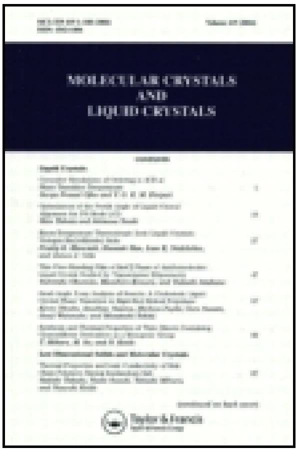

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Molecular Ferromagnets Based on Metal Complexes with 3-Imidazoline Nitroxides

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MOLECULAR FERROMAGNETS BASED ON METAL COMPLEXES WITH 3-IMIDAZOLINE NITROXIDES

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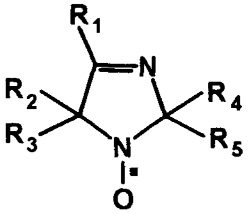
Abstract The approach to the design of molecular magnets based on metal complexes with 3-imidazoline nitroxides is discussed. Both polymeric bischelate complexes demonstrating bulk magnetization and molecular model compounds are considered. Some aspects of quantum-chemical treatment of exchange interactions in metal-nitroxide exchange clusters are presented.

INTRODUCTION

By now several approaches to the design of heterospin molecular magnets have been developed. These magnets differ in both the character of paramagnetic centers and the way of their combination in bulk ferromagnet. These approaches include i) the linking of different transition metal ions with organic diamagnetic ligands;[1] ii) the organization of stacking structures based on charge transfer complexes;[2,3] and iii) coordination compounds of transition metals with stable nitroxides.[4,5] The essence of our strategy consists in using the adducts of first row transition metals with 3-imidazoline nitroxides.[5] The coordination of the nitroxide group and/or of the imine nitrogen of the imidazoline heterocycle with a metal ion creates exchange pathways in solid complexes, while the presence of several donor functions in the structure of the ligand is favorable for the formation of 1-, 2- and 3-dimensional structures.



ZERO- AND ONE-DIMENSIONAL COMPLEXES

A convenient synthetic approach to obtaining zero- and one-dimensional metal complexes with 3-imidazoline nitroxides is the immediate interaction of metal hexafluoroacetylacetonates with the radicals or, in some cases, with corresponding hydroxylamines. As a rule, these complexes do not tend to magnetic ordering at T>4.2 K, however, magnetic ordering is not the objective of the investigation of the M(hfac)$_2$ complexes. Such complexes are good models for investigating the peculiarities of the coordination of 3-imidazoline nitroxides by various metal ions as well as for studying exchange interactions in the system M(II)---O$^{\bullet}$-N for both direct and indirect exchange.

