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Disodium Bis(*o*-chloranilato)uranyl(VI) Hexahydrate

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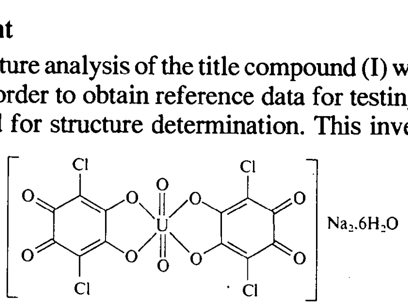
Abstract

In the title compound, disodium bis[3,6-dichloro-4,5-dihydroxy-3,5-cyclohexadiene-1,2-dionato(2−)]dioxouranium hexahydrate, $Na_2[UO_2(C_6Cl_2O_4)_2].6H_2O$, the coordination polyhedra for both uranium and sodium are pentagonal bipyramids. The uranyl anilate groups are organized in planes parallel to $(\bar{3}01)$ and are connected by Na ions which also lie in these planes. The arrangement produces channels in the [010] and [001] directions which are filled with water molecules at the intersection points. A pseudo orthorhombic F cell can be found by the transformation $a' = a - c$, $b' = b$, $c' = a + 3c$. In this cell, the anilate planes are parallel to (100). The three water molecules, O(21), O(25) and its symmetrically equivalent O(25)′, form an H_2O cluster connected by hydrogen bonding.

Comment

The structure analysis of the title compound (I) was undertaken in order to obtain reference data for testing powder data used for structure determination. This investigation is the first of a series studying the behaviour of different metals in anilate compounds. All angles and distances are in good agreement with values found in the literature (Krough Andersen, 1967; Krough Andersen & Krough Andersen, 1975).



(I)

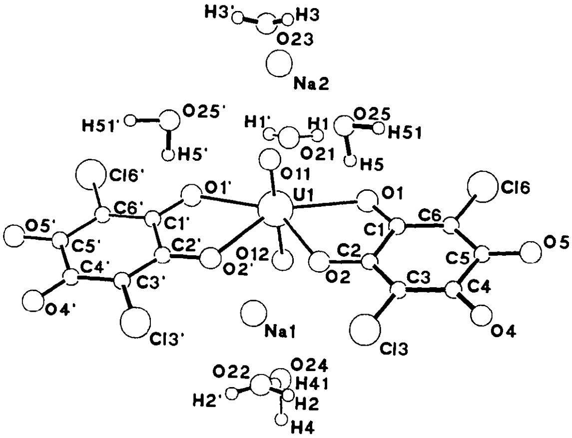
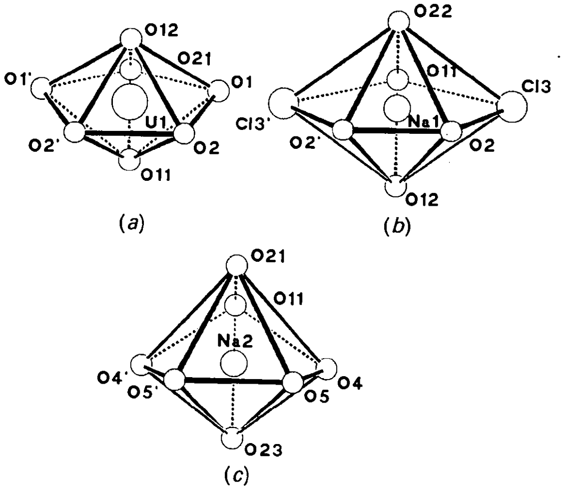


Fig. 1. View of the title compound showing the atomic numbering system; only one of the two formula units in the cell is plotted.



(*a*) (*b*) (*c*)

Fig. 2. Coordination polyhedra of (*a*) U(1), (*b*) Na(1) and (*c*) Na(2).

