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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1240). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Aqua(3,5-dimethylpyrazole)(*N*-salicylideneglycinato)copper(II)

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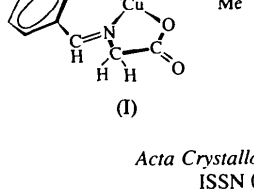
Abstract

Aqua(3,5-dimethylpyrazole-N^1)(N-salicylideneglycinato-O,N,O')copper(II), $[Cu(C_9H_7NO_3)(C_5H_8N_2)(H_2O)]$, adopts a square-pyramidal Cu^{II} coordination with the tridentate *N*-salicylideneglycinato Schiff base dianion and the 3,5-dimethylpyrazole ligand bound in the basal plane. The water molecule occupies the apical site. The complex molecules are arranged in four magnetically non-equivalent orientations, two at a time forming zigzag chains. Both the interchain Cu···Cu spacing of 7.396 Å and the intrachain Cu···Cu distance of 6.880 Å are too large for effective dipolar coupling between the paramagnetic Cu^{II} centres, in agreement with the results of electron paramagnetic resonance (EPR) spectroscopy.

Comment

Copper(II) complexes with a tridentate Schiff base dianion of the *N*-salicylideneamino alkanoate type (TSB^{2-}) represent a relatively simple model for intermediates in enzymatic reactions of amino acids (Krätsmár-Šmogrovič, Bergendi, Duncková, Švajlenová & Seressová, 1988). In recent years, however, much attention has been devoted to their structural and spectroscopic properties in the solid state, since they show an extraordinary richness of cooperative orderings. In these complexes, which are of the general type $[Cu(TSB)(L)(H_2O)_x]$, three donor atoms (O, N and O) of the Schiff base and a fourth donor atom from the neutral ligand L (N, O or S) normally define the base of a square pyramid. The apical site can be occupied by different types of donor atoms, giving rise to the observed variety of structural orderings; when a carboxylic O atom from an adjacent molecule takes the apex of the pyramid, infinite chains may be formed (Sivý, Kettmann, Krätsmár-Šmogrovič, Švajlenová, Friebel & Plesch, 1990). The apical bonding of phenolic oxygen from an adjacent molecule results in the formation of dimers (Pavelčík, Krätsmár-Šmogrovič, Švajlenová & Majer, 1991). Finally, the apical position can be occupied by a water molecule, giving rise to an isolated square-pyramidal complex (Ueki, Ashida, Sasada & Kakudo, 1969). If the coordination polyhedra are sufficiently close to one another, magnetic coupling between the Cu^{2+} ions, ranging from ferrodistortive to antiferrodistortive, distinctly influences the EPR spectra (Warda, 1994; Plesch, Friebel, Švajlenová & Krätsmár-Šmogrovič, 1995).

Since the EPR spectrum of the title compound, (I), gave no evidence for a coupled g tensor (Plesch, Friebel, Švajlenová & Krätsmár-Šmogrovič, 1987), it was of interest to analyze its crystal structure by X-ray diffraction.



(I)

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The complex molecule is characterized by an approximately square-pyramidal Cu^{II} coordination, with the tridentate dianionic Schiff base and the monodentate ligand in the basal plane and a water molecule in the apical site (Fig. 1). The apical Cu—O(4) distance of 2.328 (3) Å is very near to that for the corresponding bond in diaqua(*N*-salicylideneglycinato)copper(II) dihydrate (Ueki *et al.*, 1969).

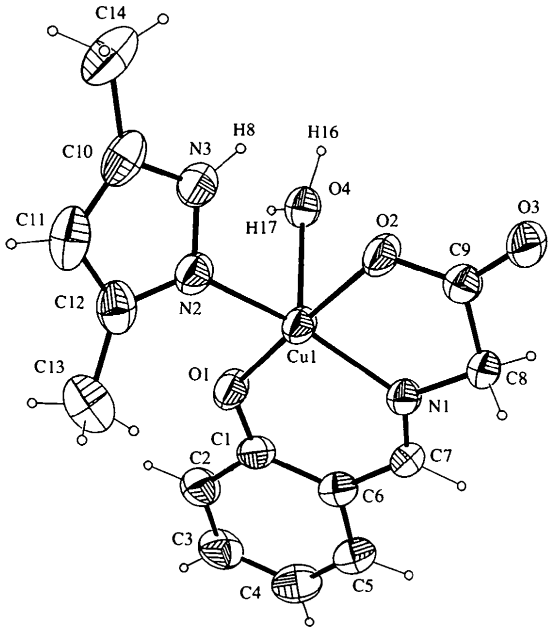

Fig. 1. Diagram of the title compound (*ORTEP*II; Johnson, 1976) with the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

The bond lengths and angles in the *N*-salicylideneglycinato ligand are very close to those reported for (*N*-salicylideneglycinato)copper(II) complexes with various neutral ligands bound in the basal plane (Ueki, Ashida, Sasada & Kakudo, 1967; Ueki *et al.*, 1969; Warda, 1994). Evidently, changing the monodentate ligand has only a small effect on the coordination of the tridentate Schiff base dianion. The Cu atom is displaced by 0.163 Å from the mean plane through the basal donor atoms in the direction of the apical O(4) atom.

