Synthesis and structural characterization of $\{[Fe(OH)(H_2bta)](H_2O)\}_n$ (3-D) (H_4bta = benzenetetracarboxylic acid)

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The coordination polymer $\{[Fe(OH)(H_2bta)](H_2O)\}_n$ from H_2O, benzenetetracarboxylate (H_4bta = benzenetetracarboxylic acid) and Fe^{III} ions has been hydrothermally synthesised and structurally characterised by single crystal X-ray crystallography.

The development of multidimensional structures from molecular building blocks is attractive due to the design and control of a wide range of supramolecular architectures.[1–4] It is driven by not only pure academic interest but also the continued discovery and development of useful applications such as chemical, physicochemical and catalytic properties.[5–10] The use of molecular units for the purpose permits reactions to take place with that the structural integrity of the building units can be maintained throughout the reaction aspect that allows for their use as modules in the assembly of extended structures. Molecular units can be designed to direct the formation of target structures and to impart desired physical properties to solid-state materials.[11] We are interested in the construction of extended structures with the bridging ligand benzenetetracarboxylic acid (H_4bta) and transitional metal ions such as Fe^{3+}, Fe^{2+} and Co^{2+}. We have reported on several 2-D coordination polymers based on this ligand.[12–14] The results show that the great ability of this ligand in fitting for the design of novel solids is very interesting. To understand the chemistry of this connector, we continued to experiment the system of this ligand and transitional metal ions and obtained a novel 3-D structure of coordination polymer $\{[Fe(OH)(H_2bta)](H_2O)_2\}_n$ **1** constructed on the basis of the H_2bta ligand and Fe–O polymeric chains. We report here the synthesis and characterization of this compound.

Using the hydrothermal method, we prepared compound **1** from a mixture of $FeCl_3{\cdot}6H_2O$ (3.00 g), NaOH (1.2 g), benzenetetracarboxylic acid ($H_4C_{10}O_8$, 1.80 g), MgO (0.30 g) and H_2O (20 ml) in a 30 cm^3 Teflon lined reactor (pH 7).†

X-ray crystal structure analysis‡ reveals that the formation of compound **1** rests on both the metal irons and organic H_2bta ligands. Figure 1 shows that the crystallographically independent unit of compound **1** is composed of the atoms C^1, C^2, C^3, C^4, C^5, O^1, O^2, O^3, O^4, O^5, O^w and Fe. The metal ion has a distorted octahedral environment with six oxygen donors, of which the equatorial four are carboxyl O atoms from four H_2bta units,

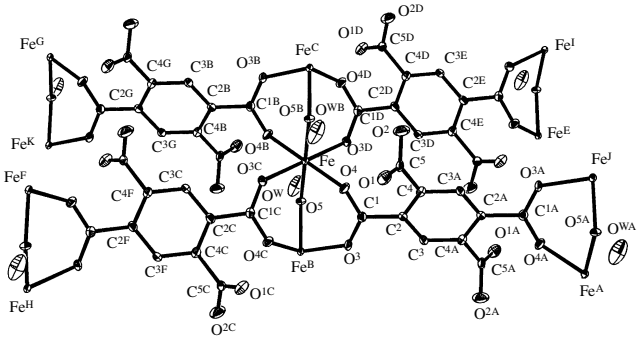

Figure 1 Molecular structure for compound **1**. Selected bond lengths (Å): Fe–O^{5B}, 1.950(2); Fe–O^5, 1.950(2); Fe–O^{3D}, 2.035(2); Fe–O^{3C}, 2.035(2); Fe–O^{4B}, 2.045(2); Fe–O^4, 2.045(2); C^5–O^1, 1.213(5); C^5–O^2, 1.304(5); C^1–O^3, 1.249(4); C^1–O^4, 1.269(4); selected bond angles (°): O^{5B}–Fe–O^5, 180.0; O^{5B}–Fe–O^{3C}, 90.58(9); O^5–Fe–O^{3C}, 89.42(9); O^{5B}–Fe–O^{3D}, 89.42(9); O^5–Fe–O^{3D}, 90.58(9); O^{3C}–Fe–O^{3D}, 180.0; O^{5B}–Fe–O^4, 90.25(10); O^5–Fe–O^4, 89.75(10); O^{3C}–Fe–O^4, 94.09(11); O^{3D}–Fe–O^4, 85.91(11); O^{5B}–Fe–O^{4B}, 89.75(10); O^5–Fe–O^{4B}, 90.25(10); O^{3C}–Fe–O^{4B}, 85.91(11); O^{3D}–Fe–O^{4B}, 94.09(11); O^4–Fe–O^{4B}, 180.0; Fe–O^5–Fe^C, 126.4(2).

