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^{237}Np MÖSSBAUER SPECTRA OF NEPTUNIUM(IV) TRIS(PYRAZOL-1-YL) BORATE COMPOUNDS*

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ABSTRACT

The compounds $Np(HBpz_3)_2Cl_2$, $Np(HBpz_3)_2(MeCp)_2$, $Np(HBpz_3)CpCl_2$, and $Np(HBpz_3)(MeCp)Cl_2$ (pz = $C_3H_3N_2$, Cp = C_5H_5, MeCp = $CH_3C_5H_4$) have been prepared as tetrahydrofuran solvates and characterized by analysis. ^{237}Np Mössbauer spectra showed magnetic splitting, except for $Np(HBpz_3)_2(MeCp)_2$. The spectra of $Np(HBpz_3)CpCl_2$ and $Np(HBpz_3)MeCpCl_2$ were distorted by intermediate relaxation effects. Isomer shifts of -0.6 cm/sec were found for both $Np(HBpz_3)_2Cl_2$ and $Np(HBpz_3)_2(MeCp)_2$, suggesting that the covalent contribution to bonding by MeCp in the latter compound is small.

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INTRODUCTION

The isomer shifts of ^{237}Np Mössbauer spectra show differences vetween Np(IV) compounds. These differences are reflected in changes in 5f electron density of the compounds. Comparison among Np(IV) organometallic compounds can be interpreted as showing the addition or withdrawal of 5f electron density by the ligands bonded to the Np(IV) ion.[1,2] In previous studies, the effect of $C_8H_8^{-2}$, C_5H_5(Cp), R, OR and acac ligands was investigated. This paper reports on the ^{237}Np Mössbauer spectra of tris(1-pyrazolyl) [$HB(N_2C_3H_3)_3$ = $HBpz_3$] and $HBpz_3$-Cp Np(IV) compounds.

Analogous Th(IV) and U(IV) - $HBpz_3$ and $HBpz_3$-Cp compounds were prepared and studied by Bagnell and coworkers.[3,4,5] An interesting possibility in the ^{237}Np Mössbauer study is the assessment of the bonding properties of Cp in a compound such as $NpCp_2X_2$. $NpCp_2X_2$ can be prepared only if X is a relatively bulky ligand compared to chloride. Previous Mössbauer studies have shown a substantial electronic contribution to bonding from the Cp ligands in $NpCp_3^+$ and essentially no contribution to bonding from Cp in $NpCpCl_3$. Therefore, the bonding contribution of a Cp_2Np^{+2} unit is of interest.

EXPERIMENTAL SECTION

General

All compounds were prepared in a purified argon atmosphere. Samples for Mössbauer magnetic susceptibility measurements were sealed in plastic holders in a glove box. Solvents [THF, toluene, petroleum ether (boiling point 20 to 40°C), and ethyl ether] were purified by standard methods in an argon atmosphere. Neptunium was determined by 1) dissolution of a weighed sample in dilute acid and 2) α-counting an aliquot of the solution; ^{238}Pu impurity was corrected from α pulse height analysis results. Chloride was determined by potentiometric titration with standard silver nitrate solution. Mössbauer spectra and magnetic susceptibility measurements were obtained as previously described.[2,6]

Preparation of Compounds

$K(HBpz_3)$

Potassium tris(1-pyrazolyl) borate was prepared by the procedure of Trofimenko.[7]

$Np(HBpz_3)_2Cl_2$

$Np(HBpz_3)_2Cl_2$ was prepared as a THF adduct by adding four equivalents of $KHBpz_3$ to a THF solution of $NpCl_4$ and stirring at room temperature for two hours. The solution was filtered, and the filtrate vacuum was evaporated to recover a glistening brown product.

$NpCp(HBpz_3)Cl_2$, $NpMeCp(HBpz_3)Cl_2$

These compounds were prepared by the reaction of equimolar quantities of $NpCpCl_3 \cdot 2THF$[5,8] with $KHBpz_3$ in THF. After stirring for two to three hours at room temperature, the mixture was filtered, and the filtrate was evaporated by vacuum to an oil. The oil was triturated with petroleum ether, and the product was recovered as a dark red powder.

