

more difficult. The spectra could suggest that both have an $e_g^1(\text{ring})$ configuration which leads to the assignment of Fe(II) $b_{2g}^2 e_g^3 a_{1g}^1$, $e_g^1(\text{ring})$ for the monoion and Fe(I) $b_{2g}^2 e_g^4 a_{1g}^1$, $e_g^1(\text{ring})$ for the diion. Taube's susceptibility results¹ indicate that both one- and two-electron reductions occur into the central metal ion. Preparations of the ions of FePc by reduction with sodium in tetrahydrofuran for electron spin resonance measurements¹⁰ apparently produced only three stages, the colors of which are the same as in the later stages in the present work while no pink first stage was evident. Their first stage (purple) exhibited an esr spectrum of nine lines with a splitting of 2.4 G and for this reason was considered to be due to central metal reduction. We do not believe our pink stage to be due to an impurity for two reasons; first, the intensity of its spectrum is of the same order of magnitude as the later stages, and, second, there is no obvious reason that

FePc should only reduce as a trinegative ion, if the first is discontinued, while the remainder of the metal phthalocyanine studies reduce to yield four steps, and five for CoPc. The nature of the reduced species for FePc must still remain in doubt although it seems probable that addition to the central metal ion does occur at some stage.

In conclusion it must be stressed that the authors are very much aware of the possibility that the reduction processes may well be assigned to other species when more data become available especially for the complexes with cobalt and iron, and possibly manganese; however, we do believe that the configurations suggested are the most consistent with the electron spin resonance and the electronic absorption data at the present time.

Acknowledgment.—The authors are extremely grateful to Dr. N. S. Hush for informative discussions.

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Mössbauer and Magnetic Susceptibility Studies of Uranium(III), Uranium(IV), Neptunium(III), and Neptunium(IV) Compounds with the Cyclopentadiene Ion¹

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Mössbauer spectra of NpCp_4 , NpCp_3Cl , and $\text{NpCp}_3 \cdot 3\text{THF}$ show isomer shifts indicative of covalent Np(IV)-Cp bonds (Cp = C_5H_5^- ion) for NpCp_4 and NpCp_3Cl and ionic Np(III)-Cp bonds for $\text{NpCp}_3 \cdot 3\text{THF}$. Quadrupole splitting of the Mössbauer spectrum of Np^{4+} in NpCp_4 suggests a site of axial symmetry for the Np^{4+} ion. The magnetic susceptibilities of UCp_4 , UCp_3Cl , $\text{UCp}_3 \cdot \text{THF}$, NpCp_3Cl , and $\text{NpCp}_3 \cdot 3\text{THF}$ were measured from 2.5 to 25–100°K. Interpretation of magnetic susceptibilities in terms of crystalline field predictions indicates that U^{4+} and Np^{4+} in $\text{UCp}_3 \cdot \text{THF}$, UCp_3Cl , and NpCp_3Cl are in sites of low symmetry; U^{4+} in UCp_4 and Np^{4+} in NpCp_4 are in sites with less than T_d symmetry, but having a threefold axis; and the Np^{3+} ion in $\text{NpCp}_3 \cdot 3\text{THF}$ is in a site descended from O_h symmetry.

Introduction

Several compounds of neptunium and uranium with the cyclopentadiene ion ($\text{C}_5\text{H}_5^- = \text{Cp}$) have been prepared, and some of their properties investigated. Infrared spectra of UCp_3Cl ,² UCp_4 ,³ UCp_3 ,⁴ NpCp_3Cl ,⁵ and NpCp_4 ⁶ have been reported and analyzed in some detail.⁷ Magnetic susceptibilities of NpCp_4 and NpCp_3Cl have been measured at low temperatures;⁸ the magnetic susceptibility of UCp_3Cl has been measured from 313 to 77°K.²

This paper reports a new synthesis for the tetrahydrofuran (THF) adducts $\text{UCp}_3 \cdot \text{THF}$ and $\text{NpCp}_3 \cdot 3\text{THF}$, Mössbauer spectra for the neptunium cyclopentadiene

compounds, and low-temperature magnetic susceptibility measurements for UCp_3Cl , UCp_4 , $\text{UCp}_3 \cdot \text{THF}$, and $\text{NpCp}_3 \cdot 3\text{THF}$.

