Table I. Quantum Yields for the Products of the 254-nm Photolysis of $[Cr(NH_3)_5OHCr(NH_3)_5]^{5+}$ [a], [b]

species	quantum yield (at $t = 0$)	species	quantum yield (at $t = 0$)
$Cr(NH_3)_5OH_2^{3+}$	0.021 ± 0.001	OH_2 erythro	0.179 ± 0.020
Cl erythro	0.087 ± 0.006	total erythro	0.266 ± 0.023

[a] $T = 5$ °C. [b] Initial moles of rhodo = 8.47×10^{-5} in all cases; solution 0.10 M in HCl.

varying concentrations of $HClO_4$. Absorption spectra were run on a Cary 14 spectrophotometer. Chromium analyses were performed on all samples following oxidation to CrO_4^{2-} in basic peroxide.

Results

When the chloride salt of the rhodo ion, in 0.10 M HCl, is put through three freeze–thaw cycles to remove dissolved oxygen and then photolyzed at 254 nm at 5 °C, in an N_2 atmosphere, three products are obtained in the ion-exchange separation of the reaction mixture: the aquo and chloro erythro ions and the aquopentaamminechromium(III) ion. The quantum yields for three replicate experiments (initial rhodo, as chloride salt, 8.47×10^{-5} mol), corrected for the small amount thermal reaction at 5 °C, are presented in Table I. When the unreacted rhodo ion was also eluted and analyzed, an average of 98% of the chromium was recovered in the experiments summarized in Table I. Similar results are obtained when the rhodo ion is photolyzed in HCl solution with O_2 present and in HNO_3 and $HClO_4$ solutions ([acid] = 0.1 M) in both oxygenated and deoxygenated solutions. In the experiments in HNO_3 and $HClO_4$ solutions the rhodo complex was first converted to the nitrate and perchlorate salts, respectively. Under some experimental conditions a small amount of the chromium ends up as Cr(VI).[7]

The apparent quantum yield for the production of $Cr(NH_3)_5OH_2^{3+}$ from the rhodo ion is constant at 0.021 ± 0.001 for irradiation times up to 10 min, corresponding to 45% conversion of the starting complex. During this same time the ratio $\phi(Cr(NH_3)_5OH_2^{3+})/\phi$(erythro complexes) is constant at 0.088 ± 0.006 and the apparent quantum yield for the total production of the erythro complexes remains constant at 0.266 ± 0.023. During this same time period, the ratio of the apparent quantum yields for the individual erythro complexes [ϕ(Cl erythro)/ϕ(OH_2 erythro)] varies from 0.48 at 2.5 min to 0.75 at 10 min. At longer times the ratio continues to rise, reaching 1.0 after 20 min of irradiation. In previous experiments on the L_1 photochemistry of the rhodo ion this latter ratio ranged from 0.0 at 1.5 min to 0.65 at longer times for similar conversion percentages.

Discussion

Several previous reports regarding ligand substitution reactions following excitation into the charge-transfer region of Cr(III) complexes have appeared in the past decade.[9-11] In those cases where two distinct photoaquation reactions were possible, it has been noted that the thermal reaction mode, which in the cases studied turns out to be the least probable photoreaction following excitation into L_1 and L_2, becomes more prominant upon excitation into the charge-transfer region. The observation of bridge-cleavage products following 254-nm excitation of the rhodo complex is another example of this phenomenon. In the reaction studied here, no thermal reaction mode products are observed following excitation into L_1 and L_2. The detection limits of our experiments are such that, if $Cr(NH_3)_5OH_2^{3+}$ is formed on L_1 or L_2 photolysis, its quantum yield is $\leq 10^{-4}$ of its yield following charge-transfer excitation.

The data reported here suggest a model in which essentially all of the photochemical reactions following 254-nm excitation of the rhodo ion arise from the charge-transfer state or the third quartet state, L_3 (this is the $^4T_1$ (^4F) state in *O* microsymmetry), which is buried under the lower energy edge of the charge-transfer band. In addition, any states which can be reached from the charge-transfer (CT) or L_3 states, but not from L_1 or L_2, could contribute to the observed photochemistry. Included in this latter set of states are highly excited vibrational levels of the ground electronic state. Other than the fact that the thermal reaction mode product is seen to become an important photoproduct following 254-nm excitation, there are currently no data which compel us to choose the "hot ground state" as the photoactive state. Quantum yield data as a function of excitation wavelength, over the range of wavelengths producing $Cr(NH_3)_5OH_2^{3+}$, would provide a more significant test of the "hot ground state" mechanism.

