

π -Complexation of Copper(I) with Allylacetone Oxime. Synthesis and Crystal Structure of the $\text{CuX} \cdot \text{C}_3\text{H}_5\text{—CH}_2\text{—C}(\text{CH}_3)=\text{N—OH}$ ($\text{X} = \text{Cl}$ or Br) Compounds

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Abstract—Crystal complexes $\text{CuCl} \cdot \text{AAO}$ (**I**) and $\text{CuBr} \cdot \text{AAO}$ (**II**) (AAO = allylacetone oxime) were prepared by an electrochemical synthesis from ethanol solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or CuBr_2 and AAO, and their crystal structures were determined [a DARCH diffractometer, MoK_α radiation, 1409 and 930 independent reflections with $F \geq 4\sigma(F)$, $R = 0.048$ and 0.037 for **I** and **II**, respectively]. The crystals of the isostructural complexes are monoclinic, space group $P2_1/a$, $Z = 4$. Unit cell parameters for **I** are $a = 15.606(6)$, $b = 7.782(4)$, $c = 7.480(7)$ Å, $\beta = 111.46(5)^\circ$, $V = 845(2)$ Å³; for **II** they are $a = 16.014(5)$, $b = 7.920(3)$, $c = 7.504(2)$ Å, $\beta = 111.27(2)^\circ$, $V = 887(1)$ Å³. In both structures, the copper atom is simultaneously π - and σ -coordinated and has a trigonal-pyramidal environment constituted of the oxime nitrogen atom, a halogen atom and the C=C bond in the equatorial plane, and an apical halogen atom. The lengths of the coordinated C=C bonds are 1.35(1) (**I**) and 1.35(2) (**II**) Å.

Owing to the additional chelating groups, azomethines are widely used as complexones in the chemistry of d elements [1]. They are σ -coordinated to the metal atoms in the complexes. It was of interest to prepare complexes with the unsaturated azomethine ligands of various structure and to study the behavior of the C=C bond in the presence of the donor nitrogen atom of the $>\text{C}=\text{N—X}$ group ($\text{X} = \text{R}, \text{OH}, \text{N}=\text{C}$, etc.). Our previous studies of the π -complexes of copper(I) chloride with *N*-allyl-2-furylaldimine and *N*-allylbenzaldimine have revealed the coordination abilities of the C=C bonds in the presence of the aldimine HC=N—R group [2]. To continue the studies on the π -complexation between copper(I) and unsaturated azomethines, we prepared crystals of the copper(I) chloride and bromide π -complexes with allylacetone oxime (AAO) of the equimolar compositions $\text{CuCl} \cdot \text{C}_3\text{H}_5\text{—CH}_2\text{—C}(\text{CH}_3)=\text{N—OH}$ (**I**) and $\text{CuBr} \cdot \text{C}_3\text{H}_5\text{—CH}_2\text{—C}(\text{CH}_3)=\text{N—OH}$ (**II**) and studied their crystal structures.

EXPERIMENTAL

The AAO ligand was synthesized by reacting allylacetone with hydroxylamine hydrochloride in an aqueous solution in the presence of sodium carbonate [3]. Compounds **I** and **II** were prepared as well-shaped single crystals by an ($U = 0.3$ V) electrochemical reduction of Cu(II) to Cu(I) in ethanol solutions containing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or CuBr_2 , respectively, and the ligand. The crystals of compound **I** were grown for 2 h as colorless air-stable needles. The crystals of complex **II** of the same habit were formed upon cooling the solution to -3°C after one day of electrolysis.

The structures were solved using the sets of diffraction data collected on a DARCH single-crystal diffractometer. The intensities of reflections were corrected for the Lorentz and polarization effects. Absorption correction was applied using the DIFABS program. The crystallographic and data collection parameters are listed in Table 1.

