

Copper(I) Sulfamate π -Complexes: Synthesis and Crystal Structure of [$\{(\text{CH}_2=\text{CHCH}_2)_2\text{N}-\text{CHO}\}\text{Cu}(\text{NH}_2\text{SO}_3)(\text{H}_2\text{O})$] Compound

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By alternating-current electrochemical synthesis, the crystalline π -complex [$\{(\text{CH}_2=\text{CHCH}_2)_2\text{N}-\text{CHO}\}\text{Cu}(\text{NH}_2\text{SO}_3)(\text{H}_2\text{O})$] (**I**) has been obtained, using copper(II) sulfamate and diallylformamide (DAFA) in water-methanolic solution and copper-wire electrodes. The single crystal of the compound was X-ray structurally characterized. The Cu atom possesses trigonal pyramidal coordination, formed by nitrogen atom of sulfamate anion and two C=C bonds of the same DAFA molecule at the equatorial plane and the oxygen atom of H_2O molecule at the apical position. Hydrogen contacts for the most part by (N)H...O and (O_w)H...O bonds of 1.98(3)–2.24(2) Å connect separate moieties of the mononuclear complex into a three-dimensional framework. The effective atomic charges in **I** are calculated.

Key words: copper(I) sulfamate, π -complex, synthesis, crystal structure

The nature of acido-ligand is one of the most significant factor in the structure formation of copper(I) π -complexes. Hardness of the anion determines the type of the coordination polyhedron of the copper atom and its coordination mode [1]. This stimulates the interest in polydentate ligands with a wide range of basic properties of the separate donor centers, which would be able to provide the sufficient lability of the metallic center in the reactions of complexes of this type. Hence, the ambivalent sulfamate anion NH_2SO_3^- is of great interest, because copper(I) sulfamate π -complexes are actually unknown. Furthermore, even the related trifluoromethane-sulfonate anion, CF_3SO_3^- , possessing CF_3 -group inactive to Cu(I), exhibits diverse coordination abilities in copper(I) π -complexes. It acts as a distant apical ligand in $[\text{Cu}(\text{cyclohexene})(\text{di}(2,6\text{-diisopropylphenylimine})\text{glyoxal})(\text{CF}_3\text{SO}_3)]$ (Cu...O 2.64(1) Å) [2], bridging ligand in $[\text{Cu}(1,5\text{-hexadiene})(\text{CF}_3\text{SO}_3)]$ (Cu...O 2.135(4) and 2.101(4) Å) [3] and $[\text{Cu}(\text{cyclooctene})_2(\text{CF}_3\text{SO}_3)]$ (Cu...O 2.049(4) and 2.433(4) Å) [4] π -complexes, and as a cross-linking triply bonded ligand in $[\text{Cu}_2(\text{benzene})(\text{CF}_3\text{SO}_3)_2]$ compound (Cu...O 2.00–2.22(1) Å) [5]. The presence of another basic group (NH_2 -) may facilitate the formation of yet more versatile acido-ligand. For these purposes, we synthesized and structurally characterized the copper(I) sulfa-

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mate-diallylformamide π -complex of composition $[(\text{CH}_2=\text{CHCH}_2)_2\text{N}-\text{CHO}]_2\text{Cu}(\text{NH}_2\text{SO}_3)(\text{H}_2\text{O})$ (**I**).

EXPERIMENTAL

Preparation of $[\text{Cu}(\text{OSO}_2\text{NH}_2)_2] \cdot x\text{H}_2\text{O}$ salt. $(\text{CuOH})_2\text{CO}_3$ was treated by 50% water solution of sulfamic acid. An excess of copper(II) hydroxocarbonate was filtered and a solution was evaporated on water bath until blue crystals of the salt appeared. On cooling copper(II) sulfamate has crystallized, which was washed with suction by cold ethanol and dried on air.

