ESR spectroscopy of copper(II) complexes with aza- and thia-containing crown ethers

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Six copper(II) chloride complexes with crown ethers containing besides oxygen also nitrogen or sulfur atoms in 15- or 18-membered cycle were studied by ESR and electron absorption spectroscopies. The g and HFI tensor components determined by spectral simulation indicate rhombic symmetry and localization of an unpaired electron on the d_{xy} orbital for all the complexes. The unpaired electron fractions on σ- and π-type metal ion and ligand AO were estimated from ESR and absorption spectra using LCAO MO method. Both σ- and π-type bond covalences were shown to be greater in these complexes compared to only oxygen-containing crown ether complexes. The temperature dependence of g and A components in some complexes may be due to conformational changes.

Key words: crown ethers, ESR, complexes with copper(II), electron absorption spectroscopy.

Macrocyclic ligands are of considerable interest for designing selective complexones, membrane ionophores, and active-site models of metalloenzymes.[1—10] There is a vast literature on the interaction of crown ethers with alkali and alkaline-earth metals;[2—4] however, little attention has been given to complexation of crown ethers with transition metal ions, in particular, copper(II) ions.[1,5—10]

A number of copper chloride complexes with oxygen-containing crown ethers has been studied by ESR.[9,10] For macrocycles with four or six heteroatoms the g-tensor anisotropy was shown to be the one typical for most copper complexes ($g_{\parallel} > g_{\perp}$), whereas for crown ethers with five oxygen atoms (15-crown-5, benzo-15-crown-5, dibenzo-15-crown-5) an unusual, inverse anisotropy ($g_{\parallel} < g_{\perp}$) was detected. According to the existing theories[11] the inverse g-tensor anisotropy is due to localization of an unpaired electron on the d_{z^2} orbital (unlike the $d_{x^2-y^2}$ ground state with the usual sign of the g-tensor anisotropy). According to ligand field theory[11] the d_{z^2} ground state is realized for the trigonal geometry of a complex or for the oblate octahedral configuration, in which the interaction of a metal ion with axial ligands is stronger than with equatorial ones.

Intensive electronic absorption bands in the visible region ($\varepsilon_{560-670} \approx (1—2) \cdot 10^3$) and ESR spectra with a small g-tensor anisotropy ($g_{\parallel} = 2.088$, $g_{\perp} = 2.0027$), similar to those of blue copper proteins, were detected in complexes of copper with macrocycles containing four sulfur atoms[6,7]. Although subsequent studies, in particular, X-ray data, showed that in plastocyanin and azurin the copper ligands are thiol, thioether (methionine), and two imidazol groups[8], it is of interest from the biomimetic point of view to determine whether it is possible to obtain the spectral and redox parameters in copper complexes with macrocyclic ligands that are similar to the corresponding parameters in blue copper proteins.

In the present study copper(II) complexes with a number of aza- and thin-containing crown ethers were obtained for the first time and the effects of the nature of the heteroatom and the macrocycle size on the electronic structure were studied by ESR and optical spectroscopy methods.

The following crown ethers were studied: 1,10-diaza-18-crown-6 (**1**), *N,N'*-dimethyl(4-bromobenzo)-4,13-diaza-18-crown-6 (**2**), *N,N'*-dimethyl(4-bromobenzo)-4,10-diaza-15-crown-5 (**3**), *N*-methylbenzo-7-aza-15-crown-5 (**4**), 4-bromobenzo-4,13-dithia-18-crown-6 (**5**), 4'-bromobenzo-4,10-dithia-15-crown-5 (**6**).

Experimental

The organic impurity content in the crown ethers did not exceed 2 % according to gas-liquid chromatography data.

Copper chloride ($CuCl_2 \cdot 2H_2O$) of "chemically pure" grade was dehydrated by heating in vacuum (4 Torr) and kept in a hermetically sealed vessel. Chloroform (of "chemically pure" grade) was purified according to a well-known procedure.[12]

Copper complexes were obtained as follows: Weighed portions of crown ether and copper(II) chloride were placed in a stoppered weighing bottle, and the appropriate amount of

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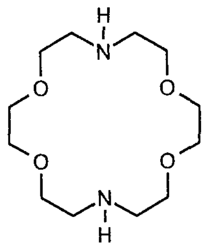

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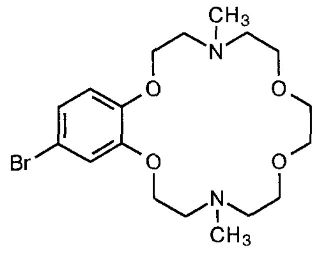

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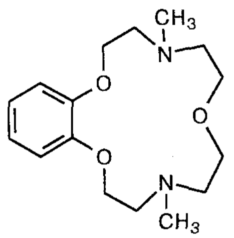

