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Magnetoactive Binuclear Copper(II) Complexes Based on β-Aminovinylimines

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Abstract—β-Aminovinylimines containing bulky substituents at the donor nitrogen atoms and copper(II) chelates based on them were synthesized. The compounds were studied by single crystal and powder X-ray diffraction, EXAFS, NMR, EPR, and UV/Vis spectroscopy, and magnetochemistry. The complexes with halide bridges exhibit a ferromagnetic type of spin–spin interaction. The metal chelate containing a phenyl substituent in the γ-position of the aminovinylimino ligand absorbs atmospheric oxygen in a methylene dichloride solution, which gives rise to a dimer with oxygen bridges exhibiting an antiferromagnetic type of spin–spin interaction.

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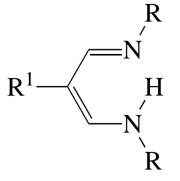
In recent years considerable attention has been devoted to magnetoactive metal complexes having a substantial potential as multi-purpose functional materials [1–9]. Among these, coordination compounds of Schiff's bases and their derivatives are widely encountered [10–17].

Metal chelates of bis(nitrogen) analogs of Schiffs bases, β-aminovinylimines, may be promising as ferromagnetic complexes [8–18]. By varying substituents in these ligands, one can obtain a broad range of complexes with different structures of the coordination polyhedron and, as a consequence, different physicochemical properties. In recent years, this compounds have attracted enhanced attention of a number of world leading schools of chemistry [19–26].

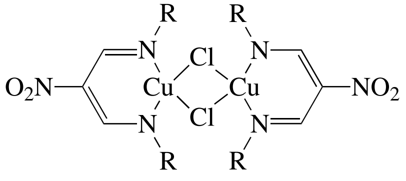
The purpose of this work is to synthesize and study the structure and magnetic properties of β-aminovinyliminate complexes using ligand systems **I** and **II** and copper metal chelates **III–V** as examples.



I, II

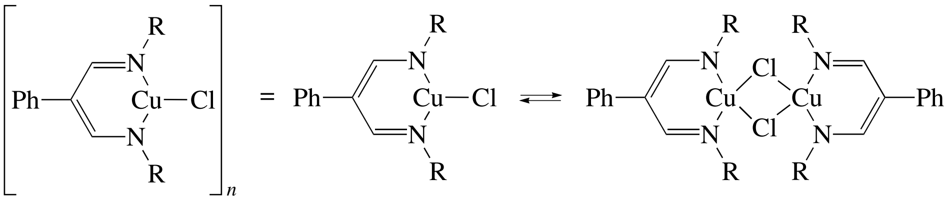
$R = 2,6\text{-}(i\text{-Pr})_2C_6H_4$

$R^1 = NO_2$ (I), Ph (II)



III

$R = 2,6\text{-}(i\text{-Pr})_2C_6H_4$

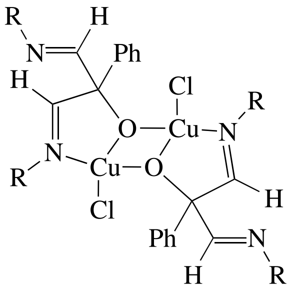


IVa,b
$n = 1–2$

IVa
$n = 1$

IVb
$n = 2$

$R = 2,6\text{-}(i\text{-}Pr)_2C_6H_4$



V
$R = 2,6\text{-}(i\text{-}Pr)_2C_6H_4$

EXPERIMENTAL

X-Ray diffraction of compound **II** was performed on a Smart 1000 CCD automated diffractometer at 293 K (MoK_α radiation, graphite monochromator, ω-scan mode, $2\theta_{max} = 57°$).

At 293 K, the crystals are monoclinic $a = 13.029(4)$, $b = 11.159(3)$, $c = 19.400(5)$ Å, $\alpha = 90°$, $\beta = 90.080(8)°$, $\gamma = 90°$, $V = 2820.6(14)$ Å^3, $\rho(calcd) = 1.099$ g cm^{-3}, space group $P2_1/c$, $Z = 4$. A total of 11703 reflections were measured, and 5634 observed reflections ($R_{int} = 0.0488$) were used in further calculations.

Table 1. Selected bond lengths and bond angles in compound **II**

Bond	d, Å	Bond	d, Å
N(1)–C(1)	1.330(3)	C(1)–C(2)	1.403(4)
N(1)–C(10)	1.430(3)	C(2)–C(3)	1.410(4)
N(2)–C(3)	1.309(3)	C(2)–C(4)	1.479(3)
N(2)–C(22)	1.426(3)	C(4)–C(9)	1.390(4)
Angle	**ω, deg**	**Angle**	**ω, deg**
C(1)N(1)C(10)	122.8(2)	C(3)C(2)C(4)	119.1(2)
C(3)N(2)C(22)	120.6(2)	N(2)C(3)C(2)	123.3(3)
N(1)C(1)C(2)	124.0(2)	C(9)C(4)C(5)	117.2(2)
C(1)C(2)C(3)	121.3(2)	C(9)C(4)C(2)	121.5(2)
C(1)C(2)C(4)	119.6(2)	C(5)C(4)C(2)	121.3(2)

The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic and isotropic approximations for F^2. The hydrogen atoms were located in the difference electron density syntheses and refined by the riding model. The final R-factors were $wR_2 = 0.1630$, $GOOF = 1.061$ for the reflections ($R_1 = 0.0660$ was calculated based on 4053 reflections with $I > 2\sigma(I)$); the calculations were carried out with the SHELXTL-Plus program package [27]. The main interatomic distances and bond angles are presented in Table 1.

