

Structure of (Di-2-pyridylamine)(*N*-phenylsalicylideneaminato)copper Perchlorate

BY M. T. GARLAND AND J. Y. LE MAROUILLE

Laboratoire de Chimie du Solide et Inorganique Moléculaire, UA au CNRS n° 254, Campus de Beaulieu,
35042 Rennes CEDEX, France

AND E. SPODINE

Facultad de Ciencias Básicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile

(Received 29 May 1985; accepted 25 October 1985)

Abstract. $[\text{Cu}(\text{C}_{13}\text{H}_{10}\text{NO})(\text{C}_{10}\text{H}_9\text{N}_3)]\text{ClO}_4$, $M_r = 530.42$, triclinic, $P\bar{1}$, $a = 10.631(3)$, $b = 11.010(2)$, $c = 11.347(4)$ Å, $\alpha = 104.16(2)$, $\beta = 113.98(3)$, $\gamma = 96.50(2)^\circ$, $V = 1142.7(6)$ Å³, $Z = 2$, $D_x = 1.542$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 11.162$ cm⁻¹, $F(000) = 542$, $T = 291$ K. Final $R = 0.044$ for 2960 observed reflections. The coordination sphere of Cu is partially tetrahedral, the dihedral angle CuN(2)N(4)-CuN(1)O(5) being 49.4°. The three Cu-N bond lengths are nearly the same, 1.961(2), 1.964(2) and 1.987(2) Å, while that of Cu-O is quite different, 1.874(2) Å. The crystal packing is mainly stabilized by hydrogen bonds and van der Waals forces.

Introduction. Several reviews contain abundant structural data related to metal complexes of Schiff bases (Casellato, Vigato & Vidali, 1977; Holm, Everett & Chakravorty, 1966; Holm & O'Connor, 1971; Maslen & Waters, 1975). However, further studies continue since these complexes have diverse applications; biological models and transition-metal-ion extraction being some of the important ones (Cimerman, Deljac & Stefanac, 1980; Leussing, 1976).

All the structures studied correspond to neutral bis-chelate complexes of copper(II). We were interested in studying an N₃O chromophore, that is a mixed complex with one salicylideneamine molecule and a

heterocyclic base. A coordination sphere with three N atoms and one phenolic O would serve as a model system for the cupric hemocyanin molecule (Préaux & Gielsens, 1984).

Experimental. The mixed complex was prepared by refluxing an ethanolic solution of a 1 mmol sample of cupric perchlorate with 1 mmol of the Schiff base, *N*-salicylideneaniline. After the solution had turned brown (0.5 h), 1 mmol of di-2-pyridylamine (dpa) dissolved in the same solvent was added to the warm reaction mixture, and heated for 1 h. The yield of the complex was greatly improved by using KOH to deprotonate the Schiff base. When cooled, steel-colored crystals of [Cu(dpa)(Ph-sal)]ClO₄ (Ph-sal = *N*-phenylsalicylideneaminato) were formed. These were washed with benzene to eliminate impurities of Cu(Ph-sal)₂, which formed during the reaction as a by-product and which grew as small yellow crystals on top of the [Cu(dpa)(Ph-sal)]ClO₄. The complex was then characterized by elemental analysis and an IR spectrum.

Crystal of dimensions 0.32 × 0.16 × 0.10 mm; Nonius CAD-4 four-circle diffractometer, cell dimensions calculated by least-squares refinement on setting angles of 25 reflections with 10.2 < 2θ < 21.0°; 4231 integrated reflections collected up to sinθ/λ < 0.595 Å⁻¹; ω-2θ scan technique, scan width (1 + 0.35 tanθ)°; -12 < h < 12, -13 < k < 13, 0 < l < 13; no significant decline in intensities of three standard reflections, 2-7% decay during 61 h of irradiation; no

