Metal–Organic Frameworks

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An In Situ High-Temperature Single-Crystal Investigation of a Dehydrated Metal–Organic Framework Compound and Field-Induced Magnetization of One-Dimensional Metal–Oxygen Chains**

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Metal–organic framework compounds have attracted considerable interest recently because of their eminently promising properties, which make them suitable for applications as gas-storage systems, sensors, and in ion exchange or catalysis,[1] and, more seldom, because of their magnetic properties.[2,3] The diversity of potential applications arises from the possibilities that the range of applicable metals and the appropriate choice of organic linking blocks offer for the intentional or inadvertent design of advantageous compounds. The common feature of most applications is that they necessitate the framework to have a sufficiently large and permanent porosity to be penetrated by guest molecules and ions. As such, coordination polymers have frequently been compared with zeolites, over which they offer a number of advantages. Among these are accessible volumes that are several times higher than for zeolites.[4] A severe disadvantage of an organic–inorganic hybrid compound with respect to zeolites, however, is often the significantly lower thermal stability. For most applications, it is necessary to remove the solvent from the pores, which is usually only achieved at elevated temperatures, and this sometimes leads to the collapse of the long-range order of the framework. Thus, the investigation of the thermal behavior of any novel porous metal–organic framework compound lies at the core of determining its suitability for applications. There have been only a few reports of single-crystal investigations of desolvated microporous metal–organic frameworks,[5] and in only one case was the study conducted in situ.[6] In all of these cases, the connectivities of the framework of the desolvated compound remained unchanged. Here, we report the synthesis and characterization of a microporous cobalt(II)-

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containing metal–organic framework. The in situ single-crystal X-ray investigation of its dehydrated form reveals that a water molecule originally coordinated to the metal center is removed as well in the course of the solvent elimination. However, the framework remains stable, with the coordination environment of the cobalt atom changing from octahedral to square pyramidal. The as-synthesized compound orders antiferromagnetically below 8 K, but it subsequently passes through a metamagnetic phase transition to display field-induced ferromagnetic ordering.

The reaction of cobalt(II) acetate and 2,5-dihydroxyterephthalic acid ($C_8H_6O_6$) in a mixture of water and tetrahydrofuran (molar ratio 2:1:556:165) under autogenous pressure at 110 °C in a Teflon-lined autoclave (50 % filling level) yielded the pink-red, needle-shaped crystalline substance $[Co_2(C_8H_2O_6)(H_2O)_2]\cdot 8\,H_2O$ (**1**). The results of the elemental analysis confirm that the channels are occupied solely by water molecules even though a solvent mixture was used in the synthesis. The crystal structure analysis revealed a three-dimensional coordination polymer with honeycomb topology that contains one-dimensional, solvent-filled channels (Figure 1 a). The cobalt atom is coordinated in a distorted octahedral fashion by six oxygen atoms. Five of the oxygen atoms are part of the organic ligand, which utilizes all of its oxygen atoms in coordinative bonds with the cobalt center. The sixth oxygen ligand at the cobalt center comes from a water molecule. Four of the Co–O distances are in the range between 2.03 and 2.06 Å, while the fifth Co–O distance is 2.190(5) Å. The water molecule is *trans* to this bond, and its Co–O bond is also elongated (2.158(7) Å). The hydroxide oxygen atom and one of the carboxylate oxygen atoms coordinate two cobalt atoms each, while the second carboxylate oxygen coordinates only one cobalt atom. This coordination arrangement results in cobalt–oxygen octahedra that are linked by *cis*-oriented edges (Figure 1 b) such that the cobalt atoms form a threefold helix parallel to the *c* axis. The framework topology is identical to that recently described for $[Zn_2(C_8H_2O_6)(dmf)_2]\cdot(H_2O)_2$ (dmf = *N*,*N*-dimethylformamide).[7]

