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Metal–Organic Frameworks

Solvent-Dependent Cation Exchange in Metal–Organic Frameworks

Carl K. Brozek,[a] Luca Bellarosa,[b] Tomohiro Soejima,[a] Talia V. Clark,[a, c] Núria López,[b] and Mircea Dincă*[a]

Abstract: We investigated which factors govern the critical steps of cation exchange in metal–organic frameworks by studying the effect of various solvents on the insertion of Ni^{2+} into MOF-5 and Co^{2+} into MFU-4*l*. After plotting the extent of cation insertion versus different solvent parameters, trends emerge that offer insight into the exchange processes for both systems. This approach establishes a method for understanding critical aspects of cation exchange in different MOFs and other materials.

Cation exchange is a powerful tool that has been used extensively to tailor the composition of materials, such as nanocrystals,[1–4] zeolites,[5,6] and, more recently, metal–organic frameworks (MOFs).[7–22] It involves the exchange of native cations in a crystalline solid with foreign cations from a surrounding solution. This process can furnish materials with properties that differ from those of the parent structure and, in certain cases, permits the isolation of metastable phases. Identifying the features underlying the exchange mechanism in a given set of materials could enable the design of new compounds with precisely engineered functionality. These studies are rare, however, because the exchange processes are undoubtedly governed by numerous parameters corresponding to both the crystalline solids and their surrounding solutions. For instance, thermodynamic values, such as cation solubility and lattice strain, are known to influence cation exchange in nanocrystals,[1] while ionic radius is significant for zeolites.[5,6] Despite the deep insight that could be gained by identifying the influence of solvent parameters on cation exchange, few if any studies have tackled this task. To endow cation exchange in MOFs with predictive power, we studied the solvent dependence for rates of exchange of native Zn^{2+} ions with Co^{2+} and Ni^{2+} in the materials known as MFU-4*l* (Zn_5Cl_4{bis(1*H*-1,2,3-triazolo-[4,5-*b*],[4′,5′-*i*])dibenzo-[1,4]-dioxin}$_6$) and MOF-5 (Zn_4O(1,4-benzenedicarboxylate)$_3$). The secondary building units (SBUs) of these materials, the sites of cation exchange, are shown in Figure 1. Our findings demonstrate that by identifying the solvent parameters that best correlate with the cation exchange rate, we can determine critical aspects of the exchange process.

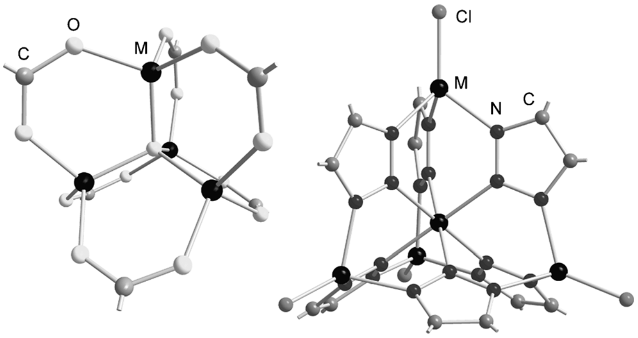

Figure 1. The SBUs of MOF-5 (left) and MFU-4*l* (right).

To examine the solvent dependence of Ni^{2+} exchanging into MOF-5, we repeated an exchange procedure previously reported for DMF with a variety of other solvents under otherwise identical conditions. In addition to DMF, we used DMSO, *N*-methyl-2-pyrrolidone (NMP), *N*-methylformamide (NMF), THF, and MeCN. MOF-5 was prepared and activated according to a literature procedure.[23] Soaking these crystals with gentle shaking for one week in 0.03 M solutions of $Ni(NO_3)_2{\cdot}x\,H_2O$ produced materials with a wide range of Ni/Zn molar ratios, as determined by inductively coupled atomic emission spectroscopy (ICP-AES).