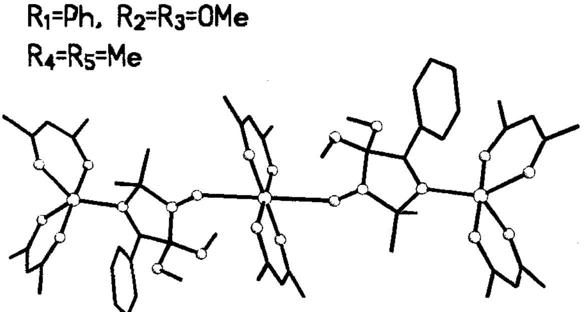


Fig.1

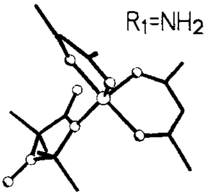


Fig 2

We have studied the products of the reactions of copper hexafluoroacetylacetonate with different 3-imidazoline radicals containing no acid groups (R_1=Me, Et, i-Pr, Ph, NH_2, PhNH, $CONH_2$; R_2=R_3=Me,OMe; R_4=Me,Et; R_5=Me)[5-7] as well as of nickel and cobalt hexafluoroacetylacetonates with some ligands of the same type (R_1=Ph,$CONH_2$, R_2=R_3=Me,OMe; R_4=R_5=Me).[8] It has been found that copper(II) complexes typically exhibit the coordination of the nitroxides by the imine nitrogen atom, which results in the formation of trinuclear (R_1=Et, i-Pr, Ph; R_2, R_3=Me, OMe; R_4=Me, Et; Fig.1)[7,9-12] or mononuclear (R_1=NH_2, PhNH, R_2, R_3=Me; R_4=R_5=Me; Fig.2)[13,14] complexes of composition $[Cu(hfac)_2]_3L_2$ or $Cu(hfac)_2L$, depending on whether the N-$^{\bullet}$O group participates or not in the coordination. The exchange interaction energy is 10-20 cm^{-1} ($H=-2JS_1S_2$) for both direct and indirect interactions. In some cases (R_1=Me, $CONH_2$; R_2=R_3=R_4=R_5=Me),[13,15] chain complexes of composition $[Cu(hfac)_2L]_\infty$ (Figs.3,4) are formed, with exchange interactions between paramagnetic centers being essentially weakened.

Nickel and cobalt hexafluoroacetylacetonates tend to form complexes involving octahedrally coordinated central atoms, with free coordination sites being occupied by N-$^{\bullet}$O groups or H_2O molecules (R_1=Ph, R_2=R_3=Me, OMe; R_4=R_5=Me; Figs.5,6),[8] depending on synthesis conditions. In the first case (complex of the composition $M(hfac)_2L_2$)), strong antiferromagnetic exchange interactions (2J<-300 K) are realized. In the second case

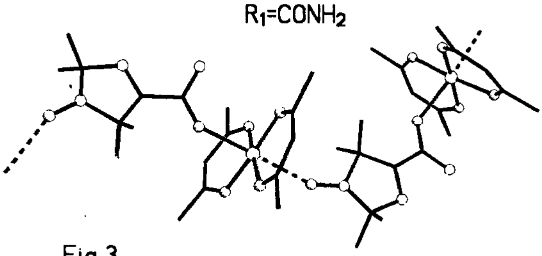


Fig.3

(complex composition $M(hfac)_2(H_2O)_2L_2$), the energy of exchange interactions between the unpaired electrons of nitroxides and of the central atom approaches zero.

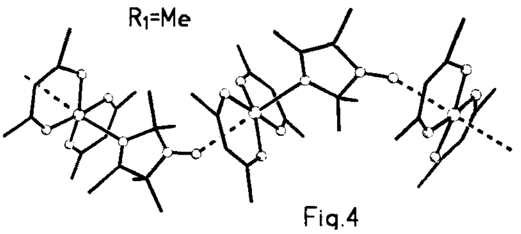


Fig.4

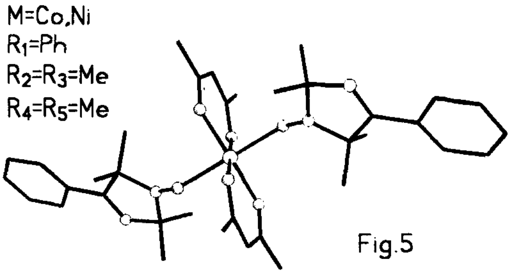


Fig.5

The presence of additional functional groups in the nitroxide radicals affects essentially the structure and properties of the complexes with $M(hfac)_2$. For instance, 4-amido-2,2-dimethyl-5,5dimethoxy-3-imidazoline-1-oxyl (R_1=$CONH_2$, R_2=R_3=OMe, R_4=R_5=Me) reacts with hexafluoroacetylacetonates of copper, nickel, and cobalt to yield coordination compounds of composition $M(hfac)_2L$, with the nitroxide coordinated by the imine nitrogen atom and by the oxygen atoms of the amide group (Fig.7)[8,15]. All these compounds are characterized by ferromagnetic exchange interactions between the unpaired electrons of the metal ion and the nitroxide. In addition, in $Cu(hfac)_2L$ the coordination abilities of the paramagnetic ligand are not exhausted, and the introduction of excessive $Cu(hfac)_2$ to the reaction leads to the formation of a chain complex $[Cu(hfac)_2]_2L$ by virtue of coordination of the nitroxyl and the amide groups of the nitroxide to additional $Cu(hfac)_2$ fragments (Fig.8).[16]

