Inorganica Chimica Acta, 65 (1982) L211–L213

Infrared and X-Ray Photoelectron Evidence for a Cation Stabilized Hydroxy-Bridged Uranyl Species, $[(UO_2^{2+})_2(OH)_2]^{2+}$

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Received July 3, 1982

This laboratory recently reported the synthesis and structure of the uranium dimer complex, di-μ-aquo-bis(dioxobis(nitrato)uranium(VI)) di-imidazole [1] (Fig. 1). Although the hydrogen atoms between the imidazole molecules and the bridging oxygen atom species were not located during the least-squares refinement of the crystal structure, they were assumed to be associated with the oxygen to form a water bridge; subsequent additional attempts using electron density difference maps to find the hydrogen atoms were also unsuccessful. This assumption of the hydrogen atoms being part of water molecules was made, because previous structurally documented hydrolysis products of uranium [2] were unstable outside the reaction medium in which they were formed. Complex (I) is stable with respect to both air and moisture and can be stored without special precautions. This report details experimental infrared and x-ray photoelectron data that would indicate the hydrogen atoms could instead be localized on the 'pyridine' nitrogen of the imidazole, thus affording a bridged hydroxy uranyl complex that is stabilized by imidazolium cations that are adjacent to hydroxy ligand bridges.

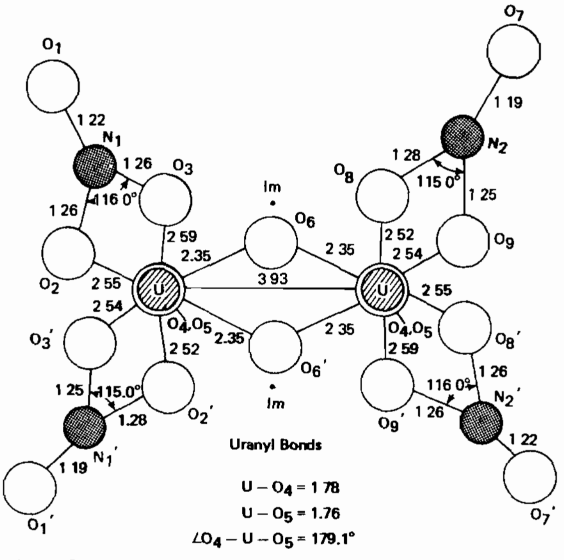

Fig. 1. Structure of Complex (I).

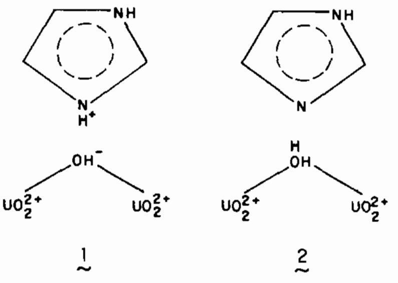

Fig. 2. Two possible bonding modes involving the imidazole-oxygen bridge.

Experimental

The same group of crystals used for the x-ray crystallographic structure work [1] was used for the present study. Infrared spectra were taken as Nujol mulls between KBr plates using a Perkin-Elmer Model 283 infrared spectrophotometer, and x-ray photoelectron spectra were obtained on a McPherson Model 36 spectrometer using Mg K_α (1253.6 eV) radiation. The photoelectron spectra were recorded as previously reported [3], assigning the contaminant principal carbon 1s photoelectron line a value of 285.0 eV. Samples were ground to fine powders and applied to double-sided Scotch brand sticky tape before being placed in the vacuum chamber for analysis. Samples were checked visually for decomposition after spectra were taken, but none was detected. The spectra were also time-independent, indicating a lack of decomposition of the samples in the X-ray beam.

Results and Discussion

As reported earlier [1], the dimeric compound (Fig. 1) consists of two uranyl ion centers that are joined by either aquo (as originally postulated) or hydroxy bridging ligands. The two uranium atoms are 3.93 Å apart. If the bridges are indeed water molecules, the complex is a coordination isomer of uranyl nitrate hexahydrate. In uranyl nitrate hexahydrate, the two coordinated terminal water molecules are *trans* to each other [4]; the two bidentate nitrate anions are also *trans* to each other. Compound I, however, presents a case in which the nitrate

0020-1693/82/0000-0000/$02.75

TABLE I. X-Ray Photoelectron Data for Complex (I) and $UO_2(NO_3)_2 \cdot 6H_2O$.

Compound	Binding energies[a,b] peak widths, and intensity ratios		
	O_{1s}	FWHM[c]	Intensity ratio
Complex (I)	533.1	2 4	2
	531.6	2.6	1
$UO_2(NO_3)_2 \cdot 6H_2O$	533.4	2.3	2
	531.8	2.3	1

[a] Binding energies and peak widths reported in electron volts, eV. [b] Calibrated against the carbon 1s line taken as 285.0 eV. [c] Full width at half maximum, in eV.

ligands are *cis* to each other, while the water ligands are also *cis* to each other *and* bridging (Fig. 1).

Two possibilities exist for the position of the hydrogen atoms between the imidazole molecules and the bridging oxygen species. In Fig. 2(2), the hydrogen atoms are associated with the bridging oxygen group; this would yield a bridging aquo complex with the water molecule hydrogen bonded to the imidazole (the originally postulated complex [1]). Fig. 2(1), however, shows an alternate situation in which the hydrogen atoms are associated with the 'pyridine' ring nitrogens of the nearby imidazole molecules. This results in a hydroxy-bridged uranyl complex in which anionic OH^- bridges are presumably stabilized by imidazolium cations.

