Hydrothermal Synthesis of a Two-Dimensional Coordination Polymer $[Fe(phen)(\mu_6\text{-bta})_{1/2}]_n$ (bta = Benzene-1,2,4,5-tetracarboxylate, phen = 1,10-Phenanthroline)

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A metal-ligand complex $[Fe(phen)(\mu_6\text{-bta})_{1/2}]_n$ (phen = 1,10-phelanthroline; bta = benzene-1,2,4,5-tetracarboxylate ligand) has been hydrothermally synthesized and structurally characterized by single crystal X-ray crystallography, showing that it possesses a novel, two-dimensional polymeric structure.

Introduction

The recent interest in the crystal engineering of special geometrical and topological coordination polymers arises from their potential application in catalysis, chemical absorption, magnetism and electrical conductivity.[1] Due to their widespread utility, the ability to modify the structures of such materials or design of new materials is of the utmost importance. A synthetic strategy widely used in this area is by coordination of metal ions to polydentate ligands that function as connectors. In this context, multi-connecting ligands which provide two or more bidentate metal-binding sites are appealing as building blocks for coordination polymers because they promise robust networks with good electronic communication between the metal centers.[2] They also offer new network architectures, many of which do not exist in natural solids. "Clay mimics" or "zeolite mimics" have the gross analogues but are based upon very different chemical components, and, most importantly, they are inherently modular and therefore fine-tunable.[3] Presently, there are considerable efforts devoted to the formation of metal-polycarboxylate assemblies.[4] A particular case in this area is the assembly of benzenetricarboxylate-based supramolecules. Interesting two-dimensional structures such as $[Cu_3(tma)_2(H_2O)]_n$,[4a] $[Ni(C_{12}H_3ON_6O_2)]_3(tma)_2\cdot 18H_2O$,[4e] and $[M_3(tma)_2]\cdot 12H_2O$[4b] (M = Co, Ni, Zn, tma = benzenetricarboxylate) etc., are all reported to be based on this bridging ligand and transition metal ions.

The benzene-1,2,4,5-teracarboxylate ligand (= bta) as a multi-connecting ligand is also an excellent candidate for the planning of coordination polymers; comparatively few examples have been reported to date in relation to applying it to the building of coordination polymers. The use of a system of one kind of metal ion and two kinds of organic ligands that contain such a ligand for the assembly of coordination polymers has also never been described. We have therefore conducted an investigation of such a system $FeCl_2$-Na_4bta-phen-H_2O by a hydrothermal method. The obtained compound $[Fe(\mu_6\text{-bta})(phen)]_n$ (**1**) is unprecedented, exhibiting a two-dimensional polymeric structure, linking the metal ions with bta bridging units. We report here the synthesis and structural characterization of this novel compound.

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Results and Discussion

Crystal analysis reveals the details for the structure of compound **1**. It consists of two-dimensional polymeric layers $[Fe(phen)(\mu_6\text{-bta})_{1/2}]_n$ formed by bta units bridging [Fe(phen)] groups. As illustrated in Figure 1, each Fe^{II} ion is six coordinated by one phen and three bta ligands. Eight oxygen atoms from four deprotonated carboxyl groups of each bta unit are all used as coordinating atoms, and bind to six metal ions. Four oxygen atoms from two neighboring carboxyl groups of one bta unit coordinate to three metal atoms, two of which bind to one Fe^{II} ion with the other two binding to two Fe^{II} ions; the remaining four oxygen atoms of the bta unit coordinate to a further three metal atoms with the same mode. The layer grids consist of two kinds of holes, one is an eight-membered-ring hole consisting of two carboxyl groups and two metal atoms, and the other is a 14-membered-ring hole, around which are two bta units and two Fe^{II} ions. The local geometry around each Fe^{II} center can be described as a slightly distorted octahedron. The Fe^{II} center coordinates to six ligating atoms with four Fe−O distances of 2.083(2), 2.091(2), 2.166(2), 2.199(2) Å and two Fe−N distances of 2.232(3) and 2.182(3) Å.

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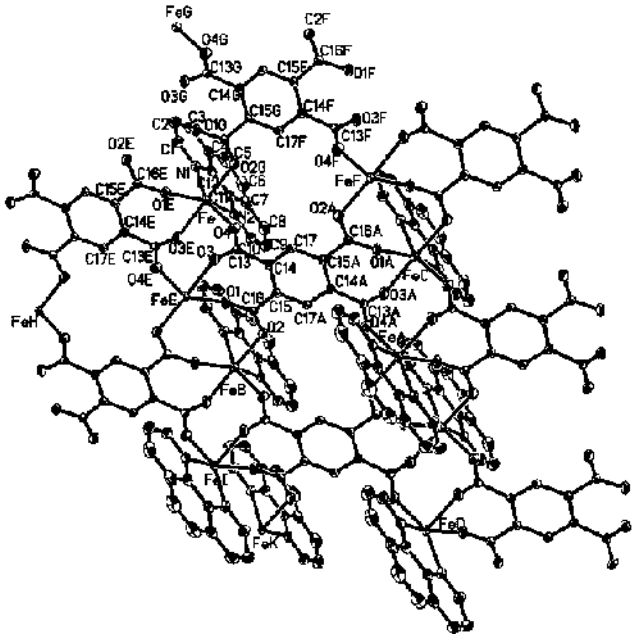

