Predetermined Ferromagnetic Coupling *via* Strict Control of M-O-M Angles.

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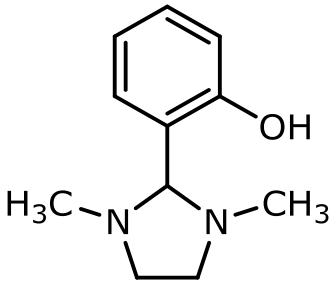
ABSTRACT: An imidazolidine-phenolate ligand HL yields quadruple bridged $(\mu\text{-NCN}_{\text{imidazolidine}})_2(\mu\text{-O}_{\text{phenolate}})_2$ ferromagnetic dinuclear nickel and cobalt complexes. Both kinds of bridges contribute to the ferromagnetic coupling but the ferromagnetism of these samples is mainly ascribed to the double $\mu\text{-O}_{\text{phenolate}}$ links, on the basis of DFT calculations. These studies demonstrate not only that the short M-O-M angles of the M_2O_2 cores favors the

parallel alignment of the electrons, but also that these angles 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 uncommon polydentate donor that induces ferromagnetism *per se* in its metal complexes by strict control of one geometric parameter, the M-O-M angle.

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,[2,3] the double exchange,[2,4] spin-polarisation,[2,5] crossed interactions[2,6] or countercomplementarity of the bridging ligands[2,7]) 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,[8] bridging *syn-anti* carboxylates,[9] a dinucleating imidazolidine ligand previously reported by us[10] and the recently described R-phenylcyanamido ligands, when they coordinate in a $\mu_{1,1}$ mode.[11] 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 an imidazolidine-phenolate donor HL (Scheme 1) that contributes to increase the scarce number of ligands that favor the ferromagnetic coupling *per se*. In this case study, the parallel alignment of the electrons is attained due to the strict control of the M-O-M angles that the ligand exerts on its complexes.



Scheme 1. HL.

EXPERIMENTAL

General considerations. Elemental analyses of C, H and N were performed on a Carlo Erba EA 1108 analyzer. Infrared spectra were recorded on a PerkinElmer TwoTM FT/IR spectrophotometer, using the ATR sampling technique, in the range 4000-400 cm^{-1}.

Syntheses. All solvents and reactants are commercially available and were used without further purification. H_3L was obtained as previously described[12] and satisfactorily characterized by elemental analysis, IR and NMR spectroscopy and mass spectrometry.

All the complexes were obtained in a similar way, exemplified by the synthesis of **1**.

*$[NiL(OAc)]_2 \cdot 2H_2O$ (**1**)*: To an acetonitrile (15 ml) solution of HL (0.101 g, 0.526 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (0.131 g, 0.526 mmol) was added. The mixture was stirred in air at room temperature for 1 h and the solid that precipitated was filtered off and dried in air. Yield: 0.114 g, (33%), mp > 300ºC. Elemental anal. calcd. for $C_{26}H_{40}N_4Ni_2O_8$ (654.00): C, 47.75; H, 6.16; N, 8.57%. Found: C, 47.54; H, 6.18; N, 8.70%. IR (ATR, ν/cm^{-1}): 3402 (OH), 1551 (COO_{asym}),

1410 (COO_{sym}). Recrystallization of **1** in hot acetonitrile gives single crystals of $[NiL(o\text{-}O\text{-}C_6H_4\text{-}CHO)]_2$ (**1b**), suitable for X-ray diffraction studies.

[Ni(L)(acac)]$_2$ (2). Yield: 0.186 g (50%), mp > 300ºC. Elemental anal. calcd. for $C_{32}H_{44}N_4Ni_2O_6$ (698.13): C, 55.00; H, 6.30; N, 8.02%. Found: C, 54.96; H, 6.38; N, 7.86%. IR (ATR, ν/cm^{-1}): 1402 (δCH_3). Slow evaporation of the mother liquor yields single crystals of $[Ni(L)(acac)]_2$ (**2**) suitable for X-ray diffraction studies.

*[Co(L)(acac)]$_2$ (**3**)*. Yield: 0.198 g (55%), mp > 300ºC. Elemental anal. calcd. for $C_{32}H_{44}N_4Co_2O_6$ (698.57): C, 54.97; H, 6.30; N, 8.02%. Found: C, 54.84; H, 6.27; N, 8.19%. IR (ATR, ν/cm^{-1}): 1402 (δCH_3). Recrystallization of **3** in hot acetone/cyclohexane (1:1) gives single crystals of $[CoL(acac)]_2$ (**3**), suitable for X-ray diffraction studies.

Crystallographic refinement and structure solution. Crystal data and details of refinement are given in Table S1. Single crystals of **1b**, **2** and **3** were obtained as detailed above. Data were collected at 100 K on a Bruker Kappa APEXII CCD diffractometer, employing graphite monochromated Mo-kα ($\lambda = 0.71073$ Å) radiation. Multi-scan absorption corrections were applied using SADABS[13]. The structures were solved by standard direct methods, employing SIR2008[14] and then refined by full-matrix least-squares techniques on F^2, using the program package SHELX-2013.[15] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure factor calculations in geometrically idealized positions.

