Magnetic properties of \( \{M_4\} \) coordination clusters with different magnetic cores (M=Co, Mn).

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We present a joint experimental and theoretical characterization of the magnetic properties of coordination clusters with an antiferromagnetic core of four magnetic ions. Two different compounds are analyzed, with Co and Mn ions in the core. While both molecules are antiferromagnetic, they display different sensitivities to external magnetic field, according to the different strength of the intra-molecular magnetic coupling. In particular, the dependence of the magnetization versus field of the two molecules switches with temperatures: at low temperature the magnetization is smaller in \( \{\text{Mn}_4\} \), while the opposite happens at high temperature. Through a detailed analysis of the electronic and magnetic properties of the two compounds we identify a stronger magnetic interaction between the magnetic ions in \( \{\text{Mn}_4\} \) with respect to \( \{\text{Co}_4\} \). Moreover \( \{\text{Co}_4\} \) displays not negligible spin-orbit related effects that could affect the spin lifetime in future antiferromagnetic spintronic applications. We highlight the necessity to account for these spin-orbit effects for a reliable description of these compounds.

1 Introduction

Molecular magnets constitute an excellent platform for molecular spintronics and quantum information storage and processing as their properties can be controlled at the nano/micro-scale during fabrication.1–3 Coordination clusters formed by an inner magnetic core and a surrounding shell of organic ligands can be synthesized to control both the magnetic interactions between the ions within the molecule and the coupling between magnetic core and environment.4 Single-molecule magnets are particularly attractive for spin-dependent quantum transport applications5 as the spin retains its orientation in the absence of an external magnetic field and applications can leverage on the technology developed for functionalization with nanoparticles.6,7

In recent years, research has concentrated on molecular magnets with large overall spin generated by ferromagnetic coupling between magnetic centers.8–10 On the other hand, the incorporation of molecular antiferromagnets in spintronic devices11,12 is still a new area of research. Recent proposals are only theoretical, and concern molecular AFM crystals13 or systems that can hardly be realized experimentally14. The expected advantages of antiferromagnetic coordination clusters are the same as for antiferromagnetic spintronic devices, i.e. robustness against perturbation due to magnetic fields, absence of stray fields, and capability to generate ultrafast dynamics and large magnetotransport effects.15 Antiferromagnetic molecules can be used to functionalize other organic systems, as carbon nanotubes, with the advantage that the current flowing through the tube does not alter the magnetic properties of the molecules16,17 and the low spin-orbit coupling allows long spin-flip lengths and spin lifetimes.

The application of molecular magnets in spintronics and quantum technologies would benefit from molecular design aimed at identifying the most suitable combinations of magnetic ions and organic ligands to ensure long spin coherence times, efficient spin injections and tunable transitions between spin states.18 In order to master this kind of applications, it is essential to understand the details of the magnetic interaction between the transition metal core ions and the subtle dependence of the magnetic properties of the molecule on the molecular structure.19 For example, Kampert et. al20 showed that the magnetic properties of a family of \( \{\text{Mn}_4\} \) antiferromagnets with the general formula \( \{(\text{RCO}_2)_3\text{Mn}_4\text{L}_2\} \) (R=CF3, CH3, Ph, H2L = 2,6-bis(1-(2-hydroxyphenyl)iminoethyl)pyridine) can be tailored by modifying the bridging carboxylate ligands, leading to a tunable exchange interaction between the magnetic ions. In this work we analyze the same molecular cluster with a different perspective by varying the chemical nature of the inner magnetic core. Through a joint experimental and theoretical characterization we compare the \( \{\text{Mn}_4\} \) acetate complex with its cobalt analogue. While MnII centers are adequately described by the spin magnetic moment (spin-only model), CoII centers in octahedral or pseudo-octahedral environments are characterized by significant orbital moments, leading to spin-orbit coupling (SOC) effects that could reasonably influence applications in more complex devices. Given the importance of magnetic fields in the study of spintronic devices, our experimental investigation mainly focuses on the changes in the magnetic properties of the complexes in an external magnetic field. The theoretical analysis, performed through a first-principles approach and a Heisenberg model Hamiltonian, is necessary to interpret the experiments and explain the differences between the two compounds, mostly due to the magnetic features of the magnetic core ions. Our computed spin dynamics highlights the key role played by electron correlation in the magnetic...
behavior of the complexes.

2 Methods

2.1 Theory

Theoretical calculations were performed in the Density Functional Theory (DFT) framework, using a pseudopotential description of the core electrons and atomic orbital basis set, as implemented in the SIESTA code. We adopted the local density approximation (LDA) for the exchange-correlation energy functional. A Hubbard correction for Mn and Co was included to account for the strong Coulomb interaction of localized $d$ electrons. We use $U = 6$ eV for Mn and $U = 4$ eV for Co, according to the literature. To evaluate the role of spin-orbit coupling, which is relevant in Co, we also performed calculations including spin-orbit correction using the formalism of Ref. The current version of the SIESTA code does not allow to simultaneously include Hubbard and spin-orbit corrections, thus the two effects are treated separately. The structure was relaxed with a tolerance on the forces on the atoms equal to 0.03 eV/Å. In the LDA+U calculations the finesse of the real-space grid (mesh-cutoff) was set to 400 Ry and the smearing of the electronic occupation (electronic temperature) to 100 K. In order to increase the accuracy in the convergence, SOC calculations where performed with 600 Ry mesh cutoff and 1K electronic temperature. The structural relaxation has been refined with SOC, starting from the LDA+U equilibrium geometry. The exchange coupling parameters $J_{i,j}$ were obtained by considering the lowest energy spin configurations of the Mn and Co centers and solving a system of equations (Heisenberg model) in the DFT energies with four $J_{i,j}$ parameters.

