Bis(cyclooctatetraenyl)neptunium(IV) and Bis(cyclooctatetraenyl)plutonium(IV)[1,2]

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Abstract: $Np(COT)_2$ and $Pu(COT)_2$ (COT = $C_8H_8{}^{2-}$) were prepared by the reaction in THF solution of K_2COT with $NpCl_4$ and $[(C_2H_5)_4N]_2PuCl_6$, respectively. Infrared spectra of both were consistent with D_{8h} molecular symmetry ("sandwich" compounds), and X-ray diffraction patterns showed both to be isomorphous with $U(COT)_2$. The isomer shift of the Mössbauer spectrum of $Np(COT)_2$ was unusually positive for a Np^{4+} compound, indicating an electron contribution from the ligand to the bonding. The magnetic moments measured between 4.2 and 44°K were 2.43 BM for $U(COT)_2$ and 1.81 BM for $Np(COT)_2$; $Pu(COT)_2$ was diamagnetic. A crystal-field model with an orbital reduction factor, *k*, of 0.8 is in reasonable agreement with the experimental results.

The reduction of cyclooctatetraene in tetrahydrofuran (THF) solution produces the planar $C_8H_8{}^{2-}$ anion (COT),[4,5] which can react with the anhydrous metal chlorides of transition metals to form M(COT), $M_2(COT)_3$, or $M(COT)_2$ complexes.[6] The preparation of $U(COT)_2$ extended these complexes to actinide(IV) ions.[7] Crystallographic studies[8] show that the $U(COT)_2$ molecule has a "sandwich" structure, with planar eight-member COT rings above and below the U^{4+} ion in D_{8h} molecular symmetry. An electronic configuration has been proposed[7] for $U(COT)_2$ that involves participation of the 5f orbitals in the bonding of the complex, with the orbitals of the two 5f electrons of the U^{4+} ion mixing with the degenerate E_{3u} orbitals of the ligands in essentially a nonbonding combination.

$Np(COT)_2$ and $Pu(COT)_2$ were prepared to allow a more thorough investigation of the nature of the actinide(IV)–COT compounds. Mössbauer measurements on $Np(COT)_2$ provide information on the shielding of s orbitals by outer electrons, and thus on the participation of ligand electrons in the bonding. Magnetic susceptibility measurements on $U(COT)_2$, $Np(COT)_2$, and $Pu(COT)_2$ (U^{4+}, $5f^2$; Np^{4+}, $5f^3$; Pu^{4+}, $5f^4$) narrow the choice of applicable molecular models.

Experimental Section

Reagents. The preparation of UCl_4, $NpCl_4$, and $[(C_2H_5)_4N]_2PuCl_6$ has been previously reported.[9] Cyclooctatetraene, benzene, and toluene were of reagent grade, and were further dried by passage through 4-Å molecular sieve. Dissolved oxygen was removed by repeatedly evacuating to about 0.3 atm. Tetrahydrofuran (THF) was purified by distillation from $LiAlH_4$ in a nitrogen atmosphere. The quality of THF was found to be a major factor in the success of preparations; addition of $LiAlH_4$ as a solution in benzene was more effective in removal of oxidizing impurities from THF than direct addition of solid $LiAlH_4$.

Preparation of Compounds. The preparation of $Np(COT)_2$ followed the general procedure for the preparation of $U(COT)_2$ as outlined by Streitwieser and Müller-Westerhoff.[7] A THF solution of cyclooctatetraene was reduced with potassium metal at −20 to −40° in an inert atmosphere, and a stoichiometric quantity of $NpCl_4$ in THF solution was added. This mixture was stirred for *ca.* 16 hr at room temperature, then the crude $Np(COT)_2$ was precipitated by the addition of deaerated water. The pure $Np(COT)_2$ was recovered by extraction of the solid material with toluene and by vacuum evaporation of the toluene until the solid $Np(COT)_2$ precipitated. *Anal.* Calcd for $Np(COT)_2$: Np, 53.3. Found: Np, 53.3.

