Full Articles

Quantum chemical interpretation of different types of exchange magnetic interactions in dinuclear copper azomethine chelates

K. V. Bozhenko,[a] S. M. Aldoshin,[a] V. I. Minkin,[b] A. D. Garnovskii,[b] I. S. Vasilchenko,[b] A. N. Utenyshev,[a] and A. A. Khrulev[a]*

[a]Institute of Problems of Chemical Physics, Russian Academy of Sciences, 1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation. E-mail: bogenko@icp.ac.ru
[b]Institute of Physical and Organic Chemistry at the Southern Federal University, 194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation. E-mail: garn@ipoc.rsu.ru

B3LYP/LANL2DZ calculations of two series of isomeric dinuclear copper chelates based on the tridentate dibasic salicylaldimines from aromatic and heterocyclic amines were performed. According to calculations, the complexes with N,N- or S,S-donor atoms in the exchange fragment are mainly characterized by ferromagnetic exchange, whereas the formation of O,O-bridging fragments leads to antiferromagnetic spin-spin interaction.

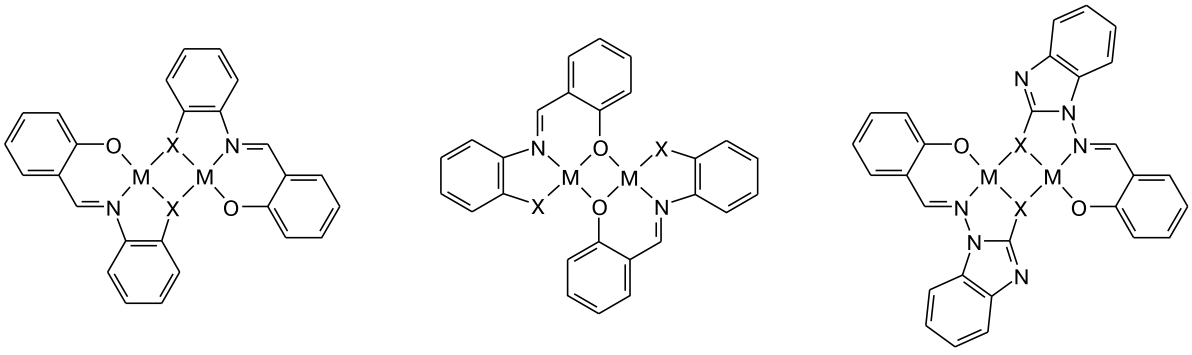
Key words: dinuclear copper chelates, quantum chemical calculations, density functional theory, ferromagnetic and antiferromagnetic exchange, spin-spin interaction, spin density, isomer structures, coordination compounds.

Azomethine metallochelates are classical objects of modern magnetochemistry.[1—5] Taking dinuclear copper complexes with aromatic (**1**) and heterocyclic (**2**, **3**) Schiff bases as examples, it was shown[6—13] that variation of the structure of the azomethine ligands (donor atoms, substituents in the aldehyde and amine fragments) can lead to systems with different types of spin-spin coupling depending on the nature of the donor atoms in the exchange fragment.

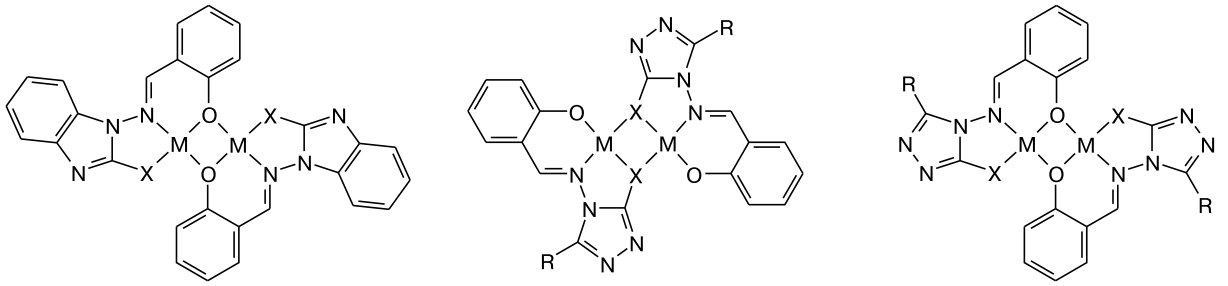
In the structures with nitrogen or sulfur bridging atoms ($(CuN)_2$ or $(CuS)_2$ fragments, respectively), dimers are mainly characterized by ferromagnetic spin-spin coupling, whereas antiferromagnetic exchange is typical of the metallochelates with oxygen bridging atoms (a $(CuO)_2$-type central metallacycle). The possibility for antiferromagnetic coordination compounds to exist as isomeric structures **1B**—**3B** was suggested.[10,13]

