Hydrothermal synthesis of the two-dimensional coordination polymer $\{[Fe(phen)(OH)](bta)_{0.5}\}_n$ (phen = 1,10-phenanthroline, bta = benzene-1,2,4,5-tetracaboxylate)

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The title two-dimensional coordination polymer was synthesised and characterised by X-ray diffraction analysis.

One of the current challenges for synthetic chemists is to understand how to control the shapes, sizes and properties of supramolecules.[1,2] By synthesising a series of complexes and characterising their structures and properties, useful information on factors responsible for the formation of supramolecules can be obtained.[2–7] Our aim was to design and prepare transition-metal compounds possessing extended molecular architectures, and our study has focused on the synthesis and structural characterization of polymeric compounds using polycarboxylates as bridging ligands. Polycarboxylates, which can form chelates as well as bridges, are of interest with respect to the preparation of unusual coordination polymers. Recent efforts have resulted in a lot of interesting architectures, and provided with facile approaches toward diverse coordination polymers.[8,9] A particularly interesting case is the construction of metal and benzenetricarboxylate (tma) assemblies, such as the syntheses of two-dimensional structures $[Cu_3(tma)_2(H_2O)]_n$,[10] $[M_3(tma)_2]\cdot 12H_2O$ (M = Co, Ni or Zn),[9] $[Ni(C_{12}H_3ON_6O_2)]_3(tma)_2\cdot 18H_2O$,[11] *etc.* Note that although benzenetetracarboxylate (bta) also belongs to the same type of excellent candidates which are appropriate for planning of ultra-large two-dimensional structures, few attempts have to date been made to use it for the construction of large supramolecular structures. By exploring the $FeCl_3$–Na_4(bta)–phen–H_2O system containing such a ligand with the hydrothermal method, we obtained a novel compound $\{[Fe(phen)(OH)](bta)_{0.5}\}_n$ **1** exhibiting a two-dimensional polymeric structure *via* linking Fe^{III} ions with bta units. We report here the synthesis and structural characterization† of this compound.

We prepared compound **1** using a mixture of $FeCl_3\cdot 6H_2O$ (0.50 g), Na_4(bta) (1.80 g), phen (0.26 g) and H_2O (23 ml) in a 30 cm^3 Teflon lined reactor (pH 10.5). The solution was sealed and heated to 160 °C for 72 h under autogenous pressure. After cooling, black crystals of the product were obtained and washed with distilled water. A grain crystal with the dimensions of 0.52×0.38×0.36 mm was selected for X-ray diffraction analysis. The yield of the crystal material based on Fe is 15%. Found (%): C, 54.10; N, 7.46; Fe, 14.87; H, 2.61. Calc. for $C_{17}H_{10}N_2O_5Fe$ (%): C, 54.00; N, 7.41; Fe, 14.77; H, 2.67. IR (KBr, ν/cm^{-1}): 3442.89 (vs), 2359.97 (m), 1625.51 (s), 1547.73 (s), 1515.11 (s), 1456.18 (vs), 1381.15 (s), 1325.03 (m), 1141.03 (m), 921.64 (m), 881.04 (s), 854.20 (m), 779.41 (m), 727.11 (s), 668.89 (m), 536.22 (m). The asymmetric and symmetric O–C–O vibrations of carboxyl groups from benzenetetracaboxylate ligands are at 1625.51 cm^{-1} and 1420 cm^{-1}, respectively. The absorption band at 1515.11 cm^{-1} can be assigned to the skeletal bending vibration of 1,10-phenanthroline ligands.

