Sterically crowded chelate complexes of copper(II) with phenoxazinyl ligands: ESR study

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A copper complex with 1-*H*-1-oxo-2,4,6,8-tetrakis(*tert*-butyl)phenoxazinyl free radical ligands was synthesized, and its magnetic properties and ESR spectra were measured at 77—290 K. It was shown that a ground electron state with one unpaired electron is typical of this complex at 77—290 K. The magnetoresonance parameters of this complex are characterized by a *g*-factor value (1.978) that is rather unusual for copper-containing compounds and by hyperfine coupling due to Cu nuclei. The considerable broadening of ESR spectral lines with increasing temperature is probably not due to the formation of a quartet state ($S = 3/2$). A model of electron states of the compound investigated was developed in the framework of ligand field theory, which made it possible to explain the pattern of the ESR spectra, which were untypical of copper complexes.

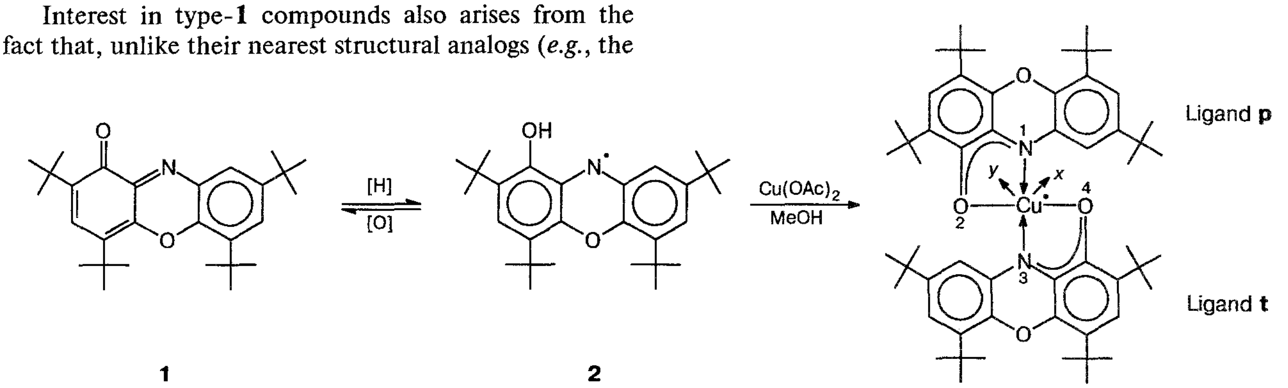
Key words: free radical ligands, complexes; ESP spectra; *g*-factor; temperature dependence.

It was reported in previous works[1—5] that 1-*H*-1-oxo-2,4,6,8-tetrakis(*tert*-butyl)phenoxazine (**1**) readily reacts with amalgams and salts of transition metals to give coordination compounds, in which stable phenoxazinyl radicals serve as ligands. An ESR study of these radicals showed that their ESR spectra have a well-resolved hyperfine structure (HFS), which makes it possible to determine their structures reliably in each particular case. In turn, the high degree of delocalization and spatial screening of an unpaired electron in such systems result in formation of highly stable paramagnetic chelate complexes, in which the unpaired electron is delocalized both along the system of ligand molecular orbitals and at the metal atom.

Interest in type-**1** compounds also arises from the fact that, unlike their nearest structural analogs (*e.g.*, the well-known *o*-quinoline complexes[6]), the N atom of the phenoxazinyl ligand in the compounds we studied is involved in the coordination environment of the metal. This affords additional information from ESR spectroscopy.

In the present work we synthesized a complex of Cu^{II} with the 1-hydroxy-2,4,6,8-tetrakis(*tert*-butyl)phenoxazinyl radical (**2**) and studied its physicochemical and spectral properties by ESR, UV, and IR spectroscopy along with magnetochemistry.

Copper complex **3** was obtained by the reaction of free phenoxazinyl radical **2** with copper(II) acetate in methanol.