In the preparation of $Pu(COT)_2$, solid $[(C_2H_5)_4N]_2PuCl_6$ was added directly to the THF solution of K_2COT; other operations were identical with those used in the preparation and purifications of $Np(COT)_2$. Attempts to synthesize $Pu(COT)_2$ with Cs_2PuCl_6 or Py_2PuCl_6 (Py = $C_5H_5N^+$) failed, although the preparation of $U(COT)_2$ with Py_2UCl_6 was successful. *Anal.* Calcd for $Pu(COT)_2$: Pu, 53.5. Found: Pu, 51.

Properties. The chemical properties of $U(COT)_2$, $Np(COT)_2$, and $Pu(COT)_2$ are nearly identical: all are stable toward water or dilute base, react rapidly with air to form oxides, and are sparingly soluble (*ca.* 10^{-3} *M*) in benzene, toluene, CCl_4, $CHCl_3$, etc. Toluene solutions of $Np(COT)_2$ are yellow viewed in 1- to 2-cm layers, and blood red in >4-cm depths. $Pu(COT)_2$ is cherry red in toluene solutions.

Mössbauer Spectra. Velocity spectra were measured at 4.2°K with a constant-acceleration Mössbauer spectrometer, using an alloy source of ^{241}Am (3 wt %) in thorium metal. The spectrometer[10] and cryogenics system[11] have been described previously. Measurements from 4.2 to 80°K were made with a variable-temperature spectrometer, using a ^{241}Am (5 wt %)– thorium metal source held at 4.3°K. Preparation and properties of americium–thorium Mössbauer sources have been described.[12] The sources used in this work[13] both emit a sharp single line with a very weak secondary line removed −2.0 cm/sec from the strong line. Absorbers of $Np(COT)_2$ contained about 50 mg/cm² of Np.

Magnetic Measurements. Magnetic susceptibilities were measured with a Foner-type vibrating-sample magnetometer[14] manufactured by Princeton Applied Research Corp., and operated in the field of a 12-in. electromagnet. The magnetometer was calibrated with a nickel standard and with $HgCo(CNS)_4$.[15] The measurements reported here were made in uniform magnetic fields of 1–10 kOe. A variable-temperature, liquid helium dewar flask provided con-

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Table I. Infrared Spectra of Actinide(IV)–COT Compounds (cm^{-1})

Solids[a]		CCl_4 solution			
U(COT)$_2$	Np(COT)$_2$	U(COT)$_2$	Np(COT)$_2$	Pu(COT)$_2$	Assignment
		3040 (sh)	3020 (sh)	3040 (w)	C–H stretching
		3005 (vs)	3005 (vs)	2970 (vs)	
		2920 (s)	2920 (s)	2920 (s)	
		2860 (w)	2840 (sh)	2860 (m)	
1470 (w)	1470 (vw)				C=C stretch
		1200 (m)	1180 (m)	1210 (w)	
		1130 (m)	1120 (s)	1120 (s)	
		960 (m)	960 (m)		2 × metal–ring stretch[b]
890 (s)	890 (s)	890 (w)	890 (w)	905 (w)	Parallel CH deformation
740 (m)	740 (m)	830 (w)	830 (w)		CH deformation[b]
690 (m)	690 (s)	690 (sh)	680 (sh)	690 (sh)	Perpendicular CH deformation
		670 (s)	670 (s)	660 (m)	
		630 (m)			
460 (s)[c]	460 (s)[c]				Metal–ring stretch[b]

[a] Paraffin oil and Fluorolube mulls. [b] Assignment speculative. [c] Raman spectra.

trolled temperatures from 2.4 to 45°K. Temperature was measured with a germanium resistance thermometer mounted directly behind the sample. Compensation was made for the effects of the field on the thermometer. The samples were encapsulated in sealed methyl methacrylate plastic containers, and showed no evidence of deterioration over the course of the experiment.

Miscellaneous. Infrared spectra, X-ray powder diffraction patterns, and metal analyses were obtained as previously reported.[8] Absorption spectra were measured in toluene solutions with a Cary Model 14 spectrophotometer. Stoppered cells prevented air oxidation of the samples. Attempts to measure Raman spectra of U(COT)$_2$ and Np(COT)$_2$ were made on a Spex Industries, Inc. Raman spectrophotometer, with a 6328-Å helium–neon exciting beam.

