Preparation and Properties of Uranocene, Di-π-cyclooctatetraeneuranium(IV)[1]

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Abstract: Details are given for the preparation of "uranocene," $U(C_8H_8)_2$, from UCl_4 and $C_8H_8{}^{2-}$ in THF. Uranocene reacts only slowly with water or acetic acid but decomposes with oxygen, bases, and strong acids. It does not undergo electrophilic substitutions or metallation reactions. Its chemistry is discussed in terms of a simple theory of the electronic structure that involves covalent interaction of the highest occupied e_{2u} ligand MO's with metal f_{xyz} and $f_{(x^2-y^2)z}$ AO's.

Our original announcement of the synthesis of "uranocene," di-π-cyclooctatetraeneuranium(IV),[3] has apparently stimulated a renaissance of rare earth organometallic chemistry.[4] In other papers we have reported the infrared,[5,6] Raman,[7] and nmr[8,9] spectra of the compound but the complete details of preparation have not been reported. The synthesis has been reproduced in other laboratories[10] but we have also been informed of several failures undoubtedly resulting from the air-sensitive nature of the compound. We have improved the preparation so that high yields of pure product are now routine, and in the present paper we report the detailed experimental procedure. We also report additional physical properties and chemical properties of the parent compound. The chemical reactions are discussed in the context of the current status of the electronic structure of uranocene and of the possible role of f electrons in the ring–metal bonding.

Experimental Section

All reactions on the vacuum line were carried out under an inert atmosphere of commercially available argon which was used without further purification. Transfer and handling of the complexes were facilitated by the use of a Vacuum Atmospheres HE-193-2 inert atmosphere glove box having an oxygen- and moisture-free recirculating argon atmosphere.

Materials. In all syntheses and further reactions, reagent grade solvents were used after having been carefully purified to remove all water and oxygen. Tetrahydrofuran (THF) was dried by transferring under vacuum onto $LiAlH_4$ and stirring for 1–2 days. After complete degassing, the THF was vacuum transferred into reactors or flasks for storage under argon atmosphere. Toluene and benzene were dried and degassed in a similar manner. Linde 4A molecular sieves, activated by heating with a cool flame under high vacuum, or calcium hydride, were used to dry other organic solvents. Anhydrous UCl_4 was prepared by reaction of uranium(VI) oxide with hexachloropropene.[11] Cyclooctatetraene from BASF was dried over molecular sieves and used without further purification.

Uranocene, Di-π-cyclooctatetraeneuranium. In the reaction vessel diagramed in Figure 1, 4.16 g (0.106 mol) of potassium sand in 100 ml of THF was prepared under argon atmosphere by melting the potassium under reflux, dispersion by vigorous stirring, and slow cooling to −30°.

The reaction vessel used was found to be especially convenient for preparation of these actinide and the related lanthanide[7] complexes. Inert atmosphere could be maintained readily and the apparatus could be used on a vacuum line and transferred in and out of the glove box. *Via* syringe under argon purge, 5.70 g (0.053 mol) of COT was added to the stirred potassium sand through the side arm of the reactor. After 3 hr at −20 to −60° all of the potassium had reacted and the solution was characterized by the dark yellow-brown color of $C_8H_8{}^{2-}$. To this solution at −20° was added 10.0 g (0.026 mol) of anhydrous UCl_4 in 50 ml of THF. The reaction mixture turned green immediately and was allowed to warm slowly to room temperature while stirring under positive argon pressure. The reaction mixture was degassed and the THF was vacuum transferred to yield a green residue.

This crude product was purified by Soxhlet extraction under argon atmosphere in the extractor diagramed in Figure 2. The design of the extractor allowed it to be used with either a continuous Soxhlet-thimble extraction or a continuous sinter-glass extraction. The Soxhlet cup was used for the larger scale preparation as in the present example; care had to be taken to pump off all traces of air from the paper thimble before beginning the extraction. The green uranocene precipitated in the bottom of the extractor. After completion of the extraction (7–9 days) the solvent was poured off into the side arm, carrying with it the organic impurities. A small amount of pure solvent was distilled back from the side arm and the solid uranocene was washed. After pouring all of the wash solvent into the side arm, the side arm was sealed off. The purified uranocene was removed from the body of the extractor in the inert atmosphere box. The yield after the THF extraction was 9.0 g (79%); yields generally were in the range of 60–80%. Uranocene prepared in this way was of sufficient purity for subsequent reactions. The material was further purified for spectroscopic studies by a second extraction with benzene. Highly purified compound was obtained by sublimation at 150° (10^{-3} Torr), but this method gives only a 35% recovery of material; however, flash vacuum sublimation of small amounts at 210° gives quantitative yields of pure sublimate.

