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: *XCAD*4 (Harms, 1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990, 1997*a*). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1996). Software used to prepare material for publication: *SHELXL*97.

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

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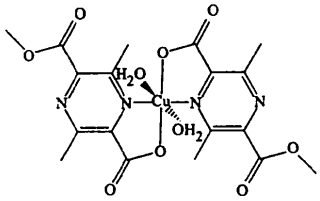
Abstract

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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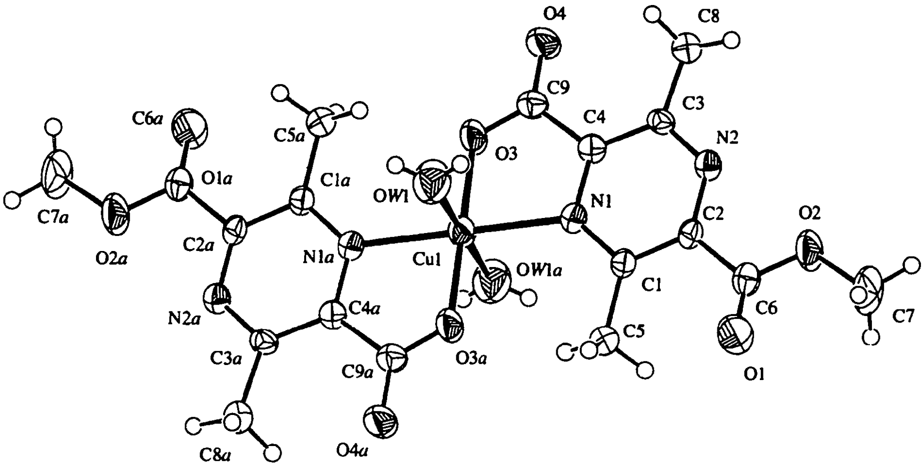

Fig. 1. Perspective view of the title complex, with displacement ellipsoids at the 50% probability level and H-atom radii arbitrary.

atoms (N1) and the carboxylato O atoms (O3) lying in the basal plane. The apical positions are occupied by two water molecules. The Cu—N(pyrazine) distance is 2.135 (4) Å, which is similar to the corresponding values [2.139 (4) and 2.140 (2) Å] observed in two copper(II) complexes prepared with the ligand pyrazinetetracarboxylic acid (Cupztc; Graf *et al.*, 1993). The corresponding distances in Cupzdc are much shorter [2.00 (1) and 2.01 (1) Å]. The Cu—O(carboxylato) distance is 1.895 (4) Å, which is again similar to those observed in the Cupztc complexes [1.904 (3) and 1.901 (1) Å]. However, the corresponding distances in the Cupzdc complex are much longer [1.99 (1) and 2.19 (1) Å]. The Cu—O(water) distance [2.470 (6) Å] is similar to that observed in the Cupzdc complex (2.473 Å). In a series of Cupztc complexes, Cu—O(water) distances of 2.03 (4), 2.37 (1) and 2.57 (3) Å have been observed. A review of the Cambridge Structural Database (Allen & Kennard, 1993) reveals that this variation is typical for copper–pyridine and copper–pyrazinecarboxylate complexes.

The methoxycarbonyl group is twisted out of the plane of the pyrazine ring by 17.7 (7)°. The pyrazine ring is twisted by 6.0 (7)° (dihedral angle between the N1, C1, C4 and N2, C2, C3 planes). Larger deformations of the pyrazine ring (9.9–11.6°) have been observed previously, notably in some Cu$^{\rm II}$, Ni$^{\rm II}$ and Zn$^{\rm II}$ binuclear complexes of the pyrazine ligand tetra-2,3,5,6-(2-pyridyl)pyrazine (Graf *et al.*, 1997; Graf & Stoeckli-Evans, 1994). Distances and angles within the methyl ester ligand are unexceptional.

In the crystal, intermolecular hydrogen bonds, each involving a coordinated water molecule and the carbonyl O atom (O4) of the carboxylato group, link the molecules to form a two-dimensional network in the *bc* plane [O*W*1···O4$^{\rm i}$ 2.984 (8), H12···O4$^{\rm i}$ 2.23 (9) Å and O*W*1—H12···O4$^{\rm i}$ 177 (9)°; symmetry code: (i) $-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$]. A three-dimensional network is then built up in the **a** direction by weak hydrogen bonds, each involving a coordinated water molecule and atom O2 of the methoxycarbonyl group [O*W*1···O2$^{\rm ii}$ 3.046 (8), H11···O2$^{\rm ii}$ 2.57 (10) Å and O*W*1—H11···O2$^{\rm ii}$ 130 (10)°; symmetry code: (ii) $-1-x$, $-y$, $-z$].