Synthesis of diallylformamide. This compound (DAFA) has been obtained starting from equimolar quantities of diallylamine (Merck production) and 90% formic acid (Reachim production) by means of azeotropic distillation of water with toluene according to modified procedure [6].

Preparation of complex I. Good quality crystals of the complex have been obtained by the alternating-current electrochemical technique [7]. To 5 ml of a water-methanol (50:50) saturated solution of $[\text{Cu}(\text{OSO}_2\text{NH}_2)_2] \cdot x\text{H}_2\text{O}$ 0.5 ml of diallylformamide (4 mmol) was added. This solution was placed into a small 6-ml test-tube and copper-wire electrodes in cork (to protect against the oxidation by air) were inserted. Under alternating current (frequency 50 Hz) of 0.40 V, the solution became colorless over a day. On cooling at -5°C , large (up to 0.5 cm) needle-shaped transparent colorless crystals of the compound **I** appeared on the copper electrodes over 20 days. These crystals are relatively stable and being vanished by cyacryne did not decompose during the X-ray experiment. The density of **I** was measured by flotation in $\text{CHCl}_3/\text{CHBr}_3$ solution.

Crystal structure of I. Approximate unit-cell dimensions and the space group were determined from rotation and Weissenberg photographs. The intensity data were measured on a DARCH diffractometer (an automated four-circle diffractometer of the former USSR production, the analogue of a Syntex P2₁) with the Zr-filtered MoK_α radiation. The crystallographic data and data collection parameters for **I** are given in Table 1. The cell parameters were obtained by the least-squares refinement with regards to the angle parameters of 24 reflections in the range $22.0 < 2\theta < 29.0^\circ$. Structure was solved by the direct methods. All H atoms were found from difference Fourier syntheses. Absorption correction has been performed using DIFABS program. A full least-squares refinement on F was performed on the positional and thermal parameters for all atoms, anisotropically for all non H-atoms. Taking into account the anharmonicity of thermal vibrations of the copper atom (including components of 4-rank polar tensor into refinement) lowered R-factor from 0.0222 to 0.0210 and resulted in a more precise positional parameters of light atoms*. The neutral atom scattering factors were taken from [9]. The intensities were not corrected for extinction. All the calculations (including absorption corrections) were performed using the CSD program package (Crystal Structure Determination) [10]. The final atomic parameters are presented in Table 2. The anisotropic thermal parameters and the list of observed and calculated structure amplitudes for **I** are available on request. The bond lengths, bond angles and the selected torsion angles in **I** are listed in Table 3.

Table 1. Crystal data and data collection parameters for compound **I**.

I	
Empirical formula	$\text{CuSO}_3\text{N}_2\text{C}_7\text{H}_{15}$
Color/shape	Colorless/brick
Crystal size, [mm]	$0.30 \times 0.20 \times 0.15$
Formula weight	302.82
Temperature [K]	293
Crystal system	monoclinic
Space group	$P2_1/n$
Table 1 (continuation)	
Unit cell dimensions	

* This procedure takes into account asphericity of filled d-orbitals rather than anharmonicity by itself [8].

a [Å]	11.384(2)
b [Å]	13.546(3)
c [Å]	7.563(2)
γ [°]	98.38(2)
V [Å ³]	1153.9(7)
Z	4
D_c [g/cm ³]	1.743(1)
D_m [g/cm ³]	1.77
Absorption coefficient, [cm ⁻¹]	21.47
Diffractometer/scan	DARCH/ θ -2 θ
λ [Å], Zr-filtered	0.71069
$F(000)$	624
$2\theta_{\max}$ [°]	53
Reflections measured	2803 (1/2 of r.l. sphere)
Unique reflections	1468
Reflections used in refinement	1467 [$F_o \geq 2\sigma(F_o)$]
No. of parameters varied	230
Weighting scheme	$[\sigma(F_o)^2 + 0.0008F_o^2]^{-1}$
Goodness-of-fit on F	1.00
$R(F)$	0.0210
$R_w(F)$	0.0238
Max./min. $\Delta\rho$ [e Å ⁻³]	0.21 / -0.17

