reaction capsules. The most important difference is in the quenching technique. The "leak quenching" procedure employed by Roy and coworkers[5,7] involves first venting the water pressure while the reactor is still at the equilibration temperature and then rapidly cooling the reactor. In relation to this procedure the statement is made that "the success of this method depends on the fact that the hydrates will not decompose rapidly at temperatures near their equilibrium dehydration temperatures in the presence of water." Although this rationale is valid near the dehydration point, it is not particularly relevant to cases in which a phase is at some temperature much higher than its dehydration point. Venting the water pressure under the latter conditions should rapidly produce the phase which is stable at the higher temperature and a water pressure of nominally 1 atm. This type of thermal decomposition accounts for the high-pressure trihydroxide and oxide phase fields observed by Shafer and Roy. It seems that the temperature–pressure diagrams reported by these investigators are incorrect because their pressure axis is a parameter which bears little or no relationship to the equilibration pressure. The essentially vertical equilibrium lines are only indicative of the decomposition temperatures of the various phases at 1 atm water pressure.

One of the most significant results of the present investigation is the characterization of nitrate ion as an oxidizing agent under the appropriate hydrothermal conditions. The *in situ* generation of gaseous reaction products from a solid substrate is a particularly powerful tool which allows convenient and accurate adjustment of oxygen to substrate ratios without elaborate or expensive equipment. Since reactions 1 and 2 proceed in the presence of a variety of cations (H^+, NH_4^+, Pr^{3+}), the method should be highly versatile. A particularly advantageous nitrate source is HNO_3, which generates only H_2O, O_2, and N_2. Although the nitrate decomposition process has not been completely characterized, it appears to be analogous to that of oxalic acid which has recently been employed for *in situ* generation of CO_2 atmospheres.[26]

A second important application of nitrate ion in the hydrothermal synthesis of ionic rare earth phases is its apparent effect as a mineralizer. Results of the present investigation suggest that nitrate might be generally applicable as a noninteracting complexing species for the rare earths at temperatures below 550°. Since essentially nothing is known about the mineralization and transport properties of nitrate, a careful examination of the conditions and limits of its application would be a worthwhile investigation.

The present investigation has resulted in a reexamination of the rare earth oxide–water phase systems and should provide a basis for the investigation of oxide crystal growth and hydroxy anion phase preparation by hydrothermal techniques.

Acknowledgment.—Katie Reimer obtained the ir spectra, Eric Miller analyzed several of the compounds and ran the tga curves, and Frederick M. Delles performed the nitrogen analysis. Their help is gratefully acknowledged. Many discussions with Dr. John Holloway were critical in the construction of the high-pressure apparatus and in obtaining the results. The support of the United States Atomic Energy Commission made these studies possible.

(26) J. R. Holloway, C. W. Burnham, and G. L. Millhollen, *J. Geophys. Res.*, **73**, 6598 (1968).

CONTRIBUTION FROM THE TRANSURANIUM RESEARCH LABORATORY,
CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE 37830

Preparation and Properties of Triindenylthorium Chloride and Triindenyluranium Chloride[1]

BY P. G. LAUBEREAU,*[2,3] L. GANGULY, J. H. BURNS, B. M. BENJAMIN, J. L. ATWOOD,[4] AND J. SELBIN

Received September 8, 1970

The syntheses of $Th(C_9H_7)_3Cl$ and $U(C_9H_7)_3Cl$ are reported. Evidence is given for the existence of $Th(C_9H_7)_4$, $U(C_9H_7)_4$, $Th(C_9H_7)_2Cl_2$, and $U(C_9H_7)_2Cl_2$. Some properties of the triindenylactinide halide complexes are described. Mass spectra, nmr spectra, infrared spectra, and electronic spectra are given and discussed together with X-ray powder diagrams and results from X-ray single-crystal data obtained with the precession method. $Th(C_9H_7)_3Cl$ and $U(C_9H_7)_3Cl$ are isomorphous. Evidence is given for the presence of metal to indenyl ligand bonds with the C_5-ring parts of the ligands centrally bonded to the metals. The indenyl to uranium bonds seem to be more covalent in character than the indenyl to thorium bond.

Cyclopentadienyl complexes of many lanthanides and actinides are known[5] and have been studied extensively, yet the nature of the ring-to-metal bond is not sufficiently understood. Recently Streitwieser, *et al.*, prepared the first cyclooctatetraenyl compounds of the actinides[6–8] and were able to postulate metal-to-ligand bonds with the participation of f electrons. Their view is supported by the structure of the dicyclooctatetraenylactinides. Determinations of the crystal struc-

---

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) Supported by the Bundesministerium für Bildung und Wissenschaft, Bonn, Federal Republic of Germany.

(3) Address correspondence to this author at Institut für Kernchemie, Universität Marburg, Marburg, Federal Republic of Germany.

(4) ORAU Research Participant, summer 1969.

(5) P. G. Laubereau and J. H. Burns, *Inorg. Chem.*, **9**, 1091 (1970), and references therein; R. V. Ammon, B. Kanellakopulos, R. D. Fischer, and P. Laubereau, *Inorg. Nucl. Chem. Lett.*, **5**, 315 (1969).

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

(7) A. Streitwieser, Jr., and N. Yoshida, *ibid.*, **91**, 7528 (1969).

(8) A. Zalkin and K. N. Raymond, *ibid.*, **91**, 5667 (1969).

tures of $U(C_5H_5)_3Cl$[9] and $Sm(C_5H_5)_3$[10] have not yielded an adequate answer because of lack of accuracy in the carbon atom positions in the former case and because of difficulties inherent with disorder in the latter. We have therefore examined the related indenyl complexes because of the possibility of producing crystal structures more tractable for the study of the bond from the metal to the pentagonal ring.

The syntheses and properties of triindenyllanthanide–tetrahydrofuran complexes have been reported,[11,12] and recently the solvent-free triindenylsamarium complex was prepared and its crystal structure determined.[13] Here we report the first syntheses and some properties of indenyl complexes of the actinide elements thorium and uranium.

Experimental Section

Physical Measurements.—X-Ray diffraction powder patterns were taken with a 114.6-mm radius powder camera; Ni-filtered Cu Kα radiation was used. Films were measured on a film reader equipped with a steel scale that could be read to within ±0.05 mm. No corrections were applied for film shrinkage. Single-crystal data for determination of unit-cell dimensions and diffraction symmetry were obtained with a precession camera equipped with a Polaroid-film cassette. Intensity data from a single crystal of $U(C_9H_7)_3Cl$ (C_9H_7 = indenyl group) were collected with a computer-controlled X-ray diffractometer and a structural analysis is in progress.

