Asymmetry and Magnetism in Bis(oximato)-Bridged Heterobimetallic Compounds: A Computational Approach

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Abstract: A density functional study of exchange coupling was carried out for a series of heterobinuclear oximato-bridged transition metal complexes. Model calculations were used to examine the influence of the electronic configuration of the metal atoms on the coupling constants. This analysis was complemented by a study of the variation of the coupling constant with the most usual structural distortions within this family of compounds. The influence of the nature of the terminal ligands as well as that of the symmetry on the bridge were also investigated.

Keywords: density functional calculations • magnetic properties • magneto–structural correlations • transition metals

Introduction

The emerging field of molecular magnetism,[1–4] that is, the study of systems in which unpaired electrons are associated with discrete molecular entities, offers promising perspectives for the synthesis of new materials with specifically designed magnetic properties if the coupling of the unpaired electrons can be controlled. In practice, we are still learning how to do this, and most experimental work has concentrated on the production of bulk ferro- and ferrimagnets. As in any developing scientific field, some progress is attributable to careful planning, but much is purely empirical or serendipitous. Because the key factors that control the coupling of the unpaired electrons are not well understood, further development in this field has been hampered. Binuclear transition metal complexes have played a key role in developing the area of molecular magnetism. Their relative simplicity with regard to exchange coupling has permitted the formulation of a number of empirical magneto–structural correlations which have been very useful for predicting magnetic properties for new compounds.

Of all binuclear transition metal complexes relevant to the field of molecular magnetism, those containing two different metal ions are especially interesting, as shown by the following two observations:

First, when the two centers within a binuclear complex with unpaired electrons are different, the exchange interaction can lead to a more interesting magnetic behavior. It was experimentally found that it is much easier to obtain ferromagnetic coupling in heterobimetallic compounds than it is in their homobinuclear analogues. Stabilization of high-spin states is apparently much easier to achieve in heterobimetallic compounds because the unpaired electrons are more easily arranged in metal-centered orthogonal orbitals of such complexes.[5–7]

The second interesting property of heterobimetallic transition metal compounds is their versatility as building blocks for the design of molecular lattices that exhibit rather peculiar spin topologies. In particular, the design and synthesis of lattices in which the spins of both types of carriers are only partially compensated led to ferrimagnetic compounds,[6, 7] for which interesting technological applications can be envisaged.

Although, in the last decades, a lot of effort has gone into the synthesis and characterization of new heterobimetallic transition metal compounds,[6] their study from a theoretical point of view, by quantum-mechanical methods, is rather limited. Great progress towards the accurate calculation of exchange-coupling constants of homobinuclear transition metal complexes has been made in recent years.[8–18] This is mainly due to the development of new strategies for solving the difficult problem posed by the existence of a manifold of states that are separated by energy differences that are up to seven orders of magnitude smaller than the total energies of these states. Combined with the increasing power of modern

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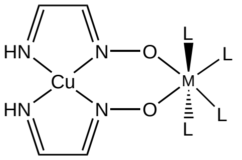
computers, these theoretical approaches nowadays permit the detailed study of magneto–structural correlations for complete families of rather complex binuclear transition metal compounds;[8, 19–23] thus, the calculated results can be compared with the qualitative models[1, 24] that are commonly used for the analysis of experimental data. Although thorough theoretical studies of exchange coupling in homonuclear bimetallic complexes can be found in the literature, its extension to heteronuclear compounds is still relatively unexplored.[9]

The main aim of this paper is to show that our recently proposed computational strategy,[8, 25] that is, the combination of DFT calculations, using the B3LYP functional, with a slightly modified version of the broken-symmetry approach of Noodelman et al.,[13, 14, 26, 27] can be extended easily to the study of exchange coupling in heteronuclear transition metal compounds. For this purpose we chose the family of bis(oximato)-bridged $\mathrm{Cu^{II}}$–M compounds,[28–36] represented by **1**; the relation between the magnetic properties and spin topologies of these compounds were studied experimentally,[28, 36] and magneto–structural correlations[30] were found for the most important structural parameters.



