Crystal structure of bis(acetato-*O,O'*)bis(μ -acetato-*O,O'*)bis(κ^3 *N*-anti-pyridine-*O*)tetraoxodiuranium, $\text{U}_2\text{O}_4(\text{CH}_3\text{COO})_4[\text{C}_6\text{H}_5\text{N}_2\text{C}_3(\text{CH}_3)_2\text{HO}]_2$

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Abstract

$\text{C}_{30}\text{H}_{36}\text{N}_4\text{O}_{14}\text{U}_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.989(9)$ Å, $b = 9.709(3)$ Å, $c = 12.22(1)$ Å, $\alpha = 112.94(5)^\circ$, $\beta = 92.84(7)^\circ$, $\gamma = 110.61(8)^\circ$, $V = 897.5$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.043$, $wR_{\text{ref}}(F^2) = 0.120$, $T = 293$ K.

Source of material

0.95 g (50 mmol) of 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (antipyrine, phenazone) was added to a boiling suspension of 0.41 g (1 mmol) of uranylacetate dihydrate in 20 mL of acetic acid. After dissolution of the uranyl salt, the yellow solution was cooled and concentrated under reducing pressure to 5 mL. Two days later, yellow needles of the title compound appeared in the solution.

Discussion

Metal amide systems are important in relation with degenerative problems concerning the nervous central system like E.S.B. or Alzheimer disease; these pathologies should be in relation with metal accumulation and protein dysfunction or denaturation. For these reasons geometrically strained amides are of current interest as models of proteic structure. Uranyl ions give easily crystalline complexes with organic ligands as recently reported [1–4].

Following our experiences on uranyl complexes [5], we studied the interactions of phenazone, a molecule of pharmaceutical interest, with uranyl diacetate.

The title complex, bis(acetato- κ^2 *O,O'*)bis(κ^3 *N*-antipyrine-*O*)-bis(μ -acetato- κ^2 *O,O'*)dioxouranium, consists of centrosymmetric dimers in which the U(VI) atoms display a UO_7 coordination. The U atoms are bridged by two acetate groups. Each U atom is in a distorted pentagonal-bipyramidal environment comparable with that previously reported in [6]. The equatorial plane contains two oxygens from a chelating acetate ion (O3 and O4), one oxygen from phenazone ligand (O14) and two oxygens from the two different bidentate bridging acetate groups (O7ⁱ and O8) [maximum deviation of 0.027(5) Å for O7ⁱ with symmetry code i: 1-*x*, -*y*, 1-*z*]. The U—O bond lengths are in the range 2.311(7) Å–2.457(8) Å. The angles subtended at the U atom are in the range 52.4(2)°–81.5(3)°. The apices of the bipyramid are occupied by the uranyl oxygens O1 and O2 with U—O bond distances of 1.765(8) Å and 1.738(7) Å, respectively, and an O1—U—O2 angle of 178.6(3)°. The U1/O7/C9/O8/U1ⁱ/O7ⁱ/C9ⁱ/O8ⁱ contour of the double bridge is in a chair conformation with the O1 and O2 in axial positions, C10, acetate group (O3/O4/C5/C6) and O14 in equatorial positions. Some bond distances and angles of phenazone for this compound differ significantly (outside 3 e.s.ds.) than those found in the phenazone molecule [6], with the maximal differences for $d(\text{C11—N12})$ [0.08(1) Å] and $\angle \text{C11—N12—C17}$ [8.6(8)°]. The dihedral angle between pyrazole and phenyl rings is 84.0 (3)°. The crystal packing of the complex is governed by numerous C—H...O interactions. The most important ones are C17—H17C...O3ⁱⁱ with 3.18(2) Å, 178°; C17—H17B...O4ⁱⁱⁱ with 3.28(2) Å, 167° (ii: -*x*+2, -*y*, -*z*; iii: *x*+1, *y*+1, *z*) and two C—H...Cg(π system) interactions [$d(\text{H6B...Cg1}^{\text{iv}}) = 2.97$ Å, $\angle \text{C6—H6B...Cg1}^{\text{iv}} = 159^\circ$; $d(\text{H10B...Cg2}) = 2.84$ Å, $\angle \text{C10—H10B...Cg2} = 137^\circ$ with Cg1 and Cg2 as centroids of the pyrazole and phenyl rings, respectively (iv: 1-*x*, -*y*, -*z*)].

Table 1. Data collection and handling.

Crystal:	yellow, parallelepipedic, size 0.20 × 0.25 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	90.81 cm ⁻¹
Diffraction, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{\text{max}}$:	49.92°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3158, 3158
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2816
$N(\text{param})_{\text{refined}}$:	226
Programs:	SIR92 [7], SHELXL-97 [8], CAMERON [9], WinGX [10]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(6A)	2i	0.3909	−0.3951	−0.1690	0.107
H(6B)	2i	0.2277	−0.3803	−0.1401	0.107
H(6C)	2i	0.2694	−0.5190	−0.1294	0.107
H(10A)	2i	0.9620	0.1893	0.6548	0.122
H(10B)	2i	0.9718	0.2593	0.5581	0.122
H(10C)	2i	0.9270	0.0723	0.5160	0.122
H(15)	2i	0.7434	0.0280	0.0034	0.064
H(16A)	2i	0.8989	0.1530	−0.1386	0.092
H(16B)	2i	1.0854	0.1947	−0.1076	0.092

