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Acta Cryst. (1978). B**34**, 1846–1849

The Crystal Structure of Diammonium Uranyl Tetraformate: $(NH_4)_2UO_2(HCOO)_4$

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(*Received* 12 *December* 1977; *accepted* 5 *January* 1978)

The crystal structure of diammonium uranyl tetraformate has been established by X-ray diffraction on a single crystal at 18 °C. This compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 9{\cdot}0850$ (9), $b = 17{\cdot}231$ (2), $c = 7{\cdot}711$ (2) Å, $\beta = 93{\cdot}13$ (1)°, $Z = 4$. The structure has been determined by the heavy-atom method from 2416 Mo $K\alpha$ intensities measured on a four-circle diffractometer, and refined by full-matrix least-squares computations. The final weighted R was 0·091 (conventional $R = 0{\cdot}110$). The U atom is at the centre of a pentagonal bipyramid. The apical O atoms are those of the uranyl group, which is nearly linear [O–U–O = 178 (1)°]. Two O atoms of the equatorial plane of the bipyramid belong to the same formato group. The ammonium groups form layers nearly perpendicular to the [100] axis. These layers are interconnected to the U polyhedra through the remaining three formato groups.

Introduction

In order to elucidate the mechanism of the photolytic decompositions of complex uranyl formates, we have undertaken, at the Laboratoire de Cinétique et Génie Chimiques, the preparation and structural studies of several of these complexes. The structures of $UO_2(HCOO)_2.H_2O$ (Mentzen, Puaux & Loiseleur, 1977) and $NaUO_2(HCOO)_3.H_2O$ (Mentzen, 1977) have recently been published, and, like both these solids, $(NH_4)_2UO_2(HCOO)_4$ is sensitive to visible, UV and X radiations. Claudel, Mentzen, Puaux & Sautereau (1977) reported the preparation and preliminary IR and X-ray investigations of diammonium uranyl tetraformate. The interpretation of the IR spectrum led to the following conclusions: (1) There are at least two types of formato groups. (2) There are two different types of ammonium groups in the solid.

Experimental results

Diammonium uranyl tetraformate has been prepared according to a method described elsewhere (Claudel, Mentzen, Puaux & Sautereau, 1977). The crystals are very soft, and owing to their high solubility in H_2O–HCOOH solutions their shape is not well defined. Nevertheless, we picked out of the mother liquor a nearly cubic crystal of 0·25 mm edge ($\mu r = 2{\cdot}27$). This crystal was mounted on the four-circle Enraf–Nonius CAD-4 automatic diffractometer of the Centre de Diffraction Automatique, Lyon. 4907 intensities corresponding to the hkl, $hk\bar{l}$, $\bar{h}k\bar{l}$ and $\bar{h}\bar{k}\bar{l}$ triplets (half reflexion sphere) were collected with the ω–2θ scan for $1 < \theta < 40°$ and $I > 2\sigma(I)$. After data reduction 2416 reflexions, of which 1412 are unique, were obtained and their intensities corrected for Lorentz and polarization factors as well as for absorption. Furthermore, the intensities were also corrected for the weakening of the intensity-control reflexion resulting from the photolytic effect of the X-rays on the crystal. Inspection of the data collected shows that the conditions limiting possible reflexions are consistent with the space group $P2_1/c$, *i.e.* $h0l$: $l = 2n$, $0k0$: $k = 2n$. The unit-cell parameters are: a = 9·0850 (9), b = 17·231 (2), c = 7·711 (2) Å, β = 93·13 (1)°, Z = 4, U = 1205·3 Å^3, M_r = 486·18, D_m = 2·680, D_x = 2·679 g cm^{-3}, $F(000)$ = 888, μ(Mo $K\bar{\alpha}$) = 128·14 cm^{-1}, t = 18 °C.

