Predetermined ferromagnetic coupling *via* strict control of M-O-M angles

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An imidazolidine-phenolate ligand HL yields quadruple bridged ferromagnetic nickel and cobalt dinuclear complexes. The ferromagnetism of these samples is mainly ascribed to the double μ-$O_{phenolate}$ bridges, on the basis of DFT calculations. These studies demonstrate that the short M-O-M angles of the M_2O_2 are the optimal ones for maximizing the ferromagnetic contribution in these complexes. And these acute angles, close to 90º, are predetermined by the geometrical constrictions imposed by the ligand itself. Thus, HL is an odd polydentate donor that induces ferromagnetism *per se* in its metal complexes by strict control of geometric parameters.

Introduction

Ferromagnetic exchange in polynuclear compounds of paramagnetic metal ions is far less common than antiferromagnetic interactions. In this way, the systematic isolation of ferromagnetic complexes remains a challenge for synthetic chemists, whose attempts to prepare high-spin ground state systems are often unsuccessful. The relevance of achieving such systems lies not only in its scarcity, but also in the fact that high spin seems to be a requirement, along with a large axial anisotropy, for a metal cluster to show single molecular magnet (SMM) behavior.[1,2] The most common strategies to obtain molecules with ferromagnetic exchange interactions (the use of orthogonal magnetic orbitals,[2] the double exchange,[2a,3] spin-polarisation,[2a,4] crossed interactions[2a,5] or countercomplementarity of the bridging ligands[2a,6]) are many times hard to come by, and the amount of failed experiments that should lead to ferromagnetic complexes is huge. In this sense, the experience seems to demonstrate that there are a reduced number of ligands that unequivocally promote ferromagnetic coupling by themselves, independent of the paramagnetic metal ion and of the presence of additional bridges. These are, basically, azide acting as $\mu_{1,1}$ donor, bridging *syn-anti* carboxylates and a dinucleating imidazolidine ligand previously reported by us.[7] Accordingly, the synthesis of ligands with such intrinsic odd characteristic is of great relevance in the field of molecular magnetism. In this sense, in this work we present a new imidazolidine-phenolate donor HL (Scheme 1), which favours the ferromagnetic coupling by strict control of the M-O-M angles in its complexes, an unusual feature that, as far as we know, has not been previously described.
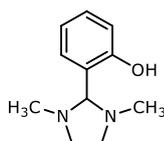
Scheme 1. HL

Results and discussion

The synthesis and characterisation of HL was previously described[8] but its coordination chemistry remains unexplored up to date. The reaction of HL with nickel(II) acetate or acetylacetonate in 1:1 molar ratio renders the dinuclear complexes [NiL(OAc)]$_2$·4H$_2$O **1** and [NiL(acac)]$_2$ **2**, respectively, **2** being isolated as single crystals from the mother liquor. Attempts to recrystallize **1** in methanol/acetonitrile leads to partial hydrolysis of HL, and yield single crystals of [NiL(OC$_6$H$_4$CHO)]$_2$ **1b**, what seems to indicate a lower stability of the acetate derivative respect to the acetylacetonate one in solution. [CoL(acac)]$_2$ **3** is also obtained by direct interaction of the ligand and cobalt(II) acetylacetonate in 1:1 molar ratio, and its recrystallisation in acetone/hexane allows isolating single crystals of **3**.

Crystal structures

Crystal structures of the **1b**, **2** and **3** show that the three complexes are isostructural (Figs. 1, S1 and 2).
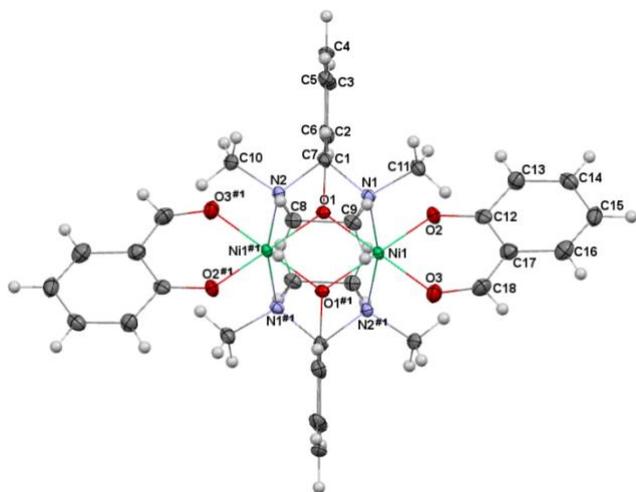
Fig. 1. Ellipsoid (50%) diagram for **1b**. Main distances (Å) and angles (⁰): Ni1—O1 2.0116(19), Ni1-O1$^{\#1}$ 2.019(2), Ni1—O2 1.980(2), Ni1-O3 2.041(2), Ni1—N1 2.252(2), Ni1-N2$^{\#1}$·2.234(2), Ni1⋯Ni1$^{\#1}$ 2.8648(7); Ni1-O1-Ni1$^{\#1}$ 90.60(8).