Table 2. Positional coordinates and equivalent thermal parameters (with e.s.d.'s in parentheses) for I.

	x	y	z	$U_{eq} \times 10^2$ *
Cu	0.24898(6)	0.05617(5)	0.18064(9)	3.34(3)
S	0.15690(5)	0.27253(4)	0.12962(8)	3.08(2)
O(1)	0.1913(2)	-0.3197(1)	0.3697(3)	5.60(7)
O(2)	0.0889(2)	0.2270(1)	-0.0172(2)	4.11(6)
O(3)	0.2081(2)	0.3752(1)	0.0947(2)	4.46(6)
O(4)	0.0985(2)	0.2590(1)	0.2988(2)	4.18(6)
O(w)	0.2250(2)	0.0031(1)	-0.1096(2)	4.92(7)
N(1)	0.2709(2)	-0.1574(1)	0.4093(3)	3.45(6)
N(2)	0.2735(2)	0.2075(1)	0.1461(2)	2.89(6)
C(1)	0.4375(2)	0.0615(2)	0.1958(4)	3.69(8)
C(2)	0.3922(2)	-0.0344(2)	0.2225(3)	3.36(8)
C(3)	0.3775(2)	-0.0839(2)	0.3995(4)	3.64(8)
C(4)	0.1577(2)	-0.1194(2)	0.4299(4)	3.92(8)
C(5)	0.1190(2)	-0.0699(2)	0.2662(4)	3.64(8)
C(6)	0.0736(2)	0.0166(2)	0.2692(4)	4.24(9)
C(7)	0.2773(2)	-0.2536(2)	0.3791(4)	4.02(9)
H(1)	0.321(2)	0.221(2)	0.043(3)	4.1(7)
H(2)	0.316(2)	0.233(2)	0.228(3)	3.1(6)
H(11)	0.451(2)	0.082(2)	0.082(3)	4.2(7)
H(12)	0.453(2)	0.104(2)	0.295(4)	4.2(8)
H(21)	0.380(2)	-0.080(2)	0.127(3)	3.5(6)
H(31)	0.443(2)	-0.120(2)	0.421(3)	3.9(7)
H(32)	0.376(2)	-0.032(2)	0.500(3)	4.0(7)
H(41)	0.099(2)	-0.181(2)	0.457(4)	5.8(8)
H(42)	0.163(2)	-0.071(2)	0.538(4)	4.8(8)
H(51)	0.123(2)	-0.114(2)	0.154(4)	4.3(8)
H(61)	0.031(2)	0.034(2)	0.166(3)	4.4(7)
H(62)	0.080(2)	0.052(2)	0.371(3)	3.3(7)
H(71)	0.362(3)	-0.263(2)	0.372(4)	4.3(7)
H(1w)	0.264(3)	-0.045(3)	-0.120(6)	10(1)
H(2w)	0.243(2)	0.037(2)	-0.201(4)	6.0(9)

*For non H-atoms $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i a_j (\bar{a}_i \bar{a}_j)$.

leads to contraction of the S–N bond. Thus, in potassium sulfamate the S–N distance equals to 1.666(6) Å [14], though, as a neutron diffraction study has shown, a configuration of N atom is tetrahedral and the conjugation of the electron pair with SO_3^- -group is negligible.

Table 3. Bond lengths (Å), bond angles ($^\circ$) (with e.s.d.'s in parentheses) and torsion angles ($^\circ$) for I.

