regard wholly ionic formulations, like $3Li^+ \cdot N^{3-}$ for Li_3N, to be exaggerated.

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Registry No. NH_3, 7664-41-7; NH_2Li, 7782-89-0; $NHLi_2$, 12135-01-2; NLi_3, 26134-62-3; NH_2^-, 17655-31-1; $NHLi^-$, 75491-75-7; NLi_2^-, 83560-66-1; NH_4^+, 14798-03-9; NH_3Li^+, 52472-72-7; $NH_2Li_2^+$, 83560-67-2; $NHLi_3^+$, 83560-68-3; NLi_4^+, 83560-69-4; Li^+, 17341-24-1.

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Cyclopentadienyl Bonding in Bis(cyclopentadienyl)neptunium(IV) Compounds from ^{237}Np Mössbauer Spectra[1]

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^{237}Np Mössbauer spectra were measured for a series of Np(IV) compounds of the general compositions NpX_4, NpX_2Y_2, and NpX_2YY' [X = acac, bis(1-pyrazolyl)borate, tris(1-pyrazolyl)borate; Y, Y′ = Cl, Cp, MeCp]. Comparison of the isomer shifts of the Mössbauer spectra showed no evidence for covalent bonding between the Cp ligand and Np(IV) in the Cp_2Np^{IV} and $CpNp^{IV}$ moieties. It is proposed that ligand repulsion in NpX_2Cp_2 and $NpX_2(MeCp)_2$ compounds lengthens the Np(IV)–Cp and Np(IV)–(MeCp) bonds and thus prevents any appreciable Np(IV)–ligand orbital overlap. Mössbauer magnetic splitting and quadrupole splitting parameters are greater for [tris(1-pyrazolyl)borato]neptunium(IV) compounds than for [bis(1-pyrazolyl)borato]neptunium(IV) compounds, a result attributed to the stronger field from the tridentate coordination of the tris(1-pyrazolyl)borate ligand.

Introduction

Previous work has used the isomer shift of the ^{237}Np Mössbauer effect to investigate covalent effects in the bonding of Np(IV) organometallic compounds.[2,3] The isomer shift (δ) of Np(IV) in $NpCl_4$ is −0.35 cm/s; δ for $NpCl_3$ is 3.54 cm/s. Covalency in Np(IV)–ligand bonding changes the isomer shift of a Np(IV) compound toward the 3+ valence shift. For example, the isomer shift of bis(cyclooctatetraenyl)neptunium(IV),[4] the Np(IV) analogue of uranocene,[5] is 1.94 cm/s, which is interpreted to indicate that the cyclooctatetraenyl ligands have contributed electron density to the Np(IV) ion equivalent to one-half that of a 5f valence electron.

The covalent contribution π-cyclopentadienyl (Cp) ligands have been of particular interest in previous work[2,3] because of recent interest in the chemistry of uranium(IV) cyclopentadienyl and uranium(IV) pentamethylcyclopentadienyl (Me_5Cp) compounds.[6-11] Compounds of Np(IV) and U (IV) are normally isostructural and have essentially identical chemical properties except for the tendency of Np(IV) compounds to reduce to Np(III) compounds. Previous work[2,3] has shown that the Cp or MeCp ligands in the Cp_3Np^{IV} moiety contribute covalently to the bonding of Cp_3NpZ (Z = Cl, BH_4, R, OR, Ar). δ for Cp_3NpCl is 1.4 cm/s; δ for $(MeCp)_3NpBH_4$ is 1.45 cm/s. R, OR, and Ar are σ-bonding ligands; their effect on the Np(IV) isomer shift is the opposite of that of the Cp ligand. δ for Cp_3NpBu is 0.27 cm/s, and δ for Cp_3NpO-*i*-Pr is 0.86 cm/s, to be compared with the 1.4 cm/s for Cp_3NpCl.[2a]

