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1,2,4,5-Benzenetetracarboxylate- and 2,2′-Bipyrimidine-Containing Cobalt(II) Coordination Polymers: Preparation, Crystal Structure, and Magnetic Properties[†]

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Three new mixed-ligand cobalt(II) complexes of formula $[Co_2(H_2O)_6(bta)(bpym)]_n \cdot 4nH_2O$ (**1**), $[Co_2(H_2O)_2(bta)(bpym)]_n$ (**2**), and $[Co_2(H_2O)_4(bta)(bpym)]_n \cdot 2nH_2O$ (**3**) (bpym = 2,2′-bipyrimidine and H_4bta = 1,2,4,5-benzenetretracaboxylic acid) have been synthesized and characterized by single crystal X-ray diffraction. **1** is a chain compound of *mer*-triaquacobalt(II) units which are linked through regular alternating bis-bidentate bpym and bis-monodentate bta groups. **2** and **3** are three-dimensional compounds where aquacobalt(II) (**2**) and *cis*-diaquacobalt(II) (**3**) entities are linked by bis-bidentate bpym (**2** and **3**) and tetrakis- (**2** and **3**) and octakis-monodentate (**2**) bta ligands. The cobalt atoms in **1**–**3** exhibit somewhat distorted octahedral surroundings. Two bpym-nitrogen atoms (**1**–**3**) and either two bta-oxygens (**2**) or one bta-oxygen and a water molecule (**1** and **3**) build the equatorial plane, whereas the axial positions are filled either by two water molecules (**1**) or by a bta-oxygen atom and a water molecule (**2** and **3**). The values of the cobalt−cobalt separation across the bridging bpym vary in the range 5.684(2)−5.7752(7) Å, whereas those through the bta bridge cover the ranges 5.288(2)−5.7503(5) Å (across the *anti-syn* carboxylate) and 7.715(3)−11.387(1) Å (across the phenyl ring). The magnetic properties of **1**–**3** have been investigated in the temperature range 1.9–290 K. They are all typical of an overall antiferromagnetic coupling with the maxima of the magnetic susceptibility at 14.5 (**1**) and 11.5 K (**2** and **3**). Although exchange pathways through bis-bidentate bpym and carboxylate-bta in different coordination modes are involved in **1**–**3**, their magnetic behavior is practically governed by that across the bpym bridge, the magnitude of the exchange coupling being $J = -5.59(2)$ (**1**), $-4.41(2)$ (**2**), and $-4.49(2)$ (**3**) with the Hamiltonian $\hat{H} = -J\hat{S}_1\hat{S}_2$.

Introduction

The design of synthetic pathways to get systems with the desired properties continues to be a challenge for inorganic chemists. In this context, many efforts have been devoted to the development of rational synthetic routes for polymeric coordination compounds which have applications as molecular-based magnetic materials.[1] One of the major challenges in molecular magnetism in the last fifteen years has been the rational design of two- and three-dimensional magnetic systems. In this respect, the role played by the oxalate ligand (the dianion of oxalic acid, H_2ox) as an assembling unit has been crucial, leading to compounds which behave as canted antiferro-, ferri- and ferromagnetic materials.[2]

The close topology of the oxalate (ox) and 2,2′-bipyrimidine (bpym), their similar behavior as ligands (the bidentate and bis-bidentate coordination modes are the more frequent ones for both ligands in their metal complexes), and their

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[†] In Memoriam of Prof. Xavier Solans. The authors have greatly benefited from numerous scientific discussions with Prof. Xavier Solans on X-ray diffraction, and they much enjoyed his enthusiasm, creativity, *savoir faire*, and pedagogic virtues. Although he passed away recently, he will remain in our memory forever.

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(1) (a) Gatteschi, D.; Kahn, O.; Miller, J. S.; Palacio, F. *Magnetic Molecular Materials*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991. (b) *Polyhedron* **2001**, *20*, 1115–1749 (issues 11–14). (c) *Polyhedron* **2003**, *22*, 1725–2408 (issues 14–17).

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remarkable ability to mediate electronic effects between the paramagnetic centers they bridge are at the origin of the interest in the mixed bpym- and carboxylate-containing polynuclear compounds.[3] The most exciting result dealing with these mixed-ligand systems was the materialization of homometallic honeycomb layered compounds of formula $[M_2(bpym)(ox)_2]\cdot nH_2O$ [M = Mn (n = 6), Cu and Fe (n = 5)] where two alternating intralayer antiferromagnetic interactions (through bis-bidentate bpym and ox) occur.[3a,h,i] The versatility as ligands of the aromatic polycarboxylate anions and the ability of the carboxylate bridge to mediate significant ferro- or antiferromagnetic magnetic interactions[4] induced us to investigate the possibility of preparing extended magnetic systems with first row-transition metal ions and bpym and bta^{4-} (H_4bta = 1,2,4,5-benzenetetracarboxylic acid) as spin carriers and linkers, respectively. Our first attempts with cobalt(II) ions afforded the chain $[Co_2(H_2O)_6(bta)(bpym)]_n\cdot 4nH_2O$ (**1**) and the two three-dimensional compounds $[Co_2(H_2O)_2(bta)(bpym)]_n$ (**2**) and $[Co_2(H_2O)_4(bta)(bpym)]_n\cdot 2nH_2O$ (**3**) whose preparation, crystal structure determination, and magnetic study are presented here.

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**–**3** were grown by slow evaporation of the solvent at room temperature (**1**), the gel technique (**2**), and hydrothermal methods (**3**) (see details below).

Preparation of the Compounds. $[Co_2(H_2O)_6(bta)(bpym)]_n\cdot 4nH_2O$ (1). H_4bta (0.12 g, 0.5 mmol), bpym (0.079 g, 0.5 mmol) and sodium carbonate (0.106 g, 1 mmol) were dissolved in 20 mL of a 1:1 (v/v) water−methanol mixture. An aqueous solution (15 mL) of cobalt(II) chloride hexahydrate (0.119 g, 0.5 mmol) was slowly added to the previous solution under continuous stirring. The resulting suspension was filtered to remove the solid which was discarded, and the orange solution was allowed to evaporate in a hood at room temperature. X-ray quality crystals of **1** as pale orange prisms were formed after a few days. They were collected and dried on filter paper. Yield (based on the cobalt): about 35%. Anal. Calcd for $C_{18}H_{28}Co_2N_4O_{18}$ (**1**): C, 30.61; H, 3.99; N, 7.93. Found: C, 30.58; H, 4.06; N, 7.89%.

