Toward a better understanding of honeycomb alternating magnetic networks

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Two new two-dimensional homometallic compounds $\{[M_2(bpm)(ox)_2]_n \cdot 5nH_2O\}$ with M = Co(II) (**1**) and Zn(II) (**2**) and the mononuclear nickel(II) complex $[Ni(bpm)_2(ox)] \cdot 2H_2O$ (**3**) [bpm = 2,2'-bipyrimidine and ox = oxalate] have been prepared and structurally characterized. **1** and **2** are isostructural compounds whose structure is made up by oxalate-bridged M(II) cations cross-linked by bis-bidentate bpm molecules to afford a honeycomb layered network extending in the crystallographic *ab* plane. The layers are eclipsed along the crystallographic *c* axis and show graphitic-like interactions between the bpm rings. The three-dimensional supramolecular network deriving from such interactions is characterized by hexagonal-shaped channels extending in the same direction. Each M(II) ion in **1** and **2** is tris-chelated with four oxygen atoms from two oxalate groups and two bpm-nitrogen atoms building a distorted octahedral surrounding. The reduced values of the angles subtended by the bis-chelating bpm [77.69(8) (**1**) and 76.59(8)º (**2**)] and oxalate [79.69(6) (**1**) and 80.01(5)º (**2**)] are the main factors accounting for this distortion. The values of the metal-metal separation through bridging bpm are 5.6956(7) (**1**) and 5.7572(9) Å (**2**) whereas those across the bis-bidentate oxalate are 5.4306(4) (**1**) and 5.4058(5) Å (**2**). **3** is a neutral mononuclear nickel(II) complex where each metal ion is six-coordinate with four nitrogen atoms from two bpm ligands in a *cis* arrangement and two oxalate-oxygen atoms building a somewhat distorted octahedral surrounding. The values of the angles subtended at the nickel(II) ion by bpm and oxalate are 78.14(4) and 80.95(5)°, respectively. The magnetic properties of **1** have been investigated in the temperature range 1.9-295 K. They are typical of an overall antiferromagnetic coupling with a maximum of the magnetic susceptibility at 22.0 K. The analysis of the susceptibility data of **1** through an effective spin Hamiltonian allowed a satisfactory simulation in the temperature range 10-295 K with the best-fit parameters $\lambda = -110$ cm^{-1}, $\alpha = 1.1$, $|\Delta| = 400$ cm^{-1}, $J_{ox} = -11.1$ cm^{-1} and $J_{bpm} = -5.0$ cm^{-1}. The values of the antiferromagnetic coupling through bpm and ox in **1** have been also supported by electronic structure calculations based on Density Functional Theory (DFT) and they compare well with those reported in the literature for bpm-bridged dicobalt(II) complexes and oxalate-bridged cobalt(II) chains.

Introduction

Polynuclear systems based on the assembling of paramagnetic metal ions and organic ligands have received great attention in the last three decades because of the structural diversity and the variety of the magnetic properties they exhibit.[1-7] The first studies focused on simple dinuclear complexes aiming at understanding the correlations between structure and magnetic properties.[8-14] On the basis of the acquired knowledge, the nuclearity was increased to move from discrete polynuclear motifs to nD systems (n = 1-3) in the search for molecule-based magnets[2c,d,e,3-5] and multifunctional materials.[6] In this respect, metal complexes with cyanide,[15] oxalate[16] and oxamato/oxamidato[17] as bridging ligands have been thoroughly investigated because of their remarkable ability to mediate electronic interactions when acting as bridges between the paramagnetic centres. Restricting ourselves to highly appealing results and for brevity reasons we can mention high-spin molecules,[18] Single Ion Magnets (SIMs),[19] Single Molecule Magnets (SMMs),[15g,h,20] Single Chain Magnets (SCMs),[21,22] and molecule-based magnets,[15a,l,16d,h,17b-d,23,24] as materials where the coexistence of different properties (conductivity, chirality, redox activity, photosensitivity, luminescent character, etc.) is of outmost interest envisaging the achievement of molecule-based multifunctional magnetic materials (MMMMs).[6,7,16h-i,16k-m,17d,23m,24]

Apart from its neutral character, 2,2'-bipyrimidine (hereafter noted bpm) well resembles the oxalate and oxamate/oxamidate ligands. In fact, it has the same topology of the donor atoms and it commonly adopts the bidentate and bis-bidentate coordination modes in its metal complexes being also a good mediator of magnetic interactions when acting as a bridge between paramagnetic centres (the values of J reaching up to -236 cm^{-1} through the spin Hamiltonian $\boldsymbol{H} = -J\boldsymbol{S}_A \cdot \boldsymbol{S}_B$).[25] The nuclearity and dimensionality of the resulting bpm-containing compounds are strongly dependent on the metal-to-bpm molar ratio and also on the nature of the anion/coligand present which is required to fulfil the charge balance. So, the dinuclear unit $[\{M^{II}(H_2O)_4\}_2(\mu\text{-bpm})]^{4+}$ (M = Mn, Fe, Co, Ni, Cu and Zn), which is formed in aqueous solution by using a 2:1 M(II):bpm molar ratio and where the water molecules act as end cap ligands, was isolated as nitrate or sulphate salt.[26-31] The fact that these coordinated water molecules represent easy leaving groups in the presence of other ligands makes this entity a suitable precursor of tailor-made polynuclear species. In fact, the replacement of one or two water molecules at each metal centre by coordinating dianions adopting monodentate (squarate, dianion of 3,4-dihydroxycyclopent-3-ene-1,2-dione) or bidentate (croconate and malonate, dianions of 4,5-dihydroxycyclopent-4-ene-1,2,3-trione and propanedioic acid, respectively) coordination modes afforded the corresponding neutral homodinuclear complexes.[32,33]