Infrared spectra in the region 4000–300 cm^{-1} were recorded with a Beckman IR-20 spectrometer. The samples were prepared as mulls of Nujol or Fluorolube; they were examined between KBr disks.

Electronic spectra were obtained at room temperature with a Cary Model 14 spectrometer.

Proton nmr spectra of $Th(C_9H_7)_3Cl$ and $U(C_9H_7)_3Cl$ were recorded at room temperature with a Varian A-60 spectrometer and, in the case of $U(C_9H_7)_3Cl$, also with a Varian HR-100 spectrometer. The concentration of the solution of $Th(C_9H_7)_3Cl$ in tetrahydrofuran (THF) was 50 mg/ml; that of $U(C_9H_7)_3Cl$ in benzene was $\leqslant 5$ mg/ml (*i.e.*, a saturated solution).

Mass spectra were recorded with the ORNL 12-in. single-focusing mass spectrometer. The electron energy was 70 eV; the temperature of the direct-inlet probe was varied up to 250°.

The thermal behavior was studied with a Du Pont differential thermal analysis (dta) apparatus.

Preparation of the Compounds.—All operations were carried out under carefully dried oxygen-free argon either with the Schlenk-tube technique or in an inert-gas box. The solvents used were intensively dried and freed of oxygen by distilling under argon from suspended sodium wire and subsequent redistillation from finely ground calcium hydride.

Uranium tetrachloride was obtained from Alfa Inorganics, Inc., and used without further purification. Thorium tetrachloride was prepared by direct reaction of the elements. Indenylpotassium was synthesized by reaction of potassium with freshly distilled indene in ether. The ether was removed and the crude dry product was used.

Elemental analyses were done by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Triindenylthorium Chloride.—In a 100-ml round-bottomed flask, equipped with a side arm and with a stopcock to introduce inert gas, 1.00 g (2.67 mmol) of $ThCl_4$ and 1.24 g (8.05 mmol) of KC_9H_7 were placed. About 50 ml of THF was added to the flask. The reaction mixture now was stirred for a period of 3 days at room temperature. During this period, the color of the solution became tan as a very fine white precipitate was formed. The THF was distilled slowly at room temperature under moderate vacuum, into a trap cooled with liquid nitrogen. The residue was a yellowish white substance, which was continuously extracted with 40 ml of pentane. Within ~0.5 hr this extract showed a first growth of light yellow crystals. The extraction was run for 3 days, when by examination with a microscope the formation of colorless and different crystals was observed. The extraction was stopped, the pentane was decanted from the residue, and the crystals were washed several times with pentane and were dried thoroughly under high vacuum.

To purify this product further it was extracted with pentane for 1 day. Voluminous fine yellow crystals were obtained; the product was identified as pure $Th(C_9H_7)_3Cl$, by comparison of the X-ray diffraction powder photographs with the ones obtained from $U(C_9H_7)_3Cl$ and by its mass spectrum; yield 0.3 g (0.49 mmol), corresponding to 17.6%, based on $ThCl_4$; $Th(C_9H_7)_3Cl$ mol wt, found by mass spectrometry, 612. A satisfactory chemical analysis was not obtained because of the compound's sensitivity to air and moisture. However, since the X-ray powder pattern proved the compound was isomorphous with $U(C_9H_7)_3Cl$, the molecular formula is known to be the same.

The infrared spectrum is as follows (positions of absorptions given in cm^{-1}; visually estimated intensities in parentheses: vw, very weak; w, weak; m, medium; s, strong; vs, very strong; br, broad; sh, shoulder): 3095 (w), 3070 (w), 3050 (w), 3010 (w), 2080 (vw, br), 1940 (w), 1915 (w), 1888 (vw), 1810 (w), 1795 (w), 1780 (w), 1685 (w), 1605 (w), 1595 (sh), 1580 (w, br), 1565 (sh), 1525 (vw), 1480 (s), 1448 (s), 1335 (vs), 1252 (w), 1215 (s), 1185 (vw), 1165 (vw), 1150 (w), 1118 (w), 1045 (sh), 1035 (m), 1015 (sh), 997 (sh), 995 (m), 970 (w), 940 (w), 910 (vw), 890 (vw, br), 860 (m), 840 (m), 815 (s, sh), 795 (s, sh), 780 (vs), 760 (sh), 740 (vs), 735 (sh), 720 (sh), 440 (sh), 430 (s), 405 (w), 380 (w).

Triindenyluranium Chloride.—In a procedure analogous to that described for the preparation of $Th(C_9H_7)_3Cl$, 1.00 g (2.64 mmol) of UCl_4 and 1.21 g (7.85 mmol) of KC_9H_7 were allowed to react in THF at room temperature for 3 days. When the components were mixed, a dark reddish brown solution was obtained instantly; it steadily turned darker with time.

At the end of the reaction time, the THF was distilled off as in the procedure for $Th(C_9H_7)_3Cl$, and the residue was dried under high vacuum for 2 hr. This maroon-brown powder then was extracted with pentane. After 2 hr, well-formed reddish brown crystals appeared in the extract. The extraction was completed after 1 week and the crystals were isolated by decanting the mother liquor, washing with pentane, and thorough drying under vacuum and were identified as pure $U(C_9H_7)_3Cl$; yield 0.48 g (0.75 mmol), corresponding to 28.4%, based on UCl_4; $U(C_9H_7)_3Cl$ mol wt, found by mass spectrometry, 618. *Anal.* Calcd for $U(C_9H_7)_3Cl$: C, 52.39; H, 3.43; Cl, 5.73. Found: C, 51.95; H, 3.70; Cl, 5.72.

The infrared spectrum is as follows [for explanations see the ir spectrum of $Th(C_9H_7)_3Cl$]: 3100 (vw), 3080 (vw), 3050 (vw), 3010 (vw), 1940 (w), 1910 (w), 1880 (vw), 1800 (w), 1780 (w), 1685 (w), 1605 (w), 1585 (sh), 1565 (sh), 1525 (vw), 1480 (m), 1448 (m), 1405 (w), 1340 (vs), 1265 (m), 1217 (s), 1190 (vw), 1150 (vw), 1120 (vw), 1055 (m), 1045 (m), 1038 (m), 1000 (m), 965 (vw), 945 (vw), 890 (vw), 865 (m), 842 (m), 825 (s), 815 ((sh), 800 (sh), 793 (vs), 785 (sh), 745 (vs), 735 (sh), 445 (s), 432 (s), 385 (sh).

