Inorganic Chemistry
Communication
pubs.acs.org/IC

Guest Molecule Release Triggers Changes in the Catalytic and Magnetic Properties of a Fe^{II}-Based 3D Metal–Organic Framework

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Supporting Information

ABSTRACT: A Fe^{II}-based metal–organic framework (MOF), $\{[Fe_2(pbt)_2(H_2O)_2]\cdot 2H_2O\}_n$, undergoes an irreversible dehydration, which triggers changes in the catalytic and magnetic properties of the MOF. These property changes are attributed to the high-spin to low-spin transition of 7.1% center Fe^{II}, which is demonstrated by ^{57}Fe Mössbauer, X-ray photoelectron spectroscopy, and UV/vis absorption spectra.

Metal–organic frameworks (MOFs) are extended structures composed of metal-based nodes, organic linkers, and sometimes guest molecules.[1] They represent an exceptionally rich field of functional materials because of their fascinating structural features and interesting properties.[2] This versatility stems from their unique structures formed through ion-covalent association of center metal ions and organic ligands and/or weak interactions.[3] Undoubtedly, center metal ions play a crucial role in the determination of the properties of MOFs. Several groups have demonstrated that changing the metal node in MOFs through a single-crystal-to-single-crystal transmetalation can make previously inert MOFs catalytically active or improve the gas-sorption properties of the framework.[4] In addition, the properties of MOFs can also be changed by modifying the organic ligands. Hupp et al. and Yaghi et al. have reported that isomorphous MOFs synthesized by the same center metal ions and ditopic carboxylate decorated with variously sized organic functional groups have different capacities.[5]

The crucial role of the metal ions or clusters and organic ligands in the determination of the structures and properties of MOFs has been extensively studied.[6] However, research on the influence of guest molecules on the properties of MOFs is still rare.[7] Actually, it is of great current interest to illustrate the subtle relationship between the guest molecules and properties of the frameworks because these insights may open new ways to study catalysis, magnetism, etc.[8] To explore the influence of the guest molecules on the properties of MOFs, it is necessary to obtain chemically and thermally stable crystals that could maintain the framework when guest molecules are exchanged or removed. It has been demonstrated that metal azolate frameworks constructed by triazolate or pyrazolate derivatives and metal ions can meet the above requirements.[9] Therefore, we chose a triazolate derivative, 5′-(pyridin-2-yl)-2*H*,4′*H*-3,3′-bis(1,2,4-triazole) (H_2pbt), to construct a Fe^{II}-based MOF, $\{[Fe_2(pbt)_2(H_2O)_2]\cdot 2H_2O\}_n$ (**1**). Interestingly, crystals of **1** were allowed to stand at 160 °C for 1 day, undergoing an irreversible release of one free water molecule to yield $\{[Fe_2(pbt)_2(H_2O)_2]\cdot H_2O\}_n$ (**2**). Moreover, dehydration triggers noticeable changes in the catalytic and magnetic properties.

Single-crystal X-ray analysis reveals that complex **1** crystallizes in the orthorhombic space group *Pbcn*. The Fe1 and Fe2 centers display distorted octahedral coordination geometry and are all coordinated by five N atoms from three pbt^{2-} ligands and one aqua O atom. As shown in Scheme S1 in the SI, there are two crystallographically independent pbt^{2-} ligands exhibiting two different conformations due to the $C_{triazole}-C_{triazole}$ rotation flexibility, but all act as tridentate ligands, binding to three Fe^{II} ions through two chelate bonds and one monodentate linkage. In such a manner, a pair of symmetry-related Fe1 centers are linked by a terminal triazole moiety of pbt^{2-} to give a $[Fe1(trz)]_2$ dimeric unit (Figure 1a), and adjacent Fe2 centers are joined by pbt^{2-} ligands to form 1D $[Fe2(pbt)]_n$ chains along the *b* axis (Figure 1b), respectively. Interestingly, each $[Fe1(trz)]_2$ unit serves as a pillar to connect four adjacent chains (Figure S2 in the SI). In this way, these 1D chains are extended into a 3D coordination framework (Figure 1c). After removal of all guest water molecules, **1** shows approximate rectangular channels, with 10.45 × 4.58 Å windows from the *c* axis encompassing a considerable solvent-accessible volume about 547.8 $Å^3$ per unit cell calculated by *PLATON* (Figure 1c).