In continuation of our studies[6—13] and taking into account the character of the atoms in the bridging, aldehyde, and amino fragments, as well as the isomerism of dinuclear complexes **1**—**3**, we calculated for the first time the relative energies and exchange interaction constants

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 479—486, March, 2010.
1066-5285/10/5903-0489



1A **1B** **2A**



2B **3A** **3B**

1: X = NR, O, S; R = H, Me, Et, Pr; **2:** X = NR, O, S; R = H, Me, Et; **3:** X = NH, O, S; R = H, Me, Et, Pr; **1**—**3:** M = Cu

for the triplet and singlet states (preliminary results have been reported earlier[14]).

Calculation Procedure

Calculations were carried out within the framework of the density functional theory (B3LYP/LANL2DZ method) with full geometry optimization using the GAUSSIAN-03 program.[15] To calculate the exchange interaction constants (J), the singlet-state geometries of the dinuclear complexes were additionally optimized with the triplet-state geometries as the starting point to determine the energies of the broken symmetry (BS) states using a known procedure.[16] This approach proved itself in studies of the magnetic properties of oxo-bridged dinuclear copper complexes.[17,18]

Tables 1—4 list the results of calculations of the geometries, total energies (E_{tot}) in the ground triplet state and in the lowest singlet state, singlet-triplet splittings (ΔE), BS energies (E_{BS}), and the corresponding exchange interaction constants (J) for complexes **1**—**3**. The results of spin density calculations for the triplet state of the complexes are presented in Tables 5—10.

Results and Discussion

In the type-**A** structures of the complexes under study, heteroatoms included in the five-membered rings are also constituents of the exchange fragments. The geometries of complexes **1A** are strongly dependent on the nature of bridging atoms (see Table 1). For instance, the molecules with the $(CuO)_2$ fragment are nearly planar in both the triplet and singlet states (Fig. 1). Replacement of the O atom by the S atom in structure **1A** leads to a tetrahedral distortion of the coordination site.

The close values of the geometric parameters of complex **1A** (X = S) in the triplet and singlet states are noteworthy. Complexes **1A** containing N atoms in the exchange fragment (S state) have a ladder structure (see Fig. 1), which is almost independent of the nature of the alkyl substituent R (see Table 1); only the complex with R = H is structurally similar to the complexes containing sulfur atoms.

As in the case of complexes **1A**, the geometry of dimers **2A** changes upon replacement of the O atom by the S atom. Similarly to dimers **1A**, the geometry of chelates **2A** (X = NR) is independent of the nature of substituent R, although its type changes. For instance, the molecule has an angular structure in the singlet state and a ladder structure in the triplet state (see Table 1).

Analysis of the energies of the triplet and singlet states shows that for all structures (**1A**—**3A**, **1B**—**3B**) the energy of the triplet state is lower than that of the singlet state (see Tables 1—4), thus suggesting the possibility of ferromagnetic ordering in these states. The factor determining the type of exchange interaction is the energy difference between the BS and triplet states (E_T), *viz.*, if $E_{BS} > E_T$, ferromagnetic ordering occurs; otherwise, antiferromagnetic ordering occurs.

Table 1. Molecular structures, total energies of the ground triplet state and lowest-lying singlet state (E_{tot}), singlet-triplet splittings (ΔE), BS state energies (E_{BS}), and the exchange interaction constants (J) of dimers **1A** and **2A**

Central fragment	R	State	Geometry	$-E_{tot}$ /au	ΔE /kcal mol^{-1}	$-E_{BS}$ /au	J/cm^{-1}
			Dimers **1A**				
$(CuO)_2$	—	S	Ladder	1804.214846	38.9	1804.27812	−350
		T	Planar	1804.276878			
$(CuS)_2$	—	S	Angular	1673.990387	26.1	1674.031399	106
		T	Angular	1674.031960			
$(CuNR)_2$	H	S	Angular	1764.463283	23.5	1764.499645	232
		T	Angular	1764.500700			
$(CuNR)_2$	Me	S	Ladder	1843.042438	24.7	1843.080820	214
		T	Planar	1843.081817			
$(CuNR)_2$	Et	S	Ladder	1921.662200	24.2	1921.699650	232
		T	Planar	1921.700723			
$(CuNR)_2$	Pr	S	Ladder	2000.276745	23.9	2000.313780	234
		T	Planar	2000.314858			
			Dimers **2A**				
$(CuO)_2$	—	S	Nearly planar	2099.307555	28.3	2099.353362	−152
		T	Planar	2099.352668			
$(CuS)_2$	—	S	Ladder	1969.079104	12.2	1969.098248	55
		T	Ladder	1969.098497			
$(CuNR)_2$	H	S	Angular	2059.560045	12.5	2059.580378	215
		T	Ladder	2059.581358			
$(CuNR)_2$	Me	S	Angular	2138.155319	9.1	2138.168913	201
		T	Ladder	2138.169828			
$(CuNR)_2$	Et	S	Angular	2216.775931	9.6	2216.790365	194
		T	Ladder	2216.791249			

Note. Here and in Tables 2—4 "S" and "T" denote the lowest-lying singlet and triplet states, respectively.

