Copper(I) Nitrate π-Complexes with 1-Allyl-2-Thiourea: Synthesis and Crystal Structure of [Cu(C₃H₅NHC(S)NH₂)(CH₃CN)]NO₃ and [Cu(C₃H₅NHC(S)NH₂)₃]NO₃

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Abstract—Crystal complexes $[Cu(C_3H_5NHC(S)NH_2)(CH_3CN)]NO_3$ (**I**) and $[Cu(C_3H_5NHC(S)NH_2)_3]NO_3$ (**II**) were synthesized in acetonitrile or benzonitrile solutions containing $Cu(NO_3)_2 \cdot 3H_2O$ and 1-allyl-2-thiourea by the ac electrochemical method. The crystal structures of **I** and **II** were determined by X-ray diffraction [a CAD-4 diffractometer, MoK_α radiation, 1757 reflections with $F \geq 4\sigma F$, 1440 reflections with $F \geq 6\sigma F$, $R = 0.049$ and 0.048 for **I** and **II**, respectively]. For π,σ-complex **I**, space group $P2_1/n$, $a = 7.9490(8)$, $b = 20.618(2)$, $c = 13.675(4)$ Å, $\beta = 95.46(2)°$, and $Z = 8$. For σ-complex **II**, space group $R\bar{3}$, $a = 12.3671(7)$, $c = 24.71(1)$ Å, and $Z = 6$. In **I**, the copper(I) atom is in a trigonal-pyramidal environment formed by two sulfur atoms, a C=C bond, and the N atom of the CH_3CN molecule. In **II**, copper(I) is in a trigonal planar environment of sulfur atoms.

Previous investigations of a number of copper(I) nitrate π-complexes—with diallyl cyanamide {CuNO₃ · (CH₂=CH–CH₂)₂NCN [1]} and diallylamine (CuNO₃ · (CH₂=CH–CH₂)₂NH (A, B) [2, 3] and [(CH₂=CH–CH₂)₂NH₂][Cu(NO₃)₂] [4]}—have shown that the olefin C=C grouping successfully competes with the σ-donor nitrogen atoms (nitrile and amine) for the site in the nearest Cu(I) surrounding. It is of interest to study the possibility of formation of the Cu(I)–(C=C) bond if the ligand is an unsaturated organic molecule containing a sulfur atom, to which copper(I) exhibits a rather high affinity. We synthesized the copper(I) nitrate complexes with 1-allyl-2-thiourea [Cu(CH₂=CHCH₂NHC(S)NH₂)(CH₃CN)]NO₃ (**I**) and [Cu(CH₂=CHCH₂NHC(S)NH₂)₃]NO₃ (**II**) and determined their crystal structures.

EXPERIMENTAL

1-Allyl-2-thiourea (ATU) was prepared by treating a water–alcohol mixture of allyl isothiocyanate with aqueous ammonia [5]. High-quality crystals of **I** and **II** were synthesized by ac ($U = 0.4$ V) electrochemical reduction of Cu(II) to Cu(I) in solutions of $Cu(NO_3)_2 \cdot 3H_2O$ and ATU in acetonitrile and benzonitrile, respectively. Crystals of **I** as elongated monoclinic prisms were grown within several hours, and tetrahedral crystals of **II** were grown within several days.

X-ray diffraction analysis of single crystals **I** and **II** was carried out on a CAD-4 diffractometer. Crystallographic data and experimental details are given in Table 1.

The structures were solved by the direct method, and light and hydrogen atoms were located from difference Fourier syntheses. Structure **I** was refined by the full-matrix least-squares method in anisotropic approximation for all

Table 1. Crystallographic data and experimental details for complexes **I** and **II**

Parameter	I	II
M	474.2	281.8
Space group	$P2_1/n$	$R\bar{3}$
a, Å	7.9490(8)	12.3671(7)
b, Å	20.618(2)	
c, Å	13.675(4)	24.71(1)
β, deg	95.46(2)	
V, Å³	2231(1)	3273(2)
Z	8	6
d_{calcd}, g/cm³	1.684(1)	1.443(1)
μ_{Mo}, cm⁻¹	22.05	13.41
Radiation	MoK_α	MoK_α
Diffractometer	CAD-4	CAD-4
Scan mode	$\theta/2\theta$	$\theta/2\theta$
Number of reflections:		
measured	6481	2404
independent	1757	1440
$(F \geq n\sigma F)$	$n = 4$	$n = 6$
$2\theta_{max}$, deg	60	55
Number of refined parameters	464	151
R	0.049	0.048
R_w	0.051	0.049