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Computational methodology

>Since a detailed description of the computational strategy adopted in this work can be found elsewhere,[8] we will limit our discussion here to its most relevant aspects. A phenomenological Heisenberg Hamiltonian [Eq. (1)] can be used to describe the exchange coupling in a binuclear compound, to easily relate the coupling constant, *J*, with the energy difference between the lowest (LS) and the highest (HS) multiplicity states [Eq. (2)].

$$H = -JS_1 \cdot S_2 \tag{1}$$

$$E_{\mathrm{HS}} - E_{\mathrm{LS}} = -\frac{J}{2}(S_{\mathrm{HS}} - S_{\mathrm{LS}})(S_{\mathrm{HS}} + S_{\mathrm{LS}} + 1) \tag{2}$$

Abstract in Spanish: *En este trabajo se presenta un estudio, basado en la teoría del funcional de la densidad, del acoplamiento de intercambio para un conjunto de compuestos heterobimetálicos de metales de transición con puente oximato. Se han realizado cálculos para diferentes compuestos modelo con el fin de analizar la influencia que ejercen sobre la constante de acoplamiento los siguientes factores: a) la configuración electrónica de los metales, b) las distorsiones estructurales más frecuentes, c) la naturaleza de los ligandos terminales y d) la simetría en el puente oximato.*

We recently found that DFT-based wavefunctions can give a reasonable estimate of the low-spin state energy directly from the energy of a broken-symmetry solution. If S_1 and S_2 (with $S_2 \leq S_1$) are used for the local spins on both centers, then *J* is expressed by Equation (3).[25] E_{BS} and E_{HS} in Equation (3)

$$J = \frac{(E_{\mathrm{BS}} - E_{\mathrm{HS}})}{(2S_1S_2 + S_2)} \tag{3}$$

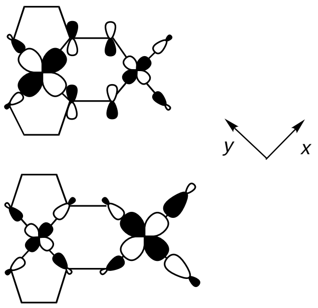
refer to the energies of the broken-symmetry (BS) and high-spin wavefunctions, respectively. Experience has shown that this equation, in which the energy of the low-spin state is estimated directly from that of the broken-symmetry solution without performing any spin-projection, leads to a good agreement with the experimental data of a large variety of compounds with exchange-coupled electrons. For a more thorough discussion of this topic the reader is referred to previous work.[8, 19–23, 25]

In practice, density functional theory is used to carry out two separate calculations to evaluate the coupling constant of each compound. The one calculation is for determining the high-spin state and the other one is for the low-spin broken-symmetry state. The hybrid B3LYP method[37] was used in all calculations as implemented in Gaussian-94,[38] so that the exact Hartree–Fock-type exchange was mixed with Becke's expression for the exchange functional[39] and the Lee–Yang–Parr correlation functional was used.[40] A basis set of double-ζ quality (triple-ζ for the transition-metal atoms), proposed by Schaefer et al.,[41] was employed throughout.

Results and Discussion

Electronic configuration and exchange coupling: All calculations presented in this work were carried out for the model bis(oximato)-bridged $\mathrm{Cu^{II}}$–M compounds (**1**), with M = $\mathrm{Cu^{II}}$,[42] $\mathrm{Ni^{II}}$, $\mathrm{Mn^{II}}$, $\mathrm{Mn^{III}}$, or $\mathrm{Cr^{III}}$. Average bond lengths and angles that were used for these model compounds were obtained from known structures.[28–36] Geometrical details for these structures can be found in the Appendix.

The M–N distances that define the coordination geometry around M are critical for the determination of the electronic configuration of the M atom in the molecule. In the experimentally characterized compounds the common $\mathrm{Cu^{II}}$ ion is in a $t_{2g}^6e_g^3$ configuration, with the $d_{x^2-y^2}$ orbital bearing the unpaired electron. The same situation is found for M when M = $\mathrm{Cu^{II}}$ (**2**). When M = $\mathrm{Ni^{II}}$, one electron is removed from the e_g set, resulting in a configuration with two unpaired electrons in the $d_{x^2-y^2}$ and d_{z^2} orbitals, respectively. For $\mathrm{Mn^{II}}$ and $\mathrm{Mn^{III}}$, experimental data show that the highest multiplicity configurations, $t_{2g}^3e_g^2$ and $t_{2g}^3e_g^1$, respectively, are found. For M = $\mathrm{Cr^{III}}$ a $t_{2g}^3e_g^0$ configuration can be deduced from experimental data. In our model compounds, the original terminal ligands surrounding the M atom are substituted by ammonia molecules. This ligand is, however, not innocent since its strong ligand field favors low-spin configurations if one uses M–N distances extracted from experimental structures. To solve this problem, the M–N distances were taken from compounds with tertiary amines[43] (see the Appendix



