Small-Molecule Binding

DOI: 10.1002/ange.201310004

Scorpionate-Type Coordination in MFU-4*l* Metal–Organic Frameworks: Small-Molecule Binding and Activation upon the Thermally Activated Formation of Open Metal Sites**

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Abstract: *Postsynthetic metal and ligand exchange is a versatile approach towards functionalized MFU-4l frameworks. Upon thermal treatment of MFU-4l formates, coordinatively strongly unsaturated metal centers, such as zinc(II) hydride or copper(I) species, are generated selectively.* Cu^I*-MFU-4l prepared in this way was stable under ambient conditions and showed fully reversible chemisorption of small molecules, such as* O_2*,* N_2*, and* H_2*, with corresponding isosteric heats of adsorption of 53, 42, and 32* $kJ\,mol^{-1}$*, respectively, as determined by gas-sorption measurements and confirmed by DFT calculations. Moreover,* Cu^I*-MFU-4l formed stable complexes with* C_2H_4 *and CO. These complexes were characterized by FTIR spectroscopy. The demonstrated hydride transfer to electrophiles and strong binding of small gas molecules suggests these novel, yet robust, metal–organic frameworks with open metal sites as promising catalytic materials comprising earth-abundant metal elements.*

Metal–organic frameworks with open metal sites have been proposed for many different applications, such as catalysis,[1] gas storage and capture,[2] separation,[3] and sensing.[4] However, most known MOFs with free metal centers are only able to bind typical Lewis bases, such as CO_2 or H_2O, whereas the activation of unreactive small molecules, such as O_2, N_2, and H_2, still remains a challenge.

Molecular dioxygen,[5] dinitrogen,[5] and dihydrogen[6] complexes have attracted significant attention in coordination chemistry. Only very few stable MOFs with open metal centers have been described that are able to bind these molecules. A structural analogue of CuBTC, $Cr^{II}_2(BTC)_3$, containing dinuclear Cr^{II} paddle-wheel units, was shown to bind oxygen at room temperature.[7] However, after the first adsorption step, only approximately 82 % of the total amount of oxygen could be desorbed, thus indicating that 18 % of the O_2 binds irreversibly. CPO-27 (also termed MOF-74) is another well-established MOF family with interesting chemisorption properties. CPO-27-Fe, for example, showed reversible chemisorption of O_2 and N_2 with initial heats of adsorption of 41 and 35 $kJ\,mol^{-1}$, respectively. However, O_2 chemisorption was reversible at −62 °C, whereas at room temperature the irreversible formation of a dimeric iron(III) peroxide was observed.[8] A weak chemisorption of hydrogen with well-defined 1:1 stoichiometry (metal sites/H_2) was reported for CPO-27-Ni, with an initial heat of adsorption of 13.5 $kJ\,mol^{-1}$, which ranks among the highest values reported for a MOF material.[9] In contrast, compound **5**, presented herein, shows fully reversible binding of O_2, N_2, and H_2 molecules under ambient conditions. To the best of our knowledge, no copper(I)-containing metal–organic framework has previously been shown to possess similar chemisorption properties, although IR investigations on monomeric CuCl embedded in an Ar matrix gave first experimental proof of the formation of a Cu^I–H_2 complex, in which H_2 binds in a side-on coordination mode.[10] The chemisorption of N_2[11] and H_2[12] on copper-exchanged zeolites has also been described previously. For these microporous compounds, Cu^I–N_2 and Cu^I–H_2 adducts were characterized by spectroscopic methods (mainly IR spectroscopy). However, presumably as a result of the relatively low Cu^I content, no accurate values of N_2 or H_2 binding energies were reported.