Results

Infrared Spectra. The infrared spectra of the actinide(IV)–COT compounds are essentially identical, and have relatively few absorption lines (Table I). Attempts to measure the Raman spectra of actinide(IV)–COT compounds were unsuccessful because of absorption of the 6328-Å exciting line by the compounds. A single strong line distinguished at 460 cm^{-1} may be due to a metal–ring stretching vibration. Strong CH stretching bands are observed in the infrared spectra of CCl_4 solutions of the COT compound, but not in the spectra taken on fluorocarbon mulls. The infrared spectra are consistent with those expected for compounds of high symmetry; only four infrared bands are predicted for D_{8h} symmetry.[5]

X-Ray Diffraction. The X-ray diffraction patterns for U(COT)$_2$, Np(COT)$_2$, and Pu(COT)$_2$ are identical within the precision of the measurements (Table II). A diffraction pattern[16] calculated from the single-crystal structure of U(COT)$_2$ agreed with the experimental diffraction patterns of Np(COT)$_2$ and Pu(COT)$_2$; from this evidence all three actinide(IV)–COT compounds are isomorphous.

Table II. Partial X-Ray Diffraction Patterns for M(COT)$_2$

U(COT)$_2$[a]		Np(COT)$_2$		Pu(COT)$_2$	
2θ	I	2θ	I	2θ	I
13.20	100	13.15	s	13.15	s
14.09	60	14.05	m	14.10	s
16.24	60	16.15	s	16.20	s
16.25	30				
16.88	25	16.85	vw	16.90	m
20.38	13			20.30	mw
22.05	24	22.15	vw	22.00	m
24.86	25	24.75	vw	24.95	m
24.88	11				
26.58	7			26.50	w
27.44	14			27.50	m
27.57	15				
29.91	16			30.00	ms
30.22	11				
31.96	16			32.05	m
32.82	14			32.85	m
32.83	11				

[a] Calculated from crystal structure; see ref 16.

Table III. Absorption Spectra of Np(COT)$_2$ and Pu(COT)$_2$

Np(COT)$_2$			Pu(COT)$_2$		
λ		ϵ_m,	λ		ϵ_m,
Å	cm^{-1}	M^{-1} cm^{-1}	Å	cm^{-1}	M^{-1} cm^{-1}
			2900	34500	sh
5175	19320	1.3×10^3	3040	32900	3.1×10^3
5360	18750	sh	3850	26000	sh
5610	17850	600	4040	24700	670
5820	17200	800	4140	24350	670
5980	16700	850	4480	22300	400
6160	16220	sh	5160	19400	300
6600	15150	sh	6500	15450	60
7200	13890	sh	7200	13890	sh
7270	13760	20	7600	13160	120
7920	12626	10	7900	12630	120
10400	9615	30	8260	12100	120
11400	8770	6	8900	11230	40
12260	8160	22	9100	11000	sh
12440	8039	12	10350	9660	12
14140	7072	sh			
14280	7003	15			

Absorption Spectra. The absorption spectra of Np(COT)$_2$ and Pu(COT)$_2$ have several strong bands in the visible region (Figure 1), and a number of weaker bands in the near-infrared region (Table III). The intensities of the strong band ($\epsilon \sim 10^3$) are reasonable for charge-transfer transitions, the intensities of weaker bands are in the range ($\epsilon \sim 10$–100) expected for 5f–5f transitions.

Mössbauer Spectra. The Mössbauer spectrum of Np(COT)$_2$ at 4.2°K (Figure 2) is similar to the spectrum of $NpCl_4$ (except for isomer shift), with combined magnetic and quadrupole splitting.[10] Analysis of the spectrum to extract the hyperfine parameters and the isomer shift is straightforward and has been described previously.[17] Table IV gives the isomer shift relative to NpO_2, the magnetic splitting parameter $g_0\mu_N H_{\mathrm{eff}}$, and the quadrupole coupling constant $eqQ/4$ for Np(COT)$_2$ at 4.2°K. Velocity spectra were also taken between

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(16) The authors are indebted to A. Zalkin and K. N. Raymond of the Lawrence Radiation Laboratory, University of California, Berkeley, for providing the computer-calculated diffraction pattern.