Table 2. Coordinates of atoms and their thermal parameters* for structures **I** and II

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
		I			H(51)	0.18(1)	−0.135(4)	0.343(6)	6(3)
Cu(1)	0.5720(1)	0.02404(5)	0.1653(1)	4.32(4)	H(52)	0.167(8)	−0.133(3)	0.233(5)	3(2)
Cu(2)	0.4359(1)	−0.08320(5)	0.30198(9)	4.00(3)	H(61)	0.192(9)	−0.023(3)	0.253(5)	4(3)
S(1)	0.4472(3)	−0.0670(1)	0.1003(2)	3.22(6)	H(71)	0.05(1)	−0.002(4)	0.408(6)	4(3)
S(2)	0.5728(3)	0.0057(1)	0.3645(2)	3.35(6)	H(72)	0.22(1)	−0.033(4)	0.451(7)	7(3)
O(1)	0.2822(8)	0.2473(3)	0.4277(6)	6.1(2)	H(101)	0.213(8)	0.217(3)	0.137(5)	3(2)
O(2)	0.5252(9)	0.2740(3)	0.3871(6)	6.7(3)	H(102)	0.28(1)	0.215(5)	0.224(8)	10(5)
O(3)	0.412(1)	0.3296(3)	0.4916(6)	7.1(3)	H(103)	0.13(1)	0.178(4)	0.230(7)	8(4)
O(4)	0.0540(9)	0.1339(4)	0.5056(5)	6.7(3)	H(121)	0.78(1)	−0.265(4)	0.278(7)	8(4)
O(5)	−0.173(1)	0.1885(4)	0.4844(7)	8.5(3)	H(122)	0.885(9)	−0.244(3)	0.356(5)	4(3)
O(6)	−0.065(1)	0.1456(5)	0.3668(7)	11.5(4)	H(123)	0.78(1)	−0.294(5)	0.369(8)	12(5)
N(1)	0.7620(8)	−0.1103(3)	0.0807(5)	3.5(2)	H(1.N1)	0.829(7)	−0.139(3)	0.079(4)	1(1)
N(2)	0.5560(9)	−0.1857(3)	0.0742(5)	3.8(2)	H(1.N2)	0.461(7)	−0.191(3)	0.082(4)	1(1)
N(3)	0.2640(9)	0.0515(3)	0.3950(5)	3.9(2)	H(2.N2)	0.630(9)	−0.219(4)	0.047(6)	5(3)
N(4)	0.480(1)	0.1230(4)	0.4088(6)	5.3(3)	H(1.N3)	0.194(9)	0.082(4)	0.408(6)	5(3)
N(5)	0.4173(9)	0.0973(3)	0.1605(6)	4.1(2)	H(1.N4)	0.416(7)	0.149(3)	0.433(4)	1(2)
N(6)	0.585(1)	−0.1583(4)	0.3180(6)	4.7(3)	H(2.N4)	0.579(8)	0.137(3)	0.412(5)	3(2)
N(7)	0.4069(9)	0.2835(3)	0.4365(5)	3.3(2)					
N(8)	−0.060(1)	0.1557(4)	0.4502(6)	5.0(3)			**II**		
C(1)	0.818(1)	0.0601(4)	0.1617(8)	4.8(3)	Cu	0	0	0.06553(3)	3.55(2)
C(2)	0.823(1)	−0.0046(4)	0.1617(7)	3.6(3)	S	0.20354(7)	0.06485(7)	0.07559(3)	3.83(3)
C(3)	0.834(1)	−0.0450(4)	0.0740(6)	3.2(2)	O	0.1094(2)	0.0238(2)	0.5784(1)	8.5(1)
C(4)	0.602(1)	−0.1235(4)	0.0849(6)	3.0(2)	N(1)	0.3234(4)	−0.0520(3)	0.1068(1)	4.9(2)
C(5)	0.181(1)	−0.1119(4)	0.2902(7)	4.6(3)	N(2)	0.1563(3)	−0.1651(4)	0.0530(1)	4.7(2)
C(6)	0.190(1)	−0.0474(4)	0.2973(7)	3.7(3)	N(3)	0	0	0.5784(3)	6.5(2)
C(7)	0.180(1)	−0.0117(4)	0.3921(7)	3.9(3)	C(1)	0.5715(6)	0.1053(6)	0.0700(2)	10.7(3)
C(8)	0.425(1)	0.0630(4)	0.3905(6)	3.3(2)	C(2)	0.5377(4)	0.1213(4)	0.1151(2)	7.8(2)
C(9)	0.328(1)	0.1392(4)	0.1689(7)	3.8(3)	C(3)	0.4124(4)	0.0521(4)	0.1391(2)	6.5(2)
C(10)	0.214(1)	0.1927(5)	0.1822(9)	5.9(4)	C(4)	0.2296(3)	−0.0590(4)	0.0790(1)	3.4(1)
C(11)	0.678(1)	−0.1968(4)	0.3222(7)	3.9(3)	H(11)	0.525(9)	0.054(6)	0.038(1)	15(6)
C(12)	0.800(1)	−0.2509(5)	0.3255(8)	5.8(4)	H(12)	0.645(5)	0.153(4)	0.055(1)	8(3)
H(11)	0.84(1)	0.083(4)	0.220(6)	6(3)	H(21)	0.596(6)	0.179(5)	0.138(2)	10(4)
H(12)	0.804(8)	0.085(3)	0.103(5)	4(3)	H(31)	0.414(4)	0.021(3)	0.173(2)	8(2)
H(21)	0.844(8)	−0.026(3)	0.219(5)	3(2)	H(32)	0.385(3)	0.110(4)	0.140(2)	10(3)
H(31)	0.764(9)	−0.011(3)	0.013(5)	3(2)	H(1*n*1)	0.333(3)	−0.110(4)	0.102(1)	6(2)
H(32)	0.951(8)	−0.051(3)	0.063(5)	3(2)	H(1*n*2)	0.106(4)	−0.169(5)	0.030(1)	7(3)
					H(2*n*2)	0.173(5)	−0.218(4)	0.051(2)	8(3)

