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Chemical and electrochemical synthesis, structure and magnetic properties of mono- and binuclear 3d-metal complexes of N-[2-[(hydroxyalkylimino)methyl]phenyl]-4-methylbenzenesulfonamides

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ABSTRACT

Complexes of Cu(II), Ni(II), Co(II) and Fe(II) ions with N-[2-[(hydroxyalkylimino)methyl]phenyl]-4-methylbenzenesulfonamides containing the $(CH_2)_n$ -spacer of a variable length (n =2-6) were synthesized by chemical and electrochemical methods. All the compounds were characterized by C, H and N elemental analysis, IR, EPR and X-ray absorption spectroscopy data. The dimeric

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structures of the copper complexes with $(CH_2)_n$ -spacers (n = 2,3) were determined by the magnetochemical method and by X-ray diffraction analysis for the copper complex with the $(CH_2)_3$ -spacer.

1. Introduction

Tridentate azomethine compounds derived from 2-hydroxybenzaldehyde, 2hydroxynaphthaldehyde, 2-N-tosylaminobenzaldehyde and alkylaminoalcohol have attracted great scientific interest as ligands for mono-, bi- and polynuclear metal complexes. Numerous binuclear copper complexes [1-8], nickel complexes [9], cubane complexes of nickel and copper [3, 10] with ligands containing a hydroxyalkylimine fragment, in which the deprotonated oxygen atoms of the hydroxyl groups act as bridging fragments, with the realization of M₂N₂O₄ coordination cores, were obtained and structurally characterized. Strong ferromagnetic exchange antiferromagnetic or interactions between the paramagnetic centers are observed in these complexes [1, 10].

In the literature there are also many examples of mononuclear intracomplex metal compounds with such azomethine ligands, in which the alcoholic groups of the hydroxyalkylimine fragments are involved neither in coordination with metals [11-18] nor in the realization of $M_2N_2O_4$ metallacycles.

Zinc complexes of azomethinic ligands containing hydroxyalkylamine groups possess photo- (PL) and electroluminescent (EL) properties and biological activities [11, 19-25]. In the literature, intracomplex metal compounds of such ligands are represented by complexes with the coordination cores MN_2O_2 and $M_2N_2O_4$, and with the length n = 2 and 3 for the (CH₂)_n-spacer.

Here we report the synthesis, structural studies and magnetic properties of metal chelates with azomethine compounds derived from 2-N-tosylaminobenzaldehyde and hydroxyalkylamines with the length of the aliphatic spacer from 2 to 6 methylene units, in which structures with coordination cores MN_4 , $M_2N_4O_2$ (M= Cu(II), Ni(II), Co(II) and Fe(II)) are realized.

2. Experimental

2.1. Materials required and general methods

All solvents, 2-amino-1-ethanol, 3-amino-1-propanol, 4-amino-1-butanol, 5amino-1-pentanol and 6-amino-1-hexanol were purchased from Alfa Aesar and used as received. 2-(N-Tosylamino)benzaldehyde has been synthesized using the reported procedure [26].

C, H and N elemental analyses were carried out on a Carlo Erba Instruments TCM 480 apparatus using sulfanilamide as a reference. The metal content was determined gravimetrically in the analytical laboratory of the Institute of Physical and Organic Chemistry (SFU, Rostov-on-Don, Russia). Melting points were measured on a Kofler table.

Infrared spectra were recorded using a Varian Excalibur-3100 FT-IR spectrophotometer for powders of compounds **1-3**.

ESR spectra were measured using a Bruker «ELEXSYS E-680X» spectrometer in the X-band at T = 293 K.

2.2. General procedure for the synthesis of the complexes of copper(II), nickel(II), cobalt(II) and iron(II) with N-[2-[(hydroxyalkylimino)methyl]phenyl]-4-methylbenzenesulfonamides (2).

Chemical synthesis (CS). A solution of 2 mmol of the corresponding amino alcohol (0.12 g of 2-amino-1-ethanol, 0.15 g of 3-amino-1-propanol, 0.18 g of 4-amino-1-butanol, 0.21 g of 5-amino-1-pentanol or 0.23 g of 6-amino-1-hexanol) in 10 ml of acetonitrile was added to a solution of 0.55 g (2 mmol) of 2-N-tosylaminobenzaldehyde in 30 ml of acetonitrile. The mixture was refluxed for 1 h. To the resulting solution was added a solution of 1 mmol of the corresponding metal acetate (0.20 g of copper(II) acetate monohydrate, 0.25 g of nickel(II) acetate tetrahydrate, 0.25 g of cobalt(II) acetate tetrahydrate or 0.34 iron(II) tetrafluoroborate hexahydrate) in 10 ml of methanol and the mixture was refluxed

for 1 h. After cooling, precipitates of the complexes were filtered off, washed with acetonitrile, methanol, hexane and dried in vacuo at 150 $^{\circ}$ C.

