First trinuclear paramagnetic transition metal complexes with redox active ligands derived from TTF: $Co_2M(PhCOO)_6(TTF\text{-}CH{=}CH\text{-}py)_2 \cdot 2CH_3CN$, M = Co^{II}, Mn^{II}†

Konstantin S. Gavrilenko,‡ Yann Le Gal, Olivier Cador, Stéphane Golhen and Lahcène Ouahab*

Received (in Cambridge, UK) 12th September 2006, Accepted 11th October 2006
First published as an Advance Article on the web 26th October 2006
DOI: 10.1039/b613191c

The first paramagnetic homo- and hetero-metallic trinuclear complexes with redox active ligands derived from TTF are synthesized, the central metal ion has an octahedral coordination sphere while the outer Co^{II} ions are in a distorted bipyramidal surrounding, bearing TTF-ligands, the magnetic properties show antiferromagnetic coupling leading to a magnetic ground state.

One of the current challenges in the field of material science is dealing with multifunctional materials in relation to the wide flexibility of the molecular building blocks for their degrees of freedom in charge, spin, color, redox properties…. In particular, designing new functional molecules or molecule-based materials, which possess synergy or interplay between two or more properties such as electrical conductivity with magnetism,[1] is attracting great interest from chemists and physicists for potential applications in devices as well as from the point of view of fundamental science.[2] The objective of this combination is to establish a coupling between conduction electrons (π electrons) and localized magnetic moments (d spins), through the so-called π–d interaction.[1] Usually, these kinds of materials with dual properties consist of co-assembling two components, namely organic donors and paramagnetic anions. However, in this type of solid, the through-space interactions between π and d electrons are very weak. In order to increase these interactions, preparation of paramagnetic transition metal complexes where the redox active ligands such as tetrathiafulvalene (TTF) derivatives are coordinated to a spin carrier appeared as a very promising alternative to achieve conducting (or superconducting) magnets through interactions between d spins and mobile electrons.[1d] Hence several ligands based on TTF derivatives bearing coordination functions well-known for their ability to coordinate to transition metal ions have been prepared. These include, for instance, pyridine-type heterocycles,[3] bipyridine,[4] acetylacetonate,[5] or phosphine substituents.[6] Although a large number of coordination complexes involving these kinds of redox active ligands have been prepared and characterized,[3–7] only a few of them have been successfully oxidized as radical cation complexes showing,[8] however, an insulating behaviour due to a dimerization and a lack of highly ordered stacking in the donor sublattice. Therefore, it is still a great challenge to achieve π–d interactions in this kind of system based on coordination complexes. Thus, we are now exploring new complexes involving redox ligands with more extended π-systems and also high-spin polynuclear complexes.

We present in this contribution the syntheses of the first homo- and hetero-metallic trinuclear transition metal complexes as well as their crystal structures, redox and magnetic properties. These compounds formulated as $Co^{II}{}_2M^{II}(PhCOO)_6(L)_2 \cdot 2CH_3CN$, with **L** being 4-[2-(tetrathiafulvalenyl)-ethenyl]pyridine (TTF-CH=CH-py), M = Co^{II} (**1**), Mn^{II} (**2**) have been successfully synthesized§ using the previously reported route for synthesis of high nuclearity transition metal complexes.[9] This method is based on the *in situ* redox-generation of carboxylate ligands, using the oxidation reaction of aromatic aldehydes by metal nitrates.

The two compounds are isostructural¶, therefore, we describe here the structure of **1** and we give in square brackets the corresponding values of **2** for comparison. The molecular structure of the title compounds is shown in Fig. 1. It consists of a centrosymmetric trimetallic unit, the three metal ions are bridged by benzoate ligands and the outer metal ions are coordinated by ligands **L** through the nitrogen atom of pyridyl. In the asymmetric unit, two benzoate anions are $\mu_2(\eta_1,\eta_1)$ bridging ligands (O1, O2 and O3, O4) and the remaining one is $\mu_2(\eta_1,\eta_2)$ ligand (O6, O5). The central metal ion (Co1) [Mn1] is lying on an inversion centre in an octahedral coordination sphere made of six oxygen atoms from different benzoates. The octahedron is quite regular as metal–oxygen distances are ranging from 2.063(3) [2.1327(18)] Å to 2.080(3) [2.154(2)] Å and the smallest O–M1–O angle is equal to 86.36(16) [87.55(7)]°. In compound **1**, these bond lengths are quite similar to those found in the trinuclear benzoate complex $[Co_3(PhCOO)_6(py)_2]$.[9] The two peripheric cobalt ions (Co2) lie in a distorted trigonal bipyramidal surrounding. The Co2 ion is bonded to four oxygen atoms and one nitrogen atom: three oxygens from three different benzoate anions with Co2–O bonds ranging from 1.930(4) [1.9459(19)] Å to 2.029(4) [2.0307(19)] Å,