The structures were solved by the direct method; the O, N, C, and H atoms were determined from Fourier difference synthesis. All the non-hydrogen atoms were refined in the full-matrix anisotropic approximation (the hydrogen atoms were refined in the isotropic approximation) using the CSD program package [4].

The atomic coordinates and the thermal parameters for structures **I** and **II** are listed in Table 2, and the bond lengths, bond angles, and torsion angles are given in Table 3.

RESULTS AND DISCUSSION

Isomorphous compounds **I** and **II** are typical molecular complexes, in which the copper atom has a trigonal-pyramidal environment constituted of the oxime nitrogen atom, a halogen atom and the C=C bond in the equatorial plane, and an apical halogen atom. Two copper(I) atoms and two halogen atoms form a planar parallelogram. The Cu—Cu distances in **I** and **II** are 3.319(5) and 3.395(3) Å, respectively. This way of arranging the inorganic fragment is quite typical for the copper halide π -complexes, e.g., for the $\text{CuCl} \cdot$ allylamine structure [5]. Owing to its extraordinary flexibility, the ligand molecule functions as a chelating π,σ -ligand and completes the trigonal pyramidal coordina-

Table 1. Crystallographic and data collection parameters for **I** and **II**

Parameter	I	II
<i>M</i>	212.2	256.6
<i>F</i> (000)	432	504
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i>
<i>a</i> , Å	15.606(6)	16.014(5)
<i>b</i> , Å	7.782(4)	7.920(3)
<i>c</i> , Å	7.480(7)	7.504(2)
β , deg.	111.46(5)	111.27(2)
<i>V</i> , Å ³	845(2)	887(1)
<i>Z</i>	4	4
ρ (calcd.), g/cm ³	1.667(4)	1.922(2)
μ_{Mo} , cm ⁻¹	29.24	72.60
Radiation	MoK α	MoK α
Diffractometer	DARCh	DARCh
Scan mode	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{\text{max}}$, deg.	60	58
Number of reflections:		
measured	1522	1016
independent with $F \geq 4\sigma(F)$	1409	930
Number of refined parameters	135	135
<i>R</i>	0.048	0.037
<i>R</i> _w	0.063	0.043
Weighing scheme	$[\sigma(F_o)^2 + 0.0055 F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0020 F_o^2]^{-1}$
GOOF	1.05	1.04

tion sphere of the copper(I) atom by its C=C bond and nitrogen atom. With such a coordination mode, the allyl group occupies a near-cisoid position relative to the oxime group (Table 3), i.e., it takes the conformation similar to that of the allylthiourea (ATU) molecule in the copper(I) nitrate complex [Cu(C₃H₅NHC(S)NH₂)(CH₃CN)]NO₃ (**III**) [6]. In complexes **I** and **II**, the torsion angles C(2)C(3)C(4)C(5) are equal to 65.4° and 63.6°, respectively. The corresponding angles in **III** are equal to 66.9° and -63.4° for two independent ATU molecules that are also π, σ -chelated to copper(I). It is noteworthy that, unlike ATU, the AAO molecule, except for its allyl group, is almost coplanar with the copper atom. Thus, the structures of **I** and **II** are formed from the centrosymmetric Cu₂X₂ · 2AAO dimers (X = Cl or Br) linked together by the van der Waals forces and weak hydrogen bonds of the C-H...O type. A fragment of structure **I** is shown in the figure.

The coordination polyhedron of Cu(I) is not subjected to a strong trigonal distortion and is close to a tetrahedron, resulting in a substantial deviation of the copper atom from the plane of equatorial ligands (by 0.32 and 0.38 Å for **I** and **II**, respectively) [7]. The orienta-

tion of the C=C bond is largely determined by the steric factors. The angles between the plane of equatorial ligands and the C=C bond are equal to 19.5° and 15.7° for **I** and **II**, respectively. Despite the efficient Cu-(C=C) interaction [the distances between Cu(I) and the midpoint of the C=C bond are 1.941(9) Å in **I** and 1.95(1) Å in **II**], the coordinated olefinic bond is slightly lengthened [1.35(1) Å in **I** and 1.35(2) Å in **II**], indicating that the (M ← L) σ component markedly predominates over the (M → L) π component, which is quite natural in the presence of a donor nitrogen atom [7].

