Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

(η^2-Allylammonium)aquabis(sulfamato-*N*)copper(**I**)

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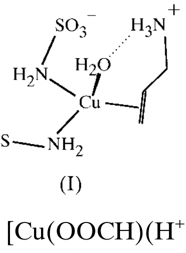
Received 30 May 2000
Accepted 6 November 2000

The Cu^I atom in the title complex, [Cu(NH_2SO_3)$_2$(C_3H_8N)(H_2O)], is coordinated by the C═C bond of the allylammonium cation, two N atoms of the sulfamate anions and the O atom of the H_2O molecule in the apical position. Thus, the central atom is in a distorted trigonal–pyramidal environment. Strong N—H···O and O—H···O contacts connect separate moieties of the complex into a three-dimensional framework. The title compound is representative of hitherto unknown copper(I)–sulfamate π-complexes.

Comment

The complexation of allylamine (AA) with copper(I) is rather diversified because of the versatile properties of AA and because of its simple structure and the abundance of related allylic compounds in organic synthesis. The dual character of the coordination ability of AA as a π,σ-ligand was manifested in Cu*X*AA (*X* = Cl, Br) complexes (Fayad *et al.*, 1991). However, AA, being in the protonated form (as the H^+AA cation), reveals new faces of its π-coordination behaviour with copper(I). The possibility of forming strong N—H···*X* hydrogen bonds promotes the participation of strong acid anions in the structure formation of copper(I) compounds, leading to the formation of a new class of mixed-ligand cationic copper(I) π-complexes, such as [Cu_2Cl_2(H^+AA)$_2$](NO_3)$_2$ (Olijnyk & Myskiv, 1995), [Cu_2X_2(H^+AA)$_2$(H_2O)]SO_4 (Myskiv *et al.*, 1994) or [Cu(OOCH)(H^+AA)]CuX_2 (*X* = Cl, Br; Mykhalichko *et al.*, 1994), as well as zwitterionic π-compounds, for instance, (H^+AA)CuX_2 (*X* = Cl, Br; Myskiv *et al.*, 1991) and [(H^+AA)CuCl($NCCH_2COO$)] (Olijnyk *et al.*, 1997). On the other hand, the nature of the copper(I) salt anion sometimes plays a decisive role in the formation of stable solid π-complexes, as occurred in the case of [$Cu_2(C_6H_6)(CF_3SO_3)_2$], in spite of the typically weak Cu^I–aromatic ring interactions (Dines & Bird, 1973). Hence, copper(I) sulfamate was chosen as an initial salt to study its complexation abilities with allylammonium salts.



(I)

The compound [Cu(H^+AA)(NH_2SO_3)$_2$(H_2O)], (I), appears to be a zwitterionic π-complex formed by copper(I) sulfamate and allylammonium sulfamate. A sulfamate anion exhibits its coordination ability with respect to the Cu^I atom through Cu^I—N bonds of 2.050 (3) and 2.066 (3) Å. The third coordination position is occupied by the C═C group of the H^+AA cation [Cu^I—(C═C) 1.935 (3) Å]. An axial O atom from the H_2O molecule [Cu—O 2.348 (3) Å] completes a trigonal pyramidal environment for the Cu^I atom. A view of the asymmetric unit of (I) with the atomic numbering scheme is shown in Fig. 1 and selected dimensions are given in Table 1. The extent of the pyramidal distortion of the coordination sphere conforms to a certain deviation (0.203 Å) of the Cu atom from the plane of the equatorial ligands (through N1, N2 and the midpoint of C1═C2). The tilt of the π-coordinated double bond from this plane equals 10.0°. The coordinated olefinic C1═C2 group is elongated to 1.359 (5) Å. The zwitterionic nature of the complex results in the monodentate function of the ligands and, in turn, the mononuclear character of (I). In zwitterionic complexes, less condensed fragments occur because of the rise of ionic interactions and the formation of strong hydrogen bonds. A similar complex structure construction with monodentate anions can be found in the zwitterionic [(C_3H_5)$_2NH_2$][Cu(NO_3)$_2$] compound (Olijnyk *et al.*, 1995). Even the copper(I) [(H^+AA)CuCl($NCCH_2COO$)] π-compound, due to its similar zwitterionic character, does not contain any polynuclear CuCl fragment, typical of copper(I) chloride complexes.

Since in copper(I) π-complexes the donor–acceptor ($M \leftarrow L$)-σ-component is more efficient than the ($M \rightarrow L$)-π-dative component, the N atom with sharply pronounced donor properties suppresses markedly the Cu^I—(C═C) interaction (Myskiv & Olijnyk, 1995). Nevertheless, in the discussed complex, the C═C bond competes successfully with the two N

