

**TRANSITION METAL-ORGANIC POLYCARBOXYLATE COORDINATION POLYMER CHEMISTRY. HYDROTHERMAL SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF A ONE-DIMENSIONAL COORDINATION POLYMER [Fe(bzta)<sub>2</sub>(ox)]<sub>n</sub> (bzta = BENZOTRIAZOLE, ox = OXALATO)**

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Complex [Fe(bzta)<sub>2</sub>(ox)]<sub>n</sub> (**1**) was synthesized from K<sub>3</sub>[Fe(ox)<sub>3</sub>]·3H<sub>2</sub>O and benzotriazole. Single-crystal X-ray diffraction study of complex **1** has established a novel structure containing several kinds of secondary bonding interactions. All these interactions make it display a three-dimensional supramolecular network.

**Keywords:** Crystal structure; Benzotriazole; Ferrous complexes; Coordination polymers; Oxalates; X-Ray diffraction.

Amongst the variety of open-framework organic/inorganic composite materials, those of the metal polycarboxylates constitute a new family. Polycarboxylates, which can be used as chelating ligand as well as bridging one, are of interest with respect to the preparation of unusual coordination polymers. Different polycarboxylates have been used in the synthesis of coordination polymers, such as benzene-1,2,4,5-tetracarboxylate<sup>1-3</sup>, *m*-benzenetricarboxylate<sup>4</sup>, etc. Among them, oxalate is also often used for preparing organic/inorganic hybrid materials. With this versatile ligand some novel complexes have been reported, such as [Fe(ox)(DPA)]<sub>n</sub> (**2**), [Ni(ox)(DPA)]<sub>n</sub> (**3**) (DPA = 2,2'-dipyridylamine)<sup>5</sup>, {K(imH)[Cd(ox)<sub>2</sub>]}<sub>n</sub> (**4**)

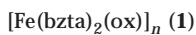
(im = imidazole) possessing channels<sup>6</sup>,  $[\text{Cu}(\text{ox})(\text{pyOH})_2]_n$  (**5**) (pyOH = 3-hydroxypyridine) and  $\{[\text{Cu}_2(\text{ox})_2(\text{ampy})_3](\text{ampy})\}_n$  (**6**) (ampy = 2-amino-4-methylpyridine) showing certain magnetic properties<sup>7</sup>.

Synthesizing diversity of active compounds and characterizing their structures and properties is fundamental to develop certain special functional materials. Our aim has been to design and prepare transition metal compounds possessing extended molecular architectures. Recent studies have focused on the syntheses and characterization of coordination polymers, using polycarboxylates, including oxalates, as bridging ligands and organic amines as auxiliary ligands. Herein we report the synthesis and structural characterization of a new one-dimensional Fe(II)-oxalate coordination polymer with benzotriazole (bzta) as subsidiary ligand.

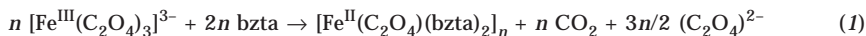
## EXPERIMENTAL

### Materials

Benzotriazole (analytical reagent grade) was used as received. The starting complex  $\text{K}_3[\text{Fe}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$  was prepared according to a standard literature procedure<sup>8</sup>.



Benzotriazole (0.238 g) was added to a well-stirred solution of  $\text{K}_3[\text{Fe}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$  (0.437 g) in distilled water (20 ml). The resulting 2 : 1 mixture was stirred at room temperature for 3 h until a homogeneous solution was obtained. The solution was then sealed in a 30 ml Teflon-lined stainless steel autoclave and heated at 160 °C for 3 days. After having slowly cooled the reaction system to ambient temperature, orange-red columnar crystals were recovered by filtration and dried in air. Yield of the target complex was *ca* 40% (based on Fe). For  $\text{C}_{14}\text{H}_{10}\text{FeN}_6\text{O}_4$  (382.1) calculated: 44.01% C, 2.54% H, 21.99% N; found: 44.03% C, 2.56% H, 21.75% N. IR (KBr,  $\text{cm}^{-1}$ ): 3 450 (w)  $\nu_{\text{N-H}}$ , 3 095 (m)  $\nu_{\text{C-H}}$ , 1 674 (s)  $\nu_{\text{C=O}}$ , 1 616 (vs) benzene-ring mode, 1 459 (w) benzene-ring mode, 748 (s)  $\delta_{\text{C-H}}$ . During the formation of complex **1**, ferric oxalate was reduced to the ferrous product, Eq. (1).



