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Delocalization Mechanism of Ferromagnetic Exchange Interactions in Complexes of Copper(II) with Nitroxyl Radicals

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On the basis of a detailed quantum-chemical (ab initio and INDO) analysis, it has been shown that the experimentally observed ferromagnetic properties of axially coordinated bischelating complexes of Cu(II) with nitroxyl ligands (in contrast to the antiferromagnetic properties of equatorially coordinated complexes of the same type) cannot be explained in the framework of the concept of direct exchange interaction. An alternative (delocalization) mechanism of ferromagnetic exchange interaction has been proposed. This mechanism is due to slight delocalization ($\rho \simeq 10^{-2}$–10^{-3}) of the unpaired electron from the π^*-antibonding MO of nitroxyl radicals onto the valence AO (mainly on the 3d$_{z^2}$ AO) of the central paramagnetic Cu(II) ions. The predicted values of the exchange interaction in a series of axially coordinated complexes of Cu(II) are in good agreement with the experimental data obtained from magnetic measurements.

In the last few years there have been a large number of papers devoted to the problem of designing a novel class of ferro- or ferrimagnetic materials based on the coordination compounds of transition metals with paramagnetic organic ligands.[1–5] Highly promising in this respect are the recently synthesized complexes of bis chelates of Cu(II) with nitroxyl radicals (L) in which the O–N< group of the radical is directly coordinated to the central Cu(II) ion.[3–18] According to magnetostructural studies the type and the magnitude of exchange interaction between the paramagnetic centers Cu$^\bullet$(II) and O–$^\bullet$N< in such complexes depends on the structural features of Cu(II)···L bonding. For example, in the equatorially coordinated complexes the strong antiferromagnetic interactions $|J| \geq 100$ cm^{-1} are usually observed[3,6–10] whereas in the axially coordinated ones only the ferromagnetic interactions 10 cm^{-1} $\leq J \leq$ 65 cm^{-1} have been detected.[3,4,11–17] Here J is the exchange parameter involved in the spin-Hamiltonian $\hat{H} = -J\hat{S}_{\mathrm{Cu}}\cdot\hat{S}_{\mathrm{L}}$. At present there is no clear theoretical interpretation in the literature of the magnetic (particularly ferromagnetic) properties of such copper(II)–nitroxyl complexes. The authors of most works assume that the main mechanism responsible for the formation of intramolecular ferromagnetism in complexes of this kind is the direct exchange interaction, i.e. the interaction determined by the overlap between the orbitals of unpaired electrons (magnetic orbitals) of paramagnetic centers Cu$^\bullet$ (3d$_{xy}$ AO) and O–$^\bullet$N< (π^*-antibonding MO). However, no convincing confirmation is available for the validity of this viewpoint. Moreover, all attempts to explain the observed magnetic behavior of the axially coordinated complexes of Cu(II) have been unsuccessful. This problem has been studied in detail by Caneschi and co-workers,[3,4] who used a well-known approach proposed by Hoffmann et al.[19] and Kahn et al.[20,21]

The present report is devoted to a detailed quantum-chemical analysis of the possible mechanisms of exchange interaction in the magnetic fragments Cu$^\bullet$(II)···O–$^\bullet$N< (or >N$^\bullet$–O···Cu$^\bullet$(II)···O–$^\bullet$N<) of bischelating complexes of Cu(II) with nitroxyl radicals and the determination of the main factors (electronic and geometrical) which govern the magnitude and the sign of the exchange parameter J in these compounds. The necessary wave functions (MO) have been obtained using ab initio (program GAUSSIAN-80)[22] and INDO (program SPIN-HAMILTONIAN)[23] Hartree-Fock (HF) calculations for models A–D of the [Cu(II)]···L complexes given in Table I. In the case of ab initio calculations we have used the familiar contracted Gaussian basis sets.[24–26] Figure 1 shows the view of the molecular structure of typical axially coordinated (a) and equatorially coordinated (b) copper(II)–nitroxyl complexes (of the type Cu(hfac)$_2$L). The chemical formulas of the complexes and the values of the exchange parameters J_{exp} obtained from magnetic measurements are listed in Table II. All calculations have been performed by using the experimental values of the geometrical parameters R, θ, ψ, φ, α, and β of the complexes.[3,4]