Figure 1. A view of the polymeric layer for compound [Fe(phen)-(μ_6-bta)$_{1/2}$]$_n$; selected bond lengths and angles: Fe−O_{1E} 2.083(2), Fe−O_4 2.091(2), Fe−O_{2G} 2.166(2), Fe−N_2 2.182(3), Fe−O_{3E} 2.199(2), Fe−N_1 2.232(3); O_{1E}−Fe−O_4 105.80(10), O_{1E} −Fe−O_{2G} 98.48(9), O_4−Fe−O_{2G} 81.08(9), O_{1E}−Fe−N_2 158.31(9), O_4−Fe−N_2 86.56(10), O_{2G}−Fe−N_2 101.05(9), O_{1E}−Fe−O_{3E} 80.64(9), O_4−Fe−O_{3E} 96.79(9), O_{2G}−Fe−O_{3E} 177.40(9), N_2−Fe−O_{3E} 80.24(9), O_{1E}−Fe−N_1 96.97(10), O_4−Fe−N_1 155.02(10), O_{2G}−Fe−N_1 85.60(10), N_2−Fe−N_1 75.34(10), O_{3E}−Fe−N_1 96.93(9)

Figure 2 is a view of the packing diagram for compound **1**. It shows that along the crystallographic *b* axis, all the two-dimensional polymeric layers are arranged in an ABAB fashion. Between two neighboring layers, the phen rings from different layers interdigitate. The alternate A···A or B···B interlayer distance is 18.504 Å, and the average interlayer distance is 9.252 Å.

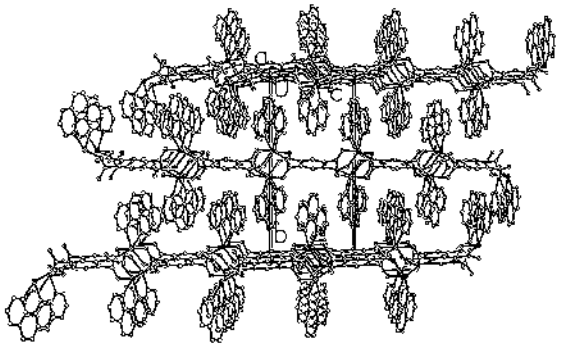

Figure 2. Crystal packing of the compound [Fe(phen) (μ_6-bta)$_{1/2}$]$_n$

Figure 3 shows that between two neighboring layers the interdigitated phen rings are parallel groups such as CQA/CQQ, CFF/CFA, CJJ/CJA, or CHH/CHA (here, the eight groups of three letters such as CQA represent 1,10-phenanthroline planes). The average distance between two adjacent parallel phen planes is small (3.2 Å), indicating that there are weak spatial π-π interactions between these phen rings. This type of π-π packing may be of high interest for the design of advanced materials.

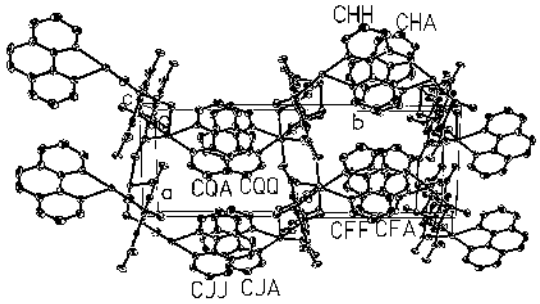

Figure 3. The parallel π-π packing of 1,10-phenanthroline plane between neighbouring polymeric layers in the crystal; the 1,10-phenanthroline planes CQA/CQQ, CFF/CFA, CJJ/CJA and CHH/CHA are parallel groups, but they are each bonded to different polymeric layers

In the chemical realization of multi-dimensional metal and polycarboxylate solids, a major challenge may come from the control of dimensionality. There are at least four problems in this respect. Firstly, since H_2O molecules are also excellent ligands for hard metal ions such as Fe^{II}, ancillary ligation of metal ions by water may result in low dimensionality such as discrete $Co(H_2bta)$[5] or $\{[Mn(H_2O)_5]_2(bta)\}\cdot H_2O$ units.[6] Secondly, in a system with a metal ion and two kinds of organic ligands, low dimensionality may come from the coordinating competition between the two kinds of organic ligands, such as full occupation of six sites per metal ion by three phen ligands, forming discrete metal complex cations $[Fe(phen)_3]^{2+}$. Thirdly, the low dimensionality may be caused by competition from polycarboxylate itself, due to its facile formation of hydrogen-bonded dimers or polymers.[7] Finally, in basic and even neutral aqueous solutions, the formation of Fe^{II}−ligand complexes will compete with the process of forming hydroxo- and oxo-bridged metal networks,[8] and result in much lower yields of the target coordination polymer.

