

Structure of (1,10-Phenanthroline)salicylaldehydato-copper(II) Perchlorate

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Abstract. $[\text{Cu}(\text{C}_7\text{H}_5\text{O}_2)(\text{C}_{12}\text{H}_8\text{N}_2)]\text{ClO}_4$, $M_r = 464.32$, triclinic, $P\bar{1}$, $a = 9.139$ (4), $b = 9.290$ (3), $c = 11.679$ (5) Å, $\alpha = 96.27$ (2), $\beta = 111.07$ (2), $\gamma = 97.00$ (2)°, $V = 906$ (1) Å³, $Z = 2$, $D_x = 1.702$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 1.396$ mm⁻¹, $F(000) = 470$, $T = 291$ K, final $R = 0.037$ for 2204 unique observed reflections. The structure consists of a dimeric unit involving a planar Cu_2O_2 group. The coordination sphere of the Cu can be described as an elongated octahedron where the basal plane is formed by the two N atoms of the 1,10-phenanthroline molecule and the two O atoms of the salicylaldehyde anion. The phenoxo O atom is the negative ligand of the monomeric unit. Two apical Cu—O distances complete the 4 + 2 coordination of the Cu atom. They correspond to one of the O atoms of the perchlorate anion and to the O atom of the nearest salicylaldehyde molecule.

Introduction. In previous work the crystal and molecular structures of salicylaldehydato(di-2-pyridylamine)copper(II) and salicylaldehydato(di-2-pyridyl)copper(II) complexes were determined (Garland, Le Marouille & Spodine, 1985, 1986). The complexes were shown to be dimeric species. To continue with the study of ternary copper(II) complexes in the solid state, the title compound was synthesized and characterized. This complex has a more rigid diamine molecule than the di-2-pyridylamine (dpa) and di-2-pyridyl (dp) ligands. The π acceptor ability of the 1,10-phenanthroline molecule is similar to that of di-2-pyridyl (Addison, Carpentier, Lau & Wicholas, 1978). These data will be used to correlate the structural properties of these dimeric copper(II) complexes with magnetic susceptibility measurements still to be determined.

Experimental. The mixed-ligand Cu^{II} complex $[\text{Cu}(\text{phen})(\text{sal})]\text{ClO}_4$ was prepared like the $[\text{Cu}(\text{dpa})(\text{sal})]$ complex (Garland, Le Marouille & Spodine, 1985). However, the hydrolysis reaction produces a green microcrystalline solid and no single crystals adequate for an X-ray structure determination are

obtained. The mixed-ligand Cu^{II} complex was crystallized from an ethanol-dichloromethane solution. Recrystallization from pure dry ethanol, methanol or acetonitrile produced the bis(1,10-phenanthroline)copper(II) complex, $[\text{Cu}(\text{phen})_2]\text{ClO}_4$.

Crystal dimensions $0.15 \times 0.13 \times 0.11$ mm; Nonius CAD-4 four-circle diffractometer, cell dimensions calculated by least-squares refinement on setting angles of 25 reflections with $13.1 < 2\theta < 25.6^\circ$; 3348 integrated reflections collected up to $(\sin\theta)/\lambda = 0.639$ Å⁻¹; ω - 2θ scan technique, scan width $(1.0 + 0.35 \tan\theta)^\circ$; $0 < h < 10$, $-11 < k < 11$, $-13 < l < 13$; no significant decline in intensities of three standard reflections; decay 1.4% during 48 h; no absorption correction and no time-decay correction applied; 3145 unique reflections after averaging ($R_{int} = 0.024$); 2204 with $F^2 > 3\sigma(F^2)$; structure solution by MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); refinement by full-matrix least squares based on F_o ; weights based on counting statistics: $1/w = \sigma^2(F) = \{[\sigma^2(F) + 0.06I]^2\}/I$ (Stout & Jensen, 1968); atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974); H atoms placed at idealized positions with fixed isotropic thermal parameters and not refined (4.5 Å²); anisotropic thermal parameters for all other atoms; refinement converged to $R = 0.037$; $wR = 0.048$, goodness of fit $S = 1.277$ for 263 refined parameters; largest shift over e.s.d. in last cycle 0.18 ; largest residual peak in final difference Fourier map 0.31 e Å⁻³. All computer programs from Enraf-Nonius SDP described by Frenz (1978).