absorption correction and no time-decay corrections applied; 3787 unique reflections after averaging ($R_{int} = 0.013$); 2960 with $F^2 > 3\sigma(F^2)$; structure solution by MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); refined by full-matrix least squares based on F_o , weights based on counting statistics $1/w = \sigma_F^2 = \{ \sigma_o^2 + (0.04I)^2 \} / I$ (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 thermal parameters (5 Å²) and not refined; anisotropic thermal parameters for all other atoms; refinement converged to $R = 0.044$ and $wR = 0.059$ and goodness-of-fit $S = 2.164$ for 308 refined parameters; largest Δ/σ in last cycle: 0.11; final difference map revealed no residuals greater than 0.50 e Å⁻³, except one maximum of 1.02 e Å⁻³ near the perchlorate. All computer programs from Enraf-Nonius SDP described by Frenz (1978).

Table 2. Intramolecular bond lengths (Å) and bond angles (°) and selected intermolecular distances (Å) with e.s.d.'s in parentheses

| | | | |
|------------------|------------|--------------------------|-----------|
| Cu—O(5) | 1.874 (2) | C(2)—C(7) | 1.413 (4) |
| Cu—N(1) | 1.964 (2) | C(3)—C(4) | 1.361 (5) |
| Cu—N(2) | 1.987 (2) | C(4)—C(5) | 1.386 (5) |
| Cu—N(4) | 1.961 (2) | C(5)—C(6) | 1.353 (5) |
| Cl—O(1) | 1.387 (3) | C(6)—C(7) | 1.416 (4) |
| Cl—O(2) | 1.371 (3) | C(8)—C(9) | 1.363 (5) |
| Cl—O(3) | 1.483 (4) | C(9)—C(10) | 1.383 (6) |
| Cl—O(4) | 1.380 (4) | C(10)—C(11) | 1.368 (5) |
| O(5)—C(7) | 1.312 (3) | C(11)—C(12) | 1.396 (4) |
| N(1)—C(1) | 1.306 (3) | C(13)—C(14) | 1.396 (4) |
| N(1)—C(18) | 1.428 (3) | C(14)—C(15) | 1.359 (4) |
| N(2)—C(8) | 1.361 (4) | C(15)—C(16) | 1.359 (4) |
| N(2)—C(12) | 1.349 (4) | C(16)—C(17) | 1.354 (4) |
| N(3)—C(12) | 1.378 (4) | C(18)—C(19) | 1.388 (4) |
| N(3)—C(13) | 1.382 (3) | C(18)—C(20) | 1.386 (4) |
| N(4)—C(13) | 1.341 (3) | C(19)—C(21) | 1.384 (5) |
