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Covalent Bonding in Copper(II) Complexes with Hetarylformazans According to EPR Spectra

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Abstract—Covalent bonding in a number of copper(II) complexes with hetarylformazans that have pseudotetrahedral or square-planar symmetry of the nearest metal environment was analyzed from EPR spectra. The dependence of the unpaired electron delocalization on the pseudotetrahedral distortion of the coordination polyhedron was determined. A change in the Zeeman coupling parameters was interpreted. Various contributions to the components of the hyperfine coupling (HFC) and ligand hyperfine coupling (LHFC) tensors were calculated. *pd*-Mixing of the AO of the copper ion was found to have a slight effect on the HFC parameters. In the components of the LHFC tensor, the contribution from isotronic LHFC is decisive.

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A study of the properties of complexes of transition metals with formazans is of considerable practical interest because they can be employed as analytical reagents and because ion-exchange polymers containing formazans are more selective toward metal ions to be sorbed [1]. Vishnevskaya et al. have examined a wide range of copper(II) complexes with hetarylformazans (HFs) by EPR spectroscopy, revealed the ways of coordinating the ligands by the metal ion, and found that the nearest environment of the copper ion in such complexes has pseudotetrahedral or square-planar symmetry [2]. At the same time, the nature of covalent bonding in copper(II) complexes with HFs has not been studied thoroughly. In addition, it remains unclear how this bonding influences the parameters of the EPR spectra of complexes. Here we analyzed the character of covalent bonding from EPR spectra and discussed the behavior of the Zeeman coupling parameters, the hyperfine coupling (HFC), and the ligand hyperfine coupling (LHFC) of the copper(II) complexes with HFs that have pseudotetrahedral (D_{2d}) or square-planar symmetry (D_{4h}).

PARAMETERS OF THE ZEEMAN, HYPERFINE, AND LIGAND HYPERFINE COUPLINGS

For the pseudotetrahedral copper(II) complex CuL_4 (D_{2d}) ($S = 1/2$, ground-state term $^2B_2$), let us set off the following shells from its electronic configuration:

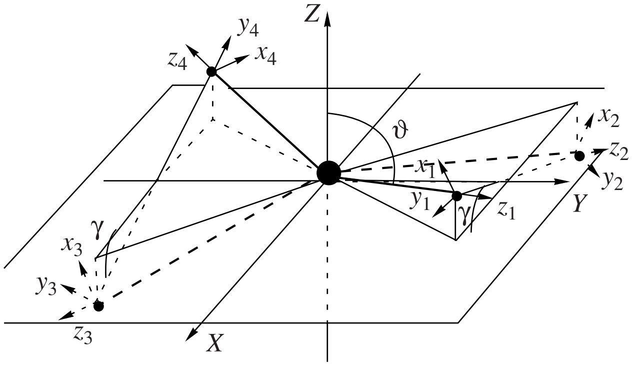
$$[b_1(d_{x^2-y^2})]^2[e_{1,2}(d_{xz,yz})]^4[b_2(d_{xy})]^1 = {}^2B_2, \tag{1}$$

where the antibonding states of the complex are considered. The molecular orbitals (MOs) for the electrons in the corresponding shell are enclosed in parentheses and d_i ($i = x^2 - y^2, xz, yz, xy$) is the 3$d$-AO of the copper ion. The sequence of the shells is written in accordance with optical data and quantum-chemical calculations of pseudotetrahedral copper(II) complexes [3, 4]. The general and local systems of coordinates and the angle of pseudotetrahedral distortion γ are shown in figure. The MO has the form:

$$\begin{aligned} b_2 = {}& x_0^d(d_{xy}) + x_0^p(p_z) \\ & + x_1^{\mathrm{L}}(\varphi_{b_2}^{p\sigma z}\sin\varphi + \varphi_{b_2}^{s\sigma}\cos\varphi) + x_2^{\mathrm{L}}\varphi_{b_2}^{p\pi x}. \end{aligned} \tag{2}$$

$$b_1 = y_0^d(d_{x^2-y^2}) + y_1^{\mathrm{L}}\varphi_{b_1}^{p\pi y}, \tag{3}$$

$$\begin{aligned} e_{1,2} = {}& z_0^d(d_{xz,yz}) + z_0^p(p_{y,x}) + z_1^{\mathrm{L}}(\varphi_{e_{1,2}}^{p\sigma z}\sin\varphi \\ & + \varphi_{e_{1,2}}^{s\sigma}\cos\varphi) + z_2^{\mathrm{L}}\varphi_{e_{1,2}}^{p\pi x} + z_3^{\mathrm{L}}\varphi_{e_{1,2}}^{p\pi y}, \end{aligned} \tag{4}$$



