

Acta Cryst. (1996). C52, 1124–1125

Diaquabis(5-isonitrosobarbiturato)-cobalt(II) Dihydrate

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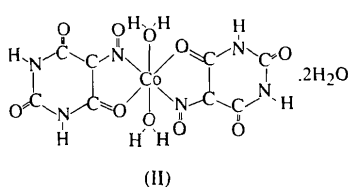
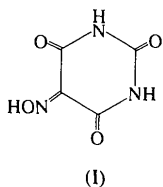
(Received 20 July 1995; accepted 23 November 1995)

Abstract

The Co^{II} atom in the title compound, diaquabis[2,4,5,6(1*H*,3*H*)-pyrimidinetetrone 5-oximato]-cobalt(II) dihydrate, [Co(C₄H₂N₃O₄)₂(H₂O)₂].2H₂O, is six-coordinate in a distorted octahedral environment. It is bonded to the two N atoms of the isonitroso groups and to two carbonyl O atoms of the two 5-isonitrosobarbiturate ligands, the four atoms constituting the equatorial plane. The two water O atoms occupy the axial positions. Molecules are linked by two types of hydrogen bond, N—H···O and O—H···O, involving water molecules.

Comment

Violuric acid (5-isonitrosobarbituric acid), (I), is a barbituric acid derivative; these derivatives have effective photoprotecting characteristics and are useful for protecting the skin from the harmful effects of ultraviolet irradiation (Bush, 1995). The *N*-nitroso compounds are known to be carcinogens (Iishi, Tatsuta, Baba, Uehara & Nakaizumi, 1994). In order to clarify the physiological effect of nitroso compounds, it is important to clarify the structures of their complexes and their analogues with biomaterials. Violuric acid also forms salts with various metals such as alkaline and transition metals (Awadallah, Issa, Belal & Peacock, 1993). Accordingly, the crystal structure of the Co^{II} complex of violuric acid, diaquabis(5-isonitrosobarbiturato-*N,O*)-cobalt(II), (II), has been determined. The structures of the related compounds violuric acid (Craven & Mascarenhas, 1964), perdeuterated violuric acid (Craven & Takei, 1964) and 1,3-dimethylvioluric acid–mercury(II) (Jaya Reddy, Chacko, Aoki, Yamazaki & Salas-peregrin, 1990) have been reported.



The molecular structure of the title complex with the atomic labelling is shown in Fig. 1. The isonitroso group (N—O—H) of the violuric acid molecule may be present in the deprotonated form owing to the resonance contribution of =N—O[−] or —N=O (Jaya Reddy *et al.*, 1990). The Co coordination sphere is a slightly distorted octahedron. The carbonyl O atoms at the 6-positions and the N atoms of the deprotonated isonitroso groups of the two violuric acid ligands are bound to the Co atom in the same equatorial plane in positions *trans* with respect to one another. Two water O atoms occupy the axial sites. The crystal structure is stabilized by two types of hydrogen bond involving water molecules: N(3)—H(3)···O(4ⁱ) 2.835 (5), N(1)—H(1)···O(3ⁱⁱ) 2.886 (6), O(3)—H(32)···O(2ⁱⁱⁱ) 2.867 (5), O(3)—H(31)···O(5^{iv}) 3.044 (6), O(1)—H(12)···O(3^v) 2.861 (6) and O(1)—H(11)···O(5^{vi}) 2.748 (6) Å [symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} - y, -z$; (ii) $\frac{3}{2} - x, -\frac{1}{2} - y, 1 - z$; (iii) $x, -y, \frac{1}{2} + z$; (iv) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (v) $-\frac{1}{2} + x, -\frac{1}{2} + y, z - 1$; (vi) $x, y - 1, z$]. There is no significant ring stacking.

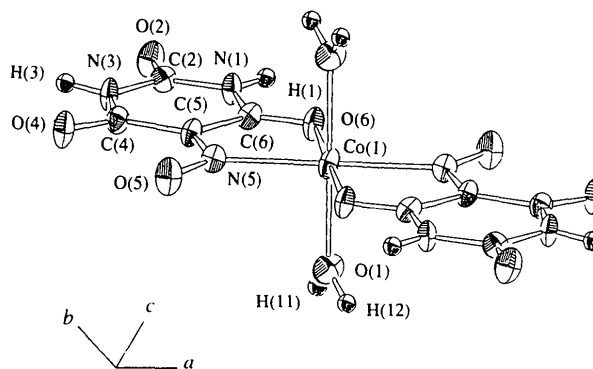


Fig. 1. An ORTEP drawing (Johnson, 1976) of the title compound with the atomic numbering scheme. Displacement ellipsoids for non-H atoms correspond to 50% probability.

Experimental

The brownish plate crystal used for analysis was obtained by slow evaporation of a 50% ethanol solution of a 3:1 mixture of violuric acid monohydrate and CoSO₄·7H₂O at room temperature.