Discussion. Final atomic parameters are in Table 1, bond distances and angles in Table 2.* The atomic numbering is shown in Fig. 1.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44104 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent thermal parameters with e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3} \sum_i \beta_i a_i^2$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Cu	0.09271 (5)	0.40570 (5)	0.11225 (4)	2.786 (9)
Cl	-0.0295 (1)	0.1906 (1)	0.30636 (8)	3.30 (2)
O(1)	-0.1288 (3)	0.4016 (3)	0.0278 (2)	3.15 (6)
O(2)	0.0979 (3)	0.2406 (3)	-0.0027 (2)	3.26 (6)
O(3)	-0.1819 (4)	0.1253 (6)	0.2255 (4)	9.9 (2)
O(4)	0.0339 (4)	0.1039 (4)	0.3967 (3)	6.9 (1)
O(5)	0.0728 (3)	0.2098 (3)	0.2387 (3)	5.03 (7)
O(6)	-0.0330 (4)	0.3307 (4)	0.3672 (3)	6.07 (9)
N(1)	0.3278 (3)	0.4362 (3)	0.2046 (3)	3.04 (7)
N(2)	0.1093 (3)	0.5712 (3)	0.2426 (3)	2.78 (6)
C(1)	0.4366 (4)	0.3657 (5)	0.1837 (4)	3.97 (9)
C(2)	0.5973 (5)	0.4018 (5)	0.2562 (4)	5.0 (1)
C(3)	0.6495 (5)	0.5141 (6)	0.3538 (4)	5.3 (1)
C(4)	0.5402 (5)	0.5924 (5)	0.3792 (4)	4.3 (1)
C(5)	0.3797 (4)	0.5485 (4)	0.3021 (3)	3.28 (8)
C(6)	0.2605 (4)	0.6226 (4)	0.3208 (3)	3.03 (8)
C(7)	0.3035 (5)	0.7411 (5)	0.4181 (4)	4.1 (1)
C(8)	0.1786 (6)	0.8071 (5)	0.4300 (4)	4.6 (1)
C(9)	0.0263 (5)	0.7542 (5)	0.3521 (4)	4.5 (1)
C(10)	-0.0057 (4)	0.6350 (4)	0.2587 (3)	3.45 (9)
C(11)	-0.5803 (6)	0.7148 (6)	0.4784 (5)	5.8 (1)
C(12)	-0.4672 (6)	0.7853 (5)	0.4947 (4)	5.4 (1)
C(13)	-0.2296 (4)	0.2826 (4)	-0.0371 (3)	2.78 (8)
C(14)	-0.3924 (4)	0.2781 (4)	-0.0621 (4)	3.62 (9)
C(15)	-0.5037 (5)	0.1557 (5)	-0.1307 (4)	4.6 (1)
C(16)	-0.4567 (5)	0.0344 (5)	-0.1803 (4)	4.9 (1)
C(17)	-0.3012 (5)	0.0360 (5)	-0.1603 (4)	4.2 (1)
C(18)	-0.1842 (4)	0.1570 (4)	-0.0880 (3)	3.06 (8)
C(19)	-0.0235 (4)	0.1504 (4)	-0.0699 (3)	3.10 (8)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) of the monomeric molecule with e.s.d.'s in parentheses

