This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Journal Name

COMMUNICATION

Multielectron oxidation in a ferromagnetically coupled dinickel(II) triple mesocate†

Jesús Ferrando-Soria,[a] Oscar Fabelo,[b] María Castellano,[c] Joan Cano,*[c,d] Stephen Fordham[a] and Hong-Cai Zhou*[a]

Triple-stranded dinuclear nickel(II) complexes of the *meso*-helicate type have been obtained from the new *N,N'*-1,3-phenylenebis(pyrazine-2-carboxamidate) ligand; they possess a multielectron redox behaviour featuring up to four stepwise, one-electron oxidations of the two ferromagnetically coupled Ni^{II} ions to afford the putative high-valent dinickel(III) and dinickel(IV) species, as supported by theoretical calculations.

Metallacyclic complexes containing multiple ligand- and/or metal-based, spin containing electrophores are of large interest as potential electronic and magnetic devices in the emerging field of molecular spintronics.[1–3] Toward this goal, we are developing new multifunctional exchange-coupled polynuclear metallacyclic complexes with new pyrazineamidate-substituted aromatic bridging ligands that would possess a rich metal-centred electrochemical activity. In fact, high-valent nickel(III) and nickel(IV) mononuclear complexes with related pyridineamidate chelating ligands were isolated by Mukherjee due to the strong σ-donor ability (basicity) of the amidate donor groups, that reduce the oxidizing character of high-valent complexes and therefore increase the stability of themselves.[4] More recently, Colacio and co-workers have obtained ferromagnetically-coupled, triple-stranded dinuclear nickel(II) complexes with the *N,N'*-1,3-phenylenebis(pyridine-2-carboxamidate) bridging ligand, but their electrochemical activity has not been investigated.[6]

Here we report the synthesis, structural and spectroscopic characterization, magnetic and electrochemical properties, and Density Functional (DF) and Complete Active Space (CAS) calculations of novel triple-stranded dinuclear nickel(II) complexes

with the *N,N'*-1,3-phenylenebis(pyrazine-2-carboxamidate) (L) bridging ligand. To our knowledge, they constitute the first members of a novel class of exchange coupled dinuclear triple *meso*-helicates ("mesocates"), exhibiting multistep metal-based redox behaviour. Based on these experimental and theoretical exploratory studies, we suggest that dinickel(II) mesocates can act as effective multielectron reservoirs for charge storage applications.

The proligand H_2-L was synthesized from the straightforward reaction of 1,3-phenylenediamine and 2-pyrazinecarboxylic acid under the presence of triphenyl phosphite (1:2:2 molar ratio) in pyridine solution in very good yields (90%) (see ESI†).[5] The anionic dinuclear nickel(II) complex, [Ni$^{II}_2$L$_3$]$^{2-}$, was synthesized from the reaction of the proligand and the nitrate salt of the Ni^{2+} ions (3:2 molar ratio) in basic methanol solution by using either potassium or *n*-tetrabutylammonium hydroxide as base, and it was isolated as its corresponding salts of formula K$_2$[Ni$^{II}_2$L$_3$] · 3MeOH · 3H$_2$O (**1a**) and (*n*Bu$_4$N)$_2$[Ni$^{II}_2$L$_3$] · 4MeOH (**1b**) respectively, in moderate to good yields (70–75%) (see ESI†).

The crystal structure of **1a** consists of dinickel(II) triple mesocate anions of the metallacryptand-type with approximate C_{3h} molecular symmetry, [Ni$^{II}_2$(μ-η^2:η^2-L)$_3$]$^{2-}$ (Fig. 1), coordinated potassium cations, together with crystallization methanol and water molecules (see ESI†). The two crystallographically independent Ni(1) and Ni(2) atoms adopt a trigonally distorted octahedral NiN$_6$ coordination environment with alternating helical chiralities (named *RS*-stereoisomers) (Fig. 1). The values of the trigonal twist angle (τ) of 50.1(2) and 51.1° at Ni(1) and Ni(2) respectively, deviate appreciably from that of an ideal octahedral geometry ($\tau = 60°$), as previously reported for the related dinickel(II) triple mesocates with

