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EDGE ARTICLE

Lattice-imposed geometry in metal–organic frameworks: lacunary Zn_4O 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_4O(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_3O(carboxylate)$_6$ "tripodal ligand" as an unusual, stronger field ligand than halides and other oxygen donor ligands. These results may inspire the widespread 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,[1] 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 $Zn_4O(BDC)_3$ (MOF-5, BDC = 1,4-benzenedicarboxylate)[2] as a tripodal ligand for metals that are typically incompatible with tetrahedral oxygen ligand fields, such as Ni^{2+} (see Fig. 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,[3] or when surrounded by bulky supporting ligands.[4] By demonstrating that the Zn_4O(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.

Our first attempts to install Ni^{2+} ions inside MOF-5 were inspired by isolated reports of post-synthetic ion metathesis at MOF nodes.[5] 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.[6] Accordingly, colourless crystals of MOF-5 were soaked in a saturated solution of $Ni(NO_3)_2 \cdot 6H_2O$ 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 CH_2Cl_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 two weeks. Albeit slow, these results indicated that

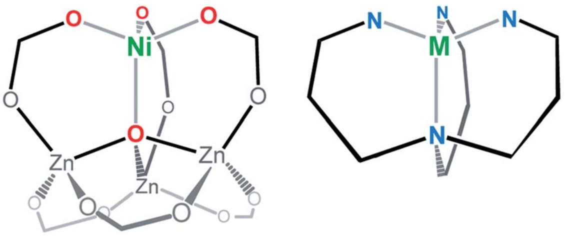

Fig. 1 Illustration of the Zn_3O(carboxylate)$_6$ SBU of MOF-5 as a tripodal support that enforces a tetrahedral oxygen ligand field, akin to standard chelating ligands such as the tetra-amine on the right.

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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. CCDC reference number 874342. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2sc20306e

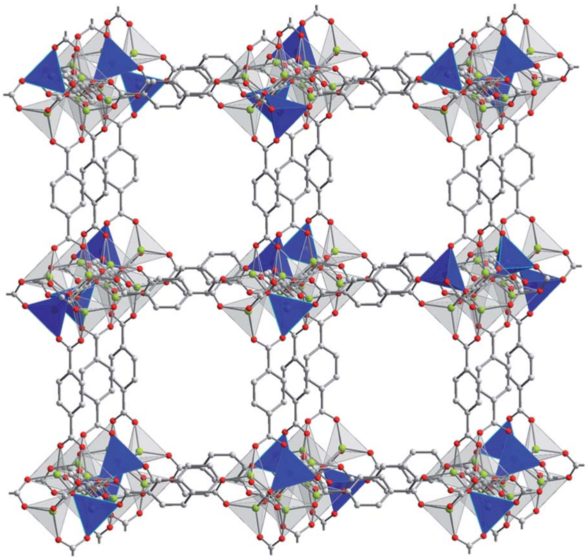


Fig. 2 Part of the crystal structure of $Ni_xZn_{4-x}O(BDC)_3$ ($x = 1$). Due to crystallographically-imposed symmetry, the position of Ni^{2+} centers (blue tetrahedra) within individual $NiZn_3$ clusters cannot be identified unambiguously, and these are depicted at random. Green, red and grey spheres represent Zn, O and C atoms, respectively. Hydrogen atoms are omitted for clarity.

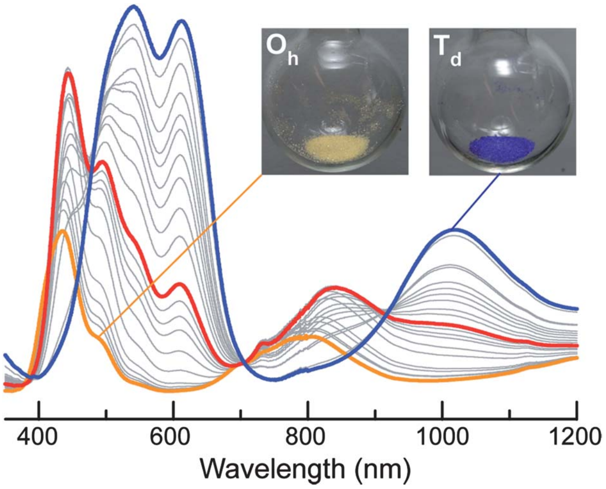


Fig. 3 *In situ* diffuse-reflectance spectra depicting the colour progression from yellow **$(DMF)_2$Ni-MOF-5** to blue **Ni-MOF-5** *via* a putative penta-coordinated Ni^{2+} intermediate (red trace). The inset shows optical images of the yellow and blue crystals.