(17) W. L. Pillinger and J. A. Stone in "Mössbauer Effect Methodology," Vol. 4, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1968.

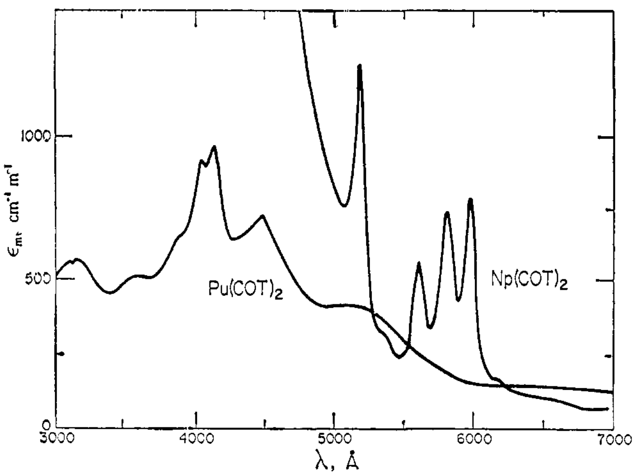

Figure 1. Absorption spectra of $Np(COT)_2$ and $Pu(COT)_2$.

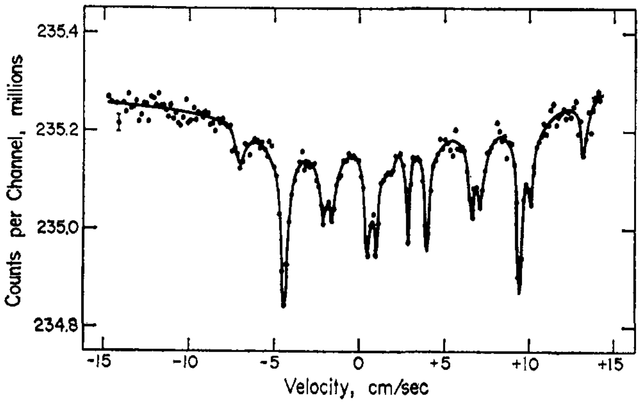

Figure 2. Mössbauer spectrum of $Np(COT)_2$ at 4.2°K.

Table IV. $Np(COT)_2$ Isomer Shift and Hyperfine Parameters at 4.2°K, From Mössbauer Spectra

Isomer shift,[a] cm/sec	$g_0\mu_N H_{eff}$, cm/sec	$eqQ/4$, cm/sec
$+2.50 \pm 0.05$	6.0 ± 0.1	-0.5 ± 0.1

[a] Relative to NpO_2.

4.2 and 80°K in a search for possible magnetic transitions. Above ~40°K the recoilless absorption became too weak to observe; magnetic splitting was present in all spectra below this temperature. No magnetic transitions were observed between 4.2 and 40°K.

Magnetic Susceptibilities. Powdered samples of $U(COT)_2$ and $Np(COT)_2$ were paramagnetic from 4.2 to 45°K; $Pu(COT)_2$ was diamagnetic over the same temperature range. The susceptibility of $Pu(COT)_2$ in the low-temperature region was unusually large, and showed a strong increase with decreasing temperature (Figure 3). Room-temperature measurement of the $Pu(COT)_2$ diamagnetic susceptibility yielded $(-218 \pm 92) \times 10^{-6}$ emu/mol, which agrees with the -187.5×10^{-6} emu/mol[18] calculated from the susceptibilities of the aromatic COT ligands $(-73.4 \times 10^{-6}$ emu/mol) and the diamagnetism of the Pu^{4+} ion $(-40.8 \times 10^{-6}$ emu/mol).[19]

