LANTHANIDES AND ACTINIDES

ANNUAL SURVEY COVERING THE YEAR 1975

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General

Sheline and Slater (1) have recently published a review of their spectroscopic studies of lanthanide and actinide carbonyls. These unstable species were produced by co-condensation of the metal vapor with carbon monoxide in an argon matrix at 4°K. Infrared data and tentative assignments are reported for $M(CO)_n$, M = U, Pr, Nd, Gd, and Ho, n = 1-6. The band pattern observed with Yb was considerably different, and the difference appears to arise from the presence of a filled 4f shell in the latter case. The most striking feature of this study is the close similarity of the actinide and lanthanide carbonyl C-O stretching frequencies and band patterns to those of transition metal (e.g., Cr, Mo, W, Ta) carbonyls. Since the C-O force constants are sensitive to the ability of the M(O) atom to act as a π-donor, these results are of considerable importance. The authors also report the response of the spectra to annealing (warming and recooling) the matrix.

Warren (2) has employed a molecular orbital approach to estimate the ordering of f orbitals in $(\eta^8\text{-}C_8H_8)_2U$ and in $(\eta^8\text{-}C_8H_8)_2Ln^-$ compounds (Ln = a tripositive lanthanide). In uranocene he finds substantial mixing of the

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uranium $5f_{xyz}$ and $5f_{z(x^2-y^2)}$ orbitals with the $C_8H_8^{=}$ e_{2u} π molecular orbital. On the other hand, the interaction between this ligand orbital and lanthanide 4f orbitals is much less. The ligand field splittings obtained for these complexes can be used to predict the temperature dependence and anisotropy of the magnetic susceptibility. The agreement with those experimental data which exist was found to be better for the 5f case than for the 4f.

Lanthanides

Tsutsui and Ely (3,4,5) have reported in considerable detail on the synthesis and properties of biscyclopentadienyl lanthanide alkyls and aryls. The highly air-sensitive new complexes were synthesized via eq. (1). They were characterized by chemical, spectral (infrared, uv-visible), and magneto-chemical means. The infrared spectra indicate, besides the fact that the cyclopentadienyl ligands are bonded in a pentahapto fashion, that the allyl groups are trihapto (4). This contrasts with the $(\eta^5\text{-}C_5H_5)_3U$- analogues where the allyl moieties are sigma-bonded (6,7). Tsutsui and Ely also synthesized a monocyclopentadienyl bisphenylacetylide complex by a similar procedure [eq. (2)]. The bonding in all of the new complexes is proposed to involve primarily ligand-to-metal charge transfer.

$$(\eta^5\text{-}C_5H_5)_2LnCl + RLi \xrightarrow{THF} (\eta^5\text{-}C_5H_5)_2LnR + LiCl \qquad (1)$$

Ln = Gd, Ho, Er, Yb; R = $C\equiv CC_6H_5$
Ln = Er, Yb; R = CH_3
Ln = Gd, Yb; R = C_6H_5
Ln = Sm, Ho, Er; R = allyl

$$(\eta^5\text{-}C_5H_5)HoCl_2 \cdot 3THF + 2LiC\equiv CC_6H_5 \xrightarrow{THF} (\eta^5\text{-}C_5H_5)Ho(C\equiv CC_6H_5)_2 + 2LiCl \qquad (2)$$

In the visible spectra, the energies of the ligand-to-metal charge transfer bands and the heightened intensities of hypersensitive transitions appear to indicate some covalency in the lanthanide alkyl bond. The magnetic moments of the biscyclopentadienyl alkyls and aryls decrease on lowering the temperature unlike the chloride analogues. This effect also appears to arise from increased covalency in the monohapto metal-ligand interaction. The high concentration of negative charge on the sigma-bonding α carbon atom is the most reasonable explanation for the enhanced covalency.

Baker, Brown, and Raymond (8) have now published a full paper on the molecular structure of the organoytterbium halide dimer $[(CH_3C_5H_4)_2YbCl]_2$. The result of the X-ray diffraction study is shown in Figure 1. The coordination geometry about the lanthanide is somewhat distorted from tetrahedral. The Cl-Yb-Cl angle is 82.05(5)°, while the ring centroid-Yb-ring centroid angle is 126.7° (no standard deviation given). The bridging by chlorine is essentially symmetrical, with Yb-Cl bond distances ranging from 2.628(2) to 2.647(2) Å. The average Yb-C distance is 2.585(7) Å.

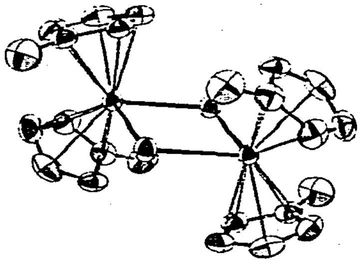


Figure 1. The molecular structure of $[(CH_3C_5H_4)_2YbCl]_2$ from ref. 8.