1 **2** **3**

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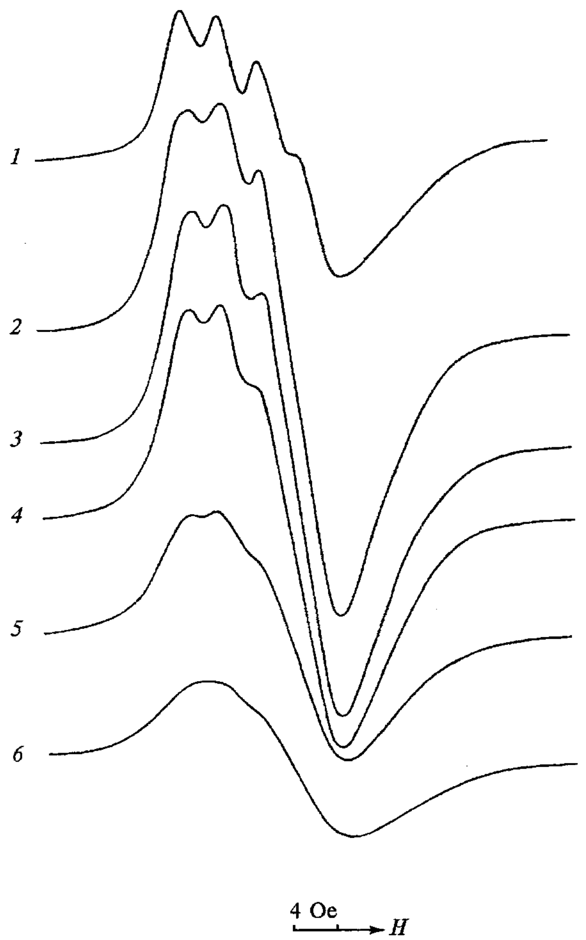

Fig. 1. ESR spectra of complex **3** in a frozen matrix (toluene) at a modulation amplitude of 0.2 Oe (spectrum *1*) or 0.4 Oe (spectra *2—6*). *1,2,* at 77 K; *3,* at 93 K; *4,* at 98 K; *5,* at 105 K; *6,* at 123 K.

Compound **3** was isolated from the reaction mixture as a fine crystalline black powder, which is very stable, highly soluble in low-polarity aprotic solvents (benzene, hexane, and other hydrocarbons), and poorly soluble in alcohols and acetonitrile. When solutions in alcohols are stored in air, they undergo oxidative hydrolysis to give phenoxazinone **1**.

The ESR spectra of complex **3** were found to differ both from the spectra of copper(II) complexes and from those of free phenoxazinyl ligands. At ~20 °C, ESR signals were not observed either in the solid state (powder) or in solutions of compound **3**. However, when the temperature was decreased to 77 K, a relatively broad single line (ΔH = 98 Oe) was found to appear. The *g*-factor of this line (1.978) is untypical of copper compounds and is less than *g* for a free electron (2.0023).

In frozen solutions, we detected a weakly anisotropic ESR spectrum characterized by $g_{\parallel} = 1.9897$, $g_{\perp} = 1.9667$, and hyperfine splitting ($A_{\parallel} = 22.4 \cdot 10^{-4}$ cm^{-1}) into four components due to interaction of the spin of an unpaired electron with those of the ^{63}Cu and ^{65}Cu nuclei (Fig. 1).

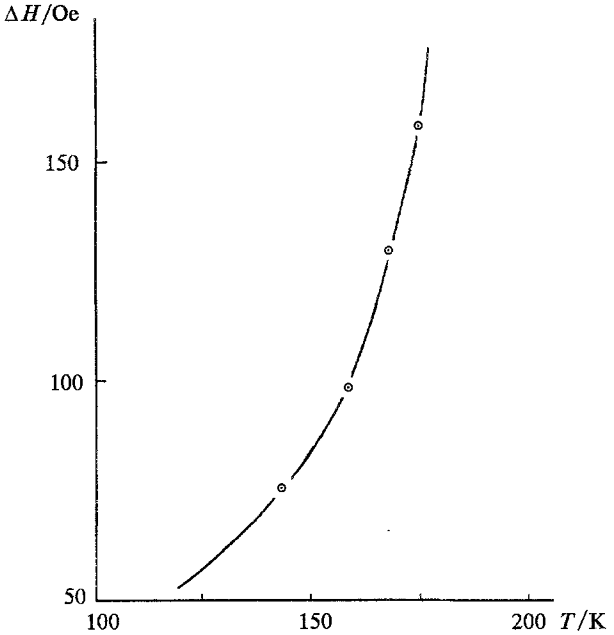

Fig. 2. Dependence of the width of an ESR spectrum line of frozen complex **3** (toluene) on temperature.