Principal and local coordinate systems for complex CuL_4 (D_{2d}). ● is copper ion; ● is L atom.

where p_i ($i = x, y, z$) is the 4p-AO of the copper ion; φ_r^t ($r = b_1, b_2, e_{1,2}$; $t = s\sigma, p\sigma z, p\pi x, p\pi y$) is the LCAO for L; x_0^d, x_0^p, y_0^d, z_0^d, z_0^p are the MO coefficients in front of the AO of the copper ion; $x_j^{\mathrm{L}}, y_j^{\mathrm{L}}, z_j^{\mathrm{L}}$ (j = 1–3), are the MO coefficients in front of the LCAO for L; $n = \tan^2\varphi$ is the degree of sp^n-hybridization of the AOs for L; b_2 is the ground-state MO (MO of the unpaired electron). In MO (2), the LCAO for L can be written as follows:

$$\left.\begin{aligned}\varphi_{b_2}^{s\sigma} &= \frac{1}{2}(s_1 - s_2 - s_3 + s_4)\\ \varphi_{b_2}^{p\sigma z} &= \frac{1}{2}(-p_{z_1} + p_{z_2} + p_{z_3} - p_{z_4})\\ \varphi_{b_2}^{p\pi x} &= \frac{1}{2}(p_{x_1} + p_{x_2} + p_{x_3} + p_{x_4})\end{aligned}\right\}, \qquad (5)$$

where s_i, $p_{z_i(x_i)}$ (i = 1–4) are the AOs in L that participate in σ- and π-bonding to the AO of the copper ion. MOs (2) and (4) describe mixed σ–π-bonding and MO (3) describes the metal–ligand π-bonding.

Expressions for the parameters of the EPR spectra of the pseudotetrahedral copper(II) complex were obtained according to a standard procedure [5] using MOs (2)–(4). In the calculations, we ignored bond covalence and pd-mixing of the AO of the copper ion in MOs (3) and (4); i.e., we believed that $y_0^d = z_0^d = 1$ and that $y_1^{\mathrm{L}} = z_0^p = z_1^{\mathrm{L}} = z_2^{\mathrm{L}} = z_3^{\mathrm{L}} = 0$. The expression for the MO of the unpaired electron was left unchanged. The correctness of these approximations is discussed below.

The components of the Zeeman coupling tensor (g tensor) can be written in the form:

$$g_{\parallel} = 2.0023 + 8\frac{\xi_{3d}}{\Delta_{\parallel}}[x_0^d(x_0^d + x_1^{\mathrm{L}}S_\sigma + x_2^{\mathrm{L}}S_\pi)], \qquad (6)$$

$$g_{\perp} = 2.0023 + 2\frac{\xi_{3d}}{\Delta_{\perp}}[x_0^d(x_0^d + x_1^{\mathrm{L}}S_\sigma + x_2^{\mathrm{L}}S_\pi)], \qquad (7)$$

where ξ_{3d} is the parameter of the spin–orbital coupling (SOC) for the 3d-electron of the copper ion, $\Delta_{\parallel} = \Delta E(b_1 \longrightarrow b_2)$ and $\Delta_{\perp} = \Delta E(e_{1,2} \longrightarrow b_2)$ are the energy differences for the electron transitions in configuration (1), and $S_{\sigma,\,\pi}$ are the group overlap integrals (GOIs), which are

$$\left.\begin{aligned}S_\sigma &= S_{p\sigma}\sin\varphi + S_{s\sigma}\cos\varphi\\ S_{p\sigma} &= \sqrt{3}S(p\sigma, d\sigma)\sin^2\vartheta\\ S_{s\sigma} &= \sqrt{3}S(s\sigma, d\sigma)\sin^2\vartheta\\ S_\pi &= -S(p\pi, d\pi)\sin 2\vartheta\end{aligned}\right\}, \qquad (8)$$

where $S(p\sigma, d\sigma)$, $S(s\sigma, d\sigma)$, and $\mathrm{S}(p\pi, d\pi)$ are the two-centered overlap integrals (TOIs); the angle ϑ is shown in figure. In (6) and (7), the bracketed expression is the Mulliken population of the $3d_{xy}$-AO of the copper ion (***Q***). In [4, 6], the components of the g tensor of the complex CuL$_4$ (D_{2d}) were considered while neglecting the density of the unpaired electron on the atoms of L; in this approximation, their expressions follow from (6) and (7) for $x_1^{\mathrm{L}} = x_2^{\mathrm{L}} = 0$.

