O1—Cu—N1	94.19 (8)	O2—Cu—N2	89.79 (8)
O1—Cu—O2	177.67 (8)	O1—Cu—O1^{i}	82.79 (7)
N1—Cu—O2	83.50 (9)	N1—Cu—O1^{i}	105.32 (8)
O1—Cu—N2	92.51 (8)	O2—Cu—O1^{i}	97.56 (7)
N1—Cu—N2	162.91 (8)	N2—Cu—O1^{i}	91.10 (7)

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H41···O5^{i}	0.90 (4)	2.19 (4)	2.997 (4)	150 (4)
O4—H42···O5^{ii}	0.90 (4)	2.02 (4)	2.895 (4)	165 (4)
O5—H51···O3^{iii}	0.90 (4)	2.04 (4)	2.914 (4)	165 (4)
O5—H52···O3	0.90 (4)	2.02 (4)	2.877 (5)	160 (4)

Symmetry codes: (i) $2-x, 1-y, -z$; (ii) $x, y, z-1$; (iii) $1-x, 1-y, 1-z$.

All H atoms, except the water H atoms, were included at calculated positions using *SHELXL*97 (Sheldrick, 1997) and refined using a riding model. The U_{iso} of H atoms of CH and CH_2 groups, and the methyl group were taken as $1.2U_{eq}$ and $1.5U_{eq}$ of the parent atoms, respectively. The H41, H42, H51 and H52 atoms were found from difference Fourier syntheses and refined with $U_{iso} = 1.2U_{eq}$ of the water oxygen; O—H distances were restrained as equal. Atom C10 may be slightly disordered; the residual electron density of 0.86 e Å^{-3} at a distance of 1 Å from H8 is unusually high. However, no disorder model proved satisfactory. An analytical absorption correction based on face indexing was carried out with the following faces and distances (mm): $0\bar{2}\bar{1}$ 0.0924, 021 0.0924, $20\bar{1}$ 0.0962, $\bar{2}01$ 0.1925, 001 0.0192 and $00\bar{1}$ 0.0192.

Data collection: *IPDS* (Stoe & Cie, 1997). Cell refinement: *IPDS*. Data reduction: *IPDS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *XP* in *SHELXTL* (Siemens, 1996*b*). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1252). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 304–306

Dimeric (Imidazole-N^3)(*N*-salicylidene-*rac*-alaninato-*O*,*N*,*O*′)copper(II)†

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Abstract

The title compound, $[Cu(C_{10}H_9NO_3)(C_3H_4N_2)]_2$, adopts a square-pyramidal copper(II) coordination with three donor atoms of the *N*-salicylidene-*rac*-alaninato Schiff base dianion and the imidazole ligand bound in the basal plane. The axial position is occupied by an oxygen ligand from an adjacent chelate at an apical distance of 2.500 (3) Å, forming a centrosymmetric dimer. These dimers are connected through hydrogen bonding to form chains parallel to [010]. All copper polyhedra belonging to one chain are oriented parallel to each other, whereas between the two types of chains they are tilted at an angle 2γ of 38.9(2)°.

Comment

Copper(II) complexes with tridentate Schiff base dianions of the *N*-salicylideneaminoacidato type (TSB^{2-}) represent a suitable model for the elucidation of structural and spectroscopic correlations. We are interested in the behaviour of the electron paramagnetic resonance (EPR) signal of Jahn–Teller ions with respect to the local geometry and the dipolar interaction between differently oriented polyhedra. For unambiguous interpretation of EPR results, X-ray structure determinations of a range of substances were undertaken.

Recently, we reported the structures of two imidazole–(TSB–Cu^{II}) complexes. In the case of imidazole(*N*-salicylidene-α-amino-2-methylpropanato)copper(II), (Warda, 1997*a*), the molecules are arranged in dimeric units connected by the phenolic O atom of a neighbouring monomer at an apical distance of 2.623 (2) Å. The tilting angle between the copper(II) polyhedra is 66.7 (2)°. The second imidazole compound, imidazole(*N*-salicylideneglycinato)copper(II) (Warda, 1997*b*), polymerizes *via* carboxylic bridging at an apical distance of 2.563 (2) Å and has a tilting angle of 88.8 (2)°. In both cases, the C8 atom is achiral.

