

Bis(2,6-dimethyl-4H-pyran-4-one)dinitratocopper(II), $[\text{Cu}(\text{NO}_3)_2(\text{C}_7\text{H}_8\text{O}_2)_2]$

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Abstract. $M_r = 435.83$, triclinic, $P\bar{1}$, $a = 15.872$ (5), $b = 8.772$ (3), $c = 8.384$ (3) Å, $\alpha = 124.35$ (1), $\beta = 106.84$ (1), $\gamma = 85.93$ (1)°, $V = 916.06$ Å³, $D_x = 1.580$, $D_m = 1.55$ (1) Mg m⁻³, $Z = 2$, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.30$ mm⁻¹, $F(000) = 446$, $T = 294$ K, $R = 0.042$ for 3440 observed diffractometer reflexions. The Cu atom is distorted square-planar coordinated with the dimethylpyrone ligands *cis* to each other and the nitrate groups unidentate. The mean Cu–O coordination distance is 1.954 (3) Å. The dimethylpyrone ligands and the nitrate groups are individually planar but not coplanar.

Introduction. The title compound was synthesized by Hill (1971) and a spectroscopic study of its properties was carried out by Briggs & Hill (1969, 1970) as part of a research project on corrosion inhibition. This investigation was undertaken to supplement that work and to study the Cu coordination and the nitrate linkages. Results have already been published for the Zn^{II} analogue (Brown & Lewis, 1984) and tris(2,6-dimethyl-4H-pyran-4-one)dinitratocadmium(II) (Banerjee, Brown, Jain & Gautam, 1984).

Experimental. Sample prepared by Drs E. M. Briggs and A. E. Hill of the Chemistry Department of this Polytechnic; blue-green platelets (*ca* 0.4 × 0.4 × 0.2 mm) which decompose in air over several months; D_m by flotation in $\text{CHCl}_3/\text{CCl}_4$; lattice parameters initially from rotation photographs and refined on the diffractometer; Mo $K\alpha$ radiation; intensities on a CAD-4 diffractometer at Queen Mary College, University of London; 3689 measured reflexions of which 249 had $|F| < 1$; index range $h -19$ to 19, $k 0$ to 11, $l -10$ to 8; four standard reflections, no significant variation in intensity; $2\theta_{\text{max}} = 54^\circ$; correction for L_p but not for absorption or extinction; structure solved first from visual intensities by Patterson and successive Fourier syntheses; refinement by least squares on F using initially B_{iso} and $\sqrt{w} = 1/(10 + F_o + 0.01F_o^2)$, then finally B_{ij} until shifts $< 0.2\sigma$; H atoms derived by calculation included in structure factors with $B_{\text{iso}} = 6.0$ Å² without refining; $R = 0.042$, $wR = 0.112$; residual electron density in final difference map within

± 0.2 e Å⁻³; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); NRC computer programs (Ahmed, Hall, Pippy & Huber, 1970) implemented on the ICL 1905E at the London Polytechnics Computer Unit and on our own DEC-20.

Discussion. The final positional and equivalent isotropic temperature parameters are given in Table 1.* The numbering of the atoms and the arrangement of the molecules in the unit cell are shown in Fig. 1. Bond lengths and angles are in Table 2.

The Cu atom is coordinated to four O atoms (two from dimethyl-4-pyrone and two from nitrate) in an almost square plane, slightly distorted in the direction of a tetrahedron. A mean plane through the Cu and four O atoms has out-of-plane distances O(1) (nitrate) +0.323 (2), O(2) (nitrate) –0.320 (2), O(3) (pyrone) +0.231 (2) and O(4) (pyrone) –0.270 (2) Å. The angles subtended at Cu are O(1)–Cu–O(3) 164.0 (1) and O(2)–Cu–O(4) 162.4 (1)°. The two dimethyl-4-pyrone ligands are *cis* to each other (as are also the two nitrate groups) whereas in the corresponding Zn compound (Brown & Lewis, 1984) the Zn–O ligands are distributed tetrahedrally with the Zn atom lying on a twofold axis. The mean Cu–O coordination distance is 1.954 (3) Å compared with Zn–O 2.008 (2) and Cd–O 2.332 (4) Å in the Zn and Cd compounds (Brown & Lewis, 1984; Banerjee *et al.*, 1984). The *trans* Cu compound has not yet been prepared.