### X-Ray Crystallography

A single crystal of complex **1** (Table I) was studied on a CCD diffractometer, using graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and  $\omega$ - $2\theta$  scans. The structure was solved using SHELXTL program<sup>9</sup>, and refined by full-matrix least-square techniques. Crystal data:  $T = 293(2) \text{ K}$ ; crystal size  $0.30 \times 0.15 \times 0.15 \text{ mm}$ ; empirical formula  $\text{C}_{14}\text{H}_{10}\text{FeN}_6\text{O}_4$ ,  $M_w = 382.11$ ; monoclinic, space group  $Cc$ ;  $a = 14.4953(19) \text{ \AA}$ ,  $b = 12.4520(16) \text{ \AA}$ ,  $c = 9.3666(13) \text{ \AA}$ ,  $\beta = 109.318(2)^\circ$ ;  $V = 1 595.4(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.591 \text{ g cm}^{-3}$ ,  $F(000) = 776$ ;  $\theta$  range for data collection from 2.21 to 27.96°; 4 755 reflections measured, of which 2 979 unique ( $R_{\text{int}} = 0.0364$ ), and used in all calculations; final  $R$  indices,  $R_1 = 0.0344$ ,  $wR_2 = 0.0781$ .

CCDC 175529 (for complex **1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

### Thermogravimetric Analysis

Thermogravimetric analysis was performed on a Perkin-Elmer TGA-7 instrument, with a heating rate of 20 °C min<sup>-1</sup> in air. The thermal behaviour of compound **1** was studied from 30 to 730 °C. The TGA curve indicates only one stage of weight loss. The compound is thermally stable up to about 240 °C; then it begins to decompose. After decomposition at high temperature, the residue is ferrous oxide (FeO), since the weight of the residue is *ca* 18.50%, comparable with the calculated value (18.80%).

## RESULTS AND DISCUSSION

With ancillary monodentate or bidentate chelating N-donor ligands, the metal centres are bridged by oxalato ligands to form an extended one-dimensional (1D) zig-zag chain, such as in complexes **2**, **3**, **5** and **6** (refs<sup>5-7</sup>). When the auxiliary ligands are bidentate and bridging, the infinite 1D zig-zag chains are further interconnected into 2D layers, such as in a family of complexes with the general formula [M<sup>II</sup>(ox)(bpy)]<sub>n</sub> (M = Fe, Co, Ni, Zn; bpy = 4,4'-bipyridine)<sup>10</sup>. Imidazole is a versatile ligand that can bind both

TABLE I

Selected bond lengths (in Å) and angles (in °) for the title compound **1** (symmetry transformations used to generate equivalent atoms: #1 *x*, -*y*, *z* + 1/2)

Fe(1)–O(2)	2.123(3)	Fe(1)–N(4)	2.147(3)
Fe(1)–O(4)#1	2.135(3)	Fe(1)–N(3)	2.163(3)
Fe(1)–O(1)	2.147(2)	Fe(1)–O(3)#1	2.181(3)
O(2)–Fe(1)–O(4)#1	166.45(8)	O(1)–Fe(1)–N(4)	93.16(11)
O(2)–Fe(1)–O(1)	77.53(10)	O(2)–Fe(1)–N(3)	92.12(11)
O(1)–Fe(1)–O(4)#1	91.20(10)	N(3)–Fe(1)–O(4)#1	98.38(11)
O(2)–Fe(1)–N(4)	98.87(11)	O(1)–Fe(1)–N(3)	168.62(11)
N(4)–Fe(1)–O(4)#1	89.12(11)	N(3)–Fe(1)–N(4)	93.11(12)
O(2)–Fe(1)–O(3)#1	95.26(10)	N(4)–Fe(1)–O(3)#1	165.84(11)
O(3)#1–Fe(1)–O(4)#1	76.83(10)	N(3)–Fe(1)–O(3)#1	87.27(11)
O(1)–Fe(1)–O(3)#1	88.96(9)		