After the hypothetical removal of the noncoordinating solvent molecules in the channels, the empty channels occupy 49 % of the total volume of the unit cell, and the average cross-sectional channel dimensions are 11.08 × 11.08 Å^2. The empty volume increases to 60 % if the coordinating water is also removed. The water molecules excluding and including the coordinating water account for 29.2 % and 36.6 % of the mass, respectively. We found that it was possible to repeatedly dehydrate and hydrate compound **1** by heating to 100 °C in a dry argon gas stream and then cooling down and admixing water vapor with the inert gas stream. A dry gas stream at room temperature actually suffices to remove 90 % of the water within 43 h. The amount of weight loss during the heating experiments indicates that the coordinatively bound water molecules are also removed. Indeed, this was confirmed by an in situ single-crystal structure determination at 95 °C which revealed that the three-dimensional framework actually remains intact upon dehydration. Because of the abscission of the coordinating water molecule, the cobalt center remains in a square-pyramidal coordination environment (Figure 1 c). At the apex of the pyramid is the oxygen atom that used to be *trans* to the vacated water position; the Co–O distance is now significantly shorter than before (2.067(5) Å). The empty coordination site is accessible for molecules from the channels, which is a necessary requirement for the metal to perform catalytic functions.[8]

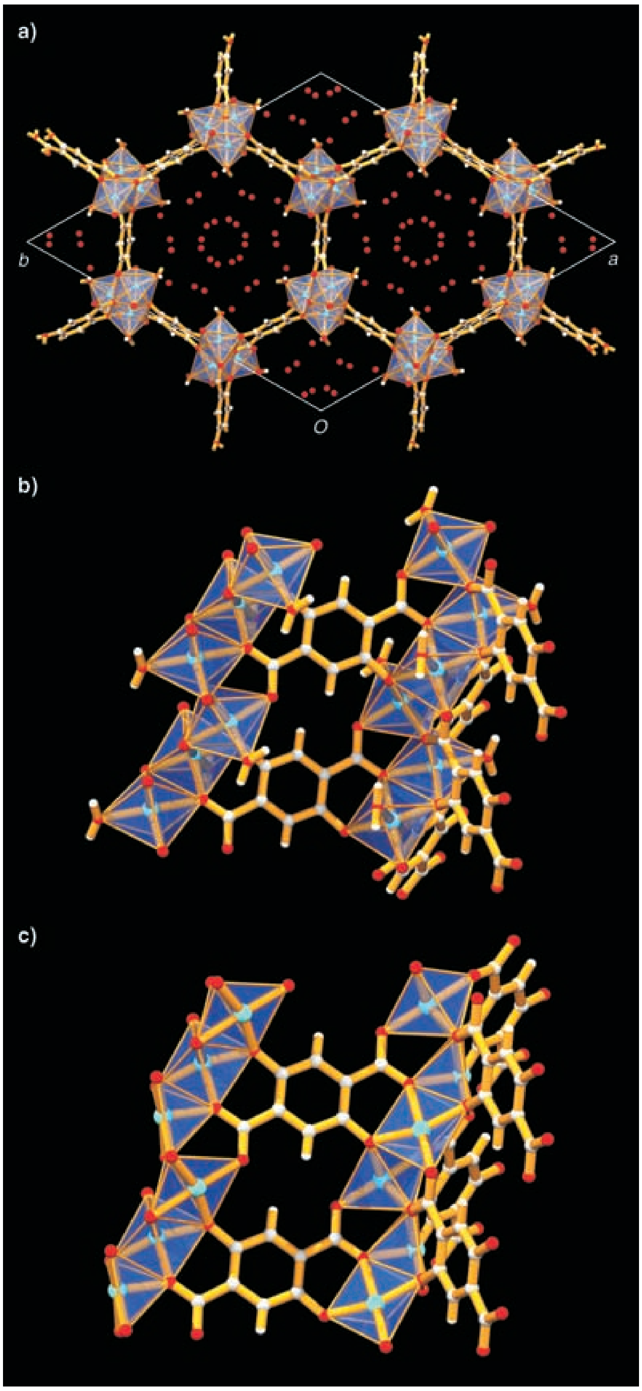

Figure 1. a) Packing diagram of **1** along [001]; b) chains of edge-connected cobalt oxygen octahedra in **1**. Neighboring chains are of opposite handedness; c) square-pyramidal environment of the cobalt center in **2** after removal of the water molecules.