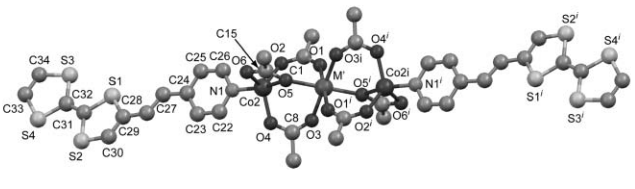

Fig. 1 Scheme of trinuclear complex with M′=Co for (**1**) and M′=Mn for (**2**). H-atoms and phenyl rings are omitted for clarity.

Organométalliques et Matériaux Moléculaires, UMR 6226 CNRS-UR1 Sciences Chimiques de Rennes, Université de Rennes 1, 35042, Rennes Cedex, France. E-mail: lahcene.ouahab@univ-rennes1.fr; Fax: +33 2 23 23 68 40; Tel: +33 2 23 23 56 59

† Electronic supplementary information (ESI) available: Physical characterization. See DOI: 10.1039/b613191c

‡ Permanent address: L. V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of the Ukraine, Prospekt Nauki 31, Kiev, 03028, Ukraine

one nitrogen from the pyridine ring of L Co2–N1 = 2.048(4) [2.057(2)] Å, the fifth position is occupied by the η_2-O5 atom from the $\mu_2(\eta_1,\eta_2)$ benzoate ligand with Co2–O5 = 2.370(4) [2.383(2)] Å. A similar coordination arrangement around the $\mathrm{Co^{II}}$ ion was found in comparable cobalt carboxylate complexes.[9] The Co2···Co1 [Mn1] distance is equal to 3.5620(7) [3.6279(3)] Å. The bond lengths and bond angles of the TTF moiety are close to those reported for the non-coordinated neutral unit,[7] indicating that **L** is neutral. The crystal structure packing pattern consists of an alternating arrangement of organic and inorganic layers. Acetonitrile molecules fit into the cavities made by the packing of trinuclear units. In the organic sublattice, the shortest intermolecular S···S contacts are equal to 3.9768(35) [3.9456(16)] Å. Finally, the length of the molecules is equal to 38.25 Å (≈4 nm).

Despite the fact that the chemical formulation of **2** is more complicated than **1**, the magnetism of **2** is more simple. Indeed, on one hand, the ground state of $\mathrm{Mn^{II}}$ (d^5) in the octahedral environment is an orbital singlet and the prototype of isotropic spin. While, the orbital contribution of the ground state of $\mathrm{Co^{II}}$ (d^7) in the octahedral environment is partially quenched in low-symmetry.[10] The $\chi_M T$ *vs.* T curve of **2** is almost completely flat down to 100 K[11] with a room temperature value equal to 9.57 $\mathrm{cm^3\ K\ mol^{-1}}$ and obeys the Curie law. Clearly, the superexchange interactions between spin carriers are not strong enough to be detected at higher temperatures than 100 K. The magnetic properties of **2** are analysed below 100 K considering purely isotropic spins and nearest neighbour superexchange interactions. The spin Hamiltonian describing the system is the following

$$H = -J\,\boldsymbol{S}_{\mathrm{Co}}\cdot\boldsymbol{S}_{\mathrm{Mn}} + g_{\mathrm{Co}}\beta\boldsymbol{H}\cdot\boldsymbol{S}_{\mathrm{Co}} + g_{\mathrm{Mn}}\beta\boldsymbol{H}\cdot\boldsymbol{S}_{\mathrm{Mn}} \text{ with } \boldsymbol{S}_{\mathrm{Co}} = \boldsymbol{S}_{\mathrm{Co}_1} + \boldsymbol{S}_{\mathrm{Co}_2} \qquad (1)$$