The geometry of the various spin configurations was kept fixed to the ground state one in order to exclusively account for the effect of the spin-flip on the total energy of the molecules. Further, we exploited the model Heisenberg Hamiltonian $H = \sum_{i,j} \vec{S}_i \cdot \vec{S}_j + \mu g \vec{S}_i \cdot \vec{B}$, where $\vec{S}_i$ is the spin vector of atom $i$ and $J$ is the matrix of the exchange parameters, to fit experimental temperature and field-dependent magnetization data, as allowed by the implementation in the PHI code. In the following we label $J_1 = J_{1,4} = J_{2,3}$, $J_2 = J_{1,3} = J_{2,4}$, $J_3 = J_{1,2}$, $J_4 = J_{3,4}$, with the atoms numbered as indicated on Figure 1.

2.2 Experiment

The complexes [M$_2$L$_2$(OAc)$_4$] ($M = Mn$, Co, Zn, {M$_4$} for short), where H$_2$L = 2,6-bis-(1-(2-hydroxyphenyl)iminoethyl)pyridine, HOOAc = acetic acid, and $M = Mn^{II}$, Co$^{II}$ or Zn$^{II}$) were synthesized by one pot reaction of 2-aminophenol, diacetylpyridine and manganese, cobalt or zinc acetate, are stable towards oxidation in the solid state as well as in solution, despite the sensitivity of the {Co$_4$} precursors to oxidation by O$_2$ during synthesis. This observation is confirmed by the cyclic voltammetry of the complex (Fig. 2), which displays two quasi-reversible ($\Delta E = 120$ mV) one-electron oxidation waves at 0.30 and 0.80 V vs. Fe$^{2+}$/Fe which can be assigned as $\{Co^{II}_4\} \rightarrow \{Co^{III}_2Co^{II}_2\} \rightarrow \{Co^{III}_2Co^{II}_2\}$. As expected, the redox couples in the manganese complexes are shifted to lower potentials and show the large peak-to-peak characteristic of Mn$^{II}$/Mn$^{III}$ processes. Finally, the zinc derivative shows irreversible ligand-centered oxidation processes above 0.5 V vs. Fe$^{2+}$/Fe.

3 Theoretical and experimental analysis

3.1 Synthesis and redox properties

The {M$_4$}, synthesized by one pot reaction of 2-aminophenol, diacetylpyridine and manganese, cobalt or zinc acetate, are stable towards oxidation in the solid state as well as in solution, despite the sensitivity of the {Co$_4$} precursors to oxidation by O$_2$ during synthesis. This observation is confirmed by the cyclic voltammetry of the complex (Fig. 2), which displays two quasi-reversible ($\Delta E = 120$ mV) one-electron oxidation waves at 0.30 and 0.80 V vs. Fe$^{2+}$/Fe which can be assigned as $\{Co^{II}_4\} \rightarrow \{Co^{III}_2Co^{II}_2\} \rightarrow \{Co^{III}_2Co^{II}_2\}$. As expected, the redox couples in the manganese complexes are shifted to lower potentials and show the large peak-to-peak characteristic of Mn$^{II}$/Mn$^{III}$ processes. Finally, the zinc derivative shows irreversible ligand-centered oxidation processes above 0.5 V vs. Fe$^{2+}$/Fe.

3.2 Molecular structure

The structure of the cobalt and zinc complexes was determined by single crystal X-ray diffraction to be analogue to that of the previously published manganese complex: the complexes consist of a cubic M$_2$O$_4$ core with two sets of two different ligand groups, for a total of 118 atoms (Fig. 1). The metallic core is a quasi-tetrahedron composed of two 7-coordinated ions (M$_1$, M$_2$) with bentapical bipyramidal coordination and two 6-coordinated ions (M$_3$, M$_4$) with pseudo-octahedral symmetry.

The metal ions with the same coordination number are almost equivalent, as they overall face a quasi-identical chemical environment. The molecular cluster has an approximately C$_2$ symmetry and can be described as two identical structures on different planes that are rotated of 90° one respect to the other (Fig. 1), taking the rotation axis along z. Seven-coordinated M$_1$ and M$_2$ lie on different planes, each being connected in-plane to a pentadentate pyridine-dimine-diphenoxide type ligand (L$^{2-}$), completed...
by the oxygen of a bridging acetate and a κ¹ phenoxy oxygen from the other L²⁻ ligand. The coordination sphere of M₃, M₄ is a pseudo octahedron of six oxygen atoms provided by a bidentate acetate ligand, the other oxygen of the two bridging acetate and two phenoxy oxygen from the L²⁻ ligand. (Relaxed coordinates available in ESI).

The inner cage of the three molecules is composed by four transition metal ions with different atomic valence configurations, 3d⁵ for Mn(II), 3d⁷ for Co(II) and 3d¹⁰ for Zinc(II). The latter complex is therefore diamagnetic; it was used experimentally to determine the diamagnetic contribution to the susceptibility of the complexes and will not be discussed further. Both Mn(II) and Co(II) ions display high spin configurations, i.e. S=5/2 for Mn and S=3/2 for Co.

Despite the similarity between the structures of the manganese and cobalt complexes, experimental evidence and DFT calculations show small differences in bond lengths in the inner core. In agreement with the larger atomic radius of Mn with respect to Co, the (M₄) central cage is slightly larger than the (Co₄) one, due to larger M-O and M-N bond-lengths. Details of the structure are reported in Table 1.

3.3 Behavior in magnetic field

In order to quantify the strength of the magnetic interaction within the molecule and the response to an external magnetic field we performed SQUID magnetometry experiments (Fig. 3). A singlet ground state is observed in both complexes, indicating the presence of antiferromagnetic coupling between the magnetic ions in the molecule. The molecular moment μₘₖₑₐₙ as a function of magnetic field (H = 0–5 T) and temperature (T = 20–300 K) was fitted to a mean field model (Curie-Weiss law, equation 1), yielding Néel temperatures of Tₙ = 23 K for (M₄) and Tₙ = 12 K for (Co₄):

$$\mu_{\text{mol}} = \frac{C H}{T - T_N}$$  \(1\)

Those values, as well as the larger slope of the molecular moment at low field/low temperature observed for (Co₄) in comparison to (M₄), suggests that the antiferromagnetic coupling between the metal atoms in (Co₄) is smaller than in (M₄). Notably, the behavior is reversed at high temperature with a larger magnetic moment for (M₄) than for (Co₄), which is in agreement with the higher spin moment of the Mn centers.