Rather than the increased positive δ expected, compared to that of $NpCp_3Cl$, δ for $NpCp_4$ is 0.72 cm/s.[12] This is explained by the crystal structures of the U(IV) analogues—UCp_4 and UCp_3Cl—which show that the U–C(ring) bond lengths in UCp_4 are 0.07 Å longer than the U–C(ring) bond lengths in UCp_3Cl.[13-15] The longer bond length decreases the overlap of Cp and Np(IV) orbitals and is reflected in a smaller isomer shift in $NpCp_4$ than in Cp_3NpCl.[2a]

The object of this work was to use the ^{237}Np Mössbauer effect to investigate the bonding properties of a Cp_2Np^{IV} moiety. The success of a variety of syntheses with the bis(pentamethylcyclopentadienyl)uranium(IV) [$(Me_5Cp)_2U^{IV}$] moiety[9,10] leads to the assumption that the ligand contributes substantial electron density to the U(IV) ion in $(Me_5Cp)_2U^{IV}$ compounds and also the expectation that $(Me_5Cp)_2Np^{IV}$, Cp_2Np^{IV}, and $(MeCp)_2Np^{IV}$ moieties might show a covalent contribution to their bonding.

A report of the preparation of UCp_2Cl_2[16] was later found to have mistaken a mixture of UCp_3Cl and $UCpCl_3L_2$ (L = solvent) for the desired compound.[17,18] Attempts to synthesize $NpCp_2Cl_2$ also yielded a mixture of $NpCp_3Cl$ and $NpCpCl_3 \cdot 2THF$.[19] However, the Cp_2U^{IV} moiety can be

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(1) The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

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stabilized by first attaching two bulky ligands to the U(IV) ion and then attaching two Cp ligands, as in the sequence[20]

$$UCl_4 \xrightarrow[THF]{2Na(acac)} [U(acac)Cl_2] \xrightarrow[THF]{2TlCp} U(acac)_2Cp_2$$

$$acac = CH_3COCHCOCH_3$$

The poly(1-pyrazolyl)borate ligands[20,21] are also bulky enough to serve in a similar reaction sequence. For this work, compounds of the Cp_2Np^{IV} and $(MeCp)_2Np^{IV}$ moieties with the acac, bis(1-pyrazolyl)borate, and tris(1-pyrazolyl)borate ligands were synthesized for Mössbauer study and related compounds synthesized for comparison purposes. It should be noted that Takats and co-workers[7,8] have also synthesized Cp_2U^{IV} compounds by the reaction of $U(NR_2)_4$ with HCp. This approach was not attempted, and attempts to synthesize $(Me_5Cp)_2NpCl_2$ yielded mainly Np(III) compounds.

Experimental Section

Materials. THF and ethyl ether were purified by distillation from $LiAlH_4$ in an argon atmosphere. Toluene and petroleum ether (bp 20–40 °C) were dried by passage through a column of 3A molecular sieve, stirred overnight with CaH_2, and filtered before use. Sodium acetylacetonate (Na(acac)) was prepared from freshly distilled Hacac and sodium metal. $NpCl_4$ was prepared as described previously.[22] Potassium tris(1-pyrazolyl)borate ($KHB(pz)_3$) and potassium bis(1-pyrazolyl)borate ($KH_2B(pz)_2$) were prepared by the procedures of Trofimenko.[23] Thallous cyclopentadienide (TlCp) was prepared by the method of Meister,[24] and sublimed and stored under vacuum before use. Thallous methylcyclopentadienide (TlMeCp) was prepared, purified, and stored in the same way, except that TlMeCp was prepared in an argon atmosphere. $NpCpCl_3{\cdot}2THF$ and $Np(MeCp)Cl_3{\cdot}2THF$ were prepared by the procedure of Bagnall and Edwards.[25] Thallous pentamethylcyclopentadienide was prepared by the procedure of Tulip and Manzer.[26]

Methods. All compounds were prepared in a glovebox in a purified argon atmosphere. Analyses[2a] were obtained by previously described methods. ^{237}Np Mössbauer spectra[3] were measured with a constant-acceleration spectrometer at 4.2 K and a 400-channel analyzer in the multiscaler mode. The spectra displayed include lines drawn to guide the viewer's eye. The only Mössbauer parameter required for the purpose of this study is the isomer shift, which is easily obtained from the spectra without detailed spectral analysis. Computer fitting of the data was therefore deemed unnecessary.

