

COORDINATION
COMPOUNDS

New Magnetoactive Copper Complexes with Schiff's Bases

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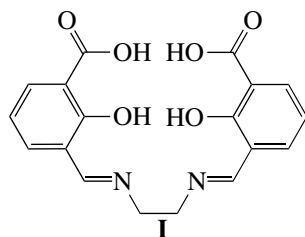
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Abstract—Tridentate azomethine ligands with N₂O and N₃ donor atoms and their copper complexes have been synthesized and characterized. Magnetochemical measurements in the temperature range of 5–300 K show that the change in the coordination environment induces the change in the sign of exchange coupling in the molecules of complexes.

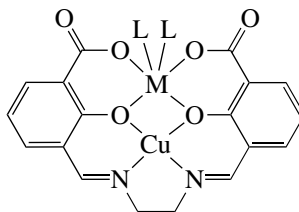
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Among molecular ferromagnets, an important place is occupied by ferromagnetic complexes of Schiff's bases. In the late 1970s, O. Kahn designed the azome-

thine ligand of type **I**, which served as the base for preparation of various homo- and heteronuclear complexes **II** with ferro- and antiferromagnetic exchange [1].



I



II:

M = Cr, Fe, VO; L = H₂O, MeOH

Cu–VO $J = +118 \text{ cm}^{-1}$

Cu–Cr $J = +115 \text{ cm}^{-1}$

Cu–Fe $J = -105 \text{ cm}^{-1}$

It was shown that the magnetic characteristics of binuclear chelates **II** obtained from **I** depend on the electronic configuration and different combinations of complexing metals [1–3]. The Kahn model is still successfully used to prepare ferromagnetic complexes [3–8].

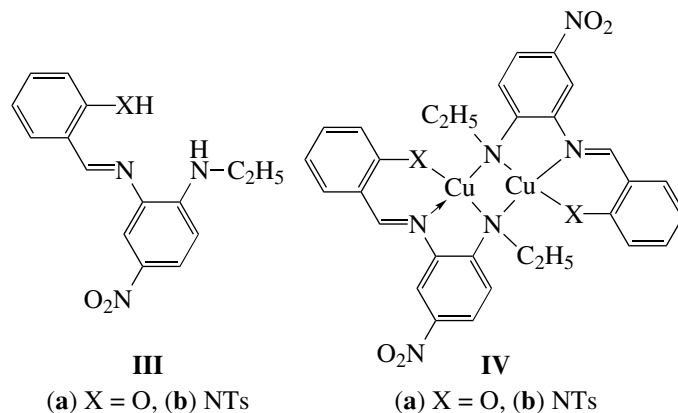
Another approach to the design of molecular magnets based on chelates of azomethine ligands involves incorporation of diverse bridging fragments between the metal ions in binuclear complexes, for example, azides [9, 10], chlorides [11], or carboxylates [12]. Ferromagnetic complexes have also been prepared by introducing salicylaliminate fragments into hexacya-

nide complexes [13–15], by using free-radical azomethine ligand systems [15–17], and by using chelates of Schiff's bases as metal ligands [18–21].

Recently, we proposed a new approach to the search for and design of ferromagnetic complexes of azomethine ligands. According to this approach, binuclear complexes with different magnetic properties can be obtained by varying the fine structure of the considered ligand system (rational design of azomethines and their analogues [29, 30]). Both ferro- and antiferromagnetic structures were prepared in this way.

As a development of this approach, this publication presents data on the synthesis and properties of new ligand systems **III** (LH₂), differing by the donor atom

X, and their copper complexes **IV** and on the magnetic properties of these complexes in the temperature range of 5–300 K.



EXPERIMENTAL

¹H NMR spectra were recorded on a Varian Unity 300 (300 MHz) spectrometer using an internal deuterium lock (CDCl₃). IR spectra were recorded on a Nicolet Impact 400 spectrophotometer in KBr pellets.

