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 H₂ and usually release it only at high temperatures, metal–organic frameworks and other high-surface-area adsorbents establish weak van der Waals interactions with H₂. The strong adsorption enthalpies of approximately 15 kJ mol⁻¹ would be optimal for H₂ 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 H₂ 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][(Mn₄Cl)₃(btt)₈(H₂O)₁₂]·12H₂O·16CH₃OH (1; DFM = N,N-dimethylformamide, btt = 1,3,5-tris(tetrazol-5-yl)benzene) could be partially desolvated to yield a material with an exceptional H₂ 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 H₂ molecules binding directly to unsaturated Mn²⁺ 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 Cu²⁺ ions in place of Mn²⁺ 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 (Fe²⁺–Zn²⁺). 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 Cu²⁺ ions in formamide/methanol mixtures, the reactions afforded insoluble, amorphous solids that were not further characterized. The reaction of H₄btt with CuCl₂·2H₂O in a mixture of DMF, methanol, and aqueous HCl at 60 °C produced green cube-shaped crystals of H[Cu(dmf)₆][(Cu₄Cl)₃(btt)₈(H₂O)₁₂]·3.5HCl·12H₂O·16CH₃OH (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 Cu²⁺ ions of chloride-centered square-planar [Cu₄Cl]²⁻ units are connected through the N₂ and N₃ atoms of tetrazolate rings from eight surrounding btt⁻³⁻ ligands (Figure 1b). In turn, each triangular btt⁻³⁻ ligand is connected to three [Cu₄Cl]²⁻ squares (Figure 1a) to generate a rare 3,8-connected network. A fundamental building unit for the structure is the truncated octahedron outlined in blue in Figure 1c, which consists of six [Cu₄Cl]²⁻ squares and eight btt⁻³⁻ ligands. Each truncated octahedron is reminiscent of a sodalite cage, and, as in sodalite, the truncated octaheda share square faces to generate the cubic framework structure. Every Cu²⁺ center in the framework is octahedrally coordinated and has a single water ligand (not shown) that can potentially be removed and replaced with an H₂ 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, H₁₂[(Co₄O)₄(tatb)]₂·(H₂tatb = 4,4',4''-s-...
triadine-2,4,6-triyltribenzoic acid), was reported recently,[7] attesting to the similarities between tetrazolate- and carboxylate-based bridging ligands.[46]

As with the related manganese-containing framework 1, soaking 2 in methanol displaces the less volatile DMF constituents, affording H[Cu(CH3OH)6]([Cu2Cl2(btt)3·3.5HCl·36CH3OH (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 H[Cu2(C6H4O)6(btt)3]·3.5HCl (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 Mn11[Mn2(Cl)12(btt)26]·20CH3OH (1d). Consistent with an intact, evacuated framework, an N2 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 m² g⁻¹ and 1710 m² g⁻¹, respectively. The latter result is somewhat lower than the BET surface area of 2100 m² 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 H2 adsorption isotherms collected for samples of 2d indicate that the framework has a strong affinity for binding H2 (Figure 2a). At 77 K and 900 torr, a fully reversible uptake of 2.42 wt% H2 is apparent, which is slightly higher than the H2 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 H2 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 H2 is adsorbed. The results are consistent with the Cu2⁺ ions of 2d having a weaker H2 binding affinity than the Mn2⁺ ions of 1d, but with 2d indeed having more open metal sites available. At 1.6 wt% of adsorbed H2, 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 [Zn4O(bdc)3]·(H2bdc = 1,4-benzenedicarboxylic acid), which does not contain any coordinatively unsaturated metal sites.

Higher-pressure H2 adsorption isotherms were collected on 2d to assess its overall storage capacity (Figure 2b). At 77 K, the excess H2 adsorption, defined as the amount of H2 taken up in excess of the bulk gas that would occupy the pores of the adsorbent,[5] reaches a maximum of 4.2 wt% at approximately 30 bar. A perhaps more informative quantity, however, is the total amount of H2 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 H2 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
The current best value of 75 mg/1075 mg, 7.0 wt% recently reported for [Zn4O(btb)2](H3btb = 1,3,5-benzenetribenzoic acid).[19] Besides the gravimetric capacity, however, the volumetric density of the adsorbed H2 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 [Zn4O-(btb)],[19] indicating that the H2 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 H2 at 1 atm and 21 K.[9] Note, however, that the H2 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 D2 molecules per formula unit were used to identify the strongest binding sites within the material (Table 1).

