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Structural studies and conductivity of $[Fe(O_3C_4)(COO)]\cdot H_2O$ based H_4btec (H_4btec = 1,2,4,5-benzenetetracarboxylic acid)

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ABSTRACT

A new metal-organic hybrid compound $[Fe(O_3C_4)(COO)]\cdot H_2O$ I has been hydrothermally synthesized and characterized by single-crystal X-ray diffraction. Rust crystals crystallize in the monoclinic system, space group $I2/a$, a = 6.9651(2) Å, b = 8.12630(10) Å, c = 19.4245(2) Å, β = 92.6600(10)°; V = 1098.25(4) $Å^3$; Z = 2 and D_x = 3.63 g/cm^3. The refinement converged into R = 0.042; R_w = 0.058. The structure, determined by single crystal X-ray diffraction, consists of a network of FeO_6 centers, octahedral coordinated by btec (btec = 1,2,4,5-benzenetetracarboxylic acid) anions giving rise to a two-dimensional sheet structure. In the compound I, $[Fe(O_3C_4)(COO)]\cdot H_2O$, the FeO_6 group bridged by the 1,2,4,5-benzenetetracarboxyl anion exist in a unit cell, with each anion lying about an inversion centre. One of the FeO_2 a distance [1.965(2)] significantly corresponds to the shortest distance as the other and the distances found in the axial direction of compound I.

Keywords: Hydrothermal Synthesis; X-Ray Diffraction; Crystal Structure

1. INTRODUCTION

During the past decade, the design and synthesis of crystalline material constructed from molecular clusters linked by extended groups have attracted great attention. Most notable fields are metal-organic frameworks (MOFs), [1-7] in which polyatomic inorganic metal-containing clusters are connected by polytopic linkers. The direct driving forces originate not only from their fascinating topological structures but also from their versatile applications in gas adsorption and separation, catalytic activities, optoelectronic material, luminescence, magnetism, and so on [8-19]. Thus, structural design or modification of the coordination polymers has become a very active field in crystal engineering [20-24]. In this process, judicious selection of ligands as basic building blocks is of great importance because slight structural changes in the organic building blocks such as length, flexibility, and symmetry can dramatically change the structural motifs of coordination polymers. It is well known that organic ligands play a rather important role in the construction of MOFs, and multicarboxylate ligands are frequently chosen owing to their rich coordination modes, coordinating to metal ions through complete or partial deprotonation of their carboxy groups, and their metal binding ability [25-30]. Especially interesting are the complexes formed by H_2bdc and H3btc having one-dimensional polymeric chain or brick-wall structures and their selective guest binding abilities [31-46].

In spite of the rich coordination chemistry exhibited by H_2bdc and H_3btc (Chart 1) in the presence of auxiliary ligands and coordinated solvents, barring a few sporadic reports, which mainly concentrate on the direct interaction between the metal ion and the ligand, there have been no serious attempts to prepare metal-organic polymeric or supramolecular structures based on 1,2,4,5-benzene tetracarboxylic acid (H_4btec) [47-65]. It may be argued that, due to steric reasons, all the four carboxyl groups of H_4btec are unlikely to take part in coordination to the metal. However, even the presence of free -COOH groups (especially in the vicinity of coordinated