Experimental

Crystal data

$Na_2[UO_2(C_6Cl_2O_4)_2].6H_2O$
$M_r = 838.04$
Monoclinic
Im
$a = 12.188$ (2) Å
$b = 16.518$ (3) Å
$c = 5.908$ (1) Å
$\beta = 102.57$ (1)°
$V = 1160.8$ (3) Å^3
$Z = 2$
$D_x = 2.398$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 5.6$–13.9°
$\mu = 7.203$ mm^{-1}
$T = 293$ K
Parallelepiped
$0.19 \times 0.12 \times 0.07$ mm
Black

Data collection

Rebuilt Philips PW1100 diffractometer (Gomm, 1991)
$\theta/2\theta$ scans
Absorption correction: Gaussian by integration from crystal shape (Busing & Levy 1957)
$T_{\min} = 0.49$, $T_{\max} = 0.68$
3862 measured reflections
2006 independent reflections

2006 observed reflections
$R_{\rm int} = 0.0215$
$\theta_{\max} = 24.5$°
$h = -14 \rightarrow 14$
$k = -19 \rightarrow 19$
$l = -6 \rightarrow 6$
6 standard reflections monitored every 100 reflections
intensity variation: 0.5%

Refinement

Refinement on *F*
$R = 0.016$
$wR = 0.019$
$S = 1.76$
2006 reflections
190 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 1.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.77$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: local software (Gomm, 1991). Cell refinement: local software (Gomm, 1991). Data reduction: local software (Gomm, 1991). Program(s) used to refine structure: *CRYSTAN* (Burzlaff & Rothammel, 1988). Software used to prepare material for publication: *CRYSTAN*.

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

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

	x	y	z	$U_{\rm eq}$
U(1)	1/2	1/2	1/2	0.0214
Cl(3)	0.2480 (1)	0.68204 (8)	−0.1689 (2)	0.0449
Cl(6)	0.5599 (1)	0.80930 (9)	0.7651 (3)	0.0456
Na(1)	0.2751 (2)	1/2	0.9199 (5)	0.0331
Na(2)	0.8088 (3)	1/2	0.6099 (5)	0.0330
O(1)	0.5229 (3)	0.6394 (2)	0.5853 (6)	0.0358
O(2)	0.3905 (3)	0.5865 (2)	0.2145 (6)	0.0320
O(4)	0.2863 (3)	0.8542 (2)	−0.0008 (6)	0.0408
O(5)	0.4241 (4)	0.9070 (2)	0.3813 (7)	0.0439
O(11)	0.6050 (8)	1/2	0.354 (1)	0.0429
O(12)	0.3908 (7)	1/2	0.662 (1)	0.0327
O(21)	0.6512 (5)	1/2	0.8405 (9)	0.0400
O(22)	0.1242 (5)	1/2	0.097 (1)	0.0376
O(23)	0.8939 (6)	1/2	0.302 (1)	0.0479
O(24)	0.1373 (6)	1/2	0.584 (1)	0.0667
O(25)	0.6810 (7)	0.6388 (3)	1.0386 (9)	0.1034
C(1)	0.4704 (4)	0.6936 (3)	0.4620 (9)	0.0292
C(2)	0.3937 (4)	0.6638 (3)	0.2394 (8)	0.0278
C(3)	0.3350 (5)	0.7187 (3)	0.0859 (9)	0.0326
C(4)	0.3394 (4)	0.8021 (3)	0.1282 (8)	0.0306
C(5)	0.4178 (5)	0.8330 (3)	0.3552 (9)	0.0322
C(6)	0.4754 (4)	0.7753 (3)	0.507 (1)	0.0295

