

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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Redetermination of a Copper(II) Complex of Violuric Acid

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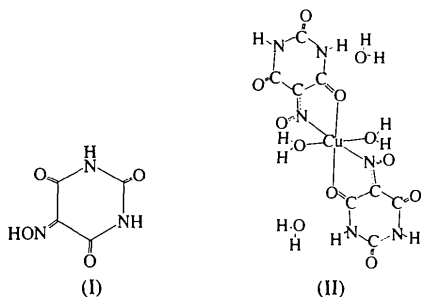
Abstract

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

positions. The crystal structure is stabilized by a three-dimensional network of N—H···O and O—H···O intermolecular hydrogen bonds. The structure was originally determined based on Weissenberg film data taken using Cu K α radiation [Hamelin (1972). *Acta Cryst.* B28, 228–235].

Comment

Violuric acid (5-isonitrosobarbituric acid), (I), and its derivatives have biologically effective photoprotecting characteristics for ultraviolet irradiation (Bush, 1995). Violuric acid contains an isonitroso group as a substituent and is known to form many kinds of metal complexes in solution (Awadallah, Issa, Belal & Peacock, 1993). It is important to accumulate structural information on metal complexes of various nitroso compounds in order to clarify their effect on many important physiological processes involving various metal enzymes, since many *N*-nitroso compounds are well known as potent carcinogens (Iishi, Tatsuta, Baba, Uehara & Nakaizumi, 1994). For this reason, the crystal structure of the copper(II) dihydrate of violuric acid, (II), has been determined as a model compound for investigating the interaction between a metal and a nitroso compound. The structure of the title compound had been determined previously (Hamelin, 1972), but the determination was based on Weissenberg film data taken using Cu K α radiation and the final *R* index of 0.114 and the estimated standard deviations on geometric parameters were rather high. The present study has yielded markedly lower uncertainties and has allowed the H-atom positions to be identified.



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 previously.

The molecular structure of (II) is shown in Fig. 1, which also indicates the atom labelling. The isonitroso (N—O—H) group of violuric acid may be present in its deprotonated form in the complex owing to the resonance contribution from =N—O⁻ or —N=O (Jaya Reddy *et al.*, 1990). The Cu coordination sphere is a slightly distorted octahedron. The

carbonyl O atom at the 6-positions and the N atoms of the deprotonated isonitroso groups of the two violuric acid ligands are bound to the Cu atom in the equatorial plane in positions *trans* with respect to each other. The O atoms of the two water molecules bind to the Cu atom in axial positions. The crystal structure is stabilized by N—H···O and O—H···O hydrogen bonds involving the water molecules; N(3)—H(3)···O(2ⁱ) 2.892 (5), N(1)—H(1)···O(3ⁱⁱ) 2.826 (5), O(3)—H(31)···O(4ⁱⁱⁱ) 2.900 (5), O(3)—H(32)···O(2^{iv}) 2.967 (5), O(1)—H(12)···O(4ⁱⁱⁱ) 2.703 (5), O(1)—H(11)···O(5^v) 2.816 (5) Å [symmetry codes: (i) 3 - x, -3 - y, -1 - z; (ii) 1 + x, y, z; (iii) x, 1 + y, z; (iv) 3 - x, -2 - y, -1 - z; (v) 1 - x, -2 - y, -z].

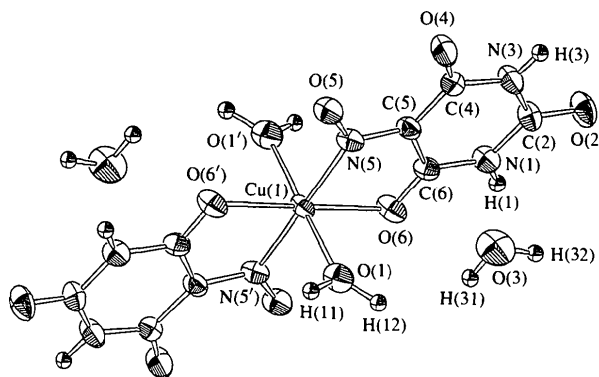


Fig. 1. An ORTEP drawing (Johnson, 1976) of the title compound, with the atomic numbering scheme, viewed along the *a* axis. Displacement ellipsoids for non-H atoms correspond to 50% probability.

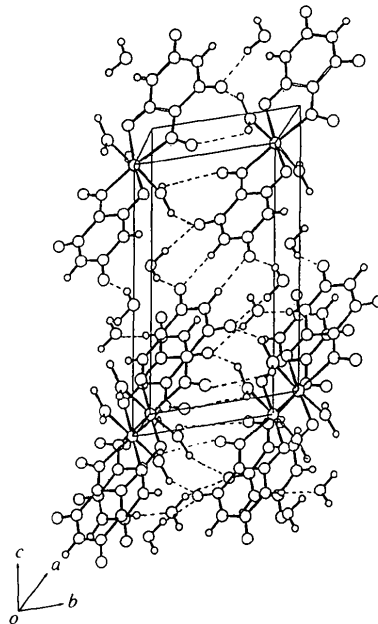


Fig. 2. Packing diagram of the title compound along the *a* axis of the unit cell, with intermolecular hydrogen bonds represented by dashed lines.

Experimental

The blue plate-like crystal used for analysis was obtained by the slow evaporation of a 50% ethanol solution of a 3:1 mixture of violuric acid monohydrate and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at room temperature.

