

DP-MS-78-62

COVALENCY OF NEPTUNIUM(IV) TRISCYCLOPENTADIENYL
COMPOUNDS FROM MÖSSBAUER SPECTRA

by

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Paper proposed for presentation at the
Southeastern ACS Meeting
Savannah, Georgia
November 8-11, 1978

MASTER

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ABSTRACT

Isomer shifts measured from the ^{237}Np Mössbauer spectra of NpCp_3OR (R = alkyl) NpCp_3R and NpCpAr (Ar = aryl) are used as a measure of the covalency in Np(IV) ligand bonding. The isomer shifts in $\text{NpCp}_3^{\text{n}}\text{Bu}$ and $\text{NpCp}_3\text{C}_6\text{H}_4\text{C}_2\text{H}_5$ show a strong σ character to the $\text{Np}^{\text{n}}\text{Bu}$ and $\text{Np}-\text{C}_6\text{H}_4\text{C}_2\text{H}_5$ bonds. The σ character of Np-OR bonding is definite, but less pronounced. The comparatively low covalency in the bonding of NpCp_4 is ascribed to longer Np-C bonds in NpCp_4 than in NpCp_3^+ compounds. The ^{237}Np isomer shift in $\text{Np}(\text{MeCp})\text{Cl}_3 \cdot 2\text{THF}$ indicates that the MeCp ligand is σ -bonded in this compound.

* The information contained in this article was developed during the course of work under Contract No. AT(07-2)-1 with the U.S. Department of Energy.

INTRODUCTION

The U(IV) compounds with cyclopentadiene (HCp), UCp_3Cl and UCp_4 were among the first actinide organometallic compounds discovered.^{1,2} The analogous Np(IV) compounds, NpCp_3Cl and NpCp_4 were synthesized later, and shown to have identical properties.^{3,4} A number of derivatives have been prepared from UCp_3Cl , such as UCp_3OR (R = alkyl), UCp_3R and UCp_3Ar (Ar = aryl).⁵⁻¹⁰ Substituted cyclopentadienes, such as MeCp, indenyl (In) and $\text{C}_5\text{H}_4\text{CH}_2\emptyset$ have also been prepared for structural studies of the UCp_3^+ compounds.^{11,12}

This study is concerned with the preparation of the Np(IV) analogs of the UCp_3^+ compounds and their study by Mössbauer spectroscopy. For several NpCp_3^+ compounds, intermediate relaxation effects did not produce interpretable Mössbauer spectra, so Cp_3NpOR and Cp_3NpAr compounds substituted on either the Cp, R, or Ar ligands were prepared and studied. Previous investigations have shown that the isomer shift of the Mössbauer spectrum reflects covalent contributions to the bonding of Np^{+4} ion.^{13,14} These covalent effects are the major interest of this study.

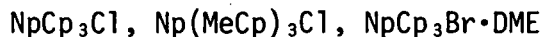
EXPERIMENTAL

General

All compounds were prepared in the dry, purified argon atmosphere of a glove box. Samples were sealed under an argon atmosphere in plastic holders for Mössbauer measurements, as performed previously.^{13,14} Solvents (THF, 1,2-DME, toluene, petroleum ether

and ethyl ether) were purified by standard methods in an argon atmosphere. Neptunium was analytically determined by destruction of a sample in dilute acid and alpha-counting an aliquot of this solution. Chloride was determined by titration with standard silver nitrate to potentiometric end-point. Organic ligands were estimated by gas chromatography of the decomposition products, formed by reacting the compounds with water or ethanol.

Preparation of Compounds

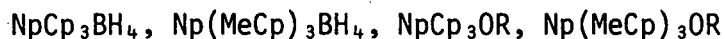


NpCp_3Cl was prepared by reacting NpCl_4 and TiCp in 1,2-dimethoxyethane (DME), as described by Marks, et al.¹⁵ Substitution of TiMeCp or NpBr_4 produced $\text{Np}(\text{MeCp})_3\text{Cl}$ or $\text{NpCp}_3\text{Br}\cdot\text{DME}$, respectively. The product of this reaction may be only 70-80% pure. To obtain pure material (>95%) the crude product was dissolved in toluene, filtered, and vacuum evaporated. The solid product was heated at 100°C in vacuum for 8 to 16 hours to remove excess solvent. In the single preparation of NpCp_3Br , solvent removal was incomplete. Calcd. for $\text{NpCp}_3\text{Br}\cdot\text{DME}$: Np 40.05%; Br, 13.6%. Found: Np, 40.6%; Br 14.5%.



