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Spin exchange between transition metal complexes and nitroxyl radicals in nonaqueous media

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New complexes of diaza- and tetraaza-containing crown ethers, *viz.*, 1,10-diaza-18-crown-6 (**1**), 1,4,8,12-tetraazacyclopentadecane (**2**), 1,4,8,11-tetraazacyclotetradecane (**3**), and 1,4,8,11-tetraazacyclotetradecane 1,4,8,11-tetrachloride tetraacetic acid tetrahydrate (**4**), with the divalent copper and nickel ions and the Cl^-, Br^-, ClO_4^-, NO_3^-, and AcO^- counterions were synthesized. The exchange interactions of these compounds and paramagnetic copper and nickel salts with the TEMPO radical in MeOH—$CHCl_3$ binary mixtures of different compositions were studied. The plots of the linewidths of the hyperfine coupling components of TEMPO *vs.* concentration of the ions and temperature show that the frequency of diffusion collisions is the rate-limiting step for spin exchange (strong exchange regime). A strong dependence of the exchange rate constant (k_{ex}) on the crown ether and counterion structure was found. The isotropic hyperfine coupling constants (a_{Cu}) and g factors (g_i) were measured for the Cu^{II} complexes with the crown ethers. In the case of the crown ether complexes **1**—**3** with $CuCl_2$, the a_{Cu} constant decreases linearly with an increase in $\Delta g_i = g_i - 2.0023$ in the series **3** < **2** < **1**, whereas k_{ex} increases linearly in the same series with a decrease in the contact HFC on the Cu^{II} nucleus (K) and a decrease in covalence of bonding. For the complexes of **2** with Cu^{II} and different axial ligands (counterions), k_{ex} increases in the series $Cl^- < ClO_4^- \le AcO^- \le Br^- < NO_3^-$. In the case of the complexes of **2** with $NiCl_2$, k_{ex} increases in the series **1** < **4** < **3** ≈ **2**. For the Cu^{II} and Ni^{II} salts with the Cl^-, ClO_4^-, and NO_3^- anions, the k_{ex} values are almost independent of the anion nature. The correlation of the k_{ex} values with the electron-spin parameters of the complexes is discussed.

Key words: ESR spectroscopy, complexes with copper ions, complexes with nickel ions, azacrown ethers, spin exchange, tetramethylpiperidineoxyl.

Spin exchange in solutions of paramagnetic species provides an information on the translational dynamics, elementary collision acts, and microtopography of biomolecules.[1—5] In the case of transition metal complexes often exhibiting the catalytic activity, it is of special interest to study the exchange of unpaired electrons in collisions with other paramagnetic species (free radicals) and the dependence of this process on the structure of organic ligands. This interest is evoked, in particular, by common features of spin exchange and electron transfer reactions. In particular, if the molecular orbitals determining the exchange integral (J) are the same as those involved in the electron transfer, then the J value and the squared electronic matrix elements for the tunneling electron transfer are related by a proportional law.[6,7]

Another important area of application of spin exchange between paramagnetic ions and nitroxyl radicals has been developed in the recent years to establish the spatial arrangement and conformation of spin-labeled proteins and peptides in membranes (see, *e.g.*, Ref. 8). Differences observed in these experiments for the spin exchange rates for different ions or complexes at different depths of the membrane[9] can be due to differences in the partition coefficients of these ions and accessibility of spin-labeled functional groups or the influence of counterions and ligands of the paramagnetic complexes themselves. In this connection, it seems important to study the mechanisms and parameters of spin exchange for simpler model systems, namely, nitroxyl radicals and transition metal complexes in nonaqueous media. Both salts of transition metals[9] and their complexes in the membrane can act as paramagnetic ions. Therefore, aza-containing crown ethers are of interest because they form complexes with transition metal ions in low-polar solvents[10—13] and, hence, can serve as ionophores for biologically active copper, nickel, iron, cobalt, and other active ions in lipid membranes.[14]

In this work we prepared new copper(II) and nickel(II) complexes with diaza- and tetraazacrown ethers and studied the regularities of spin exchange between these

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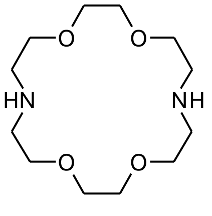
complexes and between the corresponding copper and nickel salts and TEMPO in MeOH—$CHCl_3$ mixtures, depending on the nature of the counterion and temperature.

Experimental

The nitroxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was synthesized according to a previously published procedure[15] at the Institute of Chemical Physics of the Russian Academy of Sciences. The following reagents were used: salts $NiCl_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, and $Cu(ClO_4)_2 \cdot 6H_2O$; MeOH (Merck, Germany); crown ethers (CE) 1,10-diaza-18-crown-6 (**1**), 1,4,8,12-tetraazacyclopentadecane (**2**), 1,4,8,11-tetraazacyclotetradecane (**3**), and 1,4,8,11-tetraazacyclotetradecane 1,4,8,11-tetrachloride tetraacetic acid tetrahydrate (**4**) (Fluka, Switzerland); and salts $Cu(AcO)_2 \cdot H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $NiBr_2 \cdot 3H_2O$, and $Ni(AcO)_2 \cdot 4H_2O$ (reagent grade or analytical grade). Anhydrous $CuCl_2$ and $CuBr_2$ were prepared by heating of the corresponding crystal hydrates *in vacuo* (4 Torr) at 120 °C to a constant weight as described previously.[13] Chloroform and DMSO were purified using known procedures[16] and used at most two months after purification.