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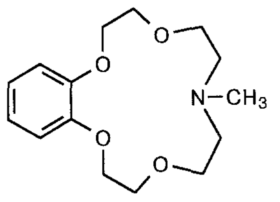

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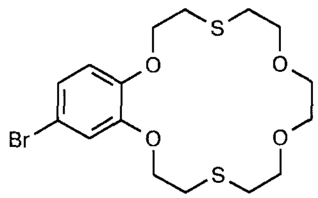

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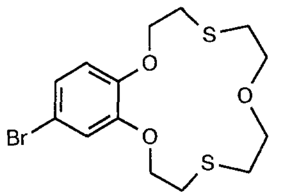

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chloroform was added. Then the mixture was allowed to stand for 24 h to complete the dissolution of Cu(II) chloride. The crown ether/$CuCl_2$ mole ratio was varied from 1:1 to 10:1 for different samples; the absolute copper(II) concentrations were in the range 10^{-2}—$5 \cdot 10^{-4}$ *M*.

The following experiments were carried out to determine the stoichiometry of the complexes. Interaction of $CuCl_2$ with compound **5** in equimolar quantities (10^{-2} *M*) results in complete dissolution of the copper(II) chloride. When $CuCl_2$ was taken in excess, the undissolved sediment was weighed after drying, and the mole ratio of crown ether to copper chloride was determined in solution and found to be equal to unity. The electronic spectra in the visible region and the ESR spectra of all the complexes in solution did not change upon changing the ligand/copper mole ratio from 1 to 10. It follows from these data that the complexes have a 1:1 stoichiometry.

The absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in the range of 200—1100 nm at 20 °C. The ESR spectra were recorded at 77 K and in the interval from −50 to +50 °C on SE/X-2547 (Radiopan) and Bruker ER-200D instruments. The ESR measurements at 77 K were carried out in quartz tubes (diameter 3÷4 mm). The samples were rapidly frozen down to 77 K in a Dewar flask before the measurements. At high temperatures the sample solutions were measured in flat quartz cells. The DPPH sample used as a reference for measuring *g*-values was stuck to the outer side of the Dewar finger. The calibration of the field scan was monitored using a nuclear gaussmeter; the klystron frequency in both spectrometers was measured with an MCM-110 frequency meter (Poland).

Programs for simulating ESR spectra in terms of models with uniaxial *g*-tensor anisotropy, with three different principal *g*-factors, and with a distribution over the *g*-values were developed. Only Zeeman and hyperfine interactions were included in the spin Hamiltonian; the angular dependence of the transition probability[11] and the Lorentz intrinsic line shape were taken into account in the simulations.

Results and Discussion

Electronic absorption spectra of the solutions are presented in Fig. 1. Copper(II) chloride is insoluble in $CHCl_3$, and crown ethers absorb at $\lambda < 300$ nm; therefore, two absorption bands in the 340—430 and 650—750 nm regions correspond to the copper complexes with crown ethers. The extinction coefficients for the shortwave and longwave bands are in the ranges of $(1—4) \cdot 10^3$ and $(1—2) \cdot 10^2$, respectively; the λ_{max} values for the longwave bands are given in Table 1.

ESR spectra of the frozen solutions at 77 K are shown in Figs. 2, 3. The spectral resolution of the hyperfine splitting (HFS) components was found to increase significantly upon increasing the concentration of a free crown ether, the spectral extremum positions being independent of the crown ether/Cu^{2+} ratio. Since pure chloroform does not vitrify on freezing, resolution enhancement at free crown ether concentrations higher than $5 \cdot 10^{-3}$ *M* demonstrates their efficient plasticization effect on the chloroform matrix.

The ESR line shapes at 77 K for all the complexes (except the complex with compound **5**, see Fig. 3) are typical for axial *g*-tensor anisotropy. However, the spectra simulated in terms of this model have a substantially smaller linewidth in the $g_\perp$ region compared to the experimental one if the linewidth values in the parallel orientation are used as the intrinsic linewidth values

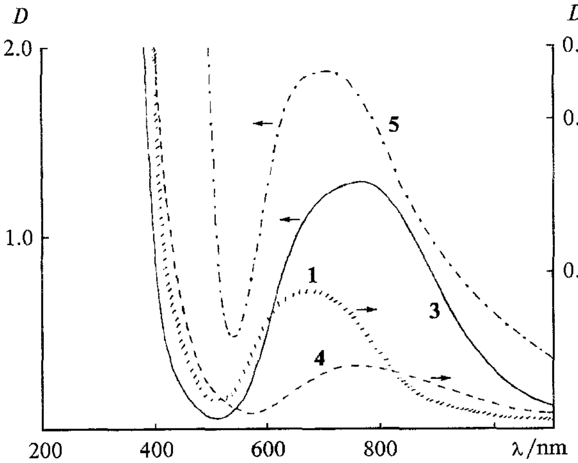

Fig. 1. Electronic absorption spectra of complexes of $CuCl_2$ with crown ethers (in chloroform) at 20 °C, *C*/mol L^{-1} : 10^{-2} (**5**), $8 \cdot 10^{-3}$ (**3**), $8 \cdot 10^{-4}$ (**1**), $5 \cdot 10^{-4}$ (**4**).

