

Slow Magnetic Relaxation in Co(III)–Co(II) Mixed-Valence Dinuclear Complexes with a Co^{II}O₅X (X = Cl, Br, NO₃) Distorted-Octahedral Coordination Sphere[⊥]

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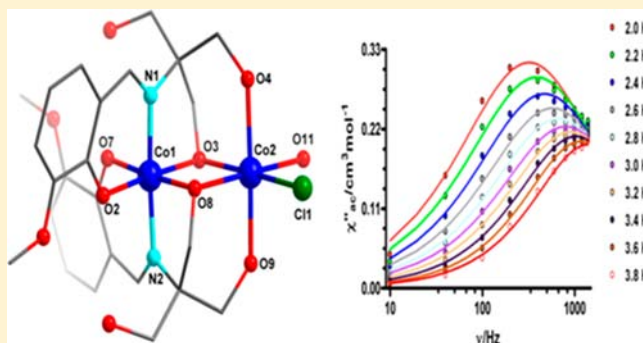
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Supporting Information

ABSTRACT: The reaction of the multisite coordination ligand (LH₄) with CoX₂·nH₂O in the presence of tetrabutylammonium hydroxide affords a series of homometallic dinuclear mixed-valence complexes, [Co^{III}Co^{II}(LH₂)₂(X)(H₂O)](H₂O)_m (1, X = Cl and m = 4; 2, X = Br and m = 4; 3, X = NO₃ and m = 3). All of the complexes have been structurally characterized by X-ray crystallography. Both cobalt ions in these dinuclear complexes are present in a distorted-octahedral geometry. Detailed magnetic studies on 1–3 have been carried out. *M* vs *H* data at different temperatures can be fitted with *S* = 3/2, the best fit leading to *D*_{3/2} = −7.4 cm^{−1}, |*E*/*D*| < 1 × 10^{−3}, and *g* = 2.32 for 1 and *D*_{3/2} = −9.7 cm^{−1}, |*E*/*D*| < 1 × 10^{−4}, and *g* = 2.52 for 2. In contrast to 1 and 2, *M* vs *H* data at different temperatures suggest that compound 3 has comparatively little magnetic anisotropy. In accordance with the large negative *D* values observed for compounds 1 and 2, they are single-molecule magnets (SMMs) and exhibit slow relaxation of magnetization at low temperatures under an applied magnetic field of 1000 Oe with the following energy barriers: 7.9 cm^{−1} (τ₀ = 6.1 × 10^{−6} s) for 1 and 14.5 cm^{−1} (τ₀ = 1.0 × 10^{−6} s) for 2. Complex 3 does not show any SMM behavior, as expected from its small magnetic anisotropy. The τ₀ values observed for 1 and 2 are much larger than expected for a SMM, strongly suggesting that the quantum pathway of relaxation at very low temperatures is not fully suppressed by the effects of the applied field.



INTRODUCTION

The discovery of polynuclear discrete complexes exhibiting slow relaxation of the magnetization and magnetic hysteresis below the so-called blocking temperature (*T*_B), without undergoing 3D magnetic ordering, has fuelled the field of molecular magnetism based on coordination compounds. These nanomagnets, called single-molecule magnets (SMMs),¹ are potential candidates for magnetic information storage and quantum computing.² The origin of the SMM behavior is the existence of an energy barrier (*U*) for the reversal of the molecular magnetization, which enables the molecule to retain its magnetization after removal of an applied field. The early examples of SMMs were clusters of transition-metal ions,³ the majority being Mn clusters containing at least some Mn^{III} centers. However, recently mixed 3d/4f metal aggregates,^{3,4} low-nuclearity 4f metal complexes,⁵ and even mononuclear complexes of lanthanide,⁶ actinide,⁷ and transition-metal ions⁸ have been shown to possess SMM behavior. These latter complexes containing a unique slow-relaxing metal ion, the so-called single-ion magnets (SIM), are now the

systems attracting more interest for studying the magnetic relaxation dynamics in the SMM field. For transition-metal clusters, the height of the energy barrier and therefore the SMM behavior depends on the large-spin multiplicity of the ground state (*S*_T) and the easy-axis (or Ising-type) magnetic anisotropy of the entire molecule (*D* < 0). The thermal energy barrier for the reversal of the magnetization between the *M*_s = ±*S* ground states can be calculated through the expressions *U* = −*D*(*S*² − 1/4) and −*DS*² for half-integer and integer spin values, respectively.

Nevertheless, recently, it has been shown that low-coordinate, high-spin iron(II) and cobalt(II) complexes with large and positive *D* values can also exhibit SMM behavior.^{8a,h} Fast quantum tunnelling magnetization (QTM) through the mixing of ±*M*_s levels may disable the observation of slow magnetic relaxation through a thermally activated mechanism. QTM is promoted by transverse zero-field splitting (*E*),

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Table 1. Details of the Data Collection and Refinement Parameters for Compounds 1–3

