New Magnetically Active Metal Complexes of Tridentate Schiff Bases of Phenylazosalicylaldehyde

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Abstract—The bidentate chelate Cu(II) complexes of phenylazosalicylaldehyde azomethines are synthesized for the first time and their magnetic properties are studied. The complexes with the intermetallic bridge of the nitrogen atoms are characterized by the antiferromagnetic interaction, whereas the ferromagnetic exchange is typical of analogous coordination compounds with the sulfur bridge.

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INTRODUCTION

Azo ligands are most important objects of the modern coordination chemistry [1–4]. In the most cases, metallochelates with five-, six- or five-, and six-membered coordination modes were obtained from the azoligating compounds. At the same time, complexes, whose azo group of the ligand is not in the composition of the coordination mode, are of considerable interest for the synthesis and study of magnetically active materials [5, 6]. This position of the azo group makes it possible to use its ability for the photoinduced E/Z- isomerization in the creation of coordination compounds with the properties of molecular switchers [7]. We synthesized earlier undescribed binuclear copper chelates (I) from 2-hydroxy-5-phenylazobenzaldehyde (L^1) and 2-((*E*)-{[2-(ethylamino)-5-nitropherelated nyl]imino}methyl)-4-(phenylazo)phenol (L^2). Their magnetic properties were studied in the temperature interval from 2 to 300 K.

EXPERIMENTAL

Synthesis of L¹ was carried out by the dinitration of aniline and the coupling of the obtained diazonium salt with salicylaldehyde. Dry NaNO₂ (1.82 g, 0.026 mol) was added during 45 min with vigorous stirring at a temperature not higher than -5° C to a solution of aniline (2.33 g, 0.025 mol) in a 12% solution of HCl (15 ml). Subsequent procedures were carried out at this temperature. After the end of the dinitration, the resulting solution was stored for 30 min. The diazonium salt was slowly added to a solution of salicylaldehyde (3.05 g, 0.025 mol) in methanol (7 ml) with vigorous stirring. The azocoupling was ceased 45 min after, and the resulting solution was stirred for 30 min. When the temperature of the solution became ambient, the pH value was brought to 7 by the addition of Na₂CO₃. The brown precipitate formed was filtered off, washed with a large amount of water, and dried in air. The product was purified by chromatography on a column packed with Al₂O₃ (chloroform as eluent), chloroform was distilled off from the eluate, and the resulting precipitate was recrystallized from benzene. The yield of L¹ was 70% (mp = $128-129^{\circ}$ C).

IR, cm⁻¹: 1664 vs (C=O). ¹H NMR (CDCl₃), δ , ppm: 7.12–8.22 (m, 8H, C_{Ar}–H), 10.04 (s, 1H, CHO), 11.33 (s, 1H, OH).

Synthesis of L². A solution of 2-ethylamino-5nitroaniline (0.544 g, 3 mmol) [8] in toluene (15 ml) was added to a solution of L¹ (0.679 g, 3 mmol) in toluene (20 ml). The mixture was refluxed under argon for 3 h. Then 1/3 of the toluene volume was distilled off on a rotary evaporator. A yellow-orange precipitate was formed on cooling, filtered off, washed with cold ethanol (4 × 5 ml), and recrystallized from a chloroform– ethanol (4 : 1) mixture. The yield of L² was 65% (mp = 233–234°C).



IR, cm⁻¹: 1605 (C=N), 1293 (Ph–O), 3408 (N–H). ¹H NMR (CDCl₃), δ , ppm: 1.37 (t, 3H, J = 7.22 Hz, CH₃), 3.37 (m, 2H, CH₂), 5.06 (br.s, 1H, NH), 6.66 (d, 1H, J = 9.1 Hz, C_{Ar}–H), 7.17 (d, 1H, J = 8.7 Hz, C_{Ar}–H), 7.47–7.57 (m, 3H, C_{Ar}–H), 7.90–8.17 (m, 6H, C_{Ar}–H), 7.90–8.17 (m, 6H, C_{Ar}–H), 8.84 (s, 1H, CH=N), 12.78 (s, 1H, OH).