Electrochemical synthesis (ES) of complexes was performed by a standard method [27] using a potentiostat EG&GPAR/173 in an acetonitrile solution with a platinum electrode as the cathode and metal plates (Cu, Co, Ni) as the anode. The working solution (25 ml) contained 0.4 mmol of the corresponding H₂L compound (**1a-e**) described and characterized in [11] and 0.020 g of [Et₄N]ClO₄ as a conductive additive.

Electrolysis was carried out in a U-shaped glass tube with undivided anode and cathode spaces under a current of 15 mA and an initial voltage of 12 V for 1.5 h. The formed precipitates of the complexes were filtered off, washed with hot isopropanol and dried in vacuo.

2.2.1. Bis{N-[2-[(Z)-2-hydroxyethyliminomethyl]phenyl]-4methylbenzenesulfonamide]copper(II) (2a). Red-brown crystals, m.p. > 250 °C. Yield (CS): 0.64 g, 92 %, (ES): 0.66 g, 94%. Anal. Calc. for $C_{32}H_{34}CuN_4O_6S_2$: C, 55.04; H, 4.91; N, 8.02; Cu, 9.1%. Found: (CS) C, 55.16; H, 5.02; N, 8.17; Cu, 9.18%. (ES) C, 55.18; H, 5.10; N, 8.12; Cu, 9.15%. IR spectrum, selected bands, cm⁻¹: 3341 v(OH), 1626 v(CH=N), 1288 v_{as}(SO₂), 1133 v_s(SO₂). μ_{eff} =1.95 μ_B (298 K); 1.85 μ_B (77 K)

2.2.2. $Bis\{N-[2-[(Z)-2-hydroxyethyliminomethyl]phenyl]-4$ methylbenzenesulfonamide $\}dicopper(II)$ (**3a**). Green crystals, m.p. decomposition > 280 °C. Yield (CS): 0.60 g, 79 %. Anal. Calc. for C₃₂H₃₂Cu₂N₄O₆S₂: C, 50.58; H, 4.24; N, 7.37; Cu, 16.73%. Found: (CS) C, 50.64; H, 4.38; N, 7.50; Cu, 16.84%. IR spectrum, selected bands, cm⁻¹: 1628 v(CH=N), 1296 v_{as}(SO₂), 1139 v_s(SO₂). $\mu_{3\phi\phi}$ =1.26 μ_B (294 K); 0.41 μ_B (77.4 K) 2J = -334 cm⁻¹, g = 2.08, f = 0.08 2.2.3. $Bis\{N-[2-[(Z)-3-hydroxypropyliminomethyl]phenyl]-4$ methylbenzenesulfonamide $\}copper(II)$ (**2b**). Red-brown crystals, m.p. > 300 °C. Yield (CS): 0.63 g, 88 %, (ES): 0.65 g, 90%. Anal. Calc. for C₃₄H₃₈CuN₄O₆S₂: C, 52.22; H, 5.27; N, 7.71; Cu, 8.75%. Found: (CS) C, 52.31; H, 5.30; N, 7.81; Cu, 8.80%. (ES) C, 52.28; H, 5.32; N, 7.79; Cu, 8.77%. IR spectrum, selected bands, cm⁻¹: 3400 v(OH), 1627 v(CH=N), 1281 v_{as}(SO₂), 1138 v_s(SO₂). μ_{eff} =2.20 μ_{B} (293 K)

2.2.4. Bis{N-[2-[(Z)-3-hydroxypropyliminomethyl]phenyl]-4-

methylbenzenesulfonamide]dicopper(II) (**3b**). Dark green crystals, m.p. > 300 °C. Yield (CS): 0.65 g, 82 %. Anal. Calc. for $C_{34}H_{36}Cu_2N_4O_6S_2$: C, 51.83; H, 4.61; N, 7.11; Cu, 16.13%. Found: (CS) C, 51.79; H, 6.71; N, 7.18; Cu, 16.20%. IR spectrum, selected bands, cm⁻¹: 1628 v(CH=N), 1282 v_{as}(SO₂), 1139 v_s(SO₂). μ_{eff} – diamagnetic (293 K).

2.2.5. $Bis\{N-[2-[(Z)-3-hydroxypropyliminomethyl]phenyl]-4-methylbenzenesulfonamide\}nickel(II) ($ **2b Ni** $). Light green powder, m.p. > 300 °C. Yield (CS): 0.60 g ,83 %, (ES): 0.63 g, 87%. Anal. Calc. for <math>C_{34}H_{38}NiN_4O_6S_2$: C, 56.60; H, 5.31; N, 7.77; Ni, 8.13%. Found: (CS) C, 56.64; H, 5.34; N, 7.80; Ni, 8.15%. (ES) C, 56.58; H, 5.28; N, 7.75; Ni, 8.17%. IR spectrum, selected bands, cm⁻¹: 3066 v(OH), 1622 v(CH=N), 1274 v_{as}(SO₂), 1126 v_s(SO₂). $\mu_{eff} = 3.42 \mu_B$ (298 K)