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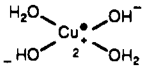
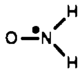
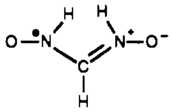
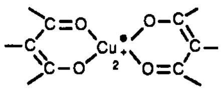
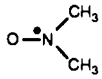
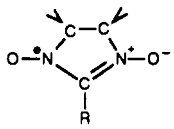
Table I. Models of Complexes [Cu(II)]···L and Method of Calculation of the Wave Functions (MO) and the Structural Formulas of Paramagnetic Fragments: [Cu(II)], Chelating Moiety of the Complex; L, Nitroxyl Radical; R, Methyl or Phenyl

method	[Cu(II)]	L	model
ab initio HF SCF			A
			B
INDO			C
			D

Results and Discussion

Direct Mechanism of Exchange Interaction. The nonempirical calculations of the parameters $J = J_{\text{dir}}$ of the direct exchange interaction in the complex [Cu(II)]···L (model A) performed in the framework of the pair orbital approximation (program HEIPAS)[27,28] by using the ab initio restricted open-shell (ROHF) and unrestricted (UHF) Hartree–Fock MOs of isolated paramagnetic fragments [Cu(II)] and L testify that (because of the smallness of the contributions to J_{dir} due to the terms associated with the effects of the spin polarization of inner shell electrons) in order to obtain reasonable estimates for the J_{dir} values it is quite sufficient to consider the exchange interaction only between the unpaired electrons that are localized mainly on the $3d_{xy}$ AO of the Cu(II) ion and the π^* MO of the O-$^{\bullet}$N< group of the radical L. In this case, the exchange parameter may be expressed as

$$J_{\text{dir}} \simeq 2\rho_{xy}J(3d_{xy},\pi^*) \qquad (1)$$

$$J(3d_{xy},\pi^*) = \langle 3d_{xy}\pi^*|\pi^*3d_{xy}\rangle - 2S\langle\pi^*|\hat{\mathbf{T}}|3d_{xy}\rangle + S^2[\epsilon_{xy} + \epsilon_{\pi}{}^* + \langle 3d_{xy}3d_{xy}|\pi^*\pi^*\rangle] \qquad (2)$$

where $\rho_{xy} \simeq 0.8$–0.9 is the density of the unpaired electron on the $3d_{xy}$ AO; $S = \langle 3d_{xy}|\pi^*\rangle$ is the overlap integral between magnetic orbitals; ϵ_{xy} and $\epsilon_{\pi}{}^*$ are the orbital energies; $\langle 3d_{xy}\pi^*|\pi^*3d_{xy}\rangle$ and $\langle 3d_{xy}3d_{xy}|\pi^*\pi^*\rangle$ are the two-electron integrals of the exchange and Coulomb types, respectively; and $\hat{\mathbf{T}}$ is the kinetic energy operator.

It was found from our calculations that the strong antiferromagnetism of equatorially coordinated complexes of Cu(II) can be explained by direct exchange interaction of unpaired electrons. Indeed, these complexes are characterized by fairly large values of the overlap integral $S \simeq 10^{-1}$. In this case, the last (proportional to S^2) term in expression 2 becomes predominate. This leads to large negative values of the exchange parameter $J_{\text{dir}} < 0$. It should be noted that a substantial overlap between magnetic orbitals causing a strong antiferromagnetic interaction is quite typical for most of the equatorially coordinated complexes.[6-10] The calculated by us values of the parameters J_{dir} are in satisfactory agreement with the experimental results J_{exp}. For instance, for the complex[6] Cu(hfac)$_2$TEMPO: $S = 0.07$, $J_{\text{dir}} = -1.7 \times 10^3$ cm^{-1}, and $J_{\text{exp}} < -450$ cm^{-1}. A considerably different picture has been observed for the axially coordinated complexes of Cu(II).[3,4,11-17] Table II summarizes the values of S, J_{dir}, and J_{exp} for a series I–VI of such complexes. A substantial discrepancy is observed with the experimental data. Despite the coincidence in the signs of the exchange parameters, the calculated values of J_{dir} are much smaller (about an order of magnitude) than the experimental values of J_{exp}. This can be explained from the fact that in such complexes the values $S \simeq 10^{-3}$–10^{-4} are very small (at $\alpha \simeq 0$–$10°$ the orbitals of the oxygen atom O(L) of radical L are approximately orthogonal to the $3d_{xy}$ AO of Cu(II), and contribution to the overlap integral S is due to the orbitals of a more distant nitrogen atom N(L)). Therefore, in expression 2 the first (positive) term is predominant; i.e., $J_{\text{dir}} \simeq 2\rho_{xy}\langle 3d_{xy}\pi^*|\pi^*3d_{xy}\rangle$. Thus, it must be concluded that the observed ferromagnetic properties of the axially coordinated complexes of Cu(II) cannot be interpreted in terms of the direct exchange mechanism.