Cu—O(1)	1.900 (2)	N(2)—C(10)	1.327 (4)
Cu—O(2)	1.941 (2)	C(1)—C(2)	1.383 (6)
Cu—O(5)	2.496 (3)	C(2)—C(3)	1.358 (7)
Cu—N(1)	1.995 (3)	C(3)—C(4)	1.399 (6)
Cu—N(2)	1.993 (3)	C(4)—C(5)	1.398 (5)
C(16)—C(17)	1.353 (6)	C(4)—C(11)	1.441 (6)
C(17)—C(18)	1.404 (5)	C(5)—C(6)	1.424 (5)
C(18)—C(19)	1.416 (5)	C(6)—C(7)	1.399 (5)
Cl—O(3)	1.386 (3)	C(7)—C(8)	1.402 (6)
Cl—O(4)	1.399 (3)	C(8)—C(12)	1.419 (6)
Cl—O(5)	1.431 (3)	C(8)—C(9)	1.354 (6)
Cl—O(6)	1.422 (3)	C(9)—C(10)	1.388 (5)
O(1)—C(13)	1.309 (4)	C(11)—C(12)	1.346 (7)
N(1)—C(1)	1.332 (5)	C(13)—C(14)	1.404 (5)
N(1)—C(5)	1.357 (4)	C(13)—C(18)	1.424 (5)
N(2)—C(6)	1.345 (4)	C(14)—C(15)	1.379 (5)
		C(15)—C(16)	1.395 (6)
		Cu—Cu'	3.369 (1)
		Cu—O(1')	2.622 (2)
O(1)—Cu—O(2)	93.5 (1)	C(1)—C(2)—C(3)	119.5 (4)
O(1)—Cu—O(5)	97.9 (1)	C(2)—C(3)—C(4)	119.6 (4)
O(1)—Cu—N(1)	173.1 (1)	C(3)—C(4)—C(5)	117.4 (4)
O(1)—Cu—N(2)	92.3 (1)	C(3)—C(4)—C(11)	125.1 (4)
O(2)—Cu—O(5)	82.4 (1)	C(5)—C(4)—C(11)	117.5 (4)
O(2)—Cu—N(1)	92.1 (1)	N(1)—C(5)—C(4)	122.8 (4)
O(2)—Cu—N(2)	173.9 (1)	N(1)—C(5)—C(6)	116.0 (3)
O(5)—Cu—N(1)	86.9 (1)	C(4)—C(5)—C(6)	121.2 (4)
O(5)—Cu—N(2)	95.0 (1)	N(2)—C(6)—C(5)	116.7 (3)
N(1)—Cu—N(2)	82.3 (1)	N(2)—C(6)—C(7)	123.4 (4)
O(3)—Cl—O(4)	111.0 (3)	C(5)—C(6)—C(7)	119.9 (3)
O(3)—Cl—O(5)	109.9 (3)	C(6)—C(7)—C(8)	116.1 (4)
O(3)—Cl—O(6)	109.9 (3)	C(6)—C(7)—C(12)	118.3 (4)
O(4)—Cl—O(5)	108.5 (2)	C(8)—C(7)—C(12)	125.6 (4)
O(4)—Cl—O(6)	108.6 (2)	C(7)—C(8)—C(9)	120.4 (4)
O(5)—Cl—O(6)	108.8 (2)	C(8)—C(9)—C(10)	119.6 (4)
Cu—O(1)—C(13)	123.6 (2)	N(2)—C(10)—C(9)	121.9 (4)
Cu—N(1)—C(1)	130.1 (3)	C(4)—C(11)—C(12)	121.0 (4)
Cu—N(1)—C(5)	112.4 (2)	C(7)—C(12)—C(11)	122.2 (4)
C(1)—N(1)—C(5)	117.5 (3)	O(1)—C(13)—C(14)	119.0 (3)
Cu—N(2)—C(6)	112.6 (2)	O(1)—C(13)—C(18)	123.5 (3)
Cu—N(2)—C(10)	128.9 (2)	C(14)—C(13)—C(18)	117.4 (3)
C(6)—N(2)—C(10)	118.5 (3)	C(13)—C(14)—C(15)	121.3 (4)
N(1)—C(1)—C(2)	123.1 (4)	C(14)—C(15)—C(16)	120.3 (4)
O(1)—Cu—N(1)	90.6 (1)	C(15)—C(16)—C(17)	120.0 (3)
O(1)—Cu—N(2)	88.87 (9)	C(16)—C(17)—C(18)	121.2 (4)
		C(13)—C(18)—C(17)	119.7 (3)
		C(13)—C(18)—C(19)	122.1 (3)
		C(17)—C(18)—C(19)	118.1 (3)
		O(1')—Cu—O(1)	85.01 (9)
		O(1')—Cu—O(2)	93.47 (9)
		O(1')—Cu—O(5)	175.06 (8)
		Cu—O(1')—Cu'	95.00 (8)

Symmetry code: (i) $-x, 1-y, -z$.

