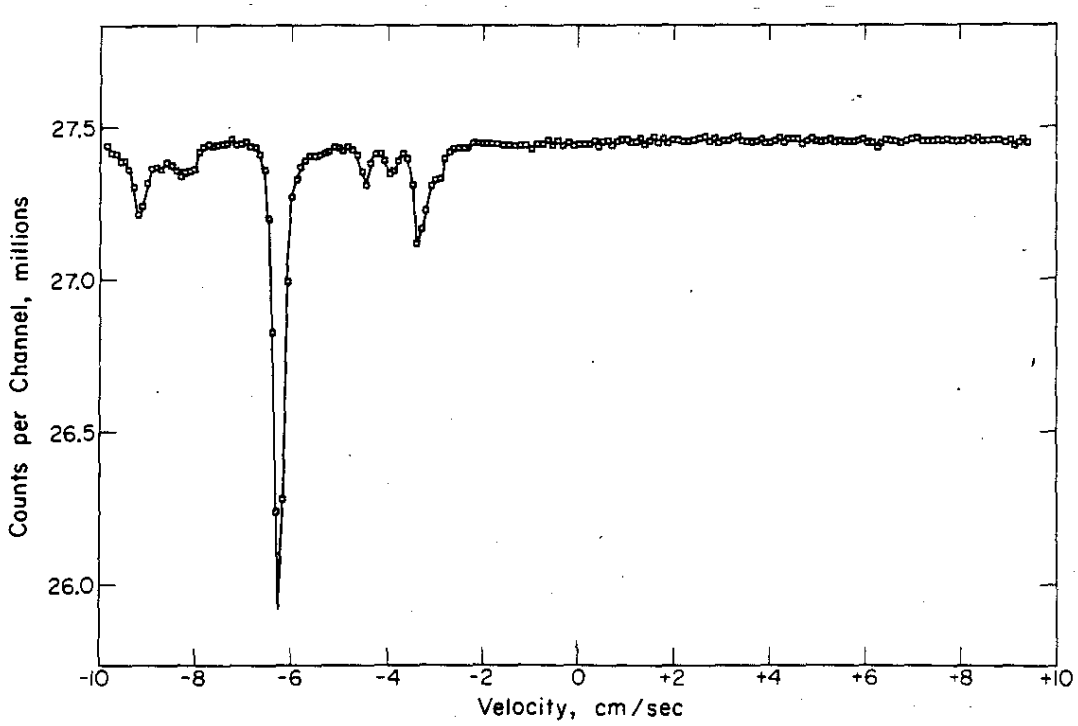


Fig. 4. Mössbauer spectrum of $Co(NH_3)_6NpO_5 \cdot xH_2O$ at 4.2°K

## Proposed $NpOCl_5^{-2}$ Compounds

Virtually all Np(V) compounds prepared in aqueous media have the neptunium as an $NpO_2^+$ ion. The neptunyl (V) ion has an ellipsoidal shape, with the two oxygen ions covalently bonded to the central Np(V) ion. Reported preparations[11] of the compounds $Cs_2NpOCl_5$ and $[(C_6H_5)_4As]_2NpOCl_5$ were quite surprising, since these compounds must have one oxygen and one to three chloride ions bonded to the Np(V) ion. As this would surely be reflected by an unusual Mössbauer spectrum, the Mössbauer spectrum of $[(C_6H_5)_4As]_2NpOCl_5$ was investigated.[12]

The $^{237}Np$ Mössbauer spectrum of $[(C_6H_5)_4As]_2NpOCl_5$ (Fig. 5a) was blurred by intermediate relaxation effects, but the center of gravity of the magnetically split spectrum has an isomer shift that corresponded to a Np(IV) ion, with some extra absorbances added.[12] Comparison of the $[(C_6H_5)_4As]_2NpOCl_5$ spectrum with the spectra of Np(IV) in $(TPAs)_2NpCl_6$ [TPAs = $(C_6H_5)_4As$] (Fig. 5b) and Np(VI) in $(TPAs)_nNpO_2Cl_{n+2}$ (Fig. 5c) showed that the spectrum of $(TPAs)_2NpOCl_5$ could be reproduced by a superposition of the major absorptions from the Np(IV) and Np(VI) compounds, and that the $NpOCl_5^{-2}$ ion was not present in $(TPAs)_2NpOCl_5$. This conclusion was later corroborated by absorption and infrared spectra. Obviously, in the preparation of $(TPAs)_2NpOCl_5$, the $NpO_2^+$ ion had disproportionated in strong HCl, as:

$$4H^+ + 2NpO_2^+ \rightarrow Np^{4+} + NpO_2^{2+} + 2H_2O$$

and the mixed Np(IV) and Np(VI) compounds were precipitated from solution by TPAsCl.

## $Np(C_8H_8)I \cdot xTHF$

$Np(C_8H_8)I \cdot xTHF$ is an unstable compound that could not be characterized by standard measurements but whose preparation was established through $^{237}Np$ Mössbauer spectra.[13] $Np(C_8H_8)I \cdot xTHF$ was prepared as green-brown solid by the reaction of $NpI_3$ and $K_2C_8H_8$ in THF solution at -20°C. The reaction mixture was warmed to room temperature, filtered and the product recovered from the filtrate by vacuum evaporation to a damp-dry solid. Further evaporation caused a color change that was an apparent sign of decomposition. Chemical analysis established that the ratio of I/Np was about 1, but the degree of solvation varied; neither x-ray or absorption spectra yielded any useful results.

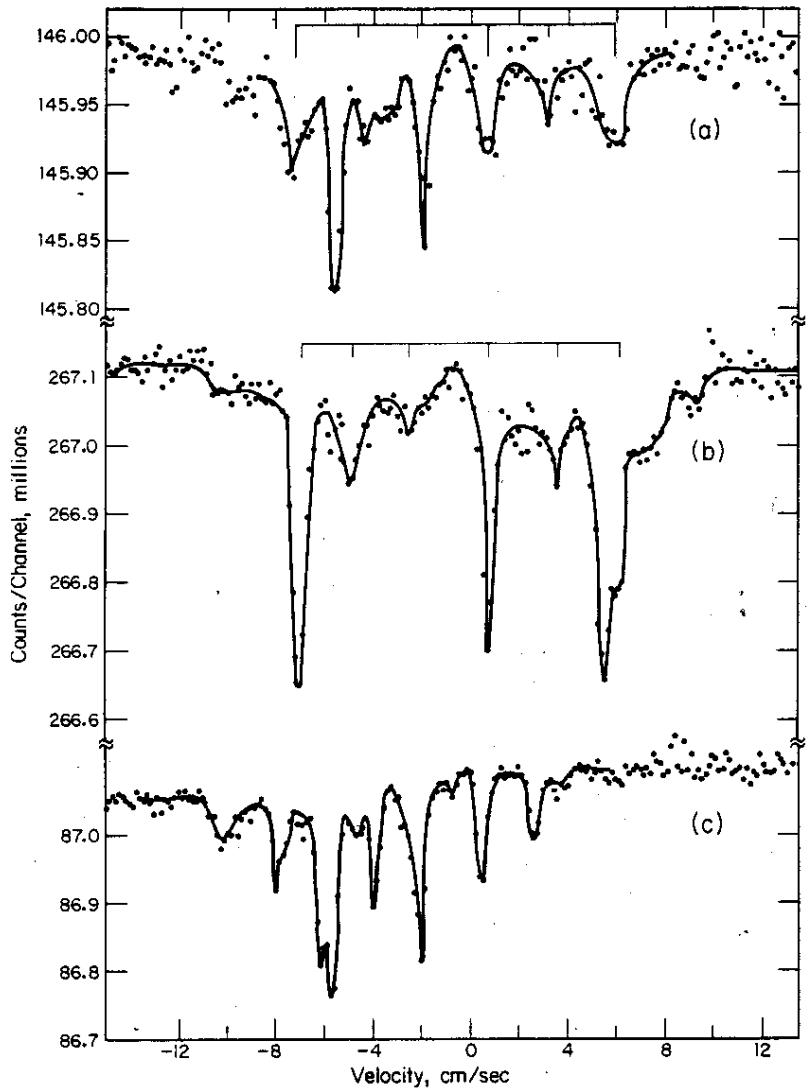


Fig. 5. Mössbauer spectra of (a) "$(TPAs)_2NpOCl_5$," (b) $(TPAs)_2NpCl_6$, and (c) $(TPAs)_nNpOCl_{n+2}$