The magnetic measurements of complexes **IVa** and **IVb** were carried out on a Quantum Design SQUID magnetometer in the temperature range of 5–300 K in a magnetic field of 5 kOe. In calculations of the paramagnetic component of the magnetic susceptibility χ , the additive diamagnetic contributions of ions were taken according to the Pascal constants to be 340×10^{-6} and 509×10^{-6} cm³/mol for **IVa** and **IVb**, respectively. The effective magnetic moment as a function of temperature was calculated by the formula

$$\mu_{\text{eff}}(T) = \left(\frac{3k}{N\beta^2} \chi T \right)^{1/2} \approx (8\chi T)^{1/2},$$

where N , k , and β are the Avogadro number, the Boltzmann constant, and the Bohr magneton, respectively.

The CuK-edge X-ray EXAFS spectra of the compounds under study were recorded on a laboratory EXAFS spectrometer based on a DRON-3 diffractometer. A BSV-21-Mo tube at $U = 17$ kV and $I = 30$ mA was used as the X-radiation source. X-radiation was expanded in the spectrum by means of a quartz monochromator crystal (1340). After standard background isolation, normalization to the K -edge step, and isolation of the atomic absorption μ_0 [31], the recorded EXAFS (χ) spectra were subjected to Fourier transform in the range of photoelectron wave vectors k from 3.0 to 13 Å⁻¹ with the weight function $n = 2$. The threshold ionization energy E_0 was chosen from the maximum of the first derivative of the K -edge and was subsequently varied during a fitting procedure. The parameters of the local environment of copper atoms were found by the

nonlinear fitting of the calculated values χ_{calcd} to experimental ones χ_{exp} carried out using the IFFFIT-1.2.5 software [32]. The phases and amplitudes of photoelectric wave scattering needed to simulate the spectrum were calculated with the FEFF7 software [33]. Copper complexes with related structures that had been determined by X-ray diffraction were taken as model compounds.

The quality function of fitting Q , which was minimized when determining the structure parameters of the local environment, was calculated by the formula

$$Q(\%) = \frac{\sum [k\chi_{\text{exp}}(k) - k\chi_{\text{calcd}}(k)]^2}{\sum [k\chi_{\text{exp}}(k)]^2} \times 10^2.$$

Synthesis of Ligands

2,4-Dinitro-*N*-ethylaniline. Ethylamine hydrochloride (8.97 g, 0.11 mol) was added to a suspension of 2,4-dinitrochlorobenzene (20.26 g, 0.1 mol) and sodium acetate trihydrate CH₃COONa · 3H₂O (29.94 g, 0.22 mol) in ethanol (50 ml). The mixture was refluxed for 2 h and cooled, and the precipitate was filtered off and washed with water and ethanol. Yield, 15.2 g (72%); mp 113–114°C (from ethanol), which is consistent with the published data [34].

2-Ethylamino-5-nitroaniline. A suspension of *N*-ethyl-2,4-dinitroaniline (21.1 g, 0.1 mol) in ethanol (40 ml) was added to a warm solution of sodium sulfide nonahydrate (Na₂S · 9H₂O) (48.01 g, 0.2 mol) and crystalline sulfur (6.41, 0.2 mol) in water (63 ml). The mixture was refluxed for 2 h, diluted with water (30 ml), and cooled. The precipitate was filtered off and washed with warm water. The yield of dark red crystals was 12.5 g (69%), mp = 138–139°C (from ethanol), which is consistent with the published data [34].

Synthesis of Azomethines **III**

A solution of 2-ethylamino-5-nitroaniline (1.81 g, 0.01 mol) in ethanol (100 ml) was added to a solution of salicylaldehyde (1.22 g, 0.01 mol) or 2-(*N*-tosylamino)benzaldehyde [35] in ethanol (30 ml), and the mixture was refluxed for 3 h. The precipitates formed after cooling were filtered off and recrystallized from ethanol.