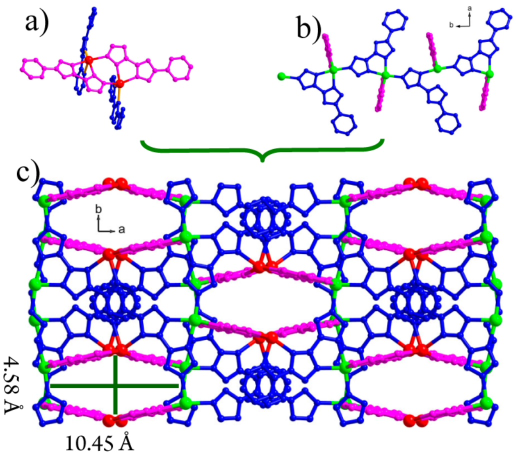

Figure 1. (a) $[Fe2(trz)]_2$ unit. (b) 1D $[Fe1Lb]_n$ chain. (c) View of the 3D structure along the *c* axis.

Received: January 2, 2014
Published: March 24, 2014

In addition, there exist strong hydrogen-bonding interactions between the water molecules and triazole N atoms in **1** (Table S2 in the SI). It is worth noting that the O3 water molecule was fastened to the framework by the strong hydrogen bonds O3−N10 [2.792(6) Å] and O3−O1 [2.925(6) Å], while the unstable O4 lattice water molecule was sited in the cavities by weak hydrogen bonds O4−O2 [3.030(6) Å] and O4−N3 [3.090(8) Å; Figures S3 and S4 in the SI). These facts may give rise to dehydration of these two lattice water molecules at different temperatures. Thermogravimetric analysis (TGA) of **1** (Figure S5 in the SI) confirms that the first weight loss of 2.85% in the range of 58−108 °C corresponds to one lattice water molecule per formula unit (calcd 2.97%), then an approximate plateau region in the range of 108−165 °C is observed, and the second weight loss of 8.62% in the range of 165−195 °C corresponds to one lattice and two coordinated water molecules per formula unit (calcd 8.91%).

Because Fe^{II} ions exhibit dynamic Jahn−Teller distortion and can provide open Lewis acid sites, Fe MOFs should be highly active catalysts for some reactions requiring Lewis acidity, such as aldol condensation, ring opening of epoxides, etc. Aiming to evaluate the catalytic activity of **1**, we have selected a representative aldol condensation reaction requiring Lewis acidity. The reaction of benzaldehyde, pyridylaldehyde, and furaldehyde with methanol to form the corresponding dimethyl acetal was investigated at 40 °C for 20 h using a small quantity of complex **1** as the catalyst.[10] Gas chromatographic analysis shows that conversion values of these reactions are 65%, 45%, and 62%, respectively.

Inspired by the lattice water molecules in the cavities, we attempt to explore the possibility of guest species dehydration. Elimination of the guest molecules disrupts the preexisting noncovalent interactions and may modify the properties of the complex.[11] After **1** stood at 160 °C for 1 day, the color of its crystals changed from yellow to dark red. TGA of the dark-red crystals shows that three water molecules are lost before 195 °C (Figure S5 in the SI). Therefore, the dark-red crystals have only one water less than **1**, and the formula should be $\{[Fe_2(pbt)_2(H_2O)_2]\cdot H_2O\}_n$ (**2**). We tried to remove the other lattice water molecule by heating. Disappointingly, the complex maintained at 180 °C for 1 day lost single crystallinity. TGA of complex **1** also shows that the O3 lattice water molecule is removed together with two coordinated water molecules in the range of 165−195 °C. The subtle component difference of these two MOFs motivates us to evaluate the catalytic activity of complexes **1** and **2**. Following the same method, the catalytic activity of complex **2** is investigated. To our satisfaction, conversion of benzaldehyde, pyridylaldehyde, and furaldehyde is improved to 87%, 56%, and 78%, respectively. The results demonstrate that the catalytic activity of **2** is higher than that of **1**. In other words, the catalytic activity of the Fe^{II}-based MOF is significantly improved by release of a free water molecule.

