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Beyond Kahn's Model: Substituent and Heteroatom Influence on Exchange Interaction in a Metal-Verdazyl Complex

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The synthesis, structure and magnetic properties of the first thiooxoverdazyl metal complex [Cu(hfac)$_2$(Svdpy)] [hfac = (1,1,1,5,5,5)-hexafluoroacetylacetonate; Svdpy = 1,5-dimethyl-3-(2-pyridyl)-6-thiooxoverdazyl] is described. The organic radical acts as a bidentate ligand leading to a six-coordinate metal complex. The fit of the thermal variations of the magnetic susceptibility reveal a ferromagnetic intramolecular exchange interaction. This finding is confirmed and analysed by using wavefunction-based methods which indicate that the exchange interaction is governed by the substituent of the radical rather than by its heteroatom.

Introduction

With an odd number of electrons, stable radicals were soon identified as interesting ligands to build molecule-based metal-radical magnetic compounds with high exchange interaction.[1–3] This field has long been dominated by nitroxide-based radicals but newcomers are now emerging.[2,3] We focus our attention on verdazyl-based compounds. We aim to develop a global approach that favours a back-and-forth motion between the synthesis of radical-containing coordination architectures[3–5] and the theoretical investigation of the intimate mechanisms that govern the exchange interaction between spin bearers with magnetic orbitals of different natures.[6,7] Because the valence-only description that forms the basis of the Kahn's model does not take into account all the mechanisms that contribute to the exchange interaction, wavefunction-based methods appear as central ones to unravel the microscopic origins of this phenomenon in molecule-based magnets. Despite their demanding requirements, they allow to bridge the gap between an incomplete picture of the exchange mechanisms and a comprehensive interpretation with spectroscopic accuracy.

The present contribution is representative of this approach. It describes the synthesis, structure and magnetic properties of the first thiooxoverdazyl metal complex. Eager to enhance the amplitude of the exchange interaction, the synthetic strategy was driven by the replacement of the electronegative oxygen atom of the oxoverdazyl analogue[8] by a sulfur atom. Following the valence-only description, such a substitution can modify significantly the magnetic orbitals and hence the exchange interaction. It has proven to be fruitful.[9] Moreover, since our recent results underline the importance of the substituent of the verdazyl radical,[7] we also play with this second ingredient. The single-crystal X-ray data obtained on the synthesized complex form a solid basis both for modelling the thermal variation of the magnetic susceptibility and for investigating by wavefunction-based methods the different contributions to the exchange interaction between the metal and the radical. The influence of both the heteroatom and the verdazyl substituent are actually inspected by means of calculations.

Results and Discussion

The synthesis of thiooxoverdazyl radical is a two-step procedure. The formation of the 1,5-dimethyl-3-(2-pyridyl)-6-thioxo-1,2,4,5-tetrazane (H$_3$Svdpy) is not significantly influenced by the change in the heteroatom. On the contrary, the oxidation of the thiooxotetrazane towards 1,5-dimethyl-3-(2-pyridyl)-6-thiooxoverdazyl (Svdpy) requires the use of specific procedures (see Supporting Information).[10] The efficient synthesis of [Cu(hfac)$_2$(Svdpy)] (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate) leads to the first coordination compound implying a thiooxovardazyl radical. In contrast with the oxidation process, it demonstrates that the coordination ability of substituted oxoverdazyl[8] is preserved upon heteroatom substitution.