IIIa, X = O. Yield, 78%. Light yellow crystals, mp 194–195°C.

For C₁₅H₁₅N₃O₃ anal. calcd. (%): C, 63.15; H, 5.30; N, 14.73. Found (%): C, 63.25; H, 5.15; N, 14.83.

¹H NMR, δ, ppm: 1.34 (t, 3H, ³J = 7.2 Hz, CH₂–CH₃), 3.31–3.40 (t, 2H, ³J_{CH₂–CH₃} = 7.2 Hz, ³J_{CH₂–NH} = 4.9 Hz, CH₂–CH₃), 5.07 (t, 1H, ³J = 4.9 Hz, NH–C₂H₅), 6.62–8.15 (t, 7H, C_{Ar}–H), 8.71 (s, 1H, CH=N), 12.31 (s, 1H, OH). IR (cm⁻¹): 3400 w (NH), 1615 s (C=N), 1275 m (Ph–O).

IIIb, X = NTs. Yield, 84%. Orange needles, mp 141–142°C.

For C₂₂H₂₂N₄O₄S anal. calcd. (%): C, 60.26; H, 5.06; N, 12.78, S, 7.31.

Found (%): C, 60.16; H, 5.16; N, 12.88, S, 7.42.

¹H NMR, δ, ppm: 1.42 (t, 3H, ³J = 7.2 Hz, CH₂–CH₃), 2.38 (s, 3H, CH₃), 3.39–3.43 (t, 2H, ³J = 7.2 Hz, CH₂–CH₃), 5.51 (t, 1H, ³J = 4.9 Hz, NH–C₂H₅), 6.67–8.17 (t, 11H, C_{Ar}–H), 8.68 (s, 1H, CH=N), 12.45 (s, 1H, NH). IR (cm⁻¹): 3446 w (NH), 1618 s (C=N), 1349 vs (ν_{as}SO₂), 1168 vs (ν_sSO₂).

Synthesis of Copper Complexes **IV**

A solution of copper acetate monohydrate (0.199 g, 0.001 mol) in ethanol (10 ml) was added to a solution of azomethine **IIIa** (0.283 g, 0.001 mol) or azomethine **IIIb** (0.438 g, 0.001 mol) in ethanol (50 ml). The mixture was refluxed for 4 h. The crystals of the complexes that precipitated on cooling were filtered off, washed with boiling ethanol (3 × 5 ml), and dried in a vacuum drying chamber at 100°C.

IVa. Yield, 63%. Dark brown crystals, mp 234–235°C, dec.

For C₃₀H₂₆N₆O₆Cu₂ anal. calcd. (%): C, 51.95; H, 3.78; N, 12.12; Cu, 18.32. Found (%): C, 52.01; H, 3.72; N, 12.32; Cu, 18.42.

IR (cm⁻¹): 1604 s (C=N), 1327 w (Ph–O).

IVb. Yield, 78%. Dark brown crystals, mp > 260°C.

For C₄₄H₄₀N₈O₂S₂Cu₂ anal. calcd. (%): C, 52.84; H, 4.03; N, 11.20; S, 6.41; Cu, 12.71. Found (%): C, 52.75; H, 4.13; N, 11.32; S, 6.51; Cu, 12.92.

IR (KBr, cm⁻¹): 1603 vs (C=N), 1283 vs, (ν_{as}SO₂), 1136 vs (ν_sSO₂).

RESULTS AND DISCUSSION

Like other azomethine systems [30], compounds **III** used as ligands tend to undergo enol–imine (**IIIa**) and amine–imine (**IIIb**) tautomerism, as follows from the IR and ¹H NMR spectra. This is indicated by the C=N stretching vibration frequencies (1615 and 1618 cm⁻¹) and the OH (12.31 ppm) and NH (12.45 ppm) proton signals for fragments **IIIa** and **IIIb**, respectively.

