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MÖSSBAUER SPECTROSCOPY OF ^{237}Np ORGANOMETALLIC COMPOUNDS

by

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A paper proposed for publication in the
Proceedings of NATO Advanced Study Institute
Sogesta, Italy
September 11-22, 1978

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I. INTRODUCTION

Mössbauer Effect (ME) spectra are an important tool in the investigation of the properties of solids. The electron charge density, electric field gradient and magnetic hyperfine field at the actinide nucleus are influenced by covalent contributions to bonding, site symmetry of the actinide ion, and magnetic interactions between the ion and the nucleus, respectively.

Isotopes of all the actinides from thorium to americium have been shown to give Mössbauer spectra, but only the ME of ^{237}Np has been extensively exploited for chemical purposes. The ^{237}Np ME has excellent resolution and is comparatively easy in experimentation; Np(IV) and Np(III) ions form most of the organometallic compounds that can be synthesized in the actinides. This paper will deal exclusively with ^{237}Np ME on Np organometallics.

II. ^{237}Np MÖSSBAUER EFFECT

The ME on ^{237}Np was discovered by Stone and Pillinger¹ at the Savannah River Laboratory and developed further by the group at Argonne National Laboratory, then directed by G. M. Kalvius. The fundamentals of the ^{237}Np ME have been discussed in two excellent reviews^{2,3} and will only be briefly reviewed here. The useful gamma ray is the 59.5 keV transition from $^{237\text{m}}\text{Np}$ ($t_{1/2}$, 63 nsec) $5/2^-$ to the ^{237}Np , $5/2^+$ ground state. The 59.5 keV - $^{237\text{m}}\text{Np}$ results from the α -decay of ^{241}Am ($t_{1/2}$, 433 yr), the β -decay of ^{237}U ($t_{1/2}$, 6.75 da) or the electron capture decay in ^{237}Pu ($t_{1/2}$, 45.6 da) (Figure 1). The most convenient of these

for a Mössbauer source is the ^{241}Am ; normally ^{241}Am is diluted in a matrix of thorium metal to give a gamma source with a narrow line width.

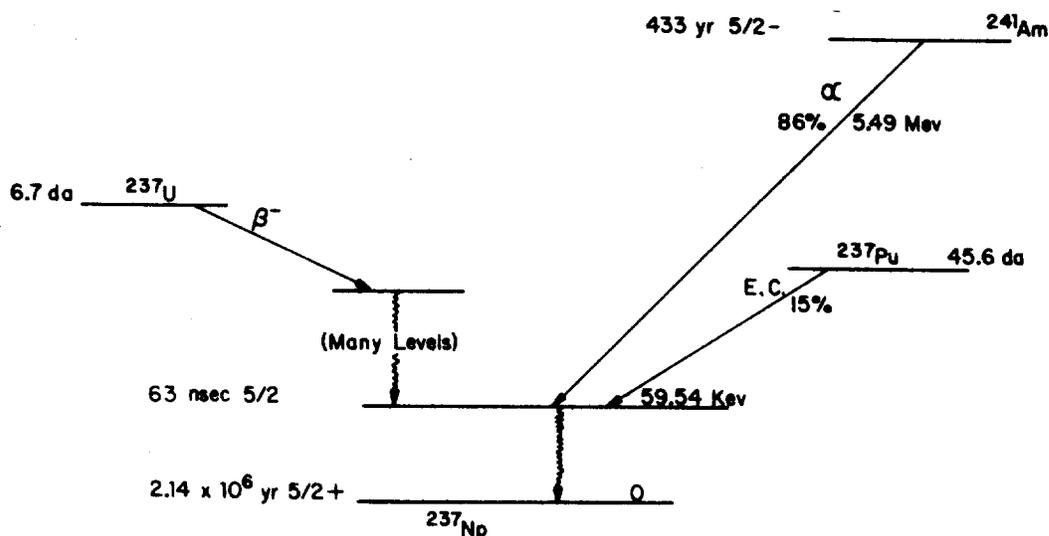


FIGURE 1. Decay Schemes to the 59.5 keV ^{237}Np Level (Simplified)

If the emitting and absorbing ^{237}Np nuclei are not in identical environments, an energy increment equal to the recoil energy of the emitting matrix must be added mechanically to achieve a resonance. The energy increment required for resonance is affected by ^{237}Np valence, site symmetry, and magnetic interactions. The Hamiltonian for the system may be written

$$H_{\text{Total}} = H_{\text{IS}} + H_{\text{Q}} + H_{\text{M}}$$

where H_{IS} represents the interactions of the central field with the nucleus (valence); H_{Q} represents the interaction of the quadrupole moment with the electric field gradient (site symmetry); and H_{M} represents the interaction of the nuclear dipole moment with the magnetic field, internal or external. The transitions induced between the $^{237\text{m}}\text{Np}$ and ^{237}Np levels are shown in Figure 2, for a single level, a quadrupole-split level, magnetically split levels, and a magnetic-quadrupole combined splitting.

The central field interactions that lead to the isomer shift in ME are spherically symmetric. Only S electrons have an appreciable density at the nucleus, so the isomer shift reflects the density of electrons in the S orbitals. In the case of ^{237}Np ,

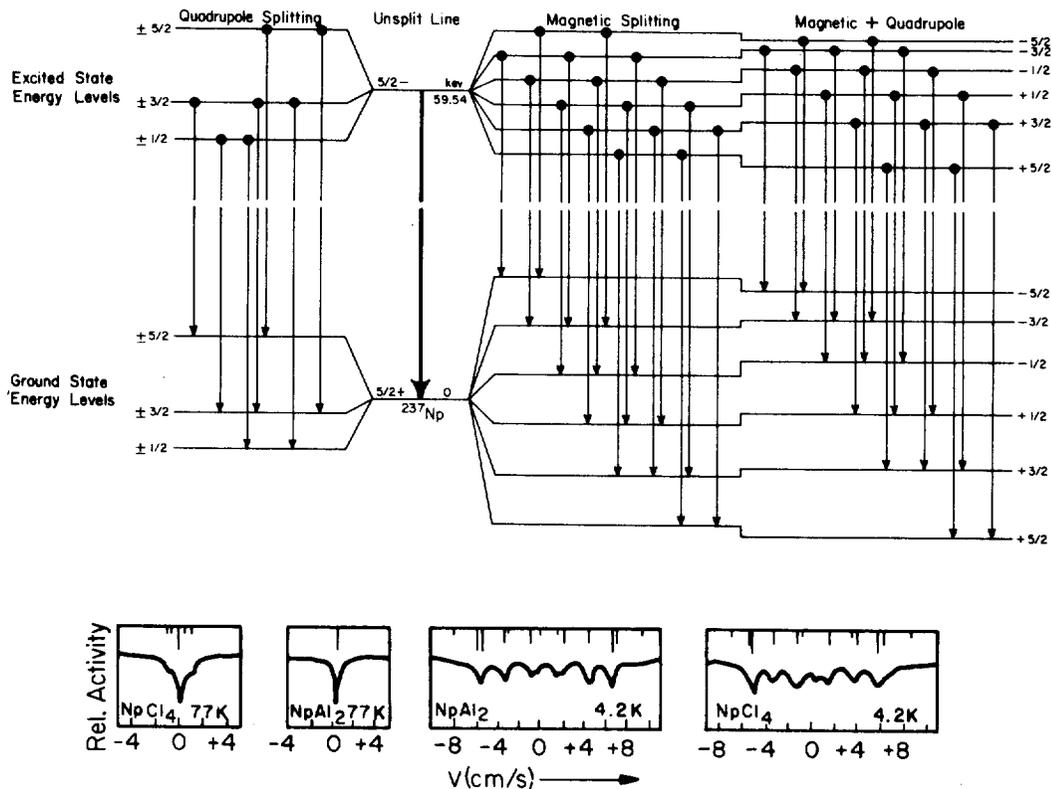


FIGURE 2. Splitting of the Ground State and 59.5 keV Level of ^{237}Np in Magnetic and Electric Fields

the 6s orbitals are shielded by the inner 5f orbitals: as the 5f shell is filled, progressing from Np(VII) to Np(III), the shielding of the 6s orbitals is increased, and the isomer shift becomes progressively more positive. Thus, the decrease in S-electron density is actually measured by the ME isomer shift of ^{237}Np compound. Figure 3 shows the effect of valence on isomer shift.³

The isomer shift in ^{237}Np is very large - from -6.9 cm/sec to +3.5 cm/sec, compared with the normal 2 to 4 cm/sec shift found for most Mössbauer isotopes. This large isomer shift allows excellent precision in determinations of the isomer shift, and can also allow a quantitative measure of covalent effects in bonding. Covalency involves electronic contribution from a ligand to the metal ion orbitals, which in the ^{237}Np ME results in an isomer shift toward a lower valence. An example (Figure 4) is the comparison of Np fluorides with oxygen-bonded Np in four valences.^{3,4}