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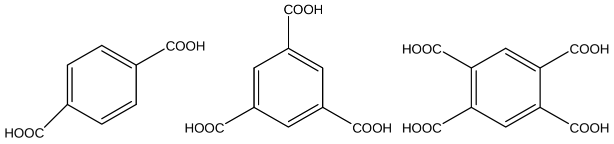
water molecules, donor solvents and added amines) would lead to formation of new extended structures aided by hydrogen bonding inter-actions. Moreover, the presence of a large number of uncoordinated water molecules within the lattice, may in turn lead to interesting possibilities for the preparation of porous solids. 1,2,4, 5-Benzenetetracarboxylic acid (H_4btec) has been well known to be an ideal ligand to encapsulated metal nodes, forming coordination compounds with unique structures and interesting properties [66-70], which may have the following advantages: 1) Higher symmetry of the ligand may cause the generation of regular structures; 2) The rigidity of the ligand may reduce the possibility of lattice interpenetration in the products [71,72]; 3) The multidentate carboxylate is known to be essential in chelating metal ions to form chain-like units with M-O-M connectivity; 4) The four carboxylic groups of this ligand may chelate to metal ions by using various coordination modes to form fascinating multidimensional compounds. In consideration of the varieties of topologies and properties, incorporating functional moieties into MOFs is often a popular method used in crystal engineering.

