Actinide Metallocarbaborane Complex: Synthesis and X-Ray Structure Determination of the Bis[η^5-(3)-1,2-dicarbollyl]dichlorouranium(IV) Dianion

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Summary The first actinide metallocarbaborane complex, [U(C$_2$B$_9$H$_{11}$)$_2$Cl$_2$]$^{2-}$, has been obtained by reaction of the 1,2-dicarbollide ion with UCl$_4$ in tetrahydrofuran (THF), and a crystal structure determination of its lithium salt has shown the complex anion to have a distorted tetrahedral geometry with pentahapto-bonded dicarbollide ligands.

THE (3)-1,2-dicarbollide ion, $C_2B_9H_{11}^{2-}$, has been shown to form complexes with transition metal ions analogous to the metallocenes of the cyclopentadienide ion.[1] Its open pentagonal face, which contains the two carbon atoms, acts as a six π-electron donor isoelectronic with $C_5H_5^-$. This bonding face, however, is substantially larger than that of cyclopentadienide, and possesses a higher formal negative charge. Both these differences should be favourable to the stability of an actinide complex because of the large co-ordination numbers and high formal oxidation states normally found in actinide organometallic chemistry. The large, highly charged cyclo-octatetraenide dianion is more tightly bound in actinide complexes than is cyclopenta-

dienide, and the same behaviour might be expected for dicarbollide dianion. Based upon these considerations, we have prepared and structurally characterized the first example of an actinide carbaborane complex, the ion [U(C$_2$B$_9$H$_{11}$)$_2$Cl$_2$]$^{2-}$.

The yellow-orange complex is obtained in high yield from the reaction of UCl$_4$ with 2 mol. equiv. of $C_2B_9H_{11}^{2-}$ in THF at 0 °C under inert atmosphere conditions. Salts of several cations were prepared. The THF-solvated lithium salt, [Li(C$_4$H$_8$O)$_4$]$_2$[U(C$_2$B$_9$H$_{11}$)$_2$Cl$_2$], was found to be most suitable for structure analysis. *Crystal data:* space group Cc, $a = 26.410(7)$, $b = 11.248(5)$, $c = 20.163(6)$ Å, $\beta = 102.35(1)°$, $D_c = 1.32$ g cm^{-3} for $Z = 4$. Intensity data were collected at room temperature by automatic diffractometer methods using Mo-K_α radiation. The sample crystal, which is oxygen- and moisture-sensitive and is extremely susceptible to loss of solvent, was mounted in a thin-walled glass capillary. Full-matrix least-squares refinement of 322 parameters using 2020 unique data for which $F^2 > 3\sigma(F^2)$ led to final discrepancy indices of $R = 0.058$ and $R_w = 0.061$.

The Figure illustrates the geometry of the $[U(C_2B_9H_{11})_2Cl_2]^{2-}$ ion, which approximates C_{2v} symmetry. The co-ordination geometry may be described as highly distorted tetrahedral, with the *pentahapto*-bonded carbaborane ligands opened such that their face centroids form an angle of 137° about the uranium atom. The Cl–U–Cl angle is 90·3(5)°.
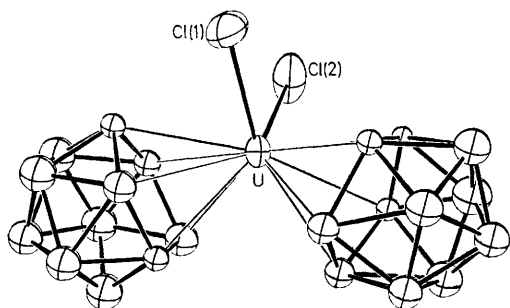

FIGURE The molecular structure of the bis(η^5-(3)-1,2-di-carbollyl)dichlorouranium(IV) dianion, with thermal ellipsoids drawn at the 20% probability level.

The two U–Cl bond lengths are experimentally identical, and average 2·599(6) Å, in good agreement with the values of 2·559(16) found in $U(C_5H_5)_3Cl$,[2] 2·627(2) in $U(C_5H_4CH_2Ph)_3Cl$,[3] and 2·593(3) Å in $U(C_9H_7)_3Cl$.[4] The identities of the carbaborane carbon atoms are not defined unambiguously by our data because of the effects of high thermal motion and possible rotational disorder of the facial boron and carbon atoms. Isotropic thermal parameters for the carbaborane atoms vary over a range of *ca.* 3—10 Å², and typical values for THF carbon atoms fall within the range 10—20 Å². All carbaborane atoms were treated as boron. The average bonded U–B (or C) distance is 2·73(2) Å, similar to U–C distances found in U^{IV} cyclopentadienyl complexes.[5] The 1,2-dicarbollide ligands have normal geometries; they exhibit approximate symmetry C_{5v} (neglecting the difference between C and B) expected of this icosohedral fragment. Within these ligands, bond distances which are clearly B–B average 1·76(3) Å, typical of the values found in transition metal dicarbollide complexes.[6] The lithium counterions exist as discrete $[Li(C_4H_8O)_4]^+$ units, in which the oxygen atoms of the THF molecules co-ordinate tetrahedrally around the lithium atom. Average values are 1·92(3) Å for the Li–O contacts and 109(1)° for the O–Li–O angles.

The precision of this determination is limited by high thermal motion, particularly in the THF molecules. Individual bond length standard deviations are *ca.* 0·01 for U–Cl, 0·03 for U–B, and 0·06 Å for B–B and C–C bonds. Collection of a low-temperature data set is in progress.

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