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Article

Study of the Influence of the Bridge on the Magnetic Coupling in Cobalt(II) Complexes

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Two new cobalt(II) complexes of formula $[Co_2(bta)(H_2O)_6]_n \cdot 2nH_2O$ (**1**) and $[Co(phda)(H_2O)]_n \cdot nH_2O$ (**2**) [H_4bta = 1,2,4,5-benzenetetracarboxylic acid, H_2phda = 1,4-phenylenediacetic acid] have been characterized by single crystal X-ray diffraction. Compound **1** is a one-dimensional compound where the bta^{4-} ligand acts as 2-fold connector between the cobalt(II) ions through two carboxylate groups in *para*-conformation. Triply bridged dicobalt(II) units occur within each chain, a water molecule, a carboxylate group in the *syn-syn* conformation, and an oxo-carboxylate with the $\mu_2 O(1);\kappa^2 O(1),O(2)$ coordination mode acting as bridges. Compound **2** is a three-dimensional compound, where the phda^{2-} group acts as a bridge through its two carboxylate groups, one of them adopting the μ-*O,O′* coordination mode in the *syn-syn* conformation and the other exhibiting the single μ_2-O″ bridging mode. As in **1**, chains of cobalt(II) ions occur in **2** with a water molecule, a *syn-syn* carboxylate group, and an oxo-carboxylate constitute the triply intrachain bridging skeleton. Each chain is linked to other four ones through the phda^{2-} ligand, giving rise to the three-dimensional structure. The values of the intrachain cobalt−cobalt separation are 3.1691(4) (**1**) and 3.11499(2) Å (**2**) whereas those across the phenyl ring of the extended bta^{4-} (**1**) and phda^{2-} (**2**) groups are 10.1120(6) and 11.4805(69 Å, respectively. The magnetic properties of **1** and **2** have been investigated in the temperature range 1.9−300 K, and their analysis has revealed the occurrence of moderate intrachain ferromagnetic couplings [$J = +5.4$ (**1**) and $+2.16$ cm^{-1} (**2**), J being the isotropic magnetic coupling parameter], the magnetic coupling through the extended bta^{4-} and phda^{2-} with cobalt−cobalt separations larger than 10 Å being negligible. The nature and magnitude of the magnetic interactions between the high-spin cobalt(II) ions in **1** and **2** are compared to those of related systems and discussed as a function of the complementarity-countercomplementarity effects of the triple bridges.

Introduction

Cobalt(II) compounds are very popular among magnetochemists, as shown in a very recent review on magnetic metal-organic frameworks (MOFs).[1] Apart from the variety of colors that they exhibit, the most common ones being pale pink under octahedral coordination to deep blue for tetrahedral coordination, the strong magnetic anisotropy which characterizes the high-spin cobalt(II) ions is at the origin of the increasing interest in the polynuclear compounds containing this metal ion.[2] In that respect, several examples of high-nuclearity compounds with six-coordinated cobalt(II) ions behaving as single molecule magnets (SMMs)[3] and single

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chain magnets (SCMs)[4] (systems that exhibit slow relaxation of the magnetization, the energy barrier responsible for it arising from the existence of an easy-axis, Ising-type magnetic anisotropy) have been reported by different research teams.

Among the different bridging ligands explored, the carboxylate group seems very appealing because of the different conformations that it can adopt (*syn-syn*, *anti-syn*, and *anti-anti*) and its ability to mediate ferro- or antiferromagnetic interactions between the paramagnetic centers that it links, as well illustrated by the thoroughly investigated carboxylate-bridged copper(II) complexes.[5] In the case of complexes with carboxylate-bridged high-spin cobalt(II) ions ($t_{2g}^5e_g^2$ electronic configuration in O_h symmetry), a few magneto-structurally characterized examples are known where weak antiferromagnetic interactions across the *syn-syn* conformation[6] and either ferro- or antiferromagnetic interactions through the *anti-anti*[7] and *anti-syn*[8] conformations occur. This versatility as a ligand of the carboxylate group has oriented the use of ligands of polycarboxylic acids with aromatic rings to build extended frameworks because of their potential applications to gas storage, heterogeneous catalysis, and magnetic materials.[9] It deserves to be noted that these works have usually focused on rigid polycarboxylate ligands, such as the deprotonated forms of the 1,4-benzenedicarboxylic[10] and 1,2,4-benzenetricarboxylic[11] acids. The use of more flexible aromatic polycarboxylic acids, 1,4-phenylenediacetic acid (H_2phda) for instance, as ligands toward transition metals is not so extended[12] and the first example of MOF resulting from the assembly of cobalt(II) ions by H_4phda is provided herein (see below).

In the context of our work based on carboxylate-bridged cobalt(II) coordination networks[8c,13] and aiming at comparing the magneto-structural effects of rigid and flexible polycarboxylate ligands, we have prepared two new compounds of formula $[Co_2(bta)(H_2O)_6]_n\cdot 2nH_2O$ (**1**) (H_4bta = 1,2,4,5-benzenetetracarboxylic acid) and $[Co(phda)(H_2O)]_n\cdot nH_2O$) (**2**) where a water molecule (**1** and **2**), a carboxylate group in the *anti-syn* (**1**)/*syn-syn* (**2**) conformation and an oxo-carboxylate with the $\mu_2O(1);\kappa^2O(1),O(2)$ (**1**)/μ_2-O″ (**2**) coordination mode constitute the triple bridging units that mediate significant ferromagnetic interactions between the high-spin cobalt(II) ions. They are quite unusual triple bridging cores in polynuclear cobalt(II) complexes, the two structurally characterized closer examples being the chain $[Co(CH_3COO)_2(H_2O)]_n$. nH_2O[14] and the dodecanuclear wheel compound $[Co_{12}(chp)_{12}(CH_3COO)_{12}(H_2O)_6(thf)_6]$[15] (chp = 6-chloro-2-pyridonate and thf = tetrahydrofurane). As far as we are aware, the magnetic properties of the former compound were not investigated where the latter one exhibits a ferromagnetic behavior. Herein, we focus on the synthesis, structural characterization, and magnetic study of the compounds **1** and **2**, with special attention being paid to the complementarity-countercomplementarity of the bridges regarding the magnetic coupling observed.

Experimental Section

Materials. Reagents and solvents used in the syntheses were purchased from commercial sources and used without further purification. Elemental analyses (C, H, N) were performed with an EA 1108 CHNS/0 automatic analyzer. Single crystals of **1** and **2** were obtained by hydrothermal methods (see details below).