	1	2	3
formula	C ₂₄ H ₃₇ ClCo ₂ N ₂ O ₁₅	C ₂₄ H ₃₆ BrCo ₂ N ₂ O ₁₅	C ₂₄ H ₃₂ Co ₂ N ₃ O ₁₇
mol wt	746.87	790.32	752.39
cryst syst	monoclinic	monoclinic	monoclinic
space group	Cc	Cc	Cc
unit cell dimens			
<i>a</i> /Å	11.663(5)	11.670(2)	12.513(2)
<i>b</i> /Å	13.228(5)	13.369(2)	13.020(2)
<i>c</i> /Å	19.690(5)	19.766(3)	19.069(3)
<i>α</i> /deg	90	90	90
<i>β</i> /deg	106.216(5)	106.395(4)	105.583(3)
<i>γ</i> /deg	90	90	90
<i>V</i> /Å ³	1539.3(11)	2958.4(9)	2992.5(8)
<i>Z</i>	4	4	4
<i>ρ</i> _c /g cm ⁻³	1.701	1.774	1.670
<i>μ</i> /mm ⁻¹	1.306	2.548	1.193
<i>F</i> (000)	1544	1612	1548
cryst size (mm ³)	0.18 × 0.15 × 0.11	0.13 × 0.11 × 0.10	0.17 × 0.16 × 0.12
<i>θ</i> range (deg)	4.41–25.03	4.30–25.03	4.41–25.03
limiting indices	–7 ≤ <i>h</i> ≤ 13 –14 ≤ <i>k</i> ≤ 15 –23 ≤ <i>l</i> ≤ 23	–13 ≤ <i>h</i> ≤ 13 –14 ≤ <i>k</i> ≤ 15 –23 ≤ <i>l</i> ≤ 15	–14 ≤ <i>h</i> ≤ 14 –12 ≤ <i>k</i> ≤ 15 –21 ≤ <i>l</i> ≤ 22
no. of rflns collected	7147	7439	7631
no. of indep rflns	3494 (<i>R</i> (int) = 0.0470)	4080 (<i>R</i> (int) = 0.0310)	4712 (<i>R</i> (int) = 0.0309)
completeness to <i>θ</i> /%	98.6	99.3	99.3
refinement method		full-matrix least squares on <i>F</i> ²	
no. of data/restraints/params	3494/6/405	4080/11/430	4712/24/435
goodness of fit on <i>F</i> ²	1.054	1.012	1.051
Flack param	0.05(3)	0.009(9)	0.00(2)
final <i>R</i> indices (<i>I</i> > 2 <i>θ</i> (<i>I</i>))			
<i>R</i> 1	0.0634	0.0337	0.0499
<i>wR</i> 2	0.1672	0.0740	0.1191
<i>R</i> indices (all data)			
<i>R</i> 1	0.0680	0.0368	0.0575
<i>wR</i> 2	0.1721	0.0757	0.1268
largest diff peak, hole/e Å ⁻³	0.760, –0.668	0.760, –0.515	0.993, –0.453

hyperfine interactions, or dipolar interactions.¹ However, for noninteger spin systems with $D < 0$, the mixing of the ground degenerate $\pm M_s$ levels through transverse anisotropy (E) is forbidden, thus favoring the observation of the thermally activated relaxation process.⁹ This, together with the fact that mononuclear species can exhibit large anisotropies in comparison with their multinuclear counterparts, has prompted the search for SMMs based on mononuclear Co²⁺ complexes with an $S = 3/2$ ground state. The results in this field are limited to four examples of Co²⁺ complexes with pseudo-tetrahedral,^{8a,c} square-pyramidal,^{8b} and octahedral^{8h} geometries, which show the suitability of the strategy. Herein, we report the syntheses, structures, and magnetic properties of three new Co(III)–Co(II) mixed-valence dinuclear complexes, which can be considered as Co²⁺ mononuclear complexes from a magnetic point of view. This study aims to find whether such magnetically diluted complexes, where the Co²⁺ ion possesses a distorted-octahedral geometry, can exhibit SMM behavior.

EXPERIMENTAL SECTION

Reagents and General Procedures. All reagents and chemicals were purchased from commercial sources and were used without further purification. The compound 2-[(2-hydroxy-3-methoxyphenyl)methylene]amino]-2-(hydroxymethyl)-1,3-propanediol (LH₄) was prepared according to a literature procedure.¹⁰

Tris(hydroxymethyl)aminomethane, Co(NO₃)₂·6H₂O, CoBr₂·6H₂O, and 3-methoxysalicylaldehyde (Sigma Aldrich) were used as purchased. All reactions were carried out under aerobic conditions.

Instrumentation. Melting points were measured using a JSGW melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating at 400–4000 cm⁻¹. Elemental analyses of the compounds were obtained from Thermoquest CE instruments CHNS-O, EA/110 model. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer.

Magnetic Measurements. Field dependence of the magnetization at different temperatures and variable temperature (2–300 K) magnetic susceptibility measurements on polycrystalline samples were carried out with a Quantum Design SQUID MPMS XL-5 device operating at different magnetic fields. ac susceptibility measurements were performed using an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. The experimental susceptibilities were corrected for the sample holder and diamagnetism of the constituent atoms by using Pascal's tables.

Preparation of the Metal Complexes 1–3. A general procedure for the preparation of the metal complexes is as follows. LH₄ (0.06 g, 0.24 mmol) was taken up in a mixture of methanol (15 mL) and acetonitrile (15 mL). CoX₂·*n*H₂O (0.24 mmol: 1, X = Cl and *n* = 6; 2, X = Br and *n* = 0; 3, X = NO₃ and *n* = 6) and tetra-*n*-butylammonium hydroxide (0.13 g, 0.50 mmol) were added to this solution. The

reaction mixture was stirred for 12 h and filtered. After 1 week brown block-shaped crystals suitable for X-ray crystallography were obtained. The characterization data for these complexes are given below.

[Co^{III}Co^{II}(LH₂)₂(Cl)(H₂O)](H₂O)₄ (**1**). Yield: 0.06 g, 67% (based on Co). Mp: 175 °C dec. IR (KBr, cm⁻¹): 3452 (b), 2978 (s), 2882 (s), 2739 (w), 2622 (s), 2497 (s), 1631 (w), 1600 (w), 1475 (s), 1443 (s), 1397 (s), 1364 (w), 1318 (w), 1243 (w), 1220(s), 1172 (w), 1073 (s) 980 (w). ESI-MS (*m/z*, ion): 660.03, [C₂₄H₃₀ClCo₂N₂O₁₀ + H]. Anal. Calcd for C₂₄H₃₂ClCo₂N₂O₁₁: C, 42.53; H, 4.76; N, 4.13. Found: C, 42.21; H, 4.48; N, 4.42.

