Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis(μ-succinato-*O*,*O*′:*O*″,*O*‴)bis[bis(2-amino-1,3-benzothiazole-N^3)copper(II)]

Lesław Sieroń† and Maria Bukowska-Strzyżewska*

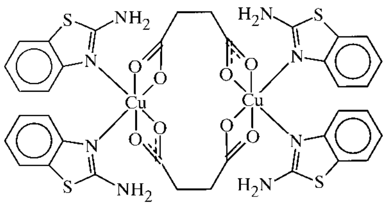
Institute of General and Ecological Chemistry, Technical University of Łódź, Żwirki 36, 90-924 Łódź, Poland
Correspondence e-mail: mbs@ck-sg.p.lodz.pl

Received 27 July 1999
Accepted 12 October 1999

In the title dimeric complex, $[Cu_2(C_4H_4O_4)_2(C_7H_6N_2S)_4]$, which possesses a centre of symmetry, the Cu atoms are enclosed in a 14-membered ring. They adopt a distorted square-bipyramidal (4+2) coordination. The four closest donor atoms are two N atoms of 2-aminobenzothiazole ligands and two O atoms of the succinate carboxylate groups. They form a square-planar *cis* arrangement, with an average Cu—N distance of 2.003 (3) Å and Cu—O distances of 1.949 (3) and 1.965 (3) Å. Two longer Cu—O bonds of 2.709 (3) and 2.613 (3) Å involving the remaining O atoms of the carboxylate groups complete the sixfold coordination of the Cu atoms. The H atoms of each amino group of the 2-aminobenzothiazole molecules form intra- and intermolecular N—H$\cdots$O hydrogen bonds. A nearly perpendicular intermolecular C—H$\cdots$*Cg* interaction (*Cg* is the centroid of the imidazole ring) is observed. The intramolecular Cu$\cdots$Cu distance is 6.384 (2) Å.

Comment

This work forms part of a continuing study of Cu^{II} complexes with benzimidazole and dicarboxylic acids (Tosik & Bukowska-Strzyżewska, 1992; Tosik *et al.*, 1995*a*,*b*; Sieroń & Bukowska-Strzyżewska, 1998, 1999*a*), and with carboxylate anions and 2-aminobenzothiazole (Sieroń & Bukowska-Strzyżewska, 1999*b*), giving a second example of Cu–(2-aminobenzothiazole) coordination. In the molecule of the title compound, (I) (Fig. 1), both succinate ions adopt the rare synclinal conformation with respect to the central C—C bonds [$C8—C9—C19^i—C18^i = -73.2 (5)°$; symmetry code: (i) $-x, -y, 1-z$] and take the bridge position between the two Cu atoms, forming a dinuclear centrosymmetrical complex with a Cu$\cdots$Cu distance of 6.384 (2) Å. A 14-membered ring is formed around a centre of symmetry. The Cu atoms adopt very distorted square-bipyramidal coordinations. The four basal bonds are formed by two *cis*-N atoms of 2-aminobenzothiazole, with an average Cu—N distance of 2.003 (3) Å, and two *cis*-O atoms of two carboxylate groups, with Cu—O distances of 1.949 (3) and 1.965 (3) Å. The square-planar coordination is visibly deformed in the direction of the tetrahedral coordination. The deviations from the N1/N11/O1/O11 least-squares plane are −0.404 (1) and −0.472 (2) Å for the *trans*-situated N1 and O1 atoms, and 0.444 (2) and 0.433 (2) Å for the N11 and O11 atoms, respectively. The deviation of the Cu atom from this plane is only 0.022 (2) Å. Two distinctly longer Cu—O2 and Cu—O12 bonds of 2.709 (3) and 2.613 (3) Å complete the sixfold coordination. The observed O2—Cu—O12 angle is only 133.2 (1)°. The dihedral angle between the planes of the two *cis*-carboxylate groups is 89.9 (5)° and between the average planes of the two 2-aminobenzothiazole ligands is 82.2 (1)°. The five and six-membered rings of the 2-aminobenzothiazole molecules are ideally planar and in one molecule ideally coplanar. In the second molecule (containing S1 and N1 atoms), the five and six-membered rings form a dihedral angle of 2.7 (2)°.