As reported previously (Kettmann, Frešová, Blahová & Krätsmár-Šmogrovič, 1993) in the 1:1 pyrazole adduct of (pyrazole-*N*)[(*S*)-salicylidenealaninato]copper(II), the coordinated pyrazole lies approximately in the basal plane of the complex. Alkyl substituents on C atoms adjacent to the donor N atom of the neutral ligand effectively disturb this coplanarity. An inclination of the 2-methylimidazole ring plane by 34.2° with respect to the basal plane has been found in 2-imidazole(*N*-salicylideneglycinato)copper(II) (Sivý *et al.*, 1990), where the complex molecules are connected by carboxylato bridges to form zigzag chains. In the title complex, the presence of methyl substituents on both sides of the pyrazole donor N atom results in an inclination of the almost planar 3,5-dimethylpyrazole by 45.9° with respect to the basal coordination plane. With this relatively bulky ligand, formation of chains or dimeric units is prevented and isolated square-pyramidal complexes are formed, which are stabilized by an intramolecular N(3)—H(8)···O(2) hydrogen bond (see Table 3).

The crystal structure is also stabilized through intermolecular hydrogen bonds between the H atom on N(3) and the carboxylic O(3) atom from a neighbouring molecule. There are also contacts shorter than the sum of the van der Waals radii between water H atoms and the O(3) atom (see Table 3).

The complex molecules are stacked to form zigzag chains propagated along [010] in which the dihedral angle between adjacent basal planes is 58.6°. Even though the intrachain Cu···Cu spacing is just 6.880 Å, molecular *g* components were observed by EPR spectroscopy. Glide-mirror planes parallel to (001) generate a second zigzag chain containing two additional orientations of Cu^{II} coordination pyramids. The shortest interchain Cu···Cu distance is 7.396 Å. In other complexes of this type (Warda, 1994), Cu···Cu spacings shorter than 8 Å give rise to a coupling of the *g* tensor components of magnetically non-equivalent Cu^{II} ions, *i.e.* centres of square pyramids with differently oriented fourfold axes. However, EPR spectroscopic properties of single crystals of the title compound present a system of four differently oriented molecular *g* tensors in agreement with the structural result.

Experimental

The title crystal was prepared by the reaction of aqua(*N*-salicylideneglycinato)copper(II) hemihydrate with 3,5-dimethylpyrazole in the ratio 1:2 using ethanol–water (3:1) as solvent (see Plesch *et al.*, 1987).

Crystal data

[$Cu(C_9H_7NO_3)(C_5H_8N_2)$-
(H_2O)]
$M_r = 354.84$
Orthorhombic
Pbca
$a = 18.308\,(2)$ Å
$b = 7.262\,(1)$ Å
$c = 22.805\,(3)$ Å
$V = 3032.0$ Å^3
$Z = 8$
$D_x = 1.555$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18.48$–$24.06°$
$\mu = 1.462$ mm^{-1}
$T = 293$ K
Needle
0.30 × 0.20 × 0.15 mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
3524 measured reflections
3076 independent reflections
2063 observed reflections $[I > 2\sigma(I)]$
$\theta_{\rm max} = 26.31°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 9$
$l = -28 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0472$
$wR(F^2) = 0.1161$
$S = 1.076$
3074 reflections
220 parameters
All H-atom parameters refined for five H atoms
$w = 1/[\sigma^2(F_o^2) + (0.0797P)^2 + 0.97P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = <0.001$
$\Delta\rho_{\rm max} = 0.76$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.82$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0035 (6)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu(1)	0.0904 (1)	0.0594 (1)	0.1288 (1)	0.036 (1)
O(1)	0.0169 (2)	0.2441 (4)	0.1265 (1)	0.047 (1)
O(2)	0.1641 (2)	−0.1359 (4)	0.1261 (1)	0.047 (1)
O(3)	0.1883 (2)	−0.4176 (4)	0.0958 (2)	0.051 (1)
O(4)	0.1672 (2)	0.2191 (4)	0.0652 (1)	0.042 (1)
N(1)	0.0328 (2)	−0.1201 (4)	0.0850 (1)	0.034 (1)
N(2)	0.1412 (2)	0.1617 (4)	0.2000 (2)	0.039 (1)
N(3)	0.2149 (2)	0.1526 (5)	0.2024 (2)	0.041 (1)
C(1)	−0.0467 (2)	0.2313 (5)	0.1013 (2)	0.035 (1)
C(2)	−0.0939 (2)	0.3847 (6)	0.1036 (2)	0.045 (1)
C(3)	−0.1616 (2)	0.3834 (7)	0.0784 (2)	0.052 (1)
C(4)	−0.1874 (2)	0.2279 (7)	0.0494 (2)	0.052 (1)
C(5)	−0.1441 (2)	0.0749 (7)	0.0466 (2)	0.045 (1)
C(6)	−0.0733 (2)	0.0725 (6)	0.0714 (2)	0.036 (1)
C(7)	−0.0318 (2)	−0.0934 (5)	0.0646 (2)	0.035 (1)
C(8)	0.0704 (2)	−0.2965 (6)	0.0759 (2)	0.039 (1)
C(9)	0.1468 (2)	−0.2831 (6)	0.1007 (2)	0.039 (1)
C(10)	0.2412 (3)	0.2036 (6)	0.2545 (2)	0.047 (1)
C(11)	0.1820 (3)	0.2441 (6)	0.2883 (2)	0.054 (1)
C(12)	0.1208 (3)	0.2189 (6)	0.2532 (2)	0.045 (1)
C(13)	0.0420 (3)	0.2474 (8)	0.2679 (2)	0.068 (2)
C(14)	0.3213 (3)	0.2108 (7)	0.2665 (2)	0.061 (1)