X-Ray diffraction spectra were obtained on a DRON-3M diffractometer with a GP-13 attachment for powder diffraction and a BSV21-Cu X-ray tube ($U = 35$ kV, $I = 25$ mA). The CuK_{α_1, α_2} radiation ($\lambda = 1.5406$ Å) was isolated from the total spectrum by means of a nickel β-filter. The spectrum was recorded using a scintillation counter in the 2θ range from 5° to 60° with a step of 0.02° and a 4 s exposure at a point.

X-Ray Cu *K*-edge EXAFS spectra of metal chelates were recorded in the absorption mode on a EXAFS spectrometer at the Siberian Synchrotron Center (Novosibirsk). The electron beam energy used as a source of X-ray synchrotron radiation was 2 GeV at an average current of 80 mA. X-radiation was monochromatized by a double-crystal Si(111) monochromator. The intensities of the incident radiation and radiation that has passed through the sample were recorded using argon-filled ionization chambers.

The standard procedures for the background isolation, normalization to the *K*-edge step, and isolation of the atomic absorption μ_0 were followed by Fourier analysis of the resulting EXAFS (χ)-spectrum (EXAFS or the far fine structure of the X-ray absorption spectra) for each sample in the 2.8 to 15 Å^{-1} range of the photoelectron wave vectors with the weighing function k^2. The Fourier transform modulus (FTM) obtained after the Fourier transform of the EXAFS spectra reflects the radial distribution function of the neighboring atoms around the absorbing Cu atom. Exact structural parameters of the nearest environment of Cu were determined by non-linear approximation of the parameters of the corresponding coordination spheres through comparison of the computed EXAFS signal for the standards compound with that isolated by the FTM. The approximation quality function (***Q***), which was minimized when finding the structural parameters of the nearest environment of Cu atom, was calculated from the formula

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

^{1}H NMR spectra were recorded on a Varian UNITY-300 spectrometer (300 MHz) in $CDCl_3$ relative to the residual proton signal of the deuterated solvent (7.24 ppm).

The EPR spectra were measured on a Bruker ER200D-SRC instrument with a double ER 4102 resonator and a ER 4111 VT temperature unit. Diphenylpicrylhydrazine (DPPH, $g = 2.0037$) was used as the reference to determine the *g*-factor.

The diffuse reflection spectra (DRS) of solid samples and electronic absorption (UV/Vis) spectra of solutions of the compounds under study in methylene dichloride were measured on a Specord M400 instrument.

The magnetic properties of the crystalline phase of the complexes were measured using a MPMS-5S SQUID Quantum Design magnetometer in the temperature range 2–300 K and in a 5 kOe magnetic field. No dependence of the magnetic susceptibility on the magnetic field has been detected. The effective magnetic moments were calculated from the formula

$$\mu_{\text{eff}}(T) = \sqrt{8\chi T},$$

where χ is the molar paramagnetic susceptibility corrected for the diamagnetic contribution. When simulating the experimental plots with allowance for the dimer–dimer exchange interactions (***zJ'***), the theoretical curves were determined by the relation

$$\chi = \chi_{\text{Cu–Cu}}/[1 - (2zJ'/Ng^2\beta^2)\chi_{\text{Cu–Cu}}],$$

where $\chi_{\text{Cu–Cu}}$ is the Bleany–Bauers magnetic susceptibility of the dimer, *g* is the Cu(II) *g*-factor, β is the Bohr magneton.

β-Aminovinylimines **I, II** and complexes **III–V** based on them were synthesized by published procedures [28–30].

2-(2,6-Diisopropylphenyl)amino-4-(2,6-diisopropylphenyl)imino-3-nitro-2-pentene (I) was prepared by a reported method [28]. 2,6-Diisopropylaniline hydrochloride (4.26 g, 0.02 mol) was added to a water–ethanol solution of the sodium salt of nitromalonodialdehyde (1.39 g, 0.01 mol). The mixture was refluxed for 5 h . After cooling, a solution of $NaHCO_3$was added to the reaction mixture up to pH 7–8. The precipitate was filtered off, washed with water and small portions of ethanol, and recrystallized from isopropyl alcohol. The yield of product **I** formed as yellow crystals was 75–78%.

For $C_{27}H_{37}N_3O_2$			
anal. calcd. (%):	C, 74.45;	H, 8.56;	N, 9.65.
Found (%):	C, 74.22;	H, 8.23;	N, 9.44.

^{1}H NMR ($CDCl_3$, δ, ppm): 1.2 (d, 24H, $8CH_3$, $^3J_{CH_3\text{–}CH}$ = 6.9 Hz); 3.05 (hept, 4H, $4CH\text{–}(CH_3)_2$, $^3J_{CH\text{–}CH_3}$ = 6.9 Hz); 7.16–7.26 (m, 6H, $2C_6H_3$); 8.74 (d, 2H, 2CH–NH, $^3J_{CH\text{–}NH}$ = 4 Hz); 12.79 (br.s, 1H, NH).