These values differ considerably from those of typical ESR spectral parameters[7] for planar (2O2N) $\mathrm{Cu^{II}}$ complexes ($g_{\parallel} \approx 2.20$—2.25, $g_{\perp} \approx 2.05$—2.06, $A_{\parallel} \approx (180$—$200) \cdot 10^{-4}$ cm^{-1}, $A_{\perp} \approx (20$—$30) \cdot 10^{-4}$ cm^{-1}). The low $A_{\parallel}$ value, like that in the case of *o*-quinoid ligands,[8] is indicative of considerable delocalization of the unpaired electron in complex **3** along the ligand—Cu atom—ligand system of orbitals.

Increase in the temperature of frozen solutions of compound **3** ($T > 77$ K) results in sharp broadening of lines of the ESR spectrum. We studied the dependence of the width of an ESR spectrum line of complex **3** in a polystyrene matrix on temperature (Fig. 2). This type of dependence is maintained for a wide range of solvents (hexane, toluene, methanol, acetonitrile).

A magnetochemical study of powders of complex **3** gave the following values of the magnetic moment: $\mu = 2.03\ \mu_B$ at ~20 °C and $\mu = 1.98\ \mu_B$ at the temperature of liquid nitrogen. These values of μ suggest that complex **3** is characterized by one ground state with one unpaired electron over the 77—290 K temperature range. Broadening of lines in the ESR spectra with increasing temperature is probably not due to the formation of a quartet state ($S = 3/2$) with three unpaired electrons.

Results and Discussion

Let us consider a model based on the ligand field theory and allowing a satisfactory explanation of the unusual pattern of the ESR spectra of compound **3**. It is assumed that in this complex the unpaired electron is located on a molecular orbital formed due to the interaction of the out-of-plane π-orbitals of the two ligands through the d-orbitals of the metal atom. The π-orbitals in the free ligands are occupied by an unpaired electron. The corresponding one-electron molecular wave functions of the complex can be written as

$$\psi_i = \alpha_p^{(i)}\varphi_p + \alpha_t^{(i)}\varphi_t + \sum_{\mathrm{M}} \alpha_{\mathrm{M}}^{(i)}\varphi_{\mathrm{M}},$$

where φ_{M} are the atomic d-functions of Cu^{II} (xy, x^2-y^2, z^2, xz, yz); φ_p and φ_t are linear combinations constructed from the wave p-functions ($\varphi_z^{(k)}$) of ligand atoms stretched along the z axes perpendicular to the ligand ring planes:

$$\varphi_p = \sum_k C_k^{(p)}\varphi_z^{(k)}, \quad \varphi_t = \sum_k C_k^{(t)}\varphi_z^{(k)}.$$

Summation was performed for all ligand atoms (**p** or **t**). The $\alpha_p^{(i)}$, $\alpha_t^{(i)}$, and $\alpha_{\mathrm{M}}^{(i)}$ coefficients and the molecular energy levels (ε_i) were calculated within the scope of the angular overlapping model[9] *vs.* the angle (γ) between the N(1)CuO(2) and N(3)CuO(4) planes characterizing the tetrahedral distortions of the chelate moiety. The nondiagonal matrix elements were described by the Wolfsberg—Helmholtz expression:

$$V_{p\mathrm{M}} = \varepsilon_0 S_{p\mathrm{M}}.$$

The dependences of the integrals of overlapping ($S_{p\mathrm{M}}$) of the atomic wave functions of the ligand and metal on angle γ were obtained using the method reported previously.[10]