The asymmetric unit of the compounds contains just hall of the [MLL']$_2$ (L' = acac or OC$_6$H$_4$CHO) molecule, the other half being generated by an inversion center. In these complexes, the exogenous L' ligands act as terminal bidentate quelate donors. The remaining coordination positions about the metal ions are filled by two deprotonated imidazolidine (L)$^-$ ligands, which act as bridging tridentate.
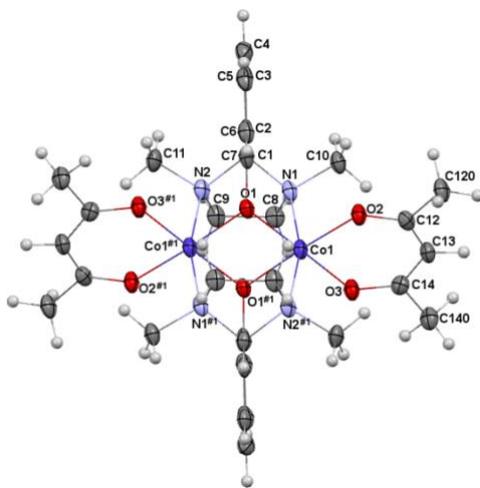
Fig. 1. Ellipsoid (50%) diagram for **3**. Main distances (Å) and angles (⁰): Co1-O1 2.029(2), Co1-O1$^{\#1}$ 2.0570(18), Co1—O2 2.0201(19), Co1-O3 2.019(2), Co1—N1 2.304(3), Ni1-N2$^{\#1}$ 2.309(3), Co1⋯Co1$^{\#1}$ 2.8926(9); Co1-O1-Co1$^{\#1}$ 90.13(8).

Accordingly, these donors use each one of its imidazolidine nitrogen atoms to link a different metal ion and the phenolate oxygen atom to act as a bridge between the mentioned centres. Thus, each ligand provides one NCN and one O-bridge, the result being a quadruple bridge between the two metal ions. These bridges lead to M$_2$O$_2$ metallacycles with short M⋯M distances (*ca.* 2.9 Å) and remarkable acute M-O-M angles (*ca.* 90º) in all cases. As a result, the described features agree with metal ions in N$_2$O$_4$ axially elongated octahedral environments (distances M-N$_{imidazolidine}$ about 2.3 Å).

It is worth of note that all the angles and distances for **1b** (Fig. 1) and **2** (Fig S1) are very similar, what seems to indicate that the substitution of the exogenous ligand does not significantly affect the geometric parameters about the metal ions. Accordingly, it looks reasonable to suggest that the structure of **1** must be very similar to that described for **1b**, just replacing the deprotonated salicylaldehyde donors by bidentate chelate acetate ones.

Magnetic studies

Magnetic dc susceptibility measurements for **1-3** were recorded in the 2-300 K temperature range. The magnetic behaviour of **1** and **2** (Figs. S2 and 3, respectively) is very similar, suggesting once again an analogous structure. In this way, as it can be seen in Fig. 3, the $\chi_M T$ product continuously increases from 300 K (*ca.* 2.7 cm^{3}mol^{-1}K) to 10 K (*ca.* 3.65 cm^{3}mol^{-1}K), then diminishing with temperature. This agrees with an intramolecular ferromagnetic coupling, the fall at low temperature being due to the zero-field splitting effect and/or intermolecular interactions in both cases. The ferromagnetic behaviour is also supported by magnetization measurements at 2 K (Fig. 3 inset), which suggest an S =2 ground state.
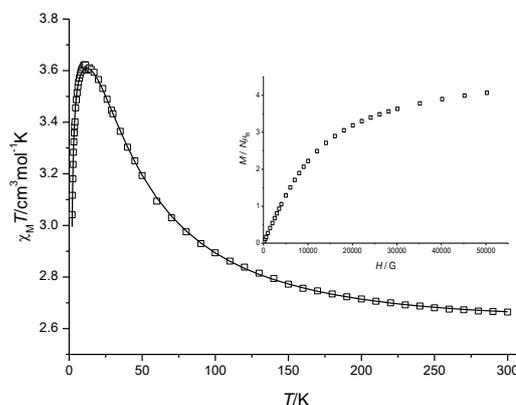
Fig. 3. $\chi_M T$ *vs* T for **2**: □ : experimental data; — : best fit. Inset: $M/N\mu_B$ *vs* H at 2 K.

