

Structure of *catena*-(Acetato)(di-2-pyridylamine)- μ -nitrate-copper(II)

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Abstract. $[\text{Cu}(\text{NO}_3)(\text{C}_2\text{H}_3\text{O}_2)(\text{C}_{10}\text{H}_9\text{N}_3)]$, $M_r = 355.79$, monoclinic, $P2_1/n$, $Z = 4$, $a = 12.859$ (3), $b = 9.674$ (2), $c = 12.247$ (3) Å, $\beta = 113.52$ (2)°, $V = 1396.93$ Å³, D_m (floatation) = 1.720 (6), $D_x = 1.692$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 15.36$ cm⁻¹, $T = 298$ K, $F(000) = 724$, 1822 unique observed reflections. $R = 0.037$. The local molecular $\text{CuN}_2\text{O}_2\text{O}'_2$ chromophore involves an elongated rhombic octahedral structure, with nearly symmetrically bonded di-2-pyridylamine (dpyam) and bidentate acetate groups bonding in the plane and bridging 'semi-coordinate' nitrate groups completing the six coordination.

Introduction. Copper metal reduction (Hathaway & Underhill, 1960) of $[\text{Cu}(\text{dpyam})_2(\text{CH}_3\text{CO}_2)][\text{NO}_3]$ in acetonitrile solution, on reoxygenation in air, yielded dark bluish-green crystals of the title complex (I). As the mode of bonding of the anions in (I) is ambiguous, (I) was reprepared from its components and the structure determined.

Experimental. (I) was prepared by adding a boiling solution containing 0.48 g (2.0 mmol) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 40 ml of water, to 0.35 g dpyam (2.0 mmol) in 60 ml of ethanol and 0.33 g (4.0 mmol) of $\text{CH}_3\text{O}_2\text{Na}$. The mixed solutions were heated to boiling, filtered, allowed to stand, and yielded bluish-green crystals of (I). Found: C, 40.66; H, 3.39; Cu, 18.11; N, 16.02%; calculated for $\text{C}_{12}\text{H}_{12}\text{CuN}_4\text{O}_5$: C, 40.50; H, 3.38; Cu, 17.87; N, 15.75%.

The unit-cell data (25 reflections, θ 3–25°) and intensities were collected on a Philips PW 1100 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Reflections with $3.0 < \theta < 25^\circ$ in one quadrant were examined, in the ω - 2θ scan mode, with a constant scan speed of $0.05^\circ \text{ s}^{-1}$, and a variable scan width of $(0.7 + 0.1 \tan \theta)^\circ$. 1882 observed reflections were collected [$I > 2.5\sigma(I)$]; h , -14–14, k , 0–11, l , 0–14] of which 1822 were unique. Lorentz and polarization corrections were applied, but no correction was made for absorption. The structure was solved by the *SHELX76* direct methods (Sheldrick, 1976) and difference Fourier techniques and

refined by full-matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$ with anisotropic temperature factors on all the non-H atoms. The positions of the H atoms were calculated geometrically and 'floated' on the adjacent C or N atoms, assuming C—H and N—H distances of 1.08 Å, and a fixed temperature factor of 0.07 \AA^2 . Maximum shift/e.s.d. was < 0.001 , with a refined weighting scheme, $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$ with $k = 1.0000$ and $g = 0.001711$. $R = 0.037$ and $wR = 0.043$, 200 parameters, 9.1 observations/parameter. The maximum and minimum residual electron densities were 0.40 and -0.38 e \AA^{-3} , respectively. Complex neutral-atom scattering factors were employed and those for Cu atoms were taken from Cromer & Waber (1974). All calculations were carried out with *SHELX76* (Sheldrick, 1976) and *XANADU* (Roberts & Sheldrick, 1979), *CHEM-X* (Davies, 1980) and *PUBTAB* (Henrick, 1980) on the UCC mainframe IBM 4341 and VAX 11/780 computers. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.† Selected bond lengths and angles are given in Table 2. Fig. 1 shows the molecular structure of (I), and the atom-numbering scheme used.

