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Chemically-Controlled Stacking of Inorganic Subnets in Coordination Networks: Metal-Organic Magnetic Multilayers

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Supporting Information

ABSTRACT: Coordination Networks (CNs), such as for instance Metal-Organic Frameworks (MOFs), can turn into remarkable magnets, with various topologies of spin carriers and unique opportunities of cross-coupling to other functionalities. Alternatively, distinct inorganic subnetworks that are spatially segregated by organic ligands can lead to coexisting magnetic systems in a single bulk material. Here, we present a system of two CNs of general formula Mn(H2O)2(OOC-(C6H11)7-COO). The compound with two water molecules and one aromatic ring (x=2; y=1) has a single 2-dimensional magnetic subnet, while the material with x=1.5 and y=2 shows, additionally, another type of magnetic layer. In analogy to magnetic multilayers that are deposited by physical methods, these materials can be regarded as Metal-Organic Magnetic Multilayers (MOMMs), where the stacking of different types of magnetic layers is controlled by the choice of an organic ligand during the chemical synthesis. This work further paves the way towards organic-inorganic nanostructures with functional magnetic properties.

In this Article, we present a system that consists of two layered CNs, in which the stacking of two types of inorganic subnetworks is controlled by the choice of the interlayer organic ligand. The formation of such Metal-Organic Magnetic Multilayers (MOMMs) further reveals the parallel between hybrid layered magnets and multilayers of inorganic materials deposited by physical methods, which have led to a multitude of technological applications.

Figure 1 shows a projection of the structures of the two CNs of general formula Mn2+(H2O)2(OOC-(C6H11)7-COO). The material with x=2 and y=1 has been reported earlier and is based on 1,4-benzenedicarboxylate (bdc). It features a single inorganic subnet labelled ‘i’. The material with x=1.5 and y=2 is reported for the first time here and incorporates 4,4’-biphenyldicarboxylate (bpdc) molecules that separate two types of inorganic subnets; layer ‘i’, as in the bdc-based material, and another type of layer labelled ‘ii’.

Both materials are formed at room-temperature by co-precipitation in water of the sodium(I) bdc or bpdc dicarboxylate with manganese(II) chloride. The pH value is determinant for their synthesis as it regulates the competition between the hydrated phases and the manganese(II) hydroxycarboxylates, namely phases of general formula Mn2+(OH)2(OOC-(C6H11)7-COO). For y=1 (bdc), the hydrate is best formed at a pH value of about 7.5, while the hydroxide is obtained as a pure phase for pH=8.5 or slightly higher; intermediate pH values yield mixtures of the two phases. This global scenario is retained for y=2 (bpdc); with the range of optimal pH values shifted to higher values. The novel phase presented here was obtained by slow addition, using peristaltic pumps, of aqueous solutions of sodium hydroxide (0.1 M) and manganese(II) chloride (5×10−4 M) into an aqueous reaction medium that contains the deprotonated ligand (pH=9). The solution of the metallic salt was incorporated at a constant rate over an hour, while the addition of the base was controlled by a loop that maintained the pH of the reaction medium at a value of 9.0±0.1. The slow mixing yields a better crystallinity of the final product, whereas the control loop on the pH is crucial to avoid the formation of competing hydroxides. The aqueous suspensions resulting
from the room-temperature co-precipitation can be hydrothermally treated under various conditions of temperature (up to 180 Celsius) and time (up to several days). Within these ranges, the only effect of this optional hydrothermal treatment is to improve the crystallinity of the final product.

Mn(H$_2$O)$_2$(bpdc) was obtained while we aimed to synthesize the bpdc analogue of Mn(H$_2$O)$_2$(bdc). The powder X-ray diffraction (PXRD) pattern is typical for layered hybrid materials (Figure 5), with a strong Bragg reflection centered on a low scattering angle. However, the solid does not crystallize into a monoclinic unit-cell that would simply account for the longer bpdc molecules. In contrast, the lattice parameter along the stacking direction, a=53.35 Å, is remarkably large. The indexation into a monoclinic using the X-Cell computer program gives b=6.49 Å, c=7.41 Å and β=90.45°, which is reminiscent of Mn(H$_2$O)$_2$(bdc) (b=6.54 Å, c=7.35 Å, β=97.85°). The half-integer water stoichiometry of the novel material can be directly evaluated from a thermogravimetric analysis in air (Figure S2a), if manganese, bpdc and water molecules are considered as the constituents of the final product. The theoretical dehydration loss of Mn(H$_2$O)$_2$(bpdc) is 8.39 %, in excellent agreement with the experimental loss of 8.32 %. This process occurs well above 350 Celsius, which indicates coordinated water molecules. The decomposition of the organic ligand is observed around 350 Celsius and the total loss of 72.66 % agrees well with the prediction for Mn(H$_2$O)$_2$(bpdc) → ½ MnO$_2$ (75.48 %, residue checked by PXRD). Chemical analysis confirms the formula CaH$_3$MnO$_6$O$_7$; Anal. (Calcd): C, 25.98 (26.71); O, 29.18 (29.68); Mn, 31.04 (30.57). The crystal structure (C2/c) of Mn(H$_2$O)$_2$(bpdc) was solved from synchrotron PXRD data by global optimization methods in the direct space, using the computer program Fox. The solution was obtained for a set of scatterers comprising one bpdc molecule in general position (8f), two Mn$^{2+}$ ions occupying special positions (Mn(1) in 4e and Mn(2) in 4c), and two oxygen atoms accounting for the presence of two water molecules (H$_2$O(1) in 4e and H$_2$O(2) in 8f). The final Rietveld refinement of the synchrotron PXRD data was performed using Fullprof$^9$ (Figure Si).