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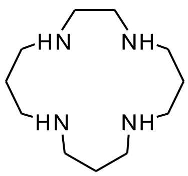

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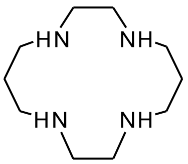

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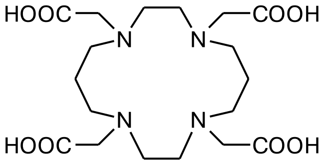

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Complexes with CE in a solution were prepared by mixing solutions of the corresponding salts in MeOH and CE in $CHCl_3$. The formation of complexes was detected by a shift of the d—d-absorption band in the visible spectral region and from a change in the rate of spin exchange with the TEMPO radical. Studies of these changes with the ratio of the molar concentrations of CE and salt showed that in the case of **1** >95% of all M^{II} ions (Ni^{II} or Cu^{II}) were bound to form a complex at [**1**] : [Me^{II}] = 4 : 1 and $CHCl_3$: MeOH = 4 : 1 (vol.) (mixture with this composition was chosen because it is conventionally used for dissolution of phospholipids). For CE **2**—**4**, the complex formation rates with transition metal ions are much higher,[17] and the almost complete ion binding in the same solvent is observed already at CE : $M^{II} \approx 1 : 1$. The reactions of several salts with CE, in particular, $Cu(ClO_4)_2$ with CE **3**, $Ni(ClO_4)_2$ with CE **2** and **3**, in a MeOH—$CHCl_3$ (1 : 4) mixture resulted in the precipitation of crystals.* In this case, a higher concentration of MeOH in a MeOH—$CHCl_3$ (1 : 2) mixture was necessary to dissolve the complexes. Neat MeOH was used as solvent in the synthesis of the $Ni(ClO_4)_2$—**4** complexes. However, the $Cu(ClO_4)_2$—**4** complex is insoluble even in neat MeOH.

TEMPO was added to a solution of a complex or salt until the final concentration achieved $\sim 3 \cdot 10^{-4}$ mol L^{-1}. Samples were placed in capillaries 1 mm in diameter, and the capillaries were sealed without removal of dissolved oxygen. ESR spectra were recorded on a Bruker ER-200 instrument at a temperature maintained constant with an accuracy of ±0.5 °C. The modulation amplitude and decreasing microwave field powder corresponded to the recording of the non-distorted line shape. To determine the *g* factors of the copper(II) complexes, the klystron frequency was measured on an MSM-10 frequency-meter (Poland) and polycrystalline powder of diphenylpicrylhydrazyl (DPPH) was used as internal standard ($g = 2.0034$). The capillary with DPPH was attached directly to the sample.

Optical spectra were recorded on a Hitachi-330 spectrophotometer in Hellma cells (USA) with blackened edges to detect the absorption maximum with the optical density >~0.01.

The viscosity of solvents was measured using a Heppler viscosimeter, which was calibrated against pure MeOH. The accuracy of measurements was at most ±2%.

The initial ESR line shape of TEMPO in the absence of paramagnetic ions or complexes is a convolution of the inhomogeneous Gaussian broadening caused by the unresolved HFS on the protons of the Me groups and the homogeneous Lorentzian broadening. The Gaussian broadening between the points of the maximum slope is[18] $\Delta H_{pp}{}^{G} = 1.19$ G for a solution of TEMPO in CCl_4. We used this value to calculate the Lorentzian linewidth ($\Delta H_{pp}{}^{L}$) by the Dobryakov—Lebedev formula[19]

$$(\Delta H_{pp}{}^{G}/\Delta H_{pp})^2 + \Delta H_{pp}{}^{L}/\Delta H_{pp} = 1,$$

where ΔH_{pp} is the observed linewidth.

Results and Discussion

Plots of ESR linewidths for TEMPO *vs.* concentration of complexes. The plots of $\Delta H_{pp}{}^{L}$ for TEMPO *vs.* concentration of the CE complexes are satisfactorily described by straight lines for all the complexes and temperatures. The examples of these plots for the copper and nickel complexes are presented in Fig. 1. Similar linear plots were obtained for solutions of copper chloride, perchlorate, and nitrate. In the case of the nickel salts with the same anions, linear concentration plots were observed only at $c > 5$ mmol L^{-1}. The measured viscosities of MeOH—$CHCl_3$ mixtures lie in an interval of 0.5—0.9 cP. According to the theoretical estimates,[1—3] at such viscosities the contribution of the dipole interaction to the concentration broadening of the ESR lines is negligible compared to the exchange interaction. Therefore, the bimolecular spin exchange rate constants were determined

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* The preparation of the complexes in the crystalline state and their ESR study will be published in more detail elsewhere.