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[Cu(hfac)$_2$(Svdpy)] crystallizes in the monoclinic $P2_1/c$ space group. The asymetric unit consists of two molecular complexes (Figure 1) with very similar geometrical features (see Supporting Information). In both complexes, the metal(II) ion is surrounded by six nearest neighbors: four oxygen atoms from the hfac groups and two nitrogen atoms from the thiooxoverdazyl radical. In both complexes, three oxygen atoms of the two hfac groups are close to the copper ion while the last one is much further away (Table S1). The nitrogen atoms of the verdazyl rings are located at 2.409(5) Å (Cu1–N4) and 2.374(5) Å (Cu2–N9) from the copper atom while those of the pyridine moieties are located at 2.019(4) Å (Cu1–N5) and 2.020(4) Å (Cu2–N10). The resulting geometries around the metal ion are elongated octahedra. This geometry is in line with the d^9 electronic structure of copper(II) which favors a Jahn–Teller distortion. The shortest Cu–N distances are those where the pyridine moieties are engaged rather than the verdazyl rings in accordance with both the relative Lewis basicity and bulkiness of these two groups. Finally the nitrogen atoms of the verdazyl moieties appear to be closer to the copper atoms than in analogous oxoverdazyl complexes.[8] The crystal packing of [Cu(hfac)$_2$(Svdpy)] is rather complex (see Supporting Information). Given its crucial influence on intermolecular exchange interaction through π-π interactions,[11–13] its analysis deserves special attention. Such interactions appear in alternating staggered π-stacks along the *a* axis (Figure 2). To figure out the possible existence of through-space exchange interactions between the radicals, these π–π interactions are described using the parameters identified by Jornet et al.:[12] for the A-type (B-type, respectively) stacking, the distance between the centroids of the verdazyl rings is 5.019(3) Å [5.268(3) Å, respectively] while for both types of stacking, the angle between the mean planes of the verdazyl rings is of 7.22(15)°. Because the stacking is more complicated than the one observed in the hydroquinone:oxoverdazyl adduct,[11] the closest contacts between atoms bearing a strong electronic density in the SOMO are also considered (see Supporting Information). For the A-type stacking, the N1–N8 distance is 3.694(7) Å. For the B-type stacking, the N3–N6 distance is worth 4.007(7) Å.

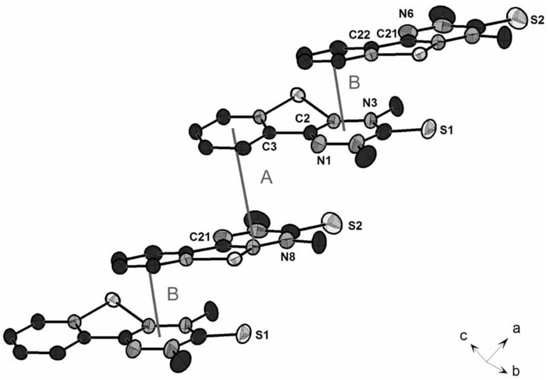

Figure 2. π-π interactions in alternating staggered stacks of [Cu(hfac)$_2$(Svdpy)] along the a axis. The hfac ligands are omitted for clarity.

Upon cooling, the $\chi_M T$ product, where χ_M is the molar magnetic susceptibility of [Cu(hfac)$_2$(Svdpy)], increases from 0.678 cm^3 K mol^{-1} at 300 K to reach a rounded maximum of 0.696 cm^3 K mol^{-1} at 48 K and then drops off with an increasing rate down to 5 K (Figure 3). The thermal evolution of $\chi_M T$ down to 48 K is characteristic of a ferromagnetic (F) coupling between the spin carriers. The steep decrease at low temperature is indicative of an additional antiferromagnetic (AF) interaction. As experimentally observed in oxygenated analogs[8] and theoretically rationalised in the following, the F contribution arises from the intramolecular exchange coupling between the axially coordinated radical and the copper(II) ion. The AF interaction is thus related to the radical-radical intermolecular interaction. This is coherent with the theoretical analysis of the evolution of this interaction with respect to the relative position of the radicals:[7] the angle between the radical is far below the crossover angle from AF to F interaction (ca. 40°) and the stacking indicates a noticeable overlap between the nitrogen atoms of the radicals (see Supporting Information).