Table 1. Electronic absorption and magnetic parameters of copper(II) complexes with crown ethers

Ligand	λ/nm	g_{zz}	g_{xx}	g_{yy}	$g_{\perp}^{*a}$	A_{zz}/G	$A_{\perp}$/G	$A_{\perp}^{*a}$	g_{iso}^{b}	a_{iso}^{b}/G
1	667	2.226	2.01	2.088	2.06	147	15—25	22.5	2.1175	64
2	725	2.2635	2.024	2.064	2.063	151	15	28	2.1358	69.3
3	740	2.2485	2.038	2.078	2.06	155.5	15	28	2.1225	70.7
4	715	2.283	2.045	2.125	—	102.2	20	—	—	—
5^c	688	2.225	—	—	2.015	113	20	23	2.085	53.3
5^c	688	2.195	—	—	—	148	—	—	—	—
6	733	2.20	2.005	2.065	2.04	148.8	10	5.5	2.093	53.3
7^d		2.335	2.081	2.081	—	147	—	—	—	—
8^d		2.345	2.077	2.077	—	126	—	—	—	—
9^d	471	2.00	2.372	2.265	—	121	—	—	—	—
10^d	476	1.995	2.321	2.321	—	130	—	—	—	—

^{a} $g_{\perp}^*$, $A_{\perp}^*$ are determined using the relations $g_{\perp}^* = 1/2 \cdot (3g_{iso} - g_{zz})$ and $A_{\perp}^* = 1/2 \cdot (3a_{iso} - A_{zz})$. ^{b} g_{iso}, a_{iso} are determined from ESR spectra of solutions at 20 °C. ^{c} Two types of complexes with different magnetic parameters are formed for ligand **5**. ^{d} The data of works[9,19].

(ΔH) (Fig. 2). Use of an angular dependence of ΔH such that $\Delta H_{zz} < \Delta H_{\perp}$ is unjustified because the width of the static distribution of the hyperfine tensor component values (A_{zz}) in glass and the relaxational linewidth must be greater in parallel orientation since A_{zz} is much greater than $A_{\perp}$ (see Table 1). This is the case, in particular, for nitroxides[13]. Agreement with experiment is not improved upon increasing $A_{\perp}$ either. The line

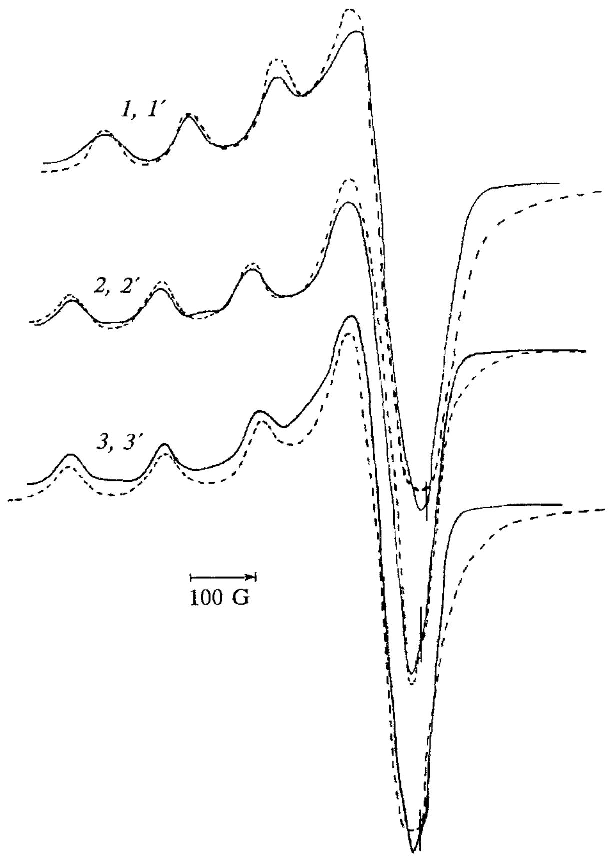

Fig. 2. ESR spectra of complexes of crown ethers **1** (*1*, *1′*), **2** (*2*, *2′*), and **3** (*3*, *3′*) with $CuCl_2$ in $CHCl_3$ at 77 K. Crown ether and copper chloride concentrations are $5 \cdot 10^{-2}$ mol L^{-1} and 10^{-2} mol L^{-1}, respectively. *1′*, *2′*, *3′* — simulated spectra (the *A*- and *g*-tensor components used in the simulations are given in Table 1).