$^{237}Np$ Mössbauer spectra for the reaction reactants and products are shown in Fig. 6. The top spectrum is a quadrupole-split of $NpI_3$ ($\delta$ = 3.33 cm/s, eqQ/4 = 0.81 cm/sec), the next lower spectrum is the THF solvate of $NpI_3$ ($\delta$ = 3.32 cm/s, eqQ/4 = 0.74 cm/s, asymmetry parameter, $\eta \cong 1$), and the next lower spectrum shows a strong single absorption with $\delta$=3.83 cm/s. This line is not the compound $KNp(C_8H_8)_2 \cdot 2THF$ ($\delta$ = 3.92 cm/s, eqQ/4 = 0.74 cm/sec, $\eta \approx 0$), and the pronounced isomer shift from $NpI_3 \cdot 6THF$ indicates a species with a small covalent contribution to its bonding. This line at $\delta$ = 3.83 cm/s is considered to demonstrate a

$Np(C_8H_8)I \cdot xTHF$ species. The bottom spectrum in Fig. 6 shows the spectrum of the decomposition products that results when the $Np(C_8H_8)I \cdot xTHF$-$NpI_3 \cdot 6THF$ mixture is thoroughly dried in vacuum - probably the spectrum of a mixture of Np(IV) products.

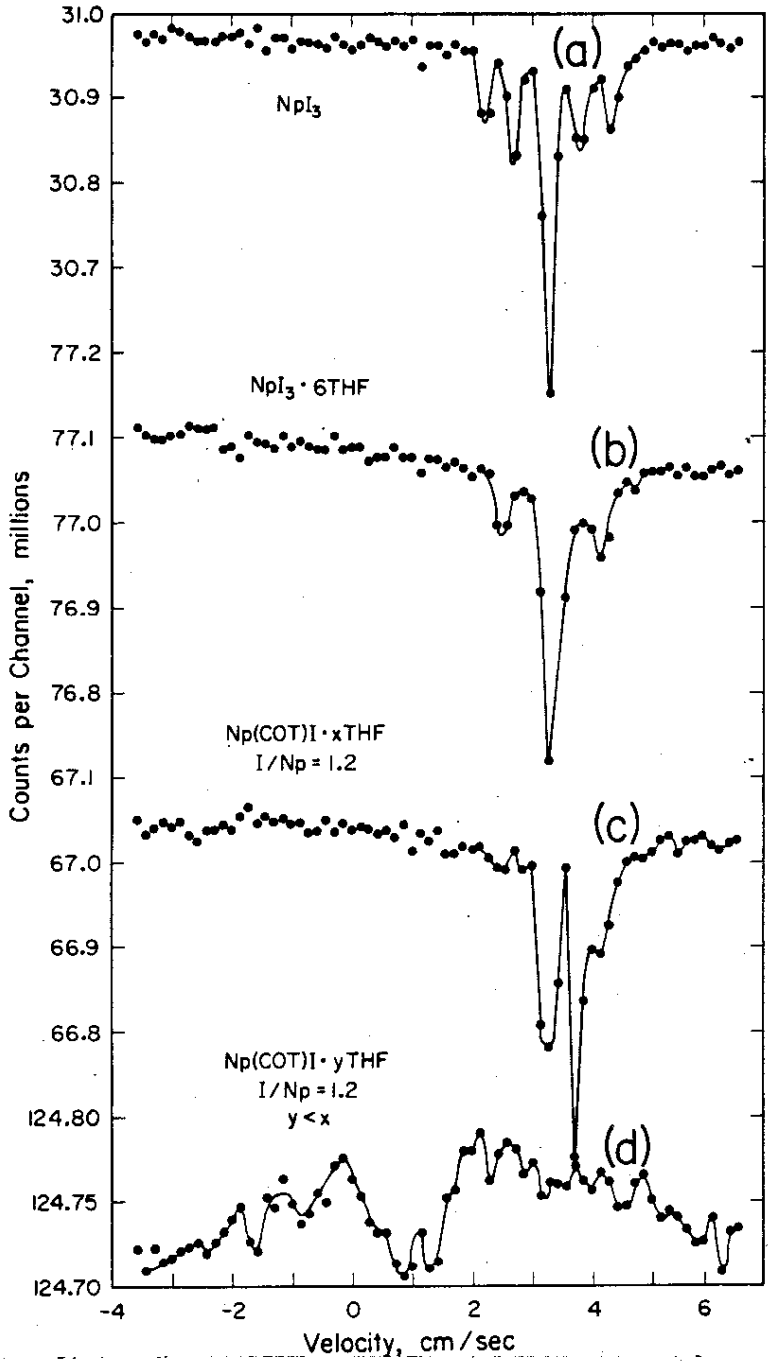


Fig. 6. Mössbauer spectra of (a) $NpI_3$, (b) $NpI_3 \cdot 6THF$, (c) $Np(COT)I \cdot xTHF$, and (d) $Np(COT)I \cdot yTHF$

