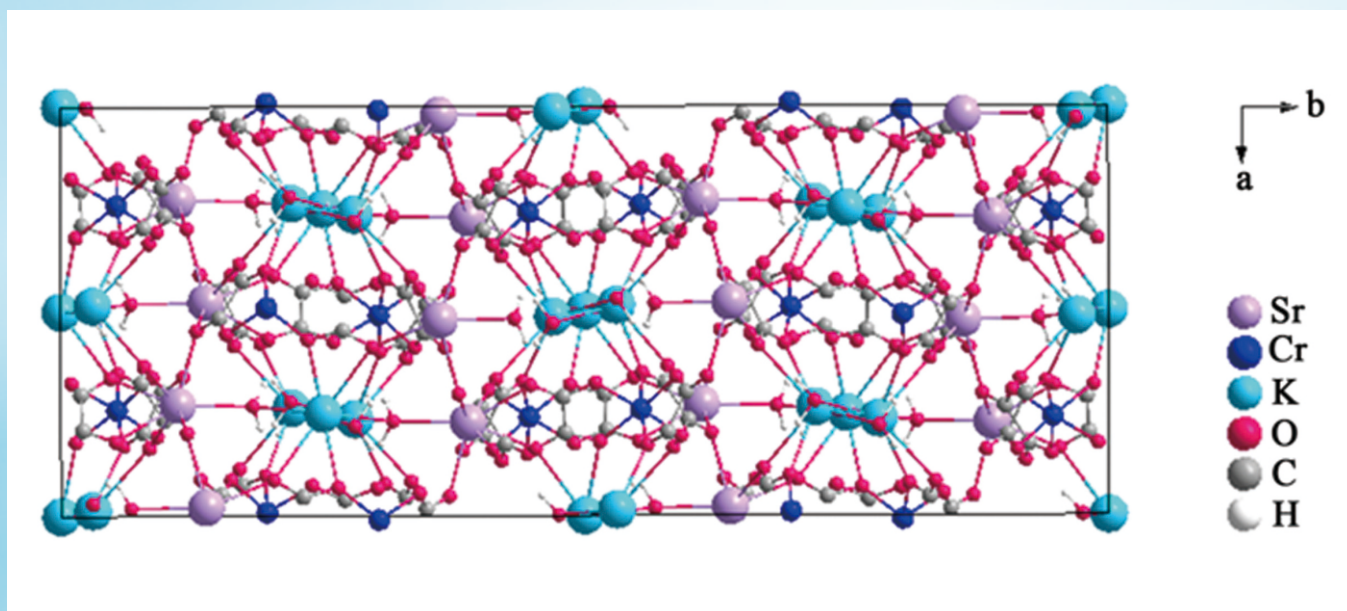




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A Chiral Three Dimensional Potassium(I)/Strontium(II)/Chromium(III) Oxalato-Bridged Coordination Polymer: Synthesis, Characterization and Thermal Analysis

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Abstract

A new compound of general formula $\{[(\text{H}_2\text{O})_2\text{K}(\mu\text{-H}_2\text{O})\text{Sr}][\text{Cr}(\text{C}_2\text{O}_4)_3]\}_n$ (1) has been synthesized in water and characterized by elemental and thermal analyses, EDX, IR and UV-Vis spectroscopies and by single crystal X-ray structure determination. Compound 1 crystallizes in the chiral space group Fdd2 of orthorhombic system with $a = 14.110$ (4) Å, $b = 36.074$ (11) Å, $c = 11.034$ (3) Å and $Z = 16$. Compound 1 is a coordination polymer in which the three-dimensional lattice framework is realized by the interconnectivity between K^+ cations, Sr^{2+} cations, aqua ligands and $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ complex anions. The asymmetric unit of 1 consists of one cationic motif formally written $[(\text{H}_2\text{O})_2\text{K}(\mu\text{-H}_2\text{O})\text{Sr}]^{3+}$ and one anionic entity, $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$. The K^+ and Sr^{2+} ions in the cationic motif are both eight-coordinate while the Cr^{3+} ions in the anionic complex are six-coordinate in a distorted octahedral geometry. Coulombic interactions between the ionic motifs and the three-dimensional H-bonding involving aqua ligands help to consolidate the bulk structure. Thermogravimetric analysis (TGA) shows that compound 1 is stable to heat up to ca. 80°C.

Keywords

Tris(Oxalato)Chromate(III) Anion, Heterometallic Complex Polymer, Chiral Compound, Crystal

*Corresponding author.

Structure, Thermal Stability

1. Introduction

One of the current research activities in the field of materials science is unarguably the rational design and synthesis of heterometallic complexes with interesting molecular topologies, crystal packing motifs and potential applications as advanced multifunctional materials [1]–[6]. In this respect, the old but evergreen oxalate dianion, $\text{C}_2\text{O}_4^{2-}$, with its π -extended system together with its ability to transmit relatively large magnetic interactions between the metal ions that it bridges, provides unique opportunities for the discovery of unusual networks in this fascinating and challenging field [7]–[9].

