

Bis(2-amino-2-thiazolinium) tetra- μ -formato- κ^8 O:O'-bis[(formato- κ O)-copper(II)]

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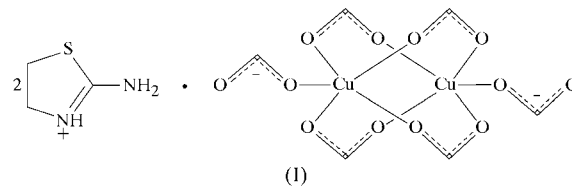
In the title dimeric compound, $(C_3H_7N_2S)_2[Cu_2(CHO_2)_6]$, each Cu^{II} atom has a square-pyramidal coordination, with the nonbridging formate ion at the apical position. The complex anion is located on a crystallographic inversion centre, with a $Cu \cdots Cu$ separation of 2.6566 (4) Å. 2-Amino-2-thiazolinium cations connect complex anions *via* hydrogen bonds to form a ribbon running along the *a* axis.

Comment

2-Amino-2-thiazoline (2-amt) derivatives have been described as compounds with M-cholinergic activity (Ivanov *et al.*, 2002). 2-Amino-2-thiazoline itself has been considered as a possible inducer of the reverse transformation of tumour cells (Brugarolas & Gosálvez, 1982). This ligand contains three donor atoms potentially available for coordination of metal ions, *viz.* the amine and heterocyclic N atoms and also the S atom. However, a search of the Cambridge Structural Database (Version 5.28, January 2007 update; Allen, 2002) identified only two structures with metal-coordinated 2-amt. This study was undertaken in order to check the possibilities of 2-amt coordination with copper(II) formate.

The title compound, (I), contains a dimeric copper(II) complex anion, $[Cu_2(\mu-HCOO)_4(HCOO)_2]^{2-}$, and two protonated 2-amt molecules (Fig. 1). Since the anion is located on a crystallographic inversion centre, the asymmetric unit is composed of a half of the anionic complex and one 2-amtH⁺ cation. Each Cu^{II} atom has a (regular within experimental error) five-coordinate square-pyramidal environment, with the basal plane defined by the O atoms of four bridging bidentate carboxylate groups of formate ligands. The apical position is occupied by the O atom of the terminal formate group, coordinating in an *anti* arrangement. The Cu^{II} atom deviates out of the mean plane formed by the four basal O atoms towards the apical O5 atom by 0.2076 (8) Å. The $Cu1^1 \cdots Cu1-O5$ [symmetry code: (i) $-x + 1, -y, -z + 1$]

angle of 178.30 (5)° indicates only a very slight deviation from the expected value of 180° for idealized D_{4h} symmetry.



Each axial formate group links to two 2-amtH⁺ cations *via* an intermolecular N—H \cdots O hydrogen bond. The first linkage forms eight-membered rings described by the $R_2^2(8)$ graph-set motif (Etter *et al.*, 1990), in the manner observed in other 2-amtH⁺ carboxylate salts (Lynch *et al.*, 1999; Lynch, 2004). The second linkage associates adjacent cations *via* carboxy atom O6 into $C_2^2(6)$ chains. The combination of these motifs results in the formation of a one-dimensional ribbon structure lying in the (021) plane and running along the *a* axis, as shown

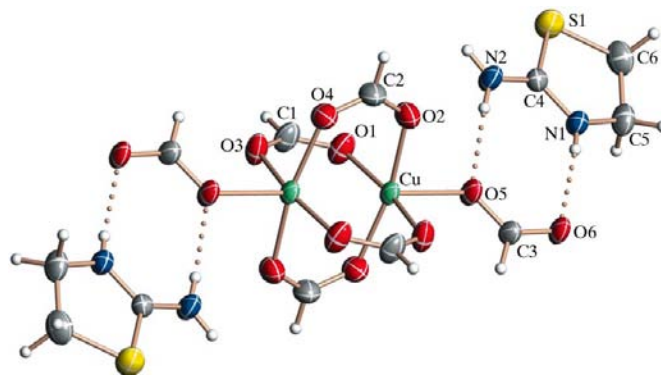


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 40% probability level. Unlabelled atoms are related to labelled atoms by the symmetry code ($-x + 1, -y, -z + 1$). Dotted lines indicate hydrogen bonds.

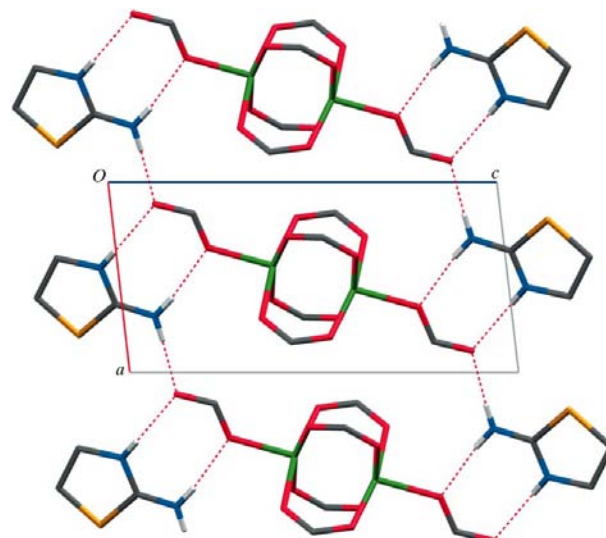


Figure 2
The packing of (I), showing a ribbon of hydrogen-bonded (dashed lines) cations and anions running along the *a* axis.

in Fig. 2. Selected bond distances and angles are listed in Table 1, and the hydrogen-bonding geometric details are summarized in Table 2.