There is substantial, although not unequivocal, evidence for the bonding scheme depicted in Fig. 2(1) in the infrared (Fig. 3) and X-ray photoelectron data (Table I), coupled with the previously reported infrared, luminescence, and structural results [1]. The arguments for this case are as follows

a) The two uranium–oxygen bonds, U–O(6) (Fig. 1) are 2.35(1) and 2.37(1) Å. The corresponding bond strengths, calculated according to Brown [5], are 0.57 and 0.55 valence units, respectively [6]. The sum, 1.02 v.u., is extremely large for an H_2O molecule; however, this value would be in good agreement with a bridging hydroxide group.

(b) The nitrogen–carbon bond lengths (the bonds involving both ring nitrogen atoms with adjacent carbon atoms) in complex (I) are equivalent [1], indicating that both nitrogen atoms are similar in their bonding. This is the situation in the imidazolium-$UO_2Cl_4^{2-}$ complex [7].

c) The bond distances and angles involved in the uranium-oxygen-uranium bridge in complex (I) are virtually identical to those reported for the $[(NO_3)_2UO_2(OH)_2UO_2(H_2O)_3] \cdot H_2O$ [8] and $Cl(H_2O)_3UO_2(OH)_2UO_2(H_2O)_3Cl$ [2] hydroxy-bridged dimers. The uranium–uranium 'bond' lengths in the complexes are also similar, being 3.927, 3.939, and 3.944 Å, respectively.

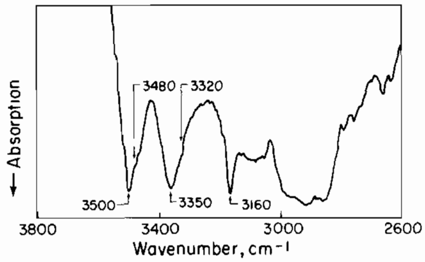

Fig. 3. Infrared spectrum of complex (I).

d) The initially reported infrared spectrum of (I) revealed two N–H stretching bands at 3350 and 3160 cm^{-1}. While both bands are in the region reported for other complexes of imidazole with transition metal ions [9], the 3350 cm^{-1} band has also been attributed to a hydroxy-bridged copper complex [10]. Another assigned OH-bridge band at 3480 cm^{-1} in the same copper system also appears in the spectrum of (I) (Fig. 3). A further study of the spectrum revealed additional bands at 355, 426, and 1090 cm^{-1} that are almost identical to those previously reported for hydroxy-bridged cobalt [11] and copper [12] complexes. Band sets involving bands at 3580, 3520, 3100 and 3400, 3220 cm^{-1} which have been reported [13] for water ligands in $UO_2(NO_3)_2 \cdot 6H_2O$ and $UO_2(NO_3)_2 \cdot 2H_2O$, respectively, were absent.

e) The oxygen-1s X-ray photoelectron spectrum (Table I) of complex (I) consisted of a peak that could be de-convoluted into two peaks with binding energies of 533.1 and 531.6 eV. A similar doublet could also be resolved for $UO_2(NO_3)_2 \cdot 6H_2O$, the binding energies being 533.4 and 531.8 eV (compared to a single, 'averaged' value of 533.3 eV that has been published [14] for $UO_2(NO_3)_2 \cdot 6H_2O$ Accordingly, the 533.1 eV peak in (I) can be assigned as resulting from the NO_3^- oxygens; this is in excellent agreement with reported values for other nitrates [15]. The 531.6 eV peak in (I), however, can easily be assigned to an OH^- functional group. It is in good agreement with the values of 531.9–532.2 eV observed for the oxygen-1s spectra of NaOH-hydrolyzed uranyl salts [16]; also, it is quite similar to the 531.5 eV value reported for the alkoxide oxygen in uranyl alkoxide compounds [3]. Values of ~531.2–531.8 eV have been observed for several other metal hydroxide compounds [17, 18]. The intensity ratios reported in Table I for these lines are also in excellent agreement with these assignments.

If the bridging species are in fact hydroxy groups rather than water groups, this would be one possible explanation for the difference in the luminescence spectra of (I) and $UO_2(NO_3)_2 \cdot 6H_2O$ which were reported by Brittain and Perry [19]. These studies showed that while the emission spectra for the two compounds are the same at room temperature, significant differences are observed on cooling to 77 K; vibronic structure is observed for (I), but none is evident for $UO_2(NO_3)_2 \cdot 6H_2O$. The existence of this hydroxy bridge, however, would still not unequivocally exclude three other possibilities for these differences: weak coupling of the two UO_2^{2+} species with the imidazole molecule in (I), coupling of the lattice waters in $UO_2(NO_3)_2 \cdot 6H_2O$ with the central UO_2^{2+} ion, or interaction of the two uranyl centers with each other in (I).

The possibility of an imidazolium-stabilized hydroxy bridge in (I) represents a potentially new approach for the study of solid-state uranyl hydrolysis products that are stable outside the reaction solution in which they are formed. The coordinated ligands about the uranyl ions could be chosen (sulfates, acetates, *etc.*, or, as in the present case, nitrates), then mild hydrolysis of that compound be effected using imidazoles as the base. One restriction to this approach might be that the compound being hydrolyzed must also contain water molecules in two coordination sites (or have two vacant coordination sites) which can then be replaced with OH^- groups to form the bridges in the dimers. In any case, complex (I) serves quite well as a spectroscopic model for a uranyl hydrolysis dimer of the nitrate salt; this is irrespective of which representation in Fig. 2 is the correct one.

Acknowledgments

This research was supported by the U.S. Nuclear Regulatory Commission, Office of Research, Division of Health, Safety, and Waste Management, Waste Management Branch, under Order No. 60-80-180, and by the U.S. Department of Energy under Contract No DE-AC03-76SF00098. The author also wishes to thank Dr. Kurt Mereiter for his extremely valuable comments regarding the data.

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