Structural Studies on the Actinide Carboxylates. II.* The Crystal and Molecular Structure of Bis(iminodiacetato)dioxouranium(VI)

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The crystal structure of bis(iminodiacetato)dioxouranium(VI) has been determined by Fourier methods and refined by least-squares calculations to $R=0.038$. The unit cell is triclinic $P\bar{1}$ with $a=8.970$ (3), $b=6.367$ (2), $c=5.843$ (2) Å, $\alpha=92.42$ (4), $\beta=76.38$ (4), $\gamma=104.15$ (4)°, $Z=1$. The iminodiacetate ligands are bridging the uranyl groups in infinite chains running in the $[0\bar{1}1]$ direction, cross-linked through hydrogen bonds. The carboxylate groups are both ionized and the proton is linked to the nitrogen atom. One carboxylate group of each ligand acts as monodentate, the other as bidentate on two adjacent uranium atoms. The geometry around the uranium is approximately hexagonal bipyramidal.

Introduction

The ability of polycarboxylic acids to form solid polymeric complexes with the uranyl(VI) ion has been proved by some X-ray structure determinations (Alcock, 1973; Bombieri, Croatto, Graziani, Forsellini & Magon, 1974). However, work on uranyl chelates of these complexes has been restricted principally to solution studies, so that, at present, it is difficult to predict what type of structure they adopt in the solid. Recently some physical properties and the infrared spectra of a series of uranyl complexes with analytically important aminopolycarboxylic acids such as ethylenediaminetetraacetic acid (H_4EDTA) and its analogue have been studied and compared (Krishnamurthy & Morris, 1969). We report here the crystal structure of bis-(iminodiacetato)dioxouranium(VI).

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Experimental

Crystals suitable for X-ray work were obtained by mixing diluted solutions of uranyl nitrate hexahydrate and iminodiacetic acid in a 1:1 ratio.

From the solution, allowed to stand for about 30 days, small prismatic pale-yellow crystals precipitated. The product obtained was the 1:2 (metal:ligand) chelate. An analogous preparation has been reported previously by Krishnamurthy & Morris (1969).

Crystal data

$C_8H_{12}O_{10}N_2U$, F.W. 534, triclinic, $a=8.970$ (3), $b=6.367$ (2), $c=5.843$ (2) Å, $\alpha=92.42$ (4), $\beta=76.38$ (4), $\gamma=104.15$ (4)°, $V=314.4$ Å^3, $F(000)=246$, $D_{obs}=2.82$ g cm^{-3}, $D_{calc}=2.83$ g cm^{-3}, $Z=1$, μ(Mo $K\alpha$)=163 cm^{-1}.

The possible space groups are $P\bar{1}$ and $P1$. The former was chosen and confirmed by the structure

Table 1. *Atomic coordinates and thermal parameters of the non-hydrogen atoms with e.s.d.'s in parentheses*

Anisotropic thermal parameters ($\times 10^4$) and e.s.d.'s in parentheses. The temperature factor is of the form:

$$T=\exp\left[-2\pi^2(U_{11}h^2a^{*2}+2U_{12}hka^*b^*+\ldots)\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	0·0	1·0	0·0	352 (4)	225 (3)	193 (3)	113 (2)	−130 (2)	−24 (2)
O(1)	0·0804 (11)	0·9052 (14)	−0·2853 (15)	488 (53)	351 (47)	316 (46)	215 (41)	−76 (39)	−80 (37)
O(2)	0·2625 (12)	1·0550 (14)	0·1292 (17)	542 (59)	360 (51)	521 (58)	140 (44)	−252 (48)	96 (43)
O(3)	0·1090 (11)	0·7257 (14)	0·1667 (16)	443 (52)	316 (46)	454 (53)	180 (40)	−186 (42)	43 (38)
O(4)	0·1922 (11)	0·3412 (14)	0·8982 (15)	494 (53)	276 (43)	350 (48)	102 (39)	−233 (41)	−20 (36)
O(5)	0·4003 (10)	0·5990 (14)	0·7192 (15)	391 (50)	393 (49)	326 (46)	108 (41)	−159 (38)	−9 (37)
N	0·3215 (13)	0·5360 (16)	0·2854 (17)	387 (58)	321 (54)	246 (52)	167 (46)	−123 (44)	10 (42)
C(1)	0·2360 (15)	0·8581 (20)	0·1828 (21)	370 (68)	323 (66)	279 (63)	111 (54)	−124 (52)	2 (50)
C(2)	0·3644 (16)	0·7797 (20)	0·2616 (24)	401 (73)	274 (63)	409 (74)	117 (55)	−169 (60)	82 (54)
C(3)	0·2036 (15)	0·4428 (21)	0·5030 (20)	392 (70)	328 (66)	226 (60)	87 (55)	−159 (52)	−29 (49)
C(4)	0·2745 (14)	0·4642 (18)	0·7196 (18)	366 (66)	300 (60)	166 (54)	170 (53)	−125 (48)	−43 (45)

