Contribution from the Department of Chemistry and Lawrence Berkeley Laboratory,
University of California, Berkeley, California 94720

Bis(π-cyclooctatetraene)protactinium

DAVID F. STARKS, THOMAS C. PARSONS, ANDREW STREITWIESER, Jr.,* and NORMAN EDELSTEIN

Received December 5, 1973 AIC30879Q

Bis(π-cyclooctatetraene)protactinium, $Pa(C_8H_8)_2$, has been prepared on a micromolar scale by reaction of $K_2C_8H_8$ with $PaCl_4$ in THF. The golden yellow sublimate was characterized by the X-ray powder pattern which is consistent with data for the isostructural compounds $Th(C_8H_8)_2$ and $U(C_8H_8)_2$. A solvent-free preparation of the latter compounds is described from the metal tetrafluoride and MgC_8H_8.

Protactinium, atomic number 91, lies between thorium and uranium in the periodic table. It shows a similarity to these elements in having a common +4 oxidation state but the lone 5f electron remaining in this oxidation state is readily lost to give a +5 oxidation state in many compounds. Only one organometallic compound of protactinium has been reported, tetrakis(cyclopentadienyl)protactinium(IV).[1] Consequently, there is a special interest in the preparation of bis(π-cyclooctatetraene)protactinium; this compound is expected to be a D_{8h} sandwich complex by analogy with the uranium[2,3] and thorium[4,5] compounds.

Experimental Section

All work involving Pa was done in negative-pressure containment glove boxes. Air- and water-sensitive materials were handled in a rebuilt argon atmosphere glove box or in a vacuum line housed in a glove box. All solvents were carefully dried and degassed prior to use. Milligram amounts of Pa materials were weighed on a Cahn gram electrobalance with a remote weighing assembly inside an argon glove box.

Ligands. A solution of $K_2C_8H_8$ was prepared as described[2,3] previously by direct reaction of cyclooctatetraene with finely divided potassium in THF. Dry $K_2C_8H_8$ (*caution*! violently pyrophoric, explodes on contact with oxygen) was obtained after vacuum transfer of solvent and was sealed in glass ampoules. The magnesium salt, MgC_8H_8, was obtained as a precipitate in the reaction between $MgBr_2$ and $K_2C_8H_8$ in THF.[6] A light green material was obtained after filtration and washing with fresh THF.

Protactinium Starting Materials. An aqueous HF solution of Pa salts was treated dropwise with concentrated ammonium hydroxide to precipitate milligram amounts of hydrated protactinium oxide. After centrifugation and washing, the protactinium oxide was allowed to air-dry for 72 hr to form a ball which could be transferred readily. Protactinium pentachloride was prepared from the hydrated oxide through reaction with thionyl chloride at 400°.[7] Protactinium tetrachloride was obtained through the reduction of $PaCl_5$ with aluminium powder.[8]

All Pa starting materials were routinely identified through X-ray powder pattern techniques prior to use. Thorium and uranium tetrafluorides were obtained from Research Organic/Inorganic and used without further purification.

Bis(π-cyclooctatetraene)protactinium. A dilute solution of 1.5 mg (4.0 μmol) of protactinium tetrachloride in 15 ml of tetrahydrofuran was mixed under argon with 1.5 mg (8.2 μmol) of dry $K_2C_8H_8$. The reaction mixture was transferred to the vacuum line, and the THF was stripped off. After evacuation to less than 10^{-5} Torr, the bottom of the reaction flask was heated with a soft blue flame. A golden yellow sublimate was obtained which was characterized by the X-ray powder pattern as $Pa(C_8H_8)_2$.

In one experiment with $PaCl_5$ in a more concentrated solution of THF, polymerization of the solvent rapidly occurred to a viscous mass apparently because of Pa radiation.

Formation of $U(C_8H_8)_2$ and $Th(C_8H_8)_2$ from the Tetrafluorides. A mixture of 14 mg (0.045 mmol) of uranium tetrafluoride and 13 mg (0.10 mmol) of dry MgC_8H_8, ground together in a mortar and pestle, was evacuated to 10^{-6} Torr. Reaction and concomitant sublimation of uranocene was effected through gentle heating with a soft blue flame. The resultant 1.4% yield of uranocene sublimate was identified through its characteristic cascade of absorption bands in the 600–700-nm region. Thorium tetrafluoride was allowed to react with MgC_8H_8 in the same manner and produced a sublimate of thorocene, $Th(C_8H_8)_2$, which was identified through its X-ray powder spectrum. One attempt to prepare the protactinium compound in an analogous fashion did not succeed, probably because the sample of protactinium tetrafluoride used was impure and could not be completely characterized.

