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Magnetic Susceptibilities of the Tetravalent Plutonium Ion in Octahedral Compounds

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The magnetic susceptibilities of Pu^{4+} in $[(CH_3)_4N]_2PuCl_6$, $[(C_2H_5)_4N]_2PuCl_6$, and Cs_2PuCl_6 were measured from 2.5 to 50°K with a Foner-type vibrating-sample magnetometer. The Pu^{4+} ion in $[(CH_3)_4N]_2PuCl_6$ showed temperature-independent susceptibility from 2.5 to 3°K and a Curie–Weiss temperature dependence from 3 to 50°K with μ_{eff} = 1.92 BM and Θ = 5.45°K. In $[(C_2H_5)_4N]_2PuCl_6$, the Pu^{4+} magnetic susceptibility was temperature independent from 2.5 to 4.5°K and had Curie–Weiss temperature dependence from 4.5 to 50°K, with μ_{eff} = 1.95 BM and Θ = 10.7°K. These and earlier measurements were employed to deduce that the $^5I_4$ ground manifold of Pu^{4+} has a Γ_1 ground level and that the splitting of the Pu^{4+} ground state is about 145 cm^{-1}. The paramagnetic temperature dependence of Pu^{4+} in Cs_2PuCl_6 at low temperature is attributed to a distortion of the $PuCl_6^{2-}$ octahedron that produces a non-Kramers doublet at the lowest level.

Introduction

Magnetic susceptibilities of Pu^{4+} in octahedral and cubic site symmetries were previously reported by Lewis and Elliott[2] and Candela, Hutchison, and Lewis.[3] A successful interpretation of the magnetic susceptibilities for $J = 4$ actinide ions, U^{4+} and Pu^{4+}, with a crystalline field model was proposed by the latter.

This paper reports measurement of the magnetic susceptibilities of Pu^{4+} in three compounds where the Pu^{4+} ion is in octahedral or near-octahedral sites. The measurements were over the temperature range 2.5–50°K; the interpretation of the data at very low temperatures provides evidence for the order of the crystalline field levels in the $^5I_4$ manifold of Pu^{4+} and also allows an estimate of the magnitude of the fourth- and sixth-degree terms in the potential of the field.

Experimental Section

$[(CH_3)_4N]_2PuCl_6$, $[(C_2H_5)_4N]_2PuCl_6$, and Cs_2PuCl_6 were prepared by adding a solution of CsCl, $(CH_3)_4NCl$, or $(C_2H_5)_4NCl$ in 6 *M* HCl to a solution of Pu^{4+} in 9 *M* HCl to precipitate the corresponding M_2PuCl_6. The precipitate was filtered, washed with anhydrous ethanol, and vacuum dried for 24 hr. The identity of the products was verified by X-ray diffraction patterns of the powdered samples.

The corresponding M_2ThCl_6 compounds were prepared as previously reported.[4] A suspension of $Th(OH)_4 \cdot xH_2O$ in absolute ethanol was dissolved by bubbling HCl gas into the chilled suspension and the M_2ThCl_6 salt precipitated by adding the appropriate MCl in a 95% ethanol solution. The precipitate was separated by filtration, washed with absolute ethanol, and vacuum dried.

Magnetic susceptibilities were measured with a Foner-type vibrating-sample magnetometer as previously described.[5] Sample measurements were made in a variable-temperature dewar; temperature control from 2.5 to 60°K was achieved by a combination of pumping and heating a stream of helium gas directed on the sample. Magnetic susceptibilities were corrected experimentally for diamagnetism from susceptibility measurements on equivalent weights of corresponding thorium(IV) compounds, over the same temperature range. For each compound, a sample from each of two separate preparations was measured. Individual measurements were reproducible within 2% and are considered accurate to ±5%. Susceptibilities at the lowest temperature measured (~2.5°K) were independent of the magnetic field.

Results

The magnetic susceptibilities of $[(CH_3)_4N]_2PuCl_6$, $[(C_2H_5)_4N]_2PuCl_6$, and Cs_2PuCl_6 are shown graphically as $1/\chi$ *vs.* T in Figures 1–3, respectively. Magnetic parameters for the Curie–Weiss law are listed in Table I for the temperature range where the data can be fitted. Cs_2PuCl_6 exhibits Curie–Weiss behavior in two temperature regions; constants for both are included in Table I.