the parent *N,N'*-1,3-phenylenebis(pyridine-2-carboxamidate) bridging ligand.[6] The NiN_6 environment at each metal ion is formed by the coordination in a *fac* disposition of three amidate and three pyridine nitrogen atoms belonging to three different bridging ligands [Ni–N$_{amide}$ = 2.063(4)–2.096(4) Å and Ni–N$_{py}$ = 2.091(4)–2.128(5) Å]. Within the $Ni_2(m\text{-}N_2C_6H_4)_3$ metallacryptand core of **1a**, the aromatic groups are disposed edge-to-face, with a weak C–H···π interaction between neighbouring benzene rings. The average torsion angle around the Ni–N–C–C bonds (ϕ) in **1a** is 94.9(1)°, a value which is slightly closer to that of 90° than those reported for the aforementioned pyridine analogues (ϕ = 95.7–96.0°).[6]
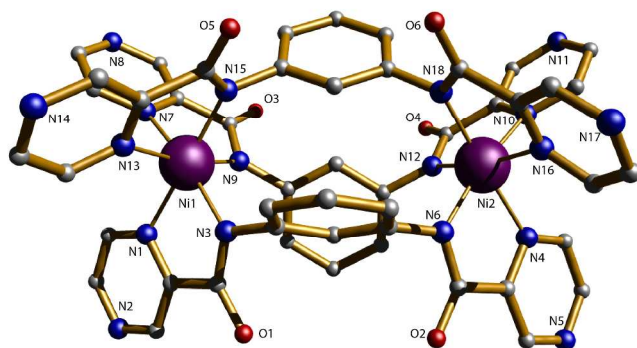

Fig. 1 The anionic dinuclear nickel(II) unit of **1a** with the atom-numbering scheme of the metal environment (hydrogen atoms have been omitted for clarity).

The binding of these heterochiral metallacryptand-type Ni^{II}_2 triple mesocates to the two crystallographically independent K(1) and K(2) atoms through the free carbonyl-oxygen atoms of the carboxamidate groups leads to heterobimetallic potassium(I)-nickel(II) 2-D coordination polymers of hexagonal-type topology (Fig. S1, ESI†). The value of the intramolecular Ni(1)–Ni(2) distance (*r*) across the triple *m*-phenylenediamidate bridge in **1a** is 6.900(1) Å, while the shortest intermolecular Ni(2)–Ni(1)^{I} separation is 9.513(3) Å [symmetry code: (I) = ½+ *x*, ½ − *y*, − ½ + *z*].

The cyclic voltammogram (CV) of **1b** in acetonitrile at 25 °C shows up to four ~~reversible~~ oxidation waves grouped in two pairs at E_1 = 0.31 V, E_2 = 0.47 V, E_3 = 0.89 V, and E_4 = 1.10 V *vs*. SCE (Fig. 2), with anodic to cathodic peak separation values ($\Delta E_{p,1}$ = $\Delta E_{p,2}$ = $\Delta E_{p,3}$ = $\Delta E_{p,4}$ = 70 mV) which are similar to that of the ferrocene under the same conditions [ΔE_p(Fc$^+$/Fc) = 70 mV (CH$_3$CN, 0.1 M *n*-Bu$_4$NPF$_6$)]. So, an almost linear plot of the peak current against the square root of the scan rate is obtained for all redox waves (see Fig. S8, ESI†), which are then stated to be pseudo-reversible on the voltammetric time-scale. Complex **1b** does not show any reduction wave at negative potentials up to –2.0 V *vs*. SCE.

The first pair of closely spaced oxidation waves of **1b** ($\Delta E_{12} = E_1 - E_2$ = 160 mV) would correspond to the stepwise one-electron oxidation of the metal centres to afford the dinickel(II,III) and dinickel(III,III) species. The second pair of oxidation waves ($\Delta E_{34} = E_3 - E_4$ = 210 mV) would then correspond to the further stepwise one-electron oxidation of the resulting dinickel(III,III) intermediate to give the corresponding dinickel(III,IV) and dinickel(IV,IV)

species. The small splitting of each pair reflects on the weak but non-negligible electronic interactions between the metal centres through the triple *m*-phenylenediamidate bridge in the resulting mixed-valent species. The calculated values of the individual comproportionation constant along this electron transfer series, however, clearly reflect the higher thermodynamic stability of the homovalent Ni_2^{III} complex (log K_c^{23} = $\Delta E_{23}/59$ = 7.12) when compared with those of the heterovalent $Ni_2^{II,III}$ and $Ni_2^{III,IV}$ ones (log K_c^{12} = $\Delta E_{12}/59$ = 2.71 and log K_c^{34} = $\Delta E_{34}/59$ = 3.56).
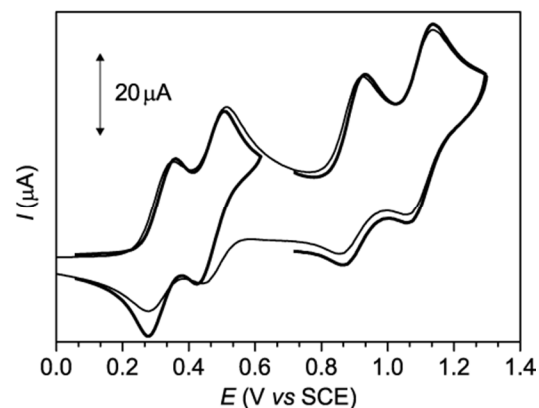