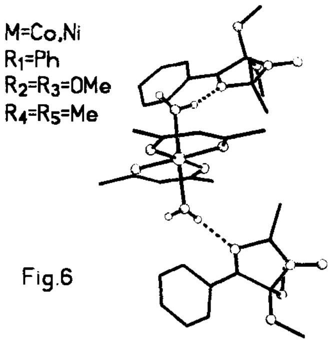


Fig.6

Thus, the use of 3-imidazoline nitroxide derivatives allows one to obtain M(hfac)-based complexes of various structures with different arrangments of paramagnetic centers, which provides a basis for quantum-chemical investigation of

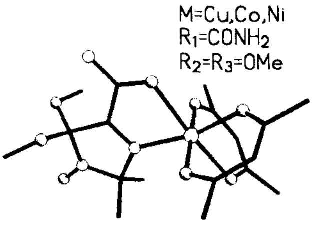


Fig.7

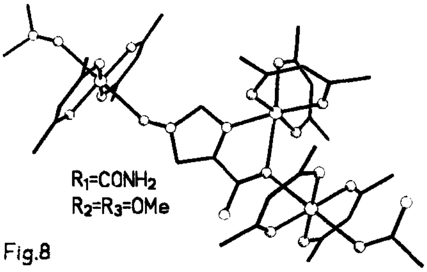
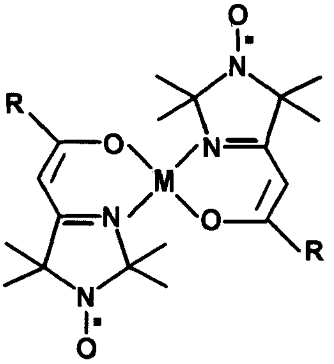


Fig.8

direct and indirect exchange interactions between transition metal ions and nitroxides.

Bischelate Complexes.

It is well known that the bischelate complexes based on 3-imidazoline radicals can be obtained if the fourth position of the radical heterocycle contains a sufficiently acid functional group.[17] In this work, we focused our attention on the derivatives involving an enamineketone group which easily releases its proton on metal ion coordination. Provided that the R-group is alkyl or aryl, the complexes of the first raw transition metals (M=Cu, Co, Ni) have molecular structure. The environment of the central atom changes from planar-square to distorted tetrahedral (Fig.9) depending on the substituent R.[18] The unpaired electrons of paramagnetic centers interact ferromagnetically at the exhange energy ≈ 10-20 cm^{-1} practically regardless of the complex geometry and the nature of the central atom. Antiferromagnetic interactions were observed only for the copper complex with $R{=}CH_3$.[19] Exchange interactions between individual molecules are essentially weaker, which allows one to describe the magnetic properties of these complexes in terms of the isolated exchange clusters $N{-}^{\bullet}O{-}M{-}O^{\bullet}{-}N$.



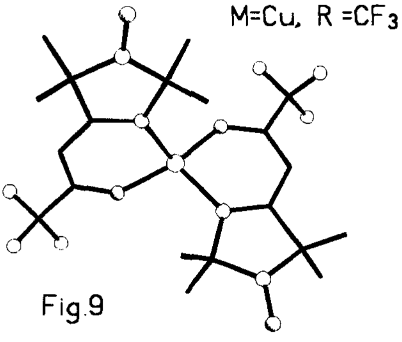


Fig.9

TWO- AND THREE-DIMENSIONAL COMPLEXES

The considerations of the above sections suggest the conclusion that for the complexes with 3-imidazoline radicals the increase in T_c to 4.2 K and higher demands the increase in structural and magnetic dimensionality of the complexes since for the molecular and chain compounds of this class the exchange (or dipole) interactions between individual molecules (chains) are weak. It is possible to increase the dimensionality of the complexes in solid 3-imidazoline bischelates by coordination of the $N{-}^{\bullet}O$ groups of neighbouring molecules. However, the participation of a weak donor,