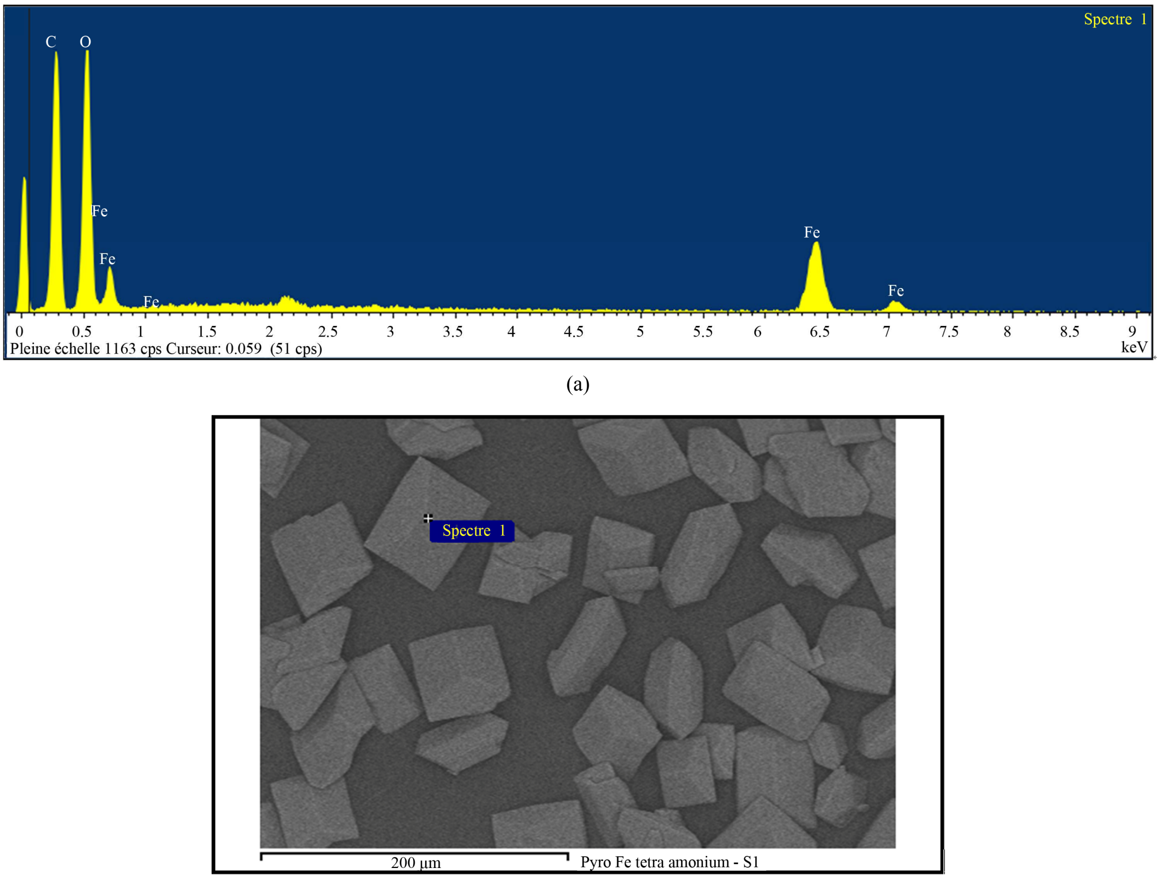


H_2BDC H_3BTC H_4BTEC

2. EXPERIMENTAL

2.1. Synthesis and Initial Characterization

The title compound was synthesized under hydrothermal conditions in the presence of tetramethylammonium nitrate. In a typical synthesis, 0.1158 g of pyromellitic acid (Acros Organics) was dispersed in 9 ml of H_2O. To this, 0.1975 g of iron nitrate monohydrate (Prolabo) was added under constant stirring. Finally, we add 0.062 g of tetramethylammonium nitrate (Alfa Aesar) and the mixture was homogenized for 15 min at room temperature, was sealed in a 23-ml PTFE-lined stainless steel autoclave and heated at 120˚C for 60 h. Then the product obtained is filtered and washed with a small amount of distilled water. The chemical purity of the product was tested by EDAX measurements. [**Figure 1(a)**] presents



(a)

(b)

Figure 1. (a) Typical EDAX spectrum of $[Fe(O_3C_4)(COO)]\cdot H_2O$ showing the presence of Fe, O and C; (b) Scanning electron microscopic image of the $[Fe(O_3C_4)(COO)]\cdot H_2O$.

the EDAX spectrum of $[Fe(O_3C_4)(COO)]\cdot H_2O$ which reveals the presence of all non-hydrogen atoms: Fe, C and O. Elemental analysis give these results: for observed we have C 34.10%, O 43.52%, Fe 2.38%; whereas for calculated we find C 43.93%, O 47.08%, Fe 8.99%. The amine used in this synthesis does not appear in the reaction product and its role remains unexplained. The [**Figure 1(b)**] shows the photograph of scanning electron microscopy (SEM) of the samples $[Fe(O_3C_4)(COO)]\cdot H_2O$ at room temperature.

2.2. Single Crystal Structure Determination

The unit-cell dimensions were refined using X-ray diffraction data collected with a Kappa CCD Enraf Noninus diffractometer using Mo Kα radiation .The structure, $[Fe(O_3C_4)(COO)]\cdot H_2O$, was analyzed with the crystallographic CRYSTALS program [73]. The structure was solved by conventional Patterson and difference-Fourier techniques. The chemical crystal data, the parameters used for X-ray diffraction data collection and strategy used for the crystal structure determination and their results, are listed in **Table 1**. **Table 2** shows the atomic coordinates and equivalent isotropic displacement. The anisotropic displacement parameters are listed in **Table 3**. Selected bond distances and angles are given in **Table 4**. Structural graphics were created by the DIAMOND program [74]. The asymmetric unit is shown in (**Figure 2**).

3. RESULTS AND DISCUSSION

The structure of compound I is representatively described in detail here. In an asymmetrical unit of 2, The structure of $[Fe(O_3C_4)(COO)]\cdot H_2O$, Compound I, is formed of a network of octahedral coordination by Fe carboxylate units btec. It also contains 11 non-hydrogen atoms. The Fe atom is octahedrally coordinated by six oxygen atoms from four different carboxylic groups. The Fe-O distances are in the range 1.965(11) - 2.038(4) (av.2.013 Å) and the O-Fe-O angles are in the range 86.34(16) - 179.994° (av.102.856°). Bond valence sum calculations 23 indicated that the valence states of the Fe, C and O in II were +2, +4 and −2 respectively. Their selected bond lengths and bond angles are listed in **Table 4**.