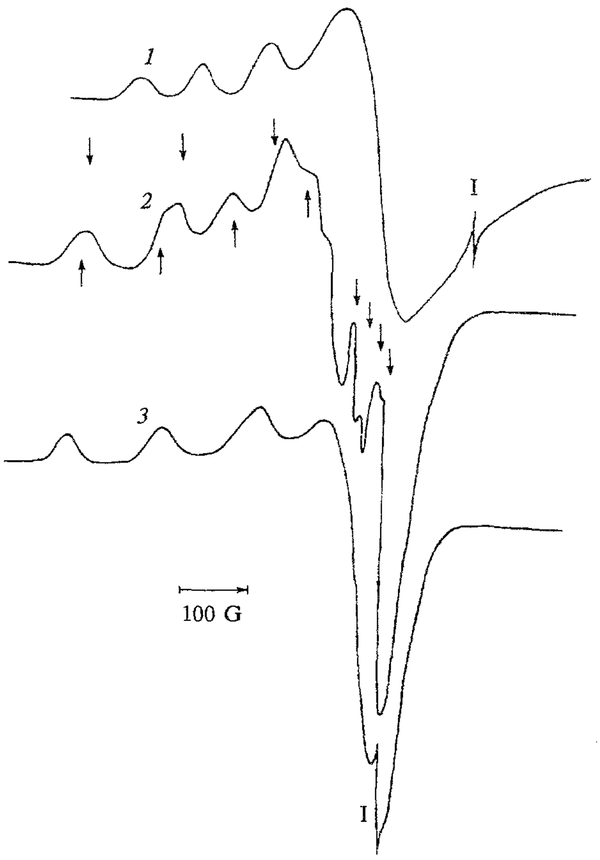

Fig. 3. ESR spectra of complexes of crown ethers **4** (*1*), **5** (*2*), and **6** (*3*) with $CuCl_2$ in $CHCl_3$ at 77 K. Positions of the hyperfine components for two conformational states of a complex with **5** are shown by arrows. I — DPPH signal.

shape depends weekly on $A_{\perp}$ at $A_{\perp} < 20$ G, and at higher $A_{\perp}$ values hyperfine splitting appears in the perpendicular orientation, which is absent in the experimental spectra (except for **5**).

Satisfactory agreement with experiment is given by introducing the model with three different principal g-factors or a distribution over the $g_{\perp}$ values (see Fig. 3). One can expect a lack of tetragonal symmetry because of the nonequivalence of the thia, aza, and oxa ligand groups. Furthermore, the X-ray data for the copper complex with **1**[14] show different bond lengths for the Cu—O and Cu—N bonds (about 2.7 and 2.03 Å, respectively). Therefore, the model with three different principal g-factors was used in subsequent spectral simulations.

Table 1 shows simulated values of A- and g-tensor components as well as $A_{\perp}$ and $g_{\perp}$ values calculated using isotropic a_{iso} and g_{iso} values obtained from ESR spectra of complexes in solution (see below): $A_{\perp} = 1/2 \cdot (3a_{iso} - A_{zz})$ and correspondingly for $g_{\perp}$. Data for copper complexes with 12-crown-4 (**7**), 18-crown-6 (**8**), 15-crown-5 (**9**), and benzo-15-crown-5 (**10**)[9,10] are also given in Table 1 for comparison.

The ESR spectrum of the copper complex with **5** (see Fig. 3) is likely to be a superposition of two ESR signals that have approximately equal statistical weights but different A_{zz} and g_{zz} values (**5a**, **5b** in Table 1). Hyperfine splitting with $A_{\perp} \approx 20$ G appears in the perpendicular orientation (shown with arrows in Fig. 3). Freezing the sample down to 77 K from different temperatures (10—50 °C) did not change the line shape significantly. No superposition was observed in the ESR spectra of this complex in the temperature interval of 20—60 °C; however, such a superposition appears upon lowering the temperature (Fig. 4). The $A_{\perp}$ value determined from the isotropic HFS constant ($a_{iso} \approx 53$ G) under the assumption that Sp A is not temperature-dependent gives for one signal ($A_{\parallel} = 116$ G) good agreement with the value obtained from the spectrum at 77 K (≈20 and ≈21 G, respectively). If one uses the same a_{iso} value for the second signal ($A_{zz} = 146$ G), the resulting $A_{\perp}$ value (6.5 G) is significantly less than the values usually obtained for copper complexes (16—40 G).[8—10,15—19] The a_{iso} value was found to be solvent-dependent: it increases from 53 to 63 G upon passage from chloroform to nitromethane.