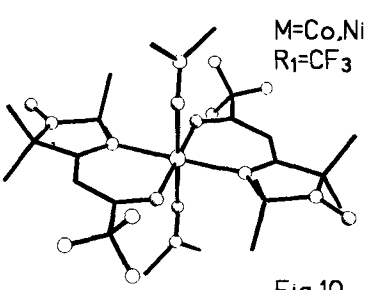


Fig.10

the nitroxyl group, in coordination necessitates an enhanced accepting ability of the bischelate molecule. In this connection, we investigated the complexes with chelating enamineketone radicals involving electron-withdrawing CF_3 and C(O)OEt groups as R. The introduction of these substituents in most cases (R=CF_3, M=Co, Ni; R=C(O)OEt, M=Co, Ni, Cu) results in the coordination of the N–•O groups of neighbouring molecules (Fig.10) and, as a consequence, in the formation of layered polymers $[ML_2]_\infty$ (Fig.11). [20,21] It is essential that on coordination of the N–•O groups the formation of new exchange channels M–O•–N occurs, which involve either weak ferromagnetic (M=Cu, 2J~10 cm^{-1}), or strong antiferromagnetic interactions (M=Co, Ni; 2J~ -100 cm^{-1}). The paramagnetic centers also are bound into the entire two-dimensional system in which both ferro- and ferrimagnetic ordering are possible. The character and energy of interlayer interactions practically determine the character of the bulk magnetic ordering. Thus, for example, the nickel complex (R=CF_3) undergoes an antiferromagnetic phase transition at 14 K.[20] The cobalt complex (R=C(O)OEt) is transferred to the ferrimagnetic state at 4.25 K, with the spontaneous magnetization being 210 G·cm^3/mol.[21] The copper complex (R=C(O)OEt) exhibits ferromagnetic intralayer ordering but does not show bulk magnetic ordering above 4.2 K because of weak interlayer exchange interactions.[21]

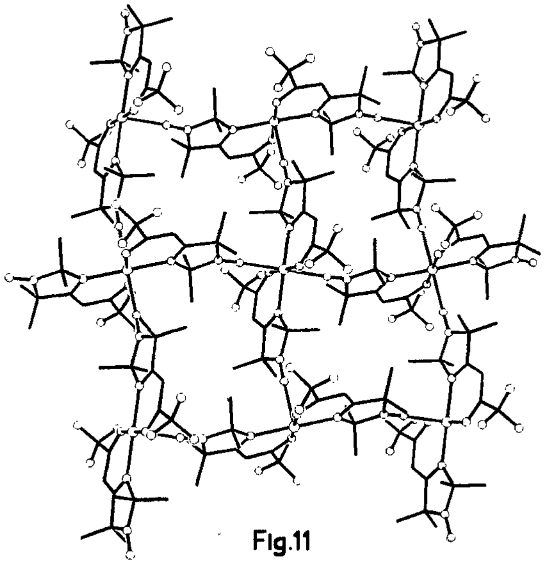


Fig.11

It should be noted that when M=Co or Ni, two intralayer exchange interactions of substantially different energy are realised: the direct exchange in N–•O–M–O•–N fragments approaching -100 ÷ -150 cm^{-3} and the superexchange through the imidazoline heterocycle (2J~10 cm^{-3}).[20] For this reason at T~10 K, when the intralayer ordering becomes operative, the paramagnetic centers in the N–•O–M–O•–N clusters are essentially coupled in antiferromagnetic way, and the cooperative magnetic moment of the layer originates from weak residual moments of the individual exchange clusters. Since the moments of the clusters are rather small, the magnetic moment of the layer appears to be insufficient to produce significant interlayer interactions. From this viewpoint the

