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IMIDAZOLIUM TETRACHLORODIOXOURANATE(VI), $[C_3N_2H_5^+]_2\ [UO_2Cl_4]^{-2}$

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ABSTRACT

The crystal and molecular structure of imidazolium tetrachlorodioxouranate(VI) has been determined by X-ray diffraction methods. The crystals, obtained by reacting imidazole and $UO_2Cl_2 \cdot 3H_2O$ in hydrochloric and maintained at pH = 2.5 - 3.0, are monoclinic, $P2_1/n$, with cell dimensions $\underline{a}$ = 9.385(5) Å, $\underline{b}$ = 10.891(5) Å, $\underline{c}$ = 6.966(4) Å, β = 104.56(5)° and V = 722 Å^3. For Z = 2 the calculated density is 2.53 g/cm^3. The structure was refined to a conventional R factor of 0.034 using 1494 data where $F^2 > \sigma(F^2)$. The $[UO_2Cl_4]^{-2}$ anion is octahedral with U-O distance of 1.770 Å and U-Cl distances of 2.692 and 2.657 Å. The imidazolium cation is planar.

INTRODUCTION

Imidazole forms complexes and salts with metal atoms in a variety of ways. A novel example is a ruthenium complex with a carbon-ruthenium bond.[2a] We studied the reaction of imidazole with uranyl choride to see if a similar derivative[2b] could be made; instead, the resultant product was a hydrogen-bonded salt of the imidazolium cation with the uranyl chloride anion, $UO_2Cl_4^{-2}$.

The coordination chemistry of the uranyl ion, UO_2^{+2}, is governed by the ability of the uranium atom to achieve a high equatorial coordination number, most commonly five or six, about the linear uranyl axis; consequently, UO_2^{+} exhibits a wide variety of structures in its complexes when it forms adducts with organic donor molecules.[3] Such compounds include mixed bridging and terminal ligands such as are found in uranyl acetate hydrates,[4] "small bite" ligands such as peroxo groups,[5] and mixed sulfur-oxygen chelates of alkoxides.[6] The $UO_2X_4^{-2}$ (where X = Cl, Br, I) series of complexes,[7] however, has not received so much attention with respect to hydrogen-bonding as have other compounds involving more complex organic ligands; these compounds exhibit the smallest equatorial coordination number (four) known for the UO_2^{+} ion and, as a result of the electronegative halide ligands, should be capable of accepting hydrogen bonds. The present report provides an example of such bonding to the imidazolium cation,[8] which is stable and readily prepared. The parent imidazole molecule is known to undergo extensive hydrogen bonding[9] in many of its metal complexes, with hydrogen-bonding playing a major role in its bioinorganic chemistry.[10]

EXPERIMENTAL

The title compound was prepared by dissolving 0.122 g. (2 mmoles) of imidazole (Aldrich Chemicals, 99% purity) and 0.341 g (1 mmole) of $UO_2Cl_2 \cdot 3H_2O$ (Alfa Chemicals, reagent grade) in hydrochloric acid which was maintained at a pH of ~ 2.5-3.0 followed by stirring for two hours. The reaction solution was allowed to evaporate slowly over a period of several days, yielding a batch of yellow, crystalline product. The crystals were filtered on a Buchner funnel and allowed to dry in air. Anal. Calcd. for $[C_3N_2H_5^+]_2[UO_2Cl_4]^{-2}$: C, 13.10; H, 1.82; N, 10.18. Found: C, 13.18; H, 1.74; N, 10.31.

A small yellow crystal, approximately 0.15 × 0.13 × 0.06 mm in size, was glued to a glass fiber in air. Preliminary cell dimensions and the space group, $P2_1/n$, were obtained from Weissenberg photography. The crystal was placed on a Nonius CAD-4 automated diffractometer equipped with a Mo tube and a graphite monochromator, ($\lambda(K\alpha_1)$ 0.70930 Å). The setting angles of 12 reflections were used to determine by least-squares the following cell parameters: $\underline{a}$ = 9.838(5) Å, $\underline{b}$ = 10.891(5) Å, $\underline{c}$ = 6.966(4) Å, β = 104.56(5)° and V = 722.41 Å^3. For Z = 2 and a molecular weight of 550.01 the calculated density is 2.53 g/cm^3.

