Mn^{II}/Co^{II}-Terephthalate Frameworks Containing Dipyridine Coligands: Syntheses, Crystal Structures, Magnetic Behaviors, and Thermal Studies

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Three new metal–organic hybrid polymeric networks of Co^{II} and Mn^{II} with the molecular formulae $[Co(bpp)(tp)(H_2O)_2]$ (**1**), $[Mn(bpds)(tp)(H_2O)_2]\cdot(bpds)$ (**2**), and $[Mn(4,4'\text{-bipy})(H_2O)_4]\cdot(tp)$ (**3**) (bpp = 4,4′-trimethylenedipyridine; bpds = 4,4′-bipyridyl disulfide; 4,4′-bipy = 4,4′-dipyridyl; tp = terephthalate) have been synthesized and characterized by single-crystal X-ray diffraction studies, low temperature (300–2 K) magnetic measurements, and thermal behaviors. The structure determination of complexes **1** and **2** reveals a parallel interpenetrated structure of 2D layers with (4,4) topology, with metal ions at the nodes connected through tp and *N*,*N*-donor coligands. The octahedral N_2O_4 chromophore surrounding the metal ion results from *trans* located tp oxygens, two water molecules, and two nitrogen donors of the co-ligands in the *cis* position. The presence of uncoordinated bpds between the interpenetrated layers leads to the formation of a wafer-like structure for **2**. In complex **3**, however, manganese(II) ions bridged by 4,4′-bipy and coordinated by four water molecules give rise to a 1D polymeric chain. The adjoining chains encapsulate terephthalate anions (tp) to give a 3D structure through H-bonding. Low-temperature magnetic data indicate weak antiferromagnetic coupling in complexes **1** and **2**.

Introduction

The construction of one- to three-dimensional functional metal-organic hybrid materials of paramagnetic metal ions is of great interest as their intriguing network topologies lead to potential applications,[1] for example in electrical, conductivity, magnetism, host–guest chemistry, ion exchange, catalysis, nanotechnology, fluorescence, nonlinear optics, etc. Research in this field has been carried out by a number of eminent groups, in particular those of Rao,[2] Yaghi,[3] Fujita,[4] Zaworotko,[5] etc. The availability of new polyfunctional ligands, as well as the discovery of alternative synthetic procedures, has led to the syntheses of unique and novel metal–organic frameworks (MOFs) that suggest routes for chemists and physicists to pursue in search of such materials. A literature survey shows that the most commonly used strategies for the synthesis of MOFs are the use of (a) anionic bridging ligands, which, in addition, can partially or fully counterbalance the charge of the metal centers, (b) anionic as well as neutral spacers to increase the possibility of enhancing the dimension of molecular materials, and (c) only neutral spacers, where charges of the metal centers are counterbalanced by noncoordinating anions.

Recently, we have reported the synthesis of some structurally and magnetically interesting MOFs using strategy (a), such as $[Ni_3(fum)_2(\mu_3\text{-}OH)_2(H_2O)_4]_n\cdot 2nH_2O$,[6] $[Cu(\mu\text{-}fum)(NH_3)_2]_n\cdot 2nH_2O$,[7] $[Mn(mal)(H_2O)_2]_n$,[8] and $[Co(H_2O)_4(fum)]_n\cdot nH_2O$,[9] where fumarate (fum) and malonate (mal) dicarboxylates act as anionic bridging ligands only. We have also reported MOFs obtained through strategies (b), where dicarboxylates are used in combination with neutral spacers, such as $[\{Cu_3(mal)_2(bpe)_3(H_2O)_2\}(NO_3)_2(H_2O)_2]_n$,[10] $[Cu_2(fum)_2(4,4'\text{-bipy})]_n\cdot 0.5nH_2O$,[11] $[Mn_2(mal)_2(4,4'\text{-bipy})(H_2O)_2]_n$,[8] $[Cu_4(mal)_4(urotropin)]\cdot 7H_2O$ and $[Co_2(mal)_2(urotropin)]\cdot 2H_2O$,[12] and $[Ni_3(maleate)_2(bpe)_4(H_2O)_4](NO_3)_2\cdot H_2O$, [Mn(adipate)(bpe)],[13] [Ni(fum)(bpe)], and $[Ni(fum)(bpp)(H_2O)]$[14] [bpe = 1,2-(bispyridine)ethane, bpp = 1,3-bis(4-pyridyl)propane], and (c), where noncoordinated dicarboxylates counterbalance the charge of the metal ions, as in $[Co(H_2O)_4(4,4'\text{-bipy})]_n(fum)_n\cdot 4nH_2O$[9] and $[\{Mn(bpe)(H_2O)_4\}(C_4O_4)\cdot 4.5H_2O]$ ($C_4O_4^{2-}$ = acetylene dicarboxylate).[15] Thus, depending on the metal ion and dicarboxylate or dicarboxylate/neutral bipyridine spacer, several MOFs with novel structural diversity and interesting

