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Covalency of Neptunium(IV) Tris(cyclopentadienyl) Compounds from Mössbauer Spectra

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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 $NpCp_3$-*n*-Bu and $NpCp_3C_6H_4C_2H_5$ show a strong σ character for the Np–*n*-Bu and Np–$C_6H_4C_2H_5$ 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 $Np(MeCp)Cl_3\cdot 2THF$ indicates that the MeCp ligand is σ-bonded in this compound.

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 $C_5H_4CH_2C_6H_5$ 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) analogues of the UCp_3^+ compounds and their study by Mössbauer spectroscopy. For several $NpCp_3^+$ compounds, intermediate relaxation effects obscured the 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 Section

General Procedure. All compounds were prepared in the dry, purified argon atmosphere of a glovebox. Samples were sealed under an argon atmosphere in plastic holders for Mössbauer measurements, as performed previously.[13,14] Solvents (THF, 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 α-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. $NpCp_3Cl$, $Np(MeCp)_3Cl$, and $NpCp_3Br\cdot DME$. $NpCp_3Cl$ was prepared by reacting $NpCl_4$ and TlCp in 1,2-dimethoxyethane (DME), as described by Marks et al.[15] Substitution of TlMeCp or $NpBr_4$ produced $Np(MeCp)_3Cl$ or $NpCp_3Br\cdot DME$, respectively. The product of this reaction may be only 70–80% pure. To obtain pure material (>95%) the crude product was dissolved in toluene and the solution filtered and vacuum evaporated. The solid product was heated at 100 °C under vacuum for 8–16 h to remove excess solvent. In the single preparation of $NpCp_3Br$, solvent removal was incomplete. Anal. Calcd for $NpCp_3Br\cdot DME$: Np, 40.05; Br, 13.6. Found: Np, 40.6; Br, 14.5.

$NpIn_3Cl$ and $NpIn_3\cdot x$THF. $NpIn_3Cl$ 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 $NpIn_3\cdot x$THF product. Mixing the reagents at −78 °C yielded a mixture with a Cl/Np ratio of 0.15, assumed to be a mixture of $NpIn_3Cl\cdot x$THF and $NpIn_3\cdot x$THF from its Mössbauer spectrum.

$NpCp_3BH_4$, $Np(MeCp)_3BH_4$, $NpCp_3OR$, and $Np(MeCp)_3OR$. 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 24–72 h, the solids (LiCl, KCl) were filtered, and the filtrate was vacuum evaporated to recover the products. Compounds prepared in this manner and their analyses are tabulated in Table I.

Table I

compd	% Np calcd	% Np found	compd	% Np calcd	% Np found
$NpCp_3BH_4$	53.04	48.9	$Np(MeCp)_3O$-*i*-C_3H_7	44.2	42.3
$Np(MeCp)_3BH_4$	48.4	46.9	$NpCp_3OCH(CF_3)_2$	39.6	40.2
$NpCp_3O$-*i*-C_3H_7	48.3	45.0	$NpCp_3O$-*t*-C_4H_9	46.9	44.4

The generally low neptunium results are considered the result of incomplete solvent removal. Solvents were removed in a fore-pump vacuum, without heating. Experience has shown that heating these compounds often leads to their decomposition.

$NpCp_3$-*n*-Bu. $NpCp_3$-*n*-Bu was prepared by adding an equimolar quantity of commercial butyllithium in hexane to $NpCp_3Cl$ suspended in diethyl ether at −78 °C.[8] The solution was stirred as it warmed to room temperature, and then the ether was removed by vacuum. The remaining solids were dissolved in toluene, the solution was filtered, and the product was recovered by vacuum evaporation of the toluene. Anal. Calcd for $NpCp_3$-*n*-Bu: Np, 48.5. Found: Np, 47.9. Cl was 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 $NpCp_3\cdot 3THF$ impurities.