Intensity data were collected at room temperature using the θ-2θ scan technique with the scan angle calculated as (0.60 + 0.35 tan θ)° and variable scan times up to a maximum of 80 seconds. The counter aperture was 173 mm from the crystal and had a height of 4 mm and a variable width of (2.50 + 0.50 tan θ) mm. Background

was estimated from an extended scan of 25% on either side of the intensity scan. For reflections where I > 50,000 cps, an attenuator was inserted in the diffracted beam that reduced the intensity by a factor of 18.17.

Three standard reflections were measured every 5400 seconds. A total of 4539 scans, including standards, was processed to yield 2810 data which resulted in 1577 unique data after processing and averaging. Data that were space group extinctions, or too weak to be observed, or whose background ratios were greater than 4.0, were deleted from the data set. An absorption correction (μ = 114 cm^{-1}) was applied[11] which ranged from 1.8 to 4.5. The crystal decay factor based on the variations of the three standard reflections ranged from 0.99 to 1.02.

With two formula units in the unit cell, the uranium atom must be on a center of symmetry. A 3-dimensional Fourier calculated with all phases positive (U on the origin) indicated the positions of two chlorines, one oxygen and one nitrogen. Subsequent least-squares refinements and difference Fouriers revealed the rest of the structure. Some of the hydrogen atoms could be observed in the difference maps, but were neither the major peaks nor well resolved. Hydrogen atoms were included at their calculated positions (0.96 Å from N and C) in the final least-squares refinements, but not refined. Least-squares refinements in which the function $\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2$ was minimized converged rapidly to the final structure. The assigned weight $w = [\sigma(F)]^{-2}$; $\sigma(F)$ was derived from $\sigma(F^2) = [S^2 +$

$(pF^2)^2]^{1/2}$, where S^2 is the variance due to counting statistics and $p = 0.02$. Scattering factors from Doyle and Turner[12] were used, and anomalous dispersion corrections[13] were applied. Anisotropic thermal parameters were applied to all but the hydrogen atoms. No extinction correction was indicated and, none was made. Because of a few large discrepancies, all 5 data below two-theta of 7.6° were zero weighted.

The discrepancy indices for 1494 data where $F^2 > \sigma$ and $7.6° < 2\theta < 60°$ are:

$$R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.034$$

$$R_w = [\Sigma(|F_o|-|F_c|)^2/\Sigma|F_o|^2]^{1/2} = 0.024$$

R for all 1577 data is 0.039. The error in an observation of unit weight is 1.02. In the last cycle, no parameter changed more than 0.005 σ. The largest peak in the final difference Fourier was 1.0 e/Å^3 and is a ripple near the uranium atom.

The list of observed structure factors is available from the authors.

RESULTS AND DISCUSSION

Atomic parameters, distances and angles are listed in Tables I-III. Figure 1 shows an ORTEP view of a formula unit with the numbering scheme used for the atoms in the tables.

The compound is a salt consisting of discrete planar imidazolium cations and octahedral tetrachlorodioxouranate anions. The closest non-hydrogen atom approaches between the two ions are 3.20 Å between O and N(1), 3.33 Å between Cℓ(1) and N(1), and 3.26 Å between Cℓ(2) and N(2). The H(1)-Cℓ(1) and H(2)-Cℓ(2) distances are 2.51 Å and 2.46 Å respectively, and the angles N(1)-H(1)-Cℓ(1) and N(2)-H(2)-Cℓ(2) are 144° and 140° respectively; these values are consistent with the criteria for N-H...Cℓ hydrogen bond.[14] Hydrogen bonding distances in $MnC\ell_2 \cdot 4H_2O$ between O and Cℓ are 3.17 to 3.32, and for N to Cℓ they should be slightly larger.[15]

The imidazolium cation is a planar five membered ring. The geometry reported here is in good agreement with other determinations,[16,17] with bond angles and distances within 4σ of the literature values.