* For all the atoms in structure **II** and non-hydrogen atoms in **I**, $B_{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* (\vec{a}_i \vec{a}_j)$, for H atoms in structure **I**, B_{iso}.

non-hydrogen atoms, and in structure **II**, all the atoms were refined anisotropically using the CSD program package [6]. The coordinates of atoms and their thermal parameters in structures **I** and **II** are listed in Table 2. Table 3 presents the interatomic distances and bond and torsion angles.

RESULTS AND DISCUSSION

Figure 1 shows a fragment of structure **I**. π,σ-Complex **I** has a typical ionic structure because even weak contacts between the Cu(I) atoms and the NO_3^- anions are absent: the shortest Cu–O(NO$_2$) distances are

Table 3. Bond lengths and bond and torsion angles in structures **I** and **II**

Bond*	d, Å	Angle*	ω, deg	Bond*	d, Å	Angle*	ω, deg
I				C(7)–H(71)	1.10(8)	N(3)C(7)C(6)	113.5(7)
Cu(1)–S(1)	2.265(2)	S(1)Cu(1)S(2)	103.5(1)	C(7)–H(72)	0.94(9)	N(3)C(7)H(71)	106(4)
Cu(1)–S(2)	2.750(3)	S(1)Cu(1)N(5)	112.3(2)			N(3)C(7)H(72)	105(5)
Cu(1)–N(5)	1.944(7)	S(1)Cu(1)m(12)	115.0(3)			C(6)C(7)H(71)	113(4)
Cu(1)–C(1)	2.101(10)	S(2)Cu(1)N(5)	94.7(2)			C(6)C(7)H(72)	118(5)
Cu(1)–C(2)	2.083(8)	S(2)Cu(1)m(12)	97.0(3)			H(71)C(7)H(72)	100(7)
Cu(1)–m(12)	1.983(8)	N(5)Cu(1)m(12)	126.7(4)	N(3)–C(7)	1.46(1)	C(7)N(3)C(8)	127.3(7)
		C(1)Cu(1)C(2)	37.2(4)	N(3)–C(8)	1.31(1)	C(7)N(3)H(1.N3)	110(5)
Cu(2)–S(2)	2.257(3)	S(1)Cu(2)S(2)	102.6(1)	N(3)–H(1.N3)	0.86(8)	C(8)N(3)H(1.N3)	121(5)
Cu(2)–S(1)	2.788(3)	S(1)Cu(2)N(6)	97.5(2)	C(8)–N(4)	1.33(1)	S(2)C(8)N(3)	124.9(7)
Cu(2)–N(6)	1.949(8)	S(1)Cu(2)m(56)	93.8(3)	C(8)–S(2)	1.729(9)	S(2)C(8)N(4)	117.1(7)
Cu(2)–C(5)	2.103(10)	S(2)Cu(2)N(6)	109.7(2)			N(3)C(8)N(4)	118.0(8)
Cu(2)–C(6)	2.081(8)	S(2)Cu(2)m(56)	115.9(3)	N(4)–H(1.N4)	0.83(5)	C(8)N(4)H(1.N4)	118(4)
Cu(2)–m(56)	1.983(8)	N(6)Cu(2)m(56)	129.1(3)	N(4)–H(2.N4)	0.84(6)	C(8)N(4)H(2.N4)	128(4)
		C(5)Cu(2)C(6)	37.2(8)			H(1.N4)N(4)H(2.N4)	112(6)