$[Co_2(H_2O)_2(bta)(bpym)]_n$ (2). An aqueous solution of 0.1 M NaOH was added dropwise to a water/methanol 1:1 (v/v) mixture (5 mL) of H_4bta (0.127 g, 0.5 mmol) and bpym (0.079 g, 0.5 mmol) to adjust the pH value to 5.0. Then, 0.25 mL of tetramethoxysilane (TMS) was added to the previous resulting solution under vigorous stirring. The gel was formed on standing after one day at room temperature. An aqueous solution (3 mL) of cobalt(II) chloride hexahydrate (0.119 g, 0.5 mmol) was carefully added on the gel. X-ray quality crystals of **2** as orange prisms were grown inside the gel at room temperature after several weeks. They were mechanically separated, washed with small amounts of a 1:1 (v:v) water–methanol mixture and air-dried. Yield (based on the cobalt): about 49%. Anal. Calcd for $C_{18}H_{12}Co_2N_4O_{10}$ (**2**): C, 38.46; H, 2.15; N, 9.97. Found: C, 37.26; H, 2.18; N, 9.88%.

$[Co_2(H_2O)_4(bta)(bpym)]_n\cdot 2nH_2O$ (3). A mixture of H_4bta (0.127 g, 0.5 mmol) and bpym (0.079 g, 0.5 mmol) was dissolved in 15 mL of water. An aqueous solution (10 mL) of cobalt(II) acetate tetrahydrate (0.125 g, 0.5 mmol) was added dropwise to the previous one under continuous stirring. The resulting mixture was sealed in a 45 mL stainless-steel reactor with a Teflon liner, and it was heated at 115 °C during 48 h. X-ray quality crystals of **3** as pale orange plates were obtained after cooling. Yield (based on the cobalt): about 60%. Anal. Calcd for $C_{18}H_{20}Co_2N_4O_{14}$ (**3**): C, 34.09; H, 3.18; N, 8.83. Found: C, 34.24; H, 3.58; N, 8.76%.

Physical Techniques. Magnetic susceptibility measurements on polycrystalline samples of **1**–**3** were carried out with a Quantum Design SQUID magnetometer in the temperature range 1.9–290 K and under applied magnetic fields ranging from 150 G to 1 T. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants[5] as -351×10^{-6} (**1**), -247×10^{-6} (**2**),

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and -299×10^{-6} cm^3 mol^{-1} (**3**) [per cobalt(II) ion]. Corrections for the magnetization of the sample holder were also performed.

Crystallographic Data Collection and Structural Determination. X-ray diffraction data on single crystals of **1**–**3** were collected at room temperature with a Nonius Kappa CCD diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Orientation matrix and lattice parameters were determined by least-squares refinement of the reflections obtained by a θ-χ scan (Dirac/lsq method). Data collection and data reduction of **1** and **3** were done with the COLLECT[6] and EVALCCD[7] programs. Empirical absorption corrections for the three structures were carried out using SADABS.[8] The indeces of data collection were $-9 \le h \le 7$, $-10 \le k \le 9$, and $-14 \le l \le 14$ (**1**), $-13 \le h \le 12$, $0 \le k \le 18$, and $0 \le l \le 17$ (**2**) and $-11 \le h \le 11$, $-12 \le k \le 14$, and $-14 \le l \le 14$ (**3**). Of the 2878 (**1**), 2177 (**2**), and 2468 (**3**) measured independent reflections in the θ range 5.45–27.50 (**1**), 5.02–27.66 (**2**), and 5.04–27.50° (**3**), 2116 (**1**), 1724 (**2**), and 2054 (**3**) have $I > 2\sigma(I)$. All the measured independent reflections were used in the analysis. All calculations for data reduction, structure solution, and refinement were done by standard procedures (WINGX).[9] The crystal of **2** was a nonmerohedral twin. The reflections for both components of the twin were indexed using DIRAX,[10] integrated using the EVALCCD,[7] and equivalent reflections were merged using the TWINABS[11] program suite. The twin refinement was performed with SHELXL97[12] using the HKLF4 data for solved and the HKLF5 format for the refinement, including the TWIN and BASF statements; all reflections having at least one contribution from the major component have been used for the HKLF5 refinement. In the final refinement, the BASF factor gives a value of (0.5875), leading to a proportion of 58.7(1)% and 41.3(1)% for each one of the twin domains. Information concerning the crystal data and details of the refinement of the structures of **1**–**3** are listed in Table 1.

The structures of **1**–**3** were solved by direct methods using the SHELXS97[12] computational program. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares technique on F^2 by using the SHELXL97[12] program. The hydrogen atoms of the coordinated water molecules in **1**–**3** and those of the crystallization water molecules in **3** were located from difference Fourier maps and refined with isotropic temperature factors. The final Fourier-difference maps showed maximum and minimum height peaks of 1.130 and -0.575 e Å^{-3} (**1**), 0.486 and -0.561 e Å^{-3} (**2**), and 0.366 and -0.355 e Å^{-3} (**3**). The final geometrical calculations and the graphical manipulations were carried out with the PARST97,[13] PLATON,[14] and DIAMOND[15] programs. Selected bond lengths and angles including the hydrogen bonds are listed in Tables 2 (**1**), 3 (**2**), and 4 (**3**).

Table 1. Crystallographic Data for the Complexes $[Co_2(H_2O)_6(bta)(bpym)]_n \cdot 4nH_2O$ (**1**), $[Co_2(H_2O)_2(bta)(bpym)]_n$ (**2**), and $[Co_2(H_2O)_4(bta)(bpym)]_n \cdot 2nH_2O$ (**3**)

	1	**2**	**3**
formula	$C_{18}H_{28}Co_2N_4O_{18}$	$C_{18}H_{12}Co_2N_4O_{10}$	$C_{18}H_{20}Co_2 N_4O_{14}$
fw	706.30	562.18	634.24
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/m$	$P2_1/c$
a (Å)	7.4812(3)	10.265(5)	8.9976(5)
b (Å)	8.4178(3)	13.915(5)	11.2478(5)
c (Å)	11.3976(4)	13.202(5)	11.3049(5)
α (deg)	80.286(3)		
β (deg)	73.181(3)	103.104(5)	108.540(4)
γ (deg)	67.702(4)		
V (Å^3)	634.28(4)	1836.104(5)	1084.72(9)
Z	1	4	2
T (K)	293(2)	293(2)	293(2)
ρ_{calc} (Mg m^{-3})	1.849	2.033	1.942
λ (Mo Kα Å)	0.71073	0.71073	0.71073
μ (Mo Kα mm^{-1})	1.404	1.881	1.618
R_1 [$I > 2\sigma(I)$] (all)	0.0494 (0.0798)	0.0387 (0.0608)	0.0317(0.0467)
wR_2, [$I > 2\sigma(I)$] (all)	0.0954(0.1061)	0.0710(0.0772)	0.0604 (0.0656)
measured reflections	5434	8683	7157
independent reflections (R_{int})	2878(0.028)	2177(−)	2468(0.022)