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(16C)	2i	1.0224	0.3344	−0.0596	0.092
H(17A)	2i	1.3156	0.4291	0.2370	0.124
H(17B)	2i	1.2611	0.4827	0.1418	0.124
H(17C)	2i	1.3152	0.3366	0.0993	0.124
H(19)	2i	1.2163	0.1152	0.3026	0.064
H(20)	2i	1.3802	0.2266	0.4955	0.076
H(21)	2i	1.4100	0.4690	0.6391	0.077
H(22)	2i	1.2689	0.6084	0.6051	0.097
H(23)	2i	1.0988	0.5026	0.4113	0.069

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
U(1)	2i	0.54691(3)	−0.07508(3)	0.25979(2)	0.0392(2)	0.0410(2)	0.0394(2)	0.0156(2)	0.0091(1)	0.0177(1)
O(1)	2i	0.492(1)	0.0713(9)	0.2380(7)	0.087(5)	0.054(4)	0.062(4)	0.040(4)	0.016(4)	0.018(3)
O(2)	2i	0.598(1)	−0.223(1)	0.2782(8)	0.091(6)	0.051(4)	0.072(5)	0.033(4)	0.008(4)	0.032(4)
O(3)	2i	0.5462(9)	−0.203(1)	0.0438(6)	0.050(4)	0.070(5)	0.047(3)	0.002(4)	0.015(3)	0.009(3)
O(4)	2i	0.3172(9)	−0.2954(9)	0.0940(6)	0.058(4)	0.060(4)	0.047(3)	0.012(3)	0.014(3)	0.017(3)
C(5)	2i	0.398(1)	−0.296(1)	0.0135(9)	0.054(6)	0.049(5)	0.051(5)	0.019(5)	0.016(4)	0.020(4)
C(6)	2i	0.314(2)	−0.408(2)	−0.1183(9)	0.084(8)	0.071(7)	0.048(5)	0.033(7)	0.013(5)	0.013(5)
O(7)	2i	0.6554(9)	0.1054(9)	0.4654(6)	0.051(4)	0.057(4)	0.041(3)	0.008(3)	0.001(3)	0.012(3)
O(8)	2i	0.6805(9)	0.141(1)	0.6536(6)	0.044(4)	0.099(6)	0.047(4)	−0.007(4)	0.015(3)	0.020(4)
C(9)	2i	0.737(1)	0.136(1)	0.5634(8)	0.052(5)	0.045(5)	0.047(5)	0.014(4)	0.013(4)	0.013(4)
C(10)	2i	0.916(1)	0.167(2)	0.574(1)	0.061(7)	0.12(1)	0.105(9)	0.047(8)	0.034(7)	0.077(9)
C(11)	2i	0.978(1)	0.198(1)	0.0371(8)	0.043(5)	0.050(5)	0.058(5)	0.020(4)	0.015(4)	0.027(4)
N(12)	2i	1.0936(9)	0.278(1)	0.1346(6)	0.041(4)	0.060(4)	0.049(4)	0.017(4)	0.012(3)	0.032(3)
N(13)	2i	1.0387(9)	0.230(1)	0.2211(7)	0.040(4)	0.058(4)	0.048(4)	0.014(3)	0.005(3)	0.026(3)
O(14)	2i	0.8081(8)	0.062(1)	0.2449(6)	0.042(3)	0.080(5)	0.052(4)	0.002(3)	0.008(3)	0.033(3)
C(14)	2i	0.884(1)	0.122(1)	0.1794(8)	0.042(5)	0.051(5)	0.054(5)	0.021(4)	0.006(4)	0.022(4)
C(15)	2i	0.843(1)	0.098(1)	0.0581(9)	0.045(5)	0.054(5)	0.057(5)	0.015(4)	0.007(4)	0.025(4)
C(16)	2i	0.998(2)	0.222(1)	−0.0777(8)	0.076(7)	0.071(6)	0.045(5)	0.033(6)	0.012(5)	0.029(4)
C(17)	2i	1.261(1)	0.391(2)	0.155(1)	0.052(6)	0.11(1)	0.081(8)	0.013(7)	0.012(6)	0.057(7)
C(18)	2i	1.141(1)	0.300(1)	0.3436(7)	0.033(4)	0.054(5)	0.042(4)	0.016(4)	0.010(3)	0.021(3)
C(19)	2i	1.225(1)	0.214(1)	0.3634(9)	0.053(5)	0.048(5)	0.062(5)	0.027(4)	0.014(4)	0.022(4)
C(20)	2i	1.324(1)	0.283(2)	0.479(1)	0.066(7)	0.079(7)	0.064(6)	0.042(6)	0.014(5)	0.037(5)
C(21)	2i	1.341(1)	0.425(2)	0.5639(9)	0.061(6)	0.081(7)	0.040(4)	0.023(6)	0.000(4)	0.023(5)
C(22)	2i	1.258(2)	0.509(1)	0.543(1)	0.078(8)	0.047(6)	0.074(7)	0.012(6)	0.014(6)	−0.004(5)
C(23)	2i	1.155(1)	0.446(1)	0.4278(9)	0.065(6)	0.052(5)	0.060(5)	0.031(5)	0.010(5)	0.022(4)

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