The low-temperature magnetic susceptibilities of $U(COT)_2$ and $Np(COT)_2$ follow a Curie–Weiss law, $\chi = C/(T + \theta)$. The low-temperature susceptibilities, corrected for diamagnetism with the experimental $Pu(COT)_2$ susceptibility, are shown in Figure 4. A least-squares fit of these data to a Curie–Weiss law gives $\mu_{eff} = 2.43$ BM for $U(COT)_2$ and $\mu_{eff} = 1.81$ BM for $Np(COT)_2$. If a constant diamagnetic correction of -187×10^{-6} emu/mol is used, the effective moments are 2.36 and 1.73 BM for $U(COT)_2$ and $Np(COT)_2$, respectively. The diamagnetic correction based upon the experimental $Pu(COT)_2$ susceptibility is considered more reliable than the calculated correction. The experimental constants derived from magnetic susceptibility data are shown in Table V.

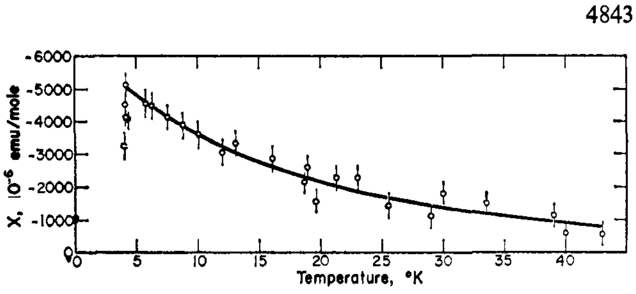

Figure 3. Molar susceptibility of $Pu(COT)_2$.

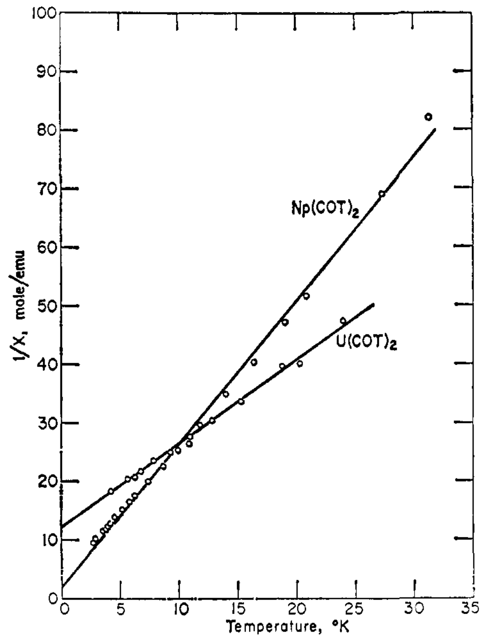

Figure 4. Reciprocal molar susceptibility of $U(COT)_2$ and $Np(COT)_2$ (corrected for diamagnetism from $Pu(COT)_2$ data).

The Mössbauer spectra of $Np(COT)_2$ between 4.2 and 40°K exhibited magnetic splitting, suggesting an ordered magnetic state in this temperature range. However, magnetic susceptibility data showed no evidence for a magnetic transition in either $U(COT)_2$ or $Np(COT)_2$. The magnetization of $U(COT)_2$ at 4.2°K was linear with applied field up to 10 kOe. The magnetization of $Np(COT)_2$ at 4.2°K was linear below 4 kOe and deviated slightly from linearity at higher fields. Since

Table V. Experimental Constants Derived from Susceptibility Data

Compound	θ,[a] °K	C,[b] (emu °K) mol^{-1}	μ_{eff}, BM/molecule	
$U(COT)_2$	9.56[c]	0.735[c]	2.43[c]	2.36[d]
$Np(COT)_2$	0.88[c]	0.739[c]	1.81[c]	1.73[d]

[a] θ = paramagnetic Curie temperature. [b] C = Curie constant. [c] Diamagnetic correction from $Pu(COT)_2$ data. [d] Constant diamagnetic correction of 187×10^{-6} emu/mol.