Synthesis of 1-(2,6-diisopropylphenyl)amino-3-(2,6-diisopropylphenyl)imino-2-phenyl-1-propene (II). An ethanol solution of KOH (0.336, 0.006 mol) was added to a hot ethanol solution of the pechlorate salt of the dimethylamine derivative of phenylmalonodialdehyde (1.51 g, 0.005 mol). The mixture was refluxed for 15 min. After cooling, the solution was filtered, di(isopropyl)aniline (1.77 g, 0.001 mol) in butanol was added to the filtrate, and 12 M HCl (1 equiv) was added dropwise. Then the reaction mixture was refluxed for 10–12 h, excess butanol was evaporated, and the mixture was left overnight. The resulting mixture was neutralized with $NaHCO_3$ and extracted with chloroform. The chloroform extract was dried for 12 h over $MgSO_4$ and filtered. Chloroform was evaporated in a vacuum to give an oily product, which was recrystallized from methanol. The yield was 55–60%.

For $C_{33}H_{42}N_2$			
anal. calcd. (%):	C, 84.93;	H, 9.07;	N, 6.00.
Found (%):	C, 84.75;	H, 8.89;	N, 5.76.

^{1}H NMR ($CDCl_3$, δ, ppm): 1.22 (d, 24H, $8CH_3$, $^3J_{CH_3-CH}$ = 6.9 Hz); 3.27 (hept, 4H, $4CH-(CH_3)_2$, $^3J_{CH-CH_3}$ = 6.9 Hz); 7.0–7.4 (m, 11H, $2C_6H_3$, C_6H_5); 7.71 (s, 2H, 2CH–NH); 12.06 (br.s, 1H, NH).

Synthesis of bis{μ(Cl_2)-(2,6-diisopropylphenyl)amino-4-(2,6-diisopropylphenyl)iminatocopper(II)-3-nitro-2-pentene} (III). A hot solution containing $CuCl_2 \cdot H_2O$ (0.17 g, 0.001 mol) in ethanol was added to a hot solution of ligand I ($R^1 = NO_2$) (0.435 g, 0.001 mol) in 10 ml of ethanol. The mixture was refluxed for 20–30 min. The precipitated brown crystals were filtered off, washed with ethanol, and dried. mp > 200°C, yield 60%.

For $C_{54}H_{72}Cl_2Cu_2N_6O_4$			
anal. calcd. (%):	C, 60.78;	H, 6.80;	N, 7.87.
Found (%):	C, 60.47;	H, 6.54;	N, 7.53.

DRS (λ_{max}, nm): 226, 270 sh, 320 sh, 344, 458, 542 sh, 622 sh, 874.

UV/Vis (CH_2Cl_2, λ_{max}, nm (ε, mol^{-1} cm^{-1})): 282 sh (17633), 340 (51734), 474 (4332), 620 sh (1199).

Bis{μ(Cl_2)(2,6-diisopropylphenyl)amino-3-(2,6-diisopropylphenyl)iminatocopper(II)-2-phenyl-1-propene} (($LCuCl)_n$) (IV) was synthesized by the procedure used to prepare complex **III** but with ligand **II** as the starting reagent. Yield 56%.

For $C_{66}H_{82}Cl_2Cu_2N_4$			
anal. calcd. (%):	C, 70.19;	H, 7.32;	N, 4.96.
Found (%):	C, 70.35;	H, 7.56;	N, 4.89.

DRS (λ_{max}, nm): 226 sh, 270 sh, 304, 372, 454, 570 sh, 608 sh, 628, 863 sh.

UV/Vis (CH_2Cl_2, λ_{max}, nm (ε, mol^{-1} cm^{-1})): 282 (37261), 330 (15212), 378 (32095), 488 sh (3472), 514 (4124), 618 sh (1017), 672 sh (884), 838 (450).

Complex V was prepared from compound **IV** by growing crystals from benzene–heptane or acetonitrile–methanol–chloroform mixtures (green crystals).

For $C_{66}H_{82}Cl_2Cu_2N_4O_2$			
anal. calcd. (%):	C, 68.26;	H, 7.12;	N, 4.82.
Found (%):	C, 68.17;	H, 7.40;	N, 4.71.

X-Ray diffraction data for chelate *V* were reported in [30].

RESULTS AND DISCUSSION

The structures of ligands **I** and **II** in a $CDCl_3$ solution were studied by NMR. The ^{1}H NMR spectra of compounds **I** and **II** exhibit broadened signals of the NH-group protons (δ 12.79 ppm (**I**), 12.06 ppm (**II**)) and the CH protons of the β-aminovinylimine ring (8,74 ppm (**I**) and 7.71 ppm (**II**)). In the ^{1}H NMR spectra of compound **I**, the CH-group protons occur as a doublet with the vicinal constant $^3J_{CH-NH}$ = 4 Hz due to the spin–spin coupling between the CH and NH protons. The vicinal spin–spin coupling constant determined is twice as low as the usual value ($^3J_{CH-NH}$ = 8 Hz). This is indicative of fast, on the NMR time scale, intramolecular chemical exchange with the NH proton being located with equal probability at any of the dianil nitrogen atoms.

In the ^{1}H NMR spectrum of ligand **II**, the CH-group protons give rise to a singlet. The broadened signal of the NH proton and the singlet for the methine fragments attest to intermolecular exchange processes. The ^{1}H NMR data indicate that dianils **I** and **II** exist in $CDCl_3$ as the amino-imine tautomers containing an intramolecular hydrogen bond [31–34].

