

RefinementRefinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.038$ $wR(F^2) = 0.123$ $S = 1.013$

4061 reflections

373 parameters

H atoms riding

 $w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 0.13P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.290 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.458 \text{ e } \text{\AA}^{-3}$

Extinction correction:

SHELXTL (Siemens, 1995)

Extinction coefficient:

0.0011 (11)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Cu1—O4	1.936 (2)	Cu1—N1	2.290 (3)
Cu1—O2	1.941 (2)	N3—C19	1.454 (4)
Cu1—O1	1.943 (2)	C19—C19 ⁱ	1.486 (7)
Cu1—O3	1.950 (2)		
O4—Cu1—O2	84.24 (9)	O4—Cu1—N1	89.88 (10)
O4—Cu1—O1	170.40 (9)	O2—Cu1—N1	91.17 (10)
O2—Cu1—O1	92.39 (9)	O1—Cu1—N1	99.19 (10)
O4—Cu1—O3	92.29 (9)	O3—Cu1—N1	96.24 (10)
O2—Cu1—O3	171.81 (9)	N3—C19—C19 ⁱ	110.7 (3)
O1—Cu1—O3	89.84 (9)		

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

The F atoms of the two CF_3 groups are disordered. The site-occupancy factors were fixed at 0.5 for each of the F atoms. All C—F distances were constrained to be equal, with an s.u. of 0.01 \AA , and the F—F distances were also constrained. These constrained C—F and F—F distances were refined as free variables. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS (Siemens, 1994). The structure was solved by direct methods and refined on F^2 using full-matrix least-squares methods. All non-H atoms were refined anisotropically. H atoms were placed in calculated positions (C—H 0.96 \AA), assigned fixed isotropic displacement parameters at 1.2 times the equivalent U_{iso} of the atoms to which they are attached (1.5 times for methyl groups) and allowed to ride on their respective parent atoms. The contributions of these atoms were included in the structure-factor calculations.

Data collection: XSCANS. Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL (Siemens, 1995). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1029). Services for accessing these data are described at the back of the journal.

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cis-Bis(2-amino-1,3-benzothiazole- N^3)bis(formato- O, O')copper(II)

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Abstract

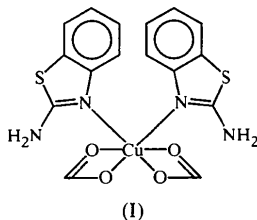
The title complex, *cis*-bis(2-amino-1,3-benzothiazole- N^3)bis(formato- O, O')copper(II), $[\text{Cu}(\text{CHO}_2)_2(\text{C}_7\text{H}_6\text{N}_2\text{S})_2]$, displays C_2 symmetry with the Cu atom adopting a distorted octahedral (4 + 2) coordination. The four closest donor atoms are two N atoms of 2-aminobenzothiazole and two O atoms of the carboxylate groups. They form a distorted square-planar arrangement, with Cu—N and Cu—O distances of 1.991 (2) and 1.993 (2) \AA , respectively. Two longer out-of-plane Cu—O bonds [2.538 (2) \AA] from the remaining O atoms of the formate groups complete the strongly distorted square-bipyramidal coordination of the Cu atom. The H atoms of each amino group of the 2-aminobenzothiazole molecules form intra- and intermolecular hydrogen bonds with O atoms from the carboxylate groups. Intermolecular S...S secondary bonding of 3.502 (2) \AA is observed between neighbouring chains of molecules connected by hydrogen bonds.

Comment

Although expected to have important biological activity (Macíček *et al.*, 1987; Armstrong *et al.*, 1992), the structures of 2-aminobenzothiazole complexes have not been intensively investigated. A search of the Cambridge Structural Database (Allen *et al.*, 1979) did not reveal any information on 2-amino-

benzothiazole—Cu^{II} complexes. The sole known structures are bis(2-aminobenzothiazole-*N*)dichlorocobalt(II) (Macíček *et al.*, 1987) and three dimolybdenum–2-aminobenzothiazolate complexes (Cotton & Ilsley, 1981). In the Co^{II} complex, 2-aminobenzothiazole coordinates through ring N atoms and in the Mo complexes, it coordinates as an *N,N'*-bidentate ligand. This work provides the first information on Cu^{II}–2-aminobenzothiazole coordination.