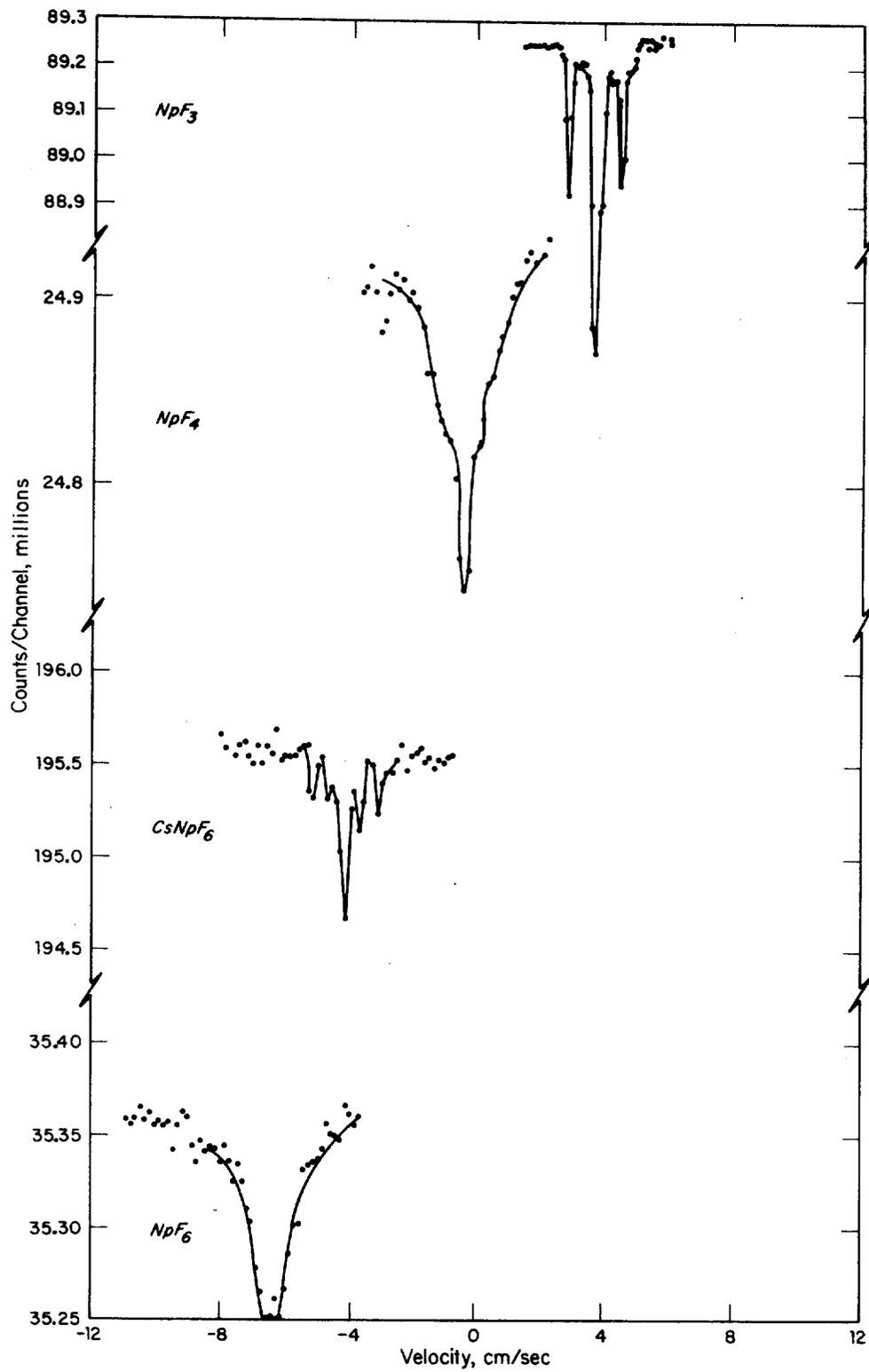


FIGURE 3. Mössbauer Spectra of Various Neptunium Fluorides

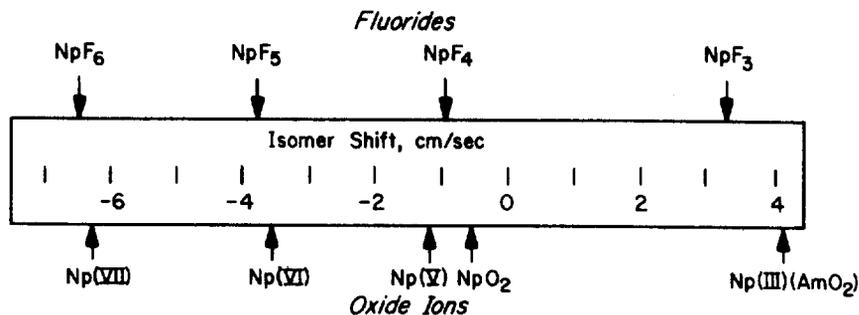


FIGURE 4. Isomer Shifts of Np Fluorides and Np Oxide Ions

Quadrupole splitting arises from the interaction between the nuclear quadrupole tensor and the electric field gradient tensor due to the distribution of charges around the ion. The nuclear quadrupole tensor is assumed to be rotating rapidly compared with the lifetime of the emitting nucleus and can be considered a scalar, the nuclear quadrupole moment Q . The electric field gradient is a more-complicated function, but in general leads to quadrupole splitting only when the field on the absorbing ^{237}Np nucleus has an n -fold axis, where $n > 2$. If the interaction is axially symmetric, the quadrupole splitting of the resonance will give a 5-line equally spaced pattern for perfect $n > 2$ axial symmetry; if the charge symmetry is nonaxial, the pattern will no longer have equal spacing and may be a three-line pattern with high asymmetry.

Magnetic splitting results from the interaction of the nuclear energy levels of the absorbing ^{237}Np nucleus with either an internal or an external magnetic field. The unpaired electrons of a paramagnetic ion produce a magnetic field on the nucleus; but at room temperature, the direction of the field changes so rapidly that the nuclear magnetic moment is unable to respond and thus no effect results. At low temperatures, the rate of relaxation will be slower, and in cases where the absorber becomes magnetically ordered - ferro or antiferromagnetic - the relaxation time becomes essentially infinite, and magnetic splitting is observed. Quadrupole splitting may occur simultaneously with magnetic splitting, but since normally $E_m \gg E_q$, quadrupole splitting only perturbs the hyperfine splitting due to the magnetic field (Figure 2) of ME spectra.

So far only the time-independent effects of ME spectra have been discussed. In these effects, the relaxation time is either much faster (single line or pure quadrupole splitting) or much slower (magnetic splitting) than the lifetime of the emitting

^{237m}Np . When the relaxation time is of the same order as the lifetime of ^{237m}Np , a ME spectrum results that is not easily predictable and is often uninterpretable. ME spectra affected by intermediate relaxation have little definition and usually appear as a broad absorption over a range of several cm/sec (Figure 5). The major mechanisms for relaxation are spin-spin and spin-lattice interactions;⁵ experimentally, intermediate relaxation seems to occur most frequently when Np ions are located close enough in the lattice to interact weakly. (Strong interactions, such as cooperative magnetic effects, result in magnetic splitting of the hyperfine levels.)