Experimental Section

Preparation of Compounds. (a) UCp_4 and NpCp_4 .—These compounds were prepared by stirring solid UCl_4 (or NpCl_4) with an excess of KCp in toluene for 3–5 days, following the procedure of Fischer and Hristidu.³ The product was recovered by extracting the solids with toluene or by sublimation from the solids at 200–220° under a low pressure of $ca. 4 \times 10^{-5}$ mm.

(b) UCp_3Cl and NpCp_3Cl .—These compounds were prepared by the reaction of a 3:1 mole ratio of KCp to UCl_4 (or NpCl_4) in THF solution.² After stirring for 16 hr to complete the reaction, the solvent was removed by vacuum, and the product was recovered by vacuum sublimation at 180–200°.

(c) $\text{UCp}_3 \cdot \text{THF}$ and $\text{NpCp}_3 \cdot 3\text{THF}$.—These compounds were prepared by the reduction of UCp_3Cl or NpCp_3Cl by potassium metal with naphthalene as a catalyst, following the procedure of Watt and Drummond.⁹ In a typical preparation, 0.51 g (1.09 mmol) of NpCp_3Cl and 2.6 mg (2×10^{-2} mmol) of C_{10}H_8 were dissolved in 30 ml of THF, 43 mg (1.1 mmol) of potassium metal was added, and the solution was stirred at room temperature until the potassium dissolved (1–3 days). KCl was filtered from the solution, and the solvent was removed by vacuum. The product was warmed gently in a low pressure of 10–20 μ for 24

(1) The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

(2) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 246 (1956).

(3) E. O. Fischer and Y. Hristidu, *Z. Naturforsch. B*, **17**, 275 (1962).

(4) B. Kanellakopoulos, E. O. Fischer, E. Dornberger, and F. Baumgärtner, *J. Organometal. Chem.*, **24**, 507 (1970).

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(7) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

(8) R. D. Fischer, P. Laubereau, and B. Kanellakopoulos, *Z. Naturforsch. A*, **24**, 616 (1969).

(9) G. W. Watt and F. O. Drummond, Jr., *J. Amer. Chem. Soc.*, **92**, 826 (1970).

hr to sublime off naphthalene. The products of the reduction of UCp_3Cl and NpCp_3Cl , respectively, were the THF adducts of the tricyclopentadienides, $\text{UCp}_3\cdot\text{THF}^4$ and $\text{NpCp}_3\cdot 3\text{THF}$. *Anal.* Calcd for $\text{UCp}_3\cdot\text{THF}$: U, 47.15. Found: U, 46.2. Calcd for $\text{NpCp}_3\cdot 3\text{THF}$: Np, 36.57. Found: Np, 36.58, 36.72. Chloride in both products was $<0.1\%$.

(d) NpCp_3 and UCp_3 .—Attempts to produce NpCp_3 or UCp_3 by heating the THF adducts under vacuum were unsuccessful. Infrared spectra demonstrated that heating removed THF, but metal analyses were 10–15% lower than theoretical values for the tris cyclopentadienides. Possibly THF was decomposed by heating, with an oxygenated fragment binding to the metal ion.

(e) Other Np(IV)-Cp Compounds.—The preparation of NpCpCl_3 and NpCp_2Cl_2 was attempted by mixing THF solutions of NpCl_4 and KCP to provide 1:1 and 1:2 mole ratios of the reactants. After stirring for 16 hr at room temperature, KCl was filtered from the solution, and the solvent was removed by vacuum. Mössbauer spectra of the solids from both reactions corresponded to mixtures of NpCp_4 and NpCp_3Cl .

(f) Reagents.—Preparation and handling of cyclopentadiene compounds was carried out entirely in an argon atmosphere. Cyclopentadiene was prepared by heating the dimer, distilling through a Vigreux column, and condensing in a Dry Ice cooled receiving flask. Other reagents and preparative materials were employed as described before;¹⁰ the methods and techniques used for experimental measurements, magnetic susceptibilities, ^{237}Np Mössbauer spectra, and infrared spectra have also been previously described.¹⁰

Results

Mössbauer Spectra.—The Mössbauer spectra of ^{237}Np in NpCp_4 , NpCp_3Cl , and $\text{NpCp}_3\cdot 3\text{THF}$ at 4.2°K are distinctly different. The spectrum of NpCp_4 is split by an electric quadrupole interaction, the spectrum of NpCp_3Cl is a broad, featureless resonance, and the spectrum of $\text{NpCp}_3\cdot 3\text{THF}$ is a sharp single line with a typical Np^{3+} isomer shift (Figure 1). Analysis