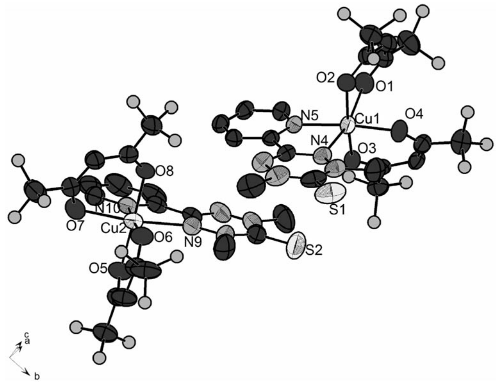

Figure 1. Crystal structure of [Cu(hfac)$_2$(Svdpy)] with numbering scheme and thermal ellipsoids at 30% probability. Hydrogen atoms and thermal ellipsoids for fluorine atoms are omitted for clarity.

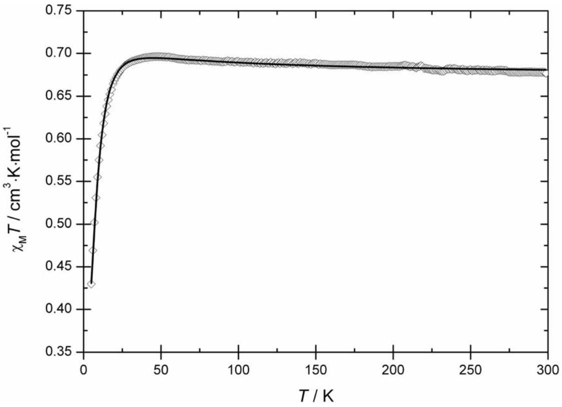

Figure 3. Thermal variation of the $\chi_M T$ product for [Cu(hfac)$_2$(Svdpy)]. The solid line is the best fit of the experimental data (see text).

Following the analysis of the crystal packing and the exponential decrease of the coupling with distances, we can estimate that the intermolecular exchange interaction J_2(B) through the B-stacks (Figure 2) is at most 30% of that occurring through the A-stacks (Figure 2).[11–13] In consequence, a first approach consists in focusing on the main intermolecular interactions by neglecting J_2(B). The system can then be considered as metal (S_1 = 1/2)-radical (S_2 = 1/2) coupled species (J_1 intramolecular exchange constant) further coupled through the A-stacking of the molecules (J_2). An analytical expression for such systems has been derived for copper tetramers.[14] For g_{av} = 1.90, J_1 = 14.5 cm^{-1} and J_2 = –14.7 cm^{-1} ($H = -J\ S_1 \cdot S_2$), this analytical law closely follows the experimental values over the whole temperature range.

The quality of the fit is much better than what has been observed in the analogous oxygenated complex [Cu(hfac)$_2$-(Ovdim)][8] [Ovdim = 1,5-dimethyl-3-(1-methyl-2-imidazolyl)-6-oxoverdazyl] leading to a good confidence in the choice of the model and the absolute values of the parameters deduced from the fit (see Supporting Information). The comparison with the system aforementioned is most instructive. The intermolecular interaction J_2 is worth 37% of the value found in [Cu(hfac)$_2$(Ovdim)]. The decrease of the intermolecular interaction observed in the present case can be ascribed to a weaker overlap between the verdazyl moieties in [Cu(hfac)$_2$(Svdpy)] compared to [Cu(hfac)$_2$-(Ovdim)].[8] The intramolecular coupling constant J_1 is more than twice the value found in [Cu(hfac)$_2$(Ovdim)]. This situation actually reinforces the relative influence of the intramolecular exchange coupling J_1 compared to the intermolecular one on the magnetic susceptibility and guarantees the ferromagnetic nature of the former by allowing the existence of a maximum in the thermal variation of the $\chi_M T$ product (Figure 3). Following the demonstrated effect of oxygen to sulfur substitution on the exchange interaction[9] and the J_1 value in the 2 to 10 cm^{-1} interval proposed for [Cu(hfac)$_2$(Ovdpy)] (Ovdpy = 1,5-dimethyl-3-(2-pyridyl)-6-oxoverdazyl),[8] the increase of J_1 could be ascribed to the modification of the heteroatom. To explore this possibility, calculations were performed to analyse the different mechanisms that govern the exchange interaction between the metal ion and the radical.