Solubility data have been reported for $(\eta^5\text{-}C_5H_5)_3Ln$ compounds (Ln = lanthanide) by Borisov, Chugunova, and Devyatykh (9). Data were reported in THF from 15-60°C for the entire lanthanide series. The heats of solution were found to be practically independent of lanthanide and to be ca. 5 kcal/mole. The solubility passes through a maximum in the early lanthanides (La-Sm) and then falls off with increasing atomic number.

Actinides

Ryan, Penneman, and Kanellakopulos (10) have determined the molecular structure of $(\eta^5\text{-}C_5H_5)_3UF$ by X-ray diffraction. This complex is of particular interest because molecular weight measurements suggest that it exists as a dimer in benzene. The structure in the solid state (Figure 2) does not reveal evidence of strong dimer formation. The intramolecular bond angles about uranium are almost identical to those in chloride analogues (11,12), viz. ring centroid-U-F, 99.7(2)°; ring centroid-U-ring centroid, 117.2(1)°. The U-F distance, 2.196(12) Å, is the shortest U-F bond yet observed for a U(IV) fluoride. The average U-C distance is 2.74 Å. The nearest intermolecular

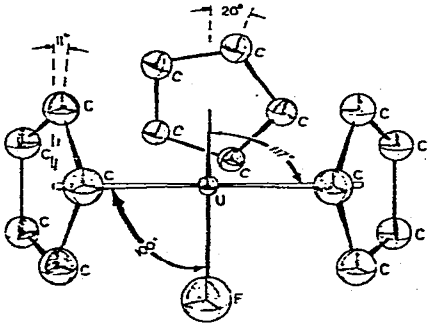


Figure 2. The molecular structure of $(\eta^5\text{-}C_5H_5)_3UF$ from ref. 10.

contact is from a fluorine to a ring hydrogen on a neighboring molecule (ca. 2.6 Å) and though probably an important factor in solid state packing, this interaction seems unlikely to be responsible for dimer formation in solution. The closest intermolecular U-F distance is 3.87 Å and is along the molecular C_3 axis.

Halstead, Baker, and Raymond have now published a full paper (13) on the molecular structure of $(\eta^5\text{-}C_5H_5)_3U$(2-methylallyl). The most interesting observation in this work is the presence of a monohaptoallyl functionality (Figure 3). This solid state result is in accord with solution pmr studies (6) of $(\eta^5\text{-}C_5H_5)_3U$(allyl) which indicate a monohaptoallyl instantaneous structure and a low barrier to sigmatropic rearrangement. The molecular geometry in this compound is quite similar to other $(\eta^5\text{-}C_5H_5)_3U$- structures, with an average ring centroid-U-C(σ) angle of 100°, an average ring centroid-U-ring centroid angle of 117°, and an average U-C(ring) distance of 2.74(1) Å. The U-C(σ) distance was 2.48(3) Å. The reason the allyl group is coordinated in a monohapto fashion, whereas $(C_5H_5)_4U$ possesses four pentahapto rings is explained on the basis of the energy required for reorganization of the uran-

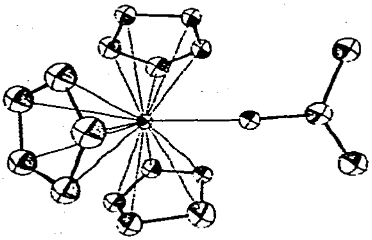


Figure 3. The structure of $(\eta^5\text{-}C_5H_5)_3U(\eta^1\text{-}C_3H_4CH_3)$ from ref. 13.

ium coordination sphere versus the stability gained on entering into a fourth polyhapto interaction.

Perego, Cesari, Farina, and Lugli (14, 15) have reported an X-ray diffraction study of the structures of $(\eta^5\text{-}C_5H_5)_3U$(n-butyl) and of $(\eta^5\text{-}C_5H_5)_3U$-(p-methylbenzyl). The coordination geometry about the uranium (Figures 4 and 5) is again very similar to that of other $(\eta^5\text{-}C_5H_5)_3U$- complexes. The

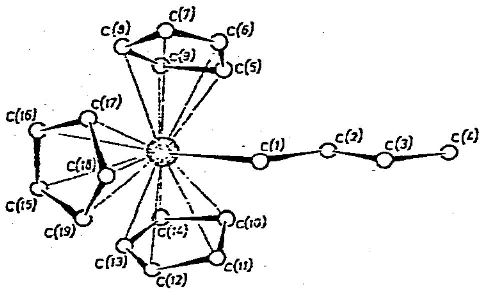


Figure 4. The structure of $(\eta^5\text{-}C_5H_5)_3U(n\text{-}C_4H_9)$ from refs. 14 and 15.

