

## The Crystal and Molecular Structure of Pyridine-2,6-dicarboxylatodioxouranium(VI) Monohydrate

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The structure has been determined by three-dimensional X-ray counter techniques. The complex crystallizes in the hexagonal space group  $P6_1$ ,  $Z=6$ ,  $a=b=14.685$  (2),  $c=9.313$  (1) Å,  $D_{\text{calc}}=2.60$ ,  $D_{\text{obs}}=2.6$  g cm<sup>-3</sup>. Full-matrix least-squares treatment of 890 observed intensities gave an unweighted  $R$  value of 0.033. The linear uranyl group coordinates a single PDC unit as a tridentate equatorial ligand through nitrogen and two oxygen atoms; each  $\text{UO}_2$ -PDC unit is linked through one of its carboxylic oxygen atoms to an adjacent  $\text{UO}_2$ -PDC unit, thus giving rise to a polymeric structure. The water molecule is also coordinated to uranium to give coordination number 7. The polymer crystallizes with helices having the same sense linked together by hydrogen bonding between coordinated water and free C=O groups. The space inside the helices is unfilled and forms a tunnel along the length of the polymer.

### Introduction

The interaction of several metal ions with pyridine-2,6-dicarboxylic acid ( $\text{H}_2\text{PDC}$ ) has been investigated by many authors. In particular the crystal structures of complexes of  $\text{Ag}^{2+}$  (Drew, Matthews & Walton, 1971),  $\text{Ni}^{2+}$  (Gaw, Robinson & Walton, 1971),  $\text{Sr}^{2+}$  (Palmer, Wong & Lewis, 1972) and some lanthanide(III) ions (Albertsson, 1972) are known, as well as the structure of the 2:1 complex with  $\text{UO}_2^{2+}$  (Marangoni, Degetto, Graziani, Bombieri & Forsellini, 1974).

In all the complexes referred to the PDC anion acts as a tridentate ligand by coordination of the nitrogen atom and one oxygen atom from each carboxylate group. The remaining oxygen atoms may coordinate to adjacent metal atoms to form polymeric structures as suggested previously (Cattalini, Baracco, Degetto, Marangoni, Maresca & Sindellari, 1974).

For the title compound, the presence of only one infrared band for the antisymmetric  $-\text{COO}-$  stretching frequency (1615 cm<sup>-1</sup>) seemed to suggest that both carboxylate groups were in similar bonding environment. Furthermore the infrared spectrum and thermal data did not show whether or not the water molecule was coordinated to the uranium atom (Degetto, Marangoni, Baracco, Gurrieri & Siracusa, 1974). In order to clarify the structure of the  $(\text{UO}_2\text{PCD} \cdot \text{H}_2\text{O})_n$  compound, a single-crystal X-ray analysis has been carried out and forms the basis of this report.

### Experimental

$(\text{UO}_2\text{PDC} \cdot \text{H}_2\text{O})_n$  was prepared as previously reported (Cattalini *et al.*, 1974). Crystals suitable for the X-ray study were obtained by dissolving the crude product in

hot water ( $\sim 70^\circ\text{C}$ ) and then cooling very slowly ( $\sim 1^\circ\text{C}$  per day) to room temperature.

### Crystal data

(Pyridine-2,6-dicarboxylato)dioxouranium(VI) monohydrate:  $\text{C}_7\text{H}_5\text{NO}_7\text{U}$ , F.W. 453.2; pale yellow rectangular prism elongated along  $c$ . Hexagonal,  $a=b=14.685$  (2),  $c=9.313$  (1) Å,  $V=1739.5$  Å<sup>3</sup>,  $D_{\text{calc}}=2.60$ ,  $D_{\text{obs}}=2.6$  g cm<sup>-3</sup> (flotation),  $Z=6$ ,  $\mu=134$  cm<sup>-1</sup> for Mo  $K\alpha$  ( $\lambda=0.7107$  Å),  $F(000)=1212$ . Space group  $P6_1$  from structure determination.

Precession and Weissenberg photographs showed the crystal to be hexagonal with  $|F_{hkl}| \neq |F_{khl}|$  and systematic absence of  $00l$  reflexions for  $l \neq 6n$ . Thus the possible space groups are  $P6_1$  or the enantiomorphic  $P6_5$ .

For the lattice parameter determination the principal rows  $h00$ ,  $0k0$ ,  $hh0$  and  $00l$  were considered. The angles for several strong reflexions with  $15^\circ < \theta < 25^\circ$  were measured by determining the centres of gravity of the peak profiles  $I=f(\theta)$ . The values for negative and positive  $\theta$  angles were averaged and their e.s.d.'s evaluated from the root-mean-square deviation of the  $\sin \theta$  values.