Starting from the structural data, the nature, intensity and origins of the intramolecular exchange coupling J_1 can be clarified by careful reading of the wavefunction. We first performed CAS[2,2]SCF (see Exp. Section) calculations for both the singlet and triplet states. As expected, the magnetic orbitals are mainly the copper-centered $d_{x^2-y^2}$ and the Svd-centered π_2* (Figure 4). Due to the quasi-orthogonality of these two orbitals, a ferromagnetic behaviour can be anticipated using Kahn's model.[15] The valence-only description indeed offers a value of J_1 that compares fairly well with the experimental one (Table 1; Figure 5).

Nevertheless, it is known that such description may not be well-adapted since non-negligible contributions arising from correlation effects (charge redistribution and spin polarization) are likely to deeply modify the minimal CAS picture.[7,16,17] Difference dedicated configuration interaction (DDCI) calculations were performed. This method can be considered as an optimal approach to deal with magnetic systems, providing quantitative estimates of the magnetic constants and a rational analysis of the leading mechanisms based on the information contained in the wavefunctions.

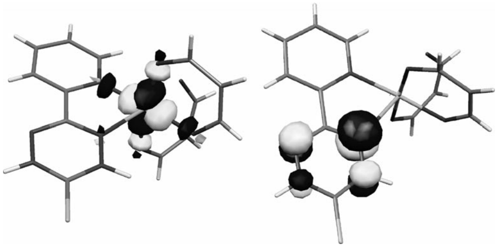

Figure 4. Magnetic orbitals in [Cu(hfac)$_2$(Svdpy)].

Table 1. Experimental and calculated values of J_1 (cm^{-1}) using different levels of calculations. The triplet state molecular orbitals were used to build the DDCI-1 and DDCI-3 spaces.

Exp.	CAS[2,2]SCF	DDCI-1	DDCI-3
14.2	15	–6.1	17

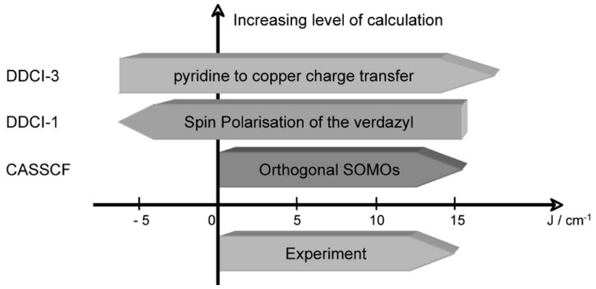

Figure 5. Main contributions to the exchange interaction J appearing when gradually increasing the level of calculation together with the corresponding J values to be read at the arrowheads.

First, an antiferromagnetic behaviour is found at the DDCI-1 level (Table 1) which can be ascribed to the stabilization of the ionic forms resulting from the electron hopping between the magnetic orbitals or to the net effect of the spin polarization (SP).[16,17] Since the ionic forms represent just 4% of the projection on the CAS, this AF contribution essentially comes from the latter. The SP effects were isolated and bring a strong AF –19.2 cm^{-1} contribution. The inspection of the DDCI-1 wavefunctions shows that the leading excitations are of SP type and involve two π orbitals (occupied and virtual ones) largely concentrated on the verdazyl moiety (see Supporting Information). Then, the ferromagnetism is quantitatively restored at DDCI-3 level. Following our recent calculations on [Cu(hfac)$_2$-(Ovdim)],[7] it is essential to determine the respective influence of the heteroatom and the substituent on the ferromagnetic exchange interaction between the metal and the radical. We thus performed similar DDCI-3 calculations for the [Cu(hfac)$_2$(Ovdpy)] complex. Since its crystallographic structure has not been described,[8] we used a hypothetical structure constructed by substituting the S atom for an O one and using rigorously the same geometry with an adapted C=O distance. The calculated exchange interaction in this complex is worth 18 cm^{-1}. For the first time for this series of complexes,[6,7] we notice an important discrepancy between the experimental[5,8] and calculated[6,7] values of the intramolecular exchange interaction. It can be tentatively related to the combination of the uncertainties on (i) the exact structure of the complex, (ii) the experimental value of the exchange interaction underlined by the authors.[8] By comparing the calculations on [Cu(hfac)$_2$(Svdpy)] and [Cu(hfac)$_2$(Ovdpy)], it appears that, in this case, the heteroatom has surprisingly little influence on the exchange interaction while the enhancement of the ferromagnetic behaviour observed for [Cu(hfac)$_2$(Svdpy)] complex compared to [Cu(hfac)$_2$(Ovdim)] is essentially due to the verdazyl substituent.