## Np(V) - Transition Metal Ion Complexes

Sullivan[14] discovered from kinetic measurements that the aqueous Np(V) ion forms complexes with a number of other cations, and particularly strong complexes with Cr(III)[15] and Rh(III)[16] ions. The suggested structure for these complexes involves the substitution of the $NpO_2^+$ ion for water in the coordination sphere of the $Cr(H_2O)_6^{3+}$ and $Rh(H_2O)_6^{3+}$ ions, presumably with an $NpO_2^+$ oxygen occupying roughly the same position as the oxygen atom of a coordinated water molecule. If this were so, there should be a marked difference in the magnetic properties of the coordinated $NpO_2^+$ induced by the Cr(III) ion ($3d^3$, high spin) and the Rh(III) ion ($4d^6$, spin = 0). A difference in these magnetic effects should be manifest in the $^{237}Np$ Mössbauer spectra of the two complexes. No solid compounds of these complexes have been prepared, but the complexes can be isolated by absorption on cation exchange resin.[14-16]

The Mössbauer spectra[17] of the Cr(III)-Np(V) and Rh(III)-Np(V) complexes absorbed on cation resin (Fig. 7) are consistent with the presumed structure of the Np(V) complex ions. The spectrum of the Np(V)-Cr(III) complex ion shows a strong magnetic splitting ($g_0\mu_N H_{eff}$); one line is beyond the negative limit of the Mössbauer drive. There is only a small quadrupole splitting. The Mössbauer parameters for the Cr(III)-Np(V) spectrum are $\delta$ = 1.69 cm/s, $g_0\mu_N H_{eff}$ = 9.91 cm/s and eqQ/4 = 2.9 cm/s.

