Uranium Compounds

DOI: 10.1002/anie.200705350

The First *cis*-Dioxido Uranyl Compound under Scrutiny

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actinides · carboxylate ligands · structure elucidation · uranium

The discovery of a *cis*-dioxido uranyl compound, an exciting event and a milestone in the history of actinide chemistry, was recently reported in this journal by P. B. Duval et al.[1] However, several peculiar points in the synthesis and structure of this compound, $[UO_2(fcdc)(thf)\cdot fc]_n$ (fcdc = 1,2-ferrocenedicarboxylate, fc = ferrocene), appeared questionable to us. The particularly easy and reversible formation of this polymeric product from uranyl acetate dihydrate and ferrocenecarboxylic acid (fccH), occurring at room temperature and involving for each uranyl unit the activation, breaking, and building of two C−H and two C−C bonds, seemed to us extraordinary and, it must be said, quite difficult to believe. The ^1H NMR spectra in CD_3OD, and their interpretation concerning the fluxional behavior of the compound in solution, were not understandable to us. The crystal structure was refined in the *Ama*2 space group to a R_1 factor of 4.99 %. However, examination of the Crystallographic Information File deposited at the Cambridge Crystallographic Data Centre revealed several anomalies. The THF moiety is affected by very large disorder effects and some displacement ellipsoids are clearly anomalous. This last point is particularly apparent in the coordinated fcdc molecule, in which some atoms of the aromatic ring bearing the acid groups are affected with extremely anisotropic displacement parameters, whereas the acid groups themselves have large, but quite isotropic parameters. The C4−C7 bond, which connects these two parts, is out of the usual range, as indicated by Duval et al. It is also surprising for the O-U-O angle of 70°, which is considerably smaller than the O-M-O angles in *cis*-dioxido transition-metal complexes, to be associated with U−O distances equal to those in *trans* uranyl complexes. All these observations indicated that a closer look at the structure, which is an essential part of the paper, was warranted, considering the importance of the claim at stake.

To settle these doubts, we decided to reproduce the synthesis of this compound. By following the same procedure as described by Duval et al, starting from a 1:2 mixture of $[UO_2(OAc)_2(H_2O)_2]$, where OAc is acetate, and fccH in CH_2Cl_2/THF, we did not obtain the 80–83 % yield of red crystals as reported in ref. [1]. We repeatedly observed instead the formation of a few small red microcrystals, not suitable for X-ray diffraction, along with a reddish-orange powder and other dark material. Dissolution of this mixture in pyridine or methanol gave red solutions which, upon addition of pentane, deposited red crystals of $[UO_2(fcc)_2(py)_2]\cdot py$ (**1**) and $[UO_2(fcc)_2(MeOH)]_2\cdot 2MeOH$ (**2**), respectively, in approximately 80 % yield. The crystal structures of **1** and **2** are shown in Figure 1 and Figure 2, respectively, together with selected bond lengths and angles; the dimeric structure of **2** is quite similar to those of $[\{UO_2(OAc)_2(L)\}_2]$ (L = Ph_3AsO,[2a] Ph_3PO,[2b] and AcOH[2c]), the *trans* uranyl units being bound to one terminal (chelating) and two bridging carboxylate ligands. It can be noted that compound **2** was obtained in the very solvent used for the NMR spectroscopic study by Duval et al. A large quantity of red crystals, also of sufficient quality for an accurate and unambiguous crystal-structure determination, was obtained when an excess of fccH (3 or 4 molar equivalents) was used in its reaction with $[UO_2(OAc)_2(H_2O)_2]$ in THF; indeed, this excess should shift the equilibrium postulated by Duval et al towards the formation of the *cis*-dioxido uranyl compound.[1] The one-dimensional polymeric crystal structure of the compound obtained from this reaction, $[UO_2(fcc)_2(H_2O)\cdot thf]_n$ (**3**; Figure 3), is quite similar

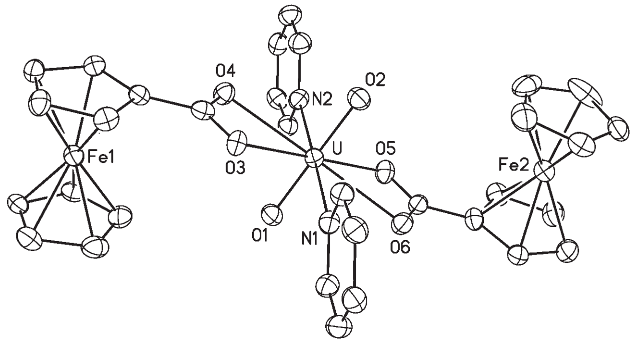

Figure 1. Crystal structure of compound **1** with thermal ellipsoids set at 50 % probability. The hydrogen atoms and the solvent molecule are omitted. Selected bond lengths [Å] and angles [°]: U–O1 1.774(3), U–O2 1.774(3), U–O3 2.451(3), U–O4 2.503(3), U–O5 2.466(3), U–O6 2.474(3), U–N1 2.596(3), U–N2 2.586(4); O1-U-O2 179.14(14).

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200705350.

