

# Synthesis, Crystal Structure and Thermal Behavior of a 3-D Barium(II)/Iron(III)-Oxalate Polymer

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## Abstract

Reaction of  $\text{Ba}(\text{NO}_3)_2$  with  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in aqueous medium readily affords, in high yield, the bimetallic complex polymer of chemical composition  $\{\text{Ba}_6(\text{H}_2\text{O})_{17}[\text{Fe}(\text{C}_2\text{O}_4)_3]_4\} \cdot 7\text{H}_2\text{O}$  (**1**), consistent with the expected ratio of  $3\text{Ba}^{\text{II}}$  vs.  $2\text{Fe}^{\text{III}}$ . Compound **1** was fully characterized by elemental and thermal analyses, vibrational FTIR spectroscopy, and by single crystal X-ray structure determination. The bulk structure of **1** is a 3-D metal-organic framework held together by intermetallic linkages across oxalate and aqua oxygen bridgings. Thermal analyses of **1** show significant weight losses corresponding to water molecules (lattice and coordinated), followed by the decomposition of the network.

## Keywords

Tris(Oxalato)Ferrate(III) Anion, Bimetallic Complex Polymer, Crystal Structure, Thermal Stability

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## 1. Introduction

During the last decades, the self-assembly *via* metal-ligand coordination bonding approach has been demonstrated to be a useful method for the design and construction of new advanced materials that are needed to foster

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emerging technologies [1] [2]. Compounds of interest in this context include optically active systems [3] [4], polymeric microporous open frameworks [5] and, most importantly, molecular magnets [3] [4] [6]-[8]. In this respect, the tris(oxalato)metalate(III) anions are suitable for building multifunctional properties in a molecular lattice [9]-[11].

It is well-known that the numerous donor sites of the flexible oxalato ligand grant it a significant versatility regarding the possible metal complexes it can form. Following the strategy of utilizing transition metals with versatile multidentate ligands like oxalate dianion, we recently synthesized the first 3-D polymeric salt,  $\{\text{Ba}_6(\text{H}_2\text{O})_{17}[\text{Cr}(\text{C}_2\text{O}_4)_3]_4\} \cdot 7\text{H}_2\text{O}$  [12], with the ionic ratio of  $3\text{Ba}^{\text{II}}$  vs.  $2\text{Cr}^{\text{III}}$ . This compound has proven to be a useful precursor for the synthesis of highly versatile complex salts with the unprecedented potential of accumulating within a single system a whole set of relevant functionalities, such as nanoscale structural features, extended hydrogen bonding, magnetic interactions [13]-[15]. Moreover, it has received great attention in the field of materials science among other reasons for its use as a convenient route for the preparation of technologically important metallic composite oxides [16].

In order to extend this family of barium(II)/metal(III)-oxalate complex salts, we now describe the synthesis, crystal structure, and thermal behavior of the new salt,  $\{\text{Ba}_6(\text{H}_2\text{O})_{17}[\text{Fe}(\text{C}_2\text{O}_4)_3]_4\} \cdot 7\text{H}_2\text{O}$ , which turns out to be the iron(III) analog of the previously well-characterized barium(II)/chromium(III)-oxalate polymer [12], where chromium(III) ions are replaced by iron(III) ions.

## 2. Experimental

### 2.1. Materials and Measurements

All the chemicals used were commercial grade materials. They were procured from Prolabo and Merck. The reagents were used without further purification. All reactions were carried out in distilled water as the solvent. Elemental analysis for carbon and hydrogen was performed on a Vario EL (Heraeus) CHNS analyzer. The infrared spectrum was recorded on a Perkin-Elmer (System 2000) FT-IR spectrometer with a pressed KBr pellet in the scan range  $4000 - 400 \text{ cm}^{-1}$ . Thermal analyses (TGA and TDA) were performed with a Mettler Toledo TGA/SDTA 851 thermal analyzer. The powdered sample (ca. 15 mg) was heated from  $25^\circ\text{C}$  to  $600^\circ\text{C}$  with a rate of  $10^\circ\text{C}/\text{min}$  in dry nitrogen gas flowing at  $60 \text{ mL}/\text{min}$ . The melting point was taken with an Electrothermal 9100 apparatus. Three capillary tubes were filled with a powder sample and lodged in a heating closure.