The Ni/Zn ratios were plotted against several solvent parameters that we expected to impact the exchange process, including the ligand field parameter of the corresponding $[Ni(solvent)_x]^{2+}$ species (*Dq*), the solvent dielectric constant, the Snyder polarity index, the Hansen solubility parameter δ_H, and the Gutmann donor number. Among these, the closest trend was observed for the *Dq* parameters, which were derived by assigning *d–d* transitions to UV/Vis–NIR spectra of $Ni(NO_3)_2{\cdot}x\,H_2O$ solutions in the various solvents using theory derived elsewhere.[24] As shown in Figure 2, the Ni/Zn ratio in-

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[a] C. K. Brozek, T. Soejima, T. V. Clark, Prof. M. Dincă
Department of Chemistry
Massachusetts Institute of Technology
77 Massachusetts Avenue, Cambridge, MA 02139 (USA)
E-mail: mdinca@mit.edu

[b] Dr. L. Bellarosa, Prof. N. López
Institute of Chemical Research of Catalonia, ICIQ
Av. Països Catalans 16, 43007, Tarragona (Spain)

[c] T. V. Clark
Boston Public Schools
John D. O'Bryant School of Math and Science
Malcom X Blvd., Roxbury, MA 02120 (USA)

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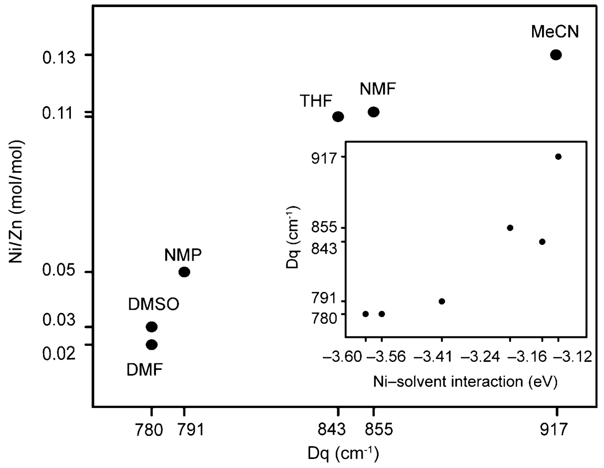

Figure 2. Ni/Zn molar ratio plotted against *Dq*. Inset: *Dq* determined from UV/Vis spectra of $[Ni(solvent)_6]^{2+}$ complexes versus calculated Ni–solvent bond strengths.

creases monotonically with increasing values of *Dq*. To interpret this trend, we employed density functional theory to compute the metal–solvent bond strengths of $[Ni(solvent)_6]^{2+}$ and $[Zn(solvent)_6]^{2+}$ following equations S1–S3 (Supporting Information). The results, plotted in the inset of Figure 1, indicate that high *Dq* values correlate with weak metal–solvent bonds. This inverse relationship reflects the solvents ranging on a spectrum from having π-donor character to being π acceptor ligands: the empty π* orbitals of MeCN lead to large *Dq*, whereas the filled π-donating orbitals from $O^{\delta-}$ on DMSO lead to small *Dq*. All the charges for the solvent atoms coordinating to the metal ions are reported in Table S1 (Supporting Information) and confirm this relationship. Thus, the Ni/Zn ratio increases for solvents that form weaker metal–solvent bonds (as shown in Figure 3 and Figure S1 in the Supporting Information).

We also plotted the Ni/Zn ratio against the Gutmann donor numbers of the solvents. This number is the formation energy of complexes between solvents and $SbCl_5$ and has been used as a metric for the Lewis basicity of the respective solvents. We reasoned that an experimental measure of Lewis basicity should follow the same trend with bond strength.[25] Indeed, less basic solvents correlate with higher Ni^{2+} incorporation (Figure S2, Supporting Information). Together, the correlations with *Dq* and the related Gutmann donor numbers suggest two possible scenarios: weak Ni^{2+}–solvent interactions (or large *Dq* values) lead to fast release of Ni^{2+}, or strong solvent association with the Zn^{2+} ions in MOF-5 leads to stable adducts in the framework, retarding the rate of exchange.

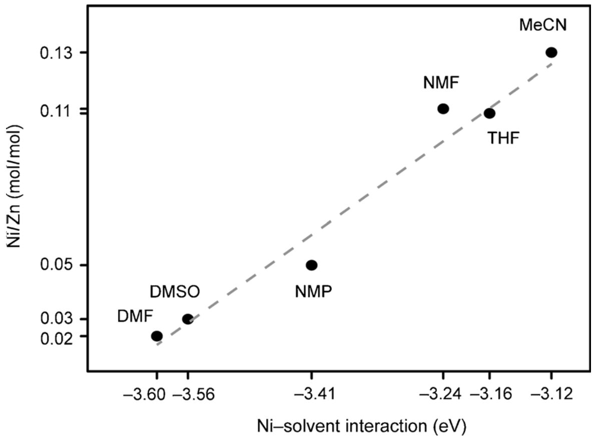

Figure 3. Ni/Zn ratio plotted against calculated Ni–Solvent interactions with a best fit line depicted by the dashed line, with $R^2=0.966$.

