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X-Ray Diffraction, Magnetochemical, and Quantum Chemical Study of the Structure and Properties of Binuclear Copper(II) Complexes

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Abstract—The binuclear chelates of copper(II) based on the tridentate azomethine ligands were synthesized and characterized by elemental analysis, IR, ^{1}H NMR spectroscopy, X-ray absorption spectroscopy (XANES and EXAFS), and magnetic measurements . The quantum-chemical study of the structure and calculation of magnetic properties of the obtained metal-chelates was performed using the density functional theory with the broken symmetry technique. The performed magnetochemical studies in the temperature range 2–300 K suggest the existence of antiferromagnetic exchange interaction in all obtained complexes. The parameters of the exchange interaction $-2J > 260$ cm^{-1} were determined experimentally for all compounds, the experimental data is in a good agreement with the results of quantum-chemical calculations.

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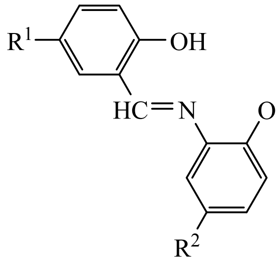
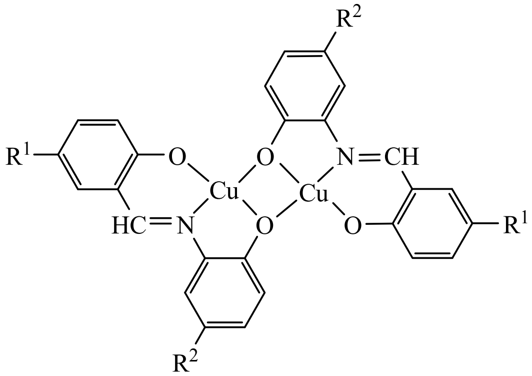
Systematic studies on the synthesis, structure, and magnetic properties of bi- and polynuclear transition metal coordination compounds with azomethine ligands have contributed significantly to a rapidly developing area of modern chemistry, the molecular design of magnetic materials [1–4]. We have previously described the binuclear copper(II) complexes with tridentate azomethine ligands exhibiting both ferromagnetic and antiferromagnetic exchange interactions [5–11]. In the extension of these studies, we synthesized and characterized ligand systems **I** and binuclear chelate complexes **II** with oxygen bridges.



I



II

$R^1 = Br, R^2 = H$ (**a**); $R^1 = Br, R^2 = NO_2$ (**b**); $R^1 = -N{=}NC_6H_4$-*p*-Me, $R^2 = H$ (**c**).

