Organometallic Chemistry

Synthesis, structures, and spectral properties of biomimetic azomethine metal chelates with chromophores CuN_2S_2, CuN_2O_2, and CuN_2Se_2. Crystal structure of bis[4-(benzyl)aldimino-3-methyl-1-phenyl-5-pyrazolothiolato]copper(II)

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Copper(II) chelates of composition CuL_2 were synthesized based on 4-aminomethylene derivatives of 5-thiopyrazoles (LH). The complexes were studied by UV, IR, ESR, and EXAFS spectroscopy, magnetochemistry, and X-ray diffraction analysis. The coordination polyhedra in the complexes are pseudotetrahedra or octahedra of the types CuN_2S_2 or CuN_4S_2, respectively, which are distorted due to the Jahn—Teller effect. The UV and ESR spectra of copper chelates with a six-coordinate metallocycle formed by the N and S atoms of the azomethine ligand and the nitrogen atom of the quinoline substituent (R) of the C=N—R fragment are most similar to the spectra observed for metals involved in the active centers of natural metalloenzymes ("blue" copper proteins).

Key words: azomethines, copper, pyrazolones, chelates, biomimetic models, "blue" copper proteins, X-ray diffraction analysis, UV, ESR, and EXAFS spectroscopy.

The construction of biomimetic models of "blue" copper proteins responsible for the outer-sphere electron transfer in bioinorganic systems[1—9] have attracted the continuing interest over many years.

The active centers in these metalloenzymes contain the chromophore CuN_2SS*, which is characterized by a "blue" band ($\lambda \approx 600$ nm, $\varepsilon = 4000—6000$), the specific ESR spectrum ($A_{\parallel} < 100 \cdot 10^{-4}$ cm^{-1}), and a rather high reduction potential of the Cu^{II}/Cu^{I} pair.[3,4,9,10] The reasons for the fact that "blue" copper proteins exhibit the above-mentioned peculiar properties have been discussed in the literature many times.[4,9] Two factors re-

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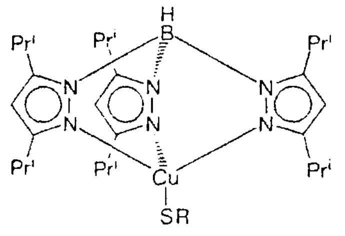
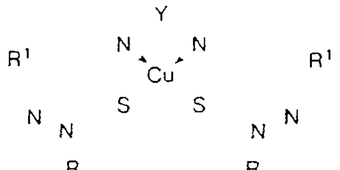
sponsible for the manifestation of these properties were revealed, *viz.*, the high degree of covalence of the Cu—S bond and the low symmetry of the coordination polyhedron. The latter factor is difficultly reproducible in the case of simple biomimetic complexes. That is the reason why only one class of compounds, which adequately reproduce the physicochemical properties of the metalloenzymes under consideration, was found among several tens of models of "blue" copper proteins.[2,7,9] This class involves a series of copper chelates containing tris(pyrazolyl)borate ligands of type **1**.[11–13]



1

R = CPh_3, Bu^t, C_6F_5

Adequate synthetic models of active centers of copper-containing proteins with the N,S-ligand environment are limited in number due to oxidation of the thiolate group of the ligand by Cu^{2+} ions.[2,9] The syntheses of stable metal chelates with the CuNS chromophore were primarily based on the use of rigid macrocyclic ligands and tetradentate Schiff's bases containing a bridging fragment (for example, complex **2**).[2,9,14]

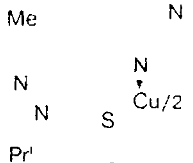


2

—Y— = —$(CH_2)_n$—,

$n = 2$—4

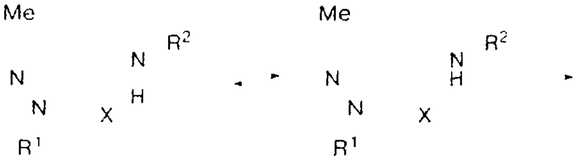
The tetrahedral distortion of the chelate unit of the complexes was achieved by either lengthening the bridges or introducing bulky substituents located in close proximity to the metal center. Up to now, complex **3** in which the dihedral angle between the NCuS planes of two different coordination units is 57° was the only example of an open structure containing the CuN_2S_2 coordination unit, which was characterized by X-ray diffraction analysis.[15]



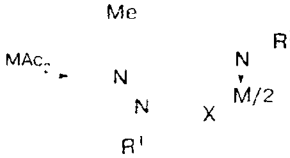
3

However, this complex was not considered[15] as a biomimetic model of the active center of "blue" copper proteins.