The ESR spectra of the complexes in nonviscous solvents ($CHCl_3$ and $MeNO_2$) correspond to complete averaging of the A- and g-tensor anisotropies (see Fig. 4). The isotropic HFS constants in the rapid rotation region do not depend on temperature (295—350 K). The dependences of the hyperfine component intensities on the nuclear spin projection qualitatively correspond to a model of relaxational line broadening due to rotational modulation of g- and A-tensor anisotropies.[20]

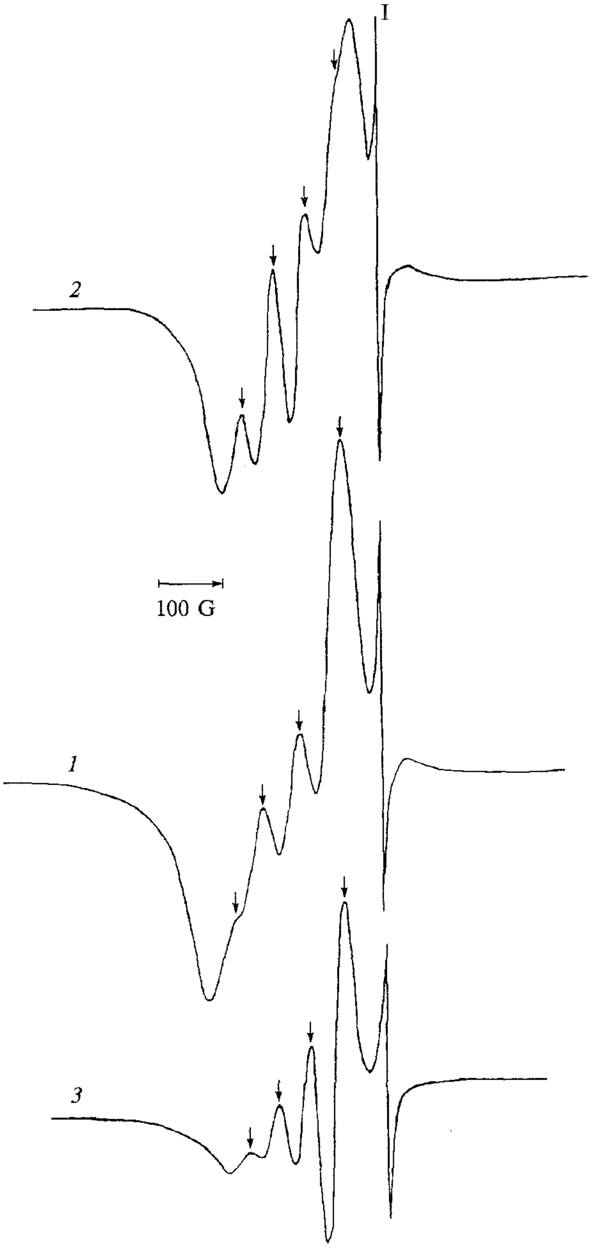

Fig. 4. ESR spectra of complexes of crown-ethers **1** (*1*), **5** (*2*), and **6** (*3*) with $CuCl_2$ in chloroform at 288 K. I — DPPH signal.

The energies and molar extinction values for the longwave bands in the electronic absorption spectra of the complexes (λ ≈ 650—750 nm, ε ≈ 10^2, see Table 1) are characteristic of parity-forbidden d—d transitions.[21] According to crystal field theory[11] the 3d level in octahedral copper complexes is split into a lower doublet ($d_{x^2-y^2}$, $d_{3z^2-r^2}$) and an upper triplet (d_{xy}, d_{xz}, d_{yz}), which are further split into two singlets and a singlet (d_{xy}) and a doublet (d_{xz}, d_{yz}) under tetragonal and rhombic distortions, respectively. The sequence of levels in the lower doublet and, accordingly, the localization of the unpaired electron can be determined from the sign of the g-tensor anisotropy. The positive and negative values of

Δg ($\Delta g = g_{zz} - g_{\perp}$) correspond to localization of the unpaired electron in the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ level, respectively. Most of the copper complexes studied have $\Delta g > 0$.[8–15,15–19] However, copper chloride complexes with oxygen-containing crown ethers were found to have $\Delta g > 0$ if a macrocycle has 4 or 6 oxygen atoms, and $\Delta g < 0$ if there are 5 oxygen atoms in a macrocycle.[9,10]

Table 1 shows that for all the complexes with crown ethers **1—6**, including ligands with five heteroatoms (**3**, **4**, **6**), g_{zz} exceeds g_{xx} and g_{yy}, the differences between g_{xx}, g_{yy} being significantly less than between the latter components and g_{zz}. Thus, the unpaired electron in these complexes occupies the $d_{x^2-y^2}$ orbital, and prolate octahedron structure is realized in which the interaction of the copper ion with axial ligands (Cl^- ions) is weaker than with equatorial ligands (macrocycle). The differences in electronic structure between the complexes **3**, **4**, **6** and the oxygen-containing analogs **9**, **10** are evidently due to the greater coordinating ability of N or S atoms compared to oxygen atoms in ethers.