Plots of the projection of the electron density along the channel direction illustrate the change from the hydrated to the dehydrated framework (surface plots in Figure 2). The

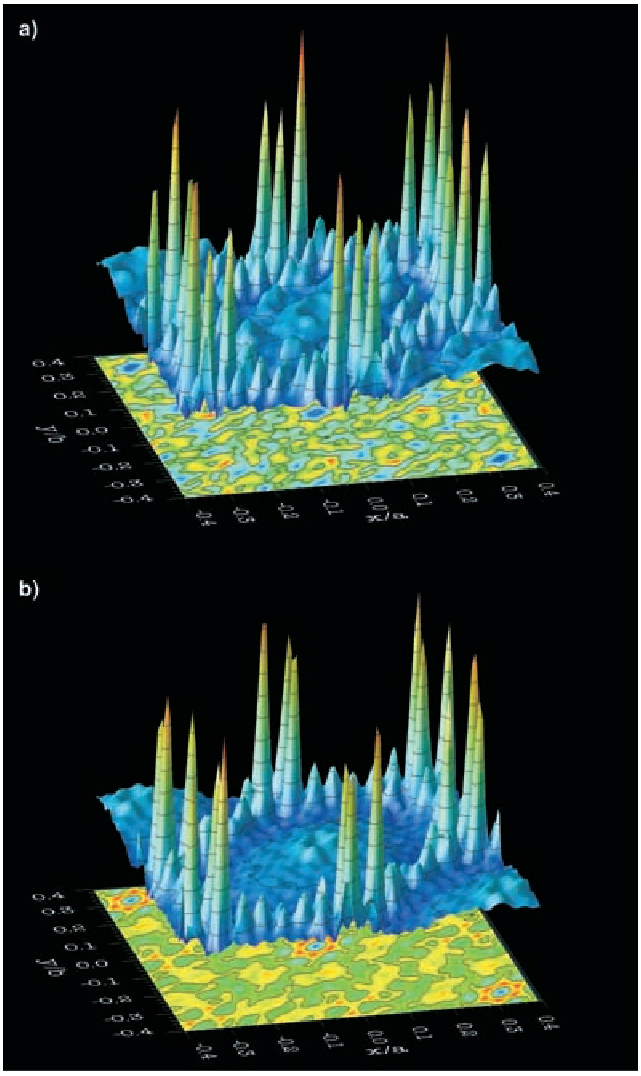

Figure 2. Projection of the electron density along [001] (surface plots) and the final difference electron maps (contour plots; line at 0.0 e$Å^{-3}$) at a) 25 °C and b) 95 °C. Observed reflections ($I > 2\sigma(I)$) were used for the calculation with the map function of WinGX.[9]

cobalt atoms stand out as the most-intense peaks in groups of three at the corners of the hexagon. Connecting these are the rows of peaks due to the organic ligand. The water molecules in the channel and at the cobalt atoms are clearly distinguishable in Figure 2 a, while they are absent in Figure 2 b. Some electron density is observed in the center of the channel at 95 °C. This might be due to the inert gas molecules that are bound to occupy the channels now, but the shape of the surface indicates that it is more likely a result of Fourier termination errors accumulating electron density around the element of symmetry. No atoms can be refined in these positions, and the final difference density maps (contour plots in Figure 2) agree well with the chosen structural models. In this context, it is noteworthy to mention that we also measured the crystal at 200 °C and the results were congruent to those obtained at 95 °C. A second crystal that had only been heated to 95 °C yielded identical results to the first crystal. It was subsequently cooled down and stored in a water-vapor-saturated atmosphere, whereupon we could again localize the coordinating water and bulk solvent water molecules.