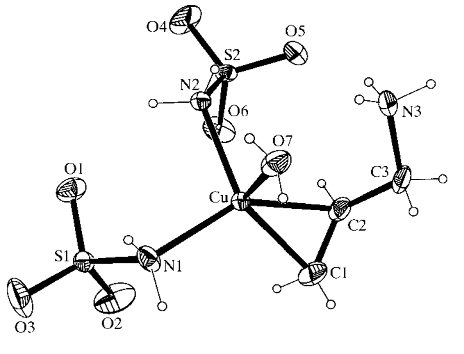


Figure 1
A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

atoms for the coordination to Cu^I. This should be attributed to N—H···O bonds of 2.08–2.32 Å (Table 2), which make the N atom more of a hard base with respect to soft acid Cu^+. Due to such contacts, the N atom of the $NH_2SO_2O^-$ moiety partially loses its donor properties and enables the Cu^I—(C═C) interaction. Actually, the Cu^+ cation is not as strongly bonded to N atoms as H^+ in the zwitterionic form of sulfamic acid. This is seen in much shorter S—N distances in (I) compared with a value of 1.772 (1) Å in the case of NH_3^+—SO_3^- (Cameron & Duncanson, 1976). Both the independent $NH_2SO_3^-$ ions are characterized by a slightly distorted tetrahedral geometry of the S and N atoms. Other hydrogen bonds in the title structure, namely $(C_3H_5N)H_3^+$···O (2.10–2.12 Å) and $(O)H_2$···O (2.02–2.10 Å) (Table 2), combine separate complex units into a three-dimensional framework (Fig. 2).

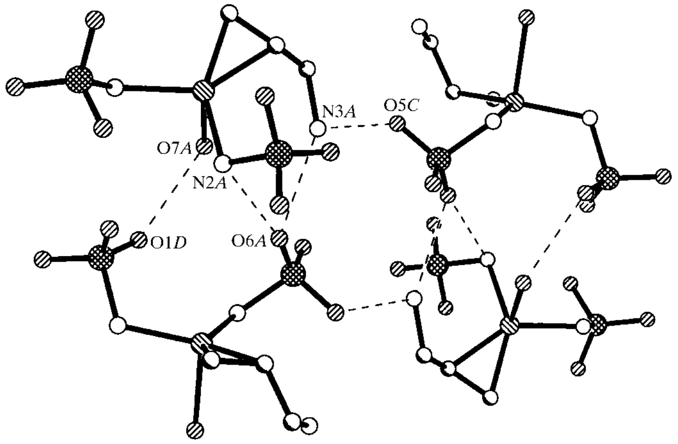


Figure 2
The two-dimensional network assembled from hydrogen bonds.

Finally, it should be noted that the title compound is not only a new representative of copper(I) zwitterionic π-complexes with the allylammonium ligand, but is one of the first copper(I) sulfamate π-complexes to be reported.

Experimental

To a water–ethanol (1:1) saturated solution of copper(I) sulfamate hydrate (3 ml), an ethanolic solution (2 ml) of allylamine (10 mmol, 0.75 ml), previously titrated by sulfamic acid to pH = 5, was added. The prepared solution was placed in a 6 ml test tube and copper-wire electrodes in cork were inserted. Under an alternating current (frequency 50 Hz) of 0.45 V, colourless crystals of the title complex appeared on the copper electrodes after 1 d.

Crystal data

$[Cu(NH_2SO_3)_2(C_3H_8N)(H_2O)]$
$M_r = 331.83$
Monoclinic, $P2_1/c$
$a = 13.5437$ (5) Å
$b = 8.89230$ (10) Å
$c = 9.7121$ (4) Å
$\beta = 103.593$ (2)°
$V = 1136.91$ (6) Å^3
$Z = 4$
$D_x = 1.939$ Mg m^{-3}
$D_m = 1.92$ Mg m^{-3}
D_m measured by flotation in a $CHCl_3/CHBr_3$ mixture
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 32.5$–37.0°
$\mu = 6.45$ mm^{-1}
$T = 298$ (2) K
Plate, colourless
0.20 × 0.17 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*CORINC*; Dräger & Gattow, 1971)
$T_{\min} = 0.359$, $T_{\max} = 0.739$
2332 measured reflections
2332 independent reflections
2303 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 74.65°$
$h = -16 \rightarrow 0$
$k = 0 \rightarrow 11$
$l = -11 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity variation: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.117$
$S = 1.251$
2332 reflections
170 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 2.2982P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.74$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0070 (5)

Table 1
Selected geometric parameters (Å, °).

Cu—C1	2.035 (4)	Cu—O7	2.348 (3)
Cu—N1	2.050 (3)	S1—N1	1.690 (3)
Cu—C2	2.066 (3)	S2—N2	1.692 (3)
Cu—N2	2.066 (3)	C1—C2	1.359 (5)
C1—Cu—C2	38.70 (15)	N2—Cu—O7	88.73 (10)
N1—Cu—N2	102.11 (11)	S1—N1—Cu	117.98 (15)
N1—Cu—O7	94.19 (11)	S2—N2—Cu	113.55 (13)
Cu—C1—C2—C3	105.9 (3)	C1—C2—C3—N3	−129.7 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H13···O1^{i}	0.73 (6)	2.10 (6)	2.818 (4)	167 (5)
O7—H14···O3^{ii}	0.68 (6)	2.02 (6)	2.682 (4)	168 (5)
N1—H1···O2^{iii}	0.90	2.32	3.180 (4)	159
N2—H4···O6^{i}	0.90	2.08	2.953 (3)	162
N3—H10···O5	0.85	2.12	2.933 (4)	160
N3—H11···O5^{iv}	0.85	2.10	2.920 (4)	161
N3—H12···O7	0.85	2.11	2.841 (4)	143

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

The H atoms of the water molecule were located in a difference electron-density map and were refined freely. The remainder of the H atoms were treated using a riding model (N—H = 0.90 Å and C—H = 0.93–0.97 Å). For the NH_3 group, variable metric rigid-group refinement (*AFIX* 135 instruction) was used. The maximum residual electron density is 1.22 Å from the Cu atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1052). Services for accessing these data are described at the back of the journal.

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