The O—C distances in all the formate groups are approximately equal and range from 1.232 (2) to 1.252 (3) Å, indicating the distinct delocalization of their π electrons (Borthwick, 1980). The planes of the two independent bridging formate groups are perpendicular within experimental error. The apical formate group is twisted by a dihedral angle of 40.2 (5)° with respect to the C1/O1/O3ⁱ mean plane. Rotation of the Cu₂(HCOO)₄ core is limited sterically by the adjacent unit, with which it forms mutual intermolecular C—H...O interactions. Other weak Csp²—H...O contacts stabilize the structure and extend it into a three-dimensional arrangement. The Cu...Cu distance of 2.6566 (4) Å is comparable to those found in other dimeric copper(II) carboxylates.

Experimental

The title complex was prepared by dissolving cupric formate [2 mmol, Cu(HCOO)₂·2H₂O] in 50 ml of water with 2-amino-2-thiazoline (2 mmol). After heating to boiling, formic acid was added dropwise until the solution became clear; it was subsequently filtered and allowed to cool. After a few days, green crystals were obtained.

Crystal data

(C ₃ H ₇ N ₂ S) ₂ [Cu ₂ (CHO ₂) ₆]	$\gamma = 67.250 (8)^\circ$
$M_r = 603.56$	$V = 551.54 (8) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 6.5347 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 7.5170 (8) \text{ \AA}$	$\mu = 2.18 \text{ mm}^{-1}$
$c = 12.4428 (5) \text{ \AA}$	$T = 294 \text{ K}$
$\alpha = 80.022 (6)^\circ$	$0.40 \times 0.22 \times 0.10 \text{ mm}$
$\beta = 80.203 (5)^\circ$	

Data collection

Kuma KM-4 CCD diffractometer	8874 measured reflections
Absorption correction: multi-scan	2530 independent reflections
(<i>CrysAlis RED</i> ; Oxford Diffraction, 2006)	2228 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.426, T_{\max} = 0.811$	$R_{\text{int}} = 0.019$

Table 1

Selected geometric parameters (Å, °).

Cu1—O1	1.963 (2)	O2—C2	1.245 (3)
Cu1—O2	1.974 (2)	O3—C1 ⁱ	1.247 (3)
Cu1—O3 ⁱ	1.967 (2)	O4—C2 ⁱ	1.251 (3)
Cu1—O4 ⁱ	1.9753 (16)	O5—C3	1.244 (3)
Cu1—O5	2.1244 (14)	O6—C3	1.232 (2)
O1—C1	1.252 (3)		
Cu1...Cu1 ⁱ	2.6566 (4)		
O1—Cu1—O2	88.45 (9)	O2—Cu1—O4 ⁱ	167.75 (7)
O1—Cu1—O3 ⁱ	167.96 (7)	O2—Cu1—O5	93.63 (6)
O1—Cu1—O4 ⁱ	88.90 (8)	O3—Cu1—O4	90.46 (8)
O1—Cu1—O5	95.79 (6)	O3—Cu1—O5	96.20 (6)
O2—Cu1—O3 ⁱ	89.65 (9)	O4—Cu1—O5	98.54 (6)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H4...O6	0.74 (3)	2.09 (3)	2.826 (2)	169 (2)
N2—H21...O5	0.80 (3)	2.05 (3)	2.841 (3)	169 (3)
N2—H22...O6 ⁱⁱ	0.81 (3)	2.05 (3)	2.849 (3)	171 (3)
C1—H1...O4 ⁱⁱⁱ	0.93	2.55	3.244 (4)	132
C5—H5B...O2 ^{iv}	0.97	2.52	3.421 (3)	154
C6—H6A...O1 ^v	0.97	2.46	3.364 (3)	155
C6—H6B...O3 ^{vi}	0.97	2.53	3.447 (3)	159

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.072$	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
$S = 1.09$	$\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$
2530 reflections	
164 parameters	

All H atoms were initially located in a difference Fourier synthesis. H atoms bonded to C atoms were positioned with idealized geometry, with C—H = 0.93 and 0.97 Å, and refined using a riding model. The amine H-atom positions and isotropic displacement parameters of all H atoms were refined freely.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2001); molecular graphics: *SHELXTL* and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* (Spek, 2003) and *publCIF* (Westrip, 2007).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3035). Services for accessing these data are described at the back of the journal.

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