Diversity in magnetic properties of 3D isomorphous networks of Co(II) and Mn(II) constructed by napthalene-1,4-dicarboxylate†

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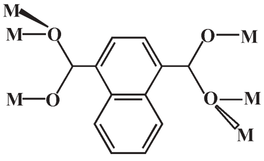
Two novel 3D isomorphous organic–inorganic hybrid frameworks, [M(1,4-napdc)]$_n$ (M = Co(II), 1 and Mn(II), 2; 1,4-napdcH$_2$ = napthalene-1,4-dicarboxylic acid) have been hydrothermally synthesized and structurally characterized, and the magnetic results exhibit metamagnetic behaviour (T_C = 5.5 K) for 1, and a weak antiferromagnetic interaction for 2, which are structurally correlated.

The chemistry of multifunctional metal–organic hybrid frameworks is recently one of the most productive areas of chemical research.[1] Currently a challenging target is the design and synthesis of molecule based magnetic materials with the strategic co-existance of multiple properties, like spin-crossover, optical properties and porous functionality.[2] In order to achieve such functionalities, one of the approaches is to link 0D clusters or 1D (M–O–M) inorganic chains having high magnetic anisotropy by using a polycarboxylate ligand to form a 3D robust framework.[3] Recently, multidimensional transition metal carboxylates (aromatic as well as aliphatic) having metal–oxygen connectivity with ferromagnetic or ferrimagnetic behavior with a high T_C and coercive field have been reported.[4] But accounts of homometallic metamagnets with 3D magnetic ordering are still few in the literature.[5] With the aim of studying the influence of organic molecules on the intra- and interlayer structural and magnetic properties in different metal systems, we decided to pursue the grafting of the planar naphthalene-1,4-dicarboxylate anion having a conjugated π-electron system and constitutional stiffness that has not, to our knowledge, been well studied as a linker to construct a functional coordination framework.[6] In this communication we report two, isomorphous 3D network of Co(II) and Mn(II) using naphthalene-1,4-dicarboxylic acid (1,4-napdcH$_2$) as a building block (Scheme 1). Variable temperature magnetic measurements of [Co(1,4-napdc)]$_n$ (**1**), exhibit intra-chain (Co–O–Co) ferromagnetic interactions and inter-chain (Co–1,4-napdc–Co) antiferromagnetic interactions and overall metamagnetic behaviour with 3D magnetic ordering (T_C = 5.5 K), whereas [Mn(1,4-napdc)]$_n$ (**2**), shows antiferromagnetic interactions along the Mn–O–Mn and Mn–1,4-napdc–Mn pathways.



Scheme 1 Binding mode of 1,4-napdc^{2-} in **1** and **2**.

Reaction of $CoCl_2{\cdot}6H_2O$ (1.0 mmol) with 1,4-napdcH$_2$ (1.0 mmol) and KOH (2.0 mmol) in water (10–12 ml) at 170 °C for 120 h resulted in deep violet colored needle-like crystals of **1** in 70% yield and under the same conditions colorless needle-like crystals of **2** were obtained in 40% yield. Recent research has revealed that the hydro(solvo)thermal reaction is a promising technique in preparing metal complexes (or metal–organic frameworks) with novel structures and special properties, which are difficult to obtain by routine synthetic methods.[7] Elemental analysis shows the formulation of [M(1,4-napdc)]$_n$ and IR spectra reveal that broad and intense bands appear at ~1540 cm^{-1} [ν_{as}(COO)] and 1356 cm^{-1} [ν_s(COO)], corroborating that the all the oxygen atoms of the carboxylate group are involved in bridging in both cases. The thermogravimetric analysis shows no weight loss from room temperature to ~400 °C, indicating that both the frameworks are very stable (Fig. SI(1)†).

X-Ray structural analysis reveals that both the frameworks crystallize in a monoclinic crystal system and the asymmetric unit comprises one metal ion and one 1,4-napdc^{2-} ligand, and therefore there is only one metal environment.‡ In the case of **1** each Co(II) is coordinated in a distorted octahedral geometry with the O_6 donor set coming from six different 1,4-napdc^{2-} ligands (Fig. 1a). Each 1,4-napdc^{2-} unit binds two Co(II) ions through one carboxylate in a *syn–syn* fashion and another Co(II) through a μ^2-carboxylate bridge, forming a one dimensional inorganic chain of [Co–μ-O$_2$]$_n$ along the crystallographic *a*-axis (Fig. 1a); thus each 1,4-napdc^{2-} ligand binds six different Co(II) centers using two carboxylate moieties. Each inorganic chain is connected to four other different chains through 1,4-napdc^{2-} ligands forming a 3D network (Fig. 1b). The four oxygen atoms O1_d, O2_a, O3 and O4_d (a = $-1 + x, y, z$; d = $1 - x, 1 - y, 1 - z$) from four different 1,4-napdc^{2-} ligands form the equatorial plane around each Co(II) ion and the axial positions are occupied by another two oxygen atoms, O1 and O4_a, from two different ligands. The deviation of each Co(II) center from the mean plane defined by the four oxygen atoms is 0.0026(7) Å and the maximum deviation of any equatorial atom (O1_d) is 0.2169(7) Å. The dihedral angle between the benzene rings of the 1,4-napdc^{2-} ligand is 6.47(6)° and the Co–O bond lengths are in the range 2.026(1)–2.145(2) Å. The degree of distortion from ideal octahedral geometry is reflected in the cisoid angles, 80.30(6)–109.14(7)° and transoid angles 161.43(6)–176.32(4)°. The angle in the μ^2-carboxylate bridge part,