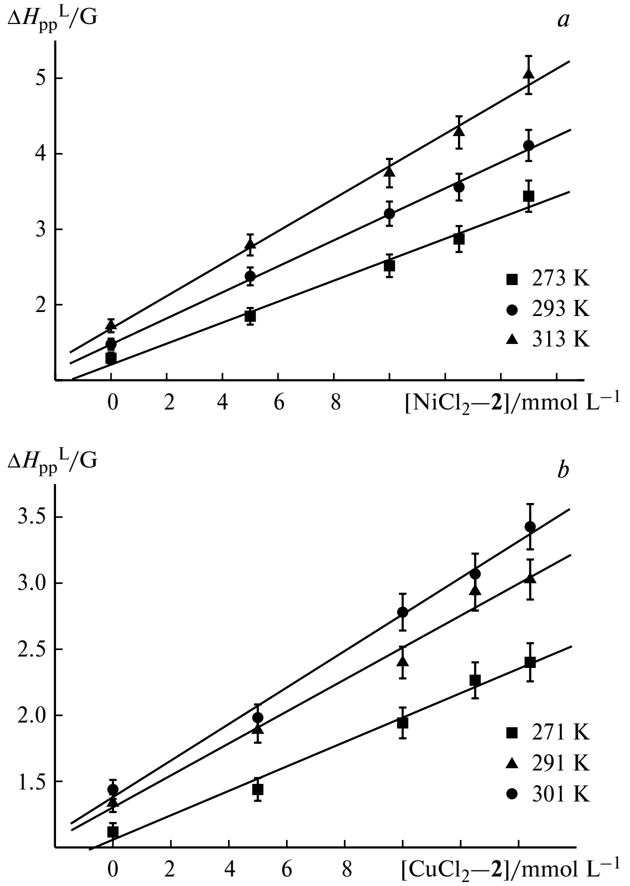

Fig. 1. Plots of the Lorents linewidths ($\Delta H_{pp}{}^L$) of the HFC component $m = 0$ for the TEMPO radical *vs.* concentration of the $NiCl_2$—**2** complexes in a MeOH—$CHCl_3$ (1 : 2) mixture (*a*) and of $CuCl_2$—**2** in MeOH—$CHCl_3$ (1 : 4) (*b*) at different temperatures.

Table 1. Temperature plots of the spin exchange constants (k_{ex}) for the nickel and copper complexes with crown ethers **1**—**3** in MeOH—$CHCl_3$ mixtures

Salt	MeOH : $CHCl_3$	T/K	$k_{ex} \cdot 10^{-9}$/L mol^{-1} s^{-1}		
			1	**2**	**3**
$NiCl_2$	1 : 2	273	0.50	2.12	2.04
		283	0.535	—	—
		293	0.66	2.62	2.53
		303	0.74	—	—
		313	0.97	3.28	3.15
	1 : 4	273	0.38	1.68	—
		293	0.74	2.3	—
		313	—	2.89	—
$CuCl_2$	1 : 4	271	1.815	1.41	0.75
		291	2.3	1.77	1.02
		301	—	2.12	1.17
$Cu(ClO_4)_2$	1 : 4	271	—	1.90	2.43
		291	—	2.70	3.32

from the slopes of the concentration plots for the ESR line broadening (see Table 1).

Temperature plots of spin exchange constants. The data presented in Table 1 show an increase in k_{ex} with temperature for all complexes. Moreover, as seen in Fig. 2, the changes in k_{ex} within the experimental error depend linearly on T/η (η is the macroscopic viscosity). This character of the temperature dependences of k_{ex} is indicative of the "strong" exchange regime.[1] Simultaneously such a character can point out to the absence of microheterogeneities from the binary solvents used because a correlation between the k_{ex} values and microviscosity was absent from other binary mixtures, where microheterogeneities were found[20] by independent methods.

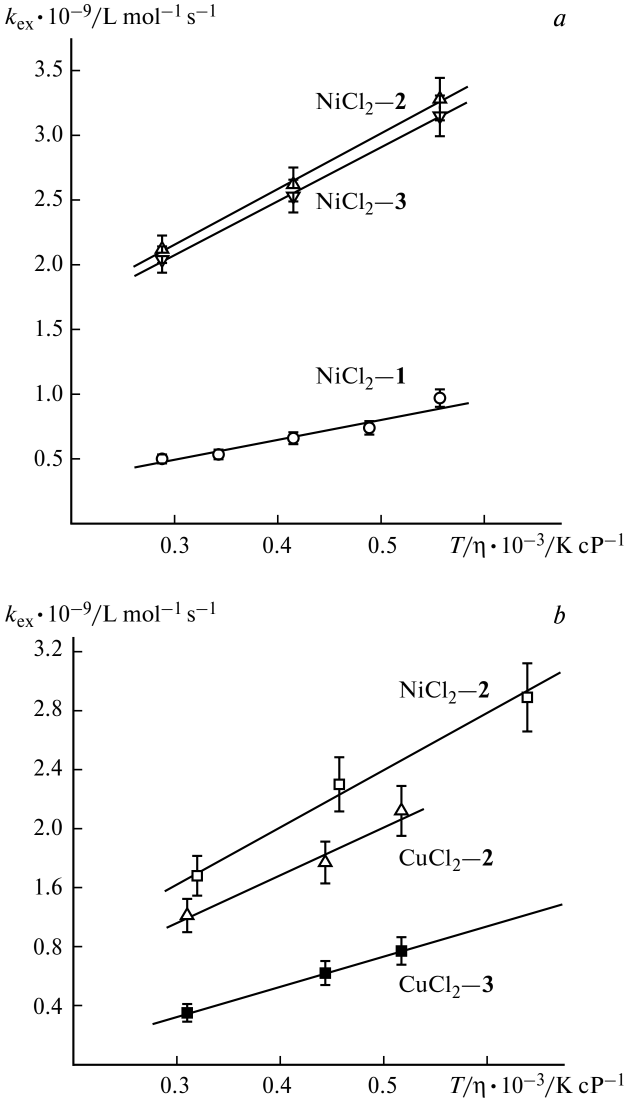

Fig. 2. Temperature—viscosity plots of the bimolecular spin exchange constants (k_{ex}) between TEMPO and the copper(II) and nickel(II) complexes with crown ethers in MeOH—$CHCl_3$ mixtures with the volume ratios of the components 1 : 2 (*a*) and 1 : 4 (*b*).