(I)

The geometry of the intra- and intermolecular hydrogen bonds, and of the intermolecular C—H$\cdots$*Cg*(π ring) interaction, where *Cg* is the centroid of the imidazole ring (containing S1 and N1), are given in Table 2. The observed H$\cdots$*Cg* distance is 2.69 Å. The molecular packing is illustrated in Fig. 2. The *trans*-situated carboxylate ions and 2-aminobenzothiazole molecules are connected by N—H$\cdots$O intramolecular hydrogen bonds, forming six-membered rings. The individual carboxylate ions are differently involved in the intermolecular N—H$\cdots$O hydrogen-bond system. The C8/O1/O2 group forms an intramolecular hydrogen bond through the O2 atom and an intermolecular hydrogen bond through the O1 atom. In the C18/O11/O12 group, only O12 is involved in hydrogen bonding, forming both inter- and intramolecular N2(12)—H$\cdots$O12 hydrogen bonds. This causes distinctly different delocalization of π bonds in both carboxylic acid groups. The bonds C8—O1 [1.284 (5) Å] and C8—O2 [1.221 (4) Å] are differentiated, while C18—O11 [1.258 (4) Å] and C18—O12 [1.255 (4) Å] are practically identical. The different structure of both Cu-coordinated carboxylic acid groups causes the differentiation of both short and long Cu—O bonds; Cu—O1 [1.949 (3) Å] is distinctly shorter than Cu—O11 [1.965 (3) Å], and Cu—O2 [2.709 (3) Å] is longer than Cu—O12 [2.613 (3) Å]. The observed regularity is consistent with the valence bond sum rule (Brown, 1994). The application of the bond valence–bond length correlation allows comparison of the relative impor-

---

† A holder of the Foundation for Polish Science (FNP) grant.

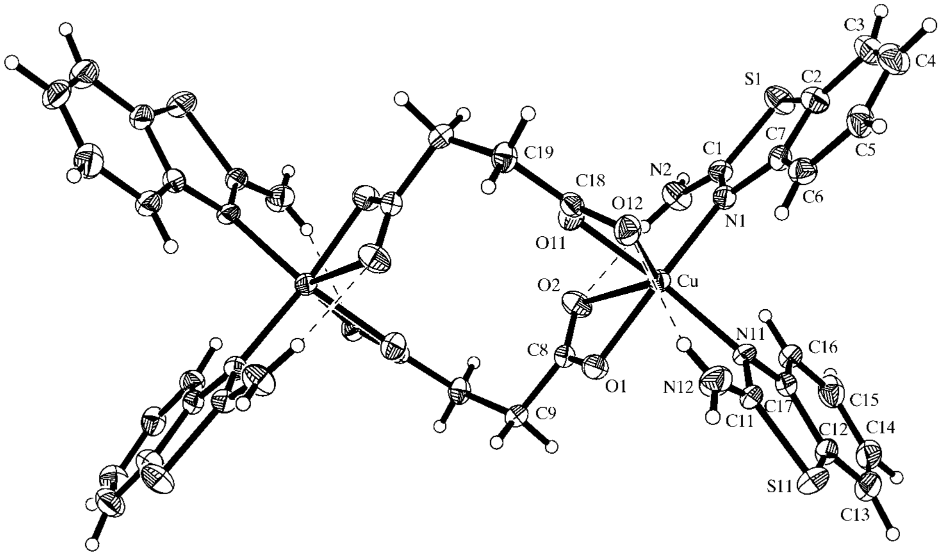


Figure 1
View of the molecule of (I). Displacement ellipsoids are drawn at the 30% probability level.

tance of Cu—N and different Cu—O bonds of the Cu^{II} polyhedron and also allows a check of the valence sum rule. According to Brown (1994), the bond length to bond valence correlation represents a measure of the strength of a bond that is independent of the atomic size. The valence sum rule states that the sum of the valences of the bond formed by an atom is equal to the valence (formal oxidation state) of the atom ($V_i = \Sigma\nu_{ij}$). The bond valences were computed according to Brown (1992, 1997) and O'Keeffe & Brese (1991) as $\nu_{ij} = \exp[(R_{ij}-d_{ij})/0.37]$, where R_{ij} is the bond-valence parameter (in the formal sense it is the single-bond length between the i and j atoms) and d_{ij} is the observed bond length. $R_{\rm Cu-O}$ and $R_{\rm Cu-N}$ were taken as 1.679 and 1.713 Å (see Sieroń & Bukowska-Strzyżewska, 1999*a*). The computed bond valences of the Cu^{II} atom are: $\nu_{\rm Cu-O1} = 0.482$, $\nu_{\rm Cu-O2} = 0.062$, $\nu_{\rm Cu-O11} = 0.462$, $\nu_{\rm Cu-O12} = 0.080$, $\nu_{\rm Cu-N1} = 0.458$, $\nu_{\rm Cu-N2} = 0.455$ v.u. (valence unit). Thus, the computed valence of the Cu^{II} atom ($V_{\rm Cu}$) is 2.00 v.u.