Hoppenjans, Hunt, and Penzhorn have shown that the bridge cleavage of the chloro erythro complex is catalyzed by Cr(II).[12] Since it is likely that the charge-transfer state in the rhodo complex involves a ligand to metal charge transfer, which may result in the formation of Cr(II), it is interesting to see if Cr(II)-catalyzed hydrolysis can account for the formation of $Cr(NH_3)_5OH_2^{+}$ in the experiments reported here. First of all, the proposed mechanism of Cr(II) catalysis of the chloro erythro complex involves formation of a Cl bridge to the Cr(II) and is thus not directly transferable to the rhodo complex. Recent experiments in ClO_4^- solutions show that the bridge-cleavage quantum yield is very similar to that in Cl^- media, ruling out an electron-transfer process involving chloro bridges. Second, the relatively low quantum yield for bridge cleavage does not demand that Cr(II) catalysis be invoked. Third, in none of our experiments is there any evidence for $Cr_2(H_2O)_8(OH)_2$, the product formed on air oxidation of Cr(II), or for any species such as $Cr(OH_2)_5Cl^{2+}$ or $Cr(OH_2)_6^{3+}$.

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Registry No. $[Cr(NH_3)_5OHCr(NH_3)_5]^{5+}$, 23329-46-6; $Cr(NH_3)_5OH_2^{3+}$, 15975-47-0; $[Cr(NH_3)_5OHCr(NH_3)_4Cl]^{4+}$, 48063-42-9; $[Cr(NH_3)_5OHCr(NH_3)_4OH_2]^{5+}$, 73465-00-6.

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Bis(η^8-1,3,5,7-tetramethylcyclooctatetraene) Compounds of Protactinium, Neptunium, and Plutonium

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Although many reports have appeared on the chemistry of the bis(cyclooctatetraene) complexes of uranium and thorium,[2]

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Table I. Partial X-ray Diffraction Patterns for $M(TMCOT)_2$

U[a]		Pa		Np		Pu	
d, Å	*I*	*d*, Å	*I*[b]	*d*, Å	*I*[b]	*d*, Å	*I*[b]
8.50	338	8.0	m	8.0	s	8.1	s
7.66	1000	7.9	m+	7.75	s	7.9	s
7.34	305			7.30	w	7.4	s
6.95	486	6.5	w	6.45	m+	7.0	w
6.20	182	6.4	m	6.20	w	6.5	m
6.03	215	5.6	w	5.6	m	5.6	w
5.82	133	5.4	w	5.4	m		
4.95	118	5.0	w	4.95	m[c]	5.0	m–[c]
4.90	93						
4.66	105	4.6	w	4.6	m	4.6	w
4.45	86						
4.10	96			4.0	m–	4.0	w

[a] Calculated; see ref 13. [b] Intensities estimated visually. [c] Probably m because of two overlapping lines.

the analogous sandwich complexes of the other actinide elements have not been as extensively studied. Karraker et al. were able to prepare the neptunium and plutonium compounds $M(C_8H_8)_2$[3] shortly after the first syntheses of uranocene[4] and thorocene.[5] Protactinocene, however, was not reported until several years later, and only minute amounts were isolated.[6,7] Further studies have included the preparation of bis(alkylcyclooctatetraene)actinide complexes of neptunium and plutonium[8,9] and of trivalent actinide complexes $KM(C_8H_8)_2$ (M = Np or Pu,[10] M = Am[11]).

Characterization and physical studies of these compounds have often been limited by the small quantities of compounds available and the strong radioactivity of these elements. Generally, X-ray powder patterns have been used to establish the identity of the compounds and in some cases visible, infrared, Raman, nuclear magnetic resonance, or Mössbauer spectra have been obtained. These studies have shown that bis(cyclooctatetraene)actinide(IV) complexes are all structurally and chemically similar. This suggests that the same bonding scheme prevails throughout the actinide(IV)–COT series, and the unusual degree of covalency demonstrated by the Mössbauer spectra of $Np(RC_8H_7)_2$[3,9] may be a common property. However, comparisons across the actinide series are hampered by the lack of data on protactinium complexes. Lying between thorium and uranium in the periodic table, Pa(IV) has a $5f^1$ electronic configuration which would simplify interpretation of magnetic and electronic spectral data and provide a better picture of the bonding and degree of ring–metal covalency in actinocene complexes. Therefore, a new study of the synthesis of bis(cyclooctatetraene)protactinium has been undertaken. In addition, a new synthetic route to actinocenes has been developed by using neptunium and plutonium borohydride complexes.

Table II. Visible Spectra (nm) of $M(TMCOT)_2$

Pa	Np	Pu
380	546	429
490 (sh)	597	470
	618	550
	635	

Table III. Maxima[a] in the Visible Spectra of Actinocenes

	Th	Pa	U	Np	Pu
COT	450		615	518	404
BuCOT	456 (6)		623 (8)	523 (5)	407 (3)
TMCOT	480 (30)	380	650 (35)	546 (28)	429 (25)

[a] λ_{max}, nm; $\Delta\lambda_{max}$ for substituent in parentheses.

