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Bis[(2-hydroxyethyl)dimethylammonium] Bis[μ-acetato-*O*:*O'*-acetato-*O*,*O'*-μ-(2-dimethylaminoethanolato-*N*,μ-*O*)-μ_3-oxo-tetraoxodiuranate(VI)]

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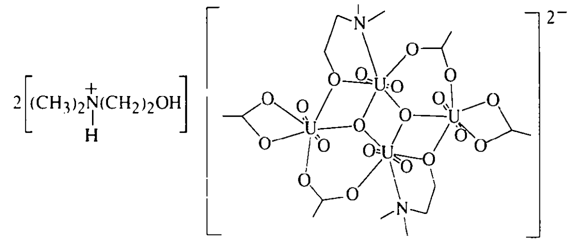
Abstract

In the centrosymmetric tetrameric $[(UO_2)_4(O)_2(C_2H_3O_2)_4(C_4H_{10}NO)_2]^{2-}$ anion {systematic name: bis(μ-acetato)-1κ*O*:2κ*O'*;3κ*O*:4κ*O'*-bis(acetato)-2κ^2*O*,*O'*;4κ^2*O*,*O'*-bis(μ-2-dimethylaminoethanolato)-1κ^2*N*,*O*:4κ*O*;2κ*O*:3κ^2*N*,*O*-di-μ_3-oxo-1:2:3κ^3*O*;1:3:4κ^3*O*-tetrakis[dioxouranate(IV)]}, the U atoms are seven-coordinate, the shortest U···U distances being 3.681 (2), 3.775 (2) and 4.214 (2) Å, and the longest 7.017 (2) Å. Four UO_2^{2+} ions are connected by two carboxylate groups, two ethanolato O atoms and two triply bridging O atoms. A (2-hydroxyethyl)dimethylammonium cation, $C_4H_{12}NO^+$, links adjacent complex anions by N—H···O(uranyl) and O—H···O(acetate) hydrogen bonds.

Comment

Several uranium complexes have been found to be dimers, trimers, tetramers or polymers. Many of these compounds are connected by O-containing bridging units such as carboxylates, water molecules or hydroxy groups. For example, uranyl acetate dihydrate is a dimer with both bridging and terminal acetate groups (Howatson, Grew & Morosin, 1975), the uranium trifluoroacetato complex (Charpin *et al.*, 1990) is tetrameric, while the uranyl benzoato complex is polymeric (Nierlich, Iroulart, Vigner, Keller & Lance, 1990). Hydrogen bonding also plays an important role in the crystallization and stabilization of uranyl complexes, as in the present compound, (I), or in a recently prepared water-bridged dimeric uranyl nitrate complex with 2-dimethylaminoethanol (Hämäläinen, Turpeinen & Mutikainen, 1996).

The present structure consists of centrosymmetric $[(UO_2)_4O_2(C_2H_3O_2)_4(C_4H_{10}NO)_2]^{2-}$ anions. The four U atoms, with distances of 3.681 (2)–7.017 (2) Å between them, are bridged by two μ_3-oxo atoms, two carboxylate groups and two ethanolato O atoms. The complex anions are hydrogen bonded by (2-hydroxyethyl)dimethylammonium cations with distances N2—H···O9($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$) 2.87 (3) and O11—H···O4($\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$) 2.82 (5) Å. The U atoms are seven-coordinate. The coordination polyhedron is a pentagonal bipyramid with an almost linear uranyl group perpendicular to five atoms (five O atoms for U1, one N and four O atoms for U2) at the corners of an irregular pentagonal base. The average bond lengths are: U—O(uranyl) 1.762 (9), U—O(μ_3-oxo) 2.262 (8), U—O(μ-ethanolato) 2.349 (8), U—O(μ-carboxylato) 2.382 (11), U—O(carboxylato) 2.513 (9) and U2—N1 2.706 (11) Å.