Mn(H$_2$O)$_2$(bpdc) is a novel CN featuring two types of inorganic subnets. Layer ‘i’, represented in red (Figure 2), is the same as in Mn(H$_2$O)$_2$(bdc). It has the stoichiometry 1 Mn(1) : 2 H$_2$O(1) and is composed of MnO$_6$ octahedra where four of the six oxygen ligands are provided by the carboxylic functions of bpdc. Layer ‘i’ forms a squared lattice of MnO$_6$ octahedra interconnected through carboxylate bridges. The second layer ‘j’ has the stoichiometry 1 Mn(2) : 1 H$_2$O(2) and is composed of MnO$_3$ distorted trigonal bipyramids. These pentahedra form zigzag chains, via carboxylate bridges, running along the c direction. The chains are connected together via strong hydrogen bonds between the hydrogen atoms of H$_2$O(2) and the acceptor oxygen atoms of the carboxylate groups in the adjacent chain. The donor–acceptor distance is ≈2.43 Å, which indicates bond energies in the range 60-170 kJ.mol$^{-1}$. The existence of two crystallographically-independent water molecules is corroborated by the infrared spectrum in the region of interest where O–H stretching vibrations are found (Figure S2b). The spectrum shows broad bands, as expected for O–H groups that are involved in hydrogen bonds. The bands are centered around three distinct frequencies, which agrees with the existence of three donor–acceptor distances around the oxygens of the water molecules (=2.69 Å and =2.81 Å for H$_2$O(1); =2.43 Å for H$_2$O(2)).

Figure 1. The system of controllable Metal-Organic Magnetic Multilayers (MOMMs) formed by Mn(H$_2$O)$_2$(bpdc) (left) and Mn(H$_2$O)$_2$(bdc) (right) Coordination Networks. Red and blue polyhedra correspond to the dihydrated ‘i’ and monohydrated ‘j’ types of layers, respectively.

Figure 2. Magnetic subnetworks ‘i’ (left) and ‘j’ (right). ‘i’ is approximated as a squared lattice with one exchange constant J$_1$. ‘j’ is approximated as an array of zig-zag chains with one exchange constant J$_2$ along the chains, and an interchain path J$_2$ via hydrogen bonds (blue dashed bonds).

The magnetic properties of both CNs were investigated by magnetization measurements recorded using a SQUID magnetometer (MPMS-XL, Quantum Design). The thermal dependence of the magnetization, M, was probed in the temperature, T, range from 1.8 to 300 K, under a moderate applied magnetic field, μ$_0$H, of 0.1 T. A simple adjustment of $H/M$ ($=\chi^{-1}$) vs. T to a Curie-Weiss law reproduces the experimental data down to a temperature of about 15 K, for both CNs (Figure 3a and 3b). The experimental data significantly deviate from this simple behavior for lower temperatures, indicating the development of magnetic correlations. This is supported by the broad bump that is centered around T=6 K in the magnetic susceptibility $\chi$ ($=M/H$) of both compounds (Figure 3c and 3d). Such a behavior is typical for low-
features a weak ferromagnetic character. This last transition, cooling reveals a third magnetic transition, at decreasing temperature, at measurements indicate the existence of multiple magnetic below reveals a more complex behavior in the bilayer change through the carboxylate bridges, stants that are extracted for layer '2' are reasonable: the ex-
significantly worse fits). With these five parameters (less parametrized fits result in