C(1)–C(2)	1.33(1)	C(2)C(1)H(11)	120(5)	N(5)–C(9)	1.13(1)	Cu(1)N(5)C(9)	172.2(7)
C(1)–H(11)	0.93(9)	C(2)C(1)H(12)	122(4)	C(9)–C(10)	1.45(1)	N(5)C(9)C(10)	178.7(10)
C(1)–H(12)	0.95(7)	H(11)C(1)H(12)	118(7)	C(10)–H(101)	0.80(6)	C(9)C(10)H(101)	111(5)
C(2)–C(3)	1.47(1)	C(1)C(2)C(3)	124.8(8)	C(10)–H(102)	0.9(1)	C(9)C(10)H(102)	97(7)
C(2)–H(21)	0.90(7)	C(1)C(2)H(21)	120(4)	C(10)–H(103)	1.04(9)	C(9)C(10)H(103)	109(5)
		C(3)C(2)H(21)	114(4)			H(101)C(10)H(102)	97(8)
C(3)–N(1)	1.470(10)	N(1)C(3)C(2)	114.5(7)			H(101)C(10)H(103)	134(7)
C(3)–H(31)	1.18(7)	N(1)C(3)H(31)	115(5)			H(102)C(10)H(103)	99(9)
C(3)–H(32)	0.97(7)	N(1)C(3)H(32)	106(4)	N(6)–C(11)	1.08(1)	Cu(2)N(6)C(11)	173.2(8)
		C(2)C(3)H(31)	100(3)	C(11)–C(12)	1.48(1)	N(6)C(11)C(12)	178(1)
		C(2)C(3)H(32)	110(4)	C(12)–H(121)	0.72(10)	C(11)C(12)H(121)	99(8)
		H(31)C(3)H(32)	111(5)	C(12)–H(122)	0.77(7)	C(11)C(12)H(122)	114(6)
		C(3)N(1)C(4)	125.3(7)	C(12)–H(123)	1.1(1)	C(11)C(12)H(123)	119(6)
N(1)–C(4)	1.304(10)	C(3)N(1)H(1.N1)	114(4)			H(121)C(12)H(122)	140(10)
N(1)–H(1.N1)	0.80(6)	C(4)N(1)H(1.N1)	120(4)			H(121)C(12)H(123)	97(10)
C(4)–S(1)	1.723(8)	S(1)C(4)N(1)	125.1(6)			H(122)C(12)H(123)	93(8)
		S(1)C(4)N(2)	117.9(6)	N(7)–O(1)	1.236(9)	O(1)N(7)O(2)	120.1(7)
C(4)–N(2)	1.338(9)	N(1)C(4)N(2)	116.9(7)	N(7)–O(2)	1.225(10)	O(1)N(7)O(3)	120.7(7)
N(2)–H(1.N2)	0.78(6)	C(4)N(2)H(1.N1)	113(4)	N(7)–O(3)	1.213(10)	O(2)N(7)O(3)	119.3(7)
N(2)–H(2.N2)	1.00(8)	C(4)N(2)H(2.N2)	122(4)	N(8)–O(4)	1.21(1)	O(4)N(8)O(5)	119.2(8)
		H(1.N2)N(2)H(2.N2)	124(6)	N(8)–O(5)	1.244(10)	O(4)N(8)O(6)	120.1(9)
C(5)–C(6)	1.34(1)	C(6)C(5)H(51)	119(6)	N(8)–O(6)	1.16(1)	O(5)N(8)O(6)	120.7(9)
C(5)–H(51)	0.86(8)	C(6)C(5)H(52)	124(4)			**II**	
C(5)–H(52)	0.90(7)	H(51)C(5)H(52)	117(7)	Cu–S	2.241(1)	SCuS'	118.79(4)
C(6)–C(7)	1.50(1)	C(5)C(6)C(7)	123.0(8)	Cu–S'	2.241(1)	SCuS'	118.79(4)
C(6)–H(61)	0.79(7)	C(5)C(6)H(61)	126(5)	Cu–S'	2.241(1)	S'CuS'	118.79(4)
		C(7)C(6)H(61)	111(5)	C(1)–C(2)	1.240(8)	C(2)C(1)H(11)	133(4)