The identification of the ground state ($d_{x^2-y^2}$ or d_{xy}, depending on the orientation of the x and y coordinate axes[19]) allows one to assign the absorption in the 650—750 nm region to the d_{xy}—$d_{x^2-y^2}$ transition. The absorption bands in the 340—430 nm (23,000—29,000 cm^{-1}) region, also observed in other copper complexes, are assigned in some publications to d—d transitions ($d_{x^2-y^2}$—$d_{xz,yz}$).[15,18] However, in our case this assignment seems to be unlikely because of the high intensities of these bands, or at least the d—d transitions are superimposed on another, more intense absorption band. The dependence of the absorption wavelength on the nature of the heteroatom ($\lambda \approx 350$ and 430 nm for the diaza- and dithiaderivatives, respectively) suggests that this absorption is due to intramolecular ligand-metal charge transfer.

Among the complexes studied, X-ray data are available only for the complex with compound **1**.[14] The Cu—Cl bond lengths are 2.284 and 2.337 Å, Cu—O — 2.7 and 2.754 Å, Cu—N — 2.03 and 2.039 Å. The Cu—S bond length in the copper complex with 1,4,8,11-tetrathia cyclotetradecane is 2.3 Å.[6] One may suppose that similar interatomic distances are realized in the remaining complexes. Thus, the difference between g_{xx} and g_{yy}, indicating rhombic symmetry of the electronic distribution in the complexes, is in agreement with X-ray data. However, the differences between g_{xx} and g_{yy} are rather small despite the significant differences in the Cu—O and Cu—N bond lengths. One notes that a difference between g_{xx} and g_{yy} was not detected in copper salicylaldimine,[22] where a copper ion is coordinated with two nitrogen and two oxygen atoms. The weaker interaction of copper ions with Cl^- compared to the equatorial ligands is in agreement with the position of these ligands in the spectrochemical series.[21]

The numerical g_{zz} and $g_{\perp}$ values (see Table 1) are indicative of the inadequacy of crystal field theory for the complexes studied. In fact, according to this theory,[11]

$$g_{zz} = 2.0023 - \frac{8\lambda}{\Delta E_{xy}},$$
$$g_{\perp} = 2.0023 - \frac{2\lambda}{\Delta E_{xz,yz}}, \qquad (1)$$

where λ is the spin-orbit coupling constant for Cu^{2+}, ΔE_{xy}, $\Delta E_{xz,yz}$ are the energy differences between the ground state level ($d_{x^2-y^2}$) and the d_{xy} and $d_{xz,yz}$ levels, respectively; $\lambda = -828$ cm^{-1} for a free copper ion, and ΔE_{xy} is 14,000—16,000 cm^{-1} for different complexes on the average (Table 1). This gives values of 2.4÷2.5 for g_{zz}, which are significantly greater than the experimental g_{zz} values (see Table 1).

The above discrepancy is evidently due to the fact that a copper-ligand bond has a covalent character to a significant extent, which is neglected by crystal field theory. Therefore, we used the LCAO MO method for interpreting the magnetic tensor values. In order to allow for the D_{2h} (rather than D_{4h}) symmetry of the complexes the x and y coordinate axes were taken along the bisecting lines of the angles between the Cu—N and Cu—O bonds rather than along these bonds.[19] As a result the $d_{x^2-y^2}$ orbital transforms into the d_{xy} orbital and vice versa. The following molecular orbitals can be formed from copper ion and equatorial ligand orbitals:

$$\Phi(B_{1g}) = \alpha\, d_{xy} - \frac{\alpha'}{2}\left[-\sigma_{xy}^{(1)} + \sigma_{xy}^{(2)} + \sigma_{xy}^{(3)} - \sigma_{xy}^{(4)}\right],$$

$$\Phi(B_{2g}) = \delta\, d_{xy} - \frac{(1-\delta^2)^{1/2}}{2}\left[p_z^{(1)} + p_z^{(2)} - p_z^{(3)} - p_z^{(4)}\right],$$

$$\Phi(A_g) = \beta\, d_{x^2-y^2} - \frac{(1-\beta^2)}{2}\left[-p_{xy}^{(1)} - p_{xy}^{(2)} - p_{xy}^{(3)} - p_{xy}^{(4)}\right], \qquad (2)$$

$$\Phi(B_{2g}) = \delta\, d_{xy} - \frac{(1-\delta^2)^{1/2}}{2}\left[p_z^{(1)} + p_z^{(2)} - p_z^{(3)} - p_z^{(4)}\right],$$

$$\Phi(B_{3g}) = d_{xz},$$

where σ_{xy}, p_{xy}, p_z are ligand orbitals.