Preparation of the Compounds. $\mathbf{[Co_2(bta)(H_2O)_6]_n\cdot 2nH_2O}$ **(1).** The pH of an aqueous solution (20 mL) of H_4bta (0.12 g, 0.5 mmol) was adjusted to 5.0 by dropwise addition of an aqueous solution of NaOH 0.1 M. Cobalt(II) chloride hexahydrate (0.119 g, 0.5 mmol) dissolved in a minimum amount of water was added to the previous solution. The resulting mixture was sealed in a 45 mL stainless-steel reactor with a teflon liner, and it was heated at 70 °C for 96 h. After cooling, X-ray quality

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crystals of **1** as red-purple prisms were obtained. They were collected by hand, washed with a minimum amount of water, and dried over filter paper. Yield about 78%, Anal. Calcd. for $C_{10}H_{18}Co_2O_{16}$ (**2**): C, 23.46; H, 3.52. Found: C, 23.40; H, 3.49%.

$[Co(phda)(H_2O)]_n \cdot nH_2O$ (2). Sodium carbonate (0.1 g, 1 mmol) dissolved in distilled water (ca. 5 mL) was added to an aqueous solution (20 mL) of H_2phda (0.097 g, 0.5 mmol). An aqueous solution of cobalt(II) chloride hexahydrate (0.238 g, 1 mmol), dissolved in a minimum amount of water, was added to the previous solution was under vigorous stirring at room temperature. The resulting mixture was sealed in a 45 mL stainless-steel reactor with a telflon linear, and it was heated at 120 °C for 48 h. After cooling, X-ray quality crystals of **2** as pink squares suitable were obtained. They were collected by hand, washed with a small amount of water, and dried over filter paper. Yield about 85%, Anal. Calcd. for $C_{10}H_{12}CoO_6$ (**2**): C, 41.85; H, 4.18. Found: C, 41.91; H, 4.22%.

Physical Techniques. Infrared spectra were performed with a ThermoNicolet Avatar 360 FT-IR spectrometer on samples prepared as KBr pellets. Magnetic susceptibility measurements on polycrystalline samples of **1** and **2** were performed in a Quantum Design SQUID magnetometer in the temperature range 1.9−300 K operating at 0.5 T ($50 < T \leq 300$ K) and 250 G ($T \leq 50$ K). Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants[16] being -227×10^{-6} (**1**) and -139×10^{-6} cm^3 mol^{-1} (**2**) [per two (**1**) and one (**2**) mol of Co(II) ions]. The values of the experimental magnetic susceptibility were also corrected for the magnetization of the sample holder.

Crystallographic Data Collection and Structure Determination. Single crystal X-ray diffraction data for **1** and **2** were collected at 293(2) (**1** and **2**) and 100(2) K (**2**) on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo−K$_\alpha$ radiation (λ = 0.71073 Å). Data were indexed, integrated, and scaled using EVALCCD.[17] The structures of **1** and **2** were solved by direct methods using the SHELXS97 computational program.[18] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares technique based on F^2 by using SHELXL97. The hydrogen atoms of the organic ligands bta^{4-} (**1**) and phda^{2-} (**2**) were positioned geometrically and included in the structure-factor calculation. The hydrogen atoms of all the water molecules in **1** and those of the coordinated water molecule in **2** were located from difference Fourier maps and refined with isotropic temperature factors. Because of the short distance between two peaks in the Fourier map corresponding to solvent molecules, the crystallization water molecules [O(2w) and O(3w)] in **2** were refined with a shared occupation factor 0.754(6)/0.246(6), for O(2w) and O(3w), respectively.

The final geometrical calculations and the graphical manipulations were carried out with PARST97,[19] PLATON,[20] and DIAMOND[21] programs. A summary of the crystallographic data and refinement conditions for **1** and **2** is given in Table 1 whereas selected bond lengths and angles are listed in Tables 2 (**1**) and 3 (**2**). Crystallographic data (excluding structure factors) for the structures of **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers 748199 and 748200, respectively.

Table 1. Crystal Data and Details of the Structure Determination for Complexes **1** and **2**

compound	**1**	**2**
formula	$C_{10}H_{18}Co_2O_{16}$	$C_{10}H_{12}CoO_6$
M	512.10	287.12
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a, Å	6.7788(4)	24.3088(5)
b, Å	8.0678(5)	7.6438(5)
c, Å	16.6512(9)	11.7779(5)
α, deg	102.104(6)	
β, deg	92.022(5)	111.780(5)
γ, deg	93.513(6)	
V, Å^3	887.65(9)	2032.3(2)
Z	2	8
index ranges	$-8 < h < 8$	$-28 < h < 31$
	$-10 < k < 10$	$-9 < k < 9$
	$-21 < l < 21$	$-15 < l < 14$
T (K)	293(2)	293(2)/100(2)
ρ_{calc} (Mg m^{-3})	1.916	1.870
λ (Mo−K$_\alpha$, Å)	0.71073	0.71073
μ (Mo−K$_\alpha$, mm^{-1})	1.953	1.703
R_1, $I > 2\sigma(I)$ (all)	0.0193 (0.0244)	0.0265 (0.0337)
wR_2, $I > 2\sigma(I)$ (all)	0.0426 (0.0444)	0.0601 (0.0628)
measured reflections	29035	11457
independent reflections (R_{int})	4016 (0.023)	2295 (0.025)
crystal size	0.21 × 0.2 × 0.08	0.2 × 0.2 × 0.10

Results and Discussion

Description of the Structures. $[Co_2(bta)(H_2O)_6]_n \cdot 2nH_2O$ (1). The structure of **1** consists of uniform chains of $[Co(1)Co(2)(H_2O)_6(bta)]$ dinuclear units which run parallel to the [01−1] direction. The fully deprotonated bta^{4-} anion acts as a 2-fold connector through four oxygen atoms from two carboxylate groups in 1,4 positions and the $[Co_2(H_2O)_6]^{4+}$ cationic units behave as 2-fold nodes (Figure 1). The chains are held together by a complex hydrogen bonding pattern affording a 3D framework (see end of Table 2), all water molecules acting as donors whereas some of the carboxylate-oxygens [O(1), O(2), O(4), O(6), O(7), and O(8)] and the crystallization water molecules [O(7w) and O(8w)] are the acceptors (Figure 2).

Two crystallographically independent cobalt(II) ions [Co(1) and Co(2)] occur in **1**. Both cobalt atoms are six-coordinated in somewhat distorted CoO_6 octahedral surroundings. The environment at the Co(1) atom is defined by three water molecules [O(1w), O(2w), and O(3w)] and three carboxylate-oxygen atoms [O(3), O(4), and O(6)], while that Co(2) is constituted by four water molecules [O(3w), O(4w), O(5w), and O(6w)] and two carboxylate-oxygens [O(3) and O(5)]. The values of the Co−O bond length vary in the ranges 2.0419(12) to 2.2001(10) Å [at Co(1)] and 2.0072(11) to 2.2506(10) Å [at Co(2)]. The two cobalt(II) ions in **1** are grouped by pairs, the bridges within each pair being a water molecule, a *syn-syn* carboxylate group, and an oxo-carboxylate with the $\mu_2O;\kappa^2O,O'$ coordination mode (Figure 1). The values of the Co(1)−O−Co(2) angle for the μ-aqua and μ-oxo are 93.89(4)° and 92.16(4)°, respectively, and the Co(1)···Co(2) distance is 3.1691(4) Å. This last value is much smaller than the shortest metal−metal separation though the *trans*-bta^{4-} carboxylate groups [10.1120(6) Å for Co(1)···Co(2)$^{h-1}$; (h-1) = $1 - x, -y, 2 - z$] and the shortest interchain metal−metal distance [5.8473(4) Å for Co(1)···Co(2)$^{g-1}$; (g-1) = $x, y-1, z$].