The Curie constant C obtained for the (M₄) complex (3.0 × 10⁻³ μₛ · K · Oe⁻¹) is in good agreement with a spin-only model (3.1 × 10⁻³ μₛ · K · Oe⁻¹ for g = 2 and S = 5/2). Such a model is not adequate for octahedral cobalt(II) complexes, with their ⁴T₁₅g...
3.4 Magnetic and electronic properties

In order to characterize the magnetic configuration of the inner cage and to ascertain the role of spin-orbit coupling in \{Co₄\} we performed ab initio calculations. DFT analysis shows that the ground state is characterized by an antiferromagnetic coupling between non-equivalent metal ions (M₁/M₂ and M₃/M₄), and a ferromagnetic one between the equivalent pairs (M₁/M₂ and M₃/M₄) giving rise to a up-up-down-down (uudd) configuration, referring to the relative alignment of the spins of the four metal ions. The magnetic moments of Co, Mn, N and O in the two molecular complexes, deduced from the Mulliken charge population, are reported in Table 2. Due to the chemical interaction with the ligands the magnetic moment of the metal atoms in the molecular complexes is reduced with respect to the isolated ions (≈ 4% in {Mn₄}, ≈ 10% {Co₄}). Accordingly, the induced magnetization of the ligands is smaller for {Mn₄} than for {Co₄}, as can be appreciated also through the small differences in the spatial distribution of the spin density (ρ_up − ρ_down on the oxygen atoms, Fig. 4). In {Mn₄} the magnetic moment of bridging oxygens (O₄ and O₆) is negligible. In {Co₄} the bridging phenoxy oxygens have opposite magnetization: O₉₂ and O₉₃ are magnetized up while O₈₂ and O₈₁ are magnetized down. Out of the eight acetate oxygens O₄, only two (O₄₁ − ) display a small positive magnetic moment while the other six (O₄ − ) have a larger (in modulus) negative magnetic moment (mean value reported in Table 2). The average magnetization of the N atoms is comparable to the average contribution of O₄ but with opposite sign. As a consequence, despite the presence of local magnetic moments, the total spin of both molecules is STOT = 0 confirming their antiferromagnetic character. Nevertheless, the major spread of the magnetic moment observed in {Co₄} is an indication of a possible large magnetic interaction of this molecule with other systems when the complex is used for functionalization.

In Figure 5 the DOS of the two molecules projected on different atoms of the complex (PDOS), is reported. The PDOS of Mn ions is characterized by a single spin population, due to the almost complete filling of the spin-up 3d electrons. In Co, instead, majority and minority spins are present, according to the more-than-half filling of the 3d orbitals. The oxygen atoms display a different PDOS depending on the group they are attached to. In particular the states of the bridging oxygen atoms O₈ partially overlap with the states of the magnetic ions, with larger extent for the seven-coordinated ones (M₁₂) in the majority-spin component and with the six-coordinated ones (M₃₂) in the minority spin component. This overlap, which appears to be slightly more intense in {Mn₄}, is responsible for the coupling between magnetic ions via superexchange interaction mechanism.⁵¹

For both complexes, the O₄ atoms are characterized by majority spin states in the [−3.5 − 1] eV energy range and minority states centered around −2.5 eV, with a moderate overlap with the metal atoms in both cases.

We can therefore conclude that they contribute to the magnetic coupling between metal centers with a similar strength.

The hybridization with states of the ligands is also responsi-
and 3.43 electrons donated in the Mn and Co case, respectively. Therefore, we expect that a stronger antiferromagnetic coupling in \{Mn_4\} than in \{Co_4\}, supporting the experimental findings.

3.5 Role of Spin Orbit Coupling

In the previous paragraphs we have analyzed the results obtained with the LDA+U approximation, necessary to account for the electronic correlation of localized 3d orbitals, but limited in the SIESTA code to a collinear-spin description of magnetism. This approximation is valid for the Mn(II) ions, as the high-spin \(d^5\) electronic configuration does not have a net orbital momentum. In Co(II) centers, instead, the \(d^7\) configuration leads to an orbital momentum \(L=3\) for an isolated ion. While the orbital momentum is quenched in low symmetry environments, including pentagonal bipyramidal, it is not in a perfect octahedron, where \(L=1\). As two of the metal centers in \{Co_4\} display a pseudo-octahedral geometry, SOC is expected to have a significant effect on the magnetic properties of this complex.

In order to investigate the role of SOC in the complexes, we have performed DFT calculations including SOC for both molecules at \(U=0\) using the fully relativistic pseudopotential formalism implemented in SIESTA. The magnetization direction has been set along the \(z\) axis for \{Mn_4\}. Indeed we verified that for this molecule the magnetic anisotropy related to spin-flip along five independent directions is at most \(\sim 100\ \mu\text{eV}\) per molecule. For \{Co_4\}, which is expected to display strong spin-orbit effects, we have explored 30 different direction of the magnetization. The easy axis for \{Co_4\} is rotated with respect to the \(z\) direction with a polar angle 150° and azimuthal angle 45°. The maximum magnetic anisotropy for spin-flip amounts to 12 meV per molecule. The results reported below are relative to \{Co_4\} with the spin along the easy axis.