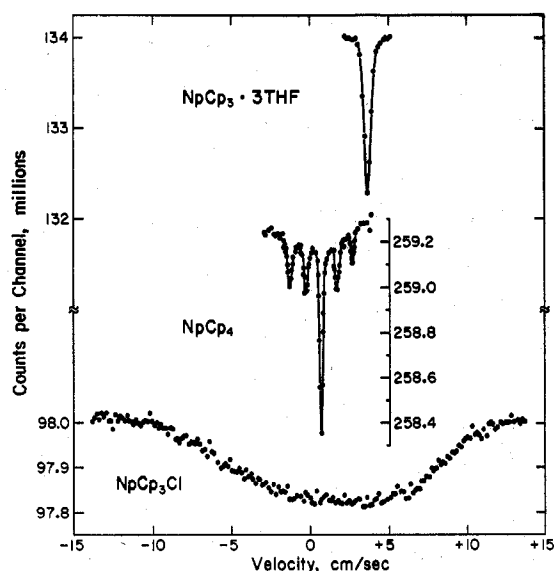


Figure 1.—Mössbauer spectra of some cyclopentadiene compounds of neptunium at 4.2°K .

of the spectra to extract isomer shifts and quadrupole coupling constants has been previously described,¹¹ and the results of the analysis are compiled in Table I. The isomer shifts of ^{237}Np in Np^{3+} and Np^{4+} compounds appropriate for comparison are listed in Table II.

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TABLE I
MÖSSBAUER PARAMETERS OF SOME CYCLOPENTADIENE
COMPOUNDS OF NEPTUNIUM AT 4.2°K

Compd	Isomer shift, ^a cm/sec	$eqQ/4$, ^b cm/sec
NpCp_4	$+0.72 \pm 0.02$	1.66 ± 0.02^c
NpCp_3Cl	$+1.4 \pm 1.0$	<i>d</i>
$\text{NpCp}_3\cdot 3\text{THF}$	$+3.64 \pm 0.10$	≤ 0.4

^a Relative to NpAl_2 at 77°K , as recommended by R. L. Cohen and G. M. Kalvius, *Nucl. Instrum. Methods*, **86**, 209 (1970).

^b Quadrupole coupling constant; signs were not determined. ^c $R = 2.03 \pm 0.06$ and $\eta \leq 0.11$, where R is the ratio of outer-pair to inner-pair splittings, as defined in ref 11, and η is the asymmetry parameter; R varies from 2 for $\eta = 0$ (axial symmetry) to 1 for $\eta = 1$ (maximum asymmetry). Tables for converting R to η have been compiled: R. Livingston and H. Zeldes, "Tables of Eigenvalues for Pure Quadrupole Spectra, Spin $5/2$," USAEC Report ORNL-1913, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1955. ^d Not determined.

TABLE II
ISOMER SHIFTS OF NEPTUNIUM(III) AND
NEPTUNIUM(IV) COMPOUNDS AT 4.2°K

Compd	Isomer shift, ^a cm/sec	Ref	Compd	Isomer shift, ^a cm/sec	Ref
NpO_2	-0.56	<i>c</i>	$\text{Np}(\text{COT})_2^b$	+1.94	<i>e</i>
NpCl_4	-0.34	<i>c</i>	NpCl_3	+3.54	<i>f</i>
NpAl_2	0.00	<i>c</i>	$\text{NpCp}_3\cdot 3\text{THF}$	+3.64	<i>d</i>
NpCp_4	+0.72	<i>d</i>			

^a Relative to NpAl_2 at 77°K . ^b COT = cyclooctatetraenyl ion, $\text{C}_8\text{H}_8^{2-}$. ^c J. A. Stone and W. L. Pillinger, *Phys. Rev.*, **165**, 1319 (1968). ^d This work. ^e Reference 10. ^f J. A. Stone and W. L. Pillinger, *Symp. Faraday Soc.*, **1**, 77 (1967).