We confirmed the stability of compound **2** in an inert atmosphere by thermodiffractometry and thermogravimetry studies. The crystallinity of **2** starts to decrease above 200 °C, and final decomposition occurs above 320 °C. A sample heated at 200 °C in argon for a total of 63 h can still take up the entire amount of water. Compound **2** is substantially less stable in air. Decomposition is observed at 234 °C and proceeds rapidly, and the crystallinity of the sample diminishes already above 140 °C. Concurrently, if a sample is dehydrated in air at 150 °C, the amount of water that it can take up again diminishes with the time it has been exposed to this temperature. Apparently, the presence of the oxygen in air promotes the collapse of the framework.

In compound **1**, the shortest metal-to-metal distance within a helical metal–oxygen backbone chain is 3.059(2) Å, while the shortest distance between cobalt atoms in adjacent chains is 7.387(2) Å. Cobalt compounds with such a large anisotropy in metal-to-metal distances have frequently been found to behave as one-dimensional magnetic systems.[10] While measurements of the magnetic susceptibility confirm the +2 oxidation state of the cobalt ($\mu = 4.67(13)\ \mu_B$, $\theta = -6(2)$ K), they do not show any noticeable deviation from three-dimensional behavior. The susceptibility drops off sharply below 8 K, which indicates antiferromagnetic ordering (Figure 3). However, on application of magnetic fields stronger than about 2 T, we observed a field-induced transition to a ferromagnetic-like ordered state.[11] The superexchange pathway in the metal–oxygen chain suggests that the magnetic moments couple ferromagnetically in the chains. The antiferromagnetic long-range order in low magnetic fields then results from the antiparallel alignment of the spins of adjacent chains. It may be the aromatic system of the organic ligand that propagates this further to give a three-dimensional interaction.[12] Stronger magnetic fields can overcome this interaction and induce the ferromagnetic-like state.

In conclusion, we would like to emphasize that metal–organic framework compounds may be very suitable systems to investigate magnetic interactions, even more so since materials with switchable magnetic properties promise to deliver the next revolution in information technology.[13] We have shown that it is possible to remove the solvent from compound **1** whilst maintaining the framework structure intact, even though the cobalt atom also loses its coordinating water molecule and remains pentacoordinate. The resulting compound **2** is stable to above 200 °C in an inert atmosphere.

The stability and the readily available coordination site at the metal atom indicate that it should be worthwhile to investigate the chemical properties of this compound further. This should encompass possible catalytic activity, while its magnetic properties suggest that a more detailed study of its magnetic structure needs to be performed.

Experimental Section

Crystals of compound **1** of a suitable size for a single-crystal structure determination were obtained by reducing the molar ratio of cobalt acetate to ligand to 1:1. They were obtained by combining a solution of cobalt(II) acetate (187 mg, 0.75 mmol) in water (10 mL) and a