In Table 5 and 4 the computed \(S, L,\) and their sum (\(J\)) are reported for both molecular complexes. In both cases, the atomic spin is slightly reduced with respect to the LDA+U calculation. The four metal ions in \{Co_4\} display an orbital moment which is smaller than the value expected for the isolated ion, but significantly larger than the manganese analogue. The quenching is stronger for the two ions in the pentagonal bipyramidal coordination, for which \(\sqrt{<L^2>}=0.11\). For the 6-coordinated pseudo-octahedral Co ions \(L\) is not negligible (\(\sim 0.4\)) and contributes to an overall value of \(\sqrt{<J^2>}>3\).

On the basis of these results we can infer that Spin-Orbit coupling plays a crucial role in determining the magnetic properties of \{Co_4\} while it is less relevant in \{Mn_4\} and in the latter case it can be disregarded.

| \(\Delta q(e)\)     | \(M_{1,2}\) | \(M_{3,4}\) | \(N\)  | \(O_A\)  | \(O_B\)  |
|---------------------|-------------|-------------|-------|----------|----------|
| \{Mn_4\}           | +1.10       | +1.32       | +0.29 | -0.39    | -0.60    |
| \{Co_4\}           | +1.49       | +1.63       | +0.22 | -0.44    | -0.70    |

Fig. 5 Density of states projected on the magnetic ions and different oxygen atoms (\(O_A\) and \(O_B\)) in the two molecular complexes. The average PDOS per atom type is reported.
Table 4 Spin (S), orbital moment (L) and their composition (J) for the four magnetic atoms of the \{Mn_4\} core. The data are reported in units of $\mu_B$.

|        | Mn_1 | Mn_2 | Mn_3 | Mn_4 |
|--------|------|------|------|------|
| $\sqrt{<S^2>}$ | 4.33 | 4.37 | 4.34 | 4.34 |
| $S_x$  | 1.43 | -1.35 | 0.17 | 0.37 |
| $S_y$  | 1.097 | -0.59 | -0.20 | 0.058 |
| $S_z$  | 3.94 | 4.11 | -4.33 | -4.32 |
| $\sqrt{<L^2>}$ | 0.052 | 0.057 | 0.058 | 0.058 |
| $L_x$  | 0.013 | -0.015 | -0.007 | -0.003 |
| $L_y$  | 0.006 | -0.008 | 0.004 | 0.01 |
| $L_z$  | 0.05 | -0.054 | -0.057 | -0.057 |
| $\sqrt{<J^2>}$ | 4.38 | 4.40 | 4.39 | 4.40 |

Table 5 Spin S, orbital moment L and their composition (J) for the four magnetic atoms of the \{Co_4\} core. The data are reported in units of $\mu_B$.

|        | Co_1 | Co_2 | Co_3 | Co_4 |
|--------|------|------|------|------|
| $\sqrt{<S^2>}$ | 2.56 | 2.56 | -2.57 | -2.58 |
| $S_x$  | -0.19 | 1.92 | -1.92 | 0.975 |
| $S_y$  | 1.355 | 1.6 | -1.62 | -0.72 |
| $S_z$  | -2.61 | -0.56 | -0.52 | 2.29 |
| $\sqrt{<L^2>}$ | 0.15 | 0.14 | 0.46 | 0.35 |
| $L_x$  | -0.004 | 0.121 | -0.33 | 0.057 |
| $L_y$  | 0.051 | 0.065 | -0.33 | 0.06 |
| $L_z$  | -0.14 | -0.033 | -0.033 | 0.33 |
| $\sqrt{<J^2>}$ | 2.71 | 2.71 | 3.03 | 2.92 |

3.6 Exchange coupling

In order to ascertain the strength of the (anti)ferromagnetic coupling in the two complexes we computed the exchange coupling parameters ($J_i$) from first-principles total energies by considering the five lowest-energy spin configurations of the molecules (uudd, udud, uduu, uudd, uudd) as explained in Section 2.1. The calculated exchange parameters are reported in Table 6, where positive and negative values correspond to ferromagnetic (FM) or antiferromagnetic (AFM) coupling. The parameters have been obtained either in the LDA+U approximation or including SOC in the calculation (with spin along the easy-axis direction).

The LDA+U simulations give $J_i$ that are of the same order of magnitude of those extracted from experimental susceptibility (see ESI), and are in fair agreement with those reported in Ref. 20 for a three-J model. Both $J_1$ and $J_2$ are negative, confirming the antiferromagnetic coupling between not equivalent atoms. One of the other two parameters describing the coupling between equivalent atoms ($J_3$ and $J_4$) is positive (FM), in agreement with the data extracted from the experiments. The overall exchange interaction, estimated as the average of the $J_i$ ($-3.7$ meV for $\{Co_4\}$ and $-1.4$ for $\{Mn_4\}$), is AFM for both molecular complexes.

The strongest $J_6$ ($J_6$ in $\{Co_4\}$, $J_2$ in $\{Mn_4\}$) corresponds to the interaction between the two pairs of not-equivalent ions and it is related to the energy difference between the AFM ground state and the high spin FM state ($S=12$ for $\{Co_4\}$ and $S=20$ for $\{Mn_4\}$) which is smaller for $\{Co_4\}$. The FM interaction between equivalent ions (intra-pair) is, instead, smaller for $\{Co_4\}$. The latter governs the transition to low-spin FM states (for example uudd) which influences the behavior of the magnetization at low fields and low temperatures, hence explaining the observed switching with temperature of the magnetization curves M(B) of the two molecules (Fig. 3). To further explore this behavior, we have exploited a model Heisenberg Hamiltonian with $J$ parameters and g-factor fitted from the experimental low-field susceptibility (ESI) and used them to calculate M(B) at two different temperatures. We find that the observed (Fig. 3) switch of M(B) with temperature is an effect of the more marked AFM character of $\{Mn_4\}$ giving rise to a positive curvature of M(B) at low field/low T. At high field/high T, instead, the most relevant factor is the larger saturation value of the magnetization in $\{Mn_4\}$ compared to $\{Co_4\}$. By increasing the range of the magnetic field beyond the experimental one, a crossing of the two theoretical curves is observed due to the combination of these two aspects (ESI).