Magnetic measurements. Magnetic susceptibility measurements for powder crystalline samples of **1-3** were carried out at the Unitat de Mesures Magnètiques of the Universitat de Barcelona with a Quantum Design SQUID MPMS-XL susceptometer. The magnetic susceptibility *dc* data were recorded in the 2-300 K temperature range, under magnetic fields of

300 G (2-30 K) and 5000 G (2-300 K). Diamagnetic corrections were estimated from Pascal's Tables. The agreement factor is based on the function $R = \Sigma(\chi_M T_{exp} - \chi_M T_{cal})^2 / \Sigma(\chi_M T_{exp})^2$. Magnetization measurements at 2 K were taken under magnetic fields ranging from 0 to 50000 G. For **3**, magnetization measurements in the 2-7 K temperature range under different fields (from 0 to 50000 G) were recorded. For **2** and **3**, dynamic *ac* magnetic susceptibility measurements as a function of the temperature (2-18 K) at 10 and 1000 Hz were recorded under an external magnetic *dc* field of 0 G (**2** and **3**) and of 1000 G (**3**).

Theoretical calculations. DFT and Ab Initio calculations were performed for **2.** DFT studies were done in order to obtain the inter- and intramolecular exchange coupling between the Ni centers and Ab initio calculations with the aim of getting the single ion parameters (*g* and ZFS values). The detailed description of the computational strategy used is outside the scope of this paper, thus we will focus our discussion here to its most relevant aspects. Previously, we have published a series of papers devoted to such purpose where more details can be found.[16-18] In this theoretical study, the employed spin Hamiltonian is:

$$\hat{H} = - \sum_{i>j} J_{ij} \hat{S}_i \hat{S}_j + D\left(\hat{S}_z^2 - \frac{1}{3}\hat{S}^2\right) + E\left(\hat{S}_x^2 - \hat{S}_y^2\right)$$

The procedure to perform DFT calculations is as follows: the original X-ray diffraction coordinates were used, without posterior optimization of the structure. Besides, a simplified model of the structure was employed to analyze the influence of the Ni-O-Ni angle in the ferromagnetic coupling. Calculations were carried out using the hybrid functional B3LYP[19] and an all-electron triple zeta basis set.[20] The guess function was generated using Jaguar 7.6 code.[21] Total energy calculations were performed using Gaussian 09 code.[22]

ORCA 3.0.3 code[23] was employed to do the Ab initio calculations, following the complete active space self-consistent field (CASSCF) methodology. The DEF2-TZVP[24] basis set was

employed. To estimate the parameters for each Ni^{II} two theoretical models have been designed, where one Ni^{II} was substituted by a diamagnetic Zn^{II} ion. For each model, a CASSCF calculation was performed, followed by an N-electron valence perturbation theory (NEVPT2)[25] calculation to introduce dynamical correlation. The spin-orbit effects were included using quasi-degenerate perturbation theory (QDPT).[26]

RESULTS AND DISCUSSION

The synthesis and characterization of HL was previously described[12] but its coordination chemistry remains unexplored up to date. The reaction of HL with nickel(II) acetate or acetylacetonate in 1:1 molar ratio in acetonitrile renders the dinuclear complexes $[NiL(OAc)]_2 \cdot 2H_2O$ (**1**) or $[NiL(acac)]_2$ (**2**), respectively. **2** can be isolated as single crystals after two weeks by slow evaporation of the mother liquor. Attempts to recrystallize **1** in acetonitrile lead to partial hydrolysis of HL, and yield a small quantity of single crystals of $[NiL(O\text{-}C_6H_4\text{-}CHO)]_2$ (**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 recrystallization in acetone/hexane also gives single crystals of **3**.

The formulations of the three complexes were confirmed by microanalysis, IR spectroscopy, and, in the case of **2** and **3**, by X-ray diffraction studies. The byproduct **1b** was only characterized by single X-ray diffraction analysis. The magnetic behavior of **1** to **3** was also studied.

The infrared spectra of the compounds agree with the different nature of the exogenous ligands in **1** and **2**, **3**. Thus, the spectrum of **1** shows two sharp bands at 1551 and 1410 cm^{-1}, assigned to COO^- vibrations of the acetate group, which are absent in the spectra of **2** and **3**.

These two latter complexes present a sharp band at 1402 cm^{-1}, which can be assigned to $\delta(CH_3)$ of the acetilacetonate group,[27] and that is not present in **1**. Besides, the spectrum of **1** shows a broad band centered at 3402 cm^{-1}, in agreement with the presence of water in the complex. This band does not exist in the spectra of **2** and **3**, in accordance with their non-hydrated nature.

X-ray diffraction studies. The single crystal structures of **1b**, **2** and **3** show that the three complexes are isostructural and, therefore, they will be discussed together.

Figures 1, S1 and 2 show ellipsoid diagrams for **1b**, **2** and **3**, respectively, and selected bond distances and angles for the three compounds are recorded in Table 1.