The 2,6-dimethyl-4-pyrone ligands and the nitrate groups are each almost exactly planar, the r.m.s. deviations of atoms from the planes of atoms [C(1)–C(7), O(3), O(9)], [C(8)–C(14), O(4), O(10)], [N(1), O(1), O(5), O(6)] and [N(2), O(2), O(7), O(8)], being 0.007, 0.007, 0.002 and 0.006 Å, respectively. The two pyrone ligands make a dihedral angle of 82.69 (5)°.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and equations of mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39976 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

There are no particularly close intermolecular contacts between non-H atoms, the shortest being O(8)...O(9) of the centrosymmetrically related molecule, 3.179 (4) Å.

Table 1. Final atomic parameters and e.s.d.'s

$$B_{eq} = \frac{4}{3}[(\beta_{11}/a^{*2}) + (\beta_{22}/b^{*2}) + (\beta_{33}/c^{*2})].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Cu	0.24652 (2)	0.40845 (3)	0.02677 (4)	3.24 (1)
O(1)	0.1920 (2)	0.6283 (3)	0.0490 (4)	5.09 (4)
O(2)	0.3662 (2)	0.5495 (3)	0.1771 (3)	4.44 (4)
O(3)	0.3004 (1)	0.1828 (3)	-0.0645 (3)	4.00 (3)
O(4)	0.1296 (1)	0.2998 (3)	-0.0369 (3)	4.09 (4)
O(5)	0.2242 (2)	0.4665 (4)	-0.2345 (4)	5.94 (5)
O(6)	0.1555 (3)	0.7097 (5)	-0.1607 (5)	9.95 (5)
O(7)	0.3063 (2)	0.6123 (3)	0.4042 (3)	4.65 (3)
O(8)	0.4407 (2)	0.7329 (4)	0.4970 (5)	6.01 (6)
O(9)	0.4085 (2)	-0.0763 (3)	0.2080 (3)	4.65 (3)
O(10)	-0.0152 (1)	-0.2042 (3)	-0.4273 (3)	3.79 (3)
N(1)	0.1909 (2)	0.6009 (4)	-0.1203 (4)	4.49 (5)
N(2)	0.3726 (2)	0.6340 (4)	0.3670 (4)	4.09 (4)
C(1)	0.3331 (2)	0.1057 (4)	0.0230 (4)	3.40 (4)
C(2)	0.3743 (2)	-0.0614 (4)	-0.0753 (4)	3.56 (4)
C(3)	0.4103 (2)	-0.1469 (4)	0.0173 (5)	4.13 (5)
C(4)	0.4530 (3)	-0.3191 (5)	-0.0751 (6)	5.76 (6)
C(5)	0.3756 (2)	0.1333 (6)	0.5145 (6)	5.52 (6)
C(6)	0.3706 (2)	0.0800 (4)	0.3099 (4)	3.67 (4)
C(7)	0.3331 (2)	0.1708 (3)	0.2235 (4)	3.31 (4)
C(8)	0.0855 (2)	0.1420 (4)	-0.1608 (4)	3.45 (4)
C(9)	0.1131 (2)	-0.0129 (4)	-0.3212 (4)	3.57 (4)
C(10)	0.0637 (2)	-0.1791 (4)	-0.4471 (4)	3.68 (4)
C(11)	0.0844 (3)	-0.3512 (6)	-0.6182 (6)	5.38 (6)
C(12)	-0.1327 (2)	-0.1169 (6)	-0.2818 (5)	4.85 (6)
C(13)	-0.0453 (2)	-0.0628 (4)	-0.2808 (4)	4.03 (5)
C(14)	0.0016 (2)	0.1058 (4)	-0.1497 (4)	3.54 (4)

Table 2. Bond lengths (Å) and angles (°)