Errors quoted for the Mössbauer data (Table II) were determined either by the deviation between duplicate spectra or, in cases where a misinterpretation of the spectra was possible, by including a large enough error limit to include either interpretation.

Synthesis. The preparation of the compounds followed generally the procedures reported by Bagnall and co-workers:[19–21]

$$NpCl_4 + 2ML \xrightarrow{THF} NpCl_2L_2{\cdot}xTHF + 2MCl$$

$$M = Na, K, Li;\ L = acac, H_2B(pz)_2, HB(pz)_3$$

$$NpCpCl_3{\cdot}2THF + ML \xrightarrow{THF} NpCpLCl_2{\cdot}xTHF + MCl$$

$$NpL_2Cl_2 + TlCp \xrightarrow{THF} NpL_2CpCl{\cdot}xTHF + TlCl$$

$$NpL_2Cl_2 + 2TlCp \xrightarrow{THF} NpL_2Cp_2{\cdot}xTHF + 2TlCl$$

$$NpCl_4 + 4KL \rightarrow NpL_4 + 4KCl \qquad L = H_2B(pz)_2, HB(pz)_3$$

All reactions were carried out at room temperature by mixing stoichiometric amounts of the reactants in THF solution. The solutions were stirred for 3–16 h; the alkali metal chloride was filtered, and the filtrate was vacuum evaporated to dryness. The product from filtrate evaporation was occasionally an oil, but in all cases it was washed with petroleum ether and redried under vacuum for 2–7 h at room temperature. This procedure did not yield solvent-free products. One to five molecules of THF were normally associated with the final product. No attempts were made to drive off the excess THF by heating under vacuum to avoid possible decomposition of the compounds. The analytical data for the compounds studied are shown in Table I.

Table I. Analytical Results

compd	% Np found	% Np calcd	% Cl found	% Cl calcd	color
$Np(acac)_2Cl_2{\cdot}THF$	40.0	41.00	12.44	12.28	green
$Np(acac)_2CpCl{\cdot}THF$	40.1	39.01	5.66	5.84	orange
$Np(acac)_2(MeCp)Cl{\cdot}{}^1/_2THF$	41.4	40.71	6.81	6.08	orange
$Np(acac)_2(MeCp)_2$	40.0	39.96	0.62		tan
$Np(acac)_2Cp_2{\cdot}2THF$	31.5	32.37	0.40		tan
$Np(HB(pz)_3)_2Cl_2{\cdot}3THF$	24.6	25.0	7.50	7.49	orange
$Np(HB(pz)_3)_2(MeCp)_2{\cdot}4THF$	21.3	21.4			brown
$Np(HB(pz)_3)_2Cp_2{\cdot}5THF$	20.7	20.55			red-brown
$Np(HB(pz)_3)_4{\cdot}2THF$	19.3	19.22			yellow-green
$Np(HB(pz)_3)CpCl_2{\cdot}THF$	37.9	36.01	11.8	10.81	red
$Np(HB(pz)_3)(MeCp)Cl_2{\cdot}3THF$	27.8	29.2	9.1	8.73	tan
$Np(HB(pz)_3)Cp_2Cl$	40.0	38.50	6.75	5.76	brown
$Np(H_2B(pz)_2)_2Cl_2{\cdot}3THF$	34.0	33.01	12.97	9.89	gold
$Np(H_2B(pz)_2)_2Cp_2{\cdot}3THF$	27.7	28.24			orange
$Np(H_2B(pz)_2)_2(MeCp)_2{\cdot}THF$	33.0	32.96			brown
$Np(H_2B(pz)_2)_4{\cdot}THF$	26.1	26.42			yellow-green
$Np(Me_5C_5)_2Cl_2{\cdot}2THF$	33.3	32.4	9.3	9.70	brown

The neptunium(IV) poly(1-pyrazolyl)borate compounds were glittering, crystalline-appearing solids as recovered by evaporation of the solvent. When the vacuum-dried solids were stored, these compounds usually coalesced into a solid mass within ~1 day.

