The present crystal structure analysis is one of the few so far reported for stable water-soluble S—Au complexes with a significantly longer (hence weaker) Au—Cl bond length. Because of this weaker linkage the chloride should be easily replaced by other bonding sites in biological systems. Thus the title compound may prove to be another phosphine-based complex with anti-arthritic activity.

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Structure of a Neutral Uranium(IV)–Dipicolinic Acid Complex*†

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Abstract. Triaquabis(dipicolinato)uranium(IV) 3·5-hydrate, $[U(C_7H_3NO_4)_2(H_2O)_3].3·5H_2O$, $M_r = 685·34$, orthorhombic, $Pn2_1a$, $a = 9·915$ (2), $b = 10·280$ (2), $c = 20·635$ (5) Å, $V = 2103·25$ Å^3, $Z = 4$, $D_m = 2·16$, $D_x = 2·164$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0·70926$ Å, $\mu = 7·387$ mm^{-1}, $F(000) = 1300$, $T = 296$ K, $R = 0·030$ for 1520 observed reflections. The structure consists of monomolecular units in which the U atom is nine-coordinated to four carboxylate O atoms, two pyridinic N atoms, and three O atoms of water molecules. The non-H atoms of each dipicolinato group are nearly coplanar, and the two groups of a given uranium polyhedron form a dihedral angle of 82 (2)° between them. Two of the interstitial water molecules are in ordered positions, while the remaining 1·5 molecules are distributed in three disordered positions with occupancies of about 0·5 each. The uranium polyhedra are interlinked by O—H···O hydrogen bonds between the water molecules in the structure.

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† Dipicolinic acid is pyridine-2,6-dicarboxylic acid.

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Introduction. Crystallographic structural studies have been reported for several complexes of pyridine-2,6-dicarboxylic acid (H_2pdc; dipicolinic acid; $C_7H_5NO_4$) with transition metals, lanthanides, alkaline earths, Pb^{2+} and actinides. The uranium–dipicolinic acid complexes which have been studied can be divided into (a) anionic U^{IV} complexes as in $[As(C_6H_5)_4]_2[U(pdc)_3].3H_2O$ (Degetto, Baracco, Bombieri, Forsellini, Graziani & Marangoni, 1974) and (b) neutral uranyl complexes as in $UO_2(pdc).H_2O$ (Immirzi, Bombieri, Degetto & Marangoni, 1975), $UO_2(pdc)(C_6H_7NO)_2$ and UO_2-$(pdc)(C_3H_7NO_2)$ (Cattalini, Baracco, Degetto & Marangoni, 1971). To our knowledge, no structure of a neutral actinide(IV) complex has been reported.

The present structure represents a prototype of neutral actinide(IV) complexes with dipicolinic acid. Normally, the multidentate anionic ligand, pyridine-2,6-dicarboxylate, pdc^{2-}, acts as a tridentate through the pyridinic N and two O atoms, one from each carboxylate group. At times, it has also been found that the O atoms not engaged in the formation of the initial monomeric units fill the coordination spheres of adjacent units to form polymeric structures as in the four uranium complexes mentioned above. Because of solubility considerations, this latter possibility was regarded as unlikely in the present case.

In anionic complexes, the coordination number of U^{IV} is normally eight or nine. A thermogravimetric analysis (TGA) of this neutral U^{IV} complex suggests that at least three water molecules are coordinated to each U atom. Thus, the uranium was expected to be nine-coordinated to two carboxylate O atoms and the pyridinic N from each of the two pdc^{2-} ligands, plus the three O atoms from water molecules. Based on the TGA, the other 3·5 water molecules in the formula unit, $U(C_7H_3NO_4)_2(H_2O)_{6.5}$, were expected to be interstitial as indicated by this crystallographic study.

Experimental. The crystals were obtained upon refluxing dipicolinic acid and UCl_4 (2:1) in toluene under nitrogen for several days and recrystallization of the crude product from water. The density was measured by flotation in an n-propanol/1,2-dibromoethane mixture. A green-coloured prismatic crystal, $0.14 \times 0.27 \times 0.32$ mm, was selected for data collection on an Enraf–Nonius CAD-4 diffractometer using Zr-filtered Mo radiation. The cell parameters were based on the angular settings of 20 reflections with $16 \le \theta \le 22°$. The intensity data were measured to $2\theta = 50°$ for $h = 0{-}11$, $k = 0{-}12$, $l = 0{-}24$, by $\omega{-}2\theta$ scans with $\Delta\omega = (0.8 + 0.35 \tan\theta)°$ plus 50% for the background. Three standard reflections measured every hour of exposure showed random variations within $\pm2.5\%$ from the mean. Of the 1955 reflections measured, 1520 were observed with $I \ge 3\sigma(I)$. The data were corrected for scale variation, Lp effects, and for absorption by the

Gaussian-integration method. The transmission factors varied from 0·337 to 0·508.