in monodentate and bidentate bridging fashion. In this regard complex  $\{K(imH)[Cd(ox)_2]\}_n$  (**4**) shows a curious and interesting structure. Cadmium and oxalate ligands form an anionic framework with formula  $[Cd(ox)_2]^{2-}$ . The reason why the structure of complex **4** is different from the others, is that the Cd atoms are eight-coordinate with respect to oxygens forming a dodecahedral arrangement, while the metal centres in the other complexes are six-coordinate in an octahedral environment. The in-plane connectivity between Cd and oxalate units in complex **4** results in the formation of honeycomb-like layers; the remaining oxalate unit then bridges these layers, giving rise to 1D elliptical channels. Benzotriazole in complex **1** has a similar character compared to imidazole. However, it contains three N-donor atoms and is bulkier, which has provoked our interest in the synthesis of polycarboxylate coordination polymers templated by bzta.

The title compound is constructed *via* a self-assembly process at a mild reaction temperature. It is built up by *cis*-[Fe(bzta)<sub>2</sub>] with two oxalate bridges forming a 1D zig-zag polymeric chain. Figure 1 displays a fragment of the polymeric chain. There is only one crystallographically unique Fe(II) centre in compound **1**. The coordination environment can be described as a slightly distorted octahedron, with four oxygen atoms from two oxalates and two nitrogen atoms from bzta. Three oxygen atoms [O(1), O(2) and O(4A)] and one nitrogen [N(3)] form the equatorial plane (maximum devia-

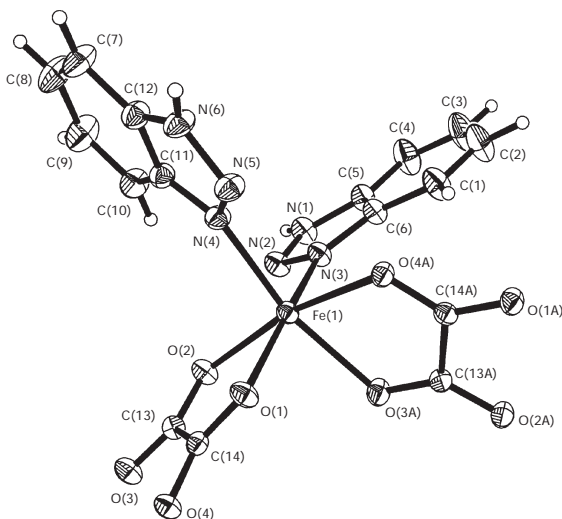


FIG. 1

An ORTEP view of the asymmetric unit of complex polymer **1** and the coordination environment of the Fe(II) centre

tion from the least-square plane is 0.0254 Å, mean deviation 0.0231 Å). The remaining two axial sites are occupied by N(4) and O(3A), being basically perpendicular to the equatorial plane (the N(4)–Fe(1)–O(3A) angle is 165°). The oxalates are nearly planar (mean deviation from the least-square plane is 0.0218 Å). The dihedral angle between the two oxalates coordinated to the same Fe(II) centre is 94.4°. The two bzta rings bound to the same Fe(II) atom display a dihedral angle of 92°. The Fe–O distances, ranging from 2.123 to 2.181 Å [Fe–O(1) = 2.147(2), Fe–O(2) = 2.123(3), Fe–O(3A) = 2.181(3), and Fe–O(4A) = 2.135(3) Å, respectively], span a narrower range than that reported in complexes **2** (2.062–2.224 Å), but the mean values of these distances are comparable with those reported for [Fe(ox)(bpy)]<sub>n</sub> possessing four equal Fe–O distances of 2.116 Å. The Fe–N distances, ranging from 2.147 to 2.163 Å [Fe–N(3) = 2.163(3) and Fe–N(4) = 2.147(3) Å, respectively] are slightly shorter than those found in [Fe(ox)(bpy)]<sub>n</sub> (2.211 Å). Therefore, the divalent iron centres are connected by bridging oxalato ligands to form an extended one-dimensional polymeric chain with Fe(ox)(bzta)<sub>2</sub> as asymmetric unit. The chain structure of the compound is depicted in Fig. 2. The distance between the adjacent Fe atoms in the same chain is 5.571 Å, which is similar to 5.548 Å reported for the Cu(II) analogue<sup>7</sup>.