A single successful preparation of $Np(Me_5C_5)_2Cl_2{\cdot}2THF$ was achieved by the reaction between $NpCl_4$ and $TlMe_5C_5$ in THF solution. Attempts to prepare $Np(Me_5C_5)_2Cl_2$ by the reaction between $NpCl_4$ and $LiMe_5C_5$ in THF, ethyl ether, and toluene solutions were unsuccessful.

^{237}Np Mössbauer Spectra

General Theory.[3] The isomer shift in ^{237}Np Mössbauer spectra is determined by the s-electron density at the Np nucleus. Differences in the isomer shift between Np compounds arise from the shielding of the 6s orbitals, principally by the inner 5f orbitals.

The isomer shifts among the different Np valences each occur in a specific velocity region, decreasing from 3.5 cm/s for Np^{3+} in rather nonlinear manner to −6.8 cm/s for Np(VII). In Np(IV) organometallic compounds, if the ligand can overlap the Np(IV) 5f orbitals, some electron density will be contributed to the 5f orbital. This increased electron density increases the shielding of the 6s orbital and results in a positive isomer shift relative to a Np(IV) compound with less covalent character in its bonding. The Introduction describes illustrative examples.

Interpretation of Spectra. The interpretation of hyperfine effects in ^{237}Np Mössbauer spectra is described by Pillinger and Stone.[27] Briefly, there are three parameters obtainable from Mössbauer spectra—the isomer shift, the magnetic splitting constant, and the quadrupole splitting constant. A simple single-line spectrum is obtained when there is no magnetic or quadrupole splitting; the isomer shift is the minimum of the absorption resonance. Figure 6 is an example

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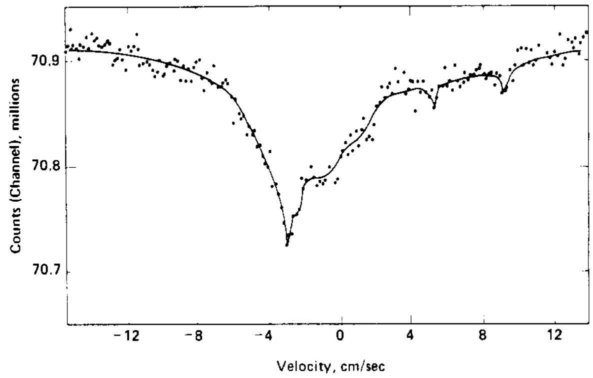

Figure 1. Mössbauer spectrum of $Np(Me_5C_5)_2Cl_2 \cdot 2THF$.

of a simple, single-line spectrum.

Magnetically split spectra theoretically have 16 lines, but in practice usually only 10 lines can be resolved. The splitting is symmetric, so the average of two symmetrically split lines determines the isomer shift. Two strong lines that occur near the outer range of velocities are normally used for determining the isomer shift. The magnetic splitting constant is obtained from separation of these lines. Since these lines are unaffected by quadrupole splitting, isomer shifts may also be extracted from their velocities when both magnetic and quadrupole splittings occur. Figure 2 is a particularly splendid example of magnetic splitting with an additional small quadrupole splitting.