Crystal data[Co(C₄H₂N₃O₄)₂(H₂O)₂].
2H₂OM_r = 443.14

Monoclinic

C2/c

a = 25.234 (3) Å

b = 5.017 (4) Å

c = 12.588 (5) Å

β = 108.83 (2)°

V = 1508 (1) Å³

Z = 4

D_x = 1.951 Mg m^{−3}D_m not measured

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25

reflections

θ = 13.05–17.65°

μ = 1.215 mm^{−1}

T = 296 K

Plate

0.50 × 0.20 × 0.10 mm

Brown

Data collection

Rigaku AFC-5R diffractometer	$R_{\text{int}} = 0.032$
ω -2 θ scans	$\theta_{\text{max}} = 27.50^\circ$
Absorption correction: none	$h = 0 \rightarrow 32$
1985 measured reflections	$k = 0 \rightarrow 6$
1939 independent reflections	$l = -16 \rightarrow 14$
1072 observed reflections	3 standard reflections
$[I > 3\sigma(I)]$	monitored every 150 reflections
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.01$
$R = 0.046$	$\Delta\rho_{\text{max}} = 0.60 \text{ e } \text{\AA}^{-3}$
$wR = 0.050$	$\Delta\rho_{\text{min}} = -0.47 \text{ e } \text{\AA}^{-3}$
$S = 1.50$	Extinction correction: none
1072 reflections	Atomic scattering factors
148 parameters	from <i>International Tables</i>
H atoms not refined	for <i>X-ray Crystallography</i>
$w = 4F_o^2/\sigma^2(F_o^2)$	(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Co(1)	1/2	0	0	1.76 (3)
O(1)	0.4829 (2)	-0.2482 (9)	-0.1349 (4)	2.5 (2)
O(2)	0.7545 (1)	-0.3628 (8)	0.1748 (3)	2.5 (1)
O(3)	0.8683 (2)	0.1874 (9)	0.7301 (3)	2.6 (2)
O(4)	0.6795 (1)	0.3283 (7)	-0.0560 (3)	2.3 (1)
O(5)	0.5645 (1)	0.3725 (8)	-0.1108 (3)	2.5 (1)
O(6)	0.5684 (1)	-0.2283 (7)	0.0906 (3)	2.0 (1)
N(1)	0.6615 (2)	-0.2854 (9)	0.1352 (4)	1.8 (2)
N(3)	0.7152 (1)	-0.018 (1)	0.0596 (3)	1.9 (1)
N(5)	0.5675 (2)	0.1777 (9)	-0.0452 (3)	1.7 (1)
C(2)	0.7132 (2)	-0.232 (1)	0.1271 (4)	1.8 (2)
C(4)	0.6706 (2)	0.140 (1)	-0.0019 (4)	1.7 (2)
C(5)	0.6170 (2)	0.0621 (9)	0.0066 (4)	1.5 (2)
C(6)	0.6128 (2)	-0.157 (1)	0.0775 (4)	1.6 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Co(1)—O(1')	2.037 (4)	N(1)—C(2)	1.368 (6)
Co(1)—O(6')	2.079 (3)	N(1)—C(6)	1.370 (6)
Co(1)—N(5')	2.156 (4)	N(3)—C(2)	1.381 (6)
O(2)—C(2)	1.212 (6)	N(3)—C(4)	1.390 (6)
O(4)—C(4)	1.229 (6)	N(5)—C(5)	1.340 (6)
O(5)—N(5)	1.266 (5)	C(4)—C(5)	1.443 (6)
O(6)—C(6)	1.237 (5)	C(5)—C(6)	1.441 (6)
O(1)—Co(1)—O(1')	180.0	O(5)—N(5)—C(5)	120.1 (4)
O(1)—Co(1)—O(6)	92.0 (2)	O(2)—C(2)—N(1)	123.0 (5)
O(1)—Co(1)—O(6')	88.0 (2)	O(2)—C(2)—N(3)	122.0 (4)
O(1)—Co(1)—N(5)	90.3 (2)	N(1)—C(2)—N(3)	115.0 (4)
O(1)—Co(1)—N(5')	89.7 (2)	O(4)—C(4)—N(3)	119.0 (4)
O(6)—Co(1)—O(6')	180.0	O(4)—C(4)—C(5)	126.4 (4)
O(6)—Co(1)—N(5)	102.4 (2)	N(3)—C(4)—C(5)	114.6 (4)
O(6)—Co(1)—N(5')	77.6 (2)	N(5)—C(5)—C(4)	126.5 (4)
N(5)—Co(1)—N(5')	180.0	N(5)—C(5)—C(6)	112.8 (4)
Co(1)—O(6)—C(6)	113.2 (3)	C(4)—C(5)—C(6)	120.6 (4)
Co(1)—N(5)—O(5)	127.3 (3)	O(6)—C(6)—N(1)	119.3 (4)
Co(1)—N(5)—C(5)	112.6 (3)	O(6)—C(6)—C(5)	123.7 (4)
C(2)—N(1)—C(6)	125.6 (4)	N(1)—C(6)—C(5)	117.1 (5)
C(2)—N(3)—C(4)	126.9 (4)		

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

Data collection: *MSCI/AFSC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCI/AFSC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Pro-

gram(s) used to solve structure: *SHELXS86* (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 1125–1127

Redetermination of a Copper(II) Complex of Violuric Acid

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(Received 21 September 1995; accepted 13 November 1995)

Abstract

In the title compound, diaquabis[2,4,5,6(1*H*,3*H*)-pyrimidinetetrone 5-oximate]copper(II) dihydrate, $[\text{Cu}(\text{C}_4\text{H}_2\text{N}_3\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, the coordination geometry about the Cu atom is distorted octahedral. The Cu atom is bonded to the N atoms of the isonitroso groups and to two carbonyl O atoms of the two violurate ligands in the equatorial plane, and to two water molecules in axial