For the components of the HFC tensor (A tensor), we have

$$\begin{aligned}A_{\parallel} &= -A_{s\mathrm{M}} - \frac{4}{7}P_{3d}(x_0^d)^2\\ &+ P_{3d}(x_0^d)^2\left(8\frac{\xi_{3d}}{\Delta_{\parallel}}\frac{6}{7}\frac{\xi_{3d}}{\Delta_{\perp}}\right) + \frac{4}{5}P_{4p}(x_0^p)^2,\end{aligned} \qquad (9)$$

$$\begin{aligned}A_{\perp} &= -A_{s\mathrm{M}} + \frac{2}{7}P_{3d}(x_0^d)^2\\ &+ \frac{11}{7}P_{3d}(x_0^d)^2\frac{\xi_{3d}}{\Delta_{\perp}} - \frac{2}{5}P_{4p}(x_0^p)^2.\end{aligned} \qquad (10)$$

where the first term is the contribution from the isotropic HFC (IHFC), the second term is the contribution from the anisotropic HFC (AHFC), the third term is the orbital contribution, the fourth term is the contribution from the mixing of the $4p_z$-AO in the MO of the unpaired electron, $A_{s\mathrm{M}}$ is the IHFC parameter, and $\mathrm{P}_{3d(4p)}$ is the AHFC parameter for the 3d(4p)-electron of the free copper ion. In [4], simplified forms of (9) and (10) have been used for quantum-chemical calculations of the parameters of the EPR spectra of pseudotetrahedral copper(II) complexes.

Under the assumption that the principal axes of the LHFC tensor (A^{L} tensor) coincide with the axes of the local systems of coordinates, the expressions for the components of the A^{L} tensor can be written in the form (with the first atom of L as an example):

$$\left.\begin{aligned}A_{z_1}^{\mathrm{L}} &= A_{s\mathrm{L}_1} + 2A_{pz_1} - A_{px_1}\\ A_{x_1}^{\mathrm{L}} &= A_{s\mathrm{L}_1} + 2A_{px_1} - A_{pz_1}\\ A_{y_1}^{\mathrm{L}} &= A_{s\mathrm{L}_1} - A_{px_1} - A_{pz_1}\end{aligned}\right\}, \qquad (11)$$

where $A_{s\mathrm{L}_1}$ is the contribution (parameter) of the ligand IHFC (LIHFC) and the second and third terms are the contributions from the ligand AHFC (LAHFC). The following relations are true:

$$A_{s\mathrm{L}_1} = \frac{1}{4}A_{s\mathrm{L}}^0(x_1^{\mathrm{L}})^2\cos^2\varphi, \qquad (12)$$

$$A_{pz_1} = \frac{1}{10}P_{\mathrm{L}}(x_1^{\mathrm{L}})^2\sin^2\varphi; \quad A_{px_1} = \frac{1}{10}P_{\mathrm{L}}(x_2^{\mathrm{L}})^2. \qquad (13)$$

where $A^0_{s\mathrm{L}}$ and P_L are the LIHFC and LAHFC parameters for the free atom of L.

The average of the components of the A^L tensor is

$$\langle A^\mathrm{L}\rangle = \frac{1}{3}SpA^\mathrm{L} = A_{s\mathrm{L}_1}. \qquad (14)$$

In [3], the expressions similar to (11) have been employed for estimation of the unpaired electron density on the ligands from experimental values of the LHFC parameters.

Formulas (2)–(4) for $x_0^p = z_0^p = x_2^\mathrm{L} = z_1^\mathrm{L} = z_3^\mathrm{L} = 0$ are the MOs of the square-planar complex CuL_4 (D_{4h}) ($S = 1/2$, ground-state term $^2B_{2g}$, $\gamma = 0$, $\vartheta = \pi/2$), where the MO of the unpaired electron describes the in-plane σ-bond and MOs (3) and (4) correspond to the in-plane and out-of-plane metal–ligand π-bonds. Expressions (6), (7), and (9)–(11) for the parameters of the EPR spectra of the pseudotetrahedral copper(II) complex is directly transformed into the respective expressions for the components of the g-, A-, and A^L tensors in the case of the complex CuL_4 (D_{4h}) [5], which ignore the covalence of the in-plane and out-of-plane π-bonds ($y_0^d = z_0^d = 1$; $y_1^\mathrm{L} = z_2^\mathrm{L} = 0$). The aforesaid expressions for the parameters of the EPR spectra of a pseudotetrahedral (or square-planar) complex are true for any copper(II) complex with this symmetry in the context of the approximations used.

