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Di-π-cyclooctatetraenethorium

Sir:

The relative stability of the recently synthesized di-π-cyclooctatetraeneuranium from cyclooctatetraene (COT) dianion and uranium tetrachloride suggests that significant stabilization is afforded by overlap of the highest occupied (E_2) molecular orbitals of the two rings with vacant f orbitals (f_{xyz},$f_{z(x^2-y^2)}$) of the central metal.[1] It is clearly important to compare the chemistry of similar complexes with other actinide and with lanthanide rare-earth metals. We report here the preparation and some of the chemistry of the thorium analog.

A suspension of dry thorium tetrachloride in tetrahydrofuran was added to 2 equiv of K_2COT in THF cooled to Dry Ice temperature. The mixture was allowed to warm to room temperature with stirring overnight. The solvent was evaporated from the yellow reaction mixture and the residue was sublimed at 0.01 Torr and 160° to produce the product as fine bright yellow crystals. The mass spectrum showed a parent peak at *m/e* 440 ($Th(COT)_2$) with important fragment peaks at *m/e* 336 (ThCOT), 111 and 109 (unassigned), and 104 (COT). Resublimation gave crystals suitable for X-ray analysis. The compound is isomorphous with di-π-cyclooctatetraeneuranium[2] (uranocene), and the thorium compound therefore also has the D_{8h} sandwich structure.[3]

$Th(COT)_2$ ("thoracene") is decomposed readily by water. It is unstable in air but does not enflame, as does uranocene; crystals of the thorium compound change in color from yellow to brown after a few minutes' exposure to air. The compound decomposes without melting at temperatures above 190° and explodes if heated to red-hot. Thoracene is insoluble in most organic solvents, *e.g.*, $CHCl_3$, CCl_4, THF, benzene, acetone, etc.; it is soluble in DMSO, but the nmr spectrum of this solution shows a complex multiplet at 6.2 ppm rather than the sharp singlet expected for a D_{8h} sandwich structure. On exposure to air for several seconds the nmr spectrum changes to the sharp singlet of COT at 5.75 ppm. We suggest that thoracene forms a complex with DMSO which destroys the symmetry of the rings and changes the structure to that of a diene–transition metal type. This chemistry may be rationalized as follows if bonding interaction with 5f orbitals is important in the di-π-cyclooctatetraeneactinide structures. We have suggested[1] that the two highest energy electrons in uranocene are in a back-bonding $f_{x(z^2-3y^2)}$, $f_{y(3y^2-x^2)}$–E_{3u} combination. These MO's are vacant in thoracene and could produce a Lewis acid capability that would lead to the observed reactions with Lewis bases such as DMSO and water. The extension of this chemistry to other actinides and to the lanthanide rare earths is in progress.

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The Reaction of a Sulfonyl-Chymotrypsin with Hydrogen Peroxide. Generation of a Hydroperoxy Enzyme

Sir:

Generating a reactive free radical at a specific site on a protein and allowing the radical to react with its surroundings would be useful as a chemical probe for three-dimensional structure in solution.[1] The present work was designed to produce a peroxide moiety (which could then be decomposed by photolysis) at the active site of the serine protease chymotrypsin. In this report the preparation of an apparently catalytically active hydroperoxy enzyme is described.

Benzylsulfonyl-chymotrypsin (modified at serine-195) was prepared according to the published procedure.[2] In all experiments it had less than 0.8% catalytic activity. When incubated at pH 7 with H_2O_2 as shown in Figure 1, catalytic activity was fairly rapidly restored until deactivation of enzyme became a significantly competing process (about 12 hr). As previously reported,[2] benzylsulfonyl-chymotrypsin was completely stable under the same conditions without H_2O_2. Native enzyme under the reaction conditions lost activity only very slowly, while the same reaction with the sulfonate and *n*-propyl hydroperoxide resulted in an extremely slow restoration of catalytic activity, probably due to H_2O_2 impurity.[3]

Variation in pH of the reactivation mixture resulted in a regular increase in the rate of reactivation from pH 4 to about pH 7 (the optimum). At much above pH 7 activity was lost at a rate comparable to its restoration.

The product of the H_2O_2 reaction was isolated by exhaustive dialysis (2 to 5 ml *vs.* two changes of 2 l. of 10^{-3} *M* HCl, then four changes of double distilled water) followed by lyophilization. Further experiments were performed on this hydrogen peroxide free material.

From the simple organic system we would expect that the dominant process might be (1) by an SN2 displace-

$$E\text{–}CH_2OSO_2CH_2C_6H_5 + {}^-OOH \longrightarrow E\text{–}CH_2OOH + C_6H_5CH_2SO_3^- \quad (1)$$

(1) A carbene approach to this problem has been taken by Westheimer: J. Shafer, P. Baronowsky, R. Laursen, F. Finn, and F. H. Westheimer, *J. Biol. Chem.*, 241, 421 (1966); R. Vaughan and F. H. Westheimer, *J. Am. Chem. Soc.*, 91, 217 (1969).
(2) A. M. Gold and D. Fahrney, *Biochemistry*, 3, 783 (1964); 5, 2911 (1966).
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