where J is the superexchange interaction parameter between $\mathrm{Co^{II}}$ ions and central $\mathrm{Mn^{II}}$, g_{Co} and g_{Mn} are the local Zeeman factors of $\mathrm{Co^{II}}$ and $\mathrm{Mn^{II}}$, respectively, the $\boldsymbol{S_i}$'s the spin operators associated with the two $\mathrm{Co^{II}}$ and the $\mathrm{Mn^{II}}$ ions. The other parameters have their usual meanings. The zero-field magnetic susceptibility is obtained applying the simplified Van Vleck formula; *i.e.*, without the second order Zeeman perturbation.[10] The best fit on χ_M *vs.* T curve in the range 2–100 K is obtained, with good agreement, by fixing g_{Mn} = 2.00, with $J = -1.80\ \mathrm{cm^{-1}}$ (antiferromagnetic), $g_{\mathrm{Co}} = 2.29$ (see Fig. 2). The shoulder at ~7 K is well reproduced. The ground state of the system corresponds to total spin $\boldsymbol{S} = 1/2$ ($\boldsymbol{S} = \boldsymbol{S}_{\mathrm{Co}} + \boldsymbol{S}_{\mathrm{Mn}}$) with S_{Mn} antiparallel to S_{Co1} and S_{Co2}. The shoulder comes from the concentration of high spin states at close energy from the ground state due to the weakness of the superexchange. These states strongly contribute to the overall susceptibility in a narrow temperature range. Amazingly, it would be possible to observe a minimum and a maximum on χ_M *vs.* T for weaker coupling. The Zeeman factor of the ground state $S = 1/2$ is a combination of local factors. The ground state corresponds to S_{Co1} and S_{Co2} pointing "up" and S_{Mn} pointing "down". It is logical that g_{Mn} is subtracted to the g_{Co}'s. Indeed, we find that $g_{S=1/2} = (8/3)g_{\mathrm{Co}}–(5/3)g_{\mathrm{Mn}}$. One may predict that for $g_{\mathrm{Co}} = (5/8)g_{\mathrm{Mn}}$ the ground state will not contribute, at first order, to the magnetic susceptibility with an effective spin $S_{\mathrm{eff}} = 0$ despite the fact that, formally, the spin is $S = 1/2$. From our analysis it appears that it is not necessary to introduce single-ion anisotropy to reproduce the experimental data down to 2 K. The field dependence at 2 K is well reproduced by the isotropic model (see ESI)† with fitted parameters in using the MAGPACK package, which supports our hypothesis.[12]

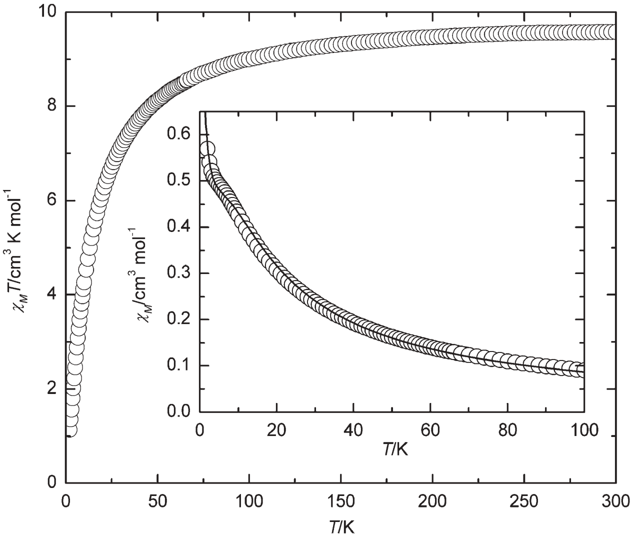

Fig. 2 Temperature dependence of $\chi_M T$ (○) of **2**. Inset: Temp. dependence of χ_M of **2** with the adjusted curve (full line).

The temperature dependence of $\chi_M T$ *vs.* T of **1** is represented in Fig. 3. At room temperature, $\chi_M T$ is equal to 8.56 $\mathrm{cm^3\ K\ mol^{-1}}$. In considering three uncoupled spins and the g_{Coi} values deduced from the analysis of the magnetic properties of **2**, the calculated Zeeman factor of octahedral cobalt (Co1) is equal to 2.78. This value falls in the range of commonly accepted g values for octahedral $\mathrm{Co^{II}}$, specially when the octahedral coordination sphere is just slightly distorted.[10] On cooling, $\chi_M T$ decreases and passes through a minimum at 7.5 K (6.23 $\mathrm{cm^3\ K\ mol^{-1}}$), then increases to reach 6.49 at 2 K. The presence of the minimum is systematic but its amplitude is sample dependent. It is worthy to note that the trinuclear benzoate complex $[\mathrm{Co_3(PhCOO)_6(py)_2}]$[9] is magnetically

