Hydrogen-Bonding and Metal-Ion-Mediated Self-Assembly of a Nanoporous Crystal Lattice

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Hydrogen-bonding and metal-ion coordination are utilized to assemble a nanoporous crystal lattice. In the initial step of the assembly process, tecton **1** (4b,5,7,7a-tetrahydro-4b,7a-epiminomethanoimino-6*H*-imidazo[4,5-*f*][1,10]phenanthroline-6,13-dione) forms an octahedrally coordinated secondary building block with Fe^{II}, which in the final step assembles through hydrogen-bonding interactions to a nanoporous network. The secondary building blocks hydrogen-bond such that ribbons with two-membered channels are formed. Sheets are generated through hydrogen-bonding of the ribbons, which results in four-membered channels. In the crystal, the sheets are stacked parallel to each other, which results in a three-dimensional porosity.

Introduction

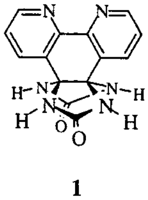
Supramolecular chemistry provides ways and means to design and generate organized equilibrium architectures of nanoscopic dimensions with novel structural and functional properties.[1,2] The final supramolecular entity (or a collection of such) evolves through a sequence of spontaneous but directed recognition, growth, and termination steps of suitably instructed components and specified interaction schemes. Non-covalent interactions, such as hydrogen bonding, metal ion coordnation, electrostatic and hydrophobic forces, permit precise positioning of molecular components in a well-defined supramolecular architecture.[1,2]

The implementation of the underlying principles of non-covalent interactions in molecular based materials allows the generation of spatially confined and macroscopically ordered ensembles. Long-range correlation of positions or orientations of the active constituents will be of paramount importance to fully explore the potential of supramolecular materials and of the derived functional devices. The improvement of existing and the development of novel methods to generate organized supramolecular assemblies represent a central objective and require the availability of structurally reliable, functional synthons to engineer periodic, three-dimensional architectures presenting specific structural characteristics.

Such is the case with nanoporous networks, which are at the focus of materials research due in particular to the commercial interest in chemical separation and heterogeneous catalysis.[3] Zeolites, pillared clays and related microporous materials, which have been studied extensively due to their useful catalytic properties, can now be engineered to some extent.[4−8] The challenges posed by the production of a well-defined porosity i.e. the formation of chiral and chemically functionalizable pores has recently stimulated the application of self-assembly principles originating from supramolecular chemistry based on hydrogen bonding and metal-ion coordination in this area.[1,2,9]

Metal-ion-containing devices are of particular interest as active components in functional materials because they possess a wide range of well-defined geometries and diverse properties that are relevant in electronic, optical, magnetic, and catalytic applications.[10] Self-assembly of the metallosupramolecular architecture is effected through ligands with suitable binding sites in a proper spatial arrangement.[1,2] On the other hand, hydrogen bonding is probably the most widely spread interaction motif in biological systems.[11] It, therefore, appeared of much interest to us to explore both interactions to pursue the goal of constructing well-defined nanoporous architectures containing functional components.[12]

Herein we describe the synthesis and structure of a nanoporous network through sequential self-assembly. Metal ion coordination of 4b,5,7,7a-tetrahydro-4b,7a-epiminomethanoimino-6*H*-imidazo[4,5-*f*][1,10]phenanthroline-6,13-dione (**1**) with Fe^{II} results in the octahedral secondary building block $[Fe^{II}(\mathbf{1})_3]Br_2$. Tecton **1** combines the versatile metal ion receptor phenanthroline[13] with urea[14] as the hy-



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drogen-bonding component. As a result of the nonplanar topology of the metal ion and hydrogen bond receptors the secondary building block forms a nanoporous, crystal lattice.