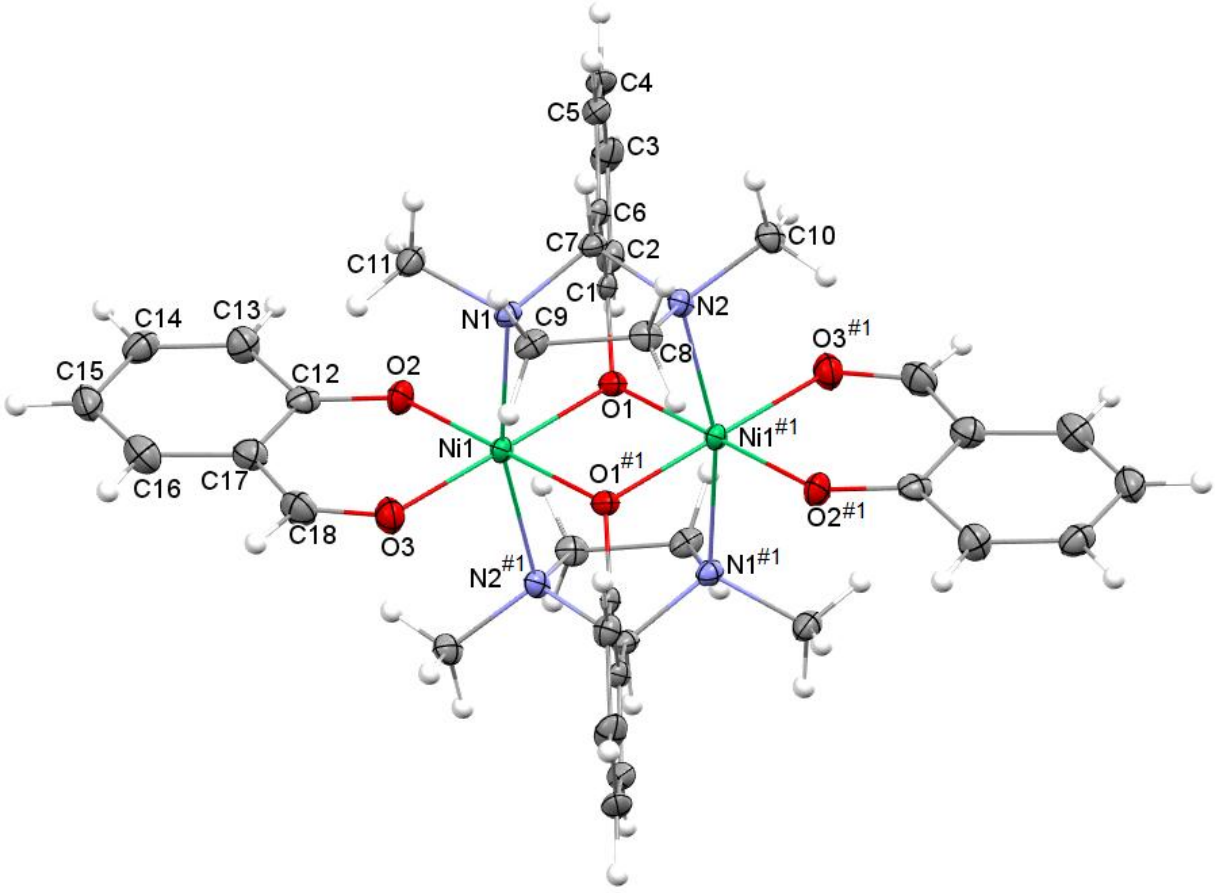


Figure 1. Ellipsoid (50% probability) diagram for **1b**.

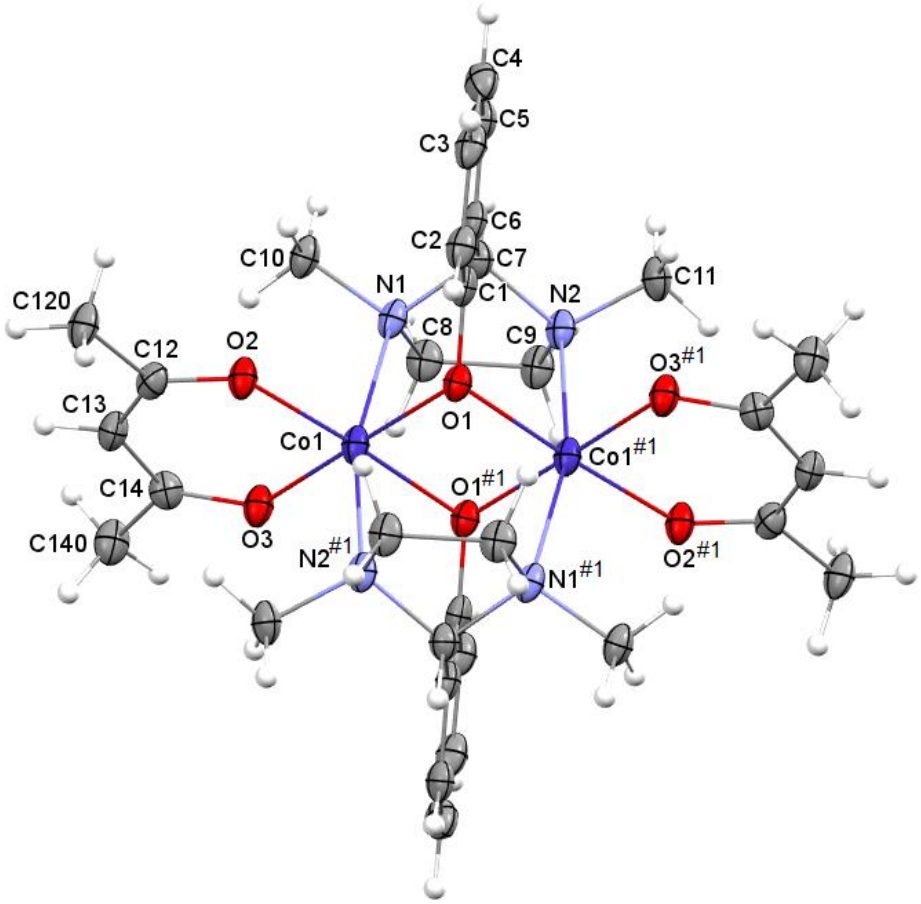


Figure 2. Ellipsoid (50% probability) diagram for **3**.