Fig. 2 CVs of **1b** in acetonitrile (0.1 M *n*Bu$_4$NPF$_6$, 25 ˚C) at a scan rate of 100 mV s^{-1}.

Variable-temperature (2.0–300 K) magnetic susceptibility measurements for **1a** and **1b** in the form of the χ_M and $\chi_M T$ *vs*. *T* plots (χ_M being the molar magnetic susceptibility per dinuclear unit and *T* the absolute temperature) are shown in Figure S2 and S3 respectively (ESI†). At room temperature the $\chi_M T$ values of 2.11 (**1a**) and 2.10 cm^3 mol^{-1} K (**1b**) are close to that expected for two magnetically non-interacting high-spin Ni^{II} ions. Upon cooling, $\chi_M T$ continuously increase for **1a** and **1b** revealing the presence of moderately weak intradimer ferromagnetic coupling between the high-spin Ni^{II} ions. In fact, since the large intermolecular metal-metal separation of *ca*. 10 Å, the interdimer magnetic interactions through the diamagnetic K^{I} ions in **1a** are certainly negligible. However, **1a** and **1b** show a maximum $\chi_M T$ value of 2.90 and 2.86 cm^3 mol^{-1} K at 3.5 and 4.7 K, respectively, and then they slightly decrease down to 2.81 cm^3 mol^{-1} K at 2.0 K, which is a consequence of a non-negligible zero-field splitting (*zfs*) of the six-coordinate, octahedral high-spin d^8 Ni^{II} ions ($^3A_{2g}$).

The magnetic susceptibility and magnetization data of **1a** and **1b** were analysed in unison through a spin Hamiltonian [eqn. (S1), ESI†] for a dimer model which takes into account the local axial (*D*) and equatorial (*E*) *zfs* of a triplet Ni^{II} ions (S_{Ni} = 1), a magnetic coupling between them (*J*), and a Zeeman effect through the Landé factor for Ni^{II} ion (g_{Ni}).[7] A good fit for **1a**/**1b** is obtained through the appropriate analytical expression[7b] with *J* = +3.3/+3.5 cm^{-1}, *D* = − 3.1/–3.1 cm^{-1}, *E/D* = 0.004/0.007, *g* = 2.040/2.035, and *F* = 3.1 x 10^{-5}/1.5 x 10^{-4} (where *F* is the agreement factor defined as $\sum[(P)_{exp} - (P)_{calcd}]^2/\sum[(P)_{exp}]^2$, where *P* is the physical property under study (solid lines in Fig. S2 and S3, ESI†). The experimental *J* and *D* values for **1a** and **1b** are similar to those reported earlier for related

dinickel(II) triple mesocates with the ligands *N,N'*-1,3-phenylenebis(oxamato) and *N,N'*-1,3-phenylenebis(pyridine-2-carboxamidate) (J = 3.2–3.6 cm^{-1} and $|D|$ = 0.5–3.5 cm^{-1}).[6,8]