Quadrupole splitting arises from the quadrupole moment of the nonspherical ^{237}Np nucleus. Interaction of this quadrupole moment with the electric field of the ligands surrounding the ^{237}Np nucleus can split each resonance into a maximum of 5 lines. The isomer shift is determined by the position of the center line. A symmetric, 5-line pattern is observed when the ^{237}Np nucleus is on a 3-fold or higher symmetry axis. An asymmetry in the external electric field can reduce the pattern to 5 unequally split lines or even 3 lines. In any case, the center line is not shifted, and its position determines the isomer shift for the compound. Examples of a quadrupole splitting produced by an asymmetric field are the patterns shown in Figure 4. The combination of a small quadrupole splitting with magnetic splitting can change the order and intensities of the resonance lines and was responsible for a previously published[3] incorrect analysis of the spectrum shown in Figure 6.

^{237}Np Mössbauer spectra are often modified by intermediate relaxation (time-dependent) effects. The electronic field on the ^{237}Np nucleus fluctuates at a frequency ω_e, producing a time-dependent charge density. The isomer shift has a frequency $\omega_{IS} = \Delta E_{IS}/\hbar$ corresponding to the difference in the isomer shift energy between two charge states. In the limit of fast electronic relaxation ($\omega_e >> \omega_{IS}$), only the isomer shift—or electron density—is observed, and the spectrum is a single line. For $\omega_e << \omega_{IS}$, a magnetically split spectrum is observed. For the intermediate relaxation case, $\omega_e \approx \omega_{IS}$, and a poorly resolved spectrum is observed. Occasionally, the spectrum is so poorly resolved as to be uninterpretable, as in Figure 1. The poor resolution in Figure 5 is also due to intermediate relaxation effects.

Results and Discussion

Table II. Mössbauer Parameters

compd[a]	isomer shift (δ), cm/s[b]	magnetic splitting const, $g_0\mu_N H_{eff}$, cm/sec	quadrupole coupling const, $^1/_4 eqQ$, cm/s
$Np(acac)_2Cl_2$	−0.42 ± 0.07	8.49 ± 0.05	−0.42 ± 0.1
$Np(acac)_2(MeCp)Cl$	−0.52 ± 0.2	6.3 ± 0.6	
$Np(acac)_2(MeCp)_2$	−0.53 ± 0.14		1.24 ± 0.1
$Np(acac)_4$[c]	−0.67	6.41 ± 0.02	0.06 ± 0.06
$Np(HB(pz)_3)_2Cl_2$	−0.60 ± 0.07	8.93 ± 0.29	
$Np(HB(pz)_3)_2(MeCp)_2$	−0.60 ± 0.07		
$Np(HB(pz)_3)_2Cp_2$	−0.46 ± 0.07		
$Np(HB(pz)_3)_4$	−0.46 ± 0.07		1.27 ± 0.15
$Np(HB(pz)_3)CpCl_2$	−0.27 ± 0.15	8.80 ± 2.5	
$Np(HB(pz)_3)(MeCp)Cl_2$	−0.06 ± 0.3		
$Np(H_2B(pz)_2)_2Cl_2$	−0.60 ± 0.07	5.78 ± 0.05	
$Np(H_2B(pz)_2)_2Cp_2$	−0.02 ± 0.4		
$Np(H_2B(pz)_2)_2(MeCp)_2$	−0.46 ± 0.2		
$Np(H_2B(pz)_2)_4$	−0.60 ± 0.07		1.05 ± 0.15

[a] Associated THF omitted. [b] Relative to $\delta(NpAl_2) = 0$. [c] Claussen, C. A.; Stone, J. A., unpublished data.

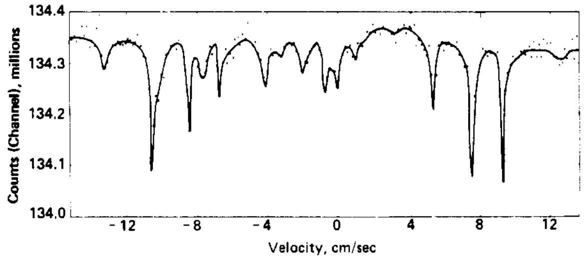

Figure 2. Mössbauer spectrum of $Np(acac)_2Cl_2 \cdot THF$.