2.2.6. $Bis\{N-[2-[(Z)-3-hydroxypropyliminomethyl]phenyl]-4-methylbenzenesulfonamide\}cobalt(II)$ (**2b** Co). Red-brown powder, m.p.= 290-293 °C. Yield (CS): 0.56 g, 78 %, (ES): 0.60 g, 83%. Anal. Calc. for C₃₄H₃₈CoN₄O₆S₂: C, 56.58; H, 5.31; N, 7.76; Co, 8.17%. Found: (CS) C, 56.61; H, 5.37; N, 7.80; Co, 8.19%. (ES) C, 56.63; H, 5.35; N, 7.81; Co, 8.21%. IR spectrum, selected bands, cm⁻¹: 3343 v(OH), 1616 v(CH=N), 1288 v_{as}(SO₂), 1129 v_s(SO₂). μ_{eff} =4.66 μ_{B} (298 K)

2.2.7. Bis{N-[2-[(Z)-3-hydroxypropyliminomethyl]phenyl]-4methylbenzenesulfonamide}iron(II) (**2b Fe**). Orange powder, m.p. > 270 °C. Yield (CS): 0.54 g, 75 %. Anal. Calc. for C₃₄H₃FeN₄O₆S₂: C, 56.82; H, 5.33; N, 7.80; Fe, 7.77%. Found: (CS) C, 56.91; H, 5.40; N, 7.78; Fe, 7.82%. IR spectrum, selected bands, cm⁻¹: 3062 v(OH), 1613 v(CH=N), 1298 v_{as}(SO₂), 1124 v_s(SO₂). μ_{eff} =5.38 μ_{B} (298 K)

2.2.8. Bis{N-[2-[(Z)-4-hydroxybutyliminomethyl]penyl]-4methylbenzenesulfonamide}copper(II) (2c). Red-brown crystals, m.p.= 267-268

°C. Yield (CS) 0.67 g, 90 %, (ES) 0.71 g, 95%. Anal. Calc. for $C_{36}H_{42}CuN_4O_6S_2$: C, 57.31; H, 5.61; N, 7.43; Cu, 8.42%. Found: (CS) C, 57.37; H, 5.72; N, 7.51; Cu, 8.52%. (ES) C, 57.18; H, 5.59; N, 7.38; Cu, 8.57%. IR spectrum, selected bands, cm⁻¹: 3340 v(OH), 1630 v(CH=N), 1287 v_{as}(SO₂), 1133 v_s(SO₂). $\mu_{eff} = 1.87 \mu_B$ (296.5 K)

2.2.9. $Bis\{N-[2-[(Z)-5-hydroxypentyliminomethyl]phenyl]-4-methylbenzenesulfonamide\}copper(II)$ (2d). Red-brown crystals, m.p.= 269-270 °C. Yield (CS): 0.73 g, 93 %, (ES): 0.74 g, 95%. Anal. Calc. for $C_{38}H_{46}CuN_4O_6S_2$: C, 58.33; H, 5.93; N, 7.16; Cu, 8.12%. Found: (CS) C, 58.45; H, 6.00; N, 7.27; Cu, 8.28%. (ES) C, 58.48; H, 6.10; N, 7.14; Cu, 8.24%. IR spectrum, selected bands, cm⁻¹: 3350 v(OH), 1626 v(CH=N), 1289 v_{as}(SO₂), 1133 v_s(SO₂). $\mu_{eff} = 1.89 \ \mu_{B}$ (296.5 K)

2.2.10. $Bis\{N-[2-[(Z)-6-hydroxyhexyliminomethyl]phenyl]-4-methylbenzenesulfonamide\}copper(II)$ (2e). Red-brown crystals, m.p.= 265-266 °C. Yield (CS) 0.70 g, 87 %, (ES) 0.72 g, 89%. Anal. Calc. for $C_{40}H_{50}CuN_4O_6S_2$: C, 59.27; H, 6.22; N, 6.91; Cu, 7.84%. Found: (CS) C, 59.40; H, 6.35; N, 7.10; Cu, 7.95%. (ES) C, 59.35; H, 6.18; N, 7.14; Cu, 7.68%. IR spectrum, selected bands, cm⁻¹: 3344 v(OH), 1626 v(CH=N), 1288 v_{as}(SO₂), 1133 v_s(SO₂). $\mu_{eff} = 1.88 \mu_B$ (296.5 K)

2.3. X-ray absorption spectroscopy

The Fe, Co, Ni and Cu *K*-edge EXAFS spectra for complexes **2a-e**, **2b Ni**, **2b Co**, **2b Fe** and **3a,b** were recorded at the "Structural Materials Science" beamline of the Kurchatov Synchrotron Radiation Source (Moscow, Russia) [28] with the storage ring operating at electron energy of 2.5 GeV and with a current of 100-120 mA. A Si(111) channel-cut monochromator was used for the energy selection. All data were measured in the transmission mode. Sample thicknesses corresponded to an absorption jump $\Delta\mu x = 0.5-1.0$.

