

Structure and magnetic property of a mixed-valence nonanuclear cobalt compound with a square-pyramidal Co^{II}_5 core†

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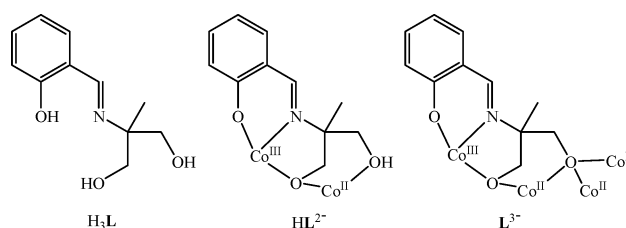
A novel cobalt compound $[\text{Co}_9(\text{HL})_4(\text{L})_4\text{Cl}_2] \cdot (\text{EtOH})_2(\text{H}_2\text{O})_2$ ($\text{H}_3\text{L} = (E)\text{-}2\text{-}2((1,3\text{-dihydroxy-}2\text{-methylpropan-}2\text{-ylimino)methyl) \text{phenol}$) has been solvothermally synthesized and structurally characterized. The compound crystallised in the space group $C2/c$ with $a = 32.624(2) \text{ \AA}$, $b = 9.4814(4) \text{ \AA}$, $c = 33.395(2) \text{ \AA}$, $\beta = 109.339(5)^\circ$ and $V = 9746.8(9) \text{ \AA}^3$. The crystal structure is a mixed-valence nonanuclear $\text{Co}(\text{II}/\text{III})$ oligomer, which contains a square-pyramidal Co^{II}_5 core formed through $\mu_4\text{-Cl}$ and $\mu_3\text{-alkoxo}$ bridges and the pentanuclear Co^{II}_5 core is surrounded by four peripheral $\text{Co}(\text{III})$ ions at the square-pyramidal base plane through $\mu_2\text{-alkoxo}$ bridges. Magnetic properties of the compound can be considered as the magnetism of the Co^{II}_5 core, and the superexchange interactions between $\text{Co}(\text{II})$ ions within the core were calculated with three $\text{Co}(\text{II})\text{-Co}(\text{II})$ superexchange parameters by using MAGPACK software package to give $J_1 = +11.1 \text{ cm}^{-1}$, $J_2 = -6.50 \text{ cm}^{-1}$, $J_3 = -3.25 \text{ cm}^{-1}$, $D = +6.0 \text{ cm}^{-1}$ and $g = 2.30$.

Introduction

High-nuclearity paramagnetic clusters (PMCs) attract a great deal of interest, due to their fascinating physical properties and the architectural beauty of their structures.¹ In the process of synthesis of PMCs, partial oxidation of divalent transition metal ions ($\text{Mn}(\text{II})$, $\text{Fe}(\text{II})$ and $\text{Co}(\text{II})$) usually produced mixed-valence PMCs, as exemplified by the first example of single-molecule magnet Mn_{12} .² Since then, a great number of mixed-valence manganese clusters have been synthesized and their magnetic properties have been widely studied, and a new field in magnetism, the so-called SMMs, has thus been springing up.³ In comparison with manganese and iron ions, cobalt ion is also easily and partially oxidized and leads to mixed-valence PMCs, whose magnetic properties are more complex due to the effect of the strong orbital contribution of $\text{Co}(\text{II})$ center to the magnetic moment and thus to a strong magnetic anisotropy. Especially at low temperature, this effect splits the ground state and thus makes the magnetic properties of cobalt clusters much more interesting.⁴