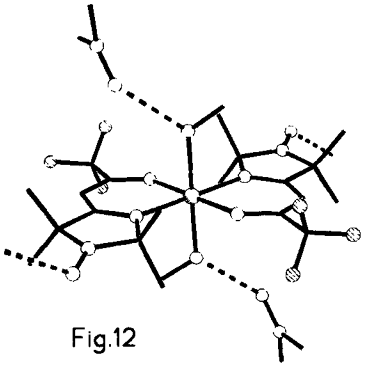


Fig.12

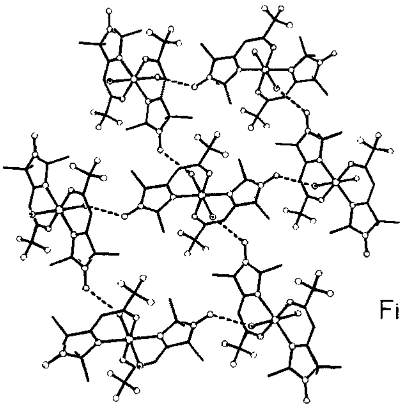


Fig.13

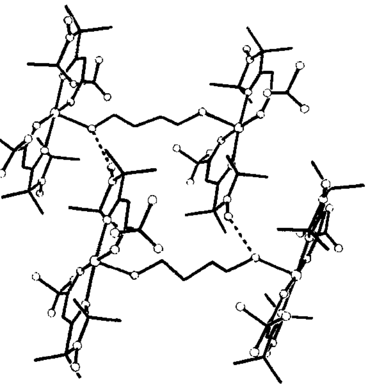


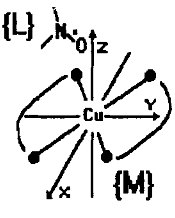
Fig.14

reduction of antiferromagnetic intralayer coupling must be favourable for increasing interlayer coupling. Such a reduction of the intralayer exchange takes place in $ML_2(R'OH)_2$ (M=Co, Ni; R'=Alk, R=CF_3) complexes, with the $N{-}^{\bullet}O{-}M{-}O^{\bullet}{-}N$ fragments being replaced by $N{-}^{\bullet}O...H{-}O(R){-}M{-}O(R){-}H...O^{\bullet}{-}N$ ones (Fig.12).[22-24] The complexes retain the layered polymeric structure, however, the $O^{\bullet}{-}N$ groups of the radicals no longer interact with the central atom but are H-bonded to the coordinated alcohol molecules. Therefore, the exchange interactions within the layers become of the same order, and the whole layer can be considered as the ensemble of sublattices involving nitroxides and metal ions, the sublattices ordering antiferromagnetically with temperature decreasing. However, in contrast to direct coordination, the residual magnetic moments in the $[ML_2(R'OH)_2]_\infty$ layers are significanly larger than the moments of the $(ML_2)_\infty$ layers. For this reason, the interlayer interactions in solid $[ML_2(R'OH)_2]$ also increase to a considerable extent, giving rise to 3-D ordering. The investigation of the magnetic properties of $ML_2(R'OH)_2$ (M=Ni; R'=CH_3, C_3H_7; C_4H_9, C_5H_{11}, C_3H_5; M=Co, R'=CH_3, C_2H_5) has shown that this materials undergo ferrimagnetic phase transition in the temperature range 4.2-8.2 K. The spontaneous magnetization is 700 G·cm^3/mol for the nickel complexes and 2500 G·cm^3/mol for the cobalt complexes.[22-24] The mixed-ligand adduct of the nickel bischelate with ethanol exhibits metamagnetic behavior with H_c about 2000 Oe. Therefore, passing from the layered bischelates ML_2 (M=Co, Ni) to the layered mixed-ligand complexes $ML_2(R'OH)_2$ we obtained a number of compounds exhibiting ferrimagnetic properties at liquid helium temperatures. It is of interest that replacing alcohol molecules with water does not change the structure of the complexes but results in the absence of magnetic phase transition above 4.2 K because of poor efficiency of H-bonded water molecules (in comparison with alcohol molecules) as superexchange pathways.[25]