Tetraindenylactinides and Diindenylactinide Dichlorides.—Samples of tetraindenylactinides and diindenylactinide dichlorides were obtained with basically the same procedures as those reported for the triindenylactinide chlorides except that an appropriate number of moles of KC_9H_7 was added, respectively.

Discussion

The Syntheses and Some Properties.—The formation of the compounds followed the general scheme $MCl_4 + 3KC_9H_7 \rightarrow M(C_9H_7)_3Cl + 3KCl$ (M = Th, U). A pure product was obtained only if the reactants MCl_4 and KC_9H_7 were added in a molar ratio of 1:3, respectively. Attempts to apply an excess of KC_9H_7, to alter the reaction time, and to extend the periods of extraction yielded products with different compositions. Powder diagrams of the products from some of these experiments indicated the formation of substances essentially free of triindenyl chlorides. Mass spectrometry of some of the products confirmed that they were predominantly $Th(C_9H_7)_4$ and $U(C_9H_7)_2Cl_2$ (*cf.* Table III).

---

(9) C. H. Wong, T. Yen, and T. Lee, *Acta Crystallogr.*, **18**, 340 (1965).

(10) C. H. Wong, T. Lee, and Y. Lee, *ibid.*, *Sect. B*, **25**, 2580 (1969).

(11) M. Tsutsui and H. J. Gysling, *J. Amer. Chem. Soc.*, **90**, 6880 (1968).

(12) M. Tsutsui and H. J. Gysling, *ibid.*, **91**, 3175 (1969).

(13) J. L. Atwood, J. H. Burns, and P. G. Laubereau, to be submitted for publication.

TABLE I
INDEXED X-RAY DIFFRACTION POWDER PATTERNS

	$Th(C_9H_7)_3Cl$		$U(C_9H_7)_3Cl$		
hkl	d_{obsd}, Å	I_{obsd}[a]	d_{obsd}, Å	I_{obsd}	d_{calcd}, Å
011			10.94	vw	10.84
002	8.43	s	8.35	s	8.36
101	7.76	vs	7.65	vs	7.63
020	7.15	s	7.11	s	7.12
111			6.75	w	6.73
021	6.52	w, br	6.52	m	6.55
102			6.00	vw	5.99
022	5.45	s	5.41	s	5.42
121	5.24	vs	5.22	vs	5.21
103	4.70	w	4.67	w	4.67
113	4.47	m	4.44	m	4.44
200	4.37	m	4.28	m	4.29
004	4.19	m	4.18	m	4.18
123	3.921	m	3.905	m	3.907
202	3.846	w	3.818	m	3.818
220	3.699	vw	3.670	w	3.673
024					3.605
221}	3.597	w, br	3.583	m, br	3.587
040					3.559
222	3.326	vw, br	3.363	w	3.363
124			3.323	w	3.323
042}	3.272	w	3.264	m	3.275
015}					3.256
141	3.218	m	3.223	m	3.226
230			3.175	vw	3.182
105	3.132	m	3.113	m	3.116
142	3.074	vw	3.058	w, br	3.059
204	3.008	m	2.988	m	2.993
214	2.945	m	2.880	m	2.929
125	2.847	s	2.851	m	2.854
301	2.795	m	2.820	m	2.818
224			2.757	m	2.759
035			2.734	vw	2.734
302	2.716	w	2.706	m	2.705
312	2.639	w, br	2.658	vw	2.657
116	2.607	m	2.607	s, br	2.606

[a] Visually estimated intensities: vw, very weak; w, weak; m, medium; s, strong; vs, very strong; br, broad.

The compounds $Th(C_9H_7)_3Cl$ and $U(C_9H_7)_3Cl$ are both very air sensitive and may be handled only under a protective atmosphere or under vacuum. Their thermal stabilities are relatively high; visually it was observed that $Th(C_9H_7)_3Cl$ melts without decomposition at 181° and $U(C_9H_7)_3Cl$ seemed to show no signs of change up to 300°. Dta measurements confirmed the melting point of $Th(C_9H_7)_3Cl$; however, a distinct endothermic transition occurred at 203° with $U(C_9H_7)_3Cl$. It is therefore believed that $U(C_9H_7)_3Cl$ melts with decomposition at this temperature. This compares with the thermal stability of $U(C_5H_5)_3F$ (decomposes at 312°)[14] and $U(C_5H_5)_3Cl$ (mp 260–265°, stable up to 300°).[15] Both indenyl complexes can be sublimed under high vacuum (better than 10^{-3} Torr) at temperatures above 160°.

Both $Th(C_9H_7)_3Cl$ and $U(C_9H_7)_3Cl$ are sparingly soluble in *n*-pentane. In benzene, 5 mg/ml solutions of $U(C_9H_7)_3Cl$ and 10 mg/ml solutions of $Th(C_9H_7)_3Cl$ could be prepared. Both substances are soluble in THF up to a concentration of at least 50 mg/ml.

On addition of deaerated water, the dark brown solution of $U(C_9H_7)_3Cl$ in benzene was immediately decolored and the aqueous phase was olive green. A similar behavior is known with $U(C_5H_5)_3Cl$[15] from which various complexes containing the cation $U(C_5H_5)_3^+$ could be isolated upon addition of suitably large anions to the aqueous solution. Attempts to precipitate a $U(C_9H_7)_3^+$-containing complex with NH_4PF_6 failed.

Single-crystal studies of $U(C_9H_7)_3Cl$ show that it crystallized as orthorhombic, space group $P2_12_12_1$, and has the unit-cell dimensions $a = 8.58$ Å, $b = 14.24$ Å, and $c = 16.73$ Å, which give a unit-cell volume of 2044 Å^3. The powder pattern calculated from these values was used to index the observed powder patterns of $U(C_9H_7)_3Cl$ and $Th(C_9H_7)_3Cl$. The latter patterns are presented in Table I as useful data for the identification of these and homologous transuranium compounds and as evidence that they are isomorphous. The calculated density 2.01 g/cm^3 for $U(C_9H_7)_3Cl$ (assuming four formula weights per unit cell) is as expected slightly lower than the value 2.18 g/cm^3 calculated for $U(C_5H_5)_3Cl$.

