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New Three-Dimensional Metal−Organic Framework with Heterometallic [Fe−Ag] Building Units: Synthesis, Crystal Structure, and Functional Studies

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Supporting Information

ABSTRACT: A new three-dimensional metal−organic framework (MOF) containing Fe^{II} and Ag^{I} ions and 2-pyrazinecarboxylic acid (pcaH) was synthesized, and its magnetic and catalytic properties were studied. The MOF has a big window size of 12.1 × 12.0 Å, with 23.8% solvent-accessible space, and shows size selectivity toward Lewis acid catalysis.

During the past decade, there has been a huge amount of worldwide activity on the research and development of microporous metal−organic frameworks (MOFs) because of their versatile promising applications in fields like gas storage, catalysis, ion exchange, and separation.[1−15] Most of the MOFs reported to date are homometallic, based on transition-metal ions or lanthanides. The synthesis of heterometallic MOFs is of special interest because the incorporation of two or more kinds of metal ions can add different functionalities. By using different coordination geometries of different metal ions, this also provides another way to control the network structure or topology. However, there are not many heterometallic MOFs reported to date compared to the large number of homometallic MOFs.[16−21] A useful strategy toward heterometallic MOFs is to use linker ligands with different functional groups and different donor atoms, like O and N atoms. According to the "soft−soft" and "hard−hard" (HSAB) interaction principle,[22−24] the different donor atoms prefer to coordinate to different metal ions. This is well-known from Prussian blue and analogous compounds.[25−28]

In our synthesis, 2-pyrazinecarboxylic acid (pcaH), which has been used before for the synthesis of different coordination complexes,[29−32] was chosen as a ligand with both N- and O-donor atoms for synthesizing heterometallic clusters made of hard and soft metal ions, namely, Fe^{II} and Ag^{I}. This resulted in a three-dimensional heterometallic MOF, $[Fe^{II}_2Ag^{I}_2(pca)_4(pcaH)(MeOH)_2](ClO_4)_2\cdot 3MeOH$ (**1**), shown in Figure 1. In this Communication, we report the synthesis, characterization, and crystal structure, as well as magnetic and catalytic studies, of this compound. It was synthesiszed by the reaction of pcaH with $Fe(ClO_4)_2\cdot 6H_2O$ and $Ag(NO_3)$ in methanol (see the Supporting Information, SI, for details).

In spite of the long-known photosensitive behavior of silver compounds, the compound was stable upon exposure to light without any observable changes.[33,34] The crystal structure was determined by single-crystal X-ray diffraction (XRD). This reveals that the compound comprises two iron and two silver ions and five linker ligands in the asymmetric unit (Figure 2). Of the latter, four ligands are deprotonated (pca) and one is protonated (pcaH). **1** represents a three-dimensionally extended network with two different kinds of channels, exhibiting window sizes of 12.12 × 12.0 or 7.2 × 4.1 Å, respectively. Calculations using the *PLATON* software suite ("nosolv") show that the compound has 1140.6 $Å^3$ of solvent-accessible space, which is 23.8% of the unit

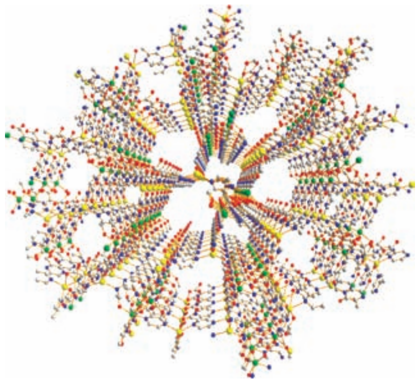

Figure 1. Central projection view of **1** as a ball-and-stick model. Color code: blue, N; gray, C; green, Fe; red, O; yellow, Ag. H atoms and solvent are omitted for clarity.