Spectral Analyses. The visible, uv, and near ir spectra were recorded on a Cary 14 spectrometer. In order to obtain reproducible results from solutions which were stable for extended periods of time, it was imperative to either heat under vacuum all of the glassware used in the preparation and spectral studies or to allow the glassware to stand in the dry inert atmosphere of the glove box for at least 24 hr. The visible spectrum of uranocene in THF is

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(2) NSF Traineeship, 1969–1972.

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

(4) R. G. Hayes and J. L. Thomas, *Organometal. Chem. Rev.*, 7, 1 (1971).

(5) F. Mares, K. O. Hodgson, and A. Streitwieser, Jr., *J. Organometal. Chem.*, **24**, C68 (1970).

(6) A. Streitwieser, Jr., and C. A. Harmon, *Inorg. Chem.*, **12**, 1102 (1973).

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

(8) N. Edelstein, G. N. LaMar, F. Mares, and A. Streitwieser, Jr., *Chem. Phys. Lett.*, 8, 399 (1971).

(9) A. Streitwieser, Jr., D. Dempf, G. N. LaMar, D. G. Karraker, and N. Edelstein, *J. Amer. Chem. Soc.*, **93**, 7343 (1971).

(10) (a) D. G. Karraker, J. A. Stone, E. R. Jones, Jr., and N. Edelstein, *J. Amer. Chem. Soc.*, **92**, 4841 (1970); (b) B. Kanellakopulos, paper presented at the Third International Transplutonium Element Symposium, Argonne National Laboratory, Argonne, Ill., Oct 20–22, 1971.

(11) J. A. Hermann and J. F. Suttle, *Inorg. Syn.*, **5**, 143 (1957).

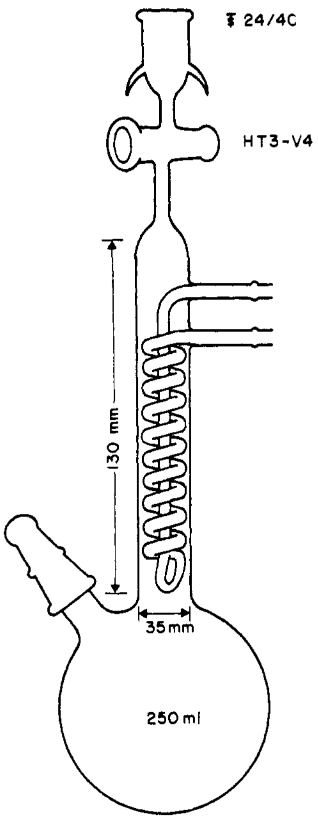

Figure 1. Schematic diagram of the reaction vessel used in the preparation of actinide and lanthanide COT complexes.

Table I. Spectra Data for Uranocene

Visible[a]–uv[b]		
λ_{max}		
nm	cm^{-1} [c]	ϵ
291[b]		6280
304[b]		6170
614.6	16270	1850
641.0	15600	890
659.6	15160	600
679.8	14710	350
689.2[d]	14510	250
760.7	14150	220
	Infrared[e]	
	Absorption peaks, cm^{-1}	
	3000 (w)[f]	
	900 (m)	
	787 (w)	
	772 (w)	
	741 (m)	
	594 (s)	

[a] Saturated THF solution. [b] Saturated cyclohexane solution. [c] Reference 20. [d] Shoulder. [e] Nujol mull except where indicated; m, sharp medium; s, sharp strong; w, weak. [f] Fluorolube mull.

reproduced in Figure 3;[12] Table I lists the bands and their molar extinction coefficients. Schatz and Mowery[12] have also found weak bands attributed to f–f transitions in the region from 850–1000 nm. These results will be reported in greater detail separately. The position of the principal band is sensitive to solvent; λ_{max} (nm) in different solvents are acetonitrile, 608; pyridine, 612; THF, 614.6; ethyl acetate, 615; benzene, 616; hexane, 617; decalin, 618. These variations suggest a weak interaction of donor solvent with the metal as acceptor.