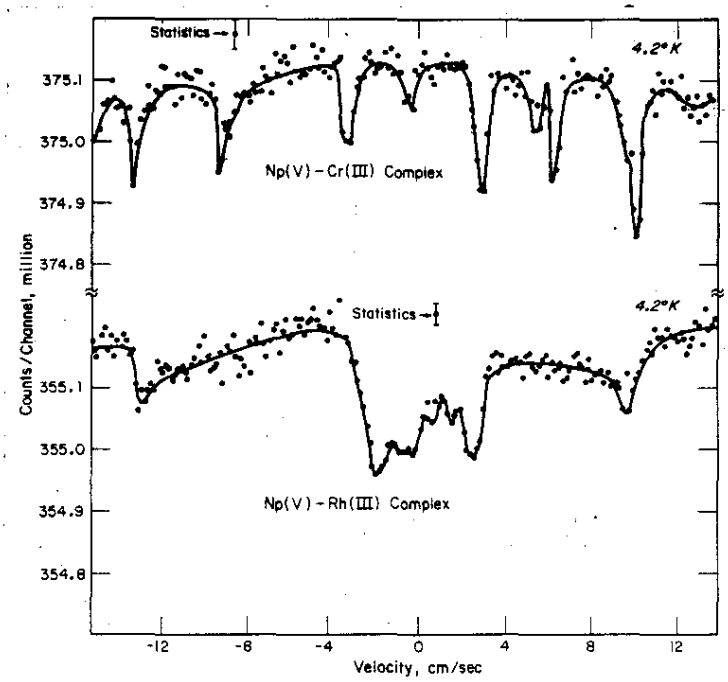


Fig. 7. Mössbauer spectra of Np(V) - Cr(III) and Np(V) - Rh(III) complexes

The spectrum of the Rh(III)-Np(V) complex shows extreme resonances that correspond to the strongest lines of a magnetically split spectrum, but the strong mixture of resonances in the center of the spectrum are due to the bulk of the Np(V) ions in the complex. These resonances are interpreted as dominated by quadrupole splitting and complicated by intermediate relaxation effects. In the fast relaxation limit, the spectrum will show single or quadrupole-split lines; at long relaxation times, the spectrum will be magnetically split. Intermediate relaxation times produce broadened resonances, and with unequal relaxation times in the different directions along the solid lattice, an extremely strange spectrum may result. However, the conclusion from this spectrum is that the major part of the Np(V) ions are in a non-magnetic environment, and that the spectrum is consistent with the suggested structure for the Rh(III)-Np(V) ion. The comparison of Mössbauer spectra for the Cr(III)-Np(V) and the Rh(III)-Np(V) ions agrees with a structure of these complex ions with an $NpO_2^+$ ion occupying a position in the octahedral coordination sphere of the Cr(III) and Rh(III) ions.

## $[(CH_3)_4N]_2NpCl_6$, $[(C_2H_5)_4N]_2NpCl_6$

These compounds have the $Np^{4+}$ ion located at the body center of the octahedron of six $Cl^-$ ions. $TMA_2NpCl_6$ (TMA = $(CH_3)_4N$) has a face-centered cubic cell ($O_h$) with the $Np^{4+}$ ion at a point of full cubic symmetry. $(TEA)_2NpCl_6$ has an orthorhombic cell ($D_{3d}$) that distorts the field on the $Np^{4+}$ sites. The ground level of the $Np^{4+}$ ion ($5f^3$) is a $\Gamma_8$ quartet[18] in cubic symmetry; the complicated splitting[19] of the $\Gamma_8$ level has been extensively studied in optical spectra,[20-23] and EPR.[24,25] In general, the $\Gamma_8$ level splitting can be described by two splitting factors, g and f, which may be unequal and are anisotropic except in special cases.

The Mössbauer spectra of $(TMA)_2NpCl_6$ and $(TEA)_2NpCl_6$ (Fig. 8) are both characterized by magnetic splitting with an additional quadrupole contribution.[26] The Mössbauer parameters for $(TMA)_2NpCl_6$ are $\delta = -0.66$ cm/s, $g_0\mu_N H_{eff} = 7.85$ cm/s and $eqQ/4 = 0.091$ cm/s. The spectra, however, show marked deviation from an isotropic splitting pattern. The hyperfine pattern expected for pure isotropic splitting is shown at the top of Fig. 8; both the line spacings and intensities are inconsistent with the hyperfine pattern expected for isotropic splitting. The explanation may be that the paramagnetic field has split the $\Gamma_8$ level, and unequal splitting has caused the anomalies in the $(TMA)_2NpCl_6$ Mössbauer spectrum.

