LANTHANIDES AND ACTINIDES

ANNUAL SURVEY COVERING THE YEAR 1971

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An excellent review article dealing with organometallic derivatives of lanthanides and actinides has appeared[1]. It covers the literature up to September 1970.

I. Organometallic derivatives of lanthanides

Full details concerning the reactions of ytterbium and europium metals with alkyl and aryl iodides have been reported[2]. Preliminary results had been published earlier[3]. Ytterbium metal reacts with alkyl and aryl iodides at –20° giving brown solutions in which species of the type "YbR(I)" were believed to be present, similar to the Grignard reagents. The assignment of structure comes from the following observations. (i) The solutions have an iodine/ytterbium ratio close to 1; (ii) the magnetic susceptibility measurements of the solutions suggest the presence of ytterbium(II) as indicated by the magnetic moment, which is substantially zero, as expected for ytterbium(II) of f^{14} configuration. Ytterbium(III) is reported to have magnetic moments around 4.5 BM; (iii) hydrolysis takes place promptly with formation of the appropriate hydrocarbon; (iv) benzophenone yielded $Ph_3C{-}OH$ by reaction with the solution obtained from ytterbium metal and iodobenzene. Some additional evidence was also gathered in support of the proposed formulation. Similar results were also obtained with europium and samarium. However, the latter metal was the slowest to react of the three, in agreement with the fact that samarium has the least stable bivalent state.

This paper and the one by Hart and coworkers[4] which appeared last year are the only reports existing in the literature concerning the existence of organometallic derivatives of lanthanides with alkyl and aryl groups.

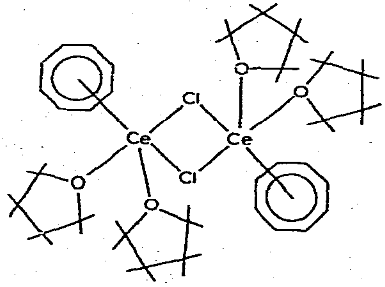
Vapour pressure measurements of tricyclopentadienyls of praseodymium, neodymium, holmium and thulium were reported[5] at different temperatures between 65 and 170°. The calculated values for the enthalpy changes of sublimation were the following.

Compound	ΔH_{subl} *(kcal/mole)*
$Pr(C_5H_5)_3$	31.3
$Nd(C_5H_5)_3$	32.3
$Ho(C_5H_5)_3$	28.6
$Tm(C_5H_5)_3$	26.1

Cyclooctatetraene complexes of cerium, praseodymium, neodymium and samarium of a new type have been prepared[6] by reacting the anhydrous trichlorides with the cyclooctatetraene dianion, abbreviated as COT^{2-}, in tetrahydrofuran as solvent, such as for example:

$$CeCl_3 + COT^{2-} + 2\,THF \xrightarrow[-15^\circ]{THF} 2\,Cl^- + \tfrac{1}{2}[Ce(COT)Cl(THF)_2]_2 \qquad (1)$$

Preliminary results of an X-ray investigation[7] show that the cerium derivative is a dimer with chloride bridges, the coordination sphere being completed by two tetrahydrofuran groups per cerium atom. The molecular structure of the cerium compound is shown schematically as (I).



(I)

A compound which was believed to contain erbium–cobalt bonds was prepared[8] by the following reaction:

$$Er + \tfrac{3}{2}\,Hg[Co(CO)_4]_2 + 4\,THF \xrightarrow{THF} \tfrac{3}{2}\,Hg + Er[Co(CO)_4]_3 \cdot 4THF \qquad (2)$$

The compound was isolated as a dark-red solid, sensitive to air and moisture. The infrared spectrum had more bands than expected if the compound has to be considered simply as an erbium derivative of the $[Co(CO)_4]^-$ anion. The products of the thermal decomposition were found to be CO and THF by mass spectrometry. More work on this and related compounds has been announced[8].

