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catena-Acetato(di-2-pyridylamine)- μ -perchlorato-copper(II) Monohydrate

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Abstract. [Cu(C₁₀H₉N₃)(C₂H₃O₂)(ClO₄)]·H₂O, C₁₂H₁₄ClCuN₃O₇, $M_r = 411.3$, monoclinic, $P2_1/c$, $Z = 4$, $a = 7.309$ (3), $b = 16.363$ (4), $c = 13.646$ (4) Å, $\beta = 103.085$ (3)°, $U = 1589.65$ Å³, $D_m = 1.75$ (2), $D_c = 1.72$ Mg m⁻³. $R = 0.0517$ for 2518 observed reflections. The local molecular CuN₂O₂O'₂ chromophore involves an elongated rhombic octahedral structure with near symmetrically bonded di-2-pyridylamine (dpyam) and acetate groups bonding in the plane and bridging semi-coordinate perchlorate groups completing the six coordination.

Introduction. In a programme to examine the bonding role of the acetate ligand (Hathaway, Ray, Kennedy, O'Brien & Murphy, 1980) in ternary complexes of the Cu^{II} ion with bis-nitrogen chelate ligands, dark-green crystals of the title complex (1) were obtained. As the

IR spectrum (Hathaway & Underhill, 1961) suggested that the perchlorate group was bonded to Cu^{II}, but failed to establish the bonding of the acetate and water molecules, the structure of (1) was determined. (1) was prepared by mixing 0.01 mol of [Cu(CH₃CO₂)₂]·H₂O and 0.01 mol of [Cu(H₂O)₆](ClO₄)₂, both in 60 ml of (1:2) aqueous ethanol, and adding 0.022 mol of dpyam in 60 ml of (1:2) aqueous ethanol. The solution was boiled, filtered, and allowed to stand and the dark-green crystals were deposited overnight.

Found: C, 35.00; H, 3.70; Cl, 8.63; Cu, 14.41; N, 9.91%; calculated for C₁₂H₁₄ClCuN₃O₇: C, 35.04; H, 3.41; Cl, 8.63; Cu, 15.46; N, 10.22%. Intensities were collected on a Philips PW 1100 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Reflections with $3.0 < \theta < 32^\circ$ in one quadrant were examined in the θ - 2θ scan mode with constant scan speed of $0.05^\circ \text{ s}^{-1}$, and a variable scan width of $(0.7 + 0.1 \tan \theta)^\circ$. 2518 unique reflections were retained [$I >$

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2.5 $\sigma(I)$). Lorentz and polarization corrections were applied, but no correction was made for absorption [$\mu(\text{Mo } K\alpha) = 15.27 \text{ cm}^{-1}$]. The structure was solved by Patterson and Fourier techniques and refined by blocked-matrix least-squares analysis with anisotropic temperature factors for all non-H atoms.

As the temperature factors of the O atoms of the ClO₄⁻ group at this stage were high and the maximum residual electron density was associated with four peaks around the ClO₄⁻ group at reasonable Cl—O bond distances of 1.4–1.5 Å, a disordered ClO₄⁻ group was introduced. With isotropic temperature factors of the Cl and O atoms fixed at 0.1 Å², the site-occupation factors (s.o.f.) of the major and minor components of the ClO₄⁻ were refined (with the constraint that they add up to one), and yielded values of 0.929 and 0.071 respectively. The s.o.f.'s were then fixed, the temperature factors of the major ClO₄⁻ made anisotropic and refinement continued with the minor component, treated as a rigid body with tetrahedral angles and Cl—O bond distances constrained to ca 1.42 Å. The