The two crystallographically independent tetracarboxylate bta^{4-} ligands in **1** [bta(1) and bta(2) corresponding

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Co(1)−O(1W)	2.0319(12)	Co(2)−O(3)	2.1478(10)
Co(1)−O(2W)	2.0072(11)	Co(2)−O(3W)	2.2001(10)
Co(1)−O(3)	2.2506(9)	Co(2)−O(4W)	2.0419(12)
Co(1)−O(3W)	2.1365(11)	Co(2)−O(5)	2.0446(11)
Co(1)−O(4)	2.1287(11)	Co(2)−O(5W)	2.0805(11)
Co(1)−O(6)	2.0449(11)	Co(2)−O(6W)	2.0438(12)
O(3)−Co(1)−O(1W)	92.93(4)	O(3)−Co(2)−O(5)	90.16(4)
O(3)−Co(1)−O(2W)	159.65(4)	O(3)−Co(2)−O(5W)	96.75(4)
O(3)−Co(1)−O(3W)	78.74(4)	O(3)−Co(2)−O(6W)	89.30(4)
O(3)−Co(1)−O(4)	60.02(4)	O(3)−Co(2)−O(4W)	167.24(4)
O(3)−Co(1)−O(6)	105.86(4)	O(3)−Co(2)−O(3W)	79.63(4)
O(4)−Co(1)−O(1W)	87.20(4)	O(5)−Co(2)−O(5W)	88.53(4)
O(4)−Co(1)−O(3W)	91.37(4)	O(5)−Co(2)−O(3W)	91.62(4)
O(6)−Co(1)−O(1W)	91.55(4)	O(5W)−Co(2)−O(3W)	176.38(4)

Hydrogen Bonds[b]

D−H···A	*d*(D···A)(Å)	*d*(H···A)(Å)	<(D−H···A)/(deg)
O(1W)−H(1Wa)···O(8W)	2.786(2)	2.02(3)	174(3)
O(1W)−H(1 Wb)···O(7W)$^{a-1}$	2.719(2)	1.93(2)	176(2)
O(2W)−H(2Wa)···O(8)$^{b-1}$	2.697(2)	1.96(3)	173(3)
O(2W)−H(2 Wb)···O(7W)	2.650(2)	1.84(2)	175(2)
O(3W)−H(3Wa)···O(7)$^{c-1}$	2.658(2)	1.82(2)	173(2)
O(3W)−H(3 Wb)···O(2)$^{c-1}$	2.612(2)	1.80(2)	176(2)
O(4W)−H(4Wa)···O(8)$^{c-1}$	2.688(2)	1.87(2)	168(2)
O(4W)−H(4 Wb)···O(4)$^{d-1}$	2.689(2)	1.93(3)	164(3)
O(5W)−H(5Wa)···O(8W)$^{d-1}$	2.787(2)	1.99(2)	173(2)
O(6W)−H(6Wa)···O(1)$^{c-1}$	2.713(2)	1.93(3)	173(3)
O(6W)−H(6 Wb)···O(1)$^{e-1}$	2.780(1)	2.06(2)	155(2)
O(7W)−H(7Wa)···O(6)$^{f-1}$	2.734(1)	1.96(2)	170(3)
O(7W)−H(7 Wb)···O(7)$^{c-1}$	2.681(1)	1.96(2)	155(3)
O(8W)−H(8Wa)···O(8)$^{g-1}$	2.898(2)	2.14(2)	168(2)
O(8W)−H(8 Wb)···O(2)	2.729(1)	1.93(2)	168(3)

[a] Symmetry code: (a-1) = x+1,+y,+z; (b-1) = x − 1,+y − 1,+z; (c-1) = x − 1,+y,+z; (d-1) = x,+y+1,+z; (e-1) = −x+1,−y+1,−z+2; (f-1) = −x,−y,−z+1; (g-1) = x, y − 1, z. [b] D = donor and A = acceptor.

Table 3. Selected Bond lengths (Å) and Angles (deg) for **2**[a]

Co(1)−O(1)$^{a-2}$	2.0319(13)	Co(2)−O(1W)$^{c-2}$	2.1440(20)
Co(1)−O(1w)	2.2122(15)	Co(2)−O(2)$^{c-2}$	2.0813(14)
Co(1)−O(3)$^{b-2}$	2.0948(15)	Co(2)−O(3)	2.0500(11)
O(1)−Co(1)−O(1^{a-2}	86.18(5)	O(1w)−Co(1)−O(1w)$^{e-2}$	175.65(4)
O(1)−Co(1)−O(1w)	89.58(5)	O(3)−Co(2)−O(1w)$^{c-2}$	81.24(5)
O(1)−Co(1)−O(3)$^{b-2}$	94.26(5)	O(3)−Co(2)−O(2)$^{c-2}$	90.09(5)
O(1)−Co(1)−O(3)$^{d-2}$	100.43(5)	O(1w)$^{c-2}$−Co(2)−O(2) $^{c-2}$	88.83(5)
Intermolecular Contacts			
O(2w)···O(1)$^{g-2}$	2.919(3)	O(3w)···O(2)$^{h-2}$	2.718(3)
O(3w)···O(1)$^{g-2}$	2.885(9)	O(3w)···O(1)$^{i-2}$	2.783(9)
O(2w)···O(2)$^{h-2}$	2.719(14)		

Hydrogen Bonds[b]

D−H···A	*d*(D···A)(Å)	*d*(H···A)(Å)	<(D−H···A)/(deg)
O(1W)−H(1wb)···O(2w)	2.594(3)	1.75(3)	163(3)
O(1W)−H(1wb)···O(3w)	2.650(9)	1.82(3)	160(3)
O(1W)−H(1wa)···O(4)$^{c-2}$	2.618(2)	1.91(3)	163(4)
O(1W)−H(1wb)···O(3w)$^{f-2}$	2.832(10)	2.16(3)	134(3)

[a] Symmetry code: (a-2) = −x+1, y,−z+3/2; (b-2) = −x+1/2,−y+1/2,−z+1; (c-2) =−x+1/2, y−1/2, −z+1/2; (d-2) = 1/2−x, 1/2−y, 2−z; (e-2) = −x, y, 3/2−z; (f-2) = −x+1, y,−z+3/2; (g-2) = x, y−1,z; (h-2) = x,−y, z+1/2; (i-2) = −x+1, y−1,−z+3/2. [b] D = donor and A = acceptor.