| N(4)—C(17) | 1.350 (3) | C(20)—C(21) | 1.383 (5) |
| C(1)—C(2) | 1.418 (4) | C(21)—C(22) | 1.361 (5) |
| C(2)—C(3) | 1.416 (4) | C(22)—C(23) | 1.391 (5) |
| O(5)—Cu—N(1) | 94.96 (8) | C(3)—C(4)—C(5) | 119.0 (3) |
| O(5)—Cu—N(2) | 96.08 (9) | C(4)—C(5)—C(6) | 121.4 (4) |
| O(5)—Cu—N(4) | 144.45 (9) | C(5)—C(6)—C(7) | 120.4 (3) |
| N(1)—Cu—N(2) | 144.6 (1) | C(6)—C(7)—C(8) | 120.4 (3) |
| N(1)—Cu—N(4) | 97.93 (9) | O(5)—C(7)—C(6) | 117.8 (3) |
| N(2)—Cu—N(4) | 92.32 (9) | C(2)—C(7)—C(6) | 118.2 (3) |
| O(1)—Cl—O(2) | 110.0 (2) | N(2)—C(8)—C(9) | 122.8 (3) |
| O(1)—Cl—O(3) | 105.1 (3) | C(8)—C(9)—C(10) | 118.9 (3) |
| O(1)—Cl—O(4) | 110.9 (2) | C(9)—C(10)—C(11) | 119.9 (3) |
| O(2)—Cl—O(3) | 103.3 (3) | C(10)—C(11)—C(12) | 118.5 (3) |
| O(2)—Cl—O(4) | 122.6 (3) | N(2)—C(12)—C(11) | 120.6 (3) |
| O(3)—Cl—O(4) | 102.9 (3) | N(2)—C(12)—C(11) | 122.4 (3) |
| Cu—O(5)—C(7) | 127.2 (2) | N(3)—C(13)—C(14) | 117.0 (3) |
| Cu—N(1)—C(1) | 122.4 (2) | N(3)—C(13)—C(14) | 120.1 (2) |
| Cu—N(1)—C(18) | 119.0 (2) | N(3)—C(13)—C(14) | 118.8 (2) |
| C(1)—N(1)—C(18) | 118.6 (2) | N(4)—C(15)—C(16) | 121.0 (2) |
| Cu—N(2)—C(8) | 118.9 (2) | C(13)—C(14)—C(15) | 118.9 (3) |
| C(8)—N(2)—C(12) | 122.8 (2) | C(14)—C(15)—C(16) | 119.5 (3) |
| C(12)—N(2)—C(8) | 117.4 (3) | C(15)—C(16)—C(17) | 117.9 (3) |
| C(12)—N(3)—C(13) | 129.7 (2) | N(4)—C(17)—C(16) | 123.6 (3) |
| Cu—N(4)—C(13) | 124.7 (2) | N(1)—C(18)—C(19) | 119.2 (3) |
| Cu—N(4)—C(17) | 116.8 (2) | N(1)—C(18)—C(19) | 120.5 (3) |
| C(13)—N(4)—C(17) | 118.4 (2) | C(19)—C(18)—C(20) | 120.3 (3) |
| N(1)—C(1)—C(2) | 127.5 (2) | C(18)—C(19)—C(20) | 118.9 (3) |
| C(1)—C(2)—C(3) | 117.9 (3) | C(19)—C(20)—C(21) | 121.1 (3) |
| C(3)—C(2)—C(7) | 118.7 (3) | C(20)—C(21)—C(22) | 119.4 (3) |
| C(2)—C(3)—C(4) | 121.9 (3) | C(18)—C(20)—C(21) | 119.2 (3) |
| O(2)—N(3) | 2.928 (4) | O(4)—C(2 ^{2a}) | 3.482 (5) |
| O(2)—C(14) | 3.281 (5) | O(4)—C(2 ^{2b}) | 3.416 (5) |