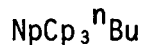
NpIn_3Cl was prepared by reacting NpCl_4 and KIn in tetrahydrofuran (THF) solution, as described by Laubereau, et al.¹¹ The product of the reaction at room temperature contained only trace amounts of chloride, and its Mössbauer spectrum showed only a

Np(III) species, consistent with a $\text{NpIn}_3 \cdot x\text{THF}$ product. Mixing the reagents at -88°C yielded a mixture with a Cl/Np ratio of 0.15, assumed to be a mixture of $\text{NpIn}_3\text{Cl} \cdot x\text{THF}$ and $\text{NpIn}_3 \cdot x\text{THF}$ from its Mössbauer spectrum.



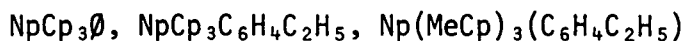
These compounds were prepared by metathesis of NpCp_3Cl (for example) with LiBH_4 ,⁵ or a potassium alkoxide.¹⁶ Stoichiometric amounts were stirred in toluene for 24 to 72 hours, the solids (LiCl , KCl) filtered, and the filtrate vacuum-evaporated to recover the products. Compounds prepared in this manner, and their analyses are tabulated below.

<i>Compound</i>	<i>Np%, Calculated</i>	<i>Np%, Found</i>
NpCp_3BH_4	53.04	48.9
$\text{Np}(\text{MeCp})_3\text{BH}_4$	48.4	46.9
$\text{NpCp}_3\text{O}^i\text{C}_3\text{H}_7$	48.3	45.0
$\text{Np}(\text{MeCp})_3\text{O}^i\text{C}_3\text{H}_7$	44.2	42.3
$\text{NpCp}_3\text{OCH}(\text{CF}_3)_2$	39.6	40.2
$\text{NpCp}_3\text{O}^t\text{C}_{11}\text{H}_9$	46.9	44.4

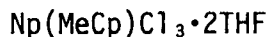


NpCp_3^nBu was prepared by adding an equimolar quantity of commercial butyl lithium in hexane to NpCp_3Cl suspended in diethyl ether at -78°C .⁸ The solution was stirred as it warmed to room temperature, then the ether was removed by vacuum. The remaining solids were dissolved in toluene, filtered and the product recovered by vacuum evaporation of the toluene. Calcd for NpCp_3^nBu : 48.5% Np. Found: 47.9% Np; Cl not detected.

Butane produced by decomposition of a sample with ethanol was measured by gas chromatography as 84% of theory. Mössbauer spectra of several preparations always showed NpCp_4 and $\text{NpCp}_3 \cdot 3\text{THF}$ impurities.



These compounds were prepared only in an impure state, by reacting NpCp_3Cl with an ether solution of the phenyl lithium¹⁷ at -78°C , similar to the method for preparing $\text{NpCp}_3^{\text{n}}\text{C}_4\text{H}_9$. After stirring a short time at room temperature, the ether was removed by vacuum, and the residue extracted with toluene. The toluene solution was evaporated by vacuum to recover the product. For $\text{NpCp}_3\emptyset$ the best preparation had a Cl/Np ratio of 0.52, indicating 52% of the sample was unreacted NpCp_3Cl . Destruction of a sample with ethanol and benzene analysis by gas chromatography showed 40% $\text{NpCp}_3\emptyset$; the Mössbauer spectrum showed a NpCp_4 impurity. The $\text{NpCp}_3(\text{C}_6\text{H}_4\text{C}_2\text{H}_5)$ and $\text{Np}(\text{MeCp})_3(\text{C}_6\text{H}_4\text{C}_2\text{H}_5)$ compounds were further purified by extraction with petroleum ether (boiling range $20-40^\circ\text{C}$).



This compound was prepared by the reaction of stoichiometric quantities of TlMeCp and NpCl_4 in THF solution, similar to the literature preparation of $\text{UCpCl}_3 \cdot 2\text{THF}$.^{18, 19} The reaction mixture was stirred for 24 hours at room temperature, filtered, and a crude product obtained by evaporation of the filtrate. The crude product was washed with toluene to remove a probable $\text{Np}(\text{MeCp})_3\text{Cl}$ impurity, and vacuum-dried. Calcd. for $\text{Np}(\text{MeCp})\text{Cl}_3 \cdot 2\text{THF}$: Np, 41.95%; Cl, 18.50%. Found: Np, 42.4%; Cl, 19.55%; Cl/Np = 3.05.