to the O(1)O(2)O(3)O(4)C(1)C(2)C(3)C(4)C(5) and O(5)-O(6)O(7)O(8)C(6)C(7)C(8)C(9)C(10) sets of atoms, respectively] are generated by an inversion center located at the middle point of the aromatic rings. Both bta(1) and bta(2) use two carboxylate groups in *trans* position to coordinate the cobalt atoms but through different coordination modes: bta(2) acts as a tetrakis-monodentate ligand [from O(5) and O(6) toward Co(2) and Co(1), respectively, and the atoms related by the inversion center] whereas bta(1) adopts the $\mu_2 O;\kappa^2 OO'$ coordination mode [bidentate through O(3) and O(4) toward Co(1) and monodentate across O(3) towards Co(2), and

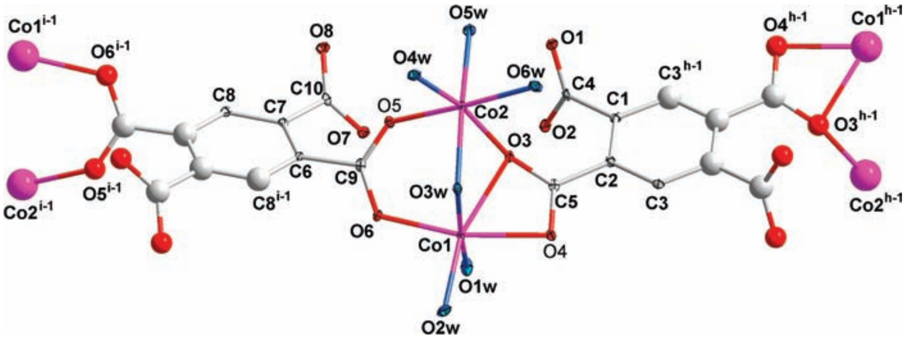

Figure 1. Perspective view of a fragment of the structure of **1** showing the two crystallographically independent cobalt atoms together with the atom numbering scheme and the coordination mode of the bta^{4-} ligand. The oxygen atom of the coordinated water molecules is in blue color and the hydrogen atoms have been omitted for the sake of clarity. [Symmetry codes: (h-1) = 1 − *x*, −*y*, 2 − *z*; (i-1) = 1 − *x*, 1 − *y*, 1 − *z*].

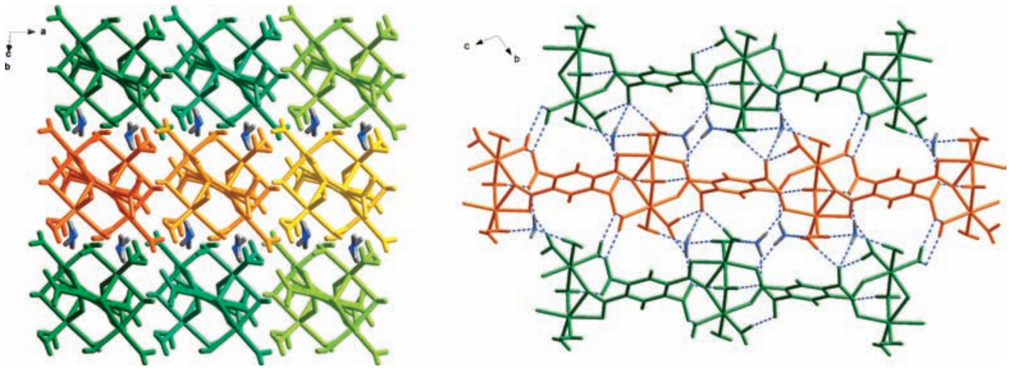

Figure 2. (a) Projection along the [01−1] of the chains in **1** (different colors are used for each chain). (b) Projection along the *a-axis* of the chains arrangement in **1** showing the intra- and interchain hydrogen bonding (blue dashed lines).

the atoms symmetry-related]. The average C−O bond lengths for the coordinated and free carboxylate-oxygen atoms are quite similar: 1.266(2) and 1.257(1) Å [at bta(1)] and 1.257(1) and 1.256(2) Å [at bta(2)]. The values of dihedral angles between the plane of the aromatic ring of bta^{4-} and those defined by the coordinated/uncoordinated carboxylate groups are 24.50(4)/70.59(5)° [bta(1)] and 56.07(5)/46.91(4)° [bta(2)]. They are all in agreement with those reported previously in other parent complexes.[13g] The values of the internal angles of the aromatic rings are slightly smaller for the substituted carbon atoms than for the non-substituted ones [average values of 119.5(1)° and 120.7(1)°, respectively], as expected.

$[\mathrm{Co(H_2O)(phda)}]_n \cdot n\mathrm{H_2O}$ (2). The crystallographic analysis of **2** shows that its structure consists of a three-dimensional MOF, the potential solvent accessible void volume space [ca. 29.5 Å^3, that is 1.4% per unit cell] being filled by disordered crystallization water molecules. Regular chains of *μ*-aqua-*μ*-oxo(carboxylate)-*μ*-carboxylate-(*syn-syn*) dicobalt(II) units that grow along the *c* axis occur in **2**. Furthermore, each chain is linked to four other ones through fully deprotonated phda^{2-} groups, these dianions acting as 4-fold connectors (Figure 3). It deserves to be noted that the dicobalt(II) entities act as 4-fold nodes, where each $[\mathrm{Co(1)(phda)_4}]^{6-}$ and $[\mathrm{Co(2)(phda)_4}]^{6-}$ units link three and five chains, respectively (Figures 4 and 5). The presence of coordination and crystallization water molecules allows the occurrence of an extensive network of hydrogen bonds which contribute to the stabilization of the three-dimensional structure (see end of Table 3 and Figure 5).

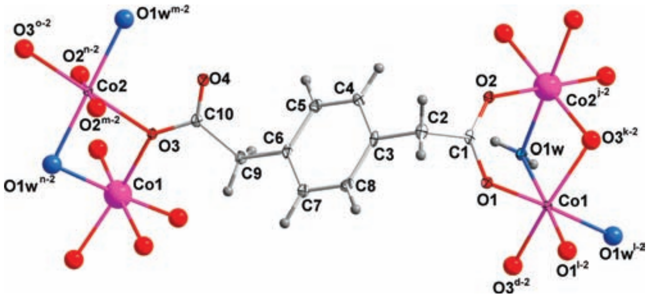

Figure 3. Perspective view of a fragment of the structure of **2** showing the coordination mode of the phda^{2-} ligand together with the atom numbering. [Symmetry codes: (d-2) = 0.5 − *x*, 0.5 − *y*, 2 − *z*; (j-2) = 0.5 − *x*, −0.5+*y*, 2.5 − *z*; (k-2) = −0.5+*x*, 0.5 − *y*, −0.5+*z*; (l-2) = −*x*, *y*, 1.5 − *z*; (m-2) = −0.5+*x*, 0.5 − *y*, −0.5+*z*; (n-2) = 1/2+*x*, 1/2 − *y*, 1/2+*z*; (o-2) = 1 − *x*, 1 − *y*, 3 − *z*].

