

Single ion magnet bevavior in Co(II)-Co(III) mixed valence dinuclear and pseudo-dinuclear complexes

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Two Co(II)-Co(III) complexes mixed-valance of molecular formula $\{ [Co_2(H_2L)_2(H_2O)_2] [Co_2(H_2L)_2(H_2O)(m-phth)] \cdot 8(H_2O) \}$ (1) and $\{ [Co_4(H_2L)_4(H_2O)_2(ppda)] \cdot 2(dmf) \cdot 3.2(H_2O) \}$ (2) $[H_2L^{2-}=$ 2-((2-hydroxy-3methoxybenzylidene)amino)-2-(hydroxymethyl)propane-1,3-diolato; *m*-phth 1.3benzenedicarboxylate; ppda = 1,4-phenylenediacrylate; dmf = N,N-dimethylformamide] have been synthesized and characterized by single crystal X-ray diffraction and magnetic studies at low temperature. The structural determination reveals that complex 1 is composed of dinuclear ion pair, namely a cationic $[Co_2(H_2L)_2(H_2O)_2]^+$ (1⁺) and an anionic $[Co_2(H_2L)_2(H_2O)(m-phth)]^-$ (1⁻) unit. In each of these ions, Co(II) and Co(III) centers present a distorted octahedral geometry. Compound 2 is a centro-symmetric tetra-nuclear complex comprising two symmetry related dinuclear Co^{III}-Co^{II} units bridged by the ppda anion.

AC/DC magnetic studies revealed that individual Co(III)-Co(II) unit exhibits field induced slow magnetic relaxation consistent with the single ion magnets (SIMs) behavior. Ab initio NEVPT2 calculations confirm large zero-field splitting (zfs) coming from a 1st order spin-orbit coupling (SOC) in both complexes (D = -62.4, -95.8 and -101.9 cm⁻¹ and E/D = 0.219, 0.216 and 0.234 for 1⁺, 1⁻ and 2, respectively).

Keywords: Co(II)-Co(III); Crystal structure; Magnetic properties; Single ion magnet

Introduction

Paramagnetic compounds in which the individual molecules exhibit slow magnetic relaxation and magnetic hysteresis are known as single-molecular magnets (SMMs).¹ Since the discovery of the first SMM (Mn₁₂OAc) in 1990, much significant work has been done on this type of magnetic materials due to their potential application in information storage,² quantum computing,³ spintronics,⁴ and magnetic refrigeration.⁵ The essential requirement for a compound to be a SMM is the presence of a spin-reversal energy barrier between the states with the spin magnetic moments of opposite directions.^{1a} The spin-reversal barrier is defined as $U=|D|S^2$ and U = |D| (S^2 -1/4) for integer and half-integer spin moments (S) of the ground states, respectively; *D* is the axial magnetic anisotropy which splits the *M_S* levels of the spin ground state (GS) under zero magnetic field.^{1a,6} Transition metal-based mononuclear and polynuclear complexes showing a SMM behavior have been widely reported in the last two decades.^{1b, 7-9} The mononuclear compounds with one spin carrier on a molecule, large Isingtype magnetic anisotropy and magnetic properties similar to polynuclear SMMs are usually known as single-ion magnets (SIMs). Literature survey reveals that most of the reported SIMs contain late lanthanide ions¹⁰ (4 f^n , n>7) and only a few examples of Co(II),¹¹ Mn(III),¹² Ni(I),¹³ Fe(II),^{7, 14} and Fe(III),¹⁵ are reported as SIMs.¹⁶

Thermally activated slow magnetic relaxation is one of the essential requirements for a SMM or SIM behaviour. But, from a mixing of the M_s levels promoted by the transverse zero-field splitting (E) and hyperfine or dipolar interactions, this process may disrupt due to a quantum tunneling magnetization (QTM). The mixing of ground degenerate M_s levels via transverse *zfs* is restricted, at least when it comes from a 2nd order SOC, for a system with non-integer spin system and negative D value. In this regard, mononuclear cobalt(II) complexes with noninteger (S = 3/2) spin state, D < 0 and a forbidden mixing of the ground degenerate M_s levels through transverse zfs (E) are suitable for a magnet-like behaviour.¹⁷ However, these rules are not so clear when the zfs is derived from a first-order SOC, which is the case in octahedral cobalt(II) complexes, and, consequently, the existence of cobalt(II) SIMs with positive D values seems to be the norm. Also, mononuclear Co(II) can show substantial axial zfs (D) that, however, can vanish in polynuclear complexes weather the zfs tensors of each metal ion are not collinear, which is usual. This inconvenient can be the main reason why the searching for molecule behaving as magnets is focused on mononuclear Co(II) complexes. But till date only a few examples of mononuclear Co(II) compounds with pseudo-tetrahedral,^{11b, 18} octahedral,^{11c} and square-pyramidal,^{11a} are reported with SMMs properties are reported showing SIMs behavior.

In the present contribution we report two new Co(II)-Co(III) mixed valence complexes $\{[Co_2(H_2L)_2(H_2O)_2][Co_2(H_2L)_2(H_2O)(m-phth)]\cdot 8(H_2O)\}$ (1) and $\{[Co_4(H_2L)_4(H_2O)_2(ppda)]\cdot 2(dmf)\cdot 3.2(H_2O)\}$ (2) [where *m*-phth = 1,3-benzenedicarboxylate; ppda = 1,4-phenylenediacrylate; $H_2L^{2-} = 2-((2-hydroxy-3-methoxybenzylidene)amino)-2-(hydroxymethyl)propane-1,3-diolato].$ Detail magnetic study reveals single ion magnet behavior for both the compounds.

Results and discussion

Synthesis of complexes 1 and 2. The complexes have been synthesized by adopting the procedures schematically given in Scheme 1.



Scheme 1. Synthesis of complexes 1-2.