Assuming space group *Pnma*, the structure was determined by the heavy-atom method from a sharpened Patterson and several Fourier and difference maps. The process was rather slow since the U atom was located near $(\frac{1}{4},\frac{1}{4},0)$. In this space group, the structure could be described as having U and one dipicolinato group in ordered positions, and the other dipicolinato and water molecules in disordered positions. Refinement of this model was terminated at $R = 0.065$.

Further refinement was carried out in space group $Pn2_1a$, assuming an ordered molecule except for 1·5 disordered water molecules in the positions O(6), O(7) and O(8). At convergence, $R = 0.030$ for the observed reflections, $wR = 0.037$, $S = 2.1$, mean and maximum $\Delta/\sigma = 0.09$ and 0.49 respectively. The refinement was by block-diagonal least squares minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = \{1 + [(|F_o| - 60)/40]^2\}^{-1}$. No attempt was made to locate the H atoms. The residual electron density in the final difference map was within -0.88 and 0.66 e Å^{-3}. The scattering-factor curves were from *International Tables for X-ray Crystallography* (1974), and all calculations were with programs from the NRC system (Ahmed, Hall, Pippy & Huber, 1973). The refined atomic parameters are listed in Table 1.*

Discussion. Fig. 1 shows the structure and the atom numbering in the triaquabis(dipicolinato)uranium(IV) molecule. Uranium is nine-coordinated; it is bonded to four carboxylic O atoms, two pyridinic N atoms and three water molecules. The whole unit has an approximate twofold symmetry about the U—O(3) bond, and each dipicolinato group is essentially planar.

Bond lengths and selected valence angles for the uranium polyhedron are listed in Table 2. The U—O(carboxylic) bonds occur in a wide range, 2·32 (1)–2·41 (1) Å, and are considerably shorter than the U—O(water) bonds [2·44 (1)–2·49 (1) Å]. The U—N bonds [2·50 (1)–2·55 (1) Å] are the longest in the structure. These U^{IV}—O and U^{IV}—N lengths are basically the same as U^{VI}—O(carboxylic) of 2·36 (1) and 2·42 (2) Å and U^{VI}—N of 2·51 (2) Å occurring in (pyridine-2,6-dicarboxylato)dioxouranium(VI) monohydrate (Immirzi *et al.*, 1975), despite the difference in the formal oxidation states of U. The O(carboxylic)—U—N(pyridinic) chelate bite angles (Table 2) are nearly equal, with a mean value of 63·6 (4)° compared with a

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Table 1. *Fractional coordinates* $(\times 10^4, U \times 10^5)$ *and equivalent isotropic temperature factors* $(Å^2)$ *for space group* $Pn2_1a$ [*No.* 33, *equivalent positions are* x, y, z; $-x, \frac{1}{2}+y, -z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; $\frac{1}{2}+x, y, \frac{1}{2}-z$]

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}/B
U	24108 (3)	25143 (28)	9950 (2)	1·9
O(11)	1242 (8)	4439 (9)	823 (5)	2·6
O(12)	−603 (10)	5670 (12)	664 (6)	4·2
C(11)	18 (14)	4599 (14)	706 (7)	2·9
C(12)	−817 (14)	3316 (13)	668 (7)	3·0
C(13)	−2174 (12)	3358 (17)	542 (8)	3·9
C(14)	−2799 (13)	2137 (15)	540 (8)	3·8
C(15)	−2071 (15)	1013 (19)	628 (9)	4·4
C(16)	−704 (11)	1169 (12)	742 (6)	2·0
N(11)	−100 (9)	2321 (16)	758 (5)	2·6
C(17)	212 (14)	31 (15)	875 (7)	3·1
O(13)	1473 (8)	348 (9)	989 (5)	3·1
O(14)	−155 (10)	−1082 (10)	824 (6)	4·4
O(21)	4148 (9)	3905 (10)	693 (4)	2·8
O(22)	5405 (10)	5737 (11)	818 (5)	3·7
C(21)	4581 (12)	4868 (14)	1017 (6)	2·4
C(22)	4079 (13)	4956 (14)	1688 (7)	2·8
C(23)	4461 (13)	5907 (13)	2147 (6)	2·6
C(24)	3908 (15)	5910 (17)	2751 (7)	3·6
C(25)	2967 (14)	4984 (13)	2884 (5)	2·5
C(26)	2588 (12)	4119 (14)	2426 (6)	2·7
N(21)	3154 (10)	4116 (10)	1836 (5)	2·1
C(27)	1528 (11)	3068 (13)	2497 (6)	2·2
O(23)	1233 (7)	2473 (19)	1987 (4)	3·7
O(24)	1052 (9)	2869 (11)	3045 (4)	3·7
O(1)	2095 (7)	2531 (25)	−201 (3)	3·1
O(2)	1978 (16)	7260 (21)	1151 (7)	7·1
O(3)	3994 (9)	1018 (10)	431 (4)	3·0
O(4)	4455 (20)	−1433 (18)	897 (9)	9·1
O(5)	3943 (10)	1409 (10)	1739 (5)	3·5
O(6)†	3501 (33)	9102 (37)	2371 (17)	7·9 (8)
O(7)†	1350 (38)	8344 (43)	2413 (20)	9·7 (10)
O(8)†	1184 (52)	9000 (59)	3058 (26)	14·5 (17)