RESULTS

Mössbauer spectra were obtained for all 16 compounds prepared. Representative spectra for the compounds studied are shown in the five figures: Figure 1, $\text{Np}(\text{MeCp})_3\text{BH}_4$; Figure 2, $\text{Np}(\text{MeCp})_3\text{Cl}$, $\text{NpCp}_3\text{Br}\cdot\text{DME}$, $\text{NpIn}_3\text{Cl}\cdot x\text{THF}$; Figure 3, $\text{NpCp}_3^{\text{n}}\text{Bu}$; Figure 4, $\text{Np}(\text{MeCp})_3\text{O}^{\text{i}}\text{C}_3\text{H}_7$; and Figure 5, $\text{Np}(\text{MeCp})\text{Cl}_3\cdot 2\text{THF}$.

Except for NpMeCpCl_3 , none of the spectra are well-resolved. The spectra of all the Cp_3Np^+ compounds investigated had their resolution decreased to varying degrees by relaxation broadening. In extreme cases, the resolution was so poor that no useful information could be obtained from the spectra of $\text{Np}(\text{MeCp})_3\text{Cl}$, $\text{NpIn}_3\text{Cl}\cdot x\text{THF}$, $\text{NpCp}_3\text{Br}\cdot\text{DME}$ (Figure 2) and NpCp_3BH_4 , and $\text{NpCp}_3\emptyset$ (not shown). The spectra of $\text{NpCp}_3\text{O}^{\text{i}}\text{C}_3\text{H}_7$, $\text{NpCp}_3\text{O}^{\text{t}}\text{Bu}$, and $\text{NpCp}_3\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ were poorly resolved, but could be interpreted within a rather generous error.

Poor resolution occurs because the relaxation time of ^{237}Np nuclei is about the same as the 62 nsec-half-life of the 59.5 keV level. At relaxation times much faster than 62 nsec, the spectra is either a single line, or quadruple-split pattern, like NpCp_4 .¹⁴ At much slower relaxation times, the spectrum is magnetically-split, like $\text{Np}(\text{C}_8\text{H}_8)_2$.¹³ Intermediate relaxation effects in $\text{Np}(\text{IV})$ compounds usually show some correlation with the distance between $\text{Np}(\text{IV})$ ions. Relaxation effects on Mössbauer spectra can sometimes be relieved by measuring a similar compound with bulkier ligands, such as $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{NpCl}_6$, which has a well-resolved

spectrum, instead of Cs_2NpCl_6 , which has an uninterpretable spectrum because of intermediate relaxation effects. This approach was used in this study with partial success. For example, NpCp_3BH_4 and $\text{NpCp}_3\emptyset$ have spectra that could not be interpreted, so measurements were made with $\text{Np}(\text{MeCp})_3\text{BH}_4$ and $\text{NpCp}_3\text{C}_6\text{H}_5\text{C}_2\text{H}_5$. Interpretation of the spectra requires the assumption that the isomer shifts are essentially the same for both the substituted and unsubstituted ligands.

The Mössbauer parameters for the compounds studied are listed in Table 1, with some previously reported data included for comparison. Isomer shifts are referred to $\text{NpAl}_2 = 0$.

DISCUSSION

The isomer shift in the ^{237}Np Mössbauer spectra depends upon the shielding of the 6s orbitals by electron density in the inner orbitals, principally the 5f orbitals.^{20,21} As the 5f orbitals add electrons proceeding from Np^{+7} to Np^{+3} , the isomer shift becomes progressively more positive, from approximately -6.5 cm/sec to 3.5 cm/sec. Similarly, as electron density is contributed to the 5f orbitals from the ligands bonded to $\text{Np}(\text{IV})$, the isomer shift of the Np^{+4} ion is shifted from its normal position of -0.4 cm/sec toward the normal value for Np^{+3} , 3.5 cm/sec. The isomer shift of the Np^{+4} ion in $\text{Np}(\text{IV})$ organometallic compounds reflects the differences in the electron density contributed by the ligands, which are equivalent to differences in covalent contributions of the ligands bonding to the $\text{Np}(\text{IV})$ ion.