Delocalization Mechanism of Exchange Interaction. The above consideration shows that in order to understand the peculiarities of the magnetic behavior of copper(II)–nitroxyl complexes it is necessary to find an alternative (indirect) mechanism of ferromagnetic exchange interaction. Note that in this case, the conventional models of indirect exchange (superexchange), which assume that the transference of interaction through orbitals of intermediate nonmagnetic particles (atoms or molecules) takes place, are unapplicable because the fragments Cu$^{\bullet}$(II)···O–$^{\bullet}$N< of these complexes contain only the directly contacting paramagnetic centers Cu$^{\bullet}$(II) and O–$^{\bullet}$N<. The performed by us INDO and ab initio ROHF analysis of spin density distribution in the model complexes [Cu(II)]···L (models A–D) show that in magnetic fragments Cu$^{\bullet}$(II)···O–$^{\bullet}$N< of the axially coordinated complexes a slight delocalization of unpaired electron from the π^* MO of the O–$^{\bullet}$N< group to the valence AO of the central Cu$^{\bullet}$(II) ion is possible[18] (Figure 2). An account of such delocalization formally corresponds to the substitution of expression 1 by $J_{\text{dir}} \simeq 2\rho_{xy}J(3d_{xy},\bar{\pi}^*)$ where $\bar{\pi}^* = \pi^* + \sum_k c_k\varphi_k$ is a new magnetic orbital containing the admixtures of φ_k = 3d, 4s, and 4p AOs of Cu(II) (except for the $3d_{xy}$ and $3d_{x^2-y^2}$ AOs because of the smallness of the overlap between these AOs and the π^* MO). It should be noted here that the magnitude of spin density delocalization from magnetic orbital of the chelating moiety of such complexes (which centered on the Cu(II) ion and is well described by the $3d_{xy}$ AO) onto the π and σ MOs of the O–N< group of the radical (L) were found to be very close to zero (do not exceed 10^{-5}). It can readily be demonstrated that the obtained (after substitution of $\bar{\pi}^*$ MO) exchange parameter J will contain two main contributions, $J \simeq J_{\text{dir}} + J_{\text{del}}$, corresponding to the two different mechanisms of interaction. In addition to the mechanism of direct exchange interaction (J_{dir}), a new delocalization mechanism of interaction arises

$$J_{\text{del}} \simeq 2\rho_{xy}\sum\nolimits_k \rho_k\langle 3d_{xy}\varphi_k|\varphi_k 3d_{xy}\rangle \qquad (3)$$

due to the appearance on the φ_k AO of Cu(II) ion of the nonzero spin density $\rho_k = c_k{}^2$ from nitroxyl radical and subsequent intratomic (ferromagnetic) exchange interaction with an unpaired electron mainly localized on the $3d_{xy}$ AO of Cu(II). Note that the delocalization onto the $3d_{z^2}$ AO of Cu(II) plays a main role in the formation of this mechanism ($\rho_{z^2} > \rho_{xz}$, ρ_{yz}), and the smallness of the delocalization ($\rho_{z^2} \simeq 10^{-2}$–$10^{-4}$) is quite well compensated for by a strong intratomic interaction ($\langle 3d_{xy}3d_{z^2}|3d_{z^2}3d_{xy}\rangle \simeq 10^4$ cm^{-1}). Neglecting a very small contribution of exchange integrals including φ_k = 4s and 4p AOs and taking into account the closeness of the values of such integrals for φ_k = $3d_{z^2}$, $3d_{xz}$, and $3d_{yz}$ AOs (0.0484, 0.0421, and 0.0421 au), the parameter J_{del} can be represented in a more simple form

$$J_{\text{del}} \simeq K\rho_{\text{d}} \qquad (4)$$

where $K = 2\rho_{xy}\langle 3d_{xy}3d_{z^2}|3d_{z^2}3d_{xy}\rangle \simeq$ constant (since $\rho_{xy} \simeq$