PARAMETERS OF COVALENT BONDS

From formulas (9) and (10), we obtain the following equation:

$$(x_0^d)^2 = \frac{C}{B} + D(x_0^p)^2, \qquad (15)$$

where

$$C = \frac{7}{4}\frac{(\langle A\rangle - A_\parallel)}{P_{3d}}, \qquad (16)$$

$$B = 1 - \frac{28}{3}\frac{\xi_{3d}}{\Delta_\parallel} + \frac{5}{6}\frac{\xi_{3d}}{\Delta_\perp}; \quad D = \frac{7}{5B}\frac{P_{4p}}{P_{3d}}. \qquad (17)$$

For the IHFC parameter, we have

$$A_{s\mathrm{M}} = -\langle A\rangle + \frac{4}{3}P_{3d}(x_0^d)^2\left(\frac{2\xi_{3d}}{\Delta_\parallel} + \frac{\xi_{3d}}{\Delta_\perp}\right), \qquad (18)$$

where $\langle A\rangle = 1/3\ (A_\parallel + 2A_\perp)$ is the average of the components of the A tensor.

By equating the expressions for the EPR parameters to their experimental values with regard to the normalization conditions for MOs, we obtain a system of equations for the parameters of covalent bonds (squared MO coefficients). When substituted into the expressions for the EPR parameters, the calculated parameters (covalence parameters) reproduce experimental data and can be used, apart from analysis of the covalent bonding character, to calculate the contributions to the expressions for the components of the g-, A-, and A^L tensors (inverse problem of EPR spectroscopy [7]).

For the complex CuL_4 (D_{2d}), the system includes five equations. By solving this system, we obtain four unknown MO coefficients of the unpaired electron and the parameter $A_{s\mathrm{M}}$. The system consists of Eqs. (6), (9), (10), and (14) and the MO normalization conditions (2). The solution of this system is based on Eqs. (6), (12), and (14)–(18). Then, using formulas (11)–(13), one should the components of the A^L tensor. For the complex CuL_4 (D_{4h}), the system consists of three equations in two unknown MO coefficients of the unpaired electron and the IHFC parameter (Eqs. (9) and (10) and the normalization conditions of MOs for the unpaired electron). The solution of this system is based on Eqs. (15) and (18).

If neglecting all coefficients in MOs (2) but that in front of the $3d_{xy}$-AO, we obtain from Eq. (15) with consideration of Eqs. (6), (7), (9), and (10) the following formula for the ground-state covalence parameter of the complex CuL_4 (D_{2d}):

$$(x_0^d)^2 = \frac{7}{4}\left(\frac{\langle A\rangle - A_\parallel}{P_{3d}} + \frac{2}{3}\Delta g_\parallel - \frac{5}{21}\Delta g_\perp\right), \qquad (19)$$

where $\Delta g_{\parallel,\perp} = g_{\parallel,\perp} - 2.0023$. For the IHFC parameter, the equation is

$$A_{s\mathrm{M}} = -\langle A\rangle + \langle\Delta g\rangle P_{3d}, \qquad (20)$$

where $\langle\Delta g\rangle = \langle g\rangle - 2.0023$ and $\langle g\rangle = 1/3(g_\parallel + 2g_\perp)$ is the average of the components of the g tensor. In the same approximation, formulas (19) and (20) are valid for the square-planar complex CuL_4 (D_{4h}). They are the known Kuska–Rogers formula for the ground-state covalence parameter [8] and the known McGarvey formula for the IHFC parameter [9].

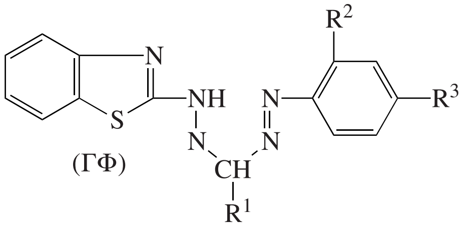
RESULTS AND DISCUSSION

Experimental parameters of the EPR spectra of copper(II) complexes with HF(I) and HF(II) are given in Table 1. The complexes were obtained for metal : ligand ratios of 1 : 2 and 1 : 1 [2]. Table 1 also contains the compositions and symmetry of the coordination polyhedra, pseudotetrahedral angles, IHFC parameters, covalence parameters, and the Mulliken populations of the $3d_{xy}$-AO of the copper ion. The structures of the ligands and their copper(II) complexes with Cu : HF = 1 : 2 and 1 : 1 were considered as described in [2].

