Spin Transitions

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Spin Transition and Exchange Interaction: Janus Visions of Supramolecular Spin Coupling between Face-to-Face Verdazyl Radicals**

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Organics radicals are fascinating objects because of both their improbable stability and their importance in biological processes and materials science. They are, for example, major actors in molecular magnetism.[1] They can be used to design purely organic materials or metal-radical architectures.[1,2] In both cases, they can exhibit versatile interactions between their unpaired electrons' spins. These interactions are mediated through intramolecular covalent or coordination bonds or through intermolecular interactions. This duality is well exemplified in one of the first organic ferromagnets built from adamantane-based ferromagnetically coupled diradicals. It displays intramolecular exchange coupling while the packing favors weak intermolecular ferromagnetic interactions, thus leading to a long-range magnetic order below 1.48 K.[3] Such interactions can lead to rather high transition temperatures[4] but are highly sensitive to crystal packing.[5] Owing to the possibility to generate labile σ- and π-bonded networks, organic-radical-based materials have been considered since magnetic and electrical properties have been observed. Spin Peierls[6] and hysteretic behavior[7] have been reported, highlighting the prime importance of such systems. Nitronyl nitroxide[3,8] and dithiazolyl[9] radicals are the most studied radicals, but recently verdazyl radicals have turned out to be interesting targets for strongly coupled systems in either their ground[2] or their excited states.[10] In these compounds, there is a wide variety of interactions between the radicals, ranging from σ-type covalent bonds to weaker intermolecular interactions.[11–13] Accordingly, the interactions between the spins of the unpaired electrons give rise to various magnetic behaviors. One way to favor strong π–π interactions between the verdazyl moieties is to introduce an intramolecular constraint to force stacking. 1,1′-bis(verdazyl)ferrocene verdazyl diradical [fc(vdO)$_2$][12] was synthesized to this end, although strong exchange interactions were found to occur only in the solid state.[12] This situation makes these compounds a laboratory for studying such behavior and for testing the different models generally used in molecular magnetism. Accurate magnetostructural studies and calculations are key factors to reach this goal.[14,15]

Herein, a strategy based solely on intermolecular constraints leads to an original face-to-face arrangement of the radicals. The crystallographic structure was determined at a variety of temperatures between 120 and 320 K, and the related exchange interaction parameters were calculated by ab initio methods. In accordance with the conclusions of this theoretical analysis, the thermal variations of the magnetic susceptibility were simulated using a spin-transition model, which is rather unusual for this type of compound. The control and flexibility of the π–π interactions in the supramolecular assembly favor the spin-transition picture over the exchange-interaction model.

During the reaction of copper(II) chloride with 1,5-dimethyl-3-(2′-imidazolyl)-6-oxo-1,2,4,5-tetrazane (imvdH$_3$O), the methanolic solution rapidly turns deep brown. Diffusion of diethyl ether into the solution leads to the formation of red single crystals of a copper(I) complex with 1,5-dimethyl-3-(2′-imidazolyl)-6-oxoverdazyl (imvdO) of formula [CuCl(imvdO)]·CH$_3$OH. The compound loses methanol above 333 K (see the Supporting Information). The formation of this compound is related to the copper-mediated oxidation of imvdH$_3$O. Such oxidation of the organic precursor has been observed in this family of radicals.[16] Structural inspections were performed at five different temperatures: 120, 180, 250, 293, and 320 K. These analyses (Figure 1 a) reveal a rather original structure. The copper(I) ion is linked to a non-bridging chloride ion (Cl21) and to the N1 nitrogen atom of the imidazole ring of imvdO. The N14–Cu1 distance is far longer than a possible coordination bond.[17] The copper(I) center is thus located in a quasi-linear environment, as the N1-Cu1-Cl21 angle ranges from 175.37(8) to 174.5(1)° between 120 and 320 K. Among the structures