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

Cu(1)—O(1)	1.900 (3)	O(3)—C(9)	1.242 (5)
Cu(1)—N(1)	1.952 (3)	N(1)—C(7)	1.285 (5)
Cu(1)—O(2)	1.959 (3)	N(1)—C(8)	1.469 (5)
Cu(1)—N(2)	2.014 (3)	N(2)—C(12)	1.334 (5)
Cu(1)—O(4)	2.328 (3)	N(2)—N(3)	1.351 (5)
O(1)—C(1)	1.302 (5)	N(3)—C(10)	1.335 (5)
O(2)—C(9)	1.257 (5)		
O(1)—Cu(1)—N(1)	94.3 (1)	O(2)—Cu(1)—O(4)	85.7 (1)
O(1)—Cu(1)—O(2)	176.4 (1)	N(2)—Cu(1)—O(4)	92.3 (1)
N(1)—Cu(1)—O(2)	82.7 (1)	C(7)—N(1)—C(8)	120.8 (3)
O(1)—Cu(1)—N(2)	95.0 (1)	C(7)—N(1)—Cu(1)	125.6 (3)
N(1)—Cu(1)—N(2)	155.3 (1)	C(8)—N(1)—Cu(1)	113.6 (2)
O(2)—Cu(1)—N(2)	88.5 (1)	N(3)—N(2)—Cu(1)	118.4 (3)
O(1)—Cu(1)—O(4)	93.4 (1)	O(3)—C(9)—O(2)	123.7 (4)
N(1)—Cu(1)—O(4)	109.9 (1)	O(3)—C(9)—C(8)	118.8 (4)
O(1)—Cu(1)—N(1)—C(7)	0.9 (3)		
O(2)—Cu(1)—N(1)—C(7)	−177.1 (3)		
N(2)—Cu(1)—N(1)—C(7)	112.9 (4)		
O(4)—Cu(1)—N(1)—C(7)	−94.3 (3)		
O(1)—Cu(1)—N(1)—C(8)	−179.7 (3)		
N(2)—Cu(1)—N(1)—C(8)	−67.7 (4)		
O(1)—Cu(1)—N(1)—O(4)	95.2 (1)		
N(2)—Cu(1)—N(1)—O(4)	−152.8 (3)		
N(1)—Cu(1)—N(2)—N(3)	105.1 (4)		
N(1)—C(8)—C(9)—O(3)	−178.1 (4)		
N(2)—N(3)—C(10)—C(14)	−177.8 (4)		
N(3)—N(2)—C(12)—C(13)	179.6 (4)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N3—H8···O2	0.86	2.57 (3)	2.88 (1)	103
N3—H8···O3$^{\rm i}$	0.86	2.20 (3)	3.05 (1)	170
O4—H16···O3$^{\rm i}$	0.97	2.02 (3)	2.91 (1)	152
O4—H17···O3$^{\rm ii}$	0.97	2.13 (3)	2.77 (1)	121

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (ii) $x, 1 + y, z$.

The title structure was solved by the Patterson method (*SHELXS*86; Sheldrick, 1985). Anisotropic displacement parameters were refined for all non-H atoms. All H atoms were located from difference Fourier maps, but the positional and isotropic displacement parameters were refined for only five of them.

