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Metal–Organic Frameworks

Assembly of the First Fullerene-Type Metal–Organic Frameworks Using a Planar Five-Fold Coordination Node**

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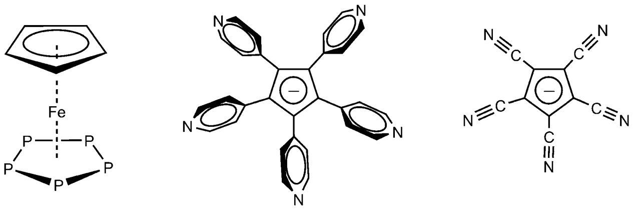
In the past twenty years there has been an explosion of interest in the controlled formation of metal–organic frameworks (MOFs),[1] not least because of the applications of extended porous materials of this class of compounds in gas storage (particularly H_2 and CO_2), gas separation, and catalysis.[2] The key structure-directing building blocks are the metal used (and its coordination preference) and the donor symmetry of the organic ligand component. These general principles of structural assembly based on the symmetry of metal- and ligand-containing nodes have also found broad applications in discrete molecular arrangements.[3] However, among the multitude of ligand nodes reported, planar five-fold nodes are particularly rare.[4–6] The major interest in these nodes stems from the fact that pentagons cannot be tiled into a planar sheet arrangement but would have to distort into a curved and domed structure. This has lead to the formation of discrete fullerene-like metal-organic arrangements, based on the linkage of twelve (and more) pentagonal nodes into a spherical supramolecule. This concept has recently been realized by the research groups of Scheer, utilizing the pentaphosphaferrocene ligand (**A**, Scheme 1),[4] and Williams, using the pentakis(4-pyridyl) cyclopentadienide ligand (**B**, Scheme 1).[5–7] Up to date this type of planar five-fold node has not been used for the formation of any network MOFs.

The coordination chemistry of the pentacyanocyclopentadienide ligand (Scheme 1, **1**)[8] has been almost unexplored to date.[5,9,10] However, recently we developed a simple synthesis of the starting material [Na{**1**}] [Eq. (1)] which greatly facilitates access to an extensive family of main group and transition-metal complexes of **1**.[11,12]

$$[Et_3NH][\mathbf{1}] + NaH \longrightarrow [Na\{\mathbf{1}\}] + H_2\uparrow + Et_3N\uparrow \qquad (1)$$



A B 1

Scheme 1. Planar, five-fold-symmetric ligand nodes with the potential for formation of fullerene-like metal–organic frameworks.

We show the key finding that readily accessed **1** can function as a five-fold symmetric ligand. However, instead of the formation of discrete supramolecules, as for all previous examples employing organic or organometallic ligands of this type, the structure of $[Na_{46}\{\mathbf{1}\}_{48}][Na]_2{\cdot}(MeNO_2)_x(Et_2O)_y$ reported here is the first example of a MOF based on fullerene units. We also show that its solvent-rich porous structure is highly metastable and solvent-directed.

During attempts to obtain single crystals of the unsolvated sodium salt [Na{**1**}] for X-ray structural determination, the complex was crystallized from $MeNO_2$ under a variety of conditions. It was found that slow crystallization of a solution of [Na{**1**}] in $MeNO_2$ by vapor diffusion using Et_2O as the non-solvent provides colorless crystals of $[Na_{46}\{\mathbf{1}\}_{48}][Na]_2{\cdot}(MeNO_2)_x(Et_2O)_y$ (cubic, *Pm*-3*n*, see the Supporting Information), whereas crystallization from hot $MeNO_2$ or layering of an $MeNO_2$ solution with toluene produces yellow-brown crystals of [Na{**1**}] (monoclinic, *C*2/*c*). Crystals of highly solvent-rich $[Na_{46}\{\mathbf{1}\}_{48}][Na]_2{\cdot}(MeNO_2)_x(Et_2O)_y$ are extremely labile and very rapidly lose solvent at room temperature and atmospheric pressure once isolated from the mother liquor. Although no meaningful TGA could be obtained owing to the rate of solvent loss, rapid handling of a few freshly isolated crystals which were dissolved immediately in [D$_6$]acetone allowed the relative ratio of $MeNO_2$ and Et_2O (x:y) to be estimated by NMR spectroscopy at around 1:2. X-ray powder diffraction reveals clean transformation of solvate $[Na_{46}\{\mathbf{1}\}_{48}][Na]_2{\cdot}(MeNO_2)_x(Et_2O)_y$ to unsolvated [Na{**1**}] and is completed after a period of around 1 h at 50 °C and 10 atm (Figure 1).