The structure of the title compound, (I), is shown in Fig. 1. The complex molecule displays C₂ symmetry. In Fig. 1, the twofold axis is perpendicular to the projection plane. The Cu atom is in a greatly distorted



octahedral environment with four short and two long bonds. The short bonds [Cu—N 1.991 (2) and Cu—O 1.993 (2) Å] are formed by ring N atoms of the two monodentate 2-aminobenzothiazole ligands and O atoms of the two formate groups. These bonds form a square-planar arrangement distorted in the direction of a flattened tetrahedron. The *trans*-N1—Cu—O1 angles are 161.65 (8)° and the deviations of the O1 and N1 atoms from the O₂N₂ least-squares plane are ±0.317 (1) and ±0.288 (1) Å, respectively. Two longer Cu—O bonds to the remaining O atoms of the formate groups are 2.538 (2) Å in length. The structure is the first example of Cu–bidentate formate coordination. The

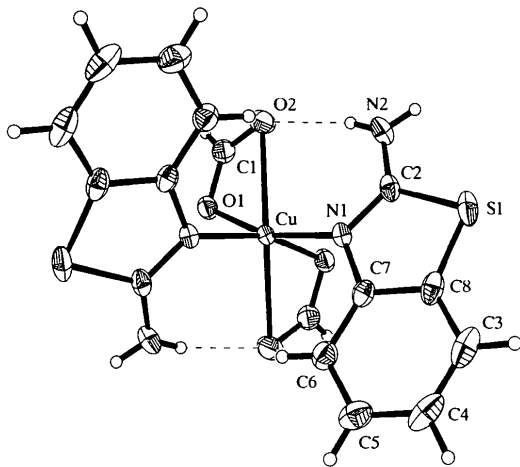


Fig. 1. View along the twofold axis of *cis*-bis(2-aminobenzothiazole)-bis(formato)copper(II). Displacement ellipsoids are drawn at the 30% probability level.

observed C1—O1 and C1—O2 bonds of 1.264 (3) and 1.225 (4) Å, respectively, indicate only an insignificant delocalization of π bonds inside the carboxylate group.

The 2-aminobenzothiazole ligand is not ideally planar. Only the six C atoms (C3–C8) of the benzene ring are exactly coplanar. The amine N2 atom is displaced from the five-membered ring plane by 0.057 (4) Å and the Cu atom is displaced by -0.479 (3) Å. The N2 atom is sp^2 hybridized as evidenced by the sum of the valence angles around it [356 (3)°], with the lone-pair electrons available for π bonding [torsion angle N1—C2—N2—H8 8 (3)°]. The N1—C2 and N2—C2 bond lengths are practically identical [1.321 (3) and 1.324 (4) Å, respectively] indicating the delocalization of π bonds along N1—C2—N2. The N1—C7 bond of 1.399 (3) Å is distinctly longer. It is also longer than the bond of 1.367 (2) Å in uncoordinated 2-amino-4-nitrobenzothiazole (Lokaj *et al.*, 1996). The two nearly identical C—S distances in the thiazole ring [1.741 (3) and 1.742 (3) Å] are similar to the average value in uncoordinated 2-amino-4-nitrobenzothiazole [C—S: 1.726 (1) and 1.754 (1) Å (Lokaj *et al.*, 1996)] and are intermediate between those reported for a single Csp^3 —S (1.819 Å) and a double C=S bond (1.611 Å), but longer than the C—S bond in thiophene (1.712 Å; Allen *et al.*, 1987).

The molecular packing is shown in Fig. 2. The molecules connected by symmetry centres at $\frac{1}{2}, 0, 0$ and

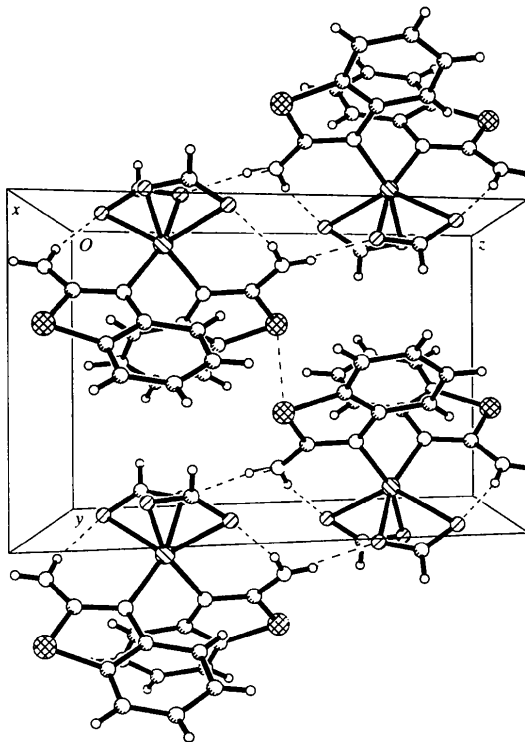


Fig. 2. The molecular packing showing intermolecular S...S secondary bonding and hydrogen bonding.