Table 1. Experimental EPR parameters, the compositions and symmetries of the coordination polyhedra, pseudotetrahedral angles, IHFC parameters, covalence parameters, and the populations of the $3d_{xy}$-AOs of the copper(II) complexes with HF

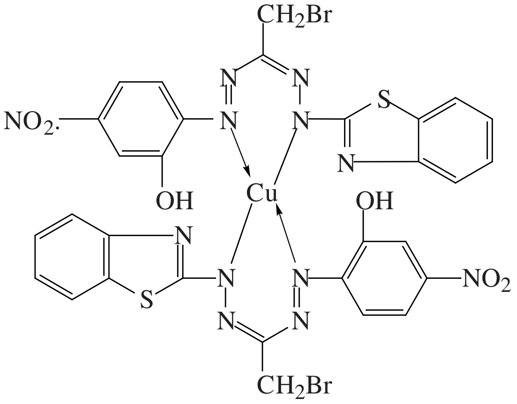
Parameter / Complex	Coordination polyhedron		γ, deg	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	$\langle A^L \rangle$	A_{sM}*	$(x_0^d)^2$**	$(x_0^p)^2$	$(x_1^L)^2$	$(x_2^L)^2$	Q
	composition	symmetry				$\times 10^4$ cm^{-1}								
Cu : HF(I) = 1 : 2	CuN_4	D_{4h}	0	2.215	2.055	183.0	14.4		118.1 (111.8)	0.76 (0.73)		0.49		0.63
Cu : HF(II) = 1 : 2	CuN_4	D_{2d}	~15	2.24	2.063	148.5	12.5	~12	111.7 (104.5)	0.75 (0.66)	0.03	0.33	0.1	0.65
Cu : HF(I) = 1 : 1	CuN_3O	D_{2d}	~25	2.276	2.05	125.4	~13***	~12	102.6 (91.0)	0.83 (0.70)	0.05	0.33	0.05	0.73

Notes: * The value in parentheses was calculated by formula (20).
** The value in parentheses was calculated by formula (19).
*** The presumed value.

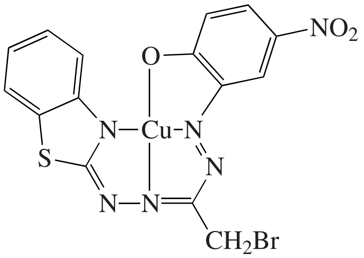


(ГФ)

HF(I): $R^1 = CH_2Br$, $R^2 = OH$, $R^3 = NO_2$;
HF(II): $R^1 = C_2H_5$, $R^3 = SO_3H$;
HF(III): $R^1 = CH_2Br$.



Cu : HF(I) = 1 : 2



Cu : HF(I) = 1 : 1

The complex with Cu : HF(II) = 1 : 2 is similar to the complex with Cu : HF(I) = 1 : 2. Experimental parameters of the EPR spectra of the complex with Cu : HF(I) = 1 : 2 are characteristic of copper(II) complexes with the square-planar coordination polygon CuN_4 (D_{4h}) [5, 10, 11]. The coordination polyhedra of the complexes with Cu : HF(II) = 1 : 2 and Cu : HF(I) = 1 : 1 should be regarded as distorted in a pseudotetrahedral manner (i.e., $CuN_4(D_{2d})$ and $CuN_3O(D_{2d})$, respectively). This is suggested by experimental parameters of their EPR spectra (rotational isomerism effect [12, 13]). The coordination polyhedra in these complexes cannot be regarded as square-planar polygons because the experimental parameters of their EPR spectra do not obey the additivity rule, which is valid for the EPR parameters for copper(II) complexes with square-planar coordination polygons and identical compositions [6, 12]. The γ values were taken from the calculations of bi- and tricyclic copper(II) chelates with the coordination polyhedron $CuN_2O_2(D_{2d})$ [12]. The covalence parameters and the IHFC parameters were determined from experimental EPR parameters by numerical solution of the corresponding systems of equations for the complexes CuL_4 (D_{4h}) and CuL_4 (D_{2d}) via iterative approximations. In the calculations, we used the sp^3-hybridization of the AOs in nitrogen and oxygen and the following atomic parameters: $\xi_{3d} = 829$ cm^{-1}, $P_{3d} = 390 \times 10^{-4}$ cm^{-1} for CuN_4 (D_{4h}) and CuN_4 (D_{2d}), $P_{3d} = 330 \times 10^{-4}$ cm^{-1} for CuN_3O (D_{2d}), $P_{4d} = 420 \times 10^{-4}$, and $P_L = 43.6 \times 10^{-4}$ cm^{-1} [5, 14, 15]. The Cu–L distance was taken to be 2 Å. In the calculation of TOI, the AO of the copper ion was taken from [16, 17] and the AOs of nitrogen and oxygen were taken from [18]. In the case of CuN_3O (D_{2d}), the TOI values were averaged. In the calculation of GOI, the ratio $\tan\gamma \times \tan\vartheta = \sqrt{2}$ was employed. We believe that the components of the A tensor are negative. The energy differences for electron transitions in the complex with Cu : HF(I) = 1 : 2 were taken to be the same as in the complex $Cu(NH_3)_4^{2+}$ with an identical coordination polyhedron (i.e., $\Delta_\parallel = \Delta_\perp = 20\ 700$ cm^{-1}