† Indicates atomic positions with occupancies of 0·5. Half the cells contain O(6) and O(8) while the other half contain O(7).

Table 2. *Bond lengths* (Å) *and selected valence angles* (°) *in the uranium polyhedron*

U−O(1)	2·488 (6)	O(23)−U−N(21)	63·6 (4)
U−O(3)	2·487 (10)	O(3)−U−O(1)	67·6 (4)
U−O(5)	2·440 (10)	O(3)−U−O(5)	67·3 (3)
U−O(11)	2·320 (9)	O(1)−U−O(5)	134·9 (4)
U−O(13)	2·413 (9)	O(3)−U−O(13)	70·7 (3)
U−O(21)	2·324 (10)	O(3)−U−O(21)	77·7 (3)
U−O(23)	2·357 (8)	O(13)−U−O(21)	148·4 (3)
U−N(11)	2·545 (9)	O(3)−U−N(11)	118·6 (4)
U−N(21)	2·503 (10)	O(3)−U−N(21)	123·1 (3)
		N(11)−U−N(21)	118·2 (4)
O(11)−U−N(11)	63·2 (4)	O(3)−U−O(11)	140·5 (3)
O(13)−U−N(11)	63·3 (4)	O(3)−U−O(23)	135·1 (4)
O(21)−U−N(21)	64·1 (3)	O(11)−U−O(23)	84·3 (4)
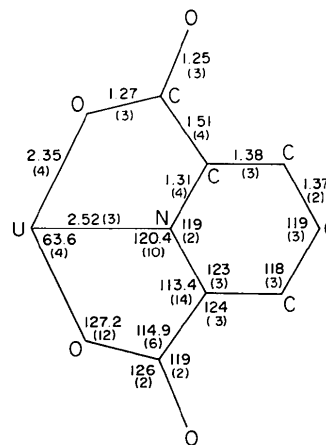
Fig. 2. Schematic drawing showing the mean bond lengths (Å) and valence angles (°) in the dipicolinato group.
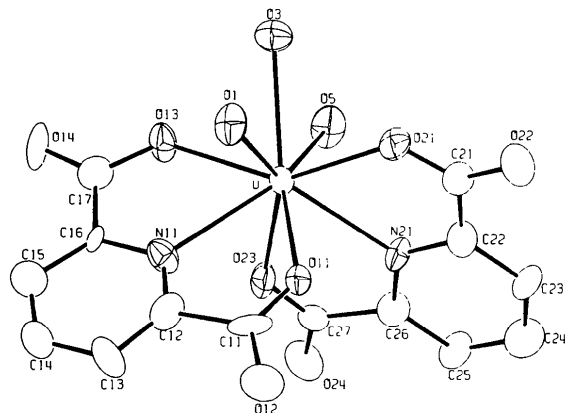

Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the triaquabis(dipicolinato)uranium(IV) molecule. The thermal ellipsoids are drawn at 50% probability.

mean value of 63·4 (10)° in the uranyl complex (Immirzi *et al.*, 1975), again indicating that the radius is nearly the same for U^{IV} and U^{VI}. The remaining 12 angles in Table 2, when considered in groups of three, give some indication of the proximity of the uranium's first neighbours to a twofold symmetry about U−O(3).

Mean bond lengths and valence angles in the dipicolinato groups are shown on the schematic drawing in Fig. 2, where the estimated standard deviations are derived from the expression $\sigma(\bar{x}) = [\sum(x - \bar{x})^2/(n - 1)]^{1/2}$ to reflect the spread in the observed values. As observed for several other dipicolinato–metal complexes, the mean C−O(bonded) and C−O(free) bond lengths are nearly equal, indicating a high degree of resonance between them. The pyridine ring is aromatic with C−C = 1·35 (2)–1·41 (2) Å, C−N = 1·26 (2)–1·34 (2) Å, and endocyclic angles in the range 114–127 (1)°.

