

## Structure of Aquabis(3,5-dimethylpyridine)(1,10-phenanthroline)copper(II) Diperchlorate

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**Abstract.**  $[\text{Cu}(\text{C}_7\text{H}_9\text{N})_2(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})](\text{ClO}_4)_2$ ,  $M_r = 675.0$ , triclinic,  $P\bar{1}$ ,  $a = 9.391(2)$ ,  $b = 12.457(2)$ ,  $c = 13.448(3)$  Å,  $\alpha = 74.81(2)$ ,  $\beta = 87.95(2)$ ,  $\gamma = 79.46(1)^\circ$ ,  $V = 1492.5(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.50$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 9.7$  cm<sup>-1</sup>,  $F(000) = 694$ ,  $T = 293$  K,  $R = 0.040$  for 3783 unique observed reflections. The four N atoms which are planar to within 0.020(3) Å and the O of the water molecule give rise to a square-pyramidal coordination geometry about the Cu atom, which is 0.237(1) Å above the basal plane. The planes of the two 3,5-dimethylpyridine rings form dihedral angles of 83.3 and 110.5° with the N-atom plane.

**Experimental.** The title compound was prepared by the reaction of bis(1,10-phenanthroline)copper(II) perchlorate with 3,5-dimethylpyridine. Crystals obtained from aqueous solution. Purple platelet data crystal 0.24 × 0.44 × 0.54 mm mounted on glass fiber. Intensities measured with an Enraf-Nonius CAD-4 diffractometer using  $\omega$ -2 $\theta$  scans of 4 to 16° min<sup>-1</sup> in  $\theta$ . Unit cell determined from least-squares analysis of angle data for 25 reflections with  $16 < 2\theta < 19^\circ$ . Analytical absorption correction based on crystal shape varied from 0.82 to 1.00. Data collected to  $\sin\theta/\lambda$  of 0.60 Å<sup>-1</sup>,  $-11 \leq h \leq 11$ ,  $-14 \leq k \leq 14$ ,  $0 \leq l \leq 16$ . Four standard reflections (402,  $\bar{3}32$ ,  $\bar{1}34$ , 145) varied less than 0.1% over 48.6 h of data collection. 5472 reflections measured, 5226 unique ( $R_{\text{int}} = 0.01$ ), 1443 reflections with  $I < 3\sigma(I)$  considered unobserved. Solved by Patterson and Fourier methods. Full-matrix least squares minimized  $\sum w(\Delta F)^2$ . All H atoms located on a difference map; for the least squares the H atoms of the water were held at the difference-map positions, other H atoms constrained to idealized (C–H = 0.95 Å) positions, and all H atoms were given isotropic  $B = 1.2 \times B$  of bonded atom. All non-H atoms refined anisotropically for a total of 379 variables,  $R = 0.040$ ,  $wR = 0.055$ ,  $S = 1.36$ , where non-Poisson  $w^{-1} =$

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) for the non-H atoms

	x	y	z	$B_{\text{eq}}$
Cu	0.36396 (4)	0.15898 (3)	0.21435 (3)	3.049 (8)
Cl(1)	0.91014 (9)	0.21126 (7)	0.18280 (6)	3.60 (2)
Cl(2)	0.6187 (2)	0.75915 (9)	0.3206 (1)	6.97 (3)
O(1)	0.8622 (4)	0.1120 (3)	0.2413 (3)	8.2 (1)
O(2)	1.0281 (3)	0.2299 (3)	0.2343 (2)	6.52 (8)
O(3)	0.9565 (4)	0.1963 (3)	0.0864 (2)	8.5 (1)
O(4)	0.7935 (4)	0.3030 (3)	0.1685 (3)	7.7 (1)
O(5)	0.6219 (7)	0.8278 (4)	0.2205 (4)	13.1 (2)
O(6)	0.5193 (7)	0.6907 (4)	0.3293 (4)	15.3 (2)
O(7)	0.5870 (7)	0.8297 (3)	0.3840 (4)	14.2 (2)
O(8)	0.7468 (7)	0.6849 (5)	0.3467 (6)	17.1 (3)
O(9)	0.5912 (3)	0.0645 (2)	0.2167 (2)	4.80 (7)
N(1)	0.3726 (3)	0.2709 (2)	0.0776 (2)	3.53 (6)
N(2)	0.3871 (3)	0.2753 (2)	0.2887 (2)	3.23 (6)
N(3)	0.2915 (3)	0.0478 (2)	0.1506 (2)	3.35 (6)
N(4)	0.2984 (3)	0.0574 (2)	0.3438 (2)	3.06 (6)
C(1)	0.2483 (4)	0.3178 (3)	0.0237 (3)	4.11 (9)
C(2)	0.2436 (4)	0.3920 (3)	-0.0726 (3)	4.55 (9)
C(3)	0.1014 (6)	0.4380 (5)	-0.1297 (4)	7.5 (1)
C(4)	0.3727 (5)	0.4204 (3)	-0.1124 (3)	4.7 (1)
C(5)	0.5016 (4)	0.3754 (3)	-0.0586 (3)	4.10 (8)
C(6)	0.6435 (5)	0.4055 (4)	-0.1012 (4)	6.2 (1)
C(7)	0.4951 (4)	0.2998 (3)	0.0373 (3)	3.61 (8)
C(8)	0.2678 (4)	0.3417 (3)	0.3118 (3)	3.84 (8)
C(9)	0.2733 (4)	0.4227 (3)	0.3645 (3)	4.14 (9)
C(10)	0.1340 (6)	0.4906 (4)	0.3907 (4)	7.3 (1)
C(11)	0.4063 (4)	0.4352 (3)	0.3921 (3)	4.11 (8)
C(12)	0.5315 (4)	0.3683 (3)	0.3704 (3)	3.61 (8)
C(13)	0.6779 (5)	0.3789 (3)	0.4028 (3)	5.06 (9)
C(14)	0.5154 (4)	0.2883 (3)	0.3185 (3)	3.40 (7)
C(15)	0.2947 (5)	0.0423 (3)	0.0529 (3)	4.70 (9)
C(16)	0.2237 (6)	-0.0321 (3)	0.0203 (3)	6.0 (1)
C(17)	0.1486 (5)	-0.1014 (3)	0.0893 (3)	5.9 (1)
C(18)	0.1455 (4)	-0.0997 (3)	0.1933 (3)	4.42 (9)
C(19)	0.0704 (5)	-0.1673 (3)	0.2718 (4)	5.8 (1)
C(20)	0.0723 (5)	-0.1620 (3)	0.3698 (4)	5.4 (1)
C(21)	0.1528 (4)	-0.0885 (3)	0.4003 (3)	4.13 (9)
C(22)	0.1626 (5)	-0.0795 (3)	0.5014 (3)	5.0 (1)
C(23)	0.2244 (4)	-0.0189 (3)	0.3243 (3)	3.14 (7)
C(24)	0.2203 (4)	-0.0231 (3)	0.2194 (3)	3.34 (7)
C(25)	0.2400 (5)	-0.0056 (3)	0.5208 (3)	5.0 (1)
C(26)	0.3073 (4)	0.0624 (3)	0.4415 (3)	3.99 (8)

