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Lattice-Imposed Geometry in Metal-Organic Frameworks: Lacunary Zn$_4$O Clusters in MOF-5 Serve as Tripodal Chelating Ligands for Ni$^{2+}$

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The inorganic clusters in metal-organic frameworks can be used to trap metal ions in coordination geometries that are difficult to achieve in molecular chemistry. We illustrate this concept by using the well-known basic carboxylate clusters in Zn$_4$O(1,4-benzenedicarboxylate)$_3$ (MOF-5) as tripodal chelating ligands that enforce an unusual pseudo-tetrahedral oxygen ligand field around Ni$^{2+}$. The new Ni-based MOF-5 analogue is characterized by porosity measurements and a suite of electronic structure spectroscopies. Classical ligand field analysis of the Ni$^{2+}$ ion isolated in MOF-5 classifies the Zn$_3$O(carboxylate)$_6$ "tripodal ligand" as an unusual, stronger field ligand than halides and other oxygen donor ligands. These results may inspire the wide-spread usage of MOFs as chelating ligands for stabilizing site-isolated metal ions in future reactivity and electronic structure studies.

The ability to tune the electronic properties of a metal ion by changing its coordination environment is the cornerstone of transition-metal chemistry. The design of ligands that enforce desired geometries around metals is the typical approach towards this goal and has been the purview of a molecular science; such tunability in the solid state is rare. With an eye towards the latter, we sought to use the inorganic clusters in metal-organic frameworks (MOFs), a class of porous crystalline materials made from simple building blocks, as chelating ligands. Although coordinatively unsaturated metal ions with unusual geometries have been isolated in MOFs in the context of gas storage and separation or catalysis, the deliberate use of MOF nodes in coordination chemistry remains virtually unexplored. As a proof-of-principle, we reconceived the secondary building unit (SBU) of the iconic Zn$_4$O(BDC)$_3$ (MOF-5, BDC = 1,4-benzenedicarboxylate) as a tripodal ligand for metals that are typically incompatible with tetrahedral oxygen ligand fields, such as Ni$^{2+}$ (see Figure 1). Normally, Ni$^{2+}$ ($d^8$) prefers octahedral coordination in oxygen ligand fields and assumes tetrahedral geometry only when trapped in condensed lattices such as ZnO, or when surrounded by bulky supporting ligands. By demonstrating that the Zn$_3$O(carboxylate)$_6$ SBU can be used as a designer chelating ligand we hope to inspire the use of these popular materials as platforms for unusual coordination chemistry.

![Figure 1](image1.png)

**Figure 1** Illustration of the Zn$_3$O(carboxylate)$_6$ SBU of MOF-5 as a tripodal support that enforces a tetrahedral oxygen ligand field, akin to standard chelating ligands such as the tetra-amine on the right.

Our first attempts to install Ni$^{2+}$ ions inside MOF-5 were inspired by isolated reports of post-synthetic ion metathesis at MOF nodes. Complete metathesis of structural units is a powerful method to access rationally designed analogues of existing MOFs, as has recently also been demonstrated by organic ligand exchange. Accordingly, colourless crystals of MOF-5 were soaked in a saturated solution of Ni(NO$_3$)$_2$•6H$_2$O...
and, to our satisfaction, turned yellow within a few days. To ensure maximal Ni\(^{2+}\) incorporation, soaking was continued for one year. The ensuing yellow crystals were washed repeatedly with \(N,N\)dimethylformamide (DMF) and \(\text{CH}_2\text{Cl}_2\) without loss of colour until the solvents no longer showed UV-Vis absorption profiles characteristic of free Ni\(^{2+}\) ions. X-ray diffraction and elemental analysis of these yellow crystals revealed a cubic lattice (\(a = 25.838(2)\) Å) nearly identical to that of MOF-5 and a Ni:Zn ratio of 1:3. Shorter soaking times engendered lower levels of Ni\(^{2+}\) substitution, and Ni:Zn ratios of 1:10 could be isolated after one year. The ensuing yellow crystals were washed repeatedly to ensure maximal Ni\(^{2+}\) incorporation, and Ni:Zn ratios of 1:10 could be isolated after one year. The ensuing yellow crystals were washed repeatedly to ensure maximal Ni\(^{2+}\) incorporation, and Ni:Zn ratios of 1:10 could be isolated after one year.