During our exploration of the above-mentioned system, we maintained the molar ratio of phen:Fe^{II} at less than 0.7:1, thus favoring the formation of compound **1**. As the ratio gets larger, $Fe(phen)_3^{2+}$ cations form more easily, resulting in the formation of low dimensional products. The pH value of the reaction system is also an important factor: it must be maintained higher than 9.5 in order to obtain the target complex.

For entropic reasons, synthesis at higher temperature can promote the formation of polymer frameworks of higher dimensionality through the loss of terminal ancillary ligands. This may be justified by the following analysis. From the viewpoint of thermodynamics, self-assembled structures represent thermodynamic minima. For compound **1**, a possible formatting reaction may be described as follows:

$$\tfrac{1}{2}n\ [bta]^{4-} + n\ [Fe(H_2O)_6]^{2+} + n\ Phen \rightarrow [Fe(phen)](bta)_{1/2}]_n + 6n\ H_2O$$

$$\tfrac{1}{2}n \qquad n \qquad n \qquad 1 \qquad 6n$$

The variation of molecular number in this reaction is $1/2n + n + n \rightarrow 1 + 6n$ (mol) and the entropy of the system increases ($\Delta S > 0$). The replacement of six water molecules with the stronger ligand phen and with carboxyl O-atoms may favor lowering the enthalpy of the system ($\Delta H < 0$). Thus giving $\Delta G = \Delta H - T\Delta S$ to be less than 0. Synthesis at higher temperature can make $T\Delta S$ greater, and thus contribute more to the variation of the free energy, facilitating the production of the target complex. This kind of consideration is easy to confirm in the crystal engineering of target complexes by self-assembly methods.[9]

This compound appears to provide a matrix for the generation of a particular metal-benzene-tetracarboxylate sheet. As a natural extension of the structural chemistry of such a network, the replacement of phen with other similar ligands, such as bipyridine, is possible, and this work is currently under way. The experimental verification of compound **1** may help us to understand more about polycarboxylate ligands, and to engineer new supramolecular architectures.

Experimental Section

Synthesis: We prepared the compound with a mixture of $FeCl_2{\cdot}4H_2O$ (1.00 g), 1,10-phenanthroline (0.33 g), sodium benzenetetracarboxylate [Na_4(bta), 1.70 g] and H_2O (24 mL) in a 30cm^3 Teflon-lined reactor (pH = 10). The reactor was sealed and heated to 160 °C for 72 hours under autogenous pressure. The obtained deep red crystals were isolated by filtration and washed with distilled water (yield 36% based on phen). IR spectra were recorded on a Perkin−Elmer 783 spectrometer as KBr pellets: $\tilde{\nu}$ = 2358(s). 1602(vs), 1510(s), 1478(s), 1423(s), 1410(s), 1370(vs), 1285(m), 1140(s),1103(s), 918(s), 852(vs), 814(s), 780(s), 740(s), 732(s), 662(m), 640(m), 600(s), 510(s), 420(m) cm^{-1}. − $C_{17}H_9FeN_2O_5$ (377.11): calcd. C 56.54, H 2.51, N 7.76, Fe 15.47; found C 56.50, H 2.55, N 7.550, Fe 15.40.

X-ray Crystal Structure Determination: Crystal data and structure refinement for the title compound are listed in the Table 1. A single crystal of compound **1** was studied on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073Å) and ω-2θ scans. The structure was solved by the heavy-atom method and successive Fourier syntheses [SHELXS and SHELXL (Version 5.03, 1993)]. The refinement was performed by full-matrix least-squares refinement.

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-151718. 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; Email: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data for compound [Fe(phen)(μ_6-bta)$_{1/2}$]$_n$

Empirical formula	$C_{17}H_9FeN_2O_4$
M	361.11
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	7.482(2)
b, Å	19.701(2)
c, Å	9.574(3)
β, deg	111.78(2)
Z	3
V, Å^3	1310.5(5),
D_{calc}, g/cm^3	1.373
μ	0.884 mm^{-1}
Final R indices [$I > 2\sigma(I)$][a]	R_1 = 0.0387, wR_2 = 0.0857

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

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