Two crystallographically independent cobalt(II) ions [Co(1) and Co(2)] are present in **2**. Co(1) is located on a 2-fold rotation axis whereas Co(2) is placed on an inversion center (see Figure 3). Both cobalt atoms are six-coordinated in distorted compressed [Co(1)] and somewhat elongated [Co(2)] octahedral environments, with geometric values *ϕ* and *s*/*h* of 58.62° and 1.21 [at Co(1)] and 58.58° and 1.24 [at Co(2)] (*ϕ* = 60° and *s*/*h* = 1.22 for an ideal octahedron).[22] The equatorial plane of Co(1) is built up by two carboxylate-oxygen atoms and two water molecules [O(1), O(1w), O(1)$^{l-2}$ and O(1w)$^{l-2}$; (l-2) = −*x*, *y*, 1.5−*z*] while the axial positions are filled by two carboxylate-oxygens [O(3)$^{k-2}$ and O(3)$^{d-2}$;

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[22] Stiefel, E. I.; Brown, G. F. *Inorg. Chem.* **1972**, *11*, 434.

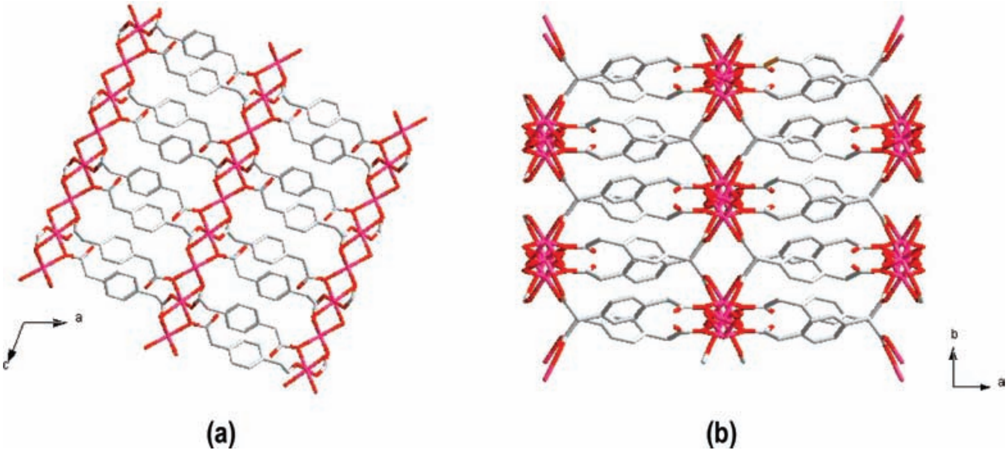


Figure 4. Views along the crystallographic *b*- (a) and *c*-axes (b) of the crystal packing in **2** showing how each phda^{2-} ligand acts as a connector between two adjacent chains (a) and the way each chain is linked to other four ones through the skeleton of the phda^{2-} group (b).

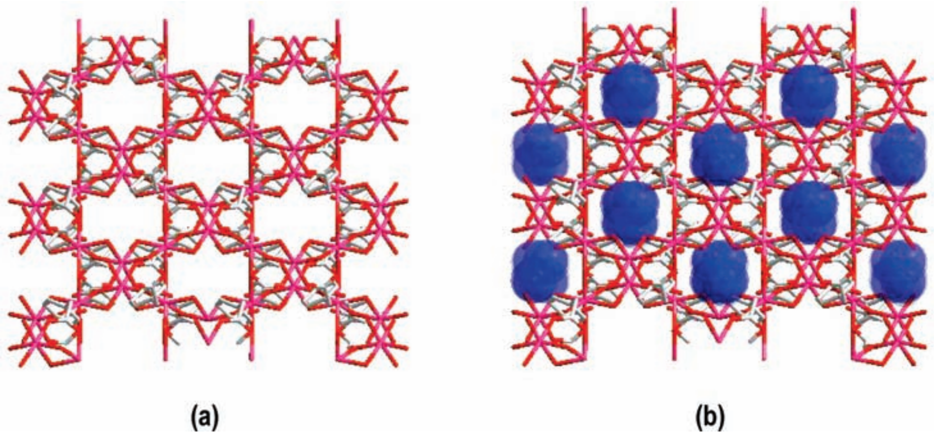


Figure 5. Views along the [101] direction of the MOF in **2** without the crystallization water molecules (a) and showing how the water molecules (space filling representation) are hosted in the cavities (b).

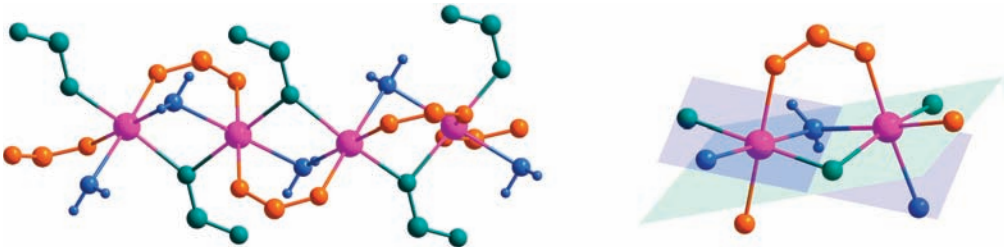
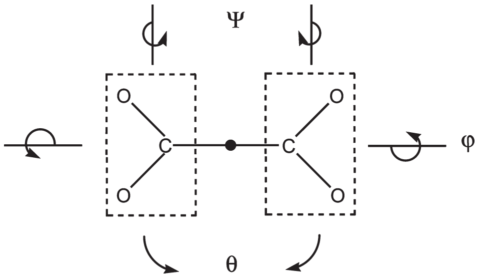


Figure 6. (a) View of a fragment of the chain [Co(1)Co(2)$(H_2O)_2]^{4+}$ in **2** focusing on the three different bridges between the cobalt atoms, *μ*-aqua, *μ*-oxo(carboxylate), and *syn-syn* carboxylato (blue, green and orange colors, respectively). (b) A detail of the Co(1)−O−Co(2) angle for the *μ*-oxo(carboxylate) and *μ*-aqua bridges is shown.