Because of the efficient Cu-N interaction, the copper atoms in the copper(I) chloride π -complexes with *N*-allyl-2-furylaldimine and *N*-allylbenzaldimine are coordinated separately in the π and σ modes [the Cu-N distances are 1.932(4) and 1.941(5) Å, respectively] [2]. In complexes **I** and **II**, the electronegative oxygen atom diminishes basicity of the oxime nitrogen [the Cu-N contacts of 2.007(7) Å in **I** and 2.004(8) Å in **II** are weaker], allowing simultaneous π - and σ -coordination of the copper atom.

The calculation of the atomic charges carried out with the HYPERCHEM program using a modified ver-

Table 2. Atomic coordinates* and thermal parameters** for structures **I** and **II**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Cu	0.01518(4)	0.1858(1)	0.11641(8)	4.88(2)
	0.01924(7)	0.1857(1)	0.1211(2)	5.13(4)
Cl	-0.09315(8)	0.1319(2)	-0.1749(2)	4.65(3)
Br	-0.09688(5)	0.1331(1)	-0.1818(1)	4.70(3)
N	0.1060(3)	0.3153(5)	0.0350(5)	3.9(1)
	0.1080(4)	0.3155(8)	0.0437(9)	4.3(2)
O	0.0901(3)	0.3132(5)	-0.1611(5)	5.0(1)
	0.0947(4)	0.3146(8)	-0.1545(8)	5.5(2)
C(1)	-0.0206(4)	0.224(1)	0.3535(8)	6.0(2)
	-0.0208(6)	0.225(1)	0.352(1)	6.1(4)
C(2)	0.0706(5)	0.250(1)	0.4008(8)	6.4(2)
	0.0672(7)	0.259(2)	0.402(1)	7.9(4)
C(3)	0.1222(6)	0.410(1)	0.4182(8)	7.4(3)
	0.1238(9)	0.411(2)	0.4224(1)	9.6(5)
C(4)	0.1980(4)	0.421(1)	0.3445(8)	6.1(2)
	0.1959(5)	0.418(1)	0.351(1)	6.0(3)
C(5)	0.1750(3)	0.4046(7)	0.1328(7)	4.4(1)
	0.1750(5)	0.4034(9)	0.141(1)	4.4(3)
C(6)	0.2342(4)	0.4982(8)	0.0484(9)	5.9(2)
	0.2350(6)	0.489(1)	0.059(2)	6.8(4)
H(O)	0.047(3)	0.255(8)	-0.204(7)	5(1)
	0.064(4)	0.233(9)	-0.19(1)	6(2)
H(1.1)	-0.064(5)	0.318(8)	0.300(8)	6(1)
	-0.048(4)	0.333(8)	0.32(1)	4(2)
H(1.2)	-0.048(5)	0.13(1)	0.378(8)	9(2)
	-0.037(4)	0.09(1)	0.38(1)	6(2)
H(2.1)	0.130(7)	0.18(1)	0.47(1)	13(3)
	0.128(6)	0.20(1)	0.45(1)	9(3)
H(3.1)	0.153(6)	0.47(1)	0.54(1)	13(3)
	0.144(4)	0.456(8)	0.558(9)	4(1)
H(3.2)	0.041(4)	0.43(1)	0.329(8)	8(2)
	0.062(4)	0.439(9)	0.34(1)	6(2)
H(4.1)	0.237(4)	0.341(7)	0.398(7)	5(1)
	0.239(6)	0.35(1)	0.39(1)	10(3)
H(4.2)	0.234(4)	0.531(9)	0.432(7)	7(1)
	0.238(7)	0.50(1)	0.41(2)	14(4)
H(6.1)	0.235(7)	0.43(2)	-0.08(1)	16(3)
	0.231(6)	0.46(1)	-0.09(1)	10(3)
H(6.2)	0.228(5)	0.59(1)	0.050(9)	9(2)
	0.231(5)	0.591(9)	0.07(1)	6(2)
H(6.3)	0.287(7)	0.44(2)	0.13(1)	15(3)
	0.298(5)	0.47(1)	0.11(2)	12(3)