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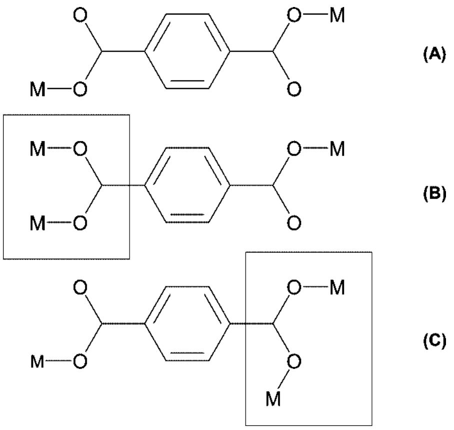
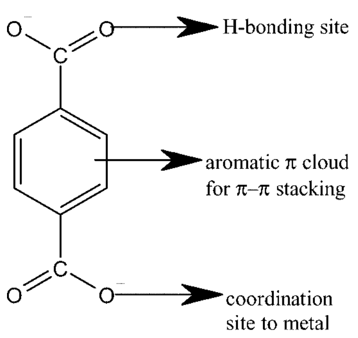
magnetic properties have been reported. This has prompted us to synthesize new MOFs using a well-known but less-documented dicarboxylate anion – terephthalate – in combination with other neutral bipyridines. The choice of terephthalate arises as it possesses versatile coordination modes (Scheme 1) and has the ability to form large and tightly bound metal cluster aggregates with specific and directional hydrogen bonds in building the molecular architecture,[16] as well as to undergo π–π stacking due to the presence of aryl rings (Scheme 2).



Scheme 1.



Scheme 2.

Herein we report the syntheses, crystal structures, low-temperature magnetic studies, and thermal behaviors of three novel Mn^{II}/Co^{II}-terephthalate frameworks containing dipyridyl coligands, namely $[Co(bpp)(tp)(H_2O)_2]$ (**1**), $[Mn(bpds)(tp)(H_2O)_2]\cdot(bpds)$ (**2**), and $[Mn(4,4'\text{-bipy})(H_2O)_4]\cdot(tp)$ (**3**) (tp = terephthalate; bpp = 4,4′-trimethylenedipyridine; bpds = 4,4′-bipyridyl disulfide; 4,4′-bipy = 4,4′-dipyridyl). Complexes **1** and **2** show unexpected 2D parallel interpenetrated structural motifs, whereas in complex **3** the use of linear 4,4′-bipy spacers gives rise to 1D coordination polymers with encapsulated tp anions. The low-temperature magnetic data of complexes **1** and **2** show weak antiferromagnetic coupling. Complex **1** exhibits thermally induced reversible octahedral (pink) ⇌ tetrahedral (blue) thermochromism upon dehydration/rehydration.

Results and Discussion

Description of the Structures

Complex 1

The crystal structure of complex **1** consists of 2D corrugated layers of square meshes of composition $[Co(tp)(bpp)(H_2O)_2]_n$, as depicted in Figure 1. The cobalt ions, with octahedral coordination geometry, occupy the 4-connecting nodes while bridging tp and bpp ligands give rise to a square grid of equal sides (11.486 × 11.486 Å). Intranet hydrogen bonds reinforce the overall structure [O(1w)–O(4) = 2.66; O(2w)–O(6) = 2.64 Å]. The N_2O_4 chromophore about the cobalt(II) center involves *trans* located tp oxygens and two water molecules, with two bpp nitrogen donors in the *cis* positions. The coordination bond lengths cover the range 2.106(2) Å [Co–O(1w)] to 2.140(2) Å [Co–N(2)] (Table 1). The bpp ligand exhibits a *TG* conformation[17] with torsion angles of –174.5(3)° and 73.4(4)° about the propyl chain. A careful analysis of the crystal structure shows parallel interpenetrated layers,[18,19] as illustrated in Figure 2, where weak π–π tp ring interactions are evident (distance between centroids = 3.807 Å). The spacing between the mean planes through the cobalt atoms of each sheet is 2.381 Å. Both the layers involved in interpenetration (A and B are structurally equal) are linked to the adjacent sheet to form a concatenated -AB-BA-AB- structure, where hyphens indicate H-bonds involving the water molecule O(1w) and the tp oxygen O(6) (O···O = 2.76 Å). As shown in Figure 3, these interactions contribute to the enhancement of molecular dimensionality. It is worthwhile to note that the aqua ligand O(1w) forms intra- and interlayer H-bonds and presents a shorter coordination distance in comparison to Co–O(2w) [2.106(2) vs. 2.132(2) Å]. The tp carboxylates are rather tilted from a coplanar conformation and form dihedral angles of 26.0(2)° and 37.6(2)° with the aromatic ring as a subtle balance to favor the intranet

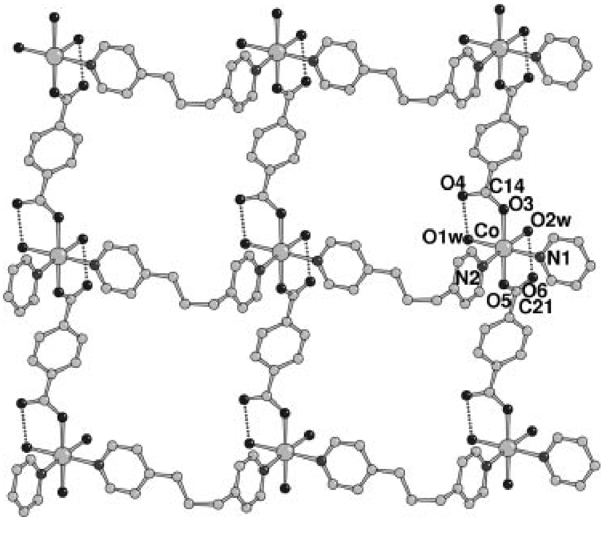


Figure 1. View down axis *c* of the 2D sheet of complex **1** with relevant atom labeling scheme about the Co atom.