Crystal structure description

The reaction of cobalt acetate with H₄L in methanol and in the presence of triethylamine and of *m*-phthalic acid (with molar ratio, cobalt acetate : H_4L : $H_2phth = 1:1:1$) leads to two ionic dinuclear complexes, a cationic $[Co_2(H_2L)_2(H_2O)_2]^+$ and an anionic $[Co_2(H_2L)_2(H_2O)(m$ phth)]⁻ species. Figure 1 shows a detail of the packing that accomplishes around a symmetry center leading to a positional disorder. As described in the experimental part, a half occupancy has been assigned to the *m*-phth anion, as well as to the coordinated aqua O(2w)and lattice water molecules O(3w)-O(9w). So that the sixth coordination site of Co(2) is occupied by a carboxylate *m*-phth oxygen atom and that of its symmetry related Co(2') by a water molecule, that the formulation for complex 1 is so $[Co_2(H_2L)_2(H_2O)_2][Co_2(H_2L)_2(H_2O)(m-phth)]\cdot 8(H_2O).$

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Figure 2 depicts an ORTEP view of the anionic fragment, where the *m*-phthalate anion (*m*-phth) acts as a monodentate ligand. The oxidation states of the cobalt centers are confirmed by considering the Co–O bond lengths and taken into account the total charge of the coordinated ligand molecules. Co(1) has a +3 oxidation state and is chelated by two polydentate H_2L^{2-} Schiff base ligands *via* the phenoxo oxygens O(1a/O1b), the imine nitrogens N(1a/1b) and the deprotonated alcoholic –OH groups (O2a/2b). These chelating ligands are such arranged that imine nitrogen donors are in trans position with phenolato mean planes almost normal to each other, as already found in polynuclear cobalt complexes containing comparable fragments.¹⁹

The values of the Co(1)-N bond lengths are of 1.887(3) and 1.889(3) Å, while the Co(1)-O distances fall in the range 1.885(3)-1.915(2) Å. On the other hand, the divalent Co(2) ion has a O₆ chromophore environment, being coordinated by the bridging alkoxido oxygen atoms O(2a) and O(2b), by the hydroxyl groups O(3a) and O(3b), and by a water molecule (O(1w)). The sixth position is occupied by an additional aqua (O(2w)) in the complex cation or by the *m*-phth carboxylate oxygen donor O(1) in its anion counterpart. The Co(2)-O bond distances are slightly longer, varying from 2.028(3) to 2.192(3) Å, but, due to the disorder, the refinement led to Co(2)-O(2w)' and Co(2)-O(1) bond length values of low accuracy, being of 2.06(2) and 2.05(2) Å, respectively.

The Co(2)-O bond lengths are significantly longer than those measured for Co(1), by 0.1–0.2 Å, consistent with the designation of the respective oxidation states of +2 and +3 for Co(2) and Co(1), respectively. The alkoxo oxygen atoms O(2a) and O(2b) of the two H₂L ligands bridge the two cobalt centers leading to an intermetallic Co^{III}-Co^{II} distance of 2.9847(7) Å.

On the other hand, by reacting cobalt acetate with H_4L in methanol, in the presence of triethylammine and of 1,4-benzenediacrylic (H_2ppda) acid (with molar ratio, cobalt acetate : H_4L : $H_2ppda = 1:1:1$), lead to the formation of a centro-symmetric tetranuclear complex of

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formula $[Co_4(H_2L)_4(H_2O)_2(ppda)] \cdot 2(dmf) \cdot 3.2(H_2O)$ (2). In fact the X-ray structural analysis of the compound revealed that it comprises a crystallographic independent dinuclear $Co^{III}Co^{II}$ unit connected to a symmetry related one by the phenylenediacrylate anion located on a center of symmetry. The molecular structure of complex 2 is illustrated in Figure 3 and a selection of bond lengths and angles is reported in Table 1. The metals in the independent unit are sixcoordinated with a distorted octahedral geometry showing a close similarity to anionic complex 1. The intermetallic distance in the $Co^{III}Co^{II}$ unit is of 2.9654(3) Å (shorter by 0.02 Å compared to the value measured in 1), and the Co(2) ions bridged by the ppda anion, are spaced by 15.225(1) Å. The same coordinating atom labels were assigned in 1 and 2 and data of Table 1 highlight close comparable geometrical values in the two complexes. Due to this similarity, we do not describe in detail the structure, being the Co-N and Co-O bond lengths well within the ranges previous indicated for 1, but the coordination bond angles in the present case indicate an octahedral geometry closer to ideal values.

It is worth of note in both complexes a rather strong intramolecular hydrogen bond occurring between the carboxylate oxygen O(2) and the adjacent coordinated water molecule O(1w) in (O...O distance of 2.654(13) and 2.625(2) Å, in **1** and **2**, respectively, see Figures 1 and 3), which reinforces the link of the carboxylate group to the dinuclear cobalt unit. However, the disorder of water molecules observed in both crystals does not allow a detailed analysis of the H-bonding pattern. The volume of lattice water molecules and dmf in **2** accounts for the 19% of the unit cell volume as derived by program Platon.²⁰

Magnetic Properties

The direct current (dc) magnetic properties of **1** and **2** in the form of the $\chi_M T$ versus *T* plot (χ_M being the dc magnetic susceptibility per {Co^{II}Co^{III}}₂ unit) were investigated in detail (Figure 4). At room temperature, the $\chi_M T$ values for **1** and **2**, of 5.80 and 5.89 cm³mol⁻¹K, respectively, are within the range expected for two isolated high-spin d⁷