All intensities were collected with a Philips PW-1100 diffractometer using a graphite monochromator and Mo  $K\alpha$  radiation ( $\lambda=0.7107$  Å). 1092 independent reflexions with  $h > 0$ ,  $k \geq 0$ ,  $l \geq 0$  were collected between  $3^\circ$  and  $25^\circ$ . The intensities were then corrected for Lorentz and polarization effects and for absorption using the program *ORABS* (Busing & Levy, 1957) on the basis of a rectangular prism of dimensions  $0.087 \times 0.058 \times 0.234$  mm with the longest edge parallel to the crystallographic  $c$  axis.

The 890 reflexions with a net intensity greater than  $3\sigma(I)$  were used in the structure refinement [ $\sigma(I)$  based

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

Temperature factor:

$$\exp(-\frac{1}{4}[B_{11}a^*{}^2h^2 + \dots + B_{12}a^*b^*hk + \dots]).$$

	x	y	z	B (Å <sup>2</sup> )
U	0.38688 (5)	0.45194 (5)	0.16674 (0)	*
O(1)	0.3680 (10)	0.4027 (10)	0.3431 (19)	2.92 (22)
O(2)	0.4059 (11)	0.5016 (11)	-0.0096 (20)	3.58 (28)
O(3)	0.2181 (14)	0.3088 (14)	0.0898 (21)	4.92 (35)
O(4)	0.5148 (10)	0.6199 (11)	0.2494 (17)	2.73 (24)
O(5)	0.6799 (12)	0.7535 (12)	0.2734 (18)	3.71 (29)
O(6)	0.4165 (11)	0.3098 (10)	0.0992 (17)	2.88 (25)
O(7)	0.5192 (11)	0.2442 (11)	0.0419 (16)	3.10 (26)
N	0.5742 (11)	0.4914 (10)	0.1572 (19)	1.74 (23)
C(1)	0.6150 (16)	0.6627 (16)	0.2389 (25)	2.86 (36)
C(2)	0.6538 (14)	0.5907 (14)	0.1851 (26)	2.57 (34)
C(3)	0.7592 (15)	0.6212 (16)	0.1706 (30)	3.13 (34)
C(4)	0.7839 (17)	0.5481 (18)	0.1225 (24)	3.03 (37)
C(5)	0.7004 (16)	0.4426 (16)	0.0908 (24)	2.51 (33)
C(6)	0.6006 (13)	0.4222 (13)	0.1059 (20)	1.53 (27)
C(7)	0.5062 (16)	0.3187 (16)	0.0777 (24)	2.63 (34)

\* Anisotropic thermal parameters for the uranium atom:

$B_{11}$	$B_{22}$	$B_{33}$
1.821 (24)	2.285 (26)	2.341 (15)
$B_{12}$	$B_{13}$	$B_{23}$
2.561 (46)	-0.053 (62)	-0.366 (54)

on counting statistics]. The data were collected by the  $\omega$  scan method (take-off angle 3°, scan width 1°, scan speed 1.8° min<sup>-1</sup>, two 10 s background counts).

### Structure determination

The structure was resolved by the standard heavy-atom method and refined by a full-matrix least-squares

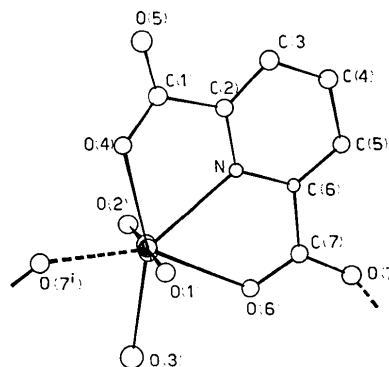


Fig. 1. Molecular model of the repeating unit  $\text{UO}_2\text{-PDC}\cdot\text{H}_2\text{O}$ .