According to the current theoretical concepts,[1,2] the spin exchange constant can be presented as the product

$$k_{ex} = fpk_D, \qquad (1)$$

where k_D is the rate constant of diffusion collisions, p is the rate constant of spin exchange during collisions, f is the steric factor that takes into account the anisotropy of spin exchange, *i.e.*, its dependence on the orientation of colliding particles. When the Stokes—Einstein law holds for the translational diffusion of the complex and nitroxyl radical and the hydrodynamic radius and collision radius are equal, the following equation is valid:

$$k_D/\text{L mol}^{-1}\text{ s}^{-1} =$$

$$= (2k_BT/3\eta)[(R_{NO} + R_{compl})^2/(R_{NO}\cdot R_{compl})]\cdot 10^{-3}N_A, \qquad (2)$$

where N_A is Avogadro´s number, and k_B is the Boltzmann constant.

The following relation holds for the p value[1]:

$$p = p_{max}J^2\tau^2/(1 + J^2\tau^2), \qquad (3)$$

where the exchange integral J is determined by the overlap of orbitals of unpaired electrons of the radical and complex in collision, and τ is the collision duration, which in the framework of the diffusion model is proportional to the solvent viscosity[21]

$$\tau \approx r(R_{NO} + R_{compl})/(D_{NO} + D_{compl}),$$

r is the size of the interaction region, D_{NO} and D_{compl} are the translational diffusion coefficients of the radical and complex, respectively; $(D_{NO} + D_{compl}) \propto \eta^{-1}$.

The p_{max} value depends on the spin value (S) and spin-lattice relaxation time (T_1) of the complex.[1] For the copper(II) complexes, $S = 1/2$, $T_1/\tau > 1$, and $p_{max} = 1/2$. In the case of nickel(II) ($S = 1$), the T_1 value is known for the aqua complex: $T_1 \approx 4\cdot10^{-12}$ s.[22,23] If the T_1 values for the nickel(II) complexes with CE also satisfy the condition $T_1/\tau < 1$, then $p_{max} \approx 1$. However, if the inverse inequality holds for these complexes ($T_1/\tau > 1$), then for $S = 1$ $p_{max} \approx 0.6$.

The proportionality $k_{ex} \propto T/\eta$ takes place if $J^2\tau^2 \gg 1$. Then according to Eqs. (1)—(3), the spin exchange is limited by the diffusional collision frequency k_Dc and the spins of the radical and complex flip-flop within the collision time with the probability close to $f/2$ (for the Cu^{II} complexes) or f (for the Ni^{II} complexes, $T_1/\tau < 1$).

The linear $k_{ex}(T/\eta)$ plots (see Fig. 2) were obtained in the restricted temperature interval for a small number of experimental points. Nevertheless, some these straight lines can be extrapolated (within the experimental error) to the coordinate origin, as it should be, according to Eqs. (1)—(3), in the case of strong exchange. However, for the Ni^{II} complexes with CE **2** and **3**, the $k_{ex}(T/\eta)$ plots cross the k_{ex} axis in a point somewhat higher than zero. The deviation from the linear $k_{ex}(T/\eta)$ plots at high T/η has previously[24,25] been observed for spin exchange between nitroxyl radicals in low-viscous media, which was explained by the transition to a weak exchange. In our case, the absence of crossing the coordinate origin for the Ni^{II}—**2** and Ni^{II}—**3** complexes can also be due to a decrease in the slope of the $k_{ex}(T/\eta)$ plot. By analogy to the earlier[1] explanation, this can be caused by the anisotropy of the exchange integral: depending on the radical orientation with respect to the symmetry axes of the complex, the exchange integral can correspond to the states of strong, weak, or intermediate exchange. The contributions of these states to the averaged k_{ex} value depend on the temperature and can result in a deviation from the linear $k_{ex}(T/\eta)$ plot.

Dependences of spin exchange constants on crown ether structure. The k_{ex} values for spin exchange between TEMPO and the complexes of **1—4** with nickel(II) chloride at 293 K are given in Table 2, and the corresponding values for the complexes of **1—3** with copper(II) chloride at 292 K are presented in Table 3. It is seen that for both ions the k_{ex} values depend significantly on the CE structure. For the complexes with nickel chloride, k_{ex} decreases in the series **2** > **3** > **4** > **1**, and on going from **2** to **1**, the k_{ex} value decreases fourfold. On the contrary, for Cu^{II} the maximum k_{ex} value corresponds to the Cu^{II}—**1** complex (**1** > **2** > **3**), and on going from **1** to **3**, k_{ex} decreases almost 2.5-fold.

In the framework of the above concepts, the dependence of k_{ex} on the structure of the equatorial ligand under the strong exchange regime should be ascribed to a change in the steric factor f. The collision time should necessarily be shorter than the rotational correlation time of the complex (the geometric sizes suggest that the latter

Table 2. Rate constants (k_{ex}) and steric factors (f) of spin exchange with TEMPO and long-wave maxima in the electronic absorption spectra (λ) for crown ether complexes **1—4** with nickel chloride in a MeOH—CHCl$_3$ (1 : 2) mixture at 293 K

Crown ether	$k_{ex}\cdot10^{-9}$ /L mol^{-1} s^{-1}	$f^a = k_{ex}/k_D$	λ_1	λ_2
			nm	
1	0.656	0.058	400	680
2	2.62	0.23	367	581
3	2.53	0.224	343	511
4 ^{b}	1.236	0.11	—	766

^{a} The f values were calculated for $p_{max} = 1$.