Results and Discussion

Ligand **1** was obtained as an insoluble white powder in 61% yield from the condensation of 1,10-phenanthroline-5,6-dione, prepared from 1,10-phenanthroline according to literature procedures,[15] and urea.[16]

When three equivalents of **1** were treated with one equivalent of $FeBr_2$ in degassed water under Ar the reaction mixture turned red (λ = 523 nm, ε = 8825 $cm^{-2}mol^{-1}$), characteristic of tris-phenanthroline Fe^{II} complexes.[17] The complex $[Fe^{II}(\mathbf{1})_3]Br_2$ (**2**) was isolated as red powder. Due to the octahedral symmetry of the complex, the imide protons are diastereotopic and their NMR resonance splits into two signals. Compound **2** is diamagnetic at room temperature in agreement with an octahedral low spin Fe^{II} complex. Compound **2** shows a quantitative loss of ether at 333 K and continuous loss of water between 373 and 564 K, after which it decomposes thermally. The elemental analysis, ^{1}H NMR spectroscopy, mass spectrometry, and single-crystal X-ray structure analysis are in agreement with the formula mentioned above.

Single crystals of **2** were obtained by crystallization from a water solution layered with *n*-pentane and diethyl ether. The compound crystallizes in the monoclinic space group *P*2/*n* (no. 13) with two cationic building blocks of the composition $[Fe^{II}(\mathbf{1})_3]^{2+}$ and four free bromide ions per unit cell. In addition, there are solvent molecules such as water and diethyl ether in strongly disordered positions. The hydrogen-bonded network made up of the cationic building blocks was identified without ambiguity. The building blocks are composed of an octahedral, monometallic Fe^{II} complex and three ligands of **1** (Figure 1 and 2). Two of the ligands, denoted *A* and *A*′, are equivalent by symmetry; the third nonequivalent ligand is referred to as *B*. The central metal atom and ligand *B* of the cationic building block are located on a C_2 axis [1/4, y, 1/4 (e)]. The coordination sphere of the iron cation can be described as a distorted octahedron of six nitrogen donor atoms, which is flattened along the pseudo-C_3 axis of the complex. A different way of describing the structure is to say that the phenanthroline units of each ligand are coordinated in a helical fashion around the metal center. The Fe−N distances vary between 1.990(8) and 2.066(8) Å. The nitrogen atoms of ligands *A* and *A*′ are denoted as N1 and N2, while those of ligand *B* are denoted as N7 and N7′. The bite angles of the bipyridyl groups are 80.1(3)° for N1−Fe−N2 (*A* and *A*′) and 82.7(4)° for N7−Fe−N7′ (B). The *trans* N−Fe−N angles are 172.3(3)° for N2−Fe−N7 and 175.1(5)° for N1−Fe−N1′. These values are similar to other phenanthroline and bipyridine complexes.[17,18] The pyridine rings in *A* and *A*′ are out of plane from each other by 8.6(5)°, whereas ligand *B* is planar. The central rings of *A* and *A*′ formed by C4, C5, C6, C7, C11 and C12 and the corresponding symmetric equivalents are not planar, with C12 and C12′ being significantly out of plane by 0.27(1) Å. The planes of the urea groups make an angle of 68.8(5)° to each other. The inner-ring angles of the pyridine groups of the phenanthroline entity vary from 114.6 to 119.3° for the C−N−C angles, from 118.8 to 125.5° for the C−C−N angles and from 115.5 to 121.8° for the C−C−C angles. The corresponding angles in the central all-carbon ring range from 114.1 to 124.5°.