The best fit of the experimental data with the MAGPACK program ($H = -2J\Sigma\Sigma S_i S_j$)[9] gives the parameters: $2J$ = +23.44 cm^{-1}, g = 2.20, $|D_{Ni}|$ = 3.55 cm^{-1} and TIP = 2.57 x 10^{-4} cm^{3}mol^{-1} (R = 9.88 x 10^{-6}) for **1**; $2J$ = +20.78 cm^{-1}, g = 2.20, $|D_{Ni}|$ = 3.83 cm^{-1} and TIP = 2.57 x 10^{-4} cm^{3}mol^{-1} (R = 1.13 x 10^{-5}) for **2**, which points to a quite strong ferromagnetic coupling in both cases.

The $\chi_M T$ *versus* T graph for **3** is shown in Figure 4, demonstrating a quite different magnetic behaviour compared with that of the nickel complexes. The $\chi_M T$ value for **3** at 300 K is 6.24 cm^{3}mol^{-1}K, which is higher than the expected spin-only value of 3.76 cm^{3}mol^{-1}K for two uncoupled Co^{II} ions with S = 3/2 and g = 2.00, but it is not exceptional for Co^{II} compounds.[10] The mentioned feature simply indicates that there is significant magnetic anisotropy (which is common for Co^{II} systems) that tends to give a larger magnetic moment at room temperature. The $\chi_M T$ product decreases gradually to 30 K and then increases between 30 and 7 K before dropping again. The global shape of the curve points towards a ferromagnetic system,[11] the final decrease being due to the zero-field splitting effect and/or intermolecular antiferromagnetic interactions once again.
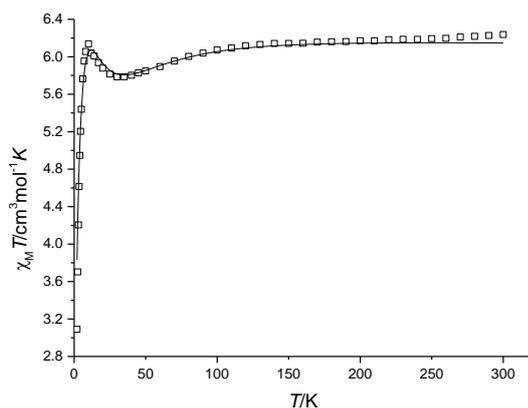
Fig. 4. $\chi_M T$ vs T for **1**: □ : experimental data; — : best fit.

The best fit of the susceptibility curve using the PHI program ($H = -2J\Sigma S_i S_j$),[12] choosing a simplified model according to Bossek et al.,[13] gives the parameters: $2J$ = +2.06 cm^{-1}, g = 2.54, D_{Co} = -18.07 cm^{-1} and zJ' = -0.065 cm^{-1} (R = 7.33 x 10^{-4}). The relatively high D_{Co} parameter is supported by magnetization measurements at 2 K (Fig. S3). The magnetization did not saturate up to 5.0 T and the value of 4.2 $N\mu_B$ is substantially smaller than the expected value (> 6.0 $N\mu_B$) when $g > 2.0$ for an $S = 3$ magnetic ground state, what is consistent with a strong magnetic anisotropy.[10,11]

Thus, the three complexes show ferromagnetic behaviour and anisotropy. Accordingly, dynamic ac magnetic susceptibility measurements as a function of the temperature at two different frequencies were performed for the crystallographically solved complexes **2** and **3**. These studies (Figs. 5 and S3) reveal that neither **2** nor **3** show frequency-dependent peaks in in-phase nor in out-of-phase components of the susceptibility. This is true for **3** even in the presence of a small external dc field of 1000 G (Fig. 5), applied in order to fully or partly suppresses the possible quantum tunnelling relaxation of the magnetization. Accordingly, despite their ferromagnetic character, these complexes do not exhibit slow relaxation of the magnetization, and therefore SMM behaviour.
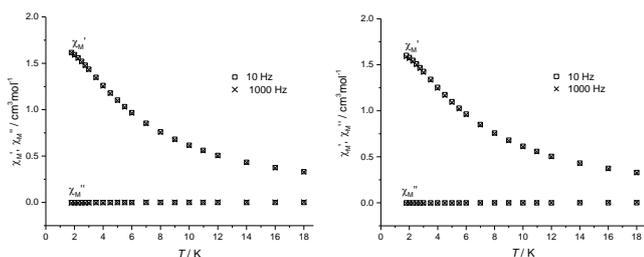
Fig. 5. Variable-temperature in-phase and out-of-phase components of the ac magnetic susceptibility data for **3** at two different frequencies: left) dc applied field of 0 G; right) dc applied field of 1000 G.