Table 1. Main distances and angles for **1b-3**.

	1b	**2**	**3**
M1—O1	2.0116(19)	2.0177(16)	2.029(2)
M1—O1$^{\#1}$	2.019(2)	2.0282(15)	2.0570(18)
M1—O2	1.980(2)	1.9989(16)	2.0201(19)
M1—O3	2.041(2)	1.9988(16)	2.019(2)
M1—N1	2.252(2)	2.2473(18)	2.304(3)
M1—N2$^{\#1}$	2.234(2)	2.2601(18)	2.309(3)
M1···M1$^{\#1}$	2.8648(7)	2.8721(8)	2.8926(9)
O2—M1—O1$^{\#1}$	179.85(8)	178.40(6)	177.05(8)
N1-M1-N2$^{\#1}$	165.68(9)	165.37(7)	165.01(8)
O1—M1—O3	179.16(9)	177.19(6)	177.26(7)
M1—O1—M1$^{\#1}$	90.60(8)	90.45(6)	90.13(8)

$^{\#1}$ -x, 1-y, -z

The asymmetric unit of the compounds contains just half of the $[MLL']_2$ (L' = acac or O-C_6H_4-CHO) molecule, the other half being generated by an inversion center. In these complexes, the exogenous L' ligands act as terminal bidentate chelate donors. The remaining coordination positions about the metal ions are filled by two deprotonated imidazolidine $(L)^-$ ligands, which behave as bridging tridentate. 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 centers. Thus, each ligand provides one NCN and one O-bridge, the result being a quadruple bis(μ-$NCN_{imidazolidine}$)bis(μ-$O_{phenolate}$) bridge between the two metal ions. These bridges lead to M_2O_2 metallacycles with short M···M distances (*ca*. 2.9 Å) and remarkable acute M-O-M angles (*ca*. 90º) in all cases. These angles are significantly more acute than those previously described for triple bridged (μ-$NCN_{imidazolidine}$)bis(μ-O) nickel complexes, which range from 95 to 100º.[28,29] In addition, as far as we know, no dinuclear $Co^{II}\cdots Co^{II}$ complexes containing imidazolidine/oxygen bridges have been previously described. Therefore, **3** is unique among its class and, to the best of our knowledge, it is the first example of a homodinuclear Co^{II} compound showing an imidazolidine bridge. Nevertheless, a reduced number of tripled bridged (μ-$NCN_{imidazolidine}$)bis(μ-O) $Co^{II}\cdots Co^{III}$ and $Co^{III}\cdots Co^{III}$ complexes were reported.[30] In these related complexes, in spite of the smaller size of the cobalt(III) ion, the Co-O-Co angles are larger than in **3**, and they range from 95 to 100º too.[30] Besides, the M···M distances are also considerably longer in the related complexes than those found for **1b-3**.[28-30] As a result, the described features agree with metal ions in N_2O_4 axially elongated octahedral environments, with the $N_{imidazolidine}$ atoms occupying the apex of the octahedrons (distances M-$N_{imidazolidine}$ about 2.3 Å).

At this point, it is worth of mention that all the angles and distances for **1b** and **2** (Table 1) 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 seems reasonable to suggest that the structure of the acetate complex **1** should be very similar to that described for the salycilaldehyde derivative **1b**, where the only difference between them should be the replacement of bidentate chelate acetate donors by deprotonated salicylaldehyde ones.

Magnetic studies. Magnetic *dc* susceptibility measurements for **1-3** were recorded in the 2-300 K temperature range. The magnetic behavior of **1** and **2** (Figure S2 and Figure 3, respectively) is very similar, suggesting once again an analogous structure. In this way, as it can be seen in Figure 3 for **2**, the $\chi_M T$ product continuously increases from 300 K (*ca*. 2.7 $cm^3mol^{-1}K$) to 10 K (*ca.* 3.65 $cm^3mol^{-1}K$), then diminishing with lowering of the temperature. This agrees with an overall intramolecular ferromagnetic coupling, the fall at low temperature being due to the zero-field splitting effect and/or intermolecular interactions. The ferromagnetic behavior is also supported by magnetization measurements at 2 K (Figure 3 inset and Figure S2 inset), which suggest an $S = 2$ ground state.

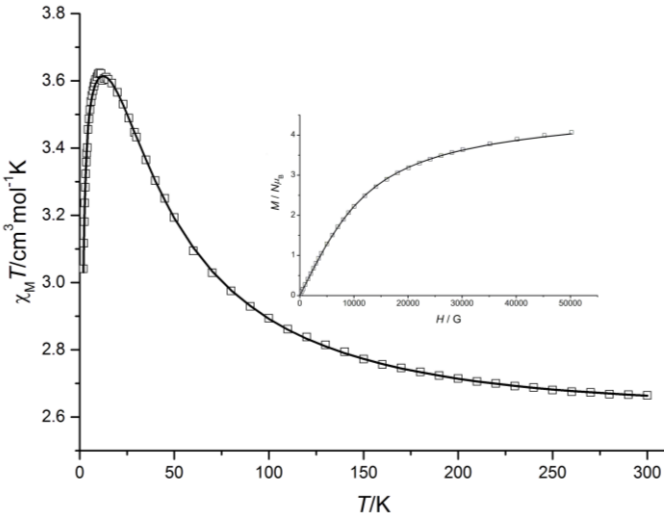


Figure 3. $\chi_M T$ *vs* T and $M/N\mu_B$ *vs* H (inset) at 2 K for **2**. □ : experimental data; — : best fit