The observed net intramolecular ferromagnetic coupling in **1a** and **1b** is supported by DF calculations on a molecular model based on the experimental geometry and including the K^{I} ions and their surrounds, which provide a calculated J value of +3.9 cm^{-1} (see Computational details, ESI†). Similar calculations on a more simple model, where K^{I} ions are excluded, give the same result (J = +3.9 cm^{-1}) or very close (J = +4.2 cm^{-1}) for its optimized geometry. From the spin density map of the quintet state of the Ni$^{II}_2$ unit shown in Figure 3a, it can be observed that a spin delocalization occurs from the e_g(z^2, x^2–y^2) magnetic orbitals of the metal ions to the coordinated amidate nitrogen atoms. The spin density on these nitrogen atoms is then pumped in the π pathway of the organic skeleton by a spin polarization mechanism leading to the alternating atomic spin densities on the exchange pathway.[9] Thus, according to the McConnell II mechanism, a ferromagnetic coupling is found because of an odd number of atoms exists through the pathway.[10]
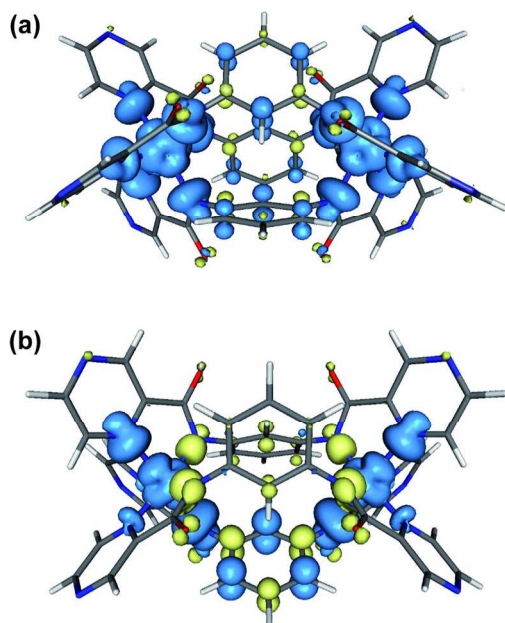
Fig. 3 Projection view of the calculated spin density distribution for the ground quintet spin configuration of **1a** (a) and optimized {Ni^{III}}$_2$ species (b). Blue and yellow contours represent positive and negative spin densities. The *iso*-density surface corresponds to a value of 0.0013 e bohr^{-3}. Even orbitals are noted as z^2 and x^2-y^2, actually, they correspond to a mixture of both.

On the other hand, CAS calculations on a more simple molecular model, where one of the high-spin Ni^{II} ions was replaced by a diamagnetic Zn^{II} ion, allowed to calculate the local magnetic anisotropy parameters of the nickel(II) centre [D = –6.0 cm^{-1} and E/D = 0.07 for centre Ni(1) and D = –6 cm^{-1} and E/D = 0.12 for centre Ni(2)]. It is worthy to say, that the $|D|$ value obtained above from the best-fit corresponds to a minimum value since a perfectly alignment of the local D tensors was considered, which is not the case. Indeed, a larger value is found by CAS calculations in agreement with an angle between z-axis of ZFS equal to 57.7º.

The stable doubly oxidized dinickel(III,III) species was prepared by both electrochemical and chemical oxidation of **1b** with *n*Bu$_4$NPF$_6$ as supporting electrolyte in acetonitrile and an applied voltage of +0.50 V (under a constant current of 0.35 µA for three days) and excess of bromine in acetonitrile, respectively [E(Br$_2$/Br$^-$) = +0.47 V *vs.* SCE] (see ESI†). Up to now, all our attempts to characterize the quadruple oxidized dinickel(IV) species obtained either by chemical or electrochemical oxidations were unsuccessful, probably because of its partial decomposition under our experimental conditions.

The Q-band EPR spectrum at 8 K of **1b** in acetonitrile solution shows a complicated spectral pattern similar to that reported in a previous paper for [Ni$_2$(μ_2-OH$_2$)(μ_2-O$_2$CBu)$_2$(O$_2$CBu)$_2$(py)(3-Mepy)][11] (py = pyridine and 3-Mepy = 3-methylpyridine) (see Figure S5). In such case, D, an probably also g_x, g_y, g_z, for each nickel(II) metal ion and J magnetic coupling constant between Ni^{II} ions are not very different from those found for us (see above), what justify the resemblance between the Q-band EPR spectra. Such as it is told by Walsh *et al.*, "*due to a very limited number of transitions falling within the available magnetic field range, ... and a significant zfs is acting on weakly coupled non-Kramer ions*" an interpretation of the spectra is extremely difficult. The complexity arises because of the two Ni^{II} ions are non-equivalents and their D tensors are not collinear. The equivalent spectrum in solid state is richer and more defined, probably due also to the observation of the hyperfine coupling (see Figure S5).