Solving a system of uniform equations for the secular problem in the perturbation theory approximation gives the following expressions for the states responsible for the magnetic properties of complex **3**:

$$\begin{cases} \alpha_p^{(1)} = -\alpha_t^{(1)} \approx \dfrac{1}{\sqrt{2}} \\ \alpha_{xy}^{(1)} = \alpha_{x^2-y^2}^{(1)} = \alpha_{z^2}^{(1)} = 0 \\ \alpha_{yz}^{(1)} = \sqrt{2}\,\dfrac{\varepsilon_p-\varepsilon_0}{\varepsilon_p-\varepsilon_{yz}} S_+^{(0)}\cos(\gamma/2) \\ \alpha_{xz}^{(1)} = -\sqrt{2}\,\dfrac{\varepsilon_p-\varepsilon_0}{\varepsilon_p-\varepsilon_{xz}} S_-^{(0)}\cos\gamma \\ \quad \varepsilon_1 = \varepsilon_p + 2(\varepsilon_p-\varepsilon_0)^2\left(\dfrac{(S_+^{(0)})^2\cos^2(\gamma/2)}{\varepsilon_p-\varepsilon_{yz}} + \right. \\ \qquad \left. + \dfrac{(S_-^{(0)})^2\cos^2\gamma}{\varepsilon_p-\varepsilon_{xz}}\right) \end{cases} \tag{1}$$

$$\begin{cases} \alpha_p^{(2)} = \alpha_t^{(2)} \approx \dfrac{1}{\sqrt{2}} \\ \alpha_{xy}^{(2)} = \sqrt{2}\,\dfrac{\varepsilon_p-\varepsilon_0}{\varepsilon_p-\varepsilon_{xy}} S_+^{(0)}\sin(\gamma/2) \\ \alpha_{x^2-y^2}^{(2)} = \dfrac{\varepsilon_p-\varepsilon_0}{\varepsilon_p-\varepsilon_{x^2-y^2}} S_-^{(0)}\sin\gamma \\ \alpha_{z^2}^{(2)} = -\sqrt{\dfrac{3}{2}}\cdot\dfrac{\varepsilon_p-\varepsilon_0}{\varepsilon_p-\varepsilon_{z^2}} S_-^{(0)}\sin\gamma \\ \alpha_{xz}^{(2)} = \alpha_{yz}^{(2)} = 0 \\ \quad \varepsilon_2 = \varepsilon_p + 2(\varepsilon_p-\varepsilon_0)^2\left(\dfrac{2(S_+^{(0)})^2\sin^2(\gamma/2)}{\varepsilon_p-\varepsilon_{xy}} + \right. \\ \qquad \left. + \dfrac{(S_-^{(0)})^2\sin^2\gamma}{2(\varepsilon_p-\varepsilon_{x^2-y^2})} + \dfrac{3}{2}\cdot\dfrac{(S_-^{(0)})^2\sin^2\gamma}{\varepsilon_p-\varepsilon_{z^2}}\right) \end{cases} \tag{2}$$

In these expressions, ε_{M} and $\varepsilon_p = \varepsilon_t$ are the energies of atomic d-orbitals of the metal and π-orbitals of free

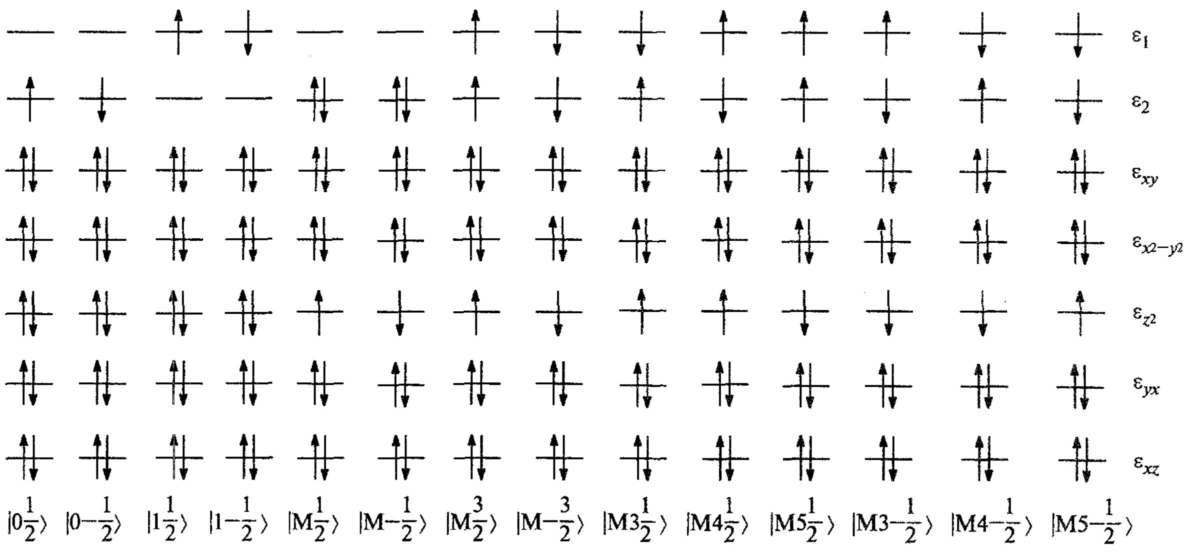

Fig. 3. Ground and excited states of the electron shell of complex **3**.