In the present work, we developed and used a procedure for the directed synthesis of biomimetic models of active centers of "blue" copper proteins based on a choice of ligands of type **4** for the preparation of metal chelates with open structures **5**, including metal chelates with coordinatively active substituents (R) at the N atom of the azomethine fragment.



4a—m **4′a—m**



5a—m

	X	R^1	R^2		X	R^1	R^2
a	S	Ph	CH_2Ph	**g**	S	Ph	(—CH—)$_2$
b	Se	Ph	CH_2Ph	**h**	Se	Ph	(—CH—)$_2$
c	O	Ph	CH_2Ph	**k**	S	Ph	8-Qin
d	S	Ph	Me	**l**	Se	Ph	8-Qin
e	S	Ph	C_6H_4Me-*p*	**m**	S	Pr^i	8-Qin
f	S	Pr^i	C_6H_4Me-*p*				

Quin is quinolyl

Results and Discussion

Compounds of type **4** (LH), like other analogous complexes,[16–20] have aminomethylene structure **4′** with a strong NH...X hydrogen bond, which is confirmed by the fact that the ^1H NMR spectra of systems **4a—m** have doublet signals for the protons of the NH groups (at δ 13—15) with $J_{NH-CH} = 12$ Hz.

Metal chelates **5** of composition ML_2 were synthesized according to known procedures[14,22,23] (Table 1). The IR spectra of these compounds have absorption bands of stretching vibrations of the coordinated pyrazoloazomethine fragment (at ~1630 cm^{-1} (X = O) and 1590 cm^{-1} (X = S)). In the studies of the magnetic properties of the metal chelates performed at −20 °C and at the temperature of liquid nitrogen, magnetic moments typical of the mononuclear Cu^{II} complexes were obtained (1.76—2.0 μB; see Table 2).

These data provide evidence in favor of formula **5**, which we assigned to the chelates under consideration. Actually, X-ray diffraction study demonstrated that complex **5a** in the crystal occupies a special crystallographic position on a twofold axes (C_2) passing through the Cu atom (Fig. 1). The geometry of the bidentate ligand is

Table 1. Properties of complexes **5**

Compound	Yield (%)	N, Found / Calculated (%)	Molecular formula
5a	60	12.36 12.43	$C_{36}H_{32}N_6S_2Cu$
5b	71	10.85 10.91	$C_{36}H_{32}N_6Se_2Cu$
5c	65	13.11 13.04	$C_{36}H_{32}N_6O_2Cu$
5d	69	15.98 16.03	$C_{24}H_{24}N_6S_2Cu$
5e	72	12.40 12.43	$C_{36}H_{32}N_6S_2Cu$
5f	63	13.18 13.08	$C_{30}H_{34}N_6S_2Cu$
5g	70	15.95 16.09	$C_{24}H_{22}N_6S_2Cu$
5h	64	13.72 13.64	$C_{24}H_{22}N_6Se_2Cu$
5k	69	14.87 14.93	$C_{40}H_{30}N_8S_2Cu$
5l	70	13.24 13.27	$C_{40}H_{30}N_8Se_2Cu$
5m	63	15.59 15.64	$C_{34}H_{32}N_8S_2Cu$