The bonded oxygen atoms of the carboxylate groups have C-O distances in the range 1.276(5) - 1.290(5)Å. The O-C-O bond angles have an average value of 125.16°. The present compound adds another example to this family of compounds. The various structural parameters observed in the present compound are in agreement with those observed before. The present compoun d adds another example to this family of compounds. The various structural parameters observed in the present compound are in agreement with those observed before. The structure of $[Fe(O_3C_4)(COO)]\cdot H_2O$, compound I, consists of a network of octahedral Fe cen-

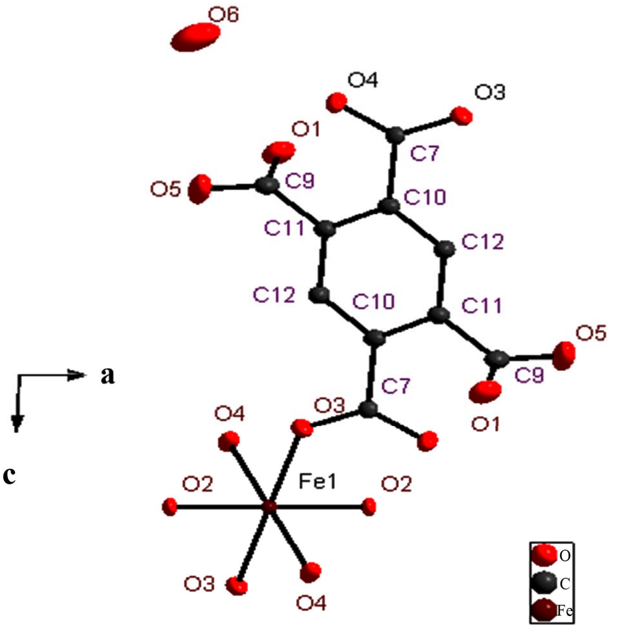


Figure 2. Asymmetric unit of $[Fe(O_3C_4)(COO)]\cdot H_2O$. Thermal ellipsoids are given at 50% probability.

Table 1. Crystallographic data for $[Fe(O_3C_4)(COO)]\cdot H_2O$.

Chemical formula $[Fe(O_3C_4)(COO)]\cdot H_2O$

Formula weight = 209.845 g·mol^{-1}

Crystal system: Monoclinic

Space group: $I2/a$

$a = 6.9651\ (2)$ Å

$b = 8.1263\ (1)$ Å

$c = 19.4245\ (2)$ Å

$\beta = 92.660\ (1)^\circ$

$V = 1098.25\ (4)$ Å^3

$Z = 2$

$2\theta^\circ\ max = 27.5^\circ$ with Mo Kα

$T = 293\ K$

$D_x = 3.631$ Mg·m^{-3}

$-9 \le h \le 9$

$-10 \le k \le 10$

$-25 \le l \le 25$

$\mu = 1.43$ mm^{-1}

Data collection instrument: Nonius Kappa CCD diffractometerRadiation, monochromator graphite $\lambda = 0.71073$ Å

Measured reflections: 17.777

Unique reflections : 8559

$R = 0.050$ and $R_W = 0.058$

ters coordinated by the btec carboxylate units (**Figure 2**). The connectivity between these units gives rise to a two dimensional hybrid layered structure in the ac and bc planes as shown in (**Figures 3** and **4**). The structure re-

Table 2. Fractional atomic coordinates and equivalent isotropic displacement for $[Fe(O_3C_4)(COO)]\cdot H_2O$.

	x	*y*	*z*	U_{iso}^*/U_{eq}	**Occupancy**
Fe1	0.5000	0.0000	1.0000	0.0092	1.000
O2	0.7500	−0.1120 (7)	1.0000	0.0122	1.000
O3	0.5712 (5)	0.1353 (5)	0.9167 (2)	0.0155	1.000
O4	0.3897 (5)	−0.1677 (5)	0.9309 (2)	0.0155	1.000
C7	0.7342 (7)	0.1644 (7)	0.8953 (3)	0.0124	1.000
C9	1.0515 (8)	0.3736 (9)	0.8420 (3)	0.0201	1.000
C10	0.7395 (9)	0.2115 (7)	0.8197 (3)	0.0132	1.000
C11	0.8953 (8)	0.3027 (7)	0.7952 (3)	0.0161	1.000
C12	0.5959 (8)	0.1636 (7)	0.7741 (3)	0.0142	1.000
O1	1.0256 (5)	0.4966 (13)	0.87741 (17)	0.0245	1.000
O6	0.2500	0.4444 (8)	0.0000	0.0475	1.000
O11	1.2191 (6)	0.3011 (8)	0.8392 (3)	0.0361	1.000

