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Preliminary communication

BIS-π-(1,3,5,7-TETRAPHENYLCYCLOOCTATETRAENE)URANIUM, AN AIR STABLE URANOCENE

ANDREW STREITWIESER, JR. and ROGER WALKER
Department of Chemistry, University of California, Berkeley, California 94720 (U.S.A.)

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Summary

Bis-(1,3,5,7-tetraphenylcyclooctatetraene)uranium has been prepared by the reaction of 1,3,5,7-tetraphenylcyclooctatetraene dianion with UCl_4. The compound sublimes unchanged at 400 °C and 10^{-5} Torr and is stable to air. This remarkable stability is undoubtedly due to steric blocking of the central uranium by the phenyl substituents.

In our continuing study of the chemistry of actinide π-complexes we have been seeking properties which would lead to greater air-stability of these highly air-sensitive compounds. Many of the reactions of uranocene (di-π-cyclooctatetraeneuranium) appear to involve attack at the central metal [1]. If this generalization extends to the facile reaction of such compounds with oxygen, the use of sufficiently bulky ring substituents could perhaps sterically inhibit such reaction. This hypothesis has now been verified by the preparation of bis-π-(1,3,5,7-tetraphenylcyclooctatetraene)uranium, a remarkably stable substance.

The ligand, 1,3,5,7-tetraphenylcyclooctatetraene (TPCOT), was synthesized via a modification of the procedure of White and Dunathon [2], and was obtained as white needles, m.p. 194-195 °C; NMR: δ 7.35 (mult., 5H); δ 6.7 (s, 1H). The hydrocarbon was converted to the dianion by treatment with potassium [3] in THF for 12 h at room temperature to give bright orange crystals of the potassium salt; NMR: δ 6.8 (s, 1H); δ 7.2, 7.6 (mult., 5H) (referred to THF).

Treatment of two equivalents of the potassium salt with one equivalent of UCl_4 in THF at room temperature for 12 h precipitated 97% of $(TPCOT)_2U$ as an olive green amorphous solid. This material was extracted with THF in a Soxhlet apparatus for 12 d and sublimed at 400 °C and 10^{-5} Torr to give 64% of green black crystalline $(TPCOT)_2U$. (Anal. found: C, 72.56; H, 4.65; U, 21.45. $C_{32}H_{48}U$ calcd.: C, 72.85; H, 4.59; U, 22.56%.) The compound is insoluble in most common solvents and is only slightly soluble in THF. The visible spectrum in THF (taken in a 10 cm cell) shows λ_{max} 658, 697 and 709 nm with shoulders at 666 and 691 nm. This spectrum is similar to that of related uranocenes with the expected shift towards longer wavelengths [3]. The mass spectrum shows *m/e* peaks at 1055 [$(C_{32}H_{24})_2U^+$], 646 ($C_{32}H_{24}U^+$) and 408 ($C_{32}H_{24}^+$), consistent with the assigned structure [1,3].

The stability of this compound is remarkable. Not only does it sublime unchanged at 400 °C but it is stable in air and has shown only slight decomposition after weeks in the open. Well formed crystals appear to exhibit even greater stability; a crystal mounted for X-ray structure determination showed no signs of decomposition after several weeks. Air oxidation was accomplished by keeping the compound at 120 °C for 4 d and regenerated TPCOT. The compound is also stable for hours in boiling aqueous THF.

The properties of this compound provide striking confirmation of the notion that the reaction of uranocenes with oxygen involves direct rate-determining attack at the metal rather than an electron transfer involving the ligand. We expect the X-ray structure determination currently in progress to show the phenyl groups twisted with respect to the COT rings to provide an effective bar to such attack at the central metal. This concept is now being expanded to other actinide derivatives.

Finally, the magnetic susceptibility of $(TPCOT)_2U$ is another significant property, particularly in view of a recent interpretation [4] of the deviation of uranocene and several substituted uranocenes from Curie—Weiss behavior at low temperatures [5]. $(TPCOT)_2U$ shows accurately linear Curie—Weiss behavior down to 4 K. The significance of this and related results will be discussed separately [6].

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