(I)

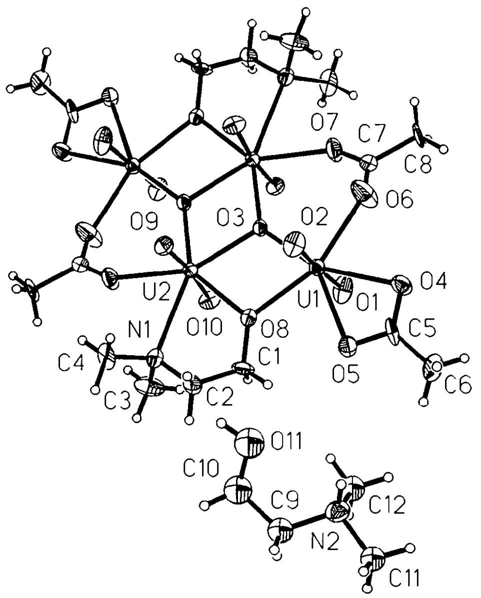


Fig. 1. View of the title structure (*SHELXTL/PC*; Sheldrick, 1990). Displacement ellipsoids are drawn at the 30% probability level. Only one set of occupied positions of the disordered ammonium cation is shown.

Experimental

Crystals of the title compound were obtained by slow evaporation at room temperature of an ethanol solution containing uranyl acetate and 2-dimethylaminoethanol in a molar ratio of 1:1.

Crystal data

$(C_4H_{12}NO)_2$-
$[U_4O_{10}(C_2H_3O_2)_4$-
$(C_4H_{10}NO)_2]$
$M_r = 1704.85$
Monoclinic
$P2_1/n$
$a = 9.242\ (7)$ Å
$b = 12.304\ (8)$ Å
$c = 18.954\ (9)$ Å
$\beta = 92.74\ (6)°$
$V = 2152.9\ (24)$ Å^3
$Z = 2$
$D_x = 2.630$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 10$–$25°$
$\mu = 15.078$ mm^{-1}
$T = 293\ (2)$ K
Bipyramid
$0.15 \times 0.15 \times 0.12$ mm
Yellow

Data collection

Nicolet $P3$ diffractometer
ω scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.52$, $T_{\max} = 1.00$
4736 measured reflections
4469 independent reflections
2966 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0454$
$\theta_{\max} = 26.53°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 15$
$l = -23 \rightarrow 23$
2 standard reflections monitored every 98 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0501$
$wR(F^2) = 0.0871$
$S = 1.170$
4469 reflections
240 parameters
H atoms refined using riding model
$w = 1/[\sigma^2(F_o^2) + (0.0100P)^2 + 10.0P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.003$

$\Delta\rho_{\max} = 1.823$ e Å^{-3} (in the vicinity of U)
$\Delta\rho_{\min} = -1.400$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00018 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
U1	0.41602 (6)	0.22350 (4)	0.10942 (2)	0.03542 (15)
U2	0.53168 (6)	−0.06798 (4)	0.08584 (2)	0.03184 (14)
O1	0.5906 (10)	0.2750 (8)	0.1032 (5)	0.060 (3)
O2	0.2347 (9)	0.1820 (7)	0.1160 (5)	0.053 (3)
O3	0.4663 (9)	0.0925 (6)	0.0328 (4)	0.036 (2)
O4	0.3468 (12)	0.4076 (7)	0.1544 (5)	0.062 (3)
O5	0.4248 (11)	0.2925 (7)	0.2342 (4)	0.050 (3)
O6	0.3377 (16)	0.3297 (9)	0.0108 (6)	0.093 (4)
O7	0.4101 (13)	0.2579 (8)	−0.0851 (5)	0.067 (3)
O8	0.4973 (10)	0.0712 (7)	0.1709 (4)	0.044 (2)
O9	0.3475 (9)	−0.1089 (7)	0.0893 (4)	0.043 (2)
O10	0.7185 (9)	−0.0381 (7)	0.0923 (4)	0.046 (2)
N1	0.5707 (13)	−0.1387 (8)	0.2206 (6)	0.046 (3)
N2	0.3897 (13)	0.2758 (10)	0.4798 (6)	0.059 (3)
C1	0.5697 (18)	0.0591 (11)	0.2381 (7)	0.056 (4)
C2	0.537 (2)	−0.0485 (11)	0.2691 (7)	0.066 (5)
C3	0.7247 (18)	−0.1687 (15)	0.2359 (8)	0.084 (6)
C4	0.476 (2)	−0.2319 (12)	0.2383 (8)	0.080 (6)
C5	0.3845 (15)	0.3887 (11)	0.2171 (8)	0.050 (4)
C6	0.3871 (17)	0.4746 (11)	0.2732 (7)	0.061 (4)
C7	0.3687 (17)	0.3364 (11)	−0.0527 (8)	0.049 (4)
C8	0.3532 (19)	0.4446 (11)	−0.0890 (8)	0.069 (5)
O11†	0.244 (3)	0.101 (2)	0.4118 (14)	0.099 (9)
C9†	0.395 (3)	0.160 (2)	0.5034 (15)	0.064 (9)
C10†	0.369 (6)	0.074 (3)	0.452 (3)	0.14 (3)
C11†	0.389 (3)	0.349 (2)	0.5401 (14)	0.063 (9)
C12†	0.507 (3)	0.302 (3)	0.4302 (15)	0.070 (10)
O110†	0.355 (4)	0.044 (3)	0.438 (2)	0.109 (13)
C90†	0.424 (4)	0.221 (3)	0.4186 (16)	0.094 (12)
C100†	0.316 (4)	0.130 (2)	0.3931 (17)	0.074 (11)
C110†	0.401 (5)	0.225 (3)	0.5489 (17)	0.121 (16)
C120†	0.460 (5)	0.388 (2)	0.487 (2)	0.113 (15)