$NpCp_2(HBpz_3)Cl$

This compound was prepared by the reaction between $NpCp(HBpz_3)Cl_2$ and TlCp in THF by a procedure similar to the preceding preparation. The product was a dark brown solid.

$Np(MeCp)_2(HBpz_3)_2$

This compound was prepared by the reaction of $Np(HBpz_3)_3Cl_2\cdot$ xTHF with TlMeCp in THF and recovered as in the preceding preparations. This product is a glossy brown solid. The analyses of these compounds are shown in Table 1.

TABLE 1

Analytical Results for Np(IV) — Tris(1-pyrazolyl) Compounds

	Np, wt %		Cl, wt %	
Compound	Found	Calcd	Found	Calcd
$Np(HBpz_3)_2Cl_2\cdot 3THF$	24.6	25.00	7.50	7.49
$Np(HBpz_3)CpCl_2\cdot THF$	37.9	36.01	11.8	10.81
$Np(HBpz_3)MeCpCl_2\cdot 3THF$	27.8	29.2	9.1	8.73
$NpCp(HBpz_3)Cl_2$	40.0	38.50	6.75	5.76
$Np(HBpz_3)_2MeCp_2\cdot 4THF$	21.3	21.4	-	-

RESULTS

^{237}Mössbauer spectra for $Np(HBpz_3)_2Cl_2 \cdot 3THF$, $Np(HBpz_3)\ CpCl_2 \cdot THF$, and $Np(HBpz_3)_2\ (MeCp)_2 \cdot 4THF$ are shown in Figure 1; the Mössbauer parameters for these spectra are shown in Table 2.

TABLE 2

Mössbauer Parameters

Compound	Isomer Shift (δ),* cm/sec	Magnetic Splitting Constant, $g_0 \mu_N H_{eff}$ (cm/sec)	Quadrupole Coupling Constant, (1/4)eqQ(cm/sec)
$Np(HBpz_3)_2Cl_2 \cdot 3THF$	-0.60 ±0.07	8.93 ±0.29	0.8 ±0.4
$Np(HBpz_3)CpCl_2 \cdot THF$	-0.27 ±0.15	8.80 ±2.5	0.5 ±0.2
$Np(HBpz_3)_2(MeCp)_2 \cdot 4THF$	-0.60 ±0.07	-	-

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* $NpAl_2$ = 0.

The Mössbauer spectra of $Np(HBpz_3)_2Cl_2$ and $Np(HBpz_3)CpCl_2$ are both magnetically split, with a small quadrupole-splitting component added.[9] The spectrum of the first compound (Figure 1) is fairly well-resolved, and the significant resonances of this spectrum are easily identified. The isomer shift and magnetic splitting parameters are quite precise. The quadrupole splitting constant is only a crude estimate because (1/4)eqQ depends on the position of two missing weak resonances at each end of the spectrum. The spectrum of $Np(HBpz_3)CpCl_2 \cdot THF$ (Figure 2) is obviously the same type as that of $Np(HBpz_3)_2Cl_2 \cdot 3THF$, but the spectrum has been distorted by intermediate relaxation effects. The large errors listed for the Mössbauer parameters reflect two possible assignments for the resonances, and the quadrupole-splitting constant is again a crude estimate, based on a guess for the location of the two missing lines. The spectrum of $Np(HBpz_3)_2(MeCp)_2 \cdot 4THF$ (Figure 3) shows a single resonance at δ = 0.60 cm/sec, but the structure of the resonance suggests that a small, unresolved quadrupole-splitting component may also be present.