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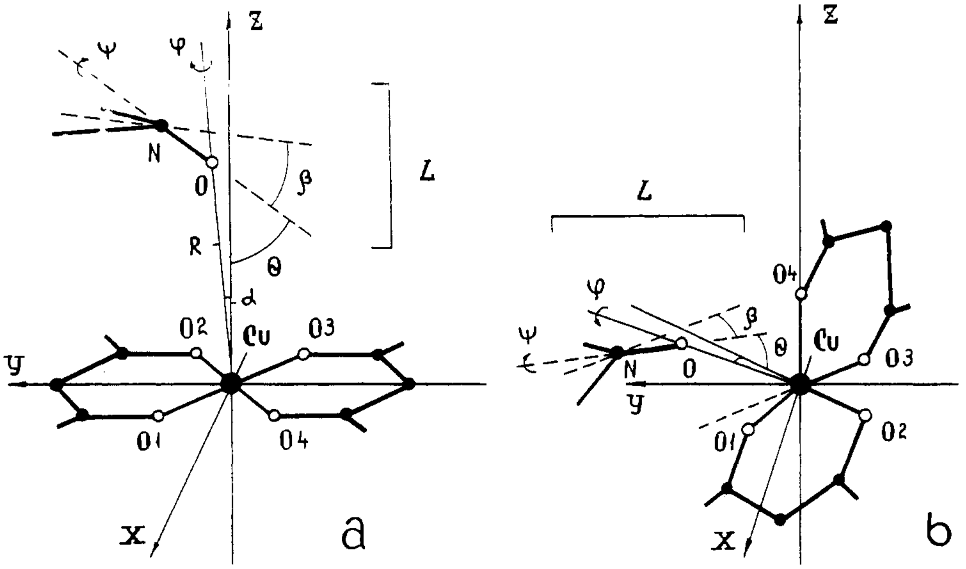

Figure 1. Schematic representation of the molecular structure and the main geometrical parameters of axially coordinated (a) and equatorially coordinated (b) complexes of Cu(II) with nitroxyl radicals (L): R, the distance Cu–O(L); θ, the angle between the N–O(L) bond and the direction Cu–O(L); ψ, the dihedral angle between the Cu–O(L)–N plane and the middle plane of the radical L; φ, angle determining the radical rotation around the Cu–O(L) bond (being equal to the angle between the projection of the N–O(L) bond on the XY plane and the Cu–O1 (chelate ring) bond); α, angle characterizing the deviation of the Cu–O(L) bond from the Z axis; β, the angle between the N–O(L) bond and the C–N–C (or H–N–H) plane of radical L.

Table II. Calculated Values of the Parameters of Direct (J_{dir}) and Delocalization (J_{del}) Mechanisms of Exchange Interaction in the Axially Coordinated Complexes of Cu(II) with Nitroxyl Radicals: J_{exp}, Parameters Obtained by the Magnetic Measurements

compound		direct mech		delocalization mech[a]			
no.	formula	$10^4 S$	J_{dir} (cm^{-1})	$10^2 \rho_d$	J_{del} (cm^{-1})	J_{exp} (cm^{-1})	refs
I	$Cu(hfac)_2TEMPOL$	0.989	2.153	0.067 (0.037)	11.149 (7.554)	13 ± 5	11–13
II	$Cu(pacTEMPOL)_2$	1.018	1.236	0.072	12.466	19 ± 5	14
		0.851	0.432	0.015	2.715		
III	$Cu(proxFORMIL)_2$	5.539	4.462	0.242	41.744	21 ± 5	15
IV	$Cu(hfac)_2NITMe$	3.159	2.735	0.127	21.508	26 ± 5	16, 17
		12.608	4.171	0.268	46.353		
V	$Cu(hfac)_2(NITPh)_2$	7.451	4.189	0.222	38.607	10 ± 5	3
VI	$Cu(tfac)_2NITMe$	17.324	6.847	0.468 (0.510)	81.425 (98.142)	65 ± 5	4

[a] Results of ab initio calculations in parentheses.