Recently, some interesting mixed-valence $\text{Co}(\text{II},\text{III})$ clusters, for examples, $\{\text{Co}^{\text{II}}_2\text{Co}^{\text{III}}_6\}$,^{5a} $\{\text{Co}^{\text{II}}_3\text{Co}^{\text{III}}_3\}$,^{5b} $\{\text{Co}^{\text{II}}_3\text{Co}^{\text{III}}_4\}$,^{5c} $\{\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_3\}$,^{5d} $\{\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_4\}$ ^{5e} and $\{\text{Co}^{\text{II}}_6\text{Co}^{\text{III}}_6\}$,^{5f} have been reported. For the synthesis of mixed-valence cobalt PMCs, the potentially polynucleating ligands possessing polyalcohol/alkoxide groups are very suitable.^{6,5d} For example, we recently adopted a Schiff-base ligand 2-((2-hydroxybenzylidene)-amino)-2-hydroxymethylpropane-1,3-diol, which contains a $\{\text{NO}\}$ chelating moiety and a tripodal alcohol unit that successfully gave rise to a mixed-valence pentanuclear $\text{Co}^{\text{II}}_3\text{Co}^{\text{III}}_2$ compound.⁷ In this compound, the tripodal alcohol unit is partially de-

protonated, which gives us an impetus to investigate a similar ligand with less alcohol groups. Aiming at extending our search of new mixed-valence PMCs that contain polyalcohol/alkoxide ligands, we report here a new mixed-valence nonanuclear cluster of formula $[\text{Co}^{\text{II}}_5\text{Co}^{\text{III}}_4(\text{HL})_4(\text{L})_4\text{Cl}_2] \cdot (\text{EtOH})_2(\text{H}_2\text{O})_2$ ($\mathbf{1} \cdot (\text{EtOH})_2(\text{H}_2\text{O})_2$) with a new ligand $(E)\text{-}2\text{-}2((1,3\text{-dihydroxy-}2\text{-methylpropan-}2\text{-ylimino)methyl) \text{phenol}$ (H_3L , Scheme 1). To our knowledge, though two nonanuclear $\text{Co}(\text{II})$ clusters have been reported,⁸ compound $\mathbf{1}$ is the first example of a nonanuclear mixed-valence $\text{Co}(\text{II},\text{III})$ cluster.



Scheme 1 H_3L and the coordination modes in $\mathbf{1}$.

Experimental

All reagents and solvents were commercially available and were used without further purification. The ligand H_3L was synthesized by condensation of salicylaldehyde and 2-amino-2-methyl-1,3-propanediol (1:1) in hot methanol solution.

A single crystal of $[\text{Co}^{\text{II}}_5\text{Co}^{\text{III}}_4(\text{HL})_4(\text{L})_4\text{Cl}_2] \cdot (\text{EtOH})_2(\text{H}_2\text{O})_2$ (dark pink block, $0.50 \text{ mm} \times 0.40 \text{ mm} \times 0.32 \text{ mm}$) was mounted on an Oxford Gemini S Ultra diffractometer equipped with a CCD camera and an enhanced graphic monochromated $\text{Mo K}\alpha$ radiation source ($\lambda = 0.71073 \text{ \AA}$). Data were collected at 223 K. Data reduction was performed with CrysAlis RED and the space group was assigned by analysis of symmetry and systematic absences determined by XPREP. The structure of the compound

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was solved by direct methods using SHELXS-97 and refined against all data in the 2θ range by full-matrix least-squares on F^2 using SHELXL-97 software.⁹ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained in their idealized positions and not refined, the hydrogen atoms on water molecules were not localized. There is only half a molecule that constitutes an asymmetric unit and it contains two water and two ethanol molecules per Co₉ cluster. The structure contains accessible voids as calculated by PLATON, it may be due to the existence of unidentified solvate which could not be modeled satisfactorily. PLATON/SQUEEZE routines were not used to refine the data.