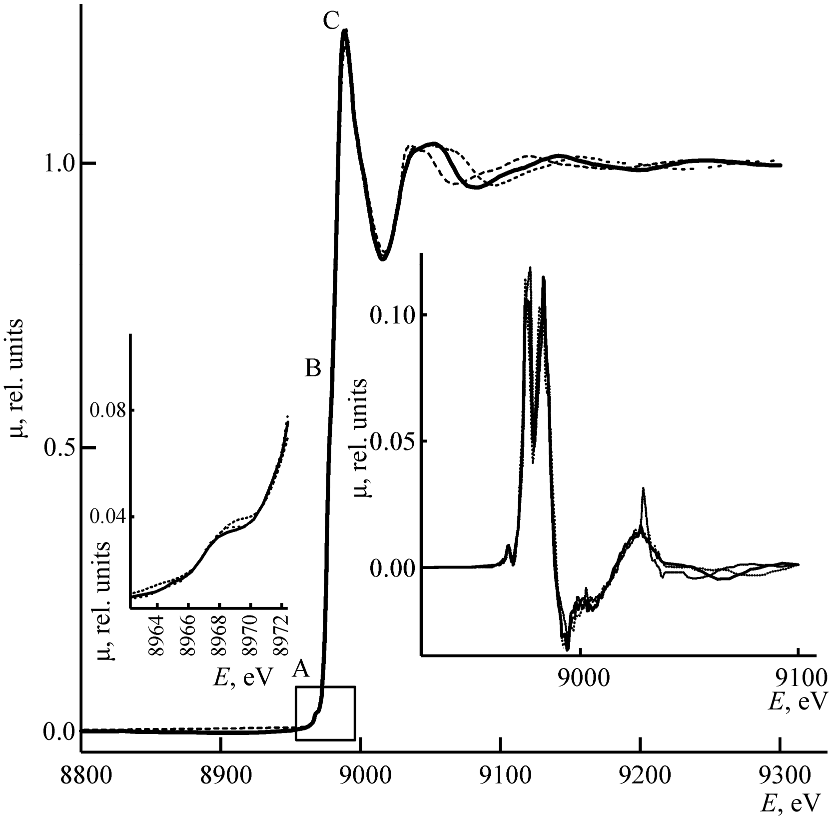


Fig. 1. XANES CuK-edge X-ray absorption spectra of metal complexes of copper. (solid line) **IIa**, (points) **IIb**, (dashed line) **IIc**. The inserts show the pre-edge area (A) and the first derivatives of the Cu*K*-absorption edges.

Elemental analysis of the complexes corresponds to the ratio M:L = 1:1, which is consistent with the expected structure of the binuclear compounds **II**. In the IR spectra of complexes **II** the stretching OH vibrations in the region 3450 cm^{-1} disappear and the frequency of the C=N stretching vibrations decreases (near 1600 cm^{-1}) by 10–15 cm^{-1}compared with the spectra of ligands **I**.

The dimeric structure and type of the ligand environment is revealed by the analysis of the Cu*K* edges of X-ray absorption of complexes **II**.

Figure 1 shows the normalized XANES (X-ray absorption near edge structure) at the Cu*K* edges in the X-ray absorption spectra of compounds **IIa**, **IIb**, and **IIc**. The XANES of the metal complexes **IIa**, **IIb**, and **IIc** are similar. The pre-edge peaks in the spectra of these compounds have the same energy position in the region of 8968 eV and similar amplitude. The appearance of the pre-edge peaks is associated with the electron transitions $1s \rightarrow 3d$ and is characteristic only of the compounds with low-symmetry coordination site (the absence of an inversion center), with the possibility of *p*–*d* mixing of the metal atomic orbitals. In addition, all the Cu*K* edges have a pronounced shoulder B, which is well seen in the first derivatives of the edges. The first derivatives of the Cu*K* edges of the complexes have two distinct peaks split by 7.5 eV. These features are usually typical of the XANES for the tetrahedral environment of the absorbing atom, in this case copper, in the metal complex **IIa**, **IIb**, and **IIc**.

Quantitative characteristics of the atomic local structures of the copper metal complexes **IIa**, **IIb**, and **IIc** were obtained by the analysis of EXAFS (Extended X-ray absorption fine structure) of the Cu*K* edges in the X-ray absorption spectra of these compounds. Figure 2 shows the Fourier transforms modules (FTM) of the EXAFS in the Cu*K*-absorption edges of copper complexes **IIa**, **IIb**, and **IIc**. As can be seen from Figure 2, the EXAFS MTS consist of the main peak at low r = 1.54 Å, which uniquely corresponds to the scattering at the nearest light coordination spheres consisting of the O and N atoms, and the peak at r = 2.46–2.50 Å, which can be candidate for the