spontaneous substitution of Ni^{2+} into MOF-5 is thermodynamically favourable and suggested that Ni^{2+}-substituted MOF-5 may also be accessible by direct synthesis. Indeed, heating mixtures of $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and H_2BDC in DMF afforded cubic yellow crystals whose diffraction pattern matched that of MOF-5. As expected for a kinetically controlled process, the Ni : Zn ratio in these samples depended on the relative concentrations of $Ni(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$, yet never exceeded 1 : 3 (Fig. S2, ESI†). In fact, increasing the Ni : Zn ratio in the reactant mixture above 6 : 1 led to selective formation of a yet unidentified crystalline green powder that did not match the X-ray diffraction pattern of any known Ni^{2+}-BDC or Zn^{2+}-BDC phases.[7] The upper limit of the Ni^{2+} content was similar to what had previously been reported as a curiosity in Co^{2+}-substituted MOF-5 materials.[8]

Table 1 Calculated Racah and ligand field parameters of various tetrahedral Ni^{2+} species based on observed transitions ν_2 and ν_3

Species	ν_3/cm^{-1}	ν_2/cm^{-1}	B/cm^{-1}	D_q/cm^{-1}	Ref.
$[Ni(NCO)_4]^{2-}$	16200	9460	511	311	11
$[NiCl_4]^{2-}$	14760	7470	405	206	11
$[NiBr_4]^{2-}$	13320	6995	379	201	11
$[Ni(OAr)_4]^{2-}$	16820	10000	867	540	4*d*
ZnO:Ni^{2+}	15720	8340	770	420	3*a*
ZnS:Ni^{2+}	12790	9750	560	475	3*a*
CdS:Ni^{2+}	12395	7840	570	400	3*a*
Ni-MOF-5	17406	9803	**1045**	**753**	This work

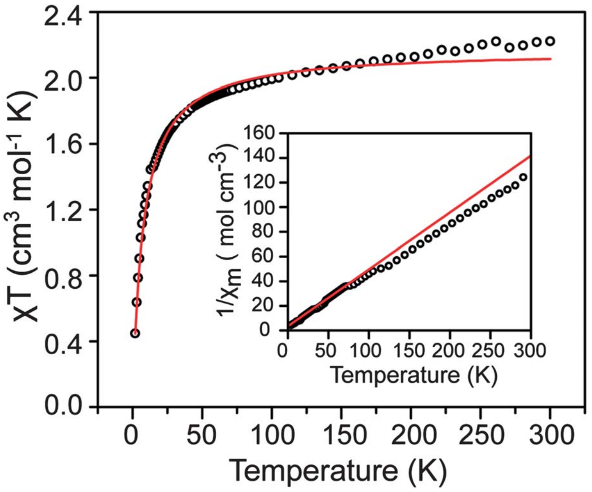
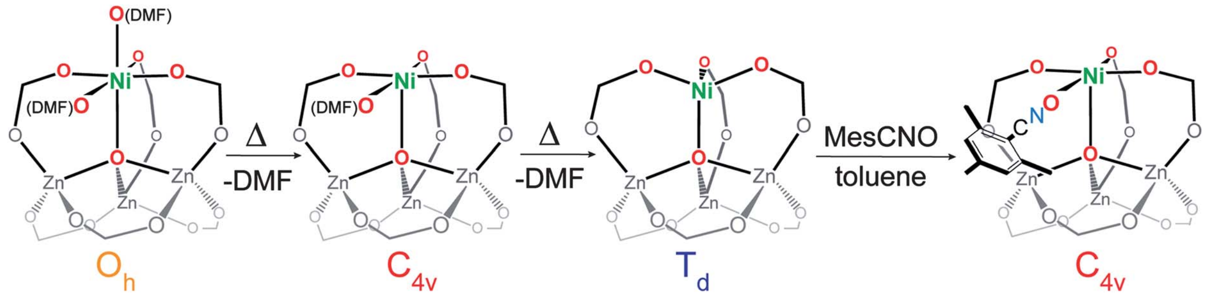


Fig. 4 The temperature dependence of $\chi_m T$ of evacuated **Ni-MOF-5** (circles). The red trace represents a fit obtained using julX.[17] We note that the observed temperature dependence of $\chi_m T$ is due to thermally accessible multiplet states of the $^3T_1(F)$ ground state, and not antiferromagnetic coupling. This is confirmed by a nearly (0,0) intercept of the Curie–Weiss plot (inset).

