Lippard, S. J. (1967). *Prog. Inorg. Chem.* **8**, 109–193.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Sheldrick, G. M. (1991). *SHELXTL/PC*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1991). *P3/P4/PC Diffractometer Program*. Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spodine, E., Manzur, J., Garland, M. T., Fackler, J. P., Staples, R. J. & Trzcinska-Bancroft, B. (1993). *Inorg. Chim. Acta*, **203**, 73–80.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

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Bis(pyridine-2,3-dicarboxylato-*N*,*O*)-copper(II)

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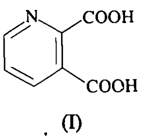
Abstract

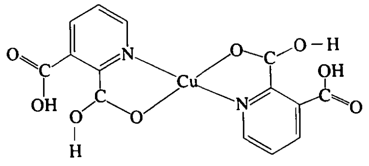
The coordination geometry of the Cu atom in the title compound, $[Cu(C_7H_5NO_4)_2]$, is distorted octahedral and the molecule displays crystallographic inversion symmetry. The Cu atom is bonded to a carboxylate O atom (at the pyridine 2 position) and the pyridine N atom of two ligands, the four atoms forming the equatorial plane, and *via* weaker axial contacts to two carboxylic acid O atoms (at the pyridine 3 position) of adjacent molecules. Strands of molecules are thus linked parallel to the x axis and hydrogen bonds link the strands parallel to the y axis.

Comment

Pyridine-2,3-dicarboxylic acid, (I), also known as quinolinic acid, is a neurotoxic tryptophan metabolite, a precursor of nicotinamide adenine dinucleotide, and an agonist of the *N*-methyl-D-aspartate receptor (Kalish, Jhamandas, Boegman & Beninger, 1994; Espey, Moffett & Namboodiri, 1995; Mawatari, Oshida, Iinuma & Watanabe, 1995). Its anion forms chelate complexes with Mn, Co, Ni and Zn; the crystal structures of the complexes with Ni and Mn have been reported previously (Goher, Youssef, Zhou & Mak, 1993). It is important to determine the precise crystal structure of the various metal complexes of quinolinic acid and its anions in order to relate the effects of this metabolite and/or related compounds on many physiological processes involving metal enzymes. The crystal structure of quinolinic acid itself has been determined by both X-ray analysis (Takusagawa, Hirotsu & Shimada, 1973) and neutron analysis (Kvick, Koetzle, Thomas & Tagusagawa, 1974; Takusagawa & Koetzle, 1978). We report herein the structure of bis(pyridine-2,3-dicarboxylato-*N*,*O*)copper(II), (II).



(I)



(II)

The molecular structure of (II) is shown in Fig. 1. The Cu atom displays distorted octahedral geometry. It lies on an inversion centre, bonded to two pyridine N atoms [Cu(1)—N(1) 1.969 (3) Å] and two carboxylate O(1) atoms of the carboxylate groups in the pyridine 2 positions [Cu(1)—O(1) 1.926 (3) Å], which form the equatorial plane. It is bonded more weakly to two O(4) atoms of the carboxylic acid groups at the pyridine 3 positions of adjacent molecules [Cu(1)···O(4)($-1+x$, y, z) and Cu(1)···O(4)($1-x$, $-y$, $1-z$) 2.660 (3) Å] in the axial directions. The carboxylate group in position 2 is almost parallel to the pyridine ring plane [O(1)—

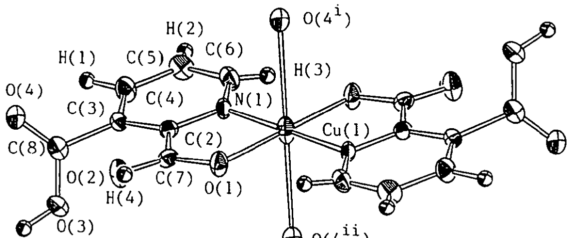


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Ellipsoids correspond to 50% probability and H atoms are drawn as circles of arbitrary radii. [Symmetry codes: (i) $1-x$, $-y$, $1-z$; (ii) $-1+x$, y, z.]

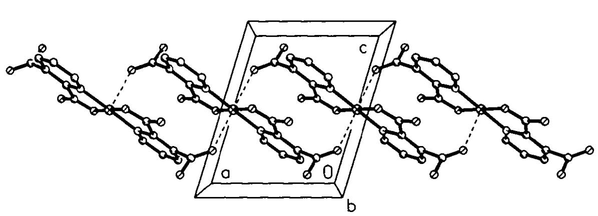


Fig. 2. A view of the weak axial contacts (dashed lines) linking molecules parallel to the x axis.

C(7)—C(2)—N(1) −6.0 (5)°], whereas the carboxylic acid group in position 3 is nearly perpendicular to it [O(4)—C(8)—C(3)—C(4) −70.9 (6)°]. Weak Cu···O interactions link the molecules into chains parallel to the x axis (Fig. 2), whereas parallel stacking of these chains in the y direction is achieved *via* hydrogen bonds between the carboxylate and carboxylic acid groups; O(3)—H(4)···O(2)($\frac{1}{2}+x$, $-\frac{1}{2}-y$, $\frac{1}{2}+z$) 2.646 (4) Å.