Magnetic Susceptibilities.—Magnetic susceptibilities were measured for UCp_4 , UCp_3Cl , $\text{UCp}_3\cdot\text{THF}$, NpCp_3Cl , and $\text{NpCp}_3\cdot 3\text{THF}$ from 2.6 to *ca.* 100°K , unless the signal from the sample became too weak for accurate measurement. The results of magnetic measurements were fitted in regions where $1/\chi$ vs. T graphs were linear to the empirical, but convenient, Curie-Weiss expression $\chi = C/(T + \theta)$. The constants obtained are listed in Table III; earlier results² on

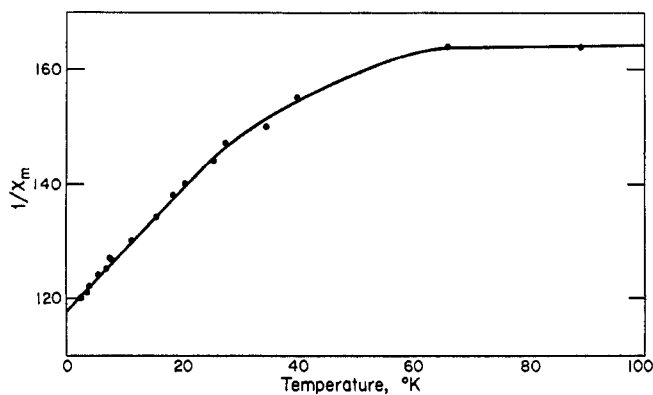
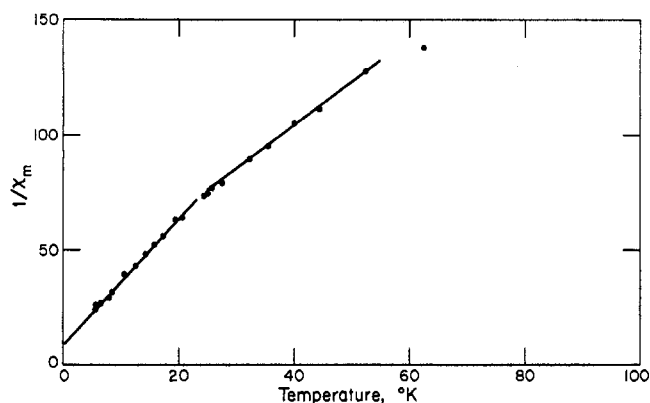
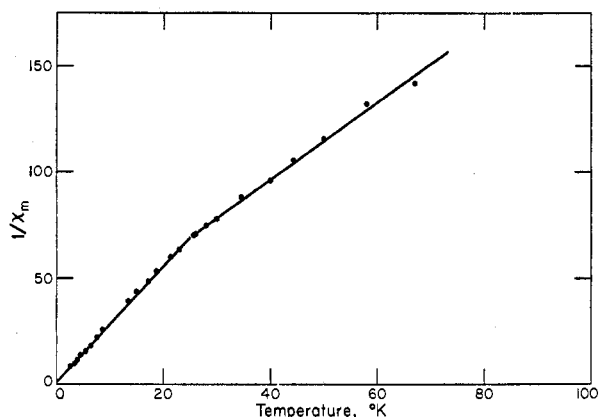
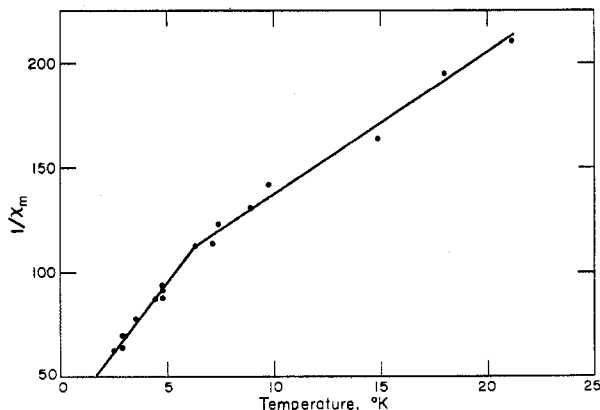
TABLE III
MAGNETIC SUSCEPTIBILITY CONSTANTS

Compd	Temp range, ^a °K	C , (emu deg)/mol	θ , °K	μ^{eff} , BM/molecule	χ , emu/mol
UCp_3Cl	2.56–90	TIP ^c			6.47×10^{-3}
	90–313	1.48	150	3.44^b	
UCp_4	2.6–25	0.95	110	2.76	6.10×10^{-3}
	60–100	TIP			
$\text{UCp}_3\cdot\text{THF}$	2.5–22	0.36	2.9	1.69	
	22–55	0.54	15	2.06	
NpCp_3Cl	2.5–25	0.36	0.40	1.69	
	25–60	0.53	11	2.07	
$\text{NpCp}_3\cdot 3\text{THF}$	2.5–6.25	0.074	2.0	0.77	
	7–25	0.145	10	1.08	

^a Signal became too weak for measurement at temperatures above maximum listed. ^b Recalculated from the data of Reynolds and Wilkinson.² ^c Temperature-independent paramagnetism.