Each dipicolinato group is approximately planar, with the maximum deviations from the mean planes occurring at the carboxylic O atoms. For one dipicolinato group the terminal atoms O(12) and O(14) are the furthest away from the mean plane at distances −0·055 (12) and 0·056 (12) Å respectively. For the other group, the atoms furthest from the mean plane are O(23) at 0·171 (14), O(21) at −0·128 (9) and O(24) at −0·122 (10) Å. The angle between the normals to the two dipicolinato mean planes is 82 (2)°.

The 3·5 water molecules which are not bonded to U have been located in two fully-occupied and three half-occupied positions. All 6·5 water molecules of the asymmetric unit appear to be involved in forming hydrogen bonds with each other and with the uranium ions to build up a complex hydrogen-bonding scheme which holds the ions and interstitial water molecules together. A list of thirteen O···O distances in the range 2·60 (2)–2·96 (5) Å, which appear to be suitable candidates for hydrogen bonding, has been deposited.

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Orthorhombic Anhydrous Zinc(II) Propionate

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Abstract. $Zn^{2+}.2C_3H_5O_2^-$, $M_r = 211·5$, orthorhombic, $Pna2_1$, $a = 9·2862$ (9), $b = 4·7937$ (4), $c = 19·0871$ (12) Å, $V = 849·7$ (1) Å^3, $Z = 4$, $D_x = 1·653$ Mg m^{-3}, $F(000) = 432$, $\lambda(Mo~K\alpha) = 0·71073$ Å, $\mu = 2·93$ mm^{-1}, $T = 293$ K, $R = 0·044$ for 1282 unique observed reflections with $F > 4\sigma(F)$. The structure consists of polymeric sheets in which tetrahedrally coordinated Zn atoms are connected by propionate bridges in a *syn–anti* arrangement.

Introduction. Various polymeric structures have been observed for anhydrous zinc(II) carboxylates. In each case Zn is tetrahedrally coordinated by carboxylate O atoms. The benzoate (Guseinov, Musaev, Usubaliev, Amiraslanov & Mamedov, 1984) and crotonate (Clegg, Little & Straughan, 1986*a*) form polymeric chains in which Zn_2(carboxylate)$_2^+$ binuclear units with three *syn–syn* bridges are connected by single *syn–anti* carboxylates. Only *syn–syn* bridges occur in the 2-chlorobenzoate, pairs of carboxylates linking Zn atoms into chains (Nakacho, Misawa, Fujiwara, Wakahara & Tomita, 1976). By contrast, two forms of zinc(II) acetate contain only *syn–anti* bridges, which link the Zn atoms into two-dimensional sheets (Clegg, Little & Straughan, 1986*b*) or a three-dimensional network (Capilla & Aranda, 1979).

A sheet structure has also been reported for anhydrous zinc(II) propionate (Goldschmied, Rae & Stephenson, 1977). Problems were encountered in this monoclinic structure determination, and were ascribed to a bent crystal and severe crystal decomposition in

the X-ray beam. We have obtained an orthorhombic form of the compound and report here its structure.

Experimental. Compound obtained from freshly precipitated $Zn(OH)_2$ and aqueous propionic acid, recrystallized from ethanol. The factors influencing the form of the crystalline product (monoclinic or orthorhombic) are unclear. Crystal size $0·35 \times 0·27 \times 0·08$ mm, Siemens AED2 diffractometer, cell parameters from 2θ values of 32 reflections measured at $\pm\omega$ ($20 < 2\theta < 25°$). Data collected in ω/θ scan mode, scan width = $1·36° + \alpha$-doublet splitting, scan time 14–56 s, $2\theta_{max}~50°$, $h~0 \rightarrow 11$, $k~0 \rightarrow 5$, $l~-22 \rightarrow 22$, no significant variation for three standard reflections, semi-empirical absorption correction, transmission $0·388$–$0·444$. 1500 reflections (no equivalents), 1282 with $F > 4\sigma(F)$ for structure determination (Patterson and Fourier recycling methods) and refinement [blocked-cascade minimization of $\sum w\Delta^2$, $\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) + 0·00116F^2$]. Anisotropic thermal parameters for non-H atoms, H atoms constrained [C–H = $0·96$ Å, H–C–H = $109·5°$, $U(H) = 1·2U_{eq}(C)$]. Isotropic extinction parameter $x = 2·7$ (5) $\times 10^{-6}$ [$F_c' = F_c/(1 + xF_c^2/\sin2\theta)^{1/4}$], polar axis direction determined by refinement of $\eta = 1·03$ (9) (Rogers, 1981). Final $R = 0·044$, $wR = 0·053$, max. $\Delta/\sigma = 0·003$, mean = $0·001$, slope of normal probability plot = $1·09$, $\Delta\rho_{max} = 1·83$ e Å^{-3} close to Zn atom, $\Delta\rho_{min} = -1·04$ e Å^{-3}, scattering factors from *International Tables for X-ray Crystallography* (1974). Programs: *SHELXTL* (Sheldrick, 1985).