Cu—O(1)	1.988 (3)	O(10)—C(10)	1.358 (4)
Cu—O(2)	1.978 (2)	O(10)—C(13)	1.346 (4)
Cu—O(3)	1.915 (2)	C(1)—C(2)	1.438 (4)
Cu—O(4)	1.934 (2)	C(1)—C(7)	1.439 (4)
O(1)—N(1)	1.294 (4)	C(2)—C(3)	1.353 (5)
O(2)—N(2)	1.296 (3)	C(3)—C(4)	1.476 (6)
O(3)—C(1)	1.246 (4)	C(5)—C(6)	1.479 (5)
O(4)—C(8)	1.257 (4)	C(6)—C(7)	1.359 (5)
O(5)—N(1)	1.231 (4)	C(8)—C(9)	1.429 (4)
O(6)—N(1)	1.233 (6)	C(8)—C(14)	1.430 (4)
O(7)—N(2)	1.235 (4)	C(9)—C(10)	1.342 (4)
O(8)—N(2)	1.222 (4)	C(10)—C(11)	1.485 (5)
O(9)—C(3)	1.359 (4)	C(12)—C(13)	1.495 (5)
O(9)—C(6)	1.353 (4)	C(13)—C(14)	1.341 (5)
O(1)—Cu—O(2)	91.9 (1)	C(1)—C(2)—C(3)	121.7 (3)
O(1)—Cu—O(4)	88.2 (1)	O(9)—C(3)—C(2)	120.5 (3)
O(2)—Cu—O(3)	88.9 (1)	O(9)—C(3)—C(4)	115.0 (3)
O(3)—Cu—O(4)	95.8 (1)	C(2)—C(3)—C(4)	124.5 (3)
Cu—O(1)—N(1)	101.5 (2)	O(9)—C(6)—C(5)	112.7 (3)
Cu—O(2)—N(2)	105.2 (2)	O(9)—C(6)—C(7)	120.6 (3)
Cu—O(3)—C(1)	131.1 (2)	C(5)—C(6)—C(7)	126.6 (3)
Cu—O(4)—C(8)	136.5 (2)	C(1)—C(7)—C(6)	121.4 (3)
C(3)—O(9)—C(6)	121.2 (3)	O(4)—C(8)—C(9)	124.1 (3)
C(10)—O(10)—C(13)	120.6 (3)	O(4)—C(8)—C(14)	121.0 (3)
O(1)—N(1)—O(5)	118.6 (3)	C(9)—C(8)—C(14)	114.8 (3)
O(1)—N(1)—O(6)	118.3 (3)	C(8)—C(9)—C(10)	121.4 (3)
O(5)—N(1)—O(6)	123.1 (3)	O(10)—C(10)—C(9)	120.7 (3)
O(2)—N(2)—O(7)	116.3 (3)	O(10)—C(10)—C(11)	112.2 (3)
O(2)—N(2)—O(8)	119.8 (3)	C(9)—C(10)—C(11)	127.1 (3)
O(7)—N(2)—O(8)	123.9 (3)	O(10)—C(13)—C(12)	113.0 (3)
O(3)—C(1)—C(2)	120.8 (3)	O(10)—C(13)—C(14)	121.3 (3)
O(3)—C(1)—C(7)	124.7 (3)	C(12)—C(13)—C(14)	125.7 (3)
C(2)—C(1)—C(7)	114.5 (3)	C(8)—C(14)—C(13)	121.1 (3)

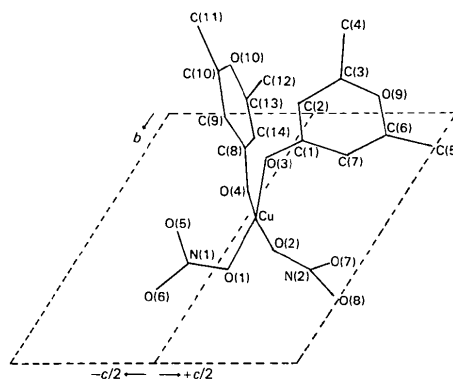


Fig. 1. The molecule in (100) projection, showing numbering of atoms.

The dimensions of the 2,6-dimethyl-4-pyrone molecule agree well with those found in other structures, e.g. 2,6-dimethyl-4-pyrone (Brown, Norment & Levy, 1957), 2,6-dimethyl-4-thiopyrone (Toussaint, 1956), 2,6-dimethyl-4-pyrone hydrobromide monohydrate (Hope, 1965), and in the Zn and Cd compounds (Brown & Lewis, 1984; Banerjee *et al.*, 1984). The N—O lengths of the nitrate group (Table 2), however, differ appreciably from those in the Zn and Cd compounds. Apart from the fact that the nitrate group in the Cd compound is bidentate, which may account for all three N—O distances being short (1.206–1.239 Å), there seems no good reason why the N—O distances in the Cu compound (one long and two short) should differ from those in the Zn compound where two are long (1.277, 1.276 Å) and one is short (1.208 Å).

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