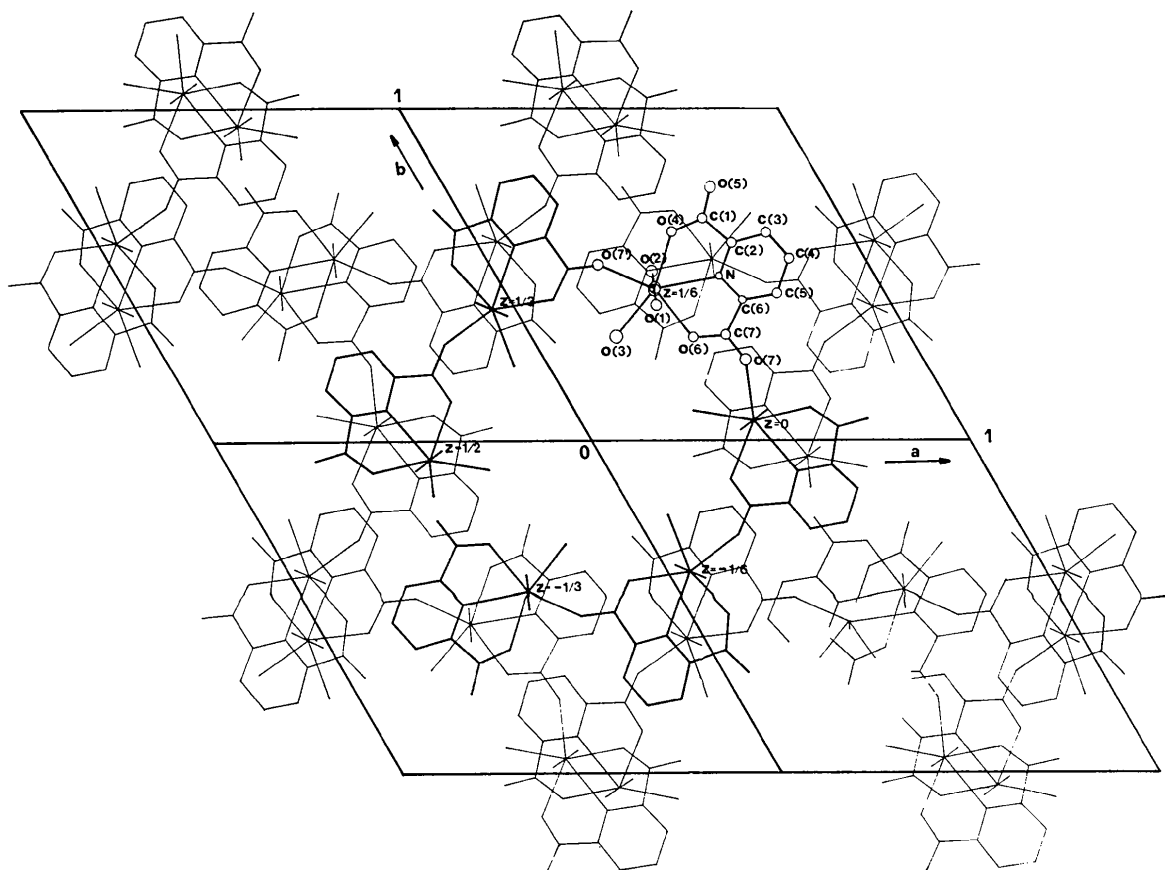


Fig. 2. Projection of the structure along the [001] direction. A single helix is drawn with heavy lines and the surrounding helices with light lines.

procedure using unitary weight factors and minimizing  $\sum w(|F_{obs}| - |F_{calc}|)^2$ . Isotropic thermal vibration parameters were used for all atoms except uranium, which was refined anisotropically with its *z* coordinate held constant to define the origin along the *z* axis. Atomic factors given by Doyle & Turner (1968) were used and the anomalous dispersion correction (Cromer & Liberman, 1970) applied to the uranium atom with  $A_f' = -10.673$  and  $A_f'' = 9.654$ . The refinement with  $P6_1$  or  $P6_5$  space groups gave significantly different results: although the *R* value was only moderately different (0.033 and 0.037 respectively), the resulting molecular geometry of the  $UO_2$  group was considerably different in the two cases. With  $P6_1$  the  $UO_2$  group turns out to be linear and symmetric as expected (U-O distances 1.76 and 1.76 Å, O-U-O angle 179.8°), whereas with  $P6_5$  symmetry a bent dissymmetric structure

results (U-O distances 1.64 and 1.89, O-U-O angle 178.1°). Thus the absolute configuration with right-handed helices can be assigned to the crystal studied. Because the starting material contained no asymmetric substances, the crystallized product would of course contain equal amounts of  $P6_1$  and  $P6_5$  crystals.

In the final difference Fourier synthesis only a random distribution of positive and negative residuals (all weaker than 0.8 e Å<sup>-3</sup>) was found, indicating the absence of water of crystallization. In these conditions, localization of hydrogen atoms was not attempted.

The final atomic coordinates and thermal parameters with their estimated standard deviations are listed in Table 1. Observed and calculated structure factors are listed in Table 2. Bond lengths and valence angles are listed in Table 3.

Table 2. Observed and calculated structure factors (10 × absolute values)