Crystallographic data for **1**·(EtOH)₂·(H₂O)₂: C₉₂H₁₁₆N₈O₂₈·Cl₂Co₉, M = 2383.20, monoclinic, space group *C2/c* (no. 8), $a = 32.624(2)$ Å, $b = 9.4814(4)$ Å, $c = 33.395(2)$ Å, $\beta = 109.339(5)^\circ$, $V = 9746.8(9)$ Å³, $Z = 4$, $T = 223$ K, 20 988 reflections measured, 9324 unique reflections ($R_{\text{int}} = 0.0411$), refinement with 628 parameters converged with agreement factors R_1 ($I > 2\sigma$) = 0.0672, wR_2 (all data) = 0.1289, GOF = 1.200, $2\theta \leq 52^\circ$.

Magnetic measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer operating in the temperature range 2–300 K with a dc magnetic field up to 7 T.

Synthesis of **1**·(EtOH)₂·(H₂O)₂

A mixture of NaOEt (0.068 g, 1 mmol) and H₃L (0.042 g, 0.2 mmol) was dissolved in absolute ethanol solution (10 mL), followed by addition of Co(OAc)₂·4H₂O (0.025 g, 0.1 mmol) and SmCl₃·6H₂O (0.036 g, 0.1 mmol). The resulting solution was stirred for 30 min and sealed in a 23 mL Teflon-lined stainless steel autoclave, heated at 140 °C for 1 day. The reaction system was then cooled to room temperature at a rate of 4 °C h⁻¹ and dark pink crystals were collected by filtration. Yield was about 30%.

Elemental percentage for C₉₂H₁₁₆N₈O₂₈Cl₂Co₉: C 46.37, H 4.91, N 4.70. Found: C 45.92, H 4.93, N 5.21. IR data (cm⁻¹): 3430 (s), 1640 (s), 1598 (s), 1540 (w), 1440 (m), 1378 (w), 1342 (m), 3111 (m), 1149 (w), 1102 (m), 1050 (w), 935 (w), 758 (m), 606 (m), 491 (w).

Results and discussion

Crystal structure

Compound **1**·(EtOH)₂·(H₂O)₂ crystallized in the monoclinic space group *C2/c* and the structure of **1** is shown in Fig. 1. The asymmetric unit comprises five independent cobalt ions with two chloride ions, two independent HL²⁻ and two independent L³⁻ ligands (Scheme 1). Symmetry operation of the space group (*C2/c*) affords a neutral and centrosymmetric nonanuclear cluster with formula of [Co₉(HL)₄(L)₂Cl₂]. Following from the charge balance of the neutral cluster, there should be four Co^{III} and five Co^{II} ions. From a structural point of view, the average Co–O bond lengths of Co1, Co2 and Co4 are 2.108, 2.064 and 2.057 Å, respectively, which are longer than those of Co3 and Co5 (which average 1.901 and 1.896 Å, respectively), thus Co1, Co2 and Co4 can be attributed to the +2 valence state and Co3 and Co5 to the +3 one. On the other hand, the values of Co–O and Co–N bond lengths of Co3 and Co5 are similar to those of typical Co^{III}–O and Co^{III}–N bonds,^{5d,6,7} confirming the +3 valence state for them. Therefore,