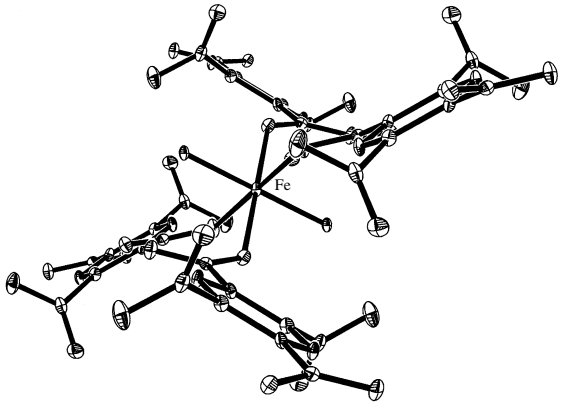

Figure 2 Two groups of benzenetetracaboxylate ligands around one metal centre.

the axial two are single bridging oxygen atoms. The Fe–O distance is 1.950(2) to 2.045(2) Å, while bond angles at the bridging oxygen atoms are 126.4°. The bond valence calculations based on the Fe–O bond lengths made using published empirical parameters[15] show that Fe is +3.07.

In Figure 1, the H_2bta units all exhibit an unexpected μ^4-connecting mode by coordinating two opposite carboxyl groups to four metal atoms (such as Fe^K, Fe^G, Fe and Fe^C), the remaining two carboxyl groups keep free. It indicates that the tetradentate ligand plays the role of a bidentate ligand but exhibits a novel μ^4-linking mode. Surrounding one central metal atom, the four H_2bta ligands are divided into two paralleled groups. The benzene rings in two opposite H_2bta units are parallel, but those in the neighbour two, such as the plane (C^2, C^3, C^4, C^{2A}, C^{3A}, C^{4A}) and the plane (C^{2D}, C^{3D}, C^{4D}, C^{2E}, C^{3E}, C^{4E}), exhibits a dihedral angle of 62.1° (Figures 1 and 2).

† The solution was sealed and heated to 160 °C for 72 h under autogeneous pressure. The obtained brown crystals were isolated (58% yield based on bta) by filtration and washing with distilled water. IR spectra (KBr, ν/cm^{-1}): 1700 (s), 1660 (m), 1540 (vs), 1490 (s), 1415 (s), 1380 (vs), 1328 (s), 1190 (vs), 1120 (s), 1070 (m), 915 (s), 848 (s), 800 (s), 760 (s), 662 (s), 575 (m), 515 (vs), 450 (m), 310 (s). Found (%): C, 35.22; H, 2.00; Fe,16.40. Calc. for $C_5H_{3.5}Fe_{0.5}O_5$ (%): C, 35.01; H, 2.06; Fe, 16.28.

‡ *X-ray structure determination for compound* **1**. Monoclinic, space group *C*2/*c*, a = 20.342(6), b = 8.124(2), c = 6.963(2) Å, β = 107.29(2)°, V = = 1098.6(5) Å^3, Z = 6, r = 1.555 g cm^{-3}, μ = 1.074 mm^{-1}, crystal size 0.32×0.38×0.42 mm.

Crystals were removed from mother liquor; a Simens P4 Four-Circle diffractometer (MoKα graphite monochromator, λ = 0.71073 Å) was used (ω scan technique). A total of 1395 reflections ($2.1 < \theta < 25$) were collected, of which 965 unique reflections were used. The structure was solved and refined using the SHELXL-97 program to R = 0.0365 for 965 reflections with $I > 2\sigma(I)$. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2002. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/117.