With evidence that the ligand strength of the solvents affects the exchange process, we turned our attention to parameters that measured electrostatic interactions. If the mechanism involved charge localization or neutralization, the rate of Ni^{2+} exchange should correlate to the polarity indices developed by Snyder.[26] Yet, a trend did not emerge from the resulting plot, displayed in Figure S3 (Supporting Information). We also investigated whether the rate of exchange correlated to the respective dielectric constants of the solvents, just as S_N1 reactions are known to proceed faster in solvents with high dielectric constants by stabilizing charged intermediates. Again, plotting the Ni/Zn ratio versus the respective dielectric constants showed no correlation (Figure S4, Supporting Information). Although electrostatics may still impact the cation exchange mechanism, our analysis indicates that the cation–solvent interaction is dominant in the rate-determining step.

To investigate whether similar effects could be observed in other systems, we turned our attention to the study of Co^{2+} exchange into MFU-4*l*. This system had been explored extensively by Volkmer et al. to impart redox activity to the MOF.[7,27] We repeated the exchange procedure in a variety of solvents under otherwise identical conditions. In addition to DMF, we used DMSO, NMP, MeCN, dimethylacetamide (DMA), and methanol (MeOH). MFU-4*l* was prepared and activated according to a literature procedure and soaked in 0.1 M solutions of anhydrous $CoCl_2$.[7,28] To observe significant differences in the extent of cation exchange between the solvents, we prevented the process from going to completion by performing the exchange at a lower temperature than used previously. Whereas the original report of Co^{2+} exchange into MFU-4*l* required stirring for 20 h at a temperature of 140 °C, we soaked the all-Zn^{2+} parent material for exactly one week at room temperature with only gentle shaking to avoid breaking the crystals, which would otherwise affect the Co^{2+} diffusion. Studying the rate of exchange at first seems complicated because the secondary building unit (SBU) of MFU-4*l* contains two crystallographically distinct Zn^{2+} sites, as shown in Figure 1. The previous study showed, however, that only the peripheral tetracoordinated sites are replaceable by Co^{2+}, whereas the central octahedral atom remains unchanged even at 140 °C.

To investigate the dependence on ligand field strength, we calculated the *Dq* for each solvent, knowing that in the UV/Vis spectra of the corresponding homoleptic metal complexes the transition $^4A_2 \rightarrow {}^4T_1(F)$ should occur at $18Dq$.[24] To our surprise, plotting the extent of Co^{2+} exchange into MFU-4*l* versus *Dq* revealed a trend that is opposite to that found for Ni-MOF-5. Unlike in the latter, the extent of Co^{2+} incorporation into MFU-

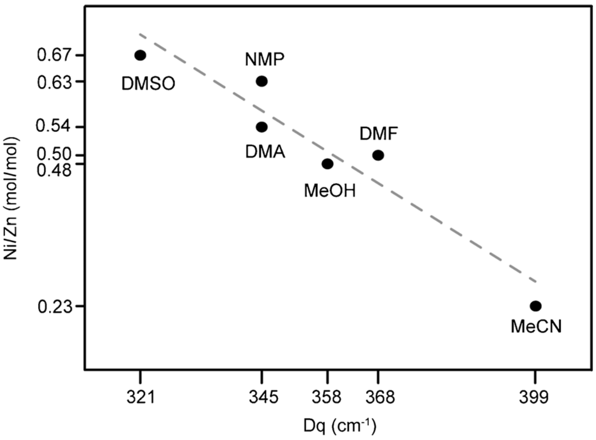

Figure 4. Co/Zn ratio plotted against ligand field parameter *Dq*. A best fit with R^2 of 0.922 is depicted by the dashed line.

4*l* increases with lower values of *Dq* and displays a linear correlation with a R^2 of 0.922, shown in Figure 4. The reversal of *Dq* dependence trends between Co-MFU-4*l* and Ni-MOF-5 suggests that solvents participate in a different rate-limiting step in the two materials.

We anticipated that if Co-MFU-4*l* shows the opposite trend from Ni-MOF-5, then the rate of exchange should increase for more Lewis basic solvents. Indeed, plotting the Co/Zn ratio against the Gutmann donor numbers revealed a convincing correlation, as shown in Figure S5 (Supporting Information). Unfortunately, because solvated $CoCl_2$ is known to exist in equilibrium between various four- and six-coordinate species,[29] extending our DFT analysis to this system is problematic and led to inferior correlations, as shown in Figure S6 and S7 (Supporting Information). Nevertheless, our experimental evidence indicates that solvents that solvate Zn^{2+} better enable faster exchange of Co^{2+} into the MFU-4*l* lattice.