Even though the chain structure of **1** is almost identical to those of complexes **2**, **3**, **5** and **6**, there exist some differences in crystal structure, since the separation between the adjacent chains is governed by the bulk of the ancillary ligands and by the position of the secondary bonding moiety. We

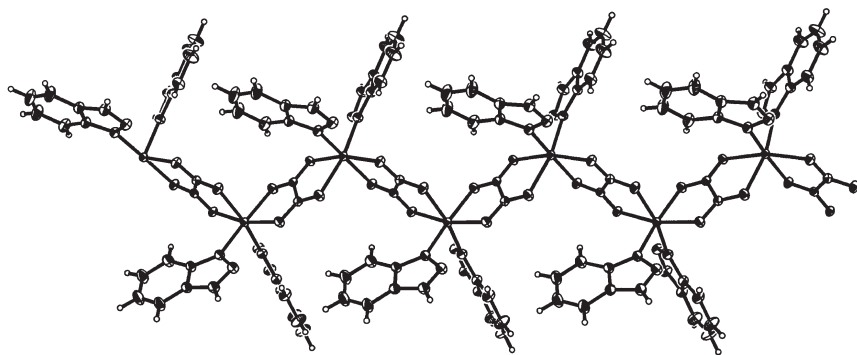


FIG. 2  
The zig-zag chain structure of complex **1**

can see in Fig. 3 that there exist three kinds of secondary bonding interactions between the neighbouring chains, *viz.*, hydrogen bonds C–H...O (C...O, 3.211 Å) and N–H...O (N...O, 2.883 Å), and weak N...N interaction (2.967 Å < 3.10 Å, the sum of the van der Waals radii of N atoms<sup>11</sup>). All these interactions, in particular the N...N one, are related to the co-ligand bzta and make compound **1** display a three-dimensional supramolecular network. Summarizing, co-ligand bzta plays an important role in controlling the crystal packing in compound **1**.

The variety of structural types reported so far and potential coordination modes of oxalato and bzta ligands suggest that a rich field of diverse structural types should be accessible. Consequently, further research is in progress, aimed at extension to other polycarboxylates and organic templating agents.

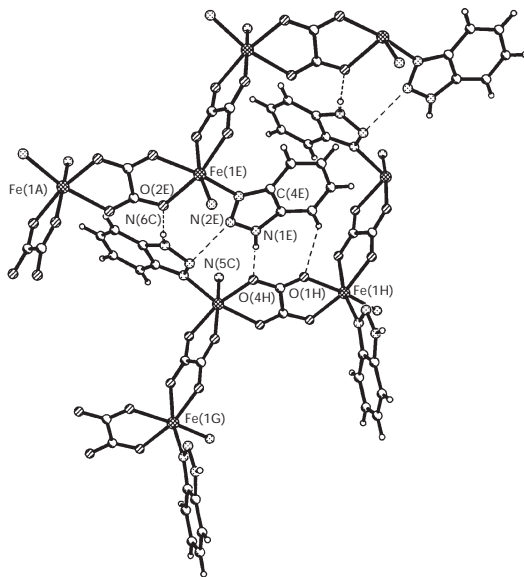


FIG. 3

The C–H...O, N–H...O hydrogen bonding and weak N...N interactions between the adjacent chains in complex **1**

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