Based on the above description of the two magnetic layers, we model their magnetic susceptibility using a 2D Heisenberg model and a 1D Fisher model with mean-field inter-
chain interactions, respectively (see Figure 3 and Supporting Information). The experimental data arising from the bdc-based MOFs are well fitted using the 2D Heisenberg model solely, yielding reasonable values for the exchange constant (J/kB=3.356(1) K – indicating an antiferromagnetic interaction) and gyromagnetic factor (g=2.11(3)). The fit can be further improved by adding a mean-field correction that accounts for interlayer interactions (Figure 3c). In this case, we obtain J/kB=-2.43(3) K, g=2.209(2), and the mean-field constant J_interlayers/kB=-0.91(2) K. In contrast, the magnetic susceptibility of the bpdc-based material is best fitted with equally-weighted contributions of 'i' and 'z' (Figure 3d). We find J_i/kB=2.593(4) K and g=2.065(9) for the 2D Heisenberg layer 'i', and J_z/kB=2.35(2) K, g=2.373(9) and J_z'/kB=1.11(7) K for the magnetic layer 'z'. We note that the fitting procedure for the bilayer (bpdc-based) material remains discriminant with these five parameters (less parametrized fits result in significantly worse fits). Moreover, the values of the exchange parameter J_i for the magnetic layer 'i' are reasonably close in the bdc- and bpdc-based materials. Finally, the constants that are extracted for layer 'z' are reasonable: the exchange through the carboxylate bridges, J_z, is similar to that in layer 'i', and the interchain coupling J_z' is significantly weaker, as expected from the larger intermetallic distance.

While the single-layer (bdc-based) material is known to order antiferromagnetically below T_N = 6.5 K, our set of macroscopic measurements (see Supporting Information) reveals a more complex behavior in the bilayer material below T_c=5 K. Both magnetic susceptibility and heat capacity measurements indicate the existence of multiple magnetic phase transitions, as expected given the intricate crystal chemistry of the material. We observe two transitions upon decreasing temperature, at T_Ni=4.3 K and T_Nz=4.0 K, which likely correspond to distinct 3-dimensional antiferromagnetic orderings of layers 'i' and layers 'z', respectively. Further cooling reveals a third magnetic transition, at T_T=3.4 K, that features a weak ferromagnetic character. This last transition, absent in the bdc-based material, may be due to a slight canting in layer 'z', where Mn^2+ is five-coordinated and therefore more likely subject to a weak single-ion anisotropy.

As evidenced in Figure 2, the two types of inorganic layers can be described using simple topologies of first-neighbor magnetic interaction pathways. A nearly squared lattice with one exchange constant through carboxylate bridges (J_i) is employed for the dihydrated layer 'i'. The intermetallic distance in 'i' is d_Mn(i)-Mn(i)=4.96 Å and d_Mn(i)-Mn(i)=4.92 Å for the bdc- and bpdc-based materials, respectively. The monohy-
drated layer 'z' requires a slightly more evolved model that corresponds to an array of chains with one intrachain inter-
action through carboxylate bridges (J_z), and one interchain interaction through hydrogen bonds (J_z'). In 'z' the interme-
tallic distances are d_Mn(z)-Mn(z)=4.48 Å along J_z and d_Mn(z)-Mn(z)=5.43 Å along J_z'. We approximate all magnetic moments as isotropic (Heisenberg-like) spins, because Mn^{2+} is an orbitally non-degenerate cation (L=0) and is, therefore, only weakly affected by crystal-electric field effects.

In conclusion, different network architectures were obtained during the auto-assembly in water of Mn^{2+} cations and the aromatic dicarboxylate linkers bdc or bpdc. This appears to be distinct from the reticular chemistry approach, where such organic ligands typically maintain the topology of the resulting MOFs. Remarkably, the change of the organic ligand from bdc to bpdc appears to trigger the formation of a second type of inorganic subunit in Mn(H_2O)_3(bpdc). Although it is relatively widespread to find different types of cluster-like Secondary Building Units (SBUs) in MOFs, the coexistence of cluster-like SBUs and extended SBUs (such as rods or layers) – or even more the coexistence of two types of extended SBUs – is rarely observed in the same structure. The layered organization found in Mn(H_2O)_3(bpdc) is most naturally compared with the structures of inorganic materials derived from perovskite blocks, as already pointed out in the study of Mn(C_4H_4O_4). The system formed by Mn(H_2O)_3(bdc) and Mn(H_2O)_3(bpdc) CNs appears remarkable in the way the structure reacts to the change of ligand. The substitution of bdc for bpdc in Mn^{2+} layered hydrates disrupts the sequence of organic and inorganic slabs along the stacking direction, while the crystal chemistry is partly conserved in the plane, where the metrics remains nearly unchanged. Our results further demonstrate the analogy between CNs, such as for instance MOFs, and nanostructures, in which different types of inorganic materials are used to tailor functional magnetic properties.

ASSOCIATED CONTENT
Supporting Information
Crystallographic data, infrared spectra and additional physical measurements and fitting details. This material is available free of charge via the Internet at http://pubs.acs.org.
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SYNOPSIS TOC. Mn(H₂O)₂(OOC-(C₆H₄)₂-COO) is a rare example of a layered Coordination Network (CN) containing two types of extended (2D) Secondary Building Units (SBUs). One of the extended SBUs is also found in Mn(H₂O)₃(OOC-(C₆H₄)₂-COO), obtained using the same synthesis procedure. Therefore, the change of organic ligand controls the stacking of different types of magnetic layers. This paradigm to prepare materials with tailored magnetic properties further demonstrates the analogy between magnetic CNs and nanostructures made of thin films of different materials.

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