(k-2) = −0.5+*x*, 0.5−*y*, −0.5+*z* and (d-2) = 0.5−*x*, 0.5−*y*, 2−*z*]. The equatorial plane in the case of Co(2) is formed by four carboxylate-oxygen atoms [O(3), O(2)$^{\text{m-2}}$ and the symmetry-related ones; (m-2) = −0.5+*x*, 0.5−*y*, −0.5+*z*] whereas the axial positions are occupied by two water molecules [O(1w) and the symmetry-related one]. The mean values of the equatorial Co−O bond distances are 2.1189(12) and 2.0648(13) Å at Co(1) and Co(2), respectively. These values are somewhat longer [Co(1)]/shorter [Co(2)] than the axial bond lengths [2.089(2) Å at Co(1) and 2.139(2) Å at Co(2)] for the elongated/compressed octahedral environments. Regular alternating of Co(1) and Co(2) atoms occurs along the *c* direction, the bridging ligands being a water molecule, a *syn-syn* carboxylate group, and a carboxylate-oxygen atom (Figure 6). The values of the angles at the aqua and oxo bridges in **2** are 93.02(5)° and 99.13(5)°, respectively. The Co(1)···Co(2) separation through the triple bridge is 3.11499(2) Å, a value that is much smaller than the shortest cobalt−cobalt distance through the aromatic ring of the phda^{2-} ligand [11.4805(6) Å for Co(1)···Co(1)$^{\text{p-2}}$; (p-2) = −0.5 − *x*, 0.5 − *y*, *1* − *z*].

One crystallographically independent phda^{2-} ligand occurs in **2**. It acts as a bridge through its two carboxylate

Scheme 1



groups, one of them [O(1)−C(1)−O(2)] adopting the *syn-syn* coordination mode [coordination of O(1) and O(2) to Co(1) and $Co(2)^{j-2}$, respectively; (j-2) = 0.5 − x, −0.5 + y, 2.5 − z] and the other [O(3)−C(10)−O(4)] exhibiting a bis-monodentate bridging mode [simultaneous coordination of O(3) to Co(2) and $Co(1)^{d-2}$]. It deserves to be noted that the $phda^{2-}$ ligand in the two previous examples of phda-containing cobalt(II) complexes also acts as a bridge but in a tetrakis-monodentate coordination mode affording (4,4)-rectangular grids of cobalt atoms.[13a] Three geometrical parameters (noted θ, ψ, and φ in Scheme 1 are used in the literature[23] to describe the distortion degree of the $phda^{2-}$ ligand: θ accounts for the bending in the center of the anion with the two carboxylate groups remaining coplanar, ψ represents the bending of the carboxylate groups toward each other, and φ is the relative twisting of the planes of two carboxylate groups. The values for these parameters in **2** are $\theta = 165°$, $\psi = 59°$, and $\varphi = 166°$. They are in agreement with those previously reported.[24] The average C−O bond length for the coordinated carboxylate-oxygen atoms [1.277(2) Å] is somewhat longer than that of the free one [1.232(2) Å], as expected. Finally, the internal C−C−C angles within the benzene ring at the substituted carbon atoms [average value of 118.8(2)°] are slightly smaller than those at the non-substituted ones [120.5(2)°].

Magnetic Properties. Compound 1. The magnetic properties of **1** under the form of $\chi_M T$ versus T plot [χ_M is the magnetic susceptibility per two Co(II) ions] are shown in Figure 7. $\chi_M T$ at room temperature is equal to 5.54 $cm^3\ mol^{-1}$ K (μ_{eff} per Co^{II} of 4.71 μ_B), a value which is greater than the expected one for the spin-only case ($\mu_{eff} = 3.87\ \mu_B$ with $S_{Co} = 3/2$ and $g_{Co} = 2.0$). This fact indicates that the distortion of the octahedral symmetry of Co(II) in **1** is not so large as to induce the total quenching of the $^4T_{1g}$ ground state. Upon cooling, $\chi_M T$ first increases smoothly until it reaches a value of 5.80 $cm^3\ mol^{-1}$ K at T of about 115 K and further decreases to a minimum value of 5.37 $cm^3\ mol^{-1}$ K at 20 K. Below this temperature, $\chi_M T$ increases to reach a maximum value of 5.74 $cm^3\ mol^{-1}$ K at 4.0 K which is followed by an abrupt decrease to 5.32 $cm^3\ mol^{-1}$ K at 1.9 K. No maximum is observed in the magnetic susceptibility in the temperature range explored. These features can be interpreted as due to an overall ferromagnetic coupling between the cobalt(II) ions. The decrease of the $\chi_M T$ in the high temperature region is due to the progressive depopulation of the high-energy Kramers doublets (spin−orbit coupling effects), as expected for six coordinated high-spin cobalt(II) complexes. This interpretation is supported by the fact that the value of $\chi_M T$ at the minimum [2.69 $cm^3\ mol^{-1}$ K per Co(II) ion at 20 K] is well above that calculated for a magnetically isolated cobalt(II) ion (1.73 $cm^3\ mol^{-1}$ K for a $S_{eff} = 1/2$ with $g \approx 4.3$).[25]

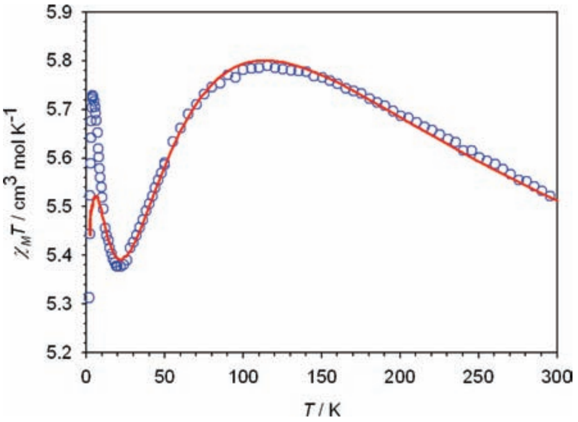


Figure 7. $\chi_M T$ versus T plot for complex **1**: (circles) experimental data;-(solid line) best-fit curve through eq 1 (see text).

In the light of the structure of **1**, two exchange pathways are possible: (i) the extended skeleton of the bta^{4-} ligand with a value for the cobalt−cobalt separation through the benzene ring greater than 10.11 Å and (ii) the triple bridge formed by the aqua, oxo-carboxylate, and *syn-syn* carboxylate groups with the cobalt atoms separated by only 3.16 Å. Having in mind the large metal−metal separation in the first pathway and the lack of magnetic coupling between Co(II) ions through the aromatic ring of the bta^{4-} ligand in previously investigated bta-bridged cobalt(II) complexes,[13b−e,g] the ferromagnetic interaction observed in **1** has to be associated to the second pathway. Consequently, from a magnetic point of view, the magnetic behavior of **1** would correspond to the triply bridged dicobalt(II) units. In general, six-coordinated Co(II) ions present an important first-order orbital momentum, and the spin Hamiltonian is insufficient to treat the magnetic properties of their complexes. It must be supplemented by consideration of orbitally dependent exchange interactions, as well as spin−orbit coupling effects.[26] Recently, we have shown that the magnetic properties of six-coordinated Co(II) in homodinuclear species can be perfectly described by using the Hamiltonian of eq 1,[8a]

$$\hat{H} = -J\hat{S}_1\hat{S}_2 - \sum_{i=1}^{2} \alpha_i\lambda_i\hat{L}_i\hat{S}_i + \sum_{i=1}^{2} \Delta_i[\hat{L}_{zi}^2 - 2/3] + \beta H\sum_{i=1}^{2}(-\alpha_i\hat{L}_i + g_e\hat{S}_i) \qquad (1)$$

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[26] (a) Herrera, J. M.; Bleuzen, A.; Dromzée, Y.; Julve, M.; Lloret, F.; Verdaguer, M. *Inorg. Chem.* **2003**, *42*, 7052. (b) Rodríguez, A.; Sakiyama, H.; Masciocchi, N.; Galli, S.; Gálvez, N.; Lloret, F.; Colacio, E. *Inorg. Chem.* **2005**, *44*, 8399. (c) Arora, H.; Lloret, F.; Mukherjee, R. *Inorg. Chem.* **2009**, *48*, 1158. (d) Sharma, A. K.; Lloret, F.; Mukherjee, R. *Inorg. Chem.* **2007**, *46*, 5128.