The best fit of the experimental data with the PHI program ($H = -JS_1S_2$),[31] using simultaneously susceptibility and magnetization data, gives the parameters: $J = +22.80$ cm^{-1}, $g = 2.21$, $|D_{Ni}| = 4.60$ cm^{-1} and $TIP = 2.36$ x 10^{-4} cm^{3}mol^{-1} ($R = 5.08$ x 10^{-7}) for **1**; $J = +20.18$ cm^{-1}, $g = 2.21$, $|D_{Ni}| = 4.91$ cm^{-1} and $TIP = 2.25$ x 10^{-4} cm^{3}mol^{-1} ($R = 1.29$ x 10^{-10}) for **2**, which points to a quite strong ferromagnetic coupling between the bridged nickel(II) centers in both cases. It should be noted that the ferromagnetism of the samples could be expected, given that DFT calculations demonstrated that the presence of the imidazolidine bridge promotes the ferromagnetic coupling in complexes with (μ-NCN$_{imidazolidine}$)bis(μ-O) bridges.[10,32] Nevertheless, the coupling of **1** and **2** thorough the bis(μ-NCN$_{imidazolidine}$)bis(μ-O) quadruple bridge, is considerably stronger than that found in related nickel complexes with the previously mentioned (μ-NCN$_{imidazolidine}$)bis(μ-O) triple bridge, where J is usually smaller than 10 cm^{-1}.[28,29,32] Accordingly, it seems that HL improves the ferromagnetic coupling with respect to the reported imidazoline donor.[10,28,29,32]

The $\chi_M T$ *versus* T graph for **3** is shown in Figure 4, demonstrating a quite different magnetic behavior compared with that of the nickel complexes.

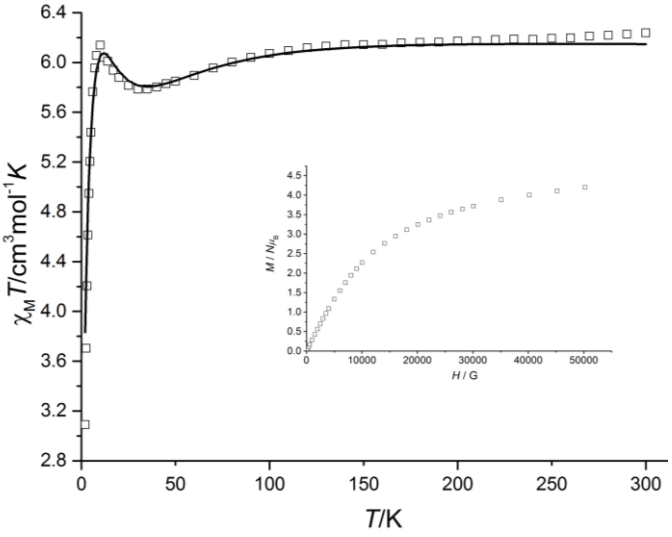


Figure 4. $\chi_M T$ *vs* T for **3**: □ : experimental data; — : best fit. Inset: $M/N\mu_B$ *vs* H at 2 K

In this case, the $\chi_M T$ value at 300 K is 6.24 $cm^3mol^{-1}K$, which is higher than the expected spin-only value of 3.76 $cm^3mol^{-1}K$ for two uncoupled Co^{II} ions with $S = 3/2$ and $g = 2.00$, but it is not exceptional for Co^{II} compounds.[33] This high value 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 from 300 K up to 30 K and then it increases between 30 and 7 K before dropping again. The global shape of the curve points towards a ferromagnetic system,[34] the final decrease being due to the zero-field splitting effect and/or intermolecular antiferromagnetic interactions.

The best fit of the susceptibility curve using the PHI program, choosing a simplified model according to Bossek et al.,[35] gives the parameters: J = +2.06 cm^{-1}, $g = 2.54$, D_{Co} = -54.10 cm^{-1} and zJ' = -0.065 cm^{-1} ($R = 7.33 \times 10^{-4}$). The relatively high D_{Co} parameter is supported by magnetization measurements at 2 K (Figure 4 inset). The magnetization does not saturate up to 50000 G 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.[33,34] Besides, this anisotropy was also confirmed by magnetization measurements in the 2-7 K temperature range under various applied fields (Figure 5).

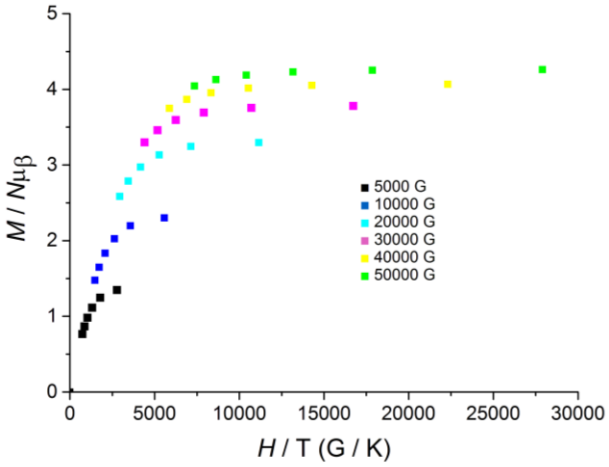


Figure 5. Plots of *M vs. H*/T curves for **3**.