Table 3. Anisotropic displacement parameters ($Å^2$).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}
Fe1	0.0104 (5)	0.0123 (6)	0.0048 (5)	0.0015 (6)	−0.0002 (3)
O2	0.0080 (8)	0.0157 (14)	0.0128 (16)	0.0000	0.0005 (6)
O3	0.0123 (8)	0.0187 (12)	0.0158 (8)	−0.0009 (9)	0.0038 (8)
O4	0.0133 (9)	0.0142 (11)	0.0185 (10)	−0.0012 (10)	−0.0047 (9)
C7	0.0086 (8)	0.0150 (17)	0.0136 (9)	0.0024 (12)	0.0007 (6)
C9	0.0138 (11)	0.032 (2)	0.0145 (13)	−0.0064 (13)	−0.0006 (12)
C10	0.0091 (14)	0.0180 (18)	0.0127 (10)	0.0015 (15)	0.0021 (7)
C11	0.0099 (13)	0.025 (2)	0.0137 (10)	−0.0012 (15)	0.0004 (9)
C12	0.0079 (15)	0.020 (2)	0.0142 (10)	0.0020 (15)	0.0000 (9)
O1	0.0276 (18)	0.0208 (18)	0.0243 (19)	−0.009 (2)	−0.0070 (14)
O6	0.088 (4)	0.007 (3)	0.046 (4)	0.0000	−0.020 (4)
O11	0.0110 (13)	0.061 (3)	0.035 (3)	−0.0020 (18)	−0.0051 (15)

Table 4. Main interatomic distances (Å) and bonds angles (deg).

Atoms	distance	atoms	distance
Fe1—O4^{i}	2.038 (4)	C7—C10	1.520 (8)
Fe1—O3^{i}	2.037 (4)	C9—C11	1.501 (8)
Fe1—O2^{ii}	1.965 (2)	C9—O1	1.231 (11)
Fe1—O2	1.965 (2)	C9—O11	1.311 (8)
Fe1—O3	2.037 (4)	C10—C11	1.416 (8)
Fe1—O4	2.038 (4)	C10—C12	1.361 (9)
O3—C7	1.249 (6)	C11—C12^{iii}	1.377 (8)
O4—C7^{ii}	1.257 (7)		
O4i—Fe1—O3i	86.34 (16)	Fe1—O3—C7	128.7 (4)
O4i—Fe1—O2ii	89.85 (14)	Fe1—O4—C7ii	129.5 (4)
O3i—Fe1—O2ii	90.09 (13)	O4v—C7—O3	126.5 (5)
O4i—Fe1—O2	90.15 (14)	O4v—C7—C10	117.9 (4)
O3i—Fe1—O2	89.91 (13)	O3—C7—C10	115.6 (5)
O2ii—Fe1—O2	179.994	C11—C9—O1	122.0 (5)
O4i—Fe1—O3	93.66 (16)	C11—C9—O11	115.1 (6)
O3i—Fe1—O3	179.994	O1—C9—O11	122.8 (5)
O2ii—Fe1—O3	89.91 (13)	C7—C10—C11	120.7 (5)
O2—Fe1—O3	90.09 (13)	C7—C10—C12	120.5 (5)
O4i—Fe1—O4	179.994	C11—C10—C12	118.8 (6)
O3i—Fe1—O4	93.66 (16)	C9—C11—C10	122.8 (5)
O2ii—Fe1—O4	90.15 (14)	C9—C11—C12iii	116.9 (5)
O2—Fe1—O4	89.85 (14)	C10—C11—C12iii	120.2 (6)
O3—Fe1—O4	86.34 (16)	C11iii—C12—C10	121.0 (5)
Fe1—O2—Fe1iv	124.8 (3)		