EXAFS data ($\chi_{exp}(k)$) were analyzed using the IFEFFIT data analysis package [29]. EXAFS data reduction used standard procedures for the pre-edge

subtraction and spline background removal. The radial pair distribution functions around the metal ions in the complexes were obtained from the Fourier transformation (FT) of the k³-weighted absorption function $\chi_{exp}(k)$ range of photoelectron wavenumbers k = 2.4-13.0 Å⁻¹. Structural parameters, including interatomic distances (R_i), coordination numbers (N_i) and distance RMS deviations due to the thermal motion and disorder-induced static deviations of atomic positions, also known as Debye–Waller factors (σ^2), were found by non-linear fitting of the theoretical spectra against the experimental ones.

$$\chi(k) = S_0^2 \sum_{i=1}^n \frac{N_i}{R_i^2} \frac{F_i(k)}{k} e^{-\frac{2R_i}{\lambda(k)}} e^{-2\sigma_i^2 k^2} \sin(2kR_i + \Psi_i(k)), \quad (1)$$

The experimental data were simulated using a theoretical photoelectron mean-free-path (λ), photoelectron backscattering amplitude $F_i(k)$ and phase functions (Eq. 1), calculated using the FEFF7 program [30]. The amplitude reduction factor due to extrinsic losses S_0^2 and the edge energy shift E_0 were calibrated by fitting EXAFS data for spectra of the reference compounds with known crystal structures. The amplitude reduction factors S_0^2 were found to be equal to 0.9 in all cases.

The accuracy of the fits was estimated by the standard mean-square deviation criterion (Eq. 2) (Q-factor),

$$Q^{2} = \frac{\sum_{i=1}^{m} w(k_{i}) \left[k_{i} \chi_{\exp}(k_{i}) - k_{i} \chi_{ih}(k_{i}) \right]^{2}}{\sum_{i=1}^{m} w(k_{i}) \left[k_{i} \chi_{\exp}(k_{i}) \right]^{2}}$$
(2)

where $w(k_i)$ is a weighting function, *m* is the number of experimental points.

2.4. X-ray crystallography analysis of the copper complex 3b

The X-ray data sets for complex **3b** were collected using a Bruker APEX II diffractometer equipped with a CCD camera and a graphite-monochromated MoK_{α} radiation source ($\lambda = 0.71073$ Å) [31]. Semi-empirical absorption corrections were applied [32]. The structure was solved by the direct method and refined by full-matrix least squares against F^2 with anisotropic thermal parameters for all non-

hydrogen atoms. The hydrogen atoms of the carbon-containing ligands were set in geometrical positions and refined using the riding model. All calculations were carried out with SHELX97 program package [33]. The crystallographic parameters for complex **3b** at T = 296(2) K were as follows: $C_{34}H_{36}Cu_2N_4O_6S_2$, fw = 787.87, dark green, parallelogram, crystal size 0.10 x 0.02 x 0.02 mm, monoclinic system, space group $P2_1/n$, a = 9.270(8) Å, b = 13.434(12) Å, c = 14.331(13) Å, $\beta = 101.86(2)^\circ$, V = 1747(3) Å³, Z = 2, $\rho_{calc} = 1.498$ g cm⁻³, $\mu = 1.387$ mm⁻¹, 10676 measured reflections, 1774 reflections with $I > 2.0\sigma(I)$, $R_{int} = 0.104$, GooF = 0.929, $R_I (I > 2\sigma(I)) = 0.061$, $wR_2 (I > 2\sigma(I)) = 0.106$, $R_I (all data) = 0.165$, $wR_2 (all data) = 0.138$, $T_{min/max} = 0.874/0.973$, residual electron density $\Delta \rho_{max}/\Delta \rho_{min} = -0.373/0.390$ e Å⁻³.

Crystallographic data for **3b** have been deposited with the Cambridge Crystallographic Data Center, CCDC 1848471. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <u>www.ccdc.cam.ac.uk</u>).

3. Results and discussion

3.1. Synthesis and spectroscopic properties of the complexes

The complex compounds of copper, nickel, cobalt and iron were obtained chemically (by the direct reaction of 2-N-tosylaminobenzaldehyde, the respective amine and metal acetate hydrate in acetonitrile in a molar ratio of 2:2:1) and electrochemically (during the anodic dissolution of the metals in an acetonitrile ligand (**1a-e**) solution) (Scheme 1).



Scheme 1. The synthesis of complexes 2a-e and 3a,b.