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for the actual values); we checked that the experimentally determined configurations of the M atoms are well reproduced. The orbital occupations obtained from a calculation for the highest multiplicity state of the different compounds are presented in Table 1. These values confirm that the configurations of the metal atoms of the models used in this work coincide with those determined experimentally. The data collected in Table 1 show that the electron populations of the e_g-type atomic orbitals are larger than their formal occupations; this indicates a certain degree of covalency in the metal–ligand bonds.

Table 1. Calculated d-orbital occupations for the highest multiplicity state in the series of model bis(oximato)-bridged Cu^{II}–M compounds studied in this work. Occupation in orbitals with unpaired electrons is indicated by boldface type. The first row gives the d-orbital occupations for the common Cu^{II} atom. Since these values are very similar for all compounds in the series, only the data for the compound with M = Cu^{II} are included in the table.

	t_{2g}			e_g		
	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}	Configuration
Cu^{II}	1.995	1.992	1.982	**1.459**	1.976	$t_{2g}^6e_g^3$
M = Cu^{II}	2.003	2.008	2.005	**1.419**	1.969	$t_{2g}^6e_g^3$
M = Ni^{II}	1.985	1.989	1.987	**1.165**	**1.175**	$t_{2g}^6e_g^2$
M = Mn^{II}	**1.016**	**1.014**	**1.013**	**1.088**	**1.079**	$t_{2g}^3e_g^2$
M = Mn^{III}	**1.049**	**1.053**	**1.072**	0.693	**1.178**	$t_{2g}^3e_g^1$
M = Cr^{III}	**1.059**	**1.076**	**1.083**	0.485	0.477	$t_{2g}^3e_g^0$

Due to the varying electronic configuration on the M atom, different coupling situations are expected for this family. Calculated exchange-coupling constants (*J*) for the model complexes (Table 2) are in excellent agreement with the experimental ones reported by Birkelbach et al.[28] The computational strategy used to extract the coupling constant can therefore also reproduce these parameters for compounds in which the different number of electrons on each metal complicates the evaluation of the energy for the HS and BS states.

Table 2. Exchange-coupling constants [cm^{-1}] for the series of model bis(oximato)-bridged Cu^{II}–M compounds studied in this work. Experimental values obtained from reference [28] are provided for comparison.

M	J_{calc}	J_{exp}
Cu^{II}	−648	−596
Ni^{II}	−201	−198
Mn^{II}	−67	−83
Mn^{III}	+127	+109
Cr^{III}	+43	+37

The calculated coupling constants follow the same trends as the experimental ones. The relative magnitudes were qualitatively discussed by various authors[28, 36] on the basis of the ideas of van Vleck[44] and Anderson.[45, 46] They suggest that the exchange interaction in a binuclear compound with magnetic centers A and B can be separated in partial contributions that involve different pairs of orbitals bearing unpaired electrons on both magnetic centers [Eq. (4)]. In

$$J = (n_A n_B)^{-1} \sum_i \sum_j J_{ij} \qquad (4)$$

Equation (4), n_A and n_B indicate the number of unpaired electrons on atoms A and B, respectively, and J_{ij} is the exchange-coupling constant between two orbitals bearing unpaired electrons. Within this model, the values of J_{ij} should be negative (antiferromagnetic coupling) if both unpaired electrons are on e_g-type orbitals and positive (ferromagnetic coupling) if one of them is in a t_{2g}-type orbital and the other in an e_g-type one. Using these qualitative ideas, one can deduce that for the compound with M = Cu^{II}, the overall coupling constant, which in this case coincides with $J_{x^2-y^2/x^2-y^2}$, should be negative. The model also suggests that the global exchange-coupling interaction for the dimers with M = Cr^{III} and M = Mn^{III} should be ferromagnetic, in good agreement with both the experimental data and our calculated *J* values. A more detailed discussion of the application of this model to cases with an intermediate situation is described in references [28] and [36].