Experimental

The title crystal was obtained by slow evaporation of a 50% 1-propanol/water solution of a mixture of quinolinic acid and $CuCl_2.2NH_4Cl.2H_2O$ (molar ratio 5:1) at room temperature and pH 7.0.

Crystal data

$[Cu(C_7H_5NO_4)_2]$
$M_r = 397.78$
Monoclinic
$P2_1/n$
$a = 6.730\,(3)$ Å
$b = 12.887\,(3)$ Å
$c = 8.274\,(2)$ Å
$\beta = 107.26\,(2)°$
$V = 685.3\,(3)$ Å^3
$Z = 2$
$D_x = 1.918$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.0–16.55°$
$\mu = 1.646$ mm^{-1}
$T = 296$ K
Needle
0.40 × 0.05 × 0.05 mm
Blue

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: none
1790 measured reflections
1657 independent reflections
1069 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.030$

$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 16$
$l = -10 \rightarrow 9$
3 standard reflections monitored every 150 reflections frequency: 137 min intensity decay: none

Refinement

Refinement on F
$R = 0.041$
$wR = 0.051$
$S = 1.56$
1069 reflections
127 parameters
H atoms not refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.37$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.50$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cu(1)	0	0	1/2	2.14 (3)
O(1)	0.1558 (4)	−0.1245 (2)	0.4938 (4)	2.0 (1)
O(2)	0.4766 (4)	−0.1901 (2)	0.5785 (4)	2.1 (1)
O(3)	0.7481 (5)	−0.1499 (3)	0.9302 (4)	2.6 (1)
O(4)	0.9365 (5)	−0.0837 (3)	0.7743 (4)	2.5 (1)
N(1)	0.2696 (5)	0.0525 (3)	0.6433 (4)	1.5 (1)
C(2)	0.4193 (6)	−0.0215 (3)	0.6724 (5)	1.4 (1)
C(3)	0.6186 (6)	−0.0024 (4)	0.7776 (5)	1.5 (1)
C(4)	0.6636 (7)	0.0961 (4)	0.8463 (6)	2.1 (2)
C(5)	0.5116 (7)	0.1708 (4)	0.8145 (6)	2.2 (2)
C(6)	0.3158 (7)	0.1458 (4)	0.7142 (6)	2.0 (2)
C(7)	0.3489 (6)	−0.1210 (3)	0.5759 (5)	1.6 (1)
C(8)	0.7858 (6)	−0.0850 (3)	0.8239 (5)	1.7 (2)

Table 2. *Selected geometric parameters (Å, °)*

Cu(1)—O(1)	1.926 (3)	N(1)—C(6)	1.328 (6)
Cu(1)—N(1)	1.969 (3)	C(2)—C(3)	1.387 (5)
Cu(1)—O(4$^{\rm i}$)	2.660 (3)	C(2)—C(7)	1.511 (5)
O(1)—C(7)	1.276 (5)	C(3)—C(4)	1.387 (6)
O(2)—C(7)	1.233 (5)	C(3)—C(8)	1.514 (6)
O(3)—C(8)	1.293 (6)	C(4)—C(5)	1.372 (6)
O(4)—C(8)	1.201 (5)	C(5)—C(6)	1.372 (6)
N(1)—C(2)	1.356 (5)		
O(1)—Cu(1)—O(4$^{\rm i}$)	95.1 (1)	N(1)—C(2)—C(7)	113.8 (3)
O(1)—Cu(1)—O(4$^{\rm ii}$)	84.9 (1)	C(3)—C(2)—C(7)	125.1 (4)
N(1)—Cu(1)—O(4$^{\rm i}$)	91.2 (1)	C(2)—C(3)—C(4)	118.2 (4)
N(1)—Cu(1)—O(4$^{\rm ii}$)	88.8 (1)	C(2)—C(3)—C(8)	122.8 (4)
O(4$^{\rm i}$)—Cu(1)—O(4$^{\rm ii}$)	180.00	C(4)—C(3)—C(8)	119.0 (3)
O(1)—Cu(1)—O(1$^{\rm iii}$)	180.00	C(3)—C(4)—C(5)	120.0 (4)
O(1)—Cu(1)—N(1)	83.7 (1)	C(4)—C(5)—C(6)	118.5 (4)
O(1)—Cu(1)—N(1$^{\rm iii}$)	96.3 (1)	N(1)—C(6)—C(5)	122.6 (4)
N(1)—Cu(1)—N(1$^{\rm iii}$)	180.00	O(1)—C(7)—O(2)	125.3 (4)
Cu(1)—O(1)—C(7)	115.7 (3)	O(1)—C(7)—C(2)	114.9 (4)
Cu(1)—N(1)—C(2)	111.6 (3)	O(2)—C(7)—C(2)	119.7 (4)
Cu(1)—N(1)—C(6)	129.0 (3)	O(3)—C(8)—O(4)	126.7 (4)
C(2)—N(1)—C(6)	119.4 (4)	O(3)—C(8)—C(3)	110.2 (4)
N(1)—C(2)—C(3)	121.1 (4)	O(4)—C(8)—C(3)	122.9 (4)

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

All H atoms were located from difference Fourier maps. Pyridine H atoms were refined isotropically and included in the subsequent least-squares refinement, whereas atom H(4) of the carboxy group was not refined, but included in the subsequent refinement with a fixed isotropic displacement parameter.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976) and *XP* (Siemens, 1994).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1106). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*. Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Espey, M. G., Moffett, J. R. & Namboodiri, M. A. A. (1995). *J. Leukocyte Biol.* **57**, 199–206.