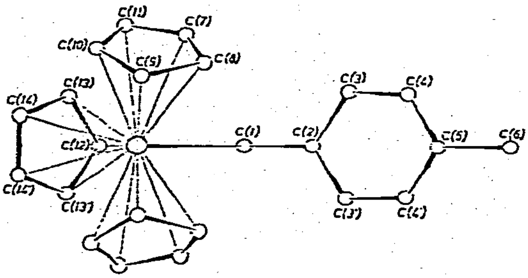


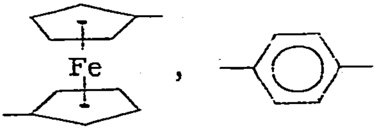
Figure 5. The structure of $(\eta^5\text{-}C_5H_5)_3U(CH_2C_6H_4CH_3)$ from refs. 14 and 15.

U-C(σ) distance in the n-butyl compound was found to be 2.553(22) Å, whereas a contact of 2.425(29) Å was found in the benzyl derivative. For both derivatives, the U-C(1)-C(2) angles were considerably larger than tetrahedral, i.e. 127.9(19)° (n-butyl) and 128.5(13)° (p-methylbenzyl). Intramolecular non-bonded repulsions do not appear to be large enough to induce such a distortion.

Tsutsui, Ely, and Gebala (16) have now related a full account of their studies of complexes containing greater than one $(C_5H_5)_3U$ moiety. These were prepared via reaction (2) and were characterized by chemical, spectral (ir,

$$RLi_2 + 2(C_5H_5)_3UCl \longrightarrow R[U(C_5H_5)_3]_2 + 2LiCl \qquad (2)$$

R =



pmr, mass), and magnetochemical means. The monometallic compounds $(C_5H_5)_3UR$, R = acetylide, ferrocenyl, were also reported. The complexes are similar to other known $(C_5H_5)_3UR$ species in most respects. Large isotropic shifts are observed in the nmr spectra. Unlike $(C_5H_5)_3UCl$ and other $(C_5H_5)_3$-UR compounds, these compounds do not exhibit a levelling off (temperature independence) of their magnetic susceptibility down to 65° K. It is not clear at present whether this interesting phenomenon arises from a difference in the ligand field strengths of the monohapto ligands [a U(IV) ion in a tetrahedral crystal field should in theory exhibit Curie-Weiss behavior down to 0° K (17)] or whether there is exchange coupling between the metal ions.

Marks and Kolb (18) have published a full description of synthetic and spectroscopic experiments with triscyclopentadienyl uranium (IV) tetrahydroborates.

The known BH_4^- derivative as well as boron-substituted derivatives can be prepared from the chloride [eq. (3)-(5)], or from the tetrahydroborate [eq. (6)].

$$(C_5H_5)_3UCl + BH_4^- \longrightarrow (C_5H_5)_3UBH_4 + Cl^- \tag{3}$$

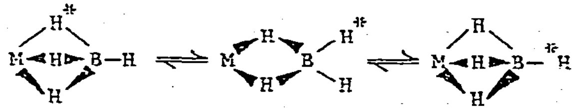
$$(C_5H_5)_3UCl + H_3BCN^- \longrightarrow (C_5H_5)_3UH_3BCN + Cl^- \tag{4}$$

$$(C_5H_5)_3UCl + (C_6H_5)_3BCN^- \longrightarrow (C_5H_5)_3U(C_6H_5)_3BCN + Cl^- \tag{5}$$

$$(C_5H_5)_3UBH_4 + R_3B \longrightarrow (C_5H_5)_3H_3BR + R_2BH \tag{6}$$

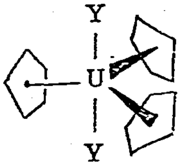
$$R = C_2H_5,\ C_6H_5$$

Vibrational spectra indicate that, with the exception of the cyano complexes, all of the above species have tridentate BH_4^- complexation, i.e. a triple hydrogen bridge between uranium and boron. The pmr spectra exhibit large isotropic shifts, and for $(C_5H_5)_3UH_3BC_6H_5$ it was possible to separate contact and dipolar contributions. This is the first contact shift data for a metal-bound hydride in a paramagnetic complex. The mechanism of unpaired spin (5f) distribution appears to be the same as for the $(C_5H_5)_3UR$ series, i.e. ligand donation to, or polarization by, metal orbitals. Advantage was also taken of the large isotropic shifts to study the fluxional process in $(C_5H_5)_3UBH_4$ which rapidly interchanges bridge and terminal hydrogens. The increased chemical shift difference between the exchanging sites expands the time resolution pmr. It was possible to approach the spectral coalescence point and to estimate $\Delta G^{\ddagger} \approx 5$ kcal/mole for what is most likely a process similar to eq. (7).