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† Electronic supplementary information (ESI) available: TG analysis of **1**, views of the coordination in **2** and a plot of *M vs. H* at 2 K for **2**. See http://dx.doi.org/10.1039/b507953e

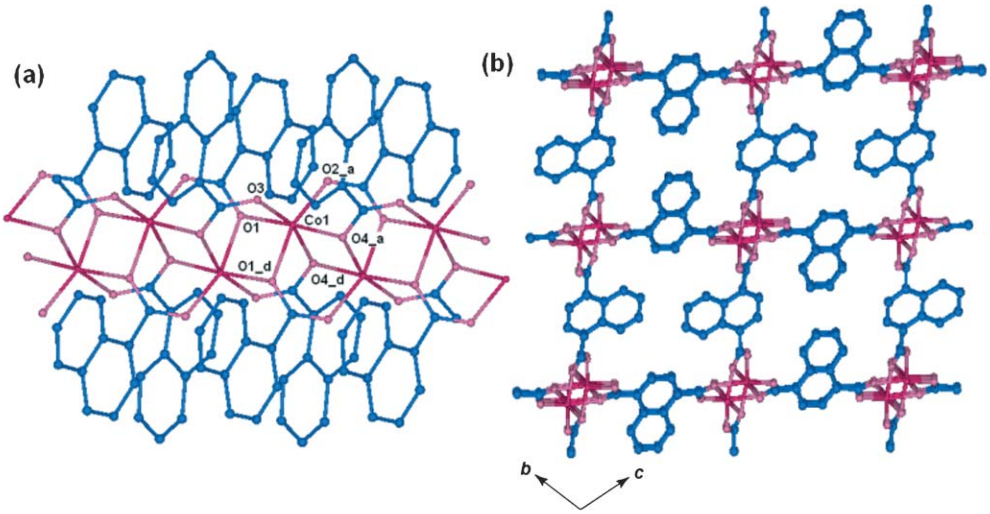

Fig. 1 (a) View of the coordination environment of Co(II) and the building unit [Co–μ-O_2]$_n$ of the inorganic chain in **1**; (b) the overall 3D coordination network of **1**.

Co1–O1–Co1_d is 85.58(6)°. The Co···Co separation in the chain through the μ^2-carboxylate bridge is very short and is about 2.91 Å, while through the 1,4-napdc^{2-} ligand, Co–1,4-napdc–Co, it is 11.12 Å. The noncovalent π–π interactions between the 1,4-napdc^{2-} ligands stabilize the overall conformation and topology of the network.

The framework **2** is isomorphous with **1**, having a 3D network with a 1D inorganic chain of [Mn–μ-O_2]$_n$ (Fig. SI(2)†). The degree of distortion from the ideal octahedral geometry of Mn(II) is reflected in the cisoid angles, 77.75(6)–113.98(8)° and transoid angles 157.59(6)–173.97(6)°. The dihedral angle between the two benzene rings of the 1,4-napdc^{2-} ligand is 5.63(9)°. The Mn–O distances are in the range 2.110(2)–2.260(2) Å and the Mn1–O1–Mn1_d angle is 87.46(8)°. The Mn···Mn separations between the μ^2-carboxylate bridge and in the Mn–1,4-napdc–Mn part are 3.07 Å and 11.21 Å, which are slightly higher compared to framework **1**.