Mass Spectra.—Some of the data obtained by mass spectrometric analysis are listed in Table II. The fragmentation pattern clearly confirms that the compositions of the compounds are $Th(C_9H_7)_3Cl$ and $U(C_9H_7)_3Cl$. In each case the molecular peak was found. However, a comparison with the known mass spectra of tricyclopentadienyl halides of uranium and of thorium[16,17] shows a strongly enhanced tendency of the triindenylactinide halides to give off the first indenyl ligand under conditions of the mass analysis. This tendency is even greater than the release of the first cyclopentadienyl ring with the tetracyclopentadienyls.

TABLE II
MASS SPECTRA[a–c] OF TRIINDENYLACTINIDE CHLORIDES

$Th(C_9H_7)_3Cl$[d]			$U(C_9H_7)_3Cl$[e]		
m/e	Ion	Rel intens[f]	*m/e*	Ion	Rel intens[f]
232	Th^+	1.0			
			273	UCl^+	5.3
			298	UC_2HCl^+	1.4
			310	UC_3HCl^+	1.3
			326	$UC_7H_4^+$	1.8
329	$ThC_5H_2Cl^+$	1.6	335	$UC_5H_2Cl^+$	0.6
			350	$UC_9H_4^+$	0.9
			351	$UC_9H_5^+$	1.0
			352	$UC_9H_6^+$	4.3
355	$ThC_7H_4Cl^+$	3.5	361	$UC_7H_4Cl^+$	0.9
356	$ThC_7H_5Cl^+$	1.4	362	$UC_7H_5Cl^+$	1.0
380	$ThC_9H_5Cl^+$	3.6	386	$UC_9H_5Cl^+$	1.3
381	$ThC_9H_6Cl^+$	6.3	387	$UC_9H_6Cl^+$	1.3
382	$ThIndCl^+$	25.0	388	$UIndCl^+$	67.7
467	$ThIndC_7HCl^+$	0.7	. . .		
469	$ThIndC_7H_3Cl^+$	0.7	. . .		
493	$ThIndC_9H_3Cl^+$	1.8	499	$UIndC_9H_3Cl^+$	0.9
495	$ThIndC_9H_5Cl^+$	1.0	501	$UIndC_9H_5Cl^+$	0.7
497	$ThInd_2Cl^+$	100.0	503	$UInd_2Cl^+$	100.0
612	$ThInd_3Cl^+$	0.3	618	$UInd_3Cl^+$	0.9

[a] Only the most intense mass peak of each ion moiety is represented; masses below a relative abundance of 0.5% are not listed with exception of the molecular peak of $Th(C_9H_7)_3Cl$. [b] Recorded at 70-eV electron energy. [c] Ind = C_9H_7. [d] Direct-inlet probe temperature 250°. [e] Direct-inlet probe temperature 220°. [f] Normalized for $MInd_2Cl^+$ (M = Th, U) = 100.0.

Similar to the tricyclopentadienylactinide halides,[16,17] the ion $M(C_9H_7)_2Cl^+$ (M = Th, U) appears as the strongest mass peak. As found by Müller[16] for the formation of cyclopentadienylmetal halide ions the relative tendency for the formation of indenylmetal halide ions is very dependent on the metal in a similar manner.

---

(14) P. G. Laubereau, Dissertation, Technische Hochschule München, 1966.

(15) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 246 (1956).

(16) J. Müller, *Chem. Ber.*, **102**, 152 (1969).

(17) M. L. Anderson and L. R. Crisler, Report CRDL 940327-2, Dow Chemical Co., Rocky Flats, Colo., 1968.

Evidently, the tendency of uranium to achieve the oxidation number 3+ very much stabilizes the formation of $U(C_9H_7)_3Cl^+$ and increases its relative abundance in the spectrum compared with $Th(C_9H_7)_3Cl^+$.

Noteworthy is the appearance of the ion Th^+ in the case of $Th(C_9H_7)_3Cl$. No evidence for U^+ was found in the mass spectrum of $U(C_9H_7)_3Cl$. However the spectrum of $U(C_9H_7)_3Cl$ shows the presence of the ion UCl^+. Because of its relatively high abundance in mass spectra of $U(C_5H_5)_3Cl$[17,18] (relative intensity 4.8–7.0%), it is reasonable to assume that the high intensity of 5.3% is not caused by an impurity in the case of $U(C_9H_7)_3Cl$. No $ThCl^+$ ion was found.

Metastable peaks were found for the decay processes (M = Th, U; Ind = C_9H_7)

$$UInd_3Cl^+ \longrightarrow UInd_2Cl^+ + C_9H_7$$

$$MInd_2Cl^+ \longrightarrow MIndCl^+ + C_9H_7$$

$$UIndCl^+ \longrightarrow UCl^+ + C_9H_7$$

$$UIndCl^+ \longrightarrow UC_9H_6^+ + HCl$$

$$ThC_9H_6Cl^+ \longrightarrow ThC_9H_5Cl^+ + H$$

The scarcity of metastable transitions where a loss of the chlorine or HCl occurs suggests that the predominant degradation of the molecules happens with a stepwise loss of C_9H_7 units. In addition, and to a small extent, the cleavage of C_2H_2 from the indenyl ligand can be observed. The situation is somewhat similar to the behavior of the tricyclopentadienylactinide halides.[16] Qualitatively, it can be said that the metal-to-chlorine bond is stronger than the metal-to-indenyl ring bond.

Although it has not yet been possible satisfactorily to isolate $Th(C_9H_7)_4$, $Th(C_9H_7)_2Cl$, and $U(C_9H_7)_2Cl_2$ in the pure state, our mass spectrometric investigations gave the first evidence for the existence of these compounds. For comparison, some of the data obtained are listed in Table III. This table also includes masses that we tentatively assign to the decay chain of $U(C_9H_7)_4$, in a spectrum which showed the presence of some $U(C_9H_7)_3Cl$ also. We were unable to find the molecular peak for $U(C_9H_7)_4$; however, it was also impossible to get evidence for a metastable transition $U(C_9H_7)_3Cl^+ \rightarrow U(C_9H_7)_3^+ + Cl$ by a thorough investigation of various $U(C_9H_7)_3Cl$ spectra. If one considers the thermal instability found for $U(C_5H_5)_4$ and its known low-intensity molecular peak (1.5–3.3% compared with 35.4% found with $U(C_5H_5)_3Cl$[16,17]), it seems reasonable to expect with $U(C_9H_7)_4$ a very much decreased appearance probability of the molecular peak. Table III also shows that, with the compounds discussed, an increased tendency of the uranium compounds, compared with thorium compounds of the same composition, exists to form fragments where uranium achieves the oxidation state 3+; $Th(C_9H_7)_4$ shows a pronounced tendency to fragment into Th^+.