† Occupancy = 0.5; $U_{\rm iso}$ (see below).

Table 2. *Selected geometric parameters (Å, °)*

U1—O1	1.743 (9)	U2—O10	1.764 (8)
U1—O2	1.762 (9)	U2—O3$^{\rm i}$	2.270 (8)
U1—O3	2.233 (8)	U2—O3	2.284 (8)
U1—O8	2.313 (8)	U2—O8	2.384 (8)
U1—O6	2.365 (11)	U2—O7$^{\rm i}$	2.398 (9)
U1—O5	2.511 (9)	U2—N1	2.706 (11)
U1—O4	2.514 (9)	U2—U2$^{\rm i}$	3.681 (2)
U1—U2	3.775 (2)	O3—U2$^{\rm i}$	2.270 (8)
U2—O9	1.779 (8)		
O1—U1—O2	175.5 (4)	O10—U2—O3$^{\rm i}$	92.4 (3)
O1—U1—O3	89.8 (4)	O9—U2—O3	91.5 (3)
O2—U1—O3	93.7 (3)	O10—U2—O3	95.0 (4)
O1—U1—O8	92.8 (4)	O3$^{\rm i}$—U2—O3	72.2 (3)
O2—U1—O8	90.9 (4)	O9—U2—O8	91.2 (3)
O3—U1—O8	70.7 (3)	O10—U2—O8	88.0 (3)
O1—U1—O6	89.7 (5)	O3$^{\rm i}$—U2—O8	140.6 (3)
O2—U1—O6	87.7 (5)	O3 U2 O8	68.6 (3)
O3—U1—O6	87.1 (3)	O9—U2—O7$^{\rm i}$	86.5 (4)
O8—U1—O6	157.7 (3)	O10—U2—O7$^{\rm i}$	89.1 (4)
O1—U1—O5	87.3 (4)	O3$^{\rm i}$—U2—O7$^{\rm i}$	81.5 (3)
O2—U1—O5	91.1 (4)	O3—U2—O7$^{\rm i}$	153.4 (3)
O3—U1—O5	149.1 (3)	O8—U2—O7$^{\rm i}$	137.9 (3)
O8—U1—O5	78.7 (3)	O9—U2—N1	87.7 (4)
O6—U1—O5	123.6 (3)	O10—U2—N1	85.2 (4)
O1—U1—O4	86.9 (4)	O3$^{\rm i}$—U2—N1	152.3 (3)
O2—U1—O4	88.8 (4)	O3—U2—N1	135.6 (3)
O3—U1—O4	159.3 (3)	O8—U2—N1	67.0 (3)
O8—U1—O4	129.9 (3)	O7$^{\rm i}$—U2—N1	70.9 (3)
O6—U1—O4	72.4 (3)	U1—O3—U2$^{\rm i}$	138.8 (4)
O5—U1—O4	51.2 (3)	U1—O3—U2	113.4 (3)
O9—U2—O10	172.5 (4)	U2$^{\rm i}$—O3—U2	107.8 (3)
O9—U2—O3$^{\rm i}$	93.0 (3)	U1—O8—U2	107.0 (3)

Symmetry code: (i) $1 - x, -y, -z$.

The dimethyl(2-hydroxyethyl)ammonium cation turned out to be disordered. Two positions were assigned to the C, H and O atoms of this cation with site occupancies of 0.5. These disordered atoms were refined isotropically. The other non-H atoms were refined anisotropically. H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms.