Table 2. Components of the g tensor and the contributions to the components of the A and A^{L} tensors for the copper(II) complexes with HF

Parameter / Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$*	$A_{\perp}$*	$A_{s\mathrm{L}_1}$	$A_{z_1}^{\mathrm{L}*}$	$A_{x_1}^{\mathrm{L}*}$	$A_{y_1}^{\mathrm{L}*}$
			$\times 10^4$ cm^{-1}					
Cu : HF(I) = 1 : 2	2.207	2.052	–118.1 – 169.4 + + 105.1 = –182.4	–118.1 + 84.7 + + 18.6 = –14.8	18.5	18.5 + 3.2 = = 21.7	18.5 – 1.6 = = 16.9	18.5 – 1.6 = = 16.9
Cu : HF(II) = 1 : 2	2.243	2.062	–111.7 – 167.1 + + 119.3 + 10.1 = = –149.4	–111.7 + 83.6 + + 21.2 – 5.1 = –12.0	12	12 + 2.2 – – 0.4 = 13.8	12 + 0.8 – – 1.1 = 11.7	12 – 0.4 – 1.1 = = 10.5
Cu : HF(I) = 1 : 1	2.279	2.071	–102.6 – 156.5 + + 115.0 + 16.8 = –127.3	–102.6 + 78.3 + + 20.4 – 8.4 = –12.3	12	12 + 2.2 – – 0.2 = 14.0	12 + 0.4 – – 1.1 = 11.3	12 – 0.2 – 1.1 = = 10.7

* The sequence of the contributions is the same as in formulas (9)–(11).

[19]). For the complexes with Cu : HF(II) = 1 : 2 and Cu : HF(I) = 1 : 1, we take $\Delta_{\parallel} = \Delta_{\perp} = 18\,000$ cm^{-1} and $\Delta_{\parallel} = \Delta_{\perp} = 17\,500$ cm^{-1}, respectively, with regard to an energy difference reduction caused by pseudotetrahedral distortion of the complex [20]. The Q values were calculated by using the bracketed expression in Eq. (6).

An analysis of the covalence parameters leads to the following conclusions. The covalence parameters $(x_0^d)^2$ and $(x_1^{\mathrm{L}})^2$ of the complex with Cu : HF(I) = 1 : 2 correspond to their values for copper(II) complexes with a square-planar coordination polygon made up of nitrogen atoms [21, 22]; the unpaired electron is noticeably delocalized. In the complexes with Cu : HF(II) = 1 : 2 and Cu : HF(I) = 1 : 1 (pseudotetrahedral distortion of the coordination polyhedra), the delocalization is lower, which is evident from the total densities of the unpaired electron in the AO of the copper ion and the AOs of nitrogen. This suggests weakening of the ground-state covalent bonding with an increase in γ. A similar dependence was found by quantum-chemical calculations of the electron density in copper(II) complexes with square-planar and pseudotetrahedral structures [4, 20]. A contamination of the $4p_z$-AO of the copper ion in the MO of the unpaired electron is several percent, increasing in more strongly distorted complexes. The covalence parameter $(x_2^{\mathrm{L}})^2$ indicates the presence of a weak π-component in the mixed ground-state σ–π-bond. The increase in Q with γ confirms the conclusion about weakening of the covalent bonding as the result of distortion of the coordination polyhedron. Replacement of the strong electron-withdrawing group $R^3 = NO_2$ by weaker SO_3H in the benzene rings of HF(I) and HF(II) and simultaneous distortion result in virtually the same character of the unpaired electron delocalization in the complexes with Cu : HF(II) = 1 : 2 and Cu : HF(I) = 1 : 2. The covalence parameters calculated by formula (19) overestimate the unpaired electron delocalization and do not correlate with its change in a number of copper(II) complexes with HF according to more thorough calculations. In [22], it has been noted that the use of expressions of the type (19) for calculation of the ground-state covalence parameter can give a wrong trend of changes in the unpaired electron delocalization in the complexes. It can also be seen in Table 1 that $A_{s\mathrm{M}}$ decreases in some copper(II) complexes with HF. Formula (20) reflects these changes in the IHFC parameter.