^{b} For the NiCl$_2$—**4** complex, measurements were carried out in neat MeOH because CE **4** is insoluble in MeOH—CHCl$_3$ mixtures. Under the condition of "strong" exchange and under the assumption that specific solvent effects, except viscosity, are absent, the k_{ex} value referred to the viscosity of a MeOH—CHCl$_3$ (1 : 2) mixture is equal to $1.25\cdot10^9$ L mol^{-1} s^{-1}.

Table 3. Rate constants (k_{ex}), steric factors (f) of spin exchange with TEMPO, and electron-spin parameters (a, Δg, λ) of crown ether complexes **1**—**4** with copper chloride in a MeOH—$CHCl_3$ (1 : 4) mixture at 292 K

Crown ether	$k_{ex} \cdot 10^{-9}$ /L mol^{-1} s^{-1}	a_{Cu}/G	Δg	f [a]	λ/nm
1	2.29	65.0	0.1153	0.4	654
2	1.77	76.4	0.1067	0.31	624
3	1.02	93.6	0.0900	0.18	526
4 [b]	1.15	69.6	0.1123	0.22	651

[a] The f values were calculated for $p_{max} = 1/2$.

[b] For the $CuCl_2$—**4** complex, measurements were carried out in pure MeOH because CE **4** is insoluble in MeOH—$CHCl_3$ mixtures. Under the condition of "strong" exchange and under the assumption that specific solvent effects, except viscosity, are absent, the k_{ex} value referred to the viscosity of a MeOH—$CHCl_3$ (1 : 4) mixture is equal to $1.26 \cdot 10^9$ L mol^{-1} s^{-1}.

is longer than the rotational correlation time of TEMPO), *i.e.*, the relative orientation of particles should not substantially change within the collision time. Otherwise, during each collision the radical would contact with the regions on the surface of the complex satisfying the strong exchange regime. Estimation of both times for the diffusion model shows, however, that the τ/τ_R ratio (τ_R corresponds to the radical) is not much lower than unity. This means that the Brownian rotation of the complex and radical during the collision time results in an increase in f. However, since the τ/τ_R ratio is virtually the same for different complexes, the f values for different complexes can characterize the fraction of the surface of the complex on which the exchange integral satisfies the strong exchange condition. The f factor was estimated by Eq. (1) using the k_D value calculated by Eq. (2). As can be seen from Eq. (2), the k_D value depends only slightly on the R_{compl} to R_{NO} ratio. For example on increasing R_{compl}/R_{NO} from 1 to 2, k_D increases by ~10%. At 292 K, for MeOH—$CHCl_3$ mixtures with component ratios of 1 : 4 and 1 : 2, $k_D \approx 1.14 \cdot 10^{10}$ and $1.13 \cdot 10^{10}$ L mol^{-1} s^{-1}, respectively. The f values calculated for the copper(II) and nickel(II) complexes are presented in Tables 2 and 3. The f and k_{ex} values depend on the CE structure. Except for CE **3**, f is higher for the copper(II) complexes than for the nickel(II) complexes.

Correlation between spin exchange rates and electron-spin parameters of complexes with different crown ethers. These values can completely be compared only for the Cu^{II} complexes because the Ni^{II} complexes do not exhibit an ESR signal due to the short spin-lattice relaxation times. Thus, for the Ni complexes positions of the long-wave absorption maxima (λ) are the only parameters of the electronic structure. The ESR spectra of the complexes of **1**—**4** with copper(II) chloride are presented in Fig. 3. The isotropic HFC constants (a_{Cu}), the deviations of the g factors from g of a free electron (Δg), and the λ values are given in Table 3. (Note that the a_{Cu}, Δg, and λ values noticeably differ for the complexes with CE **2** and **3**, although the CE themselves differ by only one CH_2 group in the macrocycle.)

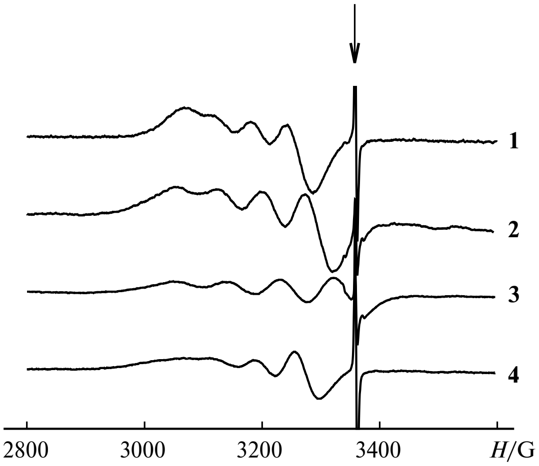

Fig. 3. ESR spectra of the copper chloride complexes with crown ethers **1**—**4** at 291 K. The signal from DPPH is marked by arrow.