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *Express*. Data reduction: *XCAD*-4 (Harms, 1994). Program(s) used to solve structure: *SHELXS*86. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93 and *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1236). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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mer-Triaqua(chloranilato-*O*,*O*′)chloroiron(III) Pentahydrate

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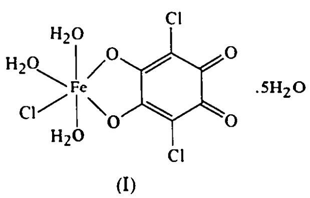
(*Received 18 October 1995; accepted 3 May 1996*)

Abstract

The crystal structure of the title compound, [FeCl($C_6Cl_2O_4$)(H_2O)$_3$].5H_2O, shows it to be a monomeric iron(III) complex with the metal ion chelated by the dianion of chloranilic acid (2,5-dichloro-3,6-dihydroxy-2,5-cyclohexadiene-1,4-dione). The octahedral coordination environment is completed by a chloride ion and three water molecules which are in a *mer* arrangement. Extensive hydrogen bonding occurs between the complex and lattice water molecules.

Comment

It has long been known that 2,5-dihydroxy-1,4-benzoquinone and its derivatives are capable of forming complexes with a variety of metals (Frank, Clark & Coker, 1950). As part of an examination of chelating ligands which have the potential to bridge metal centres, the reaction between ferric chloride and chloranilic acid in an aqueous ethanolic solution was investigated. Crystals of the title compound, (I), were obtained from this solution.



(I)

The ferric ion is octahedrally coordinated by two O atoms of a chloranilate dianion, three water molecules and a chloride ion (Fig. 1). The three aqua ligands adopt a *mer* configuration. The bite angle of the chloranilate anion and the size of the chloride ligand are largely responsible for the distortion from ideal octahedral geometry. A small degree of asymmetry is apparent in the chelation of the chloranilate ligand. The C—O atomic separations in the chloranilate dianion are significantly shorter for the non-coordinating O atoms. The variation in the ring C—C separations indicates that the canonical form of the ligand represented in the structural diagram is a major contributor to the structure. The geometry of the chelating ligand is very similar to

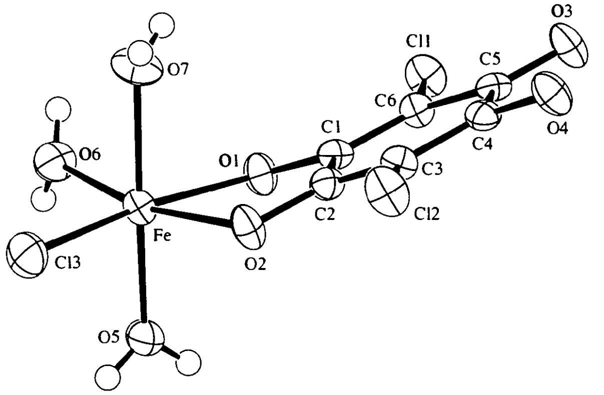


Fig. 1. An *ORTEP*II (Johnson, 1976) diagram of compound (I). Displacement ellipsoids are at the 50% probability level and H atoms are represented by spheres of arbitrary size. Solvate water molecules have been omitted for clarity.

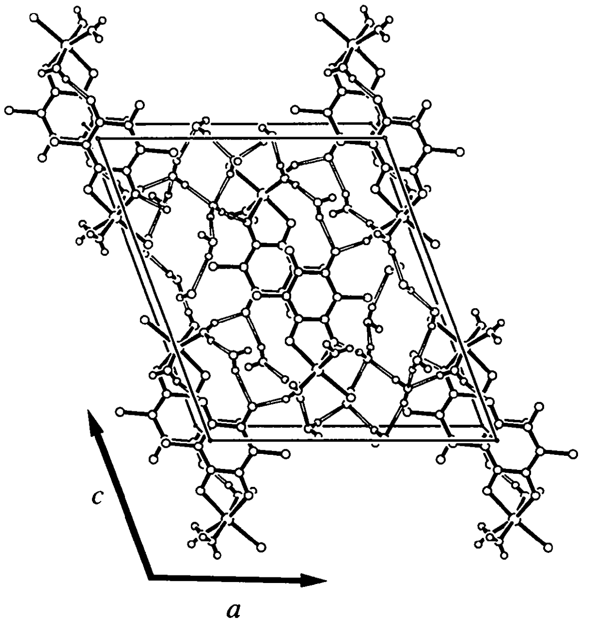


Fig. 2. An *ORTEP*II (Johnson, 1976) diagram of the unit cell of (I). Atoms are of arbitrary size and double lines represent hydrogen bonds.

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