The X-ray structure of $[Na_{46}\{\mathbf{1}\}_{48}][Na]_2{\cdot}(MeNO_2)_x(Et_2O)_y$[14] displays the anionic coordination network $[Na_{46}\{\mathbf{1}\}_{48}]^{2-}$ comprising 46 sodium ions and 48 $[C_5(CN)_5]^-$ ligands per unit cell (Figure 2 a).[15] The structure is closely related to type I gas hydrates $46H_2O{\cdot}6X{\cdot}2Y$ (X,Y = CO_2,

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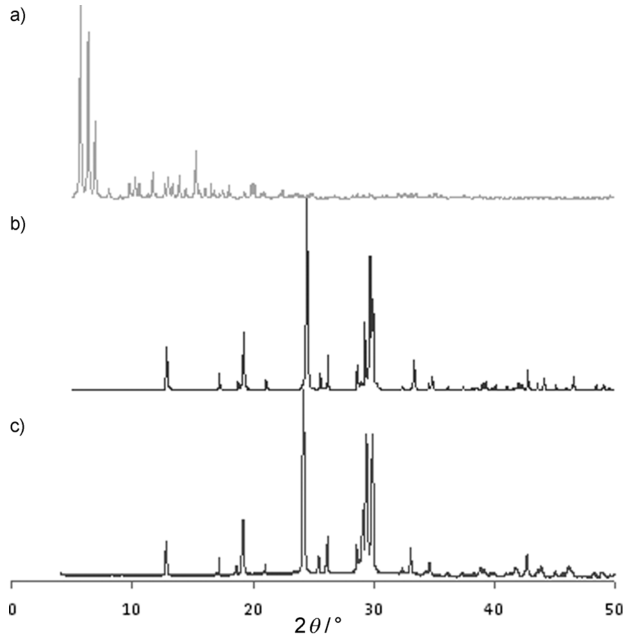

Figure 1. a) Simulated powder pattern based on single-crystal diffraction data for $[\mathrm{Na}_{46}\{\mathbf{1}\}_{48}][\mathrm{Na}]_2\cdot(\mathrm{MeNO}_2)_x(\mathrm{Et}_2\mathrm{O})_y$, b) simulated powder pattern based on single-crystal diffraction data of $\mathrm{Na}[\mathbf{1}]$, and c) measured powder pattern on $[\mathrm{Na}_{46}\{\mathbf{1}\}_{48}][\mathrm{Na}]_2\cdot(\mathrm{MeNO}_2)_x(\mathrm{Et}_2\mathrm{O})_y$ after 1 h at 50 °C and 10 atm.

$\mathrm{CH}_4)$[16] and the clathrasile mineral melanophlogite $(\mathrm{SiO}_2)_{46}\cdot 6\mathrm{X}\cdot 2\mathrm{Y}$ ($\mathrm{X}=\mathrm{N}_2$, CO_2; $\mathrm{Y}=\mathrm{CH}_4$, N_2).[17]

