

trans*-Bis(2-amino-5-methyl-1,3,4-thiadiazole- κ N)-bis(3,5-dicarboxybenzoato- κ O)copper(II) dihydrate*Daniel E. Lynch**School of Science and the Environment,
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EnglandCorrespondence e-mail:
apx106@coventry.ac.uk**Key indicators**

Single-crystal X-ray study

 $T = 150$ KMean $\sigma(\text{C}-\text{C}) = 0.005$ Å R factor = 0.049 wR factor = 0.133

Data-to-parameter ratio = 13.9

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The structure of the title compound, $[\text{Cu}(\text{C}_9\text{H}_5\text{O}_6)_2(\text{C}_3\text{H}_5\text{N}_3\text{S}_2)] \cdot 2\text{H}_2\text{O}$, comprises discrete units of the four-coordinate Cu complex linked *via* hydrogen-bonding interactions of the wtare molecules and the amino and carboxylic acid groups. The complex is *trans* and lies on an inversion centre. The thiadiazole is bound to the metal *via* a Cu–N [1.953 (3) Å] bond, while the acid binds *via* a carboxylate-O atom [Cu–O 1.971 (2) Å].

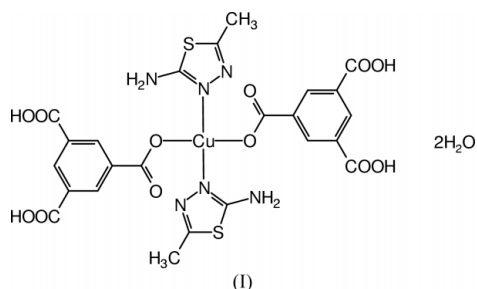
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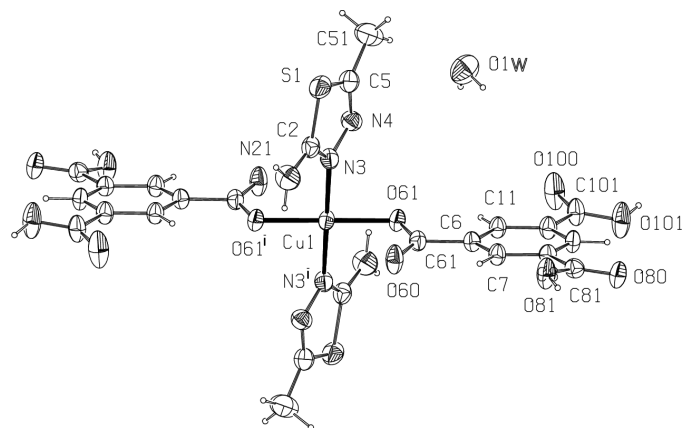
Online 27 September 2002

Comment

Copper is commonly known to form tetracarboxylato- O, O' -bridged dimers of the copper(II) acetate hydrate type (van Niekerk & Schoening, 1953) when complexed by a carboxylic acid. In the absence of other ligands, including water, these units polymerize, with each axial substituent group being a carboxylate-O atom from a neighbouring Cu dimer. When a suitable additional ligand is present, discrete units are produced (Smith *et al.*, 1996). However, none of the currently known structures of Cu with trimesic acid contain such tetracarboxylate- O, O' units. Instead a variety of five- and six-coordination geometries are observed, with only one containing a dicarboxylate- O, O' -bridged dimer (Chui, Lo *et al.*, 1999). This structure comprises a combination of Cu, benzene-1,3,5-tricarboxylate and water, although another structural variant of these ingredients is also known, in which



one carboxylate remains protonated as an acid (Pech & Pickardt, 1988). Other characterized structures based on these three components include the addition of Na^+ (Chui, Siu & Williams, 1999), pyridine (Chui, Lo *et al.*, 1999), imidazole and *N*-methylimidazole (Cheng *et al.*, 2001), whereas more complex structures include the Cu atoms coordinated by multidentate ligands, such as tris(2-pyridylmethyl)amine (Oshio & Ichida, 1995) and 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane (Ko & Suh, 2002). All except for the Oshio & Ichida (1995) complex are coordination polymers. In a series of syntheses intending to produce more Cu coordination complexes containing acid analogues of benzene-1,3,5-tricarboxylate, the title compound, (I), was prepared.


Figure 1

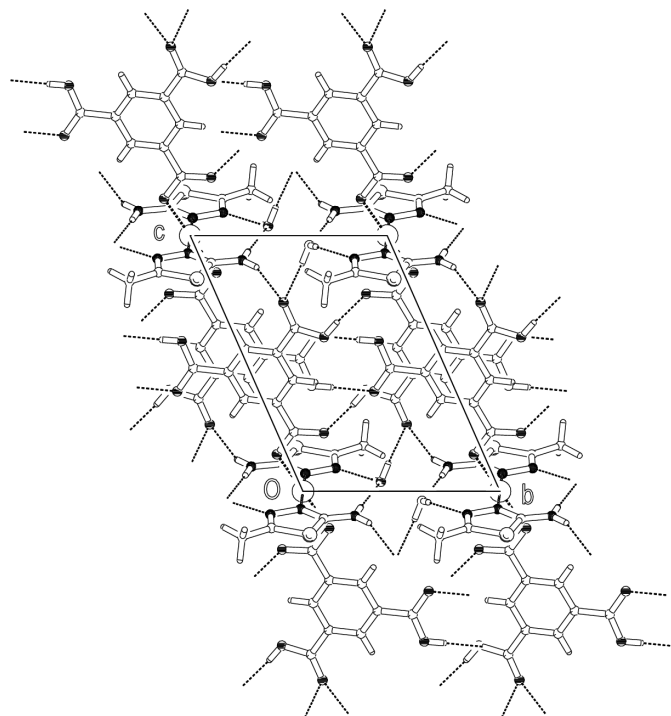
The molecular configuration and atom-numbering scheme for the title compound, showing 50% probability displacement ellipsoids [symmetry code: (i) $1 - x, 2 - y, -z$].