determination. The value of Z requires that the uranium atoms lie in special positions.

All other atoms are in general positions. Space group and approximate cell parameters were determined initially from Weissenberg and precession photographs. After alignment of the crystal on a Siemens four-circle automatic diffractometer, the cell parameters were refined by a least-squares method with 24 high-angle reflexions measured with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å).

A very small crystal of approximate dimensions $0.1 \times 0.1 \times 0.2$ mm was mounted with the c axis parallel to the φ axis of the goniometer, and the data were collected on a computer-controlled Siemens A.E.D. using the θ–2θ scan and the five-point measuring procedure up to $\theta_{max} = 27°$. 1105 independent reflexions with intensities greater than $2\sigma(I)$ were measured and used in the refinement.

The $4\bar{1}1$ reflexion was selected as the standard, and its intensity was recorded every 20 reflexions. The fluctuations in intensity of the standard reflexion were random with a maximum variation of 3%.

The intensities were corrected for Lp and absorption effects following the Kopfmann & Huber (1968, 1969) procedure.

All other calculations were carried out on the CDC 6600 computer with the X-RAY system of crystal-

Table 2. *Atomic coordinates of the hydrogen atoms and e.s.d.'s in parentheses*

	x	y	z
H(1)	0·377 (20)	0·866 (27)	0·455 (30)
H(2)	0·474 (21)	0·845 (27)	0·147 (30)
H(3)	0·409 (20)	0·479 (27)	0·295 (29)
H(4)	0·291 (20)	0·466 (27)	0·157 (31)
H(5)	0·113 (20)	0·516 (27)	0·541 (29)
H(6)	0·164 (20)	0·294 (29)	0·461 (29)

Table 3. *Observed and calculated structure factors*

Columns are h, $10F_o$, $10F_c$. Unobserved reflexions are marked by *.

lographic programs (Stewart, Kundell & Baldwin, 1970). Atomic scattering factors for uranium, nitrogen and carbon were from Cromer & Waber (1965), and for hydrogen from *International Tables for X-ray Crystallography* (1962).

Table 4. *Bond lengths* (Å), *bond angles* (°) *and e.s.d.'s in parentheses*

U—O(1)	1·80 (1)	C(3)–C(4)	1·53 (2)
U—O(2)	2·58 (1)	C(4)–O(4)	1·29 (1)
U—O(3)	2·53 (1)	C(4)–O(5)	1·24 (1)
U—O(4)	2·42 (1)	C(2)–H(1)	1·20 (18)
O(2)–C(1)	1·26 (2)	C(2)–H(2)	1·05 (15)
O(3)–C(1)	1·26 (2)	N—H(3)	0·96 (20)
C(1)–C(2)	1·53 (2)	N—H(4)	0·92 (18)
C(2)–N	1·51 (2)	C(3)–H(5)	1·01 (19)
N—C(3)	1·49 (1)	C(3)–H(6)	0·97 (17)