UCp_3Cl are also included. Magnetic data were corrected for the diamagnetism of the sample holder, but the diamagnetic correction of metal and ligands was ignored as small compared to measured values. Graphs of the inverse magnetic susceptibility vs. temperature for UCp_4 , $\text{UCp}_3\cdot\text{THF}$, NpCp_3Cl , and $\text{NpCp}_3\cdot 3\text{THF}$ are shown in Figures 2–5, respectively.

The magnetic susceptibility of UCp_3Cl was independent of temperature from 2.56 to 90°K ($\chi = 6.47 \times 10^{-3}$ emu/mol). Reynolds and Wilkinson² measured

Figure 2.—Reciprocal molar susceptibility of UCp₄.Figure 3.—Reciprocal molar susceptibility of UCp₃·THF.Figure 4.—Reciprocal molar susceptibility of NpCp₃Cl.Figure 5.—Reciprocal molar susceptibility of NpCp₃·3THF.

$\chi = 6.60 \times 10^{-3}$ emu/mol for UCp₃Cl at 77°K, in the temperature-independent paramagnetic region, and found the temperature-dependent paramagnetism $\mu_{\text{eff}} = 3.44$ BM from 90 to 313°K.

Discussion

The Mössbauer spectra of NpCp₄ and NpCp₃Cl both are appreciably different from those of ionic Np(IV) compounds. The isomer shift of Np⁴⁺ in NpCp₄ is +0.72 cm/sec, compared to -0.56 cm/sec for Np⁴⁺ in NpO₂, thus indicating considerable additional shielding of the 6s shell in NpCp₄ (Table II). Although the spectrum of NpCp₃Cl is poorly defined, the isomer shift of Np⁴⁺ in NpCp₃Cl is roughly in the same range as in NpCp₄. The additional shielding of the 6s shell in the Np(IV)-Cp complexes suggests an appreciable electron contribution from the Cp ligands to the metal orbitals. In contrast to the behavior of the Np(IV) compounds, the Mössbauer spectrum of NpCp₃·3THF is a single line with an isomer shift of +3.64 cm/sec; within experimental error this isomer shift is the same as that of Np³⁺ in NpCl₃ (+3.54 cm/sec). The isomer shift establishes the presence of the Np³⁺ ion in NpCp₃·3THF, and the close correspondence to the isomer shift of Np³⁺ in ionic compounds indicates that there is little covalency in the Np³⁺-Cp bonding.

The evidence from the Mössbauer spectra for a covalent contribution to the bonding of Np(IV) in NpCp₄ and NpCp₃Cl and the lack of such evidence for Np(III) in NpCp₃·3THF agree with earlier proposals for the bonding of actinide-cyclopentadienyl compounds. The bonding in UCp₄ and UCp₃Cl has been assumed to have covalent character from chemical evidence;^{2,3} these compounds do not react rapidly with FeCl₂ to produce ferrocene. The isomer shifts of Np(IV) in NpCp₄ and NpCp₃Cl (isomorphous with their U(IV) analogs) demonstrate the validity of this chemical evidence; using the approximation of a simple linear relationship between isomer shift and effective ionic charge, the Np(IV) ion in these compounds has an effective charge of 3.7+ rather than 4.0+ for pure ionic bonding. However, an assumption of completely covalent bonding in the Cp compounds of U(IV) and Np(IV) cannot be justified because of the behavior of the corresponding COT compounds. The isomer shift¹⁰ of Np(IV) in Np(COT)₂ corresponds to an effective charge of +3.4; this probably represents maximum covalency, so that the bonding of U(IV) and Np(IV) with Cp ligands must have both covalent and ionic contributions.