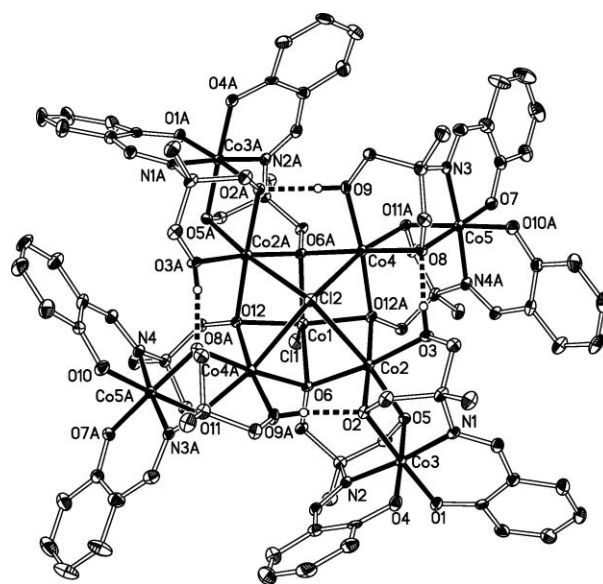


Fig. 1 ORTEP drawing at 50% probability of **1** with atom labels. Selected bond distances (Å) and angles ($^\circ$): Co1–O6 2.118(4), Co1–O12 2.098(4), Co1–Cl1 2.292(2), Co2–O2 2.065(4), Co2–O3 2.049(4), Co2–O5 2.018(4), Co2–O6 2.089(4), Co2–O12A 2.099(4), Co2–Cl2 2.667(1), Co3–O1 1.877(4), Co3–O2 1.922(4), Co3–O4 1.884(4), Co3–O5 1.920(4), Co3–N1 1.902(5), Co3–N2 1.908(5), Co4–O8 2.059(4), Co4–O9 2.045(4), Co4–O6A 2.078(4), Co4–O11A 2.024(4), Co4–O12A 2.091(4), Co4–Cl2 2.708(1), Co5–O7 1.867(4), Co5–O8 1.923(4), Co5–O10A 1.882(4), Co5–O11A 1.914(4), Co5–N3 1.897(5), Co5–N4 1.896(5), Co1–O6–Co2 90.00(14), Co1–O12A–Co2 90.28(14), Co1–O6–Co4A 90.88(14), Co1–O12–Co4A 91.08(14), Co2–O6–Co4A 110.34(16), Co2–O12A–Co4 110.88(16). Symmetry code: (A) $-x + 1, y, -z + 1/2$.

the nonanuclear can be viewed as an inner pentanuclear Co^{II}₅ core surrounded by four outer Co^{III} atoms.

The five inner Co^{II} ions form a square-pyramidal structural feature, in which Co1 locates at the apical position with a five-coordinate stereochemistry [CoO₄Cl]. The geometry about Co1 ion may be square-pyramidal or trigonal-bipyramidal, depending on the τ value ($\tau = (\beta - \alpha)/60$, where β is defined as the larger of the basal angles and α is the remaining angle).¹⁰ τ is 0 for the coordination of square-pyramidal and 1 for trigonal-pyramidal. The τ value for Co1 is 0.46%, which strongly indicates square-pyramidal geometry. Each cobalt ion (Co2 and Co4) in the basal plane of the square-pyramidal Co^{II}₅ cluster possesses an [O₅Cl] ligand donor set, giving an distorted octahedral coordination geometry, here the chloride ion (Cl2) serves as a μ_4 -bridge that is connected to four Co^{II} ions (Co2, Co2A, Co4 and Co4A) and locates above the basal plane for *ca* 1.15 Å. To our knowledge, this is the first example of a μ_4 -Cl bridge in a Co^{II} compound. The μ_4 -Cl–Co bond lengths (2.667 and 2.708 Å for Co2 and Co4, respectively) are longer than those for mono-coordinate Cl–Co^{II}, μ_2 -Cl–Co^{II} and μ_3 -Cl–Co bonds.¹³

In the square-pyramidal Co^{II}₅ cluster, the apical cobalt ion (Co1) is bridged to the basal ones (Co2, Co2A, Co4 and Co4A) through four μ_3 -alkoxo groups from the L³⁻ ligands. The Co1...Co2 and Co1...Co4 distances are 2.975 and 2.990 Å, respectively, which are much shorter than those of Co2...Co4 and Co2...Co4A (3.451 and 3.420, respectively). The values of Co_{apical}–O–Co_{basal}