[Co^{III}Co^{II}(LH₂)₂(Br)(H₂O)](H₂O)₄ (**2**). Yield: 0.05 g, 52% (based on Co). Mp: 187 °C dec. IR (KBr, cm⁻¹): 3457 (b), 2977 (s), 2872 (s), 2731 (w), 2629 (s), 2490 (s), 1625(w), 1608 (w), 1471 (s), 1446 (s), 1392 (s), 1367 (w), 1311 (w), 1248 (w), 1226(s), 1178 (w), 1079 (s) 980 (w). ESI-MS (*m/z*, ion): 705.98, [C₂₄H₃₀BrCo₂N₂O₁₀ + H]. Anal. Calcd for C₂₄H₃₂BrCo₂N₂O₁₁: C, 39.91; H, 4.47; N, 3.88. Found: C, 39.21; H, 4.38; N, 3.72.

[Co^{III}Co^{II}(LH₂)₂(NO₃)](H₂O)₃ (**3**). Yield: 0.06 g, 66% (based on Co). Mp: 162 °C dec. IR (KBr, cm⁻¹): 3363 (b), 3163(b), 2933 (s), 1631 (s), 1600 (s), 1543 (w), 1441 (s), 1381(s), 1315 (s), 1244 (s), 1219 (s), 1299 (w), 1242 (s), 1222 (s), 1170 (w), 1111 (s), 978 (s). ESI-MS (*m/z*, ion): 687.05, [C₂₄H₃₀Co₂N₃O₁₃ + H]. Anal. Calcd for C₂₄H₃₂Co₂N₃O₁₄: C, 40.92; H, 4.58; N, 5.97. Found: C, 40.31; H, 4.79; N, 5.80.

X-ray Crystallography. Crystal data and cell parameters for **1–3** are given in Table 1. Crystals suitable for single-crystal X-ray analyses were obtained by slow evaporation from the mother liquors of the reaction mixtures. The crystal data for **1–3** have been collected on a Bruker SMART CCD diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å). The program SMART^{11a} was used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT^{11a} for integration of the intensity of reflections and scaling, SADABS^{11b} for absorption correction, and SHELXTL^{11c,d} for space group and structure determination and least-squares refinements on F^2 . All structures were solved by direct methods using the program SHELXS-97^{11e} and refined by full-matrix least-squares methods against F^2 with SHELXL-97.^{11e} Hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The figures have been generated using Diamond 3.1e software.^{11f} All the complexes **1–3** crystallized in the monoclinic *Cc* space group. For complex **3**, the disordered nitrate group has been fixed by using isor, dfix, and flat commands.

RESULTS AND DISCUSSION

The ligand LH₄ reacts with CoX₂·*n*H₂O in a 1:1 stoichiometric ratio in the presence of tetra-*n*-butylammonium hydroxide to afford homometallic dinuclear mixed-valence complexes, [Co^{III}Co^{II}(LH₂)₂(X)(H₂O)](H₂O)_{*m*} (**1**, X = Cl and *m* = 4; **2**, X = Br and *m* = 4; **3**, X = NO₃ and *m* = 3) in good yields (Scheme 1; see the Experimental Section).

The molecular structures of **1–3** were confirmed by their single-crystal X-ray diffraction analyses. The X-ray crystallographic analysis reveals that **1–3** possess similar structural features. As a representative example, the structure of **3** is shown in Figure 1 and a full description of its structure is provided herein. The molecular structures of the other compounds are given in the Supporting Information (Figures S4 and S5). Selected bond parameters of **3** are given in Table 2; those of **1** and **2** are summarized in the Supporting Information (Tables S1 and S2).

The molecular structures of **1–3** reveal that the two metal ions are held together by two dianionic ligands, L²⁻ (Scheme 1; Figure 2). Both cobalt ions (Co1 (4O, 2N) and Co2 (5O, 1X)) are in a distorted-octahedral geometry (Table 2 and Tables S1 and S2). The deprotonated –CH₂O⁻ arms of each ligand (Figure 2, O3 and O8) function in a μ coordination mode to

Scheme 1. Synthesis of 1–3

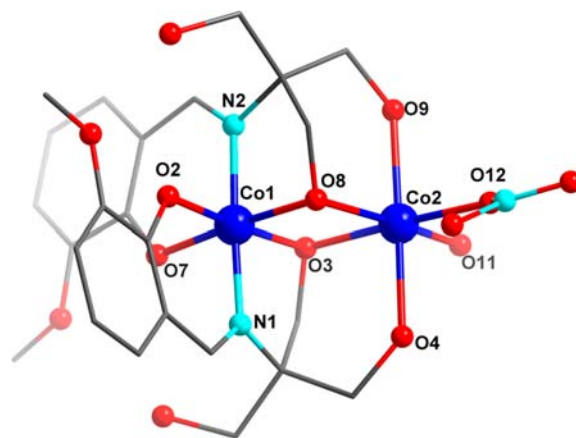
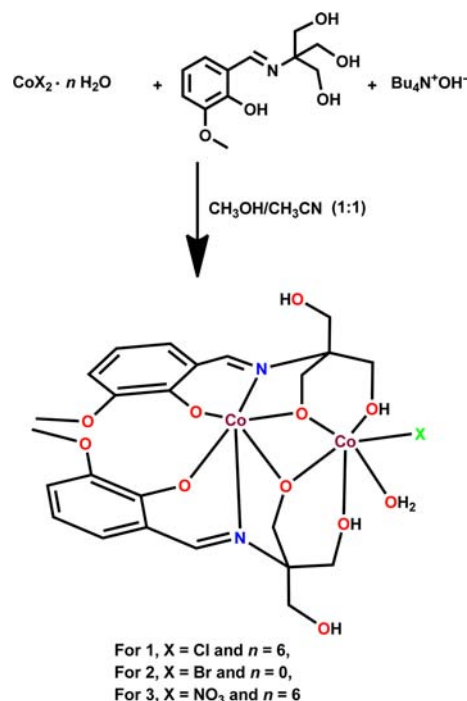