Crystal data

$[\text{Cu}(\text{C}_4\text{H}_2\text{N}_3\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	Mo $K\alpha$ radiation
$M_r = 447.76$	$\lambda = 0.7107 \text{ \AA}$
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	$\theta = 17.05\text{--}21.35^\circ$
$a = 5.177(2) \text{ \AA}$	$\mu = 1.540 \text{ mm}^{-1}$
$b = 6.410(1) \text{ \AA}$	$T = 296 \text{ K}$
$c = 11.862(2) \text{ \AA}$	Plate
$\alpha = 82.05(2)^\circ$	$0.15 \times 0.10 \times 0.05 \text{ mm}$
$\beta = 79.38(2)^\circ$	Blue
$\gamma = 76.88(2)^\circ$	
$V = 374.9(2) \text{ \AA}^3$	
$Z = 1$	
$D_x = 1.983 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Rigaku AFC-5R diffractometer	$R_{\text{int}} = 0.027$
ω - 2θ scans	$\theta_{\text{max}} = 27.55^\circ$
Absorption correction: none	$h = -6 \rightarrow 6$
1888 measured reflections	$k = -8 \rightarrow 0$
1733 independent reflections	$l = -15 \rightarrow 15$
1314 observed reflections	3 standard reflections
$[I > 3\sigma(I)]$	monitored every 150 reflections
	intensity decay: 1.70%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R = 0.051$	$\Delta\rho_{\text{max}} = 0.76 \text{ e \AA}^{-3}$
$wR = 0.052$	$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$
$S = 1.53$	Extinction correction: none
1314 reflections	Atomic scattering factors
124 parameters	from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)
H atoms not refined	
$w = 4F_o^2/\sigma^2(F_o^2)$	

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}
Cu(1)	1	-1	0	2.04 (5)
O(1)	0.7192 (6)	-0.7733 (5)	-0.0889 (3)	3.0 (2)
O(2)	1.6684 (7)	-1.2854 (6)	-0.4780 (3)	3.4 (2)
O(3)	0.8669 (8)	-0.8636 (6)	-0.3739 (4)	4.5 (3)
O(4)	0.9683 (7)	-1.5267 (6)	-0.2586 (3)	3.1 (2)
O(5)	0.7773 (6)	-1.3368 (5)	-0.0556 (3)	2.8 (2)
O(6)	1.3050 (6)	-0.9717 (5)	-0.1501 (3)	2.9 (2)
N(1)	1.4844 (7)	-1.1286 (6)	-0.3142 (3)	2.5 (2)
N(3)	1.3219 (8)	-1.4063 (6)	-0.3640 (3)	2.8 (3)
N(5)	0.9536 (7)	-1.2262 (6)	-0.0886 (3)	2.2 (2)
C(2)	1.504 (1)	-1.2725 (8)	-0.3897 (4)	2.6 (3)

C(4)	1.125 (1)	-1.4044 (7)	-0.2684 (4)	2.3 (3)
C(5)	1.1225 (9)	-1.2561 (7)	-0.1874 (4)	2.1 (3)
C(6)	1.3072 (8)	-1.1091 (7)	-0.2130 (4)	2.1 (3)

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

Cu(1)—O(1)	2.126 (4)	N(1)—C(2)	1.346 (6)
Cu(1)—O(6)	2.168 (3)	N(1)—C(6)	1.372 (6)
Cu(1)—N(5)	1.985 (4)	N(3)—C(2)	1.382 (6)
O(2)—C(2)	1.221 (6)	N(3)—C(4)	1.377 (6)
O(4)—C(4)	1.231 (5)	N(5)—C(5)	1.336 (6)
O(5)—N(5)	1.255 (4)	C(4)—C(5)	1.439 (6)
O(6)—C(6)	1.228 (5)	C(5)—C(6)	1.455 (6)
O(1)—Cu(1)—O(6)	88.9 (1)	O(2)—C(2)—N(1)	123.4 (5)
O(1)—Cu(1)—O(6')	91.1 (1)	O(2)—C(2)—N(3)	120.1 (4)
O(1)—Cu(1)—N(5)	88.9 (1)	N(1)—C(2)—N(3)	116.4 (4)
O(1)—Cu(1)—N(5')	91.1 (1)	O(4)—C(4)—N(3)	118.7 (4)
O(6)—Cu(1)—N(5)	79.2 (1)	O(4)—C(4)—C(5)	125.5 (4)
O(6)—Cu(1)—N(5')	100.8 (1)	N(3)—C(4)—C(5)	115.8 (4)
Cu(1)—O(6)—C(6)	108.6 (3)	N(5)—C(5)—C(4)	126.9 (4)
Cu(1)—N(5)—O(5)	123.1 (3)	N(5)—C(5)—C(6)	112.9 (4)
Cu(1)—N(5)—C(5)	116.1 (3)	C(4)—C(5)—C(6)	120.1 (4)
C(2)—N(1)—C(6)	125.9 (4)	O(6)—C(6)—N(1)	120.9 (4)
C(2)—N(3)—C(4)	125.4 (4)	O(6)—C(6)—C(5)	123.0 (4)
O(5)—N(5)—C(5)	120.8 (4)	N(1)—C(6)—C(5)	116.1 (4)

Symmetry code: (i) $2 - x, -2 - y, -z$.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(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: BM1036). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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