Table 3. (Contd.)

Bond*	d, Å	Angle*	ω, deg	Bond*	d, Å	Angle*	ω, deg
C(1)–H(11)	0.99(5)	C(2)C(1)H(12)	126(4)			N(2)C(4)H(1.N1)	93(1)
C(1)–H(12)	0.88(6)	H(11)C(1)H(12)	100(6)	N(2)–C(4)	1.330(5)	SC(4)N(2)	121.1(3)
C(2)–C(3)	1.469(7)	C(3)C(2)C(1)	127.6(5)	N(2)–H(1.N2)	0.83(5)	C(4)N(2)H(1.N2)	121(3)
C(2)–H(21)	0.92(5)	C(3)C(2)H(21)	113(4)	N(2)–H(2.N2)	0.78(5)	C(4)N(2)H(2.N2)	122(4)
		C(1)C(2)H(21)	119(4)			H(1.N2)N(2)H(2.N2)	114(5)
C(3)–H(31)	0.93(4)	C(2)C(3)C(1)	114.1(4)	N(3)–O	1.233(3)	ON(3)O'	120.0(4)
C(3)–H(32)	0.93(5)	H(31)C(3)N(1)	107(3)	N(3)–O'	1.233(3)	ON(3)O'	120.0(4)
		H(32)C(3)N(1)	107(3)	N(3)–O'	1.233(3)	O'N(3)O'	120.0(4)
		C(2)C(3)H(31)	112(3)				

				Torsion angles			
		C(2)C(3)H(32)	104(3)	Angle	φ, deg	Angle	φ, deg
		H(31)C(3)H(32)	112(4)			I	
N(1)–C(3)	1.446(6)	C(3)N(1)C(4)	127.0(4)	C(1)C(2)C(3)N(1)	−153.7	C(5)C(6)C(7)N(3)	154.6
N(1)–C(4)	1.313(6)	C(3)N(1)H(1.N1)	120(3)	C(2)C(3)N(1)C(4)	66.9	C(6)C(7)N(3)C(8)	−63.4
		C(4)N(1)H(1.N1)	113(3)	C(3)N(1)C(4)N(2)	−169.1	C(7)N(3)C(8)N(4)	170.3
C(4)–S	1.718(4)	SC(4)N(2)	121.1(3)	C(3)N(1)C(4)S(1)	9.4	C(7)N(3)C(8)S(2)	−8.5
		SC(4)N(1)	121.4(3)			II	
		SC(4)H(1.N1)	145(1)	C(1)C(2)C(3)N(1)	5.1	C(3)N(1)C(4)N(2)	−178.2
		N(2)C(4)N(1)	117.5(4)	C(2)C(3)N(1)C(4)	−107.7	C(3)N(1)C(4)S	2.5

* $m(12)$ and $m(56)$ are the midpoints of the C(1)=C(2) and C(5)=C(6) bonds, respectively.