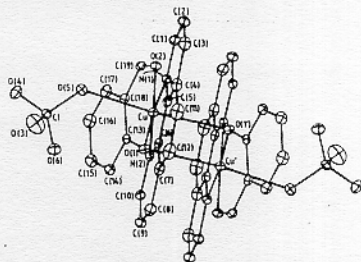


Fig. 1. A perspective view of the dimeric unit with atom numbering; H atoms excluded for clarity.

The crystal can be described as consisting of dimeric units: Cu—O(1') bonds of 2.622 (2) \AA link the two monomeric units in order to form the binuclear complex. This same distance in analogous dimeric Cu^{II} complexes is 2.436 (2) \AA for [Cu(dpa)(sal)]ClO₄ (Garland, Le Marouille & Spodine, 1985) and 2.690 (3) \AA for [Cu(dp)(sal)]ClO₄ (Garland, Le Marouille & Spodine, 1986). Therefore, the loss of the bridging amine group induces a change in the crystalline geometry, giving rise to dimeric molecules of [Cu(dp)(sal)]ClO₄ and [Cu(phen)(sal)]ClO₄ with weaker intramolecular interaction.

The coordination sphere of Cu can be described as an elongated octahedron because of the Jahn-Teller effect (Cotton & Wilkinson, 1972), the basal plane being formed by the two N atoms of the 1,10-phenanthroline molecule and by the two O atoms from the salicylaldehyde anion. The distorted octahedral coordination is completed by two large apical copper-oxygen distances [Cu—O(1') = 2.622 (2) and Cu—O(5) = 2.496 (3) \AA , compared with the basal copper-ligand bonds: Cu—O(1) = 1.900 (2), Cu—O(2) = 1.941 (2), Cu—N(1) = 1.995 (3) and Cu—N(2) = 1.993 (3) \AA]. The equatorial Cu—N(1) and Cu—N(2)

bonds of the basal plane are shorter than the corresponding Cu-N(1) = 2.005 (3) and Cu-N(3) = 2.007 (2) Å of the ternary Cu^{II} complex [Cu(dpa)(sal)]ClO₄, but similar to the corresponding distances in the [Cu(dp)(sal)]ClO₄ complex, Cu-N(1) = 1.981 (3) and Cu-N(2) = 1.983 (3) Å. The values reported in this work are similar to Cu-N distances for [Cu(phen) or (dp)₂OXO]Y complexes (Simmons, Seff, Clifford & Hathaway, 1983).

The deviations of Cu and of the four donor atoms N(1), N(2), O(1) and O(2) from their mean unweighted plane are -0.014, 0.058, -0.052, 0.055 and -0.047 Å respectively. The dihedral angle between the planes through Cu, O(1), O(2) and through Cu, N(1), N(2) is 4.7°. This value is lower than that found for (di-2-pyridylamine)salicylaldehydatocopper(II) perchlorate, 11.8° (Garland, Le Marouille & Spodine, 1986). The copper distance to the mean plane of the benzene ring is -0.536 Å, comparable to the distances, -0.700 and 0.465 Å, of the other two dimeric ternary complexes of Cu^{II}. The out-of-plane displacements of the Cu atom from the two pyridine rings of the 1,10-phenanthroline molecule are 0.026 and 0.074 Å. The corresponding values for the di-2-pyridylamine complex are 0.250 and 0.379 Å, and 0.022 and -0.086 Å for the di-2-pyridyl one.

The copper-phenoxo-oxygen-copper angle in the dimeric unit is 95.00 (8)°. This value is similar to that obtained for the ternary di-2-pyridyl complex [96.1 (2)°], but lower than the value found for the di-2-pyridylamine complex [99.2 (2)°].

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