The inclusion of SOC in the calculation leads to $Js$ with a sign that reflects the uudd magnetic order of the ground state, i.e. AFM (FM) coupling between M1/M4 and M2/M3 non-equivalent (M1/M2 and M3/M4 equivalent) ions. Nevertheless, the exchange parameters obtained with SOC are too large compared to those extracted from the experiments, suggesting that the electronic correlation cannot be neglected for a reliable estimate of the strength of the magnetic interactions.

For a deeper insight of the exchange interaction, we have computed the exchange parameters also with the Liechtenstein-Katsnelson-Antropov-Gubanov (LKAG) formula\textsuperscript{30} implemented in the TB2J package\textsuperscript{34}, which treats the local spin rotation of the numerical atomic orbitals for the magnetic atoms as a perturbation. The $Js$ evaluated with this approach present the same overall trend as those computed from total energies (Table 6), for both LDA+U and SOC case, and are reported in the ESI.

The different predictions of the various approximations (LDA or SOC) are a consequence of the complexity of the magnetic potential energy landscape of these molecular complexes. A small perturbation (geometry, electron correlation, spin alignment) can drive the results out of equilibrium and towards a different local minimum. Despite these difficulties, all the computed $J$ parameters predict the experimentally observed uudd ground state, regardless of the approach (total energies or perturbative) and inclusion of correlations or SOC. This has been verified by feeding the computed $J$ in the Heisenberg Hamiltonian and computing the various spin configurations (ESI).

Finally, we used all the computed $J$ parameters as input for spin dynamics simulations\textsuperscript{35–37} to predict the magnetic susceptibility, finding a good agreement with experiment in the LDA+U case (ESI). The results obtained without U correction are, instead, in striking contradiction with experiments, confirming the importance of taking into account electron correlation in the transitional metal sites.

4 Conclusions

Through a joint experimental and theoretical analysis we have characterized the properties of two coordination complexes, $\{Mn_4\}$ and $\{Co_4\}$, that display the same chemical structure but different inner magnetic core formed by Mn and Co atoms, respec-
tively. The theoretical analysis was performed under different approximations (LDA+U, SOC) and methods (first-principles, model Hamiltonians, perturbation theory).

The experimental data and the theoretical calculations show that by changing the magnetic core it is possible to tune the strength of the magnetic interaction inside the molecules and thus the robustness of the AFM configuration in an external magnetic field. Moreover, the different magnetic properties of the two chemical species lead to a different spatial extension of the magnetic moment and electronic charge density on the ligands, which influences the interaction with foreign systems and affects the efficiency of the two compounds when employed for magnetic functionalization.

We find and explain an unusual switch with temperature of the dependence of the magnetic moment from the applied magnetic field. Moreover, the different magnetic properties of the two chemical species lead to a different spatial extension of the magnetic moment and electronic charge density on the ligands, which influences the interaction with foreign systems and affects the efficiency of the two compounds when employed for magnetic functionalization.

The calculations clarify the role of spin-orbit effects: negligible in \( \{ \text{Mn}_4 \} \) and relevant in \( \{ \text{Co}_4 \} \), showing that SOC has to be considered for a reliable theoretical description of the magnetic moments of the latter. In perspective of future exploitation of these compounds in spintronics the SOC effects found in \( \{ \text{Co}_4 \} \) should be taken into account as possible source of spin decoherence.

Our study of the exchange coupling parameters and spin dynamics demonstrate that it is necessary to explicitly include electron correlations (for instance, via a Hubbard U parameter) to properly recover these properties. The complete description of the molecular complexes can only be performed in a framework in which electronic correlation and SOC are treated on the same footing.

**Conflicts of interest**

There are no conflicts to declare.

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Supplementary information: Magnetic properties of \{M_4\} coordination clusters with different magnetic cores (M=Co, Mn).

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1 Synthesis and characterization

1.1 Materials and synthesis

2-aminophenol (> 98%, TCI) was recrystallised from boiling water, washed with ice-cold water and diethylether and stored under inert atmosphere. 2,6-diacetylpyridine (> 98%, TCI), Co(OAc)2·4 H2O (99.999% trace metal basis, Aldrich) and Zn(OAc)2·2 H2O (99.999% trace metal basis, Aldrich) were used as received. Solvents were, when indicated, deaerated by three freeze-pump-thaw cycles using argon as inert gas. PE spatulas and PTFE cannulas were employed to avoid magnetic contamination of the samples.

[Mn4OAc4L4] (H2L=2,6-bis-(1-(2-hydroxyphenyl)iminoethyl)pyridine) \{Mn4\}

The complex was synthesized according to the literature,7 with some modifications. In particular, conducting the reaction under protective atmosphere is necessary to avoid the formation of an unidentified brown precipitate by the reaction of 2-aminophenol, cobalt acetate and dioxygen. 2,6-diacetylpyridine (439 mg, 2.5 mmol, 1 eq.), 2-aminophenol (583 mg, 5.3 mmol, 2.2 eq.) and Co(OAc)2·H2O (1.33 g, 5.3 mmol, 2.2 eq.) were introduced in a Schlenck flask under argon. Deaerated methanol (10 mL) was camulated into the flask and the resulting red solution was refluxed under argon for two hours. After the solution was returned to room temperature, deaerated diethylether (100 mL) was camulated in and allowed to mix with the solution, yielding an orange microcrystalline precipitate. The solid was filtered and washed with diethylether (3×30 mL) to yield Co4L2(OAc)4·4 CH3CN (1.0-1.2 g, 0.8-0.9 mmol, 60-70%) as a dark orange powder. The compound was recrystallised by dissolving the solid (130 mg, 0.1 mmol) in acetonitrile (25 mL), sonicating and filtering solution and setting it up for gas phase diffusion of diethylether. Dark red crystals of Co4L2(OAc)4·4 CH3CN (65-100 mg, 50-75% recrystallisation yield) were collected by filtration after 3-4 days and used for all further characterization and reactions.