For the present compounds, a study of the spin-density distribution can offer some insight into the relationship between the electronic structure and the exchange coupling. In principle, the participation of the donor atoms in a SOMO brings about some degree of delocalization of the unpaired electron, resulting in significant spin density at those atoms. As shown in previous work,[47] the amount of spin density at the donor atoms increases with the degree of covalency of the metal–ligand bonds. The spin polarization mechanism may also introduce spin density of alternating sign throughout the ligand. The combination of spin delocalization and spin polarization therefore accounts for the different magnitude and sign of the atomic spin densities. The calculated spin density on the different orbitals of the metal atoms (Table 3) reveals some interesting features of the exchange interaction. These values show that the e_g-type orbitals of the M atom bear the smallest spin densities associated with unpaired electrons. This is because the largest delocalization is expected for these

Table 3. Calculated spin densities in the highest multiplicity state for the series of model bis(oximato)-bridged Cu^{II}–M compounds studied in this work. Values of spin density coming from orbitals with unpaired electrons are indicated in boldface.

	t_{2g} (M)			e_g (M)		Cu^{II}
M	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}	$d_{x^2-y^2}$
Cu^{II}	0.000	0.000	0.001	**0.616**	0.004	**0.574**
Ni^{II}	0.004	0.003	0.004	**0.851**	**0.831**	**0.539**
Mn^{II}	**0.954**	**0.954**	**0.933**	**0.904**	**0.831**	**0.585**
Mn^{III}	**0.952**	**0.932**	**0.954**	0.199	**0.835**	**0.589**
Cr^{III}	**0.949**	**0.934**	**0.951**	0.093	0.091	**0.587**

orbitals due to their strong σ*-type interaction with the surrounding ligands. Similar reasoning shows that the largest spin densities are found for t_{2g}-type orbitals, which are essentially metal–ligand nonbonding and therefore exhibit the smallest delocalization. The spin density values on the x^2-y^2 orbital of the M atom for M = Cu^{II}, Ni^{II}, and Mn^{II} show that delocalization decreases along this series. For the copper compound, with the largest delocalization, the strongest antiferromagnetic behavior is expected. For the other two compounds two factors weaken this interaction: the contribution of ferromagnetic terms discussed above, and the increased localization of the unpaired electrons that can be deduced from the spin-density values.

To complete this discussion, the atomic spin densities on the ligand atoms directly coordinated to the metals will be analyzed (Table 4). These data show that the spin density in the coordination environment of the common Cu^{II} ion is very similar in all compounds, since the spin delocalization mechanism is responsible for the relatively large positive values of the spin density on the nitrogen atoms, at both the bridging and terminal ligands. The situation in the coordination sphere of the M atom is far more interesting. As far as the O atom of the bridge is concerned, the spin density clearly decreases with the localization of the unpaired electron in the x^2-y^2 orbital of the metal atom for the first three compounds of the series. Again, this finding is in good agreement with the predictions of the spin delocalization mechanism. For these compounds, the same trend is also observed for the nitrogen atoms of the terminal ligands. When the x^2-y^2 orbital is formally empty, as for M = Mn^{III} or Cr^{III}, the spin density is rather small at the bridging oxygen atom, and even negative at the terminal ligand nitrogen atoms; therefore, in this case, the spin polarization mechanism dominates in the coordination sphere of M. Atomic spin densities on the atoms surrounding the metal are not affected much by the presence or absence of unpaired electrons in t_{2g} orbitals, as expected from their lesser interaction with the ligand orbitals in their environment.

Table 4. Calculated atomic spin densities for the bridging (b) and terminal (t) ligand atoms directly bound to the metal atoms in the highest multiplicity state for the series of model bis(oximato)-bridged Cu^{II}–M compounds studied in this work.

M	N_b	O_b	N_t (Cu)	$N_{t\text{-eq}}$ (M)
Cu^{II}	0.109	0.138	0.094	0.112
Ni^{II}	0.115	0.109	0.085	0.061
Mn^{II}	0.112	0.079	0.092	0.018
Mn^{III}	0.079	0.004	0.121	−0.037
Cr^{III}	0.086	0.021	0.119	−0.035

Magneto–structural correlations: As found for other compounds, the molecular structure is important for the determination of the value of the exchange-coupling constant J. We will first focus on the influence of the N–O distance in the simplest model, that is, the compound with M = Cu^{II}.