H-bonding (Figure 1) and, at the same time, the stacking between phenyl rings of the interpenetrated nets (Figure 2).

Table 1. Selected bond lengths [Å] and angles [°] for complexes **1**–**3**.

1			
Co–O(1w)	2.106(2)	Co–O(5)	2.127(2)
Co–O(2w)	2.132(2)	Co–N(1)	2.136(2)
Co–O(3)	2.127(2)	Co–N(2)	2.140(2)
O(1w)–Co–O(2w)	95.02(7)	O(2w)–Co–N(2)	175.45(7)
O(1w)–Co–O(3)	88.89(6)	O(3)–Co–O(5)	172.19(6)
O(1w)–Co–O(5)	86.93(6)	O(3)–Co–N(1)	91.36(7)
O(1w)–Co–N(1)	179.68(6)	O(3)–Co–N(2)	96.43(7)
O(1w)–Co–N(2)	89.48(7)	O(5)–Co–N(1)	92.84(7)
O(2w)–Co–O(3)	84.33(7)	O(5)–Co–N(2)	90.13(7)
O(2w)–Co–O(5)	89.47(7)	N(1)–Co–N(2)	90.30(8)
O(2w)–Co–N(1)	85.20(7)	O(4)–C(14)–O(3)	125.03(19)
		O(6)–C(21)–O(5)	125.12(19)
2[a]			
Mn–O(2)	2.131(2)	Mn–N(1)	2.309(3)
Mn–O(1w)	2.204(3)		
O(2)–Mn–O(2′)	176.02(14)	O(1w)-Mn–O(1w′)	90.68(16)
O(2)–Mn–O(1w)	88.29(10)	O(1w)–Mn–N(1′)	176.41(11)
O(2)–Mn–O(1w′)	88.91(10)	O(1w)–Mn–N(1)	86.64(11)
O(2)–Mn–N(1)	88.63(10)	N(1)–Mn–N(1′)	96.14(15)
O(2)–Mn–N(1′)	94.03(10)	O(3)–C(1)–O(2)	124.8(3)
3[b]			
Mn–O(1w)	2.208(2)	Mn–N(1)	2.210(2)
Mn–O(2w)	2.188(2)	Mn–N(2)	2.269(3)
O(1w)–Mn–O(1w′)	169.87(9)	O(2w)-Mn–O(2w′)	171.29(9)
O(1w)–Mn–O(2w)	94.25(7)	O(2w)–Mn–N(1)	85.65(4)
O(1w′)–Mn–O(2w)	86.52(7)	O(2w)–Mn–N(2)	94.35(4)
O(1w)–Mn–N(1)	95.06(4)	N(1)–Mn–N(2)	180.0
O(1w)–Mn–N(2)	84.94(4)	O(3)–C(7)–O(3′′)	124.5(3)
		O(4)–C(12)–O(4′′)	124.8(3)

[a] Symmetry code: (′) –*x* + 1/4, –*y* + 1/4, *z*. [b] Symmetry code: (′) –*x* + 1/2, *y*, –*z* + 3/2; (′′) –*x* + 1/2, *y*, –*z* + 1/2.

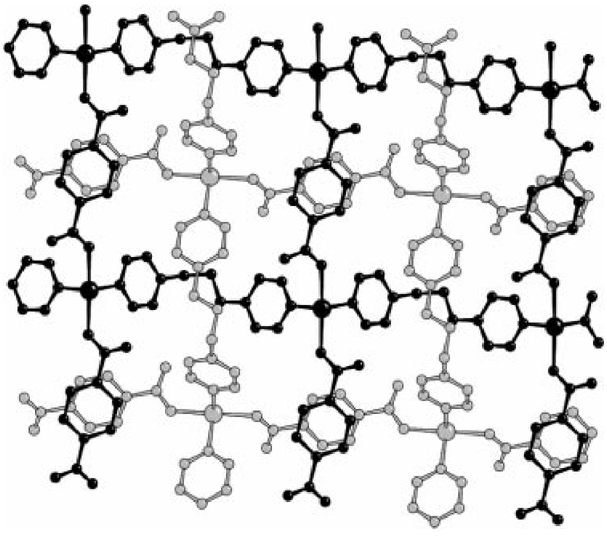


Figure 2. Parallel interpenetration of 2D sheets in complex **1** (coordinated water oxygens not shown for sake of clarity).

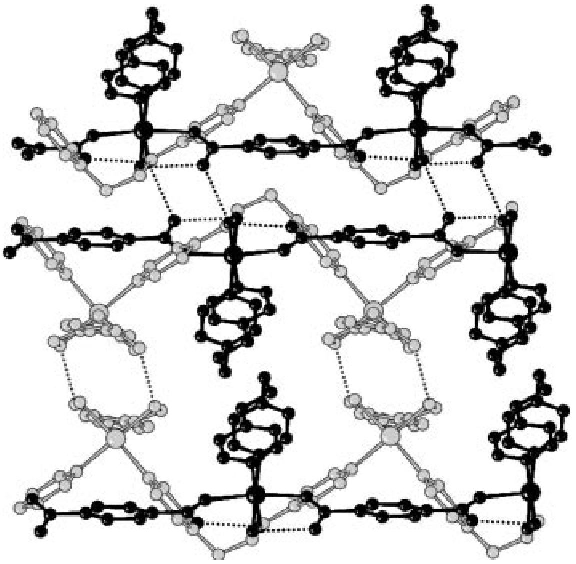


Figure 3. Interpenetrated sheets (each pair indicated in black and gray) concatenated by H-bonds (dotted lines) in complex **1**.