### 2.2. Synthesis of $\{\text{Ba}_6(\text{H}_2\text{O})_{17}[\text{Fe}(\text{C}_2\text{O}_4)_3]_4\} \cdot 7\text{H}_2\text{O}$

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.404 g, 1 mmol),  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (0.378 g, 3 mmol) and  $\text{Ba}(\text{NO}_3)_2$  (0.392 g, 1.5 mmol) were dissolved in 20 mL, 10 mL, and 10 mL of water respectively. The solutions of oxalic acid and barium nitrate were added in successive small portions in the solution of iron(III) nitrate. The resulting green mixture was stirred at 333 K for 1 hour and then filtered off. The filtrate was allowed to evaporate in darkness at room temperature. After three weeks, yellow crystals suitable for X-ray diffraction were isolated by filtration, and dried in air. Yield: 0.967 g (84.7%). M. p.:  $> 240^\circ\text{C}$ . Anal. Calcd. for  $\text{C}_{24}\text{H}_{48}\text{Ba}_6\text{Fe}_4\text{O}_{72}$  ( $2536.06 \text{ g} \cdot \text{mol}^{-1}$ ): C, 11.37; H, 1.91%. Found: C, 11.32; H, 1.79%. IR (KBr disk,  $\text{cm}^{-1}$ ):  $\nu = 3420$  (m), 1705 (m), 1644 (s), 1398 (s), 1271 (s), 897 (w), 793 (s), 531 (s), 477 (s).

### 2.3. X-Ray Crystallography

A yellow crystal with approximate dimensions  $0.4 \times 0.3 \times 0.2 \text{ mm}^3$  was selected under ambient conditions and attached to the tip of a nylon loop. It was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera. The diffraction data were collected on a Bruker APEX-II CCD diffractometer and processed using the Bruker software [17]. The structure was solved by the direct method. The positions of the hydrogen atoms were calculated. The non-hydrogen atoms were refined with anisotropic displacement coefficients, and the hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Structure solution and refinement were performed using the SHELX-2013 program package [18]. Crystallographic data and refinement parameters are listed in **Table 1**. Selected bond distances and bond angles are given in **Table 2**.

### 3. Results and Discussion

#### 3.1. Formation of $\{\text{Ba}_6(\text{H}_2\text{O})_{17}[\text{Fe}(\text{C}_2\text{O}_4)_3]_4\} \cdot 7\text{H}_2\text{O}$ (**1**)

The title compound was prepared by the reaction in aqueous medium of  $\text{Ba}(\text{NO}_3)_2$  with  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in the respective 1.5:3:1 molar ratio. Yellow good crystals were isolated from the filtrate with good yield. Elemental and full X-ray structure analyses converge to support the general formulation of **1** as  $\{\text{Ba}_6(\text{H}_2\text{O})_{17}[\text{Fe}(\text{C}_2\text{O}_4)_3]_4\} \cdot 7\text{H}_2\text{O}$ . This unambiguously demonstrates that the single crystal used for the X-ray

**Table 1.** Crystal data and structure refinement parameters for compound **1**.

Empirical formula	$\text{C}_{24}\text{H}_{48}\text{Ba}_6\text{Fe}_4\text{O}_{72}$
Formula weight	2536.06
Temperature (K)	100(1)
Wavelength (Å)	1.54178
Crystal system	triclinic
Space group	$P\bar{1}$
$a$ (Å)	10.9539(10)
$b$ (Å)	17.4492(15)
$c$ (Å)	18.700(2)
$\alpha$ (°)	88.868(5)
$\beta$ (°)	86.160(7)
$\gamma$ (°)	76.462(6)
Volume (Å <sup>3</sup> )	3467.2(6)
$Z$	2
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	2.429
Absorption coefficient (mm <sup>-1</sup> )	33.807
$F(000)$	2416.0
Crystal size (mm)	0.4 × 0.3 × 0.2
$2\theta$ Range for data collection (°)	4.736 - 140.59
Index ranges	$-13 \leq h \leq 12$ ; $-21 \leq k \leq 21$ ; $-22 \leq l \leq 22$
Reflections collected	58487
Independent reflections ( $R_{\text{int}}$ )	12756 (0.0644)
Absorption correction	Semi-empirical
Max. and min. transmission	0.470 and 0.182
Refinement method	Full-matrix least squares on $F^2$
Data/restraints/parameters	12756/38/1028
Goodness-of-fit on $F^2$	1.031
Final $R$ indices [ $I > 2 \text{ sigma}(I)$ ]	$R_1 = 0.0442$ , $wR_2 = 0.1066$
$R$ indices (all data)	$R_1 = 0.0564$ , $wR_2 = 0.1123$
Largest diff. peak and hole (eÅ <sup>-3</sup> )	2.03 and -2.64