Because elimination of the guest molecules may lead to changes in the magnetic properties of the complexes,[8a] we investigate the magnetic behavior of these two complexes. In Figure 2a is shown the $\chi_M T$ versus T plots of complexes **1** and **2** measured in an applied field of 1000 Oe over the temperature range 300−2 K. For **1**, the $\chi_M T$ value is 6.90 cm^3 K mol^{-1} at 300 K, which corresponds to two quintet spin-state Fe^{II} centers. This value is higher than the usual one for paramagnetic Fe^{II} complexes in the high-spin (HS) state, possibly because of a contribution of the orbital angular moment. The $\chi_M T$ value decreases slowly in the 300−50 K range. Below 50 K, the $\chi_M T$ value descends more rapidly, reaching a value of 2.13 cm^3 K mol^{-1} at 2 K, which is likely due to zero-field splitting. In contrast to complex **1**, the $\chi_M T$ value of complex **2** decreases more quickly than that of **1** to a value of ca. 3.70 cm^3 K mol^{-1} at 50 K and then descends more sharply, reaching a value of 0.429 cm^3 K mol^{-1} at 2 K. The quick decrease of the magnetic susceptibilities for **2** may be attributed to a reduction of the Fe−N bonds, which shortens the Fe−Fe distance and strengthens the antiferromagnetic coupling effect. It is worth noting that at 300 K the $\chi_M T$ value of **2** (6.367 cm^3 K mol^{-1}) is lower than that of **1** (6.90 cm^3 K mol^{-1}) by about 0.533 cm^3 K mol^{-1}, which amounts to 7% of the $\chi_M T$ value of **1**.

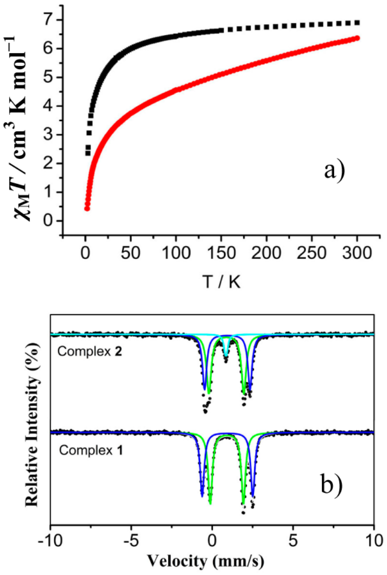

Figure 2. (a) $\chi_M T$ versus T plots for **1** (black) and **2** (red). (b) ^{57}Fe Mössbauer spectra of complexes **1** and **2**.

Why can a subtle difference in the guest molecule of the MOFs stir up considerable changes in the catalytic and magnetic properties? The difference in the magnetic and catalytic behavior was traced to intrinsic differences in the molecular structures of **1** and **2**.

First, the single-crystal X-ray structure determination reveals that through the release of one guest molecule the structure of **1** display three changes: (1) the trapped water (O4) was lost; (2) all of the Fe−O and Fe−N bonds were shortened, and especially it should be pointed out that the Fe2−O2 bond length was shortened significantly from 2.179 to 2.062 Å (Tables S4 and S5 in the SI and Figure 3); (3) the unit cell a parameter decreases from 23.507(5) to 22.696(5) Å, and the unit cell volume decreases from 4817.8(17) to 4646.7(16) $Å^3$. These changes may bear some of the responsibility for the differences in the catalytic and magnetic properties of **1** and **2**. On the one hand, **2** has one less lattice water than **1**, which is helpful for the substrates to pass through the surfaces and approach the active centers of **2**. Then the coordinated water molecules are replaced to generate the required reaction intermediates. Thus, the catalytic activity of **2** is superior to that of **1**. On the other hand, the release of the O4 water molecule and the reduction of the Fe−N and Fe−O bonds disrupt the preexisting hydrogen-bond interactions and shorten the Fe−Fe distance, which strengthens the antiferromagnetic coupling effect of the Fe^{II} centers. In this way, the magnetic properties of the complex are modified.