In fact, the ferromagnetic effect introduced by the DDCI-3 space is related to the stabilization of the triplet Ligand-to-Metal Charge Transfer (LMCT) forms produced by the coupling with specific double excitations included in the DDCI-3 space.[7,17] It is important to notice that these LMCT forms are already present in the DDCI-1 space, but too high in energy to contribute significantly. The LMCT are stabilized by the interaction with some of the double excitations of the DDCI-3 space, which manifests with larger coefficients on the DDCI-3 wavefunctions. Since the triplet LMCT are lower in energy than the singlet LMCT, their net effect is a resulting triplet ground state. This mechanism can be isolated by selected CI calculations involving only the LMCT forms and the aforementioned double excitations. This leads to a strong ferromagnetic contribution of +19.4 cm^{-1} borne by the dominant excitation in the DDCI-3 wavefunctions: a $\sigma \rightarrow 3d$ LMCT, which involves the σ-type molecular orbital of the Cu–pyridine bond (Figure 6). This analysis explains the small net effect of the DDCI-3 space on the J value with respect to the valence-only prediction, essentially due to the presence of two opposite effects of similar amplitudes, concentrated on verdazyl fragment (AF contributions) and pyridine moiety (F contributions), respectively (Figure 5).

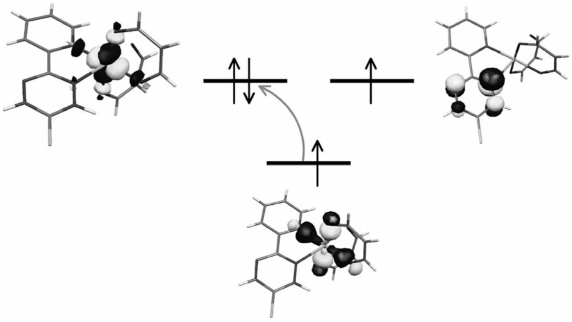

Figure 6. Dominant $\sigma \rightarrow 3d$ LMCT excitation leading to ferromagnetic exchange interaction at DDCI-3 level.

Conclusions

In summary, we have described the synthesis of a pyridine-substituted thiooxoverdazyl radical Svdpy and its use as a bidentate ligand towards a copper(II) center leading to the formation of [Cu(hfac)$_2$(Svdpy)], the first reported complex with thiooxoverdazyl radical as ligand. Ferromagnetic intramolecular exchange interaction occurs between the metal and the radical while antiferromagnetic exchange interaction is mediated by the π-stacking of the molecules. The ferromagnetic metal-radical exchange interaction is strongly enhanced compared to an oxygenated analogue [Cu(hfac)$_2$(Ovdim)]. This is indeed what was expected following a strategy based on a valence-only description of the exchange interaction. Nevertheless, our theoretical dissection of the origins of the exchange interaction indicates that this enhancement finds its foundation in the choice of the substituent rather than the heteroatom, enlightening the crucial role of this part of the organic radical generally considered as magnetically innocent. Though it has little influence on the exchange interaction, the use of sulfurated derivatives of the verdazyl radical remains an important issue for the coordination chemistry of these species. We have indeed proven that the oxygen atom of the oxoverdazyl radicals can perturb the expected coordination modes to the metal ion.[18] Using sulfurated verdazyl radical to avoid the binding to hard metal centers including 4f metal ions will be undertaken to explore the possibility to synthesize strongly coupled verdazyl-based 2p–4f systems. On the theoretical point of view, such compounds are particularly appealing since the exchange interaction mechanisms in lanthanide-containing compounds are far from being fully understood[19] though such systems can exhibit exciting magnetic properties.[20]

Experimental Section

General: H$_3$Svdpy[21] and [Cu(hfac)$_2$(H$_2$O)][22] were prepared according to literature methods. All other reagents were used as purchased.