We herein describe a new approach towards such highly active metal centers in a metal–organic framework based on MFU-4*l*, constructed from bistriazolate $BTDD^{2-}$ ligands and $\{Zn_5Cl_4\}^{6+}$ building units (Figure 1).[13] Coordination frameworks derived from the MFU-4 family show exceptional robustness against thermal and hydrolytic decomposition[14] and are therefore attractive for technical applications, such as

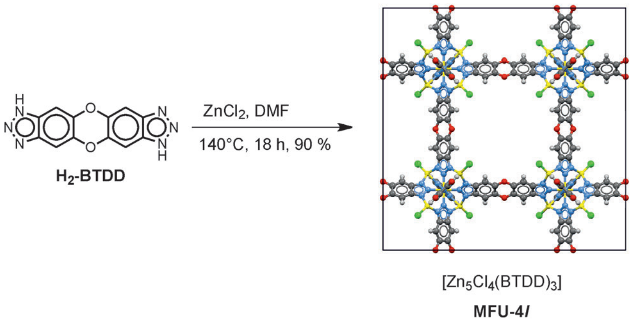

Figure 1. Solvothermal synthesis of MFU-4*l*. Atom colors: Zn (octahedral) pink, Zn (tetrahedral) yellow, Cl green, O red, N blue, C gray, H white. The black square outlines the cubic unit cell of MFU-4*l* (space group: $Fm\bar{3}m$, $a = 31.057$ Å; see Ref. [13]).

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[**] We gratefully acknowledge funding by the priority program 1362 “Porous Metal–Organic Frameworks (MOFs)” of the Deutsche Forschungsgemeinschaft (DFG).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201310004.

gas separation[15] and catalysis.[16] Their fundamental building units, so-called Kuratowski units,[17] feature coordination sites reminiscent of scorpionate-type complexes.[18] In contrast to the latter, however, the coordination sites in MFU-4 frameworks do not have to be protected from unfavorable side reactions by bulky substituents R (Figure 2a). As a result, frameworks can be generated that contain free metal centers with (almost) unconstrained substrate accessibility (Figure 2b). With the aim of constructing catalytically active frameworks, suitable MFU-4*l* derivatives can be used as starting materials, within which the required coordinatively highly unsaturated metal centers can be formed. The first example, as shown below, establishes the formation of a highly reactive zinc(II) hydride species **2**, generated from MFU-4*l*-formate (**1**), which was readily obtained from MFU-4*l* through chloride–formate ligand exchange (Figure 3, path a). Alternatively, postsynthetic metal metathesis, that is, the replacement of Zn^{II}–Cl units with Cu^{I} ions (Figure 3, path b), led to threefold-coordinated unsaturated Cu^{I} sites that showed reversible and remarkably strong chemisorption of small molecules (i.e. H_2, O_2, N_2, and C_2H_4) under ambient conditions.

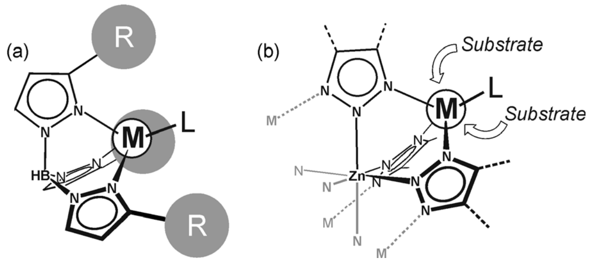

Figure 2. a) Scorpionate complex. b) Part of the fundamental building unit (Kuratowski unit) of MFU-4-type frameworks comprising coordinatively unsaturated, substrate-accessible coordination sites (M = (transition) metal, L = ligand, R = bulky substituent, for example, *t*Bu).

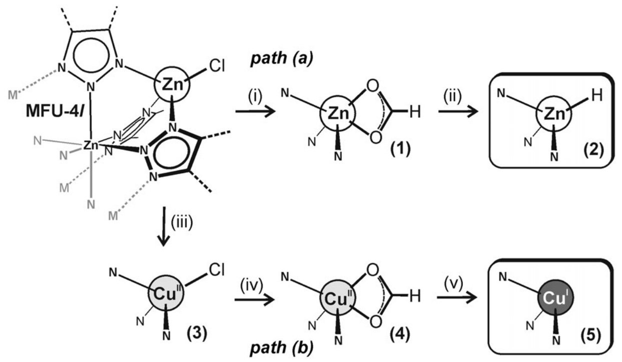

Figure 3. Reaction paths leading to MFU-4*l* derivatives **2** and **5** with active metal sites. Reaction conditions: i) HCOOLi/MeOH, room temperature; ii) 300 °C, 30 min, under vacuum; iii) $CuCl_2$, DMA, 60 °C; iv) HCOOLi/MeOH, room temperature; v) 180 °C, 1 h, under vacuum. DMA = *N*,*N*-dimethylacetamide.