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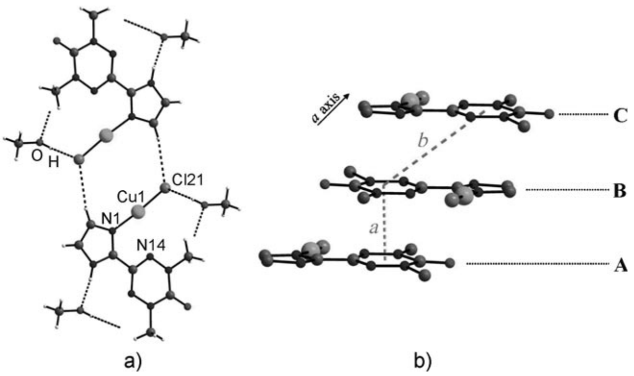

Figure 1. a) [CuCl(imvdO)]·CH_3OH with important labels and H···O and H···Cl bonds network; b) representation of [CuCl(imvdO)] pseudo-chains running along the *a* axis of the unit cell.

solved for d^{10} metal(I) ions,[18] this kind of dihedral coordination is scarce for copper(I), which is usually tetrahedrally coordinated, while the situation is balanced for silver(I), and the linear coordination is most dominant for gold(I) (see the Supporting Information for details). The absence of a Cu1−N14 bond indicates that the ligand is monodentate, a situation that has otherwise only been reported for lanthanide(III) ions.[19] The crystal packing indicates the presence of H···O and H···Cl bonds forming chains of pseudo-dimers of imidazole moieties along the *c* axis of the unit cell (Figure 1 a). Nevertheless, the main feature is the existence of stacks of complexes along the *a* axis (Figure 1 b). Within a stack, complexes are arranged in a head-to-tail manner, and the verdazyl moieties are alternatively located above one another in a face-to-face arrangement (*a*, Figure 1 b) or above an imidazole ring (*b*, Figure 1 b). Apart from $[fc(vdO)_2]$,[12] the face-to-face arrangement is only present in the simplest radicals.[20] As shown in Table 1, when the temperature is lowered, the distance between the centers of the verdazyl rings of two consecutive [CuCl(imvdO)] complexes in the face-to-face arrangement (distance *a* in Figure 1 b) decreases by 0.202 Å, while the distance between the staggered complexes (*b* in Figure 1 b) remains virtually constant (ca. 5.0 Å).

Table 1: Parameters for the crystal packing along the *a* axis.[a].

	120 K	180 K	250 K	293 K	320 K
a [Å]	3.04	3.09	3.19	3.22	3.24
b [Å]	4.97	4.95	5.01	4.98	4.99
(*a*,*b*) angle [°]	132.8	132.6	131.9	131.0	131.0
A–B [Å]	3.05	3.09	3.17	3.19	3.20
B–C [Å]	3.24	3.24	3.28	3.27	3.27

[a] The notations are those introduced in Figure 1 b

These different behaviors must strongly influence the interaction between the unpaired electrons of the radicals.[15] To quantify this influence, the exchange coupling for these two types of dimers was calculated by ab initio methods starting from the X-ray data obtained at 120, 180, 250, 293, and 320 K. The magnetic molecular orbitals (MOs) were first determined using a complete active space self-consistent field approach (CASSCF), including two electrons in two orbitals (i.e., CAS[2,2]). As expected, the magnetic MOs correspond to the bonding and antibonding linear combinations of the singly occupied MOs (SOMOs, Figure 2). Using the DDCI-1 dedicated orbitals on top of the CAS[2,2] solution, the important instantaneous π/π* electronic fluctuations within each partner were introduced at a DDCI-3 level to accurately evaluate the singlet–triplet splitting (see the Supporting Information). The resulting exchange coupling constants ($\mathcal{H} = -J S_1 S_2$) are summarized in Table 2. As expected from the exponential influence of the dimer's separation found in previous theoretical investigations,[15] the absolute J_a value is strongly reduced when the temperature is increased, while J_b remains unchanged. The thermal evolution of the two coupling constants confirms that a spin–Peierls transition can be excluded, as the decrease of one constant would be accompanied by a simultaneous increase of the second one. On the basis of the available ground- and excited-state wavefunctions, it is possible to further analyze this trend. The relevant parameters *t* (resonance integral) and *U* (electron–electron repulsion) were extracted to rationalize the antiferromagnetic (AF) contribution $-4t^2/U$. From our analysis, *U* is not sensitive to the relative positions of the two radicals and is found to be equal to 21 000 cm^{-1} in both cases. In contrast, $|t|$ is much affected (2825 and 383 cm^{-1} in AB and BC stacks, respectively), thus reflecting the deep overlap modifications. As opposed to atomic orbitals, the delocalization of the electron density over several atoms reduces the effective "on-site" repulsion, favoring the singlet state over the triplet one.[15]