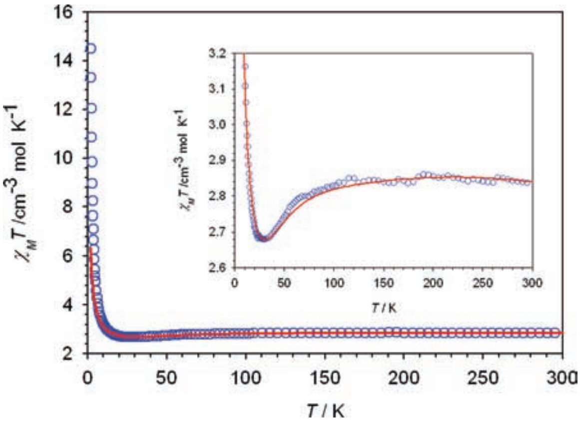

Figure 8. Temperature dependence of the $\chi_M T$ product of **2**: (circles) experimental data; (solid line) best-fit curve through eq 3 (see text). The inset shows a detail of the region in the vicinity of the minimum of $\chi_M T$.

The meaning of its different terms is as follows: the first term accounts for the magnetic interaction between the local spin quartets [$S = 3/2$ for each cobalt(II) ion]; the second one concerns the spin−orbit coupling of the $^4T_{1g}$ ground term in octahedral symmetry where λ is the spin−orbit coupling parameter and α is an orbital reduction factor defined as $\alpha = Ak$ (the value of A cover the range 1−1.5 for strong and weak crystal field limits, respectively, and k takes into account the covalency effects). In the frame of T_1 and P terms isomorphism,[26] $\boldsymbol{L}(T_{1g}) = -A\boldsymbol{L}(P)$, we can use $L = 1$ and to treat the $\alpha\lambda\hat{L}\hat{S}$ term as an isotropic Hamiltonian describing the interaction between two angular moments $L = 1$ and $S = 3/2$, $-\alpha\lambda$ being the coupling parameter. The third term is related with the axial distortion, the triplet orbital ground state $^4T_{1g}$ splitting into a singlet $^4A_2$ and a doublet ^4E levels with an energy gap of Δ; finally, the last term is the Zeeman interaction.

No analytical expression for the magnetic susceptibility (which would depends on J, α, λ, and Δ) can be derived. Numerical matrix diagonalization techniques using a Fortran program[27] (conducting extensive mappings with the aim of locating the global minimum of each system among a large number of local minima) allowed us to determine the values of these parameters for **1**. The best-fit parameters are: $J = +5.4$ cm^{-1}, $\lambda = -103$ cm^{-1}, $\alpha = 1.25$, $\Delta = -900$ cm^{-1} and $R = 2.1 \times 10^{-5}$ (R is the agreement factor defined as $\sum_i[(\chi_M T)_{\mathrm{obsd},i} - (\chi_M T)_{\mathrm{calcd},i}]^2/\sum_i[\chi_M T)_{\mathrm{obsd},i}]^2$). The calculated curve matches well the experimental data in the temperature range 10−300 K (see solid line in Figure 7). The mismatch between the experimental data and the calculated curve at $T < 10$ K must be attributed to the anisotropy effects that were discarded in our approach.

Compound 2. The magnetic properties of **2** in the form of the $\chi_M T$ against T plot [χ_M being the magnetic susceptibility for one Co(II) ion] are shown in Figure 8. At 295 K, $\chi_M T$ is 2.83 cm^3 mol^{-1} K (μ_{eff} per Co$^{\mathrm{II}}$ = 4.79 μ_B), a value which is greater than the expected one for a high-spin cobalt(II) ion through the spin-only formula ($\mu_{\mathrm{eff}} = 3.87$ μ_B). An unquenched orbital contribution typical of the $^4T_{1g}$ ground state in octahedral cobalt(II) complexes accounts for this, as in **1**. Upon cooling, $\chi_M T$ decreases first to reach a minimum value of 2.67 cm^3 mol^{-1} K at 29 K and then it increases sharply up to about 15 cm^3 mol^{-1} K at 1.9 K. The final increase of $\chi_M T$ in the low temperature region together with the fact that the value of $\chi_M T$ at the minimum (ca. 2.67 cm^3 mol^{-1} K) is well above the expected one for a magnetically isolated Co$^{\mathrm{II}}$ ion ($\chi_M T \approx 1.73$ cm^3 mol^{-1} K for a $S_{\mathrm{eff}} = 1/2$ and $g = 4.3$)[25] unambiguously support the occurrence of a significant ferromagnetic interaction between the high-spin cobalt(II) ions in **2**. The decrease of $\chi_M T$ in the high temperature region (see inset of Figure 8) is due to the thermal depopulation of the higher energy Kramers doublets of the Co$^{\mathrm{II}}$ center (spin−orbit coupling effects).

Looking at the structure of **2** and having in mind the analysis of the exchange pathways done for the previous compound, it is clear that the interaction through the aromatic ring of the bta^{4-} ligand can be discarded and the triple bridge formed by the water molecule, the carboxylate-oxo, and the *syn-syn* carboxylate would be the only possible exchange pathway in **2**. Therefore, the magnetic behavior of **2** would correspond to a uniform chain of triply bridged cobalt(II) ions which grows along the *c* axis. The full Hamiltonian to account for the magnetic behavior of **2** is given by eq 2

$$\hat{H} = \sum_{nn} -J\hat{S}_i\hat{S}_j - \sum_{nn}\alpha_i\lambda_i\hat{L}_i\hat{S} + \sum_{nn}\Delta_i[\hat{L}_{zi}^2 - 2/3] + \beta H\sum_{nn}(-\alpha_i\hat{L}_i + g_e\hat{S}_i) \qquad (2)$$

where $\sum_{nn}$ runs over all pairs of nearest-neighbor spins i and j within the chain.