Thermally activated decomposition of bulk metal formates has been reported previously. The decomposition of zinc formate, for example, leads to ZnO, whereas copper(II) formate yields the reduced products Cu_2O and Cu.[19] Our studies show that the thermally induced decomposition of coordinated formate ligands is a versatile approach for generating reactive metal sites in MFU-4*l*-type porous materials. Thus, the decomposition of **1** under flowing nitrogen gas took place in the temperature range of 190–280 °C, as shown by the curve derived from thermogravimetric analysis (TGA; see Figure S1 in the Supporting Information), whereby the crystalline order of the framework remained unchanged (see Figure S27). FTIR spectra showed clearly the formation of Zn–H species (i.e. **2**; Figure 3). Thus, a characteristic Zn–formate stretching vibration, which appeared as a shoulder in the FTIR spectrum at 1610 cm^{-1}, disappeared completely when compound **1** was heated at 300 °C (Figure 4).

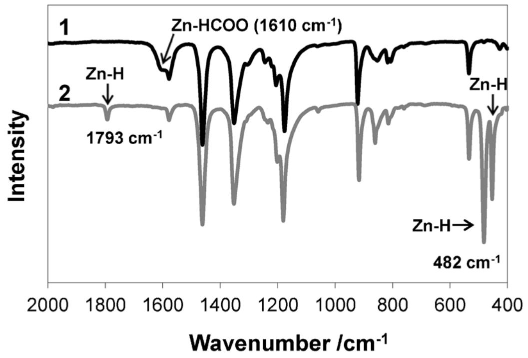

Figure 4. FTIR spectra of **1** and **2**.

Three new bands appeared upon heat treatment: at 1793, 482, and 453 cm^{-1}. On the basis of DFT calculations (using the PBE functional),[20] corrected for dispersive interactions,[21] we assign these bands to a Zn–H stretch mode and two Zn–H bending modes, respectively (see Figures S29 and S30).

Molecular hydride complexes of zinc scorpionates, prepared in a different way (either starting from ZnH_2 or by treatment of a Zn–F precursor with Et_3SiH), have been reported previously. These zinc hydride scorpionates were shown to react with various electrophiles, such as CO_2, CS_2, RNCS, RI, and CH_3COCl.[22] To demonstrate a comparable reactivity of the MFU-4*l* hydride derivative **2**, we added PhCOCl to a suspension of **2** in benzene at room temperature and obtained PhCHO as the main product, as determined by GC/MS analysis (see Figure S23). This test case indicates the potential of the hydride-containing MFU-4*l*-type framework **2** as a hydride-transfer and reducing agent.

We previously showed that all four peripheral Zn^{II} ions of each Kuratowski unit in MFU-4*l* could be substituted by Co^{II} upon heating with $CoCl_2$ in DMF.[16] An equivalent approach with $CuCl_2$ led to Cu^{II}-MFU-4*l* (**3**), in which, however, on average only two out of four tetrahedrally coordinated Zn centers per Kuratowski unit are replaced with Cu^{II} ions. Cu^{II}-MFU-4*l*-formate (**4**) could then be readily prepared by a subsequent ligand-exchange reaction, in analogy to the synthesis of **1** (Figure 3). The TGA curve (see Figure S1) shows that **4** decomposes in two steps: The first weight loss at 120–180 °C corresponds to the decomposition of Cu^{II}-formate units, and the second weight loss at 190–280 °C corresponds to the transformation of Zn-formate units. Sorption and spectroscopic studies showed that thermal activation of **4** led finally to a MFU-4*l*-type framework with free Cu^I centers, termed Cu^I-MFU-4*l* (**5**; Figure 3). As proven by gas-sorption measurements, **5** formed very stable complexes with CO and C_2H_4.