The tetrachloro dioxouranium(IV) anion is a tetragonally distorted octahedron, with four chlorine atoms in the equatorial positions and the two uranyl oxygen atoms at the apices. The anion has been well characterized by other structure determinations.[18-24] The U-O distances reported for this ion[20-24] range from 1.72 Å to 1.78 Å which compares to the 1.770 Å value reported here. The U-Cl distances reported for this ion[20-24] range from 2.62 to 2.70 Å and span the two values reported here.

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Table I. Positional and Thermal Parameters[a] with Estimated Deviations[b]

ATOM	X	Y	Z
U	0	0	0
CL(1)	.0150(1)	-.1292(1)	.3341(2)
CL(2)	.1845(1)	.1632(1)	.1948(2)
O(1)	-.1389(3)	.0881(3)	.0483(5)
N(1)	.2980(5)	.0228(5)	-.3568(8)
N(2)	.4930(5)	-.0663(6)	-.2626(8)
C(1)	.3940(7)	.1117(6)	-.291(1)
C(2)	.5183(7)	.0542(8)	-.231(1)
C(3)	.3594(7)	-.0833(6)	-.3405(9)
H(1)	.1992	.0367	-.4092
H(2)	.5626	-.1311	-.2325
H(3)	.3775	.1994	-.2841
H(4)	.6100	.0909	-.1777
H(5)	.3139	-.1619	-.3782

ATOM	B11	B22	B33	B12	B13	B23
U	1.695(8)	2.079(9)	3.44(1)	.15(1)	.567(6)	-.06(1)
CL(1)	3.14(5)	2.85(5)	3.71(6)	.23(4)	.78(4)	.10(4)
CL(2)	2.79(4)	2.94(5)	4.61(6)	-.44(4)	-.01(4)	-.17(5)
O(1)	2.3(1)	2.9(2)	4.6(2)	.8(1)	1.2(1)	.1(1)
N(1)	2.7(2)	5.2(4)	4.9(2)	.7(2)	.7(2)	.8(2)
N(2)	3.9(2)	4.5(3)	4.3(3)	1.8(2)	.8(2)	.3(2)
C(1)	6.3(4)	2.8(2)	5.1(3)	.4(3)	2.0(3)	.3(2)
C(2)	3.4(3)	5.9(3)	4.0(3)	-1.3(3)	.5(2)	.1(3)
C(3)	4.4(3)	3.7(3)	4.0(3)	-.5(2)	.8(2)	.1(2)

[a]The anisotropic temperature factor has the form $\exp(-0.25(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \ldots))$. The hydrogen atoms were all assigned an isotropic thermal parameter of 6.0 $Å^2$.

[b]Here and in the following tables the number in parentheses is the estimated standard deviation for the least significant figures.

Table II. Distances (Å)

			Corr.[a]
U	-2 O	1.770(3)	1.779
	-2 Cl(1)	2.692(2)	2.697
	-2 Cl(2)	2.657(2)	2.665
N(1)-	C(1)	1.350(7)	
	- C(3)	1.296(8)	
N(2)-	C(3)	1.303(9)	
	- C(2)	1.343(9)	
C(1)-	C(2)	1.344(8)	