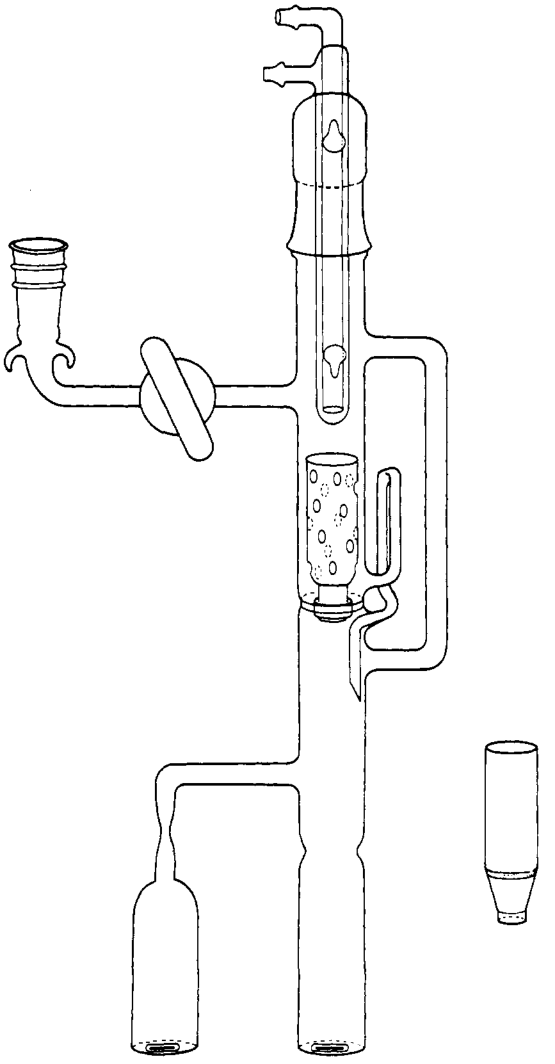

Figure 2. Diagram of side-arm Soxhlet extractor used for purification of actinide and lanthanide COT complexes.

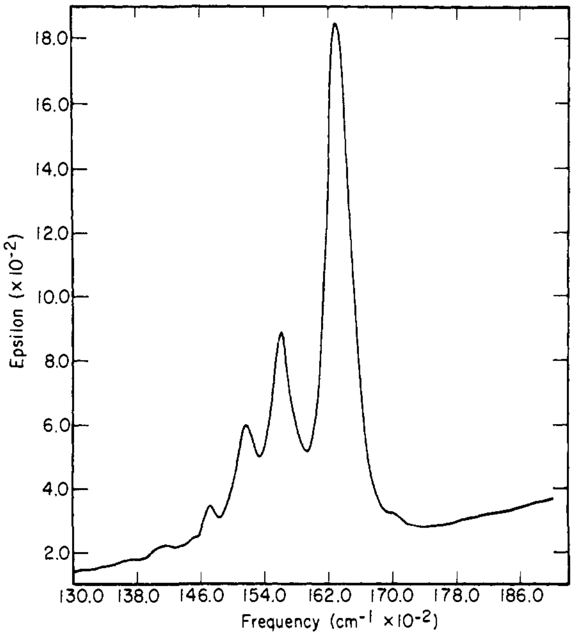

Figure 3. Visible spectrum of uranocene in THF.

The infrared spectrum of uranocene was obtained from a Nujol mull prepared in the glove box from dry, degassed Nujol. When sandwiched between NaCl plates, the mull could be handled in air

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[12] We are indebted to Professors Paul N. Schatz and Bob Mowery, University of Virginia, for accurate frequency determinations on a Cary 14 interfaced to computer facilities.

for 2-3 hr without appreciable decomposition. A diagram of a portion of the ir spectrum of uranocene has been published previously.[5,6] More accurate band positions obtained with a Perkin-Elmer 421 spectrometer are included in Table I. A similar spectrum in a Fluorolube mull located the C-H stretching band.

Solubility of Uranocene. The solubility of uranocene in a variety of solvents was determined from the visible spectrum of saturated solutions and the assumption that the molar extinction coefficient is the same in all solvents. The values obtained in this way are expected to be reliable to about 10% and are summarized in Table II.

Table II. Solubility of Uranocene

Solvent	Solubility at room temp, mmol/l.
Tetrahydrofuran	2.0
Benzene	1.3
Diphenyl ether	1.2
Tetralin	0.72
Ethyl acetate	0.40
Acetonitrile	0.30
Decalin	0.23
Cyclohexane	0.10
Hexane	~0.005
Ethyl ether	<0.005
Ethanol	<0.005
Acetic acid	<0.005
Water	<0.005
Hexachlorobutadiene	<0.005
Diisopropylbenzene	<0.005
Hexamethylphosphortriamide	Decomp

Reactions of Uranocene. Oxidation. An nmr tube containing 28.4 mg (0.0636 mmol) of uranocene and 0.31 ml of CCl_4 0.762 *M* in benzene was slowly exposed with cooling to a mixture of oxygen and air (uranocene reacts with pure oxygen with explosive violence). After the black solid had settled the nmr spectrum was taken and showed a benzene:COT ratio of 1.61 or 1.28 mmol of COT; hence, the COT:uranocene ratio was 2.01.

Reduction. Attempted hydrogenation with 5% Pd on C in THF and 40 lb of hydrogen gave no reaction. A mixture of 0.5 g of uranocene and 0.2 g of $LiAlH_4$ in 100 ml of THF was stirred for 3 days under argon. Excess hydride was decomposed with ethyl acetate. The yellow suspension was exposed to air, added to 500 ml of water, and extracted with ether. The washed and dried ether solution showed a 2:3 mixture of cyclooctatrienes:COT by gc on an SE-30 column.