The molecular structure of ligand **II** is shown in Fig. 1. Molecule **II** contains an intramolecular hydrogen bond, NH···N, the H-bonded ring being nearly planar, as found in the previous study [21–23, 34]. The N(1)–H(1) (N(2)–H(1)) and N(1)–C(1) (N(2)–C(2)) bond lengths are 1.11 (1.74) and 1.330 (1.309) Å, respectively. For these systems, the observed C–N bond lengths vary in the 1.29–1.24 Å range [22, 24].

The angle between the plane of the aromatic ring located in the γ-position of the aminovinylimine ligand and the H-bonded ring equals 37°. The aryl substituents at the nitrogen atoms are rotated relative to the H-bonded ring through 104.7° and 60.5°. The hydrogen atom at the donor nitrogen protrudes from the N(1)C(1)C(2)C(3)N(2) plane by 0.09 Å.

Complexes **III** and **IV** were prepared in ethanol by direct reaction of ligands **I** or **II** with $CuCl_2 \cdot H_2O$ in 1 : 1 molar ratio.

Complexes **III** and **IV** behave in different ways in a methylene dichloride solution. The UV/Vis spectrum of metal chelate **III** in CH_2Cl_2 exhibits the following absorption bands (nm): 340, 474, 262 sh, and 620 sh. The bands do not change for a long period of time. It is of interest that binuclear copper(II) β-aminovinyliminate complex with oxygen bridges (R = 2,4,6-$(CH_3)_3C_6H_3$) contains one intense band at ~353 nm [26]. The UV/Vis spectrum of complex **IV** has the bands (nm) at 282, 330, 378, 514, 488 sh, 618 sh, and 838 sh, which are transformed with time into a broad band with shoulders

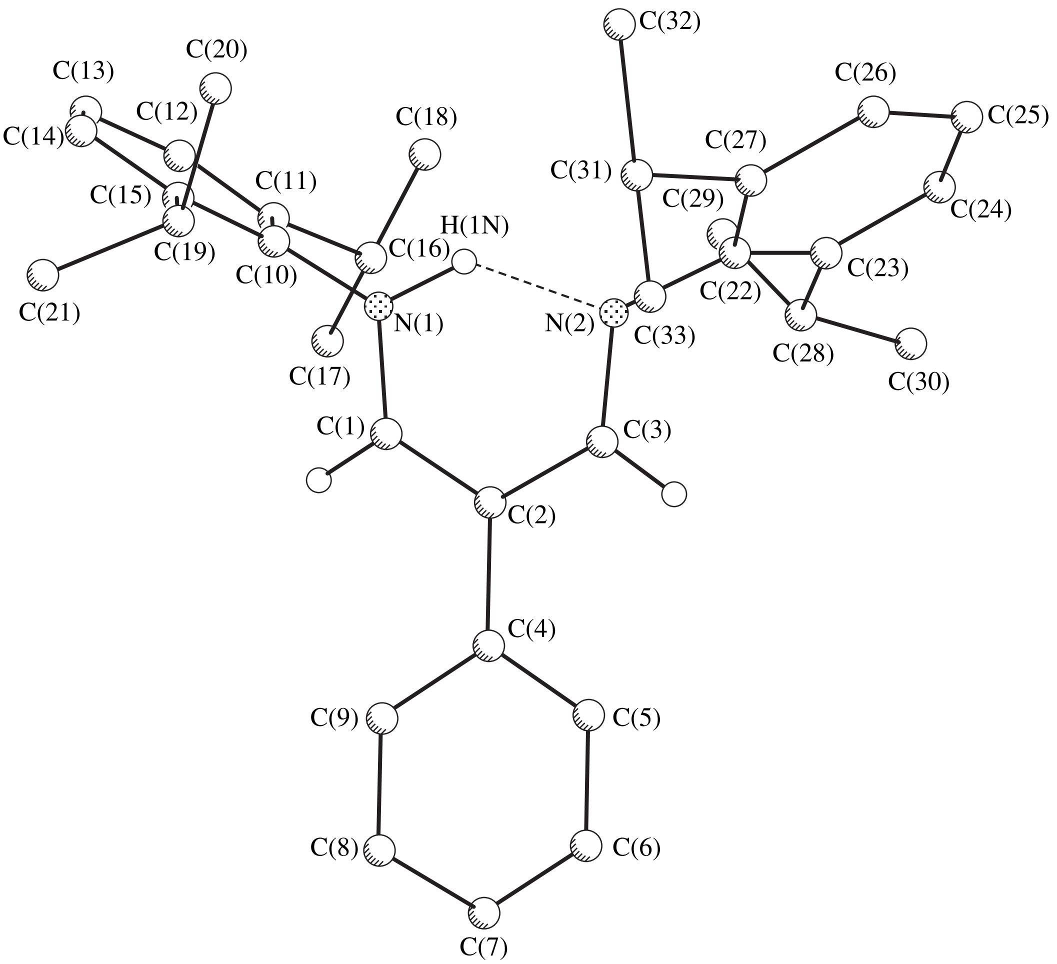


Fig. 1. Molecular structure of ligand **II**.

at 264, 290, 374 nm and weak bands ($\varepsilon = 80–98$) at 630–750 nm (Fig. 2). The UV/Vis spectrum of β-aminovinylimine complexes, in which the Cu coordination sphere contains two N atoms and one Cl atom, exhibits bands at 340, 507, 657, and 840 nm [20]. As shown previously [26] for dimeric copper complexes with dianils, the nature of the substituent and the temperature have an influence on the UV/Vis spectra of dimeric copper(II) β-aminovinyliminate chelates with chlorine bridges (for example, $R^1 = Cl$, $R = 2,6\text{-}(CH_3)_2C_6H_4$). In various temperature ranges and depending on the nature of N-substituents in the β-aminovinylimine ring, the spectra of both three-coordinate mononuclear copper and the dimer are observed. In our case, the UV/Vis spectral pattern of complex **IV** recorded immediately after dissolution in CH_2Cl_2 (Fig. 2) is virtually identical to the spectra of metal chelates described previously [26]; this implies that CH_2Cl_2 solutions contain metal chelates **IVa** and **IVb**.