Columns are *h, k, l, F<sub>o</sub>* and *F<sub>c</sub>*. Unobserved reflexions are marked by <. The phases are not listed.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>
0	0	0	1102	1102	1	1	1	1341	1392	1	1	1	1067	1396	1	1	1	632	625
0	0	1	1162	1162	2	2	2	1741	1741	2	2	2	1412	1680	2	2	2	842	842
0	0	2	1202	1202	3	3	3	2092	2092	3	3	3	1761	1944	3	3	3	1092	1092
0	0	3	1242	1242	4	4	4	2442	2442	4	4	4	2012	2208	4	4	4	1342	1342
0	0	4	1282	1282	5	5	5	2792	2792	5	5	5	2262	2472	5	5	5	1592	1592
0	0	5	1322	1322	6	6	6	3142	3142	6	6	6	2512	2736	6	6	6	1842	1842
0	0	6	1362	1362	7	7	7	3492	3492	7	7	7	2762	3000	7	7	7	2092	2092
0	0	7	1402	1402	8	8	8	3842	3842	8	8	8	3012	3264	8	8	8	2342	2342
0	0	8	1442	1442	9	9	9	4192	4192	9	9	9	3262	3528	9	9	9	2592	2592
0	0	9	1482	1482	10	10	10	4542	4542	10	10	10	3512	3792	10	10	10	2842	2842
0	0	10	1522	1522	11	11	11	4892	4892	11	11	11	3762	4056	11	11	11	3092	3092
0	0	11	1562	1562	12	12	12	5242	5242	12	12	12	4012	4320	12	12	12	3342	3342
0	0	12	1602	1602	13	13	13	5592	5592	13	13	13	4262	4584	13	13	13	3592	3592
0	0	13	1642	1642	14	14	14	5942	5942	14	14	14	4512	4848	14	14	14	3842	3842
0	0	14	1682	1682	15	15	15	6292	6292	15	15	15	4762	5112	15	15	15	4092	4092
0	0	15	1722	1722	16	16	16	6642	6642	16	16	16	5012	5376	16	16	16	4342	4342
0	0	16	1762	1762	17	17	17	6992	6992	17	17	17	5262	5640	17	17	17	4592	4592
0	0	17	1802	1802	18	18	18	7342	7342	18	18	18	5512	5904	18	18	18	4842	4842
0	0	18	1842	1842	19	19	19	7692	7692	19	19	19	5762	6168	19	19	19	5092	5092
0	0	19	1882	1882	20	20	20	8042	8042	20	20	20	6012	6432	20	20	20	5342	5342
0	0	20	1922	1922	21	21	21	8392	8392	21	21	21	6262	6696	21	21	21	5592	5592
0	0	21	1962	1962	22	22	22	8742	8742	22	22	22	6512	6960	22	22	22	5842	5842
0	0	22	2002	2002	23	23	23	9092	9092	23	23	23	6762	7224	23	23	23	6092	6092
0	0	23	2042	2042	24	24	24	9442	9442	24	24	24	7012	7488	24	24	24	6342	6342
0	0	24	2082	2082	25	25	25	9792	9792	25	25	25	7262	7752	25	25	25	6592	6592
0	0	25	2122	2122	26	26	26	10142	10142	26	26	26	7512	8016	26	26	26	6842	6842
0	0	26	2162	2162	27	27	27	10492	10492	27	27	27	7762	8280	27	27	27	7092	7092
0	0	27	2202	2202	28	28	28	10842	10842	28	28	28	8012	8544	28	28	28	7342	7342
0	0	28	2242	2242	29	29	29	11192	11192	29	29	29	8262	8808	29	29	29	7592	7592
0	0	29	2282	2282	30	30	30	11542	11542	30	30	30	8512	9072	30	30	30	7842	7842
0	0	30	2322	2322	31	31	31	11892	11892	31	31	31	8762	9336	31	31	31	8092	8092
0	0	31	2362	2362	32	32	32	12242	12242	32	32	32	9012	9600	32	32	32	8342	8342
0	0	32	2402	2402	33	33	33	12592	12592	33	33	33	9262	9864	33	33	33	8592	8592
0	0	33	2442	2442	34	34	34	12942	12942	34	34	34	9512	10128	34	34	34	8842	8842
0	0	34	2482	2482	35	35	35	13292	13292	35	35	35	9762	10392	35	35	35	9092	9092
0	0	35	2522	2522	36	36	36	13642	13642	36	36	36	10012	10656	36	36	36	9342	9342
0	0	36	2562	2562	37	37	37	13992	13992	37	37	37	10262	10920	37	37	37	9592	9592
0	0	37	2602	2602	38	38	38	14342	14342	38	38	38	10512	11184	38	38	38	9842	9842
0	0	38	2642	2642	39	39	39	14692	14692	39	39	39	10762	11448	39	39	39	10092	10092
0	0	39	2682	2682	40	40	40	15042	15042	40	40	40	11012	11712	40	40	40	10342	10342
0	0	40	2722	2722	41	41	41	15392	15392	41	41	41	11262	11976	41	41	41	10592	10592
0	0	41	2762	2762	42	42	42	15742	15742	42	42	42	11512	12240	42	42	42	10842	10842
0	0	42	2802	2802	43	43	43	16092	16092	43	43	43	11762	12504	43	43	43	11092	11092
0	0	43	2842	2842	44	44	44	16442	16442	44	44	44	12012	12768	44	44	44	11342	11342
0	0	44	2882	2882	45	45	45	16792	16792	45	45	45	12262	13032	45	45	45	11592	11592
0	0	45	2922	2922	46	46	46	17142	17142	46	46	46	12512	13296	46	46	46	11842	11842
0	0	46	2962	2962	47	47	47	17492	17492	47	47	47	12762	13560	47	47	47	12092	12092
0	0	47	3002	3002	48	48	48	17842	17842	48	48	48	13012	13824	48	48	48	12342	12342
0	0	48	3042	3042	49	49	49	18192	18192	49	49	49	13262	14088	49	49	49	12592	12592
0	0	49	3082	3082	50	50	50	18542	18542	50	50	50	13512	14352	50	50	50	12842	12842
0	0	50	3122	3122	51	51	51	18892	18892	51	51	51	13762	14616	51	51	51	13092	13092
0	0	51	3162	3162	52	52	52	19242	19242	52	52	52	14012	14880	52	52	52	13342	13342
0	0	52	3202	3202	53	53	53	19592	19592	53	53	53	14262	15144	53	53	53	13592	13592
0	0	53	3242	3242	54	54	54	19942	19942	54	54	54	14512	15408	54	54	54	13842	13842
0	0	54	3282	3282	55	55	55	20292	20292	55	55	55	14762	15672	55	55	55	14092	14092
0	0	55	3322	3322	56	56	56	20642	20642	56	56	56	15012	15936	56	56	56	14342	14342
0	0	56	3362	3362	57	57	57	20992	20992	57	57	57	15262	16200	57	57	57	14592	14592
0	0	57	3402	3402	58	58	58	21342	21342	58	58	58	15512	16464	58	58	58	14842	14842
0	0	58	3442	3442	59	59	59	21692	21692	59	59	59	15762	16728	59	59	59	15092	15092
0	0	59	3482	3482	60	60	60	22042	22042	60	60	60	16012	17000	60	60	60	15342	15342
0	0	60	3522	3522	61	61	61	22392	22392	61	61	61	16262	17264	61	61	61	15592	15592
0	0	61	3562	3562	62	62	62	22742	22742	62	62	62	16512	17528	62	62	62	15842	15842
0	0	62	3602	3602	63	63	63	23092	23092	63	63	63	16762	17792	63	63	63	16092	16092
0	0	63	3642	3642	64	64	64	23442	23442	64	64	64	17012	18056	64	64	64	16342	16342
0	0	64	3682	3682	65	65	65	23792	23792	65	65	65	17262	18320	65	65	65	16592	16592
0	0	65	3722	3722	66	66	66	24142	24142	66	66	66	17512	18584	66	66	66	16842	16842
0	0	66	3762	3762	67	67	67	24492	24492	67	67	67	17762	18848	67	67	67	17092	17092
0	0	67	3802	3802	68	68	68	24842	24842	68	68	68	18012	19112	68	68	68	17342	17342
0	0	68	3842	3842	69	69	69	25192	25192	69	69	69	18262	19376	69	69	69	17592	17592
0	0	69	3882	3882	70	70	70	25542	25542	70	70	70	18512	1964					