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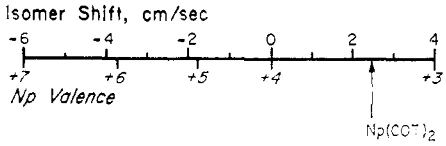

Figure 5. Neptunium isomer shifts.

the susceptibility data indicate that Np(COT)$_2$ is paramagnetic above 4.2°K, the magnetic splitting in the Mössbauer spectra must be attributed to a long spin-lattice relaxation time.[20]

Discussion

The Mössbauer spectrum of Np(COT)$_2$, the absorption spectra of U(COT)$_2$, Np(COT)$_2$, and Pu(COT)$_2$, and the magnetic susceptibilities of the actinide(IV)–COT compounds all show marked departures from these properties for normal (principally ionic) actinide compounds. The isomer shift of Np(IV) in the Mössbauer spectrum of Np(COT)$_2$ is +2.5 cm/sec compared with isomer shifts of $\sim$0 and +4.0 cm/sec for Np^{4+} and Np^{3+}, respectively[12] (Figure 5). The large positive isomer shift for Np(IV) in Np(COT)$_2$ is indicative of an unusual additional shielding of the 6s shell. This shielding suggests a strong electron contribution from the ligand to the metal orbitals.[21]

The absorption spectra for the three actinide(IV)–COT compounds show strong absorption bands in the visible region. The intensities ($\epsilon_m \sim 10^3$) of these absorption bands are a factor of 10 or more stronger than the intensities of bands resulting from normal 5f–5f transitions. The high intensity of these bands probably arises from a "borrowing" of intensity from Laporte-allowed transitions.[22]

The mechanism that permits the observation of Laporte-forbidden 5f–5f transitions is generally accepted to be the mixing of higher orbitals; the bands of unusually high intensities suggest an unusual degree of mixing between 5f and 6d orbitals. An alternative explanation for the strong bands based upon a charge transfer mechanism is possible, but is considered less likely. The bands observed are relatively narrow in width, which appears more appropriate to 5f–5f transitions than to transitions involving charge-transfer processes.

The absorption spectra include many bands in the visible and near-infrared which have the intensities and band widths typical of normal 5f–5f transitions. The energies of these bands do not correspond well with the band energies observed from solution spectra. However, large crystal-field splittings and J–J mixing in the quadrivalent actinide ions produce considerable variations in the energy levels of the ions,[23] and good agreement among U(IV), Np(IV), or Pu(IV) spectra in different compounds could only be expected for closely similar environments. Some, but not all, of the Np(IV) bands observed in toluene solutions of Np(COT)$_2$ correspond well in energy to those of Np^{4+} in a ThO_2 crystal, an eight-coordinate cubic lattice.[24] The energy correspondence between Np^{4+} in Np(COT)$_2$ and Np^{4+} in $PbMoO_4$ (S_4 point symmetry) is not as good.[23]

The magnetic data for actinide(IV)–COT compounds can be interpreted qualitatively from a simple crystal-field model with suitable approximations. The interpretation is based upon these assumptions: (a) Only the lowest crystal-field state is populated within the temperature range of the magnetic measurements. Because the first excited state is $\gg kT$, the paramagnetic susceptibilities should follow a Curie–Weiss law, as observed experimentally. (b) There is no mixing of J states by the crystal field. (c) The effects of intermediate coupling are assumed to be small and therefore neglected.

Because of the C_8 rotational axis in these molecules, the off-diagonal terms in the crystal-field Hamiltonian for the 5f electrons are all zero. The crystal-field potential may be written as $V_c = V_2^0 + V_4^0 + V_6^0$. The crystal field states are pure J_z states, doublets of $\pm J_z$ for $J_z \neq 0$, and a singlet state for $J_z = 0$. Assuming a point-charge model is valid, then $V_2^0 \gg V_4^0 \gg V_6^0$, and $V_c \approx V_2^0$. The energy matrix involves matrix elements of the type

$$\langle J,J_z|V_2^0|J,J_z\rangle = [3J_z^2 - J(J+1)]B_2^0$$

which are tabulated in the literature.[25,26] Considering the $J = 4$ ions, U^{4+} ($^3H_4$) and Pu^{4+} ($^5I_4$), the lowest state will be either the doublet $J_z = \pm 4$ or the singlet $J_z = 0$, depending upon whether the crystal-field parameter B_2^0 is positive or negative. A similar calculation for Np^{4+} ($^4I_{9/2}$) shows that the lowest state is either $J_z = \pm {}^9/_2$ or $J_z = \pm {}^1/_2$.