Complex 2

Complex **2** contains a 2D undulating $[Mn(tp)(bpds)(H_2O)_2]_n$ sheet (Figure 4), extending in the *ab* plane, where octahedral manganese ions occupy the 4-connecting nodes of the square grid, which has equal sides of 11.425 Å. The square grid is strengthened by hydrogen bonds involving the aqua ligand and the adjacent carboxylate oxygen [O(1w)–O(3′) = 2.71 Å]. The manganese(II) ion is positioned on a twofold axis with *trans* located tp oxygens, with the coordination geometry being completed by two water molecules and two bpds N donors in the *cis* position. The Mn–O(2), Mn–O(1w), and Mn–N(1) bond lengths are 2.131(2), 2.204(3), and 2.309(3) Å, respectively (Table 1). The 2D layers reveal a parallel interpenetration with a topology closely comparable to that observed in complex **1** (Figure 5). The entangled layers in the present arrangement seem more tightly connected, with the mean planes through the metals being separated by 2.228 Å and the π-stacking of tp rings being more efficient (centroid-to-centroid distance = 3.568 Å). The conformation assumed by the tp is also very similar to that found in the cobalt complex, with angles between the carboxylate groups and aromatic ring of 26.3(3)°. However, compared with complex **1**, the main difference emerges from the presence of uncoordinated bpds between the interpenetrated layers. This peculiar feature leads to the formation of a wafer-like structure, where the bidentate bpds ligands are linked to water molecules through hydrogen bonds (N···O = 2.840 Å;L N···HO = 158.9°). A view of the crystal packing is given in Figure 6.

An estimation of the torsion angles around the disulfide bonds in a series of coordination polymers indicates rigidity in the bpds ligands [C–S–S–C angles between 83.8(6)° and 95.5(8)°],[20] regardless of the different coordination environment. The present value for the coordinated bpds ligand falls in the range reported (92.5°), while it is 102.7° in free bpds. Correspondingly, the N···N distance is longer in the

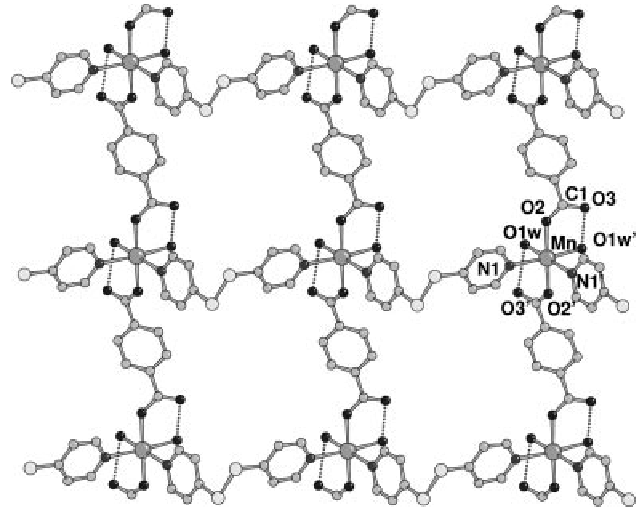


Figure 4. 2D sheet of complex **2** with relevant atom labeling scheme about the Mn ion located on a twofold axes (primed atoms at $-x + 1/4$, $-y + 1/4$, z).

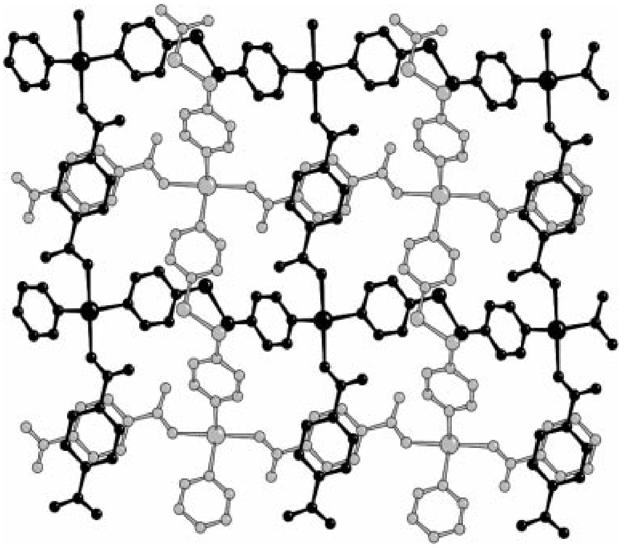


Figure 5. View of parallel interpenetration of 2D sheets (*ab* plane) in complex **2**. The larger circles represent Mn ions (coordinated water oxygens not shown for sake of clarity).

latter (8.494 vs. 8.029 Å), a conformation that appears to assist the N–OH_2 hydrogen bond.

As a comparison, in the 1D polymer [Mn(bpds)(F_6-acac)$_2$],[21] (F_6-acac = hexafluoroacetylacetonate), which represents the only known example of manganese(II) ions bridged by a bpds ligand, longer Mn–N distances of 2.282 Å are found, with the metals separated by 11.785 Å.