Table 1. Fractional atomic coordinates ($\times 10^5$ for Cu; $\times 10^4$ for the other non-H atoms) and equivalent isotropic temperature factors ($\times 10^4$ for Cu; $\times 10^3$ for the other non-H atoms)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} [*] (Å ²)
Cu	29038 (8)	11259 (3)	25330 (4)	377 (4)
N(1)	3622 (5)	2197 (2)	3101 (2)	38 (2)
N(2)	2020 (5)	1522 (2)	1157 (2)	38 (2)
N(3)	2333 (5)	2930 (2)	1617 (3)	44 (2)
O(1)	2472 (5)	-68 (2)	2304 (2)	50 (2)
O(2)	3203 (5)	434 (2)	3807 (2)	46 (2)
C(1)	4653 (7)	2207 (3)	4073 (3)	48 (3)
C(2)	5380 (7)	2912 (3)	4555 (4)	54 (3)
C(3)	5054 (7)	3627 (3)	4025 (4)	45 (3)
C(4)	4036 (8)	3637 (3)	3051 (4)	54 (3)
C(5)	3345 (6)	2902 (2)	2595 (3)	38 (2)
C(6)	1688 (6)	2318 (3)	924 (3)	36 (2)
C(7)	734 (7)	2560 (3)	-40 (3)	47 (3)
C(8)	130 (7)	1981 (3)	-764 (4)	49 (3)
C(9)	566 (8)	1164 (3)	-531 (4)	57 (3)
C(10)	1454 (7)	959 (3)	423 (3)	48 (3)
C(11)	2747 (6)	-175 (3)	3238 (4)	43 (3)
C(12)	2524 (10)	-1005 (3)	3672 (5)	68 (5)
Cl	7700 (2)	1158 (1)	2304 (1)	46 (1)
O(3)†	6387 (7)	817 (3)	2785 (5)	101 (6)
O(4)†	7706 (9)	738 (4)	1382 (4)	112 (5)
O(5)†	9511 (7)	1135 (4)	2898 (5)	106 (6)
O(6)†	7169 (8)	1997 (3)	2078 (4)	82 (6)
O(7)	2134 (8)	4482 (2)	686 (3)	86 (4)
O(3')‡	7895	1166	3361	34 (8)
O(4')‡	5855	905	1832	24 (7)
O(5')‡	9023	608	2054	37 (9)
O(6')‡	8030	1955	1972	41 (13)

$$* U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

† Occupancy = 0.929.

‡ Occupancy = 0.071.

Table 2. Selected bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses

Symmetry code: (ii) -1 + x, y, z.

Cu—N(1)	1.940 (3)	Cu—O(5 ⁱⁱ)	2.638 (4)
Cu—N(2)	1.953 (3)	Cl—O(3)	1.396 (7)
Cu—O(1)	1.992 (3)	Cl—O(4)	1.434 (6)
Cu—O(2)	2.045 (3)	Cl—O(5)	1.387 (5)
Cu—O(3)	2.541 (4)	Cl—O(6)	1.441 (5)
N(1)—Cu—N(2)	94.9 (1)	N(1)—Cu—O(5 ⁱⁱ)	95.8 (1)
O(1)—Cu—O(2)	64.7 (1)	N(2)—Cu—O(5 ⁱⁱ)	93.4 (1)
N(1)—Cu—O(1)	165.3 (1)	O(1)—Cu—O(5 ⁱⁱ)	85.0 (1)
N(1)—Cu—O(2)	101.2 (1)	O(2)—Cu—O(5 ⁱⁱ)	76.5 (1)
N(2)—Cu—O(1)	99.7 (1)	O(3)—Cl—O(4)	111.1 (4)
N(2)—Cu—O(2)	161.8 (1)	O(3)—Cl—O(5)	112.4 (4)
N(1)—Cu—O(3)	87.3 (1)	O(3)—Cl—O(6)	107.5 (4)
O(1)—Cu—O(3)	86.8 (1)	O(4)—Cl—O(5)	107.9 (4)
O(2)—Cu—O(3)	82.2 (1)	O(4)—Cl—O(6)	108.8 (3)
N(2)—Cu—O(3)	107.4 (1)	O(5)—Cl—O(6)	109.0 (3)

Table 3. Least-squares planes of the form $lX + mY + nZ = p$, where *X*, *Y* and *Z* refer to orthogonal axes, with deviations (Å) of relevant atoms in square brackets

E.s.d.'s for the atomic deviations are in the range 0.001–0.003 Å.

	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>
Plane (1): N(1), N(2), O(1), O(2) (r.m.s.d. = 0.101)	0.940 (1)	-0.140 (2)	-0.312 (2)	0.700 (2)
[N(1) 0.085, N(2) -0.087, O(1) 0.116, O(2) -0.113, Cu 0.056]				
Plane (2): N(1), C(1)–C(5) (r.m.s.d. = 0.005)	0.841 (1)	-0.134 (2)	-0.524 (2)	-0.207 (1)
[N(1) -0.008, C(1) 0.003, C(2) 0.002, C(3) 0.000, C(4) -0.005, C(5) 0.009]				
Plane (3): N(2), C(6)–C(10) (r.m.s.d. = 0.015)	0.874 (1)	0.081 (2)	-0.479 (2)	0.876 (2)
[N(2) -0.013, C(6) 0.013, C(7) 0.005, C(8) -0.023, C(9) 0.023, C(10) -0.005]				
Plane (4): O(1), O(2), C(11), C(12) (r.m.s.d. = 0.002)	0.965 (1)	-0.193 (2)	-0.178 (2)	1.233 (10)
[O(1) -0.001, O(2) -0.001, C(11) 0.003, C(12) -0.001]				

Angle between normals to planes (2) and (3) is 12.8 (1)°.