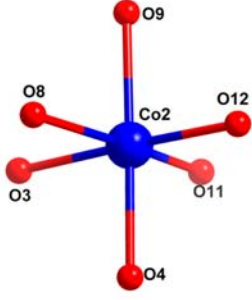


Figure 1. Molecular structure of **3** (hydrogen atoms and the noncoordinated solvent molecules have been omitted for clarity).

hold the two cobalt ions (Co1 and Co2), generating a four-membered ring. The other two –CH₂OH arms (O9 and O4) bind to Co2 in a *trans* apical manner. The fifth coordination site around Co2 is taken up by a water molecule (O11), while the sixth coordination site is occupied by a unidentate nitrate ligand (O12). In the case of **1** and **2** the sixth coordination site is taken up by a chloride and a bromide ligand, respectively (Supporting Information). The Co–O–Co bond angles in the four-membered ring of **3** are 97.7(2) and 99.3(2)°. These angles are very similar in the other two dinuclear cobalt complexes **1** and **2** (Supporting Information). The inter-Co–Co distance in **3** is 3.003(1) Å, which is very similar to the values found in **1** (3.022(7) Å) and **2** (3.022(2) Å).

In contrast to the all-oxygen coordination environment present around Co2, the coordination environment around Co1 consists of two *trans* apical imino nitrogen atoms (N1 and N2), the bridging oxygen atoms O8 and O3, and the two phenolate oxygens O2 and O7. The two Co–N bond lengths

Table 2. Bond Lengths (Å) and Angles (deg) Found in 3

	Bond Lengths/Å	Bond Angles/deg	
	N(1)-Co(1) 1.892(5)	O(2)-Co(1)-N(1)	96.15(19)
	N(2)-Co(1) 1.895(5)	O(2)-Co(1)-N(2)	85.99(19)
	O(2)-Co(1) 1.887(4)	N(1)-Co(1)-N(2)	177.2(2)
	O(3)-Co(1) 1.902(4)	O(2)-Co(1)-O(7)	91.93(19)
	O(7)-Co(1) 1.897(4)	N(1)-Co(1)-O(7)	85.62(19)
	O(8)-Co(1) 1.905(4)	N(2)-Co(1)-O(7)	96.07(19)
		O(2)-Co(1)-O(3)	176.07(19)
		N(1)-Co(1)-O(3)	86.39(19)
		N(2)-Co(1)-O(3)	91.38(19)
		O(7)-Co(1)-O(3)	91.25(17)
	O(3)-Co(2) 2.086(4)	O(12)-Co(2)-O(8)	104.32(18)
	O(4)-Co(2) 2.142(4)	O(12)-Co(2)-O(3)	177.85(19)
	O(8)-Co(2) 2.035(4)	O(8)-Co(2)-O(3)	77.63(16)
	O(9)-Co(2) 2.164(4)	O(12)-Co(2)-O(11)	91.40(19)
	O(11)-Co(2) 2.129(5)	O(8)-Co(2)-O(11)	163.36(17)
	O(12)-Co(2) 1.997(5)	O(3)-Co(2)-O(11)	86.74(17)
		O(12)-Co(2)-O(4)	91.08(18)
		O(8)-Co(2)-O(4)	93.32(17)
		O(3)-Co(2)-O(4)	87.89(16)
		O(11)-Co(2)-O(4)	91.75(17)
		O(12)-Co(2)-O(9)	90.33(18)
		O(8)-Co(2)-O(9)	86.77(16)
		O(3)-Co(2)-O(9)	90.68(17)
		O(11)-Co(2)-O(9)	87.76(17)
		O(4)-Co(2)-O(9)	178.51(18)

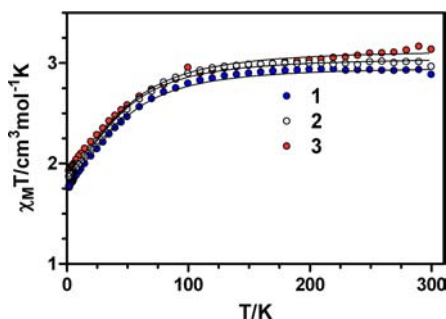


Figure 2. Temperature dependence of $\chi_M T$ for compounds 1–3. Solid lines represent the best fits with the Hamiltonian of eq 1.

(Co1–N1, 1.892(5) Å; Co1–N2, 1.895(5) Å) are comparable to the Co–O distances involving the phenolate oxygen atoms (Co1–O2, 1.887(4) Å; Co1–O7, 1.897(4) Å). In contrast, the Co–O distances involving the bridging oxygen atoms are slightly longer (Co1–O3, 1.902(4) Å; Co1–O8, 1.905(4) Å; Co2–O3, 2.086(4) Å; Co2–O8, 2.035(4) Å). The longest Co–O distances are those that involve the $-\text{CH}_2\text{OH}$ coordination (Co2–O9, 2.164(4) Å; Co2–O4, 2.142(4) Å) and the terminal water ligand (Co2–O11, 2.129(5) Å). Finally, the Co–O distance involving the unidentate nitrate ligand (Co2–O12, 1.997(5) Å) is comparable to the shorter Co–O bond distances found in these systems. It should be noted that Co–N and Co–O bond distances involving the Co^{3+} ion

(Co1) are within the range usually found for these distances in other Co^{3+} -containing complexes. As expected for its t_{2g}^6 electronic configuration, which allows the ligand donor atoms to be closer to the Co^{3+} ion, these distances are significantly shorter (~ 0.2 Å) than the analogous distances involving the Co^{2+} ion (Co2). We have also carried out bond valence sum (BVS) calculations¹² to assign the oxidation states of the two cobalt centers.¹³ The BVS values of 3.44/3.47/3.48 and 2.00/2.01/2.02 for the Co1 and Co2 centers, respectively, in complexes 1–3 support the assignment on the basis of bond lengths.

