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Early-late transition metal ferromagnetic coupling mediated by hydrogen bonding

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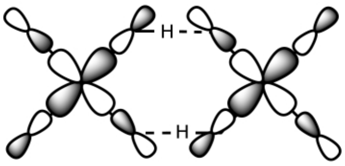
Hydrogen bonding between early and late transition metal complexes is proposed as a strategy to obtain ferromagnetic interactions based on a theoretical study using density functional calculations.

Crystal engineering of molecule-based magnets requires the control of the both the intra- and intermolecular exchange interactions. Among transition metal compounds, the intramolecular interactions can be controlled through appropriate choice of bridging ligands and interacting metal atoms.[1] However, in most cases an intramolecular ferromagnetic interaction is counterbalanced at low temperatures by antiferromagnetic intermolecular interactions that render the compound diamagnetic. The need for design principles that would allow us to make the intermolecular interactions ferromagnetic in nature is therefore obvious.

In a recent theoretical study[2] we have been able to rationalize the antiferromagnetic coupling between Cu^{II} complexes mediated by hydrogen bonds. The hydrogen bonds were shown to have only a structural role, keeping donor atoms of the two metal centers in close proximity (**1**), thus allowing for the orbital and exchange interactions that favor anti- and ferromagnetic interactions, respectively. If we supress the orbital interaction by choosing two metal atoms with unpaired electrons in orthogonal orbitals, *e.g.*, in the t_{2g} and e_g sets of metal d orbitals in an octahedral ligand field,[3] we would be left with only a ferromagnetic interaction, according to the Kahn-Briat model.[1]



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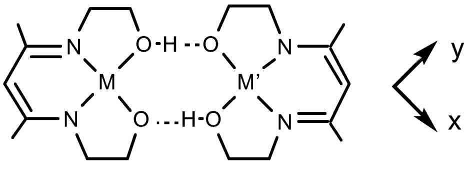
With those precedents in mind, we have carried out a computational study[4,5] of the exchange coupling between early and late transition metals through hydrogen bonds as well as an analysis of the spin density distribution,[6,7] and the results are presented in this communication.

For our study we have chosen the same tetradentate ligand used in our previous work on Cu^{II} complexes (**2**), at a constant O···O distance of 2.34 Å with two nearly coplanar molecules, and the following M/M′ metal pairs have been considered: Cu^{II}/V^{IV}, Cu^{II}/Cr^{III} and Ni^{II}/Cr^{III}. The coordination sphere of V^{IV} was supplemented with an oxo ligand making it pentacoordinate, whereas for Cr^{III} and Ni^{II} two axial ammino ligands were added to complete a pseudo-octahedral coordination sphere.[8]



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For those three compounds we have calculated the exchange coupling constant corresponding to the hamiltonian $H = -J \cdot S_1 \cdot S_2$. This was done by performing density functional theory (DFT) calculations of the energies of the highest and broken-symmetry lowest spin configurations and relating these to the coupling constant without spin projection.[9] For the DFT calculations we applied the B3LYP hybrid functional[10] using a triple-ζ basis set for the metal atoms and a double-ζ basis set for the rest.[11] The energies of the highest spin configuration (E_{HS}) and that of a broken symmetry solution with oposed spin at the two metal atoms (E_{BS}) were calculated with the Gaussian98 program,[12] from which the exchange coupling constant J is obtained without spin projection using eqn. 1, where S_1 and S_2 are the total spins of the paramagnetic centers with $S_1 > S_2$. The results are presented in Table 1 together with those reported earlier for the antiferromagnetically coupled Cu^{II} dimer.

$$E_{HS} - E_{BS} = (2S_1S_2 + S_2)J \qquad (1)$$

For the three cases studied, the computational results (see Table 1) predict ferromagnetic coupling. The calculated values are indicative of significant interaction and are comparable to, *e.g.*, the interaction between Ni^{II} and Cr^{III} mediated by cyano bridges,[13,14] that gives J values of + 5 to + 10 cm^{-1}, but significantly smaller than found, *e.g.*, between V^{IV} and Cu^{II} bridged by aryloxo groups (+ 83 cm^{-1}).[15] Even if the coupling is not strong, it should suffice to avoid the intermolecular quenching of intramolecular ferromagnetism at low temperatures.