It is seen in Table 3 that the Δg values for the complexes with CE **3** and **2** are lower than those for the complexes with **1** and **4**. This fact, along with the high binding constants and a greater shift of the long-wave electron transition toward short waves, indicates a higher covalence of bonding with ligands **2** and **3**. However, the a_{Cu} values change in opposite direction, *i.e.*, the higher a_{Cu} correspond to the lower Δg values (higher covalence of bonding). As can be seen in Fig. 4, the correlation between a_{Cu} and Δg for ligands **1**—**4** is close to linear. The a_{Cu} value itself can decrease with an increase in Δg because the HFC tensor components contain the contribution from the dipole interaction of the nuclear spin with both the spin and orbital moments of an unpaired electron, the latter contribution being not averaged to zero for the isotropic HFC constant (trace of the tensor). The approximate expression for the trace of the HFC tensor (equal to a_{Cu}) has the form[26]

$$(A + 2B)/3 = -K + (g_i - 2.0023)P, \qquad (4)$$

where A and B are the parallel and perpendicular components of the HFC tensor, respectively, K is the value of the contact isotropic interaction, and P is the parameter of the electron-nuclear dipole interaction averaged over the electron distribution. For the Cu^{II} ion, $P \approx (360—400) \cdot 10^{-4}$ cm^{-1} (~380—420 G). Equation (4) predicts a linear decrease in a_{Cu} with an increase in Δg. The slope of this plot should be equal to P, if $a_{Cu} < 0$ and K is constant. However, the slope of the $a_{Cu}(\Delta g)$ straight line is by ~2.75 times greater than the P value (~1100 G) (see Fig. 4, *a*).

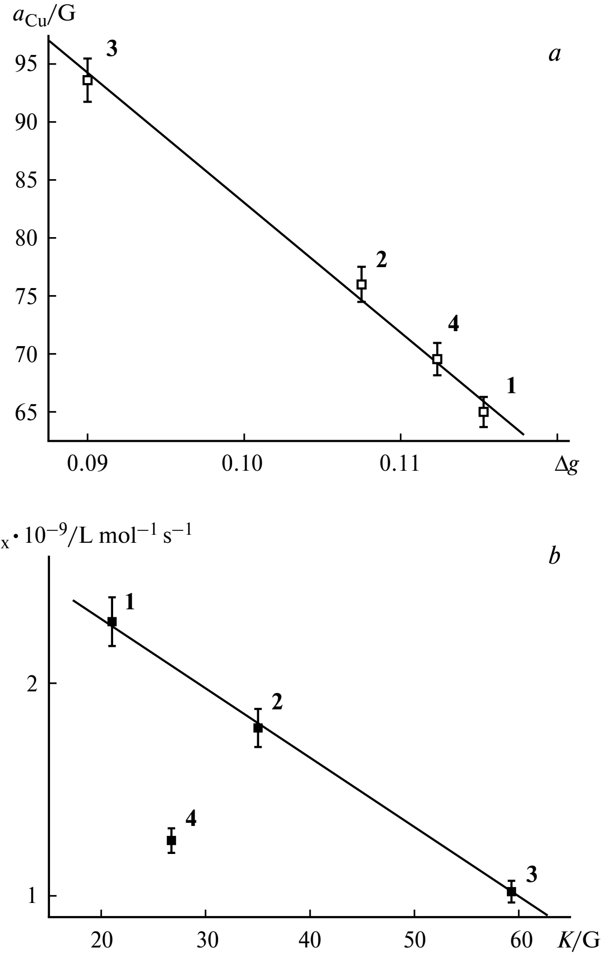

Fig. 4. Correlations between the isotropic HFC constant (a_{Cu}) and the deviation of the *g* factor from the purely spin value (Δ*g*) (*a*) and between the spin exchange constants (k_{ex}) and the contact interaction on the Cu^{II} nucleus (*K*) for the copper chloride complexes with crown ethers **1—4** (*b*).

It is of interest that the same correlation between a_{Cu} and Δ*g*, but with the twofold greater slope than *P*, has previously been observed for the copper(II) complexes with substituted acetylacetonates.[24] The results in the work[27] were explained in Ref. 25 on the basis that the contact interaction with the copper nucleus occurs because of the spin polarization of internal s-electrons by an unpaired 3d-electron. Mixing of the internal s-states with the excited 4s-states results in the promotion of the internal s-electron on the free 4s-orbital, *i.e.*, spin polarization occurs along with the effect of delocalization of the unpaired electron from the copper(II) ion to the ligands. In the presence of ligands, the electron is transferred from the ligands to the 4s orbital. Therefore, an increase in the *K* value with an increase in the electron-donating character of the ligands can also be expected.

Equation (4) makes it possible to determine the *K* value characterizing the spin density on the Cu^{II} nucleus.[26] The correlation between *K* and k_{ex} for the complexes with CE **1—3** is also close to linear (see Fig. 4, *b*). The Cu complex with CE **4** deviates from a linear plot, which is likely due to the difference in the character of copper ion binding because for this CE the acetyl groups, in addition to the N atoms of the macrocycle, are involved in binding.

It seems reasonable to believe that a decrease in the spin density on the copper nucleus (*K*) corresponds to an increase in the spin density on the equatorial ligands. This implies that, in the case of the complexes with CE **1—3**, a linear correlation exists between the exchange rate and spin density on the equatorial ligands. It is difficult to explain such a correlation in the framework of the existing theory of spin exchange. In fact, according to the semiempirical Owen relation,[28] the exchange integral (*J*) depends linearly on the spin density on ligands. However, under the strong exchange regime, as follows from Eq. (3), the exchange integral does not enter the expression for k_{ex}.

As already mentioned, the *f* value characterizes the part of the surface of the complex on which the exchange integral satisfies the strong exchange condition. Then the $k_{ex}(K)$ plot (see Fig. 4, *b*) can be explained by the fact that, on going from CE **3** to CE **1**, this fraction of the surface increases due to an increase in the total spin density on the equatorial ligands. In particular, in the case of the Cu^{II}—**1** complex, the exchange can occur through the N atoms and also through the O atoms of the macrocycle.