Magnetic Properties. Direct current magnetic susceptibility measurements were collected on powdered samples of compounds 1–3 in the 2–300 K temperature range under an applied magnetic field of 0.1 T and are given in Figure 2 and the Supporting Information, in the form $\chi_M T$ vs T . At 300 K, the $\chi_M T$ values for 1–3 are 2.89, 2.96, and 3.13 $\text{cm}^3 \text{mol}^{-1} \text{K}$, respectively. These values substantially exceed the spin-only value for high-spin cobalt(II) ($S = 3/2$, 1.875 $\text{cm}^3 \text{mol}^{-1} \text{K}$ with $g = 2$) but are close to the value expected when the spin momentum and the angular momentum exist independently (3.37 $\text{cm}^3 \text{mol}^{-1} \text{K}$). This is indicative of an unquenched orbital contribution of the Co^{2+} ion in a distorted-octahedral geometry. When the temperature is lowered, the $\chi_M T$ product first slowly decreases from room temperature to 100 K, and then the decrease becomes more pronounced to reach values of 1.77, 1.87, and 1.93 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 2 K. This behavior is due to the local anisotropy of the Co^{2+} ion promoted by the spin–

orbit coupling rather than to intermolecular interactions through the hydrogen-bond network.

The data could be analyzed through a Hamiltonian for a mononuclear model that takes into account spin–orbit coupling, axial distortion of the octahedral geometry, and Zeeman interactions:

$$\mathbf{H} = -\frac{3}{2}\kappa\lambda LS + \Delta(Lz^2 - \frac{2}{3}) + \beta[-\frac{3}{2}\kappa L + g_e S]H \quad (1)$$

where κ is the orbital reduction factor, λ is the spin–orbit coupling parameter, and Δ is the axial orbital splitting of the ${}^4T_{1g}$ term (see Figure S6 in the Supporting Information). The factor $-\frac{3}{2}$ comes from the fact that the real angular momentum for the ${}^4T_{1g}$ ground state in an ideal O_h geometry is equal to the angular momentum of the 4P free ion term multiplied by $-\frac{3}{2}$. Spin–orbit coupling and distortion were diagonalized together by solving the 12×12 secular matrix. The resulting Zeeman coefficients for the two directions parallel and perpendicular to the magnetic field were included in the van Vleck equation to obtain the expression for the average magnetic susceptibility.¹⁴ The fit of the experimental data to the theoretical equation shows that the sign of Δ cannot be unambiguously determined from the powder susceptibility data, as the agreement factor (R) for positive and negative Δ values for each compound are, in general, close. The best-fit parameters for both positive and negative Δ values were as follows: $\kappa = 0.93$, $\lambda = -89$, $\Delta = 339 \text{ cm}^{-1}$, $R = 8 \times 10^{-4}$ and $\kappa = 0.91$, $\lambda = -114$, $\Delta = -560 \text{ cm}^{-1}$, $R = 4.0 \times 10^{-5}$ for **1**; $\kappa = 0.87$, $\lambda = -83$, $\Delta = 231$, $R = 4 \times 10^{-3}$ and $\kappa = 0.87$, $\lambda = -103$, $\Delta = -394 \text{ cm}^{-1}$ and $R = 3.6 \times 10^{-5}$ for **2** and $\kappa = 0.95$, $\lambda = -113$, $\Delta = 547 \text{ cm}^{-1}$, $R = 1 \times 10^{-4}$ and $\kappa = 0.81$, $\lambda = -107$, $\Delta = -346 \text{ cm}^{-1}$, $R = 3 \times 10^{-5}$ for **3**. The fitting parameters are in good accordance with previously reported values for distorted-octahedral Co(II) complexes.¹⁵ The Δ values obtained for complexes **1–3** indicate low distortion of the octahedral geometry, in agreement with the high magnetic moment at room temperature. This is in good agreement with the calculation of the degree of distortion of the CoO_5X coordination polyhedron with respect to an ideal six-vertex polyhedra, by using the continuous shape measures theory and SHAPE software,¹⁶ which led to shape measures relative to the octahedron ($OC-6$) and trigonal prism ($TPR-6$) with values of 0.74, 1.07, and 1.43 for the former polyhedron and 15.28, 15.52 and 11.76, for the second polyhedron in complexes **1–3**, respectively. Therefore, the Co^{2+} coordination spheres are found in the $OC-6 \leftrightarrow TPR-6$ deformation pathway (deviating by less than 10% from this pathway) and are close to the octahedral geometry. These octahedral and trigonal-prismatic measures are compatible with the existence, in addition to the small Bailar distortion from $OC-6$ to $TPR-6$, of an elongated tetragonal distortion, because their square root sum (4.77, 4.62, and 4.97 for **1–3**, respectively) are higher than 4.6.¹⁷ This agrees well with the fact that the three compounds show a tetragonal elongation along the O–Co–O axis perpendicular to the $\text{Co}^{\text{III}}(\text{O})_2\text{Co}^{\text{II}}$ fragment. For such an elongation, Δ is positive and the triplet ${}^4T_{1g}$ ground term for the purely O_h symmetry splits into an orbital singlet ground state ${}^4A_{2g}$ and an orbital doublet excited state 4E_g , the energy gap between them being the axial splitting parameter, Δ (see Figure S6 in the Supporting Information). The ${}^4A_{2g}$ and 4E_g levels split by spin–orbit coupling, giving rise to two and four Kramers doublets, respectively. When Δ is large enough, only the two lowest Kramers doublets arising from the ${}^4A_{2g}$ state, Γ_6 ($M_s = \pm 1/2$)