Every $[\mathrm{C}_5(\mathrm{CN})_5]^-$ ligand in $[\mathrm{Na}_{46}\{\mathbf{1}\}_{48}][\mathrm{Na}]_2\cdot(\mathrm{MeNO}_2)_x(\mathrm{Et}_2\mathrm{O})_y$ binds five metal ions in a planar, pentagonal fashion with nearly linear $\mathrm{C{\equiv}N{-}Na}$ units (range of the Na–N bond 2.374(4)–2.481(4) Å). The overall structure comprises of dodecahedral (D) and tetradecahedral (T) cage building blocks constructed from planar and pentagonal $\mathrm{Na}_5[\mathrm{C}_5(\mathrm{CN})_5]$ faces (the ratio of D to T cages being 1:3). There are two environments of $[\mathrm{C}_5(\mathrm{CN})_5]^-$ ligands in the $[\mathrm{Na}_{46}\{\mathbf{1}\}_{48}]^{2-}$ network. The first type (L′, marked in black in Figure 2b) binds the Na atoms that form the twelve pentagonal faces of the D cages. Each of these $\mathrm{Na}_5\mathrm{L}'$ pentagonal faces is then shared with a T cage. The T cages have four of these shared $\mathrm{Na}_5\mathrm{L}'$ pentagonal faces, with the remaining eight faces being constructed from the second type of $[\mathrm{C}_5(\mathrm{CN})_5]^-$ ligand which are unshared (L″, distinguished in gray in Figure 2b). The two empty hexagonal faces of the T cages are formed from the edges of two NaL′ and four NaL″ pentagonal faces. Because both T and D cages contain large cavities, 66 % of the unit cell constitutes solvent-accessible void volume.

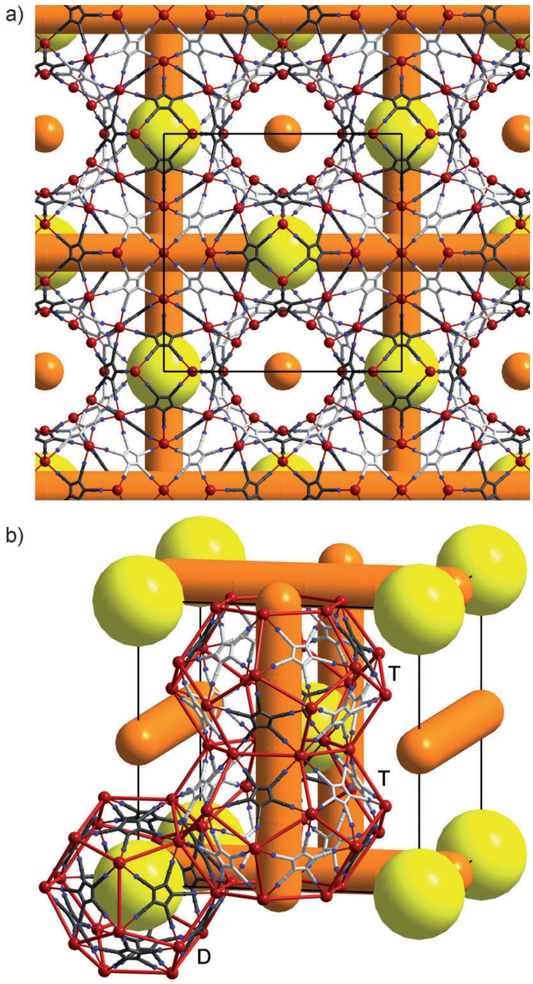

Figure 2. a) The anionic framework $[\mathrm{Na}_{46}\{\mathbf{1}\}_{48}]^{2-}$ of $[\mathrm{Na}_{46}\{\mathbf{1}\}_{48}][\mathrm{Na}]_2\cdot(\mathrm{MeNO}_2)_x(\mathrm{Et}_2\mathrm{O})_y$ (Na red, ligands L′ black, L″ light-gray, and N blue). Yellow spheres represent voids inside D cages and orange bars 1D channels running through T cages. The unit cell edges are shown as black lines. b) Schematic representation of the void structure of a unit cell. Yellow spheres represent voids inside D cages and orange bars 1D channels running through T cages.