For $\text{Np}(\text{MeCp})_3\text{BH}_4$ and NpCp_3Cl , the isomer shifts are 1.4 cm/sec. The difference between 1.4 cm/sec and -0.4 cm/sec is considered to represent the covalent contribution of the three Cp ligands. BH_4^- and Cl^- ions are assumed to have little or no covalency in their bonding to $\text{Np}(\text{IV})$. The four NpCp_3OR compounds all have isomer shifts in the range 0.8 to 0.93 cm/sec; compared with the 1.4 cm/sec shift of NpCp_3Cl , this demonstrates that the sigma bonding-OR group is withdrawing some of the electron density contributed by the three Cp ligands from the $\text{Np}(\text{IV})$ ion. The isomer shifts of $\text{NpCp}_3^{\text{n}}\text{Bu}$ 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 $^{\text{n}}\text{Bu}$ and $-\text{C}_6\text{H}_4\text{C}_2\text{H}_5$ ligands.^{9,10} The isomer shift of $\text{NpCp}_3^{\text{n}}\text{Bu}$ 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 $\text{Np}(\text{IV})$ and $\text{Np}(\text{III})$. In view of the nature of the $\text{Np}(\text{IV})$ - $^{\text{n}}\text{Bu}$ bond, it is not surprising that no $\text{Np}(\text{IV})$ or $\text{U}(\text{IV})$ tetraalkyl compounds are known.

The isomer shift of NpCp_4 (0.72 cm/sec) is less than NpCp_3Cl (1.4 cm/sec) and even NpCp_3OR compounds (0.8 - 0.95 cm/sec). The explanation for this lies almost certainly in the difference between the Cp-Np bond distances in NpCp_3^+ compounds and NpCp_4 . In the $\text{U}(\text{IV})$ analogues, single crystal studies have shown that the C-U distance is 2.72 - 2.74 Å for UCp_3Cl , $\text{UCp}_3^{\text{n}}\text{Bu}$, and UCp_3 -alkyl while the C-U(IV) distance is 2.81 Å

for UCp_4 .²² The increased C-U(IV) bond distance in UCp_4 is the result of repulsion between the four Cp ligands. Assuming that the distances between Cp ligands and Np(IV) are very close to the Cp-U distances, the smaller isomer shift in NpCp_4 probably results from a decreased overlap between Cp bonding orbitals and the 5f orbitals of the Np(IV) ion, and thus to a decreased covalent contribution in the bonding of NpCp_4 , compared to NpCp_3^+ . $\text{Np}(\text{C}_8\text{H}_8)_2$, which has the most positive isomer shift of any Np(IV) organometallic compound (1.94 cm/sec), has a Np-C distance of 2.65 Å. The shorter Np-C distance in $\text{Np}(\text{C}_8\text{H}_8)_2$ compared to NpCp_4 is a significant factor in the greater covalency of $\text{Np}(\text{C}_8\text{H}_8)_2$. The Np(IV) ion has 20 electrons available from the ligands in both NpCp_4 and $\text{Np}(\text{C}_8\text{H}_8)_2$, so the electron density available to the Np(IV) ion is the same for both $\text{Np}(\text{C}_8\text{H}_8)_2$ and NpCp_4 .

The Mössbauer spectrum (Figure 5) 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 ($\text{UCpCl}_3 \cdot 2\text{THF}$, $\text{UCpCl}_3 \cdot \text{DME}$, etc.) is probably σ -bonded also. The infrared data of Bagnall, et al.¹⁹ 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 , S = ligand) compared with an average $\nu_{(\text{U-CP})}$ of 243 cm^{-1} for

UCp₃Cl and UCp₃Br. The difference suggests a difference between the U-Cp bond in UCpX and U-Cp bond in UCp₃X compounds, consistent with the Mössbauer results.

ACKNOWLEDGMENT

The authors are indebted to B. Tiffany for the gas chromatography analyses.

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FIGURE CAPTIONS

FIGURE 1. Mössbauer Spectrum of $(\text{MeCp})_3\text{NpBH}_4$

FIGURE 2. Mössbauer Spectra of a) MeCp_3NpCl , b) In_3NpCl (the Sharp Peak at 3.5 cm/sec is In_3Np), and c) Cp_3NpBr

FIGURE 3. Mössbauer Spectra of a) $\text{Cp}_3\text{Np}^n\text{C}_4\text{H}_9$, b) Cp_4Np , and c) Cp_3Np

FIGURE 4. Mössbauer Spectrum of $(\text{MeCp})_3\text{NpOCH}(\text{CH}_3)_2$

FIGURE 5. Mössbauer Spectra of $\text{Np}(\text{MeCp})\text{Cl}_3 \cdot 2\text{THF}$