DFT studies

In spite of the non-SMM nature of **2** and **3**, further studies were done in order to gain some insight about the origin of the apparently systematic ferromagnetic coupling. Accordingly, DFT calculations for **2** were carried out, using the crystallographic atomic coordinates. Thus, initially, computations were made with the whole molecule, what renders a $2J$ value of +23.3 cm^{-1}, in good agreement with experimental results. Then, calculations

were performed with a simplified dinuclear model, where the *NCN* bridges provided by the original HL ligands were replaced by NH$_3$ terminal donors, with the aim of evaluating the contribution of *NCN* bridges to the overall magnetic behaviour. In this case, the $2J$ calculated value is +20.3 cm^{-1}. The comparison of this value with the previous one clearly indicates that the *NCN* links transmit a small positive coupling and that the major contribution to the ferromagnetic behaviour comes from the O$_{phenolate}$ bridges. This feature seems to be caused by the small M-O-M angles, close to 90º in **1**-**3**. Consequently, DFT results points towards predetermination of the ferromagnetic coupling mediated by O$_{phenolate}$ bridges with acute M-O-M angles, achieved by constrains imposed by the imidazolidine-phenolate ligands.

Accordingly, DFT studies were performed to see the influence of the Ni-O-Ni angles in the strength of the ferromagnetic coupling. For this purpose, a simplified dinuclear model, where the *NCN* bridges were replaced by NH$_3$ donors and the phenolate moieties by methanolate ones (Fig. 6), was built from the crystallographic data of **2**.
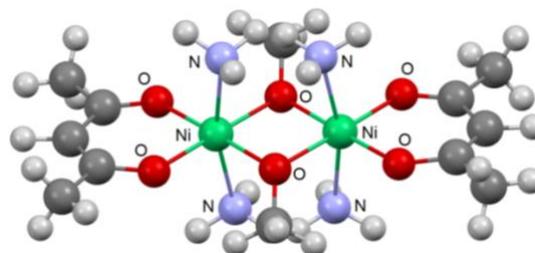
Fig. 6. Ball and sticks simplified model of **2** for DFT calculations.

The computation for the original Ni-O-Ni angle of 90º renders a $2J$ value of 19 cm^{-1}, what suggest that the replacement of the phenolate by the methanolate bridges does not have a great influence in the superexchange pathway in this case study. The global results of this study are shown in Figure 7, from which it can be clearly stated that the ferromagnetic coupling is maximum for 90º (our experimental angle) and that this coupling diminishes both when the Ni-O-Ni angles increase or decrease.
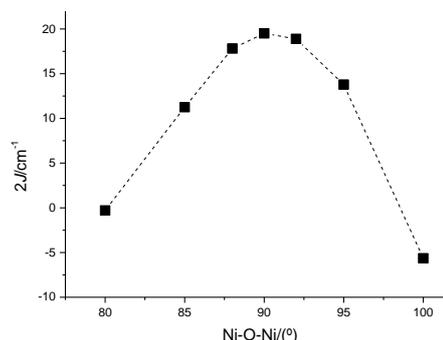
Fig. 7. Calculated variation of $2J$ with the Ni-O-Ni angle for 2. The dotted line is a guide for the eye.

This latter theoretical result is really remarkable as it demonstrates that HL not only provides two bridges that mediate ferromagnetic coupling but also determines Ni-O-Ni angles that are the optimal ones for the strongest ferromagnetic exchange.

Conclusions

HL is a tridentate ligand that act as dinucleating, providing two bridges (one NCN$_{imidazolidine}$ and one O$_{phenolate}$) between the metal ions that it binds. Both bridges promote the parallel alignment of the electrons of the linked metal ions but the main contribution to this ferromagnetic coupling comes from the geometrical restrictions imposed by the ligand over the M-O-M angles, which are ideal ones for the ferromagnetic coupling being maximun. Therefore, this ligand is not only an odd example of polynucleating ligand that predetermines the ferromagnetism of its metal complexes but also is, as far as we know, the only polynucleating ligand that encode the magnetic behaviour by strict control of one geometric parameter, the M-O-M angle.

Acknowledgements

Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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