UV (CH3CN) \(\lambda_{max}\), nm (log \(\varepsilon\)): 260sh (4.50), 321 (4.27), 398 (4.14).

CV \(E_{1/2}\), V vs. \(Fe^{3+}/Fe^{2+}\): 0.30, 0.80.

TGA (N2, 10 K min\(^{-1}\)) -12.3 % (50-150 K, -4 CH3CN (th. -12.4 %)). -30.5 % (350-400 K), -9.4 % (400-520 K).

Single crystal diffraction quality material can be obtained by gas phase diffusion of n-pentane into a saturated ethanol solution. The compound crystallizes in the P4/n space group with ethanol as a solvate. Due to twinning of the crystals and disorder of the solvate molecules we were only able to refined to a \(wR^2\) of 36 %. The asymmetric unit unequivocally contains a Co4L2(OAc)4 molecule and an ethanol molecule hydrogen bound to one of the acetate oxygens, as well as a second ethanol molecule which refines satisfactorily with a two-parts disorder of the hydroxy group with approximatively equal occupancies. The SQUEEZE routine was used to account for the residual electronic density localised in the large voids of the unit cell, which corresponds to 8 ethanol molecules per unit cell, yielding a final \(wR^2\) of 36 % \((R_1 = 18\%)\) with a formula Co4L2(OAc)4·3 EtOH. Crystal structure data is available from Cambridge Structural Database, under CCDC number 1855019.
Zn₄L₂(OAc)₄ (H₂L = 2,6-bis-(1-(2-hydroxyphenyl)iminoethyl) pyridine) ({Zn₄})

Synthesis of the complex follows the preparation of the manganese analogue,⁷ with some modifications. Specifically, 2,6-diacetylpyridine (186 mg, 1.0 mmol, 1 eq.), 2-aminophenol (250 mg, 2.3 mmol, 2.3 eq.) and Zn(OAc)₂·2 H₂O (501 g, 2.3 mmol, 2.3 eq.) were introduced in a Schlenck flask under argon. Deaerated methanol (10 mL) was cannulated into the flask and the resulting yellow solution was refluxed under argon for two hours. Note that this step can be conducted in air, but in that case a small amount of strongly red-colored 2-amino-3H-phenoxazin-3-one is formed by the oxidative dimerisation of 2-aminophenol and contaminates the product obtained before recrystallisation. After the solution was returned to room temperature, a microcrystalline yellow solid was precipitated by the addition of diethylether (200 mL). The solid (590-640 mg) was filtered, washed with diethylether (4×25 mL), and redissolved in chloroform (100 mL). Pentane was allowed to diffuse in the solution from the gas phase (to accelerate the process, the solution was divided in three fractions). Yellow single crystal diffraction quality Zn₄L₂(OAc)₄·4.5CHCl₃ (350-400 mg, 40-45 % yield) was collected by filtration after 3-4 days and used for all further characterization and reactions.

The compound crystallised in the P2₁/n space group, with 4.5 CHCl₃ molecules and a Zn₄L₂(OAc)₄ complex in the asymmetric unit. One of the chloroform molecules is located close to the inversion center at (0, 0.5, 0) and has an occupancy of 0.5. Another could be refined as an approximately 1:1 disorder between two close positions. Residual electronic density lies mostly in close proximity with the chlorine atoms of the other chloroform molecules, but attempts at refining similar disorder yielded only small occupancy factors and no significant improvement of the R factors, and were abandoned, leaving a final wR² factor of 12 % (R₁ = 4.3%). Crystal structure data is available from Cambridge Structural Database, under CCDC number 1855020.

UV (CH₃CN) λₘₐₓ, nm (log ε): 265sh (4.40), 293 (4.23), 346 (4.17), 407 (4.23).

SQUID: χdia, m³.mol⁻¹ (emu.mol⁻¹): -5.3×10⁻⁹ (4.2×10⁻⁴).
Fit of SQUID data

The experimental magnetic susceptibility was fitted exploiting an Heisenberg model Hamiltonian in which the exchange coupling parameters between pairs of ions are left as free parameters. The fit functions are reported in Figure 1 as solid lines, together with the experimental data (points) and the $J_n$ extracted from the fit.

The $J_n$ obtained are in fair agreement with those extracted from the LDA+U calculation. The fitted g-factor is $\sim 2$ in $\{\text{Mn}_4\}$ confirming the validity of the spin-only approximation, while it deviates from 2 in $\{\text{Co}_4\}$ reflecting the role of SOC.

Through the model Hamiltonian with parameters obtained from the fit of the experimental data the magnetization was calculated at different temperatures and fields. For large fields or large temperatures the magnetization of $\{\text{Mn}_4\}$ is larger than that of $\{\text{Co}_4\}$, as observed in the experiments. The saturation value ($gS\mu_B$) of $\{\text{Mn}_4\}$ ($20\mu_B$) is indeed larger than for $\{\text{Co}_4\}$ ($12\mu_B$ in a spin-only model). At low temperature, fields of 20 T for $\{\text{Co}_4\}$ and 25 T for of $\{\text{Mn}_4\}$ are needed for the magnetization to reach saturation. These values are significantly large compared to the fields accessible in our experiments (Fig. 3 in the main text).

In the low field–low-temperature limit the model shows an inversion of the magnetization curves leading to larger magnetization of $\{\text{Co}_4\}$ with respect to $\{\text{Mn}_4\}$. Moreover the two curves display opposite curvature, in agreement with SQUID data at low temperature. In particular, the magnetization of $\{\text{Mn}_4\}$ shows positive curvature, as expected for an antiferromagnet, while for $\{\text{Co}_4\}$ an almost linear dependence on the field can be observed.