In all cases, for ligands with a length of aliphatic spacer from 2 to 6 methylene units, intracomplex compounds **2a-e** of the ML₂ composition were isolated, according to elemental analysis data. In the case when n = 2 and 3, along with the copper complexes **2** of a red-brown color, green color complexes of the (ML)₂ composition of type **3** were obtained. In the IR spectra of complexes **2a-e**, broad vOH absorption bands in the region 3062-3350 cm⁻¹ were preserved. The absorption bands vCH=N in the 1613-1630 cm⁻¹ region, as well as absorption

bands at 1274-1290 cm⁻¹ ($v_{as}SO_2$) and 1122-1135 cm⁻¹ (v_sSO_2) in complexes **2a-e** shift to lower frequencies in comparison to the ligands **1a-e**.

Such spectral behavior indicates the formation of chelate structures 2a-e, in which the alcoholic groups are not involved in coordination with the metal center, regardless of the $(CH_2)_n$ -spacer length.

The complexes **2a-e** are identical, according to elemental analysis and IR spectral data, independent of the synthetic method (CS or ES). However, the ES method is carried out under milder conditions with 10-15% higher yields of the complexes compared to the CS method.

Similar changes are observed in the IR spectra of the green color complexes **3a,b**, except for the disappearance of the vOH absorption bands in the region 3305-3361 cm⁻¹.

The copper complexes **2a-e** are paramagnetic. The values of μ_{eff} in the range 1.87-2.20 μ_B (298 K) correspond to a spin value, taking into account the contribution of the orbital component, and they do not change with decreasing temperature. This evidences their mononuclear structure, which confirms the analysis of the EPR spectra.

3.2. The electron paramagnetic resonance of complexes

Figure 1 shows the EPR spectrum of compound **2a** in the polycrystalline state. The spectrum is described by the spin Hamiltonian (SH) of rhombic symmetry with the Zeeman interaction (Eq. 3):

$$\hat{H} = g_z \beta H_z \hat{S}_z + g_x \beta H_x \hat{S}_x + g_y \beta H_y \hat{S}_y$$
(3),

where g_z , g_x , g_y are, respectively, the *z*, *x*, *y* components of the monomer *g*-tensor, S_z , S_x , S_y are projections of the monomer spin operator onto the coordinate axes, S=1/2.

The parameters of the complex were found by the best approximation method between the experimental and theoretical spectra by minimizing the error functional (Eq. 4):

$$F = \sum_{i} (Y_{i}^{T} - Y_{i}^{E})^{2} / N$$
(4),

where Y_i^E is the array of experimental values of the EPR signal intensities with a constant step of the magnetic field H, Y_i^T are theoretical values for the same values of the field H, and N is the number of points. The theoretical spectra were constructed by the method described in [34]. As the line shape function, the sum of the Lorentz and Gauss functions was used [35].

During the minimization, the g-factors, widths and shapes of the lines were varied. The obtained SH parameters are given in the caption to Fig. 1.



Fig. 1. The EPR spectrum of 2a, powder, T = 293 K. 1 – experiment (solid line), 2 - simulation (circles) with parameters of SG $g_z = 2.264$; $g_x = 2.126$; $g_y = 2.023$.

The EPR spectrum of compound **3a** has the form characteristic for a complex with a total spin S = 1, when the splitting in a zero field is close to the frequency hv and this spectrum is superimposed on the spectrum of a monomeric impurity in the region of ~300 mT (Fig. 2). The presence of a monomeric impurity is confirmed by magnetic susceptibility data: at low temperatures the magnetic

moment of the compound does not decrease to zero, but remains equal to 0.41 Bohr magnetons. The SH describing the dimer spectrum has the form (Eq. 5):

$$\hat{H} = g_x \beta S_x H_x + g_y S_y H_y + g_z \beta H_z S_z + D \cdot (S_z^2 - \frac{1}{3}(S+1) \cdot S) + E \cdot (S_x^2 - S_y^2)$$
(5),

where $\hat{S} = \hat{S}_1 + \hat{S}_2$ is the total spin operator of the dimer S = 1, D and E are the fine structure tensor components. The spectrum of the monomeric impurity is described by the SH (Eq. 3).

Numerical calculations of the resonant fields of the spin Hamiltonian Eq. (3) and Eq. (5) for construction of the theoretical spectrum were carried out with the help of the Belford method [36].



Fig. 2. The EPR spectra of 3a, powder, T = 293 K. 1 – experiment (solid line), 2 - simulation (circles) with parameters of SG (1) and (2): $C_{\text{dime r}} = 75\% g_z = 2.310$; $g_x = 2.041$; $g_y = 2.031$; $D = 0.3560 \text{ cm}^{-1}$; $E = 0.0225 \text{ cm}^{-1}$. $C_{\text{monomer}} = 25\%$. $g_z = 2.310$; $g_x = 2.041$; $g_y = 2.031$.