The EPR spectrum of dimer III (powder) is a broad line (more than 100 G) with two centrosymmetric shoulders. The *g*-factor of the central component

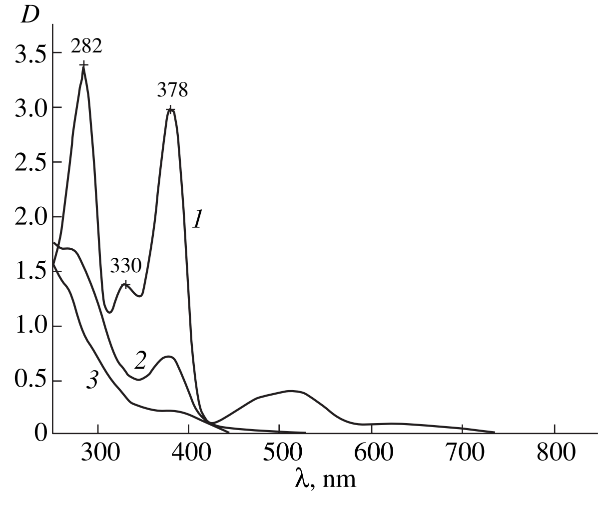


Fig. 2. UV/Vis spectrum of complex **IV** in CH_2Cl_2: (*1*) immediately after dissolution and (*2, 3*) after keeping for (*2*) 3 and (*3*) 24 h.

and the distance between the shoulder tops varies with temperature without substantial change in the line width (Fig. 3). In addition, an EPR signal occurs in the "half" field, $g = 4.33$ ($T = 130$ K). The spectra apparently belong to a radical pair (two weakly interacting electrons, the triplet ground state) with two unpaired electrons being located on Cu^{2+} ions (d^9). The zero-field splitting parameter 2D or D'' allows one to estimate the effective distance between the localization centers of the unpaired electrons for various temperatures

290 K: $g = 2.085$, 2D (D'') = 1551 G, $r = 3.3$ Å;

220 K: $g = 2.107$, 2D (D'') = 1752 G, $r = 3.17$ Å;

130 K: $g = 2.122$, 2D (D'') = 1847 G, $r = 3.11$ Å,

where g is the g-factor of the central line or the "monoradical signal"; 2D(D'') is the zero-field splitting parameter; r is the effective distance between the unpaired electrons. The g-factor value of the central line is typical of Cu^{2+} (d^9). The resulting r values are consistent with the published data for dimers with chlorine bridges [26]. The half-field signal refers to the forbidden transition with $\Delta M_S = 2$ (spin quantum number, $M_S = 1, 0, -1$). Compound **III** does not exhibit an EPR spectrum in solution. Thus, complex **III** can be assigned a dimeric structure with chlorine bridges.

The EPR spectrum of complex **IV** in 2-methyltetrahydrofuran (2-CH_3–C_4H_7O) is a broad asymmetric line with $g_{iso} \cong 2.09$. An EPR spectrum with the parameters $a_{\|}(Cu) = 131$ G, $g_{\|} = 2.23$, $g_{\perp} = 2.02$ was recorded in a glassy solvent matrix at 120 K (Fig. 4). The main values of the g-tensor ($g_{\|} = 2.23$, $g_{\perp} = 2.02$) provide grounds for assigning the spectrum to a monomeric copper(II) complex (d^9). The only unpaired electron is located predominantly on the Cu^{2+} ion. The obtained EPR parameters of complex **IV** are very similar to those for the mononuclear β-aminovinyliminate complex of three-coordinate copper containing two nitrogen atoms and one chlorine atom in the coordination sphere [20]. However, the presence of a dimer also cannot be ruled out, because it may be EPR non-detectable. This depends on the complex geometry and symmetry of the orbitals containing unpaired electrons.

Complex **V** does not produce any EPR spectrum in solutions (CH_2Cl_2, 2-CH_3–C_4H_7O). According to X-ray diffraction data [30], compound **V** is a binuclear centrosymmetric metal chelate containing an oxygen bridge. The nearest environment of the copper atom is composed of nitrogen, oxygen, and terminal chlorine atoms. A complex with a similar structure has been reported in [25].

Thus, EPR data attest to a dimeric structure of chelate **III** and to the presence of the mononuclear complex **IVa**. However, the data of UV/Vis spectra indicate that both monomer **IVa** and dimer **IVb** are present in the solution.