The slope of the magnetization is an indication of the coupling between the magnetic centers: the stronger the antiferromagnetic coupling, the smaller the slope. Moreover, the smaller the moment per atom, the stronger the linear dependence of $M$ on the field. Both these aspects explain the fast rise observed for the magnetization of $\{\text{Co}_4\}$ in the experimental data, as due to the smaller value of $S$ (or $J$) (see table 4 and 5 in the main text) and of the AFM coupling, with respect to $\{\text{Mn}_4\}$. On the other hand, the saturation value for the magnetization of $\{\text{Co}_4\}$ is smaller than for $\{\text{Mn}_4\}$, thus the two magnetization curves show a crossing for a certain value of the field which is not reached in the experiments. At high temperature the magnetization curves flatten, resulting in a slower growth as a function of the field with respect to the low temperature limit.

The linear dependence on the field $M = Ng^2S(S+1)\mu_B^2B$ in this case is governed by the value of $S$ and it is smaller for $\{\text{Co}_4\}$ than for $\{\text{Mn}_4\}$, in agreement with what observed in the experiments at high temperature.
3 Exchange parameters from different calculations

The exchange parameters where extracted by fitting a system of equation for the five lowest energy spin configurations of the molecule, as reported in the main text. For a comparison with the available experimental data and previous theoretical calculations on \(\{\text{Mn}_4\}\) we consider also a set of only three \(J\) parameters, despite we retain this choice less accurate. Indeed the assumption \(J_3 = J_{(1,2)} = J_{(3,4)}\) is not correct, as the \(M_1/M_2\) and \(M_3/M_4\) pairs are not equivalent in terms of chemical coordination and ligands groups. The obtained values are reported in Tables 1. For a system of three exchange parameters, we recover the experimental results of Kampert et al.\(^7\).

In addition, we also computed the \(J\) values with with the Liechtenstein-Katsnelson-Antropov-Gubanov (LKAG) formula\(^7\) implemented in the TB2J package.\(^7\)

Table 1: Computed exchange parameters \(J\) (meV and Kelvin) for the \(\{\text{Mn}_4\}\) molecular complex, using LDA+U and a three-J Heisenberg model. The experimental values from Ref.\(^2\) are reported for comparison.

| \(J\)             | \(J_1\) (1-4,2-3) | \(J_2\) (1-3,2-4) | \(J_3\) (1-2, 3-4) |
|-------------------|-------------------|-------------------|-------------------|
| \(\{\text{Mn}_4\}\) (meV) | -0.7              | -0.4              | -0.2              |
| \(\{\text{Mn}_4\}\) (Kelvin) | -8.1              | -4.1              | -2.0              |
| Exp\(^7\) (Kelvin) | -2.2              | -1.1              | -0.1              |

TB2J evaluates the \(J\) for each couple of atoms. So there are six \(J\) parameters. The non-equivalent \(J\) for pairs \(M_1/M_3\) and \(M_2/M_4\) is related to the not perfect symmetry of the electronic structure associated with these pairs of atoms, probably due to some orbital polarization in the Mn/Co.

When the Heisenberg equation is solved for four exchange parameters, The TB2J results for the LDA+U case give the same trend obtained using SIESTA total energies: the ferromagnetic coupling between atoms M1 and M2 is not reproduced \((J_3 < 0)\) and the exchange coupling parameters are larger for \(\{\text{Co}_4\}\) than for \(\{\text{Mn}_4\}\). With SOC included, the exchange parameters obtained with TB2J are in fair agreement with those reported in the main text supporting the robustness of the
Table 2: J of the {Mn$_4$} and {Co$_4$} molecular complexes obtained with TB2J in LDA+U and with SOC included. The values are reported in meV.

|        | $J_1$ (1-4,2-3) | $J_2$ (1-3,2-4) | $J_3$ (1-2) | $J_4$ (3-4) |
|--------|-----------------|-----------------|-------------|-------------|
| LDA+U  |                 |                 |             |             |
| {Mn$_4$} | -1.21/-1.23     | -1.77/-1.84     | -0.8        | 0.1         |
| {Co$_4$} | -3.47/-3.29     | -1.70/-1.82     | 0.03        | -2.25       |
| SOC    |                 |                 |             |             |
| {Mn$_4$} | -34.5/1.3       | -55.7/-29.2     | 12.94       | 3.29        |
| {Co$_4$} | -3.24/-5.09     | -11.84/-10.68   | 1.18        | 18.35       |

results. The comparison between the two molecules confirms indeed the larger strength of the magnetic coupling in {Mn$_4$} with respect to {Co$_4$} but the absolute value of the $J$ is too large.

All the methods agree in the qualitative description of the magnetic coupling within the two molecules and in these terms, i.e. only qualitatively, these parameters should be taken into account.
4 Spin dynamics calculation

Using the Heisenberg model constructed from DFT results, we perform Ginzburg-Landau-Lifshitz (GLL) atomic spin dynamics\(^7\) (ASD) to compute the magnetic susceptibility with the MULTIBINIT code\(^7\). The isothermal magnetic susceptibility is calculated with the fluctuation-dissipation theorem\(^7\):

\[
\chi = \frac{1}{k_B T} \left( \langle m^2 \rangle - \langle m \rangle^2 \right),
\]

where \(\langle \rangle\) means the average over the ensembles, \(m\) is the magnetization of the system.

Four sets of parameters from DFT results with either SOC or Hubbard U correction, computed by total energy (TE) method or TB2J, were used as input. Another set of exchange parameters by fitting to experimental data is also taken as comparison. The results are shown in Fig. 3.

The "\(\lambda\)"-shape of the susceptibility curves are similar to extended structures, where the susceptibility diverges at the critical temperature, which is ill-defined in molecules. Nevertheless the temperature of the peak (defined as \(T_P\)), the decay of the susceptibility above the \(T_P\), and the value of the susceptibilities, all shows that the exchange parameters from the DFT results with the "\(+U\)" correction agrees better with experiments, in which the exchange values are smaller in general.

