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Topology Control of Porous Coordination Polymers by Building Block Symmetry

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The coordination polymers $[Fe_2MO(piv)_6(bipy)_{1.5}]_n$ [M = Ni^{II}, compound **1**, and M = Co^{II}, compound **2**; piv = $(CH_3)_3CCO_2^-$ and bipy = 4,4′-bipyridine] were prepared by linking trinuclear heterometallic pivalates, possessing D_{3h} symmetry, by linear molecules of bipy. The complexes are isostructural and are built from 2D doubly interpenetrated "honeycomb" layers. The structure of the starting polynuclear building blocks is retained, which opens the way for the creation of materials with predetermined properties. Zigzag channels in the crystal structures of the compounds can adsorb N_2 and H_2. Unusual N_2 adsorption/desorption hysteresis was observed. Magnetic properties of the polymers are governed by exchange interactions in trinuclear blocks. The $\chi_M T$ vs. T curve for **2** was fitted by taking into account the zero-field splitting of the Co^{II} ion by using software specially developed for this purpose.

Introduction

Porous coordination polymers attract considerable attention due to their outstanding properties, such as high sorption capacity,[1] promising magnetic properties,[2] and by the possibility of combining these properties in one system.[2b] In addition, such compounds may be considered as a basis for creating catalysts or nanoreactors,[3] and, in some cases, as potential active bodies for sensors.[4]

To the best of our knowledge, polynuclear complexes were scarcely used as starting materials (in contrast to their formation in situ) for assembling porous nets,[4,5] though this approach may be considered to be very promising with regard to the synthesis of compounds with desired magnetic (or other) properties, which are governed by the properties of the starting polynuclear unit.

The aim of this work is to elucidate whether the topology of the coordination polymer may be controlled by appropriate choice of "building blocks", which are introduced into the reaction mixture and appear in the resulting compound without being destroyed, in contrast to the usual in situ formation of the polynuclear core. The use of thermodynamically stable and kinetically inert polynuclear complexes possessing D_{3h} symmetry and linear organic linkers may result in only two types of topologies of polymers (provided that all donors are coordinated and all coordination vacancies are filled): 2D polymers with honeycomb cavities or 3D polymers with "spiral" structure, if the bridging molecules lie in different planes. In this study, the 2D honeycomb layer was successfully assembled from appropriate trinuclear building blocks.

Results and Discussion

The coordination polymers $[Fe_2MO(piv)_6(bipy)_{1.5}]_n$ [M = Ni^{II}, compound **1**, and M = Co^{II}, compound **2**; piv = $(CH_3)_3CCO_2^-$ and bipy = 4,4′-bipyridine] were prepared by reaction of neutral trinuclear pivalates, $Fe_2MO(piv)_6(Hpiv)_3$, with 4,4′-bipyridine. Despite the fact that each of these compounds contains different metals (Fe^{III} and Ni^{II} or Co^{II}), they may be considered as pseudo-D_{3h} building blocks, because the ability of all three metal ions to coordinate these ligands is the same. Crystal structures of iso-

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structural compounds **1**·2DMF and **2**·2DMF were determined by single-crystal X-ray diffraction analysis (details of synthesis and X-ray structure determination are presented in the Supporting Information).

Compound **1** is built from trinuclear μ_3-oxocentered units $Fe_2NiO(piv)_6$, connected by bipy molecules. In $Fe_2NiO(piv)_6$ two Fe^{III} ions and one Ni^{II} ion are located at the corners of an irregular triangle (assignment of metals as Fe or Ni is arbitrary) and are bridged by μ_3-O atoms and pivalates, which is typical for μ_3-oxocentered carboxylates.[6] Each bipy links two $Fe_2NiO(piv)_6$ units, and each $Fe_2NiO(piv)_6$ unit is linked to three bipy molecules, forming a 2D layer (Figure 1a and Figures S1 and S2, Supporting Information). One of the bipy molecules is disordered between two positions, which can be seen in Figure 1. Unusual double interpenetration of these layers, which may be described as "two in one" type, leads to the formation of zigzag channels, directed along the *b* axis, with pockets (diameter about 5.5 Å) separated by "windows" (diameter about 4.1 Å, Figures 1b and S3). The channels are filled with DMF, and the composition of single crystals corresponds to **1**·2DMF and **2**·2DMF.

Estimation of solvent-accessible volume, performed by using PLATON software,[7] gives a value of 22.4% for **1** (for a probe molecule with r = 1.4 Å), which leads to an expected pore volume of about 0.21 $cm^3 g^{-1}$.