A comparison of the present results with those for Cp compounds of other transition series elements is of interest. In the 3d series iron forms ferrocene (FeCp₂), and in the 4d series ruthenium forms ruthenocene (RuCp₂), both of which are known to have strong covalency; however, Mössbauer results for these and related compounds are not directly comparable with the results for Np-Cp compounds. The 3d and 4d valence electrons of iron and ruthenium are in outer shells, whereas the 5f valence electrons of actinides are in an inner shell. Thus the details of their bonding are expected to be quite different. A comparison with the 4f series is more fruitful, although only trivalent lanthanide-Cp compounds are known. A spectral study¹²

(12) L. J. Nugent, P. G. Laubereau, G. K. Werner, and K. L. Vander Sluis, *J. Organometal. Chem.*, **27**, 365 (1971).

of actinide(III)-Cp and lanthanide(III)-Cp compounds indicates that covalency in their bonding, if present, is less than 5%. The results for Np(III) in $\text{NpCp}_3 \cdot 3\text{THF}$ are consistent with this interpretation. The covalency exhibited by the Cp compounds of U(IV) and Np(IV) appears to be a property of the quadrivalent ion rather than electronic configuration. Both U(III) and Np(IV) ions have a $5f^3$ configuration, but only the Np(IV)-Cp compounds exhibit appreciable covalency; UCp_3 appears to be ionic in bonding, from chemical evidence.⁴

Hyperfine splitting also was observed in the Mössbauer spectra of NpCp_4 and NpCp_3Cl . The spectrum of NpCp_3Cl is a broad, featureless resonance spanning 20 cm/sec and corresponding to a magnetic splitting constant ($g_0\mu_n H_{\text{eff}}$) of about 5 cm/sec if due to a magnetic interaction. The susceptibility results show that NpCp_3Cl is paramagnetic at 4.2°K, so that magnetic ordering is not responsible for the observed Mössbauer spectrum. A more probable explanation of the spectrum is found in paramagnetic relaxation effects such as observed¹⁰ for $\text{Np}(\text{COT})_2$; because the magnetic hyperfine structure is not fully resolved for NpCp_3Cl , the paramagnetic relaxation time would be in the "intermediate" region ($\sim 10^{-8}$ sec). For NpCp_4 , the observed quadrupole splitting is consistent with axial symmetry for Np^{4+} and indicates a threefold or higher axis for the NpCp_4 molecule. Magnetic susceptibility results (discussed in detail below) allow the inference that Np^{4+} is at a site whose symmetry can be obtained by a descent from O (cube) or T_d (tetrahedron) symmetries, but not from O_h (octahedron).

The destruction of $\text{NpCp}_3 \cdot 3\text{THF}$ by heat suggests that the THF ligands are held by relatively strong Np-O bonds; the Np^{3+} ion in $\text{NpCp}_3 \cdot 3\text{THF}$ is probably six-coordinate with the C_5H_5^- ions bonded locally. Analysis of the magnetic susceptibility suggests that the Np^{3+} ion is in a site descended from O_h symmetry, possibly C_{3v} , C_{3h} , etc.

Magnetic susceptibility results cannot be analyzed completely without knowledge of the site symmetry of the magnetic ions, which requires a single-crystal X-ray determination. However, the combination of experimental magnetic susceptibilities and the properties of the crystal field levels predicted by crystal field theory¹³ can be applied to limit possible site symmetries for the magnetic ions. The crystal field levels for f-electron ions in cubic site symmetries¹⁴ are defined as a function of the fourth- and sixth-order field parameters by Lea, Leask, and Wolf,¹³ the sites of actinide ions in the actinide-Cp compounds studied here can be considered to be derived from a cubic site by distortion of one of the three cubic symmetries (O , O_h , T_d). The crystal field levels, as inferred from magnetic susceptibilities, are consistent with the actinide ion in certain site symmetries. Thus, the possible site symmetries of the actinide ions in these compounds can be inferred from magnetic susceptibility results. A discussion of these results for the compounds under study follows.

The U^{4+} ion has a $5f^2$ configuration and nominally a $^3\text{H}_4$ ground level, $J = 4$. For UCp_3Cl , the experimental magnetic susceptibility is independent of tempera-

ture below 90°K and is paramagnetic² with $\mu_{\text{eff}} = 3.44$ BM from 90 to 313°K. The theoretical free ion moment is $\mu_{\text{eff}} = g_J \sqrt{J(J+1)} = 3.58$ BM, in fairly good agreement with the experimental paramagnetism. This agreement indicates that all crystal field levels are no more than 70 cm^{-1} above the ground crystal field level. Two possible site symmetries can account for the experimental magnetic susceptibility: a crystal field of such low symmetry that all degeneracy has been lifted leaving $2J + 1 = 9$ singlet levels which can only have temperature-independent paramagnetism (TIP) or a crystal field of O or T_d symmetry with two magnetic levels— Γ_4 and Γ_5 triplet levels almost coincident. The first possibility appears the more likely, when considering the magnetic evidence for Np^{4+} on the isomorphous NpCp_3Cl .