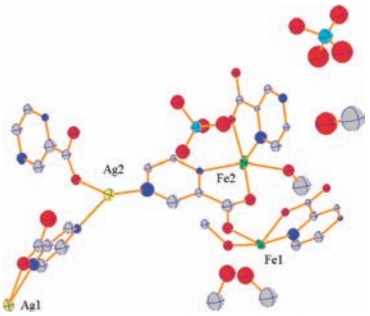

Figure 2. Crystallographic view (thermal ellipsoid with 30% probability) of the asymmetric unit of **1** along the *b* axis. Color code: blue, N; cyan, Cl; gray, C; green, Fe; red, O; yellow, Ag. H atoms are omitted for clarity.

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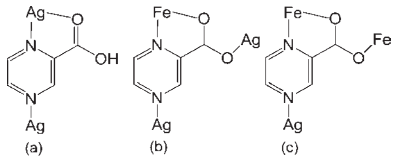
Scheme 1. Different Coordination and Bridging Modes of the pcaH Ligand in Compound 1



cell volume 4795.0(7) Å^3.[35,36] Both of the Fe^{II} ions are six-coordinate, with two N and four O donors forming a distorted octahedral coordination sphere. Fe1 is coordinated by N5, N7, O4, O6, O7, and O200 (methanol); Fe2 is coordinated by N3, N9, O3, O8, O9, and O100 (methanol). The bond lengths are in good agreement with the Fe^{II}—O and Fe^{II}—N bond lengths that can be found in the literature (see Tables S8 and S9 in the SI). However, the two Ag^{I} ions have different coordination geometries and environments. Ag1 is five-coordinate, in a distorted trigonal-bipyramidal geometry, by three equatorial N donors (N1, N8, and N10) and two axial O donors (O2 and O10). As was expected for the protonated carboxylate group that weakly coordinates Ag1, the O2—Ag1 distance is quite long [2.72(2) Å].

In contrast, Ag2 is tetrahedrally coordinated by three N donors (N2, N4, and N6) and one O donor (O5). Obviously, Fe^{II}—O "hard—hard" and Ag^{I}—N "soft—soft" interactions play an important role in the coordination of Fe^{II} and Ag^{I} ions within the title compound. Solvent MeOH molecules are involved in hydrogen bonds with coordinating MeOH molecules, e.g., Fe1···O200—(H)—O300—(H)—O400 [O200···O300 2.66(3) Å and O300···O400 2.54(3) Å] or Fe2···O100—(H)—O500 [O100···O500 2.77(4) Å]. One of the $[ClO_4]^-$ anions is located between two Fe^{II} ions, with Fe1···Cl1 and Fe2···Cl1 distances of 6.13(2) and 5.08(2) Å, respectively. Another $[ClO_4]^-$ anion is located near Fe2 [Fe2···Cl2 6.91(1) Å] but is much more distant from Fe1 [Fe1···Cl2 10.63(1) Å].

The ligand exhibits three different coordination modes, which are shown in Scheme 1. One O atom of the carboxylate group and the neighboring N atom of the pyrazine ring always coordinate to one metal ion. With its rear N atom, the pyrazine linker always coordinates to an Ag^{I} ion. In the first case (a), two Ag atoms are bridged that way. In the other two cases, the carboxylate group additionally coordinates to another metal ion, using its second O atom; thereby bridges are formed between $Fe^{II}\cdots Ag^{I}$ (b) or $Fe^{II}\cdots Fe^{II}$ (c), respectively, in a cis—trans configuration with distances of 5.35(1) or 5.61(1) Å, respectively.

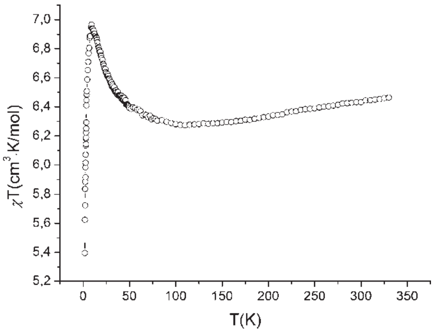
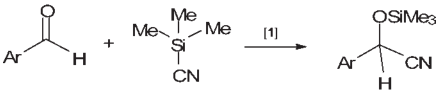


Figure 3. χT vs T plot of compound **1** measured at 500 Oe in the range of 1.79—330 K.