Calculations of the covalence parameter of copper(II) complexes with the coordination polygon CuN_4 (D_{4h}) from the EPR spectra with consideration of the in-plane and out-of-plane π-bonds show that the unpaired electron delocalization over these bonds are insignificant and the π-bonds are of distinct ionic character [21, 22]. Therefore, neglect of π-bonds in calculations of the covalence and EPR parameters for copper(II) complexes with HF having the same coordination polygon can be regarded as a “good” fit. For pseudotetrahedral copper(II) complexes, a similar approximation at relatively small γ angles ($< \pi/6$) is equivalent to neglect of the pd-mixing of the AO of the copper ion and the bond covalence in MOs (3) and (4). Thus, the approximations used to derive Eqs. (6), (7), and (9)–(11) are quite acceptable for copper(II) complexes with HF that have both the square-planar and pseudotetrahedral symmetry of the nearest metal environment.

The components of the g tensor and the contributions to the components of the A- and A^{L} tensors calculated by formulas (6), (7), and (9)–(11) with the covalence parameters taken from Table 1. Based on the data in Table 2, one can conclude that an increase in the Zeeman coupling parameter $g_{\parallel}$ in some copper(II) complexes with HF correlates with an increase in the unpaired electron density on the copper ion, its decrease on nitrogen atoms, and an increase in Q. Therefore, a change in this parameter can be associated with weakening of the ground-state covalent bonding in more strongly distorted complexes. For all complexes, the IHFC, AHFC, and orbital contributions to the components $A_{\parallel}$ are nearly equal in absolute value. In the complexes with the distorted coordination polyhedron, *pd*-mixing of the AO of the copper ion virtually does not influence the components of the *A* tensor. It is very difficult to identify a particular contribution that is decisive for the behavior of the HFC parameter $A_{\|}$. It should only be noted that the decrease in this parameter in complexes with distorted coordination polyhedra correlates with the decrease in the IHFC parameter. The negative sign of the component $A_{\|}$ is due to the sign of the sum of the IHFC and AHFC contributions; the negative sign of the component $A_{\perp}$ corresponds to the sign of the IHFC contribution. In the components of the A^{L} tensor, the contribution from LIHFC is dominant, which results in insignificant anisotropy of the LHFC tensor characteristic of copper(II) complexes with nitrogen atoms as the nearest environment.

The compositions and symmetries of the coordination polyhedra of copper(II) complexes with HF(III) were not determined reliably because their EPR spectra are poorly informative. A copper(II) complex with HF(III) is interesting in the matrix of an ion-exchange polymer with the following EPR parameters: $g_{\|}$ = 2.215, $g_{\perp}$ = 2.055, $A_{\|} = 124.1 \times 10^{-4}$ cm^{-1}, and $A_{\perp} = 11.5 \times 10^{-4}$ cm^{-1} [2]. The components of the *g* tensor indicate that this complex is identical with the complex with Cu : HF(I) = 1 : 2, while the component $A_{\|}$ suggests its similarity with the complex with Cu : HF(I) = 1 : 1. The contradiction is eliminated under the assumption that the coordination polyhedron of this complex, as well as that of the complex with Cu : HF(I) = 1 : 2, is made up of four nitrogen atoms and is distorted in a non-pseudotetrahedral fashion (CuN_4, symmetry C_{2v}). In this case, the ground-state term is $^2A_1$ and the MO of the unpaired electron is modified as follows:

$$a_1 \sim x_0^d(d_{x^2-y^2}) + x_0^{d_1}(d_{z^2}) + x_0^p(p_z) + x_0^s(s), \qquad (21)$$

where the "metal" part of the MO is written. When the $3d_{z^2}$ character in (21) is suppressed by the 4*s* character of the AO of the copper ion, this modification of the MO corresponds to the same value of the parameter $g_{\|}$ as for the complex with a square-planar coordination polygon. *sd*-Mixing of the AO of the copper ion lowers the IHFC parameter and hence decreases the component $A_{\|}$ in absolute value. In [2], it has been noted that the ligand HF(III) is less stable than the ligands HF(I) and HF(II). Apparently, this can be responsible for the non-pseudotetrahedral distortion of the coordination polyhedron in copper(II) complexes with HF(III).

