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Hydrogen Storage

Observation of Cu^{2+}–H_2 Interactions in a Fully Desolvated Sodalite-Type Metal–Organic Framework**

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The investigation of metal–organic frameworks has become one of the most active areas of chemical research, owing in part to their potential utility for hydrogen storage.[1] Unlike main-group and transition-metal hydrides, which chemically bind H_2 and usually release it only at high temperatures, metal–organic frameworks and other high-surface-area adsorbents establish weak van der Waals interactions with H_2 molecules, such that uptake and release can be achieved by a simple pressure swing. Typically, H_2 adsorption enthalpies of only 5–7 $kJ\,mol^{-1}$ characterize these weak interactions,[2] necessitating the use of cryogenic temperatures to achieve significant H_2 uptake. It has been proposed, however, that adsorption enthalpies of approximately 15 $kJ\,mol^{-1}$ would be optimal for H_2 storage at 25 °C and at fuel-cell operating pressures of 1.5–100 bar.[3] To address the challenge of producing adsorbents with an enhanced H_2 affinity, we have undertaken efforts to generate microporous metal–organic frameworks bearing a high concentration of coordinatively unsaturated metal centers.[2a,4]

Recently, we showed that the robust, sodalite-type metal–organic framework $[Mn(dmf)_6]_3[(Mn_4Cl)_3(btt)_8(H_2O)_{12}]_2\cdot 42\,DMF\cdot 11\,H_2O\cdot 20\,CH_3OH$ (**1**; DMF = *N*,*N*-dimethylformamide, H_3btt = 1,3,5-tris(tetrazol-5-yl)benzene) could be partially desolvated to yield a material with an exceptional H_2 capacity and a record-high initial binding enthalpy of 10.1 $kJ\,mol^{-1}$.[5] Furthermore, powder neutron diffraction experiments demonstrated that the strong adsorption at low loading is due to H_2 molecules binding directly to unsaturated Mn^{2+} ions. Unfortunately, however, this material retained some residual methanol, such that very few strong binding sites were accessible. Herein, we show that the same sodalite structure type can be accessed by using Cu^{2+} ions in place of Mn^{2+} ions, leading to a compound that can be fully desolvated to expose a greater number of open metal coordination sites.

To probe the generality of the framework structure, reactions analogous to those employed in forming **1**[5] were attempted using the chloride salts of a series of first-row transition-metal ions (Fe^{2+}–Zn^{2+}). The solvents used included neat dimethylsulfoxide, *N*,*N*-diethylformamide, DMF, and various combinations of these with methanol; the reaction temperatures used ranged from room temperature to 130 °C. With the exception of those with Cu^{2+} ions in formamide/methanol mixtures, the reactions afforded insoluble, amorphous solids that were not further characterized. The reaction of H_3btt with $CuCl_2\cdot 2\,H_2O$ in a mixture of DMF, methanol, and aqueous HCl at 60 °C produced green cube-shaped crystals of $H[Cu(dmf)_6][(Cu_4Cl)_3(btt)_8(H_2O)_{12}]\cdot 3.5\,HCl\cdot 12\,H_2O\cdot 16\,CH_3OH$ (**2**) in 90 % yield.

X-ray diffraction analysis of a crystal of **2** revealed a cubic metal–organic framework structure isotypic with that of **1** (Figure 1).[6] In **2**, the Cu^{2+} ions of chloride-centered square-planar $\{Cu_4Cl\}^{7+}$ units are connected through the N2 and N3 atoms of tetrazolate rings from eight surrounding btt^{3-} ligands (Figure 1 b). In turn, each triangular btt^{3-} ligand is connected to three $\{Cu_4Cl\}^{7+}$ squares (Figure 1 a) to generate a rare 3,8-connected network. A fundamental building unit for the structure is the truncated octahedron outlined in blue in Figure 1 c, which consists of six $\{Cu_4Cl\}^{7+}$ squares and eight btt^{3-} ligands. Each truncated octahedron is reminiscent of a sodalite cage, and, as in sodalite, the truncated octahedra share square faces to generate the cubic framework structure. Every Cu^{2+} center in the framework is octahedrally coordinated and has a single water ligand (not shown) that can potentially be removed and replaced with an H_2 molecule. The anionic charge of the framework is balanced by $[Cu(dmf)_6]^{2+}$ guest cations, which are situated within the truncated octahedra, and by protons, which could not be located by X-ray diffraction, but are probably bound to the nucleophilic N1 or N4 atoms of the tetrazolate rings. Notably, a proton-balanced carboxylate-based framework with the same sodalite-like topology, $H_6[(Co_4O)_3(tatb)_8]$ (H_3tatb = 4,4′,4″-*s*-