3.3 Magnetic properties of the complexes

The temperature dependences of μ_{eff} of the copper complexes are shown in Fig. 3. Such a temperature dependence of μ_{eff} (T) for 2c, 2d and 2e is characteristic

for mononuclear complexes. The nickel, cobalt and iron complexes **2b** are paramagnetic. The values of μ_{eff} are 3.42 μ_B (298 K) (**2b** Ni), 4.66 μ_B (298 K) (**2b** Co), 5.38 μ_B (298 K) (**2b** Fe) and these do not change with decreasing temperature, which indicates their mononuclear structure.



Fig. 3. Temperature dependence of μ_{eff} for the copper complexes 2c (a), 2d (b), 2e (c) and 3a (d).

The value $\mu_{eff} = 1.20 \ \mu_B \ (294 \ K)$ of the copper complex **3a** (n = 2) decreases with decreasing temperature to $\mu_{eff} = 0.41 \ \mu_B \ (77.4 \ K)$ and indicates its dimeric structure, in which an antiferromagnetic exchange interaction is observed between the copper atoms in the dimeric molecule, with parameters $2J = -334 \ cm^{-1}$, g =

2.08, f = 0.08. Such a temperature dependence of μ_{eff} (T) (Fig. 3d) is characteristic for binuclear complexes with a strong antiferromagnetic exchange interaction between the spins of the paramagnetic centers. The value of the exchange interaction parameter J/k is -483 (± 6) K.

The copper complex 3b (n = 3) is diamagnetic already at room temperature, which indicates a strong antiferromagnetic exchange interaction between the copper atoms in the dimeric molecule.

3.4. The X-ray absorption spectroscopy

The local atomic structures of all the complexes **2a-e**, **2b Ni**, **2b Co**, **2b Fe**, and **Cu 3a,b** were determined by X-ray absorption spectroscopy from the analysis of the Fe, Co, Ni, and Cu K-edges XANES and EXAFS spectra.

Figures 4a,b show the Cu K-edges XANES data and the MFT EXAFS $\chi(k)k^3$ for the copper complexes **2a-e**. Cu K-edges XANES spectra for the copper complexes **2a-e**, except **3a-Cu** and **3b-Cu**, have a shape typical for a tetrahedrally coordinated copper ion. This is particularly evident from the pre-edge structure form, which is represented by the intense peak A. The nature of the pre-edge peak A is due to 4p-3d hybridization of the copper AO in the low-symmetry coordination polyhedron. With additional coordination or with the environment symmetry of the absorbing ion without an inversion center (octahedron or plane), such hybridization does not occur and the intensity of peak A is determined only by low-intensity quadrupole electronic transitions. Such an intensity decrease of the peak A is observed in the XANES spectra for **3a-Cu** and **3b-Cu**. In addition, a peak B at the absorption edge is observed, characteristic of a plane-square environment and is associated with the manifestation of a vacant $4p_z$ AO perpendicular to the coordination plane.



Fig. 4. (a) Cu *K*-edges XANES spectra (the insets show the pre-edge structure) and (b) MFT EXAFS $\chi(k)k^3$ for the copper complexes **2a-e**, **3a-Cu** and **3b-Cu** (experiment – solid line, best fit theory – empty circles).

MFT EXAFS $\chi(k)k^3$ for copper complexes **2a-e** consist of a main peak at 1.5-

1.6 Å, corresponding to the first coordination sphere (CS), and further peaks with small amplitudes, corresponding to more distant CS's (Fig. 4b). However, MFT 3a Cu and 3b Cu evidently contain peaks at 2.6-2.7 Å with significantly larger amplitude compared to other MFT's. These peaks may correspond to the manifestation of a CS containing the copper ions with a higher scattering amplitude as compared to the lighter atoms of the ligands. To prove that these CS's contain copper ions, EXAFS wavelet analysis was used [37-40]. Light atoms (C, O, N) most effectively scatter photoelectrons with small wave vectors k (the scattering maximum is at k = 4-6 Å⁻¹), while for heavier atoms the scattering maximum shifts toward larger k. The EXAFS wavelet transform map allows the scattering by atoms in both spatial r-coordinates as well as in the wave vector k coordinates, to be observed, which makes it possible to isolate the contributions to scattering from atoms of different species that are at the same distance from the absorbing center. The WT map of copper foil (Fig. 5a) shows that the copper atoms most effectively scatter photoelectrons with $k = 8 \text{ Å}^{-1}$. The distances to the first and the next CS can also be determined from the WT map (from the y-axis without accounting for the phase shift). The EXAFS WT maps of complexes 3a Cu and 3b Cu, shown in Fig. 5b and c, reveal the existence of a region at small r and k coordinates corresponding to the first peak in the MFT of light scatterers O/N. Each map at high values of k and r has a region corresponding to scattering at the copper atoms. Thus, it can be stated that the MFT peak at r = 2.70-2.77 Å (Fig. 4b) for complexes **3a Cu** and **3b Cu** unambiguously corresponds to the Cu...Cu distance, i.e., these molecules have a dimeric structure. The EXAFS WT maps of complexes 3a Cu and 3b Cu also show additional regions with k close to the scattering at light atoms and with r coinciding with the Cu...Cu distance, which precludes the isolation of this scattering from the MFT's of the respective complexes. Based on the structure of the ligands, the appearance of these WT regions can be explained by scattering on the sulfur and oxygen atoms of the tosylamine moiety.