The exchange interaction constants J were calculated using a known procedure[16] and the equation

$$-2J = (E_T - E_{BS}).$$

For structures **1A**, the energy differences between the triplet and singlet states are rather large (from ~39 to ~24 kcal mol^{-1}); for **2A**, they are somewhat smaller (see Table 1) but sufficient for the existence of stable complexes in the triplet state.

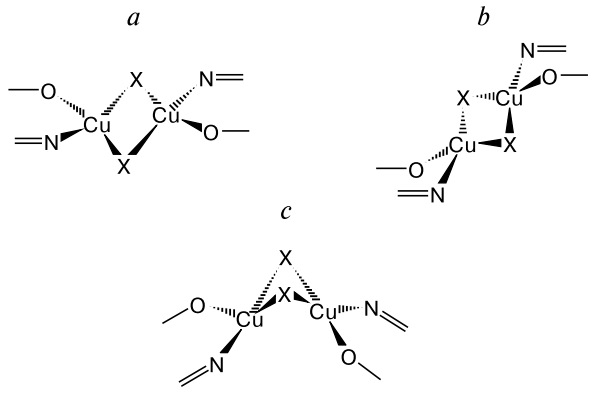


Fig. 1. Structures of the central fragment of type-**A** chelates: planar (*a*), ladder (*b*), and angular (*c*).

The exchange interaction constants J of structures **1A** and **2A** are negative for the systems with the $(CuO)_2$ central fragment and positive for the similar systems with the $(CuS)_2$ and $(CuNR)_2$ fragments (see Table 1). Since the character of the spin-spin coupling in magnetic exchange systems is determined by the sign of J, structures **1A** and **2A** are antiferromagnetic when X = O and ferromagnetic when X = NR and S. The ferromagnetic character of the complexes with the $(CuS)_2$ central fragment is less pronounced than that of the complexes with the $(CuNR)_2$ exchange fragment. The same holds for dimers **3A** (see Table 2).

The dependence between the triplet-state geometry and the sign of the exchange interaction constant in the complexes under study is noteworthy. In the dimers with ferromagnetic exchange interaction, the triplet-state geometry can be planar, ladder, and angular with a nearly 90° angle of folding along the X—X line (see Fig. 1).

To assess the effect of substituents R lying outside the exchange fragment of the complex, we calculated a number of type-**3A** structures. As for the dimers **1A** and **2A**, the geometric characteristics of dinuclear complexes **3A** are

Table 2. Molecular structures, total energies of the ground triplet and lowest-lying singlet states (E_{tot}), singlet-triplet splittings (ΔE), BS state energies (E_{BS}), and the exchange interaction constants (J) of dimers **3A**

Central fragment	R	State	Geometry	$-E_{tot}$ /au	ΔE /kcal mol^{-1}	$-E_{BS}$ /au	J/cm^{-1}
$(CuO)_2$	H	S	Angular	1824.051212	36.6	1824.110275	−166
		T	Planar	1824.109521			
	Me	S	Angular	1902.685661	36.7	1902.696934*	—
		T	Planar	1902.744177			
	Et	S	Angular	1981.297734	36.6	1981.310144*	—
		T	Planar	1981.356068			
	Pr	S	Angular	2059.911842	36.7	2059.971154*	—
		T	Planar	2059.970294			
$(CuS)_2$	H	S	Angular	1693.848795	13.2	1693.869855	−12
		T	Angular	1693.869801			
	Me	S	Angular	1772.480366	13.8	1772.502383	35
		T	Angular	1772.502439			
	Et	S	Ladder	1851.092439	13.5	1851.114199	8
		T	Angular	1851.114233			
	Pr	S	Angular	1929.706115	13.6	1929.727884	−22
		T	Angular	1929.727785			
$(CuNH)_2$	H	S	Angular	1784.318439	21.9	1784.352493	200
		T	Angular	1784.353405			
	Me	S	Angular	1862.953416	21.6	1862.986717	238
		T	Angular	1862.987803			
	Et	S	Angular	1941.565978	21.5	1941.599096	240
		T	Angular	1941.600188			
	Pr	S	Angular	2020.180500	21.5	2020.212742	251
		T	Angular	2020.213885			

* The energy does not correspond to the BS state.

independent of the nature of substituent R and vary only if atoms in the exchange fragment and the multiplicity of the system are changed. The complexes with the $(CuNH)_2$ central fragment have an angular structure in both triplet and singlet states. In the triplet state, the fragment planes make an angle of 90° (see Fig. 1), which corresponds to the largest positive values of the exchange interaction constant (see Table 2).