Compounds **1** and **2** exhibit permanent porosity, which has been confirmed by sorption of N_2 and H_2 at 78 K. At least part of the micropores are easily accessible for N_2, which is evidenced by sharp growth of adsorption isotherms at low P (<25 Torr; Figure 2). However, both compounds showed broad adsorption/desorption hysteresis in their N_2 sorption isotherms, which may be caused by some difficulties of N_2 molecules in penetrating deep into the channels.[8] Notably, the kinetic diameter of N_2 (3.64 Å[9]) is only slightly smaller than the size of the windows in **1** and **2**, determined for solvated forms, and desolvatation may even lead to some contraction of channel size. Also, sorbent–substrate interactions were shown to cause "gate-opening",[10] which may be one more reason for the nontypical sorption behavior of **1** and **2**. Such gate-opening may involve a change in the angles between intersecting 2D layers.

The estimation of micropore volume by the Dubinin–Radushkevich model gives the values 0.22 $cm^3 g^{-1}$ for **1** and 0.11 $cm^3 g^{-1}$ for **2**, which is in good agreement with the value of accessible volume derived from crystallographic data. The values of specific surface, calculated from the first parts of adsorption isotherms according to the BET model, are 520 $m^2 g^{-1}$ for **1** and 273 $m^2 g^{-1}$ for **2**. Lower surface and pore volume for **2** relative to **1** may be caused by partial structure collapse at desolvatation, or by occlusion of the pores.

Hydrogen sorption isotherms (78 K) are quite typical for microporous sorbents,[11] and at 850 Torr, the sorption capacity is 0.51 wt.-% for **1** and 0.22 wt.-% for **2** (Figure 2). The absence of hysteresis in H_2 sorption may be caused by the lower diameter of the H_2 molecule (kinetic diameter

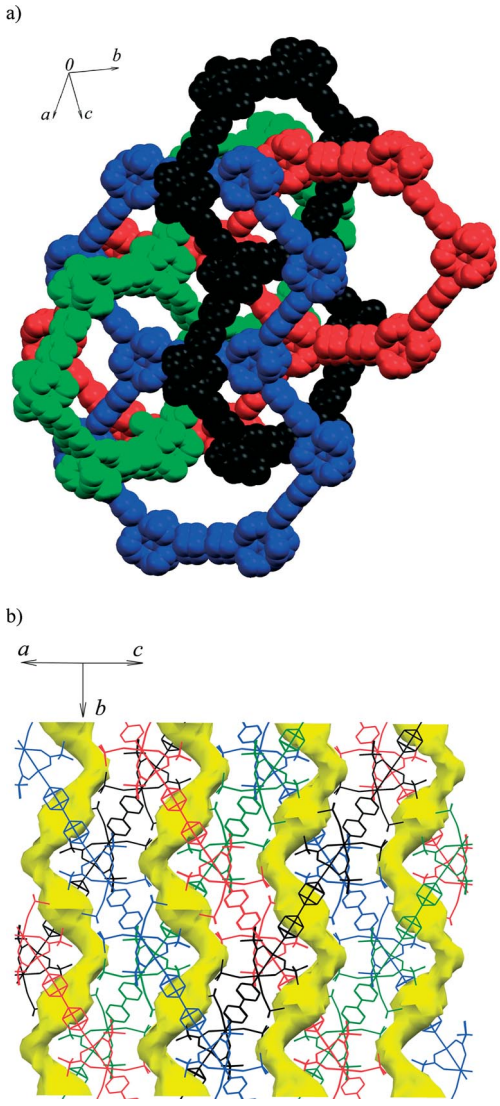

Figure 1. Interpenetration of 2D layers in **1** (*t*Bu groups of pivalates and hydrogen atoms are omitted for clarity; blue and red layers are parallel, as well as green and black ones) (a) and mercury diagram for visualization of voids in **1** calculated for a sphere with diameter 2.8 Å (b).