 Co^{II} (S = 3/2) ion with some orbital momentum contribution. Upon cooling, the $\chi_{M}T$ value continuously decreases reaching 3.54 and 3.60 $\text{cm}^3\text{mol}^{-1}\text{K}$ for 1 and 2, respectively at 2.0 K (Figures 4 and 5), revealing the occurrence of a significant spinorbit coupling (SOC). On the other hand, these temperature dependences of the magnetic susceptibility confirm that the extended bridging ligands connecting the highspin Co^{II} ions in 1 and 2 are not able to transmit a magnetic coupling strong enough to visualize its effects in the working temperature range, being the Co^{II} centres considered entirely isolated. The magnetization data also support the presence of a spin-orbit coupling or a zero-field splitting (zfs): i) even at 2 K, the saturation value of magnetization (4.30 and 4.26 N β for 1 and 2, Figures 4 and 5) is well below the expected value ($Ms = 6.0 \ N\beta$ for g = 2.0); and ii) the M vs. H/T curves do not superimpose (Figures S1 and S2). However, the latter curves are very close, featuring a system with a very small or large *zfs*. In the last case, which is usual in high-spin octahedral Co^{II} ions, the quartet ground state is split in well separated two Kramer's doublets, being at low temperatures practically only populated the Kramer doublet ground state. Thus, changes in the temperature just cause tiny adjustments on the population of the Kramer's doublets and, in consequence, in the Mvs.H/T curves (Figures S1 and S2).

Although the magnetic data susceptibility should be analyzed with a model of a first order spin-orbit coupling in case of significant SOC, a spin Hamiltonian corresponding to an isolated S = 3/2 with large *g*-factors and zero-field splitting parameters (*zfs*) can be used as well. In this case the spin Hamiltonian takes the form: $H = D[S_z^2+S(S+1)/3] + E(S_x^2+S_y^2) + \beta Hg(S_x+S_y+S_z)$, where axial and rhombic distortion of the tetragonally distorted high-spin d⁷ Co^{II} ion are taken into account through the *D* and *E* parameters, respectively. Whereas the *E* parameter cannot be unambiguously evaluated from magnetic susceptibility data, the *E* and *g*

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parameters are strongly correlated in the simulation of the magnetization data. However, these problems can be solved when magnetic susceptibility and magnetization data are analyzed in unison. Thus, the magnetic susceptibility data determines the value of the g-factor and, hence, the magnetization allows a good estimation of the rhombic anisotropy value from the determined g. However, the huge zfs leads to a collapse of the M vs. H/T curves that represents a major constraint to achieve a good estimation of the D and E parameters. Thus, we independently analyzed the thermal dependences of the magnetic susceptibility and the magnetization. The agreement factor (F) can be defined as $\sum [(P)_{exp} - (P)_{calcd}]^2 / \sum [(P)_{exp}]^2$, where P is the physical property under study. A minimum value of F for the magnetic susceptibility is reached with the following values: g = 2.501(3) and |D| = 54.7(7) cm⁻¹ with F = 3.6× 10⁻⁵ for **1** and g = 2.515(2) and |D| = 60.8(6) cm⁻¹ with $F = 2.5 \times 10^{-5}$ for **2**. The theoretical curves well match the experimental data in the whole temperature range (solid lines in Figures 4 and 5). Hence, the assumption that Co^{II} ions were magnetically isolated is validated. In cobalt(II) SIMs, these large values of the axial zfs are typical, but both negative and positive have been reported.^{11a,11b, 11c, 18} On the other hand, the large axial *zfs* allows simulating the magnetization data using a spin model that takes into account only the ground Kramer's doublet as an effective $S = \frac{1}{2}$ spin moment. In this approach the magnetic anisotropy is transferred to the g tensor, i.e., three different components should be considered. Usually, only the parallel (g_{\parallel}) and perpendicular components (g_{\perp}) are contemplated. This model is summarized in the spin Hamiltonian: $\mathbf{H} = g_{\perp}\beta H_x S_x + g_{\perp}\beta H_y S_y + g_{\parallel}\beta H_z S_z$. Thus, the best fit of the magnetization data provides the following results: $g_{\parallel} = 7.519(10)$ and $g_{\perp} =$ 1.901(9) with $F = 3.0 \times 10^{-4}$ for 1; and $g_{\parallel} = 7.349(8)$ and $g_{\perp} = 1.950(7)$ with $F = 3.6 \times 10^{-4}$ for 2 (solid lines in Figures 4 and 5). These values, especially the large values of g_{\parallel} , are those clearly typical for octahedral Co^{II} ions with negative D values.

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On the other hand, these values of the D and E/D parameters agree with those found from NEVPT2 calculations. Due to cationic (1^+) and anionic (1^-) unities coexist in 1, NEVPT2 calculations were done on both species to estimate the values of zfs parameters. In all used models, Co^{II} and Co^{III} ions are present, and the unique metal ion showing a spin density (ρ), which corresponds to a partially delocalized high-spin d^7 electronic configuration, is that was assigned to a Co^{II} ion from the crystal structure [ρ (Co) = 2.89 e]. Whereas D and E/D take values similar in 1^{-} ($D = -95.8 \text{ cm}^{-1}$, and E/D = 0.216) and 2 ($D = -101.9 \text{ cm}^{-1}$, and $E/D = -101.9 \text{ cm}^{-1}$, and $E/D = -101.9 \text{ cm}^{-1}$. 0.234), these values are lower enough in $\mathbf{1}^+$ ($D = -62.4 \text{ cm}^{-1}$, and E/D = 0.219). These values obtained from a 2nd-order perturbative approach qualitatively are similar to those reached using an effective Hamiltonian (D = +55.9, -70.4 and -73.9 cm⁻¹, and E/D = 0.294, 0.328 and 0.331 for 1^+ , 1^- and 2, respectively), which are however closer to those found from the magnetometry. However, in our experience, the approach of effective Hamiltonian usually overestimates the rhombicity in the zfs, being the E/D ratio close its maximum value (1/3) and the meaning of the sign of D is thus lost. Mainly, these results confirm the negative sign of Dsuggested from the experimental magnetization data. According to these calculations, the second-order spin-orbit coupling is the main contribution to D parameter, being the contribution of the spin-spin coupling negligible compared to the former one. Because the two first quartet excited states are much closer to the quartet ground state (786 cm⁻¹ and 1519 cm⁻¹ ¹ in $\mathbf{1}$) than other quartet and doublet excited states, the D value is largely given by the contribution from these two excited states (-108.7 and +19.4 cm⁻¹, respectively). Despite of the fact that Co^{II} ions in 1⁻ and 2 present the same coordination environment, the calculations shows that complex 2 exhibits a higher *zfs*, that is probably related to a larger distortion of the octahedral coordination sphere, supported by a major value of E/D. This provokes the two first excited quartet states to be slightly closer to the ground state (776 cm^{-1} and 1449 cm^{-1}) than in 1^{-} (786 cm⁻¹ and 1519 cm⁻¹) and they interact more strongly with it, leading to major