Interestingly, in the presence of potentially bridging monoatomic groups, regular alternating μ-bpm/di-μ-X copper(II) chains (X = OH^- and F^-)[34] or two-dimensional motifs constituted by di-μ-Y copper(II) chains (Y = Cl^- and Br^-) cross-linked by bis-bidentate bpm molecules[25a] were isolated and magneto-structurally characterized. The reaction of $[\{M^{II}(H_2O)_4\}_2(\mu\text{-bpm})]^{4+}$ with pseudohalides (cyanate, thiocyanate, azide and dicyanamide) produced nD compounds (n = 1-3). [25b,35,36] The magnetic interactions through the two types of bridges in these complexes can be of the same or opposite nature. So, the alternation of antiferro- and ferromagnetic interactions through the bis-bidentate bpm and double end-on azido bridges respectively, occurs in the honeycomb layered compounds of general formula $\{[M_2(bpm)(N_3)_4]\}_n$ [M = Mn(II) Fe(II), Co(II)][35b-e] and regular alternating antiferro- (through bis-bidentate bpm) and ferromagnetic (across the double hydroxo bridge) interactions are observed in the corresponding μ-bpm/di-μ-OH copper(II) chains.[34]

The combination of bpm and oxalate (ox) as ligands with first-row transition metal ions yielded mixed-ligand mononuclear complexes such as $[Cu(bpm)(ox)(H_2O)_2] \cdot 5H_2O$,[37] $AsPh_4[Cr(bpm)(ox)_2] \cdot H_2O$[38] ($AsPh_4^+$ = tetraphenylarsonium) as well as the neutral 2D networks of formulas $\{[NaCr(bpm)(ox)_2]_n \cdot 5nH_2O\}$,[38] $[K(H_2O)Cr(bpm)(ox)_2]_n$,[39] and $\{[M_2(bpm)(ox)_2]_n \cdot nH_2O\}$ with n = 6 [M = Mn(II)] and 5 [M = Fe(II) and Cu(II)].[37,40] Aiming at extending this work with mixed-ligand complexes to other first-row transition metal ions, we have for a long time pursued the elusive Co(II), Zn(II) and Ni(II) honeycomb analogues. We present herein the preparation and structural characterization of the two novel honeycomb layered compounds of formula $\{[M_2(bpm)(ox)_2]_n \cdot 5nH_2O\}$ [M = Co(II) (**1**) and Zn(II) (**2**)] and the mononuclear nickel(II) complex $[Ni(bpm)_2(ox)] \cdot 2H_2O$ (**3**). Variable-temperature magnetic study and density functional theory (DFT) type calculations have been performed on **1** to support the structure-function correlation.

Experimental

Materials. Bpm, $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $K_2ox \cdot H_2O$ and $(NH_4)_2ox \cdot H_2O$ were purchased from commercial sources and used as received. Elemental analyses (C, H, N) were performed by the Microanalytical Service of the Università della Calabria.

Synthesis of the Compounds. $\{[M_2(bpm)(ox)_2]_n \cdot 5nH_2O\}$ [M = Co (1) and Zn (2)]. Prismatic orange (**1**) and colorless (**2**) crystals were obtained by slow diffusion in an H-shaped tube at room temperature of an aqueous solution of $[M_2(bpm)(H_2O)_8](SO_4)_2 \cdot 2H_2O$ (0.25 mmol) [M = Co (**1**) and Zn (**2**)][28,31] at one arm and another aqueous solution containing A_2ox (0.5 mmol) [A = Na^+ (**1**) and NH_4^+ (**2**)] at the other one. Both arms were carefully filled with water, capped with parafilm and the diffusion was allowed to proceed at room temperature. X-ray quality crystals of **1** and **2** were obtained within two weeks. Anal. data for **1** ($C_{12}H_{16}Co_2N_4O_{13}$, MW = 542.15) Calcd: C, 26.59, H, 2.97, N, 10.33. Found: C, 26.67, H, 2.94, N, 10.41%. Anal. data for **2** ($C_{12}H_{16}N_4O_{13}Zn_2$, MW = 555.03) Calcd: C, 25.97, H, 2.91, N, 10.09. Found: C, 26.09, H, 2.94, N, 10.15%.

$[Ni(bpm)_2(ox)] \cdot 2H_2O$ (3). All our attempts to prepare the 2D nickel(II) derivative by means of the slow diffusion technique above mentioned were unsuccessful. For this reason, the synthetic strategy was changed starting from $[Ni(ox)(H_2O)_2]_n$ which was prepared by reaction of stoichiometric amounts of $NiSO_4 \cdot 6H_2O$ and $K_2ox \cdot H_2O$. Bpm (0.2 mmol) was added to an aqueous suspension of nickel(II) oxalate dihydrate (0.1 mmol, 20 mL) under continuous stirring and heating up to 90 °C for twenty minutes. The resulting purple-greenish solution was allowed to evaporate at room temperature. X-ray quality crystals of **3** as violet prisms were obtained by recrystallization of the obtained solid from acetonitrile. Further attempts to get the desired nickel(II) compound starting from **3** were also unsuccessful. Anal. data for **3** ($C_{18}H_{16}N_8NiO_6$, MW = 499.10) Calcd: C, 28.88, H, 3.23, N, 22.4. Found: C, 29.03, H, 3.29, N, 22.31%.

Physical Measurements. IR spectra of **1-3** were performed with a Perkin Elmer 1750 FT-IR spectrometer as KBr pellets in the 4000-400 cm^{-1} region. The magnetic susceptibility measurements on a polycrystalline sample of **1** were carried out with a Quantum Design SQUID magnetometer in the temperature range 1.9-295 K under applied dc magnetic fields of 1 T ($100 < T \leq 295$ K) and 250 G ($T \leq 100$ K). Diamagnetic corrections for **1** were estimated from Pascal's constants[41] as -246 x-10^{-6} cm^3 mol^{-1} K [per two Co(II) ions]. Corrections for the magnetization of the sample holder (a plastic bag) were also applied.