TABLE I
MAGNETIC SUSCEPTIBILITY CONSTANTS

Compd	Temp range, °K	C,[a] emu deg/mole	Θ,[a] °K	μ_{eff}, BM
$[(CH_3)_4N]_2PuCl_6$	3–50	0.455	5.45	1.92
$[(C_2H_5)_4N]_2PuCl_6$	4.5–40	0.475	10.7	1.95
Cs_2PuCl_6	2.5–7	0.119	5.77	0.97
	17–45	0.432	50.9	1.86

[a] $\chi = C/(T + \Theta)$.

Discussion

The analysis of the magnetic susceptibilities of these compounds in terms of a crystalline field model rests on the assumption that the constant susceptibilities observed for $[(CH_3)_4N]_2PuCl_6$ and $[(C_2H_5)_4N]_2PuCl_6$ at the lowest temperatures are due to temperature-independent (Van Vleck) paramagnetism. Possible alternatives are that magnetic ordering effects (ferromagnetism or antiferromagnetism) are occurring; ferromagnetism can be eliminated from consideration by the experimental observation that the measured magnetic moment was independent of magnetic field. Antiferromagnetism is discounted by the experimental measurements on the Np^{4+} analogs. $[(CH_3)_4N]_2NpCl_6$, $[(C_2H_5)_4N]_2NpCl_6$, and Cs_2NpCl_6 all follow a Curie–Weiss temperature dependence down to 2.5°K, with Θ values below 0.5°K.[6] It appears reasonable to assume that cooperative magnetic phenomena will not occur for the analogous Pu^{4+} compounds.

The Pu^{4+} ion is located at the body center of an octahedron of six Cl^- ions in the three compounds studied. $[(CH_3)_4N]_2PuCl_6$ has a face-centered cubic cell, with the Pu^{4+} ion at a point of full cubic symmetry;[7] $[(C_2H_5)_4$-

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[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.

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[4] J. P. Bibler and D. G. Karraker, *Inorg. Chem.*, **7**, 982 (1968).

[5] D. G. Karraker, J. A. Stone, E. R. Jones, and N. Edelstein, *J. Amer. Chem. Soc.*, **92**, 4841 (1970).

[6] J. A. Stone and D. G. Karraker, unpublished data, 1970.

[7] E. Staritzky and J. Singer, *Acta Crystallogr.*, **5**, 536 (1952).

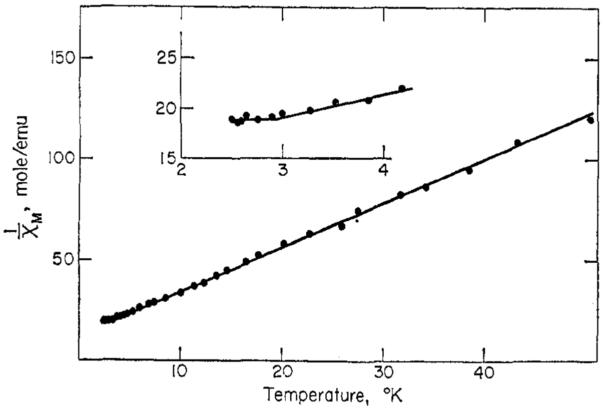

Figure 1.—Magnetic susceptibility of Pu^{4+} in $[(CH_3)_4N]_2PuCl_6$.

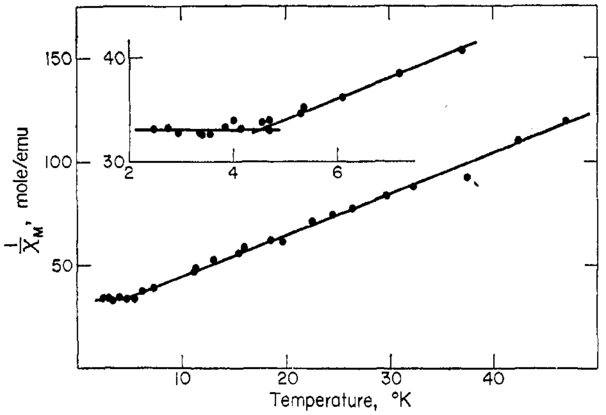

Figure 2.—Magnetic susceptibility of Pu^{4+} in $[(C_2H_5)_4N]_2PuCl_6$.