characterized by values typical of this class of compounds.[14] As expected,[15] the Cu atom in this chelate is in a distorted tetrahedral ligand environment of the N_2S_2 type. The S(1)—Cu(1)—N(1) and S(1)—Cu(1)—N(1A) bond angles are 100.74(9) and 134.25(9)°, respectively. The dihedral angle between the NCuS planes of two coordination units is 60.5°, which is somewhat larger than that in complex **3** (57.6°).[15] The Cu—N and Cu—S bond lengths in **5a** (1.982(3) and 2.2497(11) Å, respectively) are close to the corresponding values in other four-coordinate metal chelates of Cu^{II} with the N,S-ligand environment[14] (see Table 2). The Cu—N and Cu—S bond lengths in "blue" copper proteins are in the ranges of 1.99—2.15 and 2.07—2.17 Å, respectively.[9] These values are substantially smaller than the corresponding parameters observed in biomimetic complexes.[14] The tris(pyrazolyl)borate complex of type **1** is the only example[11] of model compounds in which the equally short Cu—S bond is observed. It should be noted that chelate **5a** is the second example of complexes with the CuN_2S_2 chromophore possessing an open structure, which was characterized by X-ray diffraction data (*cf.* Refs. 9, 14, and 15).

The structural data for the nearest environment about the Cu atoms in chelates **5a—c,k** were obtained by

Table 2. The Cu—X and Cu—N bond lengths (*d*) determined by X-ray diffraction analysis and EXAFS spectroscopy, the parameters of the ESR ($CHCl_3$, 77 K) and UV ($CHCl_3$) spectra, and the magnetic moments of complexes **3** and **5**

Compound	*d*/Å		ESR spectrum					UV spectrum	μ_{eff}/μB
	Cu—X	Cu—N	$g_{\parallel}$	$g_{\perp}$	g_i	$A_{\parallel} \cdot 10^{-4}$ / cm^{-1}	$A_i \cdot 10^{-4}$ / cm^{-1}	λ_{max} (ε/cm^{-1} mol^{-1})	
3	2.230	1.982	2.149	2.036	2.076	131.3	50.4	574 (1240) 710 (960)	1.8
5a	2.249 2.24*	1.982 1.97*	2.153	2.046	2.074	136.1	52.4	556 (1818) 700 (1482)	1.76
5b			2.136	2.057	2.091	131.8	63.1	554 (1010) 724 (1000)	1.78
5c	1.96*	2.05*	2.234	2.063	2.119	143.5	51.1	468 (1155)	1.81
5d			2.152	2.058	2.102	137.0	67.0	544 (1980) 680 (1470)	1.73
5e			2.152	2.041	2.072	137.6	50.4	590 (2440) 700 (2040)	1.78
5f			2.150	2.036	2.076	136.1	71.3	600 (1950) 700 (1520)	1.86
5g			2.123	2.049		183.7		432 (2217) 519 (1004) 822 (150)	1.90
5h			2.106	2.046	2.066	187.9	87.2	440 (3530) 520 (1415) 859 (350)	1.90
5k	2.30*	2.02* 2.63*	2.138 2.158**	2.047 2.041**	2.086 2.082**	<100 162.1**	58.7 74.3**	425 (13375) 580 (245)	1.82
5l	2.44*	2.04* 2.50*	2.100	2.053	2.064	<100	68.1	445 (9420) 590 (320)	1.84
5m			2.183	2.050	2.103	<100	87.0	427 (14360) 600 (260)	1.91

* Data of EXAFS spectroscopy.

** In DMF.

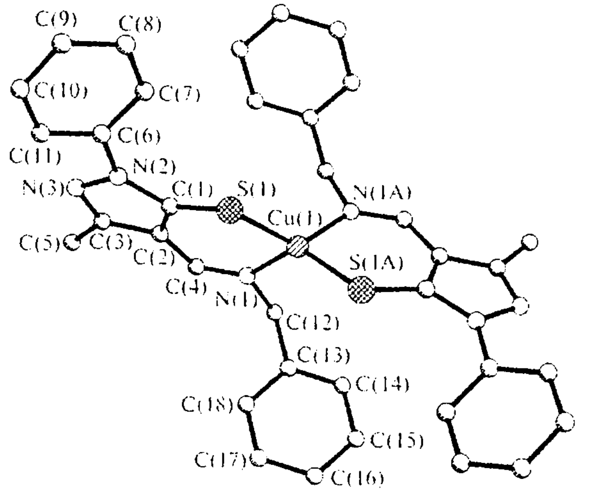


Fig. 1. Molecular structure of complex **5a**.