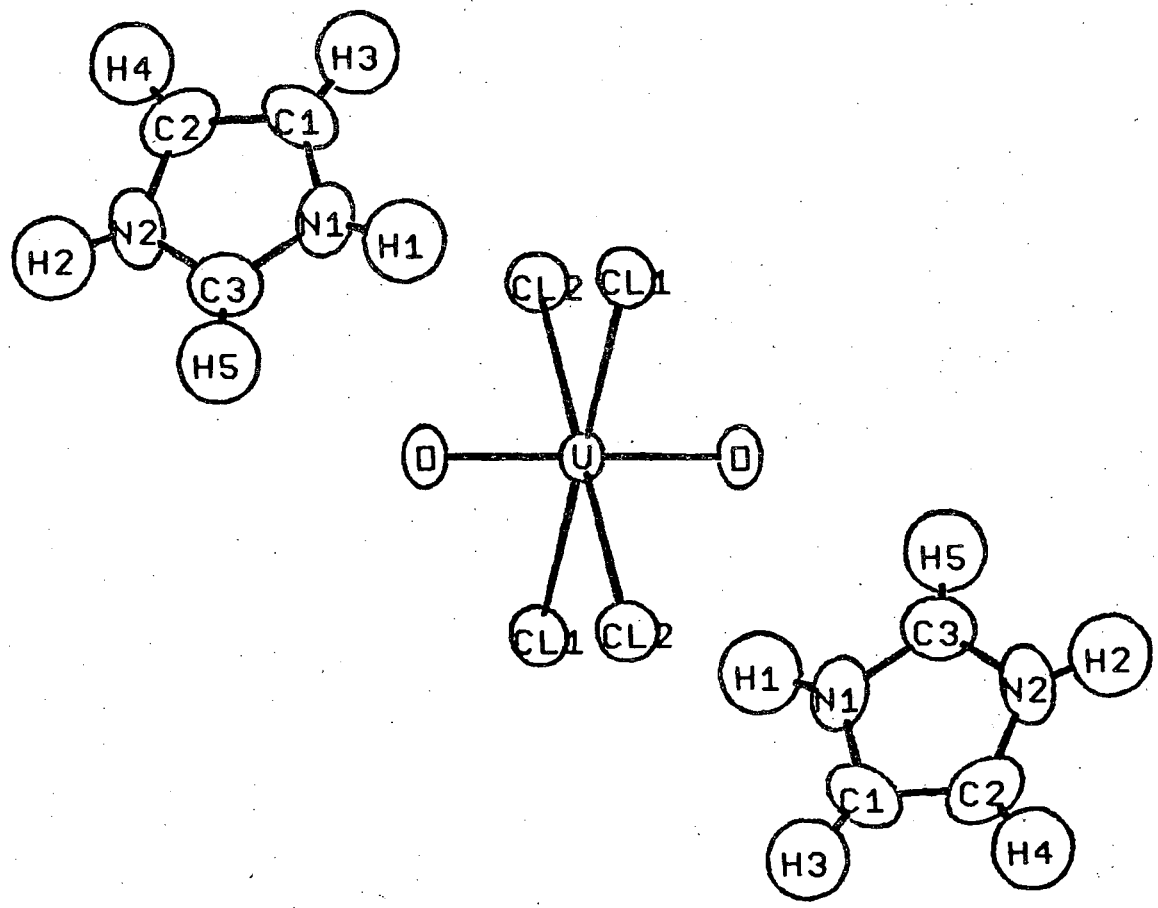
[a]Corrected for thermal motion assuming a "riding" model.

Table III. Selected Angles (deg.)

O -U -O	180.0
O -U -Cl(1)	90.2(2)
O -U -Cl(2)	90.1(2)
Cl(1)-U -Cl(1)	180.0
Cl(1)-U -Cl(2)	91.5(1)
Cl(2)-U -Cl(2)	180.0
C(1) -N(1)-C(3)	109.8(5)
C(2) -N(2)-C(3)	109.4(6)
N(1) -C(1)-C(2)	106.0(6)
N(2) -C(2)-C(1)	106.8(6)
N(1) -C(3)-N(2)	108.0(5)

FIGURE CAPTION

Fig. 1. ORTEP drawing of one formula unit.



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