The elemental analysis data of the complexes obtained by direct reaction of the ligands and metal salts [36, 37] attest to L : M = 1 : 1, i.e., to the formation of binuclear chelates M₂L₂.

The chelate structure of the complexes is also indicated by characteristic changes in their IR spectra with respect to the spectra of the ligands, namely, the OH and NH stretches disappear, the C=N stretching frequencies and symmetric and antisymmetric SO₂ vibration frequencies decrease by 10–15 cm⁻¹, and the Ph–O vibration frequency increases by 50 cm⁻¹ [38].

The dimeric structure and the type of ligand environment are confirmed by analysis of the EXAFS spectra of complexes **IVa** and **IVb**.

Figure 1 shows the Fourier transform modules (FTM) of the *K*-edge EXAFS spectra of copper complexes **IVa** and **IVb**. Table 1 summarizes the parameters of the local environment of the copper atom in these compounds determined by fitting the theoretical χ(*k*) of the chosen model to the experimental EXAFS spectra. The complex [C₃₆H₅₉Cu₂N₄O₂]⁺[CF₃O₃S]⁻ · C₅H₁₂ · C₄H₈O, bis(μ²-oxo)(*N,N'*-bis(2,6-diisopropylphenyl)-2,5-pentanediiimato)(*N,N,N',N'*-tetramethylpropane-1,3-diamino)dicopper(II)trifluoromethanesulfonate pentane tetrahydrofuran solvate) [39], containing oxygen

Table 1. Structural data found from the multisphere fitting of the EXAFS data (*R* are interatomic distances, CN is the coordination number, σ² is the Debye–Waller factor, *Q* is the quality function of fitting)

Complex	CN*	R**, Å	σ ² , Å ²	Atom	<i>Q</i> , %
IVa	2	1.99	0.0027	O/N	6.5
	2	2.02	0.0055	N	
	4	2.81	0.0062	C/N	
IVb	1	2.99	0.0038	Cu	11.3
	4	1.93	0.0035	N	
	1	2.78	0.0049	Cu	
	6	3.24	0.0066	C	

Notes: * CN is determined to a accuracy of 10% for the first coordination sphere and 20% for the subsequent coordination spheres.

** The accuracy of determination of the distances is 0.02 Å for the first coordination sphere and 0.04 Å for the subsequent coordination spheres.