The isofield lines are far from superposing on one another, thus implying significant magnetic anisotropy of the local Co_2 complex.

Hence, **1-3** show ferromagnetic behavior and anisotropy. Accordingly, dynamic *ac* magnetic susceptibility measurements as a function of the temperature at two different frequencies were performed for the crystallographically solved **2** and **3**, in order to analyze the possible single molecular magnet properties of the complexes. These studies (Figures 6 and S3 in Supporting Information) reveal that neither **2** nor **3** show frequency-dependent peaks in in-phase nor in out of-phase components of the susceptibility. Accordingly, it seems that none of the complexes is SMM.

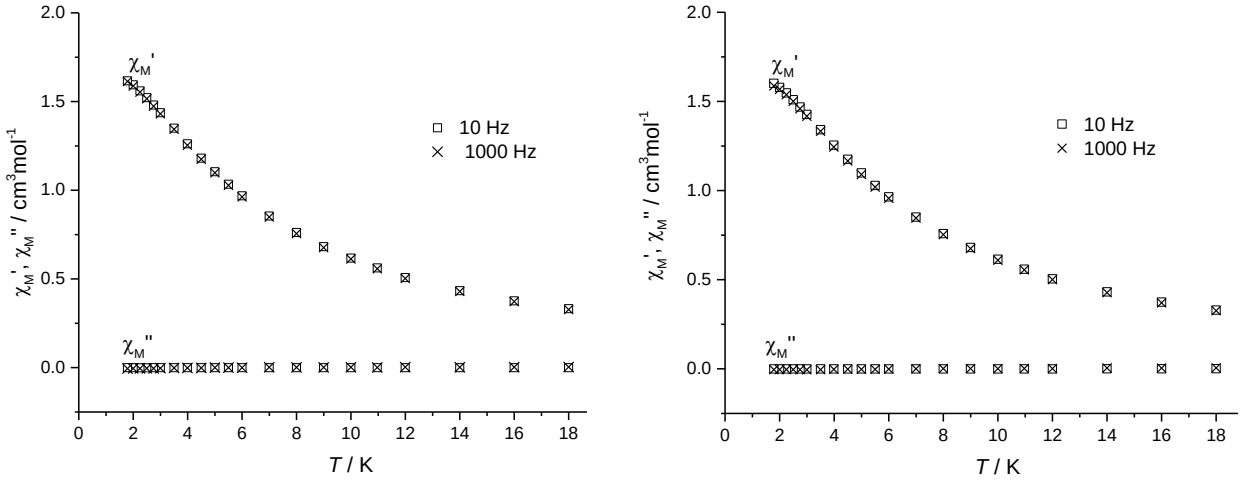


Figure 6. Variable-temperature in-phase (χ_M') and out-of-phase (χ_M'') components of the *ac* magnetic susceptibility for **3** at two different frequencies: left) *dc* applied field of 0 G; right) *dc* applied field of 1000 G.

Nevertheless, the single molecular magnetism could be hidden by quantum tunnelling relaxation of the magnetization. For this reason, and given that the cobalt complex is the one with the highest *S* ground state and highest anisotropy, χ_M' and χ_M'' for **3** were recorded once again, but now in the presence of a small external *dc* field of 1000 G (Figure 6, right), applied

with the aim of fully or partly suppressing the possible quantum tunnel. Even in these conditions, no frequency-dependence for χ_M' and χ_M'' was observed. Consequently, despite their ferromagnetic character, none of these complexes exhibit slow relaxation of the magnetization, and therefore SMM behavior.

In order to try to explain the absence of single molecular magnetism, one should remember that the two basic requirements for observing such behavior are a large ground spin state *S* and a large anisotropy *D*. Nevertheless, other factors, like the absence of intermolecular interactions that allows higher ordering, must be taken into account. Besides, it is remarkable that, usually, SMMs have large negative *D* values, although nowadays there are some notable exceptions, where positive anisotropies are found.[36] Thus, a negative uniaxial zero-field splitting parameter is not compulsory for single molecule magnet behavior.

In complexes **2** and **3**, the intermolecular interactions seem to be very weak. In addition, there are many SMMs described in literature with smaller ground state *S* values than those found in both complexes, as for example all the Ni^{II} and Co^{II} single ion magnets.[37] Thus, the non-SMM nature of **2** and **3** seems to be related to low anisotropy of the systems. The factors that control *D* in polynuclear complexes are badly understood, because there are many competing factors, such as single-ion and exchange anisotropy.[38-40] Accordingly, the effect of these two anisotropies on the magnetizations is not the same and the exchange and single-ion anisotropies are not equivalent. In particular, it can be shown that magnetic anisotropy is sensitive to the alignment of the individual axes and it is drastically reduced with increasing nuclearity if the local anisotropy axes become misaligned.[41] Therefore, it seems that in **2** and **3** the single ion magnetic anisotropies of the M(II) ions almost cancelled each other out, leading to a very small effective

energy barrier *U*, which could explain their non-SMM behavior, as it was previously suggested for other polynuclear complexes.[42]

Theoretical 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 *J* ($H = -JS_1S_2$) value of +23.3 cm^{-1}, in good agreement with experimental results. DFT calculations also render a small intermolecular exchange coupling of -0.0046 cm^{-1} that cannot justify the low temperature susceptibility behavior by itself. Ab Initio calculations were performed to obtain single ion parameters, rendering g = 2.23, D_{Ni} = 6.09 cm^{-1} and E = 0.29 cm^{-1}, which are close values to those obtained from the experimental fit. Simulations of the susceptibility and magnetization curves with the PHI program employing all these parameters are in good agreement with experimental results (Figure 7).