and Γ_7 ($M_s = \pm 3/2$), are thermally populated and then the energy gap between them may be considered as a zero-field splitting (ZFS) within the quartet state. Such a ZFS can be described by the effective spin Hamiltonian

$$\mathbf{H} = D[Sz^2 - S(S + 1)/3] + E(Sx^2 - Sy^2) + g_e\mu_B SH \quad (2)$$

where S is the spin ground state, D and E are the axial and transverse magnetic anisotropies, respectively, g_e is the average g factor, μ_B is the Bohr magneton, and H is the magnetic field. Using this Hamiltonian, the energy gap between Γ_6 and Γ_7 is $2D$ if $E = 0$.

Variable-temperature magnetization data were collected between 2 and 7 K at applied fields ranging from 0.5 to 5 T (Figures 3–5). The M vs H data at 2 K for **1–3** show that at

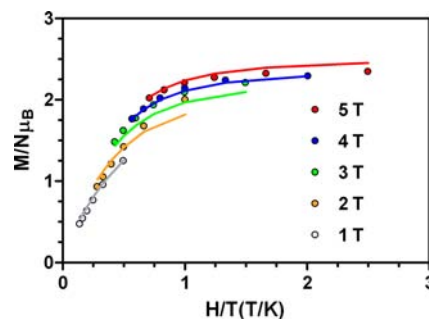


Figure 3. M vs H/T plots for **1**. Solid lines are the best fit for a ground state $S = \frac{3}{2}$ with $D = -7.3 \text{ cm}^{-1}$. The agreement factor R is 1.1×10^{-5} .

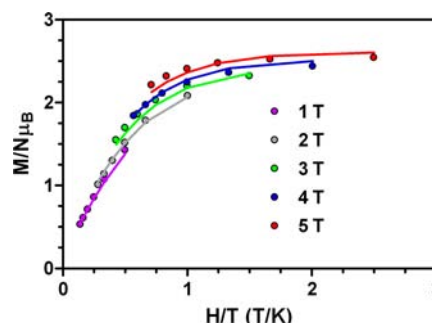


Figure 4. M vs H/T plots for **2**. Solid lines are the best fit for a ground state $S = \frac{3}{2}$ with $D = -9.7 \text{ cm}^{-1}$. The agreement factor R is 1.4×10^{-5} .

The magnetization is not fully saturated, reaching values of 2.34, 2.44, and 2.33 μ_B for complexes **1–3**, respectively. The M

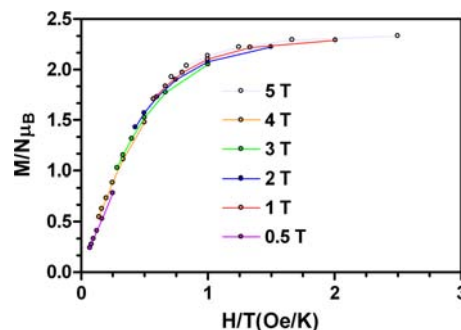


Figure 5. M vs H/T plots for **3**. Solid lines are guides for the eye.

vs H/T plots for **1** and **2** are not superimposed on a single master curve, clearly indicating the presence of a significant magnetic anisotropy in both complexes. Moreover, the anisotropy of **1** seems to be smaller than that of **2**. At variance, complex **3** shows comparatively a smaller anisotropy, as the M vs H data are almost superimposed on a single master curve.

The CoO_6 coordination polyhedron in **3** exhibits a larger distortion from the $OC-6$ geometry than do compounds **1** and **2**, as indicated by the values of the continuous shape measures and the Δ parameter extracted from the fit of the susceptibility data with the Hamiltonian of eq 1. As the zero-field splitting of the 4A_2 term (see Figure S6 in the Supporting Information) is promoted by a second-order spin-orbit coupling, D should decrease when Δ increases. Therefore, the smaller magnetic anisotropy, D , observed for **3** with regard to those found for **1** and **2** is not unexpected.

In order to determine the sign and magnitude of the magnetic anisotropy, the field dependence of the magnetization data at different temperatures was modeled according to the Hamiltonian (2). The best-fit parameters with $S = 3/2$ were $D_{3/2} = -7.4 \text{ cm}^{-1}$, $|E/D| < 1 \times 10^{-3}$, and $g = 2.32$ for **1** and $D_{3/2} = -9.7 \text{ cm}^{-1}$, $|E/D| < 1.10^{-4}$, and $g = 2.52$ for **2**. Because D is negative, the Γ_7 Kramers doublet ($M_s = \pm 3/2$) is below the Γ_6 ($M_s = \pm 1/2$) Kramers doublet. It should be noted that all attempts to extract the value of D from the M vs H/T data for **3** were unsuccessful.

In spite of the different magnetic anisotropy between compounds **1** and **2** and compound **3**, all of them exhibit very similar $\chi_M T$ vs T plots. This could be due to the fact that for Δ values in the range $200\text{--}500 \text{ cm}^{-1}$, as in the case of compounds **1–3**, the effect of D values between 0 and -10 cm^{-1} on the shape of the curve is only operative at very low temperature (typically below 10 K). Moreover, the magnitude of this effect is small and, therefore, it is not easily detected.