The crystal-field parameter B_2^0 is defined as $B_2^0 = \alpha_J A_2^0 \langle r^2 \rangle$, where α_J is the second-degree operator equivalent factor and is a function of L and S, A_2^0 is a parameter that depends upon the lattices and charges of the ions, and $\langle r^2 \rangle$ is the expectation value for the magnetic (5f) electrons. The parameter A_2^0 may be calculated exactly in the limit of a point-charge model, and is approximately constant for the three isomorphous actinide(IV)–COT compounds. $\langle r^2 \rangle$ is necessarily positive, so the algebraic sign of B_2^0 depends on the signs of α_J and A_2^0. α_J is negative for U^{4+} and Np^{4+} and positive for Pu^{4+}. Assuming A_2^0 is positive, $J_z = \pm 4$ is the lowest state for U^{4+}, $J_z = \pm {}^9/_2$ for Np^{4+}, and $J_z = 0$ for Pu^{4+}. Experimentally, U(COT)$_2$ and Np(COT)$_2$ are paramagnetic, therefore, the assumption of $A_2^0 > 0$ must be correct.

Calculating the magnetic moments from $\mu_{\text{eff}} = g|J_z|\beta$, $\mu_{\text{eff}} = 3.20$ BM for U(COT)$_2$ and 3.27 BM for Np(COT)$_2$, and Pu(COT)$_2$ is diamagnetic.

These calculated values for paramagnetic susceptibilities are larger than the experimental values, but may be brought to agree by correcting for the reduction in orbital size caused by covalent contributions to the metal–ligand bonding. Introducing the orbital reduction factor k, and replacing the conventional Zeeman operator

$$\vec{L} + 2\vec{S}$$

with

$$k\vec{L} + 2\vec{S}$$

the Landé g_J becomes $g_J - (1 - k)(2 - g_J)$.[27,28] A value of $k = 0.8$ agrees with experimental results.

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The value of $k = 0.8$ required to achieve a satisfactory fit with experiment appears quite low for actinide compounds, and corresponds to values found for d transition metal compounds.[29] However, this value of k can be interpreted to imply a strong interaction between the actinide ions and the COT orbitals, and is qualitatively consistent with the pronounced covalency inferred from the Mössbauer results of $Np(COT)_2$.

This interpretation of the magnetic susceptibility data is based on a much oversimplified model, which, however, does show the importance of covalent bonding for actinide(IV)–COT compounds and correctly predicts the diamagnetism of $Pu(COT)_2$. The temperature dependence of the diamagnetic susceptibility of $Pu(COT)_2$ is quite unusual, and no explanation for this phenomenon is apparent. Detailed studies on the optical and magnetic properties of these compounds remain to be done, and should provide experimental evidence for a more quantitative model.

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Pyrolysis of Monosilane

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Abstract: The pyrolysis of silane–silane-d_4 mixtures and silane-d_4 in the presence of hydrogen has been examined. The results from these experiments and those reported by Purnell and Walsh[1] strongly suggest that silane decomposes by the following route: $SiH_4 \rightarrow SiH_3 + H$; $H + SiH_4 \rightarrow H_2 + SiH_3$; $SiH_3 + SiH_4 \rightarrow Si_2H_6 + H$; $2SiH_3 \rightarrow Si_2H_6$. With this result, the activation energy obtained by Purnell and Walsh can be used to demonstrate that $D_{298}°(SiH_3\text{–}SiH_3)$ and $D_{298}°(SiH_3\text{–}H)$ are of the order of 81 and 94 kcal mol^{-1}, respectively. Results from the pyrolysis of methylsilane–methylsilane-d_3 mixtures suggest that in addition to the reactions present in the silane decomposition, steps forming methylsilene and hydrogen are also important in the pyrolysis of methylsilane.