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

Co(1)−O(1)	2.045(3)	Co(1)−O(7w)	2.076(3)
Co(1)−O(5w)	2.094(3)	Co(1)−N(1)	2.158(3)
Co(1)−O(6w)	2.041(4)	Co(1)−N(2)$^{a-1}$	2.173(3)
O(6w)−Co(1)−O(1)	96.67(15)	O(1)−Co(1)−O(7w)	89.52(12)
O(6w)−Co(1)−O(7w)	87.3(2)	O(1)−Co(1)−O(5w)	88.64(12)
O(6w)−Co(1)−O(5w)	172.64(15)	O(1)−Co(1)−N(1)	165.16(10)
O(6w)−Co(1)−N(1)	88.08(15)	O(1)−Co(1)−N(2)$^{a-1}$	89.56(10)
O(6w)−Co(1)−N(2)$^{a-1}$	89.84(15)	N(1)−Co(1)−N(2)$^{a-1}$	76.36(10)
O(7w)−Co(1)−N(1)	104.78(13)	O(5w)−Co(1)−N(1)	88.03(12)
O(7w)−Co(1)−N(2)$^{a-1}$	176.91(12)	O(5w)−Co(1)−N(2)$^{a-1}$	95.31(11)
O(7w)−Co(1)−O(5w)	87.61(14)		

	Hydrogen Bonds		
D−H···A	d(D···A)	d(H···A)	<(D−H···A)
O(5w)−H(51)O(4)$^{b-1}$	2.717(4)	1.96(6)	160(6)
O(5w)−H(52)O(3)	2.732(5)	1.92(7)	167(6)
O(6w)−H(61)O(3)$^{d-1}$	2.661(5)	1.82(5)	172(6)
O(6w)−H(62)O(1w)$^{d-1}$	2.758(6)	2.16(6)	167(7)
O(7w)−H(71)O(4)$^{e-1}$	2.677(5)	1.92(6)	177(6)
O(7w)−H(72)O(2)	2.652(6)	1.96(8)	161(7)

Intermolecular O···O Distances (Å)			
O(1w)O(1w)$^{g-1}$	2.952(7)	O(2w)O(6)$^{b-1}$	3.285(14)
O(1w)O(6w)$^{f-1}$	2.758(6)	O(2w)O(1)$^{b-1}$	2.833(11)
O(2w)O(1)$^{h-1}$	2.959(11)	O(2w)O(2w)$^{g-1}$	2.36(2)

[a] Symmetry codes: (a-1) = $-x$, $2 - y$, $1 - z$; (b-1) = $-x + 1$, $-y + 2$, $-z + 1$; (d-1) = $x - 1$, y, z: (e-1) = x, $y - 1$, z; (f-1) = $x + 1$, y, z; (g-1) = $-x + 2$, $-y + 1$, $-z + 2$; (h-1) = $x + 1$, $+y - 1$, $+z$.

Results and Discussion

Description of the structures. $[Co_2(H_2O)_6bta(bpym)]_n \cdot 4nH_2O$ (1). The structure of **1** consists of dinuclear $[Co_2(bpym)(H_2O)_6]^{4+}$ units, where the bpym molecule acts as a bis-bidentate ligand toward two *mer*-triaquacobalt(II) ions. The dinuclear units are linked through bis-monodentate bta ligands in a regular alternating fashion (Figure 1). These neutral chains which run parallel to the [101] direction are interlinked through hydrogen bonds with zigzag chains of crystallization water molecules to form a three-dimensional network [Figure 2(left)]. The coordinated and crystallization water molecules and all the carboxylate-oxygen atoms of the bta ligand are involved in these hydrogen bonds [O···O distances ranging from 2.652(6) to 2.959(11) Å] (Figure 2 and end of Table 2). As shown in Figure 2(right), the chains

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**^{a}

Co(1)−O(1)	2.030(2)	Co(1)−O(4w)	2.134(3)
Co(1)−O(2)	2.015(2)	Co(1)−N(1)	2.178(3)
Co(1)−O(3)$^{b-2}$	2.214(3)	Co(1)−N(2)	2.125(3)
O(1)−Co(1)−N(1)	172.36(10)	O(2)−Co(1)−O(3)$^{b-2}$	82.97(8)
O(1)−Co(1)−N(2)	95.07(3)	N(1)−Co(1)−O(3)$^{b-2}$	94.74(8)
O(1)−Co(1)−O(3)$^{b-2}$	93.97(8)	N(1)−Co(1)−O(4w)	81.37(10)
O(1)−Co(1)−O(4w)	95.96(10)	N(2)−Co(1)−O(4w)	85.29(9)
O(2)−Co(1)−O(1)	91.08(9)	N(2)−Co(1)−N(1)	77.61(10)
O(2)−Co(1)−N(2)	173.58(10)	N(2)−Co(1)−O(3)$^{b-2}$	88.86(10)
O(2)−Co(1)−O(4w)	95.93(10)	O(4w)−Co(1)−O(3)$^{b-2}$	170.03(10)
O(2)−Co(1)−N(1)	96.31(10)		

^{a} Symmetry code: (b-2) = $-0.5 + x$, $0.5 - y$, z.

Table 4. Selected Bond Lengths (Å) and Angles (°) for **3**^{a}

Co(1)−O(1)	2.1304(14)	Co(1)−O(3w)	2.075(2)
Co(1)−O(3)$^{b-3}$	2.115(2)	Co(1)−N(1)$^{a-3}$	2.176(2)
Co(1)−O(2w)	1.999(2)	Co(1)−N(2)	2.152(2)
O(1)−Co(1)−O(3)$^{b-3}$	91.41(6)	O(2w)−Co(1)−N(2)	167.07(8)
O(1)−Co(1)−O(2w)	90.78(8)	O(3w)−Co(1)−O(3)$^{b-3}$	167.59(7)
O(1)−Co(1)−O(3w)	84.46(7)	O(3w)−Co(1)−N(1)$^{a-3}$	96.23(7)
O(1)−Co(1)−N(1)$^{a-3}$	178.38(7)	O(3w)−Co(1)−N(2)	87.72(7)
O(1)−Co(1)−N(2)	102.07(7)	N(2)−Co(1)−O(3)$^{b-3}$	81.69(7)
O(2w)−Co(1)−O(3)$^{b-3}$	96.78(9)	N(2)−Co(1)−N(1)$^{a-3}$	76.51(8)
O(2w)−Co(1)−O(3W)	94.97(9)	N(1)$^{b-3}$−Co(1)−O(3)$^{b-3}$	87.61(7)
O(2w)−Co(1)−N(1)$^{a-3}$	90.62(8)		

	Hydrogen bonds		
D−H···A	*d*(D···A) (Å)	*d*(H···A) (Å)	<(D−H···A) (°)
O(1W)−H(11) O(4)$^{f-3}$	2.762(3)	1.97(4)	168(4)
O(1W)−H(12) O(4)$^{g-3}$	2.804(3)	2.06(5)	166(5)
O(2W)−H(21)O(1W)	2.695(3)	1.89(4)	173(4)
O(2W)−H(22) O(2)	2.613(3)	1.93(3)	159(4)
O(3W)−H(31)O(3)$^{e-3}$	2.832(2)	2.03(3)	174(4)
O(3W)−H(32) O(2)$^{f-3}$	2.646(3)	1.84(4)	174(4)

^{a} Symmetry codes: (a-3) = $-x, -y, -z$; (b-3) = $1 - x, -0.5 + y, 0.5 - z$; (e-3) = $-x + 1, -y + 1, -z + 1$; (f-3) = $-x, +y - 1/2, -z + 1/2$; (g-3) = $x - 1, -y + 3/2, +z - 1/2$.

of crystallization water molecules are anchored in the hydrophilic pores of the cobalt(II) chains through hydrogen bonds.