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contributions to the D parameter in 2 (-118.4 and +22.8 cm^{-1}). On the other hand, shape measurements on the 1^+ , 1^- and 2 complexes were done to check the involvement of structural distortions on the different *zfs* suggested for 1^+ . Previous theoretical studies indicate that octahedron geometries favor positive D parameters, but trigonal prismatic coordination spheres provide negative D factors.²¹ The shape measurements for our three complexes suggest that they are very similar with coordination spheres close enough to an octahedron [S = 18.4 ($\mathbf{1}^+$), 21.1 ($\mathbf{1}^-$), and 17.0 (**2**), being S the degree of conversion between an octahedron and a trigonal prism, which takes values of 0.0 and 100 for the ideal octahedron and the trigonal prism].²² However, they are distorted and deviated from the path that connects an octahedron and a trigonal prism; these deviations are also similar in the three species ($\delta =$ 11.3, 7.6 and 9.4 for 1^+ , 1^- and 2, respectively). Therefore, structural parameters are not able to explain the different calculated axial zfs between 1^+ and the similar 1^- and 2. On the other hand, the negative D values for the three unities do not agree with an octahedral geometry.²¹ On the contrary, high rhombicity, as it is proposed for complexes in 1 and 2, can inverse the sign of D or just remove its physical meaning. Nevertheless, the zfs must be associated with the electronic effects rather than to structural factors –although they can be coincident in some cases, particularly in theoretical studies where only structural distortions are applied on a specific model. In other situations, the ligands conforming the coordination sphere can display different electronic structures, but geometrical factors influencing zfs are only supporting actors. In the present case, in 1^{-} and 2 the coordination sphere is similar, but a neutral water molecule replaces one charged carboxylate group in 1^+ , provoking an apparent change in the electronic structure of this last complex despite there is not a significant structural change. This fact is the cause the D values for 1^{-} and 2 were similar, and the found difference can be associated only with structural features. But this is not the case for 1^+ , where the change of the electronic state when the water molecule is coordinated shifts up the first excited quartet (874

cm⁻¹), the main contributor to the axial *zfs* in octahedral cobalt(II) complexes, decreasing its input drastically. On the other hand, since these two excited quartet states contribute in opposite way, the control of the symmetry of the electronic distribution allows stabilizing one or other excited state and hence to obtain a positive or negative *D* value. Additionally, from these calculations, an estimation of the three components of the *g*-factor gave: $g_1 = 1.719$, $g_2 = 2.607$ ($g_{\perp} = 2.208$) and $g_3 = g_z = 7.307$ for $\mathbf{1}^+$, $g_1 = 1.517$, $g_2 = 2.350$ ($g_{\perp} = 1.978$) and $g_3 = g_z = 7.771$ for $\mathbf{1}^-$, and $g_1 = 1.510$, $g_2 = 2.392$ ($g_{\perp} = 2.000$) and $g_3 = g_z = 7.845$ for **2**, which are in agreement with those previously obtained from the magnetization data.

The alternating current (ac) magnetic susceptibility of 1 and 2 in the form of the χ_{M} and $\chi_{\rm M}$ " versus T plots ($\chi_{\rm M}$ ' and $\chi_{\rm M}$ " being the in-phase and out-of-phase ac magnetic susceptibilities per {Co^{II}Co^{III}}₂ unit) were measured in different applied static fields in the range of 0.0–2.5 kG (Figures 6-7 and S3-S6). In zero dc magnetic field, no $\chi_{\rm M}$ " signals can be observed for 1 and 2 even for the highest frequency used (v = 10 kHz), suggesting that fast zero-field quantum tunneling relaxation of the magnetization effects are present. However, when such a small static dc field as 500 G is applied, strong frequency-dependent maxima appear in both χ_{M}' and χ_{M}'' below 10 K (Figures S3 and S5) in both cases. Additional ac measurements for 1 and 2 under higher applied dc fields of 1000 and 2500 G are shown in the ESI (Figures 6-7, S4 and S6), showing the same single strong frequency-dependent χ_{M} " maxima below 10 K. Relaxation times for 1 and 2 could be calculated from the maximum of $\chi_{\rm M}$ " at a given frequency ($\tau = 1/2\pi\nu$). These follow, at higher temperatures and for all applied static dc magnetic field, the Arrhenius law characteristic of a thermally activated or Orbach mechanism (see Figures 6d, 7d and S3d-S6d), which is determined for the first preexponential factor (τ_0) and activation energy (E_a). But, in all cases, a deviation of Arrhenius law at lower temperatures is observed that is a definite indication of the presence of another additional relaxation mechanism. Among the candidates there are the quantum tunneling, direct and Raman relaxation mechanisms. The best simulation of the thermal dependence of the relaxation times was obtained using only the Orbach and Raman mechanisms through the $\tau^{-1} = \tau_0^{-1} \exp(-E_{a1}/k_BT) + AT^n$ relation. The values of first pre-exponential factor (τ_0) and activation energy (E_a) for 1 and 2 are consistent with those found for previously reported octahedral cobalt(II) SIMs (Tables 2 and 3). ^{11c} On the other hand, it is worth to note that, for a particular applied magnetic field, Raman and direct mechanism are expressed in a similar way and only the value of *n* changes, being unity in the last one and larger values for the former, usually n = 7 and 9 for non-Kramer and Kramer ions, respectively. Lower values of nare possible when phonons are considered. Thus, whereas a direct mechanism seems to be present in 2, a relaxation mechanism through a Raman process that takes into account phonons could be more appropriate in 1 (Tables 2 and 3). However, we like to note that different sets of values for the parameters associated with Orbach and Raman processes, and if it is also considered with the quantum tunneling, were able to reproduce the thermal dependence of the relaxation time. Among of these sets, it can be outlined that with energy barrier close to 100 cm⁻¹, which is a value close to that provided by the D parameter. However, the Raman A and n parameters unexpectedly ever depends on the applied static magnetic field. In the only case *n* parameter seems to be independent of the magnetic field is in 1, where this takes a value close to the unity as it is figured for a direct relaxation process. In our experience in other families of cobalt(II) complexes, additional relaxation processes together an Orbach mechanism do not provide satisfactory results because the simulations are not good enough or the dependence with the applied magnetic field is not that expected. In such cases, the inclusion of a second Orbach mechanism gives a good answer.²³ In 1 and 2, that can be also extended, obtaining values for the energy barriers and pre-exponential factors similar to other previously reported (Table S1). However, at lower temperature that we have