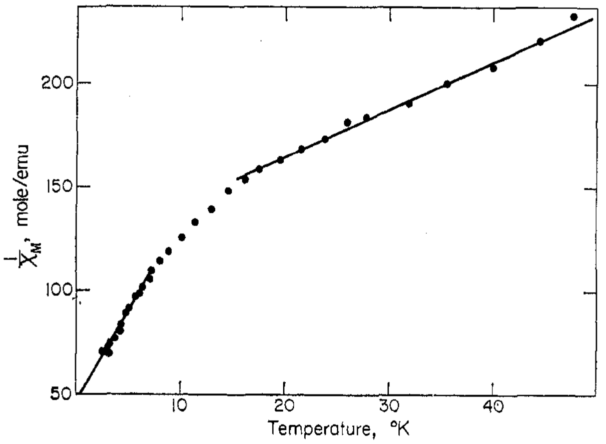

Figure 3.—Magnetic susceptibility of Pu^{4+} in Cs_2PuCl_6.

$N]_2PuCl_6$ has an orthorhombic cell that differs from the $[(CH_3)_4N]_2PuCl_6$ cell only by the greater space occupied by the $(C_2H_5)_4N^+$ cations.[7] Cs_2PuCl_6 has a trigonal cell, and the $PuCl_6^{2-}$ octahedron is slightly elongated on one axis.[8,9]

The Pu^{4+} ion has a $5f^4$ configuration and a $^5I_4$ ground state. An octahedral field splits the $J = 4$ ground level into two (magnetic) triply degenerate levels Γ_5 and Γ_4, a singlet level Γ_1, and a nonmagnetic doublet Γ_3. The energy of these levels in terms of the crystalline field parameters may be obtained from Lea, Leask, and Wolf[10] and are shown in Table II. The energies are given in terms of b_4 and b_5, defined by

TABLE II

ENERGY LEVELS FOR Pu^{4+} IN AN OCTAHEDRAL CRYSTALLINE FIELD

State	Energy	State	Energy
Γ_3	$4b_4 + 64b_6$	Γ_5	$-26b_4 - 20b_6$
Γ_4	$14b_4 + 4b_6$	Γ_1	$28b_4 - 80b_6$

$$b_4 = 60B_4 = 60A_4^0\langle r^4\rangle\langle\psi_J||\beta||\psi_J\rangle$$

$$b_6 = 1260B_6 = 1260A_6^0\langle r^6\rangle\langle\psi_J||\gamma||\psi_J\rangle$$

where B_4 and B_6 are fourth- and sixth-order parameters from the Hamiltonian, r^n is the expectation value for the 5f electrons, $\psi_J||\beta||\psi_J$ and $\psi_J||\gamma||\psi_J$ are the fourth- and sixth-degree operator equivalent factors, and A_4^0 and A_6^0 are parameters relating to the fourth- and sixth-degree potentials on the ion from the sum of ionic charges in the lattice.[11]

Depending upon the relative sizes of b_4 and b_6, either a Γ_1 or a Γ_5 level may be the ground level of the $^5I_4$ state in an octahedral or near-octahedral site, and the experimental data may be rationalized for either ground-level assignment. Considering first a Γ_1 level as the ground level, the Γ_1 (singlet) level is nonmagnetic but can contribute to temperature-independent paramagnetism by interaction with the higher Γ_4 level, as found experimentally for the Pu^{4+} ion in $[(CH_3)_4N]_2PuCl_6$ and $[(C_2H_5)_4N]_2PuCl_6$. The temperature-dependent paramagnetism above 3–4.5°K can be interpreted as showing the Γ_5 level 1.5–2.5 cm^{-1} above the Γ_1 ground level. The distortion of the $PuCl_6^{2-}$ ion in Cs_2PuCl_6 lowers the site symmetry of Pu^{4+} to C_{4v} and splits the Γ_5 level into Γ_2 and Γ_3 levels. If the Γ_2 is then lowered near the Γ_1 ground level, the two levels combine to act as a "non-Kramers doublet,"[12] which exhibits a weak temperature-dependent paramagnetism similar to that observed in Cs_2PuCl_6. A Γ_3 level is magnetically split in noncubic symmetry and would account for the paramagnetism of Cs_2PuCl_6 above ~10°K.