O(2)–U—O(3)	51·0 (3)	C(1)–C(2)–H(1)	107 (10)
O(2)–U—O(4^{iv})	62·4 (3)	C(1)–C(2)–H(2)	109 (11)
O(3)–U—O(4^{iii})	67·4 (3)	N—C(2)–H(1)	112 (8)
U—O(2)–C(1)	92·6 (8)	N—C(2)–H(2)	115 (10)
U—O(3)–C(1)	94·9 (8)	H(1)–C(2)–H(2)	103 (12)
U^v—O(4)–C(4)	142·0 (8)	C(2)–N—H(3)	113 (9)
O(2)–C(1)–O(3)	121 (1)	C(2)–N—H(4)	114 (11)
O(2)–C(1)–C(2)	118 (1)	C(3)–N—H(3)	101 (9)
O(3)–C(1)–C(2)	120 (1)	C(3)–N—H(4)	109 (9)
O(4)–C(4)–O(5)	124 (1)	H(3)–N—H(4)	102 (16)
O(4)–C(4)–C(3)	116 (1)	N—C(3)–H(5)	112 (9)
O(5)–C(4)–C(3)	120 (1)	N—C(3)–H(6)	103 (9)
C(1)–C(2)–N	111 (1)	C(4)–C(3)–H(5)	107 (10)
C(4)–C(3)–N	113 (1)	C(4)–C(3)–H(6)	114 (12)
C(2)–N—C(3)	116 (1)	H(5)–C(3)–H(6)	109 (14)

Hydrogen bonds

	N–H	H···O	N···O	N–H···O
N–H(3)···O(5^i)	0·96	1·87	2·82	171
N–H(4)···O(4^{ii})	0·92	1·97	2·88	169

The codes for symmetry-related atoms are as follows.

Symbol	Symmetry code		
None	x	y	z
(i)	$1-x$	$1-y$	$1-z$
(ii)	x	y	$z-1$
(iii)	$\bar{x}$	$1-y$	$1-z$
(iv)	x	$1+y$	$z-1$
(v)	x	$y-1$	$1+z$
(vi)	$\bar{x}$	$2-y$	$\bar{z}$

Structure determination

The structure was solved by the heavy-atom method. The uranium atom was located at the origin and all other non-hydrogen atoms were located from Fourier difference syntheses phased on the heavy atom. Three cycles of full-matrix least-squares refinement with isotropic temperature factors and $w=1$ reduced R to 8·5%. The quantity minimized was $\sum \omega(|F_o| - |F_c|)^2$.

After correction for anomalous scattering by uranium [$\Delta f'$ and $\Delta f''$ were taken from Cromer (1965)], three more cycles of least-squares refinement in which all atoms were allowed to vibrate anisotropically reduced R to 4·1%. A difference Fourier synthesis calculated at this stage showed well-resolved peaks corresponding to the hydrogen-atom positions. Two cycles of least-squares calculations with variable positional parameters assigned to the hydrogen atoms, and variable anisotropic thermal parameters assigned to all other atoms lowered R to the final value of 3·8%. The hydrogen atoms were given isotropic temperature factors based on the anisotropic values of the atoms to which they are bonded. In the last cycle no parameter shift was $>0·1\sigma$. The final atomic and thermal parameters with their estimated standard deviations are listed in Tables 1 and 2. Observed and calculated structure factors are given in Table 3. Bond lengths and bond angles are listed in Table 4 (see Fig. 1 for labelling of the atoms).

Description of the structure

The uranyl ions in the complex are surrounded by six carboxylate oxygen atoms forming an irregular hexagonal bipyramid. The best plane passing through the atoms of the equatorial plane derived by the method of least squares is given in Table 5. The deviations of the atoms coordinated to uranium from this plane are significant and are characteristic of a puckered structure. Each ligand is chelated through O(2) and O(3) to one uranyl unit and coordinated through O(4) to another uranyl unit. The carboxylic groups are both ionized and the proton is linked to the nitrogen atom, confirming the suggestions made on the basis of infrared data (Krishnamurthy & Morris, 1969).