Structure determination

The interpretation of the Patterson function gave the atomic coordinates of the heavy atom. A Fourier synthesis with the structure factors and the phases corresponding to the heavy atom revealed the positions of all the O and N atoms, and a subsequent difference Fourier synthesis revealed the missing four C atoms. The atomic coordinates and isotropic thermal parameters of the 17 atoms of the asymmetric unit were refined by minimizing $\sum w(|F_o| - |F_c|)^2$, the weighting function being $w = (2|F_o|_{\min} + |F_o| + 2F_o^2/|F_o|_{\max})^{-1}$. After seven iterations, the anisotropic thermal parameters and the weighting function $w = (a + b|F_o|)^{-2}$ (Stout & Jensen, 1968) were introduced. Introduction of anomalous-dispersion factors did not improve the model, and these were therefore rejected. Accordingly, the last refinement cycle was run for two more iterations, the final R_w $\{= [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ being 0·091, and the conventional R $(=\sum||F_o| - |F_c||/\sum|F_o|)$ 0·110.* This rather high value for R_w is related to the fact that the crystal is soft, and that the overall isotropic thermal factor is 4·68 Å^2 including the factor for the U atom (B_U = 2·5 Å^2). Therefore, it might be worth reinvestigating the crystal structure of $(NH_4)_2UO_2(HCOO)_4$ at low temperature. The refined parameters are listed in Table 1; the atomic scattering factors used were those given in *International Tables for X-ray Crystallography* (1974).

Description of the structure

The principal bond distances and bond angles are given in Table 2. The structure is built up from two distinct structural units: the first is the pentagonal bipyramid formed by the U atom and its environment of seven O atoms [OU(1) and OU(2) belong to the uranyl group and O(1) through O(5) constitute with U the equatorial plane of the bipyramid]; the second corresponds to the coordination polyhedra of the N(1) and N(2) atoms which belong to the two types of ammonium groups. Fig. 1 represents a partial projection of the structure along the [001] direction. On this figure it should be noted that the O(1)–C(2)–O(2) formato group is bidentate and forms a four-membered ring with the central U atom; the remaining three formato groups are also bidentate, but they all bridge the U atom to N atoms. Fig. 2 depicts the N polyhedra layer; from this projection along the [100] direction it is clear that the N(1) and N(2) polyhedra are interlinked through the O(7) and O(8) atoms.

Table 1. *Relative atomic coordinates, isotropic thermal parameters and standard deviations for the* U, O, N *and* C *atoms*

	x	y	z	B_{eq} (Å^2)
U	0·22175 (4)	0·09692 (2)	0·28114 (4)	2·5
OU(1)	0·2194 (9)	0·0822 (4)	0·5095 (8)	3·8
OU(2)	0·2206 (7)	0·1081 (4)	0·0547 (7)	3·3
O(1)	−0·0492 (8)	0·0682 (4)	0·2637 (9)	3·1
O(2)	0·0904 (8)	−0·0318 (4)	0·225 (1)	4·2
O(3)	0·1093 (9)	0·2145 (5)	0·299 (1)	5·4
O(4)	0·390 (1)	−0·0047 (5)	0·279 (1)	4·6
O(5)	0·427 (1)	0·1801 (4)	0·323 (1)	4·3
N(1)	0·755 (1)	0·3563 (4)	0·487 (1)	6·1
N(2)	0·7202 (9)	0·1259 (5)	0·490 (1)	4·1
O(6)	0·582 (1)	0·2672 (6)	0·250 (1)	8·9
O(7)	0·599 (1)	0·0387 (6)	0·178 (1)	6·2
O(8)	−0·085 (1)	0·2645 (5)	0·185 (1)	5·5
C(1)	0·522 (1)	−0·0135 (6)	0·224 (1)	3·7
C(2)	−0·029 (1)	−0·0040 (6)	0·226 (1)	3·6
C(3)	0·456 (2)	0·2388 (8)	0·230 (1)	6·0
C(4)	0·040 (1)	0·2709 (7)	0·244 (1)	4·3

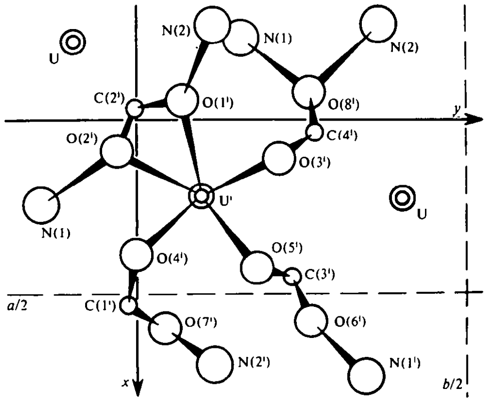

Fig. 1. Environment of the U atom. The projection is along the [001] direction.

