2132 measured reflections
2132 independent reflections
2 standard reflections
  frequency: 100 min
  intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.024$
$wR(F^2) = 0.059$
$S = 0.901$
2132 reflections
217 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.043$
$\Delta\rho_{\max} = 0.504$ e Å^{-3}
$\Delta\rho_{\min} = -0.269$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0047 (17)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.100 (13)

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

Cu1—N4	1.964 (3)	S2—C8	1.605 (3)
Cu1—N3	1.963 (3)	N1—C1	1.468 (5)
Cu1—N1	2.026 (3)	N2—C2	1.484 (5)
Cu1—N2	2.042 (3)	N3—C7	1.141 (4)
Cu1—O1	2.342 (3)	N4—C8	1.154 (4)
S1—C7	1.622 (3)	C1—C2	1.502 (6)
N4—Cu1—N3	89.48 (13)	N3—Cu1—O1	88.53 (13)
N4—Cu1—N1	90.60 (12)	N1—Cu1—O1	94.72 (12)
N3—Cu1—N1	176.65 (13)	N2—Cu1—O1	99.35 (12)
N1—Cu1—N2	86.61 (11)	N3—C7—S1	178.8 (3)
N4—Cu1—O1	102.99 (14)	N4—C8—S2	179.6 (3)

Data collection: Syntex $P2_1$ software. Cell refinement: Syntex $P2_1$ software. Data reduction: *XP*21 (Pavelčík, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). 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.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1023). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 553–555

Diaquabis(pyridazin-1-ium-3,6-dicarboxylato-N^2,O^3)copper(II) dihydrate

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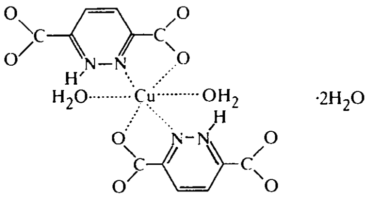
Abstract

The crystal structure of the title compound, $[Cu(C_6H_3N_2O_4)_2(H_2O)_2]\cdot 2H_2O$, shows it to exist as a monometalic and centrosymmetric complex with octahedral coordination of copper to each of two pyridazinium-3,6-dicarboxylate groups lying in the equatorial plane *via* one N and one O atom, and to two water molecules in *trans*-diaxial positions. Two additional water molecules are included in the cell. A network of hydrogen bonding links the carboxyl groups and the water molecules of the cell.

Comment

Interest in complexes of copper with small heterocyclic molecules stems from their use as organic precursors for bismuth-based metal oxides (Conflant *et al.*, 1992).

The title compound, diaquabis(pyridazin-1-ium-3,6-dicarboxylato)copper(II) dihydrate, (I), crystallizes as a monometalic cluster with a pseudo-octahedral copper(II) ion bound in the equatorial plane to each of two bidentate pyridazinium-3,6-dicarboxylate molecules *via* an N atom of the pyridazine ring and one O atom of the carboxylate group *ortho* to it [Cu—N 1.970 (2) and Cu—O 1.960 (2) Å]. Two distant and *trans*-diaxial water molecules complete the coordination sphere [Cu—O 2.506 (3) Å].



(I)

Monomeric clusters lie on parallel planes and are linked by a network of hydrogen bonding. The copper-bonded water molecules (O88) are found on the planes adjacent to those of the Cu atom (bound to the water molecule) and are seen to be involved in hydrogen bonds to the carboxylic acid O atoms O1($1+x$, y, z) and O3($2-x$, $1-y$, $1-z$) found in the same layer as the bonded H_2O group; the O···H distances are 1.98 and 1.91 Å, respectively. The water molecules (O99) not bonded to copper are similarly involved in two hydrogen bonds, to the carboxyl O atoms of the neighboring carboxylate atoms O2($1+x$, $-1+y$, z) and O4($-1+x$, y, z), with distances of 1.968 and 1.968 Å, respectively. All hydrogen-bonded interactions are intra-layer. The only interaction seen between layers is the long Cu···O interaction.