The quantity of bound species (ca. 38 $cm^3 g^{-1}$; see Figures S13 and S14) was nearly identical for both gases and very close to the calculated value (37.8 $cm^3 g^{-1}$) based on the analytically determined Cu content, thus suggesting the formation of stable 1:1 Cu^I–CO and Cu^I–C_2H_4 coordination units. The corresponding stretch modes of coordinatively bound CO and C_2H_4 molecules were observed in the FTIR spectra at 2081 and 1541 cm^{-1}, respectively (Figure 6b), in good agreement with the DFT-calculated values (2056 and 1517 cm^{-1}, respectively). Both vibrational frequencies are shifted to lower wavenumbers, as compared to those of the free gas molecules (2143 cm^{-1} for CO and 1623 cm^{-1} for C_2H_4).[23] One of the most interesting properties of **5** is the unprecedented strong and reversible chemisorption of H_2. The amount of chemisorbed H_2 (38 $cm^3 g^{-1}$; Figure 5a; see also Figure S13) was the same as for CO and C_2H_4, which indicates a 1:1 stoichiometry of Cu^I–H_2 coordination units. The adsorption/desorption isotherm measured at 273 K demonstrates full reversibility of hydrogen binding. Under equilibrium conditions (1 bar H_2 pressure), approximately 80 % of all Cu^I centers formed a 1:1 hydrogen complex at this temperature (Figure 5b). The isosteric heat of hydrogen adsorption, as calculated by using the Clausius–Clapeyron equation, is 32 kJ mol^{-1}, again in very good agreement with the DFT-calculated value of 25 kJ mol^{-1} (Table 1). The Cu–H_2 bonding energy in Cu^I-MFU-4*l* (**5**) is thus significantly higher than typical values for H_2 physisorption (5–10 kJ mol^{-1}),[24] but also significantly lower than in ionic metal hydrides or Kubas-type metal dihydrogen complexes, which normally require high desorption temperatures of 150–400 °C.[25] For example, an activation energy for hydrogen desorption of 156 kJ mol^{-1} has been measured for Mg_2NiH_4.[26] Intermetallic compounds, such as $LaNi_5$, show significantly lower desorption temperatures (as low as room temperature); however, they feature only low hydrogen-storage capacities.[25]

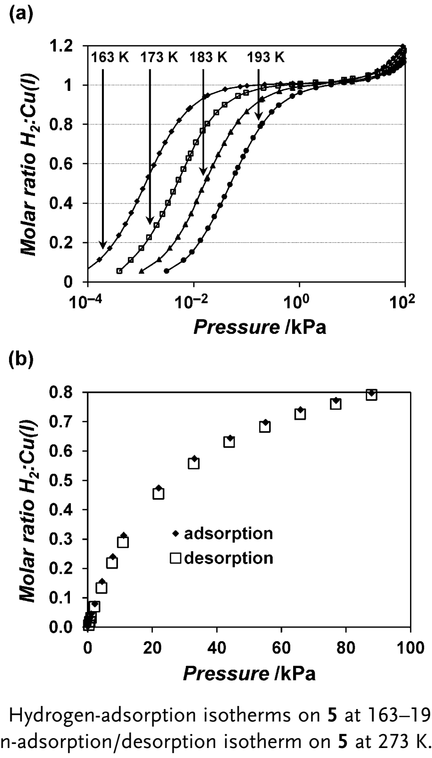

Figure 5. a) Hydrogen-adsorption isotherms on **5** at 163–193 K. b) Hydrogen-adsorption/desorption isotherm on **5** at 273 K.

Table 1: Experimental and DFT-calculated isosteric heats of adsorption in kJ mol^{-1} in Cu^I-MFU-4*l* (**5**).