Acid. In various experiments with acids the bright green uranocene color changed to yellowish. In general, the solvents were vacuum transferred and the residue was extracted into ether or other solvent; removal of the solvent by vacuum transfer generally left dark residues which did not contain COT by gc analysis. Examples of such reactions were 4 *M* CF_3COOD in benzene, acetic anhydride with BF_3 in CH_2Cl_2, acetic anhydride and $AlCl_3$ in CH_2Cl_2, and CF_3COOH in acetic acid. In some mild acid reactions, COT and cyclooctatrienes were identified among the products.

The reaction mixture of 0.5 g of uranocene with 15 ml of 2 *N* HCl and 20 ml of THF was filtered and the filtrate was extracted with petroleum ether. Evaporation of the extract left a yellow oil which contained COT and cyclooctatrienes (gc and nmr) together with other unidentified compounds.

Addition of 1.25 g (0.0033 mol) of antimony acylium hexachloride at room temperature to a suspension of 1.5 g (0.0033 mol) of uranocene in 100 ml of benzene gave a rapid color change to straw yellow. A green solid was separated and found to be air stable but was not otherwise identified. The solution contained COT.

Vilsmeier Conditions. A mixture of 1.0 g (2.4 mmol) of uranocene, 0.76 g (4.0 mmol) of zinc acetate, and 0.70 ml (6 mmol) of *N*-methylformanilide in 75 ml of THF was stirred at room temperature for 5 days. Solvent was removed by vacuum transfer and the residue was washed with water and extracted into benzene. Vacuum transfer of the benzene left uranocene in high recovery.

For a study of more vigorous conditions, a mixture of 2.0 g (4.5 mmol) of uranocene, 1.22 g (8.0 mmol) of phosphorus oxychloride and 1.08 g (8.0 mmol) of *N*-methylformanilide in 100 ml of 1:1 THF-pyridine was refluxed for 4 hr. Saturated aqueous sodium acetate was added to the brown solution. Removal of solvents by vacuum transfer left an intractible brown solid.

Attempted Mercuration. A mixture of 1.0 g (2.24 mmol) of uranocene and 0.63 g (2.24 mmol) of mercuric acetate in THF was refluxed for 24 hr. Vacuum transfer of the solvent and washing the residue with water gave only recovered uranocene.

Bromine. A solution of 0.7 g of bromine (4.4 mmol) in 100 ml of methylene chloride was added dropwise to a suspension of 2.0 g (4.4 mmol) of uranocene in 150 ml of methylene chloride maintained at −20°. The suspension was stirred for 0.5 hr and allowed to warm to room temperature. The solvent was removed by vacuum transfer, leaving a brown air-stable residue. The solid was not sublimable and was not soluble in common solvents (*e.g.*, benzene, THF, methanol, CH_2Cl_2, DMF). Identical results were obtained for iodine in place of bromine.

Bases. Addition of ethanolic sodium ethoxide to a solution of uranocene in ethanol gave an immediate change in color from green to yellow.

Addition of 10% aqueous tetraethylammonium hydroxide to a saturated solution of uranocene in THF gave an immediate color change from green to yellow. The same result was observed in the addition of 0.4 ml of 5% aqueous KOH to 4 ml of saturated uranocene in THF.

A number of metallation attempts were made. Two examples follow. A mixture of 0.50 g (1.1 mmol) of uranocene, 0.58 g (5 mmol) of tetramethylethylenediamine, and 3.5 ml of 1.6 *M* *n*-butyllithium (5 mmol in hexane) in 115 ml of cyclohexane was stirred for 3 hr at room temperature. After addition of 2.5 g of CH_3-COOD, uranocene was recovered in about 80% yield. Oxidation with air gave COT which contained no deuterium by mass spectral analysis. These reaction conditions applied to benzene give extensive metallation.[13]

Repetition of this experiment except for the inclusion of 1 ml of benzene and a reflux period of 1.5 hr gave no recovered uranocene. The recovered benzene showed 13.5% deuterium by mass spectral analysis.

A solution of 1.2 g (0.44 mmol) of uranocene in 50 ml of cyclohexane was stirred with 1 ml of 2.2 *M* *tert*-butyllithium in pentane for 1.5 hr. The solution was quenched with 2.0 g of acetic acid-*d*. COT obtained by oxidation of recovered uranocene showed no deuterium incorporation.

Kinetic Studies in Solution. A saturated solution of uranocene in decalin was sealed in a spectrometer cell under argon and was maintained at 100° with intermittent measurement of the visible spectrum after cooling to room temperature. The spectrum remained unchanged after 7 days.

Solutions of uranocene in THF containing water, acetic acid, or triethylamine showed slow decomposition. Approximate kinetic studies were carried out as in the following example. Degassed water was vacuum transferred into a spectrometer cell containing uranocene in THF and the visible spectrum was determined at intervals at ambient temperature (25 ± 2°). After decomposition was complete a sample was used to determine the water-THF ratio by nmr. The decomposition followed pseudo-first-order kinetics. A larger scale experiment showed the decomposition product to be cyclooctatrienes. Results of the kinetic runs are summarized in Table III.