Fig. 5. (a) EXAFS WT map of copper foil in r, k- coordinates, (b) EXAFS WT map of complex 3b Cu, (c) EXAFS WT map of complex 3a Cu.

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The quantitative parameters of the CS's in the **2a-e**, **3a Cu** and **3b Cu** complexes are obtained from the approximation of the experimental EXAFS by the theoretically calculated curve of the optimal model of the nearest atomic environment of the copper ions. The obtained values of the CS characteristics are given in Table 1.

Table 1. Local structure parameters of the complexes **2a-e**, **3a Cu** and **3b Cu** (R is the interatomic distance, σ^2 is the Debye-Waller factor, Q is the fit quality function).

Sample	CN	R, Å	$\sigma^2, Å^2$	CS	Q [*] , %
2a	4	1.97	0.0031	Ν	0.7
3a Cu	2	1.93	0.0035	O/N	3.2
	2	1.96	0.0035	O/N	
	1	3.03	0.0042	Cu	
3b Cu	2	1.95	0.0037	O/N	2.6
	2	1.95	0.0037	O/N	
	1	3.03	0.0067	Cu	
2c	4	1.97	0.0030	Ν	0.8
2d	4	1.96	0.0035	Ν	0.8
2e	4	1.97	0.0025	Ν	1.0
2b Co	4	2.02	0.0044	Ν	0.4
2b Ni	4	2.00	0.0033	Ν	2.9
2b Fe	4	2.05	0.0052	Ν	2.8

Consistent data were obtained for all compounds, which made it possible to relate the structural data to the magnetic and spectral characteristics of the copper complexes.

Figures 6a and b show the XANES spectra of the Fe, Ni and Co *K*-edges and the respective MFT EXAFS $\chi(k)k^3$ for the complexes **2b** Co, **2b** Ni and **2b** Fe.



Fig. 6. (a)- XANES *K*-edges (the insets show the pre-edge structure) and (b)-MFT EXAFS $\chi(k)k^3$ (experiment – solid line, theory – empty circles) of complexes **2b Co, 2b Ni** and **2b Fe**.

The XANES analysis showed that in all the **2b** Ni, Co and Fe complexes, the metal ion is in a tetrahedral ligand environment with the coordination core MN_4 . The quantitative parameters of the CS for the **2b** Ni, Co and Fe complexes obtained from fitting the experimental EXAFS to the theoretically calculated curve for the optimal model of the nearest atomic environment of metal ions are given in Table 1. The average bond lengths of the complexes depend on the ionic radius of the metal and varied from 2.00-2.02 Å for Ni and Co, up to 2.05 Å for Fe. Thus, regardless of the length of the alkyl substituent, the complexes have an ML_2 composition, in which the hydroxy group of the alcoholic fragment is not involved

in coordination with the metal.

3.5. The X-ray diffraction

The compound **3b** (Fig. 7) crystallized in the $P2_1/n$ space group as a centrosymmetric binuclear moiety, the inversion center is located at the center of the rhombic fragment Cu₂O₂ (Cu1...Cu1A 3.012 Å; selected bond lengths and bond angles are summarized in the Table 2; Fig. 7). Each Schiff base ligand is coordinated in a tridentate manner via amino- (N1) and imino-N-atoms (N2) and also alkoxy-O-atoms (O3) and in a bridging mode (Cu1-O3-Cu1A). The geometry of the copper atom environment (CuN_2O_2) corresponds to distorted square-planar (the deviation of the Cu1 atom from the N1N2O3O3A plane is 0.036(2) Å). The angle between planes of the aromatic rings C1–C6 and C8–C13 is 61.9°, that is substantially reduced in comparison with the analogous angle in the free molecule 2-tosylaminobenzaldehyde (81.85(6)°) [41, 42]. Both S–O bonds have close lengths. The Cu1...O2 distance 2.881(5) Å is non-bonding. It is worth noting that the Cu1–O3 bond is unusually short. According to analysis of the CCDC by the Mogul geometry check tool [43], only 15 earlier described copper complexes contain Cu–O bonds that fall in the range 1.891-1.927 Å. Other geometrical parameters of the organic ligands in most cases are close to common values [44].



Fig. 7. Molecular structure of the complex **3b** (atoms with character A in the atom labels are at (x-0.5, -y+0.5, z-0.5); carbon-bonded hydrogen atoms are omitted for clarity.