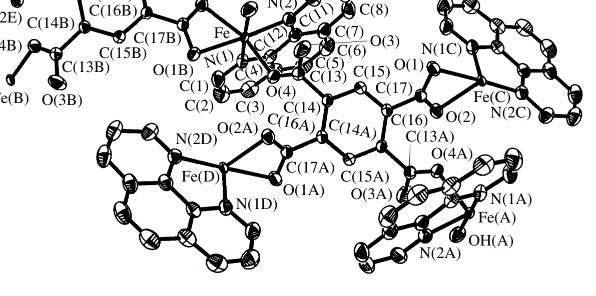

Figure 1 Molecular structure of the compound $\{[Fe(phen)(OH)](bta)_{0.5}\}_n$. Selected bond lengths (Å): Fe–O(4) 2.041(2), Fe–OH 2.044(2), Fe–N(1) 2.064(2), Fe–N(2) 2.180(0), Fe–O(1b) 2.142(2), Fe–O(2b) 2.145(2); selected bond angles (°): O(4)–Fe–OH 89.74(8), O(4)–Fe–N(1) 91.73(8), OH–Fe–N(1) 175.53(9), O(4)–Fe–N(2) 87.17(8), OH–Fe–N(2) 95.53(9), N(1)–Fe–N(2) 80.33(9), O(4)–Fe–O(1b) 99.19(7), OH–Fe–O(1b) 89.38(8), N(1)–Fe–O(1b) 94.56(8); N(2)–Fe–O(1b) 172.00(8), O(4)–Fe–O(2b) 160.38(7), OH–Fe–O(2b) 85.51(8), N(1)–Fe–O(2b) 94.47(8), N(2)–Fe–O(2b) 112.21(8), O(1b)–Fe–O(2b) 61.79(7).

Figure 1 shows the displacement ellipsoid plot (50% probability level) of compound **1** and depicts the atom numbering.

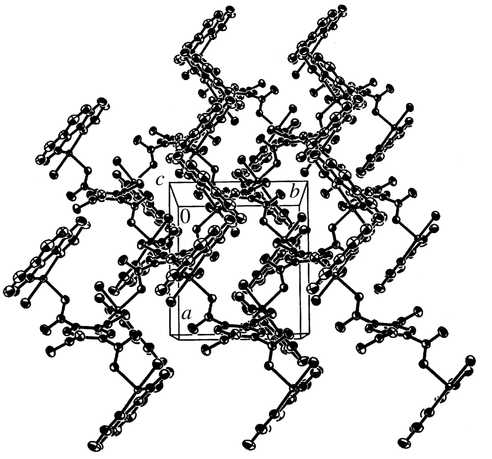

Figure 2 One layer of the compound $\{[Fe(phen)(OH)](bta)_{0.5}\}_n$.

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† *X-ray crystal structure determination.* The crystals of compound **1** were studied on a Siemens P4 four-circle diffractometer using graphite-monochromated MoKα radiation (λ = 0.70173 Å) and ω-2θ scans. Using the SHELXS and SHELXL (Version 5.03, 1994) program suite, the structure was solved by the direct method and refined with full-matrix least-square techniques. Crystal data: T = 293(2) K, $C_{17}H_{10}FeN_2O_4$, monoclinic, space group $P2_1/n$, a = 10.129(2), b = 9.265(2), c = 15.696(3) Å, β = 91.97(3), V = 1472.1(5) Å^3, Z = 3, μ(MoKα) = 0.793 mm^{-1}, d_{calc} = = 1.280 g cm^{-3}, F(000) = 576, 3553 reflections measured, 2572 reflections unique [R_{int} = 0.0183], which were used in all calculations. R_1 = = 0.0292, wR_2 = 0.0798. 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, 2001. Any request to the CCDC should quote the full literature citation and the reference number 1135/79.

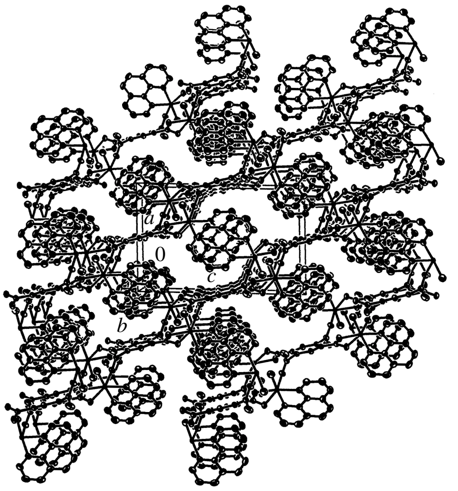

Figure 3 Crystal packing of the compound $\{[\text{Fe(phen)(OH)}](\text{bta})_{0.5}\}_n$.