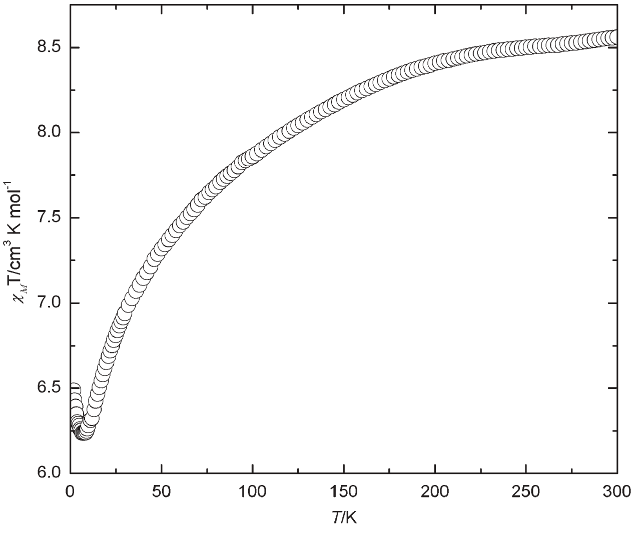

Fig. 3 Temperature dependence of $\chi_M T$ (○) of **1**.

identical to **1**. The core structure is the same with similar bond lengths and bond angles and also with the same sample dependent behaviour below 25 K. Therefore, the minimum might not be intrinsic but might be the consequence of sample pollution or decomposition. The decrease of $\chi_M T$ on lowering the temperature is the result of the combination of two phenomena: (i) Spin–orbit coupling and distortions of the octahedral environment on Co^{II} produce this decrease. At very low temperature, octahedral Co^{II} can be described by an effective spin $S_{eff} = 1/2$ with an effective Zeeman factor as high as $g' = 4.3$, and with large Temperature Independent Paramagnetism (TIP).[10,13] However, it is not sufficient to account for the experimental decrease of more than two units (ii) Superexchange interaction between central Co^{II} and the two terminal five-coordinated Co^{II} certainly operates. From the drop of $\chi_M T$ the interaction is required antiferromagnetic. As a consequence the system should be described, at low temperature, by ferrimagnetic trinuclear units with $S_{eff} = 1/2$ antiferromagnetically coupled with the S_{Coi}'s. Depending on the amplitude of the interaction, a minimum in $\chi_M T$ could be observed above 2 K. Since the experimental minimum is sample dependent, any attempts to fit the data in the low temperature regime (below 20 K) are meaningless. Single crystal measurements as well as high field EPR will aid in completing the description of the magnetism of the molecule.

In conclusion, the synthesis route[9] of homo- and hetero-metallic polynuclear complexes has been applied successfully yielding the first paramagnetic trinuclear complexes with redox active ligands derived from TTF. This opens new perspectives in the field of multifunctional materials. The length of these molecules (4 nm) is another important aspect which can be explored for molecular electronics. The complexes we have synthesized represent the first step toward functionalized high-spin molecules which might prove to be the building blocks for designing single-component magnet metals.

This work was supported by MAGMANet European excellence network and Région Bretagne.‖

Notes and references

§ All experiments were carried out under a nitrogen atmosphere. Solvents were dried and distilled by standard procedures. **TTF-CH=CH-py** (**L**) was prepared according to the literature procedure.[14]

[$Co_3(PhCOO)_6(L)_2$]·$2CH_3CN$ (1): 97 mg (0.33 mmol) of $Co(NO_3)_2·6H_2O$ were heated with 3 mL benzaldehyde over 15 min. Then, the solution was cooled down and a solution of 76 mg (0.25 mmol) of **L** in 5 mL of CH_3CN was added to the reaction mixture under an inert atmosphere and layered with 6 mL of CH_3CN. After several days, deep red crystals of **1** were collected, washed with CH_3CN and ether and dried under vacuum. Yield is 142 mg (79.9%). Anal. Calcd. for $Co_3C_{72}N_4H_{54}O_{12}S_8$: C, 54.0; H, 3.40; N, 3.50; Co, 11.0. Found: C, 54.0; H, 3.37; N, 3.26; Co, 11.1%.