Results and Discussion

The most common method of synthesis of bis(cyclooctatetraene)actinide complexes has been the reaction of a cyclooctatetraene dianion with an actinide(IV) chloride in tetrahydrofuran (eq 1). Although this technique has previously yielded small amounts of $Pa(C_8H_8)_2$,[6,7] solutions of $PaCl_4$ and K_2COT were found to readily decompose. In one case, sublimation of the reaction products gave a small amount of yellow, nonradioactive solid. Isolation of K_2COT as a yellow sublimate has previously been encountered in attempts to prepare protactinocene.[6] The facile oxidation of Pa(IV) to Pa(V) may be responsible for the failure of these reactions. The reaction of the tetramethylcyclooctatetraene dianion ($TMCOT^{2-}$) with $PaCl_4$, however, gave a light brown solution from which $Pa[(CH_3)_4C_8H_4]_2$ can be isolated in low yield. This compound, which has not previously been prepared, was soluble in THF and slightly soluble in benzene, and it was identified by its X-ray powder diffraction pattern (Table I).

$$MCl_4 + 2K_2COT \xrightarrow{THF} M(COT)_2 + 4KCl \qquad (1)$$

The synthesis of cyclooctatetraene complexes of Np and Pu is complicated by the low solubility of the halide complexes of these elements in organic solvents. Therefore, a new procedure was developed which utilizes the actinide borohydride complexes $M(BH_4)_4$. These volatile air-sensitive compounds are readily soluble in organic solvents and were allowed to react with cyclooctatetraene dianions in THF (eq 2; M = Np, black; M = Pu, green). $Np(TMCOT)_2$, which has previously been prepared from $NpCl_4$,[8,9] is readily isolated by recrystallization from THF. The visible spectrum of this black crystalline material is in agreement with that reported by Karraker,[9] and an X-ray powder pattern further established the characterization.

$$M(BH_4)_4 + 2K_2TMCOT \xrightarrow{THF} M(TMCOT)_2 + 4KBH_4 \qquad (2)$$

The value of this new synthesis is demonstrated in the reaction of tetramethylcyclooctatetraene dianion with $Pu(BH_4)_4$. Although reaction of K_2TMCOT with Pu(IV) halides has been reported to lead to reduction (to Pu(III)),[8] $Pu(TMCOT)_2$ could be isolated as a green, THF-soluble powder from the borohydride. An X-ray powder pattern was also obtained for this compound.

The X-ray powder diffraction data obtained from these sandwich compounds serve to characterize them and also to allow comparision of the structures of the three complexes with that of the uranium analogue. The crystal and molecular structure of $U(TMCOT)_2$ has been determined by Hodgson and Raymond,[12] and the computer-generated powder pattern[13]

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of this uranocene is listed in Table I along with the experimental data from the three other actinide complexes studied. Karraker has noted that, although actinocenes with differing substituents on the cyclooctatetraene ligands have different crystal structures, compounds within each series are approximately isostructural.[9] The X-ray powder patterns obtained are of poor quality, probably because of radiation damage, and many of the lines are rather weak; nevertheless, the data in Table I suggest that the Pa and Pu complexes are isostructural with $Np(TMCOT)_2$. The three complexes are therefore suggested to have the same structure as $U(TMCOT)_2$.

Visible spectra were obtained for the three TMCOT compounds studied, and the results are presented in Table II. While the spectra for the Np and Pu compounds are complex, like that of a uranocene, the spectrum from $Pa(TMCOT)_2$ contains only a single band and resembles that of a thorocene. The data for this Pa complex provide the first case in which spectra for COT complexes of all of the first five actinides can be compared. Although no clear pattern is apparent, the bathochromic shift previously observed for actinocenes with electron-donating substituents[9,14] is also found in this study (Table III). This consistency again suggests that bonding is similar in these compounds of different actinides and that these spectra are related in type, probably ring-to-metal charge-transfer transitions. In addition, the consistent observation of a bathochromic shift of about 900–1400 cm^{-1} from COT to TMCOT complexes allows the prediction of a maximum at about 365 nm in the spectrum of $Pa(COT)_2$. This compound had previously[6,7] been characterized only by its IR spectrum and X-ray powder pattern.

Experimental Section

Starting Materials. K_2TMCOT was prepared by the reaction of TMCOT with potassium and was isolated as a yellow powder by removal of the solvent. The preparation of $^{237}Np(BH_4)_4$ and $^{239}Pu(BH_4)_4$[15] has been previously published. $^{231}PaCl_4$ was prepared[16] at Harwell, England, and used as received. Tetrahydrofuran was purified by distilling twice from $LiAlH_4$ and was freeze–pump–thaw degassed before use. Due to the air-sensitive and radioactive nature of these compounds, all synthetic work was performed under an argon atmosphere or in vacuo by using an inert-atmosphere glovebox or a vacuum line equipped with containment facilities.