To rationalize the alternate assignment of a Γ_5 ground level,[13] the octahedral $PuCl_6^{2-}$ ion is assumed to be distorted enough in $[(CH_3)_4N]_2PuCl_6$ and $[(C_2H_5)_4N]_2PuCl_6$ to split a Γ_5 ground level into a Γ_2 and Γ_3 level; a Γ_2 level of 1.5–2.5 cm^{-1} below a Γ_3 level could account for the magnetic susceptibilities of the two $(R_4N)_2PuCl_6$ compounds. To account for the magnetic susceptibility of Pu^{4+} in Cs_2PuCl_6, a further descent in symmetry must be involved, and the Γ_3 level (derived from a Γ_5 ground level in O_h symmetry) must be split into Γ_1 and Γ_2 singlet levels. The Γ_1 level combines with the Γ_2 level as a non-Kramers doublet, and above 7–10°K, the three singlets act essentially as an unsplit Γ_5 level in magnetic measurements. The explanation of the magnetic susceptibility results for Pu^{4+} in this fashion requires that the Pu^{4+} site symmetry in Cs_2PuCl_6 be no higher than D_{2h},[14] which appears inconsistent with

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[13] The author is indebted to a reviewer of this paper for suggesting this possibility.

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crystal structure of Cs_2PuCl_6.[8,9] It is improbable, but not impossible, that the distortions of the field by the Cs^+ ions, 3.70 Å from the Cl^- ions, could lower the site symmetry sufficiently to split the Γ_3 level by $\sim$5 cm^{-1}. However, the assignment of a Γ_1 ground level to Pu^{4+} in the octahedral $PuCl_6^{2-}$ is preferred as more consistent with crystal structure determinations.

The earlier magnetic susceptibility measurements of Lewis and Elliott[2] on $[(CH_3)_4N]_2PuCl_6$ over the range from 77 to 334°K show a change in slope of a $1/\chi$ *vs.* T graph at about 170°K (120 cm^{-1}). From Table II, $b_4 \approx b_6$ when $E_{\Gamma_1} \approx E_{\Gamma_5}$ and a Γ_4 level would be predicted to be the next higher level. Taking the E_{Γ_4} at 120 cm^{-1}, b_4 is computed as 1.3 cm^{-1}, b_6 = 1.2 cm^{-1}, and the Γ_4 level is calculated to be $\sim$145 cm^{-1} above the ground Γ_1 level.

A total splitting of 145 cm^{-1} for the $^5I_4$ ground state of Pu^{4+} is very small, compared to the ground-state splittings calculated for U^{4+} (2298 cm^{-1})[15] and Np^{4+} (1080 cm^{-1})[16] from the absorption spectra of the analogous Cs_2MCl_6 compounds. However, a crystal field level at $\sim$120 cm^{-1} limits the ground-state splitting to a maximum of $\sim$220 cm^{-1} for Pu^{4+} with a Γ_5 ground level ($b_6 = 0$) and 290 cm^{-1} for a Γ_1 ground level ($b_4 = 0$).

From the b_4, b_6, β, and γ, $A_4\langle r^4\rangle$ and $A_6\langle r^4\rangle$ may be calculated. The $A_n\langle r^n\rangle$ depend only on the environment of the ion in the crystal and should be nearly constant for U^{4+}, Np^{4+}, and Pu^{4+} in analogous compounds. From spectral studies of Cs_2MCl_6, $A_4\langle r^4\rangle$ values of 912 and 540 cm^{-1} are derived for U^{4+} [14] and Np^{4+};[15] $A_6\cdot\langle r^6\rangle = 56$ (U^{4+}) and 150 (Np^{4+}). Neglecting the intermediate coupling corrections to β and γ for Pu^{4+}, $A_4\cdot\langle r^4\rangle = 53$ cm^{-1} and $A_6\langle r^6\rangle = 16$ cm^{-1}, roughly a factor of 10 less than the Np^{4+} values but with nearly the same ratio of fourth- to sixth-order parameters. The agreement between U^{4+} and Np^{4+} parameters is not good, and the Pu^{4+} parameters are certainly wrong. However, intermediate coupling has severe effects on β and γ for Np^{4+} [17] and Pu^{3+} [18] and may also be expected to change β and γ of Pu^{4+} drastically.

