temperature, without reaching, however, the static situation of a well-resolved paramagnetic hyperfine structure at 4.2 K.[16] The parameters of the doublet characterized by the larger quadrupole separation have been measured from the spectrum recorded at 80 K (δ/iron foil at 293 K = 0.50(1) mm s^{-1}, ΔE_Q = 1.39(2) mm s^{-1}) and are consistent with those of (μ-oxo)-diiron(III) complexes ($\delta = 0.36-0.56(1)$ mm s^{-1}, $\Delta E_Q = 1.3-1.8$ mm s^{-1}).[1, 2] Those of the doublet characterized by the smaller separation have been obtained only from the spectrum recorded at 293 K and not that at 80 K because of line broadening ($\delta = 0.72(1)$ mm s^{-1}, $\Delta E_Q = 0.67(2)$ mm s^{-1}). These parameters indicate that the corresponding iron site is in a less distorted octahedral environment. Close inspection of the structural data shows that though the N_4O_2 coordination environments of the three iron atoms are roughly equivalent, the central iron atom has the most distorted octahedral coordination (based on the standard deviation for the Fe–N distances and the average L-Fe-L angle deviation from 90°) and should thus be associated with the doublet exhibiting the larger quadrupole splitting ($\Delta E_Q = 1.39(2)$ mm s^{-1}). The crystallographically pseudo-equivalent terminal iron atoms have less distorted ligand environments and are not distinguished from each other in the Mössbauer spectra.

Complex **2** further illustrates the rich and growing chemistry of carboxylato(oxo)iron compounds. Its unprecedented structure with a bent triiron unit gives rise to unusual spectroscopic and magnetic properties. This is the first example of the transformation of a (μ-oxo)diiron(III) unit into a complex with a triiron chain. Complex **2** may represent a missing link in the series of precursors for mineralized iron(III) compounds (e.g., the polyiron core of ferritin).[1c] The presence of an exchangeable acetato ligand might allow further controlled polymerization of the iron chain.

Experimental Procedure

The synthesis of **1** is described in ref. [3e]. **2** · EtOAc: Addition of 1,2-dimethylimidazole (4.5 µL. 1.5 equiv) to **1** (30 mg, 25 µmol) in 3 mL of acetonitrile resulted in a red solution. Crystals were obtained by vapor diffusion of ethyl acetate into the mother liquor and gave satisfactory analysis (60% yield). Anal. calcd for $[Fe_3O_2(C_{12}H_8N_2)_6(CH_3CO_2)_2](ClO_4)_3 \cdot C_4O_2H_8$: C 53.82, H 3.47, N 9.42, Cl 5.95, Fe 9.38. Found: C 53.44, H 3.58, N 9.62, Cl 5.97, Fe 9.20. UV/VIS (CH_3CN, 25 °C): 378 nm (12700 M^{-1} cm^{-1}).

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[6] Diffraction-quality red crystals (0.4 × 0.2 × 0.1 mm) were obtained from ethyl acetate/acetonitrile. The complex **2** · EtOAc crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 13.336(4)$, $b = 22.804(6)$, $c = 25.181(7)$ Å, $\beta = 92.41(2)$, $V = 7668.7$ Å^3, $Z = 4$. 5299 Unique observed reflections, for which $I > 3.0\sigma(I)$, were collected at 293 K with $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) to $2\theta_{max} = 26°$ on an Enraf-Nonius CAD4F X-ray diffractometer. The structure was solved by direct methods and refined to $R = 0.074$, $R_w = 0.099$. Further details of the crystal structure investigation may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation.

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[16] To prove these relaxation phenomena it is necessary to reach a static state and observe the internal magnetic field. This can be obtained by applying a weak magnetic field. When an external magnetic field of 2 Tesla was applied at 7 K, the magnetic fluctuations were frozen, and analysis of the resulting Zeeman spectrum allowed us to measure an internal effective magnetic field of roughly 3.9 T.