ligands **p** and **t**; $S_+^{(0)}$ and $S_-^{(0)}$ are coefficients related to the integrals of overlapping between the basis functions of the metal and the N and O atoms closest to it. The $\alpha_M^{(i)} \ll 1$ inequalities are preconditions for the applicability of perturbation theory, which are likely to be actually fulfilled.

Figure 3 presents the scheme of occupation of the ε_M, ε_1, and ε_2 molecular levels in the ground state $|0\frac{1}{2}\rangle$, according to which the unusual pattern of the ESR spectra of compound **3** can be explained. It is assumed that the ε_1 and ε_2 levels are above the ε_M d-levels in the energy scale, which is indicated by the ease of the transition of the ligand molecules to the free-radical state. In the ground state, the 3d shell is completely occupied, the unpaired electron is at the lowest level ε_2, and the ε_1 level is unoccupied. In fact, such a scheme corresponds to the structure $Cu^IR^\cdot$ with transfer of the unpaired electron from the Cu atom to the ligands.

It follows from the expressions for ε_1 and ε_2 that $\varepsilon_1 > \varepsilon_2$ in the case of planar geometric positions of ligands, but when angle γ increases, levels (1) and (2) are soon reverted, which leads to degeneration of the ground state at not too high γ values. This allows us to explain broadening of lines by the Jahn—Teller effect. At the temperature of liquid nitrogen, the system is "frozen" at a point corresponding to a local minimum of the adiabatic potential. The observed spectrum reflects the geometry of the molecule at this minimum. When the temperature is increased, the Jahn—Teller effect becomes dynamic. The system is "thrown over" the point corresponding to the degenerate ground state, which results in sharp broadening of the lines, up to their disappearance at room temperature.

To calculate the components of the *g*-tensor, it is not sufficient to know the ground state of the system. In addition, data concerning its excited states are also required. Figure 3 presents electron configurations that appear when electrons are transferred from the lowest to the highest one-electron levels (ε_1 and ε_2).

All excited electron configurations can be divided into three types: 1) configurations with electron excitement $|1\frac{1}{2}\rangle$ and $|1-\frac{1}{2}\rangle$; 2) configurations with hole-type excitement $|M\frac{1}{2}\rangle$, $|M-\frac{1}{2}\rangle$ with electron transfer from ε_M levels to the ε_2 level; 3) configurations of $|M\frac{3}{2}\rangle$, $|M-\frac{3}{2}\rangle$, $|Mn+\frac{1}{2}\rangle$, $|Mn-\frac{1}{2}\rangle$ types (n = 3, 4, 5) with electron transfer from an ε_M level to an ε_1 level with different combinations of projections of spins of the interacting electrons.

In the general case, multielectron determinant wave functions, $|Mnm\rangle$, are not the own functions of the Hamilton operator. This becomes obvious if we determine the matrix elements of the interelectron coulombic interaction operator according to the rules for calculating matrix elements for a symmetric two-electron operator.[11] It can be shown that the own functions include linear combinations

$$|MNm\rangle = \sum_n C_n^{(MN)}|Mnm\rangle,$$

where $C_n^{(MN)}$ are coefficients that do not depend on *m* and are determined by the ratios between the exchange integrals

$$I_{12} = \int \psi_1(r_i)\psi_2(r_k)\frac{e^2}{|r_{ik}|}\psi_2(r_i)\psi_1(r_k)\,d\tau_1\,d\tau_2,$$

$$I_{1M} = \int \psi_1(r_i)\psi_M(r_k)\frac{e^2}{|r_{ik}|}\psi_M(r_i)\psi_1(r_k)\,d\tau_1\,d\tau_M,$$

$$I_{2M} = \int \psi_2(r_i)\psi_M(r_k)\frac{e^2}{|r_{ik}|}\psi_M(r_i)\psi_2(r_k)\,d\tau_2\,d\tau_M.$$