positions of the H atoms were calculated geometrically and 'floated' on the adjacent atoms assuming C—H 1.08 Å, and a fixed temperature factor of 0.07 Å². The data converged when the maximum shift/e.s.d. was <0.03 with a refined weighting scheme, $w = k[\sigma^2(F_o) + g(F_o)^2]$ with $k = 0.848$ and $g = 0.00433$, $R = 0.0517$ and $R_w = 0.0603$. The maximum residual electron density was 0.77 e Å⁻³. Complex atomic scattering factors were employed and those for Cu and Cl were corrected for anomalous dispersion (Cromer & Waber, 1965; Cromer & Liberman, 1970). All calculations

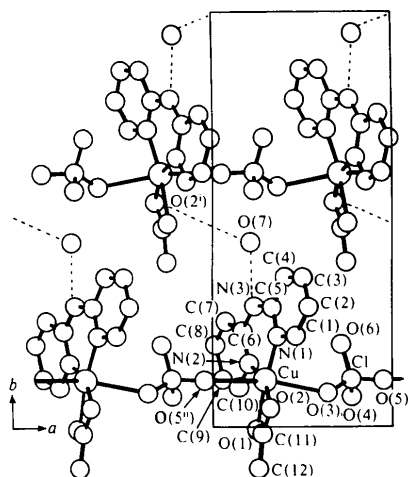


Fig. 1. The molecular structure of [Cu(dpyam)(CH₃CO₂)(ClO₄)]·H₂O viewed down *c* showing the atom-numbering scheme used. Symmetry code: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 + x, y, z$.

were carried out with *SHELX 76* and *XANADU* (G. M. Sheldrick) and *PLUTO* (S. Motherwell) on an IBM 370/138 computer. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.* Selected bond lengths and angles are in Table 2 and some mean plane data in Table 3. Fig. 1 shows the molecular structure of (1), the atom-numbering scheme, and the packing arrangement viewed down *c*.

Discussion. The local molecular structure of the Cu atom involves an elongated rhombic octahedral CuN₂O₂O'₂ chromophore. The dpyam ligand bonds in the plane almost symmetrically with Cu—N distances of 1.940 (3) and 1.953 (3) Å, mean 1.947 Å, a difference that is only just significant, with a bite angle of 94.9 (1)°. The acetate group also bonds in the plane with Cu—O 1.992 (3) and 2.045 (3) Å, mean 2.019 Å, a difference that is considered significant. Due to the near symmetrical coordination of the acetate group to the Cu atom to give a four-membered ring, the bite angle at Cu is significantly less than 90°, at 64.7 (1)°. The axial positions are occupied by O atoms from the unsymmetrically bridging perchlorate groups, major ClO₄⁻, Cu—O(3) 2.541 (4) Å and Cu—O(5ⁱⁱ) 2.638 (4) Å, mean 2.590 Å; minor ClO₄⁻, Cu—O(4') 2.576 Å and Cu—O(5'ⁱⁱ) 2.890 Å, mean 2.733 Å, distances that are consistent with semi-coordination of

* Lists of structure factors, anisotropic thermal parameters, calculated H-atom coordinates and full bond-length and bond-angle data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36655 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the bridging perchlorate groups (Procter, Hathaway & Nicholls, 1968), and yield a tetragonal *T* (=mean in-plane distance/mean out-of-plane distance) of 0.765. The four in-plane ligands, N(1), N(2), O(1) and O(2) are reasonably planar, r.m.s. deviation 0.1 Å (Table 3) with a slight tetrahedral twist. The Cu atom lies above this plane, 0.056 Å towards O(3) and the tetrahedral twist results in non-linear angles at Cu: N(1)—Cu—O(1) 165.3° and N(2)—Cu—O(2) 161.8°. There are no unusual bond lengths or angles in the dpyam ligand (Ray & Hathaway, 1978). The separate pyridine rings are planar (Table 3) and inclined to each other at an angle of 12.8°. The acetate group is planar, and consistent with the near symmetrical bidentate coordination to the Cu atom, the C(11)—O(1) and C(11)—O(2) distances of 1.257 (6) and 1.261 (5) Å not being significantly different. The symmetrical coordination of the acetate group (Oldham, 1968) is unique in the coordinating role of this ligand to Cu, which usually involves very asymmetric bonding (Hathaway *et al.*, 1980), with Cu—O distances of 2.00 and 2.5–2.9 Å, respectively, a difference in coordination of the acetate O atoms that is *not* reflected in a difference in the C—O bond distances. In addition the mean C(11)—O distance in (1) of 1.259 Å is *not* very different from the mean C—O distance of 1.25 ± 0.02 Å in the unsymmetrically bonded acetate groups of [Cu(bpy)₂(CH₃CO₂)(ClO₄)·2H₂O and [Cu(bpy)₂(CH₃CO₂)](BF₄) (bpy = 2,2'-bipyridyl), (Hathaway *et al.*, 1980), notwithstanding the different bonding role of the acetate in these three complexes. Attempts to determine the IR spectra of the acetate group in these complexes were prevented by the presence of overlapping nitrogen chelate ligand bands. The bridging role of the perchlorate group is reflected in the IR spectra of the group (Table 4): the strong ν_3 and ν_4 bands of the ionic perchlorate group are clearly split into three bands and the forbidden ν_1 band of the free ion appears with medium intensity (Hathaway & Underhill, 1961). These results are consistent with a bidentate bonding role of the ClO₄⁻ with approximate C_{2v} symmetry. The main ClO₄⁻ is reasonably tetrahedral, mean O—Cl—O angle 109.5° and mean Cl—O distance 1.42 Å, but in view of the disorder present, no attempt was made to interpret the structure in the approximate C_{2v} symmetry of a bridging ClO₄⁻ ion. The bridging role of the ClO₄⁻ group is unusual, but not unique, in Cu^{II} chemistry; it occurs in [Cu(bpy)₂(O₂ClO₂)](ClO₄) (Nakai, 1971), but with less symmetrical Cu—O distances of 2.45 and 2.73 Å.