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The Mechanisms of Substitution Reactions of Acidopentaaquochromium(III) Complexes

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The use of $(H_2O)_5CrX^{2+}$ at 25.0° in 1.0 M HCl produces 22.0, 12.0, and 15.7% $(H_2O)_5CrCl^{2+}$ (corrected for aquation) for X = Br, I, and NO_3, respectively, with small increases in the rate of disappearance of $(H_2O)_5CrX^{2+}$ as compared with the rate in 1.0 M $HClO_4$. The volume of activation for the aquation of $(H_2O)_5CrNO_3^{2+}$ in 1.1 M $HClO_4$ at 25° is -12.7 ± 1.0 cm^3 mol^{-1} over the pressure range 1–2000 bars, and this is consistent with Cr–O rather than O–N bond breaking. These and other data are best understood in terms of an associative interchange (I_a) mechanism for acid-independent substitution processes in aquochromium(III) complexes, but conjugate-base species such as $Cr(H_2O)_4(OH)X^+$ appear to react by a dissociative interchange (I_d) mechanism.

The mechanism of substitution in complexes of the type $(H_2O)_5Cr^{III}X^{n+}$ remains the subject of controversy.[1-5] Ardon[1] has demonstrated that, when $Cr(H_2O)_5I^{2+}$ is aquated at 30° in the presence of 1.06 M chloride ion ($[H^+] = 1.00$ M, $I = 1.07$ M), 12.5% of the chromium appears, after about 10 half-periods, as $(H_2O)_5CrCl^{2+}$, with little change in the rate of loss of $(H_2O)_5CrI^{2+}$ as compared with aquation in 1.0 M $HClO_4$; this yield of the chloro complex is far in excess of that expected on the basis of anation of the product $Cr(H_2O)_6^{3+}$, and Ardon[1] interpreted these findings in terms of the purely dissociative mechanism (D, or SN1 limiting)[6] of the equations.

$$Cr(H_2O)_5I^{2+} \underset{}{\overset{\text{slow}}{\rightleftharpoons}} Cr(H_2O)_5^{3+} + I^- \qquad (1)$$

$$Cr(H_2O)_5^{3+} + H_2O \longrightarrow Cr(H_2O)_6^{3+} \qquad (2)$$

$$Cr(H_2O)_5^{3+} + Cl^- \longrightarrow Cr(H_2O)_5Cl^{2+} \qquad (3)$$

However, Moore, Basolo, and Pearson[2] subsequently showed that the situation is complicated by the labilization of the aquo group trans to I in $Cr(H_2O)_5I^{2+}$, such that this water molecule undergoes exchange with solvent $H_2{}^{18}O$ about 2.2 times more rapidly than the iodo ligand is replaced (in 1.00 M $HClO_4$). The incorporation of Cl^- into a substantial fraction of the reaction products might therefore be interpreted[2] as resulting from the prior formation of some *trans*-$Cr(H_2O)_4ClI^+$, which would decompose to $Cr(H_2O)_5Cl^{2+}$ and I^- sufficiently rapidly to escape detection (eq 4–6, with X = I).

$$Cr(H_2O)_5X^{2+} + Cl^- \overset{\text{rapid}}{\rightleftharpoons} \{Cr(H_2O)_5X^{2+}, Cl^-\} \qquad (4)$$

$$\{Cr(H_2O)_5X^{2+}, Cl^-\} \xrightarrow{\text{slow}} trans\text{-}Cr(H_2O)_4ClX^+ + H_2O \qquad (5)$$

$$trans\text{-}ClCr(H_2O)_4X^+ + H_2O \xrightarrow{\text{rapid}} Cr(H_2O)_5Cl^{2+} + X^- \qquad (6)$$

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