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L-Argininium tris(acetato-*O,O'*)dioxouranium(III)–acetic acid–water (1/1/1)

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Abstract

The uranyl ion in the title compound, (C₆H₁₅N₄O₂)[UO₂(C₂H₃O₂)₃]·C₂H₄O₂·H₂O, is sixfold coordinated by three bidentate acetic acid ions. The O atoms form a hexagonal bipyramidal arrangement around the U atom. The non-crystallographic symmetry of the cation is approximately *D*_{6h}. The cation is a positively charged zwitterion. The side chain of the amino acid has a conformation where the C_γ atom is in a staggered *trans* position relative to the carboxyl group. An intricate three-dimensional network of hydrogen bonds interlinks the ions and the solvent molecules.

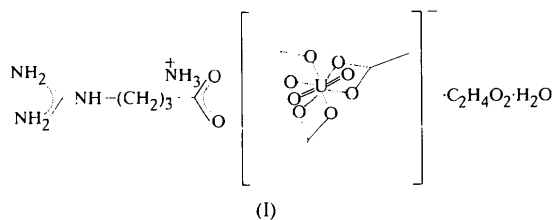
Comment

The uranyl oxocation UO₂²⁺ has a rich solution chemistry, easily forming oligomers and different types of complexes with a great variety of counter-ions (Denning, 1983). There has been much work related to the study of different chelating agents of uranyl and

mineral-surface sorption complexes, driven by the problem of radioactive waste treatment.

Uranyl acetate is commonly used in the preparation of samples to be studied by electron microscopy. Animal tissues, fibres or DNA filaments are stained with uranyl acetate, a process which is one of the most effective and least damaging for staining samples (Schmitz *et al.*, 1994).

Uranyl binds to selective amino acids in proteins, a property which has been used for multiple anomalous dispersion (MAD) phasing in protein crystallography. Uranyl often binds to the protein at the same sites as other cations, *e.g.* Ca²⁺, in living cells (Shapiro *et al.*, 1995), which justifies the renewed interest in the study of the interaction between uranyl and amino acids. We report here the structure of the title compound, (I), L-Arg⁺(Ac₃UO₂)⁻·H₂O·AcH, which crystallizes in the space group *P*2₁ with two formula units per cell.



The uranyl cation in (I) is sixfold coordinated by three bidentate acetic acid anions. The O atoms form a hexagonal bipyramidal arrangement around the U atom. The carboxy atoms lie approximately on a plane containing the U atom, with the exception of O8, which is slightly tilted out of the plane with a deviation of 0.165 (9) Å from the least-squares plane. The overall symmetry of the tris(acetato)dioxouranium anion is close to, but not exactly, *D*_{3h}. The tris(acetato)dioxouranium ion often occurs with the U atom sitting on a threefold axis, imposing a coplanar arrangement of the carboxyl O atoms and a linear configuration of the core uranyl ion. This is the case in sodium and potassium tris(acetato)dioxouranate (Navaza *et al.*, 1991; Anisimova *et al.*, 1997). The uranyl ion is linear, the O1—U—O2 bonding angle being 179.6 (3)°. The U—O2 [1.755 (6) Å] distance is larger than the U—O1 distance [1.744 (6) Å], which may be due to the fact that O2 is involved in a hydrogen bond with a water molecule. Other U—O distances vary between 2.441 (4) and 2.490 (4) Å. While the uranyl O atoms vibrate in an isotropic way, the acetate atoms exhibit the largest atomic displacement parameter almost perpendicular to the equatorial plane of the uranyl ion.

The cations exist as positively charged zwitterions, in which the guanidyl and amino groups are protonated and the carboxyl groups deprotonated. The side chain of arginine can assume many different conformations on account of its length and flexibility. The torsion angles which define the conformation observed in this structure

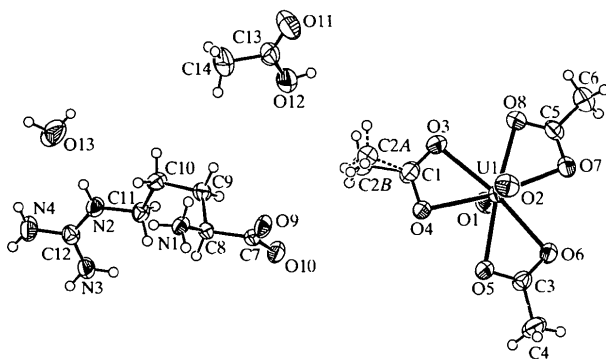


Fig. 1. ORTEP (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The two disordered components of C2 are designated *A* and *B*.