The elongation axes of the rhombic octahedral CuN₂O₂O'₂ chromophore are aligned approximately parallel to *a* (Fig. 1) and are connected by the bridging ClO₄⁻ groups in this direction. The chains of [Cu(dpyam)(CH₃CO₂)(ClO₄)] are linked by the uncoordinated water molecule into an infinite three-dimensional structure *via* some short non-bonded

Table 4. IR spectrum of the ClO₄ group (cm⁻¹)

	$\nu_1 A$	ν_2	ν_3	ν_4
(1)	930 m		1070 1110 s 1145	625 630 s 637
Ionic	935 w	460 s	1050–1170 s	630 s

distances O(7)···N(3) 2·828 (5) and O(7)···O(2ⁱ) 2·847 (5) Å.

The electronic reflectance spectrum of (1) involves a broad peak at 15 820 cm⁻¹ with a weakly resolved shoulder at ca 10 000 cm⁻¹ (Procter, Hathaway & Hodgson, 1972), and the polycrystalline ESR spectrum is axial, $g_1 = 2·074$ and $g_{11} = 2·284$. The single-crystal ESR spectrum of (1) yields three g factors 2·053, 2·065 and 2·274, but as the CuN₂O₂ plane is slightly misaligned by the monoclinic twofold axis, these crystal g factors cannot be unambiguously resolved into their local molecular g factors. Nevertheless, the electronic properties of (1) are consistent with the elongated rhombic octahedral CuN₂O₂O'₂ chromophore of (1) as reported above (Hathaway & Billing, 1970).

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Structure of Acetato(*N*-methyl-*N'*-salicylidene-1,3-propanediaminato)copper(II) Dimer

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Abstract. [Cu(C₁₁H₁₅N₂O)(C₂H₃O₂)₂]₂, (C₁₃H₁₈CuN₂O₃)₂, $M_r = 627·68$, triclinic, $P1$, $a = 8·247$ (3), $b = 9·173$ (2), $c = 10·239$ (3) Å, $\alpha = 108·88$ (2), $\beta = 111·20$ (3), $\gamma = 76·49$ (3)°, $V = 677·3$ (4) Å³, $Z = 1$, $D_m = 1·53$ (floatation), $D_x = 1·539$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 1·68$ mm⁻¹. The structure was solved by direct methods and refined by the block-diagonal least-squares technique to $R = 0·043$ for 2246 reflections with $I > 2\sigma(I)$. The tridentate Schiff base derived from salicylaldehyde and *N*-methyl-1,3-propanediamine form together with the acetate O atom the coordination plane around Cu. The axial positions are occupied by the more distant carboxyl O atoms (2·51 and 2·83 Å).

The acetate ion acts under these conditions as an unsymmetrically chelating and monoatomic bridging group.

Introduction. Several Schiff-base Cu^{II} complexes derived from L amino acids and salicylaldehyde have been analysed by X-ray methods (Ueki, Ashida, Sasada & Kakudo, 1967, 1969; Fujimaki, Oonishi, Muto, Nakahara & Konijama, 1971; Hämäläinen, Ahlgrén, Turpeinen & Rantala, 1978; Hämäläinen, Turpeinen, Ahlgrén & Rantala, 1978; Korhonen & Hämäläinen, 1979, 1981). The coordination sphere of the Cu^{II} ion in these compounds has almost invariably