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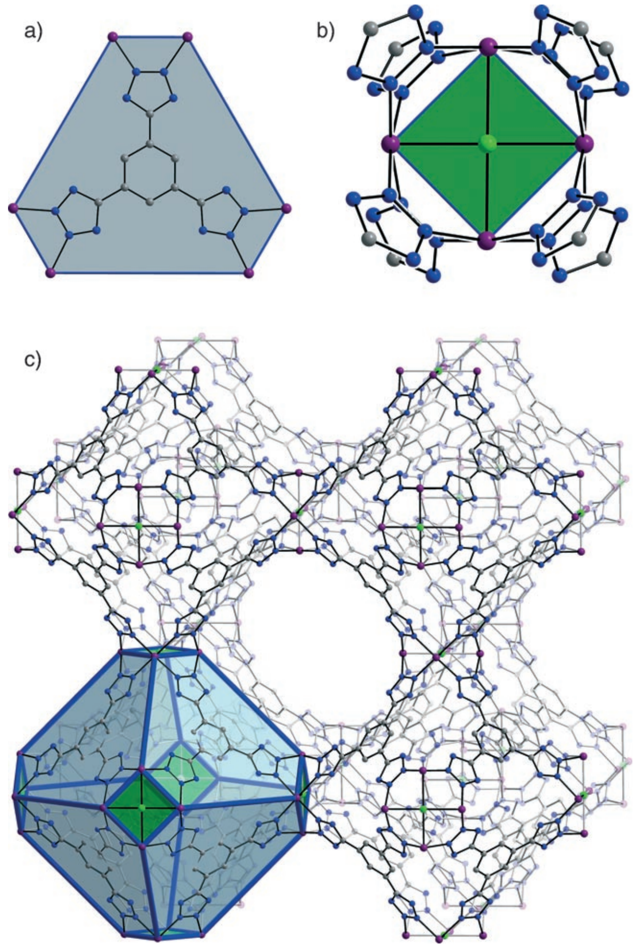

Figure 1. Portions of the crystal structure of **2**. a) The three-connected node and hexagonal face (blue) defined by a btt^{3-} ligand linked to six adjacent Cu^{2+} ions. b) The eight-connected node and square face (green) defined by four Cu^{2+} ions bridged by eight tetrazolate rings. c) A cube of eight sodalite-like truncated-octahedral cages sharing square faces. Cu purple, C gray, N blue, Cl green. Solvent molecules, hydrogen atoms, and charge-balancing $[Cu(dmf)_6]^{2+}$ ions are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Cu–Cl 2.546(1), Cu–N 2.032(4), Cu–O 2.221(8), Cu⋯Cu 3.577(1); Cu-Cl-Cu 90.0, N-Cu-N 86.6(2), 92.9(2), Cu-N-N 123.8(1), 126.3(3), N-Cu-Cl 86.4(1).

triazine-2,4,6-triyltribenzoic acid), was reported recently,[7] attesting to the similarities between tetrazolate- and carboxylate-based bridging ligands.[4b]