The Mössbauer spectra of both $NpMeCp(HBpz_3)Cl_2$ and $NpCp_2(HBpz_3)Cl$ are both distorted by intermediate relaxation effects; therefore, the spectra could not be interpreted. Previous work[1,2] has found intermediate relaxation distortions in the Mössbauer spectra of $NpCp_3X$ (X = R, OR, Cl, Br, etc.) compounds and has shown that in some cases, substituting a bulkier ligand may change the relaxation enough to allow usable spectra. A bulkier ligand increases the Np-Np distances in the solid compounds and thereby decreasing the spin-spin interactions which affect relaxation times. The distortion of the spectrum of $NpCp_2(HBpz_3)Cl$ is not unexpected, but that $NpMeCp(HBpz_3)Cl_2$ should have a heavily relaxation-affected spectrum while $NpCp(HBpz_3)Cl_2$ has an interpretable spectrum is not expected. However, substitution of MeCp for Cp may not necessarily increase Np-Np distances in a solid compound. For example, MeCp could increase Np-Np distances in one direction but shorten them in another. The net effect could be an enhancement of intermediate relaxation effects.

Discussion

The isomer shifts of these compounds, compared with isomer shifts of appropriate reference compounds, can be used to reflect changes in 5f electron density of the Np(IV) ion. Table 3 shows the changes of Np(IV) isomer shifts for one and two $HBpz_3$ ligands, and for two MeCp ligands bonding to Np(IV). The changes in isomer shift between compounds studied and reference compounds are small, and the effects observed are in the direction of withdrawing 5f electron density. These results indicate that the $HBpz_3$ and bis-methyl-cyclopentadiene are essentially electrostatically bonded in these compounds.

Biscyclopentadienyl-uranium(IV) compounds are not stable except when coordination sphere of the U(IV) ion includes other ligands that reduce access to the U(IV) ion.[3,4,10] The analogous Np(IV) compounds are almost identical in chemical behavior because the ionic radius of Np(IV) is only slightly smaller than that of U(IV). The preparation of biscyclopentadienyl-actinide(IV) compounds only in crowded coordination spheres suggests that there is a substantial repulsion between the bonding ligands. This repulsion would be expected to lengthen the bonds between the actinide(IV) ion and the ligand and decrease any covalent contribution to the bonding.

TABLE 3

^{237}Np Isomer Shifts for Ligand-Np(IV) Bond

Bond	Compound	δ, cm/sec	References	Δ•δ
$HBpz_3$ - Np(IV)	$Np(HBpz_3)Cp\ Cl_2$	-0.27	$Np(Cp)Cl_3$	-0.1
$(HBpz_3)_2$ - Np(IV)	$Np(HBpz_3)_2\ Cl_2$	-0.60	$NpCl_4$	-0.25
$(MeCp)_2$ - Np(IV)	$Np(HBpz_3)_2(MeCp)_2$	-0.60	$Np(HBpz_3)_2Cl_2$	0.00

Evidently, the tridentate $HBpz_3$ ligand bonds essentially electrostatically to Np(IV); the biscyclopentadienyl ligands appear to bond electrostatically, probably because ligand repulsion prevents any significant orbital overlap. A measurement of the Cp-Np bond distances in $Np(MeCp)_2(HBpz_2)_2$ would allow a definite conclusion to be drawn from the Mössbauer results.

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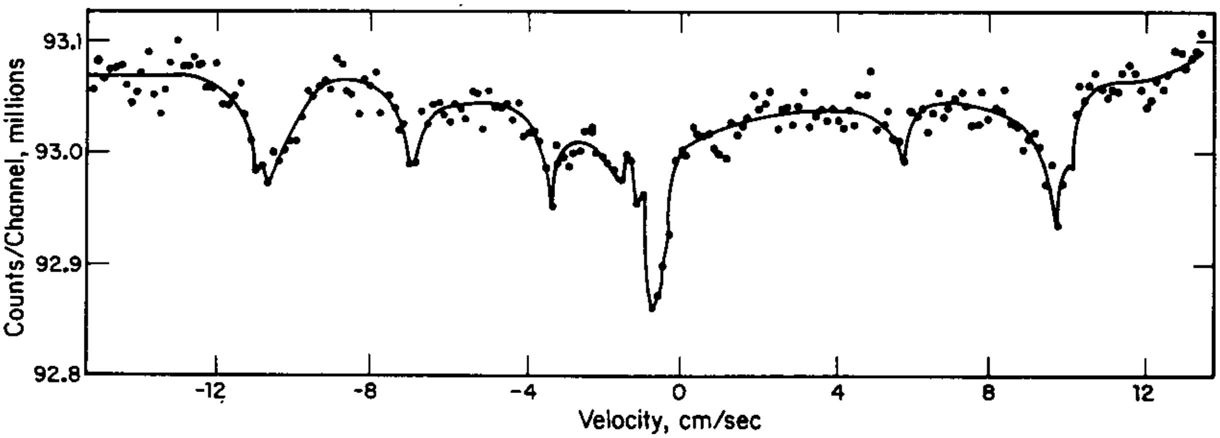