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values of relaxation times for all magnetic fields used (3.8 K), it seems there is a correlation between τ and H, therefore a direct relaxation process cannot be discarded.

It is not evident to know what unity (cationic or anionic) behaves as SIM in 1 or even whether both do. Attending to the resemblance observed particularly in the structural and electronic features between 1^{-} and 2, but also in the SIM behavior (energy barrier and relaxation times) reported for 1 and 2, it is only natural to think that the anionic species 1^{-} is the unique unity in 1 behaving as a SIM. Nevertheless, we cannot guarantee that the cationic unity $\mathbf{1}^+$ don't show this particular behavior even it is the only form of the three complexes studied here that reveals a positive D value calculated from an effective Hamiltonian. On the other hand, it is very usual in octahedral cobalt(II) complexes that the energy gap between the ground and first excited Kramers doublet was much larger than that suggested by the energy barrier obtained from the dynamic studies of the magnetization. In such cases, some authors propose that an extra energy contribution from a network relaxation via a phonon can bring down the energy that is necessary to overcome the barrier imposed by the zfs. The energy of these phonons depends directly on the how the molecules are organized in the network and the strength and nature of the contacts between them. Being the structural networks of 1 and 2 very different, it is not possible to establish a direct correlation between the found energy barriers and D values.

The Cole–Cole plots at 6.0-8.0 K of **1** and 5.0-7.0 K of **2** and under different applied dc fields of 500, 1000 and 2500 G gave almost perfect semicircles which could be fitted by the generalized Debye model²⁴ (solid lines in Figures 6c, 7c, S3c- S6c). The calculated low values of the α parameter at the different applied dc fields ($\alpha = 0.02-0.12$, Table 2) support a single relaxation process and discard thus a spin-glass behavior²⁵ ($\alpha = 0$ for a Debye model) in both compounds. We can think that **1**, with two different cobalt(II) complexes, should present a larger α value than **2** with one unique cobalt(II) unity. However, we have seen in the past that

both at the molecular level and in solid the metal complexes can display a relatively wide range of *D* values at low temperatures (5 or 10 K) caused by the geometrical changes that occur at these temperatures. Briefly, at low temperature the complexes are still in motion, showing a Gaussian distribution of the geometries and of values of *zfs* parameters, which is probably the cause of the presence of a distribution of relaxation processes and, therefore, a non-null α value.²⁶ The amplitude of these distributions depends on the molecular vibrational frequencies, but in solid also on the nature and strength of the intermolecular contacts. To establish an order of α value for 1 and 2 is not easy because the crystal structures of 1 and 2 different enough.

Conclusion

In summary, we have presented the synthesis, crystal structure, and low-temperature magnetic behavior of two novel Co(II)-Co(III) mixed-valence complexes using multidentate Schiff base and dicarboxylate ligands. AC/DC magnetic studies demonstrated that individual Co(II)-Co(III) unit exhibits field induced slow magnetic relaxation consistent with single ion magnets (SIMs) behavior. Ab initio NEVPT2 calculations ratify that large axial and rhombic *zfs* on cobalt(II) unities are responsible for the particular magnetic behavior in both compounds studied.

Experimental section

Physical measurements. Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FTIR spectrophotometer operating from 400 to 4000 cm⁻¹. Electronic absorption spectra were obtained with a Shimadzu UV-1601 UV–Vis spectrophotometer at room temperature. Quartz cuvettes of 1 cm path length and 3 cm³

volume were used for all measurements. ESI-MS spectra of the compounds in methanol were recorded on an Agilent Q-TOF 6500 mass spectrometer by using the Mass hunter software for their analysis. ¹H and ¹³C NMR spectra were recorded on a Varian 400 MHz instrument.

Crystallographic data collection and refinement. Data collections for complexes **1-2** were carried out at 120(2) K with Mo-K α radiation ($\lambda = 0.71073$ Å) on a Xcalibur, Sapphire3 diffractometer equipped with CCD. Cell refinement, indexing and scaling of the data sets were done by using the CrysAlisPropackage.²⁷ The structures were solved by direct methods using Olex2 1.2 ²⁸ software and subsequent Fourier analyses²⁹ and refined by the full-matrix least-squares method based on F^2 with all observed reflections.²⁹ Hydrogen atoms were placed at calculated positions, except those of some water molecules that were detected on the difference Fourier map, although a suitable H-bonding scheme among these was difficult to inspect for the disordered situation detected in the crystal packing. In fact in complex **1** most of the lattice water molecules and the 1,3-benzenedicarboxylate anion share the same site at half occupancy. Crystal data and details of refinements are given in Table 4.