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

U(1)—O(11)	1.69 (1)	O(1)—C(1)	1.241 (6)
U(1)—O(12)	1.80 (1)	O(2)—C(2)	1.285 (6)
U(1)—O(1)	2.361 (4)	O(21)—O(25)	2.564 (6)
U(1)—O(2)	2.385 (3)	O(25)—H(1)	1.74 (6)
U(1)—O(21)	2.414 (5)	C(1)—C(6)	1.374 (7)
Na(1)—O(12)	2.29 (1)	C(1)—C(2)	1.520 (7)
Na(1)—O(24)	2.302 (7)	C(2)—C(3)	1.369 (7)
Na(1)—O(22$^{\rm i}$)	2.305 (7)	C(3)—C(4)	1.399 (8)
Na(1)—O(2$^{\rm i}$)	2.446 (4)	C(3)—Cl(3)	1.750 (5)
Na(1)—Cl(3$^{\rm i}$)	3.058 (2)	C(4)—O(4)	1.234 (6)
Na(2)—O(23)	2.282 (9)	C(4)—C(5)	1.554 (7)
Na(2)—O(5$^{\rm ii}$)	2.434 (4)	C(5)—O(5)	1.234 (7)
Na(2)—O(4$^{\rm ii}$)	2.496 (4)	C(5)—C(6)	1.390 (8)
Na(2)—O(21)	2.585 (7)	C(6)—Cl(6)	1.736 (6)
Na(2)—O(11)	2.612 (9)		
O(1)—U(1)—O(1$^{\rm iii}$)	154.5 (1)	O(5$^{\rm ii}$)—Na(2)—O(5$^{\rm v}$)	78.3 (1)
O(1)—U(1)—O(2)	65.7 (1)	O(5$^{\rm ii}$)—Na(2)—O(11)	136.2 (2)
O(1)—U(1)—O(2$^{\rm iii}$)	139.2 (1)	O(5$^{\rm ii}$)—Na(2)—O(21)	92.4 (2)
O(1)—U(1)—O(11)	92.4 (1)	O(5$^{\rm ii}$)—Na(2)—O(23)	103.2 (2)
O(1)—U(1)—O(12)	87.3 (1)	O(11)—Na(2)—O(21)	65.4 (3)
O(1)—U(1)—O(21)	77.81 (8)	O(11)—Na(2)—O(23)	94.5 (3)
O(2)—U(1)—O(2$^{\rm iii}$)	73.6 (1)	O(23)—Na(2)—O(21)	159.9 (2)
O(2)—U(1)—O(11)	90.4 (2)	U(1)—O(1)—C(1)	123.8 (3)
O(2)—U(1)—O(12)	90.7 (2)	U(1)—O(2)—C(2)	121.1 (3)
O(2)—U(1)—O(21)	142.88 (8)	O(25)—O(21)—U(1)	112.8 (2)
O(11)—U(1)—O(12)	178.6 (4)	O(25)—O(21)—O(25$^{\rm iii}$)	126.8 (3)
O(11)—U(1)—O(21)	84.3 (3)	C(6)—C(1)—O(1)	126.8 (5)
O(12)—U(1)—O(21)	94.3 (3)	C(2)—C(1)—O(1)	114.6 (5)
O(2$^{\rm i}$)—Na(1)—O(2$^{\rm iv}$)	71.5 (1)	C(2)—C(1)—C(6)	118.7 (5)
O(2$^{\rm i}$)—Na(1)—O(12)	97.5 (2)	C(3)—C(2)—O(2)	125.7 (4)
O(2$^{\rm i}$)—Na(1)—O(22$^{\rm i}$)	94.0 (2)	C(1)—C(2)—O(2)	114.8 (4)
O(2$^{\rm i}$)—Na(1)—O(24)	144.23 (8)	C(1)—C(2)—C(3)	119.5 (5)
O(2$^{\rm i}$)—Na(1)—Cl(3$^{\rm i}$)	64.63 (8)	C(4)—C(3)—C(2)	122.7 (5)
O(2$^{\rm i}$)—Na(1)—Cl(3$^{\rm iv}$)	136.1 (1)	Cl(3)—C(3)—C(2)	118.2 (4)
O(12)—Na(1)—O(22$^{\rm i}$)	165.8 (3)	Cl(3)—C(3)—C(4)	119.2 (4)
O(12)—Na(1)—O(24)	82.3 (3)	C(3)—C(4)—O(4)	125.5 (4)
O(12)—Na(1)—Cl(3$^{\rm i}$)	86.85 (7)	C(5)—C(4)—O(4)	116.5 (4)
O(22$^{\rm i}$)—Na(1)—O(24)	83.5 (3)	C(5)—C(4)—C(3)	118.0 (4)
Cl(3$^{\rm i}$)—Na(1)—O(22$^{\rm i}$)	90.62 (7)	C(6)—C(5)—O(5)	126.2 (5)
Cl(3$^{\rm i}$)—Na(1)—O(24)	79.70 (5)	C(4)—C(5)—O(5)	116.3 (5)
Cl(3$^{\rm i}$)—Na(1)—Cl(3$^{\rm iv}$)	159.1 (1)	C(4)—C(5)—C(6)	117.6 (5)
O(4$^{\rm ii}$)—Na(2)—O(4$^{\rm v}$)	149.7 (2)	C(5)—C(6)—C(1)	123.5 (5)
O(4$^{\rm ii}$)—Na(2)—O(5$^{\rm ii}$)	65.1 (1)	Cl(6)—C(6)—C(1)	118.8 (4)
O(4$^{\rm ii}$)—Na(2)—O(5$^{\rm v}$)	142.8 (2)	Cl(6)—C(6)—C(5)	117.7 (4)
O(4$^{\rm ii}$)—Na(2)—O(11)	79.1 (1)	O(25)—H(1)—O(21)	149 (5)
O(4$^{\rm ii}$)—Na(2)—O(23)	80.5 (1)		

Symmetry codes: (i) $x, y, 1+z$; (ii) $\frac{1}{2}+x, y-\frac{1}{2}, \frac{1}{2}+z$; (iii) $x, 1-y, z$; (iv) $x, 1-y, 1+z$; (v) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$.