We herein provide a hypothesis for this surprising observation: the yellow colour of as-synthesized Ni\(^{2+}\)-substituted MOF-5 is indicative of octahedral Ni\(^{2+}\). We surmise that accommodation of octahedral Ni\(^{2+}\) must distort the original Zn\(^{2+}\) core and the MOF-5 lattice. Additional Ni\(^{2+}\) substitution into the ensuing NiZn\(^{2+}\) cluster is prevented by a large kinetic barrier as it would exert debilitating strain on the lattice. The presence and identity of the two additional ligands that complete the coordination sphere of octahedral Ni\(^{2+}\) was confirmed by thermogravimetric analysis, which showed that two DMF molecules per Ni centre are lost by heating the yellow crystals between 70 and 150 °C (Figure S3). Zn\(^{2+}\)(carboxylate)\(_6\) SBUs wherein one Zn\(^{2+}\) is hexa-coordinate and binds two DMF molecules have been reported,\(^9\) offering precedent for the formulation of Ni-substituted MOF-5 as (DMF)\(_x\)Ni\(_{1-x}\)Zn\(_{1-x}\)O(BDC)\(_x\) (0 < x < 1), (DMF)\(_x\)Ni-MOF-5.\(^{10}\)

![In-situ diffuse-reflection spectra depicting the color progression from yellow (DMF)\(_2\)Ni-MOF-5 to blue Ni-MOF-5 via a putative pentacoordinated Ni\(^{2+}\) intermediate (red trace). The inset shows optical images of the yellow and blue crystals.](image)

![The temperature dependence of χ waktu buyuk T of evacuated Ni-MOF-5 (circles). The red trace represents a fit obtained using julX.\(^{17}\) We note that the observed temperature dependence of χ waktu buyuk T is due to thermally accessible multiplet states of the \(\text{Ni}^{2+}\) ground state, and not antiferromagnetic coupling. This is confirmed by a nearly (0,0) intercept of the Curie-Weiss plot (inset).](image)

**Table 1** Calculated Racah and ligand field parameters of various tetrahedral Ni\(^{2+}\) species based on observed transitions \(\nu_2\) and \(\nu_3\).\(^{8}\)

<table>
<thead>
<tr>
<th>Species</th>
<th>(\nu_1 (\text{cm}^{-1}))</th>
<th>(\nu_2 (\text{cm}^{-1}))</th>
<th>(B (\text{cm}^{-1}))</th>
<th>(Dq (\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni(NCO)}_4]^{2-})</td>
<td>16200</td>
<td>9460</td>
<td>511</td>
<td>311</td>
</tr>
<tr>
<td>([\text{NiCl}_2]^{2-})</td>
<td>14760</td>
<td>7470</td>
<td>405</td>
<td>206</td>
</tr>
<tr>
<td>([\text{NiBr}_2]^{2-})</td>
<td>13320</td>
<td>6995</td>
<td>379</td>
<td>201</td>
</tr>
<tr>
<td>([\text{Ni(OAr)}_4]^{2-})</td>
<td>16820</td>
<td>10000</td>
<td>867</td>
<td>540</td>
</tr>
<tr>
<td>([\text{ZnO:Ni}]^{2+})</td>
<td>15720</td>
<td>8340</td>
<td>770</td>
<td>420</td>
</tr>
<tr>
<td>([\text{ZnS:Ni}]^{2+})</td>
<td>12790</td>
<td>9750</td>
<td>560</td>
<td>475</td>
</tr>
<tr>
<td>([\text{CdS:Ni}]^{2+})</td>
<td>12395</td>
<td>7840</td>
<td>570</td>
<td>400</td>
</tr>
</tbody>
</table>

![Ni-MOF-5](image)

**Figure 3** The temperature dependence of χ waktu buyuk T of evacuated Ni-MOF-5 (circles). The red trace represents a fit obtained using julX.\(^{17}\) We note that the observed temperature dependence of χ waktu buyuk T is due to thermally accessible multiplet states of the \(\text{Ni}^{2+}\) ground state, and not antiferromagnetic coupling. This is confirmed by a nearly (0,0) intercept of the Curie-Weiss plot (inset).
The pseudo-tetrahedral geometry around the Ni\(_{2}^{2+}\) and the homogeneity of Ni-MOF-5 was quantified by diffuse-reflectance UV-Vis-NIR spectroscopy (blue trace in Figure 3), and magnetic measurements (vide infra). Despite the slight deviation from tetrahedral geometry around Ni\(^{2+}\), Ni-MOF-5 exhibited a spectrum that resembled solution-phase spectra of strictly tetrahedral Ni\(^{2+}\) complexes.\(^{15}\) Thus, a peak at 1020 nm (9803 cm\(^{-1}\)) can be assigned to the \(^{3}T_{1}(F)\) – \(^{3}A_{2}\) transition of a d\(^{8}\) tetrahedral ion (\(\upsilon_6\)), while the doublet of peaks at 540 nm (18,500 cm\(^{-1}\)) and 608 nm (16,400 cm\(^{-1}\)) can be assigned to the \(^{3}T_{1}(F)\) – \(^{3}T_{1}(P)\) transition (\(\upsilon_3\)), where \(\upsilon_3\) is split by spin-orbit coupling into \(^{3}P_0\) (\(A_1\)), \(^{3}P_1\) (\(T_1\)), and \(^{3}P_2\) (\(E+T_2\)) respectively.\(^{36}\) A ligand field analysis of this spectrum using a system of equations originally derived by Ballhausen\(^{15}\) (see Supporting Information) revealed Racah and Dq parameters of 1045 cm\(^{-1}\) and 753 cm\(^{-1}\). As shown in Table 1, these are notably higher than those common for tetrahedral Ni\(^{2+}\) and suggest that spin-spin repulsion is almost as large as in unperturbed Ni\(^{2+}\) ions, thereby preserving a large spin-orbit coupling interaction.