The isomer shifts (relative to $\delta(NpAl_2) = 0$), magnetic coupling constants, and quadrupole coupling constants from the ^{237}Np Mössbauer spectra are summarized in Table II. The spectra of $Np(acac)_2CpCl$, $Np(HB(pz)_3)Cp_2Cl$, and $Np(Me_5C_5)_2Cl_2 \cdot 2THF$ (Figure 1) were so badly distorted by intermediate relaxation effects or so lacking in definition that no Mössbauer parameters could be obtained. Spectra of $Np(acac)_2(MeCp)Cl$, $Np(HB(pz)_3)CpCl_2$, $Np(HB(pz)_3)(MeCp)Cl_2$, $Np(H_2B(pz)_2)_2Cp_2$, and $Np(H_2B(pz)_2)_2(MeCp)_2$ were also distorted by relaxation effects but could be interpreted within generous limits of error.

Intermediate relaxation effects are common for Cp compounds of Np(IV) organometallic compounds, and the substitution of MeCp for Cp in a particular compound is occasionally successful in improving its Mössbauer spectrum.[12,13] The MeCp ligand probably increases the distance between Np(IV) ions in the compound and thus decreases the weak interactions (spin–spin, spin–lattice) that are considered primarly responsible for the relaxation effects.

^{237}Np Mössbauer spectra of representative compounds are shown: $Np(acac)_2Cl_2 \cdot THF$ in Figure 2, $Np(HB(pz)_3)_2Cl_2 \cdot 3THF$ and $Np(H_2B(pz)_2)_2Cl_2 \cdot 3THF$ in Figure 3, $Np(HB(pz)_3)_4 \cdot 2THF$ and $Np(H_2B(pz)_2)_4 \cdot THF$ in Figure 4, $Np(HB(pz)_3)CpCl_2 \cdot THF$ in Figure 5, and $Np(HB(pz)_3)_2(MeCp)_2 \cdot 4THF$ and $Np(H_2B(pz)_2)_2(MeCp)_2 \cdot THF$ in Figure 6. The spectra in Figures 2, 3, and 5 are magnetically split spectra; Figure 4 shows quadrupole-split spectra, and Figure 6 shows simple single-line spectra. The interpretation of these spectra is described above.

The spectrum of $Np(acac)_2Cl_2$ has been reinterpreted from that previously reported. Two interpretations are possible: (1) $\delta = -1.47$ cm/s, $g_0\mu_N H_{eff} = 7.92$ cm/s, and $eqQ/4 = 0.97$ or (2) $\delta = -0.42$ cm/s, $g_0\mu_N H_{eff} = 8.49$ cm/s, and $eqQ/4 = -0.42$ cm/s. In a previous publication,[3] the first interpretation was erroneously chosen. Comparison with the isomer shifts of other compounds in Table II leaves no doubt that the second interpretation is the correct choice.

Comparison of the isomer shifts in Table II shows no significant difference in isomer shifts among the ^{237}Np Mössbauer spectra of any of the compounds investigated, and the isomer shifts do not differ significantly from the isomer shift of $NpCl_4$, $\delta = -0.35$ cm/s. From the evidence of the ^{237}Np Mössbauer spectra, none of the ligands involved in the bonding of the