[$Co_2Mn(PhCOO)_6(L)_2$]·$2CH_3CN$ (2): A solution of 72 mg (0.25 mmol) $Co(NO_3)_2·6H_2O$ and 35.6 mg (0.125 mmol) of $Mn(NO_3)_2·6H_2O$ in a minimum amount of water was heated with 3 mL benzaldehyde until the reaction mixture become homogenous. Then a solution of 76 mg (0.25 mmol) of **L** in 5 mL of CH_3CN was immediately added to the reaction mixture. After 1 h, red crystals of complex **2** were filtered off, washed with acetonitrile and dried in vacuum. Yield 135 mg (67.6%). Anal. Calcd. for $Co_2MnC_{72}N_4H_{54}O_{12}S_8$: C, 54.2; H, 3.41; N, 3.51; Co, 7.3; Mn, 3.4. Found: C, 54.1; H, 3.39; N, 3.35; Co, 7.4; Mn, 3.5%.

¶ Structures were solved with SHELXS-97 and refined with the SHELXL-97 program by full-matrix least-squares methods on F^2.

Crystal data for 1. $C_{72}H_{54}Co_3N_4O_{12}S_8$, $M = 1600.46$, triclinic, $a = 10.7106(5)$, $b = 11.7808(7)$, $c = 15.0518(11)$ Å, $\alpha = 94.946(2)$, $\beta = 105.939(2)$, $\gamma = 90.940(4)°$, $V = 1817.82(19)$ Å^3, $T = 293$ K, space group P-1 (no. 2), $Z = 1$, μ(Mo-Kα) = 0.969 mm^{-1}, 449 parameters, 10 126 reflections measured, 6173 unique ($R_{int} = 0.0512$) which were used in all calculations. The final R and $wR(F^2)$ was 0.1172, 0.1538 (all data) and 0.0546, 0.1227 (observed data), respectively.

Crystal data for 2. $C_{72}H_{54}MnCo_2N_4O_{12}S_8$, $M = 1596.47$, triclinic, $a = 10.6124(3)$, $b = 11.7260(3)$, $c = 14.9724(5)$ Å, $\alpha = 95.594(1)$, $\beta = 106.8340(11)$, $\gamma = 90.2950(12)°$, $V = 1773.76(9)$ Å^3, $T = 293$ K, space group P-1 (no. 2), $Z = 1$, μ(Mo-Kα) = 0.937 mm^{-1}, 449 parameters, 14 183 reflections measured, 8135 unique ($R_{int} = 0.0292$) which were used in all calculations. The final R and $wR(F^2)$ was 0.0637, 0.1185 (all data) and 0.0436, 0.1064 (observed data) respectively.

CCDC 620532 and 620533. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613191c

‖ The magnetizations of compounds **1** and **2** have been measured on powders with a Quantum Design MPMS-XL SQUID magnetometer in the 2–300 K temperature range with a dc magnetic field up to 50 000 G.

1 (*a*) A. Kobayashi, E. Fujiwara and H. Kobayashi, *Chem. Rev.*, 2004, **104**, 5243; (*b*) T. Enoki and A. Miyazaki, *Chem. Rev.*, 2004, **104**, 5449; (*c*) E. Coronado and P. Day, *Chem. Rev.*, 2004, **104**, 5419; (*d*) L. Ouahab and T. Enoki, *Eur. J. Inorg. Chem.*, 2004, 933; (*e*) H. Fujiwara, K. Wada, T. Hiraoka, T. Hayashi, T. Sugimoto, H. Nakazumi, K. Yokogawa, M. Teramura, S. Yasuzuka, K. Murata and T. Mori, *J. Am. Chem. Soc.*, 2005, **127**, 14166; (*f*) R. Kato, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 515.

