Full Articles

Magnetic exchange coupling in transition metal complexes with bidentate bridging ligands: a quantum chemical study

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The exchange coupling constants (J) were calculated and the spin density distributions were analyzed in the B3LYP/TZV approximation for the complex anions $[L_2M(1)^{III}LM(2)^{II}L_2]^{n-}$, where L is ligand (L is oxalate, oxamide, dithiooxamide, hydroxamate) and M(1) and M(2) are atoms of the tri- and divalent 3d-transition metals, respectively, and $n-$ is the charge of the anion. The largest J values were found for the complexes formed by the Cr^{III}—Ni^{II} and Cr^{III}—Co^{II} pairs with the dithiooxamide ligands. Differences between the calculated and experimental J values are at most a few cm^{-1}.

Keywords: bifunctional materials, oxalate, oxamide, hydroxamate, dithiooxamide, photochromic compounds, ferromagnetics, bimetallic networks, exchange coupling constants, spin density, density functional theory, B3LYP/TZV approximation.

Bifunctional materials are of great importance for the design of new-generation displays, devices for information and energy storage and processing, sensors, *etc.*[1] Such materials, which simultaneously possess the photochromic and magnetic properties, are comprised of anionic layers of the magnetic sublattice separated by photochromic cations, *e.g.*, spiropyrans or chromenes. In turn, the magnetic sublattice is a bimetallic network formed by the complex anions (CAs) of the type $[L_2M(1)^{III}LM(2)^{II}L_2]^{n-}$, where L is a bridging ligand sometimes called the intermetallic bridge; M(1) and M(2) are the atoms of tri- and divalent 3d-transition metals, respectively; and $n-$ is the charge of the anion.

Earlier,[2,3] we have synthesized a new bifunctional compound based on a cationic spiropyran containing a quaternary N atom in the pyridine ring of the side aliphatic chain. Its magnetic sublattice is formed by the complexes $[Cr^{III}Mn^{II}(Ox)_3]^-$ containing two transition metal atoms, Cr^{III} and Mn^{II}, and an oxalate intermetallic bridge. This bifunctional compound is a ferromagnetic with a Curie temperature of 5.1 K and μ_{eff} equal to about 7 μ_B at 300 K. This is in good agreement with the calculated value 7.07 μ_B (g = 2) for two paramagnetic ions, Mn^{II} and Cr^{III}. The search for the bridging ligands and pairs of metal atoms that provide the strongest ferromagnetic-type "metal—metal" exchange coupling in the anions men-

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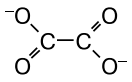
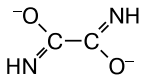
tioned above is topical in connection with the design of bifunctional materials.

In the present study, we calculated the exchange coupling constants (J) and analyzed the spin density distribution in the CAs $[L_2M(1)^{III}LM(2)^{II}L_2]^{n-}$ for four bridging ligands (oxalate, oxamide, hydroxamate, and dithiooxamide) and various pairs of atoms of di- and trivalent 3d-transition metals; in some cases, both atoms had equal valences.


Oxalate (Ox)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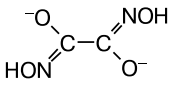
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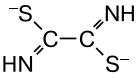
Dithiooxamide (DiSOx)

Calculation Procedure

Quantum chemical calculations were carried out within the framework of the density functional theory (DFT), in the B3LYP/TZV approximation using the ORCA program.[4]

The exchange coupling constants J were calculated using the "Broken-Symmetry" (BS) algorithm implemented in the ORCA program. It includes calculations of the total energy of the high-spin (HS) state, localization of orbitals, and subsequent BS-calculations of the low-spin state with the broken spatial and spin symmetry. This allows one to simulate the multideterminant character of the wave function within the framework of conventional one-determinant DFT calculations and thus to avoid the use of labor-consuming multiconfiguration methods for these large systems. In the ORCA program, the exchange coupling constants are calculated using expressions obtained from analysis of the spin Hamiltonian given by $H = -2J \cdot S_A \cdot S_B$ (Heisenberg—Dirac—van Fleck model):

$$J = -(E[\mathrm{HS}] - E[\mathrm{BS}])/S^2_{\max} \text{ (see Refs 5—7)}, \quad (1)$$

$$J = -(E[\mathrm{HS}] - E[\mathrm{BS}])/(S_{\max}(S_{\max} + 1)) \text{ (see Ref. 8)}, \quad (2)$$

$$J = -(E[\mathrm{HS}] - E[\mathrm{BS}])/(\langle S^2\rangle_{\mathrm{HS}} - \langle S^2\rangle_{\mathrm{BS}}) \quad (3)$$
(see Refs 9 and 10).