Interpretation of the data on the nickel chloride complexes with CE **1—4** is complicated because the T_1 values for these compounds are unknown. The *f* values for the case $T_1/\tau < 1$ ($p_{max} = 1$) are presented in Table 2. If the condition $T_1/\tau > 1$ is valid for all complexes, the *f* values (see Table 2) should be divided into 0.6. In both cases, k_{ex} and *f* depend strongly on the CE structure, although these values change in order, which is opposite to that found for the copper complexes: the highest k_{ex} and *f* values correspond to the complexes with CE **2** and **3**, whereas the lowest values correspond to the complex with CE **1**.

The long-wave region of the optical spectrum for the Ni^{II} complexes with CE is more complicated than that for the copper complexes.[29] Table 2 presents the values of two long-wave absorption maxima λ_1 and λ_2. (For the complex with CE **4**, the λ_1 maximum is not observed because of the absorption of the CE itself in this spectral region.) As for the Cu^{II} complexes, both these transitions shift to the short waves in the series **1** < **2** < **3**, corresponding to an increase in the covalence of bonding. Thus, in the case of the Ni^{II} complexes, an increase in k_{ex} and *f* (for p_{max} equal to 1 or 0.6) correlates with an increase in the bonding covalence.

A possible effect of changes in T_1 in the series of the Ni^{II} complexes with CE **1—3** on the mentioned correlation should be analyzed. It follows from the general theory of the T_1-relaxation of transition metal ions[29] that the higher T_1 value corresponds to the higher bonding covalence (higher ligand field splitting), *i.e.*, the T_1 value should increase on going in the series of CE **1**, **2**, and **3**. If in this series the inequality $T_1/\tau < 1$ would change to the inverse one, the k_{ex} values should decrease by 60—70%. However, the experiment demonstrates the increase in k_{ex}, which, hence, cannot be explained by a change in the T_1 to τ ratio in the series **1**—**3**. The complex with CE **4** somewhat falls out from this correlation due to different characters of bonding of the Ni^{II} ion with this ligand compared to ligands **1**—**3**.

The difference between the dependences of k_{ex} on the CE structure for the Ni^{II} and Cu^{II} complexes is probably related to the fact that for the Ni^{II} complexes the effects of spin polarization are less significant, and hence, the delocalization of unpaired electrons from the Ni^{II} ions to the ligands (and, hence, the k_{ex} and f values) correlates with the bonding covalence.

Influence of axial ligands (counterions) on spin exchange rates and electron-spin parameters of complexes. To study this effect, we synthesized complexes of **2** with various copper salts: chloride, perchlorate, bromide, acetate, and nitrate. The spin exchange rates (k_{ex}) for these complexes at 292 K (Table 4) depend substantially on the counterion: the highest k_{ex} value is observed for the NO_3^- anion, and k_{ex} decreases almost threefold on going from NO_3^- to Cl^-.

The replacement of the anions results in insignificant changes in the electron-spin parameters (a_{Cu}, Δg, and λ) of the Cu^{II}—**2** complexes with the listed counterions (see Table 4). This can be explained by the location of the unpaired electron in the Cu^{II} ion on the $d_{x^2-y^2}$ orbital, whose density is mainly concentrated in the *xy* plane and, hence, it is less sensitive to the axial ligands than equatorial ligands. The correlation between Δg and a_{Cu} is also observed in this case, although relative errors are high due to a smaller interval of variation of Δg (Fig. 5, *a*).

The lowest Δg value, close to the maximum shortwave shift of λ, and the highest k_{ex} value correspond to the NO_3^- anion, *i.e.*, the k_{ex} value for this anion correlates with the bonding covalence. At the same time, for the Cl^- and Br^- ions, the Δg and λ parameters are very close, although the k_{ex} values differ more than twofold. In addition, in the spectrochemical series Br^- is on the left from Cl^-,[30] but the k_{ex} value for Br^- is higher than for Cl^-.

Table 4. Rate constants (k_{ex}) of spin exchange with TEMPO and electron-spin parameters (a, Δg, λ) for the complexes of CE **2** with copper salts in a MeOH—CHCl$_3$ (1 : 4) mixture at 292 K

Anion	$k_{ex} \cdot 10^{-9}$ /L mol^{-1} s^{-1}	a_{Cu}/G	Δg	f*	λ/nm
Cl^-	1.91	76.4	0.1067	0.335	624
ClO_4^-	3.5	82.8	0.1031	0.61	579
AcO^-	3.75	79.6	0.1037	0.66	611
Br^-	3.76	78.8	0.1062	0.66	620
NO_3^-	5.18	83.5	0.1023	0.90	587

* The f values were calculated for p_{max} = 1/2.