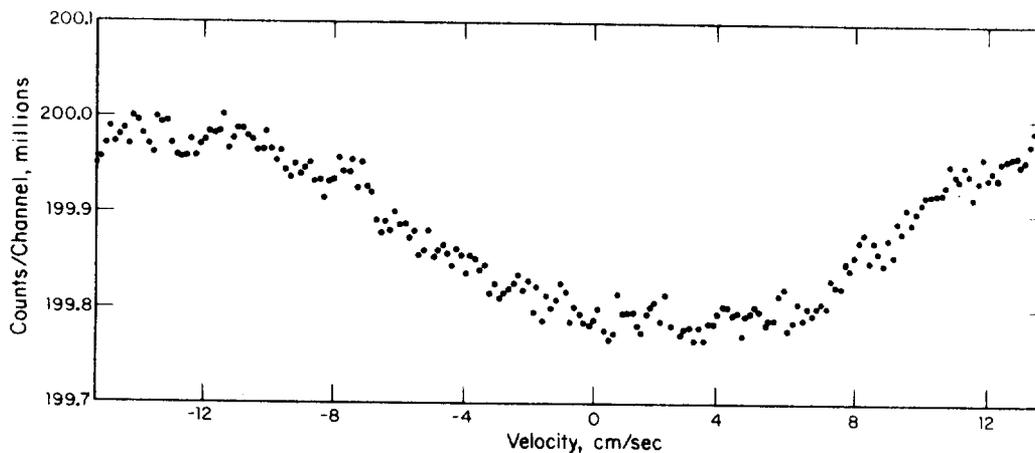


FIGURE 5. Mössbauer Spectrum of Cp_3NpCl

In principle, intermediate relaxation effects can be avoided by measuring the spectrum under conditions that increase the relaxation time (higher temperatures) or decrease the relaxation time (external magnetic field, low temperature; dilution of the sample in an inert matrix). In practice, some difficulties prevent these measures from being generally effective. The recoilless fraction is severely reduced at higher temperatures, so the running time to obtain a spectrum may be prohibitive. Applying an external magnetic field requires very expensive equipment, and dilution of the sample may not be effective within any reasonable sample size. As will be discussed later, sometimes intermediate relaxation effects can be avoided by synthesizing a compound that retains the essential of structure under investigation. For example $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{NpCl}_6$ may be studied instead of the Cs_2NpCl_6 since the ME spectrum of Cs_2NpCl_6 is dominated by uninterpretable intermediate relaxation effects. Relaxation effects are particularly important for triscyclopentadienyl neptunium(IV) compounds.

III. ME OF NEPTUNIUM - CYCLOOCTATETRAENYL COMPOUNDS

A. Np(IV) Compounds

The first compound between a quadrivalent actinide ion and the cyclooctatetraenyl dianion, $U(COT)_2$ ($COT = C_8H_8^{-2}$) was reported by Streitwieser and Müller-Westerhoff in 1968.⁶ The properties of $U(COT)_2$ - solubility in aromatic solvents, an unusual optical absorption spectra, stability to water, sublimation in vacuum at $160^\circ C$ - suggested strongly that its bonding involved some covalent contribution. Preparation and study of $Np(COT)_2$ ⁷ and substituted analogues⁸ confirmed that a strong covalent contribution was present in the bonding of $Np(COT)_2$, and by inference, in the isostructural $U(COT)_2$ and $Pu(COT)_2$ as well.

The Mössbauer spectrum of $Np(COT)_2$ (Figure 6) has combined magnetic and quadrupole splitting. The Mössbauer parameters for the three Np(IV) - cyclooctatetraenyl compounds studied are shown in Table 1.

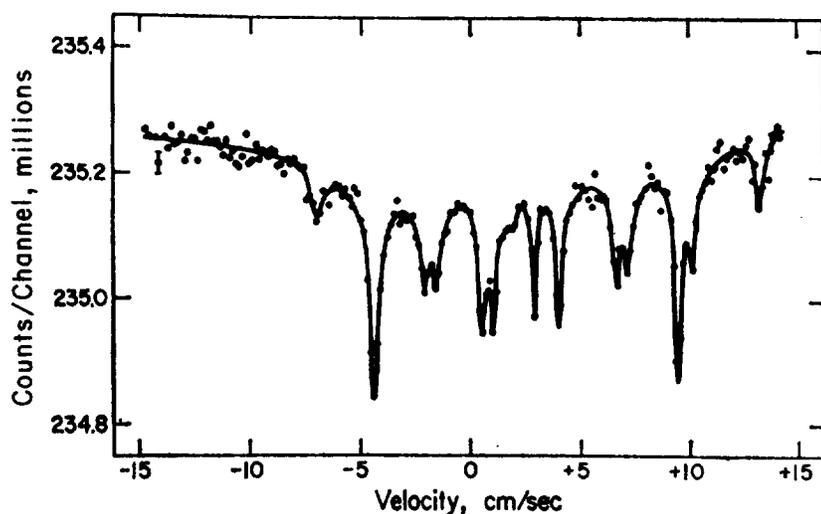


FIGURE 6. Mössbauer Spectrum of $Np(COT)_2$ at 4.2 K

Table 1. Isomer Shifts and Hyperfine Parameters

| Compound | Isomer Shift, ^a cm/sec | Magnetic Hyperfine Constant $g_0 \mu_N H_{\text{eff}}$, cm/sec | Quadrupole Coupling Constant, eqQ/4, cm/sec |
|------------------------|--------------------------------------|---|---|
| Np(COT) ₂ | +1.94 ±0.05 | 6.12 ±0.05 | -0.46 ±0.05 |
| Np(EtCOT) ₂ | +1.90 ±0.10 | 6.15 ±0.10 | -0.5 ±0.02 |
| Np(BuCOT) ₂ | +1.94 ±0.05 | 6.10 ±0.05 | -0.46 ±0.05 |

^aRelative to NpAl₂ = 0.

The most striking result from the Mössbauer spectrum of Np(COT)₂ is the isomer shift of +1.94 cm/sec. The isomer shift for a normal Np(IV) ion is about -0.4 cm/sec (compared with NpO₂, -0.56 cm/sec, or NpCl₄, -0.34 cm/sec) and for a Np(III) ion, about +3.5 cm/sec (NpCl₃, +3.54 cm/sec; NpBr₃, +3.64 cm/sec). Thus, the Np(COT)₂ isomer shift of +1.94 cm/sec shows a strong contribution to the shielding of the 6s orbitals. Presumably, the electron density from the COT ligand is contributed to the 5f orbitals of the Np⁴⁺ ion in Np(COT)₂, where it has the maximum effect in shielding.^{3,4}

Comparison of the Mössbauer parameters for substituted COT-Np(IV) compounds and Np(COT)₂ (Table 1) showed that, within the precision of the Mössbauer spectra, substituents do not add further electron density. The isomer shifts for Np(COT)₂, Np(EtCOT)₂, and Np(BuCOT)₂ were the same, even though the visible absorption bands were shifted to the red by substitution on the COT ring. These results provide qualitative understanding of the actinide (IV)-COT compounds to guide further investigations.

B. Np(III)-COT Compounds

The trivalent actinide ions Np³⁺, Pu³⁺, and Am³⁺ (References 9 and 10) form compounds of the composition KNp(COT)₂·xS (x = 1 or 2; S = solvent). These compounds are isostructural with their lanthanide analogues, which were previously discovered by Mares, Hodgson, and Streitwieser.¹¹ Structurally, the actinide (III) and lanthanide (III) ions are in a sandwich between two planar COT rings.¹² The Mössbauer spectra of KNp(COT)₂·2THF shows five-line quadrupole splitting (Figure 7) with an isomer shift of +3.92 cm/sec, a quadrupole coupling constant eqQ/4 of +0.75 cm/sec, and an asymmetry parameter of zero. This zero asymmetry parameter indicates that the Np³⁺ ion is in a site with a 3-fold or higher axis and is consistent with the D_{8d} symmetry found by x-ray studies on lanthanide analogues.

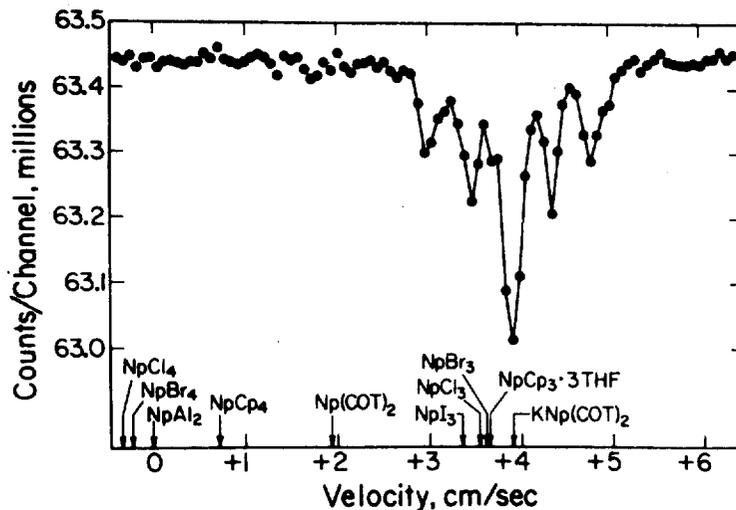


FIGURE 7. Mössbauer Spectrum of $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$

The isomer shift of +3.92 cm/sec is the largest positive shift yet observed for a Np(III) ion, but the shift is only slightly more positive than NpCl_3 (+3.54 cm/sec) or NpCp_3 (+3.64 cm/sec). The greater isomer shift for Np^{3+} in $\text{KNp}(\text{COT})_2$ indicates a covalent contribution to the bonding but not a major contribution. A study of the absorption spectra of $\text{KAm}(\text{COT})_2$ also shows that covalency in these compounds is low and is consistent with their chemical properties.¹³

The ME spectra were also used to study the reaction between NpI_3 and K_2COT in the THF solution and to identify, tentatively, the mixed COT-halide compounds $\text{Np}(\text{COT})\text{I} \cdot x\text{THF}$.¹⁴ This extremely unstable species is crudely analogous to lanthanide-COT compounds of the general composition $\text{Ln}(\text{COT})\text{Cl} \cdot 2\text{THF}$ discovered by Mares, Hodgson, and Streitwieser.¹⁵ ME spectra of the starting materials, intermediates, and products were used to follow the reaction $\text{NpI}_3 + \text{K}_2\text{COT} \xrightarrow{\text{THF}} \text{Np}(\text{COT})\text{I} \cdot x\text{THF}$ since no useful information could be obtained by normal techniques.