1,5-Dimethyl-3-(2-pyridyl)-6-thiooxoverdazyl (Svdpy): A solution of 342 mg of FeCl$_3$ (M = 162.34 g mol^{-1}, n = 2.11 mmol) in 4 mL of formic acid was added dropwise to the yellow solution of 157 mg of H$_3$Svdpy (M = 223 g mol^{-1}, n = 0.70 mmol) in 1 mL of formic acid. The mixture immediately turned dark red. After 30 min of stirring, the organic product was extracted with CH$_2$Cl$_2$. The organic solvent was removed and the solid was purified by silica column chromatography and CH$_2$Cl$_2$/AcOEt (80:20) elution (R_f = 0.44); yield 21%. IR: $\tilde{\nu}$ = 2938 [ν(C–H)], 1582, 1570 [ν(C=N)], 1461, 1442, 1417 [ν(C–C)], 1350, 1245, 1116, 794, 741, 669, 537 cm^{-1}. C$_9$H$_{10}$N$_5$S (220.27): calcd. C 49.09, H 4.55, N 31.82; found C 48.67, H 4.66, N 31.71.

[Cu(hfac)$_2$(Svdpy)]: Synthesis by carefully adding 21 mg of Svdpy (M = 220 g mol^{-1}, n = 0.1 mmol) in CH$_2$Cl$_2$ to a suspension of 49 mg of [Cu(hfac)$_2$(H$_2$O)$_2$] (M = 514.74 g mol^{-1}, n = 0.1 mmol) in 6 mL of refluxing heptane. After 10 min, the solution was filtered; slow (during 24 h) evaporation of the solvent yielded dark purple crystals suitable for X-ray diffraction; yield 69%. IR: $\tilde{\nu}$ = 2963 [ν(C–H)], 1645 [ν(C=O)], 1555, 1529 [ν(C=N)], 1484 [ν(C–C)], 1259, 1196, 1143 [ν(C–F)] cm^{-1}. C$_{19}$H$_{12}$CuF$_{12}$N$_5$O$_4$S (697.92): calcd. C 32.69, H 1.72, N 10.04, S 4.58, Cu 9.11; found C 32.50, H 1.63, N 9.64, S 4.25, Cu 8.86.

IR spectra were recorded on a Bio-Rad IRFT spectrometer as KBr pellets in the 4000–250 cm^{-1} region. Magnetisation of an assembly of single crystals was measured between 5 and 300 K at 0.1 T on a Quantum Design MPMS5 SQUID magnetometer and corrected for temperature-independent effects.

A single crystal of [Cu(hfac)$_2$(Svdpy)] was selected, mounted onto a glass fiber and transferred in a cold nitrogen gas stream to 200(2) K.

Crystal Data for [Cu(hfac)$_2$(Svdpy)]: $C_{19}H_{12}Cu_1F_{12}N_5O_4S_1$, monoclinic, $P2_1/c$, a = 10.1872(17) Å, b = 18.232(6) Å, c = 28.497(8) Å and β = 94.85(2)°; V = 5274(2) Å^3, Z = 8, ρ = 1.758 g cm^{-3}, μ = 1.029 mm^{-1}, M = 697.96 g mol^{-1}, 72645 reflections collected, 14962 independent [R(int) = 0.0622], 7149 observed [$I > 2\sigma(I)$], 779 parameters. Intensity data were collected with a Bruker–Nonius Kappa-CCD with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Unit-cell parameter determinations, data collection strategy and integration were carried out with the Nonius EVAL-14 suite of programs.[23] Multi-scan absorption correction was applied.[24] The structure was solved by direct methods using the Sir92 program[25] and refined by full-matrix least-squares methods using the SHELXL-97 software package to R_1 = 0.0752 with $I > 2\sigma(I)$ and wR_2 (all data) = 0.2743 for all reflections; GOF on F^2 = 1.039, max./min. residual electron density 1.315/–0.750 e Å^{-3}.[26]