2 T. Mori and M. Katsuhara, *J. Phys. Soc. Jpn.*, 2002, **71**, 826.

3 (*a*) S. Bouguessa, A. K. Gouasmia, S. Golhen, L. Ouahab and J.-M. Fabre, *Tetrahedron Lett.*, 2003, **44**, 9275; (*b*) S.-X. Liu, S. Dolder, E. B. Rusanov, H. Stoeckli-Evans and S. Decurtins, *C. R. Chim.*, 2003, **6**, 657; (*c*) S.-X. Liu, S. Dolder, M. Pilkington and S. Decurtins, *J. Org. Chem.*, 2002, **67**, 3160; (*d*) C. Jia, D. Zhang, Y. Xu, W. Xu, H. Hu and D. Zhu, *Synth. Met.*, 2003, **132**, 249; (*e*) J. Becher, A. Hazell, C. J. McKenzie and C. Vestergaard, *Polyhedron*, 2000, **19**, 665; (*f*) T. Devic, N. Avarvari and P. Batail, *Chem.–Eur. J.*, 2004, **10**, 3697; (*g*) A. Ota, L. Ouahab, S. Golhen, O. Cador, Y. Yoshida and G. Saito, *New J. Chem.*, 2005, **29**, 1135; (*h*) S.-X. Liu, S. Dolder, P. Franz, A. Neels, H. Stoeckli-Evans and S. Decurtins, *Inorg. Chem.*, 2003, **42**, 4801; (*i*) H. Xue, X.-J. Tang, L.-Z. Wu, L.-P. Zhang and C.-H. Tung, *J. Org. Chem.*, 2005, **70**, 9727; (*j*) N. Benbellat, Y. Le Gal, S. Golhen, A. Gouasmia, L. Ouahab and J.-M. Fabre, *Eur. J. Org. Chem.*, 2006, 4237.

4 K. Hervé, S.-X. Liu, O. Cador, S. Golhen, Y. Le Gal, A. Bousseksou, H. Stoeckli-Evans, S. Decurtins and L. Ouahab, *Eur. J. Inorg. Chem.*, 2006, 3498.

5 J. Massue, N. Bellec, S. Chopin, E. Levillain, T. Roisnel, R. Clérac and D. Lorcy, *Inorg. Chem.*, 2005, **44**, 8740.

6 (*a*) P. Pellon, G. Gachot, J. Le Bris, S. Marchin, R. Carlier and D. Lorcy, *Inorg. Chem.*, 2003, **42**, 2056; (*b*) B. W. Smucker and K. R. J. Dunbar, *J. Chem. Soc., Dalton Trans.*, 2000, 1309; (*c*) T. Devic, P. Batail, M. Fourmigué and N. Avarvari, *Inorg. Chem.*, 2004, **43**, 3136; (*d*) N. Avarvari and M. Fourmigué, *Chem. Commun.*, 2004, 1300.

7 (*a*) F. Iwahori, S. Golhen, L. Ouahab, R. Carlier and J.-P. Sutter, *Inorg. Chem.*, 2001, **40**, 6541; (*b*) L. Ouahab, F. Iwahori, S. Golhen, R. Carlier and J. P. Sutter, *Synth. Met.*, 2003, **133–134**, 505; (*c*) C. Jia, S.-X. Liu, C. Ambrus, A. Neels, G. Labat and S. Decurtins, *Inorg. Chem.*, 2006, **45**, 3152; (*d*) S. Ichikawa, S. Kimura, H. Mori, G. Yoshida and H. Tajima, *Inorg. Chem.*, 2006, **45**, 7575; (*e*) L. Wang, B. Zhang and J. Zhang, *Inorg. Chem.*, 2006, **45**, 6860.

8 (*a*) Y. Umezono, W. Fujita and K. Awaga, *J. Am. Chem. Soc.*, 2006, **128**, 1084; (*b*) F. Setifi, L. Ouahab, S. Golhen, Y. Yoshida and G. Saito, *Inorg. Chem.*, 2003, **42**, 1791; (*c*) K. Hervé, Y. Le Gal, L. Ouahab, S. Golhen and O. Cador, *Synth. Met.*, 2005, **153**, 461.

9 K. S. Gavrilenko, S. V. Punin, O. Cador, S. Golhen, L. Ouahab and V. V. Pavlishchuk, *J. Am. Chem. Soc.*, 2005, **127**, 12246.

10 O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.

11 W. Clegg, P. A. Hunt, P. Brian and M. A. Mendiola, *J. Chem. Soc., Dalton Trans.*, 1989, 1127.

12 (*a*) J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *Inorg. Chem.*, 1999, **38**, 6081; (*b*) J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *J. Comput. Chem.*, 2001, **22**, 985.

13 A. Bencini, A. Beni, F. Costantino, A. Dei, D. Gatteschi and L. Sorace, *Dalton Trans.*, 2006, 722.

14 R. Andreu, I. Malfant, P. G. Lacroix and P. Cassoux, *Eur. J. Org. Chem.*, 2000, 737.