bond angles cover the range 90.00–91.08° and those of Co_{basal}–O–Co_{basal} 110.34–110.88°. The ligand H₃L (Scheme 1, left) is bound to Co^{II}/Co^{III} ions in two ways: partially deprotonated HL²⁻ in η¹,η¹,η¹,η²-μ² coordination mode (Scheme 1, middle) and fully deprotonated L³⁻ in η¹,η¹,η²,η³-μ⁴ coordination mode (Scheme 1, right). Each HL²⁻ ligand is coordinated to one outer Co^{III} ion and an inner Co^{II} one, for example, the HL²⁻ ligand associated with N1 atom is chelated to the Co3 ion by the phenolate oxygen (O1) and imide nitrogen (N1) atoms, its deprotonated alcohol hydroxyl O2 atom is μ₂-bridged to Co2 and Co3 ions and another one (O3) is coordinated to Co2 ion, and adjacent HL²⁻ ligands form strong inter-ligand hydrogen bonds (O3–H···O8 2.527 and O9–H···O2A 2.536 Å, respectively). Each L³⁻ ligand is coordinated to one outer Co^{III} ion and three inner Co^{II} ones, for example, the L³⁻ ligand associated with N2 atom is chelated to the Co3 ion with its phenolate oxygen (O4) and imide nitrogen (N2) atoms, its alcohol hydroxyl O5 atom is μ₂-bridged to Co2 and Co3 ions, while its alcohol hydroxyl O6 atom is μ₃-bridged to Co1, Co2 and Co4A ions.

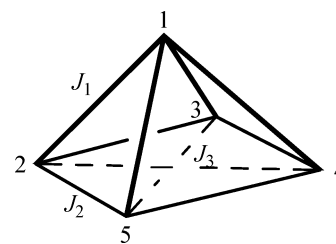
Magnetic properties

The dc magnetic susceptibility of 1·(EtOH)₂(H₂O)₂ was measured in the temperature range of 2–300 K and shown in Fig. 2. Since the Co^{III} ions are low-spin (t_{2g}⁶, S = 0), the magnetic properties are thus attributed to the square-pyramidal Co^{II}₅ cluster. At room temperature, the χ_MT value of 13.53 cm³ K mol⁻¹ differs from the spin-only value for five isolated Co^{II} ions (5 × 1.875 cm³ K mol⁻¹), indicating an orbital contribution to the g-value. The four Co^{II} ions in the basal plane in the octahedral environments represent high-spin centers and exhibit significant spin–orbital coupling, however, the Co^{II} ion in the apical position (Co1) with square-pyramidal coordination may be high-spin or low-spin. Regarding a Co^{II} ion with five-coordination, an increase of the out-of-plane displacement of the Co^{II} ion from 0 to 0.45–0.74 Å will stabilize the high-spin (S = 3/2) state,¹⁴ thus the out-of-plane displacement of the Co1 ion of 0.58 Å indicates a high-spin configuration. In the same way, the d-block orbitals of an ML₅ compound with a square-pyramidal geometry where the angle between the apical and the basal bonds varies from 90 to about 110° could lead to a rapid decrease in the quartet-state energy,^{15a} especially when

θ > 102° (θ = ∠apical–Co–L_{basal}).^{15b} The θ values for Co1 are 105.94 (C11–Co1–O6) and 106.09° (C11–Co1–O12), respectively, which also indicate a high-spin state of Co1 ion.

On lowering the temperature, χ_MT slowly decreases until 100 K and then it falls drastically reaching a value of 6.09 cm³ K mol⁻¹ at 2 K. This value is far below the expected one for five magnetically isolated Co^{II} ions (χ_MT = 5 × 1.73 cm³ K mol⁻¹), indicating the occurrence of antiferromagnetic interactions.⁶ Meanwhile, owing to spin–orbital coupling, the S = 3/2 state is split into two Kramer's doublets, so the depopulation of the higher energy Kramer's doublets also causes the decrease of χ_MT. In order to evaluate the magnetic coupling in 1, we apply the Hamiltonian of eqn (1), where J₁ represents the coupling parameter of apical–basal interactions, J₂ the nearest-neighbor basal–basal ones and J₃ the next-nearest-neighbor basal–basal ones (Scheme 2).