For the dimers **3A** with the $(CuNH)_2$ central fragment, the energy difference between the triplet and singlet state (~21.5—21.9 kcal mol^{-1}) is intermediate between the corresponding values for the other two types of exchange fragments, being large enough for stabilization of the triplet state. Complexes **3A** (X = O) and chelates **1A** and **2A** with the $(CuO)_2$ exchange fragment are characterized by antiferromagnetic exchange interaction, complexes **3A** (X = S) exhibit either antiferromagnetic or weak ferromagnetic exchange interaction, while the structures with the $(CuNH)_2$ central metallacycle possess ferromagnetic properties and maximum values of the exchange interaction constant. Thus, the ferromagnetic properties should be most pronounced for the type-**A** complexes containing nitrogen atoms in the central fragment.

The results of calculations for type-**B** dimers with the same exchange fragment $(CuO)_2$ are listed in Tables 3 and 4.

The geometry of dimers **1B** is noticeably affected by the nature of the donor X. In the case of X = NR, the structure of these complexes is almost independent of the substituent R, namely, both parts of the dimer in the singlet state lie in nearly parallel planes, thus forming a ladder structure, while in the triplet state the dimer fragments lie in intercrossing planes (Fig. 2) and form an angular structure (except for the groups R). The geometry of dimers **2B** also depends on the nature of the donor X and changes upon

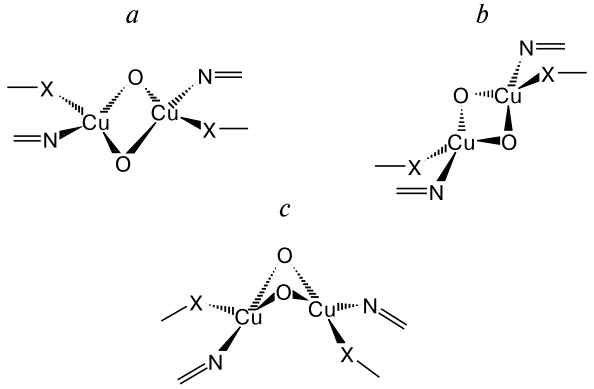


Fig. 2. Structures of the central fragment of type-**B** chelates: planar (*a*), ladder (*b*), and angular (*c*).

Table 3. Molecular structures, total energies of the ground triplet and lowest-lying singlet states (E_{tot}), singlet-triplet splittings (ΔE), BS state energies (E_{BS}), and the exchange interaction constants (J) of dimers **1B** and **2B** with the $(CuO)_2$ central fragment

X	R	State	Geometry	$-E_{tot}$/au	ΔE/kcal mol^{-1}	$-E_{BS}$/au	J/cm^{-1}
				Dimers **1B**			
O	—	S	Ladder	1804.230945	24.9	1804.230939*	—
		T	Ladder	1804.270685			
S	—	S	Angular	1674.016223	17.6	1674.046047	−392
		T	Angular	1674.044263			
NR	H	S	Ladder	1764.444620	36.9	1764.467825*	—
		T	Angular	1764.503419			
	Me	S	Ladder	1843.039570	35.6	1843.097613	−293
		T	Angular	1843.096280			
	Et	S	Ladder	1921.658539	30.9	1921.709154	−303
		T	Angular	1921.707773			
	Pr	S	Ladder	2000.272982	30.7	2000.323293	−315
		T	Angular	2000.321858			
				Dimers **2B**			
O	—	S	Ladder	2099.298783	37.6	2099.318891*	—
		T	Planar	2099.358701			
S	—	S	Ladder	1969.076283	31.9	1969.129084	−442
		T	Angular	1969.127071			
NR	H	S	Ladder	2059.549373	34.9	2059.607103	−451
		T	Angular	2059.605048			
	Me	S	Angular	2138.148872	31.8	2138.200843	−294
		T	Angular	2138.199503			
	Et	S	Angular	2216.767870	29.8	2216.816900	−343
		T	Angular	2216.815338			

* The energy does not correspond to the BS state.