Magnetic measurements. Variable temperature (2.0 - 300 K) direct current (dc) magnetic susceptibility measurements under an applied field of 250 G (T < 30 K) and 0.5 T ($T \ge 30 \text{ K}$), and field-dependence (0–5.0 T) magnetization measurements at low temperatures in the range of 2.0–10.0 K were carried out with a Quantum Design SQUID magnetometer. Variable-temperature (2.0–14.0 K) alternating current (ac) magnetic susceptibility measurements under ±4.0 G oscillating field at frequencies in the range of 1.0–10.0 kHz were carried out under different applied static fields in the range of 0.0–2.5 kG with a Quantum Design Physical Property Measurement System (PPMS). The magnetic susceptibility data were corrected for the diamagnetism of the constituent atoms and the sample holder. Dc and ac magnetic measurements were performed on powdered micro-crystals (18.69 and 13.07 mg for **1** and **2**,

respectively) and restrained the sample with *n*-eicosane (27.84 and 28.47 mg for 1 and 2, respectively) in order to avoid any field induced torquing.

Computational details. Since the magnetic coupling between Co^{II} ions through extended dicarboxylate ligands is negligible, all calculations were performed on the experimental geometries of {Co^{II}Co^{III}} unities, i.e., only one of the two Co^{II} ions was considered. Thus, all ligands of a{Co^{II}Co^{III}} unity has been fully taken into account, but in order to gain efficiency without loss of accuracy, the dicarboxylate bridging ligands were simplified in the distant region from the Co^{II} ion. A view of the molecular models used in these calculations is shown in Figure S7. The parameters that determine the axial (D) and rhombic (E) zfs were estimated from calculations based on a second order N-electron valence state perturbation theory (NEVPT2) applied on a wave function, which was previously obtained from a complete active space (CAS) calculation. These calculations were carried out with the ORCA program version 3.0³⁰ using the TZVP basis set proposed by Ahlrichs³¹ and the auxiliary TZV/C Coulomb fitting basis sets.³² The 2nd order contributions to *zfs* from 10 quartet and 20 doublet excited states were generated from an active space with seven electrons in the d orbitals. The g-tensor was calculated for the ground and excited Kramer's pairs using Multi-Reference Configuration Interaction (MRCI) wave functions with a first-order perturbation theory on the SOC matrix.³³

Materials. High-purity 1,4-phenylenediacrylic acid (H₂ppda) (97%) and cobalt(II) acetate tetrahydrate (98%) were purchased from the Aldrich Chemical Co. Inc. and used as received. All other chemicals were of AR grade and the reactions were carried out under aerobic conditions. Solvents used for spectroscopic studies were purified and dried by standard procedures before use.³⁴

Synthesis

 (1.77×10^4) .

2-((2-hydroxy-3-methoxybenzylidene)amino)-2-(hydroxymethyl)propane-1,3-diol (H₄L). To a methanolic solution (50 mL) of 2-hydroxy-3-methoxybenzaldehyde (0.608 g, 4 mmol) and a methanolic solution (50 mL) of tris(hydroxymethyl)amino methane (0.484 g, 4 mmol) was added under stirring condition at room temperature (27 °C). The stirring was continued for next 2 h. The filtered solution was allowed to evaporate at room temperature and solid yellow compound was obtained after a few days. Yellow crystals of H₄L were obtained by recrystallization of the compound in methanol. Yield: 0.714 g (70%). C₁₂H₁₇NO₅ (255.27): ESI-MS (m/z, ion): $[M + H]^+$, m/z, 256.118, calcd.: m/z, 255.27 (100%). Anal. Calc.C, 56.46; H, 6.71; N, 5.48 %; Found: C, 56.44; H, 6.70; N, 5.51 %. ¹H NMR (DMSO-d₆, 400 MHz, δ, ppm): 8.456 (s, 1H, imine), 6.944, 6.924, 6.890, 6.871 (double doublet, 1H, Ar, J = 21.6, 8 Hz), 6.581, 6.563, 6.542 (t, 1H, Ar, J = 7.6 Hz), 4.907 (s, phenolic –OH), 3.611 (s, 6H, CH₂), 3.718 (s, 3H, OMe). ¹³C NMR (DMSO-d₆, 400 MHz, δ, ppm): 164.266 (-CH=N-), 159 (Ar-C-OMe), 149.754 (Ar-C-OH), 124.343 (Ar-C-imine), 114.551-117.174 (Ar-C), 66.520 (-CH₂-OH), 61.311 (tertiary carbon), 55.881 (-OCH₃). FT-IR (KBr, cm⁻¹): 3425 (br), 2988 (w), 2949 (w), 2916 (w), 2832 (w), 2606 (w), 1952 (w), 1880 (w), 1818 (w), 1646 (vs), 1545 (vs), 1467 (s), 14149 (vs), 1372 (vs), 1300 (s), 1232 (vs), 1167 (s), 1072 (s), 1023 (s), 962 (m), 913 (m), 877 (w), 851 (s), 727 (w), 662 (w), 613 (w), 528 (s), 414 (vs). UV-Vis spectra [λ_{max} , nm $(\epsilon, L \text{ mol}^{-1}\text{cm}^{-1})$] (CH₃OH solution) 202 (6.77 × 10⁴), 241 (5.56 × 10⁴), 294 (4.15 × 10⁴), 420

 $\{ [Co_2(H_2L)_2(H_2O)_2] [Co_2(H_2L)_2(H_2O)(m-phth)] \cdot 8(H_2O) \}$ (1). A methanolic solution (20 mL) containing H₄L (0.5 mmol, 0.128 g) and triethylamine (Et₃N) (1mmol, 0.101 g) was added to a methanolic solution (20 mL) of Co(CH₃COO)₂·4H₂O (0.5mmol, 0.124 g) and stirred for 1 h. To the resulting deep brown color solution, a mixture of *m*-phthalic acid (0.5mmol, 0.083g) and Et₃N (1mmol, 0.101 g) in methanolic solution (20 mL) was added dropwise and the