Figure 8 shows the ME spectra for a) NpI_3 , b) $\text{NpI}_3 \cdot 6\text{THF}$, c) $\text{NpI}_3 \cdot 6\text{THF}$ and $\text{Np}(\text{COT})\text{I} \cdot x\text{THF}$ (damp-dry), and d) the decomposition products after thorough drying of c) in vacuum. The NpI_3 spectrum shows quadrupole splitting with an asymmetry parameter, $\eta \approx 0$ (Reference 4), which indicates the Np^{3+} ion lies on an axis of 3-fold or higher symmetry. Solvation of NpI_3 with THF does not change the isomer shift, but solvation does change the quadrupole splitting pattern to give an asymmetry parameter approaching unity; thus, solvation creates a loss of symmetry for the Np^{3+} ion. The third spectrum shows the product of the reaction between $\text{NpI}_3 \cdot x\text{THF}$ and K_2COT ; the major species with

isomer shift of +3.83 cm/sec is tentatively identified as $\text{Np}(\text{COT})\text{I}\cdot x\text{THF}$, and the presence of excess $\text{NpI}_3\cdot x\text{THF}$ is also observed in this spectrum. The bottom spectrum of Figure 8 is that of the thoroughly dried $\text{Np}(\text{COT})\text{I}\cdot x\text{THF}$; no trivalent Np^{3+} is observed, and the lines near +1 cm/sec are from unidentified Np^{4+} species. This spectrum demonstrates the instability of this compound toward desolvation.

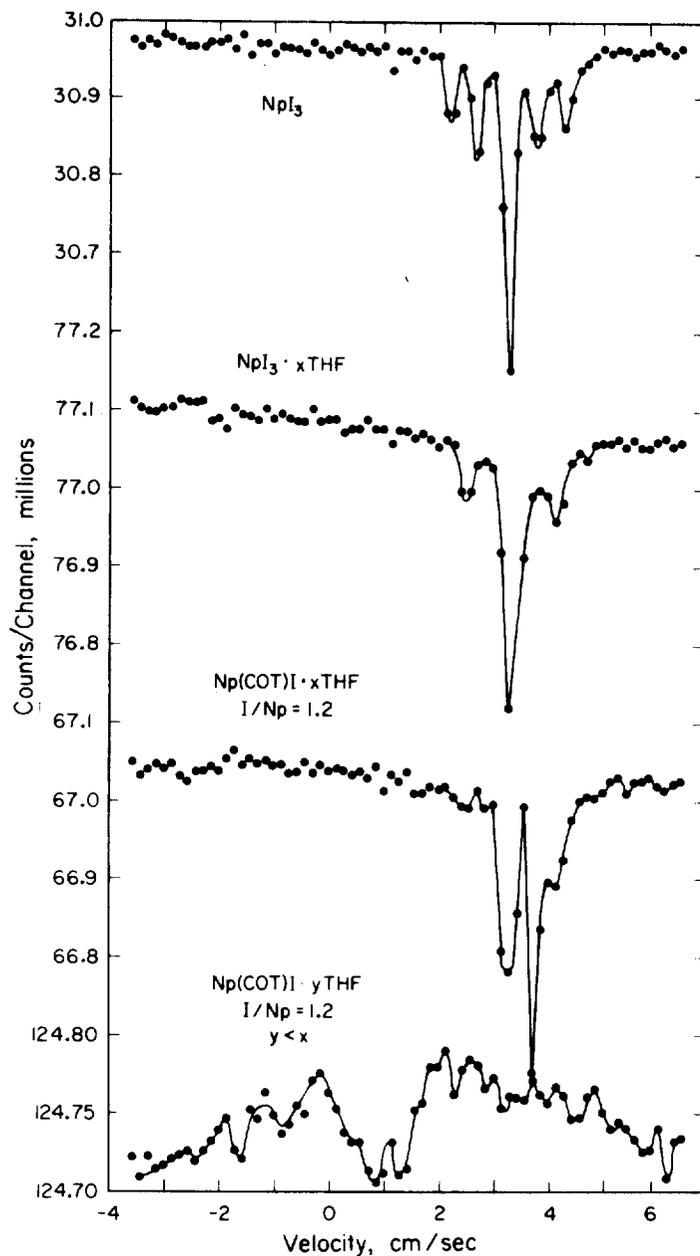


FIGURE 8. Mössbauer Spectra of NpI_3 , $\text{NpI}_3\cdot x\text{THF}$, $\text{Np}(\text{COT})\text{I}\cdot x\text{THF}$, and $\text{Np}(\text{COT})\text{I}\cdot y\text{THF}$

The new resonance line in spectrum c of Figure 8 is considered evidence for $\text{Np}(\text{COT})\text{I}\cdot x\text{THF}$. The isomer shift of +3.83 cm/sec is intermediate between NpI_3 (+3.33 cm/sec) and $\text{KNp}(\text{COT})_2\cdot 2\text{THF}$ (+3.92 cm/sec), as would be expected for a $\text{Np}(\text{COT})\text{I}\cdot x\text{THF}$ species. The Mössbauer parameters for these compounds are listed in Table 2.

Table 2. Mössbauer Parameters of Np(III) Compounds

| Compound | ^{237}Np Isomer ^a Shift, cm/sec | eqQ/4, cm/sec | Asymmetry Parameter, η |
|--|--|------------------|-----------------------------------|
| NpI_3 | +3.33 | 0.81 | ~ 0 |
| $\text{NpI}_3\cdot 6\text{THF}$ | +3.32 | 0.74 | ~ 1 |
| $\text{Np}(\text{COT})\text{I}\cdot x\text{THF} (?)$ | +3.83 | - | - |
| $\text{K}_2\text{Np}(\text{COT})_2\cdot 2\text{THF}$ | +3.92 | 0.73 | ~ 0 |

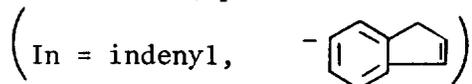
^aRelative to NpAl_2

IV. MO OF NEPTUNIUM - CYCLOPENTADIENE COMPOUNDS

A. Np-Cp Compounds

The U(IV) compounds with Cp, UCp_3Cl (Reference 16) and UCp_4 (Reference 17) were among the first actinide organometallic compounds discovered. The analogous neptunium compounds NpCp_3Cl (Reference 18) and NpCp_4 (Reference 19) were synthesized soon after and were shown to have identical properties. The chemical properties of these compounds - solubility in aromatic solvents, sublimation in vacuum, slow reaction with water and ferrous chloride - indicated a substantial degree of covalency. The Mössbauer spectrum²⁰ of NpCp_4 (Figure 9) is quadrupole-split ($\text{eqQ}/4 = 1.66 \pm 0.02$ cm/sec) and has an isomer shift of +0.72 cm/sec. This isomer shift can be compared with the isomer shift of Np^{4+} in NpO_2 at -0.56 cm/sec and shows a strong covalent contribution to the bonding in NpCp_4 . From the difference in the isomer shifts of +3 and +4 ionic compounds of Np, an isomer shift of +0.72 cm/sec corresponds to an effective valence of 3.7 for the Np^{4+} ion in NpCp_4 . The quadrupole splitting has an asymmetry parameter $\eta \approx 0$ which indicates a 3-fold or higher axis through the Np^{4+} site. A subsequent single-crystal x-ray study of UCp_4 (Reference 21) showed its molecular structure to be a distorted tetrahedron.²²

The Mössbauer spectra of $\text{NpCp}_3 \cdot 3\text{THF}$ (Figure 9)²⁰ is a single sharp line with an isomer shift of +3.64 cm/sec, not appreciably different from NpCl_3 whose isomer shift is +3.54 cm/sec. The ME spectrum of $\text{In}_3\text{Np} \cdot x\text{THF}$



(Reference 23), is quadrupole-split (Figure 10) and has the Mössbauer parameters $\delta = +3.55 \pm 0.15$ cm/sec and $eqQ/4 = 1.37 \pm 0.07$ cm/sec. The Mössbauer results for both $\text{NpCp}_3 \cdot 3\text{THF}$ and $\text{NpIn}_3 \cdot x\text{THF}$ indicate that both are ionic compounds, analogous to the lanthanide-Cp compounds.