Computational Details. Calculations were performed through the Gaussian09 package using the B3LYP functional and the quadratic convergence approach.[42-44] Triple-ζ and double-ζ all electron basis sets, as proposed by Ahlrichs *et al*., were used for the metal ions and for the rest of atoms, respectively.[45,46] An approach based on the use of broken-symmetry (BS) functions built from localized orbitals was used to evaluate the energies of several spin states.[47,48] The BS functions, which provide positive or negative spin densities on the paramagnetic centres, were obtained from the guess functions generated with the fragment tool implemented in Gaussian09 [Frisch, M. J. *et al.* Gaussian 09 (Revision B.1) ed.; Gaussian, Inc: Pittsburgh, PA, 2009] The molecular geometries for each dinuclear model were extracted from the experimental crystal structure. To stabilize the electronic surplus on the charged ligands coordinated to M^{II} ions, a polarizable continuum model (PCM) was introduced in the calculations. Parameters corresponding to the acetonitrile solvent were included to simulate the electronic effects of the surrounding molecules.[49]

Table 1. Summary of the Crystal Data and Refinement Details for $\{[M_2(bpm)(ox)_2]_n \cdot 5nH_2O\}$ [M = Co (**1**) and Zn (**2**)] and $[Ni(bpm)_2(ox)] \cdot 2H_2O$ (**3**).

	1	**2**	**3**
formula	$C_{12}H_{16}Co_2N_4O_{13}$	$C_{12}H_{16}N_4O_{13}Zn_2$	$C_{18}H_{16}N_8NiO_6$
*M*r	542.15	555.03	499.10
crystal system	monoclinic	monoclinic	monoclinic
space group	*C*2/*m*	*C*2/*m*	*C*2/*c*
a/Å	9.4514(2)	9.534(1)	19.038(2)
b/Å	16.7427(4)	16.614(2)	8.8357(8)
c/Å	6.1969(2)	6.1915(6)	15.294(1)
β/°	101.455(1)	101.659(3)	128.246(6)
V/Å^3	961.08(4)	960.4(2)	2020.5(3)
Z	2	2	4
D_c/g cm^{-3}	1.873	1.919	1.641
T/K	293	293	293
F(000)	548	560	1024
μ(Mo-Kα)/mm^{-1}	1.804	2.576	1.017
θ range/deg	2.43-31.29	2.45-30.51	2.68-32.02
refl. collected	7834	10829	18070
refl. indep. [R_{int}]	1603 [0.0234]	1520 [0.0356]	3204 [0.0211]
refl. obs. [$I > 2\sigma(I)$]	1361	1359	2860
$R_1{}^a$ [$I > 2\sigma(I)$] (all)	0.0355 (0.0456)	0.0307 (0.0829)	0.0259 (0.0298)
$wR_2{}^b$ [$I > 2\sigma(I)$] (all)	0.0934 (0.1004)	0.0357 (0.860)	0.0724 (0.0745)
Goodness-of-fit on F^2	1.076	1.096	1.061
$\Delta\rho_{max, min}$/e Å^{-3}	1.014 / -0.377	1.087 / -0.368	0.373/ -0.210

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2\}^{1/2}$ and $w = 1/[\sigma^2(F_o)^2 + (mP)^2 + nP]$ with $P = (F_o^2 + 2F_c^2)/3$, m = 0.0569 (**1**), 0.0475 (**2**) and 0.0395 (**3**), and n = 0.7362 (**1**), 0.9680 (**2**) and 0.9090 (**3**).

X-ray Crystallographic Analysis. X-ray diffraction data on single crystals of **1-3** were collected with a Bruker-Nonius APEXII CCD area detector diffractometer using graphite-monochromated Mo-Kα radiation (α = 0.71073 Å). Data for compounds **1-3** were processed through the SAINT[50] reduction and SADABS[51] multi-scan absorption software. The structures were solved by direct methods and subsequently completed by Fourier recycling using the SHELXTL software package.[52] All non-hydrogen atoms were refined anisotropically except for the oxygen atoms of the water molecules of crystallization in **1** and **2**. The hydrogen atoms on the bpm ligand were placed in calculated positions and refined as riding atoms, while those on the water molecules of crystallization in **3** were found and refined with restraints. The hydrogen atoms on the water molecules of **1** and **2** were not located. The final full-matrix least-squares refinements on F^2, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, reached convergence with the values of the discrepancy indices given in Table 1. The graphical manipulations were performed with the DIAMOND[53] program and the XP utility of the SHELXTL system. CCDC reference numbers 1039718-1039720 (**1-3**). See Supporting Information for the crystallographic data in CIF format.

Results and discussion

Synthesis and IR Characterization of 1-3. The easy replacement of the coordinated water molecules from the dinuclear species $[\{M(H_2O)_4\}_2(\mu\text{-bpm})]^{4+}$ by the oxalate ligand accounts for the formation of the neutral and insoluble honeycomb layered compounds **1** and **2**. This preparative route was successfully used to prepare the parent 2D compounds $\{[Cu_2(bpm)(ox)_2]_n \cdot 5nH_2O\}$ (**4**),[37] $\{[Fe_2(bpm)(ox)_2]_n \cdot 5nH_2O\}$ (**5**)[40b] and $\{[Mn_2(bpm)(ox)_2]_n \cdot 6nH_2O\}$ (**6**).[40a] However, in the case of the Ni(II) derivative, all out attempts to get single crystals failed, a poorly diffracting solid being obtained. The use of the chain compound $[Ni(ox)(H_2O)_2]_n$ as source of nickel(II) and oxalate afforded the mononuclear complex **3** in its reaction with bpm.

The infrared spectra of **1** and **2** exhibit strong and broad absorptions in the high frequency range centred at ca. 3486 (1) and 3495 cm^{-1} (**2**) [O-H stretching vibrations) which are due the presence crystallization water molecules being associated by hydrogen bonds. The occurrence of a very asymmetric doublet at 1580s and 1565w cm^{-1} (**1**) and 1578s and 1563w cm^{-1} (**2**) (ring stretching modes of bpm) is a diagnostic of the bis-chelating character of bpm in them.[25b,28,36c] The pattern of the peaks concerning the oxalate ligand in **1** and **2** {1680s (**1**) and 1675s cm^{-1} (**2**) [ν_{as}(CO)], 1350m and 1315s (**1**) and 1363m and 1317s cm^{-1} (**2**) [ν_s(CO)] and 810m (**1**) and 803m cm^{-1} (**2**) [δ(OCO)]} also supports the bis-bidentate coordination of such a ligand.[54] Finally, the peaks concerning the oxalate {1720w, 1660s and 1645s cm^{-1} [ν_{as}(CO)], 1430m and 1290s cm^{-1} [ν_s(CO)] and 795 cm^{-1} [δ(OCO)]} and bpm groups [quasi symmetric doublet at 1570s and 1550m cm^{-1} (ring stretching modes)] in **3**, point out their coordination to the metal ions as bidentate ligands.[25b,55] All these spectroscopic suggestions of **1-3** have been confirmed by their X-ray structures (see below).