$NpCp_3Ph$, $NpCp_3C_6H_4C_2H_5$, and $Np(MeCp)_3(C_6H_4C_2H_5)$. These compounds were prepared only in an impure state by reacting $NpCp_3Cl$ with an ether solution of the phenyllithium[17] at −78 °C, similar to the method for preparing $NpCp_3$-*n*-C_4H_9. After the mixture was stirred a short time at room temperature, the ether was removed under vacuum and the residue extracted with toluene. The toluene solution was evaporated under vacuum to recover the product. For $NpCp_3Ph$ 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% $NpCp_3Ph$; the Mössbauer spectrum showed a $NpCp_4$ impurity. The $NpCp_3(C_6H_4C_2H_5)$ and $Np(MeCp)_3(C_6H_4C_2H_5)$ compounds were further purified by extraction with petroleum ether (bp 20–40 °C). $Np(MeCp)_4$ was obtained, in an impure state, from an unsuccessful attempt to prepare $Np(MeCp)_3Ph$.

$Np(MeCp)Cl_3\cdot 2THF$. This compound was prepared by the reaction of stoichiometric quantities of TlMeCp and $NpCl_4$ in THF solution, similar to the literature preparation of $UCpCl_3\cdot 2THF$.[18,19] The reaction mixture was stirred for 24 h at room temperature and filtered, and a crude product was obtained by evaporation of the filtrate. The crude product was washed with toluene to remove a probable $Np(MeCp)_3Cl$ impurity and vacuum-dried. Anal. Calcd for $Np(MeCp)Cl_3\cdot 2THF$: 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, $Np(MeCp)_3BH_4$; Figure 2, $Np(MeCp)_3Cl$, $NpCp_3Br\cdot DME$, $NpIn_3Cl\cdot x$THF; Figure 3, $NpCp_3$-*n*-Bu; Figure 4, $Np(MeCp)_3O$-*i*-C_3H_7; Figure 5, $Np(MeCp)Cl_3\cdot 2THF$.

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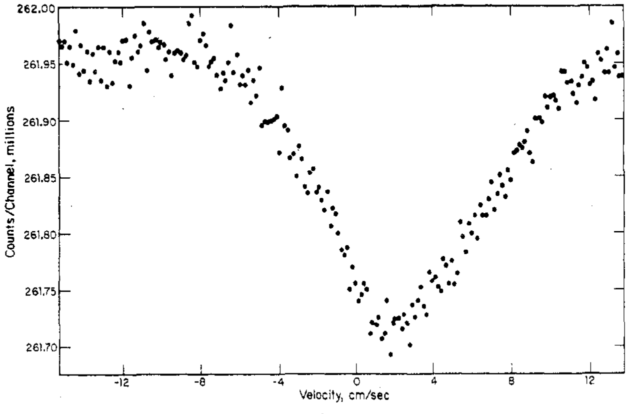

Figure 1. Mössbauer spectrum of $(MeCp)_3NpBH_4$.