Mutually Interpenetrating Sheets and Channels in the Extended Structure of [Cu(4,4'-bpy)Cl]**

O. M. Yaghi* and Guangming Li

In memory of Mouannes A.-F. Yaghi

The development of synthetic strategies for the design of solid-state structures from soluble components is of intense current interest.[1] The building-block approach has been utilized for the rational assembly of inorganic[2] and organometallic[3, 4] crystalline solids. We have initiated a program aimed at using this approach in the preparation of crystalline materials possessing open-framework structures with cavities or channels. Simple ligands such as 4,4'-bipyridine (4,4'-bpy) are chosen for their demonstrated ability to act as rods linking together metal centers to give extended solids with diverse topologies.[5] This report shows how chloro-bridged Cu^I dimers with M–M bonding may be combined with 4,4'-bpy to form sheets of [Cu(4,4'-bpy)Cl]-containing cavities with dimensions of nearly 16 × 26 Å.

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In the overall structure, these sheets are interlocked with other sheets to form a three-dimensional, neutral network containing a two-dimensional, intersecting system of channels of smaller aperture.

Crystals of [Cu(4,4'-bpy)Cl] were obtained by diffusing solutions of CuCl and 4,4'-bpy into ethylene glycol. The compound was formulated by elemental analysis[6] and characterized by X-ray single-crystal analysis.[7, 8] The extended structure is made up of the building-block unit shown in Figure 1: dimeric Cu^I centers are bridged by two chloro ligands, and each metal atom is linked to two 4,4'-bpy ligands to form a slightly distorted tetrahedron with N2-Cu-N1 = 125.6(6)°, N1-Cu-Cla = 99.6(4)°, and Cl-Cu-Cla = 104.9(4)°. In addition, the N1 and N2 pyridine rings are twisted by 22.0(5)° and 15.60(4)° relative to the N1b and N2c rings. These distortions are due to the fact that each 4,4'-bpy acts as a bismonodentate ligand linking two Cu^I dimeric units, as shown in Figure 2; this results in formation of an infinite hexagonal array made up of Cu^I dimers with M–M bonding and 4,4'-bpy ligands, and containing pores measuring around 16 × 26 Å. However, in the absence of large guest molecules to fill the pores during the molecular assembly process, other perpendicular and symmetry-equivalent sheets of the same structure and composition are found to occupy the pores. Although, these two infinite sheet arrays are mutually perpendicular, they are not bound to each other, but are instead interlocked, like catenanes, as independent two-dimensional networks.[9]

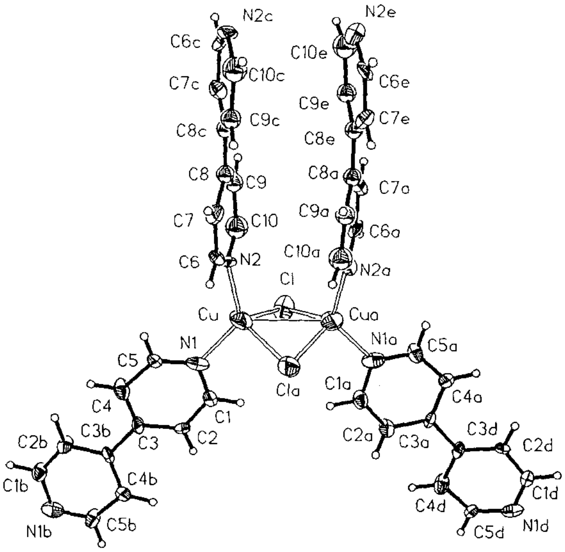

Fig. 1. A perspective drawing of the μ_2-chloro-bridged dinuclear building-block unit present in crystalline [Cu(4,4'-bpy)Cl] Non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of electron density. Hydrogen atoms are represented by arbitrarily small spheres. Atoms labeled with a–e are related to atoms without these letters by the following symmetry operations: for a, $1 - x, 1/2 - y, z$; b, $-1/4 + y, 1/4 + x, 1/4 - z$; c, $3/4 - y, 3/4 - x, -1/4 - z$; d, $5/4 - y, 1/4 - x, 1/4 - z$; and e, $1/4 + y, -1/4 + x, -1/4 - z$. Selected interatomic distances [Å] and angles [°]: Cu-Cl 2.415(6), Cu-Cla 2.475(6), Cu-Cua 2.763(7), Cu-N1 1.97(1), Cl-Cu-N1 105.1(5), Cl-Cu-N2 108.3(4), Cl-Cu-Cla 104.9(2), N1-Cu-Cla 99.6(4), N2-Cu-Cla 115.5(5), N1-Cu-N2 125.6(6), Cl-Cu-Cua 56.6(2), Cu-Cl-Cua 68.8(2), Cua-Cu-Cla 54.6(2), N1-Cu-Cua 101.9(4) (cf. ref. [8]).