Description of the Structures. $\{[M_2(bpm)(ox)_2]_n \cdot 5nH_2O\}$ [M = Co(II) (1) and Zn(II) (2). The structures of **1** and **2** are made up of parallel neutral sheets containing an hexagonal array of cobalt(II) (**1**) or zinc(II) (**2**) ions bridged by bis-bidentate oxalate and bpm ligands [Figs. 1 and 2]. Each (6,3) honeycomb layer grows in the *ab* plane and it is formed by repeating hexanuclear rings, while the crystallization water molecules are placed in the interlayer space [Fig. 2 (right)]. The layers interact each other through π - π stacking between the aromatic bpm rings [the separation between the bpm planes of neighbouring layers is 3.551(3) (**1**) and 3.529(3) Å (**2**)] and hydrogen bonds where the crystallization water molecules and some oxygen atoms of the ox groups are involved (Fig. 3).

The crystallization water molecules are arranged into five-membered planar rings [the maximum deviation from the mean plane being 0.058(6) (**1**) and 0.082(6) Å (**2**) at O(3w)], which are placed between two sheets and fit into the hexagonal channels generated by the superposition of the layers. They are linked together by means of hydrogen bonds within the ring [2.90(1) (**1**), 2.91(1) (**2**), 2.80(1) (**1**), 2.77(1) (**2**), and 2.67(1) (**1**), 2.68(1) Å (**2**) for O(1w)···O(2w), O(2w)···O(3w) and O(3w)···O(3we), respectively; (e) = 2-*x*, *y*, 2-*z*], between adjacent rings [2.95(2) (**1**) and 2.94(2) Å (**2**) for O(2we)···O(2wn); (a) = *x*, *y*, -1+*z*] and between the ring and the channel wall [2.915(4) (**1**) and 2.931(4) Å (**2**) Å for O(1w)···O(2i) and 2.84(1) Å (**1** and **2**) for O(3we)···O(2p); (i) = 1.5-*x*, -0.5+*y*, 1-*z*; (p) = 1.5-*x*, 1.5-*y*, 1-*z*].

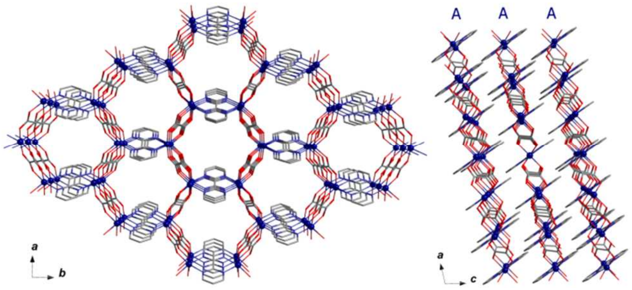

Figure 1. Projection views along the crystallographic *c* (left) and *b* (right) axes of the structure of **1** and **2** showing the arrangement of the neutral layers. The water molecules were omitted for clarity.

These hydrogen bonds contribute all together to the stabilization of the two-dimensional structure. Each metal ion in **1** and **2** exhibit a distorted octahedral MN_2O_4 geometry [M = Co(II) (**1**) or Zn(II) (**2**)**]** being coordinated to four oxygen atoms of two oxalate ligands and two nitrogen atoms of the bpm molecule.

The reduced values of the angles subtended at the cobalt(II) and zinc(II) ions by the bis-chelating bpm [N(1)–M(1)–N(1a)] = 77.69(8) (**1**) and 76.59(8)° (**2**)] and ox [O(1)–M(1)–O(2) = 79.69(6) (**1**) and 80.01(5)° (**2**)] ligands are the main factors accounting for this distortion. The cobalt and zinc atoms lie exactly in the bpm plane and they are slightly shifted from the ox planes [0.062(3) (**1**) and 0.029(3) Å (**2**)]. The bpm and ox ligands are planar and they form a dihedral angle of 69.2(1) (**1**) and 70.3(1)° (**2**). The plane of the five-membered ring of the water molecules makes dihedral angles with the ox plane of 82.6(2) (**1**) and 82.4(2)° (**2**). The intra-ring carbon–carbon bond distances in bpm [1.479(5) (**1**) and 1.487(5) Å (**2**)] are significantly shorter than the carbon–carbon bond lengths in the oxalate ligand [1.552(4) (**1**) and 1.550(4) Å (**2**)]. The values of the bond lengths and angles within the bpm and ox ligands are in agreement with those reported in the literature.

1 and **2** are isostructural to the parent copper(II) and iron(II) complexes of formula $\{[Cu_2(bpm)(ox)_2]_n \cdot 5nH_2O\}$[37] (**4**), $\{[Fe_2(bpm)(ox)_2]_n \cdot 5nH_2O\}$ (**5**)[40b] and similar to both the homometallic manganese(II) compound $\{[Mn_2(bpm)(ox)_2]_n \cdot 6nH_2O\}$ (**6**)[40a] (which features hexanuclear instead of pentanuclear water rings), and the heterometallic Cr(III)–Na(I) complex $\{[NaCr(bpm)(ox)_2]_n \cdot 5nH_2O\}$ (**7**).[38] The values of the bond distances in **1** and **2** around the cobalt(II) and zinc(II) ions are close but shorter than those observed in **5** and **6**, in agreement with the decreasing ionic radius of the respective metal ions (see Table 2). As a consequence of the geometrical variations around the divalent metal ion, smaller six-membered metal rings occur in **1** and **2** with respect to **5** and **6**, as highlighted by the values of the intra-ring M···M distances (see Table 3).

