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Crystal Structure of Photosensitive Uranyl Ethoxycarboxylate Complexes

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Two photosensitive uranyl complexes have been prepared and examined by a single-crystal X-ray diffraction study. Both compounds crystallize in the monoclinic system. In bis-(β-ethoxypropionato)dioxouranium(VI), uranyl ions are equatorially coordinated by six carboxylate oxygen atoms, forming one-dimensional infinite chains. In bis(ethoxyacetato)dioxouranium(VI), uranyl ions are equatorially coordinated by four carboxylate and one ethoxy oxygen atoms, forming two-dimensional network of uranyl-ligand infinite chains.

In the course of studies on photochemistry of uranyl complexes in the crystalline state, two photosensitive uranyl complexes have been found. They were prepared from powdered uranyl hydroxide and a large excess of β-ethoxypropionic and ethoxyacetic acid, respectively. Crystals suitable for X-ray analysis were obtained by keeping the mixture in a dark place for a few days at 60 °C. Bis(β-ethoxypropionato)dioxouranium(VI) (1) is pale yellow needle crystal. Bis(ethoxyacetato)dioxouranium(VI) (2) is pale yellow hexagonal plate crystal. These complexes are easily soluble in water and ethanol, soluble in acetone and chloroform, and insoluble in diethyl ether and benzene. Uranyl ions of these complexes are reduced under ultraviolet radiation. To our knowledge, there have been reported no other photosensitive uranyl complexes in the crystalline state than formato complexes.[1] Elemental analyses of these complexes for uranium, carbon, and hydrogen proved the chemical formulas of compounds 1 and 2 to be $UO_2(C_2H_5OC_2H_4CO_2)_2$ and $UO_2(C_2H_5OCH_2CO_2)_2$, respectively.

Table 1. Crystal Data of Uranyl Complexes Synthesized

Compound	1	2
Chemical formula	$C_{10}H_{18}O_8U$	$C_8H_{14}O_8U$
Formula weight	504.28	476.22
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/n$
Lattice constants	a = 8.603(3) Å	a = 9.664(4) Å
	b = 9.243(3) Å	b = 11.030(4) Å
	c = 18.276(4) Å	c = 12.889(4) Å
	β = 96.92(2)°	β = 108.61(3)°
Volume of unit cell	V = 1442.7(7) Å^3	V = 1302.1(9) Å^3
Z	4	4
Density, D_{obsd}	2.25 g cm^{-3}	2.33 g cm^{-3}
D_{calcd}	2.32 g cm^{-3}	2.43 g cm^{-3}

Crystal data of these compounds are tabulated in Table 1. The X-ray intensity data were collected on a single crystal by using a Rigaku AFC-5R diffractometer with graphite-monochromated Mo Kα radiation (0.71069 Å) at 23 °C. Absorption effects were corrected by the program TEXSAN (μ = 107.0 and 118.4 cm^{-1} for compounds 1 and 2). The determination of the crystal structure was based on the independent 2007 and 2092 reflections with $I > 3\sigma(I)$ for compounds 1 and 2, respectively. The structure was solved by the heavy-atom method and refined to final R and R_w values of 0.04 and 0.051 for compound 1, and 0.056 and 0.065 for compound 2.

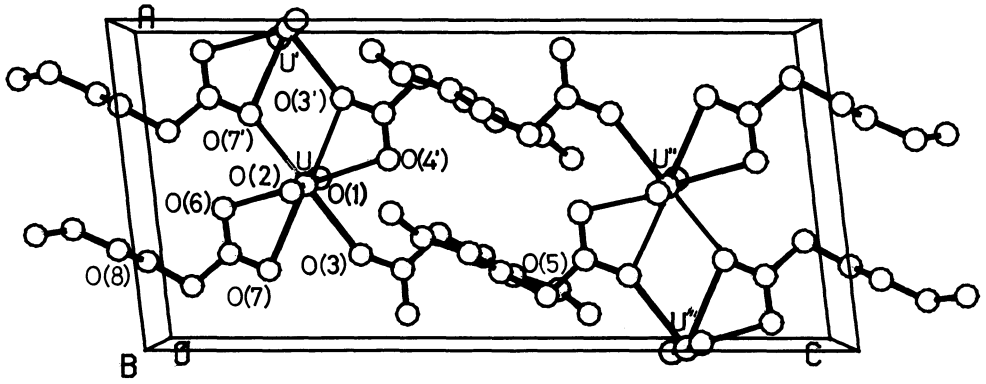

Fig. 1. Diagram of one unit cell in the crystal structure of compound 1, viewed down the b axis. Hydrogen atoms are omitted for clarity. U and U' lie close on a plane $y = \frac{1}{4}$, and U'' and U''' on a plane $y = \frac{3}{4}$.

A perspective view of crystal structure of compound 1 is shown in Fig. 1. The uranyl ions are nearly linear with O(1)–U–O(2) angle of 179.3(4)°. One uranyl unit is surrounded by six carboxylate oxygen atoms, O(3), O(7), O(6), O(7'), O(3'), and O(4'). The six O atoms lie at U–O distances of 2.442(7) to 2.555(7) Å and form a puckered hexagon,[2] deviating within ±0.28 Å from the least-squares plane defined by the O and U atoms. Both ethoxy O atoms, O(5) and O(8), do not coordinate the U atoms.