The dodecahedral D cages contain isolated voids with a diameter of 13 Å (highlighted by the yellow spheres in Figure 2). The center of the each D cage (the origin of the unit cell) is marked by a large residual electron density peak, which refines fittingly as a unique sodium ion. This ion is surrounded by residual peaks, which can be attributed to O atoms of coordinated solvent molecules. The distance of these peaks to Na (around 2.3 Å) compares well with Na–O bond lengths of sodium ions that are solvated by ether ligands.[18] The high point group symmetry of this site ($m3$) and the diffuse character of the electron density prevented a detailed determination of the coordination environment of the encaged sodium ion. However, the site multiplicity demands that there are two D cages and two encaged ions per unit cell which is equal to the number of ions that are required to balance the negative charge of the coordination network.

Each of the T cages is joined through their hexagonal faces to two T cages to form linear channels that run parallel to the crystallographic *a*, *b*, and *c* axes without intersecting (marked by the orange bars in Figure 2). The group of six Na^+ cations that form the vacant hexagonal faces of each T cage mark the narrowest point of these channels (Na···Na distance of ca. 14.3 Å). A careful examination of the residual electron density around these Na^+ cations suggests that they are coordinated by $\mathrm{Et}_2\mathrm{O}$ ligands with partial site occupancy. All other Na^+ cations in the structure of $[\mathrm{Na}_{46}\{\mathbf{1}\}_{48}][\mathrm{Na}]_2\cdot(\mathrm{MeNO}_2)_x(\mathrm{Et}_2\mathrm{O})_y$ are four-coordinate and tetrahedral.

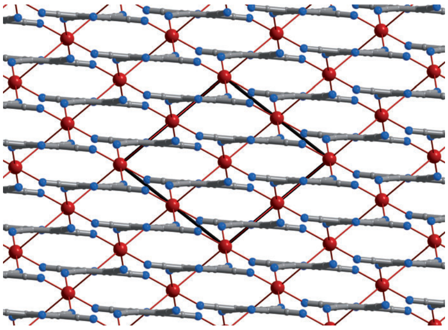

Figure 3. Structure of unsolvated [Na{**1**}] (Na red, N blue, and C gray).

The structure of the unsolvated [Na{**1**}] precursor material (Figure 3) makes a particularly interesting comparison with the solvated structure.[19] In this highly condensed arrangement the Na^+ cations exhibit distorted octahedral coordination. In return, the ligands (which display crystallographic C_2 symmetry) coordinate to six Na^+ cations through all five C≡N groups. However, in contrast to the linear C≡N–Na coordination in the solvate framework, the C≡N–Na angles in [Na{**1**}] are bent, ranging from 119.57(2) to 137.62(7)°. In addition, one N center of the ligand coordinates to two sodium ions so that **1** acts as a six-fold node. These contacts are considerably longer (2.7735(6) Å) than those involving N centers that only bind one Na ion (2.4278(8) and 2.4689(9) Å), which are comparable to the Na–N bond lengths observed in the solvate. The dense packing of [Na{**1**}] is facilitated by π stacking interactions between the ligands (ca. 3.35 Å) resulting in a layered arrangement (Figure 3). Underpinning the facile transformation of the solvate $[\mathrm{Na}_{46}\{\mathbf{1}\}_{48}][\mathrm{Na}]_2\cdot(\mathrm{MeNO}_2)_x(\mathrm{Et}_2\mathrm{O})_y$ to unsolvated [Na{**1**}] is the flexibility of the C≡N–Na interactions.