$$H = -2J_1(S_1S_2 + S_1S_3 + S_1S_4 + S_1S_5) - 2J_2(S_2S_3 + S_3S_4 + S_4S_5 + S_5S_2) - 2J_3(S_2S_4 + S_3S_5) + \mu_B g H \sum S_i^z + D \sum [(S_i^z)^2 - 5/4] \quad (1)$$



Scheme 2

The experimental data were fitted by using MAGPACK software package¹⁶ to give J₁ = +11.1 cm⁻¹, J₂ = -6.5 cm⁻¹, J₃ = -3.25 cm⁻¹, D = +6.0 cm⁻¹ and g = 2.3. The fitting results revealed ferromagnetic interaction between the apical Co^{II} ion and the basal ones, which is in agreement with the values of the Co_{apical}–O–Co_{basal} bond angles (90.00–91.08°) that give rise to orthogonal magnetic orbitals.¹⁷ While the antiferromagnetic interactions between the basal nearest-neighbor Co^{II} ions and the next-nearest-neighbor ones may be ascribed to the large Co_{basal}–O–Co_{basal} (110.34–110.88°) and Co–Cl–Co (129.26 and 129.52°) bond angles, respectively. However, the field dependence of the magnetization at 2 K (Fig. 2, inset) cannot be easily reconciled with the susceptibility in Fig. 2. The magnetization of 6.42Nβ at 7 T could be reproduced for g ~ 4.2–4.8 and a total spin S = 3/2, which may imply an intermediate ground state. This is consistent with the presence of competing interactions and spin-frustration effects because of ferromagnetic (J₁) and antiferromagnetic (J₂ and J₃) for Co_{apical}–Co_{basal} and Co_{basal}–Co_{basal}, respectively. On the other hand, the magnetic anisotropy on the cobalt centers may also play an important role.

Conclusions

A new mixed-valence nonanuclear cobalt(II,III) compound containing a square-pyramidal arranged {Co^{II}₅} inner core and four peripheral Co(III) ions has been synthesized by using a Schiff-base ligand. Magnetic studies reveal the existence of competing ferro- and antiferromagnetic interactions and consequently an intermediate ground state.

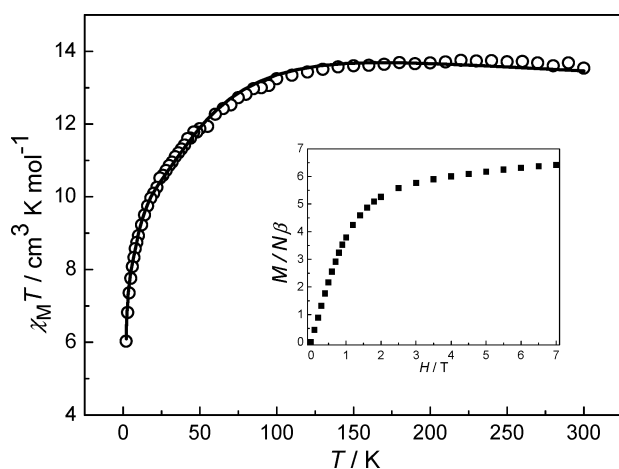


Fig. 2 Temperature-dependent susceptibility of 1·(EtOH)₂(H₂O)₂ under an applied field of 1000 Oe, inset: Magnetization at 2 K.