Experimental

The ligand dimethyl 3,6-dimethylpyrazine-2,5-dicarboxylate (MeL1) was synthesized by a one-pot reaction combining catalytic reduction of methyl 2-oximinoacetoacetate (Iida *et al.*, 1973) over an Rh/C catalyst at low pressure (3.0–3.5 atm; 1 atm = 101 325 Pa), followed by self-condensation and oxidation. It was not necessary to isolate the active intermediate methyl 2-aminoacetoacetate. The title compound was prepared by adding a suspension of MeL1 (116 mg, 0.5 mmol) in 10 ml of water to a solution of $Cu(ClO_4)_2.6H_2O$ (371 mg, 1 mmol) in 10 ml of water with stirring at 343 K. Green precipitates were formed over a variable period. The precipitates were filtered off, washed with ethanol and water, and dried in air (yield: 67%, 87 mg). A small number of very small pale green–blue single crystals of the title complex were found on the walls of the glassware. M.p. > 573 K (decomposition).

Crystal data

$[Cu(C_9H_9N_2O_4)_2(H_2O)_2]$
$M_r = 517.94$
Monoclinic
$P2_1/c$
$a = 8.907\ (1)$ Å
$b = 10.042\ (2)$ Å
$c = 11.927\ (2)$ Å
$\beta = 103.64\ (1)°$
$V = 1036.7\ (3)$ Å^3
$Z = 2$
$D_x = 1.659$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 19 reflections
$\theta = 14.0–19.5°$
$\mu = 1.097$ mm^{-1}
$T = 295\ (2)$ K
Lozenge
0.30 × 0.11 × 0.11 mm
Pale green–blue

Data collection

Stoe AED-2 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1356 measured reflections
1356 independent reflections
893 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 22.51°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 12$
2 standard reflections
frequency: 60 min
intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.116$
$S = 1.144$
1352 reflections
163 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 1.6057P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$

$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0010 (11)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu1—O3	1.895 (4)	Cu1—*O*W1	2.470 (6)
Cu1—N1	2.135 (4)		
O3—Cu1—N1	80.6 (2)	N1—Cu1—*O*W1	91.8 (2)
O3—Cu1—*O*W1	91.6 (2)		

The crystal did not diffract significantly beyond 45° in 2θ and diffraction data were not measured beyond this limit. Water H atoms were located from difference maps and refined isotropically. The remainder were included in calculated positions and treated as riding atoms using *SHELXL*93 (Sheldrick, 1993) default parameters, except that one parameter was refined for each methyl group to define its orientation.

Data collection: *DIF*4 (Stoe & Cie, 1995). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1996). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *PLATON*/*PLUTON* (Spek, 1990). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1367). Services for accessing these data are described at the back of the journal.

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cis-Dichloro(2-diphenylphosphinoethylamine-*N*,*P*)palladium(II)

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Abstract

The coordination geometry about the palladium(II) ion in $[PdCl_2\{Ph_2P(CH_2)_2NH_2\}]$ is distorted square planar. Individual atoms are displaced from the $PdCl_2PN$ coordination plane by no more than 0.094 Å, while in-plane distortion of the bond angles at the metal atom is more marked. The greater *trans* influence of phosphine over amine is reflected in the mean Pd—Cl bond lengths of 2.383 Å, *trans* to P, and 2.293 Å, *trans* to N.

Comment

Hybrid ligands with both hard and soft donor atoms are able to form hemi-labile complexes which have been noted for their utility in catalytic systems (Bader & Lindner, 1990; Wehman *et al.*, 1995). To this end, we are currently studying the complexes of a series of tridentate Schiff base ligands having P-, N- and O-donor atoms. The title compound, (I), was obtained unexpectedly from the reaction of one of those ligands, o-$C_6H_4(OH)\{C{=}N(CH_2)_2PPh_2\}$ (Dilworth *et al.*, 1994), with $[PdCl_2(NCPh)_2]$ in chloroform. We believe that the ligand (either free or complexed) undergoes acid-catalysed hydrolysis of the imine linkage (there is often a trace of HCl in $CHCl_3$) to give 2-diphenylphosphinoethylamine and hence its palladium chloride complex. The preparation of this compound has been noted previously (Suzuki *et al.*, 1996).