Discussion. The asymmetric unit of (I) consists of the $[\text{Cu}(\text{dpyam})(\text{CH}_3\text{CO}_2)(\text{NO}_3)]$ complex. It involves a six coordinate $\text{CuN}_2\text{O}_2\text{O}'_2$ chromophore, with a basic elongated rhombic octahedral stereochemistry (Fig. 1). The octahedra are linked into infinite chains in the elongation direction, parallel to the a axis, by bridging bidentate nitrate groups (Addison, Logan, Wallwork & Garner, 1971). The dpyam ligand bonds almost symmetrically in the plane with Cu—N distances of 1.954 (3) and 1.960 (3), mean 1.957 (4) Å, and with a bite angle of 94.5 (1)°. The acetate group also bonds in the plane, nearly symmetrically, with Cu—O distances of 2.007 (2) and 2.024 (3), mean 2.015 (3) Å, and with a bite angle at the Cu atom of

† Lists of structure factors, anisotropic thermal parameters, full bond lengths and bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53361 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional atomic coordinates and thermal parameters (\AA^2) with *e.s.d.*'s in parentheses
$$U_{eq} = (1/3)\sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}(\text{\AA}^2)$
Cu	0.48468 (4)	0.23760 (4)	0.75450 (4)	0.0402 (2)
N(1)	0.4601 (2)	0.0383 (3)	0.7341 (2)	0.045 (1)
C(1)	0.4977 (3)	-0.0260 (3)	0.6588 (3)	0.058 (1)
C(2)	0.4938 (3)	-0.1659 (3)	0.6423 (3)	0.066 (1)
C(3)	0.4502 (3)	-0.2466 (3)	0.7075 (3)	0.062 (1)
C(4)	0.4109 (3)	-0.1847 (3)	0.7828 (3)	0.056 (1)
C(5)	0.4170 (2)	-0.0402 (3)	0.7959 (3)	0.047 (1)
N(3)	0.3762 (2)	0.0167 (3)	0.8740 (2)	0.067 (1)
C(6)	0.3670 (2)	0.1514 (3)	0.9051 (3)	0.047 (1)
C(7)	0.3168 (3)	0.1730 (4)	0.9859 (3)	0.067 (1)
C(8)	0.3055 (3)	0.3043 (4)	1.0205 (3)	0.070 (1)
C(9)	0.3414 (3)	0.4138 (4)	0.9724 (3)	0.068 (1)
C(10)	0.3898 (3)	0.3871 (3)	0.8936 (3)	0.060 (1)
N(2)	0.4036 (2)	0.2574 (2)	0.8593 (2)	0.047 (1)
O(1)	0.5435 (2)	0.4310 (2)	0.7616 (2)	0.062 (1)
O(2)	0.5873 (2)	0.2663 (2)	0.6670 (2)	0.069 (1)
C(11)	0.5979 (3)	0.3907 (3)	0.7010 (3)	0.061 (1)
C(12)	0.6722 (3)	0.4881 (4)	0.6711 (4)	0.101 (1)
O(3)	0.3121 (3)	0.3323 (3)	0.5988 (2)	0.092 (1)
N(4)	0.2543 (2)	0.2765 (3)	0.5024 (2)	0.050 (1)
O(4)	0.2933 (2)	0.1901 (3)	0.4575 (2)	0.079 (1)
O(5)	0.1552 (2)	0.3201 (3)	0.4531 (2)	0.079 (1)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

