Structure of Some Uranium(IV) Chelates in Solution

By T. H. SIDDALL, TERT.,* and W. E. STEWART
(*Savannah River Laboratory, E. I. du Pont de Nemours and Co., Aiken, South Carolina* 29801)

Summary N.m.r. data in solution indicate that acetylacetonatouranium(IV) and related compounds have a less symmetrical structure than a D_2 square antiprism or a D_{2d} triangular dodecahedron.

X-RAY data in the *solid state*[1,2] and various arguments[3,4] indicate that acetylacetonatouranium(IV) and related compounds might have either the D_2 square antiprism or the D_{2d} triangular dodecahedron as the ground-state co-ordination polyhedron. We report here ^{1}H n.m.r. data that indicate a less symmetrical structure for acetylacetonatouranium(IV) and related compounds *in solution.*

The large chemical shifts that arise, because of the paramagnetism of U^{IV},[5,6] provide a sensitive probe for structural variations. While *intra*molecular exchange processes are rapid (on the n.m.r. time scale) in these compounds, intermolecular exchange is slow. Mixing two different chelates such as $U[EtC(O)CHC(O)Et]_4$ and $U[Bu^tC(O)$-$CHC(O)Bu^t]_4$ produces separate n.m.r. signals for all five molecular species including the three mixed chelates. A similar situation has been reported for 8-co-ordinate chelates of other metals.[7–9] N.m.r. data are given in the Table for the methide [–C(O)CHCO–] proton of several chelates. N.m.r. data for other protons in these chelates show the expected large chemical shifts due to U$^{\mathrm{IV}}$ paramagnetism and multiplicity consistent with the methide signals, but are not relevant to the discussion and are not given.

N.m.r data for U$^{\mathrm{IV}}$ *chelates* (*methide signal*) *in* $\mathrm{CDCl_3}$ *at* 30°

Chelate	Shift downfield p.p.m. from $\mathrm{Me_4Si}$
$\mathrm{U[CH_3C(O)CHC(O)CH_3]_4}$	12·5
$\mathrm{U[EtC(O)CHC(O)Et]_4}$	11·7
$\mathrm{U[Pr^iC(O)CHC(O)Pr^i]_4}$	12·0
$\mathrm{U[Bu^tC(O)CHC(O)Bu^t]_4}$	12·7
$\mathrm{U[Bu^tC(O)CHC(O)Bu^t]_3[EtC(O)CHC(O)Et]}$	14·1[a] (Bu^t), 7·7(Et)[a]
$\mathrm{U[Bu^tC(O)CHC(O)Bu^t]_2[EtC(O)CHC(O)Et]_2}$	15·2[a] (Bu^t), 8·7(Et)[a]
$\mathrm{U[Bu^tC(O)CH(CO)Bu^t][EtC(O)CHC(O)Et]_3}$	17·1[a] (Bu^t), 9·8(Et)[a]

[a] Assigned in solutions of mixtures by varying relative concentration. See ref. 7.

The methide proton shifts for unmixed complexes all lie within 1 p.p.m., but for the mixed chelates the shifts are spread out over more than 9 p.p.m. We believe that this observation can be explained only by assuming *two* (or more) nonequivalent sites for chelate rings in all of these molecules, unmixed as well as mixed. Signals from the different sites are not separately observable because the observed shifts reflect the averaged shifts for the sites. Because the internal geometry of the chelate ring is essentially independent of the alkyl substituents, only second-order effects are available to change the shifts of the two sites from molecule to molecule. As a consequence, the observed shifts for unmixed chelates vary little. However, in the mixed chelates, each ligand may occupy one site preferentially. Therefore, the shifts for each ligand are not averages from equal populations. (However, separate shifts in a mixed chelate, when averaged together on a weighted basis, are very close to those for the unmixed molecules). The range of shifts for methide protons in mixed chelates might, on this basis, be less for similar ligands and more for dissimilar ligands. This we observe. For mixtures of $\mathrm{U[Pr^iC(O)CHC(O)Pr^i]_4}$ and $\mathrm{U[EtC(O)CHC(O)Et]_4}$ the range is only 3·2 p.p.m. For mixtures of $\mathrm{U[EtC(O)CHC(O)Et]_4}$, with a variety of $\mathrm{U[R^1C(O)CHC(O)R^2]_4}$, where $\mathrm{R^2}$ is a perfluoroalkyl group, the range of shifts is at least 25 p.p.m.

On this basis, the ground state polyhedron for these U$^{\mathrm{IV}}$ chelates *in solution* cannot be the D_2 square antiprism or the D_{2d} dodecahedron. In both of these polyhedra, all four sites are equivalent and there cannot be two (or more) nonequivalent sites.

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