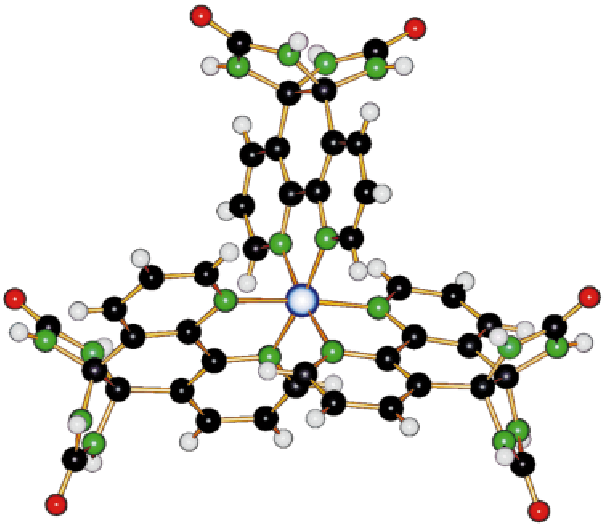

Figure 1. Crystal structure of the $[Fe^{II}(\mathbf{1})_3]$ building block

In the crystal, cationic units $[Fe(\mathbf{1})_3]^{2+}$ of the same helicity are arranged along the C_2 axes within one plane, the Λ-chains being oriented antiparallel to the Δ-chains. These linear strands of Λ- and Δ-building blocks are alternately linked to each other by hydrogen bonds through the urea part of the ligand, leading to a two-dimensional layered network. Thus, ligands *A* and *A*′ each form three (ligand *B* two) hydrogen bonds with two neighboring molecules of the same plane. In one cationic unit, the oxygen O1 of the urea group of *A* is bonded to H5(N5) of ligand *A*′ of the next cationic unit and vice versa: the oxygen O1′ of this neighboring molecule is hydrogen bonded to H5(N5) of the first cation. A crystallographic inversion center is found in the geometric middle of the hydrogen bonding system formed by O1−H5′(N5′) and O1′−H5(N5). The oxygen O2 of the second urea group of *A* is hydrogen bonded to H9(N9) of ligand *B*′ of a second neighboring molecule. The oxygen atom O3 of ligand *B* and its symmetry equivalents do not form hydrogen bonds to neighboring molecules because they point out of the plane in which the other hydrogen bonds are formed. In addition, the distance to the next layer is 11 Å (Fe−Fe distance), which is too far for binding. As a result, a Δ-helical cation only binds to four Λ-cations, and vice versa. Two types of channels are thus formed in the structure, one with an average diameter of about 10 Å, assembled from the formation of two hydrogen bonds between two ligands *B* and two ligands *A* of two neighboring