Cu—N(1)	1.954 (3)	O(3)—N(4)	1.240 (3)
Cu—N(2)	1.960 (3)	O(4)—N(4)	1.213 (3)
Cu—O(2)	2.024 (3)	O(5)—N(4)	1.246 (3)
Cu—O(1)	2.007 (2)	O(2)—C(11)	1.263 (4)
Cu—O(3)	2.454 (3)	O(1)—C(11)	1.268 (4)
Cu—O(5)	2.603 (3)		
N(1)—Cu—N(2)	94.5 (1)	O(1)—C(11)—O(2)	118.3 (3)
O(2)—Cu—N(1)	100.0 (1)	O(3)—Cu—O(5')	165.7 (1)
O(2)—Cu—N(2)	164.4 (1)	N(1)—Cu—O(5')	83.1 (1)
O(1)—Cu—N(2)	99.8 (1)	N(2)—Cu—O(5')	86.6 (1)
O(1)—Cu—N(1)	164.7 (1)	O(1)—Cu—O(5')	92.3 (1)
O(1)—Cu—O(2)	65.2 (1)	O(2)—Cu—O(5')	89.8 (1)
O(3)—Cu—N(1)	102.7 (1)	C(6)—N(3)—C(5)	132.1 (3)
O(3)—Cu—N(2)	85.4 (1)	O(4)—N(4)—O(3)	122.1 (3)
O(3)—Cu—O(2)	96.7 (1)	O(5)—N(4)—O(3)	115.0 (3)
O(3)—Cu—O(1)	83.9 (1)	O(5)—N(4)—O(4)	122.8 (3)

O(5') is related to O(5) by the operation $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

65.2 (1) $^\circ$, significantly less than the bite angle of the dpyam ligand. The two O atoms from the asymmetrically bridging nitrate groups occupy the tetragonal positions above and below the CuN_2O_2 plane, at Cu—O distances of 2.454 (3) and 2.603 (4), mean 2.528 (4) \AA , distances that are consistent with 'semi coordination' of the bridging nitrate groups (Procter, Hathaway & Nicholls, 1968). This yields a tetragonality, T (= mean in-plane distance/mean out-of-plane distance), of 0.785. The O(3)—Cu—O(5) angle is nearly linear, 165.7 (1) $^\circ$, and lies approximately parallel to the *a* axis. The atoms O(1), O(2), N(1) and N(2) are essentially planar, r.m.s. deviation 0.002 \AA , and the Cu atom lies 0.083 \AA above this plane towards O(3). There are no unusual bond lengths or

bond angles in the dpyam ligand (Ray & Hathaway, 1978), the separate pyridine rings are planar, and inclined to each other at an angle of 2.0 $^\circ$. The C—O distances of the acetate group are not significantly different. The two-coordinate (Hathaway, 1988) bridging nitrate groups have a mean N—O distance of 1.233 \AA , and mean O—N—O angle of 120.0 (5) $^\circ$ (Addison *et al.*, 1971). The N—O distances of the two coordinating O atoms, 1.240 (3) and 1.246 (3) \AA , are significantly longer than the non-coordinating O atom, 1.213 (4) \AA , due to the greater N(4)—O(3) double-bond character. The O(1)—N(4)—O(2) angle of 115.0 (5) $^\circ$, opposite to the shorter N—O distance, is significantly then less than 120 $^\circ$.

The elongated rhombic octahedral $\text{CuN}_2\text{O}_2\text{O}'_2$ chromophore of (I) has been previously observed in $[\text{Cu}(\text{dpyam})(\text{CH}_3\text{CO}_2)(\text{ClO}_4)] \cdot \text{H}_2\text{O}$, (II), (Ray, Tyagi & Hathaway, 1982), which also involves a symmetrically bonded in-plane dpyam and acetate ligand, but differs in the presence of a long bonded bridging perchlorate group rather than the bridging nitrate group of (I). The symmetrical coordination of the acetate group to the Cu atom in (I) and (II) (Oldham, 1968), is unusual, as this anion is normally involved in very asymmetric bonding (Hathaway, 1973, 1988), with Cu—O distances of approximately 2.00 and 2.5–2.9 \AA , respectively. Attempts to determine the infrared spectrum of the acetate group were unsuccessful, due to overlap with the bands of the dpyam ligand in the region of 1500 cm^{-1} , but bands at 1390 and 825 cm^{-1} are associated with the