Principal bond lengths (*d*) and bond angles (ω):

Bond	*d*/Å	Angle	ω/deg
Cu(1)—N(1)	1.982(3)	N(1A)—Cu(1)—N(1)	94.8(2)
Cu(1)—S(1)	2.2497(11)	N(1A)—Cu(1)—S(1)	134.25(9)
S(1)—C(1)	1.728(4)	N(1)—Cu(1)—S(1)	100.74(9)
N(1)—C(4)	1.288(4)	N(1A)—Cu(1)—S(1A)	100.74(9)
N(1)—C(12)	1.469(5)	N(1)—Cu(1)—S(1A)	134.25(9)
N(2)—C(1)	1.360(5)	S(1)—Cu(1)—S(1A)	98.47(6)
N(2)—N(3)	1.381(4)	C(1)—S(1)—Cu(1)	102.71(14)
N(2)—C(6)	1.427(5)	C(4)—N(1)—C(12)	118.0(3)
N(3)—C(3)	1.310(5)	C(4)—N(1)—Cu(1)	127.4(3)
		C(12)—N(1)—Cu(1)	114.5(2)
		C(1)—N(2)—N(3)	112.3(3)
		C(1)—N(3)—C(6)	130.7(3)

EXAFS spectroscopy. The moduli of Fourier transforms (MFT) of the EXAFS spectra for chelates **5a—c,k**, which represent the function of radial distribution of the adjacent atoms about the Cu atom, are shown in Fig. 2. The structural data obtained from analysis of these MFT are given in Table 3.

As can be seen from Fig. 2, the MFT curve for complex **5c** has a major peak consisting of two similar coordination spheres formed by light atoms. The best fit corresponds to a model in which the Cu atom is surrounded by two O atoms and two N atoms. The Cu—O and Cu—N radii of the coordination spheres are 1.96 and 2.05 Å, respectively (see Table 3).

Table 3. Structural data obtained from analysis of the EXAFS spectra of complexes **5**

Complex	*R*/Å	σ^2/Å	Atom	*Q* (%)
5a	2.00	0.0030	N	2.0
	2.27	0.0037	S	
5b	2.04	0.0017	N	1.9
	2.46	0.0057	Se	
5c	2.05	0.0020	N	2.5
	1.96	0.0038	O	
5k	2.00	0.0023	N	1.3
	2.50	0.0048	N	
	2.30	0.0035	S	

Note: *R* is the radius of the coordination spheres, the coordination number *N* = 2; σ^2 is the Debye—Waller factor. The *Q* value characterizes the accuracy of fitting.