Each cobalt atom exhibits a somewhat distorted octahedral surrounding with values of the degree of compression (*s/h*) and twisting angle (φ) of 1.226 and 60.20°, respectively (the ideal values for an octahedron are 1.22 and 60°).[16] The best equatorial plane is formed by two bpym-nitrogen atoms [N(1) and N(2)$^{a-1}$; (a-1) = $-x, 2 - y, 1 - z$] and two oxygen atoms, one from a water molecule [O(7w)] and the other from a carboxylate-bta group [O(1)]. The apical positions are then occupied by two water molecules [O(5w) and O(6w)]. The equatorial bond lengths vary in the range 2.041(3)−2.173(3) Å, the Co−N distances [mean value is 2.165(4) Å] being longer than the Co−O ones [av value is 2.060(3) Å]. The main source of distortion of the cobalt environment is caused by the reduced bite of the bis-chelating bpym. In this respect, the angle subtended by the bpym ligand at the cobalt atom is only 76.36(10)°, a value which is in agreement with those observed in other bpym-bridged cobalt(II) complexes.[3f,17]

Both the bpym and bta ligands in **1** are centrosymmetric, the inversion centers being located in the middle of the inter-ring carbon−carbon bond [C(10)−C(10)$^{a-1}$] and in the center of the benzene ring, respectively. The bta group in **1** adopts a *trans*-bis-monodentate coordination mode through O(1) and O(1)$^{b-1}$ to Co(1) and Co(1)$^{b-1}$, respectively [symmetry code: (b-1) = $1 - x, 1 - y, 2 - z$]. A search in the Cambridge Structural Data Base shows that there are several structural reports of cobalt(II) complexes where this coordination mode of the fully deprotonated bta^{4-} ligand is present.[18] The average values of the C−O bond distances for the coordinated [1.259(5) Å] and free [1.250(4) Å] carboxylate-oxygen atoms are very close. The values of the dihedral angle between the aromatic ring and the coordinated and noncoordinated carboxylate groups are 50.19(13)° and 54.81(11)°, respectively. The values of the internal angles in the benzene ring of the bta ligand are slightly smaller for the substituted carbon atoms [average value of 119.6(3)° versus 120.8(3)° for the unsubstituted ones]. The cobalt−cobalt separation between the cobalt atoms through the bridging bpym and bta ligands are 5.7751(7) Å and 11.204(1) Å, respectively. The shortest interchain metal−metal distance is 6.0754(7) Å [Co(1)···Co(1)$^{c-1}$; (c-1) = $1 - x, 1 - y, 1 - z$].

[Co$_2$(H$_2$O)$_2$bta(bpym)]$_n$ (2). The structure of **2** consists of bpym-bridged [Co$_2$(bpym)(H$_2$O)$_2$]$^{4+}$ units (Figure 3) similar to those found in **1**, which are carboxylate-bridged to form quadratic (4,4) layers in the *ab* plane [Figure 4(left)]. These layers are stacked perpendicular to the *ab* plane, being linked in pairs through the carbon skeleton of an octakis-monodentate bta ligand (represented in green in Figures 3 and 4). Additionally, each bilayer is connected to the two adjacent ones through the skeleton of a tetrakis-monodentate bta ligand (represented in orange in Figures 3 and 4) leading to a three-dimensional network [Figure 4(right)]. The structure is stabilized by hydrogen bonds involving the coordinated water molecule and some of the carboxylate-oxygen atoms [2.869(4) and 2.647(4) Å for O(4w)−H(2w)···O(2)$^{a-2}$ and O(4w)−H(1w)···O(5), respectively; symmetry code: (a-2) = $0.5 + x, 0.5 - y, z$]. Weak $\pi\cdots\pi$ interactions between a bta ligand and a pyrimidyl ring of the bpym ligand are present in the structure of **2**, the value of the centroid-centroid distance and that of the angle between the normal to the ring and the centroid−centroid vector being about 3.232 Å and 11.7°, respectively. These values are typical for slightly displaced off-set $\pi\cdots\pi$ interactions.[18]

Each cobalt atom exhibits a somewhat distorted octahedral surrounding. As in **1**, the main source of the distortion of the cobalt environment in **2** is the reduced bite of the bis-chelating bpym [77.61(9)° for N(1)−Co(1)−N(2)]. The

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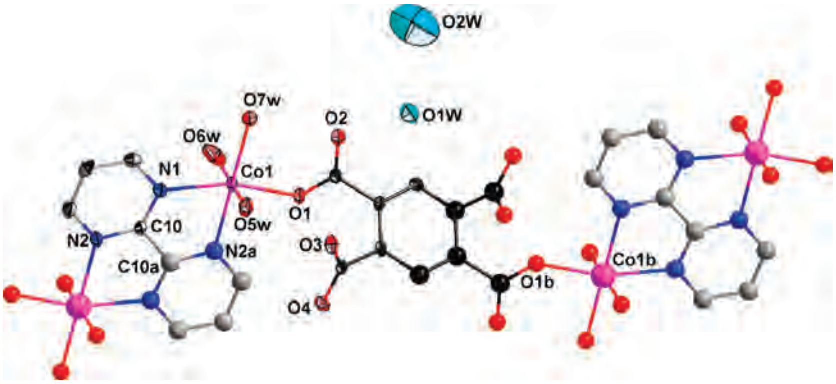

Figure 1. Perspective view of a fragment of the structure of **1** with the atom numbering scheme. An ORTEP (Oak Ridge thermal ellipsoid plot) representation has been used to denote the crystallographically independent unit. The coordination modes of bta^{4-} and bpym ligands are also shown.

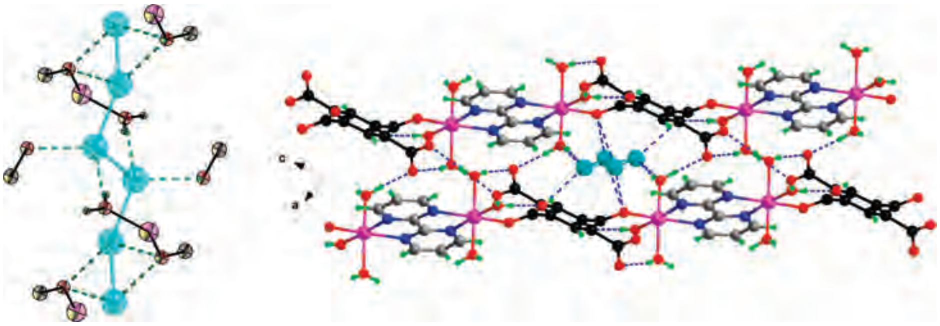

Figure 2. (left) Detailed view of the hydrogen bonds (dashed lines) of the chain of the crystallization water molecules with the carboxylate-oxygen atoms and coordinated water molecules. (right) Perspective view of the crystal packing down the *b* axis showing the interchain connections through the hydrogen bonds [broken blue lines].