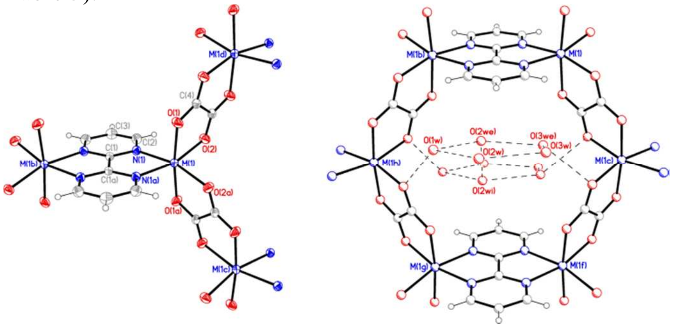

Figure 2. (Left) The asymmetric unit in a fragment of **1** (M = Co) and **2** (M = Zn) showing the atom numbering scheme. **(**Right**)** The hexanuclear repeating unit and two adjacent water rings in **1** and **2**. Hydrogen bonds are drawn as broken lines.

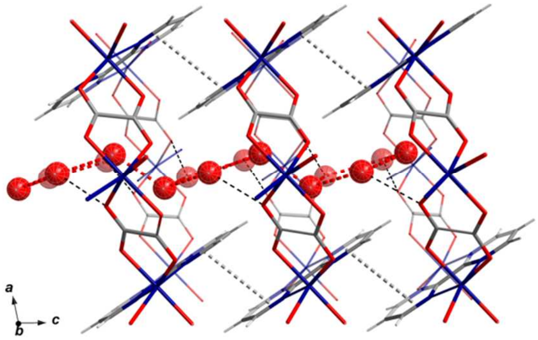

Figure 3. A view along the crystallographic *b* axis of the layers showing the π–π type interactions between the bpm molecules of adjacent layers and the hydrogen bonds between the water rings as well as between the water rings and the oxalate oxygen atoms of the channel walls.

$[Ni(bpm)_2(ox)] \cdot 2H_2O$ (**3**). The structure of **3** is made up of neutral $[Ni(bpm)_2(ox)]$ mononuclear units and crystallization water molecules linked together by hydrogen bonds involving one oxalate-oxygen [O(2)], a bpm-nitrogen [N(4)] and the two water molecules. Weak π-π off-set face-to-face type interactions between bpm ligands from adjacent mononuclear units contribute to the stabilization of the resulting supramolecular three-dimensional network. Perspective views of the tris-chelated entity and the supramolecular layer generated by the mentioned hydrogen bonding interactions are shown in Figs. 4 and 5 respectively, whereas selected bond lengths and angles together with the hydrogen bonds are listed in Table 4.

Each nickel(II) ion in **3** exhibits a distorted octahedral MN_2O_4 geometry, being coordinated to four nitrogen atoms from two bpm ligands in *cis* positions and two oxygen atoms from a bidentate oxalate. The Ni-O_{ox} bond distance (ca. 2.03 Å) is basically identical to the Ni-N_{bpm} bond lengths (ca. 2.08 Å). The reduced values of the angles subtended at the nickel atom by the chelating bpm [78.14(4)° for N(1)–Ni(1)–N(3)] and ox [80.95(5)° for O(1)–Ni(1)–O(1a); symmetry code: (a) = -*x*, +*y*, 0.5-*z*] ligands are the main factors accounting for this distortion.

Table 2. Selected bond distances (Å) and angles (deg) for **1**, **2**, **4**, **5** and **6**.[a]

M =	Mn(II) (**6**)	Fe(II) (**5**)	Co(II) [**1**]	Cu(II) (**4**)	Zn(II) [**2**]
M(1)-O(1)	2.128(5)	2.101(3)	2.079(2)	2.076(3)	2.082(2)
M(1)-O(2)	2.159(3)	2.126(3)	2.089(2)	2.086(3)	2.074(2)
M(1)-N(1)	2.313(3)	2.191(3)	2.135(2)	2.129(3)	2.165(2)
O(1)-M(1)-O(1a)	162.8(1)	171.9(1)	173.04(9)	173.8(1)	173.23(8)
O(1)-M(1)-O(2)	76.7(1)	78.3(1)	79.69(6)	79.7(1)	80.01(5)
O(1)-M(1)-N(1)	102.8(1)	97.9(1)	97.48(7)	97.0(1)	98.14(6)
O(1)-M(1)-N(1a)	89.2(1)	88.5(1)	87.96(6)	87.8(1)	87.20(6)
O(2)-M(1)-O(1a)	93.1(1)	96.3(1)	95.54(6)	96.0(1)	95.50(6)
O(2)-M(1)-O(2a)	104.2(1)	97.1(2)	94.5(1)	94.6(1)	97.93(9)
O(2)-M(1)-N(1)	92.9(1)	95.0(1)	95.26(6)	95.2(1)	94.22(6)
O(2)-M(1)-N(1a)	156.9(1)	163.0(1)	164.93(6)	164.9(1)	163.11(6)
N(1)-M(1)-N(1a)	72.3(1)	76.1(1)	77.69(8)	77.7(1)	76.59(8)

[a] Symmetry code used to generate equivalent atoms: (a) = -x+1, y, -z+1.

Table 3. Values of the intra-ring M···M distance (Å) for **1**, **2**, **4**, **5** and **6**.[a]

M =	Mn(II) (**6**)	Fe(II) (**5**)	Co(II) [**1**]	Cu(II) (**4**)	Zn(II) [**2**]
M(1)···M(1c)	5.608(1)	5.513(1)	5.4306(4)	5.406(1)	5.4058(5)
M(1)···M(1b)	6.052(1)	5.824(1)	5.6956(7)	5.680(1)	5.7572(9)
M(1)···M(1f)	9.750(1)	9.674(3)	9.4514(2)	9.445(2)	9.534(1)
M(1)···M(1h)	10.233(1)	9.754(2)	9.6131(2)	9.559(2)	9.577(1)
M(1)···M(1g)	11.748(1)	11.292(2)	11.0349(4)	11.022(2)	11.137(1)

[a] Symmetry codes used to generate equivalent atoms: (b) = x, -y+1, z; (c) = x+1/2, -y+3/2, z; (f) = x+1, y, z; (g) = x+1, -y+1, z; (h) = x+1/2, y-1/2, z.