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Notes and references

- (a) Y.-L. Bai, V. Tangoulis, R.-B. Huang, L.-S. Zheng and J. Tao, *Chem.-Eur. J.*, 2009, **15**, 2377; (b) X.-J. Kong, Y.-P. Ren, W.-X. Chen, L.-S. Long, Z.-P. Zheng, R.-B. Huang and L.-S. Zheng, *Angew. Chem., Int. Ed.*, 2008, **47**, 2398; (c) G. N. Newton, G. J. T. Cooper, P. Kögerler, D.-L. Long and L. Cronin, *J. Am. Chem. Soc.*, 2008, **130**, 790; (d) T. Liu, Y.-J. Zhang, Z.-M. Wang and S. Gao, *J. Am. Chem. Soc.*, 2008, **130**, 10500.
- (a) R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141; (b) R. Sessoli and D. Gatteschi, *Angew. Chem., Int. Ed.*, 2003, **42**, 268.
- (a) D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets*, Oxford University Press, 2006; (b) G. Aromí and E. K. Brechin, *Single-Molecule Magnets and Related Phenomena*, *Struct. Bonding*, 2006, **122**, 1.
- F. Lloret, M. Julve, J. Cano, R. Ruiz-García and E. Pardo, *Inorg. Chim. Acta*, 2008, **361**, 3432.
- (a) M. Dincă, T. D. Harris, A. T. Iavarone and J. R. Long, *J. Mol. Struct.*, 2008, **890**, 139; (b) Y.-S. Xie, Q.-L. Liu, H. Jiang and J. Ni, *Eur. J. Inorg. Chem.*, 2003, 4010; (c) L. F. Chibotaru, L. Ungur, C. Aronica, H. Elmoll, G. Pilet and D. Luneau, *J. Am. Chem. Soc.*, 2008, **130**, 12445; (d) A. Ferguson, A. Parkin, J. Sanchez-Benitez, K. Kamenev, W. Wernsdorfer and M. Murrice, *Chem. Commun.*, 2007, 3473; (e) G. I. Chilas, M. Stylianou, M. Kubicki, T. Vaimakis, P. Kögerler, A. D. Keramidis and T. A. Kabanos, *Inorg. Chem.*, 2008, **47**, 4451; (f) V. A. Milway, L. K. Thompson and D. O. Miller, *Chem. Commun.*, 2004, 1790.
- V. Tudor, G. Marin, F. Lloret, V. Ch. Kravtsov, Y. A. Simonov, M. Julve and M. Andruh, *Inorg. Chim. Acta*, 2008, **361**, 3446.
- L.-L. Hu, Z.-Q. Jia, J. Tao, R.-B. Huang and L.-S. Zheng, *Dalton Trans.*, 2008, 6113.
- (a) E. K. Brechin, S. G. Harris, S. Parsons and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 1997, **36**, 1967; (b) A. Tsohos, S. Dionyssopoulou, C. P. Raptopoulou, A. Terzis, E. G. Bakalbassis and S. P. Perlepes, *Angew. Chem. Int. Ed.*, 1999, **38**, 983.
- G. M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.
- A. W. Addison, T. N. Rao, J. Reedijk, J. Vm Riju and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
- (a) T. M. Kooistra, K. F. W. Hekking, Q. Knijnenberg, B. de Bruin, P. H. M. Budzelaar, R. de Gelder, J. M. M. Smits and A. W. Gal, *Eur. J. Inorg. Chem.*, 2003, 648; (b) G. C. Chiumia, D. J. Phillips and A. Davis Rae, *Inorg. Chim. Acta*, 1995, **238**, 197.
- G. R. Willey, D. R. Aris and W. Errington, *Trans. Metal Chem.*, 2000, **25**, 534.
- E. K. Brechin, S. G. Harris, A. Harrison, S. Parsons, A. G. Whittaker and R. E. P. Winpenny, *Chem. Commun.*, 1997, 653.
- R. Kapoor, A. Kataria, P. Venugopalan, P. Kapoor, G. Jundal and M. Corbella, *Eur. J. Inorg. Chem.*, 2005, 3884.
- (a) Y. Jean, *Molecular Orbitals of Transition Metal Complexes*, Oxford University Press, 2005, p. 60; (b) M. A. Hitchman, *Inorg. Chim. Acta*, 1978, **248**, 237.
- J. J. Vorrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *J. Comput. Chem.*, 2001, **22**, 985.
- I. Castro, J. Faus, M. Julve, C. Bois, J. A. Real and F. Lloret, *J. Chem. Soc., Dalton Trans.*, 1992, 47.