**Table 2.** Selected bond lengths [Å] and angles [°] for **1**.

Bond Lengths		Bond Angles	
Fe1-O1	2.016(5)	O1-Fe1-O3	81.1(2)
Fe1-O3	2.021(5)	O11-Fe1-O9	80.6(2)
Fe1-O5	2.013(5)	O5-Fe1-O7	80.7(2)
Fe1-O7	2.041(5)	O5-Fe1-O9	170.9(2)
Fe1-O9	2.024(5)	O11-Fe1-O1	167.4(2)
Fe1-O11	2.003(5)	O3-Fe1-O7	165.4(2)
Fe2-O13	2.063(5)	O15-Fe2-O13	79.4(2)
Fe2-O15	2.012(5)	O23-Fe2-O21	83.0(2)
Fe2-O17	2.049(5)	O19-Fe2-O17	80.1(2)
Fe2-O19	2.001(6)	O17-Fe2-O21	165.7(2)
Fe2-O21	2.050(6)	O23-Fe2-O13	168.7(2)
Fe2-O23	1.992(7)	O19-Fe2-O15	170.2(3)
Fe3-O25	2.041(5)	O27-Fe3-O25	80.1(2)
Fe3-O27	2.027(5)	O29-Fe3-O31	81.3(2)
Fe3-O29	1.986(5)	O33-Fe3-O35	79.9(2)
Fe3-O31	2.029(5)	O29-Fe3-O33	170.2(2)
Fe3-O33	2.018(5)	O35-Fe3-O27	168.3(2)
Fe3-O35	2.016(5)	O31-Fe3-O25	163.9(2)
Fe4-O37	2.001(5)	O47-Fe4-O45	81.7(2)
Fe4-O39	2.035(6)	O41-Fe4-O43	79.6(2)
Fe4-O41	2.014(6)	O37-Fe4-O39	80.1(2)
Fe4-O43	2.023(5)	O43-Fe4-O39	169.3(2)
Fe4-O45	2.014(5)	O37-Fe4-O47	169.3(2)
Fe4-O47	2.003(5)	O41-Fe4-O45	164.6(2)

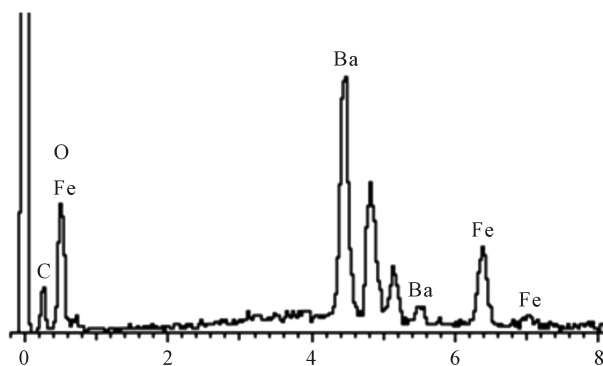
structure determination is representative of the entire complex synthesized. Compound **1** is a light-sensitive material soluble in water. It does not melt up to 240°C.