Table 5. *Least-squares planes*

Coordinates refer to the directions of the crystallographic axes. Deviations (Å) of the atoms from the plane are given in square brackets.

Plane	Atoms in plane	Equation of plane
1	U, O(2), O(3), O(4) O(2^{vi}), O(3^{vi}), O(4^{iv})	$-2·3858x + 2·4384y + 4·8116z = 0$
	[U 0·0, O(2) 0·13, O(3) −0·13, O(4) −0·12, O(2^{vi}) −0·13, O(3^{vi}) 0·13, O(4^{iv}) 0·12]	
2	U, O(2), O(3)	$-2·7724x + 1·8443y + 4·8477z = 0$
3	C(1), O(2), O(3)	$-2·3855x + 1·6812y + 5·0012z = 0·1124$
4	C(4), O(4), O(5)	$5·6916x − 5·3172y − 1·0376z = −0·6148$

Angles (°) between planes
1–2 6·7; 1–3 7·3; 1–4 46·1
2–3 2·8; 2–4 49·3; 3–4 51·8

The first carboxylate group C(1), O(2), O(3) is quasi-coplanar with plane U, O(2), O(3) and make an angle of 7·3° with the equatorial plane, whereas the second carboxylate group C(4), O(4), O(5) makes an angle of 46·1° with the same equatorial plane. The resulting structure consists of polymeric chains running parallel to [0Ī1], as shown in Figs. 1 and 2 in which the crystal structure is projected down the c and the a axes respectively. The two nitrogen protons H(3) and H(4) are involved in linear hydrogen bonding with the oxygens of adjacent chains: H(3)····O(5) (i) 1·87 Å roughly in the direction of the a axis [N–H(3)····O(5) (i) 171°] and H(4)···O(4) (ii) 1·97 Å roughly in the direction of the c axis [N–H(4)···O(4) (ii) 169°].

In particular a ten-membered ring is formed by the two halves H(3)–N–C(3)–C(4)–O(5) related by a centre of symmetry and presents a chair configuration. Analogous rings are found in a monoclinic phase of iminodiacetic acid (Boman, Herbertsson & Oskarsson, 1974) and in iminodiacetic acid hydroiodide (Oskarsson, 1974).

In this way the chains are linked to each other through a network of hydrogen bonds.

The U–O distances in the equatorial plane are significantly different, ranging from 2·42 to 2·58 Å.

A similar situation has been found in (NH₄)₂UO₂(NO₃)₄ (Kapshukov, Volkov, Moskvichev, Lebedev & Yakovlev, 1971), in which the nitrate groups act as both monodentate and chelate towards the uranyl groups. The U–O(4) bond, 2·42 (1) Å, due to the monodentate carboxylate groups, compares favourably with the value of 2·44 Å reported in the above-mentioned compound in which are also present unsymmetrical U–O bonds to the chelate nitrate, attributed to an interaction between the NH_4^+ cation and the oxygen atom involved in the longer bond. A difference between the two U–O(2) and U–O(3) bonds, respectively 2·53 (1) Å and 2·58 (1) Å, in the chelate carboxylate group also exists in the present case, but the possible cause could be the existence of some strain in the ligand shared between two different uranium atoms. The various internal rotation angles defining the conformation of the ligand, following the Klyne & Prelog (1960) nomenclature, are listed in Table 6.

The bond distances and angles in the organic residue, apart from some difference due to the coordination, agree with those found in iminodiacetic acid hydrochloride and hydrobromide (Oskarsson, 1973), hydroiodide (Oskarsson, 1974) and in iminodiacetic acid (monoclinic phase) (Boman et al., 1974).

The non-hydrogen atoms of the ligand N, C(1), C(2), O(2), O(3) are almost coplanar (Table 7) and form an angle of 60° with the plane passing through the other half of the ligand: N, C(3), C(4), O(4), O(5).