The equivalence of the C7—O1, C7—O2, C8—O3 and C8—O4 bond lengths argues that neither carboxylate group is protonated and is consistent with the presence of the proton on the N2 atom. This H atom is hydrogen bonded to the O3 atom (2.359 Å) of the same ligand molecule and to the O1($1-x$, $1-y$, $1-z$) atom (2.716 Å) of the molecule related by the center of symmetry at copper.

It is notable that this structure does not display the double hydrogen bonding typical of pairs of carboxylic acid molecules. However, this behavior is also absent in the structure of the hydrated parent ligand pyridazine-3,6-dicarboxylic acid, where water molecules are found hydrogen bonded to carboxylic acid groups (Sueur *et al.*, 1987).

The ligand pyridazine-3,6-dicarboxylic acid, with one or more unshared pairs of electrons localized on six different atoms, presents numerous possible modes of coordination to transition metals, both in monoanionic and in dianionic form. Indeed, a number of these have been observed. The complex $[Cu_2(3,6\text{-dicarboxylatopyridazine})_2(H_2O)_2]$ (Mernari *et al.*, 1999) shows dianionic ligands acting in a tetradentate fashion and linking Cu atoms in dimers. The arrangement of organic ligands is coplanar, with axial water molecules completing the coordination sphere, similar to that observed in the title structure. However, the diaxial positions are occupied by one water molecule and by the carboxylate O atom of a molecule on an adjacent layer.

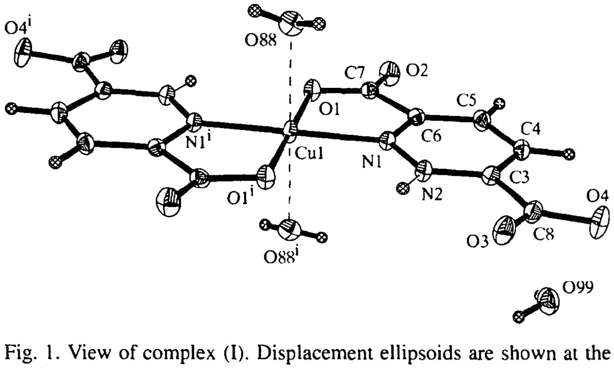


Fig. 1. View of complex (I). Displacement ellipsoids are shown at the 50% probability level.

The existence of the complexes $[Mn(3,6\text{-carboxycarboxylatopyridazine})_2(H_2O)_2]\cdot 2H_2O$, (II), and $[Mn_2(3,6\text{-dicarboxylatopyridazine})_2(H_2O)_4]$, (III), has been suggested by physical measurements (El Gueddi *et al.*, 1998). Complex (II) (El Gueddi *et al.*, 1996) has been shown by single-crystal X-ray diffraction studies to be monomeric and similar to the title structure. Both show a *trans* orientation of two N atoms (and also of two O atoms) in the equatorial plane. The monomeric manganese and copper structures differ in the details of their hydrogen bonding.

Experimental

$Cu(NO_3)_2\cdot 2H_2O$ and 0.5 *M* HNO_3 were mixed together to form a solution to which a stoichiometric quantity of pyridazine-3,6-dicarboxylic acid (Sueur *et al.*, 1987) was added. The resulting blue precipitate was collected by filtration and heated in 0.5 *M* HNO_3. The solution was allowed to cool slowly, producing blue–green plates and green–blue needles.

Crystal data

$[Cu(C_6H_3N_2O_4)_2(H_2O)_2]\cdot 2H_2O$
$M_r = 469.81$
Triclinic
$P\bar{1}$
$a = 5.406\,(4)$ Å
$b = 6.512\,(4)$ Å
$c = 13.118\,(5)$ Å
$\alpha = 74.52\,(3)^\circ$
$\beta = 79.40\,(3)^\circ$
$\gamma = 70.30\,(3)^\circ$
$V = 416.7\,(4)$ Å^3
$Z = 1$
$D_x = 1.872$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 15.0\text{–}29.6^\circ$
$\mu = 1.391$ mm^{-1}
$T = 293\,(2)$ K
Needle
0.2 × 0.1 × 0.1 mm
Green–blue