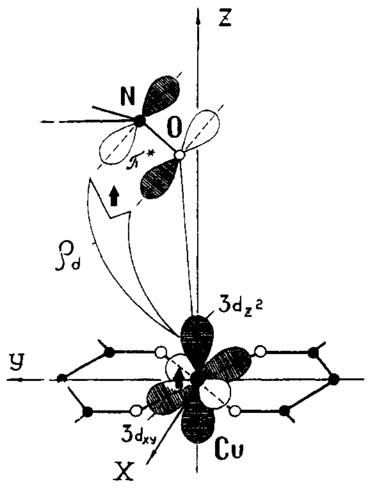

Figure 2. Qualitative scheme for the delocalization mechanism of exchange interaction in the axially coordinated copper(II)–nitroxyl complexes.

constant in the series of the studied complexes), and $\rho_d = \rho_{z^2} + \rho_{xz} + \rho_{yz}$ is the total delocalized spin density on the 3d AOs of the Cu(II) ion.

Table II gives the values of ρ_d and J_{del} calculated by using expression 3 with INDO and ab initio (in brackets) MOs for complexes I–VI (models A–D). The analysis of the obtained data shows that the delocalization mechanism allows one to correctly reproduce both the sign ($J_{del} > 0$) and the order of magnitude of the exchange interaction. The values of J_{del} substantially exceed those for J_{dir}, and moreover, a certain correlation between the calculated (J_{del}) and the experimental (J_{exp}) values is observed. The best agreement with experiment was achieved for complexes I and VI in whose crystals all magnetic fragments of the type Cu$^\bullet$(II)···O–$^\bullet$N< are structurally equivalent. In the case of complexes II–V, the comparison with experimental results is more difficult because the crystals of these complexes contain the two types of the fragments Cu$^\bullet$(II)···O–$^\bullet$N< with different structural parameters (from magnetic measurements only the averaged values for J_{exp} are available). On the whole, the obtained results allow us to conclude that the decisive role in the ferromagnetic exchange interactions in the copper(II)–nitroxyl complexes belongs to the delocalization mechanism.

Structural Dependence of Exchange Interaction. In order to determine the geometrical conformations that are most favorable for the formation of strong ferromagnetic interactions, we have calculated the values of J_{dir} and J_{del} as the functions of the geometrical parameters R, θ, ψ, and φ ($\alpha = \beta = 0°$) for the axially coordinated complexes [Cu(II)]···L (models A and C). Figure 3 represents the $J_{del}(R)$ and $J_{dir}(R)$ dependences calculated for the four different values of the angle ψ of the radical L rotation around the O–N bond at the constant values of angles $\theta = 40°$

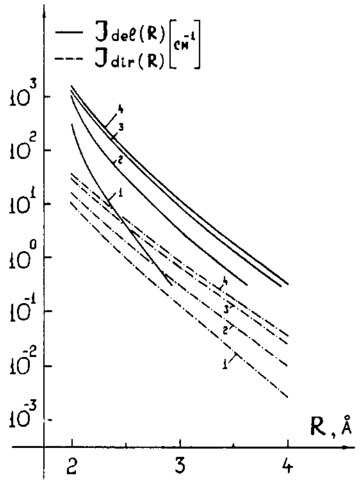

Figure 3. Variations of the values of the exchange parameters J_{dir} (dash–dot lines) and J_{del} (solid lines) with R and ψ (for $\theta = 40°$, $\varphi = 30°$) in the axially coordinated copper(II)–nitroxyl complexes. The plotted curves correspond to the four values of the ψ angle: (1) $\psi = 0°$; (2) $\psi = 30°$; (3) $\psi = 60°$; (4) $\psi = 90°$. Note that the ordinate is logarithmic.

and $\varphi = 30°$. The analysis of these dependences demonstrates that the contributions of both mechanisms rapidly increase (almost exponentially) with decreasing distance R between the paramagnetic centers. The contributions of the direct $J_{\mathrm{dir}}(R)$ exchange mechanism are approximately an order of magnitude less than the corresponding contributions of the delocalization $J_{\mathrm{del}}(R)$ mechanism. For the distances $R \simeq 2$ Å, the value of the ferromagnetic exchange interaction becomes fairly large, $J_{\mathrm{del}} \simeq 10^3$ cm^{-1}. Of interest is also a strong dependence of the J_{del} value on the ψ angle. When $\psi = 90°$, the axes of the $2p_\pi$ AO of the O–N< group are directed toward the Cu(II) ion, thus providing a better overlap between the π^* MO and the $3d_{z^2}$ AO of Cu(II). Such an orientation is especially favorable for the delocalization of an unpaired electron onto the $3d_{z^2}$ AO and, consequently, corresponds to the largest J_{del} value.