Discussion

The present structure determination provides one more example of heptacoordinated U (pentagonal bipyramid). To the best of our knowledge the structure

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33335 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic bond distances* (Å) *and bond angles* (°)

For the sake of clarity the symmetry-code superscripts have only been used for the distances and angles involving N(1) and N(2).

U–OU(1)	1·78 (2)	OU(1)–U–OU(2)	177·9 (6)
U–OU(2)	1·76 (2)	O(1)–U–O(2)	50·9 (5)
U–O(1)	2·51 (2)	O(2)–U–O(4)	69·2 (4)
U–O(2)	2·54 (2)	O(4)–U–O(5)	86·8 (5)
U–O(3)	2·28 (2)	O(5)–U–O(3)	78·8 (5)
U–O(4)	2·33 (2)	O(3)–U–O(1)	74·7 (5)
U–O(5)	2·36 (2)	O(1)–U–OU(1)	87·7 (6)
O(1)···O(2)	2·17 (3)	O(2)–U–OU(1)	90·8 (6)
O(2)···O(4)	2·77 (3)	O(3)–U–OU(1)	86·7 (6)
O(4)···O(5)	3·22 (3)	O(4)–U–OU(1)	90·2 (6)
O(5)···O(3)	2·94 (3)	O(5)–U–OU(1)	92·1 (5)
O(3)···O(1)	2·91 (3)	O(1)–U–OU(2)	90·9 (6)
		O(2)–U–OU(2)	87·1 (6)
Formato groups		O(3)–U–OU(2)	92·5 (6)
C(1)–O(4)	1·30 (3)	O(4)–U–OU(2)	91·8 (6)
C(1)–O(7)	1·21 (3)	O(5)–U–OU(2)	89·1 (6)
C(2)–O(1)	1·29 (3)	O(3)–C(4)–O(8)	121·4 (7)
C(2)–O(2)	1·18 (4)	O(5)–C(3)–O(6)	117·1 (7)
C(3)–O(5)	1·28 (3)	O(4)–C(1)–O(7)	123·7 (7)
C(3)–O(6)	1·24 (4)	O(1)–C(2)–O(2)	122·3 (7)
C(4)–O(3)	1·21 (4)	O(6^{i})–N(1^{i})–O(2^{vi})	105·4 (8)
C(4)–O(8)	1·20 (4)	O(6^{i})–N(1^{i})–O(7^{iv})	114·8 (8)
		O(6^{i})–N(1^{i})–O(8^{vii})	101·3 (7)
Environment of		O(2^{vi})–N(1^{i})–O(7^{iv})	98·1 (7)
N(1) and N(2)		O(2^{vi})–N(1^{i})–O(8^{vii})	121·3 (8)
N(1^{i})–O(2^{vi})	2·94 (3)	O(7^{iv})–N(1^{i})–O(8^{vii})	116·3 (8)
N(1^{i})–O(7^{iv})	2·77 (3)	O(8^{vii})–N(2^{i})–O(8^{viii})	110·9 (8)
N(1^{i})–O(8^{vii})	2·92 (2)	O(8^{vii})–N(2^{i})–O(7^{i})	156·4 (8)
N(1^{i})–O(6^{i})	2·80 (3)	O(8^{vii})–N(2^{i})–O(1^{v})	95·2 (7)
N(2^{i})–O(8^{vii})	2·94 (3)	O(4^{viii})–N(2^{i})–O(7^{i})	90·6 (7)
N(2^{i})–O(4^{viii})	2·95 (3)	O(4^{viii})–N(2^{i})–O(1^{v})	112·9 (8)
N(2^{i})–O(7^{i})	2·99 (3)	O(7^{i})–N(2^{i})–O(1^{v})	66·5 (7)
N(2^{i})–O(1^{v})	2·97 (2)		