The wave functions $\Phi(B_{1g})$, $\Phi(A_{1g})$, $\Phi(B_{3g})$ represent σ-bonding and in-plane and out-of-plane π-bonding, respectively (the symbols B_{1g}, B_{2g}, B_{3g}, and A_g denote irreducible representations of the group D_{2h}). Overlap is included in (2) only for the d_{xy} and σ_{xy} ligand orbitals having the maximum σ-character. The following expressions for the g- and A-tensors are obtained when passing to the spin Hamiltonian with the above wave functions[18,19]:

$$g_{zz} = g_0 - \frac{8\lambda}{\Delta E_{x^2-y^2}}\left[\alpha^2\,\beta^2 - f(\beta)\right],$$
$$g_{xx} = g_0 - \frac{2\lambda}{\Delta E_{xz}}\left[\alpha^2 - \alpha\alpha' S\right], \qquad (3)$$
$$g_{yy} = g_0 - \frac{2\lambda}{\Delta E_{yx}}\left[\alpha^2\,\delta^2 - \alpha\alpha' S\delta^2\right],$$

$$A_{zz} = p\left\{-\alpha^2\left(\frac{4}{7} + \text{æ}\right) - 2\lambda\alpha^2\left[\frac{4b}{\Delta E_{x^2-y^2}} + \frac{3}{14}\left(\frac{\delta}{\Delta E_{yz}} + \frac{1}{\Delta E_{xz}}\right)\right]\right\}$$
$$A_{\perp} = p\left[\alpha^2\left(-\frac{2}{7} - \text{æ}\right) - \frac{22}{14}\frac{\lambda\alpha^2}{\Delta E_{xy}}\right], \qquad (4)$$

$$f(\beta) = \alpha\alpha'\beta^2 S + \alpha\alpha'(1 - \beta^2)^{1/2} \cdot T(n)/2, \qquad (5)$$

where S are the overlap integrals between the d_{xy} and σ ligand orbitals; $P = 0.036\ \text{cm}^{-1}$, $\text{æ} = 3/7$.

The $T(n)$ values are expressed in terms of the effective charges on the O, N, and S atoms. According to the estimates[18,19] these values are 0.220, 0.330, and 0.440, respectively.

The α^2 values, which characterize the unpaired electron density on the d_{xy} orbital, can be calculated using the approximate relation[18]

$$\alpha^2 = -(A_{zz}/0.036) + (g_{zz} - 2) + 3/7(g_{\perp} - 2) + 0.04, \qquad (6)$$

where A_{zz} is measured in cm^{-1}.

The overlap integrals S are needed for determining the α', β, and δ values from equations (3)—(6). The normalization condition gives

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha' S = 1, \qquad (7)$$

where $S = 1/2(S_1 + S_2 + S_3 + S_4)$, $S_i = \langle d_{xy}/\sigma_{xy}^{(i)}\rangle$ is the overlap integral with the σ-orbital of the i-th ligand. The S_i values were estimated[18,19] for the N, S, and O atoms using hydrogenlike wave functions and a ligand-metal distance of 1.9 Å. We took the bond lengths for complexes **1**—**6** from the X-ray data: $R_{Cu-N} = 2.035$ Å, $R_{Cu-S} = 2.3$ Å, $R_{Cu-O} = 2.7$ Å obtained, for complexes with **1** [14] and tetrathiacrown ether[6]. The estimates of S_i using these distances gives 0.045, 0.01, and 0.0015 for the nitrogen, sulfur, and oxygen atoms, respectively.

Self-consistent estimates of the coefficients α^2, α'^2, β^2, and δ^2 of equations (3)—(7) using iterations show that the δ^2 value, which characterizes the π-bonding in the plane perpendicular to the macrocycle, is close to 1 on the average. However, a significant scatter in the δ^2 values is observed when this quantity is determined from different parameters (g_{xx}, g_{yy}, $A_{\perp}$) with allowance for experimental uncertainties (Table 1). Therefore, we put $\delta^2 = 1$ and determined the parameters α^2, α'^2, and β^2 in the axial anisotropy approximation. Table 2 shows these values for the complexes studied in the present work as well as the values calculated by us for the complexes with **7** and **8**, and the α^2 values for the complexes with **9** and **10** taken from published data[9,10].

Table 2. Unpaired electron fraction in the d_{xy} (α^2), $d_{x^2-y^2}$ (β^2) orbitals of a copper(II) ion and σ ligand orbitals (α'^2)

Ligand	α^2	α'^2	β^2
1	0.67	0.38	0.845
2	0.716	0.33	0.84
3	0.716	0.33	0.78
4	0.615	0.39	0.97
5*	0.58	0.43	0.84
5*	0.64	0.37	0.73
6	0.65	0.40	0.72
7	0.815	0.185	0.89
8	0.77	0.23	0.96
9	0.936	0.064	—
10	0.936	0.064	—

* See explanations to Table 1.