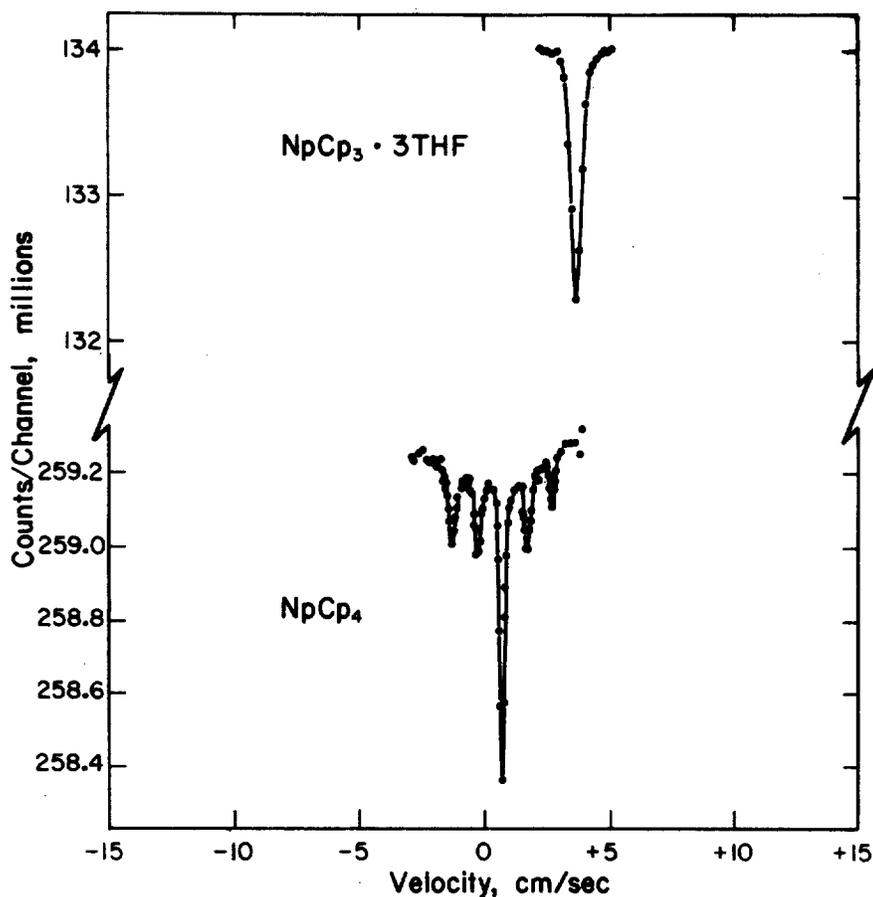


FIGURE 9. Mössbauer Spectra of NpCp_4 and $\text{NpCp}_3 \cdot 3\text{THF}$ at 4.2 K

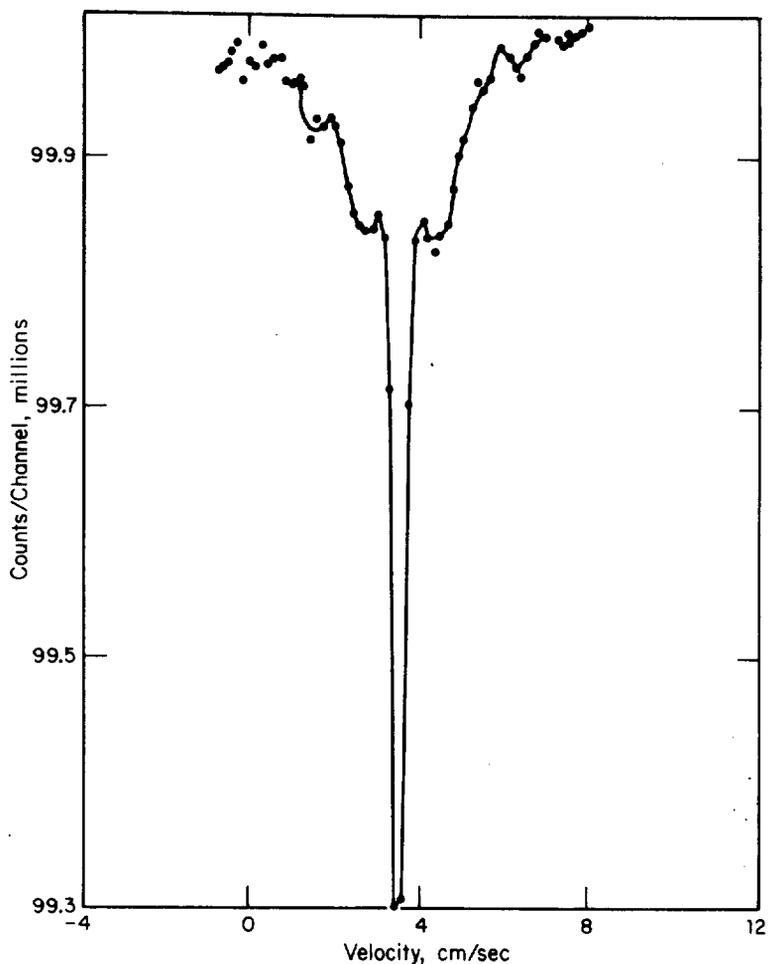


FIGURE 10. Mössbauer Spectrum of $\text{NpIn}_3 \cdot x\text{THF}$

B. Cp_3NpX Compounds

The Mössbauer spectra of Cp_3NpX compounds ($X = \text{Cl}, \text{Br}, \text{BH}_4$) are dominated by intermediate relaxation, but offer some useful information. Cp_3NpCl (Figure 5) and $(\text{MeCp})_3\text{NpCl}$ (Figure 11a) have broad, featureless spectra. Assuming that the relaxation time of Cp_3NpCl is near the fast relaxation limit, an isomer shift of $+1.4 \pm 1.0$ cm/sec can be derived. Substitution of a bulkier Cp ligand, indenyl, was attempted to reduce the interactions responsible for the relaxation effects; the spectrum of In_3NpCl (Figure 11b)²³ still lacks sufficient definition for analysis, but appears to be approaching a magnetically split spectrum. The spectrum of Cp_3NpBr (Figure 11c)²³ showed no more resolution than Cp_3NpCl .