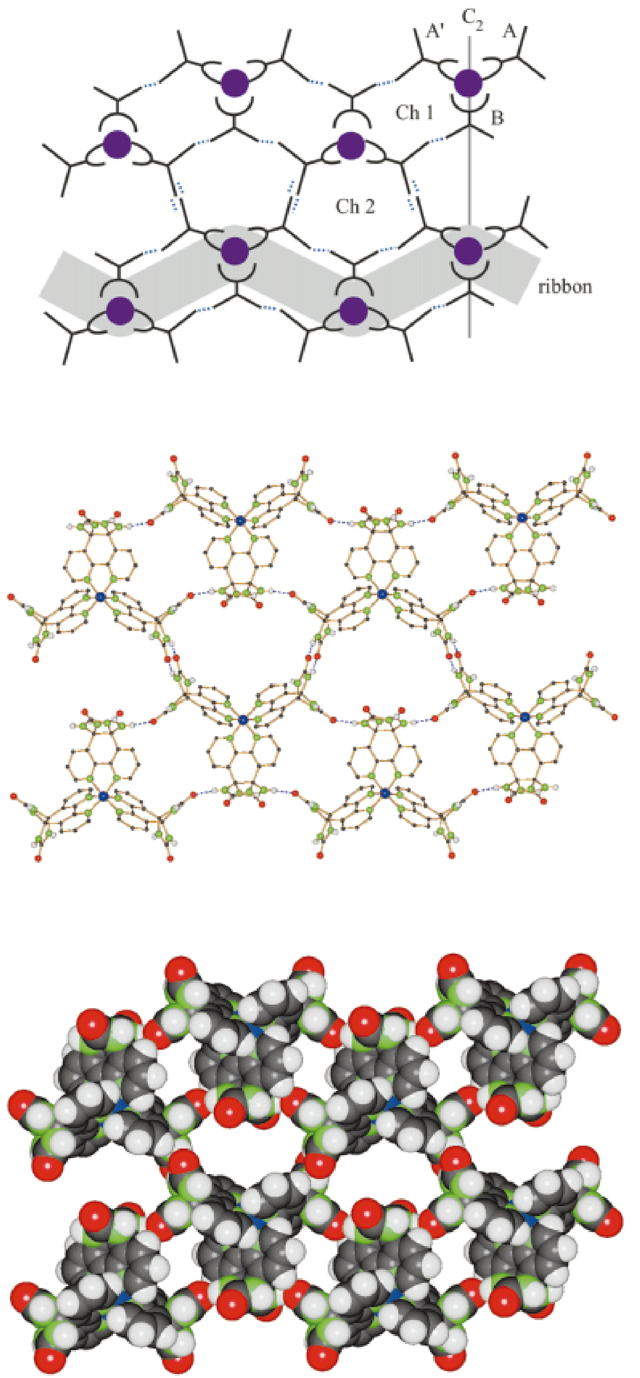

Figure 2. Schematic illustration, X-ray structure, and space-filling representation of a single sheet of the crystal lattice; ligands located on the C_2 axes are denoted *B* (in the plane of the sheet) while the other two ligands are denoted *A*; cationic units $[Fe^{II}(\mathbf{1})_3]$ of opposite chirality are hydrogen-bonded between *A* and *B* ligands, which results in an extended ribbon and a square cavity with a diameter of 1 nm (Ch 1); the ribbons form an extended sheet through the hydrogen bonds of *A* ligands such that homochiral $[Fe^{II}(\mathbf{1})_3]$ building blocks are located along the C_2 axes; four cationic units form a cavity with a diameter of approximately 1.2 nm (Ch 2) (all metal ions are in the plane of the sheet, some hydrogen atoms omitted for clarity)

cationic units, leading to a square two-membered ring system (channel 1). The other channel is due to six hydrogen bonds between ligands *A*, *A′*, and *B* of four cationic units and has the approximate dimensions 8 × 12 Å. It yields a heart-shaped, four-membered cavity (channel 2).

As the cationic units are arranged in a parallel manner, the maximum number of hydrogen bonds is formed with adjacent units in order to stabilize the structure. The bulky urea groups prevent a close approach and consequently a development of pi-stacking interactions of adjacent phenanthroline groups.

The total number of hydrogen bonds for one cationic building block, counting the donors and acceptors, is 18, six H-acceptors (oxygen) and 12 donors (N−H). Considering that the hydrogen bonds are only formed between ligands of different cationic units and that each acceptor reacts with one donor at a time, the maximum number of H-bonds formed is 12, of which only eight (4 donors + 4 acceptors) are used. The remaining donors and acceptors do not participate in bonding interactions due to the two-dimensional structure. Each of the six urea fragments of one cationic building block is thus involved in at least one H-bond. Considering the helical way in which the ligands are arranged around the metal ion, four of the six oxygen atoms come to lie in approximately one plane, whereas the other two are oriented perpendicular to this plane and cannot participate in H-bonding as the next layer is too far away. As for the N−H fragments, four of them are oriented in approximately the same plane as the four coplanar oxygen atoms and participate in the structure formation whereas the other eight point out of the plane of the layer.

The maximum number of strong, linear H-bonds is formed if the cationic units are arranged anti-parallel to each other on C_2 axes. This arrangement results in the formation of a ribbon with two-membered square channels of 1 nm diameter (channel 1). The ribbons are stacked in a plane by formation of six H-bonds to yield a four-membered ring with a heart-shaped cavity of approximately 1.2 nm in diameter (channel 2). Both channels run parallel to the *a* axis of the unit cell [1 0 0]. In the crystal, the layers are stacked parallel to each other in an alternating ABA-type fashion. Due to intercalating solvent molecules the interlayer distance is approx. 9.5 Å, which is too large for direct (short range) interactions.

Conclusion

In conclusion, we describe a potential tecton with a reliable structural paradigm such as is needed for the systematic design of metallosupramolecular crystalline materials with predictable structures and tailorable functions. Complex **2** yields a nanoporous, two-dimensional architecture which is stable up to 564 K. The formation of this material demonstrates self-organization by spontaneous self-assembly involving two types of molecular recognition phenomena, namely metal ion recognition in the first step and hydrogen bonding in the final step to establish the 3D architecture. Finally, it should be pointed out that the connectivity is reminiscent of inorganic architectures such as zeolites and clays. However, the intrinsically chiral metallosupramolecular constituents permit, in contrast to many achiral aluminosilicate precursors of other inorganic materials, the formation of chiral porous networks, which would offer attractive possibilities in recognition and catalysis. The nonparticipating H-bonding donors and acceptors may furthermore serve as anchors, for example for suitable amphiphiles, to functionalize the interior. Further studies on creating nano- and microporous architectures based on this compact synthon are in progress.