Expressions (1)—(3) give almost equal J values differing from one another by 1—2 cm^{-1}.

We also studied the applicability of relations (1)—(3) to the calculations of the constants J of anionic complexes formed by different ligands. To this end, we calculated two complexes, $(NCS)_4Cr^{III}(Ox)Cr^{III}(NCS)_4$ and $(NCS)_4Fe^{III}(Ox)Fe^{III}(NCS)_4$, which contain the Cr^{III}—Cr^{III} and Fe^{III}—Fe^{III} pairs, oxalate intermetallic bridges, and four isocyanate groups (NCS).

The coupling constants J for anions with different metal atoms and ligands were calculated earlier.[11—13] However, these were ony preliminary calculations because they correctly gave only the sign of the J constants, which is a criterion for classification of the exchange coupling as ferromagnetic ($J > 0$) or antiferromagnetic ($J < 0$). In these studies, the structures of the CAs shown in Fig. 1 were calculated in the B3LYP/LANL2DZ approximation with optimization of the geometry of the complexes in the ground state with the maximum spin multiplicity using the GAUSSIAN-03 program.[14] It was shown that the CAs $[L_2M(1)^{III}LM(2)^{II}L_2]^{n-}$ are the most efficient models for bimetallic networks because the resulting geometric and electronic structures are almost the same as those obtained using much larger complexes, but at lower computational cost. Also, if one deals with identical pairs of metal atoms in the same oxidation state, these complex anions can be treated isolated in ionic crystals because they are connected to the environment through the ionic bonds only.[15—17]

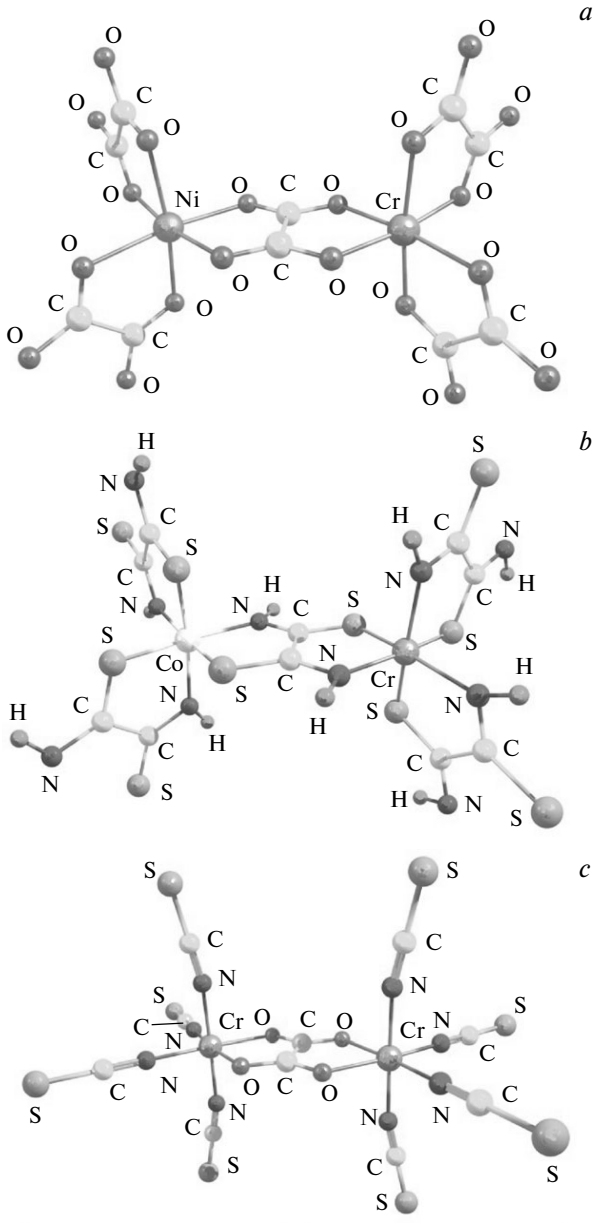

Fig. 1. Molecular structures of the anions $[(Ox)_2Cr^{III}(Ox)Ni^{II}(Ox)_2]^{5-}$ (*a*), $[(DiSOx)_2Cr^{III}(DiSOx)Co^{II}(DiSOx)_2]^{5-}$ (*b*), and $[(NCS)_4Cr^{III}(Ox)Cr^{III}(NCS)_4]^{4-}$ (*c*).