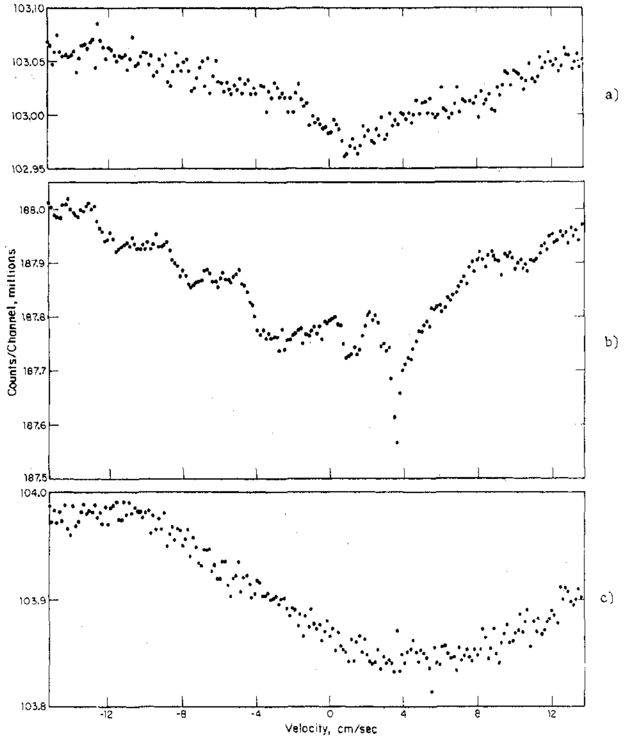

Figure 2. Mössbauer spectra of (a) $(MeCp)_3NpCl$, (b) In_3NpCl (the sharp peak at 3.5 cm/s is In_3Np), and (c) Cp_3NpBr.

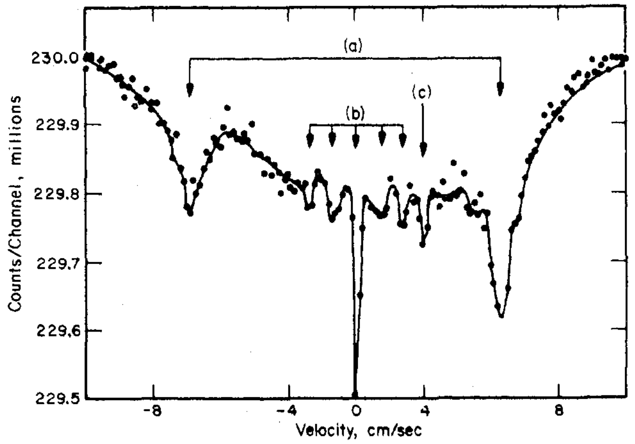

Figure 3. Mössbauer spectra of (a) Cp_3Np-*n*-Bu, (b) Cp_4Np, and (c) Cp_3Np.

Except for that of $NpMeCpCl_3$, 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. Examples are the spectra of $Np(MeCp)_3Cl$, $NpIn_3Cl·x$THF, and $NpCp_3Br·DME$ (Figure 2) and $NpCp_3BH_4$ and $NpCp_3Ph$ (not shown). The spectra of $NpCp_3O$-*i*-C_3H_7, $NpCp_3O$-*t*-Bu, and $NpCp_3C_6H_5C_2H_5$ were poorly resolved but could be interpreted within a rather generous error.

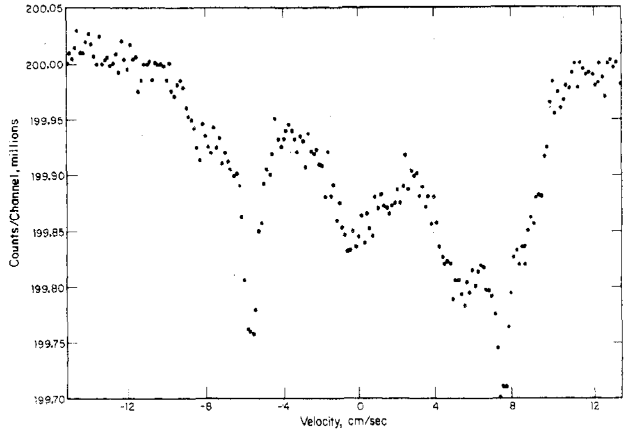

Figure 4. Mössbauer spectrum of $(MeCp)_3NpOCH(CH_3)_2$.

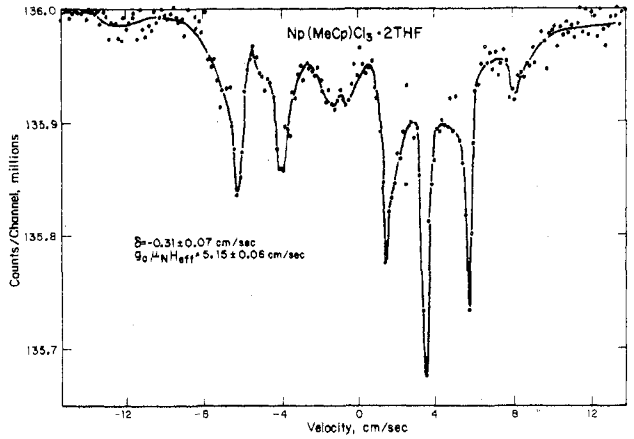

Figure 5. Mössbauer spectrum of $Np(MeCp)Cl_3·2THF$.