Table 3. Bond lengths (Å), bond angles (°) and *e.s.d.*'s in parentheses

U—O(1)	1.76 (2)	C(2)—N	1.36 (2)
U—O(2)	1.76 (2)	C(2)—C(3)	1.39 (3)
U—O(3)	2.42 (2)	C(3)—C(4)	1.37 (4)
U—O(4)	2.36 (1)	C(4)—C(5)	1.45 (3)
U—O(6)	2.42 (2)	C(5)—C(6)	1.35 (3)
U—O(7 <sup>1</sup> )	2.33 (2)	C(6)—N	1.34 (3)
U—N	2.51 (2)	C(6)—C(7)	1.48 (2)
C(1)—O(4)	1.28 (3)	C(7)—O(7)	1.25 (4)
C(1)—O(5)	1.23 (2)	C(7)—O(6)	1.27 (3)
C(1)—C(2)	1.52 (4)		
O(1)—U—O(2)	179.8 (7)	C(3)—C(4)—C(5)	119 (2)
O(3)—U—O(6)	73.8 (7)	C(4)—C(5)—C(6)	118 (2)
O(6)—U—N	62.7 (5)	C(5)—C(6)—N	124 (2)
N—U—O(4)	64.1 (6)	C(6)—N—C(2)	117 (2)
O(4)—U—O(7 <sup>1</sup> )	82.2 (7)	U—N—C(2)	120 (2)
O(7 <sup>1</sup> )—U—O(3)	77.6 (8)	U—N—C(6)	122 (1)
U—O(4)—C(1)	127 (2)	N—C(6)—C(7)	111 (2)
O(4)—C(1)—O(5)	126 (3)	C(5)—C(6)—C(7)	124 (2)
O(5)—C(1)—C(2)	119 (2)	C(6)—C(7)—O(7)	118 (2)
O(4)—C(1)—C(2)	115 (2)	C(6)—C(7)—O(6)	118 (2)
C(1)—C(2)—N	113 (2)	O(6)—C(7)—O(7)	124 (2)
C(1)—C(2)—C(3)	124 (2)	U—O(6)—C(7)	125 (1)
N—C(2)—C(3)	123 (2)	U—O(7 <sup>1</sup> )—C(7)	150 (2)
C(2)—C(3)—C(4)	118 (2)		