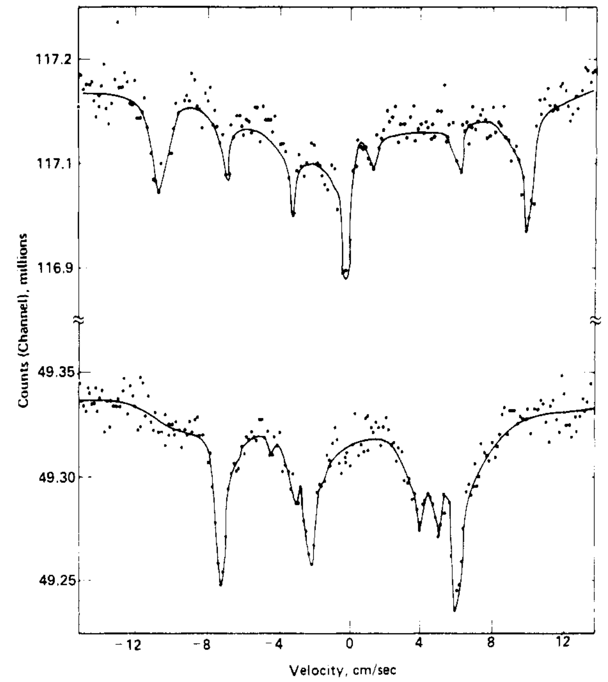

Figure 3. Mössbauer spectra of $Np(HB(pz)_3)_2Cl_2{\cdot}3THF$ (top) and $Np(H_2B(pz)_2)_2Cl_2{\cdot}3THF$ (bottom).

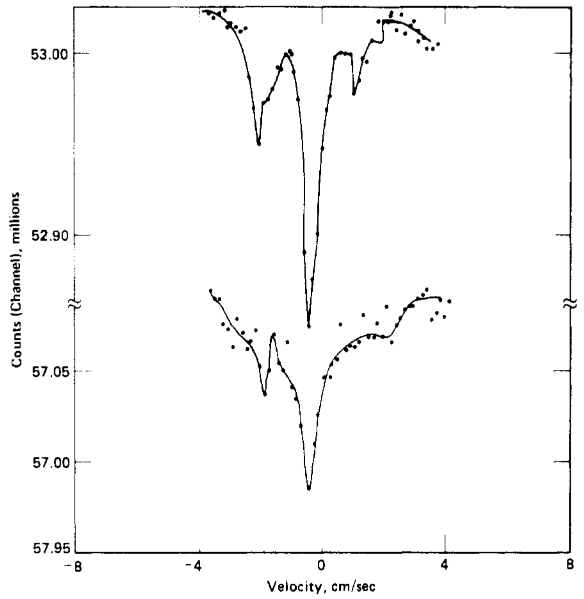

Figure 4. Mössbauer spectra of $Np(HB(pz)_3)_4{\cdot}2THF$ (top) and $Np(H_2B(pz)_2)_4{\cdot}THF$ (bottom).

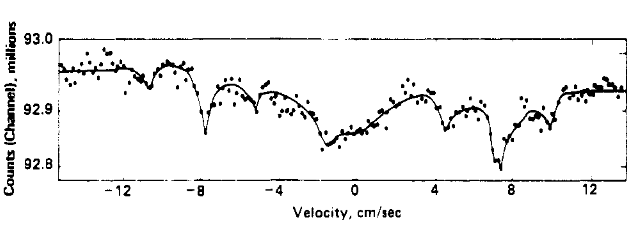

Figure 5. ^{237}Np Mössbauer spectrum of $Np(HB(pz)_3)CpCl_2{\cdot}THF$.

compounds here measured contributes any appreciable electron density to the 5f orbitals of the Np(IV) ion. This is in contrast to the striking covalent effects shown by the isomer shifts of $Np(C_8H_8)_2$ ($\delta = +1.94$ cm/s)[4] and $NpCp_3Cl$ ($\delta = +1.4$ cm/s).[12]