Coordination sphere			
Cu–O(w)	2.313(3)	O(w)–Cu–N(2)	100.5(1)
Cu–N(2)	2.044(4)	O(w)–Cu–m(12)	94.8(1)
Cu–C(1)	2.140(3)	O(w)–Cu–m(56)	94.8(1)
Cu–C(2)	2.201(3)	N(2)–Cu–m(12)	107.3(1)
Cu–m(12) *	2.065(3)	N(2)–Cu–m(56)	125.1(2)
Cu–C(5)	2.188(4)	C(1)–Cu–C(2)	35.9(1)
Cu–C(6)	2.100(3)	C(5)–Cu–C(6)	36.6(1)
Cu–m(56) *	2.036(4)	m(12)–Cu–m(56)	123.7(2)
Anion			
S–O(2)	1.440(3)	O(2)–S–O(3)	112.7(2)
S–O(3)	1.452(3)	O(2)–S–O(4)	114.9(2)
S–O(4)	1.442(3)	O(2)–S–N(2)	104.3(2)
S–N(2)	1.702(3)	O(3)–S–O(4)	113.4(2)
		O(3)–S–N(2)	105.9(2)
		O(4)–S–N(2)	104.5(2)
N(2)–H(1)	0.95(3)	Cu–N(2)–S	121.7(2)
N(2)–H(2)	0.83(2)	S–N(2)–H(1)	108(2)
		S–N(2)–H(2)	107(2)
		H(1)–N(2)–H(2)	104(2)
Molecule of ligand			
C(1)–C(2)	1.340(5)	C(2)–C(1)–H(11)	118(2)
C(1)–H(11)	0.91(3)	C(2)–C(1)–H(12)	119(2)
C(1)–H(12)	0.95(3)	H(11)–C(1)–H(12)	123(2)
C(2)–C(3)	1.496(4)	C(1)–C(2)–C(3)	124.9(3)
C(2)–H(21)	0.95(2)	C(1)–C(2)–H(21)	121(2)
		C(3)–C(2)–H(21)	113(2)
C(3)–N(1)	1.455(4)	C(2)–C(3)–N(1)	112.3(3)
C(3)–H(31)	0.96(3)	C(2)–C(3)–H(31)	110(2)
C(3)–H(32)	1.04(3)	C(2)–C(3)–H(32)	111(1)
		N(1)–C(3)–H(31)	106(2)
		N(1)–C(3)–H(32)	109(1)
		H(31)–C(3)–H(32)	108(2)
N(1)–C(4)	1.464(4)	C(3)–N(1)–C(4)	117.0(3)
N(1)–C(7)	1.336(4)	C(3)–N(1)–C(7)	120.0(3)
		C(4)–N(1)–C(7)	122.5(3)
C(4)–C(5)	1.504(4)	N(1)–C(4)–C(5)	113.5(3)
C(4)–H(41)	1.02(3)	N(1)–C(4)–H(41)	104(2)
C(4)–H(42)	1.04(3)	N(1)–C(4)–H(42)	109(1)
		C(5)–C(4)–H(41)	109(2)
		C(5)–C(4)–H(42)	111(1)
		H(41)–C(4)–H(42)	109(2)
C(5)–C(6)	1.348(5)	C(4)–C(5)–C(6)	123.2(3)
C(5)–H(51)	1.04(3)	C(4)–C(5)–H(51)	112(2)
		C(6)–C(5)–H(51)	124(2)
C(6)–H(61)	0.97(3)	C(5)–C(6)–H(61)	118(2)
C(6)–H(62)	0.91(3)	C(5)–C(6)–H(62)	118(2)
		H(61)–C(6)–H(62)	124(2)
C(7)–O(1)	1.229(4)	O(1)–C(7)–N(1)	124.7(3)
C(7)–H(71)	0.99(3)	N(1)–C(7)–H(71)	109(2)
		O(1)–C(7)–H(71)	126(2)

Table 3 (continuation)