The codes for symmetry-related atoms are as follows:

Symbol	Symmetry code			
	None	<i>x</i>	<i>y</i>	<i>z</i>
i		$x-y$	$x$	$\frac{1}{6}+z$
ii		$y-x$	$1-x$	$-\frac{1}{3}+z$
iii		$1-y$	$x-y$	$\frac{1}{3}+z$
iv		$1-x$	$1-y$	$\frac{1}{2}+z$
v		$y$	$1-x+y$	$-\frac{1}{6}+z$

All the programs used throughout the structure determination were those written by Immirzi (1967, 1973). The calculations were performed with the Univac 1108 computer at the Politecnico di Milano.

### Description of the structure

In Fig. 1 the projection of the asymmetric unit along [001] is shown together with the labelling of the atoms.

The repeating unit consists of a linear uranyl group equatorially surrounded by five ligand atoms: two carboxylate oxygens and the nitrogen atom of one PDC ion, a bridging oxygen atom of an adjacent PDC unit, and one water molecule. The carboxylate bridging between adjacent uranyl groups leads to a polymeric structure in the form of a helix orientated parallel to the  $6_1$  axis.

The five equatorial atoms coordinated to the uranyl group are not exactly coplanar. The deviations from the plane of best fit are significant and are characteristic of a puckered structure. The equations of several least-squares planes, together with the deviations of the individual atoms, are shown in Table 4.

Within the  $\text{UO}_2$ -PDC unit the three U-O bond lengths are not equal, ranging between 2.33 and 2.42 Å. These differences could be attributed to different negative charges on the oxygen atoms as well as to the strain of the polymeric structure. The U-O(4) distance 2.36 Å, which is not affected by polymer strain compares well with the U-O distance 2.37 Å observed in oxydiacetatodioxouranium(VI) (Bombieri, Croatto, Graziani, Forsellini & Magon, 1974): in both cases carboxylate groups are bonded to the metal with one oxygen atom only and a major negative charge can reasonably be supposed to exist on the bonded oxygen atoms. On the other hand the U-O(6) and U-O(7<sup>1</sup>) distances (2.42 and 2.33 Å), which in principle should be very similar, may have different values because of polymeric strain. The value of the U-N bond, 2.51 (2) Å, which is significantly shorter than the analogous bond in  $(\text{Ph}_4\text{As})_2[\text{UO}_2(\text{PDC})_2] \cdot 6\text{H}_2\text{O}$  (Marangoni *et al.*, 1974) (2.73 Å), could be attributed to a different charge on the metal due to the presence of only one PDC group.

The configuration of the PDC ligand is approximately planar, but the uranium atom is displaced by 0.20 Å from the best plane passing through the carbon and nitrogen atoms of the ligand. Although the carboxylate group C(1)-O(4)-O(5) is not twisted with respect to this plane, the O(7) atom bonded to the adjacent uranium atom is out of the plane by 0.08 Å. A larger

Table 4. Least-squares planes

The equations are referred to an orthogonal reference system  $x, y, z$  with  $x$  and  $z$  coincident with the corresponding crystal axes directions. Deviations (Å) of the atoms from the plane are given in square brackets.

Plane	Atoms in plane	Equation of the plane
1	O(3), O(4), O(6), N, O(7 <sup>1</sup> ) [U 0.034, O(1) 1.793, O(2) -1.728, O(3) -0.077, N -0.117, O(4) 0.054, O(5) -0.256, O(6) 0.124, O(7) -0.008, O(7 <sup>1</sup> ) 0.017]	$0.04220x - 0.34182y + 0.93882z = -0.44082$
2	C(1), C(2), C(3), C(4), C(5), C(6), C(7), N [U -0.202, O(3) -0.622, N 0.024, O(4) 0.038, O(5) 0.031, O(6) -0.014, O(7) 0.082, C(1) -0.003, C(2) -0.010, C(3) -0.006, C(4), -0.002, C(5) 0.017, C(6) -0.017, C(7) -0.006, O(7 <sup>1</sup> ) -0.465]	$0.18217x - 0.28247y + 0.94182z = 0.47095$
3	C(1), C(2), C(3), C(4), C(5), C(6), C(7), N, O(4), O(6) [U -0.211, O(3) -0.629, N 0.018, O(4) 0.021, O(5) 0.014, O(6) -0.012, O(7) 0.094, C(1) -0.012, C(2) -0.017, C(3) -0.010, C(4) 0.002, C(5) 0.024, C(6) -0.014, C(7) -0.001, O(7 <sup>1</sup> ) -0.486]	$0.18538x - 0.28582y + 0.94018z = 0.46664$

Interplanar angles  $\angle_{12} = 8.7$ ,  $\angle_{13} = 8.8$ ,  $\angle_{23} = 0.3^\circ$ .

displacement is present for the O(7<sup>i</sup>) atom (0.47 Å). The last two features may be attributed to the strain imposed by the conformation of the polymeric chain.