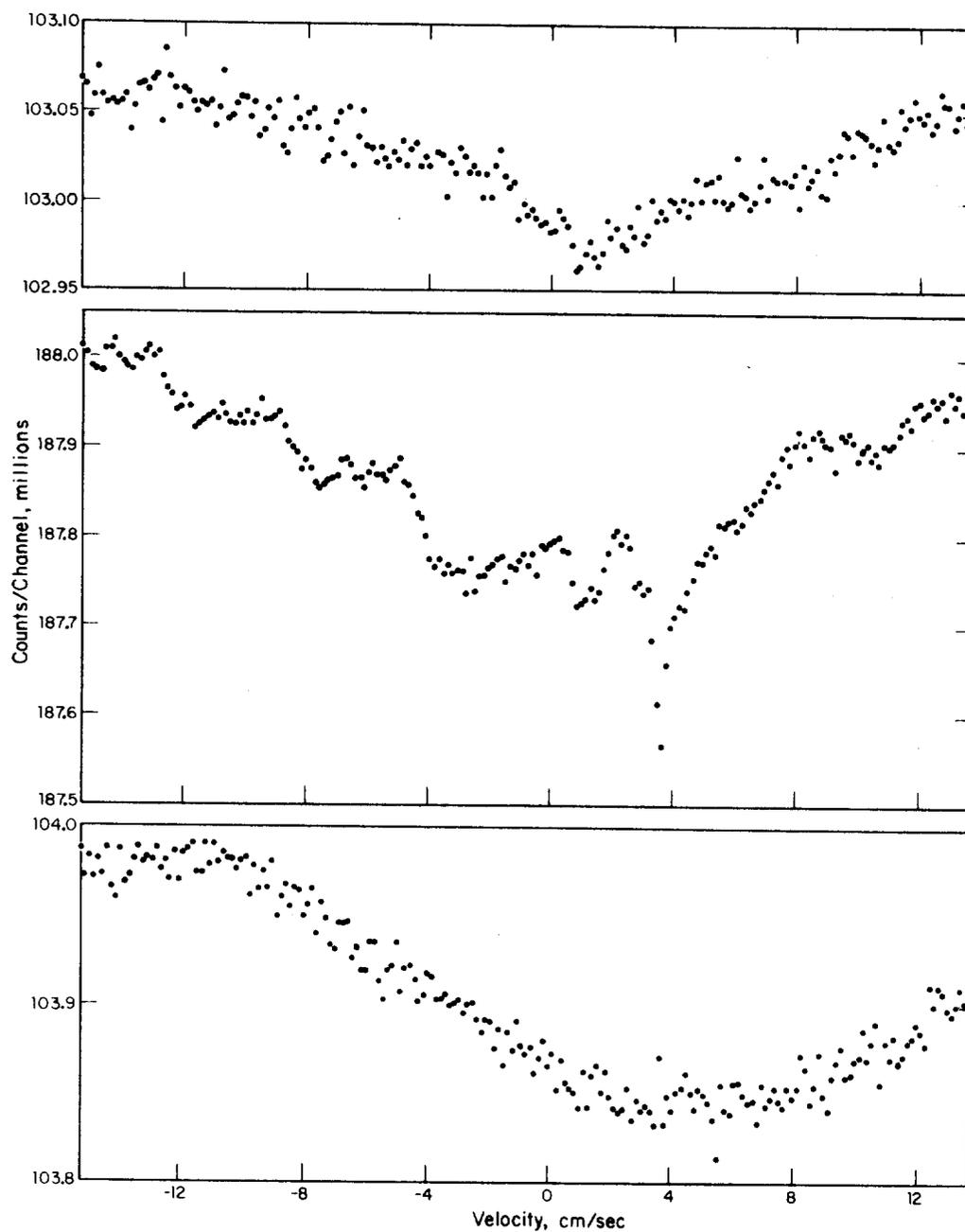


FIGURE 11. Mössbauer Spectra of a) MeCp_3NpCl , b) In_3NpCl (the Sharp Peak at 3.5 cm/sec is In_3Np), and c) Cp_3NpBr

The Mössbauer spectrum of $(\text{MeCp})_3\text{NpBH}_4$ (Figure 12),²³ though influenced by relaxation broadening, shows a broad, wide resonance with an isomer shift of 1.45 ± 0.4 cm/sec. This large isomer shift (compared with NpCp_4 , $\delta = 0.72$ cm/sec) indicates a greater covalent contribution in the bonding of $(\text{MeCp})_3\text{NpBH}_4$ than for NpCp_4 .

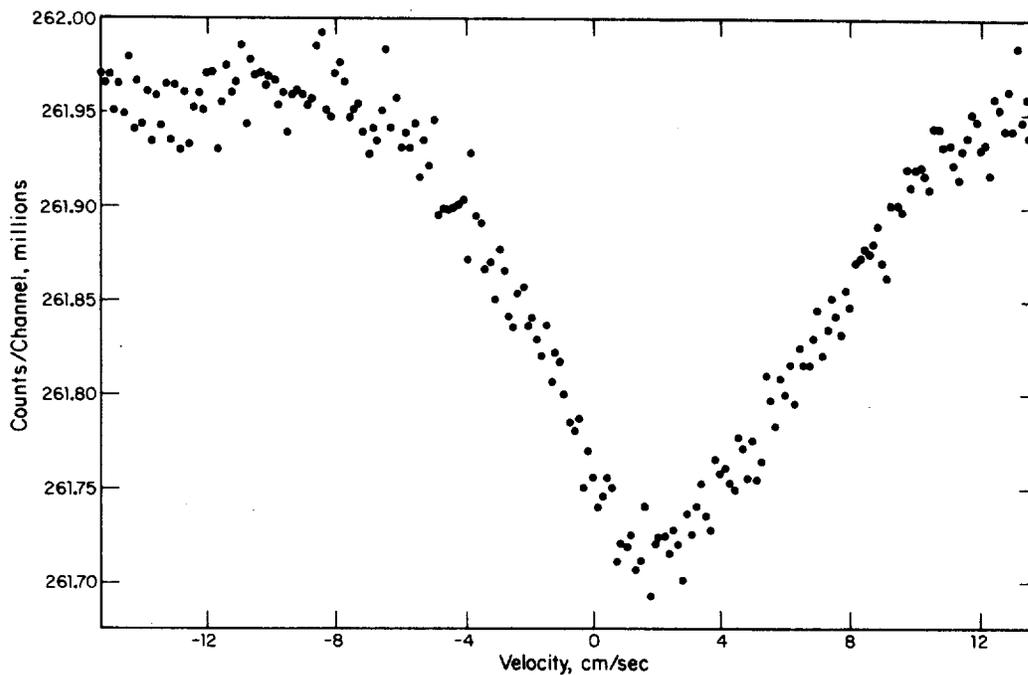


FIGURE 12. Mössbauer Spectrum of $(\text{MeCp})_3\text{NpBH}_4$

C. $\text{Cp}_3\text{Np}^n\text{Bu}$, $\text{Cp}_3\text{Np}\phi$

Cp_3NpR (where R is alkyl or aryl) compounds have been extensively studied since their discovery.^{24,25,26} Since Np(IV) organometallics are less stable toward reduction than U(IV) organometallics, $\text{Cp}_3\text{Np}^n\text{Bu}$ and $\text{Cp}_3\text{Np}\phi$ could not be prepared in high purity. Gas chromatographic analyses of the products of the decomposition of Cp_3NpR compounds by ethanol showed that $\text{Cp}_3\text{Np}^n\text{Bu}$ preparations were 80 to 90% pure. The best preparation of $\text{Cp}_3\text{Np}\phi$ was 40% pure, with NpCp_4 and NpCp_3Cl major impurities.

The Mössbauer spectrum of $\text{Cp}_3\text{Np}^{\text{n}}\text{Bu}$ (Figure 13)²³ showed three species in the spectrum – the five-line spectrum of NpCp_4 , a single line probably due to $\text{NpCp}_3 \cdot 3\text{THF}$, and two strong resonances broadened by relaxation effects that are interpreted as magnetically-split resonance due to $\text{Cp}_3\text{Np}^{\text{n}}\text{Bu}$. The Mössbauer parameters are $\delta = 0.27$ cm/sec, and $g_0\mu_{\text{N}}H_{\text{eff}} = 5.8$ cm/sec. The isomer shift for $\text{Cp}_3\text{Np}^{\text{n}}\text{Bu}$ is more negative than the shift for NpCp_4 (0.72 cm/sec) and is consistent with an assignment of a sigma bond to the $\text{Cp}_3\text{Np}^{\text{n}}\text{Bu}$ link. Sigma bonding of the $\text{Cp}_3\text{U}^{\text{n}}\text{Bu}$ link has been proposed for the analogous U(IV) compounds.²⁴⁻²⁶

The Mössbauer spectrum of an impure sample of $\text{Cp}_3\text{Np}\phi$, after subtracting the resonance absorption due to NpCp_4 and $\text{NpCp}_3 \cdot 3\text{THF}$ impurities, was broadened too much by intermediate relaxation to be interpreted. The spectrum (not shown) was similar to the spectrum of In_3NpCl (Figure 11b).

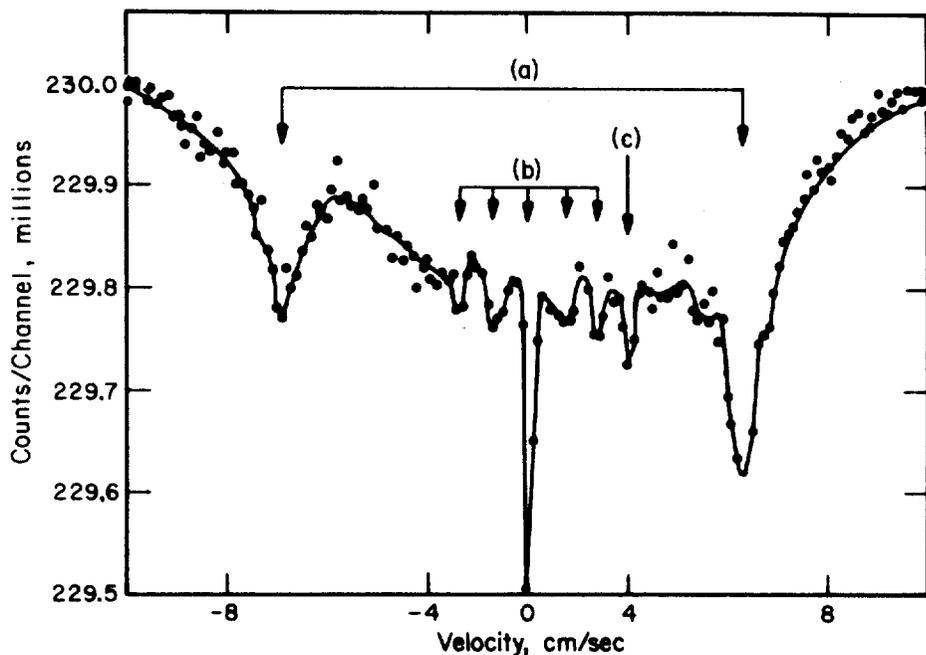


FIGURE 13. Mössbauer Spectra of a) $(\text{C}_5\text{H}_5)_3\text{Np}^{\text{n}}\text{C}_4\text{H}_9$, b) $(\text{C}_5\text{H}_5)_4\text{Np}$, and c) $(\text{C}_5\text{H}_5)_3\text{Np}$