As with the related manganese-containing framework **1**, soaking **2** in methanol displaces the less volatile DMF constituents, affording $H[Cu(CH_3OH)_6][(Cu_4Cl)_3(btt)_8(H_2O)_{12}]\cdot 3.5\,HCl\cdot 36\,CH_3OH$ (**2m**). In the IR spectrum of **2m**, the C=O stretching peak at 1651 cm^{-1}, which was observed in the IR spectrum of **2**, is absent, and a new peak attributable to the C–O stretching frequency of methanol is present at 1019 cm^{-1}. These changes indicate a complete exchange of DMF for methanol, as further verified by an elemental analysis. A thermogravimetric analysis of **2m** indicated a weight loss of 32.2%, corresponding to the loss of all of the solvent molecules, by approximately 190 °C, above which framework decomposition occurs.

To prevent partial collapse of the framework structure, a mild evacuation sequence was adopted, wherein a sample of **2m** was slowly heated to 120 °C under reduced pressure. After approximately 24 h, elimination of all methanol and water molecules was indicated by the disappearance of the C–O stretching peak at 1019 cm^{-1} in the IR spectrum. A formula of $HCu[(Cu_4Cl)_3(btt)_8]\cdot 3.5\,HCl$ (**2d**) was confirmed by an elemental analysis. Powder X-ray diffraction data show that **2d** retains the framework structure of **2**. Importantly, the complete desolvation of the material should expose more metal coordination sites than are available in the manganese-containing analogue, for which a similar procedure resulted in a compound of composition $Mn_3[(Mn_4Cl)_3(btt)_8]_2\cdot 20\,CH_3OH$ (**1d**). Consistent with an intact, evacuated framework, an N_2 adsorption measurement performed at 77 K gave a type-I isotherm characteristic of a microporous material. Langmuir and BET fits to the data yielded surface areas of 1770 $m^2\,g^{-1}$ and 1710 $m^2\,g^{-1}$, respectively. The latter result is somewhat lower than the BET surface area of 2100 $m^2\,g^{-1}$ determined for **1d**.[5] This discrepancy is most likely a result of the shorter bond lengths within the copper-containing framework (Cu–Cl 2.546(1) Å and Cu–N 2.032(4) Å versus Mn–Cl 2.736(1) Å and Mn–N 2.227(3) Å), which contract the unit-cell parameter a from 19.116(1) Å in **1** to 18.595(7) Å in **2**.

Low-pressure H_2 adsorption isotherms collected for samples of **2d** indicate that the framework has a strong affinity for binding H_2 (Figure 2a). At 77 K and 900 torr, a fully reversible uptake of 2.42 wt% H_2 is apparent, which is slightly higher than the H_2 uptake of 2.25 wt% for **1d**. The improvement is associated with a steeper initial slope for the isotherm at low pressures (Figure 2a, inset). This behavior suggests the presence of a higher concentration of strong binding sites in **2d**. As a further test, a second H_2 adsorption isotherm was measured at 87 K, and the two data sets were used to determine the isosteric heat of adsorption.[2,5] As shown in Figure 3, the enthalpy of adsorption for **2d** actually starts out slightly lower than that of **1d**, but then quickly surpasses it as more H_2 is adsorbed. The results are consistent with the Cu^{2+} ions of **2d** having a weaker H_2 binding affinity than the Mn^{2+} ions of **1d**, but with **2d** indeed having more open metal sites available. At 1.6 wt% of adsorbed H_2, the enthalpy of adsorption curves reach similar values near 6 $kJ\,mol^{-1}$, suggesting that the stronger binding sites in **2d** have been saturated. Significantly, both of these curves track well above the analogous curve for $[Zn_4O(bdc)_3]$ (H_2bdc = 1,4-benzenedicarboxylic acid), which does not contain any coordinatively unsaturated metal sites.