Experimental Section

Ligand 1: Condensation of 1,10-phenanthroline-5,6-dione (4 g, 119 mmol) and urea (2.5 g, 41.7 mmol) in toluene (100 mL) with trifluoroacetic acid (10.6 g, 93 mmol) yielded 61% (3.4 g, 11.6 mmol) of **1** as an insoluble white powder.[16] 1,10-Phenanthroline-5,6-dione was prepared from 1,10-phenanthroline according to literature procedures in 45% yield.[15] − MS: m/z = 295.2; calcd. 294.3 [M + H]. − ^{1}H NMR ([D$_6$]DMSO, room temperature): δ = 8.73 (d, J_1 = 4.3 Hz, 2 H), 8.32 (s, 4 H), 8.08 (d, J = 7.8 Hz, 2 H), 7.74 (dd, J_1 = 7.7 Hz, J_2 = 4.6 Hz, 2 H). − $C_{14}H_{10}N_6O_2$ (294.27): calcd. C 57.14, H 3.43, N 28.56; found C 57.29, H 3.51, N 28.52.

[Fe^{II}(1)$_3$]Br$_2$ (2): Three equiv. of **1** (1 g, 3.4 mmol) were treated with 1 equiv. of $FeBr_2$ (237 mg, 1.1 mmol) in degassed water (40 mL) under Ar. The reaction mixture turned red as a result of formation of the tris-phenanthroline Fe^{II} complex.[16] Complex **2** was isolated as red powder in 60% yield (725 mg) after recrystallisation. − MS: m/z = 724; calcd. 723 [Fe^{II}(**1**)$_2$Br]$^+$. − ^{1}H NMR ([D$_6$]DMSO, room temperature): δ = 7.39 (1 H), 7.71 (1 H), 8.27 (1 H), 8.43 (1 H), 8.70 (1 H). − ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 °C): δ = 159.62, 155.39, 151.02, 137.62, 135.14, 129.58, 75.31. − $C_{42}H_{30}Br_2FeN_{18}O_6(H_2O)_{2.5}$ 1143.52): calcd. C 44.12, H 3.09, N 22.05; found C 44.13, H 3.02, N 21.9. − UV/Vis (H_2O): λ (ε [cm^{-2} mol^{-1}]) = 523 nm (8825), 493 (shoulder), 315 (34440).

Compound **2** shows quantitative loss of ether at 333 K and continuous loss of water between 373 and 564 K after which it decomposes thermally.

Crystal Structure Data for 2: $[Fe(C_{14}H_{10}N_6O_2)_3]\cdot 2Br\cdot 2CH_3CN\cdot (CH_3CH_2)_2O\cdot 9H_2O$. Diffractometer and data collection: STOE IPDS (−70 °C), graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), monoclinic, space group $P2/n$, a = 11.098(2) Å, b = 16.720(3) Å, c = 19.760(4) Å, β = 96.79(3)°, V = 3640.9(13) Å^3, Z = 2, μ = 1.373 mm^{-1}, F(000) = 1388, ρ = 1.261 Mg/m^3, $2\Theta_{max}$ = 51.8°. Primary structure solution by direct methods (SHELXS-92).[20] Anisotropic refinement for all non-hydrogen atoms of the cationic complex (SHELXL-93).[21] 6232 Measured reflections, 5961 independent [R(int) = 0.1994] of which 5961 reflections were used to refine 437 parameters. The solvent and anionic structure parts show multifold disorder. Therefore atoms of solvent were refined isotropically on split positions. The structure was refined against F^2 (full-matrix least-squares). $R1$ = 0.1395 [for 2994 reflections with $F > 4\sigma(F)$, $R1$ = 0.2717 (all data)] and $wR2$ = 0.2461 [$wR2$ = 0.3288 (all data)]. GooF on $F^2 = S$ = 1.117; max./min. residual density +1.045/−0.403 e/Å^3. Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146338. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.)+ 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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