Powder Pattern Techniques. X-Ray powder patterns were obtained using a 57.3-mm Debye–Scherrer camera modified for easy loading of long capillaries. A Jarrell–Ash Microfocus X-ray source was employed using Cu Kα radiation with Ni filter. A Norelco film reader was employed with a vernier scale readable to 0.05 mm. Films were uncorrected for shrinkage which was determined to be less than 0.05 mm.

Two different $Pa(C_8H_8)_2$ samples were photographed and were found to be identical within experimental error. Each film contained 11 reflections and was measured twice. The reflections could be indexed by comparison with the calculated powder patterns for $U(C_8H_8)_2$ and $Th(C_8H_8)_2$.[9,10] The resultant four sets of data were fitted by a least-squares refinement to the lattice constants of a monoclinic unit cell.[11]

Results and Discussion

The reaction of stoichiometric amounts of $K_2C_8H_8$ and $PaCl_4$ resulted in a golden yellow sublimate which the X-ray powder pattern showed to be $Pa(C_8H_8)_2$. The average values of the observed $Pa(C_8H_8)_2$ reflections are compared with the calculated values for the thorium and uranium analogs in Table I. The absence of unidentified reflections indicates that this sublimate is pure $Pa(C_8H_8)_2$. Table II shows the lattice constants of $Pa(C_8H_8)_2$ compared with those obtained from single-crystal studies on the thorium and uranium analogs.

Powder pattern analysis of the unsublimable white residue from the reaction of $PaCl_4$ with $K_2C_8H_8$ demonstrated the presence of KCl. Consequently, the net reaction appears, as expected, to be

$$PaCl_4 + 2K_2C_8H_8 \rightarrow Pa(C_8H_8)_2 + 4KCl$$

The high radioactivity of protactinium and the small amount of material available unfortunately hinders further study of

---

(1) F. Baumgaertner, E. O. Fischer, B. Kanellakopulos, and P. Laubereau, *Angew. Chem., Int. Ed. Engl.*, 8, 202 (1969).

(2) A. Streitwieser, Jr., and U. Muller-Westerhoff, *J. Amer. Chem. Soc.*, 90, 7364 (1968).

(3) A. Streitwieser, Jr., U. Muller-Westerhoff, G. Sonnichsen, F. Mares, D. G. Morrell, K. O. Hodgson, and C. A. Harmon, *J. Amer. Chem. Soc.*, 95, 8644 (1973).

(4) A. Streitwieser, Jr., and N. Yoshida, *J. Amer. Chem. Soc.*, 91, 7528 (1969).

(5) J. Goffart, J. Fuger, B. Gilbert, B. Kanellakopulos, and G. Duyckaerts, *Inorg. Nucl. Chem. Lett.*, 8, 403 (1972).

(6) H. Lehmkuhl, S. Kintopf, and K. Mehler, *J. Organometal. Chem.*, 46, C1 (1972).

(7) D. Brown and P. J. Jones, *J. Chem. Soc. A*, 874 (1966).

(8) D. Brown and P. J. Jones, *J. Chem. Soc. A*, 719 (1967).

(9) D. K. Smith, Report No. UCRL-7196, Lawrence Berkeley Laboratory, University of California, Berkeley, Calif., 1963.

(10) A. Avdeef, K. N. Raymond, K. O. Hodgson, and A. Zalkin, *Inorg. Chem.*, 11, 1083 (1972).

(11) D. E. Williams, Report IS-1052, Ames Laboratory, Iowa State University, Ames, Iowa, 1964.

Table I. Partial Powder Pattern Data for Bis(π-cyclooctatetraene)actinides

	$U(C_8H_8)_2$[a]		$Pa(C_8H_8)_2$[b]		$Th(C_8H_8)_2$[a]	
hkl	2θ, deg	Intens	2θ, deg	Intens	2θ, deg	Intens
011	13.20	10.0	13.27 (0.04)[c]	s[d]	13.06	10.0
−101	14.09	6.0	14.14 (0.04)	m	14.13	5.8
110	16.24	6.1	16.19 (0.02)	s	16.19	6.0
101	16.25	3.1			16.20	3.0
002	16.88	2.6	16.87 (0.04)	m	16.75	2.6
020	20.38	1.3	20.26 (0.07)	m−	20.14	1.3
−112	22.05	2.4	21.99 (0.07)	m−	21.97	2.4
−121	24.86	2.5	24.77 (0.03)	m−	24.69	2.5
112	24.88	1.1			24.70	1.1
013	27.44	1.4	27.47 (0.03)	w+	27.21	1.3
−211	27.57	1.5			27.62	1.4
211	29.91	1.6	29.95 (0.06)	w+	29.87	1.6
103	30.22	1.1			30.00	1.1
031	31.96	1.6	31.84 (0.06)	w+	31.58	1.6
220	32.82	1.4	32.84 (0.06)	w+	32.72	1.4
202	32.83	1.1			32.74	1.1

[a] Calculated[9] from the reported structure.[10] [b] Average values from four films. [c] Maximum deviation from the average. [d] Estimated intensities; s = strong, m = medium, w = weak.