Symmetry operations: (i) $x, y, 1-z$; (ii) $1-x, -y, 1-z$; (iii) $-x, -y, 1-z$.

Table 1. Fractional atomic coordinates and equivalent isotropic B (Å²) with e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3} (\sum_i \sigma_i^2 \beta_i) \text{Å}^2$$

| | x | y | z | B_{eq} |
|-------|-------------|-------------|-------------|----------|
| Cu | 0.58725 (4) | 0.53094 (4) | 0.76592 (4) | 3.02 (1) |
| Cl | 0.3012 (1) | 0.0828 (1) | 0.7995 (1) | 5.70 (3) |
| O(1) | 0.3046 (4) | 0.2019 (3) | 0.8810 (4) | 6.8 (1) |
| O(2) | 0.1599 (6) | 0.0085 (4) | 0.8785 (4) | 14.3 (2) |
| O(3) | 0.4046 (5) | 0.1123 (6) | 0.7476 (5) | 13.2 (2) |
| O(4) | 0.1741 (6) | 0.0356 (6) | 0.6824 (5) | 12.6 (2) |
| O(5) | 0.7345 (2) | 0.4725 (3) | 0.8132 (3) | 3.76 (7) |
| O(6) | 0.4690 (3) | 0.3743 (3) | 0.6119 (3) | 2.95 (7) |
| N(2) | 0.6799 (3) | 0.1758 (3) | 0.8180 (3) | 3.42 (7) |
| N(1) | 0.4712 (3) | 0.7867 (3) | 0.8162 (3) | 3.66 (8) |
| N(4) | 0.4424 (3) | 0.5736 (3) | 0.8233 (3) | 2.69 (7) |
| N(3) | 0.5208 (4) | 0.2779 (4) | 0.5750 (4) | 3.33 (9) |
| C(2) | 0.6636 (4) | 0.2682 (4) | 0.6304 (4) | 3.35 (9) |
| C(1) | 0.6983 (4) | 0.1587 (4) | 0.5708 (4) | 4.5 (1) |
| C(4) | 0.8327 (5) | 0.1414 (4) | 0.6207 (5) | 5.1 (1) |
| C(5) | 0.9378 (4) | 0.2232 (4) | 0.7390 (5) | 5.1 (1) |
| C(6) | 0.9102 (4) | 0.3409 (4) | 0.8419 (4) | 4.1 (1) |
| C(7) | 0.7726 (3) | 0.3635 (4) | 0.7512 (3) | 3.27 (8) |
| C(8) | 0.8133 (4) | 0.7476 (4) | 0.8305 (4) | 4.5 (1) |
| C(9) | 0.8750 (4) | 0.8682 (5) | 0.8416 (4) | 5.6 (1) |
| C(10) | 0.7991 (6) | 0.9624 (4) | 0.8395 (5) | 5.8 (1) |
| C(11) | 0.6653 (5) | 0.9343 (4) | 0.8283 (4) | 4.5 (1) |
| C(12) | 0.4095 (4) | 0.8101 (4) | 0.8211 (3) | 3.41 (9) |
| C(13) | 0.4122 (4) | 0.6896 (3) | 0.8449 (3) | 2.91 (8) |
| C(14) | 0.3133 (4) | 0.7140 (4) | 0.8936 (4) | 4.0 (1) |
| C(15) | 0.2473 (4) | 0.6191 (4) | 0.9208 (4) | 4.2 (1) |
| C(16) | 0.2780 (4) | 0.4977 (4) | 0.8977 (4) | 3.67 (9) |
| C(17) | 0.3745 (4) | 0.4803 (4) | 0.8497 (4) | 3.17 (9) |
| C(18) | 0.3200 (4) | 0.3625 (4) | 0.5413 (3) | 3.02 (8) |
| C(19) | 0.2722 (4) | 0.4635 (4) | 0.4981 (4) | 3.8 (1) |
| C(20) | 0.216 (5) | 0.4526 (3) | 0.4322 (4) | 5.4 (1) |
| C(21) | 0.0112 (4) | 0.3445 (6) | 0.4114 (5) | 5.9 (1) |
| C(22) | 0.0795 (4) | 0.2466 (5) | 0.4553 (5) | 5.4 (1) |
| C(23) | 0.2240 (4) | 0.2535 (4) | 0.5201 (4) | 4.1 (1) |

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

The coordination sphere of Cu can be described as partially tetrahedral consisting of two N atoms from the dipyridylamine moiety and one O atom and one N atom from the salicylideneamine moiety.

The deviations of Cu, N(2), N(4), N(1) and O(5) from their mean unweighted plane are -0.008 , 0.631 , -0.573 , 0.556 and -0.608 Å, respectively. The dihedral angle θ adopted as a measure of tetrahedrality (Holm & O'Connor, 1971) and defined as the angle between planes through CuN(2)N(4) and CuN(1)O(5) is 49.4° . This geometry is quite different from the one which we found in the analogous planes of (di-2-pyridylamine)salicylaldehydato-copper(II) perchlorate due to the steric hindrance of the salicylideneamine group (Garland, Le Marouille & Spodine, 1985). Bond lengths involving N donor atoms are nearly the same, 1.961 (2), 1.964 (2) and 1.987 (2) Å, while the bond length involving the O atom is different, 1.874 (2) Å.