The magnetic susceptibility of U^{4+} in UCp_4 ($J = 4$ ground level) has $\mu_{\text{eff}} = 2.76$ BM up to ca. 25°K and then gradually becomes TIP above 60°K (Figure 2). The experimental results are consistent with a magnetic ground level with a singlet level lying 30–40 cm^{-1} higher. A U^{4+} ion in O or T_d site symmetry, with the proper ratio of field parameters, can have this ordering of crystal field levels, and a slight distortion would not alter the magnetic results significantly. X-Ray powder patterns¹⁵ indicate that UCp_4 and NpCp_4 are isomorphous, and the Mössbauer spectrum of NpCp_4 shows axial symmetry for the Np^{4+} ion; thus U^{4+} in UCp_4 must also be on a threefold or higher axis of symmetry. Analysis of the magnetic susceptibility of NpCp_4 ⁸ indicates a small splitting of the quartet Γ_3 ground state, which demonstrates a distortion from an O or T_d site symmetry for the Np^{4+} ion. Consistency with both Mössbauer and magnetic susceptibility results requires that the Np^{4+} ion in NpCp_4 be at a site of C_{3v} , C_3 , or D_3 symmetry. (C_{3v} and C_3 groups are subgroups of the T_d group; C_3 and D_3 groups are subgroups of the O group.¹⁶)

U^{3+} in $\text{UCp}_3 \cdot \text{THF}$ and Np^{4+} in NpCp_3Cl are isoelectronic and have $5f^3$ configurations with a $^4\text{I}_{9/2}$ ground state. The magnetic susceptibilities of both compounds are nearly the same and show a crystal field level about 15 cm^{-1} above the ground level (Figures 3 and 4). For O or T_d crystal fields, the ground level for a $J = 9/2$ ion is the quartet Γ_8 level, or for an O_h crystal field, the ground level is either Γ_8 or the doublet Γ_6 , depending on the ratio of fourth- and sixth-order field parameters. A Γ_6 level is a Kramers doublet and cannot be split by a crystal field; the quartet Γ_8 level is split by any symmetry less than a cubic field into Γ_6 and Γ_7 levels, both Kramers doublets. A crystal field level 15 cm^{-1} above ground could result from the splitting of a Γ_8 level; both U^{3+} in $\text{UCp}_3 \cdot \text{THF}$ and Np^{4+} in NpCp_3Cl must be at sites of low symmetry and possibly near the same site symmetry since their magnetic susceptibilities are so nearly identical. X-Ray powder data indicate that NpCp_3Cl and UCp_3Cl have the same structure.¹⁵ A low symmetry for NpCp_3Cl thus indicates a low symmetry for UCp_3Cl and eliminates the possibility that the TIP observed for UCp_3Cl results from a field of high symmetry.

The Np^{3+} ion has a $5f^4$ configuration and a $^5\text{I}_4$ ground

(13) K. R. Lea, M. J. M. Leask, and W. P. Wolf, *J. Phys. Chem. Solids*, **23**, 1381 (1962).

(14) W. A. Runciman, *Phil. Mag.*, **1**, 1075 (1956).

(15) D. G. Karraker, unpublished data.

(16) J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge University Press, Cambridge, England, 1961, p 387.

state ($J = 4$) and, in $\text{NpCp}_3 \cdot 3\text{THF}$, was found to be weakly paramagnetic, like the isoelectronic Pu^{4+} ion.¹⁷ For cubic symmetries, temperature-dependent paramagnetism is consistent only with the Np^{3+} in an O_h site and a field dominated by the fourth-order term for a Γ_5 ground level. T_d and O symmetries have the nonmagnetic singlet Γ_1 ground level, which can have TIP but not temperature-dependent paramagnetism in any symmetry. The experimental susceptibility for Np^{3+} in $\text{NpCp}_3 \cdot 3\text{THF}$ indicates two paramagnetic levels; descending in symmetry from O_h , the Γ_5 level is split

(17) D. G. Karraker, *Inorg. Chem.*, **10**, 1564 (1971).

into Γ_1 and Γ_3 (magnetic doublet) levels for hexagonal-class levels,¹⁴ which, in this instance, implies a threefold axis. The symmetries D_{3v} , D_{3h} , C_{3v} and C_{3h} are all consistent with the magnetic susceptibility results for Np^{3+} in $\text{NpCp}_3 \cdot 3\text{THF}$. Lower symmetries split the Γ_5 level into nonmagnetic singlets and permit only TIP unless the splitting is so small as to allow temperature-dependent paramagnetism *via* "non-Kramers doublets."¹⁸ An explanation of the magnetic properties of Np^{3+} in $\text{NpCp}_3 \cdot 3\text{THF}$ based upon a threefold axis (a D_{3v} , D_{3h} , etc., site) appears more probable.