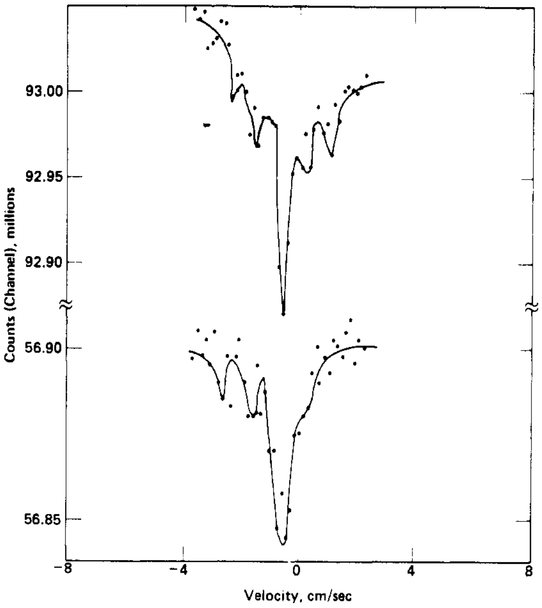

Figure 6. Mössbauer spectra of $Np(HB(pz)_3)_2(MeCp)_2{\cdot}4THF$ (top) and $Np(H_2B(pz)_2)_2(MeCp)_2{\cdot}THF$ (bottom).

The Cp and MeCp ligands are ligands that can donate electron density to the Np(IV) ion. Their failure to make any significant contribution is probably because the Np–Cp bond distance in the compounds studied is too long to allow an appreciable overlap between the ligand and the 5f orbitals of the Np(IV) ion. Bis(cyclopentadienyl)actinide(IV) compounds are not stable[16-19] unless access to the actinide(IV) coordination sphere is restricted by other ligands, so there must be substantial repulsion between the bonding ligands. This repulsion would be expected to lengthen the metal ion–Cp bonds and, thus, decrease any covalent contribution to the bonding.

A resonance line necessary for the analysis of the Mössbauer spectrum of $Np(Me_5C_5)_2Cl_2$ (Figure 1) is missing; thus, this spectrum cannot be interpreted. This is a distinct disappointment, because the chemical behavior of its uranium analogue indicates that there is a strong covalent contribution to the bonding of $U(Me_5C_5)_2X_2$ compounds.[9,10] This covalent contribution can be partly withdrawn to stabilize the bonding to U(IV) of σ-bonding ligands, as was previously found for $NpCp_3X$ compounds.[2a] These same consideratios also apply to the Me_5C_5 compounds of other strongly electropositive ions such as Zr(IV).[28]

The Mössbauer spectra of analogous bis- and tris(1-pyrazolyl)borate compounds show differences in magnetic splitting (Figure 3) and quadrupole splitting (Figure 4). The possible cause of these differences is in the field on the Np(IV) ion from the two ligands. The bis(1-pyrazolyl)borate ligand acts as a bidentate ligand, and the tris(1-pyrazolyl)borate acts as a tridentate ligand. The larger magnetic splitting for $Np(HB(pz)_3)_2Cl_2{\cdot}3THF$ (Figure 3) and the larger quadrupole splitting for $Np(HB(pz)_3)_4{\cdot}2THF$ would be expected for the more strongly coordinating $HB(pz)_3$ ligand. The field from the tridentate $HB(pz)_3$ ligand shows both stronger magnetic and electric effects on the ^{237}Np Mössbauer spectra than the field from the bidentate $H_2B(pz)_2$ ligand.

Registry No. $Np(acac)_2Cl_2$, 80844-40-2; $Np(acac)_2(MeCp)Cl$, 83947-35-7; $Np(acac)_2(MeCp)_2$, 80844-41-3; $Np(acac)_4$, 26679-42-5; $Np(HB(pz)_3)_2Cl_2$, 83947-36-8; $Np(HB(pz)_3)_2(MeCp)_2$, 83947-37-9; $Np(HB(pz)_3)_2Cp_2$, 83947-38-0; $Np(HB(pz)_3)_4$, 84041-59-8; $Np(HB(pz)_3)CpCl_2$, 83947-39-1; $Np(HB(pz)_3)(MeCp)Cl_2$, 83947-40-4; $Np(H_2B(pz)_2)_2Cl_2$, 83947-41-5; $Np(H_2B(pz)_2)_2Cp_2$, 83947-42-6; $Np(H_2B(pz)_2)_2(MeCp)_2$, 83966-20-5; $Np(H_2B(pz)_2)_4$, 83966-21-6; $NpCl_4$, 15597-84-9; $NpCpCl_3$, 83947-43-7; TlCp, 34822-90-7.

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[28] Walozanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121.