#### Molecular packing

The structure is characterized by a pattern of helices all with the same sense with a van der Waals diameter of about 21 Å. Each helix is surrounded (see Fig. 2) by six other helices (as required by the space-group symmetry) with an axis-to-axis distance of  $a = 14.68$  Å; thus the polymeric chains are partly interpenetrating. A short intermolecular distance of 2.61 Å is present between the water oxygen O(3) and the free carboxylate oxygen atom O(5<sup>ii</sup>) belonging to an adjacent chain. This distance and the suitable angles on O(3) and O(5) suggest the presence of a hydrogen bond which limits the interpenetration of the helices. As a result the latter have a large hollow screw shape. In projection along the helical axis the complete structure has a honeycomb appearance which in three dimensions produces a matrix of wide empty tunnels of van der Waals diameter about 8 Å (see Fig. 3). Along the  $z$  direction there are close contacts (see Table 5) between PDC groups of adjacent helices.

Similar large cavities were encountered in the rare-earth carboxylate complexes (Albertsson, 1972; Han-

Table 5. Selected intra- and intermolecular contacts (Å) less than 3.65 Å with *e.s.d.*'s in parentheses

(a) Intramolecular			
N·····O(4)	2.59 (3)	O(3)···O(7 <sup>i</sup> )	2.98 (3)
N·····O(6)	2.57 (2)	O(4)···O(7 <sup>i</sup> )	3.09 (2)
O(6)···O(3)	2.91 (3)		
(b) Intermolecular			
O(3)···O(5 <sup>ii</sup> )	2.61 (3)	C(1)···O(6 <sup>iv</sup> )	3.44 (3)
O(6)···C(4 <sup>iii</sup> )	3.61 (3)	O(1)···C(2 <sup>iv</sup> )	3.21 (3)
O(7)···C(5 <sup>iii</sup> )	3.59 (3)	O(1)···C(6 <sup>iv</sup> )	3.41 (3)
C(7)···C(5 <sup>iii</sup> )	3.53 (3)	C(1)···C(3 <sup>v</sup> )	3.62 (3)
C(2)···O(2 <sup>iv</sup> )	3.08 (3)	O(4)···C(4 <sup>v</sup> )	3.34 (3)
O(5)···O(3 <sup>iv</sup> )	3.62 (3)	O(2)···C(5 <sup>v</sup> )	3.35 (2)
C(1)···O(2 <sup>iv</sup> )	3.26 (3)	C(1)···C(4 <sup>v</sup> )	3.41 (3)

son, 1972), but generally they are filled by solvent water or cations. In the present case, the final difference synthesis failed to reveal any appreciable residue that could be attributed to disordered water molecules in the tunnel. Also in the thermogravimetric analysis of the compound only one water molecule per uranium atom was detected.

The observation of only one asymmetric stretching vibration at 1615 cm<sup>-1</sup> for the two different -COO- groups could be explained by hydrogen bonding to the non bridging -COO- group. The frequency is thus