Table II. Lattice Constants for Bis(π-cyclooctatetraene)actinides

Lattice parameters	$U(C_8H_8)_2$[a]	$Pa(C_8H_8)_2$	$Th(C_8H_8)_2$[a]
a, Å	7.084 (0.003)[b]	7.09 (0.04)[b]	7.0581 (0.0011)[b]
b, Å	8.710 (0.003)	8.75 (0.04)	8.8192 (0.0017)
c, Å	10.631 (0.005)	10.62 (0.04)	10.7042 (0.0018)
β, deg	98.75 (0.03)	98.5 (0.4)	98.44 (0.03)

[a] Reference 11. [b] Estimated standard deviations.

the chemistry of the compound. However, one of the significant aspects of the complex is expected to be the electronic spectrum. With a single 5f electron this spectrum should be interpretable and should provide evidence concerning electronic structure. This research is currently in progress.

During preliminary preparation of $Pa(C_8H_8)_2$ by reaction of $PaCl_4$ with $K_2C_8H_8$, an excess of the compound was used. The product sublimate contained Pa as demonstrated by its pronounced radioactivity and the presence of $Pa(C_8H_8)_2$ bands in the X-ray powder pattern. However, this pattern contained additional intense bands which were subsequently identified as belonging to $K_2C_8H_8$. Independent experiments showed that $K_2C_8H_8$ has substantial volatility and does give a yellow sublimate. The gas-phase structure of $K_2C_8H_8$ is probably that of a planar cyclooctatetraene dianion ring with a potassium cation centered above and below the ring plane.

In the course of these studies we sought a solvent-free preparation of bis(π-cyclooctatetraene)actinides that could be adapted to protactinium. The direct reaction of the finely divided metal with cyclooctatetraene provides one such route[12] but pure protactinium metal is difficult and laborious to prepare.[13] The recent preparation of cyclooctatetraenemagnesium[6] as a nonvolatile solid gave impetus to another preparation. A mixture of solid MgC_8H_8 with either UF_4 or ThF_4 gave on heating under vacuum a sublimate in low yield of the corresponding bis(π-cyclooctatetraene)actinide. This method promises to be a useful route to such sandwich compounds despite the low yield, because the product is isolated directly as a pure sublimate. It should apply to PaF_4 but the single experiment tried thus far did not succeed. The small sample of protactinium fluoride that we had available was black and may have contained acidic impurities.

The present preparation of $Pa(C_8H_8)_2$ completes the isostructural series of bis(π-cyclooctatetraene) complexes with the lower actinides, Th,[4] U,[2] Np,[14] and Pu.[14] Analogous compounds of the higher actinides americium and curium have not yet been reported but would be expected to be similar to the lanthanide complexes $[Ln(C_8H_8)_2]K$ (Ln = Y, La, Ce, Pr, Nd, Sm, Gd, Tb)[15] because of the predominance of the +3 oxidation state in these elements.[16]

Acknowledgment. Part of this work was performed under the auspices of the U. S. Atomic Energy Commission; part was supported by NSF Grant No. GP-31803. We are pleased to acknowledge helpful discussions with Professors G. T. Seaborg, K. N. Raymond, N. Bartlett, and Dr. A. Zalkin.

Registry No. $Pa(C_8H_8)_2$, 51056-18-9; $PaCl_4$, 13867-41-9; $U(C_8H_8)_2$, 11079-26-8; $Th(C_8H_8)_2$, 12702-09-9.

---

(12) D. F. Starks and A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, 95, 3423 (1973).

(13) R. L. Dod, Ph.D. Thesis, University of California; Report LBL-659, Lawrence Berkeley Laboratory, University of California, Berkeley, California., 1972.

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

(15) K. O. Hodgson, F. Mares, D. F. Starks, and A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **95**, 8650 (1973).

(16) Note Added in Proof. After this paper was submitted, we received a preprint from J. Goffart, J. Fuger, D. Brown, and F. Duyckaerts reporting the synthesis of $Pa(C_8H_8)_2$ which was characterized by ir spectroscopy and X-ray powder diffraction analysis. At a symposium entitled, "Recent Aspects in Actinide Chemistry" held in Liege on May 3–4, 1973, J. Goffart reported ir data attributed to $Pa(C_8H_8)_2$. At that time no X-ray data were available.