II. Organometallic derivatives of actinides

The preparation of a compound containing an uranium–carbon bond to a cyclohexylisocyanide group, *i.e.* to a two-electron carbon donor, was achieved[9] by the reaction of uranium tetraiodide with the ligand in hexane:

$$UI_4 + 4\,C_6H_{11}NC \rightarrow UI_4(CNC_6H_{11})_4 \qquad (3)$$

Reaction (3) was carried out at –5°. The yellow compound is extremely sensitive to moisture and its infrared spectrum has the CN stretching vibration at 2190 cm^{-1} which represents a 55 cm^{-1} increase with respect to the value for the free ligand. This, of course, is to be attributed to the relatively high oxidation state of the central metal atom.

The nuclear magnetic resonance spectrum of tetraallyluranium(IV) has been reported[10]. Three resonances were observed upfield with respect to tetramethylsilane as internal standard: the resonances were found at +18.70 ppm (doublet), +35.33 ppm (broad peak) and +59.75 ppm (doublet), in agreement with the π-allyl structure of the complex.

Dicyclopentadienyldichlorouranium(IV) was prepared[11] by treating UCl_4 with thallium cyclopentadienide in dimethoxyethane:

$$UCl_4 + 2\,TlC_5H_5 \xrightarrow[3\ h]{\text{room temp.}} 2\,TlCl + U(C_5H_5)_2Cl_2 \qquad (4)$$

The compound was reported to be green-brown, soluble in coordinating solvents, such as tetrahydrofuran and acetone. The magnetic moment was $\mu_{eff} = 2.65$ BM.

^1H NMR measurements on $Th(C_5H_4Me)_4$ and $U(C_5H_4Me)_4$ have indicated[12] that the rotation of the five-membered rings is hindered severely in these methyl-substituted compounds already at room temperature.

Vapor pressure at different temperatures have been carried out[5] on $U(C_5H_5)_3Cl$. The enthalpy of sublimation for this compound was found to be 27.7 kcal/mole.

Triindenylchloro derivatives of thorium(IV) and uranium(IV) were prepared[13]. These compounds were obtained by the following general reaction:

$$MCl_4 + 3\,KC_9H_7 \rightarrow 3\,KCl + U(C_9H_7)_3Cl \qquad (5)$$

$$(M = Th, U)$$

The thorium and uranium derivatives appear to be rather stable thermally. The thorium derivative was reported to melt without decomposition at 181°, whereas the uranium compound does not apparently change upon heating up to 300°. The mass spectra of the two compounds show the molecular ions. The ^1H NMR spectrum of the diamagnetic thorium(IV) derivative has an A_2B pattern for the five-membered ring protons at room temperature. In the absence of measurements at variable temperature, it was not possible to make suggestions about the type of bonding between the metal and the indenyl group; the infrared spectra of the two compounds as nujol mull, on the other hand, would tend to exclude the presence of σ-bonded (*monohapto*) indenyl rings.

The latter conclusion was confirmed by an X-ray study[14] of the uranium compounds, $U(C_9H_7)_3Cl$. The three indenyl rings and the chlorine atom are in an approximate tetrahedral arrangement around the central metal atom, as indicated in Fig. 1. The uranium–carbon distances are in the range 2.67–2.89 Å; however, three of the U–C distances within the five-membered rings are shorter than the other two. For one of the indenyl groups, the three carbon atoms to which correspond the shorter uranium–carbon distances are indicated below as A, B, and C. The reported figures are the uranium–carbon distances. While the results of this X-ray investigation exclude the σ-bonded (*monohapto*) arrangement of the indenyl groups, a *trihapto* arrangement could still be conceivable.

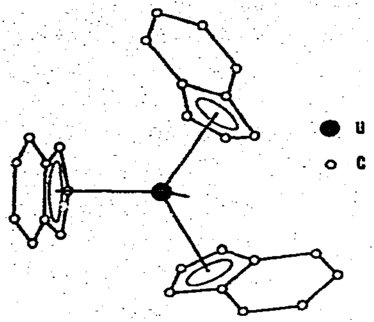
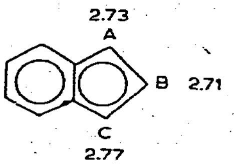


Fig. 1. Molecular structure of triindenylchlorouranium(IV). (From J.H. Burns and P.G. Laubereau, *Inorg. Chem.*, 10 (1971) 2789.)