The overall structure thus formed is a neutral three-dimensional framework, in which the interpenetrating two-dimensional networks fill up most of the pore space with channels of only small diameter (≈ 2 × 4 Å) remaining open (Figs. 3 and 4). It was found from the X-ray analysis that these channels are too small to accommodate acetonitrile or dimethyl sulfoxide (DMSO) solvent molecules as guests in the crystal. This was confirmed by thermal gravimetric analysis performed on a 35.306 mg sample, which showed that the material begins to degenerate at 175 °C to give only pyridine, chloride, and copper metal. Also, ^{13}C CPMAS (cross polarization magic angle spinning) solid-state NMR data showed only resonances due to the 4,4'-bpy carbon atoms and none that could be attributed to possible guest species.

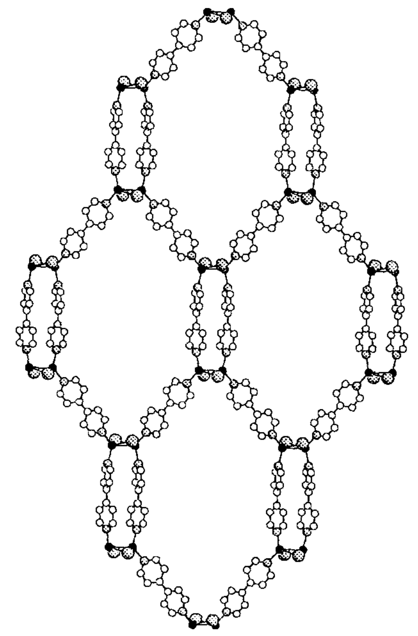

Fig. 2. A SCHAKAL drawing showing how the organization of the building-block unit $[Cu(4,4'\text{-bpy})Cl]_4$ results in the construction of infinite porous sheets that are a fragment of the crystal structure of [Cu(4,4'-bpy)Cl]. The hydrogen atoms on the bipyridine units have been omitted for clarity. Dark spheres, Cu; large shaded spheres, Cl; small shaded spheres, N; and open spheres, C.

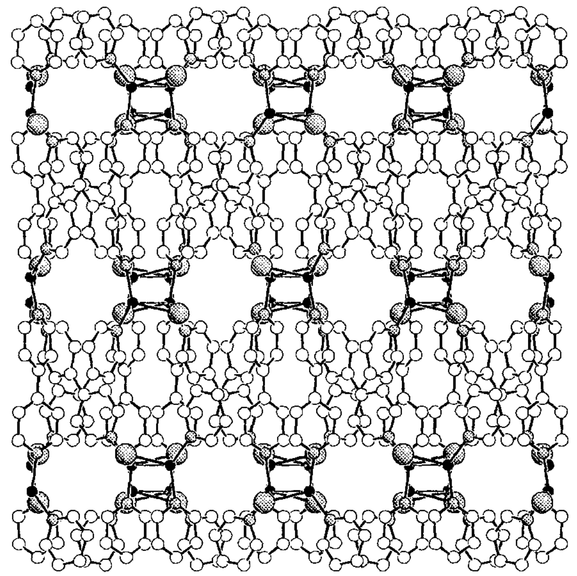

Fig. 3. A SCHAKAL drawing of the overall crystal structure of [Cu(4,4'-bpy)Cl] showing how infinite sheets are interlocked to fill the pores (shown in Fig. 2) leaving only small empty channels in the structure. The omissions and shadings are as in Figure 2.