D. Cp_3NpOR

The Mössbauer spectra of $\text{Cp}_3\text{NpOCH}(\text{CF}_3)_2$ and $(\text{MeCp})_3\text{NpO}^i\text{C}_3\text{H}_7$ have broadened resonances because of relaxation effects but are better resolved than Cp_3NpX or Cp_3NpR compounds and provide some data of interest. These compounds were synthesized by treating Cp_3NpCl with the corresponding potassium alkoxide.²⁷ The spectrum of $(\text{MeCp})_3\text{NpO}^i\text{C}_3\text{H}_7$ (Figure 14) is magnetically split, with an isomer shift $\delta = 0.93 \pm 0.07$ cm/sec, and $g_0\mu_{\text{NH}}\text{eff} = 5.72 \pm 0.40$ cm/sec. The spectrum of $\text{Cp}_3\text{NpOCH}(\text{CF}_3)_2$ (Figure 15) is more seriously affected by intermediate relaxation, but if magnetic splitting is assumed, $\delta = 0.79 \pm 0.3$ cm/sec and $g_0\mu_{\text{NH}}\text{eff} = 5.7 \pm 1$ cm/sec. The isomer shifts of the two alkoxide derivatives are about the same, within the resolution of the spectra, and slightly greater than the isomer shift (0.72 cm/sec) of Cp_4Np .

These isomer shifts indicate that a σ -bonding alkoxy ion may be substituted for a π -bonding Cp ligand without an appreciable change in covalency of the Np^{4+} ion. This surprising result may be explained by reference to the structure of the analogous Cp_3U^+ compounds.

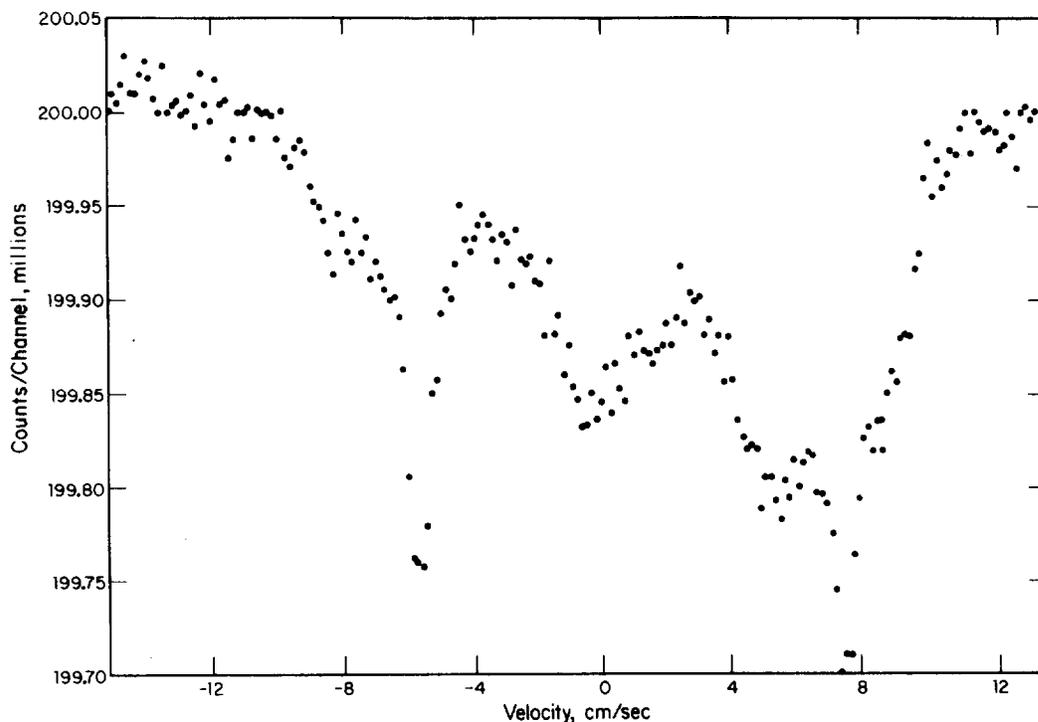


FIGURE 14. Mössbauer Spectrum of $(\text{MeCp})_3\text{NpOCH}(\text{CH}_3)_2$

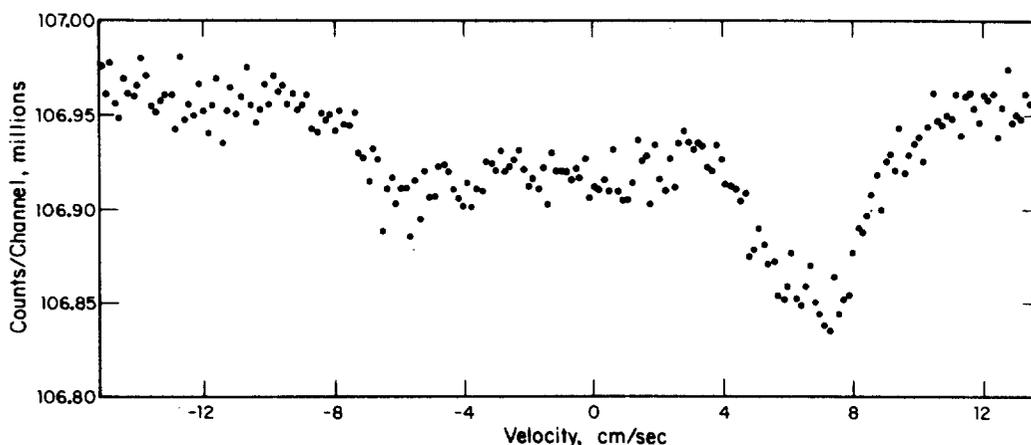


FIGURE 15. Mössbauer Spectrum of $\text{Cp}_3\text{NpOCH}(\text{CF}_3)_2$

Structure studies²² on U(IV)-Cp compounds find a distance of 2.72 to 2.74 Å between the U(IV) ion and Cp-carbons for Cp_3UX and Cp_3UR compounds. The U-C distance for U-Cp_4 was found to be 2.84 Å.²¹ The greater U-C distance probably acts to reduce the overlap of the ligand and metal orbitals and thus reduces the covalency. Although all four Cp ligands in NpCp_4 are equivalent, the addition of a fourth Cp ligand to the Cp_3Np^+ ion acts to reduce covalency by forcing the Cp ligands to a greater distance from the Np^{4+} ion.

V. DISCUSSION

Mössbauer spectra provide a valuable body of data (Table 3) for the interpretation of covalency of neptunium organometallic compounds and are considered to apply also the analogous uranium organometallics. Appreciable covalency is observed from the isomer shifts of Np(IV) compounds but not for Np(III) compounds. The probable explanation lies in the difference in size between +3 and +4 actinide ions. The ionic radii of U^{3+} and U^{4+} ions are 1.06 Å and 1.0 Å, respectively; for Np^{3+} and Np^{4+} the radii are 1.04 Å and 0.98 Å.²⁸ The larger size of the +3 ions shields the 5f orbital to an extent that interaction between the 5f orbitals and the ligand orbitals is small. For the smaller +4 ions, there is less shielding of the 5f orbitals, and 5f-ligand orbital interactions can occur.