In conclusion, the $[\mathrm{C}_5(\mathrm{CN})_5]^-$ ligand (**1**) has been shown to be capable of behaving as a planar five-fold symmetric node in the formation of framework MOFs based on fullerene-like units. The fullerene-based architecture found in the highly solvent-rich complex $[\mathrm{Na}_{46}\{\mathbf{1}\}_{48}][\mathrm{Na}]_2\cdot(\mathrm{MeNO}_2)_x(\mathrm{Et}_2\mathrm{O})_y(\mathrm{H}_2\mathrm{O})_z$ is unique in the area of coordination networks. In common with many other network MOFs this arrangement is solvent-directed.[1] However, the particularly unstable situation found here is rare (i.e., at room temperature and atmospheric pressure), whereas it is very common in porous MOFs for the structure to collapse into more condensed phases upon removal of the host molecules (particular where the framework bonds are weak, as in this case).[20] The ability to interconvert solvated $[\mathrm{Na}_{46}\{\mathbf{1}\}_{48}][\mathrm{Na}]_2\cdot(\mathrm{MeNO}_2)_x(\mathrm{Et}_2\mathrm{O})_y$ and unsolvated [Na{**1**}] under mild solvent/vacuum conditions is a particularly interesting feature. In the light of our results we are currently undertaking further studies of the coordination and host–guest (gas and liquid) behavior of [Na{**1**}] and the use of complexes of **1** containing more robust metal–ligand bonds.[11]

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[13] This result is also consistent with BET measurements of the surface area of desolvated material (see the Supporting Information).

[14] Crystals of the solvate were mounted directly from solution using the oil-drop technique, thus preventing rapid desolvation.[13] Crystal data were collected on a Bruker Apex diffractometer using MoK_α radiation ($\lambda = 0.71073$ Å). Crystal structures were refined by full-matrix least squares against F^2 using all data (G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112). There was a sharp decline in reflection intensities at around 1.0 Å resolution, therefore the data were truncated at $2\theta = 45°$. The SQUEEZE routine in PLATON (A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7) was used for removing the contributions of diffuse solvent from diffraction intensities (a total of 3653 electrons for a void volume of 20240.9 $Å^3$), $\mathrm{C}_{10}\mathrm{N}_5\mathrm{Na}$, $M_r = 213.14$, $T = 100$ K, cubic space group $Pm\bar{3}n$, $a = 31.251(8)$, $V =$

30 522(14) Å^3, $Z = 48$, $\rho = 0.557$ g cm^{-3}, $R1$ $(I > 2\sigma(I)) = 0.0639$, $wR2$ (all data) = 0.1925. Na(3) is disordered and was split during the refinement on two positions. All atoms were refined anisotropically. An alternative refinement was carried out using the original dataset in order to determine the location of solvent molecules. Five unique solvent positions were obtained, three of which coordinate to Na ions and two which are because of lattice solvent in the channels. Only the O atoms of solvent molecules bound to Na(3) and Na(4) could be refined. The other three solvents refined well as disordered ether molecules, one of which is coordinated to Na(2), whereas the other two are noncoordinated and located inside the channel. It should be noted that this refinement does not account for all solvent molecules. There are void spaces that contain electron density that is too diffuse to model. Ether molecules were refined isotropically with restraints. $(C_{10}N_5Na)_{48}\cdot 54\,C_4H_{10}O$, $M_r = 13\,993.0$, $R1$ $(I > 2\sigma(I)) = 0.1081$, $wR2$ (all data) = 0.341 (CCDC 822358 and 822359).

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[19] $C_{10}N_5Na$, $M_r = 213.14$, $T = 180$ K, monoclinic $C2/c$, $a = 9.4453(5)$, $b = 10.2788(5)$, $c = 9.6495(5)$ Å, $\beta = 101.913(3)°$, $V = 916.66(8)$ Å^3, $Z = 4$, $\rho = 1.544$ g cm^{-3}, $R1$ $(I > 2\sigma(I)) = 0.0359$, $wR2$ (all data) = 0.1148. The data were collected on a Nonius KappaCCD diffractometer and refined by full-matrix least squares on F^2 (G. M. Sheldrick, SHELX-97, Göttingen, **1997**). (CCDC 822230).

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