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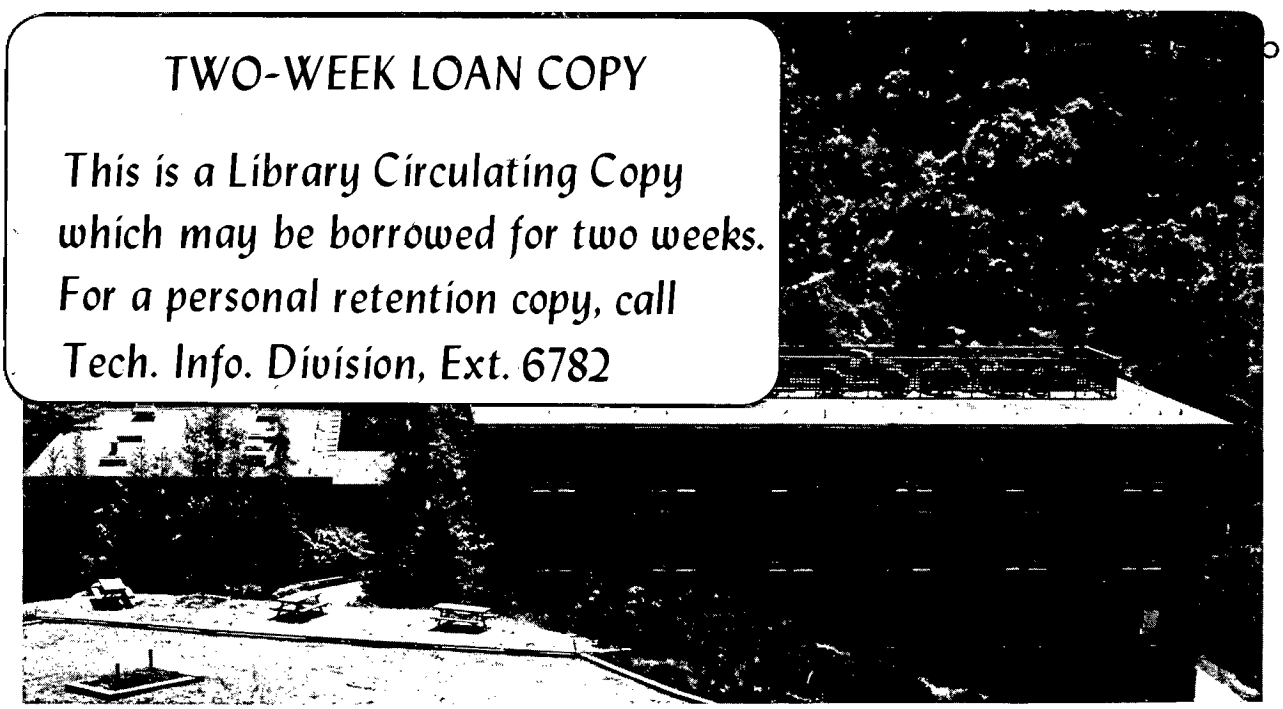

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Bis(η^8-1,3,5,7-Tetramethylcyclooctatetraene) Compounds of Protactinium, Neptunium, and Plutonium

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Abstract

Bis(η^8-tetramethylcyclooctatetraene) complexes of neptunium and plutonium, $M(TMCOT)_2$, have been prepared by the reaction of the volatile actinide-tetrahydroborates $M(BH_4)_4$ with tetramethylcyclooctatetraene dianion. The analogous protactinium compound has been prepared by the reaction of $PaCl_4$ with $TMCOT^{=}$. X-ray powder patterns and visible spectra have been obtained from these compounds allowing comparison amongst the COT complexes of the first five actinide elements.

Although many reports have appeared on the chemistry of the bis(cyclooctatetraene) complexes of uranium and thorium[2], the analogous sandwich complexes of the other actinide elements have not been as extensively studied. Karraker etal. 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 small 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 Mossbauer 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 Mossbauer spectra $Np(RC_8H_7)_2$[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 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 using Np and Pu borohydride complexes.

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:

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

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, non-radioactive 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 tetramethylcyclooctatetraene dianion ($TMCOT^{=}$) 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, is soluble in THF and slightly soluble in benzene and was identified by its x-ray powder diffraction pattern (Table 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

utilizing 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:

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

(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.

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 both as characterization and allow comparison of the structure of the three complexes with that of the uranium analog. The crystal and molecular structure of $U(TMCOT)_2$ has been determined by Hodgson and Raymond[12] and the computer generated powder pattern[13] of this uranocene is listed in Table 1 along with the experimental data from the three other actinide complexes studied. Karraker has noted that, although actinocenes with differing substituents on the cyclo-

octatetraene ligands have different crystal structures, compounds within each series are approximately isostructural.[9] The data in Table 1 suggest that the Pa and Pu complexes are isostructural with $Np(TMCOT)_2$, and therefore the three complexes are 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 2. 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 3). 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 $Pa(COT)_2$.

Experimental

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 and used as received.

Tetrahydrofuran was purified by distilling twice from $LiAlH_4$ and freeze-pump-thaw degassed before use. Due to the air sensitive and radioactive nature of these compounds, all synthetic work was performed in an argon atmosphere or in vacuo using an inert atmosphere dry box 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 drybox. X-ray powder patterns were obtained from samples loaded into quartz capillaries, sealed with grease in the drybox, and flame sealed immediately after removal from the box. Cu radiation, with a Ni filter to remove the k_β, was used and exposure times varied from 8 to 12 hours.

Reaction of $PaCl_4$ with K_2COT:

In an argon filled dry box, 10.5 mg (0.0576 mmole) of K_2COT was added to a solution of 13.0 mg (0.0349 mmole) 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 non-radioactive.

Bis(η^8-tetramethylcyclooctatetraene)protactinium(IV), $Pa(TMCOT)_2$:

A 25 mL reaction tube was loaded with 7.6 mg(0.032 mmole) of K_2TMCOT and 5.8 mg(0.016 mmole) of $PaCl_4$. The tube was sealed with a stopcock and evacuated to 10^{-6} torr. THF (16 mL) was transfered in vacuo onto the solids and the mixture was allowed to warm slowly. After thawing, 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 transfered 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 extracted on the final cycle and the solvent was removed in vacuo. The small amount of product was dissolved in THF and a visible spectrum was obtained.

Bis(η^8-tetramethylcyclooctatetraene)neptunium(IV), $Np(TMCOT)_2$:

A reaction tube was loaded with 16.5 mg(0.069 mmole) of K_2TMCOT and evacuated to 10^{-6} torr. THF(5 ml) was added by vacuum transfer and 9.4 mg(0.032 mmole)[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 transfered 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^8-tetramethylcyclooctatetraene)plutonium(IV), $Pu(TMCOT)_2$:

Following the procedure used in the preparation of $Np(TMCOT)_2$, 15 mg(0.063 mmole) of K_2TMCOT and ca. 9 mg(0.03 mmole)[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 mmole, 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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(17) Based on the vapor pressure of $Np(BH_4)_4$.

Table 1. Partial X-Ray Diffraction Patterns for $M(TMCOT)_2$

U[a]		Pa		Np		Pu	
D	I	D	I[b]	D	I[b]	D	I[b]
8.50	338	8.0	m	8.0	s	3.1	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	5.0	m-
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 reference 13

b) Intensities estimated visually

Table 2. Visible Spectra of $M(TMCOT)_2$ (nm)

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

Table 3. Maxima in The Visible Spectra of Actinocenes, ($\Delta\lambda_{max}$) for substituent

	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)

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