### 3.2. Energy Dispersive X-Ray Analysis

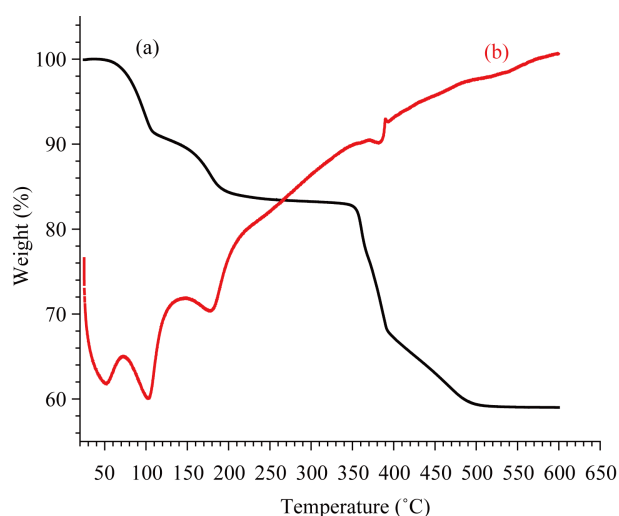
The EDX spectrum of **1** is shown in **Figure 1**. This spectrum clearly confirms the presence of chemical elements C, O, Ba and Fe in the crystal.

### 3.3. Thermal Analysis

The thermal behavior of **1** has been studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in the temperature range of 25°C to 600°C at a heating rate of 10°C per minute under nitrogen atmosphere. TGA and DTA curves are depicted in **Figure 2**. This compound shows two steps of weight loss with endothermic change between 60°C and 200°C. The first step occurs from 70°C - 109°C and this corresponds to the release of twelve H<sub>2</sub>O molecules (calc.: 8.5%, exp.: 8.6%) and the second from 130°C - 200°C represents the release of 10 H<sub>2</sub>O molecules (calc.: 7.1%, exp.: 7.0%). Above 350°C, the decomposition of the crystal network



**Figure 1.** EDX spectrum of compound **1** showing the nature of its different chemical elements.



**Figure 2.** TGA (curve *a*) and DTA (curve *b*) of compound **1**.

commences with the major weight loss in the temperature range 350°C - 394°C, which can be attributed to the release of a combined mass of  $8\text{CO}_2 + 2\text{H}_2\text{O}$  (calc. 15.3%, exp.: 15.1%) and formation of a mixture of  $2(\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O})$  and  $\text{BaC}_2\text{O}_4$ . Further, a small loss of weight is finally observed between 395°C - 500°C, which may be due to the release of a combined mass of  $4\text{CO}_2 + 2\text{H}_2\text{O}$  (calc. 8.4%, exp.: 8.5%) and formation of the residual compounds,  $\text{Fe}_2\text{O}_3$  and  $\text{BaCO}_3$ .

### 3.4. Crystal Structure

The molecular structure of **1** has been determined by X-ray study, which shows that it crystallizes in the triclinic space group  $P\bar{1}$ . The asymmetric unit is shown in **Figure 3**. Compound **1** is a 3-D polymeric structure with oxalate anions and water molecules bridging  $\text{Ba}^{2+}$  and  $\text{Fe}^{3+}$  ions. This compound is isostructural with its chromium analog  $\{\text{Ba}_6(\text{H}_2\text{O})_{17}[\text{Cr}(\text{C}_2\text{O}_4)_3]_4\} \cdot 7\text{H}_2\text{O}$  characterized earlier [12]. It seems relevant, therefore, to compare the structural features of **1** with those of the chromium analog. As to be expected from structural isomorphism, the crystal data of **1** compare with the reported values (in brackets) as follows:  $a = 10.9539(10)$  [10.941(1)] Å;  $b = 17.4492(15)$  [17.595(1)] Å;  $c = 18.700(2)$  [18.577(1)] Å;  $\alpha = 88.868(5)$  [88.850(1)]°;  $\beta = 86.160(7)$  [85.813(1)]°;  $\gamma = 76.462(6)$  [76.546(1)]°;  $V = 3467.2(6)$  [3469.0(3)] Å<sup>3</sup>;  $Z = 2$  [2];  $D_x = 2.429$  [2.413] g/mm<sup>3</sup>.