Table III. Rates of Decomposition of Uranocene in Solutions

Addend to THF solution	Mole fraction of addend	Molarity of addend	k, 10^5 sec^{-1}
Water	0.59	13.0	12.9
Water	0.42	7.7	7.1
Acetic acid	0.16	2.0	0.86
Triethylamine	0.26	2.9	6.0[a]

[a] Triethylamine showed deviation from first-order behavior after the first half-life.

Radicals. In small portions, 2.4 g (10 mmol) of benzoyl peroxide was added to a refluxing mixture of 1.0 g (2.2 mmol) of uranocene in 150 ml of benzene. The color changed rapidly from bright

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(13) M. D. Rausch and D.J. Ciappenelli, *J. Organometal. Chem.*, **10**, 127 (1967).

Table IV. D_{8h} Character Table

	E	$2C_8$	$2C_4$	$2C_8^3$	C_2	$4C_2'$	$4C_2''$	i	$2S_8$	$2S_4$	$2S_8^3$	σ_h	$4\sigma_d$	$4\sigma_v$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	s, d_{z^2}
A_{2g}	1	1	1	1	1	−1	−1	1	1	1	1	1	−1	−1	
B_{1g}	1	−1	1	−1	1	1	−1	1	−1	1	−1	1	1	−1	
B_{2g}	1	−1	1	−1	1	−1	1	1	−1	1	−1	1	−1	1	
E_{1g}	2	$\sqrt{2}$	0	$-\sqrt{2}$	−2	0	0	2	$\sqrt{2}$	0	$-\sqrt{2}$	−2	0	0	d_{xz}; d_{yz}
E_{2g}	2	0	−2	0	2	0	0	2	0	−2	0	2	0	0	d_{xy}; $d_{x^2-y^2}$
E_{3g}	2	$-\sqrt{2}$	0	$\sqrt{2}$	−2	0	0	2	$-\sqrt{2}$	0	$\sqrt{2}$	−2	0	0	
A_{1u}	1	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	
A_{2u}	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	1	1	p_z, f_{z^3}
B_{1u}	1	−1	1	−1	1	1	−1	−1	1	−1	1	−1	−1	1	
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	
E_{1u}	2	$\sqrt{2}$	0	$-\sqrt{2}$	−2	0	0	−2	$-\sqrt{2}$	0	$\sqrt{2}$	2	0	0	p_x, f_{xz^2}; p_y, f_{yz^2}
E_{2u}	2	0	−2	0	2	0	0	−2	0	2	0	−2	0	0	f_{xyz}; $f_{z(x^2-y^2)}$
E_{3u}	2	$-\sqrt{2}$	0	$\sqrt{2}$	−2	0	0	−2	$\sqrt{2}$	0	$-\sqrt{2}$	2	0	0	$f_{x(x^2-3y^2)}$; $f_{y(3x^2-y^2)}$

green to milky. Vacuum transfer of the solvent gave a yellow benzene distillate that contained COT (gc analysis) and an air-stable salt-like residue.

In small batches and with stirring, 5.0 g of solid *p*-anisolediazonium fluoroborate was added to a mixture of 40 ml of 0.1 *N* aqueous acetate buffer solution and 1.0 g of uranocene in 75 ml of CH_2Cl_2 maintained at 0°. Immediate gas evolution was noted concomitant to a dulling of the color of the suspension. Vacuum transfer of the volatile materials gave a yellow distillate containing COT and left an air-stable solid.

A mixture of 15 g of degassed acrolein and 0.01 of uranocene in 25 ml of THF was stored in the dark overnight. Vacuum transfer gave a volatile fraction that contained no acrolein and a nonvolatile gelatinous residue.

Discussion

The compound prepared by reaction of uranium tetrachloride with cyclooctatetraene dianion has been established to have the D_{8h} sandwich structure of a di-π-cyclooctatetraeneuranium(IV)[14] by X-ray crystal structure analysis. The U(IV) character of the central metal is established by its magnetic moment and by Mössbauer spectroscopy of the analogous neptunium compound.[10a,15] The compound is rather stable and, indeed, the ring-metal bonds in the di-π-cyclooctatetraeneactinides appear to be the strongest of any comparable sandwich structures of planar cyclooctatetraenes with other classes of central metals. For example, the lanthanide complexes, $[(C_8H_8)_2Ln]^-$ and $(C_8H_8LnCl)_2$, are highly sensitive to water and show facile ligand mobility.[7] Various complexes of cyclooctatetraene with hafnium and zirconium are currently under study in several laboratories;[16] these compounds react immediately with UCl_4 to produce uranocene.[16c]

By contrast, the uranocene structure appears to be thermodynamically rather stable. The compound can be prepared directly from uranium metal and cyclooctatetraene at 150°;[17] it can be sublimed without apparent decomposition above 200°. A decalin solution showed no measurable decomposition after 1 week at 100°. Ligand exchange has not yet been accomplished, even at elevated temperatures.[6]