Table 4. Molecular structures, total energies of the ground triplet and lowest-lying singlet states (E_{tot}), singlet-triplet splittings (ΔE), BS state energies (E_{BS}), and the exchange interaction constants (J) of dimers **3B** with the $(CuO)_2$ central fragment

X	R	State	Geometry	$-E_{tot}$/au	ΔE/kcal mol^{-1}	$-E_{BS}$/au	J/cm^{-1}
NH	Me	S	Ladder	1862.939266	32.6	1862.992990	−396
		T	Angular	1862.991188			
	Et	S	Ladder	1941.551392	32.8	1941.605512	−400
		T	Angular	1941.603688			
	Pr	S	Ladder	2020.166000	32.7	—	—
		T	Ladder	2020.218126			
O	H	S	Planar	1824.071279	25.2	—	—
		T	Planar	1824.111401			
	Me	S	Ladder	1902.685605	38.0	1902.705643*	—
		T	Planar	1902.746180			
	Et	S	Ladder	1981.297996	38.2	1981.360600	−393
		T	Planar	1981.358810			
	Pr	S	Ladder	2059.912656	38.7	—	—
		T	Planar	2059.973296			
S	H	S	Angular	1693.862118	17.0	1693.891223	−434
		T	Angular	1693.889246			
	Me	S	Angular	1772.493368	17.2	1772.522694	−410
		T	Angular	1772.520827			
	Et	S	Angular	1851.105943	17.3	1851.135281	−399
		T	Angular	1851.133463			

* The energy does not correspond to the BS state.

replacement of the oxygen atom by the sulfur atom; however, as for the complexes **1B**, the nature of the substituent R has almost no effect on their structure when X = NR.

For structures **1B**, the energy difference between the triplet and singlet states decreases from 36.9 to 17.6 kcal mol^{-1} in the following order of the donors X: NH > O > S (see Table 3). Apparently, by varying the substituents R adjacent to the exchange fragment one can stabilize the triplet state. The energy differences between the triplet and singlet states of dimers **2B** are much larger, lying between 37.6 and 29.8 kcal mol^{-1} for different donors X (see Table 3). The *J* constants for both groups of dimers (**1B** and **2B**) are negative, which indicates antiferromagnetic character of exchange interactions.

The structure of complexes **3B** (X = NH) is almost independent of the substituent R (see Table 4), namely, it is angular in the triplet state and ladder in the singlet state. At X = O, the complex has a ladder structure in the singlet state and a planar structure in the triplet state (irrespective of R). At X = S, the complexes have an angular structure regardless of the spin state and substituent R.

The triplet state of dimers **3B** is much more stable than the singlet state (by ~17—39 kcal mol^{-1}), while the exchange interaction constants are negative, as for the structures **1B** and **2B**. Thus, exchange interaction in the complexes containing the $(CuO)_2$ central fragment is antiferromagnetic.

The spin densities (SD) calculated for the triplet state of complexes **1A**—**3A** are listed in Tables 5—7. In all structures **1A** and **2A**, the spin density is localized on two copper atoms and six donor centers included in the coordination site; these eight atoms bear from ~1.93 to ~1.98 of maximum possible two unpaired electrons in the triplet state (see Tables 5 and 6). In complexes **1A**, the highest spin density is localized on the copper atoms irrespective of the substituent R. Note that the spin density on the copper atoms decreases in the following order of donors X: O > NR > S; it simultaneously increases on other atoms of the exchange fragment, being equal to about 1.5 on the central fragments ($(CuS)_2$, $(CuNR)_2$, and $(CuO)_2$).

A similar situation with the spin density magnitude and localization on particular atoms and with trends of its changes for different donors X is observed for structures **3A** (see Table 7). In dimers **3A**, the substituents R are bound to the terminal fragments rather than the central fragment. Therefore, the changes in the spin density on

Table 5. Spin densities (SD) on atoms in triplet structures **1A** with different central fragments

$(CuO)_2$		$(CuS)_2$		$(CuNR)_2$				
Atom	SD	Atom	SD	Atom	SD for R			
					H	Me	Et	Pr
Cu	**0.596**	**Cu**	**0.406**	**Cu**	**0.515**	**0.508**	**0.507**	**0.507**
O	**0.135**	**S**	**0.356**	**N**	**0.252**	**0.290**	**0.285**	**0.284**
O	**0.134**	**S**	**0.356**	**Cu**	**0.515**	**0.508**	**0.507**	**0.507**
O	0.128	O	0.116	**N**	**0.252**	**0.290**	**0.285**	**0.284**
Cu	**0.596**	**Cu**	**0.406**	O	0.100	0.083	0.085	0.085
N	0.132	N	0.093	O	0.100	0.083	0.085	0.085
N	0.132	N	0.093	N	0.096	0.087	0.088	0.088
O	0.128	O	0.116	N	0.096	0.087	0.088	0.088

Note. Here and in Tables 6, 7 and 10 the atoms of the central fragment and the spin densities on them are given in bold.