In the iminodiacetic acid this angle is 41°, in the chloride and bromide derivatives 0° (the iminodiacetic

The two independent O····O distances O(2)···O(3) across the chelated carboxylic group and O(4)···O(5) across the monodentate carboxylic group [2·20 (2) and
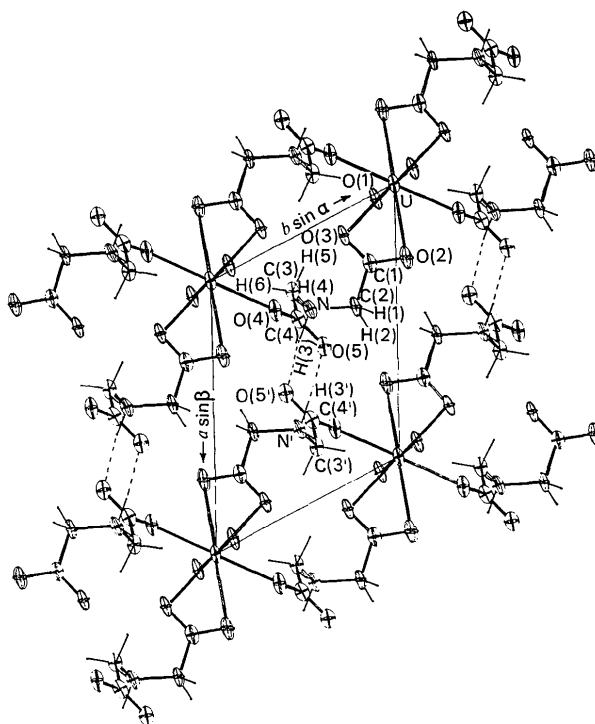

Fig. 1. The crystal structure viewed along the c axis. Figs. 1 and 2 were drawn by the program ORTEP (Johnson, 1965) and the dotted lines represent hydrogen bonding. (Thermal motion ellipsoids of 50 % probability.)
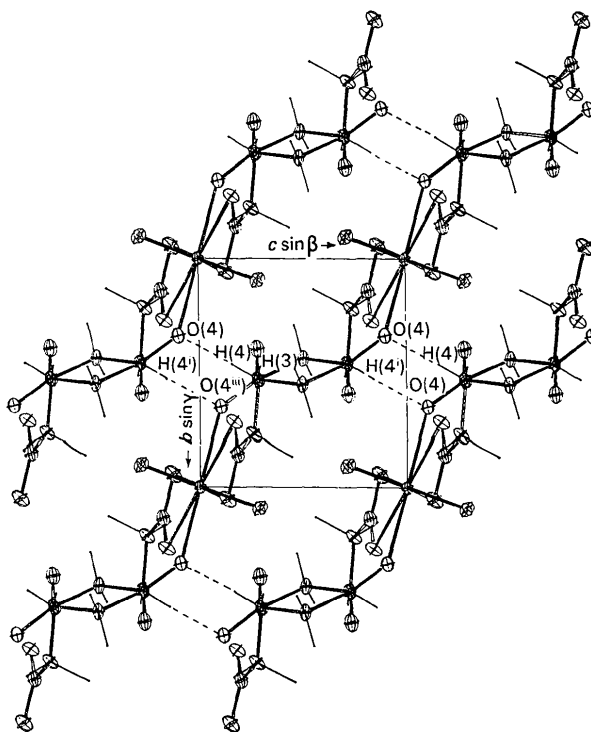

Fig. 2. The crystal structure viewed along the a axis.

Table 6. *Internal rotation angles in the organic residue described following the Klyne & Prelog* (1960) *nomenclature*

O(2)–C(1)–C(2)–N	172·04 (+ap)°
O(3)–C(1)–C(2)–N	6·07 (−sp)
C(1)–C(2)–N——C(3)	−78·46 (−sc)
C(2)–N——C(3)–C(4)	−76·99 (−sc)
N——C(3)–C(4)–O(4)	163·05 (+ap)
N——C(3)–C(4)–O(5)	19·53 (+sp)

Table 7. *Deviations* (Å) *from the least-squares planes through the independent halves in the ligand*

Atoms defining plane (I) N, C(2), C(1), O(2), O(3); (II) N, C(3), C(4), O(4), O(5). The angle between the planes is 60°.