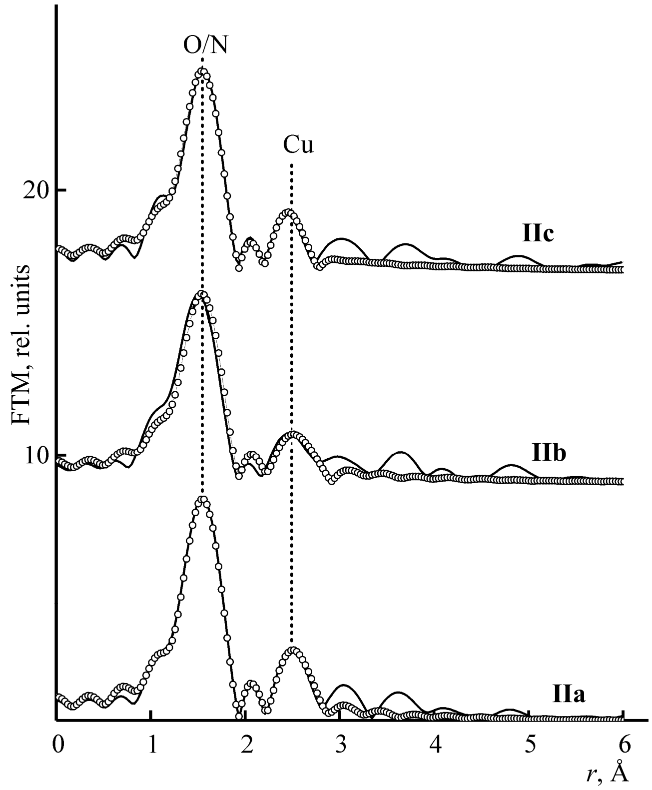


Fig. 2. Modules of the Fourier transformed EXAFS Cu*K*-edges of the X-ray absorption spectra of the metallocomplexes **IIa**–**IIc**. (Solid line) experiment; (circles) calculation.

manifestation of the Cu···Cu distances. Varying the integration limits of the Fourier transformation of EXAFS clearly showed that this peak in the case of complexes **IIa**, **IIb**, and **IIc** corresponds to the scattering of the photoelectron wave at the adjacent copper atoms, that is, points to a dimeric structure of the **IIa**, **IIb**, and **IIc** molecules.

Table 1. Structural data on the local atomic environment of the copper metallocomplexes obtained by fitting the EXAFS data[a]

Comp. no.	*N*	*r*	σ^2	Atom	*Q*
IIa	4 1	1.92 2.98	0.0042 0.0052	O/N Cu	0.5
IIb[b]	4 1	1.92 2.99	0.0054 0.0076	O/N Cu	1.1
	4 0.7	1.92 2.98	0.0054 0.0052	O/N Cu	0.9
IIc[b]	4 1	1.92 2.93	0.0050 0.0068	O/N Cu	1.3
	4 0.7	1.92 2.92	0.0050 0.0052	O/N Cu	0.8

[a] *r* is interatomic distance, *N* is coordination number, σ^2 is Debye-Waller factor, *Q* is quality fit function. [b] Fit in the range of *k* 1.1–2.87 Å^{-1}.

Table 1 lists the results of calculation of the parameters of local atomic environment in the complexes at the choice of appropriate models of atomic structure of the coordination site. Analysis of these data shows that the first coordination shell of the copper atom in compounds **IIa**, **IIb**, and **IIc** with oxygen bridges consists of four nitrogen and oxygen atoms with the same distance Cu···O/N, *r* = 1.92 Å. Since the peak corresponding to the appearance of Cu···Cu distances in these compounds have different amplitudes, the parameters of this coordination sphere were found using two models. In one case the same coordination numbers *CN* = 1 were selected and values of the Debye–Waller factor σ^2 were varied, in the other the σ^2 value was fixed and the *CN* value was found. The choice of these models is due to the strong correlation of these parameters. The best model was selected on the basis of the lowest values of the *Q* factor. As can be seen from Table 1, in the case of complexes **IIb** and **IIc**, the lowest *Q* values are obtained for the model of dimeric molecular structure, but with a lower coordination number (~0.7). Such a lowering of the coordination numbers can be associated with an admixture of monomeric copper complexes. For the complex **IIa** we obtained the single-phase state with dimeric structure of molecules, the Cu···Cu distance was 2.98 Å.