A suspension of solid anhydrous sodium chloranilate in 300 ml of a hot acetone solution of uranyl(VI) nitrate (0.1 *M*) was refluxed for 2 h with constant stirring. After the solvent had been expelled the remaining solid mass was mixed with about 1 l of distilled water and the system left to digest for 3 h in a water bath. A deep cherry-red complex formed gradually; nearly black crystals were obtained.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71534 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1025]

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trans-Dichlorobis(metronidazole)palladium(II), $[PdCl_2(C_6H_9N_3O_3)_2]$

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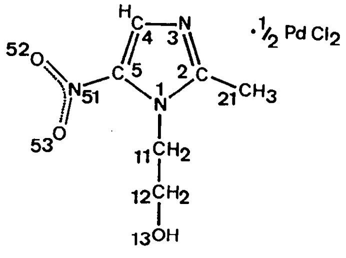
Abstract

The title complex, dichlorobis(2-methyl-5-nitroimidazole-1-ethanol-N^3)palladium(II), is *trans* square planar. The imidazole ring forms an angle of 88.8 (3)° with the square plane around the Pd atom, and an angle of 3.9 (4)° with the nitro group.

Comment

Nitroimidazoles are generally known as antiprotozoic and radiosensitizing drugs (Edwards, 1981). The structure of the title compound (I) has been determined to examine the influence of the coordination on the geometry of the heterocycle.



(I)

On the basis of a physicochemical study, Bales *et al.* (1983) concluded that the coordination of $Pt^{II}Cl_2$ to the basic imidazole was responsible for a withdrawal of electron density from the imidazole ring; however, they did not observe any change in the geometric properties of the metronidazole molecule. The structural analysis of the title compound is more appropriate for the evaluation of the effect of coordination since: (i) in the title compound the metronidazole scattering is less overpowered because of the lighter heavy atom, and (ii) the present structural model fits the measurements considerably better (R = 3.1 instead of 4.6%). However, the coordination effects, evaluated as the imidazole ring-angle differences between the title compound and the uncomplexed metronidazole (Blaton, Peeters & De Ranter, 1979), are, from the statistical point of view, still unobservable.

Since the bond angles at Pd do not deviate significantly from 90°, $PdCl_2$(metronidazole)$_2$ is square planar, as expected from the electron population of the 4*d* orbital of Pd^{II}. The complex has the Cl atoms and the metronidazole ligands *trans* to one another (Fig. 1).

The dihedral angle between the plane of the imidazole ring and the square plane around Pd is 88.8 (3)°. The dihedral angle between the plane of the imidazole ring and that of the nitro group is 3.9 (4)° [4.3 (1)° in the uncomplexed form (Blaton *et al.*, 1979)].

Each molecule forms a hydrogen bond with a symmetrically related neighbour [$O13—H13\cdots Cl^i$: $O13\cdots Cl^i$ = 3.185 (2), $H13\cdots Cl^i$ = 2.48 (3) Å, $O13—H13\cdots Cl^i$ = 158 (4)°; symmetry code: (i) $-x+1, -y, -z$].

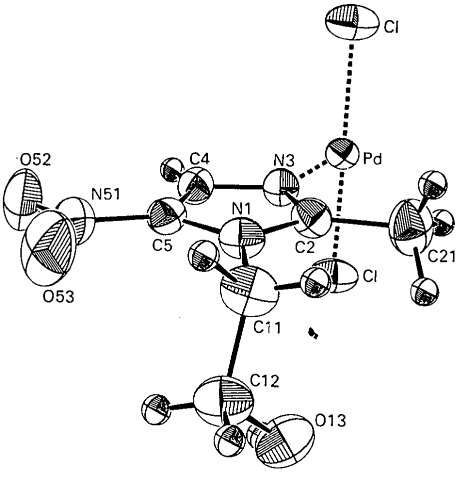


Fig. 1. View of $PdCl_2$(metronidazole)$_2$ showing the conformation.

Experimental

Crystal data

$[PdCl_2(C_6H_9N_3O_3)_2]$
M_r = 519.62
Monoclinic
$P2_1/a$

Cell parameters from 18 reflections
θ = 9–11°
μ = 1.266 mm^{-1}

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