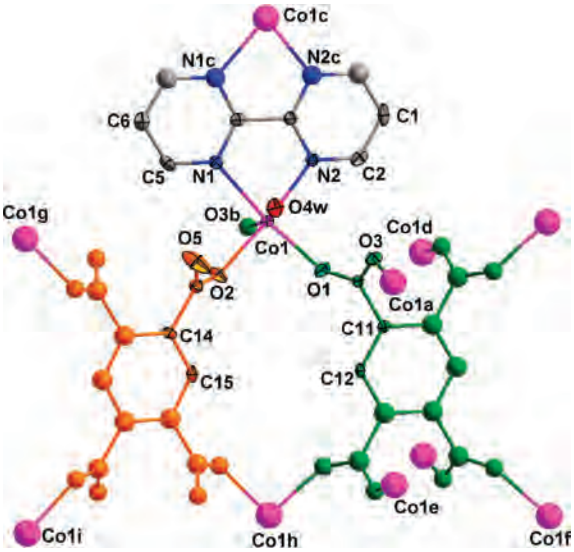

Figure 3. Perspective view of a fragment of the structure of **2** with the atom numbering scheme. The ORTEP representation has been used to denote the crystallographically independent unit. The coordination modes of the bta^{4-}(tetrakis-monodentate (orange) and octakis-monodentate (green) and bpym ligands are also shown.

degree of compression (*s/h*) and twisting angle (φ) for the metal environment are 57.68° and 1.244, respectively (to be compared with those for the regular octahedron which are 60° and 1.22, respectively).[16] The equatorial plane is formed by two bpym-nitrogen atoms [N(1) and N(2)] and two oxygen atoms from two carboxylate groups [O(1) and O(2)] of two crystallographically independent bta ligands. The axial positions are occupied by a water molecule [O(4w)] and an oxygen atom from a symmetry-related carboxylate group [O(3)$^{b-2}$; (b-2) = $-0.5 + x$, $0.5 - y$, z]. The equatorial bond lengths vary in the range 2.015(2)−-2.178(3) Å, the Co−N distances [av value 2.152(5) Å] being longer than the Co−O ones [mean value 2.023(5) Å], as in **1**. The axial Co−O bonds [2.134(3) and 2.214(3) Å] are also longer than the equatorial Co−O ones.

The bpym ligand adopts the bis-bidentate coordination mode linking two cobalt atoms through its nitrogen atoms [N(1) and N(2) to Co(1) and N(1)$^{c-2}$ and N(2)$^{c-2}$ to Co(1)$^{c-2}$; symmetry code: (c-2) = x, $-y$, z]. The C(1)C(3)C(4)C(6) set of bpym-carbon atoms lie on a mirror plane. The value of the cobalt−cobalt separation through bis-chelating bpym is 5.685(2) Å [Co(1)⋯Co(1)$^{c-2}$]. There are two crystallographically independent bta ligands in **2** which are noted bta(1) [O(1)O(3)C(10)C(11)C(12) and symmetry-related atoms] and bta(2) [O(2)O(5)C(13)C(14)C(15) and symmetry-related atoms]. Each one is generated by the application of *2/m* symmetry sites that are located in the center of the aromatic rings. The bta(1) group acts as an octakis-monodentate ligand (Figure 3), each carboxylate group exhibiting the *antisyn* bridging conformation [O(1) and O(3) are bound to Co(1) and Co(1)$^{a-2}$, respectively]. The bta(2) group adopts a tetrakis-monodentate coordination mode (Figure 3) with the crystallographically independent carboxylate group acting as a monodentate ligand [O(2) bound to Co(1)]. Examples of bta^{4-}-containing cobalt(II) complexes with these coordination modes were already known[18] but **2** is the first example where both occur in the same species. The average value of the C−O bond distance of the bta(1) group is 1.252(4) Å,

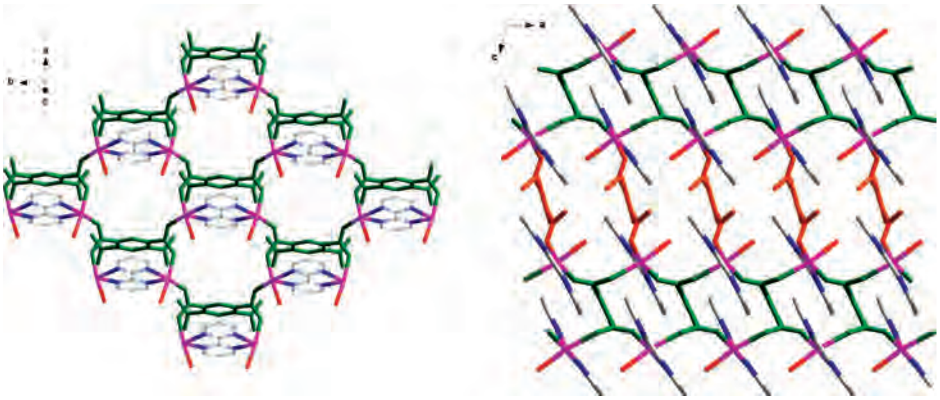

Figure 4. (left) Perspective view of the $[Co_2(bpym)(H_2O)_2]^{4+}$ units of **2** linked through the carboxylate-bridged forming the (4,4) a quadratic layer. (right) A view down the crystallographic *b* axis of a fragment of **2** showing the connection of two double layers (green) through the tetrakis-monodentate bta^{4-} ligand (orange). Hydrogen atoms have been omitted for the sake of clarity.