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as:  $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ .

$[\sigma^2(I) + 0.0036I^2]/4F^2$ . Final  $(\Delta/\sigma)_{\text{max}} < 0.01$ ,  $\Delta\rho_{\text{max}} = 0.52(3)$  and  $\Delta\rho_{\text{min}} = -0.39(3)$  e Å<sup>-3</sup> on final difference map. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for*

Table 2. Selected bond distances (Å) and bond angles (°)

Cu–N(1)	2.005 (2)	Cu–N(4)	2.016 (2)
Cu–N(2)	2.010 (2)	Cu–O(9)	2.238 (2)
Cu–N(3)	2.031 (2)		
N(1)–Cu–N(2)	91.0 (1)	N(2)–Cu–N(3)	166.4 (1)
N(1)–Cu–N(3)	92.9 (1)	N(1)–Cu–O(9)	97.2 (1)
N(2)–Cu–N(4)	91.7 (1)	N(2)–Cu–O(9)	101.7 (1)
N(3)–Cu–N(4)	81.3 (1)	N(3)–Cu–O(9)	90.7 (1)
N(1)–Cu–N(4)	164.8 (1)	N(4)–Cu–O(9)	97.0 (1)

*X-ray Crystallography* (1974) and programs used were those of Enraf–Nonius (1982) *SDP*.<sup>\*</sup> Table 1 gives the atom coordinates and Table 2 selected bond distances and angles. Fig. 1 shows the complex cation with the numbering scheme.

**Related literature.** Square-pyramidal geometry for five coordinate Cu<sup>II</sup> is well established (O'Brien, 1984; Hathaway, 1982, 1983). Structures of similar phenanthroline complexes with an apical water molecule have been determined, but these have mixed atom coordination in the basal plane. These include complexes with the following ligands: malonate (Kwik, Ang, Chan, Chebolu & Koch, 1986), oxalate (Fabretti, Franchini, Zannini & Divaira, 1985), phthalate (Krstanović, Karanović & Stojaković, 1985), and acetylacetonate (Bailey, Fenton, Franklin & Hall, 1980).

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<sup>\*</sup> Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44033 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

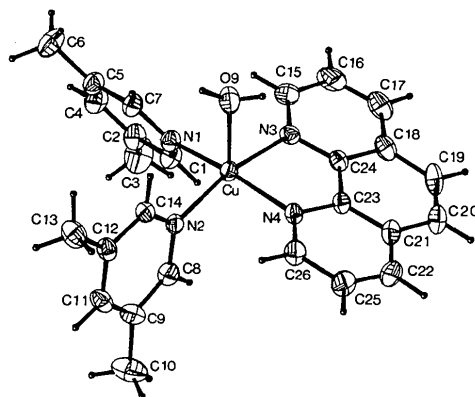


Fig. 1. ORTEP diagram (Johnson, 1976) and atom-numbering scheme. Non-H ellipsoids at 30% probability level, H atoms given arbitrary radii.

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## Structure of Dicarboxyl( $\eta^5$ -cyclopentadienyl)(*O,O'*-diethyl dithiophosphato)iron(II)

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**Abstract.** [Fe(C<sub>5</sub>H<sub>5</sub>)(C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>PS<sub>2</sub>)(CO)<sub>2</sub>], *M<sub>r</sub>* = 362.18, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 7.440 (1), *b* = 14.545 (1), *c* = 14.454 (1) Å,  $\beta$  = 94.415 (3)°, *V* = 1559.5 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.543 Mg m<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.7107 Å,  $\mu$  = 1.329 mm<sup>-1</sup>, *F*(000) = 744, room temperature, final *R* = 0.042 (*wR* = 0.041) for 2517

[*I* > 3 $\sigma$ (*I*)] observed reflections. The compound belongs to a series of cyclopentadienyl–Fe<sup>II</sup> derivatives which contains a very uncommon monodentate dithiophosphate ester ligand, linked to Fe through an S atom. The cyclopentadienyl ligand is situated on one side of the Fe atom with the carbonyl and dithiophosphate ligands on