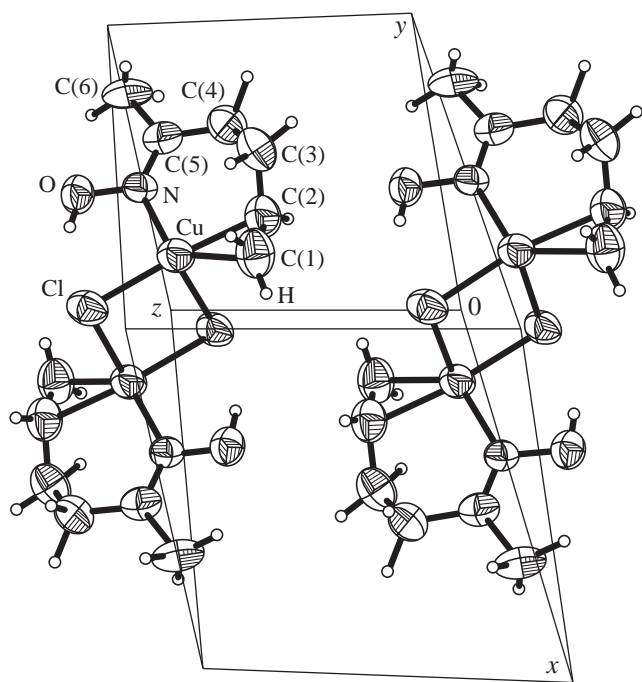
* The atomic coordinates and thermal parameters in the upper line correspond to compound **I** and those in the lower line are for **II**.