(7)

Fischer, Sienel, Landgraf, and Wagner (19) have presented a preliminary report on organouranium compounds of the general type $[(\text{trans-}Y_2)(\eta^5\text{-}C_5H_5)_3\text{-}U(IV)]^{\pm q}$. These are proposed to have pseudo trigonal bipyramidal (D_{3h})



uranium coordination geometries. A number of new $(\eta^5\text{-}C_5H_5)_3UY$ compounds appear to fall into this category, when Y is a bridging ligand such as $C(CN)_3^-$, $Ni(CN)_4^{-2}$, $Pt(CN)_4^{-2}$, and CN^- (20). The new complexes were characterized by near-infrared and visible spectra as well as by temperature-dependent magnetic susceptibility. They all appear to have polymeric structures where each Y ligand bridges two uranium ions. Monomeric examples of this class of compounds include $(C_5H_5)_3U(H_2O)_2^+$ and $(C_5H_5)_3U(DMF)_2^+$.

The syntheses of (indenyl)$_3$ThBr and (indenyl)$_3$UBr have been communicated by Goffart, Fuger, Gilbert, and Hocks (21). These were prepared by the reaction of the actinide tetrabromide with potassium indenide [eq. (8)], followed

$$MBr_4 + 3\,C_9H_7^-K^+ \xrightarrow{THF} (C_9H_7)_3MBr + 3\,KBr \qquad (8)$$
$$M = Th,\ U$$

by extraction with benzene, then pentane. The new compounds were characterized by chemical, spectral (ir, Raman, uv-visible) and X-ray powder diffraction methods. The structures are believed to involve pentahaptoindenyl coordination; the compounds are not isomorphous with the analogous chlorides (22).

Condorelli, Fragala, Tondello, and Zanella (23) have reported and analyzed the gas phase He (I) photoelectron spectra of $(\eta^8\text{-}C_8H_8)_2U$, $(\eta^5\text{-}C_5H_5)_3UCl$, and

$(\eta^5\text{-}C_5H_5)_3UBH_4$. The uranocene data are in agreement with a molecular orbital scheme invoking substantial participation of 5f orbitals in the metal-ligand bonding. Shifts in band positions observed on going to the cyclopentadienyl compounds can be understood in terms of increased positive charge on the uranium ion

Reasons for the thermal instability of uranium(IV) tetraalkyls continue to attract attention. Further evidence that it arises from coordinative unsaturation is provided by the work of Andersen, Carmona-Guzman, Mertis, Sigurdson, and Wilkinson (24). Anionic, presumably six-coordinate complexes could be prepared by the addition of six equivalents of methyllithium, trimethylsilylmethyllithium, or 2-benzyldimethylaminelithium to UCl_4. The crystalline complexes $Li_2U[CH_2Si(CH_3)_3]_6 \cdot 7$tmeda and $Li_2U(C_9H_{12}N)_6 \cdot 7$tmeda (tmeda = tetramethylethylenediamine) are stable at room temperature. The methyl complex decomposes at about 0°C. Isotropically shifted pmr resonances of the hexakis(trimethylsilylmethyl) complex were observed in tetrahydrofuran.

Stretwieser and Walker (25) have reported the synthesis and characterization of the highly substituted uranocene, bis(1,3,5,7-tetraphenylcyclooctatetraene)-uranium(IV). It was prepared by reacting the dianion of the substituted cyclooctatetraene with uranium tetrachloride. In contrast to the unsubstituted analogue, this remarkable new complex is completely air-stable and sublimes unchanged at 400°C/10^{-5} mm.

The electronic and magnetic properties of uranocene have been extensively investigated by Amberger, Fischer, and Kanellakopulos (26). The magnetic susceptibility has now been measured from 1.25 to 298°K, and the results have been interpreted in terms of theoretical crystal field parameters obtained by three different methods: purely electrostatic considerations, the angular overlap model, and Wolfsberg-Helmholtz molecular orbital calculations. The final results are in best agreement with a singly degenerate ground state for uranocene and a doubly degenerate excited state which lies only 17 cm^{-1} higher in energy. An alternative explanation based upon a lower symmetry crystal field and a split doublet ground state cannot be completely ruled out.

Lugli, Brunelli, and Mazzei (27) have communicated chemical and spectroscopic results on the new alkoxyallyl compound $[(CH_3)_3CO]_2U(allyl)_2$. This was prepared by treating tetraallyluranium with t-butanol. Variable temperature isotropically shifted pmr spectra in tetrahydrofuran reveal exchange of free and coordinated THF as well as other dynamic processes indicative of stereochemical nonrigidity.

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