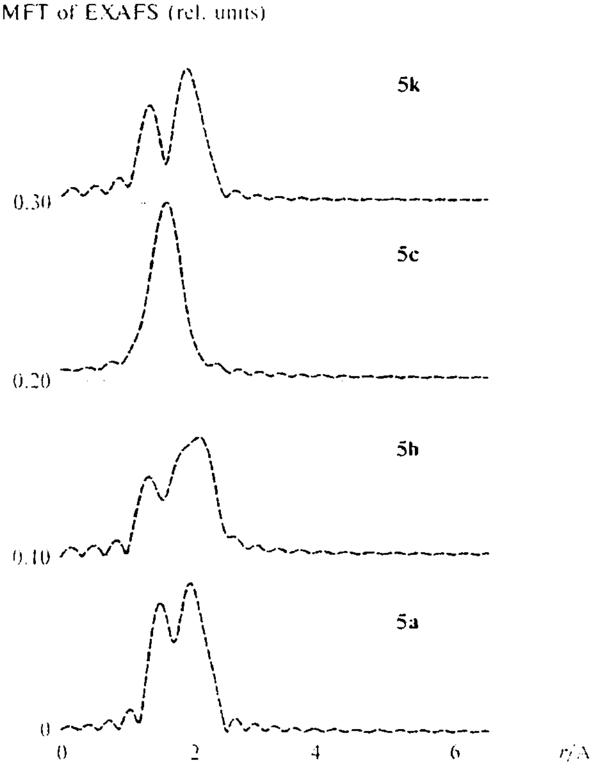


Fig. 2. Moduli of Fourier transforms of EXAFS of the X-ray absorption CuK spectra for complexes **5a**, **5b**, **5c**, and **5k** (solid lines). The model MFT obtained based on the structural data are indicated by dashed lines.

The shapes and the parameters of MFT for complexes **5a** and **5k** are very similar. It is therefore concluded that the nearest coordination environments about the Cu atoms in these complexes have similar structures. In complex **5a**, the distances to two N atoms and two S atoms coordinated to the Cu atom (2.00 and 2.27 Å, respectively), which were determined by the fitting method, are in good agreement with the X-ray diffraction data (1.982(3) and 2.2497(11) Å, respectively). However, the best results of fitting for complex **5k** correspond to a model containing two additional N atoms, which are located at a distance of 2.55 Å from the Cu atom due to the Jahn-Teller effect. Becase of the large Cu—N distance, these atoms are characterized by higher Debye—Waller factors (the average displacements of the atoms from the equilibrium positions) and, correspondingly, by a small contribution to the EXAFS spectra.

The nearest environment about the Cu atom in complex **5b** is characterized by the presence of two N atoms at a distance of 2.04 Å and two Se atoms at a substantially larger distance (2.46 Å).

The ESR spectral data for complexes **5** are given in Table 2. The $g_\parallel$ and $A_\parallel$ values indicate that pseudotetrahedral complexes **5a—f** (unlike tetragonal metal chelates **5g,h**) are similar in the ESR characteristics to "blue" copper proteins. The replacement of the donor S atom in complex **5a** by the O atom leads to an increase in the $g_\parallel$ value, which is consistent with a decrease in the degree of covalence of the Cu—O bond compared to the Cu—S bond.[4] The results obtained in the present work reflect the tendencies for an increase in the nephelauxetic effect, an increase in the degree of covalence, and a decrease in the electronegativity in the series $N_2O_2 > N_4 > N_2S_2$ (see Ref. 9). The ESR characteristics of complexes **5a—f** differ substantially from those of natural compounds.[3,6] As can be seen from Table 2, parameters of the ESR spectra similar to those of "blue" copper proteins were achieved by introducing the quinoline R substituent into the amine fragment of chelates **5** (compounds **5k—m**). Apparently, a considerable effect of this substituent on the parameters of the ESR spectra of complexes **5** is attributable to an additional coordination of the N atom of the quinoline fragment (*cf.* Refs. 24 and 25), the distortion of the chelate unit, and a change in the efficiency of overlapping of the atomic orbitals of the Cu, N, and S atoms. Therefore, metal chelates **5k—m** are similar in the ESR spectral properties to the active centers of "blue" copper proteins.

The electronic absorption spectra of natural "blue" enzymes are characterized by an intense band in the region of 600—700 nm, which was assigned to the S—Cu charge transfer band.[4] The UV spectra of complexes **5a—f** have absorption bands in the region of 500—700 nm, which we assigned to the $S\sigma—Cu^{II}$ (λ 500—600 nm) and $S\pi—Cu^{II}$ (λ 700 nm) charge transfer bands. In the spectrum of compound **5c**, absorption in this region is absent. In the spectra of metal chelates **5k—m**, strong absorption at 450—500 nm prevails, whereas only weak peaks are observed in the region of 600—700 nm.

Previously,[24,25] it has been demonstrated that the introduction of the coordinatively active quinoline fragment into the ligand system is of fundamental importance for constructing biomimetic models of nitrile hydratase based on pyrazole complexes of Fe^{III}. In the present work, we used the same ligand systems for the construction of new biomimetic models of "blue" copper proteins whose ESR spectral properties are similar to those of the metalloenzymes.