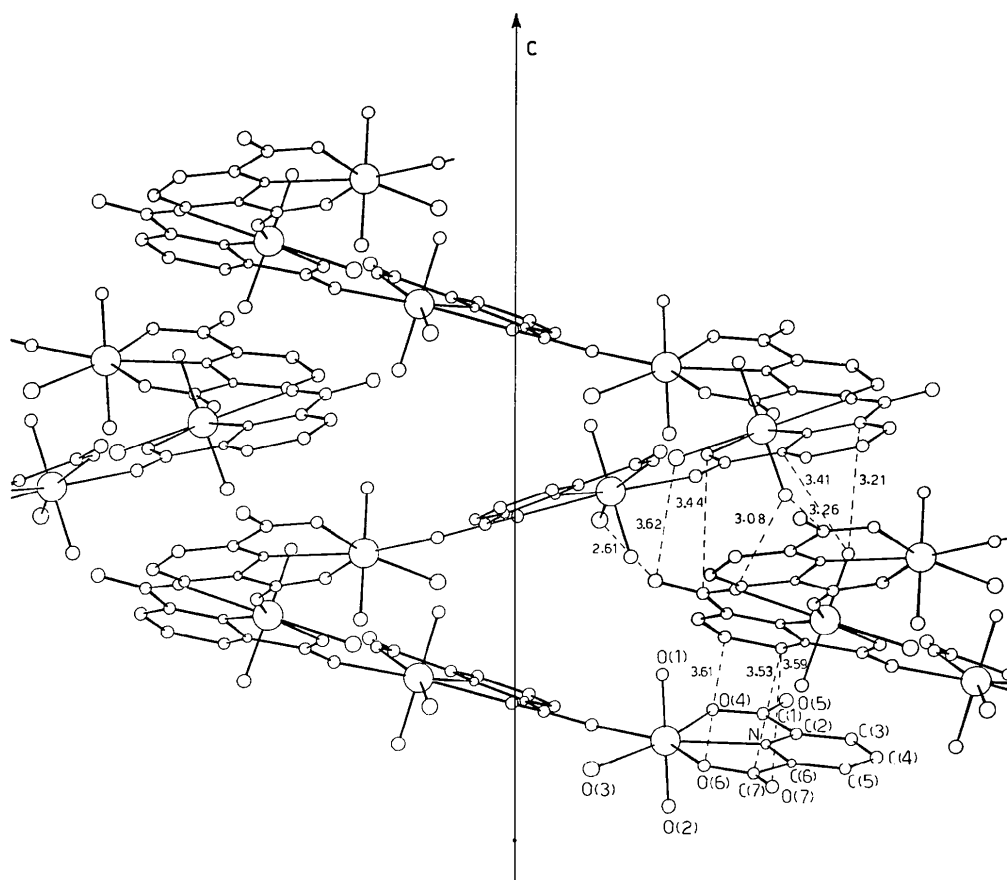


Fig. 3. Projection of the structure normal to the  $z$  direction and rotated by  $+20^\circ$  with respect to the  $x$  direction.

lowered with respect to that found for free carboxylate groups such as in monomeric  $[\text{UO}_2(\text{PDC})\text{L}_2]$  (L = PyNO, DMSO) (Degetto *et al.*, 1974) and becomes approximately equal to the value for the bridging carboxylate group.

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## X-ray Crystallography of the $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$ Compounds.

### III. *trans* Nongeminal 2,4,6-Trichloro-2,4,6-trisdimethylaminoclotriphosphazatriene\*

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*trans* Nongeminal  $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$  forms monoclinic crystals,  $P2_1/a$ , with  $a=18.118$ ,  $b=7.054$ ,  $c=13.411$  Å,  $\beta=99.74^\circ$ , and  $Z=4$ . The structure has been determined by a direct method, and refined by least-squares calculations to  $R=0.051$  for the 2027 observed reflexions. The  $\text{P}_3\text{N}_3$  ring adopts a slight sofa conformation, with one P 0.15 Å out of the mean plane of the other five atoms. The bond formed between this P and the *trans* Cl is 2.068 (2) Å, while the two *cis* P–Cl bonds are 2.034 (2) and 2.049 (2) Å. The exocyclic P–N(CH<sub>3</sub>)<sub>2</sub> bonds are of equal lengths, 1.623 ± 0.002 Å. For the PNP segment between the two *cis* Cl atoms, P–N = 1.568 ± 0.002 Å and P–N–P = 121.6 (3)°, while the corresponding values for the other two segments are 1.576 ± 0.005 Å and 120.1 ± 0.3°, respectively. The endocyclic N–P–N are 118.9, 119.4 and 118.6 (2)°. The exocyclic Cl–P–N(CH<sub>3</sub>)<sub>2</sub> are 104.9, 104.2 and 105.7 (2)°, and the C–N–C are 113.2, 114.1 and 114.3 (5)°.

### Introduction

The wide involvement of phosphorus compounds in living processes and industrial applications is a direct result of the high capacity of phosphorus for covalent bond formation (Corbridge, 1974). The crystal structures of some of these compounds provide the essential background to the understanding of their properties and behaviour. The present series examines the effect of conformation on the bonding mechanism in the three isomers of  $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$ . In parts I and II Ahmed & Pollard (1972*a,b*) described the structures of the geminal and *cis* nongeminal isomers; this part is concerned with the structure of the *trans* nongeminal isomer.

Suitable crystals for this study were prepared, with difficulty, by Professors R. A. Shaw and R. Keat. The crystals are transparent and colourless flat prisms, with the longest dimension parallel to **b** and the largest face corresponding to the 100 planes. Only thin crystals were found to be single.

### Experimental

#### Crystal data

*trans* Nongeminal  $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$ ; M.W. 373.53; monoclinic,  $P2_1/a$ ;  $a=18.118$  (4),  $b=7.054$  (2),  $c=13.411$  (4) Å,  $\beta=99.74$  (2)°,  $V=1689.28$  Å<sup>3</sup>;  $Z=4$ ,  $D_x=1.468$ ,  $D_m=1.467$  g cm<sup>-3</sup>;  $\mu(\text{Cu})=76.3$  cm<sup>-1</sup>,  $\mu(\text{Mo})=8.3$  cm<sup>-1</sup>.

The X-ray measurements were carried out on an automatic Picker diffractometer (Gabe, Alexander &

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