This unique stability of the uranocene structure has important implications for the electronic structure. A simple molecular orbital description of uranocene derives from the symmetry-permitted combination of metal atomic orbitals with plus and minus combinations of the π orbitals of two planar eight-membered ring ligands under the D_{8h} point group. The corresponding D_{8h} character table has not, to our knowledge, been discussed previously in the chemical literature; hence, it is given as Table IV.[18] For the purposes of this table the molecular axis is the *z* coordinate and the "plus" combination of ligand orbitals, for example, $\psi_1' + \psi_1''$, is taken as that in which the lobes of the p-ligand orbitals on the side facing the central metal have the same sign. This table also includes the assignment to irreducible representations of s, p, d, and f orbitals.

As a present working hypothesis we assume that the f orbitals are ordered as in a D_{8h} crystal field with $l_z = \pm 3$ having lowest energy, $l_z = \pm 2$ next, etc., and $l_z = 0$ being a lone level of highest energy, that is, three doublets and a singlet.[7,10a] The $l_z = \pm 2$ f level (f_{xyz} and $f_{z(x^2-y^2)}$) interacting with the e_{2u} ligand combination gives the interaction shown in Figure 4. It should be emphasized that the recognition of the homologous nature of the e_{2u} interaction in Figure 4, compared to the e_{1g} interaction (Figure 5) that appears to be so important in d-transition metallocenes, was the motivating inspiration that preceded the original successful synthesis of uranocene.[3] We assume for the present that these levels are approximately matched in energy with the f orbitals somewhat the higher in energy. At present this assumption is justified only from an interpretation of the visible spectrum and from qualitative observations that alkyl substituents provide more stable complexes;[7] such substituents should raise the energy of the ligand e_{2u} levels and give greater ligand–metal bonding. Qualitatively also, the interaction shown in Figure 4 is conducive to favorable overlap. Other symmetry-permitted combinations as given in Table

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(14) A. Zalkin and K. N. Raymond, *J. Amer. Chem. Soc.*, **91**, 5667 (1969); A. Avdeef, K. N. Raymond, K. O. Hodgson, and A. Zalkin, *Inorg. Chem.*, **11**, 1083 (1972).

(15) A comparison of the Mössbauer spectrum of $(C_8H_8)_2Np$ with analogous cyclopentadienyl compounds establishes further uniqueness of the former compound: D. G. Karraker and J. A. Stone, *Inorg. Chem.*, **11**, 1742 (1972).

(16) (a) H. J. Kadlitz, R. Katlweit, and G. Wilke, *J. Organometal. Chem.*, **42**, C49 (1972); D. J. Brauer and C. Krüger, *ibid.*, **42**, 129 (1972); (b) J. Schwartz and J. E. Sadler, *J. Chem. Soc., Chem. Commun.*, 172 (1973); (c) A. Streitwieser, Jr., K. O. Hodgson, and D. F. Starks, unpublished results.

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

(18) A D_{8h} character table has been published recently in F. A. Cotton, "Chemical Applications of Group Theory," 2nd ed, Wiley-Interscience, New York, N. Y., 1971, p 360; however, the f orbitals are not treated in this work.

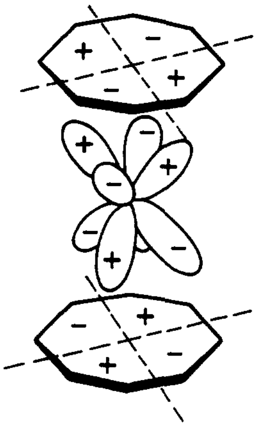

Figure 4. Proposed e_{2u}–f_{xyz}, $f_{z(x^2-y^2)}$ interaction in uranocene.

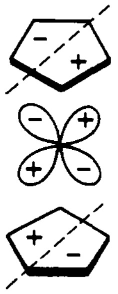

Figure 5. e_{1g}–d_{xz}, d_{yz} interaction as in ferrocene.

III are: $l_z = 0$ (f_{z^3}) with a_{2u}, $l_z = \pm 1$ (f_{xz^2}, f_{yz^2}) with e_{1u}, and $l_z = \pm 3$ ($f_{(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$) with e_{3u}. In all of these cases, energy matching is less favorable and interaction is expected to be substantially less. The 7s, 7p, and 6d orbitals of uranium(IV) are assumed to be too high in energy to contribute significantly to covalent bonding. This assumption is justified by the chemistry of U^{+4},[19] SCF calculations of U^{+4},[20] and state energies derived from spectral and thermodynamic data.[21] The resulting qualitative ordering of MO energy levels shown in Figure 6 constitute our working hypotheses for the electronic structure of uranocene.

