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Uranium-to-Uranium Bonds: Do They Exist?

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Over the last few years (although the roots go back further) there has been an avalanche of work showing that both molybdenum and tungsten in oxidation states from II to V have a profound tendency to form metal–metal bonds of orders from 1 to 4. Hundreds of compounds with Mo–Mo, W–W (and even some W–Mo) bonds of all orders are well established, and such bonding is one of the most important features of the chemistry of these two elements [1, 2]. Naturally, this has repeatedly provoked the question "What about the next group VI element, uranium?" No deliberate effort has previously been made to answer this question, nor was an answer forthcoming spontaneously from the literature, apart from whatever interpretation one might choose to place upon the fact that no structure has yet appeared containing a U–U bond of any order. Conversely, however, it did not appear that anyone had performed a planned, definitive experiment, *i.e.*, had attempted to foster the formation of such bonds by choosing auspicious combinations of oxidation state and ligands.

We report here the results of such an experiment. It is well documented that for binuclear molybdenum and tungsten compounds in their oxidation states III–V the presence of alkoxide ligands (either terminal or bridging) regularly leads to the formation of M–M bonds of orders 3, 2 or 1 for oxidation numbers III, IV and V, respectively [1, 2]. Alkoxo-bridged binuclear compounds of Mo^{IV} or W^{IV} contain double bonds [3–7] and those containing Mo^{V} or W^{V} have single bonds [8–10]. For trinuclear compounds of molybdenum and tungsten in oxidation state IV M–M single bonds are formed [1, 11, 12]. There are also tetranuclear species with OR bridges and M–M bonds [13]. We therefore reasoned that if uranium had any significant tendency to resemble molybdenum and tungsten in forming U–U bonds, this tendency should manifest itself in the structures of the alkoxides of uranium(IV) and uranium(V), $[U(OR)_4]_x$ and $[U(OR)_5]_x$. Such compounds had been prepared but we found no reports of structural investigations [17]. We therefore undertook structural studies of representative compounds by means of X-ray crystallography. We first attempted to prepare what Gilman *et al.* [14] had described as uranium(IV) t-butoxide. In our hands, this preparation has given the considerably more interesting oxo compound $U_3O(OBu)_{10}$ [15]. An ORTEP view of the $U_3O(OC)_{10}$ core and some key distances [16] are presented in Fig. 1. The trinuclear unit is strikingly similar to that in $Mo_3O(OCH_2CMe_3)_{10}$ in general structure. The U···U distance of 3.576(1) Å, however, shows that no metal–metal bonds are formed, whereas in the $Mo_3O(OR)_{10}$ compounds [12] there are Mo–Mo single bonds (*ca.* 2.5 Å).

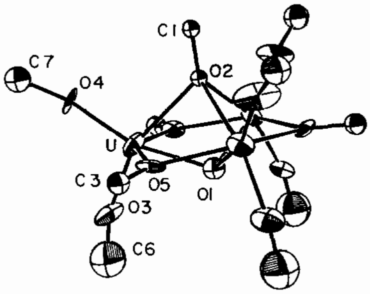

Fig. 1. ORTEP view of the central $U_3O(OC)_{10}$ skeleton. Pertinent distances are U···U = 3.576(1) Å, U–(μ_3-O) = 2.27(3) Å, U–(μ_3-OR) = 2.61(3) Å, U–(μ_3-OR) = 2.375(7) Å, U–OR(av) = 2.10(3).

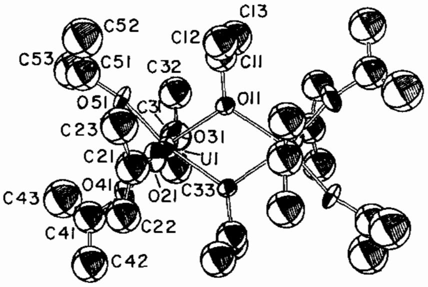

Fig. 2. ORTEP view of $U_2(OPr^i)_{10}$. Some important average distances are: U···U = 3.789(1) Å, U–(μ_2-O) = 2.29(1) Å, U–OR = 2.03(1) Å.

We next prepared $U_2(OPr^i)_{10}$ by following, without difficulty, a procedure of Gilman *et al.* [18]. The structure was determined [19] and, as shown in Fig. 2, it lacks a U–U bond, even though its general shape would be conductive to the formation of such a bond. The U···U distance is 3.789(1) Å.

While we are not suggesting that on the basis of these two structural results all hope of observing U–U bonds is futile, we do feel that such hopes are rather dim. Only, perhaps, in oxidation state III might such bonds occur, but chemistry in this state is limited and difficult. As for the oxidation states IV and V, the types of compounds we have chosen

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would appear to be as favorable as possible and thus indicate that U^{IV} and U^{V} have little if any capacity to form U=U or U–U bonds. The reason for this would appear to be that in these ions the electrons reside in 5f orbitals and that these orbitals are unsuitable for adequate overlap with similar orbitals on adjacent metal atoms. While it is fairly obvious [20] that the strong shielding of 4f orbitals by the $5s^2 5p^6$ shell virtually excludes them from participation in all kinds of bonding (including Ln–Ln bonds), the situation is less clean-cut for the actinides. The 5f functions extend appreciably into the $6s^2 6p^6$ shell [20] and there is evidence from PE [21a] and electronic [21b] spectroscopy that 5f electrons participate in some forms of bonding. We feel that our observations show that in spite of this, 5f–5f overlap is insufficient to stabilize U–U bonds.

Acknowledgement

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16 Pale green crystals were obtained by slow cooling of a hexane solution. Space group $P6_3mc$ (#186), $a = b =$ 18.256(4) Å, $c =$ 11.013(2) Å, $V =$ 3178. (2), graphite monochromated Mo Kα, R = 0.048, R_w = 0.058.

17 After the completion of our work we did find one pertinent report in which the structure of $(\eta^3\text{-}C_3H_5)_2(OPr^i)U(\mu\text{-}OPr^i)_2U(OPr^i)(\eta^3\text{-}C_3H_5)_2$, a compound of uranium(IV) is described. The U···U distance is not given but can be calculated to be 3.861(1) Å. *Cf.* M. Brunelli, G. Perego, G. Lugli and A. Mazzei, *J. Chem. Soc. Dalton,* 861 (1979). This result adds further weight to our conclusion that neither U^{IV} nor U^{V} is inclined to form U–U bonds.

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19 Yellow-green dichroic crystals were obtained by slow cooling of an isopropyl alcohol solution: Space group $P\bar{1}$ (#2), a = 10.974(3) Å, b = 12.226(3) Å, c = 10.002(2) Å, α = 111.56(2)°, β = 110.09(2)°, γ = 67.87(2)°, V = 1122.9(4) Å^3, graphite monochromated Mo Kα, R = 0.048, R_w = 0.059.

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