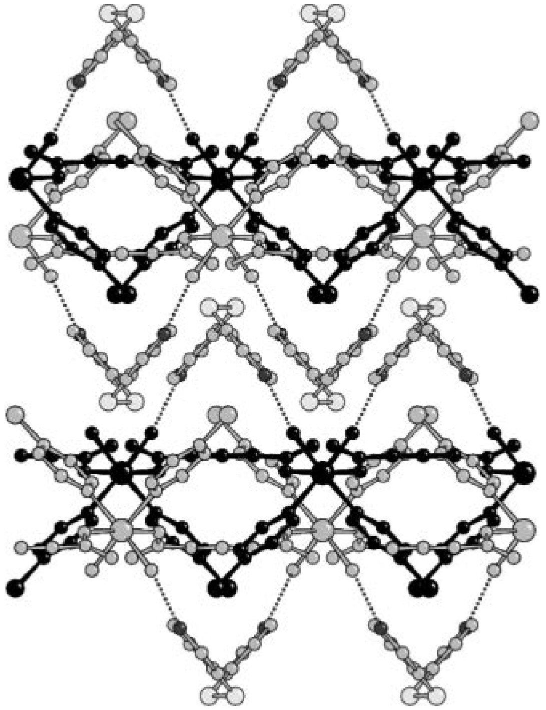


Figure 6. Crystal packing (view along axis *b*) of complex **2** with uncoordinated bpds ligands sandwitched between the parallel interpenetrated layers and connected through H-bonds (dotted lines) to coordinated water molecules. The larger circles indicate Mn ions.

Complex 3

The $Mn(H_2O)_4$ units in complex **3** are bridged by 4,4′-bipy ligands to give a 1D coordination polymeric array along the crystallographic *b* direction, with metals located on twofold axes. A drawing of the packing with the atom labeling scheme is shown in Figure 7; a selection of bond lengths and bond angles is given in Table 1. The MnN_2O_4 chromophore presents a slightly distorted octahedral coordination geometry, with the equatorial oxygens showing a tetrahedral distortion (±0.18 Å). The Mn–O(1w) and Mn–O(2w) distances are 2.208(2) and 2.188(2) Å, respectively; the nitrogen bipy donors N(1) and N(2) occupy the *trans* axial positions with Mn–N(1) and Mn–N(2) distances of 2.210(2), 2.269(3) Å, respectively. The rings of the 4,4′-bipy ligand are not coplanar, but are tilted by about 20°. The terephthalate dianions are also located on twofold axes and are sandwiched by 4,4′-bipy ligands of contiguous polymeric chains to give rise to a three-dimensional structure through a H-bonding scheme with the water molecules. In fact, O2w is involved in H-bonding with the sandwiched tp anions (O3 and O4 at 2.74 Å, mean value), while O1w is connected to O4 at a longer distance (2.90 Å) and also a symmetry-related O3 of a side-located tp at 2.71 Å (not shown in Figure 7).

The 4,4′-bipy ligand spans the metal ions at a distance correspondening to the length of the crystallographic *b* axis, namely 11.565 Å (Figure 7), while the shortest interchain Mn···Mn separation in the 3D architecture is 6.562 Å. The orientations (dihedral angles) taken up by carboxylate groups with respect to the phenyl ring are 4.86(5)° and 22.03(6)°, which is assumed to favor the H-bonding.

The overall structure presents structural features comparable to those observed in the analogous Mn polymeric derivative with croconate $(C_5O_5)^{2-}$ dianions.[22] However, accounting for the smaller dimensions of $(C_5O_5)^{2-}$ (with re-

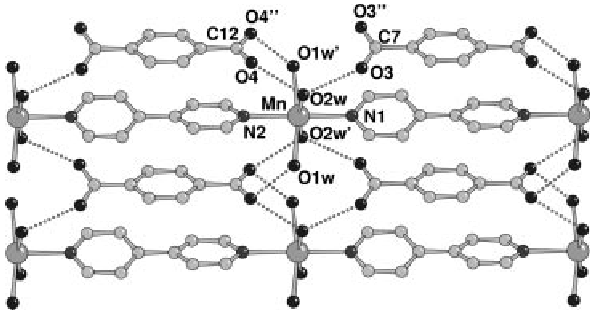


Figure 7. Crystal packing of complex **3** viewed down the *c* axis showing the terephthalate anions encapsulated between the -$Mn(H_2O)_4$-(4,4′-bipy)- polymers [dotted lines indicate H-bonds, symmetry operation: (′) $-x + 1/2$, y, $-z + 3/2$; (′′) $-x + 1/2$, y, $-z + 1/2$].

spect to tp) in the latter, an additional water molecule was detected in the lattice in order to favor the H-bonding interactions.

Magnetic Properties

Although the crystal nets consist of a two-dimensional structure with terephthalate and bpp or bpds as bridging ligands in complexes **1** and **2**, respectively, we assumed the possible couplings between the long amines bpp and bpds to be zero. With this hypothesis, the magnetic data can be interpreted as being derived from a pseudo-one-dimensional structure formed by cobalt(II) and manganese(II) ions (for **1** and **2**, respectively) linked by terephthalate at a long distance. For complex **3**, the terephthalate dianion remains encapsulated and the manganese ions are bridged by long 4,4′-bipy ligands (Mn···Mn = 11.565 Å). Such a type of bridging ligand usually gives negligible antiferromagnetic interactions,[23] therefore we did not study the magnetic behavior.