Table 6. Spin densities (SD) on atoms in triplet structures **2A** with different central fragments

$(CuO)_2$		$(CuS)_2$		$(CuNR)_2$			
Atom	SD	Atom	SD	Atom	SD for R		
					H	Me	Et
Cu	**0.597**	**Cu**	**0.402**	**Cu**	**0.520**	**0.510**	**0.509**
O	**0.178**	O	0.172	**N**	**0.193**	**0.218**	**0.220**
Cu	**0.597**	**Cu**	**0.402**	**N**	**0.193**	**0.218**	**0.220**
N	0.112	N	0.081	O	0.151	0.135	0.133
N	0.112	N	0.081	**Cu**	**0.520**	**0.510**	**0.509**
O	**0.178**	O	0.172	N	0.081	0.076	0.076
O	0.101	**S**	**0.297**	N	0.081	0.076	0.076
O	0.101	**S**	**0.297**	O	0.151	0.135	0.133

Table 7. Spin densities on atoms in triplet structures **3A**

Central fragment	Atom	R			
		H	Me	Et	Pr
$(CuO)_2$	**Cu**	**0.601**	**0.600**	**0.598**	**0.602**
	O	0.099	0.102	0.102	0.103
	O	0.099	0.102	0.102	0.103
	O	**0.181**	**0.175**	**0.175**	**0.173**
	N	0.107	0.109	0.109	0.109
	Cu	**0.600**	**0.599**	**0.598**	**0.601**
	O	**0.181**	**0.176**	**0.175**	**0.173**
	N	0.107	0.108	0.109	0.109
$(CuS)_2$	**Cu**	**0.408**	**0.407**	**0.407**	**0.407**
	S	**0.325**	**0.339**	**0.338**	**0.315**
	S	**0.326**	**0.339**	**0.338**	**0.315**
	O	0.152	0.140	0.141	0.157
	N	0.079	0.080	0.079	0.079
	Cu	**0.408**	**0.407**	**0.407**	**0.407**
	O	0.152	0.140	0.142	0.157
	N	0.107	0.080	0.080	0.079
$(CuNH)_2$	**Cu**	**0.521**	**0.517**	**0.516**	**0.516**
	N	**0.228**	**0.236**	**0.237**	**0.236**
	O	0.127	0.120	0.120	0.120
	N	0.079	0.079	0.079	0.079
	Cu	**0.521**	**0.517**	**0.516**	**0.516**
	O	0.127	0.120	0.120	0.119
	N	0.079	0.079	0.079	0.079
	N	**0.228**	**0.236**	**0.237**	**0.238**

Table 8. Spin densities on atoms in triplet structures **1B** with the $(CuO)_2$ central fragment

Atom	X = O	X = S	X = NR for R			
			H	Me	Et	Pr
Cu	0.587	0.480	0.588	0.538	0.534	0.535
O	0.121	0.114	0.119	0.109	0.108	0.108
O	0.121	0.114	0.119	0.109	0.108	0.108
O (S, N)	0.156	0.295	0149	0.190	0.193	0.193
N	0.133	0.120	0.143	0.125	0.138	0.139
Cu	0.588	0.480	0.588	0.538	0.534	0.535
O (S, N)	0.156	0.295	0.149	0.190	0.193	0.193
N	0.133	0.120	0.143	0.125	0.138	0.139

the copper atoms at different substituents R in complexes **3A** are small.

Thus, the following regularities were revealed for structures **1A**—**3A**: 1) the spin density is mainly localized on four atoms of the exchange fragment; 2) the exchange interaction constant is positive for the dimers with planar, ladder, and angular structure; 3) at X = NR, the spin density distributions in all complexes and the geometries of their exchange fragments are almost independent of the nature of substituent R.

The spin density distributions in type-**B** dimers are listed in Tables 8—10. In structures **1B**, the spin density is localized on four atoms of the central fragment and on the adjacent four donor atoms (see Table 8). In all complexes **1B**, the highest spin density is localized on the copper atoms and decreases in the following order of X: O > NR > S (as for the previously studied groups of complexes). A decrease in the spin density on the copper atoms on going from X = O to X = S is accompanied by its increase on two sulfur atoms. Type-**B** complexes differ from the type-**A** ones in that the spin density is transferred from the copper atoms to adjacent atoms beyond the exchange fragment. In the dimers **2B** and **3B** (see Tables 9 and 10, respectively), the spin density is also mainly localized on four atoms of the central fragment and on the nearest four atoms, the maximum spin density being localized on the copper atoms.