The large and negative zero-field splitting D parameter for compounds **1** and **2** indicate the existence of an important uniaxial anisotropy and therefore the possibility of slow magnetic relaxation. This fact prompted us to carry out an ac dynamic susceptibility study to find if compounds **1** and **2** exhibit SMM behavior. Under zero applied dc field at frequencies between 1 and 1500 Hz , no out-of-phase susceptibility signal (χ_M'') was observed. This somewhat unexpected result can be attributed to the existence of a fast resonant zero-field quantum tunneling of the magnetization (QTM) through the thermal relaxation barrier between the degenerate ground $\pm 3/2$ levels, which dominates on other relaxation pathways in the absence of an applied field. For a noninteger spin system with $D < 0$, such as **1** and **2**, transverse anisotropy cannot promote the quantum tunneling process through mixing of the wave functions corresponding to the $\pm M_s$ levels due to parity effects;⁹ therefore, the QTM is most likely due to hyperfine and dipolar mediated relaxation processes.¹ The application of a magnetic field of 1000 Oe (this field was chosen because it induces the slower relaxation) during the ac measurement splits the energy of the $\pm M_s$ Kramers doublets, and then the quantum tunneling is not an easy relaxation pathway. Consequently, the QTM is partly or fully suppressed, the relaxation dynamic is slowed down and a frequency dependent out-of-phase signal can be observed for complexes **1** and **2** (see Figure 6 and Figures S7 and S8 in the Supporting Information). As expected, compound **3** shows no slow relaxation under an applied field of 1000 Oe , which is most likely a direct consequence of the comparatively very

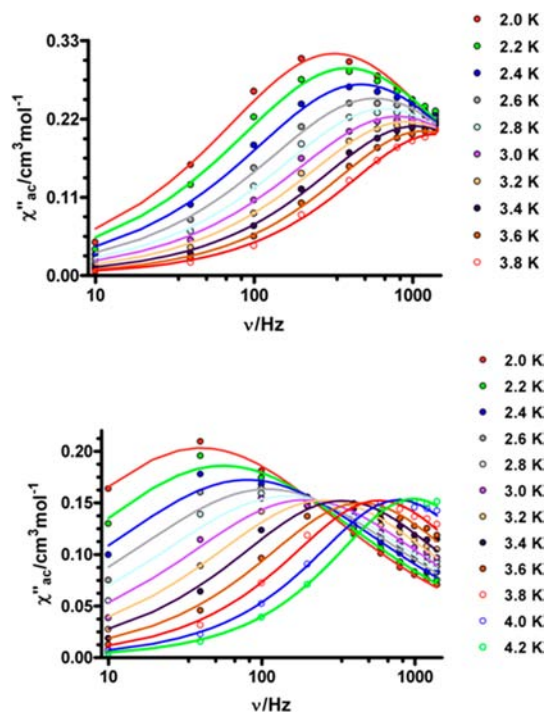


Figure 6. Variable-temperature frequency dependence of the χ_M'' signal for **1** (top) and **2** (bottom) in a 1000 Oe dc field. Solid lines represent the best fit to the Cole–Cole equation.

small anisotropy observed for this compound. The Cole–Cole diagrams in the temperature range $2\text{--}3.8 \text{ K}$ for **1** and $2\text{--}4 \text{ K}$ for **2** (Figures S9 and S10 in the Supporting Information) exhibit semicircular shapes. The fit of the χ_M'' vs χ_M' data at each temperature using the generalized Debye mode (see equation S1 in the Supporting Information) yielded the values of χ_0 (isothermal susceptibility), χ_S (adiabatic susceptibility), and α (this parameter determines the width of the distribution of relaxation times, so that $\alpha = 1$ corresponds to an infinitely wide distribution of relaxation times, whereas $\alpha = 0$ represents a relaxation with a single time constant). The α values are found within the ranges $0.03\text{--}0.22$ and $0.07\text{--}0.40$ for **1** and **2**, respectively, suggesting multiple relaxation processes and the presence of a non-negligible remaining QTM relaxation. As the temperature is increased, the QTM process moves beyond the high-frequency range of the magnetometer ($<1500 \text{ Hz}$) and, as expected, at 4 K only a well-defined semicircle due to the thermally activated process can be observed. The set of χ_0 , χ_S , and α obtained in the above fits were further used to fit the frequency dependence of χ_M'' at each temperature to the Cole–Cole equation (see equation S2 in the Supporting Information), which permits the relaxation time τ to be extracted.

The temperature dependence of the magnetic relaxation times, τ , for **1** and **2** were used in constructing the Arrhenius plots (Figure 7).

The fits of the linear portion of the data (high-temperature regime of the relaxation where it is thermally induced, between 3 and 3.8 K for **1** and between 4.2 and 3.4 K for **2**) afforded the following effective energy barriers for the reversal of the magnetization: 7.9 cm^{-1} ($\tau_0 = 6.1 \times 10^{-6} \text{ s}$) for **1** and 14.5 cm^{-1} ($\tau_0 = 1.0 \times 10^{-6} \text{ s}$) for **2**. The τ_0 values observed for **1** and **2** are at the higher end of the experimental range found for SMMs¹⁸ and are similar to those found for other Co^{2+} SIMs.^{8b,c} This

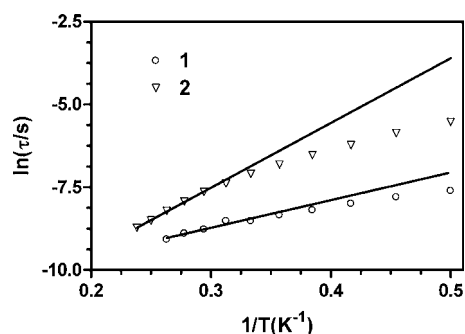


Figure 7. Arrhenius plots of relaxation times for **1** and **2**. The solid lines correspond to the best fit to the highest temperature data.