Complex 1

Considering the spin-orbit coupling due to the $^4T_{1g}$ ground state for octahedral Co^{II} complexes,[24] precise calculations to derive the *J* parameter from experimental data in all the temperature range are not possible except for dinuclear[25] or small polynuclear complexes.[26] One-dimensional systems of Co^{II} are frequently associated with anisotropic Ising systems, and they can be fitted in the low-temperature zone by assuming again an effective spin, *S*′, of ½.[27] More recently, Rueff et al.[28] have proposed a phenomenological approach for some low-dimensional Co^{II} systems that allows an estimation of the strength of the antiferromagnetic exchange interactions. They postulated the phenomenological equation:

$$A\chi_M T = A \exp(-E_1/kT) + B \exp(-E_2/kT)$$

where $A + B$ is the Curie constant [approx. 2.8–3.4 $cm^3 mol^{-1}$ K for octahedral cobalt(II) ions], and E_1 and E_2 represent the "activation energies" corresponding to the spin-orbit coupling and the antiferromagnetic exchange interaction, respectively. E_1/k, the effect of spin-orbit coupling and site distortion, is of the order of +100 K.[28,29] Excellent results have been reported in one- and two-dimensional cobalt(II) complexes.[28]

The $\chi_M T$ vs. T plot for **1** (χ_M is the molar magnetic susceptibility for one Co^{II} ion) is shown in Figure 8. A $\chi_M T$ value of 3.27 $cm^3 mol^{-1}$ K at 300 K is a typical value for the Co^{II} system.[30,31] Upon decreasing the temperature, the $\chi_M T$ values decrease continuously to 1.91 $cm^3 mol^{-1}$ K at 2 K. To calculate an estimated *J* value we used the Rueff expression, which suitable for any temperature greater than the possible T_c.[28] The fit values obtained with this procedure are: A + B = 3.5 $cm^3 mol^{-1}$ K, in agreement with those given in the literature.[28] The E_1/k value of 69.09 K is of the same magnitude as those reported by Rueff et al. for several one- and two-dimensional cobalt(II) complexes.[30b] As for the value found for the antiferromagnetic exchange interaction, it is very weak ($E_2/k = 0.21$ K), corresponding to $J = -0.42$ K (ca. $-0.3\ cm^{-1}$), according to the Ising chain approximation, $\chi_M T = \exp(J/2kT)$ (Figure 8). The reduced magnetization curve, $M/N\beta$, at 2 K tends to 2.35 $N\beta$ at 5 T, a typical value for isolated or quasi-isolated cobalt(II) ions (Figure 8 inset).

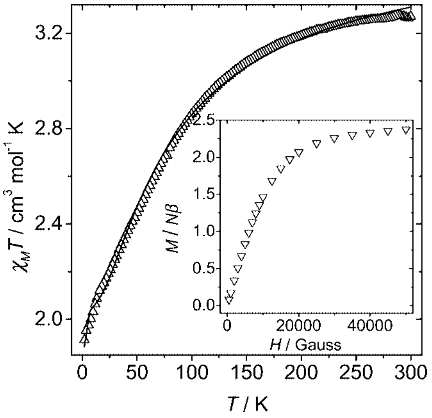


Figure 8. Plot of $\chi_M T$ vs. T for complex **1** (solid line represents the best fit using the Rueff formula). Inset: plot of the reduced magnetization ($M/N\beta$) vs. H at 2 K for complex **1**.

Complex 2

The $\chi_M T$ vs. T plot is given in Figure 9 for one manganese(II) ion. The $\chi_M T$ values start at 4.35 $cm^3 mol^{-1}$ K, corresponding to the value for one isolated manganese(II) ion (with g ≈ 2.00). This value decreases smoothly to close to 4.0 $cm^3 mol^{-1}$ K at 2 K. Such behavior is typical for a very weak antiferromagnetic coupling between manganese(II) ions in the chain. The magnetism of this kind of one-dimensional Mn^{II} system has been studied theoretically mainly by Fisher by assuming an infinite number of classical spins ($S = 5/2$).[32] The best-fit parameters were: $J = -0.045 \pm 0.01$, $g = 2.00 \pm 0.004$, and $R = 4.1 \times 10^{-3}$ (*R* is the agreement factor defined as $\Sigma_i[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\Sigma_i[(\chi_M T)_{obs}]$).[33] The *g* value agrees perfectly with that expected for a manganese(II) ion ($S = 5/2$, $g = 2.00$). The reduced magnetization (Figure 9, inset) is also indicative of a very weak antiferromagnetic coupling. The experimental values tend to 4.8 $N\beta$ and practically follow the Brillouin formula at 2 K for $S = 5/2$ and $g = 2.0$.

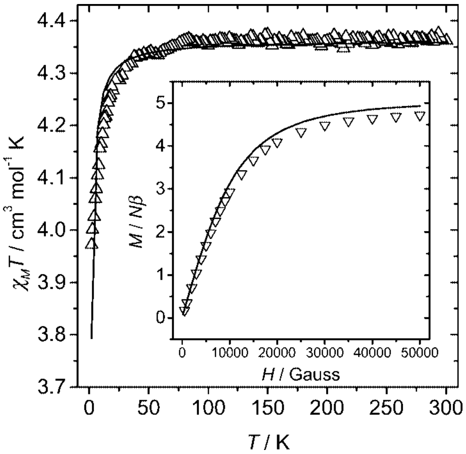


Figure 9. Plot of $\chi_M T$ vs. T for complex **2** (solid line represents the best fit). Inset: plot of the reduced magnetization, $M/N\beta$ (solid line indicates the Brillouin formula for $S = 5/2$ and $g = 2.0$).