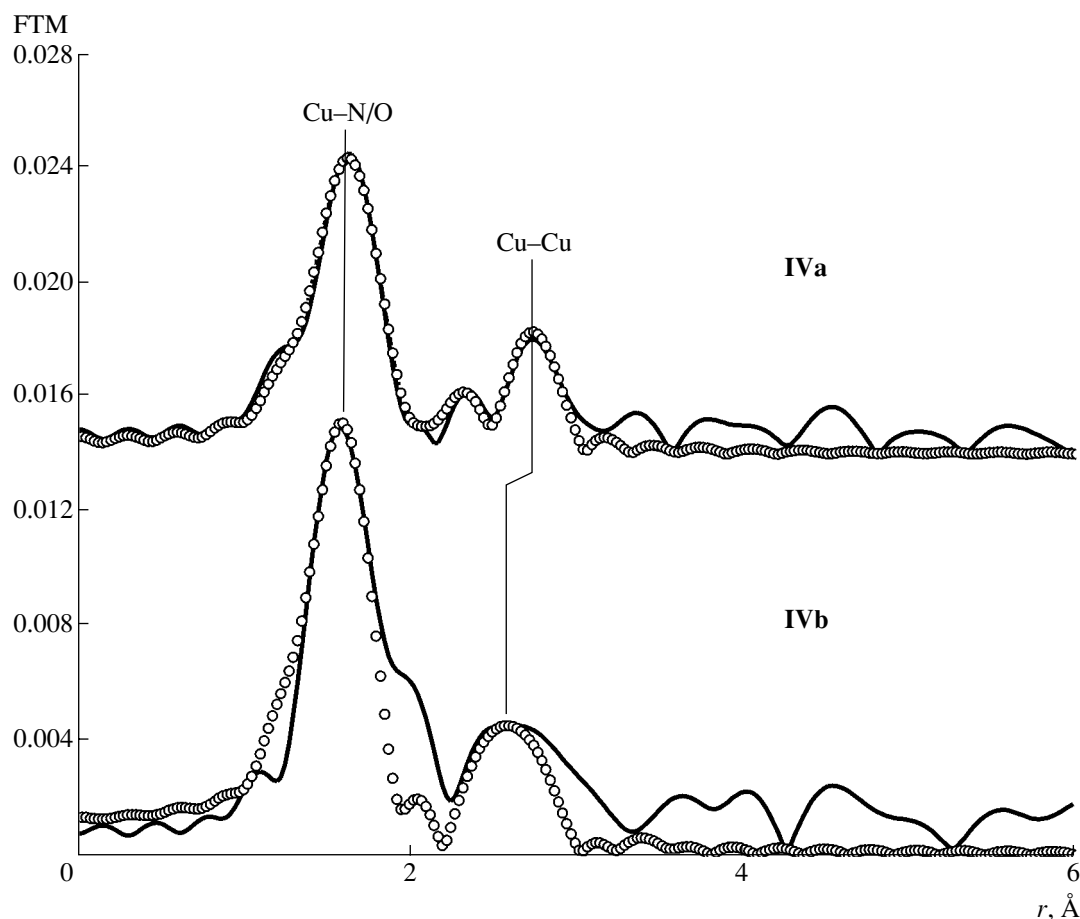


Fig. 1. FTMs of the CuK-edge EXAFS spectra for complexes **IVa** and **IVb**. The solid line shows the experimental results and the circles correspond to theoretical FTMs. The phase correction was not applied.

bridges with $R = 1.818 \text{ \AA}$ for Cu–O distances and $R = 2.849 \text{ \AA}$ for Cu–Cu distances was used as the model.

It can be seen from Fig. 1 that the FTM of both samples consist of the major peak with $r = 1.59 \text{ \AA}$ (FTM for **IVa**) and $r = 1.63 \text{ \AA}$ (FTM for **IVb**) and a minor peak with $r = 2.75 \text{ \AA}$ (FTM for **IVa**) and $r = 2.61 \text{ \AA}$ (FTM for **IVb**). The major peak corresponds to photoelectron wave scattering on the nearest coordination spheres of nitrogen (or nitrogen and oxygen for **IVa**) whose radii were found from fitting and are summarized in Table 1. The radii for the first coordination spheres of the compounds are typical of copper complexes. The second peak in the FTM may be due to the Cu...Cu distance, which is in line with the proposed dimeric model for the structure of the complexes. Note that the Cu...Cu distance in **IVb** is 0.2 \AA shorter than that in **IVa**.

Thus, EXAFS studies of two copper complexes confirm the proposed dimeric structure of these compounds.

The results of magnetic measurements for complexes **IVa** and **IVb** are presented in Figs. 2 and 3, respectively. As can be seen, the effective magnetic moments μ_{eff} of the complexes at room temperature

correspond to two unpaired electrons per molecule. The decrease in μ_{eff} with decreasing temperature and the magnetic susceptibility maximum at $\sim 20 \text{ K}$ for **IVa**