It demonstrates that an asymmetric crystallographic unit in the structure contains one phen, one OH^-, half a bta unit and one Fe^{III} ion. Figure 2 accounts for that the bta units behave as linkages to bring Fe^{III} ions together and result in a layered structure with the two-dimensional infinite extended motif $[\text{Fe(bta)}_{0.5}]_n$. In one layer (Figures 1 and 2), four deprotonated carboxylates from one bta unit are alternately used as mono- and bidentate ligands to bind to Fe^{III} ions. Four ligands (two bta units, one phen and one OH group) provide with four oxygen atoms and two nitrogen atoms to coordinate to one Fe^{III} ion. Each of the six-coordinated Fe^{III} ions links two bta units by sharing three oxygen atoms with them. With six oxygen atoms, each bta unit bridges four [Fe(phen)OH] blocks. In the opposite two blocks, the two phen rings are parallel, but in the neighbouring two blocks, they exhibit a dihedral angle of 85.5°. The four phen rings in the four blocks alternately locate over and down the bta unit. Thus, the phen rings in the crystal are divided into two different parallel groups. The dihedral angle is also equal to 85.5°. In the crystal, all the benzene rings of the bta units are parallel. There exist large 30-membered-ring holes with the dimensions of 9.348×5.424 Å in the layer. Around each hole are four bta units and four Fe atoms. The two-dimensional layers pack along the crystallographic *a* axis. Between two neighbouring layers, the phen rings on different layers interdigitate and form walls of the channel (Figure 3).

Figure 4 shows that six phen rings are linked by two neighbouring polymeric layers. They are three paralleled groups (CN, CM), (CJ, CK) and (CQ, CP), among which the two different paralleled groups (CQ, CP) and (CJ, CK) [or (CN, CM)] exhibit a dihedral angle of 85.5°. The average distance of the two adjacent paralleled phen planes is close (3.39 Å), indicating the existence of weak spatial π–π interactions between the adjacent parallel phen rings. This type of π–π packing may be of interest to the designing of advanced materials.

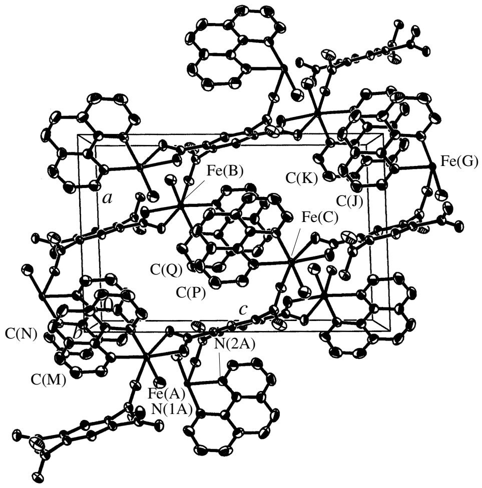

Figure 4 The paralleled π–π packing of 1,10-phenanthroline plane between three polymeric layers in the crystal. The 1,10-phenanthroline planes (CN, CM), (CJ, CK) and (CQ, CP) are parallel groups, but they are respectively bonded to different polymeric layers.

In coordination polymers of metal ions and polycarboxylates, a major challenge may come from the control of dimensionality; ancillary ligation of metal ions by water or other solvent ligands may result in low dimensionality.[8] Two cases related to benzenetetracarboxylate are the compounds $[\text{Co(H}_2\text{O)}_6][\text{H}_2\text{(bta)}]$[12] and $\{[\text{Mn(H}_2\text{O)}_5]_2\text{(bta)}\}\cdot\text{H}_2\text{O}$.[13] However, they are both discrete species.

From the standpoint of thermodynamics, a self-assembled structure represents a thermodynamic minimum. Here, a possible reaction may be as follows:

$$\begin{array}{lllll} 0.5n[\text{bta}]^{4-} + & n[\text{Fe(H}_2\text{O)}_6]^{3+} + & n\text{phen} + & n\text{HO}^- & \longrightarrow \\ 0.5n & n & n & n & \end{array}$$

$$\begin{array}{cc} \{[\text{Fe(phen)OH}](\text{bta})_{0.5}\}_n & +\ 6n\text{H}_2\text{O} \\ \mathbf{1} & 6n \end{array}$$

The replacement of H_2O with the stronger ligand phen and carboxylate O-atoms is obviously in favour of lowering enthalpy of the system ($\Delta H < 0$). Because H_2O molecules are also excellent ligands to Fe^{III} ions, the enthalpies of the interactions holding these molecules together may be relatively week. The contribution of entropy ($\Delta S > 0$) in the formation might be more important. The synthesis at a higher temperature can make $T\Delta S$ greater and contribute greater to the variation of free energy ΔG ($\Delta G = \Delta H - T\Delta S < 0$), and hence favour the formation of the target complex. This kind of considerations may be applied to the crystal engineering of complexes by self-assembly methods.[13]

The replacement of phen with other similar ligands such as bipyridine may also be possible. The experimental verifications of this coordination polymer may help us to understand more of polycarboxylate ligands and to generate new architectures.

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