CCDC-721854 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The calculations have been performed on both complexes of the asymmetric unit leading to comparable results at each level of calculation (see Supporting Information). Complete active space self-consistent field (CASSCF) calculations including 2 electrons in 2 active molecular orbitals (CAS[2,2]SCF) were performed using the Molcas 7.2 package.[27] A simplified structure was constructed by replacing the CF_3 groups by H atoms. The carbon, sulfur, nitrogen and copper atoms were depicted with ANO RCC-type DZP basis sets.[27,28] A minimal basis set (8s)/[1s] was used for the hydrogen atoms and the hfac ligands. Whatever the definition of the active space, it has been clearly demonstrated that the singlet-triplet energy difference cannot be accurately evaluated ignoring the dynamical correlation effects.[16] A bare-valence picture limited to CAS[2,2]SCF calculations might be not sufficient to understand the microscopic origins of the phenomena even if numerical accuracy seems to be reached. CI expansions are then required to take into account all the physical effects. Using the molecular orbitals of the triplet state, the CI spaces are constructed from selected excitations on top of the CAS wavefunctions. The procedure we used has been described previously.[6] It relies on the Difference Dedicated CI (DDCI) method[29] as implemented in the CASDI code.[30] The singlet-triplet energy differences (i.e. the J values) are then computed at the different DDCI-1 and DDCI-3 levels. Class-partitioned CI calculations are employed to isolate the leading mechanisms on each space.[17] The DDCI-1 space contains all the single excitations. This allows a more realistic evaluation of the charge transfers between the magnetic centres and the inclusion of the spin polarization effects. The stabilization of the ionic forms resulting from the electron hoping (kinetic exchange) favours the singlet state over the triplet, i.e. brings an antiferromagnetic contribution. In contrast, the net effect of the spin polarization is hard to predict. However, it has been shown that quantitative agreement demands a DDCI-3 level of calculations.

Supporting Information (see also the footnote on the first page of this article): Supporting Information for this article is available on the WWW under http://www.eurjic.org/ or from the author. It contains details on the synthetic process, on the crystal structure (distances and angles, crystal packing), on the fitting procedure (choice of the model) and on the theoretical study (J_1 for the second complex of the asymmetric unit; spin-polarisation process).

Acknowledgments

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[1] a) A. Caneschi, D. Gatteschi, P. Rey, *Prog. Inorg. Chem.* **1991**, *39*, 331–429; b) O. Kahn, *Magnetism: A Supramolecular Function*, Kluwer, Dordrecht, The Netherlands, **1996**; c) *Magnetism: Molecules to Materials*, vol. I–V (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001–2005**; d) D. Luneau, P. Rey, *Coord. Chem. Rev.* **2005**, *249*, 2591–2611; e) K. E. Vostrikova, *Coord. Chem. Rev.* **2008**, *252*, 1409–1419.

[2] a) B. D. Koivisto, R. G. Hicks, *Coord. Chem. Rev.* **2005**, *249*, 2612–2630; b) K. E. Preuss, *Dalton Trans.* **2007**, 2357–2369.

[3] C. Train, L. Norel, M. Baumgarten, *Coord. Chem. Rev.* **2009**, *253*, 2342–2351.

[4] F. Pointillart, C. Train, P. Herson, J. Marrot, M. Verdaguer, *New J. Chem.* **2007**, *31*, 1001–1006.

[5] 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.

[6] J.-B. Rota, L. Norel, C. Train, N. Ben Amor, D. Maynau, V. Robert, *J. Am. Chem. Soc.* **2008**, *130*, 10380–10385.

[7] J.-B. Rota, C. J. Calzado, C. Train, V. Robert, *J. Chem. Phys.* **2010**, *132*, 154702–154706.