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stirring was continued for additional 2 h. Then the deep brown solution was filtered and the filtrate was allowed to evaporate at room temperature. After 2 days a brown colored crystalline compound was collected by filtration. Yield: 0.523 g, 65%. Anal. Calcd. for $C_{56}H_{86}Co_4N_4O_{35}$ (1611.00): C, 41.75; H, 5.38; N, 3.47 %. Found: 41.72; H, 5.41;N, 3.49 %. FT-IR (KBr, cm⁻¹): 3431 (br), 2982 (s), 2946 (w), 2154 (w), 1639 (vs), 1551 (vs), 1467 (vs), 1413 (vs), 1372 (w), 1300 (vs), 1245 (s), 1219 (w), 1171 (w), 1138 (w), 1078 (vs), 1017 (s), 978 (s), 881 (w), 738 (w), 629 (w). UV-Vis spectra [λ_{max} , nm (ϵ , L mol⁻¹cm⁻¹)] (CH₃OH solution) 250 (3.13 × 10⁴), 313 (3.91 × 10³), 393 (2.71 × 10³).

{[Co₄(H₂L)₄(H₂O)₂(ppda)]-2(dmf)-3.2(H₂O)} (2). Complex 2 was synthesized by following the same procedure as adopted for 1, using 1,4-benzenediacrylic acid (0.5 mmol, 0.109 g) instead of *m*-phthalic acid. The filtrate was left for slow evaporation at room temperature. After a few days, a brown coloured compound was collected and it was dissolved in DMF and filtered. Brown crystals suitable for X-ray analysis were obtained after 4 weeks. Yield: 0.511 g, 60%. Anal. Calcd. For C₆₆H_{92.40}Co₄N₆O_{31.20} (1704.77): C, 46.49; H, 5.46; N, 4.92 %. Found: C, 46.51; H, 5.44; N, 4.95%.FT-IR (KBr, cm⁻¹): 3428 (br), 2983 (s), 2946 (w), 2151 (w), 1642 (vs), 1551 (vs), 1467 (vs), 1411 (vs), 1373 (w), 1300 (vs), 1245 (s), 1219 (w), 1170 (w), 1138 (w), 1076 (vs), 1014 (s), 979 (s), 882 (w), 729 (w), 632 (w). UV-Vis spectra [λ_{max} , nm (ε , L mol⁻¹cm⁻¹)] (CH₃OH solution) 250 (2.37 × 10⁴), 312 (1.26 × 10⁴), 398 (2.40 × 10³). CCDC numbers are 1518364 and 1518365 (for complexes 1 and 2, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

Supporting Information. Results of FT-IR, electronic absorption and mass spectral study, Figures and Tables for magnetic analysis are provided as supplementary material.

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	1	2
Co(1)-N(1a)	1.889(3)	1.8861(15)
Co(1)-N(1b)	1.887(3)	1.8899(15)
Co(1)-O(1a)	1.885(3)	1.8749(12)
Co(1)-O(1b)	1.899(3)	1.9005(13)
Co(1)-O(2a)	1.915(2)	1.9123(12)
Co(1)-O(2b)	1.894(3)	1.8870(12)
Co(2)-O(1)	2.05(2)	2.0213(14)
Co(2)-O(2a)	2.028(3)	2.0379(13)
Co(2)-O(2b)	2.050(3)	2.0235(12)
Co(2)-O(3a)	2.192(3)	2.1971(14)
Co(2)-O(3b)	2.155(3)	2.1895(14)
Co(2)-O(1w)	2.078(3)	2.0904(15)
Co(2)-O(2w)'	2.06(2)	-
Co(1)-Co(2)	2.9847(7)	2.9654(3)
N(1a)-Co(1)-N(1b)	177.43(13)	176.69(6)
O(1a)-Co(1)-O(2a)	175.19(11)	176.35(5)
O(1b)-Co(1)-O(2b)	176.11(11)	175.52(6)
O(3a)-Co(2)-O(3b)	176.75(12)	177.72(6)
O(2b)-Co(2)-O(1w)	179.74(11)	173.69(6)
O(2a)-Co(2)-O(1)	162.4(4)	170.38(5)
O(2a)-Co(2)-O(2w)'	173.5(4)	_
Co(1)-O(2a)-Co(2)	98.36(11)	97.25(5)
Co(1)-O(2b)-Co(2)	98.30(11)	98.57(5)

Table 1. Coordination bond lengths (Å) and angles (°) for complexes 1-2.

Symmetry code for O(2w)' in 1 = -x+1, -y+1, -z+1.

$H^{a}(\mathbf{G})$	$\tau_0{}^b \times$	E_{a}^{b}	A^b	n^b	α^{c}	χs^{c}	χτ ⁶	$\frac{1}{1}$ (temp)
						(cm ^s mol ⁻¹)	(cm [°] m	iol ¹)
					0.07	0.26	0.74	(5.0 K)
500	4.29	16.4	2019	1.08	0.02	0.24	0.62	(6.0 K)
					0.05	0.20	0.54	(7.0 K)
					0.12	0.10	0.72	(5.0 K)
1000	2.81	19.0	1682	1.19	0.07	0.10	0.62	(6.0 K)
					0.04	0.10	0.54	(7.0 K)
					0.08	0.04	0.72	(5.0 K)
2500	7.71	15.3	1341	1.05	0.09	0.04	0.61	(6.0 K)
					0.06	0.02	0.52	(7.0 K)

Table 2. Selected ac magnetic data for 1 at different dc applied fields.