TABLE III
PARTIAL MASS SPECTRA[a] OF TETRAINDENYLACTINIDES AND DIINDENYLACTINIDE DICHLORIDES

m/e	Ion	Rel intens[d]	m/e	Ion	Rel intens[d]
	$ThInd_4$[b]			$UInd_4$[c]	
232	Th^+	5.3	238	U^+	No
347	$ThInd^+$	3.8	353	$UInd^+$	≤130.0
462	$ThInd_2^+$	62.0	468	$UInd_2^+$	270.0
577	$ThInd_3^+$	100.0	583	$UInd_3^+$	100.0
692	$ThInd_4$	2.1			
	$ThInd_2Cl_2$[c]			$UInd_2Cl_2$[c]	
			238	U^+	No
267	$ThCl^+$	≤2.0			
302	$ThCl_2^+$	4.0	308	UCl_2^+	51.4
417	$ThIndCl_2^+$	100.0	423	$UIndCl_2^+$	100.0
431	$ThIndCH_2Cl_2$	≤14.0	437	$UIndCH_2Cl_2^+$	8.0
458	$ThIndC_3H_5Cl_2^+$	≤14.0	464	$UIndC_3H_5Cl_2$	29.7
532	$ThInd_2Cl_2^+$	12.0	538	$UInd_2Cl_2^+$	15.7

[a] Recorded at 70-eV electron energy. [b] Direct-inlet probe temperature 275°. [c] Direct-inlet probe temperature 250°. [d] Normalized for $MInd_3^+$ and $MIndCl_2^+$ (M = Th, U) = 100.0, respectively.

The following metastable transitions for compounds listed in Table III were found (Ind = C_9H_7)

$$UInd_3^+ \longrightarrow UInd_2^+ + C_9H_7$$

$$UInd_2^+ \longrightarrow UInd^+ + C_9H_7$$

$$UInd_2Cl_2^+ \longrightarrow UIndCl_2^+ + C_9H_7$$

$$UIndCl_2^+ \longrightarrow UCl_2 + C_9H_7$$

However in addition to the case of the decay of $U(C_9H_7)_3Cl$ mentioned already, *no* metastable transitions were found for

$$UInd_2Cl_2^+ \longrightarrow UInd_2Cl^+ + Cl$$

$$UCl_2^+ \longrightarrow UCl^+ + Cl$$

Nmr Spectra.—The nmr data obtained are listed in Table IV. The numbering scheme shown in the table was used because of its convenience in spectral analysis and it applies to the following discussion. Because $Th(C_9H_7)_3Cl$ is reasonably soluble in THF and is diamagnetic, a well-resolved spectrum was obtained in that solvent. All resonance lines were well separated downfield from solvent lines. On the other hand, some of the resonance lines for $U(C_9H_7)_3Cl$ were overlapped by THF lines. Therefore spectra for the uranium compound were obtained in benzene solution as were spectra for the cyclopentadienyl complexes[5] previously reported. Chemical shifts listed in Table IV are related to internal TMS for the thorium compound and to external TMS for the uranium compound. The very low solubility of $U(C_9H_7)_3Cl$ in benzene, as well as broadening of the signals attributed to paramagnetism, resulted in decreased quality of the spectrum, and a complete analysis could not be made.

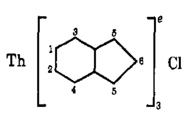
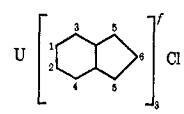
The nmr spectra of $Th(C_9H_7)_3Cl$ and $U(C_9H_7)_3Cl$ are comparatively simple and seem to indicate that only one type of indenyl ligand and one type of ligand-to-metal bond is present in the dissolved compounds. Each spectrum shows two sets of signals, one belonging to the protons of the C_6 ring and the other to the protons of the C_5 ring. The compound $Th(C_9H_7)_3Cl$ shows an AA′BB′ pattern for the protons 1,2 and 3,4 of the C_6 ring, with the presence of two groups of signals. A fairly large para-coupling constant $J_{3,4} = 0.93$ Hz was found, in contrast to the situation normally found with substituted benzenes. A coupling constant $J_{5,4} = 0.6$ Hz, for the case of the neighboring protons H(4) of the C_6 ring and H(5) of the C_5 ring, indicates only a weak exchange between the ring currents of the two rings of the indenyl ligand, as was found also for other indenyl complexes.[19]

The signals for the five-membered ring in $Th(C_9H_7)_3Cl$ give a typical A_2B pattern. The doublet of doublets (relative intensity 2) appearing 2.06 ppm upfield from

(18) P. G. Laubereau, unpublished results.

(19) H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, **4**, 198 (1965).

TABLE IV

		
$\delta_1 = \delta_2{}^a$	7.71	+3.51 or −0.24
	AA′BB′ multiplet	AA′BB′ multiplet
$w_{1/2}{}^b$	0.55	~2
I^c	2	2
$\delta_3 = \delta_4$	7.18	−0.24 or +3.51
	AA′BB′ multiplet	AA′BB′ multiplet
$w_{1/2}$	<0.55	~2
I	2	2
δ_5	5.84	−1.64
	Doublets of doublets	
$w_{1/2}$	<0.5	~6.5
I	2	2
δ_6	6.34	−5.48
	Triplet	
$w_{1/2}$	0.70	~7
I	1	1
$J_{1,3} = J_{2,4}{}^d$	8.63	
$J_{1,4} = J_{2,3}$	1.08	
$J_{1,2}$	6.81	
$J_{3,4}$	0.93	
$J_{4,5}$	0.6	
$J_{5,6}$	3.42	⩽2.3