In the title compound, (I), the monomeric unit of which is shown in the formula scheme, the C8 atom is chiral; the compound crystallizes as a racemate. The

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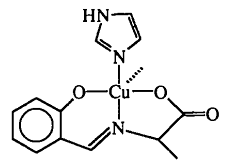
copper ions adopt (4+1) square-pyramidal geometry defined by the tridentate *N*-salicylidene-*rac*-alaninato dianion (ONO^{2-} chelator) and the neutral monodentate imidazole ligand in the basal plane. The Cu atom is shifted from this plane by 0.130 (1) Å toward the apical ligand (*PLATON*; Spek, 1995).



(I)

The O1 atom (Fig. 1) is part of the basal plane of one molecule and acts at the same time as the apical ligand at the copper centre of a second monomer forming centrosymmetric dimers. The imidazole ring is twisted from the mean plane (O1, N1, O2, N2) with an angle of 20.9 (2)°. All the equatorial copper distances are in the normal range. The most variable copper distance in this class of compounds is the apical one, which is 2.500 (3) Å in (I).

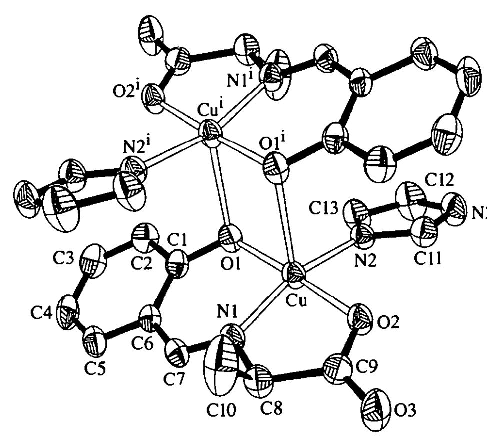


Fig. 1. The dimeric unit of the title compound with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

The structure is further stabilized by hydrogen bonding N3—H31···O3($-x$, $-y$, $2-z$), forming chains of dimers. The copper(II) polyhedra in these chains are oriented parallel to each other and [010]. The symmetry-related chains ($-x$, $-y$, $-z$) are tilted by 2γ = 38.9 (2)°.

As a consequence of this ordering (Warda, 1994), EPR patterns of (I) display a slightly coupled *g* tensor (non-molecular), indicating a distorted ferrodistortive ordering ($0 < 2\gamma < 45°$). The value of the *g* tensor allows the tilting angle between the differently oriented copper(II) polyhedra to be estimated as 39°, which is in good agreement with X-ray data.

Experimental

The title compound was synthesized from aqua(*N*-salicylidene-*rac*-alaninato)copper(II) dihydrate by a method analogous to that reported by Ueki *et al.* (1967) and Warda (1994) with imidazole.

Crystal data

$[Cu(C_{10}H_9NO_3)(C_3H_4N_2)]$
M_r = 322.80
Monoclinic
$P2_1/n$
a = 7.9688 (9) Å
b = 9.9716 (10) Å
c = 17.2571 (13) Å
β = 98.592 (9)°
V = 1355.9 (2) Å^3
Z = 4
D_x = 1.581 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 19.98–22.96°
μ = 1.621 mm^{-1}
T = 293 (2) K
Prism
0.384 × 0.180 × 0.060 mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: empirical with ψ scans (*SHELXTL*; Sheldrick, 1996)
T_{min} = 0.575, T_{max} = 0.909
2562 measured reflections
2382 independent reflections