Table 9. Spin densities on atoms in triplet structures **2B** with the $(CuO)_2$ central fragment

Atom	X = O	X = S	X = NR for R		
			H	Me	Et
Cu	0.615	0.490	0.607	0.536	0.547
O	0.138	0.123	0.130	0.117	0.120
Cu	0.615	0.490	0.607	0.536	0.547
O	0.138	0.123	0.130	0.117	0.120
O (S, N)	0.125	0.286	0.138	0.190	0.181
N	0.110	0.100	0.113	0.090	0.098
N	0.110	0.100	0.113	0.090	0.098
O (S, N)	0.125	0.286	0.138	0.190	0.181

Table 10. Spin densities on atoms in triplet structures **3B** with the $(CuO)_2$ central fragment

X	Atom	R		
		H[a]	Me[b]	Et[c]
O	**Cu**	**0.618**	**0.616**	**0.616**
	O	**0.138**	**0.136**	**0.136**
	O	**0.138**	**0.136**	**0.136**
	O	0.131	0.132	0.132
	Cu	**0.618**	**0.616**	**0.616**
	O	0.131	0.132	0.132
	N	0.105	0.106	0.107
	N	0.105	0.106	0.107
S	**Cu**	**0.490**	**0.490**	**0.490**
	O	**0.122**	**0.122**	**0.122**
	O	**0.122**	**0.122**	**0.122**
	S	0.298	0.294	0.293
	Cu	**0.490**	**0.490**	**0.490**
	S	0.298	0.294	0.293
	N	0.091	0.095	0.095
	N	0.091	0.095	0.095
NH	**Cu**	**0.589**	**0.589**	**0.590**
	O	**0.124**	**0.124**	**0.124**
	O	**0.124**	**0.124**	**0.124**
	N	0.160	0.160	0.159
	Cu	**0.589**	**0.589**	**0.587**
	N	0.160	0.160	0.161
	N	0.101	0.101	0.102
	N	0.101	0.101	0.100

[a] Me for X = NH.
[b] Et for X = NH.
[c] Pr for X = NH.

Thus, the results of quantum chemical calculations suggest ferromagnetic ordering in the chelate azomethine complexes with the $(CuNR)_2$ (R = H, Me, Et, Pr) or $(CuS)_2$ central metallacycles. The strongest spin-spin coupling is expected for the $(CuNR)_2$ central metallacycle. For the type-**A** and type-**B** complexes with the $(CuO)_2$ central fragment, calculations predict antiferromagnetic exchange interaction. In all dimers studied, the spin density is almost completely localized on the four atoms of the exchange fragment and on the four adjacent donor atoms, which suggests that the magnetic properties of these complexes are determined by the nature of the exchange fragment. The substituents studied (R = H, Me, Et, Pr) do not affect the geometry and spin density distribution in the complexes studied. The calculated exchange interaction constants are close to experimental ones (see, *e.g.*, Refs 7 and 10).

This work was financially supported by the Council on Grants at the President of the Russian Federation (Program of State Support of Leading Scientific Schools, Grant

NSh-3233.2010.3), the Ministry of Education and Science of the Russian Federation (Program "Development of Research Potential", Grant RNP.2.2.1.1/2348), and the Russian Foundation for Basic Research (Project No. 08-03-00223).