For these reasons, anions of the type $[L_2M(1)^{III}LM(2)^{II}L_2]^{n-}$ were chosen for simulation of exchange coupling in the magnetic sublattice of bifunctional compounds. Optimization of nine key structural parameters of these complexes (even assuming the same geometry of five bridging ligands) leads to almost the same results as those obtained by full geometry optimization. This allows one to conserve the symmetry of the complexes in the solid state and simultaneously reduce the number of parameters to be optimized by nearly an order of magnitude .

In this connection, geometry optimization of the complex anions with different metal atoms involved variation of only nine most important structural parameters taking into account the same molecular structure of five bridging ligands. This corresponds to their involvement in a bimetallic network where all ligands are chemically equivalent. Calculations of the complex anions containing the same metal atoms were carried out with full geometry optimization because the geometric parameters of the intermetallic bridge are different from those of the other four bridging ligands. The geometry of the complex anions thus obtained was used for calculations of the exchange coupling constants J and the corresponding spin density distributions.

Results and Discussion

The J values calculated using expressions (1)—(3) for two types of geometry optimization of the complex containing two Fe^{III} atoms and the dithiooxamide intermetallic bridge are listed in Table 1. As can be seen, in the case of full geometry optimization, the J values differ by at most 1.06 cm^{-1}. The J constants obtained using formula (3) are the most theoretically substantiated;[18] therefore, it is these values that are mainly discussed in the text below.

The calculated J values listed in Table 2 are in reasonable agreement with the experimental data (differences between them are at most 3 cm^{-1} except a value of nearly 8 cm^{-1} for $[(Ox)_2Ni^{II}(Ox)Ni^{II}(Ox)_2]^{6-}$). Changes in the constants J calculated using any of the relations (1)—(3) are similar to the changes in the corresponding negative and positive experimental values.

From the data of Table 2 it follows that the J values calculated for the complex anions formed by identical pairs of metal atoms in the same oxidation states are negative; this corresponds to antiferromagnetic exchange coupling and agrees with experimental data. In particular, for the Cr^{III}—Cr^{III} and Fe^{III}—Fe^{III} pairs, the strongest antiferromagnetic exchange coupling was found in the complexes with dithiooxamide (for the complex with Cr, the J constant is nearly 1.9 times higher in absolute value than for the complex with Fe). For both pairs, Cr^{III}—Cr^{III} and Fe^{III}—Fe^{III}, the absolute values of the constants J decrease in the same order (see Table 2), namely, J(DiSOx) > J(Oxam) > J(Ox) > J(HA). The complex anion containing a Ni^{II}—Ni^{II} pair and the oxalate ligand showed the strongest antiferromagnetic exchange among all same-type complexes.

Table 1. Exchange coupling constant J (cm^{-1}) calculated using expressions (1)—(3) for two types of geometry optimization of the complex anion $[(DiSOx)_2Fe^{III}(DiSOx)Fe^{III}(DiSOx)_2]^{4-}$

Expression	Geometry optimization	
	Full	Nine parameters
(1)	−6.35	−7.40
(2)	−5.29	−6.17
(3)	−6.35	−7.39

From data of Table 2 it also follows that for the complexes formed by the Cr^{III}—Ni^{II} and Cr^{III}—Co^{II} pairs the J values are positive, *i.e.*, one deals with ferromagnetic exchange coupling for all compounds used as ligands in these complexes. For both pairs, Cr^{III}—Ni^{II} and Cr^{III}—Co^{II}, the absolute values of J decrease in the same manner depending on the ligand, *viz.*, J(DiSOx) > J(Oxam) > J(Ox) > > J(HA). This order of changes is the same as that observed for identical pairs of metal atoms. In both cases, the strongest magnetic properties (ferromagnetic or antiferromagnetic) are due to the presence of the dithiooxamide ligand. However, the sign of the exchange coupling constant is determined by the pairs of the metal atoms that form these complex anions.