	H_2	N_2	O_2	C_2H_4	CH_4
experiment	32.3 ± 0.4	41.6 ± 0.6	52.6 ± 0.6	88 ± 4	14.9 ± 0.4
DFT-B3LYP	25	44	46	84	15

In fact, the hydrogen binding at the Cu^I centers matches well a suggested optimal binding energy of approximately 25 kJ mol^{-1} for hydrogen storage, thus enabling the accumulation and release of hydrogen at close to ambient temperature.[24] Although the amount of chemisorbed hydrogen in **5** is not high (0.34 wt %), owing to the low volumetric density of Cu^I centers, this degree of chemisorption is possible at close to ambient temperature and pressure, thus indicating the great potential of copper(I)-containing materials with a higher density of active metal sites for hydrogen storage. Higher storage capacities have only been observed either at low temperature or at high pressure.[27] For example, CPO-27-Ni showed less than 0.3 wt % H_2 uptake at 298 K and 65 bar.[28] Compound **5** also showed reversible chemisorption of N_2 and O_2 with the same 1:1 stoichiometry (see Figure S13) and isosteric heats of adsorption of 42 and 53 kJ mol^{-1}, respectively (Figure 6a). In contrast, methane showed only physisorption, as indicated by the low value of 15 kJ mol^{-1} determined for the isosteric heat of adsorption (Figure 6a; see also Figure S14). This value was also confirmed by DFT calculations (Table 1), which showed only dispersive interactions between Cu^I centers and CH_4 (see Figure S31). The fact that methane does not bind to Cu^I centers suggests **5** as a potential candidate for CH_4/N_2 separation with highly selective N_2 uptake. In the case of normal physisorption, most frequently observed in porous materials, CH_4 is adsorbed preferentially over N_2.[29] The exceptionally high difference of 73 kJ mol^{-1} between the heats of adsorption of C_2H_4 and CH_4 indicates that **5** is a very promising material for alkene/alkane separation or alkene capture. The isosteric heat of ethylene adsorption on CPO-27-Fe, for comparison, is about 45 kJ mol^{-1} and is the highest within the series of CPO-27 frameworks containing different metal ions (Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}), whereas the heat of CH_4 adsorption on CPO-27-Fe is 20 kJ mol^{-1}.[30] As summarized in Table 1, all isosteric heats of adsorption were very well reproduced in DFT calculations, thus confirming the picture

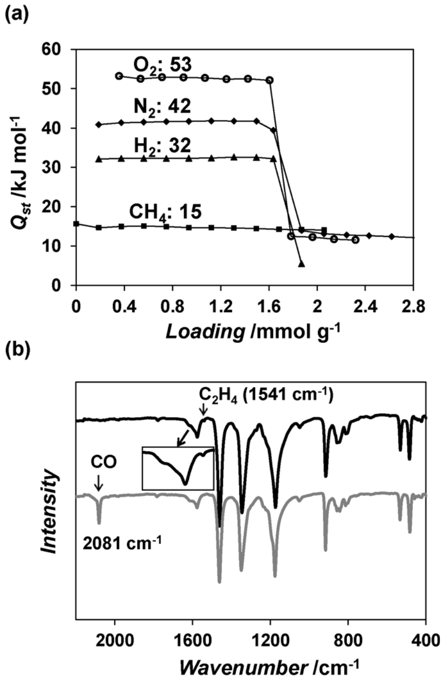

Figure 6. a) Dependence of isosteric heat of adsorption on loading for different gases on **5**. b) FTIR spectra of CO and C_2H_4 complexes of **5**.

of highly reactive and accessible Cu^I centers in Cu^I-MFU-4*l* (**5**).