Higher-pressure H_2 adsorption isotherms were collected on **2d** to assess its overall storage capacity (Figure 2b). At 77 K, the excess H_2 adsorption, defined as the amount of H_2 taken up in excess of the bulk gas that would occupy the pores of the adsorbent,[8] reaches a maximum of 4.2 wt% at approximately 30 bar. A perhaps more informative quantity, however, is the total amount of H_2 taken up within the volume of the sample, which climbs to 5.7 wt% at 90 bar. Consistent with the lower surface area of **2d**, these values are slightly lower than the maximum excess and total H_2 adsorption of 5.1 wt% and 6.9 wt%, respectively, determined for **1d** at 77 K. In addition, the excess adsorption is lower than the

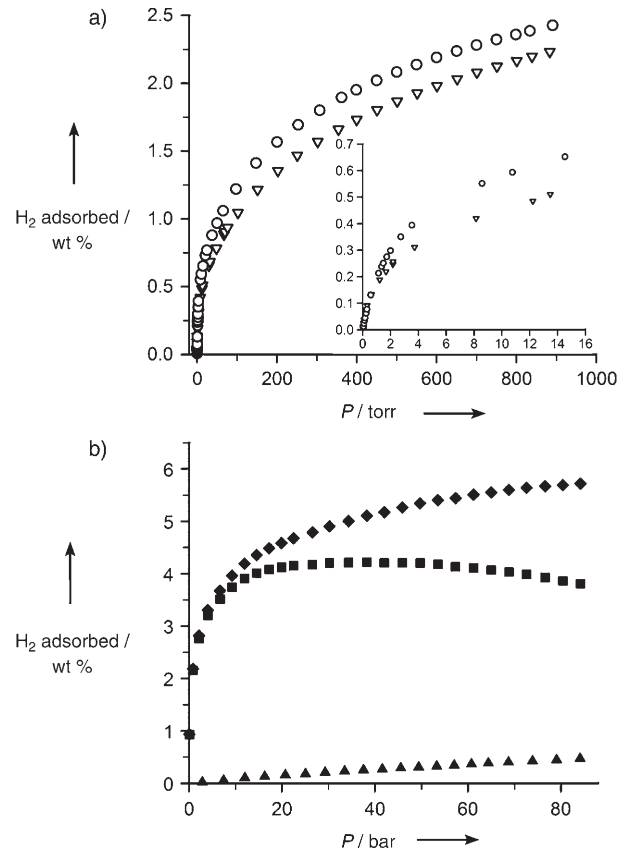

Figure 2. a) Adsorption isotherms for the uptake of H_2 within **1d** (▽) and within **2d** (○) at 77 K (inset: enlargement of the low-pressure region). b) Adsorption isotherms for the uptake of H_2 within **2d**: excess (■) and total (◆) adsorption at 77 K; adsorption at 298 K (▲).

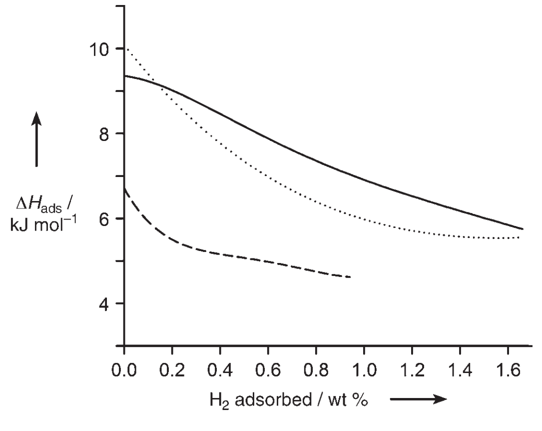

Figure 3. Enthalpy of adsorption as a function of H_2 uptake within **1d** (•••••), **2d** (——), and $[Zn_4O(bdc)_3]$ (-----).

current best value of 75 mg/1075 mg, 7.0 wt % recently reported for $[Zn_4O(btb)_2]$ (H_3btb = 1,3,5-benzenetribenzoic acid).[1j] Besides the gravimetric capacity, however, the volumetric density of the adsorbed H_2 is a critical storage parameter, which in **2d** reaches excess and total values of 38 and 53 g L^{-1}, respectively. Significantly, the excess volumetric density is 4 g L^{-1} higher than that measured for $[Zn_4O(btb)_2]$,[1j] indicating that the H_2 molecules pack more closely within **2d**. Indeed, the total volumetric density of 53 g L^{-1} at 77 K is 75 % of the density of liquid H_2 at 1 atm and 21 K.[9] Note, however, that the H_2 adsorption isotherm measured at 298 K indicates very little uptake, consistent with adsorption enthalpies still well below 15 kJ mol^{-1}.