Each bidentate ligand forms a six-membered chelate ring with the Cu atom. The salicylideneamine chelate ring is planar and deviates from planarity within 0.025 Å, while the dipyridylamine chelate ring is less planar with deviations from the mean plane within 0.204 Å.

The dipyridylamine rings deviate from planarity by -0.020 and ± 0.004 Å respectively. The out-of-plane displacements of the Cu atom from these rings are

-0.120 and 0.390 Å which are comparable with the analogous values of 0.250 and 0.379 Å found by us in (di-2-pyridylamine)salicylaldehydato-copper(II) perchlorate (Garland *et al.*, 1985).

The two aromatic rings of the *N*-phenyl-salicylideneamine group deviate from planarity by 0.022 and -0.006 Å respectively. The distances of Cu from these rings are 0.192 and -1.398 Å which are not comparable with those found in [4-methoxymethyl-6-methyl-2-(salicylideneamino)-3-(salicylideneamino-methyl)pyridinato(2-)-*N,N',O,O'*]copper 1.5 hydrate (Galčič, Trojko, Cimerman & Štefanac, 1984). We found an undefined maximum near the perchlorate group which is due to a probable occupational disorder of the perchlorate group.

The crystal packing is mainly stabilized by hydrogen bonds between the O atoms of the perchlorate and the non-donor N atom of the dipyridylamine. There are also van der Waals forces between the O atoms of the perchlorate and the C atoms of the dipyridylamine and of the *N*-phenylsalicylideneamine (Table 2).

This research was supported in part by the Departamento de Desarrollo de Investigación y Bibliotecas, Universidad de Chile (DIB 1872-8414).

References

- CASELLATO, U., VIGATO, P. A. & VIDALI, M. (1977). *Coord. Chem. Rev.* **23**, 31-117.
- CIMERMAN, Z., DELJAC, A. & ŠTEFANAC, Z. (1980). *Int. Solvent Extr. Conf.*, Liège, Belgium, Proc. 1, pp. 80-87.
- FRENZ, B. A. (1978). *The Enraf-Nonius CAD-4 Structure Determination Package. A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination. In Computing in Crystallography*, edited by H. SCHENK, R. OLTROP-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64-71. Delft, Univ. Press.
- GALČIČ, N., TROJKO, R., CIMERMAN, Z. & ŠTEFANAC, Z. (1984). *Acta Cryst.* **C40**, 232-235.
- GARLAND, M. T., LE MAROUILLE, J. Y. & SPODINE, E. (1985). *Acta Cryst.* **C41**, 855-858.
- HOLM, R. H., EVERETT, G. W. & CHAKRAVORTY, A. (1966). *Prog. Inorg. Chem.* **7**, 83-214.
- HOLM, R. H. & O'CONNOR, M. J. (1971). *Prog. Inorg. Chem.* **14**, 241-401.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- LEUSSING, D. L. (1976). *Metal Ions in Biological Systems*, Vol. 5, edited by H. SIGEL, pp. 1-77. New York: Marcel Dekker.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MASLEN, H. S. & WATERS, T. N. (1975). *Coord. Chem. Rev.* **17**, 137-176.
- PREAUX, G. & GIELENS, C. (1984). *Copper Proteins and Copper Enzymes*, Vol. 2, edited by R. LONTJE, pp. 159-204. Cleveland, Ohio: CRC Press.
- STOUT, G. H. & JENSEN, L. H. (1968). In *X-ray Structure Determination*. New York: Macmillan.

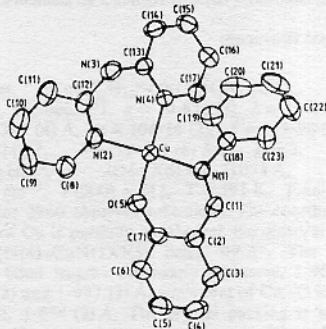


Fig. 1. A perspective view of the molecule with atom numbering and H atoms excluded for clarity.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares-planes' data and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42603 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.