$\frac{1}{2}, 0, \frac{1}{2}$ are linked by two short intermolecular N—H...O hydrogen bonds forming infinite chains along the *z* axis. These chains are linked by intermolecular S...S secondary bonds of 3.502 (2) Å. The S...S secondary bonds are nearly perpendicular to the thiazole rings, with C2—S1—S1ⁱⁱⁱ and C8—S1—S1ⁱⁱⁱ angles of 79.4 (1) and 89.9 (1)°, respectively [symmetry code: (ii) $-x, -y + 2, -z$]. The S...S interaction approximately along [210] results in a two-dimensional molecular network. Details of the of inter- and intramolecular N—H...O hydrogen bonds are given in Table 2.

Experimental

The title complex was prepared by dissolving cupric formate [2 mmol, Cu(HCOO)₂·2H₂O] in 30 ml of water with 2-aminobenzothiazole (4 mmol, C₇H₆N₂S). After heating to boiling, a few drops of formic acid were added to clear the solution. The solution was filtered and allowed to cool. After several hours, dark-green crystals were obtained.

Crystal data

[Cu(CHO₂)₂(C₇H₆N₂S)₂]

M_r = 453.97

Monoclinic

*C*2/*c*

a = 18.3481 (16) Å

b = 8.3075 (7) Å

c = 13.2995 (9) Å

β = 113.960 (6)°

V = 1852.5 (3) Å³

Z = 4

D_x = 1.628 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 48 reflections

θ = 3.24–15.69°

μ = 1.435 mm⁻¹

T = 293 (2) K

Prism

0.30 × 0.30 × 0.16 mm

Dark green

Data collection

Siemens *P3* diffractometer

ω–2θ scans

Absorption correction:

ψ scan (North *et al.*, 1968)

T_{min} = 0.673, *T_{max}* = 0.803

1998 measured reflections

1917 independent reflections

1716 reflections with

I > 2σ(*I*)

R_{int} = 0.020

θ_{max} = 26.5°

h = –23 → 21

k = 0 → 10

l = 0 → 16

3 standard reflections

every 100 reflections

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.033

wR(*F*²) = 0.080

S = 1.142

1917 reflections

152 parameters

All H atoms refined

w = 1/[σ²(*F_o*²) + (0.0251*P*)²

+ 4.1788*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.279 e Å⁻³

Δρ_{min} = –0.370 e Å⁻³

Extinction correction:

SHELXL97 (Sheldrick, 1997*a*)

Extinction coefficient:

0.0013 (2)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu—N1	1.991 (2)	O1—C1	1.264 (3)
Cu—O1	1.9925 (19)	O2—C1	1.225 (4)
Cu—O2	2.538 (2)	N1—C2	1.321 (3)
S1—C2	1.742 (3)	N1—C7	1.399 (3)
S1—C8	1.741 (3)	N2—C2	1.324 (4)
O1—Cu—O1 ⁱ	87.24 (11)	O1—C1—O2	124.2 (3)
O1—Cu—O2	56.57 (7)	C2—N1—C7	111.4 (2)
O1—Cu—O2 ⁱ	90.06 (8)	C2—S1—C8	89.41 (13)
O2—Cu—O2 ⁱ	135.36 (12)	N1—C2—N2	124.4 (3)
O1—Cu—N1	161.65 (8)	N1—C2—S1	115.0 (2)
O1—Cu—N1 ⁱ	90.09 (8)	N2—C2—S1	120.6 (2)
O2—Cu—N1	105.31 (8)	N1—C7—C6	126.0 (2)
O2—Cu—N1 ⁱ	103.57 (8)	S1—C8—C7	110.2 (2)
N1—Cu—N1 ⁱ	97.91 (12)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

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>
N2—H7...O1 ⁱ	0.83 (4)	2.02 (4)	2.835 (3)	170 (3)
N2—H8...O2	0.80 (4)	2.12 (4)	2.905 (4)	166 (4)

Symmetry code: (i) $x, 1 - y, z - \frac{1}{2}$.

The title structure was solved by direct methods and refined by full-matrix least-squares calculations. All non-H atoms were refined anisotropically. All H atoms were located from a difference synthesis and refined isotropically.

Data collection: *P3 Software* (Siemens, 1990). Cell refinement: *P3 Software*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1298). Services for accessing these data are described at the back of the journal.

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