are, according to the nomenclature of the IUPAC–IUB Commission on Biochemical Nomenclature (1970), $\varphi^1 = -18.1(6)$, $\varphi^2 = 163.6(4)$, $\chi^1 = -58.8(7)$, $\chi^2 = -74.3(9)$, $\chi^3 = 166.9(6)$, $\chi^4 = -164.0(6)$, $\chi^{51} = -5.2(8)$ and $\chi^{52} = 174.6(5)^\circ$. The C10 atom is in a staggered *trans* position relative to the carboxyl group.

The absolute structure of (I) was determined, taking advantage of the significant anomalous dispersion of U at the Mo $K\alpha$ wavelength. The Flack (1983) parameter was refined to a value of $-0.004(7)$, confirming the expected chirality of the L-arginine molecule.

It was not possible to locate the H atoms of the solvated water molecule on a difference Fourier synthesis. Tentative coordinates for the water-H atoms were obtained from a force field calculation which performs an energy minimization of the van der Waals and Coulomb non-bonded energy profiles around a set of starting points that takes into account the neighbouring hydrogen-bond acceptors and reasonable geometric criteria for hydrogen bonding (Nardelli, 1999). An O–H bond distance of 0.850 Å was assumed. The best coordinates for the water-H atoms, corresponding to the minimum of the energy profile, were then included in the refinement riding on the O atom with $U_{iso} = 1.5U_{eq}(O)$. The atomic displacement tensor of the water-O atom is still abnormally anisotropic, which may indicate that the water molecule exhibits orientational disorder. It was checked that the occupancy of the water site does not deviate significantly from unity. The structure contains an additional acetic acid molecule which does not belong to the coordination shell of the uranyl. Inspection of the carboxyl bond distances [C13–O11 1.201(8) and C13–O12 1.300(10) Å] clearly shows that this molecule is not ionized.

An intricate three-dimensional network of hydrogen bonds links all the molecules in (I). The solvent acetic acid molecule is hydrogen bonded to two neighbouring arginine cations. The bare O atom is an acceptor from an amino group, while the OH group is a donor to the carboxylate group of the amino acid. This latter

hydrogen bond is the strongest present in the structure [O12–H14···O9^{vi} = 2.565(7) Å; symmetry code: (vi) $1-x, y-\frac{1}{2}, 1-z$]. Each arginine ion is both a donor and an acceptor of protons and is hydrogen bonded to three acetate ions, two molecules of acetic acid, the water molecule and to another arginine ion with a strong bifurcated hydrogen bond where the carboxyl O10 accepts two protons from the amino and guanidyl groups.

Experimental

The title compound was synthesized by mixing uranyl acetate dihydrate with L-arginine in a water–acetic acid solution. After a few weeks of slow evaporation, single crystals of the title compound were obtained. A specimen of good quality was selected and tested prior to data collection by photographic methods.

Crystal data

$(C_6H_{15}N_4O_2)[UO_2(C_2H_3O_2)_3] \cdot C_2H_4O_2 \cdot H_2O$
 $M_r = 700.45$
 Monoclinic
 $P2_1$
 $a = 9.602(5)$ Å
 $b = 7.636(6)$ Å
 $c = 16.661(5)$ Å
 $\beta = 92.16(3)^\circ$
 $V = 1220.7(11)$ Å³
 $Z = 2$
 $D_x = 1.900$ Mg m⁻³
 D_m not measured

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{min} = 0.128$, $T_{max} = 0.228$
 3513 measured reflections
 2977 independent reflections
 2653 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.017$
 $wR(F^2) = 0.043$
 $S = 1.047$
 2977 reflections
 297 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 0.2714P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.429$ e Å⁻³
 $\Delta\rho_{min} = -0.805$ e Å⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 11.4$ – 14.3°
 $\mu = 6.714$ mm⁻¹
 $T = 293(2)$ K
 Irregular
 $0.34 \times 0.29 \times 0.22$ mm
 Yellow