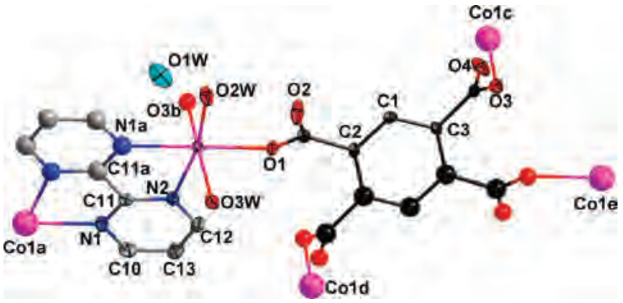

Figure 5. Perspective view of a fragment of the structure of **3** with the atom numbering scheme (the ORTEP representation denotes the crystallographically independent unit). The coordination modes of bta^{4-}and bpym ligands are also shown.

whereas those for the coordinated and free carboxylate-oxygen atoms of the bta(2) ligand are 1.277(5) and 1.226 (5) Å, respectively. The values of the dihedral angle between the plane of the aromatic ring and the monodentate and bridging *antisyn* carboxylate groups are 46.14(10)° and 62.79(12)°, respectively. The internal angles in the aromatic rings of the bta ligands are slightly smaller for the substituted carbon atoms than for the unsubstituted ones with average values of 119.6(2)° and 120.7(4)°, respectively. The value of the cobalt−cobalt separation through the *antisyn* carboxylate bridge is 5.288(3) Å [Co(1)$\cdots$Co(1)$^{a-2}$] whereas those through two carboxylate groups in *ortho*-, *meta*- and *para*-positions are 5.491(2) [Co(1)$\cdots$Co(1)$^{d-2}$; (d-2) = 0.5 − *x*, 0.5 − *y*,1 − *z*], 5.684(2) [Co(1)$^{a-2}\cdots$Co(1)$^{e-2}$], and 8.771(2) Å [Co(1)$\cdots$Co(1)$^{f-2}$; (f-2) = 0.5 − *x*, 0.5 + *y*,1 − *z*] for bta(1) and 7.716(3) [Co(1)$\cdots$Co(1)$^{g-2}$; (g-2) = −*x*, *y*, −*z*], 8.230(3) [Co(1)$\cdots$Co(1)$^{h-2;}$ (h-2) = *x*, 1 − *y*, *z*] and 11.282(3) Å [Co(1)$\cdots$Co(1)$^{i-2;}$ (i-2) = −*x*, 1 − *y*, −*z*] for bta(2), respectively.

$[Co_2(H_2O)_4(bta)(bpym)]_n \cdot 2nH_2O$ (3). The structure of **3** is made up of bpym-bridged $[Co_2(bpym)(H_2O)_4]^{4+}$ dinuclear units (Figure 5) similar to those of **1** and **2**which are interlinked through tetrakis-monodentate bta ligands into three chains, one along the [111] direction and the other two along the [1$\bar{1}$1] direction (Figure 6) affording a three-dimensional structure. It deserves to be noted that adjacent parallel chains are displaced by one unit along the growing direction with weak π-type interactions between bpym and bta ligands occurring in the node between perpendicular adjacent chains (Figure 7). This π pattern gives rise to a chain running parallel to the crystallographic *a* axis. The average values of the centroid-centroid distance and those of the angle between the normal to the ring and the centroid-centroid vector are about 3.537 Å and 10.9°. They are typical for slightly displaced face-to-face $\pi\cdots\pi$ alignment.[19] The crystal packing is strongly influenced by these $\pi\cdots\pi$ interactions. The presence of hydrogen bonds involving all the water molecules and some carboxylate-oxygen atoms (see Figure 7 and end of Table 4) contributes to the stabilization of the structure.

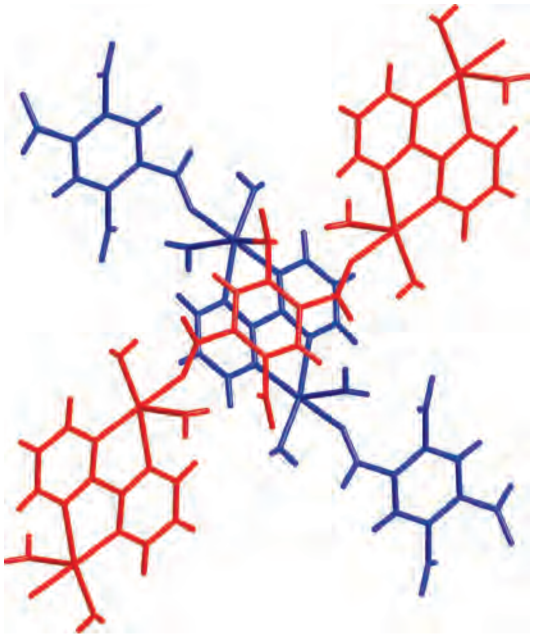

Figure 6. View of the crossing chains of **3** along the [111] (red) and [1$\bar{1}$1] (blue) directions.

Each cobalt atom exhibits an elongated octahedral surrounding with geometric values $\varphi = 58.57$ and $s/h = 1.236$.[16] The best equatorial plane is defined by two nitrogen atoms from the bpym ligand [N(1)$^{a-3}$ and N(2); (a-3) = −*x*, −*y*, −*z*], a water molecule [O(2w)], and one bta-carboxylate oxygen [O(1)]; therefore, the axial positions are filled by two oxygen atoms, one from a water molecule [O(3w)] and

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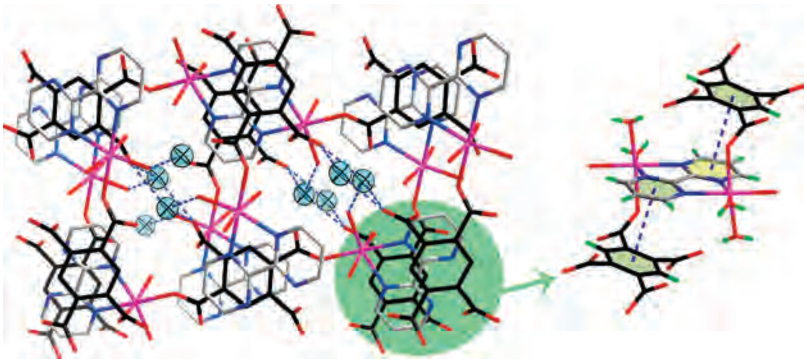

Figure 7. View of the crystal packing of **3** showing the main hydrogen bonds (blue broken lines). The $\pi\cdots\pi$ interactions among bta^{4-} and bpym ligands are highlighted.

the other from a symmetry-related bta-carboxylate [O(3)$^{b-3}$; (b-3) = 1 − x, −0.5 + y, 0.5 − z]. The mean values of the equatorial Co−O and Co−N bond distances are 2.065(2) and 2.164(2) Å, respectively. The average axial Co−O bond length is 2.095(2) Å. The value of the angle subtended at the cobalt atom by the bis-chelating bpym is 76.51(8)°. All these values are similar to those observed in **1** and **2**.

The pyrimidine rings of the bpym ligand are *quasi*-planar but the bpym molecule is not [the value of the dihedral angle between the pyrimidyl rings is 6.2 (6)°]. An inversion center is located at the middle of the C(11)−C(11)$^{a-3}$ bond of the bpym molecule. The inter-ring carbon−carbon bond length in **3** is 1.481(3) Å [1.482(6) and 1.484(6) Å for **1** and **2**, respectively], a value which, being somewhat shorter than the classical value of 1.54 Å for the C−C bond distance, is close to that found in the free bpym in the solid state [1.502(4) Å].[20] The bta ligand in **3** is centrosymmetric, and it adopts the tetrakis-monodentate bridging mode being coordinated to Co(1) and Co(1)$^{c-3}$ through the O(1) and O(3) atoms, respectively [(c-3) = 1 − x, 0.5 − y, 0.5 − z]. The average value of the C−O bond distances for the coordinated carboxylate-oxygen atoms [1.265(3) Å] is slightly longer than that for the free ones [1.242(3) Å]. The values of the dihedral angle between the plane of the benzene ring and the planes of the crystallographically independent carboxylate groups are 46.26(7)° and 51.96(7)°. The values of the internal angles in the benzene ring are slightly smaller at the substituted carbon atoms [mean value 119.3(2)°] compared to those at the unsubstituted ones [av value 121.4(2)°].