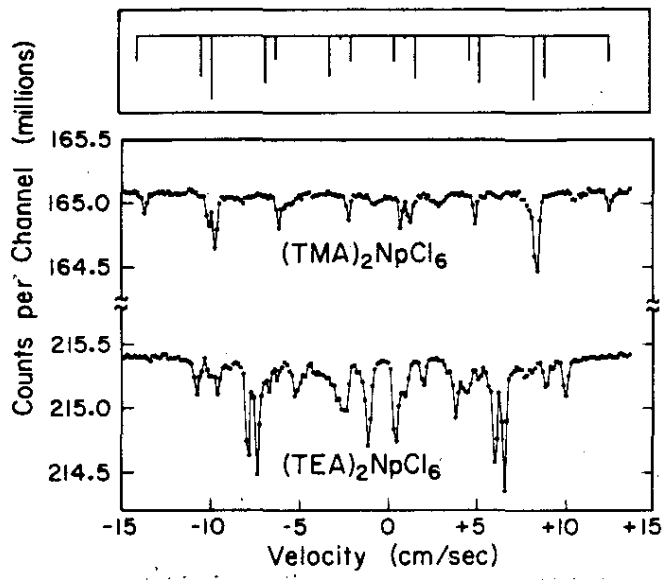


Fig. 8. Mössbauer spectra of $Cs_2NpCl_6$, $(TMA)_2NpCl_6$, and $(TEA)_2NpCl_6$

The Mössbauer spectrum of $(TEA)_2NpCl_6$ (Fig. 8) is quite complex, with about twice the number of lines expected for a magnetically split spectrum. The optical absorption spectrum[21] at 4.2°K was interpreted as resulting from $Np^{4+}$ ions in two unequal sites. The Mössbauer spectrum confirms this interpretation; the parameters for the two sites are (A) $\delta$ = 0.75 cm/s, $g_0\mu_N H_{eff}$ = 5.78 cm/s, eqQ/4 = 0.35 cm/s and (B) $\delta$ = 0.71 cm/s, $g_0\mu_N H_{eff}$ = 6.26 cm/s, eqQ/4 = 0.27 cm/s. As with the $(TMA)_2NpCl_6$ spectrum, the line spacings and intensities are not consistent with an isotropic splitting pattern. However, the spectrum does confirm the presence of two $Np^{4+}$ sites found by optical studies.

## Covalency of Np(IV) Organometallic Compounds

The wide range of isomer shifts in $^{237}Np$ Mössbauer spectra, besides identifying the valence of Np in compound, can also show more subtle effects within compounds of the same valence. This is of particular interest for organometallic compounds, where the orbitals of highly Π-bonding ligands contribute appreciable electron density to the shielding 5f orbitals. The isomer shift of $Np^{4+}$ in covalency-bonded compounds is shifted toward more positive values, sometimes quite dramatically. Table I compares the isomer shift of some $Np^{4+}$ organometallics, with the isomer shifts of $NpCl_4$ and $NpCl_3$ included for reference. As this work has been both reported[27-29] and reviewed,[30,31] this discussion is necessarily brief.

Table 1. Isomer Shifts of Np(IV) Organometallic Compounds

| Compound | Isomer Shift, cm/s | Hyperfine Splitting |
|---|---|---|
| $NpCl_4$ | -0.35 ± 0.05 | MAG |
| $NpCp_3Cl$* | 1.4 ± 1.0 | - |
| $NpCp_3C_4H_9$ | 0.27 ± 0.07 | MAG |
| $NpCp_3OC(CH_3)_3$ | 0.86 ± 0.3 | MAG |
| $NpCp_4$ | 0.72 ± 0.02 | QUAD |
| $Np(C_8H_8)_2$ | 1.94 ± 0.05 | MAG |
| $NpCl_3$ | 3.54 ± 0.05 | QUAD |
| $KNp(C_8H_8)_2$ | 3.92 ± 0.10 | QUAD |

* Cp = $C_5H_5^-$, cyclopentadienyl anion.

## Future

Mössbauer studies[32,33] of the charge states of $^{237}Np$ following alpha-decay of the $^{241}Am$ source have shown a general persistence of the same valence in the $^{237}Np$ daughter as in the $^{241}Am$ parent. Experiments of the same nature with the $^{237}U$ or $^{237}Pu$ as the Mössbauer sources are considerably more difficult, but may lead to the application of the $^{237}Np$ Mössbauer effect to uranium or plutonium chemical studies.

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