Along the crystallographic *c*-axis, Fe–O polymeric chains are formed through the connection of metal ions with oxygen atoms (Figures 1 and 3). By bridging the Fe–O chains with H_2bta spacers, a 3-D architecture is thus built up with different channels along this direction. Note that it is such a structure that led to the coexistence of inorganic Fe–O polymers and polycarboxylate H_2bta ligands. The guest H_2O molecules are also introduced into the largest channels along *c*-axes and bonded to the adjacent carboxyl O atoms forming hydrogen bonds (Figure 3).

Because the hydrogen atom cannot be revealed by X-ray structure analysis, and the occupation factors for Fe, O^5 and O^w are equal to 0.5 (Figure 1), the reasonable formula for this compound is $[C_5H_{3.5}Fe_{0.5}O_5]$. By comparison of the C–O bond lengths [C^1–O^3, 1.249(4); C^1–O^4, 1.269(4) and C^5–O^1, 1.213(5); C^5–O^2, 1.304(5) Å], the two free carboxyl groups of each unit may take the electrically uncharged form of COOH, and the two coordinating carboxyl groups may be deprotonated $COO^–$. The remaining 0.5H atoms (according to the uncharged formula $C_5H_{3.5}Fe_{0.5}O_5$) can be added to O^5. Thus, in one Fe–O polymeric chain, the bridging anion units might be the alternate $OH^–$ units.

The TGA analysis of compound **1** indicates that weight-loss occurred in two stages. The first stage occurred from 30 to 279.34 °C, which can be attributed to the loss of small water molecules. The second stage is between 279.34 and 445.05 °C, which can be attributed to the release of H_2bta and phen organic ligands and metal oxides. The compound is rather stable.

For the rational synthesis of this solid, a chief difficulty may come from the replacement of ligated oxygen around the metal centres with other atoms from organic ligands. In this structure, two oxygen atoms around the metal centres such as O^{5B} and O^5 are kept, the other four sites around a metal centre are occupied with carboxylate oxygen atoms such as O^{3C}, O^{4B}, O^4 and O^{4D}.

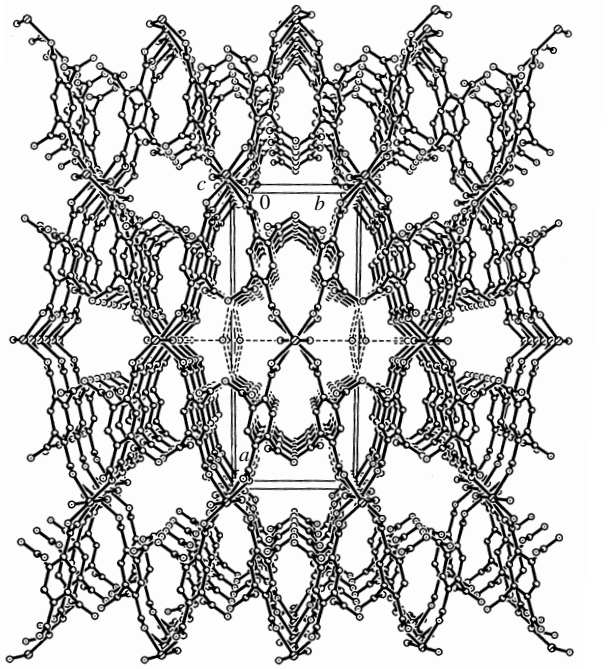

Figure 3 Packing of compound **1** along the crystallographic *c*-axis.

In summary, we described a novel complex with an unusual 3-D porous structure. It is of special interest that Fe–O clusters and organic H_2bta spacers occur in the assembled framework. Since the processes by which solid materials form in hydrothermal crystallization are usually very complicated and poorly understood, the synthesis of new solid materials and an understanding of their mode of formation is of paramount importance.[16] The reported structure mode may provide with a matrix for the further designing of functional organic connector and metal ion assemblies. The experimental verification of compound **1** may help us to understand the role of polycarboxylate ligands and metal oxide clusters and to engineer organic–inorganic hybrid materials.

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