Synthesis of bis[2-((*E*)-{[2-(ethylamino)-5-nitrophenyl]imino}methyl)-4-(phenylazo)phenolato]dicopper(II) (Ia). A boiling solution of copper acetate dihydrate (0.119 g, 0.00058 mol) in methanol (10 ml) was added to a hot solution of azomethine L² (0.232 g, 0.00058 mol) in a dioxane–methanol (3 : 1) mixture (20 ml). The resulting mixture was refluxed for 2.5 h. A brown precipitate of compound Ia was formed during reflux. After cooling, the precipitate was filtered off, washed with hot methanol (4×5 ml) and hexane (5 ml), and dried in a vacuum drying oven at 100°C. The yield of compound Ia was 45% (mp > 250°C). IR, cm⁻¹: 1602 s (C=N), 1344 w (Ph–O).

Synthesis bis[2-{(*E*)-[(2-mercaptopheof nyl)imino]methyl}-4-(phenyldiazenyl)phenolato]dicopper(II) (Ib). A hot solution of *o*-aminothiophenol (0.125 g, 0.001 mol) in methanol (10 ml) and a solution of copper acetate dihydrate in the same solvent (10 ml) were added to a hot solution of L^1 (0.226 g, 0.001 mol) in dioxane (10 ml). The resulting mixture was refluxed for 15 ml, and then a hot solution of copper acetate dihydrate (0.200 g, 0.001 mol) in methanol (10 ml) was added. Then the mixture was refluxed for 1.5 h. A black precipitate was formed during reflux. The mixture was cooled down, filtered off, washed with hot methanol $(4 \times 5 \text{ ml})$ and then with hexane (5 ml), and dried in a vacuum drying oven at 100°C. The yield of compound **Ib** was 60% (mp > 250° C).

For C38H26N6O2S2Cu2

No. 7

2009

anal. calcd, %: C, 57.78; H, 3.32; N, 10.64; Cu, 16.09. Found, %: C, 57.61; H, 3.41; N, 10.71; Cu, 16.20.



Fig. 1. The FTM EXAFS of the X-ray K-edge absorption of complexes (1) Ia and (2) Ib. Solid line is experiment, and circles show theoretical calculation.

IR, cm⁻¹: 1611 vs (C=N), 1324 w (Ph–O).

¹H NMR spectra were recorded on a Varian Unity-300 instrument (300 MHz) in the mode of internal stabilization of the ²H polar resonance line in CDCl₃. IR spectra were measured on a Nicolet Impact-400 instrument (suspensions in Nujol).

Structure parameters of the nearest environment of the Cu atoms obtained from the multisphere fitting of the EXAFS data (*R* are the interatomic distances, *N* is the coordination number, σ^2 is the Debye–Waller factor, and *Q* is the fitting quality function)

Compound	Ν	<i>R</i> , Å	σ^2 , Å ²	Atom	<i>Q</i> , %
Ia	2	1.87	0.0035	O/N	5.1
	2	1.99	0.0037	Ν	
	1	2.79	0.0074	Cu	
Ib	2	1.92	0.0040	Ν	4.3
	2	2.24	0.0057	S	
	1	2.99	0.0060	Cu	

The Cu*K*-edge EXAFS spectra of the studied compounds were detected on an EXAFS laboratory spectrometer based on a DRON-3 diffractometer. A BSV-21-Mo tube was used as an X-ray radiation source at the voltage U = 17 kV and the current I = 30 mA. The X-ray radiation was decomposed into the spectrum using a SiO₂(13 $\overline{4}$ 0) monochromating crystal.