The conformations on the two terminal C—C bonds of the succinate ion are different. On the C18—C19 bond, the conformations are synperiplanar and antiperiplanar [torsion angles O11—C18—C19—C9^{i} = 5.0 (6)° and O12—C18—C19—C9^{i} = −175.2 (4)°], and on the C8—C9 bond, the conformations are antiperiplanar and synclinal [torsion angles O1—C8—C9—C19^{i} = 151.4 (4)° and O2—C8—C9—C19^{i} = −32.0 (6)°]. The structure illustrates the influence of weak hydrogen bonds on the conformation of the aliphatic chain and the differentiation of Cu—O bond lengths.

Compound (I) is a second example of bis(μ-dicarboxylate) coordination in a Cu^{II} complex with formation of a dimeric molecular structure. A similar coordination was observed in the complex bis[(μ_2-adipato-*O,O′*:*O″,O‴*)(*N,N*-diethylenediamine)copper(II)] (Pajunen & Nasakkala, 1977).

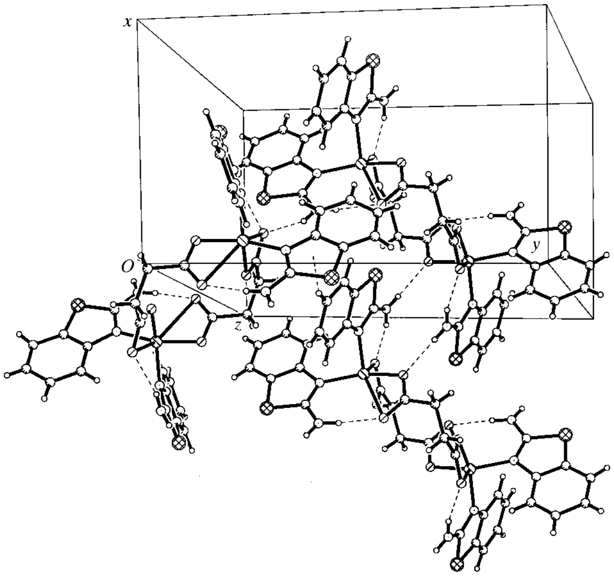


Figure 2
The molecular packing of (I) showing intra- and intermolecular hydrogen bonds, and intermolecular C—H···π interactions.

Experimental

The title complex was prepared by dissolving equimolar quantities (1 mmol) of 2-aminobenzothiazole, succinic acid and copper(II) chloride dihydrate in water (80 ml). After heating to boiling, the solution was filtered and allowed to cool. After several hours, green crystals of (I) were obtained.

Crystal data

$[Cu_2(C_4H_4O_4)_2(C_7H_6N_2S)_4]$
M_r = 960.08
Monoclinic, $P2_1/n$
a = 9.239 (2) Å
b = 15.643 (3) Å
c = 13.859 (3) Å
β = 102.37 (2)°
V = 1956.5 (7) Å^3
Z = 2

D_x = 1.630 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 32 reflections
θ = 4.19–14.27°
μ = 1.364 mm^{-1}
T = 293 (2) K
Prism, green
0.23 × 0.13 × 0.13 mm

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.949 (3)	N1—C1	1.317 (5)
Cu—O2	2.709 (3)	N1—C7	1.403 (5)
Cu—O11	1.965 (3)	N2—C1	1.327 (5)
Cu—O12	2.613 (3)	O11—C18	1.258 (4)
Cu—N1	2.002 (3)	O12—C18	1.255 (4)
Cu—N11	2.004 (3)	S11—C11	1.751 (4)
O1—C8	1.284 (5)	S11—C12	1.740 (5)
O2—C8	1.221 (4)	N11—C11	1.310 (5)
S1—C1	1.751 (4)	N11—C17	1.400 (5)
S1—C2	1.750 (4)	N12—C11	1.331 (6)