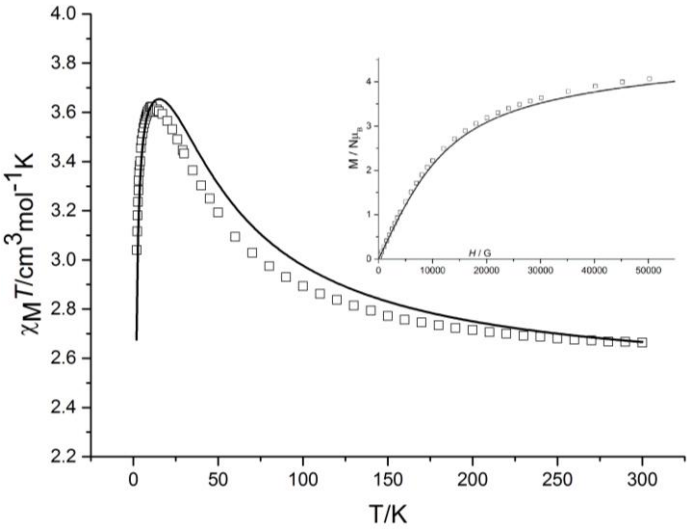


Figure 7. $\chi_M T$ *vs* T for **2**: □ : experimental data; — : simulation using theoretical parameters. Inset: $M/N\mu_B$ *vs* H at 2 K

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 the NCN bridges to the overall magnetic behavior. In this case, the *J* calculated value is +20.3 cm^{-1}. The comparison of this value with the original one (+23.3 cm^{-1}) indicates that the NCN links transmit a small positive coupling. This finding clearly contrasts with previous results, as we ourselves have previously demonstrated that the presence of an $NCN_{imidazolidine}$ bridge is the reason for the ferromagnetic behavior observed in imidazolidine/oxygen bridged complexes of a dinucleating ligand.[10,32] The smaller contribution to the ferromagnetic coupling in this case study could be associated with the longer $Ni\text{-}N_{imidazolidine}$ bonds in **2** compared with related complexes.[28,29,32]

In any case, the major contribution to the ferromagnetism in **2** comes from the $O_{phenolate}$ bridges and this seems to be caused by the small M-O-M angles, close to 90º. In this sense, earlier proposed magnetostructural correlations for diphenolate bridged dinuclear nickel complexes[43,44] suggest that the crossover from antiferromagnetic to ferromagnetic coupling occurs at 97º or 93.5º, depending on the type of phenolate ligand. Thus, taking these previous results into account, the ferromagnetic coupling in **1** and **2** could be an expected result, in view of the acute Ni-O-Ni angles in these complexes. At this point it should be noted that, in spite of known magnetostructural/correlations, the experience demonstrates that the number of ferromagnetic nickel complexes with a Ni_2O_2 core is still small,[28a] maybe because it is difficult to achieve so acute angles. In fact, the best way of decreasing this Ni-O-Ni angles and, therefore, promoting the parallel alignment of the electrons, seems to be by introduction of a third one atom bridge, as a water bridge,[45] a process that is not easy to control. In our case study, the relevant fact is that the acute M-O-M angles are attained by constrains imposed by the imidazolidine-

phenolate ligand, and that the final structure of the complexes is completely under control by the ligand itself. Thus, this ligand shows the outstanding characteristic of predetermining the ferromagnetic coupling by control of the M-O-M parameter, as DFT calculations demonstrates.

With all the above considerations in mind, additional 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 was built from the crystallographic data of **2**, where the NCN bridges were replaced by NH_3 donors and the phenolate moieties by methanolate ones (Figure 8).

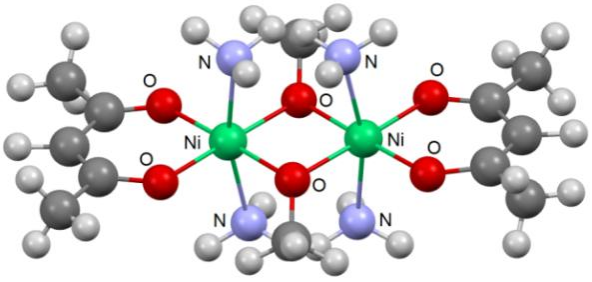


Figure 8. Ball and sticks simplified model of **2** for DFT calculations.