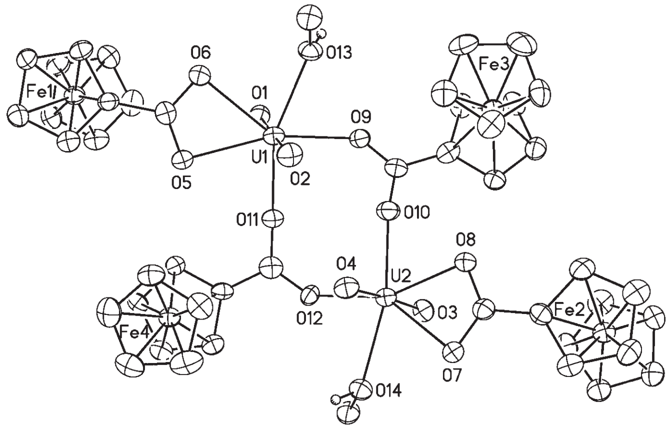

Figure 2. Crystal structure of compound **2** with thermal ellipsoids set at 40% probability. The carbon-bound hydrogen atoms and the solvent molecules are omitted. Selected bond lengths [Å] and angles [°]: U1–O1 1.781(5), U1–O2 1.758(5), U1–O5 2.431(6), U1–O6 2.492(6), U1–O9 2.378(6), U1–O11 2.279(5), U1–O13 2.401(6), U2–O3 1.763(6), U2–O4 1.740(6), U2–O7 2.489(5), U2–O8 2.435(6), U2–O10 2.263(5), U2–O12 2.349(5), U2–O14 2.416(6); O1-U1-O2 177.5(3), O3-U2-O4 176.2(2).

to that of $[UO_2(OAc)_2(H_2O)\cdot H_2O]_n$.[3] As expected, crystallization of **3** from pyridine/pentane gave crystals of **1**.

In none of our experiments did we obtain crystals with unit cell parameters equal to those reported for the *cis*-dioxido uranyl complex $[UO_2(fcdc)(thf)\cdot fc]_n$, but it can be noted that the *a*, *b*, and *c* parameters in compound **3** are close to *b*, 2*a*, and *c*, respectively, in the reported compound. However, the crystal system is different since **3** crystallizes in the monoclinic, centrosymmetric space group $P2_1/c$ with a β angle of 92.774(4)°. The origins of this discrepancy between the two experiments cannot be traced with certainty at present, but the hypothesis of a twinned crystal having led to an erroneous structure with a spurious *cis*-dioxido group seems possible. Unfortunately, we were unable to get the structure factors file for the *cis*-dioxido species from Duval et al. In any case, **1**, **2**, and **3** are the expected, and quite unremarkable, reaction products, resulting from substitution of OAc for fcc ligands, and their crystal structures do not present any anomaly. It may appear quite puzzling that these or similar simple compounds were seemingly never obtained by Duval et al. during their study of this system.

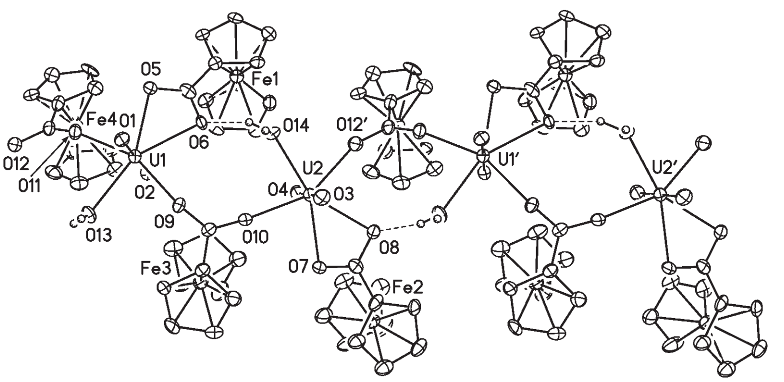

Figure 3. Crystal structure of compound **3** with thermal ellipsoids set at 40% probability. The carbon-bound hydrogen atoms and the solvent molecules are omitted, hydrogen bonds are drawn as dashed lines. Symmetry code: $' = x+1, y, z$. Selected bond lengths [Å] and angles [°]: U1–O1 1.762(7), U1–O2 1.758(7), U1–O5 2.447(7), U1–O6 2.463(6), U1–O9 2.309(6), U1–O11 2.285(6), U1–O13 2.430(7), U2–O3 1.762(7), U2–O4 1.758(8), U2–O7 2.421(7), U2–O8 2.511(6), U2–O10 2.295(7), U2–O12′ 2.302(7), U2–O14 2.402(6); O1-U1-O2 179.3(4), O3-U2-O4 178.8(4).

The ^1H NMR spectra of **1**–**3** in CD_3OD (200 MHz) at 25 °C exhibit, in addition to the signals corresponding to the pyridine (in **1**) or THF (in **3**) molecules, three resonance signals in the intensity ratio of 5:2:2 assigned to the fcc ligand. The chemical shifts of these resonance signals are identical for **1**–**3**, and are also identical to those which are visible in the spectra attributed to $[UO_2(fcdc)(thf)\cdot fc]_n$. Upon lowering the temperature, these resonance signals were split into two sets of three signals in the same intensity ratio of 5:2:2. These features, which were also observed on the spectra attributed to the *cis*-dioxido uranyl complex, can be easily explained by the presence in solution of an equilibrating mixture of two conformers of $[UO_2(fcc)_2(CD_3OD)_x]$, the two fcc ligands being, respectively, in *cis* and *trans* positions with respect to the uranyl equatorial plane. The strong absorption band at 933 cm^{-1} in the IR spectrum of **3** in Nujol mull is assigned to the UO_2 stretching vibration mode; the IR spectrum of **3** is distinct from that reported for $[UO_2(fcdc)(thf)\cdot fc]_n$, but it is peculiar that the two bands assigned to the *cis* dioxido group in this compound, 935 and 916 cm^{-1}, are also visible on the spectrum of fccH.

In conclusion, we have failed to reproduce the results reported by Duval et al., but we have isolated instead three compounds of much more usual nature, containing *trans*-dioxido uranyl ions and indicating no strange reaction of fcc. It seems therefore that the existence of *cis*-dioxido uranyl ions should still be considered as an open question.

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