On the contrary, the Q-band EPR spectrum at 8 K of the doubly oxidized species obtained by either electrochemical or chemical oxidation of **1b** in acetonitrile solution is characteristic of a doublet from a Ni^{III} species (S_{Ni} = 1/2) and with g_1 = 2.05, g_2 = 2.07 and g_3 = 2.20 (see Figure S6). A similar spectrum was registered on a crystalline sample obtained from electrocrystallization (g_1 = 2.05, g_2 = 2.05 and g_3 = 2.30), unfortunately any good single-crystal was obtained (see Figure S7). However, the experimental spectra is more complicated than the theoretical ones obtained with these g_i values and some signals at lower magnetic field are also observed, which correspond to an anisotropic spin state generated from a weak ferromagnetic coupling between the two Ni^{III} ions. The stabilization of the trivalent oxidation state of nickel in **1b** is explained in terms of the well known strong electron donating character of the amidate groups,[4] as reported earlier for the dicopper(II) metallacyclophane with the innocent ligand *N,N'*-2-methyl-1,3-phenylenebis(oxamate) (E_1 = +0.43 and E_2 = +0.65 V *vs*. SCE).[3a]

Usually in coordination chemistry, DF calculations provide a correct description of the electronic structure but it is not possible in an easy way to correlate the obtained molecular orbitals with those usually used in simplified but useful schemes. In such cases, the formal magnetic orbitals are split into several molecular orbitals and any physical information cannot be directly extracted from them, e.g. their energies. An answer can be found in the natural orbitals that allow us to find a composition and shape of the magnetic orbitals. As an approach, it is possible to find an estimation of their energies carrying out a calculation using frozen natural orbitals, as illustrated in Figure S4 (ESI†). In **1a**, the energy gaps between pairs of the magnetic orbitals are very small (125 and 173 cm^{-1}), i.e., they are

nearly degenerated and following the Hay-Thiebault-Hoffman mechanism a ferromagnetic is expected, in agreement with our calculations. In fact, these orbitals should be symmetric and antisymmetric combinations of the local magnetic orbitals, but as in some ferromagnetic diradical species, they are non-bonding in the skeleton, avoiding the mixture of them, what support the ferromagnetic nature of the interaction.

It is very usual thinking that oxidation processes occur by removing electrons of the HOMO, i.e., the highest occupied molecular orbital, but, sometimes, in modern coordination chemistry this is not the case, because a reorganization of the molecular orbitals occurs after removing one electron, what can stabilize an oxidation from a more intern orbital. Thus, following the description in the preceding paragraph, an oxidized Ni_2^{III} complex should be expected, but the only way to rule out a radical form is looking for the most stable of them. So, from the optimized molecular geometry of the simple model of **1a** we removed two electrons and optimized the molecular geometry. Evidently, an oxidation of one electron in each metal centre to reach a $\{Ni^{III}\}_2$ configuration were studied, but also other where the electrons were removed from the organic bridge to arrive at $\{Ni^{II}L^{\bullet}\}_2$ species with different arrangements of the local spin moments on Ni^{II} and $L^{\bullet}$ paramagnetic centres. A double oxidation in only one of the metal ions to generate a Ni^{IV}-Ni^{II} specie was logically discarded. The radical species were all placed to above 3400 cm^{-1} from the most stable $\{Ni^{III}\}_2$ configuration and above 2600 cm^{-1} for a configuration, $\{Ni^{II}Ni^{III}LL^{\bullet}\}$, where the oxidized is mixed between a metal ion and one organic bridge.

DF calculations on the $\{Ni^{III}\}_2$ species showed that a weak ferromagnetic coupling ($J = +20.4$ cm^{-1}) mediates between doublet ($S = \frac{1}{2}$) Ni^{III} ions, being, in agreement with the EPR study, a triplet as a spin ground state. As in **1a**, the McConnell mechanism makes possible a ferromagnetic coupling in the oxidized species, such as it is shown in Figure 3b. However, three phenyl ring are operative to transmit the magnetic coupling in **1a**, but now only one of them is pertinent because the x^2-y^2 magnetic orbital is empty. Indeed, a lost of spin density is observed in the basal plane of the Ni^{III} ion that leads to a spin polarization instead of a delocalization on the nitrogen atoms of two pyrazineamidate ligands, but the spin polarization on the pathway is conserved but its magnitude is largely decrease. On the other hand, as in **1a**, the larger spin density on the z axis is delocalized on the amidate nitrogen atoms and then polarized through the pathway being effective the McConnell mechanism, observing hence a net ferromagnetic coupling. Comparing the $n_A n_B J$ parameter, where n_A and n_B are the unpaired electrons in each centre, closed values are found for **1a** (16.8 cm^{-1}) and its oxidized species (20.4 cm^{-1}) showing that the magnetic coupling in both compounds is similar.