Figure 1 shows the variation of J with the N–O distance in the region of the experimentally found values. The antiferromagnetic coupling is significantly weakened when the N–O bonds are stretched. This behavior can be easily rationalized if one analyzes the interaction between metal and ligand orbitals (**2**) that splits the in- and out-of-phase combinations of the metal x^2-y^2 orbitals that accommodate the unpaired electrons in this compound (the single-occupied molecular orbitals, SOMOs). These metal orbitals interact with a combination of N–O nonbonding and π* orbitals of the ligand. When this bond is elongated, the π* orbital is significantly stabilized, resulting in a poorer energy match with the metal x^2-y^2 orbitals, that effectively reduces the splitting of the SOMOs. According to the qualitative orbital-based model developed by Hay, Thiebault, and Hoffmann[24] (HTH) the antiferromagnetic coupling constant should decrease with the square of the splitting between SOMOs, a trend that is also found in our calculations, confirming the validity of the HTH model in this case.

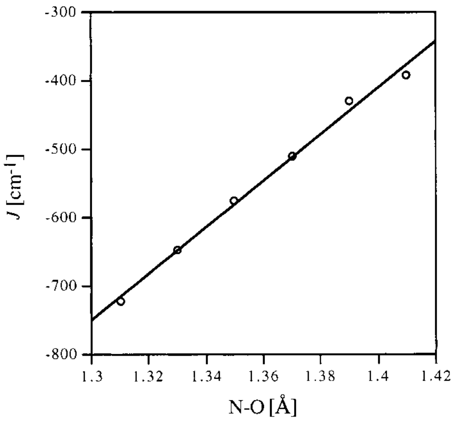


Figure 1. Exchange-coupling constants, calculated for the model bis(oximato)-bridged Cu^{II}–Cu^{II} compound as a function of the N–O distance of the bridging ligand.

The analysis of experimental data given by Dominguez-Vera et al.[30] did not show any correlation of the magnetic properties with the N–O distance. The discrepancy between that analysis and our computational results is probably due to the structural complexity of the compounds used by Dominguez-Vera et al. in their study. The simultaneous presence of other structural distortions (see discussion below) and the comparison of data for compounds with differences both in the oximate ligand itself and in the terminal ligands hides the simple correlation between J and the N–O distance that appears in our calculations.

Table 5 shows that the decrease in the exchange-coupling strength when the N–O distance is increased is a general feature for all the compounds considered in this work, regardless of the sign of the coupling constant. It is, however,

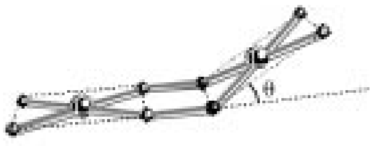
Table 5. Exchange-coupling constants [cm^{-1}] for the series of model bis(oximato)-bridged Cu^{II}–M compounds studied in this work calculated for two different N–O distances in the bridging oximato ligand.

M	d_{N-O} = 1.35 Å	d_{N-O} = 1.41 Å
Cu^{II}	−577	−394
Ni^{II}	−159	−100
Mn^{II}	−139	−67
Mn^{III}	+142	+102
Cr^{III}	+59	+43

0947-6539/00/0602-0330 $ 17.50+.50/0

not straightforward to justify this behavior by qualitative arguments similar to those presented above for the simplest case. This is due to the inability of the simple HTH model to predict magneto–structural correlations for the ferromagnetic component of the exchange coupling.