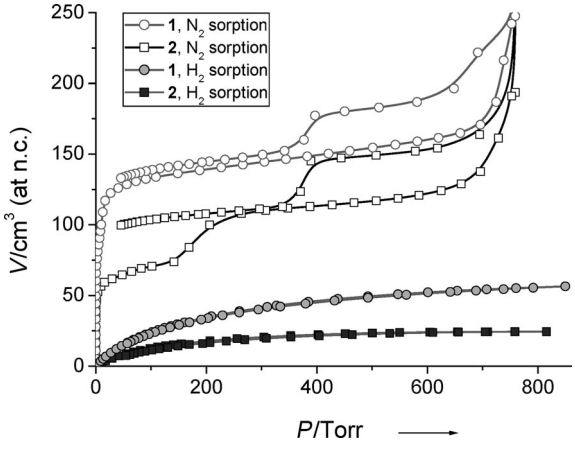

Figure 2. N_2 and H_2 sorption isotherms for **1** and **2** (78 K). The lines are to guide the eye.

2.8 Å[9]), which allows it to pass through the "windows" in the zigzag channel without obstacles.

The temperature dependence of $\chi_M T$ for **1** is shown in Figure 3. The $\chi_M T$ vs. T curve can be fitted with an isotropic model (details are presented in the Supporting Information). The best agreement is obtained with $J_{Fe–Fe}$ = –80.5(2) cm^{-1}, $J_{Fe–Ni}$ = –37.5(2) cm^{-1}, g_{Ni} = 2.120(3), zJ' = –0.72(1) cm^{-1} and g_{Fe} = 2.00 (fixed) ($R^2 = 3.0 \times 10^{-5}$). The nonzero zJ' clearly shows that superexchange interactions operate between Fe_2Ni units through bipy.

Spin–orbit coupling (SOC) and axial splitting at Co^{II} sites in **2** are incorporated in the zero-field splitting and in the Zeeman tensor.[12] For compound **2** the $\chi_M T$ vs. T curve (Figure 3) could be simulated[13] above 13 K with the parameters $J_{Fe–Fe}$ = –82.1 cm^{-1}, $J_{Fe–Co}$ = –36.7 cm^{-1}, zJ' = –0.8 cm^{-1}, $g_{Co\perp}$ = 2.15, D_{Co} = 40 cm^{-1}, and *tip* = 8×10^{-5} (temperature-independent paramagnetism); g_{Fe} and $g_{Co\parallel}$ were fixed at 2.0023 ($R^2 = 4.5 \times 10^{-4}$). Desolvatation of **2**·2DMF had some effect on the electronic structure of the Fe_2Co unit, most probably by distortion of the Co^{II} donor set, leading to a change in D_{Co} (Supporting Information) or in exchange interactions between Fe_2Co units.

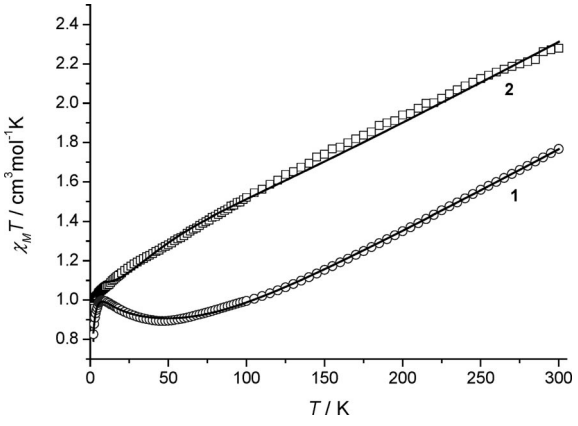

Figure 3. $\chi_M T$ vs. T curves for samples **1** and **2** without solvent and calculated curves with parameters from the text.

Absolute values of J for **1** and **2** are higher than those reported for acetato- and trifluoroacetato-bridged trinuclear carboxylates, which is consistent with the higher electron-donating ability of the *t*Bu group in pivalates relative to CH_3 or CF_3 groups.[6b]

Conclusions

We have shown that linking of building blocks with trigonal topology by linear bridges result in the formation of hexagonal honeycomb 2D layers, exactly as it could be predicted from geometry considerations. The compounds possess nontrivial N_2 adsorption/desorption hysteresis, which may be associated with structural rearrangement. Magnetic properties were simulated by taking into account the SOC of Co^{II} and were shown to be governed by exchange interactions within trinuclear units. This example of porous coordination polymers assembled from presynthesized polynuclear units without their destruction opens the way for the synthesis of coordination polymers possessing the properties of the starting polynuclear building blocks.

Supporting Information (see footnote on the first page of this article): Experimental details, details of X-ray structure determination, additional figures illustrating the X-ray structure, and details of magnetic data fitting.

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[13] The program Mjöllnir and a detailed manual may be obtained from the authors free of charge upon request.

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