The small antiferromagnetic J values for **1** and **2** may be interpreted as being due to the terephthalate bridging ligand. When the coordination mode is that shown in Scheme 1A (complexes **1** and **2**), the terephthalate bridging ligand shows a very small antiferromagnetic coupling for M = Mn^{II}, Co^{II}, Ni^{II}, and Cu^{II}.[33] To the best of our knowledge, only two Mn complexes with this kind of coordination have been reported to date – $[\{Mn(dca)(terpy)(MeOH)\}_2(\mu\text{-ta})]$[34] and $[Mn_2(phen)_4(H_2O)_2(\mu\text{-ta})](ClO_4)_2$.[35] The calculated J values of $-0.06\ cm^{-1}$ and $-0.065\ cm^{-1}$, respectively, are in good agreement with that found in complex **2**. All these very weak J values are in accordance with the MO calculations made by Cano et al.,[35] which show that a terephthalate bridge is not a suitable bridging unit to mediate significant exchange coupling.

Thermal Studies

The pink complex **1** starts to lose its coordinated water molecules, upon heating, at around 125 °C and becomes dehydrated at 190 °C, yielding the species [Co(bpp)(tp)] (**1a**, blue), which reverts to **1** in a humid atmosphere (relative humidity of ca. 60%) at ambient temperature. This dehydration-rehydration process involves an octahedral $\rightleftharpoons$ tetrahedral transformation of Co^{II} that shows thermochromism, as evidenced from the solid state electronic spectra [(19455, ca. 16666, and 8510 cm^{-1} for **1**) and (19300, 17985, 14000–15500, and 8802 cm^{-1} for **1a**; Figure S1)] and room temperature magnetic measurements [μ_{eff} for **1** (see magnetic properties) and for **1a** 4.82 μ_B (at 300 K)].

Complex **2** starts to lose water molecules, upon heating, at 110 °C and shows continuous decomposition with concomitant formation of an intermediate species. The initial temperature of dehydration suggests the presence of coordinated water molecules as well as their involvement in H-bonding. It should be noted that after dehydration the network in **2** collapses as the terephthalate carboxylate fails to function here as a chelate to attain octahedral geometry, which is a requirement for the existence of Mn^{II} in the polymeric networks according to the crystal structure (Figure 4).

Complex **3** is thermally stable up to 100 °C, a lower temperature than that of **2**. It undergoes dehydration in two steps that overlap each other and is fully dehydrated at 150 °C. The dehydrated species collapses immediately upon further heating as the manganese centers fail to attain the required geometry after removal of their water molecules.

Conclusions

We have reported the syntheses, crystal structures, low-temperature magnetic studies, and thermal behaviors of three metal–organic hybrid polymeric networks. The tp and bipyridine ligands in complexes **1** and **2**, respectively, take part in formation of a covalently bonded 2D parallel interpenetrated polymeric architecture, whereas in complex **3** the tp anions are encapsulated by 1D Mn(4,4′-bipy) chains. The presence of uncoordinated bpds ligands in **2** between the interpenetrated layers leads to formation of a wafer-like structure where bpds is anchored to coordinated water molecules through H-bonds. All these crystal structures contain extensive H-bonding between the water molecules and the tp oxygens, which increases the dimensionality of the architectures to 3D. As a consequence, in order to favor H-bonding connections the tp carboxylate groups show different conformations, as indicated by the dihedral angles of the carboxylates with respect to the phenyl ring. These are about 30° in complexes **1** and **2**, and quite different in **3** (about 5° and 22°). The variable-temperature magnetic data reveal weak antiferromagnetic coupling for **1** and **2**.

Experimental Section

Materials: High purity 4,4′-trimethylenedipyridine (98%), 4,4′-bipyridyl disulfide (Aldrithiol-4; 98%), 4,4′-dipyridyl (98%), disodium terephthalate (96%), and manganese(II) chloride tetrahydrate (98%) were purchased from the Aldrich Chemical Co. Inc. and were used. All other chemicals were of AR grade.

Physical Measurements: Elemental analyses (carbon, hydrogen, and nitrogen) were performed with a Perkin–Elmer 240C elemental analyzer. IR spectra were measured as KBr pellets on a Nicolet 520 FTIR spectrometer. Magnetic measurements were carried out with polycrystalline samples (20–30 mg) by the Servei de Magnetoquímica, Universitat de Barcelona, with a Quantum Design MPMS SQUID magnetometer operating at a magnetic field of 0.1 T, in the temperature range 2–300 K. The diamagnetic corrections were evaluated from Pascal's constants. Thermogravimetric analyses were carried out with a Mettler Toledo Star system. The UV/Vis reflectance spectra were recorded between 300–1400 nm with a Hitachi U-3501 spectrophotometer at room temperature in the solid state.