^{*a*} Applied dc magnetic field. ^{*b*} The values of the pre-exponential factor (τ_0) and activation energy (E_a) are calculated through the Arrhenius law [$\tau^{-1} = \tau_0^{-1} \exp(-E_a/k_BT) + A T^n$].^{*c*} The values of the α parameter, adiabatic (χ_s) and isothermal (χ_T) susceptibilities are calculated from the experimental data through the generalized Debye law (see text).

$H^{a}(\mathbf{G})$	$\tau_0^{\ b} \times 10^7$	E_{a}^{b}	A^b	n^b	α^{c}	χs ^c	χ_{T}^{c}	(temp)
						$(\text{cm}^3\text{mol}^{-1})$	(cm ³ m	ol^{-1})
					0.11	0.20	0.59	(6.0 K)
500	4.61	22.3	481.0	2.34	0.09	0.18	0.52	(7.0 K)
					0.06	0.16	0.46	(8.0 K)
					0.12	0.09	0.60	(6.0 K)
1000	0.82	32.3	227.5	2.67	0.09	0.09	0.52	(7.0 K)
					0.07	0.08	0.46	(8.0 K)
					0.05	0.05	0.59	(6.0 K)
2500	0.50	35.1	100.6	3.08	0.08	0.05	0.51	(7.0 K)
					0.05	0.05	0.45	(8.0 K)

Table 3. Selected ac magnetic data for 2 at different dc applied fields.

^{*a*} Applied dc magnetic field. ^{*b*} The values of the pre-exponential factor (τ_0) and activation energy (E_a) are calculated through the Arrhenius law [$\tau^{-1} = \tau_0^{-1} \exp(-E_a/k_BT) + A T^n$].^{*c*} The values of the α parameter, adiabatic (χ_s) and isothermal (χ_T) susceptibilities are calculated from the experimental data through the generalized Debye law (see text).

Complex	1	2
Empirical formula	$C_{56}H_{86}Co_4N_4O_{35}$	$C_{66}H_{92.40}Co_4N_6O_{31.20}$
Formula mass, $g \text{ mol}^{-1}$	1611.00	1704.77
Crystal system	Triclinic	Triclinic
Space group	PĪ	PĪ
<i>a</i> , Å	9.0902(4)	8.9043(2)
b, Å	10.2821(4)	10.0665(2)
<i>c</i> , Å	19.6120(8)	21.2197(5)
α, deg	97.720(3)	77.346(2)
β, deg	99.862(3)	80.303(2)
γ, deg	105.991(4)	77.212(2)
$V, Å^3$	1703.91(12)	1795.36(7)
Ζ	1	1
$D_{\text{(calcd)}}, \text{ g cm}^{-3}$	1.570	1.577
μ (Mo-K α), mm ⁻¹	1.054	1.002
<i>F</i> (000)	838	888
Theta range, deg	2.84 - 27.88	1.98 - 30.51
No. of collected data	26400	57856
No. of unique data	7878	10969
R _{int}	0.0515	0.0454
Observed reflections $[I > 2\sigma(I)]$	5506	9262
Parameters refined	553	555
Goodness of fit (F^2)	1.030	1.039
$R1, wR2 (I > 2\sigma(I))^{[a]}$	0.0607, 0.1397	0.0405, 0.0996
R1, wR2 (all data)	0.0933, 0.1616	0.0506, 0.1055
Residuals, e $Å^{-3}$	1.649, -0.566	0.776, -0.535

 ${}^{[a]}R1(Fo) = \Sigma | |Fo| - |Fc| | / \Sigma |Fo|, wR2(Fo^{2}) = [\Sigma w (Fo^{2} - Fc^{2})^{2} / \Sigma w (Fo^{2})^{2}]^{\frac{1}{2}}$

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Caption of the Figures

Figure 1. Crystal packing of compound **1**: the *m*-phth anion, the coordinated aqua O2w and lattice water molecules O4w-O9w (all at half occupancy) share the same area due to the crystallographic symmetry center represented by the black dot.

Figure 2. ORTEP drawing (40% probability ellipsoids) of the anionic complex $[Co_2(H_2L)_2(H_2O)(m-phth)]^-$ of compound **1**. The labels of C atoms are omitted for clarity.

Figure 3. ORTEP drawing (50% probability ellipsoids) of the centro-symmetric molecular structure of compound **2** (labels of C atoms omitted for clarity).

Figure 4. Thermal dependence of $\chi_M T$ of compound **1** under an applied dc field of 0.25 (*T* < 30 K) and 5.0 kG ($T \ge 30$ K): (O) experimental data; (—) best-fit curve (see text). The inset shows the dependence of *M* with *H* of **1** at 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, 8.0, 9.0 and 10.0 K (from black to palest grey dots). The solid lines are the best-fit curves (see text).

Figure 5. Thermal dependence of $\chi_M T$ of compound **2** under an applied dc field of 0.25 (*T*< 30 K) and 5.0 kG ($T \ge 30$ K): (O) experimental data; (—) best-fit curve (see text). The inset shows the dependence of *M* with *H* of **2** at 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, 8.0, 9.0 and 10.0 K (from black to palest grey dots). The solid lines are the best-fit curves (see text).

Figure 6. Temperature dependence of χ_{M} ' (a) and χ_{M} " (b) of **1** in a dc applied static field of 1.0 kG and under ±4.0 G oscillating field at frequencies in the range of 1.0–10 kHz. The Cole-Cole plot (c) at 5.0–7.0 K and the Arrhenius plot in the high temperature region (d) for an applied static field of 1.0 kG.

Figure 7. Temperature dependence of χ_{M} ' (a) and χ_{M} " (b) of **2** in a dc applied static field of 1.0kG and under ±4.0 G oscillating field at frequencies in the range of 1.0–10 kHz. The Cole-Cole plot (c) at 6.0–8.0 K and the Arrhenius plot in the high temperature region (d) for an applied static field of 1.0 kG.



Figure 1



Figure 2



Figure 3



Figure 4





Figure 6



Figure 7