Visible spectra were run on a Cary 17 spectrophotometer using THF solutions prepared and loaded into a stoppered glass cell in an argon-filled glovebox. X-ray powder patterns were obtained from samples loaded into quartz capillaries, sealed with grease in the glovebox, and flame sealed immediately after removal from the box. Cu radiation, with a Ni filter to remove the $K\beta$, was used, and exposure times varied from 8 to 12 h.

Reaction of $PaCl_4$ with K_2COT. In an argon-filled glovebox, 10.5 mg (0.0576 mmol) of K_2COT was added to a solution of 13.0 mg (0.0349 mmol) of $PaCl_4$ in 10 mL of THF. Removal of the solvent in vacuo gave a green residue which was heated to ca. 400 °C under high vacuum (10^{-6} torr). The brown sublimate was found to be nonradioactive.

Bis(η^8-tetramethylcyclooctatetraene)protactinium(IV), $Pa(TMCOT)_2$. A 25-mL reaction tube was loaded with 7.6 mg (0.032 mmol) of K_2TMCOT and 5.8 mg (0.016 mmol) of $PaCl_4$. The tube was sealed with a stopcock and evacuated to 10^{-6} torr. THF (16 mL) was transferred in vacuo onto the solids, and the mixture was allowed to warm slowly. After the solution thawed, the $PaCl_4$ dissolved, and the solution darkened. Removal of the solvent in vacuo gave a dark powder. A powder pattern of this material indicated the presence of KCl and the sandwich complex.

The powder was loaded into the left arm of an H-tube extractor, and the extractor was evacuated. THF (ca. 5 mL) was transferred onto the solids. After warming to room temperature, the solution was filtered into the right arm of the extractor. About 1–2 mL of the THF was distilled back into the left side by cooling the left arm in liquid nitrogen. The solution was again filtered into the right side and this process was repeated twice. Little colored material was extracted on the final cycle, and the solvent was removed in vacuo. The small amount of product was dissolved in the THF, and a visible spectrum was obtained.

Bis(η^5-tetramethylcyclooctatetraene)neptunium(IV), $Np(TMCOT)_2$. A reaction tube was loaded with 16.5 mg (0.069 mmol) of K_2TMCOT and evacuated to 10^{-6} torr. THF (5 mL) was added by vacuum transfer, and 9.4 mg (0.032 mmol)[17] of $Np(BH_4)_4$ was sublimed into the frozen mixture. As the solution thawed, the green color of $Np(BH_4)_4$ faded, and the solution turned a dark brown. The solvent was removed by vacuum transfer.

The dark powder was transferred to the H-tube and extracted with benzene in the manner described previously. A visible spectrum and a powder pattern were obtained from the product.

Bis(η^5-tetramethylcyclooctatetraene)plutonium(IV), $Pu(TMCOT)_2$. By use of the procedure used in the preparation of $Np(TMCOT)_2$, 15 mg (0.063 mmol) of K_2TMCOT and ca. 9 mg (0.03 mmol)[17] of $Pu(BH_4)_4$ were allowed to react in ca. 8 mL of THF. Extraction with THF using the H-tube gave 2.5 mg (0.004 mmol, 15%) of green product and an insoluble white powder that was identified as KBH_4 by its X-ray powder pattern. A powder pattern and a visible spectrum were obtained from the green product.

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Registry No. $Pa(TMCOT)_2$, 73574-67-1; $Np(TMCOT)_2$, 12715-86-5; $Pu(TMCOT)_2$, 73587-37-8; K_2TMCOT, 56726-06-8; $PaCl_4$, 13867-41-9; $Np(BH_4)_4$, 66615-98-3; $Pu(BH_4)_4$, 66615-99-4.

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Equilibrium Thermodynamic and Activation Parameters for Isomer Exchange in $[MoI(CO)_2((CH_3)_2PC_2H_4P(C_2H_5)_2)_2]I$

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Recently, we reported that compounds of the type $MX(CO)_2(\text{unsymmetric, bidentate phosphine})_2^{n+}$ [M = Ta, n = 0; M = Mo, n = 1; X = Cl, Br, I; unsymmetric, bidentate phosphine = $Me_2PC_2H_4PEt_2$ (dmdepe) and others] exist as cis and trans isomers with respect to the unsymmetric ends of the chelate.[1] The isomer distributions were as expected for the Ta(I) derivatives, i.e., the less crowded trans isomer (eq 1) being favored (1.8/1 for **2** at 30 °C). However, although the Mo(II) ion should be smaller and have shorter M–P bonds than Ta(I), the isomer distribution in **1** appeared to be more nearly equal (1.2/1 at −30 °C).

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