Among the other solvent parameters we tested for the formation of Co-MFU-4*l*, the polarity indices reveal a strong correlation for the aprotic solvents. Figure 5 illustrates that Co^{2+} incorporates to a greater extent in solvents with higher indices, giving a linear fit with $R^2 = 0.905$ when MeOH, the only protic solvent, is excluded. Although this parameter provides a convincing trend, the presence of MeOH as an extreme outlier suggests that the metal–solvent interaction (i.e. *Dq*) exerts a more reliable influence on the cation exchange mechanism because it demonstrates a strong correlation whether the solvent is protic or not. Nevertheless, the strong correlation between the Co/Zn ratio and the Snyder polarity indices suggests that the exchange process involves a highly polarized intermediate, and thus offers additional insight into the overall mechanism. Solvents with higher indices might better stabilize this polarized intermediate and enhance the rate of the exchange. This is not surprising since for MFU-4*l* the exchange process involves Cl^- transfer between Co^{2+} and Zn^{2+}. Indeed, we surmise that MeOH performs better than expected from the polarity trend because its protic groups enhance Cl^- solvation. Furthermore, it is possible that the Ni^{2+} exchange into MOF-5 does not correlate well to polarity indices because it lacks participating anions.

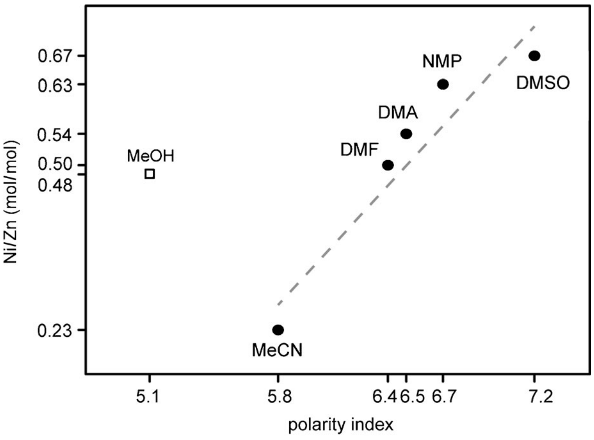

Figure 5. Co/Zn ratio plotted against Snyder polarity indices. A best fit with R^2 of 0.905 is depicted by the dashed line.

While *Dq* and polarity values correlate well to the rate of Co^{2+} exchange into MFU-4*l*, other potentially relevant solvent parameters do not. Prompted by our hypothesis for why MeOH is the outlier in Figure 5, we plotted the Co/Zn ratio against the Hansen solubility parameter δ_H to determine the influence of hydrogen bonding.[30] As shown in Figure S8 (Supporting Information), no clear trend emerges. While hydrogen bonding may still influence the exchange process, our analysis suggests that it does not govern the rate through a clear relationship, and is likely not a significant factor prior to or during the rate-determining step.

Encouraged by the relevance of polarity indices on the Co^{2+} exchange in MFU-4*l*, we also investigated whether the rate of exchange correlates to the solvent dielectric constants. We expected this parameter to correlate with the exchange rate at least as well as the polarity index, yet the resulting plot also did not display a convincing trend (Figure S9, Supporting Information). This result reinforces that the solvent participates in the exchange process (probably by coordinating and decoordinating from metal centers) and thus cannot be treated as a homogeneous dielectric continuum when investigating the mechanism.

In conclusion, these studies illustrate that solvents influence the cation exchange mechanism, as might be expected, but only a select group of relevant parameters correlate with the exchange rates. These studies also reveal that cation exchange in Ni-MOF-5 and Co-MFU-4*l* relies on different rate-determining steps. The trends displayed by solvent polarity and ligand field strength suggest that the replacement of Zn^{2+} by Co^{2+} in MFU-4*l* involves a polarized intermediate and is limited by the ability of the solvent to solvate the dissociating Zn^{2+} ions. Similar analyses of Ni-MOF-5 suggest instead that the dissociation of solvent from Ni^{2+} or the stability of solvent-MOF (i.e. Zn^{2+}) adducts dictates the rate of exchange in MOF-5. Mechanisms of cation exchange may differ from material to material, but systematic studies of solvent dependence are a first step towards understanding these mechanisms. In identifying the few parameters with the greatest influence on the exchange rate, future studies will glean not only mechanistic insight, but acquire a handle for manipulating the exchange process to control physical properties a priori.

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