Our magnetochemical studies showed that in all the described complexes the exchange interaction of antiferromagnetic type was realized. The temperature dependence of magnetic susceptibility of the copper(II) complexes were satisfactorily interpreted in the framework of the model of exchange-linked dimer (for the Hamiltonian $H = -2JS_1S_2$) [12]. The $2J$ parameter of the antiferromagnetic exchange interaction was calculated using the modified Bleaney–Bowers equation [13], taking into account the presence in the complex of some fraction of paramagnetic impurities:

$$\chi'_m = \frac{N_A g^2 \beta^2}{3kT}\left\{(1-p)\left[1+{}^{1}/_{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}+pS(S+1)\right\}+N_\alpha.$$

Here χ'_M is the molar magnetic susceptibility corrected for the atomic diamagnetism within the Pascal additive scheme, *p* is the mole fraction of paramagnetic

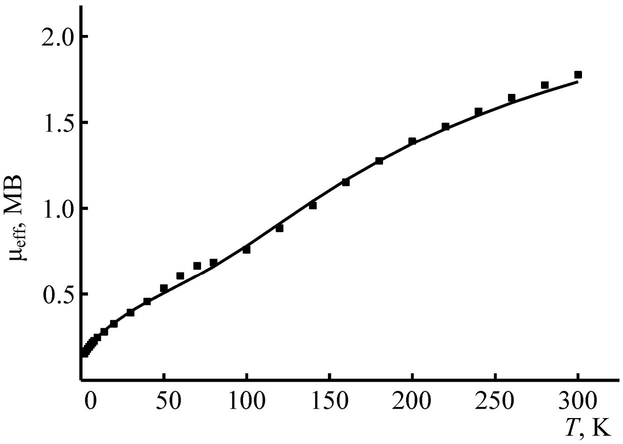


Fig. 3. The temperature dependence of the effective magnetic moment of complex **IIa**.

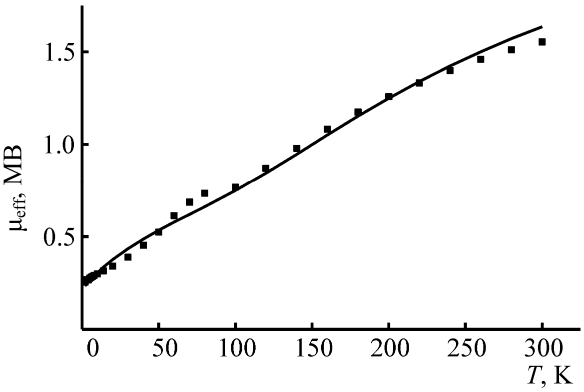


Fig. 4. The temperature dependence of the effective magnetic moment of complex **IIb**.

impurity, N_α is the temperature-independent paramagnetism that for the Cu(II) ion is taken equal to 60×10^{-6}.

The experimental curves of $\mu_{eff.}(T)$ of the complexes **II** are shown in Figs. 3–5, solid lines correspond to theoretical curves. Table 2 lists the optimum parameters.

The values of the parameters of antiferromagnetic exchange interaction $2J$ in the complexes **IIa**–**IIc** are –322 cm^{-1} ($g = 2.00$, $p = 0.005$), –405 cm^{-1} ($g = 2.00$, $p = 0.005$) and –263 cm^{-1} ($g = 2.10$, $p = 0.018$), respectively.

The exchange interaction in complex **IIc** is somewhat weaker than in **IIa** and **IIb**, which may be caused by distortion of the exchange fragment due to the presence of bulky substituents R^1. This assumption is consistent with the structural parameters of the complexes obtained from the data of EXAFS (Table 1). A decrease in the Cu···Cu distance in complex **IIc** compared with **IIa** and **IIb** is connected, apparently, with a bend of the binuclear molecules along the line connecting the bridging atoms, which reduces the Cu–O$_{phen}$–Cu bond angle. The value of the latter affects considerably the strength of antiferromagnetic exchange in binuclear copper complexes with phenoxide bridges [4, 14–17].