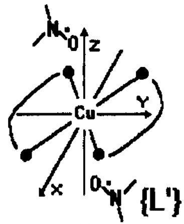
The mixed-ligand complexes $ML_2(R'OH)_2$, however, are unstable under usual conditions with respect to the decomposition into the starting bischelate and corresponding alcohol. We have found that in these adducts the distance between the hydroxyl oxygens in the adjacent layers is close to the length of the tetramethylene fragment. Reasoning from these considerations the butane-diol-1,4 adducts of NiL_2 and CoL_2 were synthesized. Like the mixed-ligand complexes with alcohols, these materials exhibit ferrimagnetic behavior at low temperatures, but they are stable under normal conditions. The investigation of the structure of the complexes has shown that the butanediol molecules, as expected, link neighbouring layers in an entire 3-D framework (Fig. 14).[24,26]

QUANTUM-CHEMICAL ANALYSIS

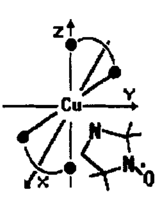
To gain some understanding of the magnetic properties of the compounds in question we performed a detailed quantum-chemical investigation of exchange interaction mechanisms which are responsible for ferromagnetic exchange in {M}...{L} and {L'}...{M}...{L} heterospin exchange systems:[20,27]



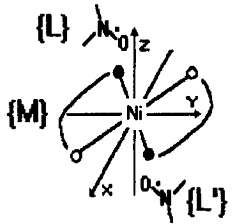
I



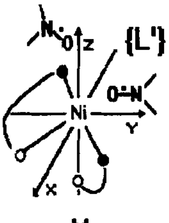
II



III



IV



V

In this contribution we also consider the existing approaches to calculating the exchange parameters J ofr the spin Hamiltonian $H=-2JS_1S_2$. Here {M} is the chelating moiety of the complexes, and {L} is the coordinated stable 3-imidazoline nitroxide.

Molecular orbitals

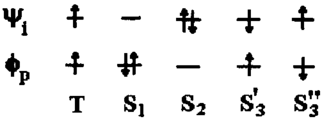
The electronic structure of the complexes I-V was calculated in terms of the INDO RHF (Restricted Hartree-Fock) approach. An analysis of obtained spin density distribution has shown that in such complexes the unpaired electrons of the { M } fragments are mainly localized on the 3d atomic orbitals with small delocalization towards the chelate group atoms and { L } and { L'} radicals. This allows one to represent in a good approximation the ψ_i (i=1 for {Cu} and i=1,2 for {Ni}) MO's of these unpaired electrons as the sum: $\psi_i = \varphi_i + \varphi_i^{del}$, where φ_i generally can be represented as a linear combination of 3d AO's of M; $\varphi_i^{del} = \varphi_i^{L} + \varphi_i^{L'}$ is the delocalization part of the MO, involving the contributions of 2s and 2p AO's of the $O^{\bullet}-N$ groups of { L } and { L'}. The unpaired electron of the { L } ligand is mainly localized on the π^* -antibonding MO's of the $O^{\bullet}-N$ groups. The ϕ_p MO of this electron can also be represented as the sum: $\phi_p = \chi_p + \chi_p^{del}$, where the $\chi_p = \pi^*$ MO of the { L }; $\chi_p^{del} = \chi_p^{M} + \chi_p^{L'}$ is the delocalization part of MO, including contributions from both the 3d AO's of M and the 2s and 2p AO's of the $O^{\bullet}-N$ group of the second radical {L'}.