Goher, M. A. S., Youssef, A. A., Zhou, Z. Y. & Mak, T. C. W. (1993). *Polyhedron*, **12**, 1871–1878.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kalish, B. E., Jhamandas, K., Boegman, R. J. & Beninger, R. J. (1994). *Brain Res.* **668**, 1–8.
Kvick, A., Koetzle, T. F., Thomas, R. & Takusagawa, F. (1974). *J. Chem. Phys.* **60**, 3866–3874.
Mawatari, K., Oshida, K., Iinuma, F. & Watanabe, M. (1995). *Anal. Chim. Acta*, **302**, 179–183.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
Siemens (1994). *XP. Interactive Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Takusagawa, F., Hirotsu, K. & Shimada, A. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2372–2380.
Takusagawa, F. & Koetzle, T. (1978). *Acta Cryst.* B**34**, 1149–1154.

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Bis(2-amino-4-chloromethylthiazolium) Tetrachlorocuprate at 200 and 100 K and Bis(2-amino-4-methylthiazolium) Tetrachlorocuprate at 100 K

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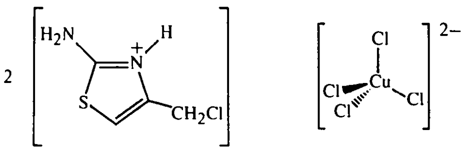
Abstract

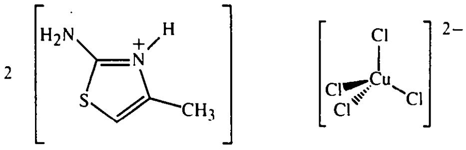
The title compounds, $(C_4H_6ClN_2S)_2[CuCl_4]$ and $(C_4H_7N_2S)_2[CuCl_4]$, show thermochromic properties. In both compounds, the thiazole ring is protonated at the N atom.

Comment

Thermochromism is often associated with temperature-dependent changes in the coordination geometry of the chromophore (Bloomquist & Willett, 1982; Sone & Fukuda, 1987). The title compounds, (1) and (2), are thermochromic coordination compounds; the thermochromism is expected to be caused by deformation of the $[CuCl_4]^{2-}$ group as a function of temperature. The crystals are amber at room temperature and yellow between 120 and 77 K. The colour change with temperature is a reversible process. In this paper we report the crystal structure of compound (1) at 200 and 100 K and compound (2) at 100 K.



(1)



(2)

Comparison of the crystal structure of (2) at 100 K with that determined at 295 K (Fernández, Morán, Doadrio, Conradi, Willing & Müller, 1987) shows that the maximum angle difference in the anion is

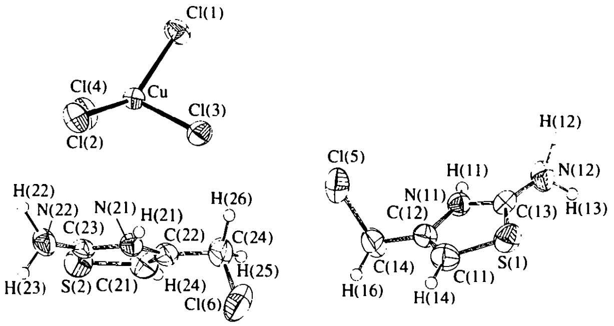


Fig. 1. *EUCLID* (Spek, 1982) plot of compound (1) at 200 K showing the atom-numbering scheme. The ellipsoids are drawn at 50% probability.

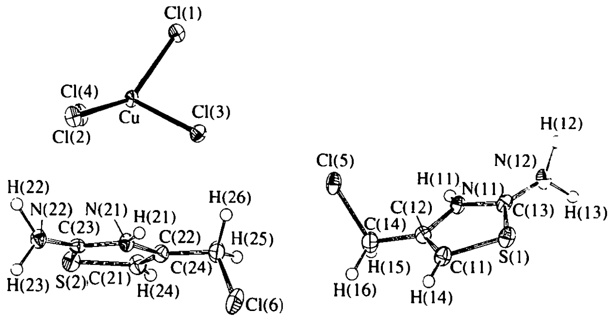


Fig. 2. *EUCLID* (Spek, 1982) plot of compound (1) at 100 K showing the atom-numbering scheme. The ellipsoids are drawn at 50% probability.