Scheme 2. Cyanosilylation Reaction Using Two Different Aldehydes (Ar = Benzaldehyde and 2-Naphthalenealdehyde)



The magnetic susceptibility measurement of **1** (Figure 3) reveals a χT product of 6.43 $cm^3 \cdot K \cdot mol^{-1}$ at room temperature, which is close to the expected value of 6.00 $cm^3 \cdot K \cdot mol^{-1}$ (with $g_{av} = 2$) for two high-spin Fe^{II} ions.[37] The slightly higher χT value is possibly due to the spin—orbit coupling of the high-spin d^6 ions.[38] From the χT vs T plot, it can be seen that the χT value decreases very slowly with a decrease in the temperature because of a weak antiferromagnetic coupling that may occur for Fe^{II} ions bridged by carboxylate groups.[39-41] However, at low T (110 K), the χT value starts to rise with a decrease in the temperature and reaches 6.97 $cm^3 \cdot K \cdot mol^{-1}$ at 9 K before a sharp fall to 5.40 $cm^3 \cdot K \cdot mol^{-1}$ at 1.79 K. The rise of χT at low T might be due to the presence of an untraceable amount of iron oxide or might represent the result of structural reorientation, which is common for this kind of coordination network.[42-45] However, low-temperature crystal measurements will be necessary to gain further insight. The sharp decrease of χT at very low temperature might be a result of the zero-field-splitting parameter (D).

The thermal stability of the compound was studied using thermogravimetric analysis (TGA; Figure S1 in the SI). The compound loses lattice solvents slowly at the beginning. At the first visible step (204 °C), the slope suggests a weight loss of 22%, which counts for the detachment of five coordinated and noncoordinated MeOH and four O molecules, which possibly form as the decomposition products of two $[ClO_4]^-$ anions as $2[ClO_4]^- \rightarrow 2Cl^- + 4O_2$. This is in accordance with the calculated residual weight of 77.9%. Finally, the compound loses all of the organic components and results into a residual weight of 35.4% at 1000 °C. Powder XRD reveals clear peaks only for Ag_2O (Figure S2 in the SI). Iron most likely forms some residual amorphous chlorides/oxides.

Some recent investigations on using MOFs as potential Lewis acid catalysts for cyanohydrin synthesis are noticeable.[46-50] The title compound possesses some interesting features in this regard: (a) big channel windows of the compound, (b) 23.8% solvent-accessible space, and (c) solvents coordinated to Fe^{II} ions, which may act as Lewis acid catalytic sites upon solvent removal and thus the formation of exposed metal centers. Because the compound is insoluble in CH_2Cl_2, it was used as a heterogeneous catalyst for cyanohydrin formation in CH_2Cl_2, using two aldehydes of different sizes (Scheme 2 and Table 1). A conversion of 51% was observed in 3 h with a turnover number (TON) of 31 when benzaldehyde was used as a reagent. However, for the bulkier substrate 2-naphthaldehyde, the yield was only 9.2% after 3 h. The reactions were reproduced successfully for each study. This behavior correlates exactly with the expected size selectivity of the MOF according to easier access of less bulky substrates to the exposed metal sites through the channels. It supports the assumption that catalysis takes place in the channels of the title compound and not only on the surface.[10] A catalytic effect of some other species was excluded by means of powder XRD and elemental analysis in accordance with the expected values.

Table 1. Results of the Exploration of the Catalytic Activity of Compound 1 (Room Temperature, Ar Atmosphere, and Gas Chromatography Monitoring of the Conversion)[a]

substrate	*t* (h)	*T* (°C)	conversion (%)
benzaldehyde	3	25	51
2-naphthaldehyde	3	25	9.2

[a] The given data represent the averages of two independent studies.

In summary, a new three-dimensional [Fe—Ag] MOF with a large channel window and 23.8% solvent-accessible space was synthesized, and its magnetic properties and size-selective Lewis acid catalysis for cyanosilylation reactions were studied.

ASSOCIATED CONTENT

S **Supporting Information.** CIF of **1**, crystal packing diagrams, TGA plot, XRD pattern, synthesis and characterization details of **1**, and details of catalysis experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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