Direct exchange mechanism

To elucidate the role of direct exchange interaction in the formation of the magnetic properties of complexes I - V, we performed calculations of the exchange parameters J for simple heterospin systems { M }...{ L }, taking into account the interaction only between unpaired electrons. The following expression was used :[28] $J = (1/n_M\, n_L)\Sigma_i^{n_M} J(i,p)$, where $J(i,p) = K_{ip} - 2S_{ip}\, T_{pi} + S_{ip}^2\, [\varepsilon_i + \varepsilon_p - \langle p|U_M|p\rangle - \langle i|U_L|i\rangle + J_{ip}]$ is the contribution to the exchange interaction from the two MO's φ_i and φ_p belonging to the weakly interacting subsystems { M } and { L }. Here n_M and ε_i or n_L and ε_p are, respectively, the number of unpaired electrons and orbital energies of the subsystems {M} or {L}; $S_{ip} = \langle i|p\rangle$ is the overlap integral of the φ_i and φ_p MO's ; $T_{pi} = \langle p|T|i\rangle$, where T is the kinetic energy operator; U_M or U_L are the electrostatic potentials formed by the core and the electronic shells of the subsystem {M} or {L}; $K_{ip} = \langle ip|pi\rangle$ and $J_{ip} = \langle ii|pp\rangle$ are the two-electron exchange and Coulomb integrals, correspondingly. The above INDO RHF MO's φ_i and φ_p localized on the M ion and on the O$^\bullet$–N group were taken as magnetic orbitals of the subsystems.

Indirect exchange mechanism

Currently, the most widespread method for investigation of indirect exchange interactions with due account of the main molecular characteristics of the exchange systems {A}...{B} (A and B are the paramagnetic subsystems) is the molecular orbital approach proposed by Hoffmann *et al.* [29] However, we have recently shown that the use of this approch requires rigorous account of the difference between the symmetrical system {A}+{B} and nonsymmetrical system {A}≠{B}.[20] A schematic diagram of one-electron molecular energy levels as well as many-electron configurations possible in exchange systems with two unpaired electrons is given below.



In the symmetrical systems {A}...{A} two frontier MO's ψ_i and ϕ_p differ in parity with respect to the mirror plane. Hence, in determining the energy E^S_{min} of the lowest singlet state in the framework of a configuration interaction (CI) in the basis of frontier MO's, one may restrict oneself to the consideration of the interaction $\Psi^S = c_1S_1 + c_2S_2$ of only two singlet wave functions S_1 and S_2, since the function $S_3 = 1/\sqrt{2}\,(S'_3 - S''_3)$ differs in parity from S_1 and S_2 and is not mixed with them in the CI. Let **R** be the 2x2 CI matrix for two singlet states S_1 and S_2. Then the solution of the secular equation $|\mathbf{R} - \lambda\mathbf{I}| = 0$ for the transformed matrix yields directly the energies of singlet-triplet splitting $\lambda_n = E^S_n - E^T$ (n=1,2) and, hence, the exchange parameter $2J = E^S_{min} - E^T$.

$$\tilde{R} = R - E^T \cdot I = \begin{bmatrix} \Delta\varepsilon + J_{pp} - J_{ip} + K_{ip} & K_{ip} \\ \text{———} & -\Delta\varepsilon + J_{ii} - J_{ip} + K_{ip} \end{bmatrix}$$

Here **I** is the unit matrix; $J_{ii} = \langle ii|ii\rangle$ and $J_{pp} = \langle pp|pp\rangle$ are the two-electron Coulomb integrals of the ψ_i and ϕ_p MO's; $\Delta\varepsilon = \varepsilon_i - \varepsilon_p$ is the difference of orbital energies. In the case of the complexes with heterospin (nonsymmetrical) exchange systems { M }...{ L } the situation is more complicated since the CI leads to the mixing of all three singlet configurations $\Psi^S = c_1S_1 + c_2S_2 + c_2S_2$, and for correct estimation of the energies of the singlet states $E^S{}_n$ (n=1,2,3) one should diagonalize the 3x3 CI matrix. Let this matrix be denoted as **D**. It can easily be shown that the transformed matrix **D** of the secular equation $|\mathbf{D} - \lambda\mathbf{I}| = 0$ for determining the singlet-triplet splittings $\lambda_n = E^S{}_n - E^T$ (n=1,2,3) is given by:

$$\tilde{D} = D - E^T \cdot I = \left[\begin{array}{c|c} \tilde{R} & \begin{array}{c}\sqrt{2}\,G_{ip} \\ \sqrt{2}\,G_{pi}\end{array} \\ \hline - \;\; - & 2\,K_{ip} \end{array}\right]$$