The binuclear coordination compounds based on the ligands of type **I** are known [4] to be capable to exist as two isomers differing by the inclusion into the exchange fragment of the heteroatoms of either five-membered or six-membered metallocycles (structures **II** and **III**, respectively). To clarify the structure of compounds **IIa**, **IIb**, and **IIc**, we performed the quantum-chemical study of the structures **II** and **III** simulating their coordination sites.

The calculations showed that structure **II** has almost planar metal-chelate rings. The geometry of the isomeric structure **III** is characterized by a rotation of two ligands relative to each other (at an angle of 19°) due to their repulsive interactions. It follows from Fig. 6 that the Cu···Cu distances in the structures **II** and **III** are similar: 3.06 and 3.04 Å, respectively. The calculated values of the $2J$ constants for these structures (–250 and –342 cm^{-1} for **II** and **III** respectively) are also consistent with the experimental data of the magnetochemical investigations of the complexes **IIa**–**IIc**. Thus, the characteristics of structures **II** and **III** calculated by DFT method do not allow us to make a choice in favor of one or another stereochemistry of the coordination site. However, destabilization of structure **III** with respect to **II** by 4.5 kcal mol^{-1} indicates a disadvantage of this structure for the complexes **IIa**, **IIb**, and **IIc**.

Table 2. The magnetic properties of complexes **II**

Comp. no.	T, K	μ_{eff}, BM	$2J$, cm^{-1}	g	p
IIa	300 2	1.556 0.153	–322	2.00	0.005
IIb	300 2	1.554 0.254	–405	2.00	0.015
IIc	300 2	1.722 0.246	–263	2.10	0.018

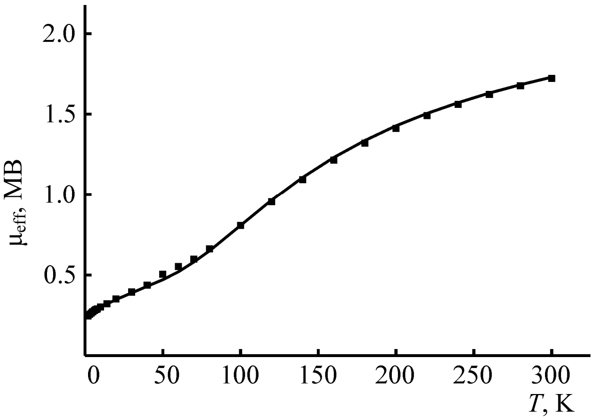


Fig. 5. The temperature dependence of the effective magnetic moment of complex **IIc**.

EXPERIMENTAL

IR spectra were obtained on a Varian 3100-FTIR Excalibur instrument from the powders by the method of attenuated total internal reflection. The ^{1}H NMR spectra were recorded on a Varian Unity-300 device (300 MHz) in the mode of internal stabilization of the polar-resonance ^{2}D line in $CDCl_3$.

The X-ray Cu*K*-edge absorptions were obtained in the transmission mode on an EXAFS-spectrometer of the Structural Material Research station at the Kurchatov synchrotron center (Moscow). The energy of the electron beam used as a source of X-ray synchrotron radiation was 2.5 GeV at a current of 80–100 mA. For monochromation of the X-ray radiation a double-crystal Si(111) monochromator was used.

The spectra processing was performed using the standard procedures of the background abstraction, normalization according to the value of the *K*-edge jump, and isolation of the atomic absorption μ_0 [18], followed by Fourier transformation of the obtained EXAFS (χ)-spectra in the range of photoelectron wave vector k from 2.6 to 13 Å^{-1} with the weight function k^3. The threshold ionization energy E_0 was chosen corresponding to the maximum of the first derivative of the *K*-edge and further was varied for fitting.