Thus, the strongest magnetic exchange coupling of a desired type in the anionic layers of the magnetic sublattice is attained by combining particular pairs of metal atoms and bridging ligands. In the anionic complexes we have studied, the most pronounced ferromagnetic properties of the magnetic sublattice can be obtained by combining the Cr^{III}—Ni^{II} and Cr^{III}—Co^{II} pairs with dithiooxamide. This conclusion can be useful for the design and targeted synthesis of the magnetic sublattices of bifunctional compounds.

The spin density in the complexes under consideration is almost completely localized on the metal atoms, in particular, on the Cr—Ni pair (more than 95%) and on the Cr—Co pair (more than 97%), as can be seen in Fig. 2 and

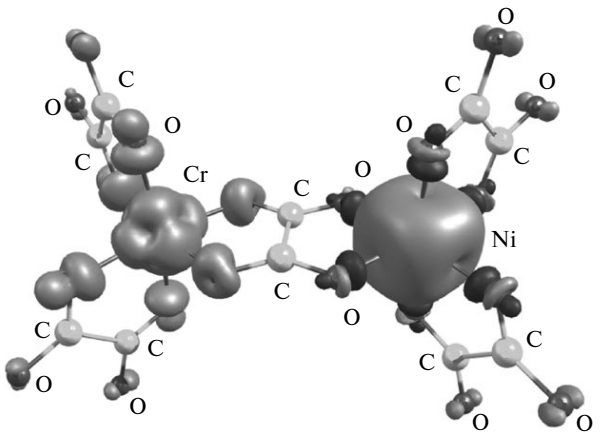

Fig. 2. Spin density distribution in the complex anion $[(Ox)_2Cr^{III}(Ox)Ni^{II}(Ox)_2]^{5-}$ with ferromagnetic character of exchange coupling.

Table 2. Total energy differences between the high-spin (E_{HS}) and broken-symmetry (E_{BS}) states of the complex anions, the anion charges ($n-$), the maximum spin values (S_{max}) corresponding to the total energy E_{HS}, and the exchange coupling constants (J) calculated using expressions (1)—(3) and the corresponding experimental values

Structure $[CA]^{n-}$	$n-$	$(E_{HS} - E_{BS})$ /kcal mol^{-1}	S_{max}	J/cm^{-1}			
				(1)	(2)	(3)	Experiment
$(Ox)_2Cr^{III}(Ox)Cr^{III}(Ox)_2$	4–	0.104	3	–4.01	–3.01	–4.01	–3.1[19]
$(HA)_2Cr^{III}(HA)Cr^{III}(HA)_2$	4–	0.088	3	–3.40	–2.55	–3.40	—
$(DiSOx)_2Cr^{III}(DiSOx)Cr^{III}(DiSOx)_2$	4–	0.262	3	–10.16	–7.62	–10.17	—
$(Oxam)_2Cr^{III}(Oxam)Cr^{III}(Oxam)_2$	4–	0.231	3	–8.98	–6.73	–8.98	—
$(Ox)_2Cr^{III}(Ox)Ni^{II}(Ox)_2$	5–	–0.144	5/2	7.99	5.7	8.32	3.55[20]
$(DiSOx)_2Cr^{III}(DiSOx)Ni^{II}(DiSOx)_2$	5–	–0.251	5/2	13.85	9.90	14.42	—
$(Oxam)_2Cr^{III}(Oxam)Ni^{II}(Oxam)_2$	5–	–0.176	5/2	9.88	7.06	10.29	—
$(HA)_2Cr^{III}(HA)Ni^{II}(HA)_2$	5–	–0.094	5/2	5.32	3.80	5.54	—
$(Ox)_2Ni^{II}(Ox)Ni^{II}(Ox)_2$	6–	0.168	2	–14.66	–9.77	–14.65	–22.8[15]
$(Ox)_2Fe^{III}(Ox)Fe^{III}(Ox)_2$	4–	0.289	5	–4.05	–3.37	–4.04	–3.44[21]
$(HA)_2Fe^{III}(HA)Fe^{III}(HA)_2$	4–	0.119	5	–1.66	–1.38	–1.66	—
$(DiSOx)_2Fe^{III}(DiSOx)Fe^{III}(DiSOx)_2$	4–	0.454	5	–6.35	–5.29	–6.35	—
$(Oxam)_2Fe^{III}(Oxam)Fe^{III}(Oxam)_2$	4–	0.393	5	–5.51	–4.59	–5.51	—
$(DiSOx)_2Cr^{III}(DiSOx)Co^{II}(DiSOx)_2$	5–	–0.232	3	8.93	6.70	8.92	—
$(Oxam)_2Cr^{III}(Oxam)Co^{II}(Oxam)_2$	5–	–0.182	3	7.01	5.26	7.01	—
$(HA)_2Cr^{III}(HA)Co^{II}(HA)_2$	5–	–0.082	3	3.13	2.35	3.13	—
$(Ox)_2Cr^{III}(Ox)Co^{II}(Ox)_2$	5–	–0.132	3	5.09	3.82	5.09	1.85[20]
$(NCS)_4Cr^{III}(Ox)Cr^{III}(NCS)_4$	4–	0.117	3	–4.53	–3.40	–4.53	–3.23[22]
$(NCS)_4Fe^{III}(Ox)Fe^{III}(NCS)_4$	4–	0.342	5	–4.78	–3.98	–4.78	–3.84[23]