Second, the color change from yellow of **1** to dark red of **2** and the reduction of the Fe−N and Fe−O bonds are attributed to the

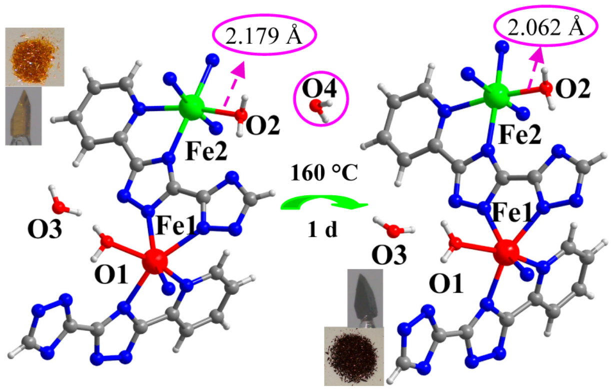

Figure 3. View of the difference of the asymmetric unit of complexes **1** (left) and **2** (right) and the color change from **1** to **2**. Symmetry codes: A, −0.5 + *x*, 0.5 + *y*, 0.5 − *z*; B, 1 − *x*, 1 − *y*, 1 − *z*.

spin-state transition of the Fe^{II} centers from HS to low spin (LS). We consider that the HS → LS transition may play a crucial role in the changes of the catalytic and magnetic properties from **1** to **2**. For one thing, the HS → LS transition empties the e_g orbitals. This implies that the presence of unoccupied antibonding e_g orbitals of the Fe^{II} centers can favor the electron-pair acceptance from the substrates and, therefore, formation of the required reaction intermediates.[12] For another, associated with the HS → LS transition, there is a decrease in the relative number of unpaired electrons, and hence the $\chi_M T$ value of **2** is lower than that of **1** at room temperature. Also, the reduction of the Fe−N bonds shortens the Fe−Fe distance and strengthens the antiferromagnetic coupling effect of the Fe^{II} centers.

^{57}Fe Mössbauer spectroscopy and XPS show that all Fe atoms of the two complexes are in the oxidation state of II (Figures 2b and S10 in the SI). As shown in Figure 2b, at 300 K, the spectrum of complex **1** displays a quadrupole doublet, with the isomer shift (δ) and quadrupole splitting (ΔEQ) characteristic of HS Fe^{II} (Table S1 in the SI). Because all Fe^{II} centers in complex **1** are equivalent with a [FeN5O] octahedral geometry, there are only two doublets at 300 K. As for complex **2**, apart from the main doublet (blue and green lines) characterized by the quadrupole splitting with $\Delta EQ = 2.17$ and 2.82 mm s^{-1} and isomer shift $\delta =$ 0.98 and 1.04 mm s^{-1} corresponding to the HS state of Fe^{II} ($S = 2$), a poorly resolved doublet (turquoise line) of relative area 7.1% appears with $\Delta EQ = 0.21$ mm s^{-1} and an isomer shift value of 0.55 mm s^{-1} and is assigned to LS Fe^{II} ($S = 0$). The existence of LS is also confirmed by the UV/vis absorption spectra. As shown in Figure S6 in the SI, the spin-allowed $^1A_1 \rightarrow {}^1T_1$ d−d transition of the LS Fe^{II} appears as a 620 nm shoulder of the intense singlet metal-to-ligand charge-transfer band at 480 nm.[13] This result is consistent with the 7% reduction of the $\chi_M T$ value of **1**.

In conclusion, a Fe^{II}-based MOF, **1**, loses a free water molecule and converts to **2**. Dehydration bears the responsibility for the reduction of the Fe−O and Fe−N bonds and for the HS → LS transition of 7.1% of the center ions. These results give rise to changes in the catalytic and magnetic properties of the Fe^{II}-based MOF.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, experimental details, and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by the National Natural Science Foundation (Grants 21371155 and 91022013) and the Research Foundation for the Doctoral Program of Higher Education of China (Grant 20124101110002).

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