Table 3. Mössbauer Parameters for Np-Cp and Np-COT Compounds

| Compound | Isomer Shift, ^a δ , cm/sec | Quadrupole Coupling Constant $eqQ/4$, cm/sec | Magnetic Hyperfine Constant $g_0^{149}\text{Np}H_{\text{eff}}$, cm/sec |
|---|---|---|---|
| NpCp ₄ | 0.72 ±0.02 | 1.66 ±0.02 | |
| NpCp ₃ ·3THF | 3.65 ±0.10 | | |
| NpIn ₃ ·xTHF | 3.55 ±0.15 | 1.37 ±0.07 | |
| NpCp ₃ Cl | 1.4 ±1.0 | | |
| Np(MeCp) ₃ BH ₄ | 1.45 ±0.4 | | |
| NpCp ₃ ⁿ Bu | 0.27 ±0.07 | | 5.8 ±0.2 |
| Np(MeCp) ₃ O ⁱ C ₃ H ₇ | 0.93 ±0.07 | 5.0 ±1.0 | 5.7 ±0.2 |
| NpCp ₃ OCH(CF ₃) ₂ | 0.79 ±0.3 | | 5.7 ±0.5 |
| NpCp ₃ C ₆ H ₄ C ₂ H ₅ | 0.42 ±0.28 | | 5.5 ±0.4 |
| NpCp ₃ O ⁱ C ₃ H ₇ | 0.86 ±0.2 | | 5.4 ±0.5 |
| NpCp ₃ O ^t Bu | 0.86 ±0.3 | | 5.2 ±0.4 |
| Np(MeCp)Cl ₃ ·2THF | -0.31 ±0.07 | | 5.15 ±0.06 |
| Np(COT) ₂ | 1.94 ±0.05 | 0.46 ±0.05 | 6.12 ±0.05 |
| KNp(COT) ₂ | 3.92 ±0.10 | 0.75 ±0.10 | |
| Np(COT)I·xTHF(?) | 3.83 ±0.10 | | |
| NpCl ₄ | -0.34) Included for | | |
| NpCl ₃ | 3.54) comparison | | |

^aRelative to $\delta = 0$ for NpAl₂

The isomer shift of Np(COT)₂ indicates a greater degree of covalency than for NpCp₄, although if 10 π electrons per COT ligand and 5 π electrons per Cp ligand are considered, their covalencies could be equal. However, the U-C bond length is 2.65 Å for U(COT)₂, and the U-C bond is 2.81 Å for UCp₄; the crowding²² of the Cp ligands forces longer bonds in the UCp₄. The lower covalency of NpCp₄ indicated by the isomer shifts in the Mössbauer spectra of the isostructural NpCp₄ and Np(COT)₂ probably arises from the differences in bond distances; the longer Np-C bond in NpCp₄ diminishes the overlap of 5f and Cp orbitals.

For Np(MeCp)₃BH₄ and NpCp₃Cl, the isomer shifts are 1.4 cm/sec, and the difference between 1.4 cm/sec and -0.4 cm/sec is considered to represent the covalent contribution of the three Cp ligands. BH₄⁻ and Cl⁻ ions are assumed to have little or no covalency in their bonding to Np(IV). The four NpCp₃OR compounds all have isomer shifts in the range 0.8 to 0.93 cm/sec; compared with the 1.4 cm/sec shift of NpCp₃Cl, this demonstrates that the sigma bonding -OR group is withdrawing some of the electron density contributed by the three Cp ligands from the

Np(IV) ion. The isomer shifts of $\text{NpCp}_3^{\text{nBu}}$ and $\text{NpCp}_3\text{C}_6\text{H}_4\text{C}_2\text{H}_5$, 0.27 and 0.4 cm/sec, respectively, show a much stronger electron-withdrawing tendency, and verify the strong sigma bonding reported for the $^{\text{nBu}}$ and $-\text{C}_6\text{H}_4\text{C}_2\text{H}_5$ ligands.^{10,11} The isomer shift of $\text{NpCp}_3^{\text{nBu}}$ represents a withdrawal of electron density of more than 1 cm/sec with respect to NpCp_3^+ , equivalent to about 1/4 the isomer shift difference between Np(IV) and Np(III). In view of the nature of the Np(IV)- $^{\text{nBu}}$ bond, it is hardly surprising that no stable Np(IV) or U(IV) tetraalkyl compounds are known.

The Mössbauer spectra of $\text{Np}(\text{MeCp})\text{Cl}_3 \cdot 2\text{THF}$ has an isomer shift of -0.31 cm/sec, about the same as the isomer shift of NpCl_4 (-0.35 cm/sec). Comparing these isomer shift values, the MeCp ligand and the chloride ion are essentially equivalent in donation of the electron density to the Np^{4+} ion. This equivalence indicates that the MeCp ligand is σ -bonded in $\text{NpMeCpCl}_3 \cdot 2\text{THF}$ and infers that the Cp ligand in analogous compounds ($\text{UCpCl}_3 \cdot 2\text{THF}$, UCpCl_3 DME, etc.) is probably σ -bonded also. The infrared data of Bagnall, et al²⁹ show an average $\nu(\text{U-Cp})$ of 262 cm^{-1} for seven compounds of the general formula $\text{UCpX}_3 \cdot x\text{S}$ ($\text{X} = \text{Cl}^-$ or Br^- , $x = 1$ or 2 , $\text{S} = \text{ligand}$) compared with an average $\nu(\text{U-Cp})$ of 243 cm^{-1} for UCp_3Cl and UCp_3Br . The difference suggests a difference between the U-Cp bond in UCp_3X and the U-Cp bond in UCp_3X compounds, consistent with the Mössbauer results.

ACKNOWLEDGMENT

The author is deeply indebted to John A. Stone for experimental assistance, theoretical advice, and, over all, many illuminating discussions on "what to do next."

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APPENDIX

Other Actinide and Lanthanide Mössbauer Isotopes

Recoilless resonant absorption or emission of nuclear gamma rays, now known as the Mössbauer effect, was discovered by R. L. Mössbauer in 1957.¹ Since then, over 73 isotopes of 43 elements have been shown to have a detectable Mössbauer effect, among them isotopes of all the lanthanides except cerium and lutetium, and isotopes of the first six actinides.^{2,3} For a variety of reasons, only a few of these isotopes can be used to explore the chemical bonding, and none has the potential of the ^{237}Np Mössbauer effect. Actinide isotopes, other than ^{237}Np , either have very broad resonances (2 to 5 cm/sec); or the half-life of the source isotope is inconveniently short. The ^{243}Am Mössbauer effect has a very large isomer shift, 5.3 cm/sec between Am^{3+} and Am^{4+} compounds; but the disadvantages of a short source half-life (^{243}Pu , 5 hr) source and the self-damage to absorbers from the ^{243}Am radiation have prevented application to chemical problems.

Isotopes of eight lanthanides have useable Mössbauer resonances and have been exploited in studies of the magnetic properties. A potential for the study of chemical bonding is best for Sm, Eu, and Yb compounds, where compounds with both dipositive and tripesitive valences can be studied. The ^{151}Eu Mössbauer effect has a well-resolved spectrum and an isomer shift of about 1.5 cm/sec between the +2 and +3 valences. The ^{151}Eu Mössbauer effect is also experimentally convenient, with either of two long-lived sources possible, and a large recoilless fraction at room temperature. Consequently, almost all of the chemical studies on lanthanide chemistry have been with europium compounds. A recent review by Barton and Greenwood⁴ compiles the data for studies with ^{151}Eu Mössbauer effect.

The isomer shifts found in ^{151}Eu Mössbauer spectra fall in three ranges: Eu(II) -1.2 ± 0.2 cm/sec, Eu(III) 0 ± 0.1 cm/sec and metallic alloys and band systems -0.7 to -1.1 cm/sec with the EuF_3 isomer shift taken as zero. The isomer shift of a number of representative Eu(II) and Eu(III) compounds are compiled in the following table:

Isomer Shifts of Eu Compounds^a

| Compound | Isomer Shift ^b cm/sec |
|--|-------------------------------------|
| EuF ₂ | -1.36 |
| EuCl ₂ | -1.37 |
| EuBr ₂ | -1.34 |
| EuSO ₄ | -1.40 |
| Eu(C ₅ H ₅) ₂ | -1.22 |
| Eu ₂ (SO ₄) ₃ | 0.052 |
| EuCl ₃ ·6H ₂ O | 0.050 |
| Eu(C ₅ H ₅)Cl ₂ ·3THF | 0.041 |
| Eu(C ₉ H ₇) ₃ ·3THF ^c | 0.058 |

^aReference 4

^bEuF₃ isomer shift = 0

^cC₉H₇ = indenyl

In general, the isomer shifts are fairly constant for compounds and coordination complexes of both Eu(II) and Eu(III). A small effect in Eu(III) chelates has been attributed to a change in coordination number⁵ and also to a small contribution to the 6s orbitals from the ligands.⁶ No real evidence for ligand contribution to the 4f orbitals is apparent from these studies. These results conform to a model that assumes the 4f orbitals of the lanthanides are so well shielded from interaction with ligand that covalent effects will be very small for trivalent ions, and even less for divalent ions. Appreciable covalent effects are observed in ²³⁷Np Mössbauer only for Np(IV) and higher valences.

The isomer shifts for both Sm and Yb isotopes are quite small, 0.16 cm/sec for the ¹⁵²Sm Mössbauer effect between Sm(II) and Sm(III) and 0.063 cm/sec between Yb(II) and Yb(III) for the ¹⁷¹Yb effect. Chemical studies of isomer shifts effects on Sm and Yb would be quite difficult to perform successfully.

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