Symmetry codes: (i) $-x + 1, -y, -z + 2$; (ii) $x - 1/2, -y, z$; (iii) $-x + 3/2, -y + 1/2, -z + 3/2$; (iv) $-x + 3/2, y, -z + 2$; (v) $x + 1/2, -y, z$.

sembles a 4-connected network in which each Fe atom is connected to four btec anions and each btec anion is linked to two Fe^{2+} ions. The water molecules also occupy the interlamellar region.

4. CONCLUSION

In this work, we report a novel metal–organic complex $[Fe(O_3C_4)(COO)]\cdot H_2O$ (I), which is prepared by the hydrothermal synthesis route. It crystallizes in the monoclinic symmetry, space group *I*2/*a*. Compound I exhibits a novel bi-dimensional network constructed from bridging btec ligand. The successful isolation of compound I not only confirms that such metal–organic compounds may be designed and synthesized according to the inherent stereo and interactive information stored in the organic ligands and metal ions [75], but also further proves the strong capability of hydrothermal reactions in preparing novel metal–organic materials with mixed or-

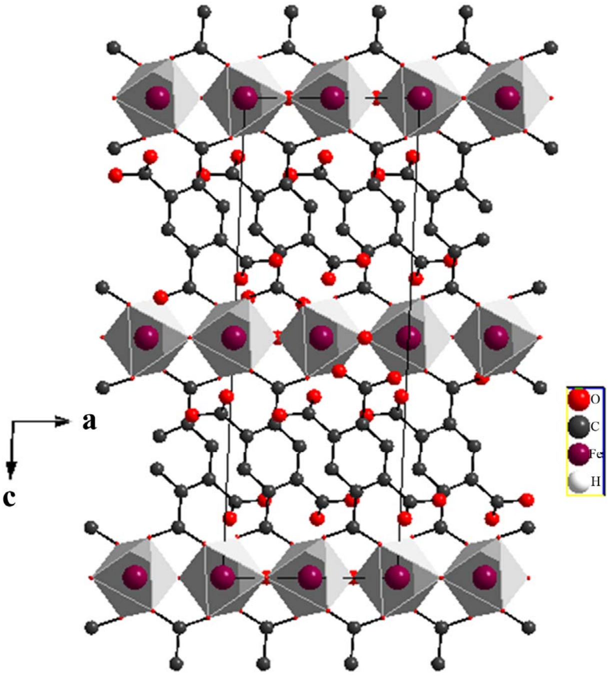


Figure 3. The projection structure of $[Fe(O_3C_4)(COO)]\cdot H_2O$, in the *ac* plane showing a single layer.

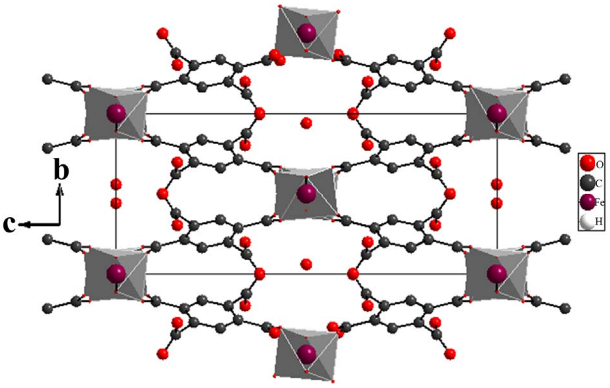


Figure 4. The projection structure of $[Fe(O_3C_4)(COO)]\cdot H_2O$, in the *bc* plane showing a single layer.

ganic ligands.

5. ACKNOWLEDGEMENT

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