$R_{int} = 0.018$
 $\theta_{max} = 27.5^\circ$
 $h = -11 \rightarrow 12$
 $k = 0 \rightarrow 9$
 $l = -21 \rightarrow 21$
 3 standard reflections
 frequency: 180 min
 intensity decay: 1%

Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0084(4)
 Scattering factors from *International Tables for Crystallography* (Vol. C)
 Absolute structure: Flack (1983)
 Flack parameter = $-0.004(7)$

Table 1. Selected geometric parameters (\AA , $^\circ$)

U1—O1	1.744 (5)	U1—O8	2.486 (4)
U1—O2	1.755 (6)	U1—O6	2.488 (4)
U1—O7	2.441 (4)	U1—O4	2.490 (3)
U1—O5	2.464 (3)	O11—C13	1.201 (8)
U1—O3	2.469 (3)	O12—C13	1.300 (10)
O1—U1—O2	179.6 (3)	O8—U1—O6	120.90 (14)
O7—U1—O5	121.62 (12)	O8—U1—O4	119.37 (12)
O5—U1—O3	118.99 (12)	O6—U1—O4	119.51 (12)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N2—H2...O13	0.86	1.98	2.840 (7)	175
N1—H82A...O10 ⁱ	0.89	1.98	2.820 (6)	157
N1—H82B...O11 ⁱⁱ	0.89	2.27	2.882 (7)	126
N1—H82B...O8 ⁱⁱⁱ	0.89	2.41	2.968 (5)	121
N1—H82C...O3 ⁱⁱⁱⁱ	0.89	2.03	2.899 (8)	165
N3—H85A...O10 ^v	0.86	2.11	2.946 (5)	164
N3—H85B...O4 ^{vi}	0.86	2.09	2.917 (6)	160
N4—H4D...O5 ^{vii}	0.86	2.09	2.937 (6)	167
N4—H4E...O6 ^{viii}	0.86	2.45	3.143 (7)	138
O12—H14...O9 ^{ix}	0.82	1.75	2.565 (6)	170
O13—H13A...O2 ^x	0.85	2.32	2.965 (9)	133
O13—H13B...O7 ^{xi}	0.85	1.93	2.762 (6)	164

Symmetry codes: (i) $-x, \frac{1}{2}+y, 1-z$; (ii) $x-1, y, z$; (iii) $1-x, \frac{1}{2}+y, 1-z$; (iv) $-x, y-\frac{1}{2}, 1-z$; (v) $x-1, y, z-1$; (vi) $1-x, y-\frac{1}{2}, 1-z$.

All H atoms were placed at calculated positions and refined as riding using the *SHELXL97* (Sheldrick, 1997) defaults, except those of the water molecule, which could not be located directly and were positioned at calculated positions given by an energy profile calculation (see *Comment*). One of the methyl groups (C2) is disordered over two alternate positions with occupancies close to 50%. The two disordered C atoms were refined isotropically with a common atomic displacement parameter. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no further solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *HEL-ENA* (Spek, 1997). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1332). Services for accessing these data are described at the back of the journal.

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Absolute configuration of *exo-syn-syn*-dicarbonyl(η^5 -cyclopentadienyl)-[(1,2,3- η)-(1*R*,2*S*,3*S*)-1-phenylbut-2-en-1-yl]molybdenum(II)

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Abstract

The absolute configuration of the title complex, $[\text{Mo}(\text{C}_5\text{H}_5)(\text{C}_{10}\text{H}_{11})(\text{CO})_2]$, has been determined. The allyl moiety adopts an *exo* conformation with respect to the cyclopentadienyl group.

Comment

We report herein the structure and absolute configuration of *exo-syn-syn*-dicarbonyl(η^5 -cyclopentadienyl)-[(1,2,3- η)-(1*R*,2*S*,3*S*)-1-phenylbut-2-en-1-yl]molybdenum(II), (I), a key intermediate in the on-going synthesis of cryptophycin antibiotics (Golakoti *et al.*, 1995). As Fig. 1 reveals, the η^3 -allyl moiety adopts an *exo* conformation with respect to the cyclopentadienyl ligand and is nearly fully eclipsed with respect to the $\text{Mo}(\text{CO})_2$ fragment. The three C atoms of the η^3 -allyl unit in (I) are more symmetrically bonded to the Mo atom than in a related tris-pyrazolylborate complex (Ward *et al.*,