We further note that **5** is air-stable (meaning that it is not oxidized irreversibly or destroyed in air like many copper(I)-containing compounds) and changes its color reversibly from slightly yellow (in a vacuum) to dark-gray (in air), which indicates the reversible binding of O_2 molecules at the Cu^I centers. Quantitative information about this process was gleaned by UV/Vis spectroscopy (see Figure S3). The binding of nitrogen was followed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The experimental frequency for the IR-active N–N bond stretch (2242 cm^{-1}; see Figure S10) is typical for Cu^I–N_2 adducts, as previously described,[11] and close to the DFT-calculated value (2215 cm^{-1}). As observed for CO and C_2H_4, the N–N vibrational frequency was shifted to lower wavenumbers as compared to that of the free N_2 molecule (2331 cm^{-1}).[23]

The DFT-calculated geometries of the formed Cu^I–H_2, Cu^I–N_2, Cu^I–O_2, and Cu^I–C_2H_4 complexes in the Kuratowski unit are presented in Figure 7. H_2 binds in an η^2 (side-on) mode with a H–H bond distance of 0.83 Å and a Cu–H bond distance of 1.66 Å (Figure 7a). N_2 binds in an η^1 (end-on) mode with a N–N bond distance of 1.12 Å and a Cu–N bond distance of 1.83 Å; the Cu-N-N angle is 180° (Figure 7b). O_2 also binds in an η^1 (end-on) mode with an O–O bond distance of 1.29 Å, a Cu–O bond distance of 1.92 Å, and a Cu-O-O angle of 105.7° (Figure 7c). C_2H_4 forms an η^2 (side-on) complex with a C–C bond distance of 1.39 Å and a Cu–C bond distance of 2.03 Å (Figure 7d). All atomic distances within the bound species are longer than in the free molecules (0.74, 1.10, 1.21, and 1.34 Å for H_2, N_2, O_2, and C_2H_4, respectively),[23] in agreement with the experimentally observed red shifts of the stretch frequencies for N_2 and C_2H_4.

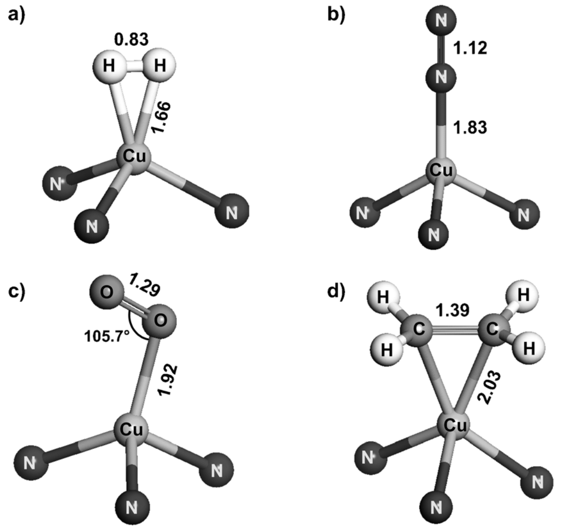

Figure 7. Binding geometries for a) H_2, b) N_2, c) O_2, and d) C_2H_4 at the Cu^I sites within the Kuratowski unit of MFU-4*l*, as determined by DFT calculations (interatomic distances in Å).

In summary, we have provided sound experimental and theoretical evidence for the synthesis, structure, and reactivity of robust metal–organic frameworks featuring open metal sites. The reactivity of these frameworks, which are derived from the MFU-4*l* structural family, towards small molecules was demonstrated by hydride transfer to electrophiles and by strong binding of small gas molecules. Since both processes are fundamental steps of catalytic transformation processes, further investigations in this direction should be highly rewarding. Selective chemisorption properties of Cu^I centers are of great interest for the storage, separation, and sensing of small gas molecules.

Experimental Section

Detailed synthetic procedures and characterization, TGA, XRPD, and GC/MS data, FTIR and UV/Vis/NIR spectra, gas-sorption isotherms, crystallographic data, and details of the DFT calculations are provided in the Supporting Information. CCDC 971404 (**1**), 971402 (**3**), and 971403 (**4**) contain 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.

Received: November 18, 2013
Revised: March 11, 2014

Keywords: chemisorption · copper · hydrides · hydrogen · metal–organic frameworks

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