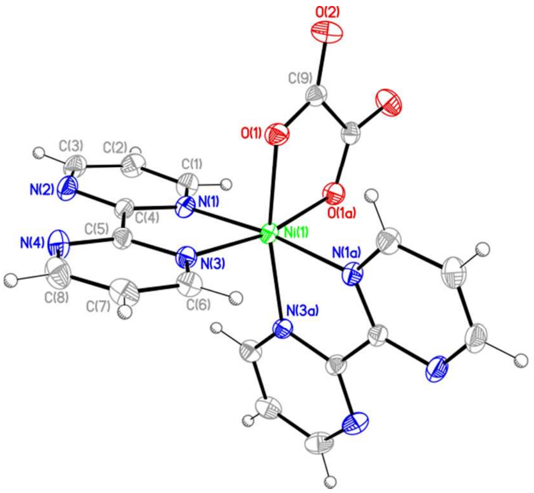

Figure 4. Crystal structure of the neutral mononuclear unit of **3** showing the atom numbering scheme.

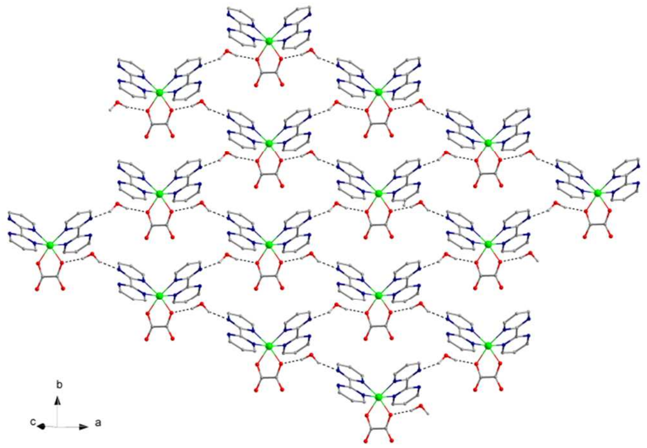

Figure 5. A view of the supramolecular layered structure of **3**. Hydrogen bonds are depicted as dashed lines.

These values agree with those previously reported for the oxalate-containing mononuclear complexes $K_2[Ni(ox)_2(H_2O)_2] \cdot 4H_2O$[55a] and $[Ni(bpy)_2(ox)] \cdot nH_2O$ [bpy = 2,2'-bipyridine and n = 4 and 5).[56b,c] The bpm and ox ligands are practically planar and they are almost perpendicular to each other. The values of the dihedral angle between the oxalate and the two bpm planes are 93.8(1) and 86.2(1)º respectively, whereas that between the bpm planes is 73.3(1)º. The shortest intermolecular metal-metal separation is 7.679(1) Å [Ni(1)···Ni(1b); symmetry code: (b) = -0.5-*x*, 1.5-*y*, -*z*].

Table 4. Selected bond distances (Å) and angles and hydrogen bonds details for **3**.[a]

Ni(1)-O(1)	2.032(1)	Ni(1)-N(3)	2.081(1)
Ni(1)-N(1)	2.084(1)		
O(1)-Ni(1)-O(1a)	80.95(5)	N(1)-Ni(1)-N(3)	78.14(4)
O(1)-Ni(1)-N(1)	91.64(4)	N(1)-Ni(1)-N(3a)	97.09(4)
O(1)-Ni(1)-N(1a)	93.86(4)	N(1) -Ni(1)-N(1a)	172.76(6)
O(1)-Ni(1)-N(3)	90.56(4)	N(3)-Ni(1)-N(3a)	98.93(5)
O(1)-Ni(1)-N(3a)	168.23(4)		

D-H···A	**D-H/Å**	**H···A/Å**	**D···A/Å**	**(DHA)/°**
O(1w)-H(1w)···N(4b)	0.937(9)	2.03(1)	2.897(2)	154(2)
O(1w)-H(2w)···O(1)	0.947(9)	1.88(1)	2.803(1)	166(2)

[a] Symmetry codes used to generate equivalent atoms: (a) = -*x*, *y*, -*z*+1/2; (b) = -*x*+1/2, *y*-1/2, -*z*+1/2.

Magnetic Properties of 1. Because of the diamagnetic character of the Zn(II) ion, only the magnetic behaviour of the cobalt(II) derivative was investigated. The magnetic properties of **1** under the form of both χ_M and $\chi_M T$ and versus T plots [χ_M is the magnetic susceptibility per Co(II) ion] are shown in Figure 6. $\chi_M T$ at room temperature is equal to 2.58 cm^3 mol^{-1} K, a value that is larger than the expected one for the spin-only case ($\chi_M T$ = 1.875 cm^3 mol^{-1} K 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.[56] Upon cooling, $\chi_M T$ continuously decreases to practically vanishes when T approaches to zero. The susceptibility curve exhibits a maximum value of 0.027 cm^3 mol^{-1} at 22.0 K. Moreover, the extrapolated value of χ_M at T = 0 K is practically equal to 2/3 its value at the temperature at which it is a maximum. This is the signature that we are dealing with a three-dimensional antiferromagnet.[57]

Although the decrease of $\chi_M T$ in the high-temperature region is mainly due to the depopulation of the higher energy Kramers doublets of the six-coordinate high-spin cobalt(II) ions, the presence of a maximum in the magnetic susceptibility unambiguously support the occurrence of relatively large antiferromagnetic interactions between these paramagnetic centres across the bis-bidentate bpm and oxalate ligands. In this respect, previous magneto-structural studies on bpm- and ox-bridged cobalt(II) ions have illustrated the ability of these extended bridges to mediate antiferromagnetic interactions with J values from -4.7 to -7.0 cm^{-1} (across bridging bpm)[28,36a,58] and up to -20 cm^{-1} (through bridging oxalate),[59] the cobalt-cobalt separation being greater than 5.4 Å.