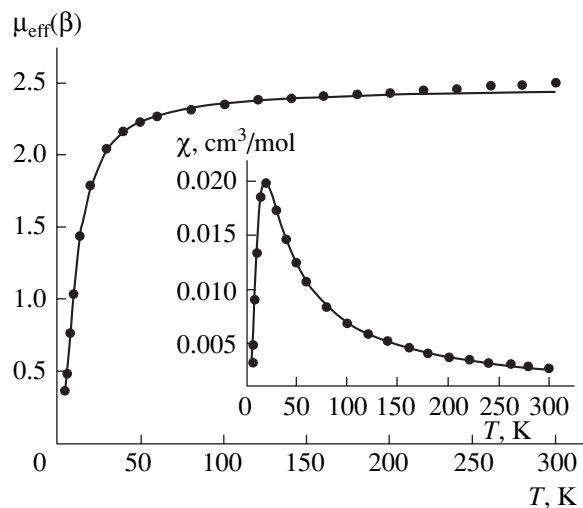


Fig. 2. Temperature dependences of the effective magnetic moment $\mu_{\text{eff}}(T)$ and magnetic susceptibility $\chi(T)$ (inset) for complex **IVa**.

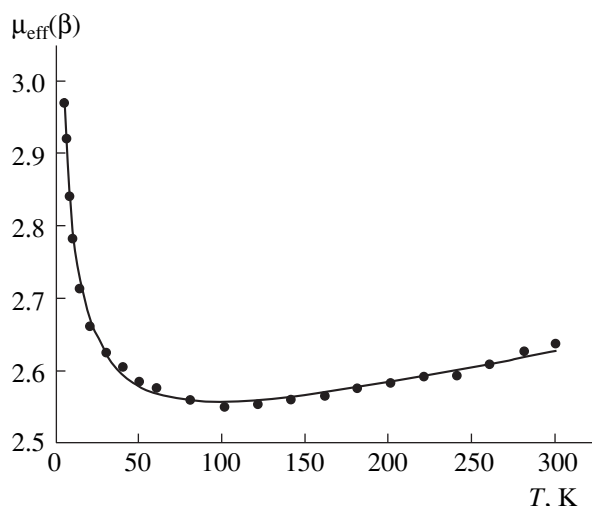


Fig. 3. Temperature dependence of the effective magnetic moment $\mu_{\text{eff}}(T)$ for complex **IVb**.

point to antiferromagnetic exchange interactions in the dimeric complex molecules. Conversely, μ_{eff} of complex **IVb** increases with a decrease in temperature to reach a value of 2.97β at 5 K, which exceeds the ferromagnetic limit of the dimer (2.83β at $g = 2$).

The theoretical simulation of the experimental curves was carried out using the known Bleaney–Bowers equation for the magnetic susceptibility of a dimeric cluster with the spins $1/2$ [40]:

$$\chi_{\text{CuCu}} = \frac{N\beta^2 g^2}{3kT} \left[1 + \frac{1}{3} \exp\left(\frac{-2J}{kT}\right) \right]^{-1} + N\alpha,$$

where N is the Avogadro number, g is the g -value of the Cu(II) ion, J is the exchange coupling parameter of the paramagnetic ions in the dimer, and $N\alpha$ is a temperature-independent constant term. The dimer–dimer exchange interactions were considered in the molecular field approximation using the relation [40]

$$\chi = \frac{\chi_{\text{CuCu}}}{1 - (2zJ'/Ng^2\beta^2)\chi_{\text{CuCu}}},$$

where χ_{CuCu} is the magnetic susceptibility of the isolated dimer, z is the number of the nearest neighbors of the dimers, and J' is the exchange parameter between the dimers. The results of simulation are shown in the

Table 2. Model parameters

Complex	g	J, cm^{-1}	zJ', cm^{-1}	$N\alpha, \text{cm}^3/\text{mol}$
IVa	2.05	-10.1	-2.6	–
IVb	2.02	4.0	0.27	0.00029

plots by solid lines. The optimal parameters of the model are presented in Table 2.

Attention is attracted by the positive ferromagnetic exchange between the dimers in complex **IVb**, which creates the possibility for ferromagnetic ordering of the complex at lower temperatures.

Thus, variation of the coordination core of binuclear copper azomethine complexes (**IV**) by changing the donor atoms in their aldehyde fragments gives rise to two types of magnetically anomalous structures, namely, antiferromagnetic ($X = \text{O}$) and ferromagnetic ($X = \text{NTs}$) coordination compounds.

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