The exact values of the structural parameters of the nearest environment of copper ion were determined by nonlinear fitting the parameters of the coordination spheres comparing the calculated EXAFS signal and the signal extracted from the full EXAFS spectrum by Fourier filtering of the Fourier-transformed modules. The non-linear fitting was performed using the IFFEFIT-1.2.5 software package [19]. The phases and amplitudes of the photoelectron wave scattering for the model spectrum were calculated using the FEFF7 program [20]. The initial atomic coordinates to calculate the phase and amplitude of the scattering and further adjustment were taken from the X-ray data found in the Cambridge structural database for the complex with similar local environment of copper ions.

The fit quality function Q minimized for finding the parameters of the nearest environment structure was calculated by formula (1).

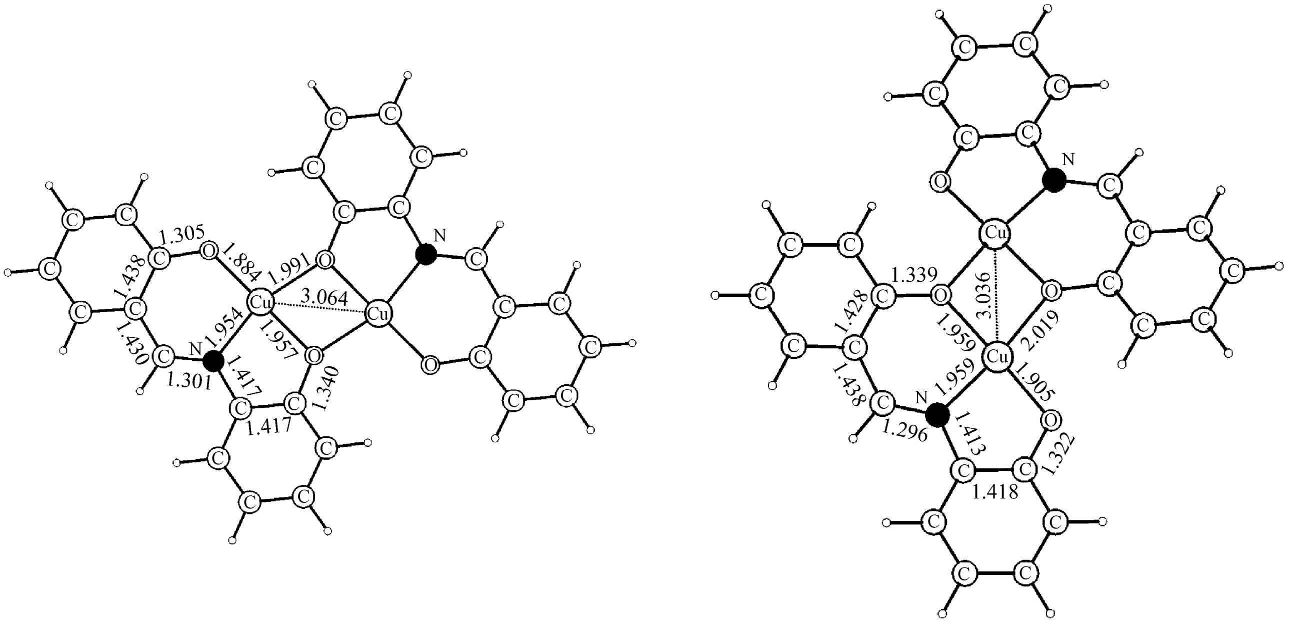


Fig. 6. The results of quantum-chemical calculations of structure of the intra-chelate complexes **II** and **III**.

$$Q(\%) = \frac{\Sigma[k\chi_{\text{exp}}(k) - k\chi_{\text{th}}(k)]^2}{\Sigma[k\chi_{\text{exp}}(k)]^2} \times 100\%. \qquad (1)$$

The magnetic properties of polycrystalline samples were studied on a Quantum Design SQUID magnetometer MPMS-*XL* in the temperature range 2–300 K, in the magnetic field of 5 kOe. At calculating the paramagnetic component of the molar magnetic susceptibility (χ) corrections were introduced in accordance with the diamagnetic Pascal additive scheme. In the paramagnetic region, the effective magnetic moment was determined from Eq. (2).