TABLE 1

Mössbauer Parameters for NpCp_3^+ Compounds

<i>Compound</i>	<i>Isomer Shift^a</i> δ , cm/sec	<i>Quadrupole</i> <i>Coupling Constant</i> $eqQ/4$, cm/sec	<i>Magnetic Hyperfine</i> <i>Constant</i> $g_0^{14}\text{N}^{\text{H}}_{\text{eff}}$, cm/sec
NpCp_4^b	0.72 ± 0.02	1.66 ± 0.02	
NpCp_3Cl^b	1.4 ± 1.0		
$\text{Np}(\text{MeCp})_3\text{BH}_4$	1.45 ± 0.4		
$\text{NpCp}_3^{\text{n}}\text{Bu}$	0.27 ± 0.07		5.8 ± 0.2
$\text{NpCp}_3\text{C}_6\text{H}_4\text{C}_2\text{H}_5$	0.42 ± 0.28		5.5 ± 0.4
$\text{Np}(\text{MeCp})_3\text{O}^{\text{i}}\text{C}_3\text{H}_7$	0.93 ± 0.07	5.0 ± 1.0	5.72 ± 0.20
$\text{NpCp}_3\text{O}^{\text{i}}\text{C}_3\text{H}_7$	0.86 ± 0.2		5.4 ± 0.5
$\text{NpCp}_3\text{OCH}(\text{CF}_3)_2$	0.79 ± 0.2		5.7 ± 0.4
$\text{NpCp}_3\text{O}^{\text{t}}\text{Bu}$	0.86 ± 0.3		5.2 ± 0.4
$\text{NpIn}_3 \cdot x\text{THF}$	3.55 ± 0.15	1.37 ± 0.07	
$\text{Np}(\text{MeCp})\text{Cl}_3 \cdot 2\text{THF}$	-0.31 ± 0.07		5.15 ± 0.06

a. Relative to $\delta = 0$ for NpAl_2 .

b. From Reference 14.