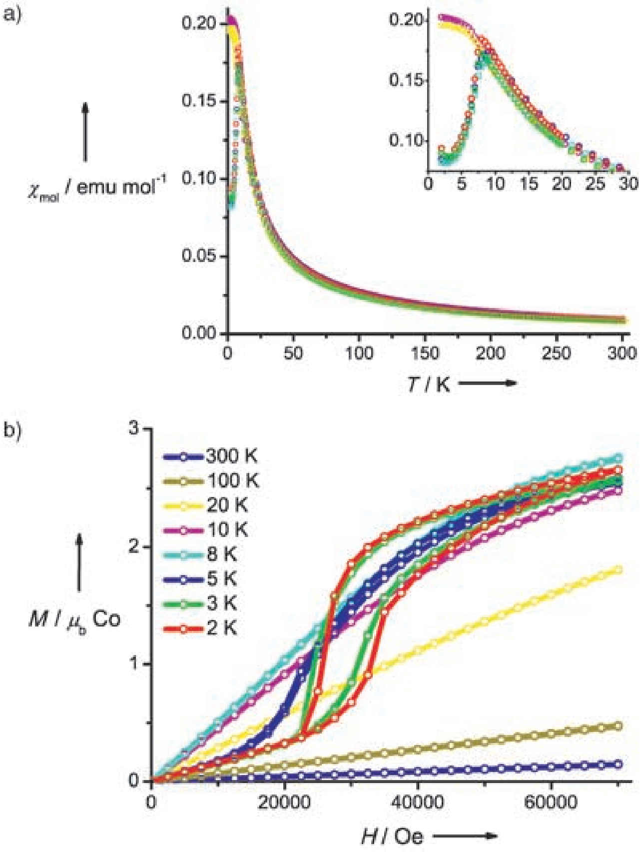

Figure 3. a) Molar magnetic susceptibility χ_{mol} as a function of the temperature for compound **1** and various fields (zero-field-cooled: 1000 Oe red, 10^4 Oe blue, 4×10^4 Oe magenta; field-cooled: 1000 Oe green, 10^4 Oe cyan, 4×10^4 Oe yellow); b) magnetization *M* per cobalt atom [μ_B] as a function of magnetic field and temperature.

solution of 2,5-dihydroxyterephthalic acid (149 mg, 0.75 mmol) in THF (10 mL) in a Teflon-lined steel autoclave and heating at 110 °C for three days. The crystals were isolated after filtration in 54 % yield (95 mg, 0.2 mmol) with respect to cobalt. Elemental analysis (%): calcd: C 19.52, H 4.47, Co 23.95, O 52.05; found: C 19.60, H 4.38, Co 23.95, O 52.06.

Single-crystal X-ray crystallography: A hemisphere of data was collected on a Bruker D8 diffractometer with an Apex II detector and an Oxford Cryosystems Cryostream Plus device. After data integration with SAINT and semiempirical absorption correction with SADABS,[14] structures were solved by direct methods and refined on F^2 with the SHELX program suite.[15]

Compound **1**: Crystal dimensions $0.02\times0.02\times0.20$ mm^3, trigonal, space group $R\bar{3}$ (no. 148), $a=26.1102(19)$, $b=26.1102(19)$, $c=6.7192(10)$ Å, $V=3967.1(7)$ Å^3, $\rho_{calcd}=1.793$ g cm^{-3}, $Z=18$, $2\theta_{max}=50°$, Mo$_{K\alpha}$ radiation, $\lambda=0.71073$ Å, ω scans, $T=293$ K, 12577 reflections collected, 1544 unique reflections, 1093 observed data ($I>2\sigma(I)$), $R_{int}=0.115$, $\mu=1.959$ mm^{-1}, min/max transmission 0.712/0.962, 124 parameters, final $R_1(I>2\sigma(I))=0.0626$, wR_2(all data) = 0.1647, GOF = 1.15, $\Delta\rho_{min}=-0.59$ e Å^{-1}, $\Delta\rho_{max}=0.73$ e Å^{-1}. Compound **2**: A crystal of dimensions $0.03\times0.03\times0.30$ mm^3 was attached carefully oriented and with a minimum of glue to the tip of a capillary to avoid obstructing the channels; it was then slowly heated at 20 °C h^{-1} to 95 °C; trigonal, space group $R\bar{3}$ (no. 148), $a=25.885(3)$, $b=25.885(3)$, $c=6.8058(17)$ Å, $V=3949.0(12)$ Å^3, $\rho_{calcd}=1.181$ g cm^{-3}, Z = 18, $2\theta_{max}=50.6°$, Mo$_{K\alpha}$ radiation, $\lambda=0.71073$ Å, ω scans, $T=368$ K, 6446 reflections collected, 1598 unique reflections, 1150 observed data ($I>2\sigma(I)$), $R_{int}=0.066$, $\mu=1.89$ mm^{-1}, min/max transmission 0.590/0.945, 73 parameters, final $R_1(I>2\sigma(I))=0.058$, wR_2(all data) = 0.209, GOF = 1.24, $\Delta\rho_{min}=-0.76$ e Å^{-1}, $\Delta\rho_{max}=1.30$ e Å^{-1}.

CCDC 270292 (**1**) and 270293 (**2**) 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.

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