Table 1: Occupation of D2 adsorption sites[1] within 2d as a function of approximate D2 loading, as determined by the Rietveld refinement of powder neutron diffraction patterns.

<table>
<thead>
<tr>
<th>D2 loading[1]</th>
<th>Site I</th>
<th>Site II</th>
<th>Site III</th>
<th>Site IV</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>4.4(1)</td>
<td>3.1(1)</td>
<td>0</td>
<td>0</td>
<td>7.5(2)</td>
</tr>
<tr>
<td>12</td>
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<td>5.2(1)</td>
<td>0</td>
<td>0</td>
<td>13.0(2)</td>
</tr>
<tr>
<td>18</td>
<td>10.7(1)</td>
<td>5.7(1)</td>
<td>1.2(1)</td>
<td>0</td>
<td>17.6(2)</td>
</tr>
<tr>
<td>30</td>
<td>11.1(2)</td>
<td>5.5(1)</td>
<td>8.0(2)</td>
<td>4.3(2)</td>
<td>28.9(4)</td>
</tr>
</tbody>
</table>

[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 (12f). [b] Molecules of D2 per formula unit of 2d.

The difference Fourier map obtained with a loading of 12 D2 molecules per formula unit clearly identifies the positions of the first two adsorption sites (Figure 4). As expected, the D2 centroid of one of the strongest adsorption positions, site I, is just 2.47 Å from the exposed Cu2+ ions within the framework. The slight elongation of the Cu–D2 distance compared to the Mn–D2 distance of 2.21 Å found in 1d[19] is probably associated with a Jahn–Teller distortion of the coordination environment of the Cu2+ ions. Such a distortion could also account for the slightly lower enthalpy

![Figure 2. a) Adsorption isotherms for the uptake of H2 within 1d (●) and within 2d (■) at 77 K (inset: enlargement of the low-pressure region). b) Adsorption isotherms for the uptake of H2 within 2d: excess (●) and total (■) adsorption at 77 K; adsorption at 298 K (△).](image)

![Figure 3. Enthalpy of adsorption as a function of H2 uptake within 1d (----), 2d (---), and [Zn4O(bdc)](-----).](image)

![Figure 4. Difference Fourier map after loading 12 D2 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 D2 molecules; adsorption sites I and II are labeled.](image)
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 $2d$ bears saturation, with a site occupancy of 93%. This result confirms that, perhaps also because of the Jahn–Teller effect, residual metal molecule adsorptions 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.[9] To our knowledge, the only previous detection of $Cu^{2+}$–$H_2$ interactions was in the dehydrated Prussian-blue analogue $Cu_6[Co(CN)_6]_4$. [10] Electronic-structure calculations for $H_2$ adsorbed within $Cu^{2+}$-exchanged mordenite, a porous aluminosilicate with the formula (Ca,Na$_2$K$_2$Al$_2$Si$_{10}$O$_{24}$·7H$_2$O 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 planes of four different tetrazolate rings. Sites II 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: $2\left(C_{18}H_{12}ClCu_3Ni_2O_{30}\right)$: $M_2 = 3754.48$, green crystal, 0.36 × 0.28 × 0.24 mm$^3$, cubic, space group $Pn2_1m$ (no. 221), $a = 18.595(7)$ Å, $V = 6460(4)$ Å$^3$, $Z = 1$, $F(000) = 1850$, $\rho_{calc} = 0.970$ g cm$^{-3}$, $\mu_{MoK}\alpha = 1.136$ mm$^{-1}$, $\lambda_{MoK}\alpha = 0.7073$ Å, $\beta = 159.2(2)$ K. 18413 reflections collected ($2\theta_{max} = 44.83^\circ$), 953 independent ($R_{int} = 0.0869$), 62 parameters, $wR_{2} = 0.1538 (1 > 2\sigma(I)), \omega R_{2} = 0.1650$ (all data), $R_{1} = 0.0726 (1 > 2\sigma(I))$, GOF = 1.086. A crystal of 2 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 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 SHEXLXTL 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.