Poor resolution occurs when the relaxation time of the absorbing ^{237}Np nuclei is about the same as the 62-ns half-life of the 59.5-keV excited level. At relaxation times much faster than 62 ns, the spectrum is either a single line or a quadrupole-split pattern, like $NpCp_4$.[14] At much slower relaxation times, the spectrum is magnetically split, like $Np(C_8H_8)_2$.[13] Intermediate relaxation effects in Np(IV) compounds usually show some correlation with the distance between Np(IV) ions. Relaxation effects on Mössbauer spectra can sometimes be relieved by measuring a similar compound with bulkier ligands, such as $[(C_2H_5)_4N]_2NpCl_6$, 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 $NpCp_3Ph$ have spectra that could not be interpreted, so measurements were made with $Np(MeCp)_3BH_4$ and $NpCp_3C_6H_5C_2H_5$. Interpretation of the spectra requires the assumption that the isomer shifts be essentially the same for both the substituted and unsubstituted ligands. The Mössbauer spectra of $NpCp_4$ and $Np(MeCp)_4$ have the same isomer shifts within experimental error, in accord with this assumption.

The Mössbauer parameters for the compounds studied are listed in Table II, with some previously reported data included for comparison. Isomer shifts are referred to $NpAl_2$ = 0.

Table II. Mössbauer Parameters for $NpCp_3^+$ Compounds

compd	isomer shift, cm/s[a]	$eqQ/4$, cm/s[c]	$g_0\mu_nH_{eff}$, cm/s[d]
$NpCp_3Cl$[b]	1.4 ± 1.0		
$Np(MeCp)_4$	0.71 ± 0.07	1.29 ± 0.08	
$Np(MeCp)_3BH_4$	1.45 ± 0.4		
$NpCp_3$-*n*-Bu	0.27 ± 0.07		5.8 ± 0.2
$NpCp_3C_6H_4C_2H_5$	0.42 ± 0.28		5.5 ± 0.4
$Np(MeCp)_3O$-*i*-C_3H_7	0.93 ± 0.07	5.0 ± 1.0	5.72 ± 0.20
$NpCp_3O$-*i*-C_3H_7	0.86 ± 0.2		5.4 ± 0.5
$NpCp_3OCH(CF_3)_2$	0.79 ± 0.2		5.7 ± 0.4
$NpCp_3O$-*t*-Bu	0.86 ± 0.3		5.2 ± 0.4
$NpIn_3 \cdot x$THF	3.55 ± 0.15	1.37 ± 0.07	
$Np(MeCp)Cl_3 \cdot 2$THF	−0.31 ± 0.07		5.15 ± 0.06

[a] Isomer shift relative to $\delta = 0$ for $NpAl_2$. [b] From ref 14. [c] Quadrupole coupling constant. [d] Magnetic hyperfine constant.

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/s to 3.5 cm/s. Similarly, as electron density is contributed to the 5f orbitals from the ligands bonded to Np(IV), the isomer shift of the Np^{4+} ion is shifted from its normal position of −0.4 cm/s toward the normal value for Np^{3+}, 3.5 cm/s. The isomer shift of the Np^{4+} ion in Np(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 Np(IV) ion.