4.336(9) and 4.547(9) Å. Two independent copper(I) atoms and two sulfur atoms of two ATU molecules form a planar parallelogram with a Cu–Cu distance of 3.152(2) Å. The S(1)Cu(1)S(2)Cu(2) and S(2)Cu(1)S(1)Cu(2) torsion angles are 2.3° and 2.7°, respectively.
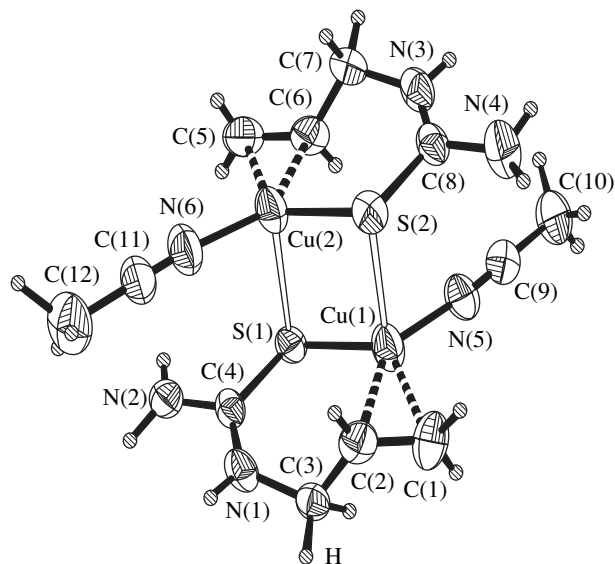
In the ionic copper(I) π-complexes, such a combination of the copper and sulfur atoms, which belong to the inorganic and organic components of a metallocomplex, respectively, was found for the first time (however, in copper halide π-complexes, e.g., in CuCl · (allylamine) [7], such a combination is rather widely encountered).

Each of the two independent copper atoms in the dimeric cation has a trigonal-pyramidal coordination. The C=C bond, the sulfur atom of ATU, and the nitrogen atom of acetonitrile are in the basal plane of the polyhedron. The sulfur atom of the other independent ATU molecule occupies the apical site. Because of its extraordinary flexibility, the ATU molecule functions as a chelating π,σ-ligand, in which the allyl group is nearly in the *cisoid* position to the thiocarbamide moiety (see torsion angles in Table 3). Although the nearest copper environment contains three σ-donor ligands—two sulfur atoms and the nitrile nitrogen atom—the copper(I) atom exhibits a pronounced tendency to form a Cu–(C=C) π-bond. The efficiency of this π-interaction is indicated by rather short distances between Cu(I) and the midpoint of (C=C) [1.983(8) Å]. However, the coordinated C=C bonds do not experience noticeable elongation [the C=C distances are 1.33(1) and 1.34(1) Å], and this is evidence that the $(M \longleftarrow L)_\sigma$ component essentially dominates the $(M \longrightarrow L)_\pi$ component, which is quite natural in the presence of the three σ-donor atoms [8].

Fig. 1. Structure of dimeric cation [Cu$_2$(C$_3$H$_5$NHC(S)NH$_2$)$_2$(CH$_3$CN)$_2$].

Rather strong hydrogen bonds of the N(H)···O type [1.99–2.47(8) Å] and weaker bonds of the N(H)···S, C(H)···S, and C(H)···O types are essential for structure **I**. The geometry of the most significant H-bonds of different types is given in Table 4. The following correlation stands out: the stronger the N–H···O hydrogen bond is, the longer the N–O distance in the NO_3^- ion is. For example, the H(2.N2)···O(5) bond length is 1.99(8) Å, whereas the length of the corresponding N(8)–O(5) bond in the nitrate ion is 1.24(1) Å, which is greater than the N(8)–O(6) distance [1.16(1) Å] in the same anion. The O(6) atom is mainly involved in the weak C–H···O contacts. The strong H···O bonds also lead to elongation of the N–H and C–H bonds.