Table 3. From Fig. 2 it follows that the neighbors of the Cr atom bear almost no spin density while the atoms adjacent to the Ni atom have nonzero spin densities.

Interrelations between the exchange coupling constants and the spin density distributions in the complexes forming the bimetallic network are also of interest. Elucidation of the mechanism of exchange coupling in the complexes under study will help to strengthen this coupling in the magnetic sublattices.

Table 3. Spin populations ($\rho(M)$) on the metal atoms in the complexes containing the Cr—Co and Cr—Ni pairs and an intermetallic bridge and the total changes in the spin populations on the pairs of metal atoms compared to the corresponding spin population values for isolated cations ($[\Delta\rho(M(1)) + \Delta\rho(M(2))]$) obtained from B3LYP/TZV calculatuions, and the calculated constants J (see Table 2)

Parameters of complexes	Bridging ligand			
	DiSOx	Oxam	Ox	HA
	Cr—Co pair			
ρ(Cr)	3.209	3.073	3.046	3.009
ρ(Co)	2.687	2.794	2.792	2.812
$[\Delta\rho(Cr) + \Delta\rho(Co)]$	0.522	0.279	0.254	0.197
J/cm^{-1}	8.92	7.01	5.09	3.13
	Cr—Ni pair			
ρ(Cr)	3.210	3.074	3.045	3.008
ρ(Ni)	1.599	1.737	1.738	1.765
$[\Delta\rho(Cr) + \Delta\rho(Ni)]$	0.611	0.337	0.307	0.243
J/cm^{-1}	14.42	10.29	8.32	5.54

Table 3 lists the spin populations on the metal atoms in the complexes formed by the Cr—Co pair and one of intermetallic bridge, the total changes in the spin populations on the Cr—Co pair compared to their values for isolated cations Cr^{3+} and Co^{2+}, and the J constants calculated using expression (3) (see Table 2). From the data of Table 3 it follows that the changes in these parameters correlate. In particular, an increase in the degree of spin density transfer from the Co^{II} to the Cr^{III} atom is accompanied by an increase in the J constant, *i.e.*, the intermetallic bridge acts as a kind of conductor as the spin density is transferred from one metal atom to the other.

Thus, one deals with a spin density exchange between atoms. Taking into account this fact gives a deeper insight into the nature of exchange coupling in these complexes. The higher the degree of spin density transfer from one metal atom to the other the higher the exchange coupling constant; *i.e.*, this type of the spin density redistribution causes the magnetic properties to become more pronounced. Clearly, systems in which the lone electron pair orbitals are aligned to the chemical bonds of the intermetallic bridge should show a higher degree of the spin density transfer. Unlike the cobalt atom, in the case of nickel atom this phenomenon does occur, being accompanied by the higher degree of the spin density transfer and by an increase in the exchange coupling constant J (see Table 3).

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