Data collection: Nicolet $P3$ software (Nicolet XRD Corporation, 1980). Cell refinement: Nicolet $P3$ software. Data reduction: Nicolet $P3$ software. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1337). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Isomorphous Polymeric Complexes of Ca^{2+} and Pb^{2+} with 9,10-Dihydro-9-oxo-10-acridineacetate (CMA^-) Ligands: $[M(CMA)_2(H_2O)_2]$

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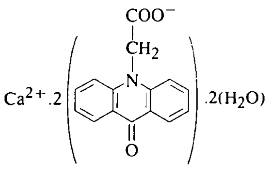
Abstract

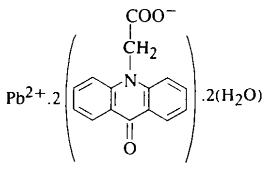
The title compounds, *catena*-poly[diaquacalcium-bis-μ-(9,10-dihydro-9-oxo-10-acridineacetato-*O*,*O*′:*O*)], $[Ca(CMA)_2(H_2O)_2]$, and the analogous lead(II) compound, $[Pb(CMA)_2(H_2O)_2]$ (CMA = $C_{15}H_{10}NO_3$), are carboxylate-bridged linear polymers in the solid state. Each ligand chelates one metal ion and bridges to the next metal ion. Two water molecules complete eightfold coordination around the Ca and Pb atoms. Adjacent polymer chains show stacking interactions of parallel acridone groups and there are hydrogen bonds linking aqua ligands to carboxylate and ketone O atoms.

Comment

This investigation is a continuation of our earlier studies on the ligating properties of the 9,10-dihydro-9-oxo-10-acridineacetate anion, a powerful interferon inducer (Inglot, Młochowski, Szulc, Inglot & Albin, 1985). We have found that the CMA^- anion in its metal complexes exhibits a variety of carboxylate bonding modes. Bridges through a single O atom have been observed in $[Cu(CMA)_2(H_2O)_2]$ (Miernik, Lis, Palus & Reedijk, 1993), whereas both μ_3 single-atom bridging and *syn-syn* bridging by the OCO group are present in $[Na_2Zn(CMA)_4(EtOH)_2(H_2O)_7]$ (Miernik & Lis, 1994). In this article we describe the preparation and crystal structure of two isomorphous complexes of CMA^-, namely $[Ca(CMA)_2(H_2O)_2]$, (I) and $[Pb(CMA)_2(H_2O)_2]$, (II), in which the CMA^- anions act as both chelating and single-atom bridging ligands.



(I)



(II)

The atomic numbering scheme for the repeating unit of the Ca compound is shown in Fig. 1. The Pb complex is essentially the same, except for a twofold disorder of one aqua ligand. A packing diagram is shown in Fig. 2. The crystal structures consist of $[Ca(CMA)_2(H_2O)_2]$ or $[Pb(CMA)_2(H_2O)_2]$ repeating units. The Ca and Pb atoms are eight-coordinate, being bonded to six O atoms from carboxylate groups and two water O atoms. Each carboxylate group forms a chelate ring with one metal ion and is also coordinated to a centrosymmetrically related neighbouring metal ion in a monodentate manner. Thus, the repeating units are linked by monatomic carboxylate bridges to form polymer chains. The van der Waals interactions between ring systems of CMA^- result in interleaving of adjacent polymer chains, with stacks of ligands along the *a* axis, separated by about 3.5 Å.

The main features of coordination around the metal ions observed in compounds (I) and (II), namely a co-

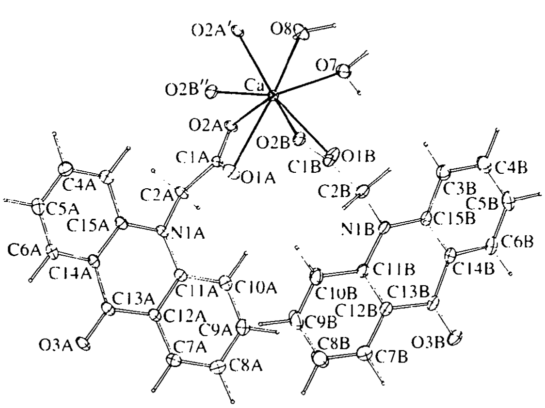


Fig. 1. Molecular geometry around the Ca atom in (I). Displacement ellipsoids are plotted at the 50% probability level.