[a] Chemical shifts are given in ppm relative to TMS at 0. Negative values for chemical shifts are for signals at higher field strength than TMS. [b] Width at half-height ($w_{1/2}$) is given in Hz. The spectrum for $Th(C_9H_7)_3Cl$ was reproduced using 0.55 Hz for the AA′BB′ portion. Some lines appeared to be broader because of near coincidence of two transitions. [c] Intensity (I) is given in arbitrary units. [d] Coupling constants (J) are given in Hz. The spectrum of the thorium compound was analyzed as an AA′BB′ system using the program NMRIT [R. C. Ferguson and D. W. Marquardt, *J. Chem. Phys.*, **41**, 2087 (1964)] and was confirmed using the program LAOCN3 [S. Castellano and A. A. Bothner-By, *ibid.*, 41, 3863 (1964); LAOCN3, Mellon Institute, Pittsburgh, Pa., 1966]. The spectrum of the uranium compound could not be analyzed because of its limited solubility and poor resolution due to broadened lines. [e] The thorium compound was nearly insoluble in benzene. Its spectrum was recorded in tetrahydrofuran solution. [f] Spectra were taken for saturated solutions in benzene. Chemical shifts were slightly concentration dependent. Tetrahydrofuran could not be used as solvent because some signals were obscured by solvent signals.

external benzene [5.84 ppm downfield from external tetramethylsilane (TMS)] is assigned to the equivalent hydrogens in position 5 (*cf.* Table IV). The triplet (relative intensity 1) found at lower fields, 1.46 ppm upfield from external benzene (6.34 ppm downfield from external TMS), can be correlated to hydrogen 6.

A rather large coupling constant $J_{5,6} = 3.4$ was found. According to Fritz, *et al.*,[19] this could be evidence for a comparatively high electron density on the indenyl C_5 ring, thus indicating that a possible π-electron donation from the ring to thorium is fairly low. The value found would be comparable to $J_{5,6} = 3.4$ given by Fritz, *et al.*,[19] for NaC_9H_7 although a different solvent was used in this case. NaC_9H_7 presumably has a predominantly ionic metal-to-ligand bond. The $J_{5,6}$ values for π-bonded *pentahapto*indenylmetal complexes are somewhat lower.[19-21]

The signals for the 5 and 6 protons in $Th(C_9H_7)_3Cl$ are shifted to higher fields compared with the signals for the free indenyl ion studied by Fritz.[19] Similar observations can be made with π-indenyl complexes.[19] Values for the chemical shifts of the possibly free anion $C_9H_7^-$ are also given by Tsutsui, *et al.*,[12] for NaC_9H_7 dissolved in THF. However there the position of the signal for H(6) is at considerably higher fields than reported by Fritz, *et al.*[19] This difference could be caused by the known coordination of NaC_9H_7 with THF.

The chemical shifts of H(5) and H(6) in $Th(C_9H_7)_3Cl$ are about the same as found for the compounds $M(C_9H_{11})_2Cl$ (M = Ti, Zr; C_9H_{11} = tetrahydroindenyl anion),[21] all of which have a similar A_2B pattern for the C_5-ring hydrogens. A fair degree of bond delocalization for the C_5 ring–metal bond was assumed for these Zr and Ti complexes.

The nmr data alone for $Th(C_9H_7)_3Cl$ do not unambiguously define the type of metal to indenyl bond present in dissolved molecules. The discussion by Cotton, *et al.*,[22] of nmr spectra of diindenylmercury can be applied, to a certain extent, to $Th(C_9H_7)_3Cl$. A comparison of low- and high-temperature spectra could help to distinguish among various possibilities of contributions of 1-monohapto, 1,2,3-trihapto, or other multihapto structures to the spectrum. Thus, it seems noteworthy to remark that the spectrum of $Th(C_9H_7)_3Cl$ resembles very much the "high-temperature" spectrum of $Hg(C_9H_7)_2$. Taking into account this similarity as well as the large value for the coupling constant $J_{5,6}$ and the dissimilarity with spectra known for some molecules with predominantly π-bonded indenyl ligands one cannot exclude the possibility of the presence of fluxional mono- to polyhapto bonds with σ character. On the other hand, the nmr spectrum of $Th(C_9H_7)_3Cl$ gives no support for the assumption of a localized nonfluxional bond with a high degree of covalency, as was found with the complex $Sm(C_9H_7)_3 \cdot THF$,[11,12] which until now was the most extensively studied case of an f-element indenyl complex. $Sm(C_9H_7)_3 \cdot THF$ seems to present a unique bond arrangement. Since $La(C_9H_7)_3 \cdot THF$ does not show an ABX pattern for the C_5 ring, but shows a A_2B pattern with a singlet at $\delta = 5.58$ and a triplet at $\delta = 3.19$, the possibility of a somewhat greater delocalization of the metal-to-ligand bond was proposed.[12]

The replacement of thorium by uranium has a profound effect on the nmr spectrum. The group of signals for the C_6-ring protons 1, 2, 3, and 4 are considerably shifted upfield, appearing in two groups at δ = 3.51 ppm and $\delta = -0.24$ ppm as an AA′BB′ multiplet. Hydrogen 5 gave a broadened signal (relative intensity 2) at −1.64 ppm (upfield from TMS) and hydrogen 6 gave a signal (relative strength 1) at −5.48 ppm. The half-width of the signals for hydrogens 5 and 6 was about 7 Hz and no observable coupling could be observed. We estimate the coupling $J_{5,6}$ to be about 2.3 Hz. The large shift to higher field strength of the hydrogens, especially hydrogen 6, is attributed to interactions with the paramagnetic metal, uranium. The phenomenon has been called the "Knight shift"[23] and thus avoids the implication of a particular mechanism. However the large shifts are similar to those in other paramagnetic metal complexes[6,7,11,12,19,24] and probably are a consequence principally of participation

---

(20) J. H. Osiecky, C. J. Hoffman, and D. P. Hollis, *J. Organometal. Chem.*, **3**, 107 (1965).

(21) E. Samuel, *Bull. Soc. Chim. Fr.*, **11**, 3548 (1966).

(22) F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 3178 (1969).

(23) E. W. Randall and D. Shaw, *J. Chem. Soc. A*, 2867 (1969).

(24) (a) E. Samuel and R. Setton, *J. Organometal. Chem.*, **4**, 156 (1965); (b) T. H. Siddall, III, W. E. Stewart, and D. G. Karraker, *Chem. Phys. Lett.*, **3**, 498 (1969); (c) R. V. Ammon, B. Kanellakopulos, and R. D. Fisher, *ibid.*, **2**, 513 (1968); (d) *ibid.*, **4**, 553 (1970).

of unpaired f electrons.[24b,c,d] Other effects on the position of the signal for hydrogen 6 caused by different steric arrangements were discussed earlier by Fritz.[25]

The lower value of $J_{5,6}$ in $U(C_9H_7)_3Cl$ may indicate a higher degree of electron donation from the rings to the metal and thus could be a sign for a more delocalized but more rigid bond. It is not possible to separate these effects from lowering of the coupling due to paramagnetism of the compound.