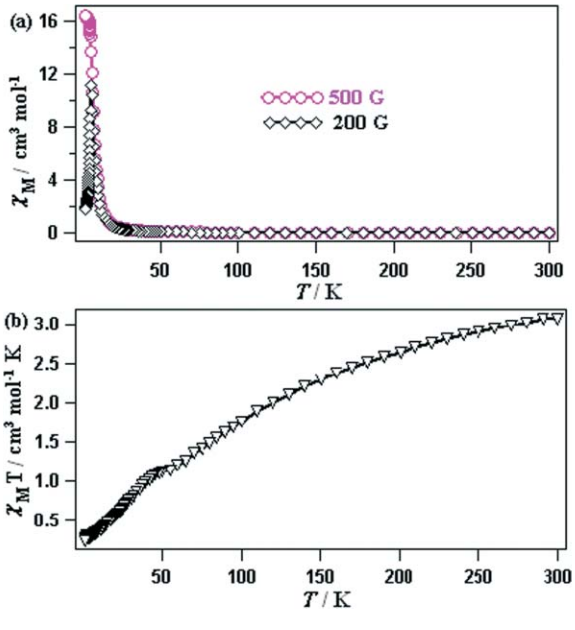

Fig. 2 (a) Temperature dependent χ_M *versus* T plots for **1** at two different applied fields (H = 500 and 200 G); (b) temperature dependent $\chi_M T$ *versus* T plots for **2** (H = 500 G).

Temperature dependent (300–1.8 K) magnetic measurements were carried out for both compounds using powder samples. Fig. 2a shows χ_M *versus* T plots of **1** at 200 and 500 G. The value of χ_M at 300 K is 1.06 × 10^2 cm^3 mol^{-1} (5.09 μ_B), which agrees with the expected spin-only value for an isolated high-spin Co(II) ion including an orbital contribution to $^4T_{1g}$ (4.5–5.2 μ_B). Upon cooling in a field of 200 G, the χ_M value gradually increases up to a maximum value of 11.1 cm^3 mol^{-1} (22.2 μ_B) at 5.5 K and then suddenly decreases to 1.80 cm^3 mol^{-1} (5.11 μ_B) at 1.8 K. The magnetic behavior above 5.5 K and the maximum χ_M value suggests a ferromagnetic coupling between Co(II) ions within the chain. The 1/χ_M *versus* T plot in the range 70–300 K obeys the Curie–Weiss law and gives a positive Weiss constant of +24.7 K, which also supports the ferromagnetic interaction between Co(II) ions. The drop in χ_M values below 5.5 K indicates the operation of an antiferromagnetic interchain interaction and an overall metamagnetic nature.[8] The ac magnetic susceptibilities (Fig. 3) confirm the onset of magnetic ordering with a sharp peak in the

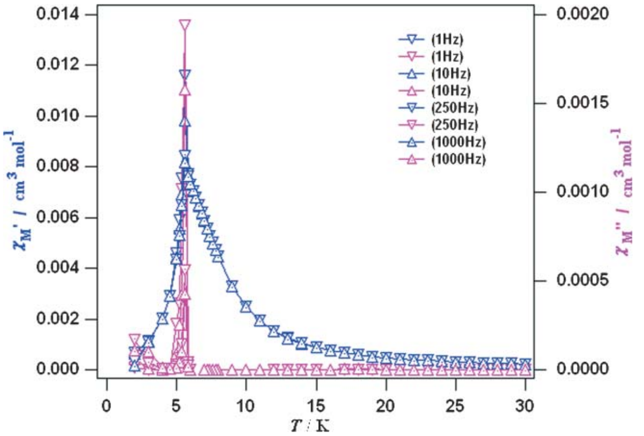

Fig. 3 The temperature dependence of the in-phase (χ_M') and the out-of-phase (χ_M'') ac magnetic susceptibilities for **1**.

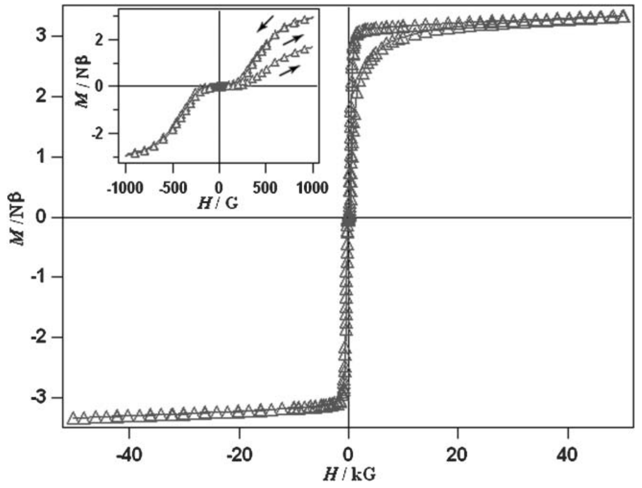

Fig. 4 Magnetic hysteresis loop at 2 K for **1** (inset: details in a low field showing a sigmoidal curve corresponding metamagnetic behaviour).

in-phase ($\chi_M{'}$) and out-of-phase components ($\chi_M{''}$) at 5.5 K, which suggest 3D magnetic ordering with $T_C = 5.5$ K. The ac magnetic behavior does not depend on the frequency between 1 and 1000 Hz. The magnetic hysteresis loop (Fig. 4 (inset)) shows a sigmoidal nature with an inflection point around 250 G, a saturation magnetization value of 3.32 μ_B at 5 T and a slight remnant magnetization (Fig. 4).[8] The first magnetization curve does not correspond to the second one (Fig. 4 (inset)). The inflection point means a critical magnetic field for spin flipping and this behavior suggests the metamagnetic nature of framework **1**. Actually, the drop of the χ_M value below 5.5 K is not observed in the χ_M *versus* T plot under 500 G (Fig. 2a), which suggests the weak antiferromagnetic interchain interaction is overcome by the external magnetic field.