Compound **IV** in solutions (for example, in CH_2Cl_2) is converted with time into dimer **V**. The UV/Vis spectrum of chelate **IV** changes with time both in the UV and in the visible regions (Fig. 2). The spectrum of complex **IV** having been kept for 24 h is virtually identical to the spectrum of crystals of **V** dissolved in CH_2Cl_2. Similar changes in the UV/Vis spectra have

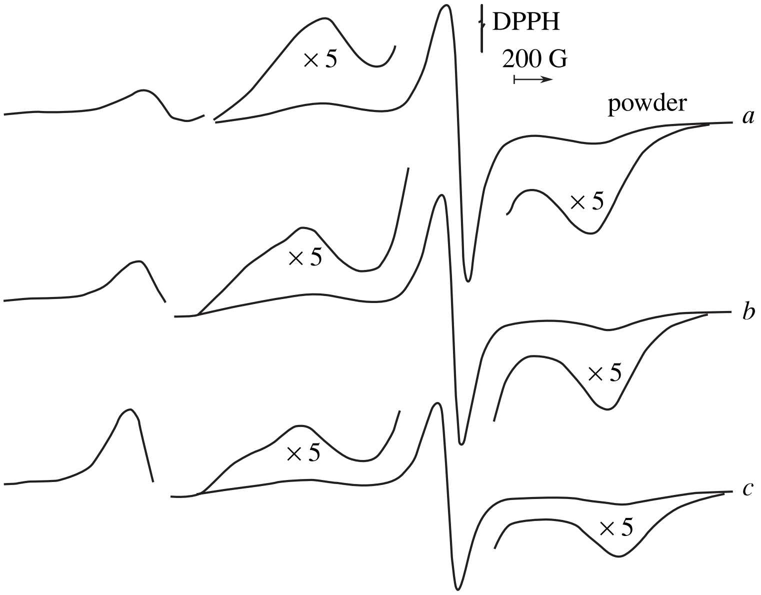


Fig. 3. EPR spectra of complex **III** at *T* of (*a*) 290, (*b*) 220, (*c*) 130 K.

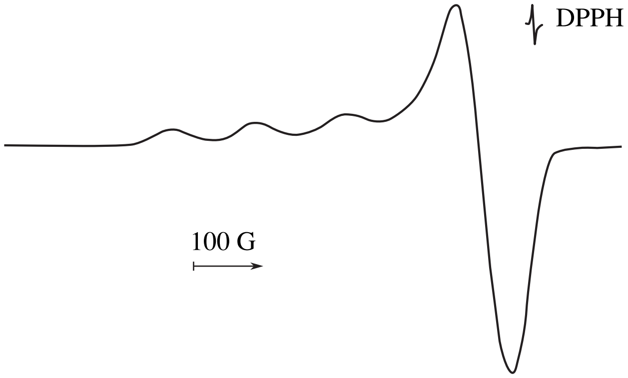


Fig. 4. EPR spectra of complex **IV**.

been noted in oxidation of copper(II) β-aminovinyliminates [20, 25].

Spectroscopic studies of a freshly prepared solution of complex **IV** in CH_2Cl_2 and the crystal of **V** confirm the results of powder X-ray diffraction, attesting to their different structures (Fig. 5).

The composition and characteristics (radius, coordination numbers, and Debye–Waller factors) (Table 2) for the atoms of the nearest coordination spheres in complexes **IV** and **V** were studied by EXAFS. The experimental FTM EXAFS spectra of complexes **IV** and **V** are similar and contain two well-resolved major peaks corresponding to scattering of the photoelectron wave on the nearest coordination sphere and weaker peaks with great *r* corresponding to the long-range coordination sphere (Fig. 6). Table 2 presents the parameters of the nearest environment of the copper atom in the complexes, which have been determined by approximating the theoretically calculated $\chi(k)$ values of the models chosen to the experimental EXAFS spectra. The coordination sphere parameters obtained from approximation for complex **V** are close to the corresponding X-ray diffraction values [30] and describe the model of a copper dimer with two oxygen bridges and two terminal chlorine atoms. In the case of freshly prepared complex **IV**, the best approximation corresponds to the model in which the first coordination sphere consists of two nitrogen atoms and two bridging chlorine atoms.

On the basis of the physicochemical studies and published data [20, 25], we suggest that the reaction of dianil **II** with $CuCl_2 \cdot 2H_2O$ yields complex **IV**, which is oxidized by air oxygen in a CH_2Cl_2 solution, being