The values of the cobalt−cobalt separation through bis-bidentate bpym and the carboxylate groups in *ortho*- positions are 5.7503(5) [Co(1)$\cdots$Co(1)$^{a-3}$] and 5.6623(3) Å [Co(1)$\cdots$Co(1)$^{d-3}$; (d-3) = x, 0.5 − y, 0.5 + z)], respectively. These values are much shorter than the metal−metal distance across the bta-carboxylate groups in *trans* positions [11.4694(7) Å for Co(1)$\cdots$Co(1)$^{e-3}$; (e-3) = 1 − x, 1 − y, 1 − z].

Magnetic Properties. The magnetic behavior of **1**–**3** under the form of both $\chi_M T$ and χ_M versus T plots [χ_M is the magnetic susceptibility per two cobalt(II) ions] is shown in Supporting Information, Figures S1 (**1**), 8 (**2**) and S2 (**3**). The three plots exhibit the same trend: $\chi_M T$ continuously decreases upon cooling with $\chi_M T$ = 5.80 (μ_{eff} per Co^{II} = 4.82 μ_B; **1**), 5.74 (4.79 μ_B; **2**), and 5.60 cm^3 mol^{-1} K (4.73 μ_B; **3**) at 290 K and an extrapolated value that vanishes when T approaches zero. The susceptibility curves show maxima at 14.5 (**1**) and 11.5 K (**2** and **3**). These features reveal the occurrence of an overall antiferromagnetic coupling between the metal centers with a low-lying singlet spin state. Also, the fact that the values of μ_{eff} per Co^{II} ion are all above that calculated for the spin-only case (μ_{eff} = 3.87 μ_B for S = 3/2 with g = 2.0) indicates that a significant orbital contribution is involved. So, the degree of distortion of the CoN_2O_4 octahedron in **1**–**3** is not so important as to induce a total quenching of the orbital momentum of the $^4T_{1g}$ ground-state under O_h symmetry.

An examination of the crystal structures of the three compounds shows that several exchange pathways are involved: the bis-chelating bpym (**1**–**3**) and the bta ligand through an *antisyn* carboxylate bridge (**2**) and two carboxylate groups in 1,4 (**1**–**3**) and 1,2 and 1,3 (**2** and **3**) positions of the benzene ring. Previous magneto-structural studies with bpym-bridged cobalt(II) ions have shown the remarkable ability of the bpym molecule to mediate relatively important antiferromagnetic interactions when adopting the bis-bidentate bridging mode [-J values varying in the range 7.0–4.7 cm^{-1} with the exchange Hamiltonian defined as $\hat{H} = -J\hat{S}_1\hat{S}_2$]. The magnetic interaction between the cobalt(II) ions through the bta-carboxylate in adjacent or opposite positions is predicted to be very weak having in mind the vary small magnetic couplings observed through these pathways in isophthalate- and terephthalate-bridged copper(II) complexes.[21] Finally in the case of complex **2**, because of the presence of *antisyn* carboxylate bridges, weak ferro- or antiferromagnetic interaction could be involved through this pathway in the light of the magneto-structural results obtained with analogous carboxylate-bridged copper(II) complexes.[22]

In the light of the these considerations, we have attempted to analyze the magnetic behavior of **1**–**3** considering that the antiferromagnetic interaction between the high-spin cobalt(II) ions observed in this family is mediated only by the bpym bridge. Thus, we are dealing with a bypm-bridged cobalt(II) dinuclear model. However, the first-order isotropic exchange interaction (Heisenberg–Dirac−Van Vleck model)

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Table 5. Best-Fit Parameters for **1**–**3**[a]

compound	J	α	λ	Δ
1	−5.59(2)	1.29(1)	−140(2)	340(10)
2	−4.41(2)	1.24(1)	−150(2)	310(10)
3	−4.49(2)	1.25(1)	−150(2)	460(10)

[a] Values of J, λ, and Δ in cm^{-1}.

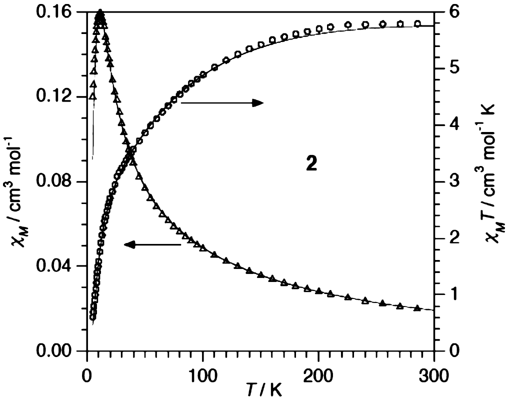

Figure 8. Temperature dependence of χ_M (△) and $\chi_M T$ (○) for **2**. The solid line is the best-fit curve through the Hamiltonian of eq 3 (see text).

is insufficient to discuss the magnetic properties of polynuclear compounds of six-coordinated cobalt(II) ions because of the need to consider orbitally dependent exchange interactions as well as spin–orbit coupling effects.[17c,23] The Hamiltonian describing the spin–orbit coupling is given by eq 1

$$\hat{H}_{SO} = -\alpha\lambda\hat{L}\hat{S} \qquad (1)$$

where λ is the spin–orbit coupling and α is an orbital reduction factor defined as $\alpha = Ak$ [the k parameter considers the reduction of the orbital momentum caused by the delocalization of the unpaired electrons and A contains the admixture of the upper $^4T_{1g}$ (^4P) state into the $^4T_{1g}$ (^4F) ground state]. The values of A range between 1.5 (weak crystal-field limit) and 1 (strong crystal field limit). In the frame of the isomorphism of the T_{1g} and P terms, $\mathbf{L}(T_{1g}) = -A\mathbf{L}(P)$, we can use $L = 1$ and treat eq 1 as an isotropic Hamiltonian describing the interaction between two angular moments $L = 1$ and $S = 3/2$, the coupling parameter being $-\alpha\lambda$.

In addition, the cobalt atoms in **1**–**3** have distorted octahedral surroundings. Under an axial distortion, the triplet orbital ground state $^4T_{1g}$ splits into a singlet $^4A_2$ and a doublet ^4E level with an energy gap of Δ which is considered positive when the orbital singlet is the lowest and negative when the orbital doublet is the lowest. The one-center operator responsible for such axial distortion can be expressed by the Hamiltonian of eq 2, which represents the zero-field splitting of the triplet $L = 1$.