Symmetry code

(i) x, y, z
(ii) $-x, -y, -z$
(iii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$
(iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$
(v) $1+x, y, z$
(vi) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$
(vii) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$
(viii) $1-x, -y, 1-z$

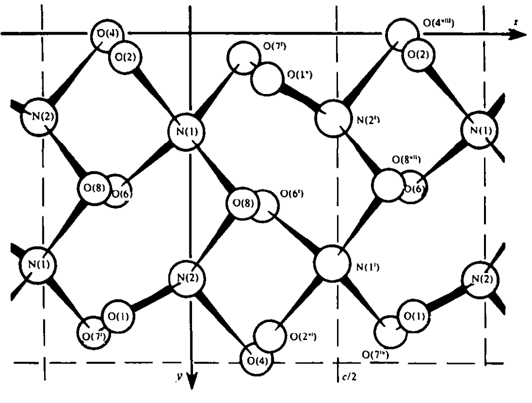

Fig. 2. The N(1) and N(2) polyhedra layer viewed along the [100] direction.

of $(NH_4)_2UO_2(HCOO)_4$ is the only complex uranyl formate where a bidentate formato group is linked to the same central U atom. Carboxylic groups which with a central atom form four-membered rings have already been reported for uranyl diacetate dihydrate (Howatson, Grev & Morosin, 1975) and uranyl oxalates (Jayadevan & Chackraburtty, 1972; Alcock, 1973; Legros & Jeannin, 1976). Although the equatorial plane of the pentagonal bipyramid in $(NH_4)_2UO_2(HCOO)_4$ is almost planar, the presence of the four-membered U–O(1)–C(2)–O(2) ring introduces large differences in the U–O bond distances in the pentagon (see Table 2). The three other formato groups are bidentate and they all bridge U polyhedra to N polyhedra; accordingly, the complex may be formulated $[NH_4]_2(HCOO)_3[UO_2(HCOO)]$. On inspecting the standard deviations on the carboxylic C–O bond distances one can consider that there are two symmetric [O(5)–C(3)–O(6) and O(3)–C(4)–O(8)] and two asymmetric formato groups [O(1)–C(2)–O(2) and O(4)–C(1)–O(7)]. Thus, the ν_{as}(CO) infrared bands at 1744 and 1600–1560 cm^{-1}, respectively, correspond to the shorter (1·18–1·21 Å) and the normal (1·24–1·30 Å) C–O distances. The two N(1) and N(2) coordination polyhedra are quite different and, if we consider only the N–O distances shorter than 3 Å, it clearly appears that N(1) has a nearly regular tetrahedral environment of O atoms and that N(2) has a very distorted one. On the other hand, if we assume that the H atoms of the NH_4 groups lie nearly on the N–O bonds, the previously observed IR bands can now be interpreted, *i.e.* the ν_{as}(NH) bands at 3395 and 3190 cm^{-1}, respectively, correspond to the shorter [N(1)–H···O = 2·77–2·80 Å] and the longer [N–H···O = 2·92–2·99 Å] H–N distances.

Accordingly, from the above description it appears that the framework of the crystal structure of diammonium uranyl tetraformate is comprised of layers of interconnected ammonium groups which are interlinked to the U polyhedra through three of the four bidentate formato groups.

All the computations have been performed on an IBM 370-168 computer at Orsay (CIRCE), through the terminal of the Institut de Recherches sur la Catalyse, Lyon, and by means of a program library available at the Laboratoire de Chimie Analytique II, Université Claude Bernard, Lyon I.