References

1. O. Kahn, *Molecular Magnetism*, Wiley—VCH, 1993, 380 pp.
2. D. Gatteschi, R. Sessoli, A. Cornia, *Magnetism: General Introduction*, in *Comprehensive Coordination Chemistry II*, Eds J. A. McCleverty, T. J. Meyer, Elsevier—Pergamon Press, 2003, **2**, 393.
3. P. Przychodzen, K. Lewinski, M. Balanda, R. Pelka, M. Rams, T. Wasiutynski, C. Guyard-Duhayon, B. Sieklucka, *Inorg. Chem.*, 2004, **43**, 2967.
4. S. Saha, D. Mal, S. Koner, A. Bhattacherjee, P. Gütlich, S. Mondal, M. Mukherjee, K.-I. Okamoto, *Polyhedron*, 2004, **23**, 1811.
5. T. Glaser, M. Heidemeier, J. B. H. Strautmann, H. Bögge, A. Stammler, E. Krickemeyer, R. Huenerbein, S. Grimme, E. Bothe, E. Bill, *Chem. Eur. J.*, 2007, **13**, 9191.
6. I. S. Vasilchenko, T. A. Kuz´menko, T. E. Shestakova, R. N. Borisenko, L. N. Divaeva, A. S. Burlov, N. I. Borisenko, G. S. Borodkin, I. E. Uflyand, A. D. Garnovskii, *Arkivoc*, 2005, 82.
7. A. I. Uraev, I. S. Vasilchenko, V. N. Ikorskii, T. E. Shestakova, A. S. Burlov, K. A. Lyssenko, V. G. Vlasenko, T. A. Kuz´menko, L. N. Divaeva, I. V. Pirog, G. S. Borodkin, I. E. Uflyand, M. Yu. Antipin, V. I. Ovcharenko, A. D. Garnovskii, V. I. Minkin, *Mendeleev Commun.*, 2005, **15**, 133.
8. A. S. Burlov, Yu. V. Koshchienko, V. N. Ikorskii, V. G. Vlasenko, I. A. Zarubin, A. I. Uraev, I. S. Vasilchenko, D. A. Garnovskii, G. S. Borodkin, S. A. Nikolaevskii, A. D. Garnovskii, *Zh. Neorgan. Khim.*, 2006, **51**, 1143 [*Russ. J. Inorg. Chem. (Engl. Transl.)*, 2006, **51**, 1065].
9. A. S. Burlov, V. N. Ikorskii, A. I. Uraev, Yu. V. Koshchienko, I. S. Vasilchenko, D. A. Garnovskii, G. S. Borodkin, S. A. Nikolaevskii, A. D. Garnovskii, *Zh. Obshch. Khim.*, 2006, **76**, 1337 [*Russ. J. Gen. Chem. (Engl. Transl.)*, 2006, **76**, 1282].
10. A. D. Garnovskii, V. N. Ikorskii, A. I. Uraev, I. S. Vasilchenko, A. S. Burlov, D. A. Garnovskii, K. A. Lyssenko, V. G. Vlasenko, T. E. Shestakova, Y. V. Koshchienko, T. A. Kuz´menko, L. N. Divaeva, M. P. Bubnov, V. P. Rybalkin, O. Yu. Korshunov, I. V. Pirog, G. S. Borodkin, V. A. Bren, I. E. Uflyand, M. Yu. Antipin, V. I. Minkin, *J. Coord. Chem.*, 2007, **60**, 1493.
11. A. S. Burlov, A. I. Uraev, V. N. Ikorskii, S. A. Nikolaevskii, Yu. V. Koshchienko, I. S. Vasilchenko, D. A. Garnovskii, V. G. Vlasenko, Ya. V. Zubavichus, L. N. Divaeva, G. S. Borodkin, A. D. Garnovskii, *Zh. Obshch. Khim.*, 2008, **78**, 1002 [*Russ. J. Gen. Chem. (Engl. Transl.)*, 2008, **78**, 1230].
12. A. S. Burlov, V. N. Ikorskii, S. A. Nikolaevskii, Yu. V. Koshchienko, V. G. Vlasenko, Ya. V. Zubavichus, A. I. Uraev, I. S. Vasilchenko, D. A. Garnovskii, G. S. Borodkin, A. D. Garnovskii, *Zh. Neorgan. Khim.*, 2008, **53**, 1677 [*Russ. J. Inorg. Chem. (Engl. Transl.)*, 2008, **53**, 1566].
13. I. S. Vasilchenko, T. E. Shestakova, V. N. Ikorskii, T. A. Kuz´menko, V. G. Vlasenko, L. N. Divaeva, A. S. Burlov, A. I. Uraev, I. V. Pirog, G. S. Borodkin, P. B. Chepurnoi, I. G. Borodkina, O. A. Beletskii, O. A. Karpov, I. E. Uflyand, A. D. Garnovskii, *Koordinats. Khim.*, 2007, **33**, 176 [*Russ. J. Coord. Chem. (Engl. Transl.)*, 2007, **33**, 184].
14. K. V. Bozhenko, S. M. Aldoshin, V. I. Minkin, A. D. Garnovskii, I. S. Vasilchenko, A. N. Utenyshev, A. A. Khrulev, *Materialy IX Mezhdunar. seminara po magnitnomu rezonansu (spektroskopiya, tomografiya i ekologiya)* [*Proc. IX Int. Seminar on Magn. Reson. (Spectroscopy, Imaging, and Ecology*)] *(Rostov-on-Don, Russia, September 15—20, 2008*), Rostov-on-Don, 2008, 50 (in Russian).
15. *Licence to Use Agreement*, Gaussian, Inc., 340 Quinnipiac Street, Building 40, Wallingford, CT 06492.
16. L. Noodleman, *J. Chem. Phys.*, 1981, **74**, 5737.
17. E. Ruiz, P. Alemany, S. Alvarez, J. Cano, *J. Am. Chem. Soc.*, 1997, **119**, 1297.
18. E. Ruiz, P. Alemany, S. Alvarez, J. Cano, *Inorg. Chem.*, 1997, **36**, 3683.

Received April 20, 2009;
in revised form October 16, 2009