1736 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 25.03°
$h = -9 \rightarrow 0$
$k = 0 \rightarrow 11$
$l = -20 \rightarrow 20$
2 standard reflections frequency: 120 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.097
S = 1.029
2382 reflections
181 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0530P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.513 e Å^{-3}
$\Delta\rho_{min}$ = −0.350 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu—O1	1.930 (2)	Cu—N2	1.966 (3)
Cu—N1	1.933 (3)	Cu—O1^{i}	2.500 (3)
Cu—O2	1.965 (2)	N1—C7	1.277 (5)
O1—Cu—N1	93.12 (11)	O2—Cu—N2	91.34 (11)
O1—Cu—O2	176.25 (10)	O1—Cu—O1^{i}	82.74 (10)
N1—Cu—O2	83.16 (11)	N1—Cu—O1^{i}	104.60 (11)
O1—Cu—N2	92.37 (11)	O2—Cu—O1^{i}	97.68 (10)
N1—Cu—N2	163.73 (13)	N2—Cu—O1^{i}	91.27 (11)

Symmetry code: (i) $-x, 1-y, 2-z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N3—H31···O3^{i}	0.91	1.85	2.751 (5)	170

Symmetry code: (i) $-x, -y, 2-z$.

All H atoms, except for H31, were placed in calculated positions with *SHELXL*97 (Sheldrick, 1997*b*) and refined using a riding model. The U_{iso} values of the H atoms were set to 1.2 times greater than U_{eq} of the parent atoms (CH, NH, CH_2)

and 1.5 times as large as U_{eq} of C10. The position of the H31 atom was found from a difference Fourier synthesis and refined using a riding model.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *XCAD4* (Harms, 1997). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990, 1997*a*). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1996). Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1251). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 306–308

Diaquabis(5-methoxycarbonyl-3,6-dimethylpyrazine-2-carboxylato-N^1,*O*)copper(II)

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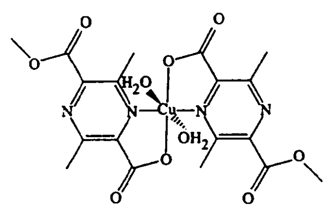
Abstract

The reaction of the bis(methyl ester) of 3,6-dimethylpyrazine-2,5-dicarboxylic acid with copper perchlorate leads to the formation of the centrosymmetric mononuclear complex [Cu($C_9H_9N_2O_4$)$_2$(H_2O)$_2$]. Two partially hydrolysed (ionized) ligands are coordinated, in a bidentate fashion, to the Cu atom. The Cu coordination sphere is completed by two water molecules. Symmetry-related molecules are linked by a strong hydrogen bond, involving the carbonyl O atom of the carboxylato group and the coordinated water molecules, to form a two-dimensional network.

Comment

Metal-catalysed hydrolysis of amino acid esters is a well known phenomenon (Dugas, 1989). We have shown recently (Neels *et al.*, 1997) by powder diffraction analysis that the reaction of the bis(methyl ester) of pyrazine-2,3-dicarboxylic acid with $CuCl_2$ leads to partial hydrolysis of the ligand and the formation of a two-dimensional coordination polymer. This structure is quite different from that which results from the reaction of pyrazine-2,3-dicarboxylic acid (H2pzdc) with $CuCl_2$. That reaction leads to the formation of a one-dimensional coordination polymer (Cupzdc; O'Connor *et al.*, 1982) in which the ligand coordinates in a bis-bidentate fashion, symmetry-related ligands being perpendicular to one another along the chain. The fivefold coordination of the Cu atom is completed by a Cl atom. Interestingly, this complex was shown to be ferromagnetic. Hence, quite different compounds can be synthesized using the ester derivatives of these unusual amino acids.

We report here on the reaction of the bis(methyl ester) of 3,6-dimethylpyrazine-2,5-dicarboxylic acid (MeL1) with $Cu(ClO_4)_2$, in a metal-to-ligand ratio of 2:1. This results in the formation of a mononuclear complex, (I), with two partially ionized ligands coordinated, each in an *N*,*O*-bidentate fashion, to the Cu atom, the coordination sphere of which is completed by two water molecules (Fig. 1). The same compound was obtained irrespective of the metal-to-ligand ratio used. The presence of two different C═O bonds, contained in coordinated and uncoordinated carboxylic groups, was indicated by the presence of two absorption bands centred at 1647 and 1737 cm^{-1}.



(I)

The molecule possesses C_i symmetry. The Cu atom sits on a centre of symmetry, adopting square-bipyramidal coordination geometry with the pyrazine N

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