Experimental

The ^1H NMR spectra of compounds **4** were recorded on a Varian UNITY-300 spectrometer (300 MHz) in solutions in $CDCl_3$.

The ESR spectra of solutions of metal chelates **5** were measured on an SE/X-2543 Radiopan instrument (Poland) in the X range at 298 and 77 K.

The electronic absorption spectra of the complexes in solutions in $CHCl_3$ and C_6H_6 were recorded on a Specord M-40 spectophotometer.

The magnetic moments of the complexes in the crystalline state were determined at 299 K on an instrument designed at the Rostov State University[26] using the Faraday method: $Hg[Co(NCS)_4]$ was used as the standard. The effective magnetic moments were calculated by the formula $\mu_{eff} = (8T\lambda_m)^{1/2}$, where λ_m is the molar magnetic susceptibility taking into account the Pascal magnetic corrections. Information on the structures of the nearest environments about the Cu atoms in the complexes under study were obtained by Fourier analysis of the extended X-ray absorption fine structure (EXAFS) of X-ray absorption CuK spectra.[27]

X-ray absorption CuK spectra were recorded on an EXAFS spectrometer devised based on a DRON-3M diffractometer[28] with the use of a (1340) quartz crystal as the monochromator. The Fourier transformations of the EXAFS spectra were performed in the range of wave vectors of photoelectrons k = 2.5—12.5 $Å^{-1}$ with the k^2 weighting function. The amplitudes and scattering phases of photoelectrons required for the Fourier analysis were determined with the use of the FEFF 7.0 program[29] based on analogous compounds whose crystal structures are known. The parameters of the structures of the nearest environments about the Cu atoms (the interatomic distances, the coordination numbers, and the Debye—Waller factors) were determined using nonlinear fitting of the parameters of the corresponding coordination spheres by comparing the model EXAFS signal and the signal, which was extracted from the total EXAFS spectrum by the Fourier-filtering method. The target function Q minimized in the course of fitting of the structural parameters was no higher than 3%, which corresponds to the accuracy of determination of interatomic distances equal to 0.02 Å.

X-ray diffraction study of complex 5a. The crystals are monoclinic, at 293 K a = 28.862(8) Å, b = 6.957(2) Å, c = 17.483(5) Å, β = 106.90(2)°, V = 3359(2) $Å^3$, d_{calc} = 1.337 mg m^{-3}, space group $C2/c$, Z = 4. The intensities of 2425 reflections were measured on an automated four-circle Siemens P3/PC diffractometer at 298 K (Mo-Kα radiation, graphite monochromator, $\theta/2\theta$ scanning technique, $2\theta_{max}$ = 50°) and 1758 observed reflections were used in subsequent calculations. The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic-isotropic approximation based on F^2. The positions of the hydrogen atoms were located from difference electron density syntheses and refined using the riding model. The final values of the R factors were as follows: wR_2 = 0.1299, GOF = 1.067 using all reflections (R_1 = 0.0462 calculated using 1758 reflections with $I > 2\sigma(I)$) with the use of the SHELXTL PLUS program package.[30] The complete tables of the atomic coordinates, thermal parameters, bond lengths, and bond angles were deposited with the Cambridge Structural Database.

Synthesis of aminomethylene derivatives 4 was carried out by the reactions of the corresponding aldehydes[31] with amines (RNH_2) in ethanol or an ethanolic-ethereal mixture according to known procedures.[16,19,22,23] The reaction mixtures were heated for 15—30 min. The precipitates of compounds **4** that formed were washed with ethanol and ether and recrystallized from propan-2-ol or toluene. The yields were 60—80%.

Metal chelates 5 were synthesized from sodium salts of compounds **4** and Cu^{II} acetate in methanol. The mixtures were refluxed for 5—20 min. The crystals that precipitated were filtered off, washed with methanol and ether until the filtrates became colorless, and dried in a vacuum desiccator.

The data of chemical analysis are given in Table 1. The complexes are characterized by very high melting points (>250 °C).

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