The addition of trimesic acid to a digestion of copper(II) carbonate in 50% aqueous ethanol yielded an instant emerald green precipitate. Total evaporation of the solvent, following removal of the insoluble material, yielded very little coloured product that was not suitably crystalline for single-crystal analysis. The same result was obtained each time, when suitable *N*-heterocyclics were added in an attempt to prevent instant precipitation of the emerald green material. However, total evaporation of the filtered solvent following the use of 2-amino-5-methyl-1,3,4-thiadiazole yielded a sprinkling of purple-coloured prisms, which were suitable for structure determination.

The structure of (I) comprises discrete units of the four-coordinate Cu complex, linked *via* hydrogen-bonding interactions of water molecules and the amino and carboxylic acid groups. Selected coordination geometry is given in Table 1, while hydrogen-bonding parameters are given in Table 2. As (I) is a symmetrical square-planar *trans* complex, the Cu atom is located on an inversion centre, with one ligand of each type and a water molecule in the asymmetric unit (Fig. 1). The thiadiazole binds to atom Cu1 *via* N3 and, following the loss of one acid H atom, the trimesic acid binds *via* atom O61, leaving the remaining two acid groups intact. The dihedral angle between the thiadiazole ring and the benzene ring is 85.1 (1)°. The 3-carboxy group (O81) associates to the non-bound carboxylate–O atom (O60) in another molecule, whereas the 5-carboxy group associates across another inversion centre to a symmetry equivalent of itself (O101–H···O100^{iv}) (Fig. 2 and Table 2). The water molecule hydrogen bonds to both N4 and the carbonyl–O atom of the 3-carboxy group (O80). One amino association also binds O80, while both O61 and O1W are subject to the other. The overall result is a complex three-dimensional hydrogen-bonded network that is totally different from the other Cu–trimesate complexes.

Experimental

The title compound was prepared according to the literature procedure of Smith *et al.* (1996), by the partial digestion of excess


Figure 2

Packing diagram for the title compound. Hydrogen-bonding associations are shown as dotted lines.

copper(II) carbonate in a 50% aqueous ethanol solution containing equimolar amounts of trimesic acid and 2-amino-5-methyl-1,3-thiadiazole. Crystals were obtained by the total evaporation of the filtered solvent.

Crystal data

[Cu(C₉H₅O₆)₂(C₃H₅N₃S)₂]₂·2H₂O
 $M_r = 748.15$
 Triclinic, $P\bar{1}$
 $a = 8.4671$ (4) Å
 $b = 8.7971$ (5) Å
 $c = 11.6748$ (6) Å
 $\alpha = 112.096$ (4)°
 $\beta = 90.354$ (3)°
 $\gamma = 110.549$ (2)°
 $V = 744.84$ (7) Å³

$Z = 1$
 $D_x = 1.668$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3147 reflections
 $\theta = 2.9$ – 27.5°
 $\mu = 0.95$ mm⁻¹
 $T = 150$ (2) K
 Prism, purple
 0.07 × 0.07 × 0.02 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.936$, $T_{\max} = 0.981$
 5879 measured reflections

3222 independent reflections
 2353 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$
 $\theta_{\text{max}} = 27.7^\circ$
 $h = -10 \rightarrow 10$
 $k = -11 \rightarrow 10$
 $l = -12 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.133$
 $S = 1.06$
 3222 reflections
 232 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0527P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.78$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Cu1—N3	1.953 (3)	Cu1—O61	1.971 (2)
N3—Cu1—O61	90.40 (9)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N21—H21...O1W ⁱ	0.88	2.04	2.904 (5)	168
N21—H22...O80 ⁱⁱ	0.88	2.13	2.949 (3)	155
O81—H81...O60 ⁱⁱⁱ	0.84 (2)	1.75 (2)	2.570 (3)	167 (4)
O101—H101...O100 ^{iv}	0.83 (2)	1.81 (2)	2.631 (3)	169 (4)
O1W—H1W...O80 ^v	0.83 (2)	2.23 (3)	2.993 (4)	152 (5)
O1W—H2W...N4 ^{vi}	0.86 (2)	2.30 (4)	3.071 (4)	150 (6)

Symmetry codes: (i) $x, 1+y, z$; (ii) $x, y, z-1$; (iii) $2-x, 3-y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $2-x, 2-y, 1-z$; (vi) $1-x, 1-y, -z$.

All methyl and amino H atoms were included in the refinement, at calculated positions, as riding models with C—H set to 0.98 Å (CH₃) and N—H set to 0.88 Å, while the three aromatic H atoms were included at calculated positions with C—H set to 0.95 Å; their isotropic displacement parameters were freely refined. The two water H atoms were initially located from a difference map, but were then restrained to an O—H distance of 0.83 Å, while their isotropic displacement parameters were freely refined. The two carboxylic acid H atoms were generated positions likely to form hydrogen bonds with adjacent hydrogen-bond acceptor atom, and were restrained to an

O—H distance of 0.83 Å, while the isotropic displacement parameters were set equal to 1.25 times U_{eq} of the preceding normal atom. In the difference map, the deepest hole of $-0.78 \text{ e } \text{Å}^{-3}$ was 0.88 Å from Cu1.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLUTON94* (Spek, 1994) and *PLATON97* (Spek, 1997); software used to prepare material for publication: *SHELXL97*.

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