observation, together with the low-temperature curvature of the relaxation times (Figure 7), strongly suggests that the quantum pathway of relaxation at very low temperatures is not fully suppressed by the effects of the applied field (1000 Oe). This fact could be due to the presence of strong enough intermolecular interactions in **1** and **2** as to persist even after eliminating the nearest neighboring spins by the action of the applied dc field. The energy barriers for the flipping of the magnetization in **1** and **2** are in general lower but similar to those observed for the other four examples of reported cobalt(II) SIMs.^{8a–c} The thermally activated relaxation process observed at the high-temperature regime indicates that the spin system follows an Orbach relaxation pathway¹⁹ through the excited $M_s = \pm 1/2$ levels (also named thermally assisted quantum tunneling of the magnetization). Thus, the system is excited to the $M_s = \pm 1/2$ level by absorption of phonons from the lattice followed by an emission of phonons to reach the $M_s = \pm 3/2$ ground state.⁷ As indicated above, the energy gap between the $M_s = \pm 1/2$ and $M_s = \pm 3/2$ levels is $2D$. Using the D values derived from the magnetization data, U values of 14.8 and 19.4 cm^{-1} are predicted for **1** and **2**, respectively. As usual, these estimated values are larger than the U_{eff} values, determined through ac susceptibility measurements, of 7.9 and 14.5 cm^{-1} for **1** and **2**, respectively, which is most likely due to the existence of a significant quantum pathway of relaxation at very low temperature that, as indicated elsewhere, is not fully suppressed by the dc field. In fact, the temperature dependence of the out-of-phase ac magnetic susceptibility (χ''_M) at different frequencies (Figures S7 and S8 in the Supporting Information) shows that the signals do not go to zero below the maxima at low temperature, which is a clear indication of the non-negligible presence of QTM.

An alternative explanation of the relatively high τ_0 values found for **1** and **2**, as well as of the curvature at low temperature of the relaxation time vs $1/T$ plot for these compounds, would be to consider the existence of direct and Raman spin–lattice relaxation processes. The spin–lattice relaxation time can be expressed as: $\tau^{-1} = AT + BT^n + C \exp(-\Delta/\kappa_B T)$.²⁰ The first term corresponds to the single-phonon direct process, the second to the Raman process, and the third to the Orbach process. For Kramers ions $n = 9$, but when optical and acoustic phonons are considered, n values between 1 and 6 are reasonable.²¹ The relaxation times for **1** and **2** can be fitted to T^{-n} with $n = 2.22$ and 4.31 for **1** and **2**, respectively (see Figure S11 in the Supporting Information), but the $\ln \tau$ vs $\ln T$ plot for the latter exhibits some degree of curvature. These results would suggest that the single-phonon direct process and the Raman process could be dominant. However, the fact that the

thermal energy barriers for **1** and **2** follow the same order as the D values extracted from the variable-temperature variable field magnetization data and the fact that compound **3** with comparatively very small anisotropy does not exhibit slow relaxation of the magnetization support that the observed relaxation is of a thermally activated type rather than of direct and Raman-like types.

CONCLUSION

We have reported the syntheses, crystal structures, and magnetic properties of a new family of Co(III)–Co(II) dinuclear mixed-valence complexes of general formula $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\text{LH}_2)_2(\text{X})(\text{H}_2\text{O})](\text{H}_2\text{O})_m$ (**1**, X = Cl and $m = 4$; **2**, X = Br and $m = 4$; **3**, X = NO_3 and $m = 3$). Although compounds **1** and **2** have negative D values of -7.4 and -9.7 cm^{-1} , respectively, and thereby significant uniaxial anisotropy, they do not exhibit slow relaxation of the magnetization and SMM behavior at zero magnetic field above 2 K. This somewhat unexpected behavior is due to the fast quantum tunneling of the magnetization (QTM), the dominant relaxation pathway at zero field. However, in the presence of a small magnetic field, the QTM relaxation pathway is partially suppressed, the relaxation of the magnetization is slowed down, and compounds **1** and **2** show SMM behavior. As expected, compound **3** with comparatively little magnetic anisotropy shows no slow relaxation of the magnetization. These results support that the height of the energy barrier in these Co^{3+} – Co^{2+} dinuclear mixed-valence complexes depends on the magnetic anisotropy D . It should be noted that complexes **1** and **2** represent the first examples of Co^{2+} – Co^{3+} mixed-valence systems that exhibit SMM behavior. The predicted energy barriers for the flipping of the magnetization, $U = 2D$, for **1** and **2** of 14.6 and 19.4 cm^{-1} respectively, are larger than the U_{eff} values determined through ac susceptibility measurements, of 7.9 and 14.5 cm^{-1} , respectively. This fact is most likely due to the existence of a significant quantum pathway of relaxation at very low temperature that is not fully suppressed by the dc field.

We feel that, in addition to the distortion of the octahedral geometry of the Co^{2+} ion that fine-tunes the magnitude of D , the existence of a diamagnetic Co(III) ion linked to the Co(II) ions mitigates the intermolecular interactions between the Co^{2+} ions, thus diminishing the QTM process and favoring the observation of slow relaxation of the magnetization in these “mononuclear” Co^{2+} complexes. In fact, intermolecular hydrogen bonds do not directly involve atoms coordinated or close to a pair of Co^{2+} sites but to one Co^{2+} atom and one Co^{3+} atom. Nevertheless, more examples of these kinds of compounds with different coordination spheres, geometries, and ligand fields are needed to support our intuitive feeling. Work along this line is in progress in our laboratories.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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DEDICATION

[†]This work celebrates 100 years of Chemistry at the University of Granada.

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