Infrared Spectra.—The infrared spectrum of $Th(C_9H_7)_3Cl$ is presented in Figure 1. $Th(C_9H_7)_3Cl$ and $U(C_9H_7)_3Cl$ have similar spectra and the positions of the absorptions are listed in the Experimental Section. The absorption patterns closely resemble ones reported for $Ti(C_9H_7)_2Cl_2$ and $Zr(C_9H_7)_2Cl_2$.[24]

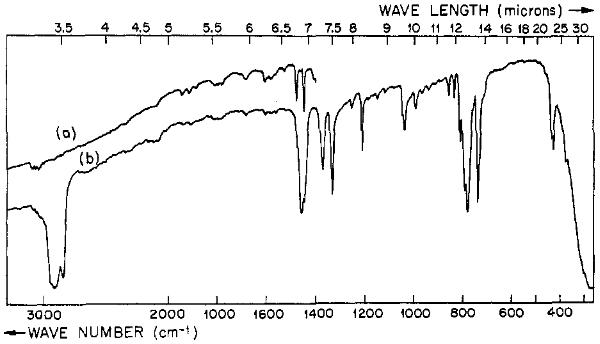


Figure 1.—The infrared spectra of $Th(C_9H_7)_3Cl$: (a) Fluorolube mull; (b) Nujol mull.

Special attention was given to the infrared spectra of various types of indenyl compounds by Samuel in several publications.[21,24,26,27] This, as well as additional material given in ref 17, 19, 20, 28, and 29, provides a basis for assignments and a discussion of the absorptions found here.

A group of weak absorptions [four in the case of $U(C_9H_7)_3Cl$] observed in the region 3000–3100 cm^{-1} for both compounds can be attributed to aromatic C–H stretching vibrations. No indications of absorptions in the region 2800–3000 cm^{-1} could be found for $U(C_9H_7)_3Cl$ and only very slight indication was noticed in the case of $Th(C_9H_7)_3Cl$. Thus $Th(C_9H_7)_3Cl$ and $U(C_9H_7)_3Cl$ do not show the absorption pattern found for compounds with σ-bonded indenyl systems such as HgC_9H_7Cl and $Hg(C_9H_7)_2$.[27]

Several sharp and moderately intense absorptions are found in the region 1700–1200 cm^{-1}. Because of the lack of additional data for partially deuterated ring systems or for tetrahydroindenyl derivatives of uranium and of thorium, a satisfactory direct assignment is somewhat difficult here and in the 1200–300-cm^{-1} region. The characteristic absorptions in the vicinity of 1600, 1480, and 1450 cm^{-1} were also observed for $Ti(C_9H_7)_2Cl$[22,24] and lie in a region where ω(C–C) vibrations for aromatic C_5 and C_6 rings could be expected. With $Ti(C_9H_7)_2Cl$, a band at 1500 cm^{-1} is strongly affected by hydrogenation of the C_6 ring. The same can be said for an absorption band of $Ti(C_9H_7)_2Cl$ found at 1350 and 1230 cm^{-1}. Therefore, it is assumed that the bands found with the actinide indenyls at 1480, 1350, and 1230 cm^{-1} also belong to the C_6 ring system; presumably, the latter two are generated by δ(C–H) vibrations.

By comparison of the absorptions of the actinide indenyls found for the region 1200–300 cm^{-1} with the discussions given for other indenyl complexes,[20,21,24–28] the following general assignment can be made. The medium strong bands at 1040 cm^{-1} belong to the δ(C–H) vibration mode of an aromatic C_5 ring. Absorptions in the same position were found for instance in the cases of $Fe(C_9H_7)_2$ at 1025 cm^{-1} and $Fe(C_9H_{11})_2$ at 1030 cm^{-1}.[20] With $U(C_9H_7)_3Cl$ this band is split into three peaks and with $Th(C_9H_7)_3Cl$ into two peaks.

At 1000 cm^{-1} a δ absorption of the C_6 ring appears. The two bands at about 860 and 840 cm^{-1} are characteristic of the triindenylactinide chlorides and may result from Δ(C–C) or ω(C–C) vibrations of the ring systems. The very strong absorptions around 790 cm^{-1} are γ(C–H) vibrations of the C_5 ring, whereas the very strong band (with strong shoulder) at 740 cm^{-1} can be assigned to γ(C–H) vibrations of the C_6 rings. The fact that the γ(C–H) bands of the C_5 ring are centered around 790 cm^{-1} and are not split in a manner found for HgC_9H_7Cl[27] is taken as evidence of C_5 rings with a relatively high degree of aromatic character. For the free anion $C_9H_7^-$, as assumed in the case of KC_9H_7, we found a very strong sharp single absorption for the C_5 ring γ(C–H) vibration at 755 cm^{-1} and a similar sharp absorption at 725 cm^{-1} for the C_6 ring σ(C–H) vibration mode. In the case of π-bonded complexes the following positions and band shapes were found: $Ti(C_9H_7)_2Cl_2$ at ~860 cm^{-1} (sharp but indication of shoulder),[24] $Zr(C_9H_7)_2Cl_2$ at ~840 cm^{-1} (splitting into two absorptions),[24] $Fe(C_9H_7)_2Cl$ at 808 cm^{-1},[20] and $Ru(C_9H_7)_2Cl$ at 808 cm^{-1}.[20]

As can be seen, the γ(C–H) vibrations of the triindenylactinide chlorides lie between the ones found for the presumably predominantly ionic compound KC_9H_7 and the positions known from π-indenyl complexes. If the same general trend applies as found with the cyclopentadienyl complexes,[29] a higher degree of ionic character could be deduced for the metal-to-ligand bond in the case of the triindenylactinide chlorides when compared with the known π-indenyl compounds. Furthermore the fair amount of splitting might be indicative of some distortion of one or more of the C_5 rings in a molecule.

The absorptions found at 440 cm^{-1} probably belong to Γ(C–C) vibrations of the C_6 ring parts of the ligands.

Electronic Spectra.—The pale yellow $Th(C_9H_7)_3Cl$ (in benzene or THF solution) shows the beginning of a strong absorption in the near-ultaviolet spectrum (absorption edge ~380 nm), which can be attributed to ligand transitions. The spectrum of $U(C_9H_7)_3Cl$ (in benzene solution) is shown in Figure 2. It should be most appropriate to compare the spectrum found here with those known for complexes of the type $U(C_5H_5)_3X$ (X = F, Cl, Br, I, C_5H_5) particularly where X = Cl.[15,17,30–32]

---

(25) H. P. Fritz, F. H. Köhler, and K. E. Schwarzhans, *J. Organometal. Chem.*, **19**, 449 (1969).