FIGURE 1. ^{237}Np Mössbauer Spectrum of $Np(HBpz_3)_2Cl_2 \cdot 3THF$

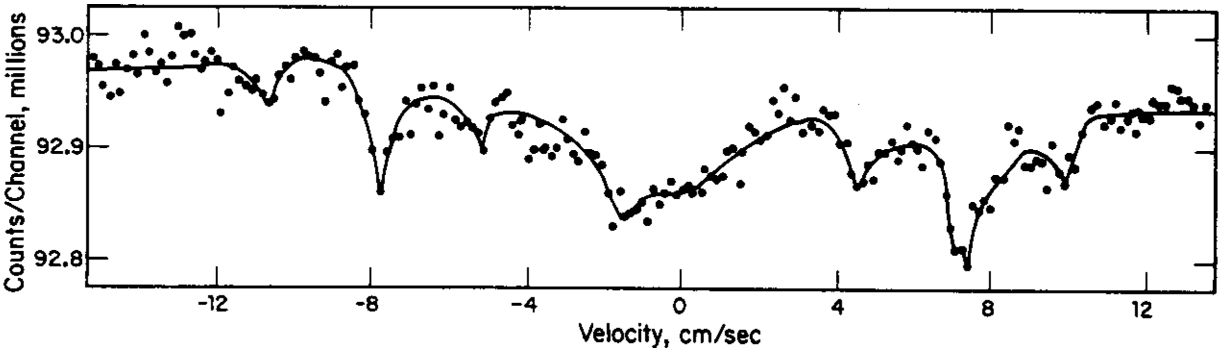

FIGURE 2. ^{237}Np Mössbauer Spectrum of $Np(HBpz_3)CpCl_2 \cdot THF$

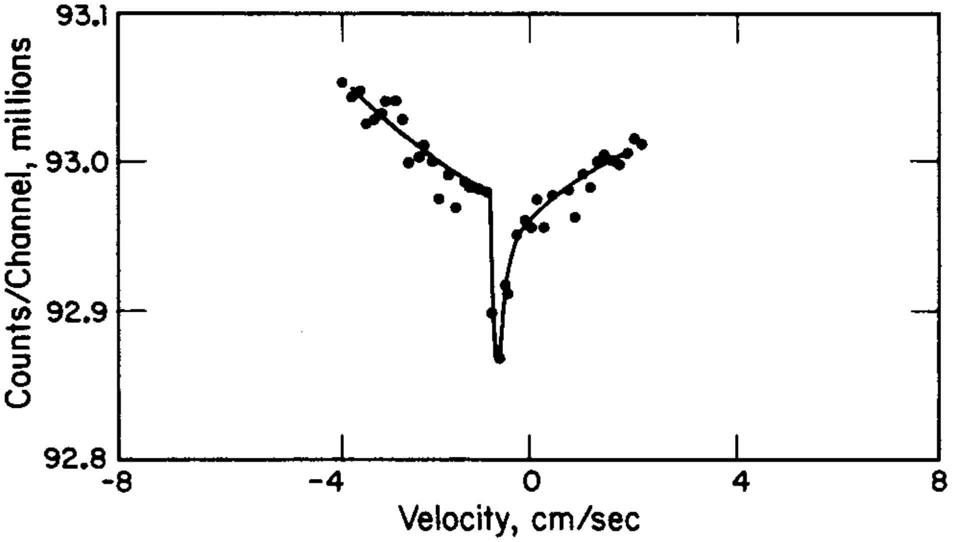

FIGURE 3. ^{237}Np Mössbauer Spectrum of $Np(HBpz_3)_2(MeCp)_2 \cdot 4THF$