The presence of significant spin-orbit coupling was also evidenced by magnetic measurements. A \(\mu_\text{eff}\) vs. T plot of Ni-MOF-5, shown in Figure 4, revealed the presence of magnetically dilute Ni\(^{2+}\) ions and a room temperature magnetic moment of 4.21 \(\mu_B\) per Ni\(^{2+}\) ion. This value is higher than the spin-only value expected for Ni\(^{2+}\), but is expected for tetrahedral d\(^8\) ions subject to unquenched orbital angular momentum.\(^{16}\) The value of \(\mu_\text{eff}\) is further elevated by a temperature independent paramagnetism value of 0.2 \(\times\) 10\(^{-6}\) cm\(^{3}\)/mol as determined by a fit of the susceptibility data using julX.\(^{17}\)

Hints at the reactivity of Ni\(^{2+}\) centers within Ni-MOF-5 came from an in-situ UV-Vis-NIR study of the striking color change that occurs when heating (DMF)$_2$Ni-MOF-5. These experiments, plotted in Figure 3, evidenced an isosbestic point around 700 nm, which suggested that DMF loss occurred in two kinetically independent processes via a well-defined five-coordinate Ni\(^{2+}\) species. The identity of this species was probed by treating Ni-MOF-5 with various nucleophiles. Although the reaction of Ni-MOF-5 with small ligands such as PMe$_3$, THF, and MeCN rapidly produced octahedral Ni\(^{2+}\), indicated by a color reversal to yellow, stericly-demanding MesCNO afforded an orange adduct, whose spectrum matched that of the putative pentacordinate (DMF)Ni-MOF-5 adduct (Figure S5). Thus, Figure 3 shows a straightforward six-(O\(_h\)) to five-(C\(_{4v}\)) to four-(pseudo-T\(_d\)) coordinate conversion of Ni in a +2 formal oxidation state. These transformations, illustrated in Scheme 1, are supported by computational modeling of (DMF)$_2$NiZn(O(benzoate))\(_y\) (\(y = 0, 1, 2\)) clusters containing six-, five-, and four-coordinate Ni\(^{2+}\) ions with two, one, or no bound DMF molecules. As shown in Figure S7, time-dependent DFT calculations using optimized geometries of these clusters predicted electronic absorption spectra that agreed well with the assigned yellow, red, and blue traces in Figure 3.

**Conclusions**

The use of the inorganic nodes in MOF-5 as unusual chelating ligands illustrates a potentially rich area of exploration in coordination chemistry. Extending this concept to other metals and MOF systems will enable synthetic inorganic chemists to pursue a variety of important goals, including the isolation of "hot" intermediates from industrial and biological catalytic processes.

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**Notes and references**

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‡ Electronic Supplementary Information (ESI) available: Experimental procedures, X-ray structure refinement tables and details, computational details, relevant equations for LF analysis, powder X-ray diffraction patterns, ICP-AES results, TGA, FT-IR spectra, additional diffuse reflectance spectra, calculated electronic transitions, and an N\(_2\) isotherm plot and data table. See DOI: 10.1039/b000000x/
References

32. Repeated attempts to grow single crystals of this NiII-BDC phase were not successful. A search of the Cambridge Crystallographic Database indicated, to our surprise, that no pure NiII-BDC MOF has been reported so far (i.e. containing no other chelating/bridging ligands).
35. Accordingly, we propose that the materials reported in reference 6 may also be formulated as (DMF)_2Co,Zn_4(O(BDC)).