Powder neutron diffraction experiments were carried out to test whether the improved overall adsorption enthalpy in **2d** is indeed due to an increased number of open metal coordination sites. Differences in the neutron diffraction patterns recorded upon charging a pulverized sample of **2d** at 4 K with approximately 6, 12, 18, and 30 D_2 molecules per formula unit were used to identify the strongest binding sites within the material (Table 1).

Table 1: Occupation of D_2 adsorption sites[a] within **2d** as a function of approximate D_2 loading, as determined by the Rietveld refinement of powder neutron diffraction patterns.

D_2 loading[b]	D_2 occupation[b]				
	Site I	Site II	Site III	Site IV	Total
6	4.4(1)	3.1(1)	0	0	7.5(2)
12	7.8(1)	5.2(1)	0	0	13.0(2)
18	10.7(1)	5.7(1)	1.2(1)	0	17.6(2)
30	11.1(2)	5.5(1)	8.0(2)	4.3(2)	28.9(4)

[a] Crystallographic sites (and Wyckoff positions) at maximum loading: I = 0.2713, 0.5, 0 (12h); II = 0, 0.3123, 0 (6e); III = 0.2115, 0.2115, 0.5 (12j); IV = 0.1727, 0.1727, 0 (12i). [b] Molecules of D_2 per formula unit of **2d**.

The difference Fourier map obtained with a loading of 12 D_2 molecules per formula unit clearly identifies the positions of the first two adsorption sites (Figure 4). As expected, the D_2 centroid of one of the strongest adsorption positions, site I, is just 2.47 Å from the exposed Cu^{2+} ions within the framework. The slight elongation of the Cu–D_2 distance compared to the Mn–D_2 distance of 2.21 Å found in **1d**[5] is probably associated with a Jahn–Teller distortion of the coordination environment of the Cu^{2+} ions. Such a distortion could also account for the slightly lower enthalpy

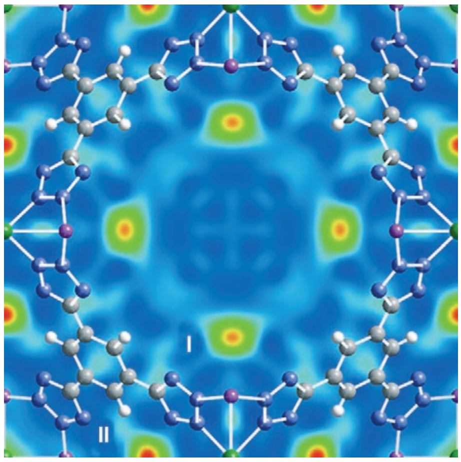

Figure 4. Difference Fourier map after loading 12 D_2 molecules per formula unit within **2d** at 4 K, calculated from powder neutron diffraction data. The view is down a fourfold rotational axis. Red maxima indicate the centroids of the adsorbed D_2 molecules; adsorption sites I and II are labeled.