(18) J. M. Baker and B. Bleaney, *Proc. Roy. Soc., Ser. A*, **245**, 156 (1958).

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Thermal and Photochemical Aquation of Some Substituted Acetatopentaamminechromium(III) Ions

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The acid hydrolysis of four $\text{Cr}(\text{NH}_3)_5(\text{OCOR})^{2+}$ complex ions, where $\text{R} = \text{CCl}_3$, CHCl_2 , CH_2Cl , or CH_3 , has been studied in 0.1–0.01 M HClO_4 at constant ionic strength, 0.13. For $\text{R} = \text{CCl}_3$, as usual, the reaction is one of aquation of the acido group and is acid catalyzed. Comparison with the $\text{R} = \text{CF}_3$ analog indicates that the rate varies inversely with the base strength of RCOO^- . NH_3 aquation is the primary step for the three other species with rates increasing with RCOO^- basicity. The results are interpreted in terms of a progressive strengthening of the Cr–O bond and weakening of the Cr–N bond *cis* to the carboxylate, consistent with hydrogen bonding between the carbonyl oxygen and adjacent H of an ammonia ligand. Possible steric effects are discussed. Irradiation of the four complexes and of that with $\text{R} = \text{CF}_3$ in the long-wavelength ligand-field band leads mainly to ammonia aquation with quantum yields ranging between 0.25 and 0.45, unconnected with the electron-withdrawing ability of R. The mode of photoreaction is that predicted by the chromium(III) photochemical rules. No conclusions can be drawn about stereospecific implications from the configuration of the photoproduct, *cis*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OCOR})^{2+}$.

Introduction

All the known acidopentaammine complexes of chromium(III), like those of cobalt(III), rhodium(III), and iridium(III), are known to undergo the primary aquation of the acido group.^{1,2} Among the $\text{Cr}(\text{NH}_3)_5\text{X}^{2+}$ systems, detailed acid hydrolysis studies have been reported for $\text{X} = \text{NCS}$,^{3,4} F ,⁵ Cl , Br , I ,^{6,7} and ONO .⁸

Recently a series of variously substituted acetatopentaamminechromium(III) complexes of the general formula $\text{Cr}(\text{NH}_3)_5(\text{OCOR})^{2+}$, where $\text{R} = \text{CH}_3$, CHCl_2 , CCl_3 , or CF_3 , has been prepared⁹ and it seemed proper to study the aquation reactions of such a homologous series of coordination compounds. The purpose of this research was (i) to study the effect of a virtually continuous variation of the basicity of the acetato ligand and (ii) to compare these reactions with the reported results for analogous $\text{M}(\text{NH}_3)_5(\text{OCOR})^{2+}$

complexes, where either $\text{M} = \text{Co(III)}$ and $\text{R} = \text{CH}_3$, CH_2Cl , CHCl_2 , CCl_3 , CF_3 ¹⁰ or $\text{M} = \text{Co(III)}$, Rh(III) , Ir(III) and $\text{R} = \text{CH}_3$, $\text{C}(\text{CH}_3)_3$, CF_3 ,¹¹ the aquation of which is subject to acid catalysis since the leaving acido group may be protonated.¹¹ Some of the reaction paths were reported to involve the cleavage of the oxygen to carbon (rather than metal to oxygen) bond.¹¹ Arguments have however been presented¹² that C–O bond breaking is much less common than previously assumed.¹¹

The results reported here refer to the aquation reactions of (trichloroacetato)-, (dichloroacetato)-, (chloroacetato)-, and acetatopentaamminechromium(III) in acid solution. While this work was in progress, a note by other authors has appeared on the acid and alkaline hydrolysis of (trifluoroacetato)pentaamminechromium(III).¹³ Also the photochemical behavior of the five new coordination compounds has been examined, on irradiation of their long-wavelength ligand-field band, indicated as L_1 and due to the $^4A_{2g} \rightarrow ^4T_{2g}$ transition in O_h symmetry. Chromium(III) photoreactions following light absorption in the

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