A structural distortion common to this family of compounds is the bending of the MO_2N_2 moiety around the O–O hinge (**3**). The value of θ is between 10°–60° for the structurally characterized compounds. Using the qualitative HTH model, Dominguez-Vera et al.[30] analyzed the effect of this structural distortion on exchange coupling. Their conclusion is that the change in the dihedral angle between the basal and oximate planes should only moderately decrease the energy gap (and hence the antiferromagnetic contribution to J), even for extremely large deviations from planarity. To check the validity of the HTH model for this structural distortion, we evaluated the variation of J with the hinge angle θ for values between 10°–60° in the model compound **1** with $M = Cu^{II}$ and $N-O = 1.33$ Å. We found that the coupling constant is practically invariant with the bending around the O–O hinge, with variations of less than $-10\,cm^{-1}$ for values of J around $-650\,cm^{-1}$, in good agreement with the HTH model. In their report, Dominguez-Vera et al. comment that the nature of the end-cap ligands may be, at least, as important in determining the exchange coupling as the structural parameters. As an example they considered two compounds with $M = Cu$, with practically the same geometrical distortions ($\theta = 29°$ and 26.7° for the two compounds), but with significantly different values of J. The compound with 2,2′-bipyridyl (bipy) as terminal ligand has a coupling constant[36] of $-674\,cm^{-1}$, while for the one with 1,10-phenanthroline (phen), $J = -866\,cm^{-1}$ (derived from experimental data).[35] To check if this significantly different magnetic behavior can be ascribed to the nature of the terminal ligand, we calculated the coupling constants for the complete structures of both compounds to avoid variations in J that could be attributed to poor modeling of the coordination environment around the copper atoms. The calculated results agree very well for the bipy compound: $J = -638\,cm^{-1}$. For the compound with phen, however, the calculated value $J = -524\,cm^{-1}$ deviates significantly from the experimental value. Our previous experience in calculating exchange-coupling constants indicates that a difference of over $300\,cm^{-1}$ is too large to be due to errors in the computational procedure. The discrepancy between the experimental and theoretical data for this compound remains therefore an open question. Despite the problem of determining J, our calculations for both complete structures indicate that, as noted by Dominguez-Vera et al.,[30] the nature of the terminal ligand is indeed as important as the structural distortions in determining the magnetic behavior for these compounds.



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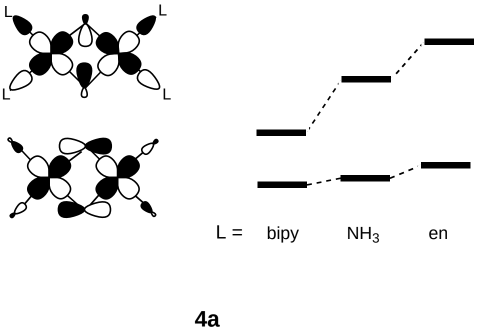
Effect of the terminal ligands on exchange coupling: As shown previously,[19, 48] the electronegativity of the atoms directly coordinated to the paramagnetic centers significantly influences the coupling constant of compounds with oxalato, hydroxo, and alkoxo bridges. The general trend for these compounds is that decreasing the electronegativity of the atoms on the terminal ligands that are directly coordinated to the paramagnetic centers, results in increased hybridization of the SOMOs towards the bridge. This increased hybridization towards the bridge results in a stronger interaction and hence in a larger energy gap between both SOMOs. According to the HTH model, this should produce a larger antiferromagnetic term in the coupling constant. This same effect leads to another interesting observation:[19] for terminal ligands that have the same type of atom coordinating directly to the metal, N for example, the strength of the antiferromagnetic coupling follows the same trend as the basicity of the terminal ligand: en ($pK_b = 4.07$) > NH_3 ($pK_b = 4.75$) > aromatic N-ligand ($pK_b = 8.77$).

To deepen our understanding of the effect of the terminal ligands on the exchange-coupling constant, we performed a series of calculations on model oximato-bridged compounds **1**, with $M = Cu^{II}$, and with different terminal ligands on the two copper atoms. We firstly analyzed the effect of the basicity of the terminal ligands coordinated to the copper atom that is bonded to the oxygen atoms of the bridge. When the NH_3 ligands in the original model are replaced by en or bipy, the coupling constant is modified in the following way: bipy ($-705\,cm^{-1}$), NH_3 ($-648\,cm^{-1}$), en ($-593\,cm^{-1}$). The trend that emerges is exactly opposite to that found for hydroxo and alkoxo bridges:[19] when the basicity of the terminal ligand of the oximato-bridged compounds is increased, the strength of the antiferromagnetic coupling is reduced.

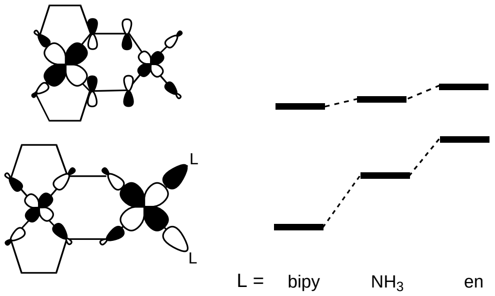
The explanation for the different behavior of oximato- and hydroxo-bridged complexes lies in the participation of the orbitals of the terminal ligands in the composition of the SOMOs. For the hydroxo-bridged compounds, in which both copper atoms have the same coordination environment, the terminal ligands participate in the two SOMOs, but they contribute more to the higher-lying one (**4a**). When the basicity of the ligand is increased, the participation of the terminal ligands in the SOMOs is also increased. Since both SOMOs are of metal–ligand antibonding nature, the in-