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Acta Cryst. (1978). B**34**, 1849–1853

The Crystal Structure of Bis(triphenylphosphine)(perfluoro-1,2-3,4-5,6-triethanobenzene)platinum(0)

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(*Received 7 December* 1977; *accepted* 13 *January* 1978)

Bis(triphenylphosphine)(perfluoro-1,2-3,4-5,6-triethanobenzene)platinum(0).$\frac{1}{2}C_5H_{12}$ (?) is triclinic, space group $P\bar{1}$, with $a = 17{\cdot}435$ (9), $b = 12{\cdot}795$ (6), $c = 11{\cdot}248$ (5) Å, $\alpha = 104{\cdot}39$ (2), $\beta = 108{\cdot}08$ (4), $\gamma = 95{\cdot}37$ (3)°, $Z = 2$. Refinement gave $R = 0{\cdot}061$ for 3316 counter reflexions. The coordination at the Pt atom is essentially trigonal planar and bonding of the $C_{12}F_{12}$ is *via* a double bond of its benzene ring. The C atoms of the bond coordinate symmetrically and are almost coplanar with the Pt and the P atoms of the two coordinating triphenylphosphine ligands. Bond lengths around the $C_{12}F_{12}$ benzene ring alternate, with the exception of the bond coordinated to the Pt atom which is also long [1·52 (2) Å].

Introduction

The structures of the cyclic fluorocarbons perfluoro-1,2-3,4-5,6-triethanobenzene ($C_{12}F_{12}$) (Cobbledick & Einstein, 1976) and perfluorododecahydrotetracyclopentacyclooctene ($C_{20}F_{24}$) (Cobbledick & Einstein, 1977) have been determined. These compounds can coordinate to a transition metal and the structure of the title compound was studied to investigate the bonding of the $C_{12}F_{12}$ moiety to the Pt atom.

Experimental

Weissenberg and precession photographs (Cu $K\alpha$ radiation) showed the yellow crystals to be triclinic. Cell dimensions were obtained by least-squares refinement of the setting angles of ten reflexions with $2\theta > 30°$ centred on a Picker FACS-I automatic four-circle diffractometer [λ(Mo $K\alpha_1$) = 0·70926 Å]. Crystal data are given in Table 1. Intensities were collected (crystal dimensions 0·20 × 0·10 × 0·08 mm) with the diffractometer using a graphite monochromator and a scintillation counter with pulse-height discrimination. A θ–2θ scan was used with a scan speed of 2° min^{-1} in 2θ. The data were collected in two shells; reflexions having $0 < 2\theta \leq 20°$ were measured with a scan base width of 1·3° and reflexions with $20 < 2\theta \leq 40°$ had a width of 1·0° (both widths were increased for dispersion). Background measurements of 4 s duration were made at either side of the reflexions. Intensities were measured for 4265 unique reflexions, of which 3316 were classed as observed ($I > 2{\cdot}3\sigma I$, where σI is the standard deviation). Lorentz and polarization corrections were applied. No absorption correction was made [μ(Mo $K\alpha$) = 34·1 cm^{-1}] and this could give a maximum error of 3% in F.

The space group was assumed to be $P\bar{1}$ and was confirmed by successful refinement. The positions of the Pt and P atoms were obtained from a Patterson synthesis. After least-squares refinement, the remaining non-hydrogen atoms were located from a difference synthesis.

Table 1. *Crystal data*

$C_{48}H_{30}F_{12}P_2Pt.\frac{1}{2}(C_5H_{12})$, $M_r = 1127{\cdot}88$

$a = 17{\cdot}435$ (9) Å	Space group: $P\bar{1}$
$b = 12{\cdot}795$ (6)	$V = 2270{\cdot}3$ Å^3
$c = 11{\cdot}248$ (5)	$Z = 2$
$\alpha = 104{\cdot}39$ (2)°	$D_o = 1{\cdot}65$ g cm^{-3}
$\beta = 108{\cdot}08$ (4)	$D_c = 1{\cdot}650$
$\gamma = 95{\cdot}37$ (3)	μ(Mo $K\alpha$) = 34·1 cm^{-1}