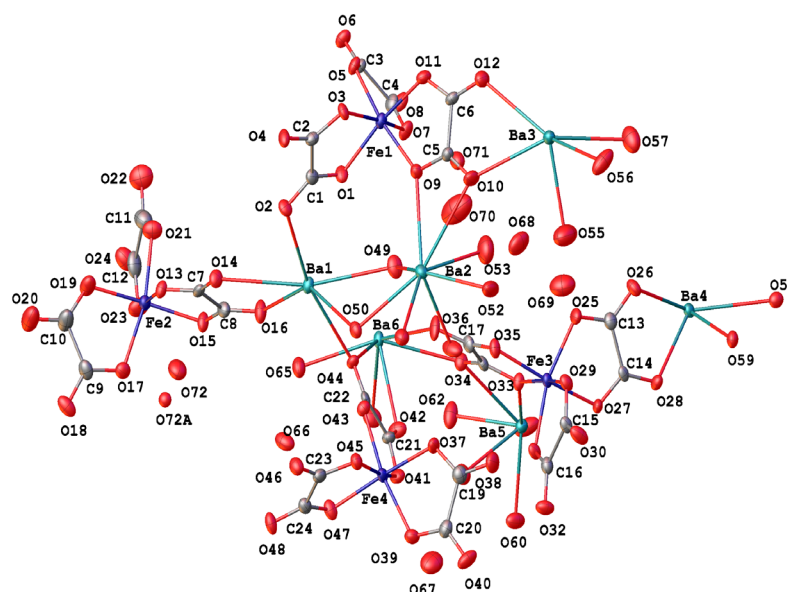
The constitutive ionic building blocks of the structure of **1** are the tris(oxalato)ferrate(III) anion,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ , and  $\text{Ba}(\text{II})$  cations. The anionic building unit,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ , functions as a metalloligand or else as an “*internetting bridge*” [19]. Hence, this internetting bridge interconnects, across its twelve O atoms as numbered, the six independent metallic sites Ba1, Ba2, Ba3, Ba4, Ba5 and Ba6—differently coordinated both by  $\text{H}_2\text{O}$  and oxalate

ligands—into a three-dimensional polymeric network. Each of the four independent Fe<sup>III</sup> sites is pseudo-octahedrally chelated by three oxalate (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) ligands with helical orientation. Selected geometrical parameters are presented in **Table 2**. The Fe-O<sub>oxalate</sub> bond lengths range from 1.986(5) Å to 2.063(5) Å and the bite angles, O-Fe-O, vary from 79.4(2) to 83.0(2)°. These bond lengths and bond angles are in good agreement with those found in other tris(oxalato)metalate(III) complexes [12] [20] [21].

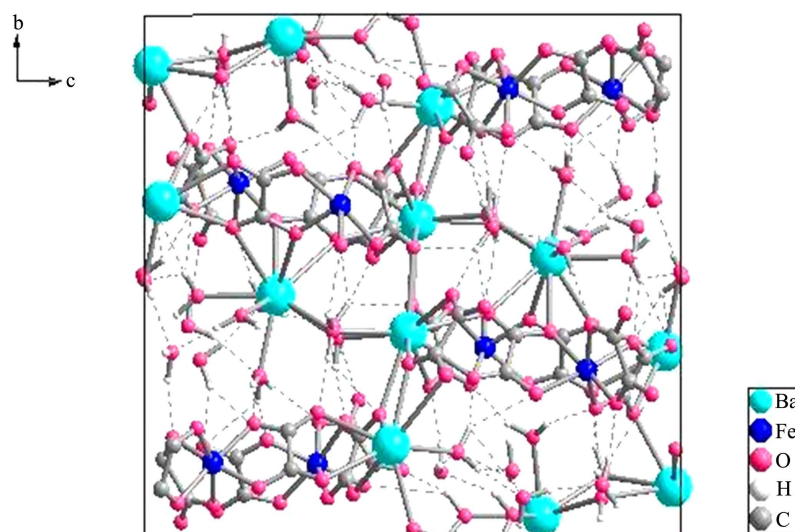
The packing diagram for **1** showing hydrogen bonding interactions as viewed along the *a*-axis is shown in **Figure 4**. The bulk structure of **1** is consolidated by a three-dimensional network of hydrogen-bonding of the type O-H···O, with O···O distances ranging from 2.645(14) to 3.277(11) Å (**Table 3**).

#### 4. Conclusion

A new complex salt, {Ba<sub>6</sub>(H<sub>2</sub>O)<sub>17</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>4</sub>}·7H<sub>2</sub>O (**1**), obtained from aqueous solution as yellow crystals,



**Figure 3.** The asymmetric unit of compound **1**. All atoms are drawn as 50% thermal probability ellipsoids. All H atoms are omitted for clarity.