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

where k is Boltzmann constant, N_A is Avogadro number, β is the Bohr magneton.

All quantum-chemical calculations were performed within the density functional theory DFT B3LYP/6-311++G(d,p) [21] with the Gaussian 03 program [22]. To find the stationary points on potential energy surface a full geometry optimization of molecular structures was carried out. Calculation of exchange coupling constant J was performed using the technique according to the formula proposed in [23]: $E_T - E_{BS} = -2J$, where E_T is the triplet state energy, E_{BS} is the energy of the symmetry breakdown state.

Azomethines **Ia**, **Ib** were obtained by the known method [24].

2-{[(2-Hydroxyphenylimino)methyl]-4-(*p*-tolyldiazenyl)}phenol (Ic). A suspension of 0.721 g (3 mmol) of 2-hydroxy-5-[(4-methylphenyl)diazenyl]benzaldehyde and 0.327 g (3 mmol) of 2-aminophenol in 15 ml of toluene was refluxed for 5 h. The red precipitate was filtered off, washed with hot isopropyl alcohol (3×5 ml), then with hexane (2×5 ml). Yield 98%, mp 239–240°C. Found, %: C 72.35; H 5.22; N 12.60. $C_{20}H_{17}N_3O_2$. Calculated, %: C 72.49; H 5.17; N 12.68. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.42 s (3H, CH_3), 5.75 br.s (1H, OH-phenol), 6.98–8.10 m (11H, Ar), 8.83 s (1H, CH=N), 12.87 br.s (1H OH of salycilic aldehyde). IR spectrum, (ν, cm^{-1}): 3415 s (OH), 1608 v.s (C=N), 1288 w (Ph–O).

Synthesis of metal-chelates. To a solution of 0.001 mol of an azomethine **Ia–Ic** in 25 ml of ethanol was added a solution of 0.199 g (0.001 mol) of copper acetate monohydrate in 20 ml of ethanol. The resulting mixture was refluxed for 4 h. The precipitated fine crystalline complexes were filtered off, washed with boiling ethanol (3×5 ml) and hexane (2×5 ml), and dried in a vacuum drying cabinet at 100°C.

Bis{4-bromo-2-[2-(hydroxyphenylimino)methyl]-phenoxido}dicopper(II) (IIa). Yield 65%. Green powder, mp > 250°C. IR spectrum, ν, cm^{-1}: 1613 v.s (C=N), 1337 s (Ph–O). Found, %: C 44.19, H 2.35, N 3.97. $C_{26}H_{16}Br_2Cu_2N_2O_4$. Calculated, %: C 44.15, H 2.28, N 3.96.

Bis{4-bromo-2-[5-nitro-2-(hydroxyphenylimino)-methyl]-phenoxydo}dicopper(II) (IIb). Yield 67%. Brown powder, mp > 250°C. IR spectrum (cm^{-1}): 1611 v.s (C=N), 1337 s (Ph–O). Found, %: C 40.01, H 1.58, N 7.13. $C_{26}H_{14}Br_2Cu_2N_4O_8$. Calculated, %: C 39.17, H 1.77, N 7.03.

Bis{[2-(hydroxyphenylimino)methyl]4-(*p*-tolyldiazenyl)phenoxido}dicopper(II) (IIc). Yield 57%. Black powder, mp > 250°C. IR spectrum, (ν, cm^{-1}): 1617 v.s (C=N), 1332 m (Ph–O). Found, %: C 61.08, H 3.99, N 10.57. $C_{40}H_{30}Cu_2N_6O_4$. Calculated, %: C61.14, H 3.85, N 10.69.

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