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_4O core and the MOF-5 lattice. Additional Ni^{2+} substitution into the ensuing $NiZn_3O$ 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 (Fig. S3, ESI†). $Zn_4O(carboxylate)_6$ 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 $(DMF)_{2x}Ni_xZn_{4-x}O(BDC)_3$ ($0 < x < 1$), (**$(DMF)_2$Ni-MOF-5**).[10]

Remarkably, heating **$(DMF)_2$Ni-MOF-5** under vacuum afforded deep blue–purple crystals of $Ni_xZn_{4-x}O(BDC)_3$ (**Ni-**



Scheme 1 Sequential loss of DMF molecules from a $(DMF)_2NiZn_3O(carboxylate)_6$ cluster and isolation of a MesCNO adduct. Symmetry labels indicate the idealized geometries at the Ni^{2+} centers.

MOF-5), a new analogue of MOF-5 that contains pseudo-tetrahedral Ni^{2+} supported only by oxygen ligands, shown in Fig. 2. Single-crystal X-ray diffraction analysis revealed that the asymmetric unit of **Ni-MOF-5** contains a single metal site, indicating that Ni^{2+} substitutes Zn^{2+} inside the SBU of a structure otherwise identical to MOF-5. Functional similarity to MOF-5 was also established by porosity measurements: blue **Ni-MOF-5** adsorbed 825 cm^3 of N_2/g at 1 atm and 77 K and exhibited a BET surface area of 3300(100) $m^2\ g^{-1}$, analogous to original MOF-5 (Fig. S9, ESI†).[12] FT-IR analysis of **Ni-MOF-5** confirmed the absence of a C=O stretch at 1660 cm^{-1} that would be expected if DMF were still coordinated to Ni^{2+} (Fig. S4, ESI†). In contrast to Be^{2+} and Co^{2+} analogues of MOF-5,[13] **Ni-MOF-5** is built from SBUs that do not have molecular analogues, highlighting the importance of the lattice in stabilizing otherwise inaccessible molecular species. Soaking basic zinc acetate crystals, $Zn_4O(O_2C{-}CH_3)_6$,[14] in an anhydrous DMF solution of $Ni(NO_3)_2{\cdot}6H_2O$ for up to three weeks led to the decomposition of the metal cluster, not the incorporation of Ni^{2+}. Therefore, $NiZn_3O(carboxylate)_6$ clusters can only be stabilized in the MOF lattice.

The pseudo-tetrahedral geometry around the Ni^{2+} and the homogeneity of **Ni-MOF-5** was quantified by diffuse-reflectance UV-Vis-NIR spectroscopy (blue trace in Fig. 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 $^3T_1(F){-}^3A_2$ transition of a d^8 tetrahedral ion (ν_2), while the doublet of peaks at 540 (18 500) and 608 nm (16 400 cm^{-1}) can be assigned to the $^3T_1(F){-}^3T_1(P)$ transition (ν_3), where ^3P is split by spin–orbit coupling into $^3P_0$ (A_1), $^3P_1$ (T_1), $^3P_2$ (E + T_2), respectively.[3a] A ligand-field analysis of this spectrum using a system of equations originally derived by Ballhausen[15g] (see ESI†) revealed Racah and D_q 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 $\chi_m T$ *vs.* T plot of **Ni-MOF-5**, shown in Fig. 4, revealed the presence of magnetically dilute Ni^{2+} ions and a room-temperature magnetic moment of 4.21 μ_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 μ_{eff} is further elevated by a temperature independent paramagnetism value of 0.2×10^{-6} $cm^3\ mol^{-1}$ 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 colour change that occurs when heating **$(DMF)_2$Ni-MOF-5**. These experiments, plotted in Fig. 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 colour reversal to yellow, sterically-demanding MesCNO afforded an orange adduct, whose spectrum matched that of the putative penta-coordinate **(DMF)Ni-MOF-5** adduct (Fig. S5, ESI†). Thus, Fig. 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 $(DMF)_yNiZn_3O(benzoate)_6$ (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 Fig. S7 (ESI†), 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 Fig. 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.

Acknowledgements

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