For the problem under consideration, one can expect that $I_{12} \gg I_{1M}$, I_{2M}. In this case, diagonalization of the Hamilton operator matrix gives the states

$$N = 3{:}\quad C_3^{(M3)} = C_4^{(M3)} = \frac{1}{\sqrt{2}},\quad C_5^{(M3)} = 0,\quad E_{M3} = E'_M - I;$$

$$N = 4{:}\quad C_3^{(M4)} = C_4^{(M4)} = \frac{1}{\sqrt{2}},\quad C_5^{(M4)} = 0,\quad E_{M4} = E'_M + I;$$

$$N = 5{:}\quad C_3^{(M5)} = C_4^{(M5)} = 0,\quad C_5^{(M5)} = 1,\quad E_{M5} = E'_M - I.$$

Here $I = I_{12}$, $I_{1M} = I_{2M} = 0$, and E'_M is a member common to all $|MNm\rangle$, which includes the energy of coulombic repulsion.

If we know the ground and excited states of a system, the components of the *g*-tensor can be determined by diagonalization of the matrix of the spin-orbital and Zeeman interactions, taking into account that the matrix elements between the determinant wave functions should be calculated in this case. Skipping the intermediate calculations, we present expressions for g_{zz}, g_{xx}, and g_{yy}, assuming that $|0m\rangle$ is the ground state, while $|1m\rangle$, $|Mm\rangle$, and $|MNm\rangle$ are excited states (Eqs. (3)—(5)).

$$g_{zz} - g_0 = -\frac{2\lambda|\langle\psi_1|\hat{l}_z|\psi_2\rangle|^2}{E_1 - E_0} + 2\lambda\sum_M \frac{|\langle\psi_M|\hat{l}_z|\psi_2\rangle|^2}{E_M - E_0} - {} - 2\lambda\sum_{M,N}\frac{(C_5^{(MN)})^2 - (C_3^{(MN)})^2}{E_{MN} - E_0}|\langle\psi_M|\hat{l}_z|\psi_1\rangle|^2 \tag{3}$$

$$g_{xx} - g_0 = -\frac{2\lambda|\langle\psi_1|\hat{l}_x|\psi_2\rangle|^2}{E_1 - E_0} + 2\lambda\sum_M \frac{|\langle\psi_M|\hat{l}_x|\psi_2\rangle|^2}{E_M - E_0} - {} - 2\lambda\sum_{M,N}\frac{C_4^{(MN)}(C_3^{(MN)} - C_5^{(MN)})}{E_{MN} - E_0}|\langle\psi_M|\hat{l}_x|\psi_1\rangle|^2 \tag{4}$$

$$g_{yy} - g_0 = -\frac{2\lambda|\langle\psi_1|\hat{l}_y|\psi_2\rangle|^2}{E_1 - E_0} + 2\lambda\sum_M \frac{|\langle\psi_M|\hat{l}_y|\psi_2\rangle|^2}{E_M - E_0} - {} - 2\lambda\sum_{M,N}\frac{C_4^{(MN)}(C_3^{(MN)} - C_5^{(MN)})}{E_{MN} - E_0}|\langle\psi_M|\hat{l}_y|\psi_1\rangle|^2 \tag{5}$$

In the above expressions, g_0 = 2.0023, λ = 830 cm^{-1} is the constant of the spin-orbital bond for the Cu atom, and $\hat{l}_z$, $\hat{l}_x$, and $\hat{l}_y$ are components of the orbital moment (the matrix elements are calculated between one-electron wave functions). As usual, Eqs. (3)—(5) can be used provided that $\lambda \ll (E_1 - E_0)$, $(E_M - E_0)$, $(E_{MN} - E_0)$.