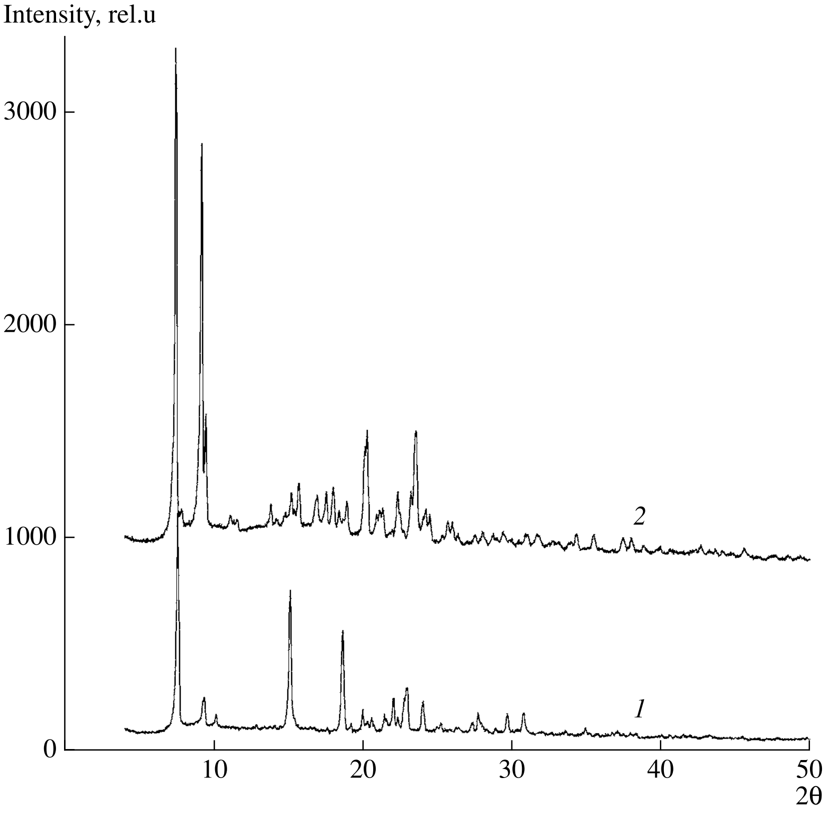
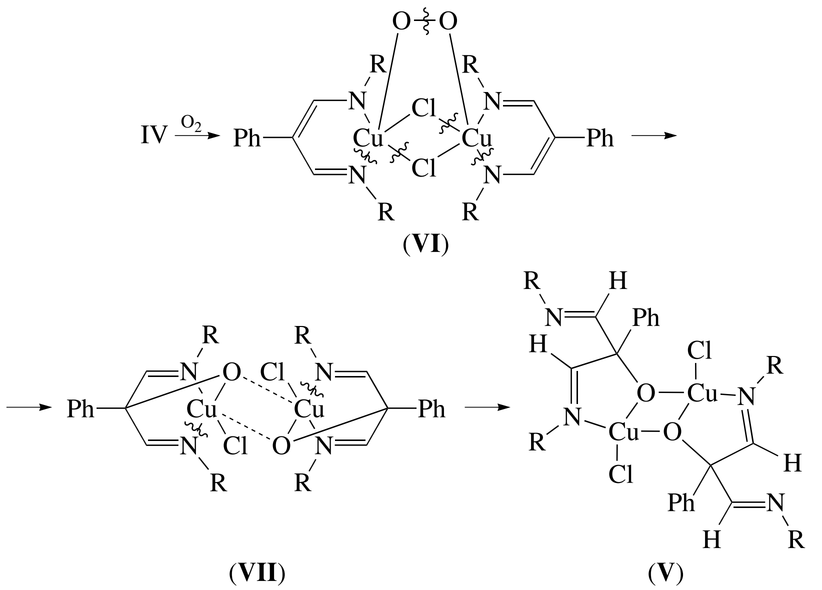


Fig. 5. X-ray diffraction patterns of complexes **IV** and **V**: (*1*) compound isolated immediately after the reaction, **IV**; (*2*) oxidized compound, **V**. Wavelength λ = 1.5406 Å.

converted into dimer **V**. The hypothetical mechanism of this reaction that includes oxidation of chelate **IV** with atmospheric oxygen to give intermediate compounds **VI** and **VII** can be represented as follows:



(**VI**)

(**VII**)

(**V**)

The magnetochemical investigations demonstrated that complex **III** tends to exhibit a ferromagnetic type of spin–spin coupling. The temperature dependence of the magnetic moment and exchange parameters of complex **III** are presented in Fig. 7. Study of a large group of compounds in which the exchange coupling

Table 2. Structural data for the copper coordination spheres in complexes **IV** and **V** found by the multisphere approximation of EXAFS data*

Compound	C.N.	*r*, Å	σ^2, Å^2	Atom	*Q*, %
Complex **IV** (immediately after the reaction)	2	1.95	0.0049	N	3.5
	2	2.30	0.0054	Cl_{bridge}	
	3	2.94	0.0060	C	
	1	3.01	0.0088	Cu	
Complex **V**	2	1.91	0.0076	C_{bridge}	2.5
	1	2.05	0.0022	N	
	2	2.33	0.0052	Cl_{term}	
	5	2.93	0.0065	C	
	1	2.97	0.0080	Cu	

* *r* are the radii of the coordination spheres; C.N. is the coordination number, σ^2 is the Debye–Waller factor, *Q* is the approximation quality function.