To determine the intrachain magnetic interaction in **2**, we have used an approach that we reported very recently.[2] This approach is able to analyze the magnetic data of high-spin cobalt(II) compounds in the whole temperature range in the limit of the weak magnetic coupling as compared to the spin−orbit coupling, $|J/\lambda| < 0.1$. The cobalt(II) ions in axial symmetry are treated therein as effective spin doublets ($S_{\mathrm{eff}} = 1/2$) which are related with the real spins ($S = 3/2$) by $S_{\mathrm{eff}} = (3/5)S$. For that, the value of the g_0 Landé factor of the ground Kramers doublets is replaced by the $G(T,J)$ function which takes into account the magnetic behavior of the magnetically isolated cobalt(II) ions as well as the influence of the magnetic interactions between the ground Kramers doublets of different Co(II) centers on the g_0 value. So, this $G(T,J)$ is an effective g factor depending on the temperature, J (magnetic coupling), λ (spin−orbit coupling), α (orbital reduction), and Δ (energy gap between the singlet $^4A_2$ and doublet ^4E levels issued from the splitting of the orbital triplet $^4T_{1g}$ ground state under an axial distortion).

Following the above approach and from a magnetic point of view, complex **2** can be viewed as a uniform chain of ferromagnetically interacting spin doublets. In this sense, the magnetic data of **2** in the whole temperature

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(27) Cano, J. *VPMAG package*; University of Valencia: Spain, 2003.

range can be treated as those of a uniform chain of interacting spin doublets through the numerical expression of Baker-Rushbrooke [eq 3][28] where the g factor has been replaced by the $G(T,J)$ function.

$$\chi_M = \frac{\mathcal{N}[G(T,J)]^2\beta^2}{kT}(N/D)^{2/3} \qquad (3)$$

where

$$N = 1.0 + 5.7979916y + 16.902653y^2 + 29.376885y^3 + 29.832959y^4 + 14.036918y^5$$

$$D = 1.0 + 2.79799y + 7.0086780y^2 + 8.653844y^3 + 4.5743114y^5$$

and

$$y = (25/18)J/kT$$

The two crystallographically independent six-coordinated Co(1)O_6 and Co(2)O_6 which alternate regularly within the chain are considered equivalent to avoid the overparametrization in the fitting procedure. A very good fit (solid line in Figure 8) is obtained for the magnetic data of **2** in the whole temperature range through eq 3 with the following set of best-fit parameters: $J = +2.16\ \mathrm{cm}^{-1}$, $\lambda = -126\ \mathrm{cm}^{-1}$, $\alpha = 1.20$, and $\Delta = 480\ \mathrm{cm}^{-1}$ with $R = 2.5 \times 10^{-5}$. The low value of the $|J/\lambda|$ quotient (0.017) in **2** justifies the use of the above approach, and the values of the λ, α, and Δ parameters obtained for both **1** and **2** lie within the range of those observed in other six-coordinated high-spin complexes.[8a,13,26]

Influence of the Bridges on the Nature of the Magnetic Coupling in 1 and 2. The analysis of the magnetic data of **1** and **2** shows that the μ-aqua, μ-oxo(carboxylate), and μ-COO(*syn-syn* carboxylate) triple bridge provide the exchange pathway for the ferromagnetic couplings observed in those compounds. It is clear that the *syn-syn* carboxylate conformation would cause an antiferromagnetic coupling, as supported by the large number of magneto-structural studies on acetato-bridged dicopper(II) complexes.[5a] As far as the monatomic carboxylate-oxo bridge is concerned, no data are available for cobalt(II) complexes. However, ferromagnetic interactions are observed in di- and trinuclear nickel(II) complexes through the oxo(phenolato) bridge with values of the Ni−O−Ni angle smaller than 93.5° (so-called magic angle), the magnetic interaction being antiferromagnetic for larger values of this angle.[29] A similar situation occurs in the di-μ−hydroxodicopper(II) binuclear complexes where a correlation between the magnitude and nature of the magnetic coupling and the value of the Cu−O−Cu angle (θ) has been established (ferro- for $\theta < 97.5°$ and antiferromagnetic for larger values of θ).[30] Most likely, these features can be extended to the cobalt(II) complexes and the ferromagnetic interaction observed in **1** and **2** would have its origin in the reduced values of the angles at the single carboxylate-oxo [99.13(5)° (**1**) and 92.16(4)° (**2**)] and aqua [93.02(5)° (**1**) and 93.89(4)° (**2**)] bridges. This is in agreement with the fact that antiferromagnetic couplings are observed in the cobalt(II) complexes of formula $[Co_2(butca)(H_2O)_5]_n \cdot 2nH_2O$ (**3**) (H_4butca = 1,2,3,4-butanetetracarboxylic acid) ($J = -1.2\ \mathrm{cm}^{-1}$)[13f] and $[Co_2(bta)(H_2O)_4]_n \cdot 2nH_2O$ (**4**) ($J = -1.9\ \mathrm{cm}^{-1}$)[13c] where *syn-syn* carboxylate and aqua coexist as bridges with larger values of the Co−O_w−Co angle [113.10(8) and 120.78(7)°, respectively]. An alternative explanation to the ferromagnetic coupling observed for **1** and **2** is based on the fact that when the bridging ligands are different, they can add or counterbalance their effects. This problem was treated by Nishida et al.[31] and McKee et al.,[32] and the two situations are referred to as orbital complementarity and countercomplementarity, respectively. The *syn-syn* carboxylato and the oxo-carboxylate/aqua as bridges are countercomplementary and the magnetic coupling becomes ferromagnetic (case of **1** and **2**), as observed in several examples of ferromagnetically coupled copper(II) complexes where *syn-syn* carboxylato and hydroxo,[33] alkoxo,[34] or end-on azido[35] coexist as bridges. In the case of high-spin cobalt(II) complexes, given that the number of magnetic orbitals on each spin carrier is increased [from one for Cu(II) to three for Co(II)], the possibilities of a net overlap between the magnetic orbitals also increases. This could counterbalance the countercomplementary effects and lead to an antiferrromagnetic coupling, as observed in the above-mentioned butca- and bta-containing cobalt(II) complexes.

Conclusions

In the compounds **1** and **2**, the metallic centers are linked through [(μ-aqua)(μ-oxo-carboxylate)(μ-carboxylate$_{syn\text{-}syn}$)] bridges, forming dinuclear units in **1** and chains in **2**; these inorganic nodes are extended through the skeleton of the ligands [bta^{4-} (**1**) and $phda^{2-}$ (**2**)] to give one- or three-dimensional structures for **1** and **2**, respectively. From the magnetic point of view, the behavior of both complexes is quite similar, showing ferromagnetic interactions. The exchange pathways are similar to those previously observed in compounds **3** and **4**, [13f,c] where the cobalt(II) ions are linked through μ-aqua/μ-carboxylate$_{syn\text{-}syn}$ bridges. Nevertheless, the nature of the magnetic coupling in the two families is different: the cobalt(II) ions in **1** and **2** are ferromagnetically

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coupled whereas they are antiferromagnetically coupled in **3** and **4**. This different magnetic behavior can be explained on the base of either the values at the angle at the monatomic bridges or the complementarity/countercomplementarity effects of the bridges.

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