The calculated spin population at the H atoms involved in hydrogen bonding is negligible, thus confirming the strictly structural role of those bonds and their indirect participation in the exchange coupling of the two metal atoms. The calculated spin populations for other atoms can be rationalized within the usual conceptual framework based on bonding principles:[6] (a) the spin density is mostly localized at the metal atoms, (b) the unpaired electrons in e_g orbitals show significant delocalization toward the donor atoms whereas the t_{2g} unpaired electrons are essentially localized at the metal atoms, (c) the donor atoms connected to Cu^{II} or Ni^{II} present sizeable positive spin densities due to unpaired electron delocalization and the rest of the ligands' atoms present small spin densities whose sign is determined by the spin polarization mechanism.

The study of the present heteronuclear systems gives us new views on the topology of the spin density distribution that deserve some comments. In the case of the vanadyl compound,

Table 1 Calculated coupling constants and metal-centered spin densities for the ground state of hydrogen-bonded heterodinuclear species.

M	M′	J (cm^{-1})	ρ(M)	ρ(M′)	ref.
Cu^{II}	Cu^{II}	−100	0.55	−0.55	2
V^{IV}	Cu^{II}	+8.3	1.22	0.58	this work
Cr^{III}	Cu^{II}	+9.0	3.08	0.57	this work
Cr^{III}	Ni^{II}	+5.6	3.08	1.61	this work

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no orbital interaction is allowed by symmetry between the atomic orbitals of the oxo ligand and the vanadium d_{xy} orbital that hosts the unpaired electron. Consequently, there is no positive spin delocalization to that ligand and only negative spin arises for the four oxo electron pairs as a result of spin polarization. The outcome is a large negative calculated spin density (-0.18), compared to those found for other spin-polarized atoms within the same molecule (0.03 at most), that can be seen as an island of negative spin in a sea of positive spin population in Fig. 1.

Another interesting aspect of the spin density topologies can be illustrated with the Cr/Ni compound. There (Fig. 2), the spin density corresponding to the chromium $t_{2g}{}^3$ shell has a cubic shape, with the faces of the cube perpendicular to the metal-ligand bonds, whereas that corresponding to the nickel $e_g{}^2$ shell has the shape of a octahedron with vertices in the metal–ligand bond directions. Superposition of cubic and octahedral spin densities in the same metal atom, say a high spin d^5 metal ion, must result in a spherical spin density, as recently found both from computation and from polarized neutron diffraction experiments in a Mn^{II} compound.[7] In contrast, in the V/Cu compound (Fig. 1), in which there is only one unpaired electron in the t_{2g} and e_g shell, respectively, the spin density distribution is basically two-dimensional and has the shape of the corresponding d orbitals.

In summary, the rational use of hydrogen bonding to connect hetero-mononuclear transition metal complexes should allow one to design molecule-based crystal structures with the desired exchange-coupled magnetic properties and spin density topology.

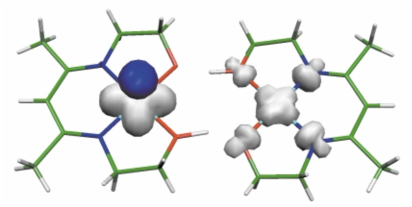

Fig. 1 Calculated spin density distribution for the hydrogen-bonded vanadyl–copper compound showing positive spin population at the metal and copper-bound donor atoms and negative spin density at the apical oxo ligand of the vanadyl group.

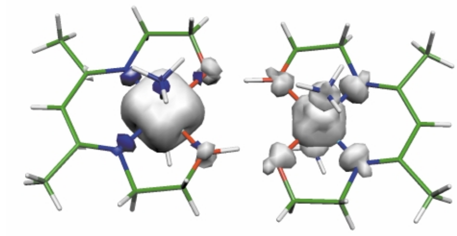

Fig. 2 Spin density distribution for the hydrogen-bonded Cr/Ni compound showing cubic and octahedral topologies around the metal atoms.

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