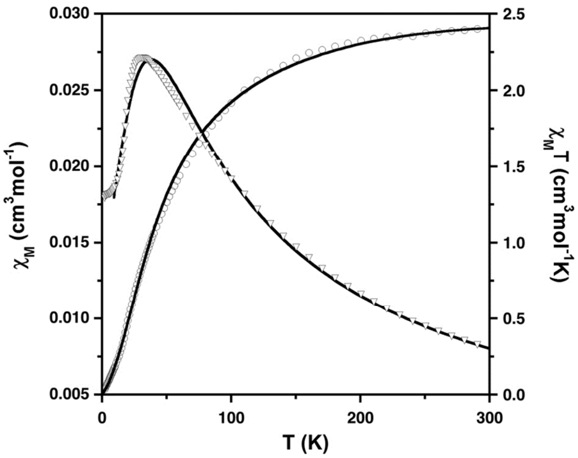

Figure 6. Thermal dependence of χ_M (▽) and $\chi_M T$ (○) for **1**. The solid line is the best-fit curve (see text).

Consequently, **1** can be viewed as a magnetic plane with alternating intralayer antiferromagnetic interactions between the high-spin cobalt(II) ions through bpm and ox bridges with coexistence of spin-orbit coupling effects and axial orbital splitting. There is no theoretical law to analyse the magnetic data of such a complex magnetic system. The inclusion of the spin-orbit coupling can be introduced in different ways: via a magnetic anisotropy or an L-S spin-orbit coupling. In systems with weak second-order spin-orbit coupling, their magnetic behavior can be easily simulated considering a magnetic anisotropy for the magnetic center. However, this approach is too simple to study the magnetic behavior of systems with large first-order spin-orbit coupling, in particular in the high temperature region. This last case is that usually observed in five- and six-coordinate cobalt(II) complexes. That is why a spin-orbit coupling has been used instead of an anisotropic model, although, unfortunately, one extra parameter had to be considered (α, λ and Δ instead of *g* and *D*).

In an attempt to evaluate the magnitude of the magnetic coupling parameters in **1**, its magnetic data were fitted by an approach that introduces the spin-orbit coupling through the *T-P* formalism and the Hamitonian of eq (1)

$$\hat{H} = -\alpha\lambda\hat{L}\cdot\hat{S} + \Delta\left[\hat{L}_z^2 - 2/3\right] + \beta H\left(-\alpha\hat{L} + g_e\hat{S}\right) \qquad (1)$$

where λ is the spin-orbit coupling parameter, α is the orbital reduction factor, and Δ is the axial orbital splitting of the T_1 term.[56] From this approach, each cobalt(II) ion can be considered as a Kramer's doublet with an effective spin value S_{eff} = ½ and an effective temperature-dependent g-factor extrapolated from the value of $\chi_M T$ provided by the *T-P* approach. Within this framework, an effective coupling between Kramer's doublets (J_{eff}) can be related to the real magnetic coupling between two cobalt(II) ions (J) through the ratio J_{eff} = (25/9)J. These effective parameters are related to the real values, which are those that we will get by fit, through the energies, wavefunctions and spin densities for each site in the corresponding spin states. Thus, no extra parameters were included and only a way to operate was used to allow the simulation of the complex network. The thermal population of each state is responsible for the temperature-dependence of the effective parameters. Details will be further published in a theoretical paper. On the other hand, the magnetic topology of **1** can be visualized as an alternating honeycomb network where uniform chains of oxalate-bridged cobalt(II) ions chains are connected via the bpm ligand. Hence, the experimental magnetic behaviour could be simulated by using a law for an antiferromagnetic alternating honeycomb for $S = 1/2$ local spins and an effective temperature-dependent g value related to the spin-orbit coupling observed in the cobalt(II) ions. As far as we are aware, no law has been derived for this alternating magnetic network and therefore, we have developed it in the present work. For such a purpose, a method based on an effective Hamiltonian that operates through three temperature-dependent effective parameters [g-factor, J (magnetic coupling) and S (local spin moment)] was employed. Herein, we used a largely improved version of that reported in a previous work.[60]

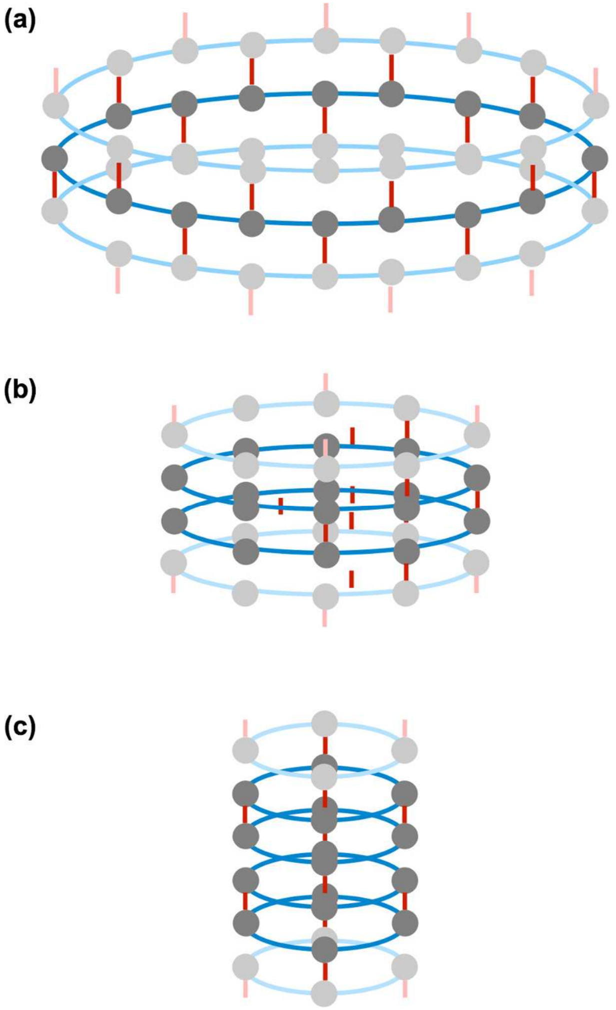

Figure 7. J interaction pattern showing 16 x 1 (a), 8 x 2 (b) and 4 x 4 (c) rings representation that were exactly solved (in strong colors). The rings were connected by means of the model based on effective Hamiltonian along the only free direction, i.e., a chain of rings is built.