Here **R** is the submatrix equivalent to the above 2x2 CI matrix of singlet-triplet splittings; $G_{ip} = \langle ip|pp\rangle$ and $G_{pi} = \langle pi|ii\rangle$ are the two-electron "hybrid" integrals. The value of exchange parameter J in this case is determined as above. Using the INDO RHF MO's $\psi_i = \varphi_i + \varphi_i{}^{del}$ and $\phi_p = \chi_p + \chi_p{}^{del}$ obtained for the simplest model { M } ... { L } of the complexes I - V, we calculated the singlet-triplet splittings λ_n (n=1,2,3) for all possible pairs (i,p) of unpaired electrons as well as the exchange parameters $2J = E^S{}_{min} - E^T$ in terms of three different approximations: (i) disregarding the CI (only the diagonal elements of the **D** matrix are considered), (ii) taking into account the 2x2 CI (diagonalization of the submatrix **R** of the **D** matrix), and (iii) taking into account the 3x3 CI (**D** matrix diagonalization).

Main results

1. The observed magnetic properties of these complexes cannot be explained in terms of the direct exchange interaction mechanism determined by the overlap between magnetic orbitals strongly localized on the paramagnetic fragments {M} and {L}. The dominating role in the realization of ferromagnetic exchange interaction in complexes of type I - V belongs to the delocalization mechanism of interaction caused by slight spin density redistribution between {M} and {L} fragments.

2. The lowest singlet state energies (and, hence, the values and the sign of the exchange parameters J) for heterospin systems like {M}...{L} or {L'}...{M}...{L} with the unpaired electrons residing mainly on the metal and $O^{\bullet}$–N paramagnetic centers can be estimated correctly only in terms of 3x3 configuration interaction including (along with ground S_1 and doubly excited S_2) singly excited S_3 singlet configuration in the basis of frontier MO's of these systems.

3. In the case of the complexes of types I and II ferromagnetic exchange interaction is due to small delocalization of unpaired electron in the direction {L} => {M}, namely, from the π^* -antibonding MO of nitroxide onto the valence AO's (mainly on the $3d_{z^2}$ AO) of Cu(II) ion with the subsequent strong intratomic (ferromagnetic) exchange interaction with unpaired electron localized on the $3d_{xy}$ AO of Cu(II).

4. The stronger ferromagnetic exchange interaction in the complexes of type {L'}...{M}...{L} as compared to that in the complexes of type {M}...{L} may be explained in terms of an electrostatic model: the appearance of the second ligand {L'} with an effective negative charge of the coordinated atom O of the $O^{\bullet}$–N group results in destabilization of the energy level of the filled $3d_{z^2}$ AO as well as in its approaching the level of the π^* MO of nitroxide in the system {M}...{L}. This increases

considerably the degree of delocalization in the direction N–•O(π*) => Cu(3d$_{z^2}$), and, consequently, the magnitude of the ferromagnetic exchange interaction in the Cu(II) ion.

5. For the complexes of type III ferromagnetic exchange interaction is caused by the small delocalization of the unpaired electron in the direction {M} => {L}, namely, from 3d valence AO's of the Cu(II) ion along the σ-bonds of nitroxide onto σ MO of the O•–N group with the subsequent π-σ (ferromagnetic) exchange interaction with unpaired electron localized on the π* MO of the O•–N group.

6. The magnetic properties of the complexes of types IV and V are almost completely determined by the delocalization of spin density in the directions {M} => {L} and {L} => {M} which give rise to a rather strong (both ferro- and antiferromagnetic) exchange interaction in the Ni(II) ion and O•–N group. Ferromagnetic exchange interaction in the complexes of these types are best realized when the orientations of {L} with respect to {M} are such that the overlap between their magnetic orbitals is minimum. In this case the following delocalization channels are dominant: N–•O(π*) => Ni(3d$_{xz}$,3d$_{yz}$) and Ni(3d$_{z^2}$) => O•–N(σ).

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