Figure 3: The susceptibilities computed with spin dynamics using various set of parameters. TE-SOC: fit from DFT (with SOC) energies. TE-LDAU: fit from DFT (with +U correction). TB2J-SOC: computed with TB2J from DFT with SOC. TB2J-LDAU: computed from TB2J with DFT+U. Experimental: fit from experimental data. The left and the right panels are from Mn4 and Co4, respectively.
5 Relaxed structures

The atomic coordinates (in Å) obtained through structural relaxation performed in DFT-LDA and SOC included are reported below for \{Co₄\} and \{Mn₄\}.

\{Co₄\}:
- Co 11.784660 24.970504 9.657395
- Co 10.497270 22.083542 10.349018
- Co 13.826910 21.350956 8.956570
- Co 11.640250 22.423558 7.355454
- O 12.276659 23.190641 10.768667
- O 13.053111 23.738692 8.233238
- O 12.150853 21.350956 8.965670
- O 10.536075 23.509294 8.730816
- N 11.150917 25.250576 11.697139
- N 10.234291 26.256309 9.631992
- N 11.898964 25.955696 7.819901
- C 12.573409 23.459183 12.047217
- C 13.501743 22.723520 12.800231
- H 14.089320 21.934242 12.292846
- C 13.683728 23.040467 14.147378
- H 14.424537 22.471937 14.743995
- C 12.967844 24.084959 12.800231
- H 13.125847 24.329670 15.812985
- C 12.094520 24.862400 11.948916
- H 11.619728 25.748710 14.42161
- C 11.894341 24.565336 12.624100
- C 10.126773 26.025442 11.948916
- C 9.578037 26.345785 13.287772
- H 10.175627 27.151091 13.781884
- H 8.530036 26.715922 13.221056
- C 9.604646 25.444738 13.951800
- C 9.538585 26.565027 10.740648
- C 8.341386 27.295998 10.668957
- H 7.820799 27.608225 11.593808
- H 7.833021 27.603089 9.415343
- H 6.862677 28.154448 9.327204
- C 8.583412 27.341326 8.274367
- H 8.239272 27.639455 7.265994
- C 9.816490 26.700082 8.429924
- H 10.790725 26.483101 7.373647
- C 10.499096 26.837914 5.965518
- C 11.18355 26.205940 5.283527
- H 9.420716 26.654751 5.742013
- H 10.706556 27.914849 5.751836
- C 13.024326 25.741449 7.058258
- C 13.537698 26.594422 6.071137
- H 13.031246 27.555676 5.858676
- C 14.722039 26.250453 5.422129
- H 15.143996 26.930256 4.657679
- C 15.384636 25.058139 5.746152
- H 16.319763 24.794952 5.214912
- C 14.880653 24.193928 6.719788
- H 15.372314 23.244492 6.981271
- C 13.696788 24.573235 7.377188
- N 11.408346 20.414618 11.203267
- N 10.045893 22.163800 12.313801
- N 8.804952 23.970605 10.567973
- C 12.292475 20.027330 9.077568
- C 12.842500 19.207261 8.088787
- H 13.105214 19.659644 7.110727
- C 13.063406 17.859247 8.376878
- H 13.502886 17.200660 7.602911
{Mn₄}
Mn 11.810113 24.985996 9.743006
Mn 10.424819 22.105112 10.320622
Mn 13.969259 22.519930 9.574551
Mn 11.607671 22.312376 7.271543
O 12.349963 23.147982 10.831958
O 13.140464 23.571435 8.098263
O 12.345050 21.326161 8.840598
O 10.496148 23.528278 8.643963
N 11.103152 25.197501 11.777895
N 10.216281 26.274131 9.676366
N 11.890695 25.881198 7.790930
C 12.598813 23.438037 12.113694
C 13.538059 22.730289 12.880143
H 14.135978 21.938064 12.381465
C 13.716597 23.053512 14.225799
H 14.46366 22.503444 14.828710
C 12.981132 24.093676 14.810091
H 13.138995 24.358651 15.873515
C 12.083104 24.839617 14.047557
H 11.583453 25.17635 14.497662
C 11.870084 24.527046 12.689523
C 10.080681 25.994708 12.005918
C 9.546066 26.384103 13.338673
H 10.158648 27.184771 13.798833
H 8.501386 26.750637 13.269521
H 9.564052 25.494243 14.036190
C 9.519736 26.565525 10.790827
C 8.322393 27.297096 10.700291
H 7.771295 27.596526 11.612739
C 7.835847 27.640072 9.438633
H 6.864361 28.162054 9.339557
C 8.588967 27.345740 8.297761
H 8.238350 26.736652 7.288881
C 9.816809 26.695904 8.461386
H 10.779240 26.441424 7.388195
H 10.469343 26.827821 5.989159
C 11.084954 26.222383 5.280743
H 9.388972 26.652695 5.766540
H 10.676751 27.911245 5.802432
H 13.005069 25.665510 7.012250
C 13.513339 26.561176 6.054061
H 12.985913 27.517018 5.868582
C 14.713268 26.281899 5.401472
C 15.114912 27.003092 4.663350
C 15.418169 25.105071 5.685767
H 16.370640 24.891407 5.162735
C 14.920698 24.193405 6.616684
H 15.436848 23.237961 6.848087
C 13.721749 24.467567 7.279225
N 11.478065 20.440099 11.180512
C 10.003855 22.178942 12.333361
C 8.775266 23.494498 10.565036
C 12.408593 19.997149 9.045486
C 12.918357 19.125851 8.079778
H 13.195354 19.548705 7.091340
C 13.081014 17.774955 8.386179
H 13.483453 17.082870 7.621038
C 12.750828 17.293427 9.650596
H 12.879629 16.219411 9.896550