The first members, corresponding to electron excitations, give negative contributions to $(g_{ii} - g_0)$, while the second members, characterizing "hole" excitations, give positive contributions. Usually, only the "hole" contributions are important for Cu^{II} complexes, therefore g_{xx}, g_{yy}, and g_{zz} for these compounds always exceed 2.0023. The signs of the third members in Eqs. (3)—(5) depend on the $C_n^{(MN)}$ coefficients. The matrix elements involved in expressions (3)—(5) can be easily determined as the general form of the ψ_1, ψ_2, and ψ_M wave functions is known. When the molecule of the complex has a planar configuration, these equations become especially simple, as the $\alpha_{xy}^{(1)}$, $\alpha^{(1)}{}_{x^2-y^2}$, $\alpha^{(1)}{}_{z^2}$, and all $\alpha_M^{(2)}$ coefficients equal zero. Assuming that $I_{1M} = I_{2M} = 0$ and $I_{12} = 1$, summing by N and calculating the matrix elements, one can obtain the following expressions for $(g_{ii} - g_0)$:

$$g_{zz} - g_0 = -\frac{2\lambda(\alpha_{xz}^{(1)})^2 K_{xz}^2 I}{(E_{yz} - E_0)^2 - I^2} - \frac{2\lambda(\alpha_{yz}^{(1)})^2 K_{yz}^2 I}{(E_{xz} - E_0)^2 - I^2}; \qquad (6)$$

$$\begin{aligned} g_{xx} - g_0 = &-\frac{2\lambda(\alpha_{xz}^{(1)})^2 K_{xz}^2 I}{(E_{xy} - E_0)^2 - I^2} - \frac{2\lambda(\alpha_{yz}^{(1)})^2 K_{yz}^2 I}{(E_{x^2-y^2} - E_0)^2 - I^2} - \\ &- \frac{6\lambda(\alpha_{yz}^{(1)})^2 K_{yz}^2 I}{(E_{z^2} - E_0)^2 - I^2}; \end{aligned} \qquad (7)$$

$$\begin{aligned} g_{yy} - g_0 = &-\frac{2\lambda(\alpha_{yz}^{(1)})^2 K_{yz}^2 I}{(E_{xy} - E_0)^2 - I^2} - \frac{2\lambda(\alpha_{xz}^{(1)})^2 K_{xz}^2 I}{(E_{x^2-y^2} - E_0)^2 - I^2} - \\ &- \frac{6\lambda(\alpha_{xz}^{(1)})^2 K_{xz}^2 I}{(E_{z^2} - E_0)^2 - I^2}. \end{aligned} \qquad (8)$$

where K_{xz} and K_{yz} are coefficients, which can be represented as $K_{xz} = (\varepsilon_{yz} - \varepsilon_0)/(\varepsilon_1 - \varepsilon_0)$ and $K_{yz} = (\varepsilon_{xz} - \varepsilon_0)/(\varepsilon_1 - \varepsilon_0)$ for the model under consideration. In the case of a planar configuration, Eqs. (6)—(8) do not contain electron and "hole" contributions, and the $(g_{ii} - g_0)$ values are solely determined by the third members in expressions (3)—(5). These contributions are negative. Because $(E_{yz} - E_0)$, $(E_{xz} - E_0) > (E_{xy} - E_0)$, $(E_{x^2-y^2} - E_0)$, the following inequalities should be fulfilled:

$$|g_{zz} - g_0| < |g_{xx} - g_0|, |g_{yy} - g_0|.$$

However, a planar molecule should not display hyperfine splitting on ^{63}Cu and ^{65}Cu nuclei due to the absence of spin density on them in the ground state ($\alpha_M^{(2)} = 0$). The appearance of hyperfine splitting in the ESR spectrum of complex **3** ($|A_z| > |A_x|$, $|A_y|$) can be explained by assuming that $\alpha_{xy}^{(2)}$ or $\alpha^{(2)}{}_{x^2-y^2}$ differs from zero, probably due to distortion of the planar structure of the molecule. The following expressions are valid for A_{zz}, A_{xx}, and A_{yy}:

$$\begin{aligned} A_{zz} &= \mathcal{P}_0(\alpha_{xy}^{(2)})^2(-K_0 - \tfrac{4}{7}) + \mathcal{P}_0(g_{zz} - g_0) + \\ &+ \tfrac{3}{14}\mathcal{P}_0(g_{xx} - g_0) + \tfrac{3}{14}\mathcal{P}_0(g_{yy} - g_0); \\ A_{xx} &= \mathcal{P}_0(\alpha_{xy}^{(2)})^2(-K_0 + \tfrac{2}{7}) + \mathcal{P}_0(g_{xx} - g_0) - \\ &- \tfrac{3}{14}\mathcal{P}_0(g_{yy} - g_0); \\ A_{yy} &= \mathcal{P}_0(\alpha_{xy}^{(2)})^2(-K_0 + \tfrac{2}{7}) + \mathcal{P}_0(g_{yy} - g_0) - \\ &- \tfrac{3}{14}\mathcal{P}_0(g_{xx} - g_0). \end{aligned} \qquad (9)$$