Conclusions

The self-assembly of the novel *N,N'*-1,3-phenylenebis(pyrazine-2-carboxamidate) ligand with Ni^{II} ions renders a unique example of ferromagnetically coupled dinickel(II) metallacryptand of the triple mesocate-type. Interestingly, the two metal centres function as electron reservoirs to impart a multielectron (charge storage) oxidation behaviour to this electroactive magnetic molecule with several chemically accessible oxidation levels at the exchange-coupled spin carriers that can store and deliver an electric charge by the application of the appropriate electric potential.

Notes and references

[a] Department of Chemistry, Texas A&M University, College Station, 77843 Texas, United States. E-mail: zhou@mail.chem.tamu.edu
[b] Institut Laue Langevin, 6 Rue J. Horowitz, 38000, Grenoble, France.
[c] Instituto de Ciencia Molecular (ICMol), Universitat de València, 46980 Paterna, València, Spain. E-mail: joan.cano@uv.es
[d] Fundació General de la Universitat de València (FGUV), Universitat de València, 46980 Paterna, València, Spain.

† Electronic Supplementary Information (ESI) available: Synthesis, crystallographic, magnetic, electrochemical, and computational details. See DOI: 10.1039/c000000x/

1 (*a*) J. M. Lehn, *Angew. Chem. Int. Ed.*, 2004, **43**, 3644; (*b*) L. K. Thompson and O. Waldman, *Coord. Chem. Rev.*, 2005, **249**, 2677.

2 (*a*) A. Dei, D. Gatteschi, C. Sangregorio, L. Sorace and M. G. F. Vaz, *Inorg. Chem.*, 2003, **42**, 1701; (*b*) S. Mukherjee, T. Weyhermüller, E. Bothe, K. Wieghardt and P. Chaudhuri, *Dalton Trans.*, 2004, 3842.

3 (*a*) E. Pardo, J. Ferrando-Soria, M. C. Dul, R. Lezcouëzec, Y. Journaux, R. Ruiz-García, J. Cano, M. Julve, F. Lloret, L. Cañadillas-Delgado, J. Pasán and C. Ruiz-Pérez, *Chem. Eur. J.*, 2010, **16**, 12838; (*b*) J. Ferrando-Soria, M. Castellano, R. Ruiz-García, J. Cano, M. Julve, F. Lloret, J. Pasán, C. Ruiz-Pérez, L. Cañadillas-Delgado, Y. Li, Y. Journaux and E. Pardo, *Chem. Commun.*, 2012, **48**, 8401.

4 A. K. Patra and R. Mukherjee, *Inorg. Chem.*, 1999, **38**, 1388.

5 D. J. Barnes, R. L. Chapman, R. S. Vagg and E. C. Watton, *J. Chem. Eng. Data*, 1978, **23**, 349.

6 (*a*) M. A. Palacios, A. Rodriguez-Dieguez, A. Sironi, J. M. Herrera, A. J. Mota, J. Cano and E. Colacio, *Dalton Trans.*, 2009, 8538; (*b*) M. A. Palacios, A. Rodriguez-Dieguez, A. Sironi, J. M. Herrera, A. J. Mota, V. Moreno, J. Cano and E. Colacio, *New J. Chem.*, 2009, **33**, 1901.

7 (*a*) A. P. Ginsberg, R. L. Martin, R. W. Brookes and R. C. Sherwood, *Inorg. Chem.*, 1972, **11**, 2884; (*b*) G. De Munno, M. Julve and F. Lloret, *J. Chem. Soc., Dalton Trans.*, 1993, 1179.

8 M.-C. Dul, R. Lescouëzec, L.-M. Chamoreau, Y. Journaux, R. Carrasco, M. Castellano, R. Ruiz-García, J. Cano, F. Lloret, M. Julve, C. Ruiz-Pérez, O. Fabelo and E. Pardo, *CrystEngComm*, 2012, **14**, 5639.

9 I. Fernández, R. Ruiz, J. Faus, M. Julve, F. Lloret, J. Cano, X. Ottenwaelder, Y. Journaux and M. C. Muñoz, *Angew. Chem. Int. Ed.*, 2001, **40**, 3039.

10 H. M. McConnell, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, 1967, **11**, 144.

11   J. P. S. Walsh, S. Sproules, N. F. Chilton, A.-L. Barra, G. A. Timco,
     D. Collison, E. J. L. McInnes and R. E. P. Winpenny, *Inorg. Chem.*,
     2014, **53**, 8464.

ChemComm Accepted Manuscript