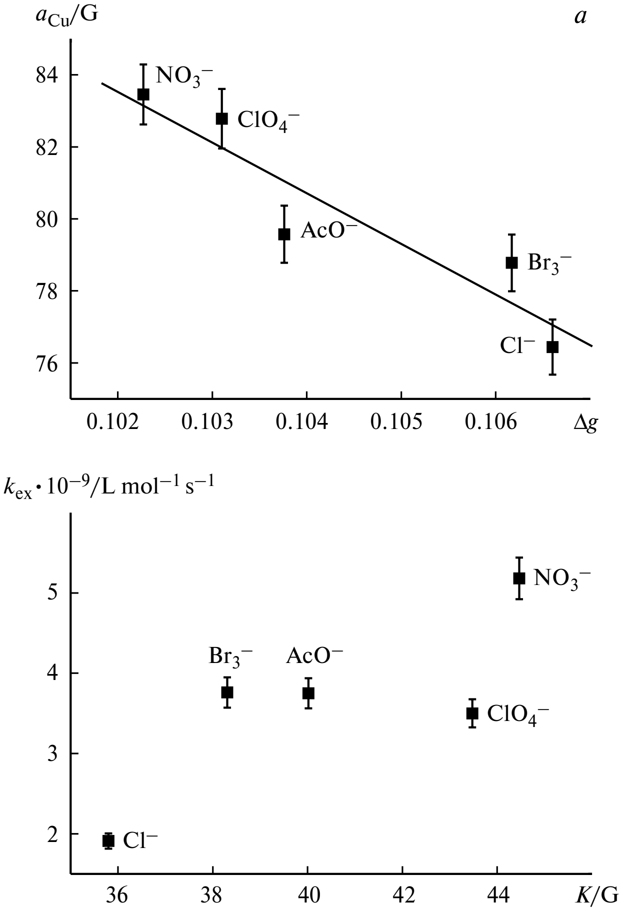

Fig. 5. Correlations between the isotropic HFC constant (a_{Cu}) and the deviation of the g factor from the purely spin value (Δg) (*a*) and between the spin exchange constant (k_{ex}) and the contact interaction on the Cu^{II} nucleus (K) for the Cu^{II}—**2** complexes with different counterions (*b*).

It is likely that there is a correlation (or a tendency) between the k_{ex} and K values for the same complexes (see Fig. 5, *b*), but it is inverse compared to the $k_{ex}(K)$ plot in Fig. 4, *b*, namely, the spin exchange rate increases with an increase in the spin density on the Cu^{II} nucleus. The nature of this correlation is not quite clear. Probably, the replacement of the counterions results in such a redistribution of the spin density that its value on the equatorial ligands increases and, correspondingly, k_{ex} increases. Another possible explanation is that the efficiency of spin exchange through the axial ligands is determined by the orbital shapes, in particular, by the overlap of orbitals of the ligand and radical rather than the spin density on the axial ligands. Quantum-chemical calculations of the spin density distribution for the copper complexes with different axial ligands are thus necessary to choose between

Table 5. Rate constants (k_{ex}) and steric factors (f) of spin exchange with TEMPO for the paramagnetic nickel salts in a MeOH—$CHCl_3$ (1 : 1) mixture and for the paramagnetic copper salt in a MeOH—$CHCl_3$ (1 : 4) mixture at 292 K

Anion	$k_{ex} \cdot 10^{-9}$/L mol^{-1} s^{-1}		f*	
	Ni^{II}	Cu^{II}	Ni^{II}	Cu^{II}
Cl^-	1.85	2.88	0.164	0.50
ClO_4^-	1.6	2.65	0.141	0.465
NO_3^-	1.75	2.25	0.155	0.395

* The f values were calculated for p_{max} = 1 and 1/2 in the case of the nickel and copper salts, respectively.

different hypotheses. They are also needed to understand the nature of the qualitative distinction in the dependences of k_{ex} on the CE structure for the copper and nickel complexes. These problems will be studied elsewhere.

Spin exchange with paramagnetic salts of nickel and copper ions. Nickel and copper chlorides, perchlorates, and nitrates were used in these studies. The absolute values of the k_{ex} and f parameters for these salts (Table 5) are close to those for the complexes with CE. However, unlike the latter, the spin exchange constants for both ions depend only slightly on the nature of the anion. Like for the complexes with CE, the spin exchange of TEMPO with the copper(II) ions is more efficient than that with the nickel(II) ions.

The ESR spectra of the copper salts in a MeOH—$CHCl_3$ mixture are broadened and have a poorly resolved hyperfine structure, which is possibly caused by a weak binding and the fast exchange of the ligands (anions and solvent molecules) between the ligand shell and solution. The isotropic HFC constants and g factors cannot exactly be determined from these spectra without detailed spectral simulation. However, the Δg values for these salts are much higher and, hence, the covalence of the bonding with the ligands is lower than that for the complexes with CE. The high Δg values and, probably, the higher rate of ligand exchange can explain why k_{ex} and f depend weakly on the anion.

Thus, the series of new complexes of di- and tetraaza-substituted CE with the copper(II) and nickel(II) ions and various counterions was prepared in this work. These complexes were shown to interact in nonaqueous media with the nitroxyl radical in the "strong" exchange regime when the frequency of diffusional collisions is the limiting step of spin exchange. At the same time, the spin exchange constant depends rather strongly on the nature of CE and axial ligands (counterions). Such relations under the strong exchange conditions can be accounted for the anisotropy of the steric factor if the collision time is much shorter than the correlation time of rotation of paramagnetic complexes. For the copper complexes upon the replacement of the equatorial ligands, the increase in k_{ex} in the series **1** > **2** > **3** correlates linearly with a decrease in the spin density on the copper nucleus. This correlation is lading when the axial ligands are varied.

The dependences of the k_{ex} values on the ligand structure and the correlations of k_{ex} with the spin density in the strong exchange regime are of considerable interest, in our opinion, for the theory of elementary acts of spin exchange. However, the quantitative interpretation of these effects requires quantum-chemical calculations. In addition, the results obtained are important for the correct interpretation of experiments on the paramagnetic relaxation of spin labels induced by various complexes of transition metal ions in biological systems.

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