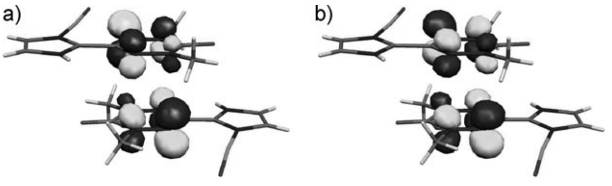

Figure 2. The a) bonding and b) antibonding quasi-degenerate magnetic MOs for a [CuCl(imvdO)] face-to-face dimer.

Table 2: Exchange coupling constants J_a and J_b in dimers AB and BC, respectively, calculated using the crystal structure at different temperatures.

	120 K	180 K	250 K	293 K	320 K
J_a [cm^{-1}]	−1520	−1245	−720	−580	−465
J_b [cm^{-1}]	−28	−29	−28	−27	−27

These theoretical predictions must be faced with the experimental magnetic behavior of the material, keeping in mind that the contribution of magnetic excitons to crystal changes can be neglected, since $|J_a|$ is much larger than kT over the entire temperature range explored. The $\chi_M T$ product of [CuCl(imvdO)]·CH_3OH has a value of 0.173 $cm^3 K mol^{-1}$ at 325 K and exhibits a steep decrease down to 150 K. Then the slope goes to zero, and the magnetic susceptibilityeventually decreases again below 10 K (Figure 3). The low value of the $\chi_M T$ product at 325 K together with the overall shape of the curve is indicative of very strong AF interactions. Nevertheless, the fitting of the thermal variation of the magnetic susceptibility with a dimer model or, to be closer to the topological description (Figure 1 b), an alternating chain model led to very poor agreement with the experimental data (see the Supporting Information for details). This result can be easily understood from the theoretical study, since the leading phenomenon featured by J_a is very sensitive to the temperature (Table 2). Temperature dependence of exchange interaction has been previously observed and tentatively modeled in other organic radical crystals by using a set of constant J parameters for the different temperature intervals.[21] Nevertheless, such a treatment is not adapted when the magnitude of the exchange interaction variation is large.[22] To propose a description adapted to our situation, it is necessary to question the hypothesis of a model based on exchange interactions that are temperature-independent. A situation in which the energy of spin states of the consecutive units (singlet and triplet) varies with temperature is strongly reminiscent of spin-transition case. Therefore, a $S=0$ to $S=1$ spin-transition model (Figure 4) was used to fit the experimental magnetic data (see the Supporting Information for details). An excellent agreement was reached (Figure 3) with $\Delta H^\circ = 8.06\ \text{kJ}\,\text{mol}^{-1}$ ($674\ \text{cm}^{-1}$) and $\Delta S^\circ = 18.7\ \text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$, corresponding to $T_{1/2} = 431\ \text{K}$. As expected from the dual proposed vision, ΔH° is of the same order of magnitude as the calculated J_a values (Table 2). Besides, it compares well with the values observed in metal-based spin transition.[23] A relatively smooth spin transition is observed, reflecting a weak cooperativity within the material. This observation is consistent with the small J_b value (Table 2). For an $S=0$ to $S=1$ spin transition, the electronic contribution to the entropy is $R\ln 3 = 9.13\ \text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$, which amounts to half of the total entropy variation. By analogy with iron(II)-based systems,[23] the other half can be attributed to modifications of the vibrations associated with the increase of the intermolecular distance with temperature (Table 1). It should be noted that the low value of the entropy variation pushes the crossover temperature upwards.