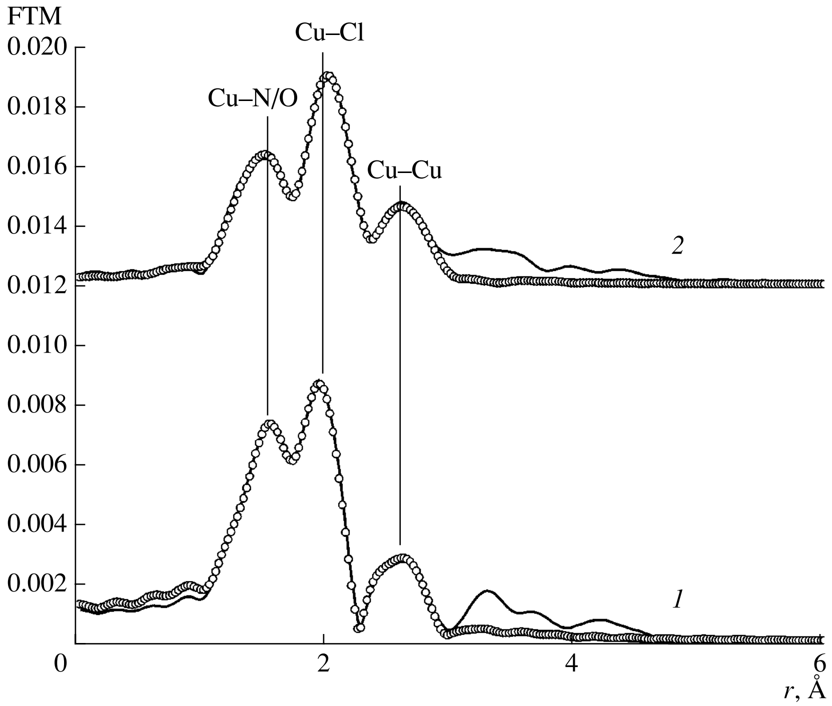


Fig. 6. FTM for complexes (*1*) **IV** and (*2*) **V** in the integration range from 2.8 to 13 $Å^{-1}$. (–) Is the experimental FTM, (○) is the theoretical FTM obtained by approximation.

between Cu^{2+} ions occurs through the halide ions showed that they mainly have the antiferromagnetic type of spin–spin coupling [26, 35]; the cases of ferromagnetic exchange are very seldom [11]. In this connection, note that the dimeric copper complex with a similar structure containing ethyl rather than isopropyl groups in the N-aryl fragments exhibits weak antiferromagnetism ($J = -0.3$ cm^{-1}) [26].

Complex **IVb** obtained immediately after the reaction exhibits, like **III**, the ferromagnetic type of spin–spin coupling (Fig. 8). However, binuclear complex **V** shows a very weak antiferromagnetic exchange (Fig. 9).

These data imply that the physicochemical properties and the reactivity of copper β-aminovinyliminate chelates depend on the nature of substituents both at

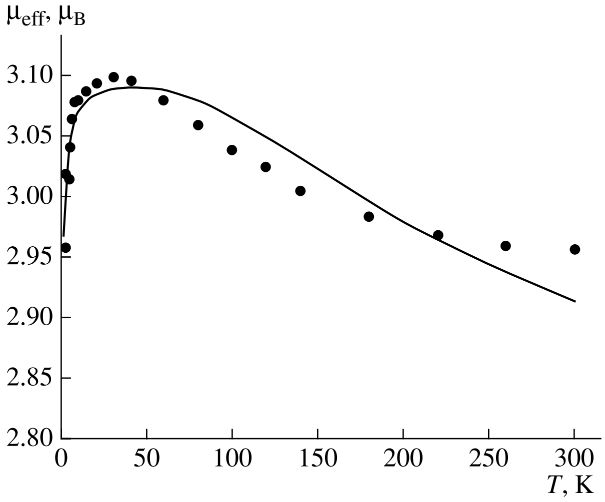


Fig. 7. Temperature dependence of the magnetic susceptibility of complex **III** ($g = 2.19$, $J = 99$ cm^{-1} (142 K), $J'z = 0.08$ cm^{-1} (–0.11 K)).

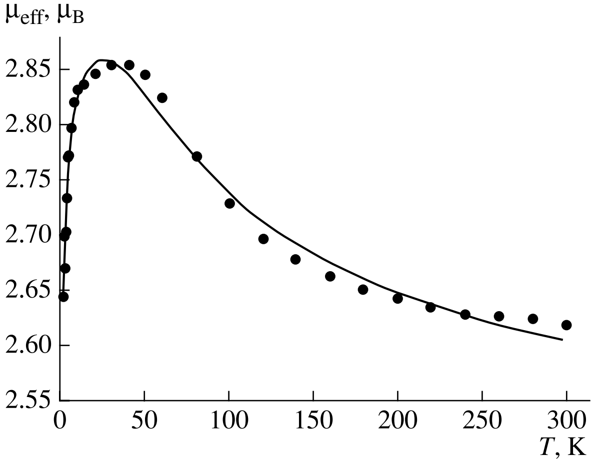


Fig. 8. Temperature dependence of the magnetic susceptibility of complex **IV** ($g = 2.05$, $J = 39$ cm^{-1} (56 K), $J'z = 0.2$ cm^{-1} (–0.3 K)).

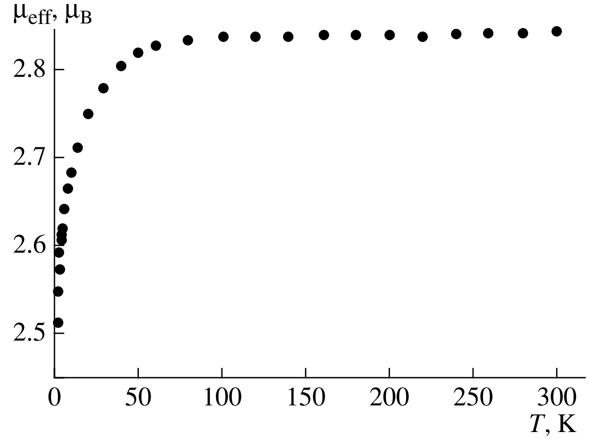


Fig. 9. Temperature dependence of the magnetic susceptibility of complex **V**.

nitrogen and in the β-aminovinylimine ring. In particular, it was shown that rational design of these ligand systems opens up the way to magnetoactive binuclear copper complexes with different types of spin–spin coupling. Treatment of compound **IV** in CH_2Cl_2 with atmospheric oxygen gives metal chelate **V** with an unusual ligand coordination.

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