The performed analysis of the covalent bonding and the EPR parameters for copper(II) complexes with HF leads to the following conclusions. The unpaired electron in the complexes with the square-planar coordination polygon is distinctly delocalized and the covalence of the in-plane and out-of-plane π-bonds in them is insignificant. When the coordination polygon is distorted in a pseudotetrahedral manner, the ground-state covalent bonding weakens, which increases the component $g_{\|}$ in distorted complexes. This reflects the influence of the unpaired electron delocalization on the Zeeman coupling parameters in copper(II) complexes with HF. The MO of the mixed σ–π ground state of the complexes with a pseudotetrahedral coordination polyhedron has a small π-component. A contamination of the $4p_z$-AO of the copper ion in the ground-state MO is insignificant and *pd*-mixing virtually does not influence the HFC parameters. The covalence parameters calculated by the Kuska–Rogers formula overestimate the unpaired electron delocalization and provide a wrong pattern of its changes. In some copper(II) complexes with HF, the IHFC parameter decreases. Among the components of the A^{L} tensor, the main contribution is made by LIHFC, which makes the LHFC tensor only slightly anisotropic. In copper(II) complexes with HF(III), the coordination polygon can undergo non-pseudotetrahedral distortions.

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REFERENCES

1. Lipunov, I.N., Pervova, I.G., Lipunova, G.N., et al., *Koord. Khim.,* 1997, vol. 23, no. 12, p. 934 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 23, no. 12, p. 877].
2. Vishnevskaya, G.P., Frolova, E.N., Pervova, I.G., et al., *Koord. Khim.,* 2005, vol. 31, no. 11, p. 873 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 31, no. 11, p. 828].
3. Deeth, R.J., Hitchman, M.A., Lehmann, G., and Sachs, H., *Inorg. Chem.*, 1984, vol. 23, no. 10, p. 1310.
4. Bencini, A. and Gatteschi, D., *J. Am. Chem. Soc.*, 1983, vol. 105, no. 17, p. 5535.
5. McGarvey, B.R. *Transition Met. Chem.*, New York: Dekker, 1966, vol. 3, p. 89.
6. Rakitin, Yu.V. and Kasumov, R.D., *Koord. Khim.*, 1985, vol. 11, no. 9, p. 1179.
7. Murav'ev, V.I., *Koord. Khim.*, 1989, vol. 15, no. 10, p. 1314.
8. Kuska, H.A. and Rogers, M.T., *ESR of First Row Transition Metal Complex Ions*, New York: Interscience, 1968.
9. McGarvey, B.R., *J. Phys. Chem.*, 1967, vol. 71, no. 1, p. 51.
10. Gusy, C.M., Raynor, J.B., and Symons, M.C., *J. Chem. Soc., A*, 1969, p. 2299.
11. Vishnevskaya, G.P., Molochnikov, L.S., and Safin, R.Sh., *EPR v ionitakh* (EPR in Ion Exchangers), Moscow: Nauka, 1992.
12. Rakitin, Yu.V., Kasumov, R.D., Larin, G.M., et al., *Teoriya EPR nizkosimmetrichnykh kompleksov v modeli uglovogo perekryvaniya* (Theory of EPR of Low-Symmetry Complexes in the Angular Overlap Model), Moscow: VINITI, 1981.
13. Rakitin, Yu.V., Larin, G.M., and Minin, V.V., *Interpretatsiya spektrov EPR koordinatsionnykh soedinenii* (Interpretation of the EPR Spectra of Coordination Compounds), Moscow: Nauka, 1993.

14. Scharnoff, M., *J. Chem. Phys.*, 1965, vol. 42, no. 10, p. 3383.
15. Morton, J.R. and Preston, K.F., *J. Magn. Res.*, 1978, vol. 30, p. 577.
16. Richardson, J.W., Nieupoort, W.C., Powell, R.R., and Edgell, W.F., *J. Chem. Phys.,* 1962, vol. 36, no. 4, p. 1057.
17. Richardson, J.W., Powell, R.R., and Nieupoort, W.C., *J. Chem. Phys.,* 1963, vol. 38, no. 4, p. 796.
18. Clementi, F. and Roetti, C., *Atomic Data and Nuclear Data Tables*, 1974, vol. 14, no. 2, p. 177.
19. Hichman, M.A., *Inorg. Chem.*, 1985, vol. 24, no. 26, p. 4762.
20. Yamabe, T., Hori, K., Minato, T., et al., *Inorg. Chem.*, 1982, vol. 21, no. 5, p. 2040.
21. Murav'ev, V.I., *Zh. Strukt. Khim.,* 1986, vol. 26, no. 3, p. 56.
22. Murav'ev, V.I., *Koord. Khim.*, 2005, vol. 31, no. 9, p. 643 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 31, no. 9, p. 609].