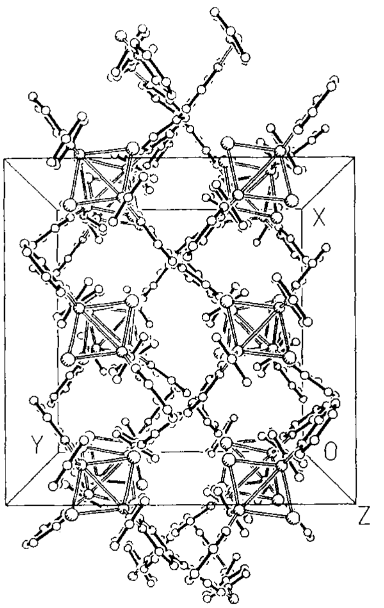

Fig. 4. A plot of the structure showing the unit cell packing and the perpendicular interpenetrating arrangement of the Cu–Cu units. Small partially shaded spheres, N; medium-sized partially shaded spheres, Cu; large partially shaded spheres, Cl; open spheres, C.

The size of the channel openings is very similar to those observed in some zeolite molecular sieves, such as, analcime (2.2–2.4 Å) and natrolite (2.6 × 3.9 Å),[10, 11] where water (kinetic diameter ≈ 2.8 Å) is known to penetrate and diffuse into the channels. We found that the material synthesized is stable in air indefinitely and in boiling water for up to 1 h. Currently, we are attempting to evaluate its potential use in water adsorption and in gas separation processes.

Experimental Procedure

[Cu(4,4'-bpy)Cl]: The addition of an acetonitrile solution (10 mL) of 4,4'-bpy (0.78 g, 5.0 mmol) to an acetonitrile solution (50 mL) of CuCl (0.50 g, 5.0 mmol) resulted in the immediate formation of a dark red, microcrystalline material. This solid was collected and washed with ethanol (3 × 20 mL) followed by diethyl ether (3 × 20 mL), and dried under vacuum for 24 h to give 1.2 g (94%) [7]. Crystals suitable for X-ray single-crystal analysis were obtained by diffusing a DMSO solution of 4,4'-bpy (0.10 M) into an acetonitrile solution of CuCl (0.10 M) through ethylene glycol (3 mL). This results in the formation of red, rectangular parallelepiped-shaped crystals at the acetonitrile/ethylene glycol interface. Alternatively, large crystals were obtained by diffusing solutions of the reactants in a 5 mm thick mineral oil.

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[8] Single crystals of [Cu(4,4'-bpy)Cl] were analyzed at 20 °C. Tetragonal, space group $I4_1/acd$, (no. 142) with $a = 14.246(4)$, $c = 38.596(12)$ Å, $V = 7833(3)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.731$ g cm^{-3} and $\mu_a(\mathrm{Mo_{K\alpha}}) = 2.46$ mm^{-1}. A total of 1345 independent absorption-corrected reflections having $2\theta(\mathrm{Mo_{K\alpha}}) < 45.8°$ (the equivalent of 0.6 $\mathrm{Cu_{K\alpha}}$ spheres) were collected on a computer-controlled Nicolet autodiffractometer with full 2.00° wide ω scans and graphite-monochromated $\mathrm{Mo_{K\alpha}}$ radiation. The structure was solved by direct methods (SHELXTL-PC) and the resulting structural parameters were refined by least-squares techniques to converge ($R1$ (unweighted, based on $|F|) = 0.050$ for 465 independent absorption-correction reflections having $2\theta < 45.8°$ and $I > 2\sigma(I)$) using counter-weighted full-matrix least-square techniques and a structural model which incorporated anisotropic thermal parameters for C8, C9, and C10 and for all hydrogen atoms. The hydrogen atoms were fixed at idealized sp^2-hybridized positions with C–H bond lengths of 0.96 Å, and their isotropic thermal parameters were fixed at values 1.2 times the equivalent isotropic thermal parameters of the carbon atoms to which they are covalently bonded. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-58460.

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Investigation of Self-Assembled Supramolecular Species in Solution by IL-ESMS, a New Mass Spectrometric Technique**

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Alain Van Dorsselaer, and Jean-Marie Lehn*

The spontaneous assembly of complementary components into designed architectures has developed recently into a central theme of supramolecular chemistry.[1] In particular, hydrogen bonding has been used for the generation of supramolecular assemblies in solution, in liquid crystals, and in the solid state.[2–5] Whereas solid-state structures may be determined by X-ray crystallography, procedures are greatly needed for investigation of organized species formed in solution, in particular to determine whether their structures are the same as in the solid. Vapor-phase osmometry, membrane osmometry, and gel permeation chromatography have been used and generally yield molecular weights with degrees of error that can be as large as

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