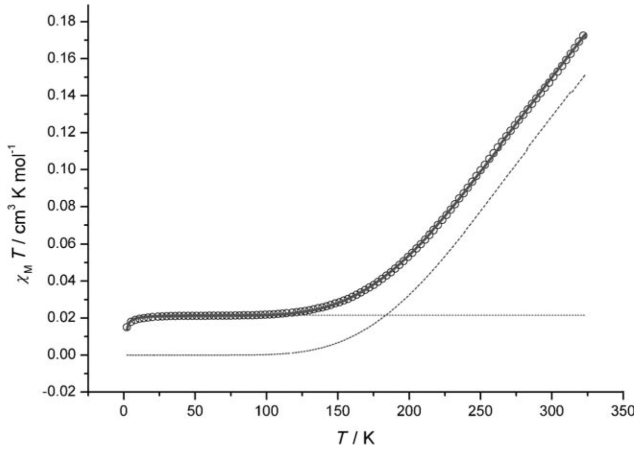

Figure 3. Thermal variation of the molar magnetic susceptibility times temperature product $\chi_M T$ of [CuCl(imvdO)]·CH_3OH. The solid line represents the best fit obtained by combining a leading contribution from spin-transition units (-----) and a fraction below 6% of a weakly coupled impurity (•••••; see the Supporting Information for details). Every third experimental point is presented for clarity.

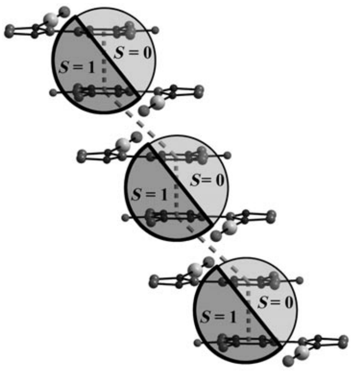

Figure 4. Schematic presentation of the magnetic behavior of [CuCl(imvdO)]·CH_3OH. The system should be seen as face-to-face dimer-based spin-transition units with cooperativity arising from the staggered interactions.

The situation encountered in [CuCl(imvdO)]·CH_3OH must be compared to other situations in which the interaction between the unpaired electrons is governed by π–π overlap. In particular, the face-to-face interaction in [fc(vdO)$_2$][12] generates a strong AF exchange interaction comparable in magnitude to that calculated at 120 K (Table 2). The interaction definitely has a common origin. Nevertheless, the molecular breathing is suppressed in [fc(vdO)$_2$] because of the intramolecular constraints imposed by the ferrocene moiety, and the entropic changes are negligible. In contrast, important structural variations with temperature (Table 1) in the [CuCl(imvdO)] intermolecular face-to-face stacking are observed. Therefore, entropic factors are likely to strongly influence the magnetic interaction. Through this comparison, it appears that the exchange interaction model and spin transition model are much closer to one another than generally considered. A proper way to identify the appropriate model is to have a close look at the structural variations with temperature. Indeed, the distances and volume changes observed in [CuCl(imvdO)]·CH_3OH (Table 1) are comparable to those observed in metal-based spin-transition systems.[24]

The structure of [CuCl(imvdO)]·CH_3OH shows how much the presence of a coordination bond within the compound can influence crystal packing of the verdazyl radicals compared to the situation in purely organic compounds.[11,25] In the present case, it leads to the occurrence of face-to-face interactions that are associated with fairly strong magnetic interactions. The enhancement of the exchange interaction results from the molecular character of the magnetic orbitals. The effective on-site repulsion is reduced, favoring the low-spin state over the high-spin one. Following the increase of 0.202 Å of the AB inter-radical distance (Figure 1 b, distance a) between 120 and 320 K, the leading exchange parameter J_a varies by a factor of more than three.

In contrast, J_b remains constant. The latter corresponds to the archetype of usual spin-coupled systems, while the temperature dependence of the former makes interpreting the spin–spin interaction with a spin-transition model more appropriate (Figure 4). This situation is, at first glance, surprising for this type of system. Rationalizing the use of this model allows us to underline that exchange-interaction and spin-transition models have common origins but are adapted to different systems, the latter being operative when there are structural changes that switch on specific entropic contributions.