	(I)		(II)
N	−0·053	N	0·124
C(2)	0·061	C(3)	−0·158
C(1)	0·020	C(4)	−0·012
O(2)	−0·048	O(4)	0·096
O(3)	0·020	O(5)	−0·050

ion exhibits in this case symmetry *mm*) and in the iodide 81°.

The oxygen–oxygen distances along the edges of the uranium coordination polyhedron together with some inter- and intramolecular non-bonded distances are reported in Table 8.

Table 8. *Some intra- and intermolecular contacts in the structure*

O(2)···O(3)	2·20 (1)	N·····O(5)	2·78 (1)
O(4)···O(5)	2·24 (1)	N·····O(5^i)	2·82 (2)
O(2)···O(4^{iv})	2·59 (2)	N·····O(4^{ii})	2·88 (1)
O(3)···O(4^{iii})	2·74 (2)	O(3)···C(2)	2·42 (2)
O(4)···O(3^{ii})	3·00 (1)	O(2)···C(2)	2·40 (2)
O(1)···O(4^{iv})	2·96 (1)	O(4)···C(3)	2·40 (2)
N·····O(3)	2·72 (2)	O(5)···C(3)	2·40 (2)

2·24 (2) Å] are comparable with the values reported in Na(UO$_2$)(OAc)$_3$ (Zachariasen & Plettinger, 1959), in [UO$_2$(OAc)$_2$Ph$_3$PO]$_2$ (Panattoni, Graziani, Bandoli, Zarli & Bombieri, 1969), and in (NH$_4$)$_4$UO$_2$(CO$_3$)$_3$

(Graziani, Bombieri & Forsellini, 1972), and the other O···O approaches in the equatorial plane [2·59 (1) and 2·74 (1)] are slightly shorter than the sum of the van der Waals radii (Allinger, Darooge & Hermann, 1961). This influences the puckered arrangement previously mentioned.

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References

ALCOCK, N. W. (1973). *J. Chem. Soc. Dalton*, pp. 1614–1616, 1616–1620.

ALLINGER, N. L., DAROOGE, M. A. & HERMANN, R. B. (1961). *J. Org. Chem.* 26, 3626–3628.

BOMAN, C. E., HERBERTSSON, H. & OSKARSSON, Å. (1974). *Acta Cryst.* B30, 378–382.

BOMBIERI, G., CROATTO, U., GRAZIANI, R., FORSELLINI, E. & MAGON, L. (1974). *Acta Cryst.* B30, 407–411.

CROMER, D. T. (1965). *Acta Cryst.* 18, 17–23.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* 18, 104–109.

GRAZIANI, R., BOMBIERI, G. & FORSELLINI, E. (1972). *J. Chem. Soc. Dalton*, pp. 2059–2061.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

KAPSHUKOV, I. I., VOLKOV, YU. F., MOSKVICHEV, E. P., LEBEDEV, I. A. & YAKOVLEV, G. N. (1971). *Zh. Strukt. Khim.* 12, 94–98.

KLYNE, W. & PRELOG, V. (1960). *Experientia*, 16, 521–523.

KOPFMANN, G. & HUBER, R. (1968). *Acta Cryst.* A24, 348–351.

KOPFMANN, G. & HUBER, R. (1969). *Acta Cryst.* A25, 143–152.

KRISHNAMURTHY, M. & MORRIS, K. B. (1969). *Inorg. Chem.* 8, 2620–2624.

OSKARSSON, Å. (1973). *Acta Cryst.* B29, 1747–1751.

OSKARSSON, Å. (1974). *Acta Cryst.* B30, 780–783.

PANATTONI, C., GRAZIANI, R., BANDOLI, G., ZARLI, B. & BOMBIERI, G. (1969). *Inorg. Chem.* 8, 320–325.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). *X-RAY 70* system, version of July, Univ. of Maryland.

ZACHARIASEN, W. H. & PLETTINGER. H. A. (1959). *Acta Cryst.* 12, 526–530.