A previous MO description by Fischer[22] was given in somewhat different terms. His rough calculations at that time predicted little covalent stabilization for uranocene. In particular, the unique e_{2u}–f ($l_z = \pm 2$) interaction as shown in Figure 4 was not given explicit recognition in his work. However, Fischer's ordering of resulting MO levels corresponds to that in Figure 5 and does represent the first recognition that $U(C_8H_8)_2$ may be a significant f-orbital organometallic compound. More detailed calculations of Hayes and Edelstein[23] are in qualitative accord with the working hypothesis presented in Figure 6; in particular, the overlap integral between the e_{2u} ligand combination and the $5f_{xyz}$ and $5f_{z(x^2-y^2)}$ ($l_z = \pm 2$) of uranium has the relatively high magnitude required for such bonding.

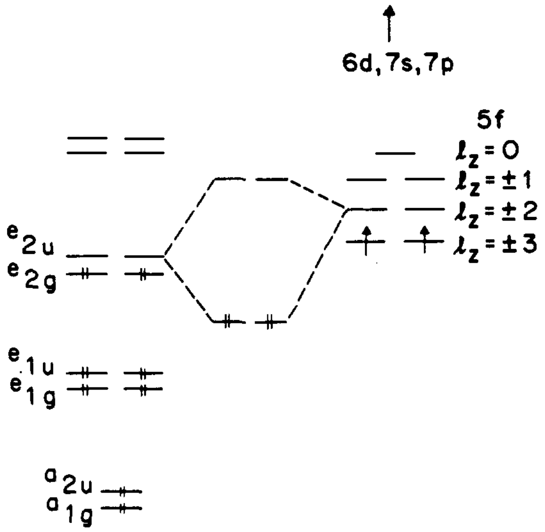

Figure 6. Working hypothesis of the electronic structure of uranocene.

Of the 22 valence electrons in uranocene, 16 electrons are retained in predominantly ligand MO's as shown in Figure 6, four are used for the bonding e_{2u}–f ($l_z = \pm 2$) MO's responsible for the covalent metal–ring interaction and two electrons are left for the remaining, essentially pure, f orbitals. Bonding produces net charge transfer from ligands to metal. Finally, it should also be recognized that spin–orbit coupling which mixes together various f functions and exchange interaction which produces spin polarization within filled orbitals are not readily pictured in a simple one-electron description such as that in Figure 6.

The foregoing theoretical analysis has the following significance. If the compound $U(C_8H_8)_2$ does have significant covalent bonding between the ligand rings and the central metal and if the metal 5f orbitals are important in such bonding in the sense represented in Figure 6, then this compound represents a new class of metallocene-like compounds homologous to the d transition metal metallocenes and could be regarded as a new "aromatic" organometallic system. However, these bonding properties are not simple to establish, in large part because such bonding concepts are themselves approximations, albeit useful ones. Consequently, our approach is to test how well the above theoretical scheme will accommodate a range of experimental observations, such as physical and spectral properties and chemical reactivities. This study is a continuing one but enough chemistry has already been established to show that the above hypothesis is successful and that $U(C_8H_8)_2$ may indeed be considered to be an f-orbital organometallic aromatic system. One corollary of this result is that even in other organouranium(IV) compounds that do not have the D_8 symmetry of uranocene, f orbitals probably play a significant role in bonding. The present work would then give added support to previous suggestions of significant f-orbital involvement in actinide compounds.[24] We next apply the theory to a rationalization of the chemical reactions of uranocene.

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(19) R. E. Connick and Z. Z. Hugus, *J. Amer. Chem. Soc.*, **74**, 6012 (1952).

(20) A. C. Larson and J. T. Waber, "Self-Consistent Field Hartree Calculations for Atoms and Ions," Report no. LA-4297, TID-4500, Los Alamos Scientific Laboratory, 1969.

(21) L. Brewer, *J. Opt. Soc. Amer.*, **61**, 1666 (1971).

(22) R. D. Fischer, *Theor. Chim. Acta*, **1**, 418 (1963).

(23) R. G. Hayes and N. Edelstein, *J. Amer. Chem. Soc.*, **94**, 8688 (1972).

(24) For some examples, see K. Street, E. M. Diamond, and G. T. Seaborg, *J. Amer. Chem. Soc.*, **76**, 1461 (1954); J. C. Eisenstein, *J. Chem. Phys.*, **25**, 142 (1956); C. A. Coulson and G. R. Lester, *J. Chem. Soc.*, 3650 (1956); W. Moffitt, *J. Inorg. Nucl. Chem.*, **2**, 246 (1956); and ref 19.

Reactions of Uranocene

Oxidation. Organouraniums with the U^{4+} oxidation state are generally sensitive to air oxidation and uranocene is no exception. U^{4+} has two electrons outside the radon core that are readily lost to form the stable +6 oxidation state. Uranocene enflames in air but on controlled air oxidation, for example, by bubbling oxygen through a solution, uranium oxides are precipitated with quantitative liberation of cyclooctatetraene. This air sensitivity requires working in completely inert atmosphere with carefully purified and degassed solvents. The quantitative recovery of ligand by air oxidation is generally true for uranocene compounds and serves to monitor reactions.