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[1] a) A. Caneschi, D. Gatteschi, P. Rey, *Prog. Inorg. Chem.* **1991**, *39*, 331 – 429; b) K. Itoh, M. Kinoshita, *Molecular Magnetism*, Kodansha (Gordon and Breach), Tokyo, **2000**; c) P. M. Lahti, *Magnetic Properties of Organic Materials*, Marcel Dekker, New York, **1999**.

[2] a) B. D. Koivisto, R. G. Hicks, *Coord. Chem. Rev.* **2005**, *249*, 2612 – 2630; b) C. Train, L. Norel, M. Baumgarten, *Coord. Chem. Rev.* **2009**, *253*, 2342 – 2351.

[3] R. Chiarelli, M. A. Novak, A. Rassat, J. L. Tholence, *Nature* **1993**, *363*, 147 – 149.

[4] A. J. Banister, N. Bricklebank, I. Lavender, J. M. Rawson, C. I. Gregory, B. K. Tannner, W. Clegg, M. R. J. Egglewood, F. Palacio, *Angew. Chem.* **1996**, *108*, 2648 – 2650; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2533 – 2535.

[5] J. Luzón, J. Campo, F. Palacio, G. J. McIntyre, A. E. Goeta, E. Ressouche, C. M. Pask, J. M. Rawson, *Physica B* **2003**, *335*, 1 – 5.

[6] W. Fujita, K. Kikuchi, K. Awaga, *Angew. Chem.* **2008**, *120*, 9622 – 9625; *Angew. Chem. Int. Ed.* **2008**, *47*, 9480 – 9483.

[7] W. Fujita, K. Awaga, *Science* **1999**, *286*, 261 – 262; R. G. Hicks, *Nat. Chem.* **2011**, *3*, 189 – 191.

[8] a) M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi, M. Kinoshita, *Chem. Phys. Lett.* **1991**, *186*, 401 – 404; b) Y. Pei, O. Kahn, M. A. Aebersold, L. Ouahab, F. Leberre, L. Pardi, J. L. Tholence, *Adv. Mater.* **1994**, *6*, 681 – 683; c) M. Deumal, F. Mota, M. J. Bearpark, M. A. Robb, J. J. Novoa, *Mol. Phys.* **2006**, *104*, 857 – 873; d) M. Deumal, J. Cirujeda, J. Veciana, J. J. Novoa, *Adv. Mater.* **1998**, *10*, 1461 – 1466.

[9] a) J. L. Brusso, O. P. Clements, R. C. Haddon, M. E. Itkis, A. A. Leitch, R. T. Oakley, R. W. Reed, J. F. Richardson, *J. Am. Chem. Soc.* **2004**, *126*, 14692 – 14693; b) J. L. Brusso, O. P. Clements, R. C. Haddon, M. E. Itkis, A. A. Leitch, R. T. Oakley, R. W. Reed, J. F. Richardson, *J. Am. Chem. Soc.* **2004**, *126*, 8256 – 8265; c) A. Alberola, R. J. Less, C. M. Pask, J. M. Rawson, F. Palacio, P. Oliete, C. Paulsen, A. Yamaguchi, R. D. Farley, D. M. Murphy, *Angew. Chem.* **2003**, *115*, 4930 – 4933; *Angew. Chem. Int. Ed.* **2003**, *42*, 4782 – 4785; d) C. M. Robertson, A. A. Leitch, K. Cvrkalj, R. W. Reed, D. J. T. Myles, P. A. Dube, R. T. Oakley, *J. Am. Chem. Soc.* **2008**, *130*, 8414 – 8425; e) A. A. Leitch, J. L. Brusso, K. Cvrkalj, R. W. Reed, C. M. Robertson, P. A. Dube, R. T. Oakley, *Chem. Commun.* **2007**, 3368 – 3370.

[10] a) Y. Teki, S. Miyamoto, M. Nakatsuji, Y. Miura, *J. Am. Chem. Soc.* **2001**, *123*, 294 – 305; b) Y. Teki, T. Toichi, S. Nakajima, *Chem. Eur. J.* **2006**, *12*, 2329 – 2336.

[11] R. G. Hicks, M. T. Lemaire, L. Ohrstrom, J. F. Richardson, L. K. Thompson, Z. Q. Xu, *J. Am. Chem. Soc.* **2001**, *123*, 7154 – 7159.