The structure of complex **II** ($CuNO_3$: ATU = 1 : 3) is quite different (Fig. 2). In this ionic compound, the copper atom is in a special position in axis $\bar{3}$ and has the planar trigonal environment of the sulfur atoms at distances of 2.241(1) Å. The C=C bond in the uncoordinated allyl moiety of ATU [1.240(8) Å] is close in length to the similar bond in the free ATU (1.27 Å [9]). The nitrogen atoms of the NO_3^- anions also occupy special positions in axis $\bar{3}$. The nitrate ions have no contacts with the copper atoms [the $Cu–O(NO_2)$ distance is 6.303(3) Å, and the shortest Cu–Cu distance is 3.238(1) Å]. Contrary to **I**, the oxygen atoms of the NO_3^- anions form in structure **II** rather weak hydrogen bonds of the O···H(N) type. For this reason, the N–O distances in anions remain unaltered [1.233(3) Å], so that **II** has a rather high-symmetry rhombohedral lattice. Structure **II** also exhibits weak S···H(N) [2.71(4) Å] and even S···H(C) [2.58(5) Å] contacts. In general, the conformations of the ATU molecules in structures **I** and **II** are
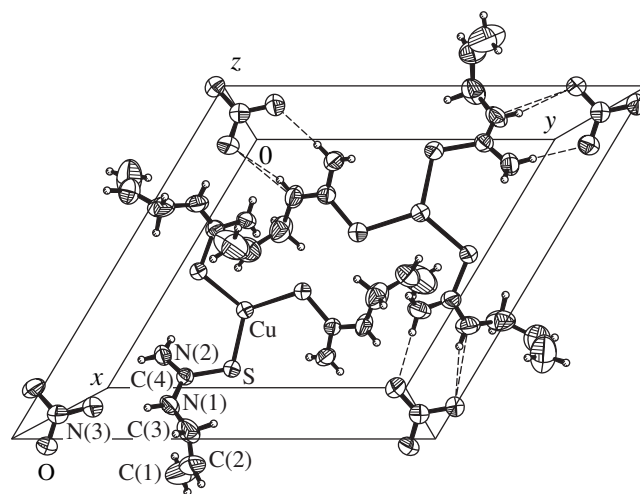

Fig. 2. Structure **II**.

similar; however, they differ in the mutual arrangement of the olefin group and the C(3)–N(1) bond with respect to the C(2)–C(3) bond: *transoid* in **I**, and *cisoid* in **II**.

What is responsible for the formation, from the same components, of the complexes that are so different in composition and structure? First of all, complexes **I** and **II** were synthesized in different solvents: acetonitrile and benzonitrile, respectively. Nitriles are required to obtain the single crystals because in the absence of nitriles the powdered $CuNO_3$ adducts with ATU form. Being readily soluble in more polar acetonitrile, $Cu(NO_3)_2 \cdot 3H_2O$ promoted, in the presence of ATU, the formation of 1 : 1 : 1 complex **I**, including a small-sized solvent molecule. In benzonitrile, copper(II) nitrate is noticeably less soluble, as distinct from

Table 4. Geometry of hydrogen bonds in structures **I** and **II**

A–H···B	d(H···B), Å	ω, deg	A–H···B	d(H···B), Å	ω, deg
			I		
N(1)–H(1.N1)···O(2)	2.16(6)	162(6)	C(10)–H(103)···O(6)	2.61(9)	173(7)
N(1)–H(1.N1)···O(3)	2.44(6)	143(5)	C(12)–H(123)···O(3)	2.6(1)	140(8)
N(2)–H(1.N2)···O(1)	2.30(5)	153(5)	C(1)–H(11)···O(6)	2.44(9)	172(7)
N(2)–H(2.N2)···O(5)	1.99(8)	150(6)	C(1)–H(12)···O(3)	2.53(7)	149(6)
N(3)–H(1.N3)···O(4)	2.12(8)	152(7)	C(3)–H(31)···S(1)	2.71(7)	168(5)
N(3)–H(1.N3)···O(6)	2.47(8)	151(7)	C(5)–H(51)···O(5)	2.61(8)	171(7)
N(4)–H(1.N4)···O(1)	2.29(5)	149(5)	C(5)–H(51)···O(2)	2.86(7)	147(5)
N(4)–H(2.N4)···O(5)	2.37(6)	157(6)	C(7)–H(72)···S(2)	2.93(9)	140(7)
C(10)–H(102)···O(1)	2.87(11)	134(8)			
			II		
N(1)–H(1.N1)···O	2.17(4)	162(4)	N(1)–H(1.N1)···O	2.67(4)	146(4)
N(2)–H(1.N2)···S	2.71(4)	148(4)	N(2)–H(2.N2)···O	2.30(5)	152(5)

ATU. This fact, as well as considerably greater molecular dimensions of C_6H_5CN compared to CH_3CN, favored the formation of crystals of the 1 : 3 copper(I) nitrate complex with ATU.

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