The following conclusions can be drawn from the data presented in Tables 1 and 2. The α^2 values for the complexes with the crown ethers **1**—**6** are in the range of 0.61—0.72, *i.e.*, they are noticably different from 1, indicating significant covalence of the σ-bonds between a copper ion and a crown ether (the lower the α^2 value, the greater the bond covalence). No distinctive dependence of the parameters A, g, ΔE_{xy}, α^2, α'^2, β^2 on the number of heteroatoms (or the macrocycle size) was detected (compare **2**, **3** and **5**, **6**). It appears that because of conformational flexibility complex formation also occurs when the cavity size exceeds the copper ion radius. It is seen (Table 2) that the α^2 and β^2 values for diaza- and dithiaderivatives are similar, though some tendency toward greater covalence is observed for dithiacrown ethers, which correlates with the somewhat smaller g_{zz}—g_0 values for these complexes. A substantially smaller A_{zz} value and, correspondingly, greater covalence of the σ-bonds with ligands compared to diazacrown ethers are observed for the monoazaderivative **4**. It is to be noted that the α^2 value is definitely higher (the covalence is lower) for the usual crown ethers **7**,**8** that contain neither sulfur nor nitrogen. The σ-bond covalence has the least values (i.e., the bonding is essentially ionic) in the complexes with the compounds **9**, **10**, where an unpaired electron occupies the $d_{3z^2-r^2}$ orbital.

The coefficient β^2 similarly characterizes the covalence of the in-plane π-bonds of a copper ion with a crown ether. One can see that although $\beta^2 > \alpha^2$, β^2 also certainly differs from unity for the complexes with compounds **1**—**3** and **5**,**6**. Similarly to α^2 there is also a tendency toward greater covalence in dithiaderivatives compared to diazacrown ethers. Of interest is the virtual absence of in-plane π-bonding in the complex with monoazacrown ether **4** as well as in the complexes with oxygen-containing ligands **7** and **8**.

The ESR signals of the complex with **5** with different parameters A_{zz} and g_{zz} apparently correspond to two different conformational states of the complex. The second state (A_{zz} = 146 G) is observed only at 77 K, while at ~20 °C the first form predominantly exists, for which a_{iso} = 53 G in solution and the relation $a_{iso} = 1/3 \cdot (A_{zz} + 2A_{\perp})$ holds. The increase in a_{iso} from 53 to 63 G upon passage from chloroform to nitromethane is difficult to explain by the direct influence of the solvent molecules on the copper ion, because the coordination sites in the complex are occupied, and both chloroform and nitromethane are weak ligands. At the same time the use of a_{iso} = 63 G instead of 53 G in $CHCl_3$ gives reasonable $A_{\perp}$ values for second state: $A_{\perp} = 1/2 \cdot (3a_{iso} - A_{zz})$ = 23.5 G. Therefore, one can suppose that in the more polar nitromethane at ~20 °C second conformation is predominantly stabilized, to which greater solvation of the crown ether and higher a_{iso} value correspond.

It can be concluded from the data presented in Table 1 that the conformation of the copper complexes with compounds **2**,**3**, and **6** is also temperature-dependent. Thus, the $A_{\perp}$ values for **2** and **3** determined by simulation of the ESR spectra measured at 77 K and the values calculated from the expression for the trace ($A_{\perp}$*) using a_{iso} values measured at 20 °C are substantially different. The $A_{\perp}$* value for the complex with **6** calculated from the tensor trace is too low (5—6 G). The existence of different conformations of crown ethers and their complexes with alkali metals follows from IR spectral data and quantum-mechanical calculations[3].

Thus, the electronic parameters of the crown ether complexes that include different heteroatoms (O, N, and S) in a macrocycle differ substantially from those of the complexes with only oxygen- or thia-containing crown ethers.[6,7] In contrast to the first ones they have greater covalence of the σ-bonds and a greater contribution of π-bonding to the stability of the complex. Ligands with five heteroatoms apparently do not form oblate octahedra upon interaction with copper chloride because of greater covalence and bond energies. At the same time, the electronic parameters of the complexes do not depend strongly on the macrocycle size due to "conformational adjustment."

The magnetic and electronic absorption parameters of the complexes studied differ substantially from those of the tetrathiacrown ether complexes as well: the *g*-tensor anisotropies are greater, correspondingly the bond covalences are smaller, and whereas the positions of the absorption maxima in the electronic spectra are close together, the extinction of the longwave band ($\approx 1 - 2 \cdot 10^2$) is much less than in the tetrathiaderivatives ($\varepsilon \approx 1 - 2 \cdot 10^3$) and copper blue proteins[8]. In this respect the ligands studied are not adequate models of the ligand environment in these proteins. However, it cannot be excluded that deformation of the ligands including the N, O, and S heteroatoms, which can be stabilized in a protein due to its ternary structure, can result in an increase in the probabilities of d—d transitions and a decrease in magnetic anisotropy. The preparation and investigation of these conformationally nonequilibrium crown ether model complexes is the subject of our next study.

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