In the case of **2**, the $\chi_M T$ value at 300 K is 3.06 cm^3 mol^{-1} K (4.95 μ_B) and then simply decreases down to 0.24 cm^3 mol^{-1} K (1.39 μ_B) at 1.8 K (Fig. 2b). This behaviour is characteristic of an antiferromagnetic interaction between the Mn(II) centers. The anomaly around 50 K is attributed to effect of oxygen. The residual oxygen was not completely removed by repeated evacuation. The M *versus* H curve of **2** (Fig. SI(3)†) with a magnetization value of 0.256 μ_B at 5 T also suggests an antiferromagnetic interaction between Mn(II) ions through the μ^2-carboxylate bridge. In spite of having the same bridging structure, the dominant magnetic interaction nature is opposite between **1** and **2**. Here in the frameworks, **1** and **2**, all metal centers are in an octahedral environment. The magnetic interaction between dσ (e_g) unpaired electrons should be ferromagnetic due to accidental orthogonality of the M–O–M bridging angle (85.58° for **1** and 87.46° for **2**). However, the interaction of Co(II) usually stronger than that of Mn(II) because of the shorter M–O bond distances. In addition, Mn(II) (d^5, high spin) has more unpaired electrons in the dπ (t_{2g}) orbitals, which give an antiferromagnetic contribution, and an antiferromagnetic interchain interaction also operates. Accordingly, weak antiferromagnetic interactions operate in **2** as a sum of such magnetic contributions.

In summary, we have synthesized two isomorphous 3D coordination networks of Co(II) and Mn(II) by hydrothermal techniques using 1,4-napdc^{2-} as a bridging ligand. The framework **1** shows overall metamagnetic behaviour ($T_C = 5.5$ K) with strong ferromagnetic intrachain interactions and antiferromagnetic interchain interactions. Whereas framework **2**, having Mn(II) in a d^5 high spin configuration, shows simple antiferromagnetic interactions. So, this novel result shows the diversity of magnetic properties in two isomorphous frameworks by a simple change of the metal ion.

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Notes and references

‡ Crystal and structure refinement parameters for **1** and **2**. Framework **1**: $C_{12}H_6CoO_4$, Mw = 273.11, monoclinic, space group $P2_1/n$ (No. 14), a = 4.728(5) Å, b = 14.84(2) Å, c = 13.48(3) Å, β = 90.46(6)°, V = 946.0(2) Å^3, Z = 4, D_c =1.917 g cm^{-3}, $\mu(\mathrm{Mo}_{K\alpha})$ = 1.811 mm^{-1}, T = 223 K, $\lambda(\mathrm{Mo}_{K\alpha})$ = 0.71069 Å, θ_{max} = 27.5°. Total data = 9938, unique data = 2128, R_{int} = 0.029, observed data [$I > 2\sigma(I)$] = 1661, R = 0.0253, wR_2 = 0.0417, GOF = 1.08. Framework **2**: $C_{12}H_6MnO_4$, Mw = 269.11, monoclinic, space group $P2_1/n$ (No. 14), a = 4.892(9) Å, b = 14.99(2) Å, c = 13.37(4) Å; β = 91.82(6)°; V = 980(3) Å^3, Z = 4; D_c = 1.824 g cm^{-3}; $\mu(\mathrm{Mo}_{K\alpha})$ = 1.343 mm^{-1}, T = 233 K; $\lambda(\mathrm{Mo}_{K\alpha})$ = 0.71069 Å, θ_{max} = 27.5°. Total data = 8752, unique data = 2221, R_{int} = 0.039, observed data [$I > 2\sigma(I)$] = 1514; R = 0.0293, wR_2 = 0.0395, GOF = 0.89. Data were collected on a Rigaku Mercury CCD diffractometer with graphite monochromated $\mathrm{Mo}_{K\alpha}$ radiation (λ = 0.71069 Å). Both the structures were solved by direct methods by using SIR97 program and expanded by using Fourier techniques. For both compounds, the non-hydrogen atoms were placed in the ideal positions. CCDC 274483 for **1** and 274484 for **2**. See http://dx.doi.org/10.1039/b507953e for crystallographic data in CIF or other electronic format.

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