	-	-	-
Bond	<i>d</i> , Å	Bond	d, Å
Cu1–N1	1.935(4)	N1-S2	1.599(4)
Cu1–N2	1.953(5)	N2-C14	1.273(7)
Cu1–O3	1.895(3)	N2-C15	1.475(8)
Cu1–O3A	1.926(4)	C15–C16	1.344(9)
C1–C2	1.324(8)	C16–C17	1.372(9)
C2–C3	1.384(10)	O3–C17	1.404(6)
C3–C4	1.312(11)	O1–S2	1.428(4)
N1–C8	1.424(6)	O2–S2	1.430(4)
Angle	ω, deg.	Angle	ω, deg.
N1-Cu1-N2	92.2(2)	O3–Cu1–N2	95.0(2)
O3–Cu1–N1	168.8(2)	O3A–Cu1–N2	163.0(2)
O3A-Cu1-N1	99.1(2)	O3–Cu1–O3A	76.0(2)

Table 2. Selected bond lengths d (Å) and bond angles ω (deg.) for **3b**.

It is known that molecules of complexes structurally related to **3b** tend to dimerize by the formation of axial Cu–O bonds with adjacent molecules in the crystal [45]. However, the non-interacting O2 atom position of the SO₂ group in one fragment of the complex molecule as well as the deviation (36.6°) of the closely located phenyl fragment C8–C13 from the plane Cu1N1N2O3O3A in another fragment creates sterical hindrance and prevents such bond formation. As a result, only short C–H…O contacts (C14-H…O1A 3.433 Å, H-O1A 2.55 Å, angle C14-H…O1A 158.5°, where atom with character A in the atom label is at (*x*-0.5, -*y*+0.5, *z*-0.5)) could be observed.

Conclusion

Thus, based on the set of experimental data of IR, EXAFS, XANES, EPR spectroscopy, magnetochemistry and XRD, it was established that N-[2-

[(hydroxyalkylimino)methyl]phenyl]-4-methylbenzenesulfonamides with the $(CH_2)_n$ -spacer (n = 2-6) form mononuclear Cu(II), Ni(II), Co(II) and Fe(II) complexes, regardless of the spacer length, in which the alcoholic group of the hydroxyalkylamine fragment does not participate in coordination with the metal. For copper complexes (n = 2 and 3), when the length of the hydroxyalkyl moiety is allowed to be realized by additional five- or six-membered metallacycles, dimeric structures for the copper complexes with bridging oxygen atoms of alcoholic groups are formed. In these copper complexes, a strong antiferromagnetic exchange interaction is observed between the copper atoms in the dimeric molecule. The dimeric structure of bis{N-[2-[(2hydroxypropylimino)methyl]phenyl]-4-methylbenzenesulfonamide}dicopper(II) was determined by the X-ray diffraction method.

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Fig. 1. The EPR spectrum of 2a, powder, T=293 K. 1 – experiment (solid line), 2 - simulation (circles) with parameters of SG $g_z = 2.264$; $g_x=2.126$; $g_y = 2.023$.

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Fig. 2. The EPR spectrum of **3a**, powder, T=293 K. 1 – experiment (solid line), 2 - simulation (circles) with parameters of SG (1) and (2): C_{dimer} =75% g_z = 2.310; g_x =2.041; g_y =2.031; D = 0.3560 cm⁻¹; E = 0.0225 cm⁻¹. $C_{monomer}$ = 25%. g_z = 2.310; g_x =2.041; g_y =2.031.

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Fig. 3. Temperature dependence of μ_{eff} of copper complexes 2c (a), 2d (b), 2e (c), 3a (d).



Fig. 4. (a)- Cu *K*-edges XANES spectra (the insets show the pre-edge structure) and (b) - MFT EXAFS $\chi(k)k^3$ for the copper complexes **2a-e**, **3a-Cu** and **3b-Cu** (experiment – solid line, best fit theory – empty circles).



Fig. 5. (a)- EXAFS WT map of copper foil in r, k- coordinates, (b)- EXAFS WT map of complex **3b Cu**, (c)- EXAFS WT map of complex **3a Cu**.

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Fig. 6. (a)- XANES *K*-edges (the insets show the pre-edge structure) and (b)-MFT EXAFS $\chi(k)k^3$ (experiment – solid line, theory – empty circles) of complexes **2b Co, 2b Ni,** and **2b Fe**.



Fig. 7. Molecular structure of the complex **3b** (atoms with character A in the atom labels are at (x-0.5, -y+0.5, z-0.5); carbon-bonded hydrogen atoms are omitted for clarity.











Complexes of Cu(II), Ni(II), Co(II) and Fe(II) ions with N-[2-[(hydroxyalkylimino)methyl]phenyl]-4-methylbenzenesulfonamides were synthesized.

The dimeric structures of the copper complexes with $(CH_2)_n$ -spacers (n = 2 and 3) were determined by the Accepting magnetochemical method, X-ray absorption spectroscopy and X-ray diffraction.

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