4a

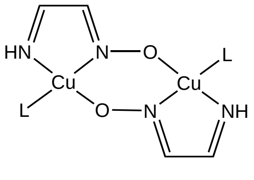
creased participation of the terminal ligands in the SOMOs causes destabilization of both SOMOs, a destabilization that is more pronounced for the SOMO which has a higher energy. The net result is an increase in the gap between both SOMOs and a stronger antiferromagnetic coupling, as predicted by the HTH model.

In the oximato-bridged compounds the situation is quite different. The different coordination environment of the two copper atoms leads to very different participation of the terminal ligands on each SOMO (**4b**). Whereas the lower lying out-of-phase combination of the metal $d_{x^2-y^2}$ orbitals mixes strongly with the orbitals of the terminal ligands, the participation of these in the high-lying SOMO is much smaller. Increasing the basicity of the terminal ligands again results in destabilization of both SOMOs, but since the terminal-ligand participation is much more important in the low-lying SOMO, the net effect in this case is a reduction of the gap and, following the HTH model, a weaker antiferromagnetic coupling. The same effect is found when the electronegativity of the atom on the terminal ligand that coordinates directly to the copper atom is changed. When NH_3 in model **1** is replaced by H_2O, the antiferromagnetic coupling constant increases from $J = -648$ cm^{-1} to $J = -1281$ cm^{-1}.



4b

We showed so far that dioximato- and dihydroxo-bridged complexes respond differently to changes in the terminal ligands, and that the different coordination environments of the two copper atoms in the dioximato-bridged compounds are responsible for this behavior. An interesting question that arises is whether the existence of an inversion center that would make both copper atoms symmetry-related, as in **5**, would affect the magnetic exchange or not. To explore this possibility, we computed the exchange-coupling constant for model **5**. J was found to be -666 cm^{-1}, a value that corresponds to slightly more antiferromagnetic coupling than found for the noncentrosymmetrical model **1**, whose J value is -648 cm^{-1}. As expected, the energy gap between the two SOMOs is practically the same for both cases. This fact, together with the difference between the J values, suggests that the changes in the two-electron terms that are neglected or considered constant in the qualitative models[1, 24] that are used to rationalize the variations in J, are extremely important in this case. A more thorough analysis of the relation between J and the symmetry at the bridge is currently being developed in our group.



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Conclusion

The use of a recently developed computational strategy was expanded to investigate exchange interactions in oximato-bridged heterobimetallic transition metal complexes. Model calculations could semiquantitatively reproduce the magnetic behavior of a number of physical situations, with quite diverse total numbers of unpaired electrons. These results confirm previous qualitative theoretical models which were used in the last decades to design new molecular materials with interesting magnetic properties. Some aspects that are sometimes difficult to study experimentally, such as magneto–structural correlations, the effect of the terminal ligands, or the effect of symmetry at the bridge on the exchange coupling, were analyzed with simplified models. This aided the rationalization of experimentally observed trends, trends that are sometimes obscured when various modifications are simultaneously made to the basic structure of these compounds.

Appendix

The average bond lengths and angles of molecular model **1**, used throughout this work, were obtained from known structures.[28] The M–N distances were taken from compounds with tertiary amines as terminal ligands, and are: 1.980 Å (Cu–N), 2.115 Å (Ni–N), 2.354 Å (Mn–N), and 2.200 Å (Cr–N). The N–O distance of the bridging oximato ligands also plays an important role in determining the exchange-coupling constant. This distance is found to vary significantly with M.[28–36] For $M = Cu^{II}$, the N–O distance is shortest, with an average value of 1.33 Å. Although no structural determination has been performed for the known compounds with $M = Ni^{II}$, a related compound with an N–O distance of 1.30 Å has been characterized.[49] The distance is longer for $M = Mn^{III}$ and $M = Cr^{III}$, with values of 1.37 Å and 1.41 Å, respectively. The structural details of compounds with $M = Mn^{II}$ are still unknown. In our models we adopted the experimental values for each compound, assuming that the N–O distance for the Mn^{II} compounds will be practically the same as for the Mn^{III} ones.

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