** For non-hydrogen atoms, $B_{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$.

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

Bond*	<i>d</i> , Å		Angle*	ω, deg.	
	I	II		I	II
Cu–X	2.255(7)	2.394(3)	XCuX'	96.9(2)	98.3(1)
Cu–X'	2.719(5)	2.778(4)	XCuN	99.4(3)	101.7(2)
Cu–N	2.007(7)	2.004(8)	XCum(12)	139.9(4)	135.4(4)
Cu–C(1)	2.066(9)	2.08(1)	X'CuN	100.4(3)	101.0(2)
Cu–C(2)	2.043(9)	2.05(1)	X'Cum(12)	99.1(3)	101.1(4)
Cu– <i>m</i> (12)	1.941(9)	1.95(1)	NCum(12)	113.4(4)	113.3(4)
			C(1)CuC(2)	38.4(3)	38.1(4)
C(1)–C(2)	1.35(1)	1.35(2)	C(2)C(1)H(1.1)	121(4)	103(4)
C(1)–H(1.1)	0.98(7)	0.95(7)	C(2)C(1)H(1.2)	128(5)	115(4)
C(1)–H(1.2)	0.88(9)	1.13(8)	H(1.1)C(1)H(1.2)	112(6)	142(6)
C(2)–C(3)	1.46(1)	1.48(2)	C(1)C(2)C(3)	129.9(8)	137(1)
C(2)–H(2.1)	1.0(1)	1.0(1)	C(1)C(2)H(2.1)	138(6)	140(6)
			C(3)C(2)H(2.1)	91(6)	83(6)
C(3)–C(4)	1.48(1)	1.44(2)	C(2)C(3)C(4)	120.3(8)	122(1)
C(3)–H(3.1)	0.94(8)	1.02(6)	C(2)C(3)H(3.1)	123(6)	110(4)
			C(4)C(3)H(3.1)	97(6)	111(4)
C(3)–H(3.2)	1.20(7)	0.98(8)	C(2)C(3)H(3.2)	68(3)	71(5)
			C(4)C(3)H(3.2)	127(4)	122(5)
			H(3.1)C(3)H(3.2)	123(7)	115(6)
C(4)–C(5)	1.50(1)	1.49(1)	C(3)C(4)C(5)	118.3(7)	119.3(9)
C(4)–H(4.1)	0.86(6)	0.8(1)	C(3)C(4)H(4.1)	108(4)	122(7)
			C(5)C(4)H(4.1)	107(4)	98(7)
C(4)–H(4.2)	1.10(6)	0.9(1)	C(3)C(4)H(4.2)	97(3)	115(8)
			C(5)C(4)H(4.2)	125(3)	113(8)
			H(4.1)C(4)H(4.2)	100(5)	83(10)
C(5)–N	1.265(9)	1.26(1)	C(4)C(5)N	118.9(6)	117.9(8)
C(5)–C(6)	1.49(1)	1.48(1)	C(4)C(5)C(6)	117.5(6)	118.2(8)
			NC(5)C(6)	123.6(7)	123.9(8)
C(6)–H(6.1)	1.1(1)	1.2(1)	C(5)C(6)H(6.1)	109(6)	120(5)
C(6)–H(6.2)	0.71(8)	0.82(8)	C(5)C(6)H(6.2)	112(6)	109(6)
C(6)–H(6.3)	1.0(1)	1.0(1)	C(5)C(6)H(6.3)	90(7)	120(7)
			H(6.1)C(6)H(6.2)	123(9)	110(8)
			H(6.1)C(6)H(6.3)	94(9)	93(9)
			H(6.2)C(6)H(6.3)	124(9)	103(9)
N–O	1.395(8)	1.424(9)	NOH(O)	104(4)	101(5)
O–H(O)	0.78(6)	0.80(8)			
Angle	φ, deg.		Angle	φ, deg.	
	I	II		I	II
CuNC(5)C(4)	–1.0	–0.4	C(3)C(4)C(5)N	29.3	30.9
CuNC(5)C(6)	–177.9	–178.8	C(3)C(4)C(5)C(6)	–149.7	–150.6
CuC(1)C(2)C(3)	–98.6	–99.2	C(4)C(5)NO	178.5	179.0
C(1)C(2)C(3)C(4)	138.7	135.9	C(6)C(5)NO	0.4	2.6
C(2)C(3)C(4)C(5)	65.4	63.6			

* X corresponds to the Cl atom in structure **I** and to the Br atom in structure **II**, and *m*(12) is the midpoint of the multiple C(1)–C(2) bond.

Fragment of structure **I**.

sion of the iterative SCF MO LCAO method in the INDO approximation [8] shows that the charge on the copper atom in **I** is $-0.12\bar{e}$. Such a relatively large negative charge on the Cu atom in the molecular copper(I) chloride π -complexes (the charges on the copper atoms in the π -complexes with aldimines lie between $-0.01\bar{e}$ and $+0.03\bar{e}$) is due to the charge redistribution caused by the formation of the strong hydrogen bonds of the O-H...X type [in **I**: H...Cl 2.47(6) Å and OHCl angle

148.5°; in **II**: H...Br 2.71(7) Å and OHBr angle 135.7°]. The hydrogen H(O) atom in **I** bears a substantial positive charge of $+0.29\bar{e}$, while the chlorine atom bears a negative charge of $-0.48\bar{e}$; the charges on the chlorine atoms in the aldimino π -complexes are equal to $-0.33\bar{e}$. Owing to the $p-d_{\pi}$ Cu-Cl interaction in structure **I**, the charge on the copper atom is equal to $-0.12\bar{e}$.

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