[12] B. D. Koivisto, A. S. Ichimura, R. McDonald, M. T. Lemaire, L. K. Thompson, R. G. Hicks, *J. Am. Chem. Soc.* **2006**, *128*, 690 – 691.

[13] a) Y. Morita, S. Suzuki, K. Fukui, S. Nakazawa, H. Kitagawa, H. Kishida, H. Okamoto, A. Naito, A. Sekine, Y. Ohashi, M. Shiro, K. Sasaki, D. Shiomi, K. Sato, T. Takui, K. Nakasuji, *Nat. Mater.* **2008**, *7*, 48 – 51; b) H. Nishimaki, T. Ishida, *J. Am. Chem. Soc.* **2010**, *132*, 9598 – 9599; c) K. Lekin, S. M. Winter, L. E. Downie, X. Bao, J. S. Tse, S. Desgreniers, R. A. Secco, P. A. Dube, R. T. Oakley, *J. Am. Chem. Soc.* **2010**, *132*, 16212 – 16224.

[14] a) J. Jornet, M. Deumal, J. Ribas-Arino, M. J. Bearpark, M. A. Robb, R. G. Hicks, J. J. Novoa, *Chem. Eur. J.* **2006**, *12*, 3995 – 4005; b) J.-B. Rota, L. Norel, C. Train, N. Ben Amor, D. Maynau, V. Robert, *J. Am. Chem. Soc.* **2008**, *130*, 10380 – 10385; c) O. Oms, J. B. Rota, L. Norel, C. J. Calzado, H. Rousselière, C. Train, V. Robert, *Eur. J. Inorg. Chem.* **2010**, 5373 – 5378.

[15] J. B. Rota, B. Le Guennic, V. Robert, *Inorg. Chem.* **2010**, *49*, 1230 – 1237.

[16] a) D. J. R. Brook, S. Fornell, B. Noll, G. T. Yee, T. H. Koch, *J. Chem. Soc. Dalton Trans.* **2000**, 2019 – 2022; b) L. Norel, F. Pointillart, C. Train, L.-M. Chamoreau, K. Boubekeur, Y. Journaux, A. Brieger, D. J. R. Brook, *Inorg. Chem.* **2008**, *47*, 2396 – 2403.

[17] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751 – 767.

[18] F. H. Allen, *Acta Crystallogr. Sect. B* **2002**, *58*, 380 – 388.

[19] L. Norel, L.-M. Chamoreau, Y. Journaux, O. Oms, G. Chastanet, C. Train, *Chem. Commun.* **2009**, 2381 – 2383.

[20] S. V. Rosokha, J. Zhang, J. Lu, J. K. Kochi, *J. Phys. Org. Chem.* **2010**, *23*, 395 – 399.

[21] a) S. M. Winter, K. Cvrkalj, P. A. Dube, C. M. Robertson, M. R. Probert, J. A. K. Howard, R. T. Oakley, *Chem. Commun.* **2009**, 7306 – 7308; b) M. Deumal, J. M. Rawson, A. E. Goeta, J. A. K. Howard, R. C. B. Copley, M. A. Robb, J. J. Novoa, *Chem. Eur. J.* **2010**, *16*, 2741 – 2750.

[22] S. L. Veber, M. V. Fedin, A. I. Potapov, K. Y. Maryunina, G. V. Romanenko, R. Z. Sagdeev, V. I. Ovcharenko, D. Goldfarb, E. G. Bagryanskaya, *J. Am. Chem. Soc.* **2008**, *130*, 2444 – 2445.

[23] T. Nakamoto, Z. C. Tan, M. Sorai, *Inorg. Chem.* **2001**, *40*, 3805 – 3809; M. Sorai, M. Nakano, Y. Miyazaki, *Chem. Rev.* **2006**, *106*, 976 – 1031.

[24] P. Gütlich, *Struct. Bonding (Berlin)* **1981**, *44*, 83 – 195.

[25] L. Norel, L.-M. Chamoreau, C. Train, *Polyhedron* **2010**, *29*, 342 – 348.