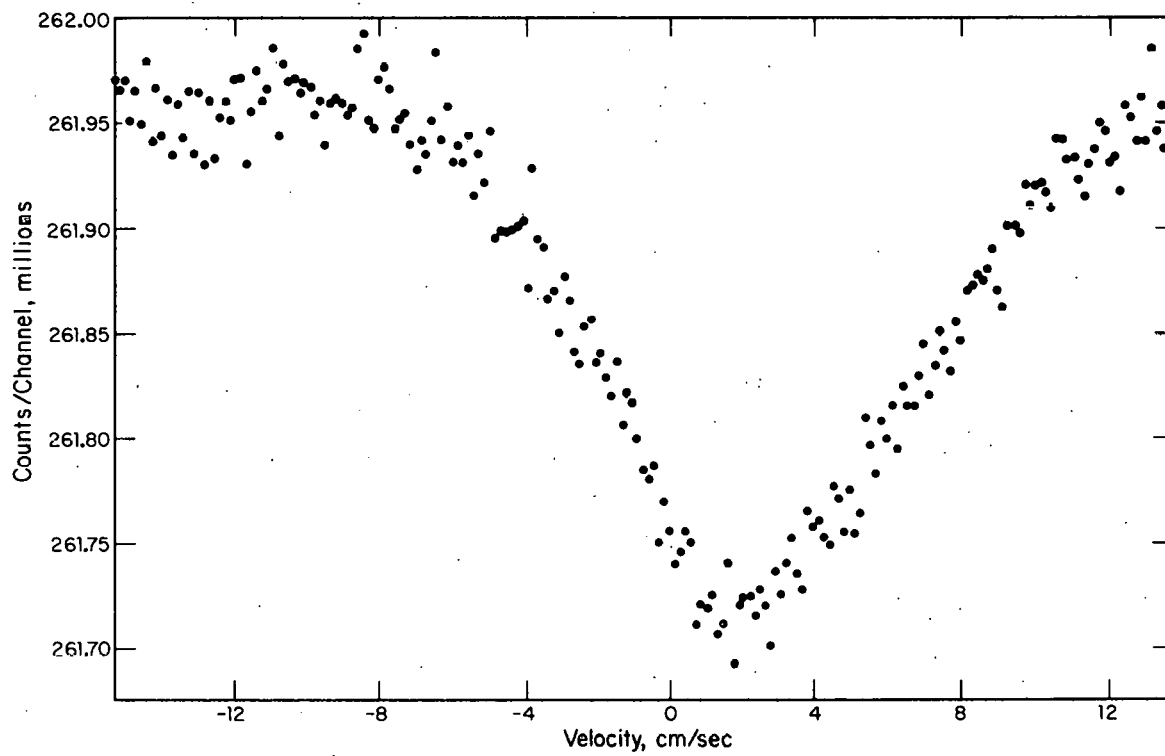


FIGURE 1. Mössbauer Spectrum of $(\text{MeCp})_3\text{NpBH}_4$

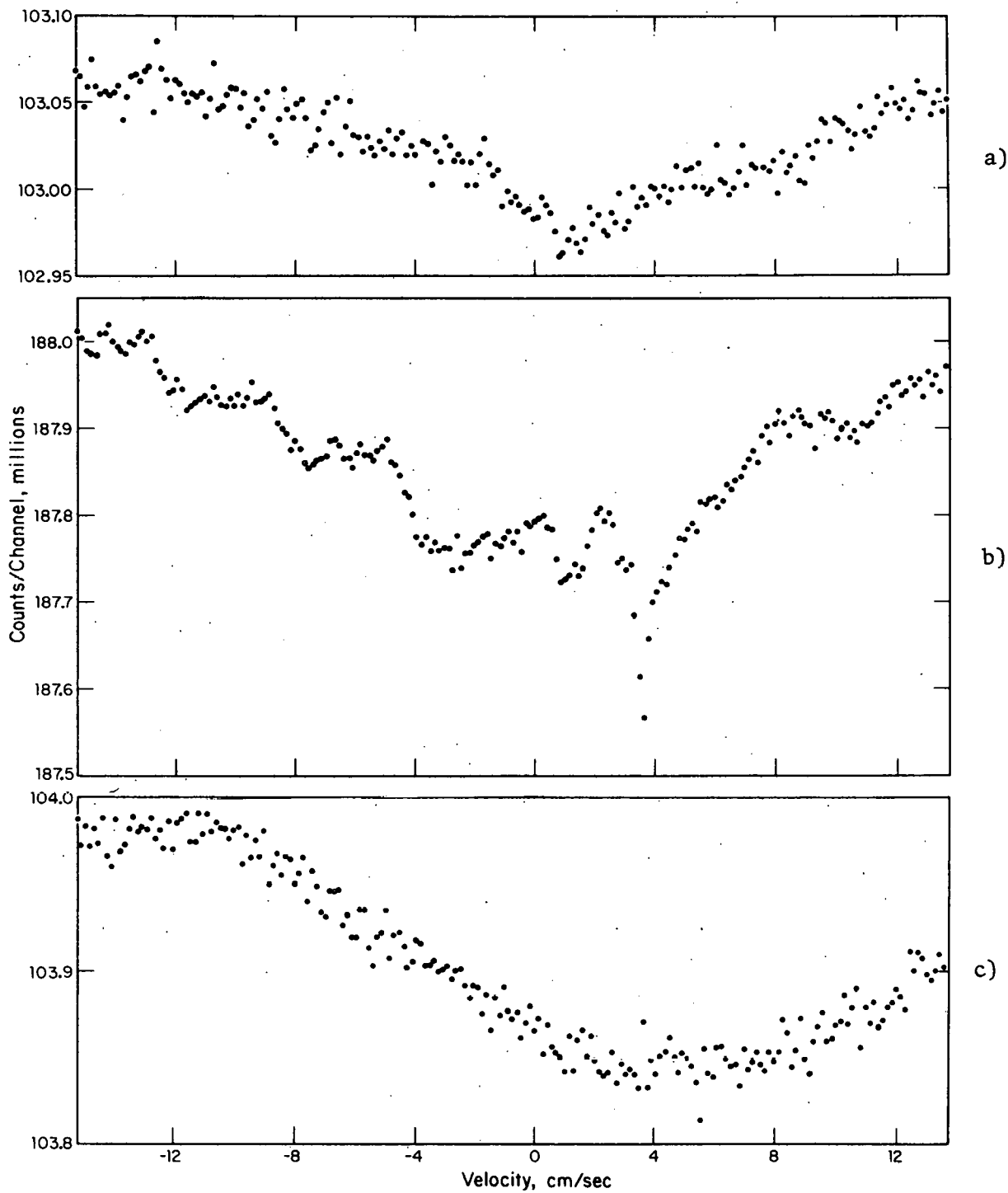


FIGURE 2. Mössbauer Spectra of a) MeCp_3NpCl , b) In_3NpCl (the Sharp Peak at 3.5 cm/sec is In_3Np), and c) Cp_3NpBr