For $Np(MeCp)_3BH_4$ and $NpCp_3Cl$, the isomer shifts are 1.4 cm/s. The difference between 1.4 and −0.4 cm/s 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 Np(IV). The four $NpCp_3OR$ compounds all have isomer shifts in the range 0.8–0.93 cm/s; compared with the 1.4-cm/s shift of $NpCp_3Cl$, this demonstrates that the σ-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 $NpCp_3$-*n*-Bu and $NpCp_3C_6H_4C_2H_5$, 0.27 and 0.4 cm/s, respectively, show a much stronger electron-withdrawing tendency and verify the strong σ bonding reported for the *n*-Bu and $C_6H_4C_2H_5$ ligands.[9,10] The isomer shift of $NpCp_3$-*n*-Bu represents a withdrawal of electron density of more than 1 cm/s 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}–*n*-Bu bond, it is not surprising that no Np(IV) or U(IV) tetraalkyl compounds are known.

The isomer shift of $NpCp_4$ (0.72 cm/s) is less than that of $NpCp_3Cl$ (1.4 cm/s) and even $NpCp_3OR$ compounds (0.8–0.95 cm/s). The explanation for this lies almost certainly in the difference between the Cp–Np bond distances in $NpCp_3^+$ compounds and the distances in $NpCp_4$. In the U(IV) analogues, single-crystal studies have shown that the C–U distance is 2.72–2.74 Å for UCp_3Cl, UCp_3-*n*-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. On the assumption 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 $NpCp_3^+$. $Np(C_8H_8)_2$, which has the most positive isomer shift of any Np(IV) organometallic compound (1.94 cm/s), has a Np–C distance of 2.65 Å. The shorter Np–C distance in $Np(C_8H_8)_2$ compared to $NpCp_4$ is a significant factor in the greater covalency of $Np(C_8H_8)_2$. The Np(IV) ion has 20 electrons available from the ligands in both $NpCp_4$ and $Np(C_8H_8)_2$, so the electron density available to the Np(IV) ion is the same for both $Np(C_8H_8)_2$ and $NpCp_4$.

The Mössbauer spectrum (Figure 5) of $Np(MeCp)Cl_3 \cdot 2$THF has an isomer shift of −0.31 cm/s, about the same as the isomer shift of $NpCl_4$ (−0.35 cm/s). Comparing these isomer shift values, one observes that 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 $NpMeCpCl_3 \cdot 2$THF and implies that the Cp ligand in analogous compounds ($UCpCl_3 \cdot 2$THF, $UCpCl_3 \cdot$DME, etc.) is probably σ bonded also. The infrared data of Bagnall et al.[19] show an average ν(U–Cp) of 262 cm^{-1} for seven compounds of the general formula $UCpX_3 \cdot x$S ($X = Cl^-$ or Br^-, $x = 1$ or 2, S = ligand) compared with an average ν(U–Cp) of 243 cm^{-1} for UCp_3Cl and UCp_3Br. The difference suggests a difference between the U–Cp bond in UCpX and the U–Cp bond in UCp_3X compounds, consistent with the Mössbauer results.

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Registry No. $NpCp_3BH_4$, 70480-21-6; $Np(MeCp)_3BH_4$, 70479-75-3; $NpCp_3O$-*i*-C_3H_7, 70480-19-2; $Np(MeCp)_3O$-*i*-C_3H_7, 70479-76-4; $NpCp_3OCH(CF_3)_2$, 70479-77-5; $NpCp_3O$-*t*-C_4H_9, 70479-78-6; $NpCp_3$-*n*-Bu, 70479-79-7; $NpCp_3Ph$, 70479-80-0; $NpCp_3C_6H_4C_2H_5$, 70470-76-7; $Np(MeCp)_3(C_6H_4C_2H_5)$, 70470-77-8; $Np(MeCp)Cl_3$, 70470-86-9; $NpCp_3Br$, 70414-75-4; $NpIn_3$, 70480-18-1; $NpIn_3Cl$, 70479-81-1; $NpCp_3Cl$, 1317-00-6; $NpCp_4$, 37216-56-1; $Np(MeCp)_4$, 70479-82-2; $NpCl_4$, 15597-84-9; $NpBr_4$, 15608-32-9; $NpCp_3$, 63757-59-5.

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