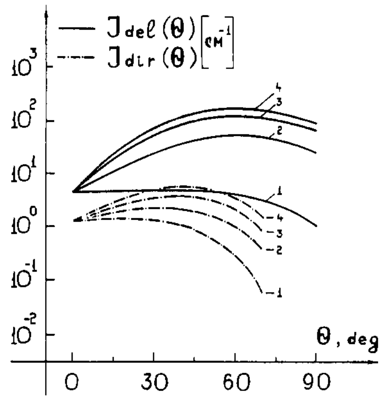

Figure 4. Variations of the values of the exchange parameters J_{dir} (dash–dot lines) and J_{del} (solid lines) with θ and ψ (for $R = 2.5$ Å, $\varphi = 30°$) in the axially coordinated copper(II)– nitroxyl complexes. The plotted curves correspond to the four values of the ψ angles: (1) $\psi = 0°$; (2) $\psi = 30°$; (3) $\psi = 60°$; (4) $\psi = 90°$. Note that the ordinate is logarithmic.

Figure 4 depicts the $J_{\mathrm{del}}(\theta)$ and $J_{\mathrm{dir}}(\theta)$ dependences calculated for the same four angles ψ at $R = 2.5$ Å and $\varphi = 30°$. It is seen that the increase of the θ angle, i.e. the transition from the rigorously axial to the angular conformation of the Cu(II)···O–N< fragment, considerably increases the J_{del} value. This is due to the fact that the increase of the θ angle leads to a more efficient overlap between the π^* MO of the radical and the $3d_{z^2}$ AO of Cu(II). We have performed also the calculation of the $J_{\mathrm{del}}(\varphi)$ and $J_{\mathrm{dir}}(\varphi)$ dependences for the various values of the angle ψ at the constant values $R = 2.5$ Å and $\theta = 40°$. The analysis of the obtained results indicated that varying the φ angle of the radical rotation around the Cu(II)–O(L) bond (around the Z axis, since $\alpha = 0°$) leads to the change of the overlap between the magnetic orbitals within $0 \leq |S| \leq 10^{-3}$ (the orbitals are strictly orthogonal $S = 0$ at $\varphi = 45°$ and $\psi = 90°$) but has practically no effect on the magnitudes of the exchange interactions J_{del} and J_{dir}. In the case of the direct exchange mechanism, the obtained dependence $J_{\mathrm{dir}}(\varphi) \simeq$ constant is quite clear because with such a small value of the overlap integral S the magnitude of interaction is mainly determined by the two-electron integral $\langle 3d_{xy}\pi^* | \pi^* 3d_{xy} \rangle$ which weakly depends on the angle φ. For the delocalization mechanism, the invariability of the interaction value $J_{\mathrm{del}}(\varphi) \simeq$ constant can readily be explained by expression 4. Indeed, the overlap between the π^* MO and the $3d_{z^2}$ AO does not vary with rotation of the radical around the Z axis (see Figure 2), and hence, the degree of delocalization from the O–N< group of the radical onto the $3d_{z^2}$ AO of Cu(II) remains unchanged; i.e., $\rho_{z^2}(\varphi) \simeq$ constant.

Analyzing the obtained $J_{\mathrm{del}}(R, \theta, \psi, \varphi)$ dependences, it should be concluded that the strongest ferromagnetic interaction can be expected for such geometrical conformations of the axially coordinated cooper(II)–nitroxyl complexes that satisfy the following conditions: (a) the distance R must be minimal ($R \simeq 2.0$–2.3 Å), (b) the angle θ must be within the range 60°–90°, (c) $\psi \simeq 90°$, and (d) the angle φ can have any value. Among the considered complexes I–VI, the structure of complex VI is the closest to the optimal structure. The greatest experimental value $J_{\mathrm{exp}} = 65$ cm^{-1} was obtained for just this complex.

Registry No. I, 72692-66-1; II, 65652-96-2; III, 85646-32-8; IV, 106865-83-2; V, 106681-95-2; VI, 112506-21-5.