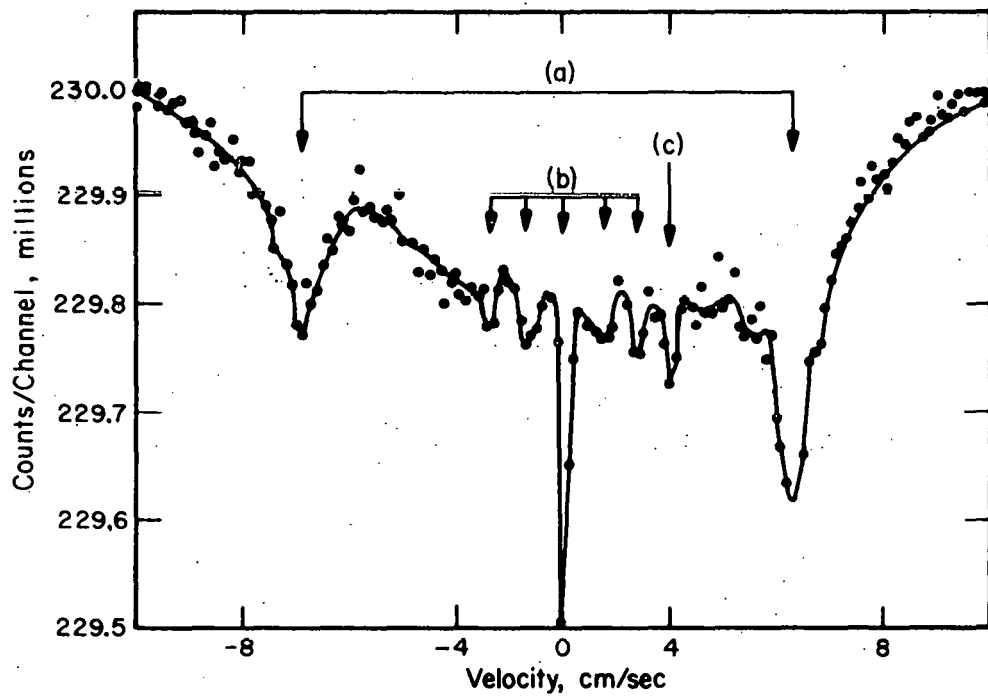


FIGURE 3. Mössbauer Spectra of a) $\text{Cp}_3\text{Np}^{14}\text{C}_4\text{H}_9$, b) Cp_4Np , and c) Cp_3Np