Samples for detection were thoroughly mixed with the Apiezon lubricant and placed between thin lavsan films. The thickness of the samples was selected in such a way that the intensity of the passed X-ray beams decreased by 2.5–3.0 times. After standard procedures on the isolation of the background, normalization to the *K*-edge jump, and isolation of the atomic absorption μ_0 [9], the Fourier transformation of the obtained EXAFS spectra was performed in the interval of wave vectors of photoelectrons k from 3.0 to 13 Å⁻¹ with the weight function k^2 . The threshold ionization energy E_0 was chosen by the value of the maximum of the first derivative of the K-edge and further was varied during fitting. The exact values of the structure parameters of the nearest environment of metal atoms were determined by the nonlinear fitting of the parameters of the corresponding coordination spheres by the comparison of the calculated EXAFS signal and that isolated from the full EXAFS spectrum by the Fourier filtration method of the Fourier transformant modules (FTM). This non-



Fig. 2. Temperature plot of the effective magnetic moment for complex Ia.

linear fitting was carried out using the IFFEFIT-1.2.10 programs [10]. The photoelectron wave scattering phases and amplitudes, being necessary for the construction of theoretical spectra, were calculated using the FEFF7 program [7] and the X-ray structural data for the model compounds. The model compounds were bis((μ^2 -azido-N,N)-(7-amino-4-methyl-5-aza-3-hep-tyl-2-onato-N,O)-copper(II) (C₁₄H₂₆Cu₂N₁₀O₂) [12] and *N*,*N*-(2,6-dimethylene-4-methylthiophenyl)-1,3-diaminopropane)-bis(methanol-copper(II)) nitrate hexafluorophosphate ethanol solvate (C₂₉H₄₃Cu₂F₆N₅O_{6.5}PS₂) [13] for compounds **Ia** and **Ib**, respectively. They have local environment of the metal atoms close to the assumed one in the compounds under study.

The fitting quality function Q, which was minimized by finding the structure parameter of the nearest environment, was calculated by the formula

$$Q(\%) = \frac{\sum [k\chi_{\exp}(k) - k\chi_{\text{theor}}(k)]^2}{\sum [k\chi_{\exp}(k)]^2} 100,$$

where χ_{exp} and χ_{theor} are the experimental and theoretical EXAFS values, respectively; *k* is the wave vector of a photoelectron.

The magnetic properties of the compounds were measured on an MPMSXL SQUID magnetometer (Quantum Design) in the temperature interval from 2 to 300 K and a magnetic field of 5 kOe. The paramagnetic components of the magnetic susceptibility (χ) were determined with allowance for the diamagnetic contribution estimated from Pascal's constants. The effective magnetic moment (μ_{eff}) was calculated by the formula

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



Fig. 3. Temperature plot of the effective magnetic moment for complex Ib.

are Avogadro's number, Bohr's magneton, and the Boltzmann constant, respectively.

RESULTS AND DISCUSSION

According to the data of the IR and ¹H NMR spectra, the enolimine form can be ascribed to the Schiff base L² as to other *o*-hydroxyazomethines [14–17]. The intense peak of the absorption band of stretching vibrations of the HC=N bond appears at 1605 cm⁻¹ in the IR spectrum, whereas the band corresponding to vibrations of the NH groups appears at 3408 cm⁻¹.

The enolimine tautometic form of L^2 is also confirmed by the ¹H NMR signals at 5.06 (NH), 8.84 (HC=N), and 12.78 (OH) ppm.

The formation of chelate structure of type I by analogy to [18, 19] is confirmed by the disappearance of the v(NH) stretching vibrations in the IR spectrum of the complexes and the signals of the NH groups in their ¹H NMR spectra and by an insignificant decrease in the frequencies of vibrations of the HC=N bond.

For the first time the dimeric structure can be ascribed to synthesized complexes I, which is confirmed by the EXAFS spectral data.

The FTM of the copper *K*-edge EXAFS spectra of compounds **Ia** and **Ib** are shown in Fig. 1. The parameters of the nearest environment of the copper atom in these compounds obtained by the fitting of theoretically calculated $\chi_{\text{theor}}(k)$ of the chosen models to $\chi_{\text{exp}}(k)$ are given in the table.