[8] J. B. Gilroy, B. D. Koivisto, R. McDonald, M. J. Ferguson, R. G. Hicks, *J. Mater. Chem.* **2006**, *16*, 2618–2624.

[9] R. Vicente, J. Ribas, S. Alvarez, A. Segui, X. Solans, M. Verdaguer, *Inorg. Chem.* **1987**, *26*, 4004–4009.

[10] F. A. Neugebauer, H. Fischer, C. Krieger, *J. Chem. Soc. Perkin Trans. 2* **1993**, 535–544.

[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] 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.

[13] a) J.-B. Rota, B. Le Guennic, V. Robert, *Inorg. Chem.* **2010**, *49*, 1230–1237; b) L. Norel, L. M. Chamoreau, C. Train, *Polyhedron* **2010**, *29*, 342–348.

[14] G. V. Rubenacker, J. E. Drumheller, K. Emerson, R. D. Willett, *J. Magn. Magn. Mater.* **1986**, *54–57*, 1483–1484.

[15] O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, **1993**.

[16] a) C. J. Calzado, J. Cabrero, J. P. Malrieu, R. Caballol, *J. Chem. Phys.* **2002**, *116*, 3985–4000; b) C. J. Calzado, J. Cabrero, J. P. Malrieu, R. Caballol, *J. Chem. Phys.* **2002**, *116*, 2728–2747.

[17] C. J. Calzado, C. Angeli, D. Taratiel, R. Caballol, J. P. Malrieu, *J. Chem. Phys.* **2009**, *131*, 044327.

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

[19] a) M. L. Kahn, R. Ballou, P. Porcher, O. Kahn, J. P. Sutter, *Chem. Eur. J.* **2002**, *8*, 525–531; b) L. F. Chibotaru, L. Ungur, A. Soncini, *Angew. Chem. Int. Ed.* **2008**, *47*, 4126–4129.

[20] a) L. Bogani, C. Sangregorio, R. Sessoli, D. Gatteschi, *Angew. Chem. Int. Ed.* **2005**, *44*, 5817–5821; b) C. Aronica, G. Pilet,

G. Chastanet, W. Wernsdorfer, J. F. Jacquot, D. Luneau, *Angew. Chem. Int. Ed.* **2006**, *45*, 4659–4662; c) J. K. Tang, I. Hewitt, N. T. Madhu, G. Chastanet, W. Wernsdorfer, C. E. Anson, C. Benelli, R. Sessoli, A. K. Powell, *Angew. Chem. Int. Ed.* **2006**, *45*, 1729–1733; d) Y. G. Huang, X. T. Wang, F. L. Jiang, S. Gao, M. Y. Wu, Q. Gao, W. Wei, M. C. Hong, *Chem. Eur. J.* **2008**, *14*, 10340–10347.

[21] O. Oms, L. Norel, L.-M. Chamoreau, H. Rousselière, C. Train, *New J. Chem.* **2009**, *33*, 1663–1672.

[22] R. J. Casey, W. R. Walker, *J. Inorg. Nucl. Chem.* **1967**, *29*, 1301.

[23] A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J. Appl. Crystallogr.* **2003**, *36*, 220–229.

[24] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.

[25] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

[26] G. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

[27] G. Karlstrom, R. Lindh, P. A. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P. O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady, L. Seijo, *Comput. Mater. Sci.* **2003**, *28*, 222–239.

[28] a) J. Almlof, P. R. Taylor, *J. Chem. Phys.* **1990**, *92*, 551–560; b) B. O. Roos, R. Lindh, P. A. Malmqvist, V. Veryazov, P. O. Widmark, *J. Phys. Chem. A* **2005**, *109*, 6575–6579.

[29] J. Miralles, O. Castell, R. Caballol, J. P. Malrieu, *Chem. Phys.* **1993**, *172*, 33–43.

[30] N. Ben Amor, D. Maynau, *Chem. Phys. Lett.* **1998**, *286*, 211–220.

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