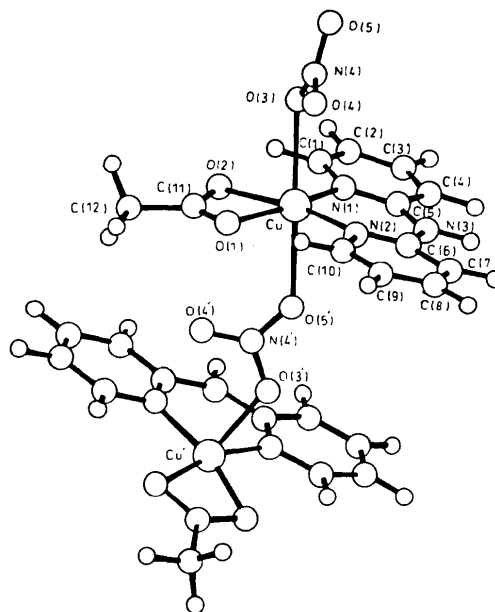


Fig. 1. The molecular structure of $[\text{Cu}(\text{dpyam})(\text{O}_2\text{CCH}_3)(\text{O}_2\text{NO})]$, viewed approximately down the *c* axis, and the atom-numbering scheme used.

bidentate bridging role of the nitrate group (Nakamoto, 1978). The electronic reflectance spectrum of (I) has a broad peak centred at 15 000 cm⁻¹, with a weakly resolved shoulder at 10 200 cm⁻¹, consistent with its stereochemistry, and comparable with the electronic spectra of (II), which has a main band at 15 800 cm⁻¹ and a weakly resolved shoulder at 10 000 cm⁻¹ (Ray, Tyagi & Hathaway, 1982). The lower energy of the main band in (I) is then consistent with the slightly higher tetragonality of (I) than of (II), 0.785 and 0.765, respectively. The polycrystalline ESR spectrum of (I) is axial, $g_1 = 2.073$ and $g_{11} = 2.299$ and consistent with the elongated rhombic octahedral chromophore present, but due to some misalignment of the local molecular axes ($2\gamma = 80^\circ$), these g values do not equate with the local molecular g values (Hathaway & Billing, 1970).

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Structure of Bis[cyanatobis(di-2-pyridylamine)copper(II)] Sulfate Bis(di-2-pyridylamine) Monohydrate

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Abstract. [Cu(NCO)(C₁₀H₉N₃)₂](SO₄)_{0.5}·C₁₀H₉N₃·0.5H₂O, $M_r = 676.20$, monoclinic, $I2/c$ [equivalent positions: $\pm(x, y, z)$; $\pm(-x, y, \frac{1}{2}-z)$], $Z = 8$, $a = 17.688$ (3), $b = 20.596$ (4), $c = 17.519$ (2) Å, $\beta = 96.886$ (2)°, $V = 6336.17$ Å³, $D_m(\text{floatation}) = 1.42$ (6), $D_x = 1.417$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.733$ mm⁻¹, $T = 298$ K, $F(000) = 2792$, 1893 unique observed reflections, $R = 0.077$. The CuN₄N' chromophore involves a square pyramidal structure, distorted towards a trigonal bipyramidal stereochemistry, $\tau = 0.31$. The NCO⁻ anion is bonded to

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the copper(II) ion *via* the N atom. The two non-coordinated dpyam (dpyam = 2,2'-dipyridylamine) molecules are disordered about a centre and a two-fold axis of symmetry, respectively, and both are poorly defined. The [SO₄]²⁻ anion is also disordered about a centre of symmetry, SOF = 0.5, and the non-coordinated water molecule is also disordered, SOF = 0.5.

Introduction. The structure determination of the [Cu(dpyam)₂(NCO)]⁺ cation has been undertaken to establish (a) the mode of bonding of the NCO⁻ anion to the copper(II) cation, (b) the stereo-

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