This approach works from quantum exact solutions of discrete fragments that provide the effective parameters necessary to develop them to the real network. In our honeycomb network, we have used this approach from several fragments (4 x 4 unit and 8 x 2 and 16 x 1 rings, see Figure 7), but the empirical law employed here was that developed from the 16 x 1 ring fragment. In order to test this methodology, theoretical simulations were compared with those obtained from exact solutions of 4 x 4 spheres [61] and from Quantum Monte Carlo (QMC) techniques through the decoupled cell method (DCM),[62] although the former provide a larger applicability range in reduced temperatures (T/J). 16 x 1, 8 x 2 and 4 x 4 open cells were used in QMC simulations to simulate and build a 96 x 96 2D honeycomb network with boundary conditions. From this coupled set of approaches, it was possible to find a quite satisfactory simulation of the experimental data with the following set of values: $\lambda = -110$ cm^{-1}, $\alpha = 1.1$, $|\Delta| = 400$ cm^{-1}, $J_{ox} = -11.1$ cm^{-1} and $J_{bpm} = -5.0$ cm^{-1}. The magnitude of the values of λ, α and Δ are as those usually observed for these parameters in six-coordinate high-spin cobalt(II) complexes[28,57,59a,b, 63] and the size and nature of the magnetic interactions are also within the range of those reported for bpm- and oxalate-bridged cobalt(II) complexes either in simple dinuclear species or uniform chain compounds.[28,36a,58,59] These results were indeed supported by electronic structure calculations based on density functional theory (DFT) on cut fragments on the real structure that provided values of the intralayer magnetic couplings very close to the above ones (J_{ox} = -11.1 and J_{bpm} = -3.6 cm^{-1}). Finally, we would like to outline the great efforts we carried out to analyse successfully the variable-temperature magnetic data of compound **1** [a honeycomb lattice with anisotropic six-coordinate cobalt(II) ions and two different intralayer magnetic interactions], an approach that is presented here for the first time and that will be source of inspiration for other scientists working in molecular magnetism.

Conclusions

The honeycomb layered compounds **1** and **2** described herein show the known architecture of the isostructural complexes with Cu(II) and Fe(II) and very similar to that of the analogous species with Mn(II). They represent two more puzzle tiles in the first-row transition metal ions series from Mn(II) to Zn(II), where only the Ni(II) compound is still missing. Our attempts to grow single crystals of the nickel(II) derivative were unsuccessful so far, the tris-chelated species $[Ni(bpm)_2(ox)] \cdot 2H_2O$ (**3**) being obtained instead in the course of this work. It is interesting to note that the size of the hexagonal-shaped cavities/channels featured by this family of compounds shrinks within the series, following the trend exhibited by the ionic radii. Related to this structural feature is the fact that only the Mn(II) compound is able to accommodate six-membered rings of water molecules in its supramolecular channels five-membered water rings occur in the other members of the family from Fe(II) to Zn(II). The magnetic data of **1** from room temperature to 10 K were successfully reproduced by the use of an effective Hamiltonian operating on three temperature-dependent effective parameters (g, J and S) and the results tested by Quantum Monte Carlo (QMC) techniques through the decoupled cell method (DCM). Intralayer antiferromagnetic interactions between the paramagnetic metal ions through bridging ox (J_{ox} = -11.1 cm^{-1}) and bpm (J_{bpm} = -5.0 cm^{-1}) are observed, the former being larger than latter in agreement with the greater ability of the bis-bidentate oxalate to mediate electronic interactions compared to bpm. DFT type calculations provide additional support to both the nature and magnitude of the magnetic interactions obtained by fit.

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Crystallographic Information Files (CIFs) available: [CCDC 1039718, 1039719 and 1039720 contain the X-ray crystallographic data for **1**, **2** and **3** respectively, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org]. See DOI: 10.1039/b000000x/

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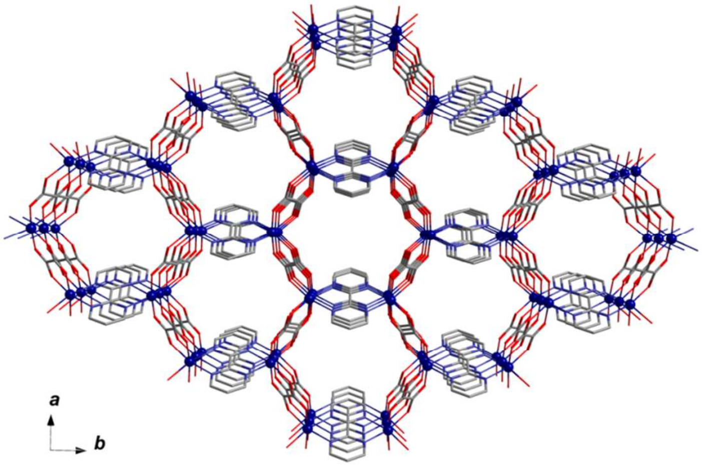
TOC Graphic and Synopsis:



The so far elusive Co(II)-based honeycomb 2D mixed-ligand complex of formula $\{[Co_2(bpm)(ox)_2]_n \cdot 5nH_2O\}$ was prepared and magneto-structurally characterized. The interpretation of the magnetic behavior of this species was attempted and the values of the antiferromagnetic coupling through the bpm (J_{bpm} = -5.0 cm^{-1}) and ox (J_{ox} = -11.1 cm^{-1}) ligands were supported by DFT calculations.