Proton magnetic resonance shifts of $U(C_8H_8)_2$ have been reported[15]. The spectra were recorded as a function of temperature and the shifts were found to fall in the range +34.9–+67.7 ppm (with respect to $C_8H_8^{2-}$) between 353 and 198 K. These largely positive contact shifts suggest a certain degree of covalency.

More direct information concerning the bonding in these uranium(IV) complexes were obtained by the measurements[16] of the proton chemical shifts in the methyl-substituted compound $U(1,3,5,7\text{-}C_8H_4Me_4)_2$. The spectra were measured in THF-d_8 at variable temperature and two peaks were found with an intensity ratio 3/1; these resonances were accordingly attributed to the methyl and ring protons, respectively. The contact shifts were found to be of opposite sign for the methyl and the ring protons; this was taken to suggest spin density in molecular orbitals of the π-type. Similar results were also obtained for the corresponding neptunium(IV) derivative[16].

The X-ray structure of bis(1,3,5,7-tetramethylcyclooctatetraene)uranium(IV) $U(1,3,5,7\text{-}C_8H_4Me_4)_2$ has been solved[17]. The structure consists of two tetramethyl-substituted cyclooctatetraene rings bonded to uranium, as expected. However, an interesting feature of the structure is that there are two crystallographically independent molecules in the unit cell, which are different because of the orientation of the methyl groups. In one of the molecules the methyl groups are almost eclipsed, whereas in the other the same groups are almost staggered.

Absorption spectra of tricyclopentadienyl-americium and -curium derivatives have been reported[18]. The data have been compared with those for the corresponding derivatives of the lanthanides: praseodymium, neodymium and erbium. The conclusion was that in both series the degree of covalency was very low, relative to the corresponding aquo-ions, and that the lanthanide series was even less covalent than the actinide one.

A compound of formula $C_6H_6Al_3Cl_{12}U$ was obtained[19] by the reaction of UCl_4 with Al and benzene in the presence of $AlCl_3$. After 7 h reflux and cooling to room temperature, black crystals were obtained, insoluble in all common organic solvents, decomposed by basic solvents, such as tetrahydrofuran. The X-ray structure has now shown that this compound is an arene complex of uranium(III) and its formula is therefore $U(C_6H_6)(AlCl_4)_3$. The molecular structure consists of an uranium atom to which three $AlCl_4$ tetrahedra are bonded through UCl_2Al bridges. The mean uranium–carbon distance is 2.91 ± 0.01 Å. The molecular structure of this compound is schematically shown in Fig. 2.

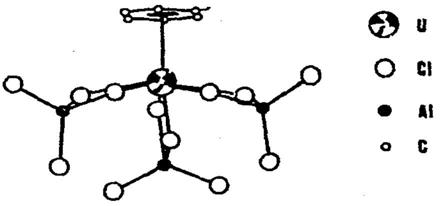


Fig. 2. Molecular structure of $U(C_6H_6)(AlCl_4)_3$. (From M. Cesari, U. Pedretti, A. Zazzetta, G. Lugli and W. Marconi, *Acta Chim. Inorg. (Padua)*, 5 (1971) 439.)

A compound believed to contain uranium–manganese bonds was obtained[20] by the reaction of UCl_4 with $Na[Mn(CO)_5]$ in tetrahydrofuran as solvent at room temperature:

$$UCl_4 + 4\,Na[Mn(CO)_5] \xrightarrow{THF} 4\,NaCl + U[Mn(CO)_5]_4 \tag{6}$$

The compound shows some bands at higher wavenumbers than expected for the $[Mn(CO)_5]^-$ anion. It is unstable in air, forming $Mn_2(CO)_{10}$ and with bromine in carbon tetrachloride yields the expected products of oxidation:

$$U[Mn(CO)_5]_4 + 4\,Br_2 \rightarrow UBr_4 + 4\,MnBr(CO)_5 \tag{7}$$

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