		Water molecule	
O(w)-H(1w)	0.84(4)	H(1w)-O(w)-H(2w)	103(3)
O(w)-H(2w)	0.84(3)		
		Cu-N(2)-S-O(2)	57.2
		Cu-C(1)-C(2)-C(3)	-100.1
		C(1)-C(2)-C(3)-N(1)	144.5
		C(2)-C(3)-N(1)-C(4)	76.8
		C(2)-C(3)-N(1)-C(7)	-95.5
		C(3)-N(1)-C(4)-C(5)	-71.6
		C(3)-N(1)-C(7)-O(1)	-173.6
		C(4)-N(1)-C(7)-O(1)	-1.8
		C(7)-N(1)-C(4)-C(5)	100.5
		N(1)-C(4)-C(5)-C(6)	136.7
		C(4)-C(5)-C(6)-Cu	-103.4

* $m(12)$ and $m(56)$ – the mid-points of C(1)=C(2) and C(5)=C(6) distances, respectively.

Table 4. Hydrogen bond lengths (Å) and bond angles (°) with e.s.d.'s (in parentheses) in the crystals of **I**.

D-H...O	D-H (Å)	H...O (Å)	D...O (Å)	D-H...O (°)
N(2)-H(1)...O(4)	0.95(3)	2.06(3)	2.490(3)	171(2)
N(2)-H(2)...O(2)	0.83(2)	2.24(2)	2.485(3)	168(2)
C(2)-H(21)...O(1)	0.95(2)	2.45(2)	3.374(4)	167(2)
C(3)-H(32)...O(3)	1.04(3)	2.56(2)	3.454(4)	144(2)
C(4)-H(41)...O(1)	1.02(3)	2.37(3)	2.832(4)	106(2)
O(w)-H(1w)...O(1)	0.84(4)	1.98(4)	2.792(4)	163(4)
O(w)-H(2w)...O(3)	0.84(3)	1.98(3)	2.817(3)	176(3)

A well-developed system of rather strong hydrogen bonds of the N(H)...O, O(H)...O, and C(H)...O types (Table 4) combines the asymmetric units of **I** into layers in the (100) plane (Fig. 2). Both hydrogen atoms at the N-atom of NH_2SO_3^- molecule, and at the O(w)-atom of water molecule, form H-contacts of 1.98(3)–2.24(2) Å. The strong =C(2)-H...O(1) contact deserves attention, because it is in favour of the stronger interaction of the C=C bond with the copper atom [15]. H-bonds of C-H...O type and the van der Waals interactions between related by a centre of symmetry layers complete the structure. Thus, hydrogen bonds cause a formation of mononuclear π -complexes **I** and **II** of a remarkable stability.

A calculation of the effective atomic charges in **I** was performed, using the program package HYPERCHEM (ZINDO/1 semiempirical method – a modified version, including the transition metal atoms of the iterative SCF method in the MNDO approximation) [16]. The largest possible and the most closed cluster with the structure determined was selected (310 atoms, 840 orbitals). Considerable negative charge for Cu atom, being proper for copper(I) π -complexes with ionic salts [15], has been revealed in this case too: $q_{\text{Cu}} = -0.23$ e. The atomic charges for N(2), O(w) and H-atoms, which take part in hydrogen bonds of N(H)...O and O(H)...O types, are respectively equal to -0.39, -0.40 and +0.22/+0.28 e. An increase in the polarity of the $\text{O}^{\delta-}\dots\text{H}^{\delta+}-\text{X}^{\delta-}\dots\text{Cu}^{\delta+}$ chain stabilizes an electron donation of the metal atom. This is corroborated by the calculation of the effective atomic charges in the cluster neglecting H-bonds: in this case, the charge for Cu atom equals -0.27 e. The total charge of