O1—Cu—O2	53.45 (10)	N1—C1—N2	124.7 (4)
O1—Cu—O11	91.98 (11)	N1—C1—S1	115.3 (3)
O1—Cu—O12	106.69 (11)	N2—C1—S1	120.0 (3)
O1—Cu—N1	152.89 (12)	C3—C2—S1	128.2 (4)
O1—Cu—N11	87.75 (12)	C7—C2—S1	110.1 (3)
O2—Cu—O11	81.17 (10)	C6—C7—N1	126.3 (4)
O2—Cu—O12	133.15 (9)	C2—C7—N1	114.5 (3)
O2—Cu—N1	102.25 (11)	O1—C8—O2	123.0 (4)
O2—Cu—N11	117.82 (11)	C11—S11—C12	88.9 (2)
O11—Cu—O12	55.36 (9)	C11—N11—C17	111.8 (3)
O11—Cu—N1	95.97 (12)	N11—C11—N12	124.9 (4)
O11—Cu—N11	154.90 (12)	N11—C11—S11	115.5 (3)
O12—Cu—N1	99.11 (11)	N12—C11—S11	119.6 (3)
O12—Cu—N11	100.77 (11)	C13—C12—S11	129.4 (4)
N1—Cu—N11	95.60 (13)	C17—C12—S11	110.6 (3)
C1—S1—C2	89.04 (19)	N11—C17—C12	113.2 (4)
C1—N1—C7	111.1 (3)	O11—C18—O12	122.4 (3)

Data collection

Siemens *P*3 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.740$, $T_{\max} = 0.848$
3561 measured reflections
3414 independent reflections
2516 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.035$
$\theta_{\max} = 25°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 16$
2 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.090$
$S = 1.033$
3414 reflections
326 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0290P)^2 + 2.5110P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.334$ e Å^{-3}
$\Delta\rho_{\min} = -0.277$ e Å^{-3}

Refined C—H distances are in the range 0.82 (6)–0.98 (4) Å.

Data collection: *P*3 software; cell refinement: *P*3 software; data reduction: *XDISK* in *SHELXTL*/*PC* (Sheldrick, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *XP* in *SHELXTL*/*PC*; software used to prepare material for publication: *SHELXL*97.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H21···O2	0.84 (5)	2.01 (5)	2.852 (5)	176 (5)
N2—H22···O12$^{\rm i}$	0.81 (4)	2.12 (4)	2.890 (5)	159 (5)
N12—H121···O12	0.84 (5)	2.09 (5)	2.894 (5)	161 (5)
N12—H122···O1$^{\rm ii}$	0.82 (5)	2.09 (5)	2.859 (5)	157 (5)
C14—H14···*Cg*$^{\rm iii}$	0.91 (5)	2.69	3.563	162

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $1 - x, -y, 1 - z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$.

This work was supported by the Polish State Committee for Scientific Research (KBN) (grant No. 3 T09A 142 15).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1341). Services for accessing these data are described at the back of the journal.

References

Brown, I. D. (1992). *Acta Cryst.* B**48**, 553–572.
Brown, I. D. (1994). *Bond-Length–Bond-Valence Relationships in Inorganic Solids*, in *Structure Correlation*, Part III, edited by H.-B. Bürgi & J. D. Dunitz, pp. 405–429. Weinheim/New York: VCH Publishers.
Brown I. D. (1997). *Acta Cryst.* B**53**, 381–393.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
O'Keeffe, M. & Brese, N. E. (1991). *J. Am. Chem. Soc.* **113**, 3226–3229.
Pajunen, A. & Nasakkala, E. (1977). *Finn. Chem. Lett.* pp. 104–109.
Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997*a*). *SHELXS*97. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sieroń, L. & Bukowska-Strzyżewska, M. (1998). *Acta Cryst.* C**54**, 1431–1435.
Sieroń, L. & Bukowska-Strzyżewska, M. (1999*a*). *Acta Cryst.* C**55**, 1230–1234.
Sieroń, L. & Bukowska-Strzyżewska, M. (1999*b*). *Acta Cryst.* C**55**, 167–169.
Tosik, A. & Bukowska-Strzyżewska, M. (1992). *J. Crystallogr. Spectrosc. Res.* **22**, 225–229.
Tosik, A., Sieroń, L. & Bukowska-Strzyżewska, M. (1995*a*). *Acta Cryst.* C**51**, 1985–1987.
Tosik, A., Sieroń, L. & Bukowska-Strzyżewska, M. (1995*b*). *Acta Cryst.* C**51**, 1987–1989.