**Figure 4.** Packing diagram of compound **1** showing the H-bonding O-H···O (dashed lines) as viewed along the *a*-axis.

**Table 3.** Hydrogen bond lengths [Å] and angles [°] for **1**.

D-H...A	<i>d</i> (D-H)	<i>d</i> (H...A)	<i>d</i> (D...A)	<(DHA)
O49-H49A...O70	0.96	2.02	2.810(12)	139.1
O49-H49B...O36	0.95	1.97	2.915(8)	170.9
O50-H50B...O43	0.95	1.81	2.736(7)	163.3
O52-H52A...O69	0.96	1.78	2.742(11)	175.7
O52-H52B...O70	0.96	1.77	2.645(14)	148.9
O53-H53A...O20 <sup>1</sup>	0.95	2.41	3.277(11)	151.1
O53-H53A...O55	0.95	2.32	2.978(11)	125.7
O55-H55A...O69	0.96	1.99	2.705(12)	129.5
O55-H55B...O19 <sup>2</sup>	0.96	2.01	2.913(9)	156.0
O60-H60A...O17 <sup>3</sup>	0.96	2.01	2.888(8)	150.2
O61-H61A...O66 <sup>3</sup>	0.96	2.00	2.880(9)	152.0
O61-H61B...O42	0.95	2.01	2.947(8)	167.3
O62-H62A...O64	0.95	2.08	2.907(9)	143.8
O62-H62B...O48 <sup>3</sup>	0.96	1.91	2.792(8)	152.7
O64-H64A...O47 <sup>3</sup>	0.96	2.09	2.896(8)	140.4
O64-H64B...O66 <sup>3</sup>	0.95	1.94	2.873(9)	163.7
O65-H65A...O16	0.95	1.79	2.690(8)	155.4
O65-H65B...O67 <sup>3</sup>	0.96	1.81	2.746(9)	163.5
O66-H66A...O65	0.96	1.94	2.864(9)	159.9
O67-H67A...O72 <sup>3</sup>	0.96	1.91	2.788(11)	150.5
O67-H67A...O72A <sup>3</sup>	0.96	1.91	2.83(3)	157.8
O67-H67B...O41	0.95	1.93	2.769(9)	146.3
O68-H68A...O25	0.96	1.99	2.855(9)	150.3
O69-H69A...O29	0.95	1.91	2.838(9)	164.1
O71-H71A...O8	0.96	1.76	2.708(8)	169.7
O72-H72A...O32 <sup>3</sup>	0.96	1.92	2.828(9)	159.0
O72-H72B...O23	0.95	1.98	2.928(10)	171.6
O73-H73A...O37	0.95	1.81	2.736(8)	163.1
O73-H73B...O35	0.96	2.06	2.954(8)	155.8

Symmetry transformations used to generate equivalent atoms (D, donor; A, acceptor): <sup>1</sup>1 - X, 1 - Y, 1 - Z; <sup>2</sup>+X, +Y, -1 + Z; <sup>3</sup>1 - X, -Y, 1 - Z.

has been characterized. It is the analog of the well-known barium(II)/chromium(III)-oxalate polymer, {Ba<sub>6</sub>(H<sub>2</sub>O)<sub>17</sub>[Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>4</sub>}·7H<sub>2</sub>O [12], with Fe<sup>3+</sup> in lieu of Cr<sup>3+</sup> ions. The bulk structure of **1** is a 3-D metal-organic framework held together by intermetallic linkages across oxalate and aqua oxygen bridgings with extensive hydrogen-bonding interactions stabilizing the crystal packing. Thermal analysis of compound **1** reveals that it is stable up to ca. 80°C. The synthesis of compound **1** provides, no doubt, a path for the preparation of further new metal(II)/meta(III)-oxalate frameworks, which may lead to the formation of a wide variety of topologies.

Work is in progress in our laboratory on extending this interesting family of oxalate-based precursor materials.

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## Supplementary Material

Detailed crystallographic data in CIF format for this paper were deposited with the Cambridge Crystallographic Data Centre (CCDC-961313). The data can be obtained free of charge at

[www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 IEZ, UK; fax: +44 (0) 1223-336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

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