The U atoms in a unit cell lie close on the *a* glide planes ($y = \frac{1}{4}$ and $\frac{3}{4}$) and aligned in parallel with the *a* axis ($z = 0.236$ and 0.764) at intervals of approximately 4.30 Å. An O atom of each carboxylic group links two uranyl units. Thus two hexagonal bipyramids share an edge to form a one-dimensional infinite chain. There is no special bond between adjacent infinite chains except van der Waals forces. No other uranyl complex has been reported in which a carboxylate O atom links two uranyl ions, although there has been many examples where uranyl ions are bridged through the O–C–O bond of carboxylate ion.[3]

A perspective view of crystal structure of compound 2 is shown in Fig. 2. The uranyl ions are nearly linear with O(1)–U–O(2) angle of 179.4(5)°. One uranyl unit is equatorially coordinated by five oxygen atoms, forming a pentagonal bipyramid. Each of the four atoms O(3), O(6), O(4'), and O(7") belongs to a different carboxylic group, and the atom O(5') to an ethoxy group. The U-to-carboxylate O bond lengths of 2.34(1) to 2.39(1) Å are normal for pentacoordinated uranyl complexes. However, the U–O(5') bond length of 2.56(1) Å is rather long, suggesting a weaker coordination. The U atoms in a unit cell lie nearly on the *n* glide planes ($y = \frac{1}{4}$ and $\frac{3}{4}$) and around the twofold screw axes ($\frac{1}{4}$, y, $\frac{1}{4}$) and ($\frac{3}{4}$, y, $\frac{3}{4}$), as shown in Fig. 3. The neighboring uranium atoms

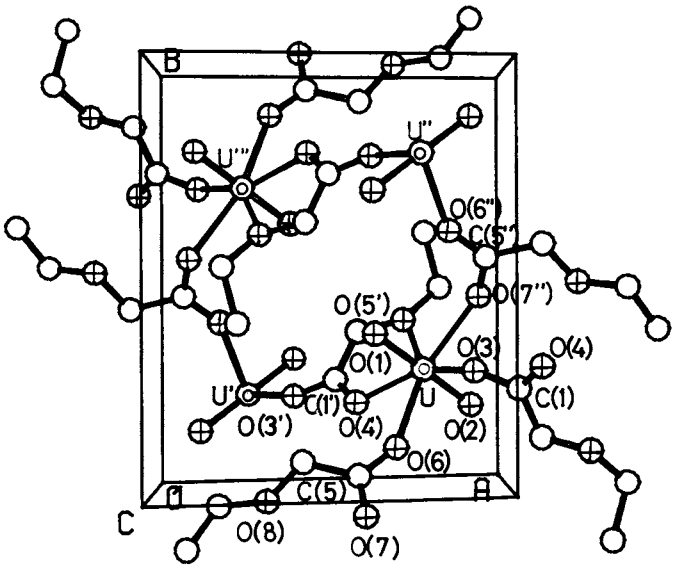

Fig. 2. Diagram of one unit cell in the crystal structure of compound 2, viewed down the *c* axis. Hydrogen atoms are omitted for clarity. Double, crossed, and open circles represent U, O, and C.

along a screw axis are connected through a carboxylic group O(6)–C(5)–O(7), forming a spiral around the screw axis. The neighboring uranium atoms on an *n* glide plane are linked along the glide vector $\frac{1}{2}(\underline{a} + \underline{c})$ through a carboxylic group O(3)–C(1)–O(4). Thus a two-dimensional uranium-ligand network is formed. There is no special bond between adjacent layer networks except van der Waals forces.

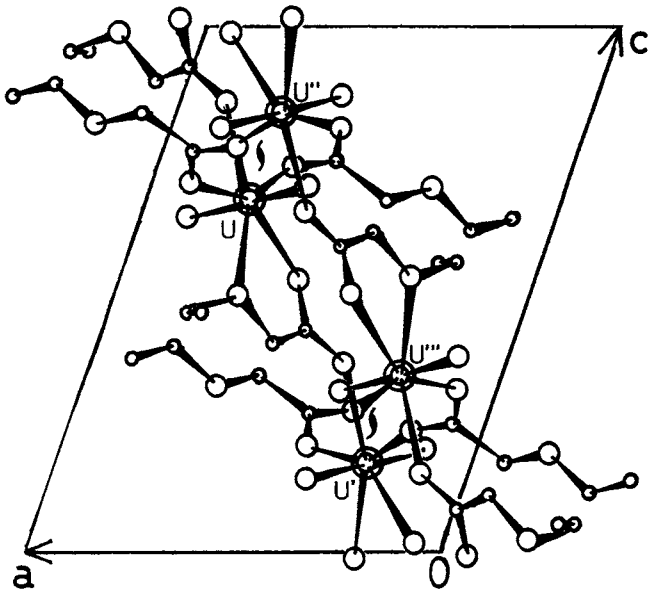

Fig. 3. Projection of compound 2, viewed down the *b* axis. Double, medium, and small circles represent U, O, and C.

The spiral structure of uranyl-ligand group found in compound 2 seems to be favorable for the coordination of the carboxylic acid with an oxygen atom at α position, because a similar spiral structure appears in the crystal of bis(hydroxyacetato)dioxouranium(VI),[4] whereas it is not the case with β-alkoxy carboxylic acid, such as compound 1.

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