(26) E. Samuel, *ibid.*, **19**, 87 (1969).

(27) E. Samuel and M. Bigorgne, *ibid.*, **19**, 9 (1969).

(28) R. B. King, *Inorg. Chem.*, **3**, 797 (1964).

(29) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 262 (1964).

(30) M. L. Anderson and L. R. Crisler, *J. Organometal. Chem.*, **17**, 345 (1969).

(31) R. V. Ammon, B. Kanellakopulos, and R. D. Fischer, *Radiochim. Acta*, **11**, 162 (1969).

(32) R. D. Fischer, R. V. Ammon, and B. Kanellakopulos, personal communication; *J. Organometal. Chem.*, in press.

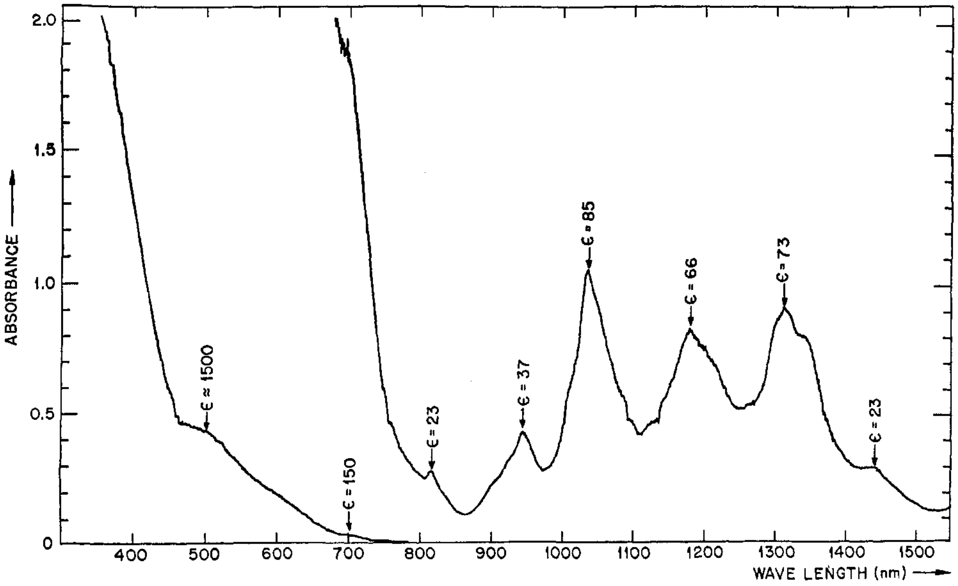


Figure 2.—Electronic absorption spectrum (ε is molar absorptivity) of triindenyluranium chloride (dissolved in benzene at room temperature) in the visible and near-infrared regions.

The prominent feature of the $U(C_9H_7)_3Cl$ spectrum is the appearance of a strong absorption covering nearly the whole visible region up to a wavelength of ~720 nm; the absorption must be attributed to a ligand-to-metal electron transfer. The absorption edge lies at lower energies than the ones found for the complexes $U(C_5H_5)_3X$.[17,31]

In the part of the spectrum not covered by the electron-transfer absorption (essentially the region 720–1500 nm), a series of sharp absorptions is found which can be attributed to f–f transitions. Most of the intensities of the sharp absorptions (given in Figure 2) are of about the same order of magnitude as the ones given in the literature[15] or derived therefrom[17,32] for tricyclopentadienyluranium halides. In addition, it is interesting to note that there is a fairly close agreement between the position of the major absorptions found for $U(C_5H_5)_3Cl$ and for $U(C_9H_7)_3Cl$. The main difference seems to be the far lower intensity of a band at ~1130 nm generally observed with $U(C_5H_5)_3Cl$. Despite this, the $U(C_9H_7)_3Cl$ spectrum is of the same type as $U(C_5H_5)_3X$ ($X = Cl, Br, I$)[31] and unlike the one found for $U(C_5H_5)F$.[32] It is therefore not unreasonable to consider a basically similar electron distribution around the uranium and ligand field effects for $U(C_9H_7)_3Cl$ and $U(C_5H_5)_3Cl$.

Anderson, *et al.*,[30] used the procedure of Gaus[33] to classify the spectrum of $U(C_5H_5)_3Cl$ and attempted to obtain some information on the local symmetry around U. Because of the above arguments, $U(C_9H_7)_3Cl$ should be treated in the same manner and thus would belong in the classes of compounds with no center of symmetry giving "medium" or "strong" spectra. However, we feel there is need for additional information also obtained from crystalline material. This information is needed to provide a term assignment of the energy levels found in the electronic spectra. Even a tentative assignment was not justified at this stage of the investigation.

Solutions of $U(C_9H_7)_3Cl$ in THF and pentane show essentially the same color as the solid and solutions in benzene. Therefore the same basic molecular symmetry could be expected in all these systems. As mentioned, with water a green solution is obtained that showed major broad absorptions in the vicinity of 600–670, 1090, 1270, and 1380 nm.

Conclusions

The macroscopic properties, such as solubility, thermal stability, sublimation behavior, and sensitivity to air, of $Th(C_9H_7)_3Cl$ and $U(C_9H_7)_3Cl$ are suggestive of their structural similarities. X-Ray powder photographs show they are isomorphous. The mass spectral fragmentation modes show successive loss of indenyl rings by both compounds.

Information on the type of metal-to-ligand bond was obtained by spectrographic methods. Infrared spectra gave evidence for aromatic character in the C_5 ring. A localized metal-to-ligand σ bond is excluded in favor of covalent π-type bonds. Support for this conclusion is found in the nmr and ultraviolet spectra and the data indicate somewhat more covalency in the uranium compound. The nmr spectra also show a high degree of symmetry in the C_5 rings of both compounds while infrared data show the absence of the diene structure.

The complete X-ray analysis of the compounds is now in progress and will give additional information on the structure and bonding involved.

Acknowledgments.—We thank W. H. Christie and W. T. Rainey for their great help in obtaining the mass spectra. We also want to express our thanks to J. L. Roberts for his important assistance.

---

[33] P. Gaus, B. J. Hathaway, and B. C. Smith, *Spectrochim. Acta*, **21**, 1589 (1965).