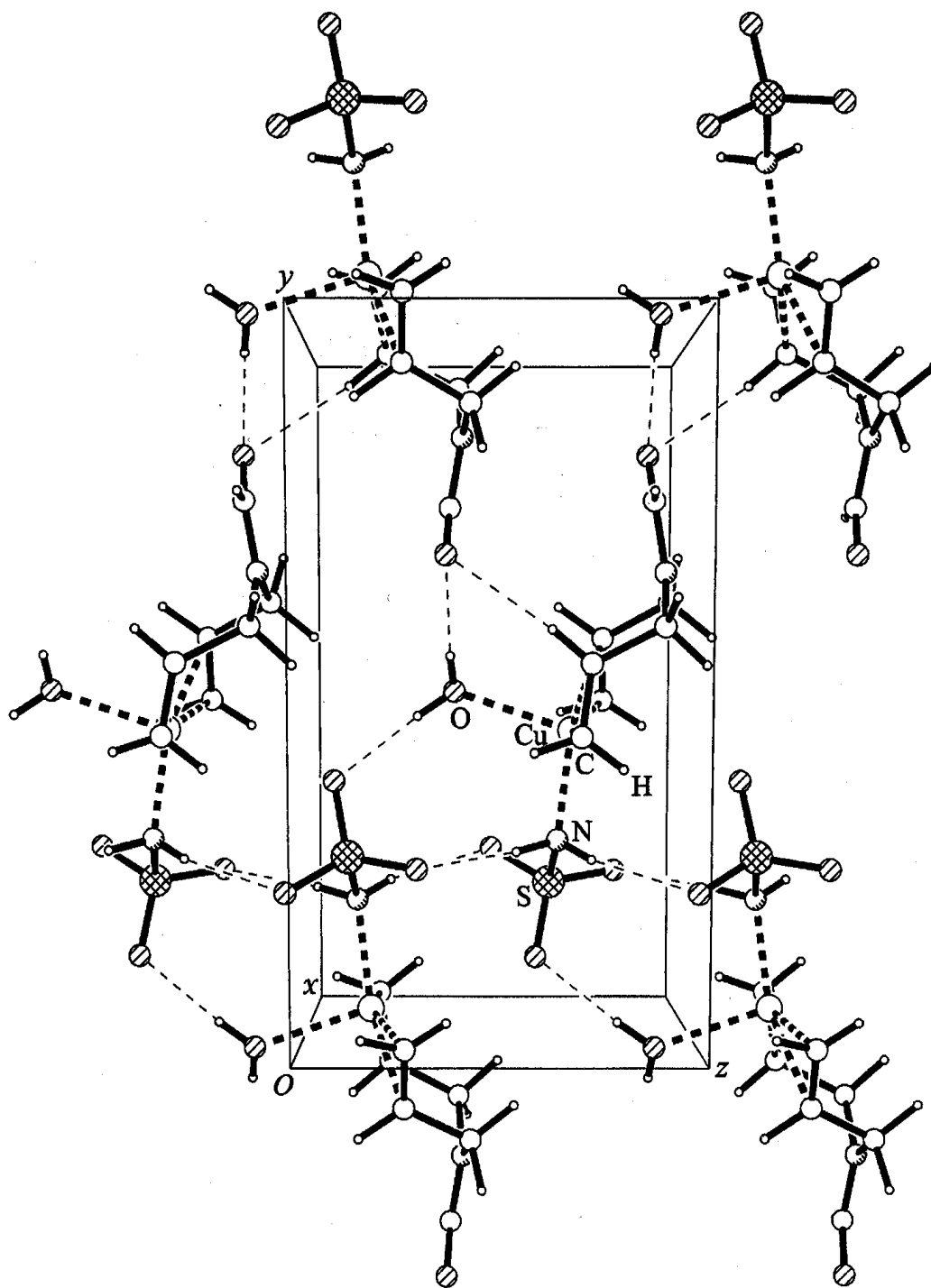


Figure 2. Crystal structure of I.

DAFA molecule equals to $+0.67 e$; the oxygen atom of the amide group possesses a charge of $-0.45 e$ and may be involved in coordination under appropriate conditions.

This considerable charge is induced in part by appreciable conjugation with nitrogen atom: deviation of N(1) from the plane of its neighbours equals to 0.06 Å.

Finally, it should be emphasized that the compound discussed is representative for hitherto practically unknown copper(I) sulfamate π -complexes.

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