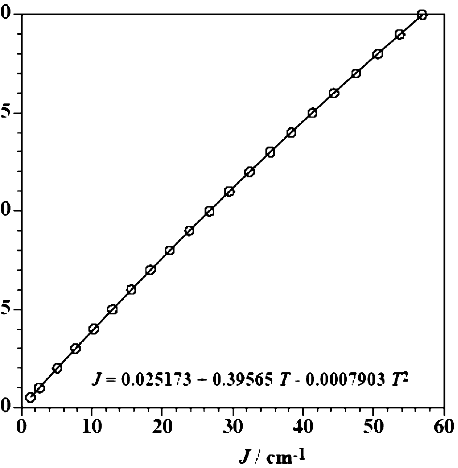

Figure 9. T_{max} versus $-J$ plot for antiferromagnetically coupled dinuclear cobalt(II) complexes. The solid line is the least-squares fit [eq 4] to the (T_{max}, $-J$) pairs obtained through the Hamiltonian of eq 3.

$$\hat{M}_{ax} = \Delta\lfloor\hat{L}_z^{\,2} - \frac{1}{3}L(L+1)\rfloor \qquad (2)$$

Therefore, the full Hamiltonian describing the magnetic properties of **1**–**3** is given by eq 3

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

where the first term accounts for the magnetic interaction between the two local spin quartets [S = 3/2 for each cobalt(II) ion] and the last one is the Zeeman interaction. The values of J, α, λ, and Δ could be determined by matrix diagonalization techniques. The values of the best-fit parameters are listed in Table 5. The calculated curves (solid lines in Figures 8, Supporting Information, Figures S1 and S2) match the magnetic data very well in the whole temperature range explored, and the values of the parameters obtained are within the range of those reported for high-spin octahedral Co(II) complexes.[17c,23] The similarity of the values of α, λ, and Δ for compounds **1**–**3** is related to the fact that the cobalt atoms in these compounds have the same CoN_2O_4 chromophore in a roughly C_{2v} point group. Finally, the somewhat larger antiferromagnetic coupling for **1** is due to the smaller deviation of the cobalt atom from the mean bpym plane in this compound [ca. 0.0882(6), 0.2959(2), and 0.2818(3) Å for **1**, **2**, and **3**, respectively].

In our theoretical simulation of the magnetic data of **1**–**3**, an examination of the shape of the theoretical χ_M versus T curves for the dinuclear cobalt(II) complexes, (the variable parameters being J, α, λ, and Δ) shows that in the case that a maximum of susceptibility is present (situation of significant antiferromagnetic coupling), its position is mainly determined by the value of J. Slight shifts of the position of

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Table 6. Selected Magneto-Structural Data for Bpym-Bridged Cobalt(II) Complexes

compound[a]	nuclearity	$d_{\mathrm{Co-N(bpym)}}$, Å[b]	$d_{\mathrm{(Co\cdots Co)}}$, Å[c]	$-J$, cm^{-1} [d]	ref
$[Co_2(hfa)_4(bpym)]$	dimer	2.15	5.75	7.0	17e
$[Co_2(bpym)(H_2O)_8](NO_3)_4$	dimer	2.16	5.76	5.4	17c
$[Co_2(bpym)(H_2O)_8](SO_4)\cdot 2H_2O$	dimer	2.17	5.78	4.7	17c
$[Co_2(bpym)_3(NCS)_4]$	dimer	2.23	5.94	6.2	17c
$[Co_2(bpym)_3(H_2O)_4](NO_3)_4\cdot 2H_2O$	dimer	2.14	5.74	5.4	17b
$[Co_2(bpym)_3(H_2O)_2(SO_4)_2]\cdot 12H_2O$	dimer	2.15	5.74	5.1	17b
$[Co(bpym)(H_2O)_2]_n(NO_3)_{2n}$	1D	2.17	5.80	5.6	17b
1	1D	2.165(4)	5.77	5.6	this work
2	3D	2.146(5)	5.68	4.4	this work
3	3D	2.164(2)	5.75	4.5	this work

[a] Abbreviations used: hfac = hexafluoroacetylacetonate; 1D = one-dimensional; 3D = three-dimensional. [b] Average value for the cobalt to nitrogen (bridging bpym) bond. [c] Metal−metal separation through bridging bpym. [d] Exchange coupling through bridging bpym.

this maximum are caused by the Δ parameter when comparing cases where very different values of Δ are involved. This effect can be neglected under the usual distortions, and a simple relationship between the value of the magnetic coupling and that of the temperature of the maximum of susceptibility could be derived as shown by Figure 9. In this graphics, the temperature of the maximum of the magnetic susceptibility calculated through the full Hamiltonian [eq 3], is plotted against $-J$ in the range $1 \geq -J \geq 55$ cm^{-1}). A least-squares fit leads to the following empirical expression [eq 4] (solid line in Figure 9)

$$J = 0.02517 + 0.39565T - 0.00079T^2 \qquad (4)$$

The value of J (in cm^{-1}) can be determined through this expression by substituting T by the value of the temperature (in K) of the maximum of the magnetic susceptibility. In the present case, for example, the calculated values of J through eq 4 are -5.60 cm^{-1} for **1** and -4.47 cm^{-1} for **2** and **3**. As one can see, they are equal to those determined by the fit through the full Hamiltonian of eq 3.

The values of the antiferromagnetic interactions through the bridging bpym in **1**–**3** compare well with those measured in previous bpym-bridged cobalt(II) complexes (Table 6). Once more, the results of the present work support the remarkable ability of the bpym ligand to mediate magnetic interactions between the paramagnetic centers that it bridges; the best examples illustrating this ability being the bpym-bridged copper(II) complexes where antiferromagnetic interactions as large as -230 cm^{-1} were observed.[3d,24]

In summary, we have shown here how the combination of bpym and the tetracarboxylate ligand bta^{4-} provides new extended cobalt(II) magnetic systems where the overall connectivity of the structures is ensured by the bis-chelating bpym and different coordination modes of the polycarboxylate ligand. The extension of these studies to other transition metal ions in a very near future will produce a wide family of coordination polymers with interesting architectures and, probably, new spin topologies.

Conclusions

The present work affords a new strategy to build multidimensional coordination polymers that is based on the use of the dicobal(II) unit $[Co_2(bpym)]^{4+}$ as a "building block". These compounds are suitable examples to be used as models to investigate the influence of the nature of the peripheral carboxylate ligands on the magnitude of the exchange coupling and also as coligands in the building blocks for the preparation of extended magnetic systems. These features have to be taken into account when analyzing the magnetic properties of extended arrays of complicated magnetic systems which have started to become more and more common in the literature in the last years.

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Supporting Information Available: Crystallographic data in CIF format for **1** (CCDC 666364), **2** (CCDC 666365), and **3** (CCDC 666366). This material is available free of charge via the Internet at http://pubs.acs.org.

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