Since the $(g_{ii} - g_0)$ shifts are very small for the complex studied, the equations are easily simplified. It is known that $\mathcal{P}_0 = 360 \cdot 10^{-4}$ cm^{-1}, $K_0 = 0.43$. It thus follows that at $A_{zz} = 22.4 \cdot 10^{-4}$ cm^{-1}, $\alpha_{xy}^{(2)} = 0.062$, which is at least an order of magnitude less than the usual α_{xy} for copper complexes.

Thus, the model considered above makes it possible to explain both the values of g-tensor components untypical of bivalent copper compounds, which are lower than the g-factor for a free electron (2.0023), and "diffusion" of spectral lines with increasing temperature due to the possibility of degeneration of the ground orbital state. In addition, the model satisfactorily predicts correct relations between the experimental parameters of ESR spectra:

$$|g_{xx} - g_0|, |g_{yy} - g_0| > |g_{zz} - g_0|; \quad |A_z| > |A_x| > |A_y|.$$

Experimental

IR spectra were recorded in Vaseline oil on a Specord M-80 spectrophotometer. ESR spectra were recorded in toluene on a Varian E-12A spectrometer. UV spectra were obtained in heptane on a Specord UV-VIS spectrophotometer.

Synthesis of free 1-hydroxy-2,4,6,8-tetrakis(*tert*-butyl)-fenoxazinyl radical (2). A mixture of 3,5-di-*tert*-butyl-*o*-quinone (12.0 g) and 3,5-di-*tert*-butylpyrocatechol (12.1 g) in isopropanol (165 mL) and 25 % aqueous ammonia (25 mL) was refluxed for 6 h. The crystals that precipitated on cooling were filtered off to give 12.52 g of radical **2**. Partial evaporation of the mother liquor gave an additional 3.23 g of the product. The overall yield of **2** was 68 %. Recrystallization from aqueous isopropanol gave dark-blue crystals, m.p. 177 °C (from isopropanol).

In addition, 1.80 g of 1-*H*-1-oxo-2,4,6,8-tetrakis(*tert*-butyl)phenoxazine (**1**) was obtained from the reaction mixture, m.p. 212 °C. Found (%): C, 79.74; H, 9.42; N, 3.20. $C_{28}H_{40}NO_2$. Calculated (%): C, 79.57; H, 9.54; N, 3.31. IR, ν/cm^{-1}: 3280, 1650, 1630, 1590. ESR (20 lines), a/Oe: $a_{H(3)} = 3.81$; $a_{H(7)} = 4.17$; $a_{H(9)} = 2.63$; $a_N = 7.67$. UV, λ_{max}/nm: 230, 275.0, 367.7, 565.7.

Synthesis of bis(1-hydroxy-2,4,6,8-tetrakis(*tert*-butyl)phenoxazinyl)copper(II) (3). A solution of radical **2** (0.5 g) in ethanol (8 mL) was mixed with a solution of $Cu(OAc)_2 \cdot H_2O$ (0.13 g) in a mixture of water (2 mL) and ethanol (2 mL). The precipitate that formed was filtered off, washed with cold ethanol, and dried to give 0.42 g (78 %) of complex **3**. Recrystallization from an ethanol—hexane mixture gave a black amorphous powder, m.p. 302 °C. Found (%): C, 73.89; H, 8.79; N, 3.02; Cu, 6.90. $C_{56}H_{78}N_2O_4Cu$. Calculated (%): C, 74.18; H, 8.67; N, 3.09; Cu, 7.01. IR, ν/cm^{-1}: 1590, 1520. UV, λ_{max}/nm: 240.0, 291.5, 380.7, 402.1, 521.2, 797.0. Magnetic weighing (μ/μ_B): 1.98 (78 K); 2.03 (292 K).

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