Reduction. Uranocene is stable to attempted catalytic hydrogenation over palladium catalyst but it is reduced by $LiAlH_4$ in THF. The reaction is complex and produces a mixture of COT and cyclooctatrienes.

Reaction with Bases. Uranocene is not significantly soluble in water and may be washed with water without decomposition. Aqueous potassium hydroxide added to a THF solution or ethanolic sodium ethoxide causes immediate decomposition. Even water in a THF solution causes slow hydrolysis to cyclooctatrienes. Acetic acid in THF solution also causes hydrolysis but apparently at a rate slower than with water; that is, acetic acid may be reacting as a base rather than as an acid.

Reaction with a base may generally be considered to occur with the lowest vacant orbitals of the substrate; in the case of uranocene the lowest vacant orbitals are undoubtedly 5f orbitals on the metal. Consequently, these reactions of uranocene may occur at the metal to liberate cyclooctatetraene dianions which then protonate.

No evidence could be obtained for metallation of uranocene despite many attempts under varying conditions, including conditions known and demonstrated to metallate benzene. It should be noted that some substituted uranocenes do give evidence of metallation.[25]

Electrophilic Substitution

Although acetic acid in THF solution reacts slowly with uranocene, stronger acids such as CF_3COOH or HCl in THF give immediate decomposition. The inorganic products of these reactions were not identified and the ligand moieties polymerized to tars under the experimental conditions. This acid sensitivity limits the types of electrophilic substitutions that can be attempted and, in general, all such attempts have given either no reaction or complete decomposition. For example, no deuterium exchange was found in acetic acid-*d* alone; 1% CF_3COOD in acetic acid-*d* caused decomposition. A mixture of $CH_3CO^+SbCl_6^-$ in benzene gave decomposition; COT was identified among the products. All attempted Vilsmeier reactions failed; phosphorus oxychloride gave decomposition as did phosphoric acid in methanol. Attempted mercuration with mercuric acetate gave no reaction.

Electrophilic reagents are expected to react with the highest occupied electrons in a substrate. In uranocene these electrons are the two 5f electrons remaining on the uranium; hence, reaction with electrophilic reagents, when it occurs at all, is expected to be at uranium with resultant decomposition of the complex. Bromine or iodine in methylene chloride give insoluble brown amorphous solids which appear to be 1:1 complexes. The reaction is not reversible and the products have air stability, but no further characterization was made at this time. These products may be charge-transfer complexes related to the halogen complexes with bis(phthalocyaninato)uranium(IV) identified by Dempf.[26]

The chemistry of uranocene itself is limited, but this limitation can be rationalized on the basis that both the highest occupied and lowest vacant orbitals are predominantly metal orbitals. Reactions generally occur at the metal with consequent decomposition of the metal–ligand bonds. It will be interesting and important to extend these concepts to substituted uranocenes and particularly to other actinide compounds such as di-π-cyclooctatetraenethorium, which has no extra 5f electrons, and the higher actinide complexes, which are rich in 5f electrons.

Finally, the relationship between uranocene and the several known cyclopentadienyl derivatives of uranium[27] is still not clear. Although the cyclopentadienyl compounds do not have the symmetry required for the kind of f-orbital interaction that appears to be present in uranocene, covalent bonding appears to be important and the 5f orbitals may well be significant in such bonding. Chemical reactivity studies are clearly required for comparison with uranocene but little such information is currently available. It would seem significant, however, that the Mössbauer isomer shift of cyclopentadienylneptunium compounds is much less than that of di-π-cyclooctatetraeneneptunium.[15,28]

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(25) C. A. Harmon and A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **94**, 8926 (1972).

(26) D. Dempf, Dissertation, Technical University, Munich, July, 1970.

(27) Many of these compounds are reviewed in ref 4 and in a review chapter by B. Kanellakopulos and K. W. Bagnall, "International Review of Science, Inorganic Chemistry, Series 1, Vol. 7, Lanthanides and Actinides," K. W. Bagnall, Ed., Butterworths, London, 1972, p 299. Recent additional examples include L. Doretti, P. Zanella, G. Faraglia, and S. Faleschini, *J. Organometal. Chem.*, **43**, 339 (1972); A. E. Gebala and M. Tsutsui, *Chem. Lett.*, 775 (1972); T. J. Marks, A. M. Seyam, and J. R. Kolb, *J. Amer. Chem. Soc.*, **95**, 5529 (1973).

(28) L. J. Nugent, P. G. Lauberean, G. K. Werner, and K. L. Vander Sluis, *J. Organometal. Chem.*, **27**, 365 (1971), have interpreted the electron spectra of $Cm(C_5H_5)_3$ and $Am(C_5H_5)_3$ to indicate little covalency in ring–metal bonding; however, a comparable analysis has not yet been accomplished with any corresponding actinide cyclooctatetraene compounds.