The pyrolysis of monosilane has been investigated by a number of workers.[2] A more recent kinetic study has been carried out by Purnell and Walsh.[1] They demonstrated that the pyrolysis of silane was homogeneous when carried out over a silicon mirror. Their results were most consistent with either mechanism A, molecular hydrogen elimination

$$SiH_4 \longrightarrow SiH_2 + H_2 \qquad (1)$$

$$SiH_2 + SiH_4 \rightleftharpoons Si_2H_6 \qquad (2)$$

$$SiH_2 + Si_2H_6 \rightleftharpoons Si_3H_8 \qquad (3)$$

or mechanism B, H atom formation (free-radical chain)

$$SiH_4 \longrightarrow SiH_3 + H \quad \text{initiation} \qquad (4)$$

$$\left.\begin{array}{l} H + SiH_4 \longrightarrow H_2 + SiH_3 \qquad (5) \\ SiH_3 + SiH_4 \longrightarrow Si_2H_6 + H \qquad (6) \end{array}\right\} \text{chain}$$

$$2SiH_3 \longrightarrow Si_2H_6 \quad \text{termination} \qquad (7)$$

Although it was not possible to determine which route was operative, they felt that a mechanism involving silene was most probable.

In this paper, we present our results, which, when combined with those of Purnell and Walsh,[1] allow for an analysis of the pyrolysis of monosilane.

Experimental Section

All reactions were carried out in a Pyrex glass vacuum system. Separations were made by trap-to-trap distillations with the use of standard slush baths. Silane and silane-d_4 were prepared by the reduction of silicon tetrachloride with lithium aluminum hydride or deuteride. The silane-d_4 had present a small (~5%) amount of silane-d_3. Infrared spectra were obtained in 10-cm gas cells on a Perkin-Elmer Model 337 spectrophotometer, while mass spectra were obtained on a Hitachi Model RMU-6E mass spectrometer.

The static pyrolyses were carried out in a cylindrical vessel of 198-cm^3 volume whose walls were coated with a silicon mirror.[1] The temperature was measured with a thermometer inserted into a well in the reaction vessel which was inside an electric furnace. An equimolar silane–silane-d_4 mixture was expanded from a trap on the vacuum line into the heated reaction zone. After 10 sec, the pressure was noted and the stopcock between the trap and the reaction vessel was closed. After 2.5 min, the reaction mixture was returned to the vacuum system for analysis.

The pyrolysis of silane-d_4–hydrogen mixtures was carried out in the same manner from previously prepared silane-d_4–hydrogen mixtures.

The flow pyrolyses were carried out in a Vycor reaction tube previously described.[3] For these reactions, 1.08 mmol of an equimolar silane–silane-d_4 mixture was cycled with a Toepler pump through a silicon-mirrored heated tube (at 460°) and two traps cooled to −130°. The average pressure before the heated tube was 67 mm. A −112° bath was used in the pyrolysis of equimolar mixtures of methylsilane and methylsilane-d_3.

The silane fractions were analyzed from infrared spectra. The infrared spectrum[4] of SiH_3D, SiH_2D_2, or $SiHD_3$ each has a strong band which has zero overlap with bands from other silanes. Therefore, it was possible to obtain at least an approximate analysis of our silane mixtures. The disilane mixtures were analyzed from mass spectra of the disilane fractions. The mass spectrum of each disilane has been previously reported.[5] These analyses are most accurate for ratios of $Si_2D_6:HSi_2D_5:H_2Si_2D_4:H_3Si_2D_3$. The ratios of the more highly hydrogenated species are less reliable. The hydrogen mixture was also analyzed by mass spectra.

In a separate control experiment it was demonstrated that an H_2–D_2 mixture does not exchange H atoms over a silicon mirror under conditions used in our experiments.

Results

The pyrolysis of equimolar silane–silane-d_4 mixtures was examined in a static system and in a circulating flow system with low-temperature (−130°) trapping

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