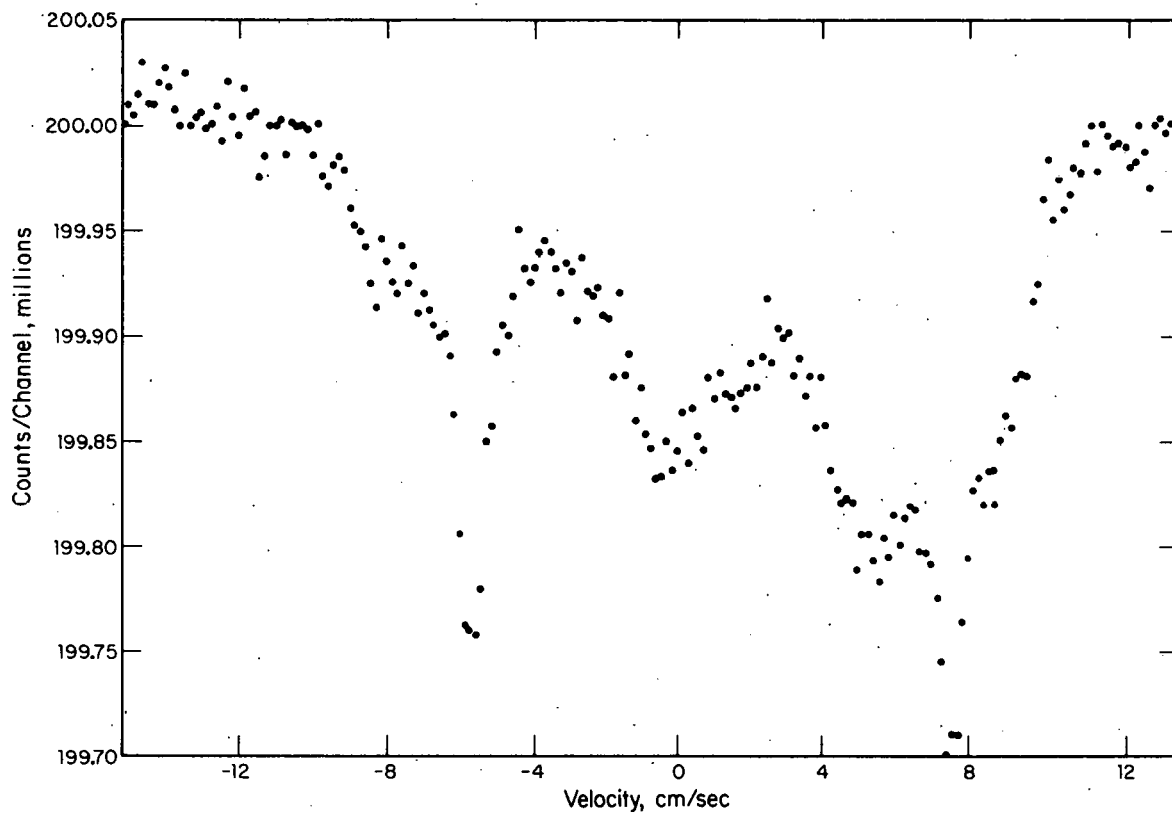


FIGURE 4. Mössbauer Spectrum of $(\text{MeCp})_3\text{NpOCH}(\text{CH}_3)_2$

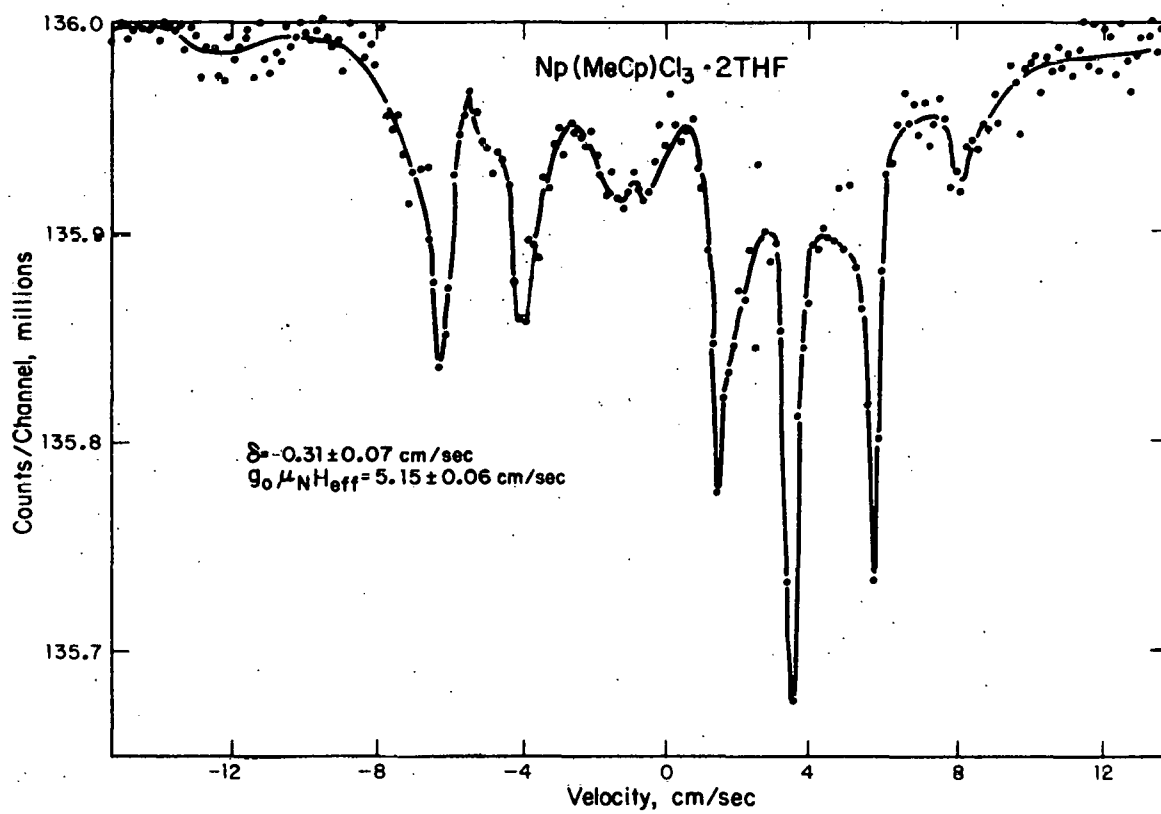


FIGURE 5. Mössbauer Spectra of $\text{Np}(\text{MeCp})\text{Cl}_3 \cdot 2\text{THF}$