of adsorption at zero coverage of **2d** (9.5 kJ mol^{-1}) compared to that of **1d** (10.1 kJ mol^{-1}). Importantly, however, at an increased D_2 loading of 30 D_2 molecules per formula unit, adsorption at site I in **2d** nears saturation, with a site occupancy of 93%. This result confirms that, perhaps also because of the Jahn–Teller effect, residual methanol molecules are easily desorbed from **2m** to produce **2d**, in which essentially all the Cu^{2+} sites are available for H_2 binding. In contrast, high D_2 loadings in **1d** saturate site I at an occupancy of just 29%, with the remaining sites being blocked by bound methanol.[5] To our knowledge, the only previous detection of Cu^{2+}–H_2 interactions was in the dehydrated Prussian-blue analogue $Cu_3[Co(CN)_6]_2$.[10] Electronic-structure calculations for H_2 adsorbed within Cu^{2+}-exchanged mordenite, a porous alumino-silicate with the formula $(Ca,Na_2,K_2)Al_2Si_{10}O_{24}\cdot 7H_2O$ have been performed, however, and some results indicate a binding energy of 11 kJ mol^{-1}.[11]

Three additional D_2 adsorption sites were also identified in **2d**. D_2 molecules in site II, which is comparable to site I in binding energy, are situated with their centroids 3.46 Å from the framework Cl^- ions and within van der Waals contact of the planes of four different tetrazolate rings. Sites III and IV are considerably weaker in binding energy and only become occupied at loadings of 18 and 30 D_2 molecules per formula unit, respectively. These sites place the D_2 molecules within van der Waals contact of two tetrazolate rings (site III) or two benzene rings (site IV). At the highest loading measured, a total of 29 D_2 molecules per formula unit are accounted for, corresponding to a total H_2 uptake of 1.8 wt%. Thus, it is expected that experiments performed at still higher loadings will reveal increased occupancy of site IV and many additional weaker adsorption sites.

The results herein demonstrate that the replacement of Mn^{2+} ions with Cu^{2+} ions in a sodalite-type metal–organic framework provides a material that can be fully desolvated to give a higher density of exposed coordination sites for H_2 binding. Future efforts will focus on the preparation of frameworks containing metal centers having a stronger interaction with H_2 and having structures with more open sites per metal ion. In addition, the reactivity and catalytic activity of the exposed metal sites within these frameworks will be explored.

Experimental Section

Experimental details are provided in the Supporting Information.

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[6] Crystallographic analysis: **2** ($C_{90}H_{24}Cl_3Cu_{13}N_{102}O_{18}$): $M_r = 3754.48$, green crystal, $0.36 \times 0.28 \times 0.24$ mm^3, cubic, space group $Pm\bar{3}m$ (no. 221), $a = 18.595(7)$ Å, $V = 6430(4)$ Å^3, $Z = 1$, $F(000) = 1850$, $\rho_{calcd} = 0.970$ g cm^{-3}, $\mu Mo_{K\alpha} = 1.136$ mm^{-1}, λ-$(Mo_{K\alpha}) = 0.71073$ Å, $T = 159(2)$ K, 18413 reflections collected ($2\theta_{max} = 44.83°$), 953 independent ($R_{int} = 0.0869$), 0 restraints, 62 parameters, $wR_2 = 0.1538$ ($I > 2\sigma(I)$), $wR_2 = 0.1650$ (all data), $R_1 = 0.0726$ ($I > 2\sigma(I)$), GOF = 1.086. A crystal of **2** was coated with Paratone-N oil, attached to a Kapton loop, transferred to a Siemens SMART APEX diffractometer, and cooled in a nitrogen stream. A full hemisphere of data was collected, and the unit-cell parameters were refined against all data. The crystal did not show significant decay during data collection. Data were integrated and corrected for Lorentz and polarization effects using SAINT 7.07b, and were corrected for absorption effects using SADABS 2.10. The space-group assignment was based upon systematic absences, *E* statistics, and successful refinement of the structure. The structure was solved by direct methods and expanded through successive difference Fourier maps. It was refined against all data using the SHELXTL 5.0 software package. Hydrogen atoms were inserted at idealized positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom. Thermal parameters for all non-hydrogen atoms in the framework skeleton were refined anisotropically. The oxygen, nitrogen, and methyl carbon atoms in each DMF molecule were disordered over four equivalent sites around the crystallographic four-fold rotation axis, and were consequently refined with 25% of the normal occupancies. CCDC-624533 contains 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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