As can be seen from Fig. 1, the FTM of the EXAFS spectra of the both samples consist of the main peak $(r \approx 1.48-1.50 \text{ Å})$ corresponding to the first coordination sphere of the light N and O atoms and the peaks with the lower amplitude (r = 2.43 (Ia), 2.64 (Ib) Å). The main FTM peak of sample Ib (X = S) also has an addi-

Vol. 35

No. 7

2009

tional shoulder ($r \approx 1.77$ Å) corresponding to the photoelectron wave scattering on two different coordination spheres. We interpreted the second peak as the manifestation of the Cu···Cu distance in the complexes. As found by the analysis of the FTM of the EXAFS spectra on the basis of the proposed models of the local atomic structure of the copper atoms in the complexes under study, metallochelates **Ia** and **Ib** have a dimeric structure with a Cu···Cu distance of 2.79 Å, two sets of bond lengths Cu···N/O 1.87 Å and Cu···N 1.99 Å in **Ia**, and the distances Cu···Cu 2.99 Å, Cu···N/O 1.92 Å, and Cu···S 2.24 Å in **Ib**.

The temperature magnetochemical studies made it possible to determine the dependence of the character of exchange interactions on the type of bridging atoms in dimeric complexes **Ia** and **Ib**.

The experimental curves $\mu_{\text{eff}}(T)$ for complexes **Ia** and **Ib** are presented in Figs. 2 and 3. Taking into account the dimeric structure of the complexes, we used the Bleaney–Bowers equation for the magnetic susceptibility of the dimer [20] in the theoretical modeling of the obtained dependences [20]

$$\chi_{(Cu-Cu)} = \frac{N_A \beta^2 g^2}{3k_B T} \left[1 + \frac{1}{3} \exp\left(\frac{-2J}{k_B T}\right) \right]^{-1} + N\alpha;$$

with allowance for intermolecular exchange interactions zJ'

$$\chi' = \frac{\chi_{(Cu-Cu)}}{(1-(2zJ'/N_A g^2 \beta^2)\chi_{(Cu-Cu)})};$$

and a possible admixture of the monomer *p* with the spin S = 1/2

$$\chi = \chi'(1-p) + \frac{N_A \beta^2 g^2 S(S+1)}{3k_B (T-\theta)} p$$

Here N_A , $N\alpha$, k_B , β , J, g, and θ are Avogadro's number, van Vleck paramagnetism, the Boltzmann constant, Bohr's magneton, the exchange interaction parameter, the Lande factor, and the Weiss constant, respectively.

The introduction of the azophenyl group into the azomethine fragment induces no basic changes in the magnetic behavior of the binuclear copper complexes with the NC₂H₅ intermetallic bridges: compound **Ia**, as similar chelates containing no N=NPh group [18, 19, 21], is characterized by the exchange interaction of the ferromagnetic type (Fig. 2).

The comparison of the characteristics of magnetic exchange in complex **Ia** and in the analogous chelate without the azo fragment [19, 21] indicates that the introduction of the N=NPh group increases the zJ parameter by 2 cm⁻¹.

Complex **Ib** is characterized by the ferromagnetic exchange (Fig. 3). An analog of this compound containing no azo group in the aldehyde fragment is diamagnetic [18, 19, 21].

Thus, the main structural factor determining the type of magnetic interactions in the binuclear copper complexes with azosalicylaldehyde anils is the nature of the bridging atoms.

It is known that the compounds containing the azo group are characterized by *cis–trans*-isomerization, which was observed under external effects [22–24]. Taking into account the crossover effect [25–27] and based on the ligand systems L² and the data presented, we can assume a possibility of the synthesis of other metal complexes (for Fe²⁺, Fe³⁺, Cr³⁺, Co²⁺) with both thermo- and photocontrolled magnetic properties.

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RUSSIAN JOURNAL OF COORDINATION CHEMISTRY Vol. 35 No. 7 2009

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