The computation for the original Ni-O-Ni angle of 90º renders a *J* 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 analysis are shown in Figure 9, from which it can be clearly stated that the ferromagnetic coupling is maximum for 90º (the experimental angle) and that this coupling diminishes both when the Ni-O-Ni angles increase or decrease. Thus, this latter theoretical study demonstrates that the variation of the coupling strength with the Ni-O-Ni angle is not linear and that more acute angles do not mean a stronger ferromagnetic coupling, in agreement with previous studies, where it was established that the Ni-O-Ni angle is not the only factor affecting the magnetic coupling in Ni_2O_2 cores.[44]

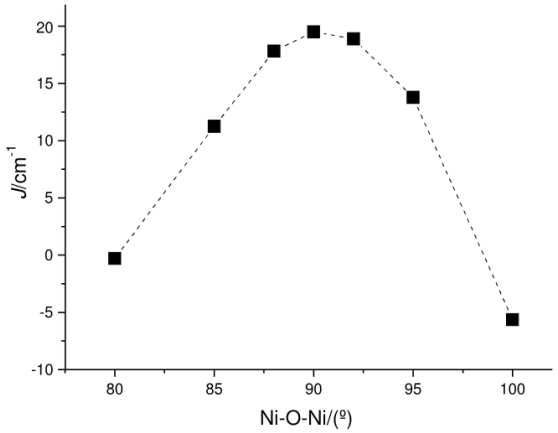


Figure 9. Calculated variation of *J* with the Ni-O-Ni angle for **2**. The dotted line is a guide for the eye.

But, more interestingly, the really remarkable result of this analysis is that HL not only provides bridges that mediate the ferromagnetic coupling but also predetermines Ni-O-Ni angles that are the optimal ones for the strongest ferromagnetic exchange.

In addition, further studies were done with the purpose of going more deeply into the magnetostructural correlation of the calculated DFT *J* values with the bridging angle for **2**. In this way, the dependence of the calculated *J* values with the orbital energy gap was analyzed in terms of the Hay-Thibeault-Hoffmann model.[46] This study shows that there is a rough correlation between the calculated *J* values with the highest and lowest energies of the four unoccupied magnetic orbitals (Figure S4). It is well-known that unoccupied orbitals provide much better correlations than the occupied ones,[47] because the occupied orbitals show a larger mixing. Hence, the points on both sides of the maximum (around 90º, Figure 10) show a slightly different dependence.

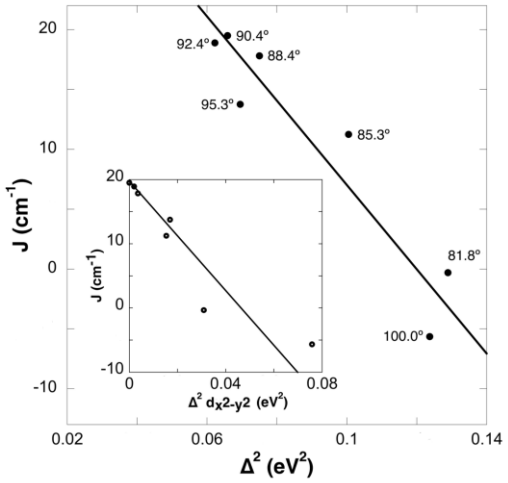


Figure 10. Dependence of the DFT calculated *J* values for the model structures with the square of the energy gap calculated with the highest and lowest energies of the four unoccupied magnetic orbitals. In the inset, the dependence was calculated with the square of the energy gap of the in-phase and out-phase dx^2-y^2 orbital combinations.

However, if we consider only the square of the energy gap involving the two combinations with the metal dx^2-y^2 orbital (inset of Figure 9), the correlation improves. Thus, this fact indicates that the variation in the calculated *J* value (and consequently in the magnetic behavior) with the bridging angle is mostly determined by the change of combination of dx^2-y^2 orbitals while those including the dz^2 ones have a minor role.

CONCLUSIONS

The coordination chemistry of HL is explored for the first time in this paper and the achieved results are really remarkable. Thus, 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 connected metal ions but the main contribution to the ferromagnetic coupling comes from the phenolate links, due to the

geometrical restrictions imposed by the ligand over the M-O-M angles. These angles, which are very acute (*ca*. 90º), are the ideal ones for the ferromagnetic coupling being maximum, as DFT studies demonstrate. Therefore, HL is not only an uncommon 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 behavior by strict control of one geometric parameter, the M-O-M angle, which is optimal for ferromagnetic coupling being maximun.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF) for **1b**, **2** and **3**, Table S1 and Figures S1-S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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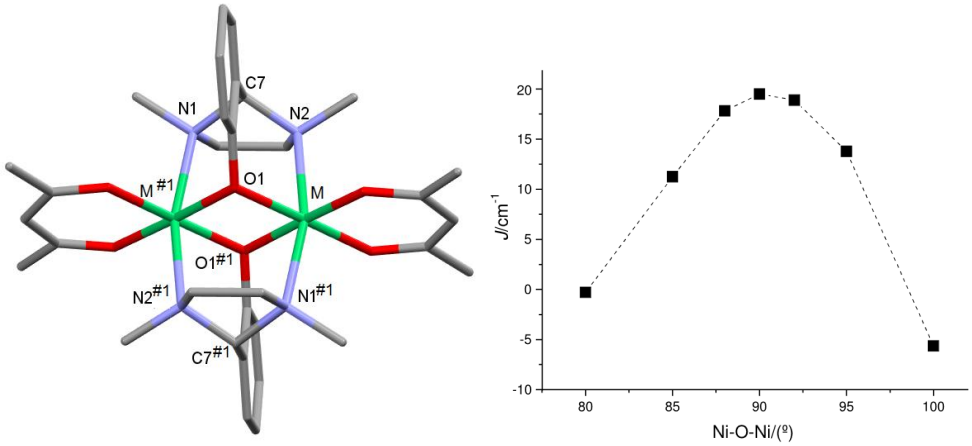
Table of Contents Graphic and Synopsis



An imidazolidine-phenolate ligand predetermines the M-O-M angles of the phenolate bridges in such a way that they are optimal for ferromagnetic coupling being maximum.