Data collection

Phillips PW1100 diffractometer
ω–2θ scans
Absorption correction: none
2343 measured reflections
2253 independent reflections
2144 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.017$
$\theta_{\rm max} = 30.05^\circ$
$h = -7 \rightarrow 7$
$k = -8 \rightarrow 9$
$l = 0 \rightarrow 18$
3 standard reflections every 97 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.035$
$wR(F^2) = 0.090$
$S = 1.083$
2253 reflections
133 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 0.2065P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.49$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.57$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu1—O1^{i}	1.9603 (19)	C4—C5	1.372 (3)
Cu1—N1^{i}	1.9701 (18)	C5—C6	1.386 (3)
N1—N2	1.321 (2)	C7—O2	1.222 (3)
N1—C6	1.333 (3)	C7—O1	1.271 (3)
N2—C3	1.324 (3)	C7—C6	1.516 (3)
C3—C4	1.388 (3)	C8—O3	1.246 (3)
C3—C8	1.507 (3)	C8—O4	1.261 (3)
O1^{i}—Cu1—N1^{i}	82.26 (8)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1^{i}	0.90	2.72	3.109 (3)	108
N2—H2···O3	0.90	2.36	2.688 (3)	102
O88—H88*A*···O1^{ii}	0.85	1.98	2.825 (3)	177
O88—H88*B*···O3^{iii}	0.85	1.91	2.682 (3)	151
O99—H99*A*···O2^{iv}	0.85	1.97	2.804 (3)	168
O99—H99*B*···O4^{v}	0.85	1.97	2.694 (3)	143

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

The crystal was lost before measurements for absorption corrections could be made. Other available crystals showed insignificant diffraction. The range of expected transmission factors is relatively small (0.76–0.87) due to the crystal size (0.2 × 0.1 × 0.1 mm) and the low value of μ (1.391 mm^{-1}). The H atoms of the aromatic ring were placed in calculated positions. The two H atoms associated with each of the water molecules and that on N2 were located from a difference Fourier synthesis and their positions improved with the *HIMP* facility of *XP* (Siemens, 1990).

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1155). Services for accessing these data are described at the back of the journal.

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(1-Phenyl-1*H*-1,2,3,4-tetrazole-5-thiolato-*S*)bis(triphenylphosphine)silver(I) methanol solvate

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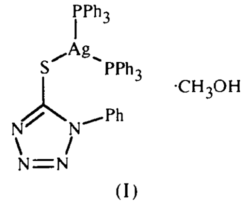
Abstract

The title compound, $[Ag(C_7H_5N_4S)(C_{18}H_{15}P)_2]\cdot CH_3OH$, contains trigonal-planar silver coordinated to the thiotetrazole ligand *via* sulfur. The presence of methanol, which hydrogen bonds to the tetrazole ring, weakens the donor capacity of the ring N atoms, preventing their interaction with silver.

Comment

The structure of $(Ph_3P)_2Ag(SCN_4Ph)$, solvated with a molecule of non-coordinating CH_2Cl_2, has been reported recently (Noth *et al.*, 1998). We now report and compare the crystal structure of the same compound as its methanol solvate, which forms part of our general interest in the coordination chemistry of thiotetrazoles (Deeth *et al.*, 1992). The gross structure adopted by the title compound, (I), is essentially the same as that reported previously (Noth *et al.*, 1998); silver is coordinated in a trigonal-planar manner by two triphenylphosphine ligands and the thiotetrazole ligand is coordinated *via* its S atom. In the discussion below, the numbering scheme of Fig. 1 is applied to both determinations for clarity of comparison.



(I)

The key difference between the two determinations is the angle at sulfur and the role of the N4 atom. In the earlier work, the angle at sulfur is acute [90.8 (2)°], which allows close approach of N4 to silver (2.897 Å) from above the P_2AgS plane (torsion angle N4—C37—S1—Ag1 117.5°). Although this does not perturb the planarity of the P_2SAg unit (sum of angles at Ag 359.9°), it was deemed responsible for the 4.8° (not 5.2° as cited) difference in the two P—Ag1—S1 angles.

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