Crystallographic Data Collection and Refinement: Crystal data and details of data collections and refinements for the structures reported are summarized in Table 2. Diffraction data for all complexes were carried out on a Rigaku Mercury CCD area detector using graphite-monochromated Mo-K_α radiation. Cell refinement, indexing, and scaling of the data sets were carried out using the Crystal package.[36] All the structures were solved with SIR97[37] and subsequent Fourier analyses[38] and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[38] Most of the water hydrogens detected in the difference Fourier map were restrained with a fixed O–H bond length (0.85 Å). All the calculations were performed using the WinGX System, Ver 1.64.05.[39]

CCDC-262151 to -262153 (for **1**–**3**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystallographic data and details of structure refinements for complexes **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{21}H_{22}CoN_2O_6$	$C_{28}H_{24}MnN_4O_6S_4$	$C_{18}H_{20}MnN_2O_8$
M_r [g mol^{-1}]	457.35	695.70	447.30
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	*C*2/*c*	*Fddd*	*P*2/*n*
a [Å]	16.883(7)	15.635(7)	6.995(4)
b [Å]	15.579(6)	16.663(8)	11.565(6)
c [Å]	18.317(8)	45.74(2)	11.420(6)
β [°]	123.778(3)	90.00	101.824(6)
Volume [Å^3]	4004.3(29)	11916.2(95)	904.2(8)
Z	8	16	2
$D_{calcd.}$ [g cm^{-3}]	1.517	1.551	1.643
μ (Mo-K_α) [mm^{-1}]	0.899	0.773	0.782
F(000)	1896	5712	462
θ_{max} [°]	27.48	27.48	27.48
Reflection collected	32844	49378	14916
Unique reflections	4735	3696	2165
R_{int}	0.035	0.079	0.038
Observed reflections $I > 2\sigma(I)$	3643	2125	1625
Parameters refined	287	201	152
Goodness of fit (F^2)	1.087	1.058	1.019
R_1 [$I > 2\sigma(I)$] [a]	0.0397	0.0517	0.0350
wR_2 [a]	0.0798	0.0983	0.0684
$\Delta\rho$ [e Å^{-3}]	0.264, –0.232	0.381, –0.337	0.282, –0.295

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

[Co(bpp)(tp)(H_2O)$_2$] (1): A methanolic solution (5 mL) of bpp (1 mmol, 0.198 g) was added dropwise to a methanolic solution (5 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (1 mmol, 0.291 g) with constant stirring. An aqueous solution (10 mL) of disodium terephthalate (1 mmol, 0.210 g) was added to the resulting light-pink reaction mixture and stirred for 1 h. A deep-pink complex separated out. Single crystals suitable for X-ray analysis were obtained by diffusing a methanolic solution (10 mL) of bpp into an aqueous (10 mL) layer containing $Co(NO_3)_2 \cdot 6H_2O$ and disodium terephthalate (1:1) in a tube. The deep-pink crystals deposited at the junction of the two layers after a few days. Yield: 0.320 g (70%). $C_{21}H_{22}CoN_2O_6$ (457.35): calcd. C 55.10, H 4.81, N 6.12; found C 55.18, H 4.80, N 6.16. IR: ṽ = 3604 (vs), 3256 (s), 3071 (w), 2943 (s), 2872 (vw), 1615 (vs), 1546 (vs), 1501 (w), 1380 (s) 1018 (w), 795 (s), 757 (s), 510 (w) cm^{-1}.

[Mn(bpds)(tp)(H_2O)$_2$]·(bpds) (2): A methanolic solution (10 mL) of manganese(II) chloride tetrahydrate (1 mmol, 0.197 g) was allowed to react with an aqueous solution (10 mL) of disodium terephthalate (1 mmol, 0.210 g) and stirred for 20 min. Then, a methanolic solution (5 mL) of bpds (1 mmol, 0.220 g) was poured slowly into it and the resulting mixture was refluxed for 4 h. It was then allowed to cool and filtered. The filtrate was kept in a $CaCl_2$ desiccator and shiny, yellowish single crystals suitable for X-ray determination were obtained after a few days. Yield: 0.500 g (72%). $C_{28}H_{24}MnN_4O_6S_4$ (695.70): calcd. C 48.30, H 3.45, N 8.05; found C 48.29, H 3.45, N 8.04. IR: ṽ = 3500–3090 (s), 3008 (w), 2904 (w), 1579 (vs), 1566 (vs), 1379 (s), 1319 (w), 1222 (vw), 815 (w), 758 (w), 704 (w) cm^{-1}.

[Mn(4,4′-bipy)(H_2O)$_4$]·(tp) (3): This complex was synthesized following the procedure adopted for complex **2** using 4,4′-bipy (1 mmol, 0.156 g) instead of bpds. Colorless crystals of **3** suitable for X-ray diffraction were obtained from the $CaCl_2$ desiccator after a few days. Yield: 0.313 g (70%). $C_{18}H_{20}MnN_2O_8$ (447.30): calcd. C 48.29, H 4.47, N 6.26; found C 48.28, H 4.48, N 6.27. IR: ṽ = 3500–3020 (s, v br.), 1656 (vw), 1610 (s), 1559 (vs), 1419 (vw), 1368 (vs), 1067 (vw), 807 (w), 752 (w), 632 (vw) cm^{-1}.

Supporting Information: A table containing H-bonding parameters, the thermogravimetric curves of complexes **1**, **2**, and **3**, and the solid-state electronic spectra for complexes **1** and **1a**, see also footnote on the first page of this article.

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