In our research group, we recently have been interested in the design and construction of polymetallic oxalate-based architectures by following the so-called “complex-as-ligand approach”. In this synthetic strategy, a molecular building block, the homoleptic $[\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{3-}$ tris(oxalato)metalate(III) octahedral complex is used as a ligand towards the divalent Ba^{2+} cations to generate 3-D polymeric complexes of general formula, $\{\text{Ba}_6(\text{H}_2\text{O})_{17}[\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]_4\} \cdot 7\text{H}_2\text{O}$ ($\text{M} = \text{Cr}, \text{Fe}$) [10] [11], with the ionic ratio of 3Ba^{II} vs. 2M^{III} . This family of complexes, indeed, has proven to be a useful precursor for the synthesis of highly versatile materials with the potential of accumulating within a single system a whole set of relevant functionalities, such as nanoscale structural features [12] [13], extended hydrogen bonding and magnetic interactions [14] [15]. Furthermore, introducing chirality into these materials may give place to potential applications in research fields such as chiral spintronics or magneto-chiral dichroism [16].

In the course of a systematic search for new members of this interesting family of heterometallic complexes involving oxalate dianions, we herein report the synthesis, crystal structure and thermal behavior of a chiral three-dimensional oxalato-bridged coordination polymer, $\{[(\text{H}_2\text{O})_2\text{K}(\mu\text{-H}_2\text{O})\text{Sr}]@[\text{Cr}(\text{C}_2\text{O}_4)_3]\}_n$ (**1**), obtained from a metathesis reaction in water of the $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ and SrCl_2 salts with the stoichiometric ratio of 2:3.

2. Experimental

2.1. Materials and Measurements

All reagents for the syntheses were purchased from commercial sources and used as received, except for the starting potassium salt, $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, which was synthesized according to the literature [17]. Microanalyses (carbon and hydrogen) were performed on a Vario EL (Heraeus) analyzer. The FT-IR spectrum was recorded from KBr pellets in the range of 4000 - 400 cm^{-1} on a Perkin-Elmer spectrometer. The UV-Vis spectrum was obtained on a Perkin-Elmer Lambda 900 spectrophotometer in water at room temperature within the range 300 - 700 nm. The chemical analysis was obtained using Energy Dispersive X-ray Spectroscopy (EDX), with a JDX-7000F X-ray spectrometer. TGA experiments were performed with a Mettler Toledo TGA/SDTA 851 thermal analyzer, heated from room temperature to 600°C under nitrogen gas with a heating rate of 10°C/min. The melting points were measured using an Electrothermal 9100 apparatus.

2.2. Synthesis of $\{[(\text{H}_2\text{O})_2\text{K}(\mu\text{-H}_2\text{O})\text{Sr}]@[\text{Cr}(\text{C}_2\text{O}_4)_3]\}_n$

The title compound was obtained by metathesis from the potassium salt as follows: $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ (0.98 g, 2 mmol) was dissolved in 50 mL of water. Simultaneously, an aqueous solution (30 mL) of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (0.80 g, 3 mmol) was prepared and subsequently added in successive small portions into the $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ one. The resulting violet mixture was stirred at 333 K for 1 hour and then filtered off. The filtrate was allowed to evaporate at room temperature. After a few weeks, violet needle crystals suitable for X-ray diffraction were isolated by filtration, and dried in air. Yield: 0.82 g (85.5%). M. p.: > 240°C. Anal. Calcd. for $\text{C}_6\text{H}_4\text{CrKO}_{14}\text{Sr}$ (478.81 $\text{g} \cdot \text{mol}^{-1}$): C, 15.05; H, 0.84%. Found: C, 14.96; H, 0.79%. IR (KBr disk, cm^{-1}): $\nu = 3449$ (w), 1708 (m), 1672 (s), 1419 (s), 1277 (s), 907 (w), 853 (s), 806 (s), 543 (s), 477 (s). UV-Vis (H_2O solution, nm): 417, 569.

2.3. X-Ray Crystallography

A violet crystal with approximate dimensions $0.281 \times 0.085 \times 0.038 \text{ mm}^3$ was selected under ambient condi-

tions 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 crystal evaluation and data collection were performed on a Bruker QuazarSMART APEXII diffractometer with MoK α ($\lambda = 0.71073$ Å) radiation. The program SMART [18] was used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT [18] for integration of the intensity of reflections and scaling, SADABS [19] for absorption corrections, and SHELXTL [20] [21] for space group and structure determination and least-squares refinements on F^2 . The structure was solved by direct methods using the program SHELXS-97 [22] and refined by full-matrix least-squares methods against F^2 with SHELXL-97 [22]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All 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. The figures have been generated using Diamond 3.1e software [23]. Crystallographic data and refinement parameters are listed in **Table 1**. Selected bond distances and bond angles are given in **Table 2**.

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

Empirical Formula	C ₆ H ₄ CrKO ₁₄ Sr
Formula weight	478.81
Temperature (K)	100 (1)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Fdd2
<i>a</i> (Å)	14.110 (4)
<i>b</i> (Å)	36.074 (11)
<i>c</i> (Å)	11.034(3)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	5616 (3)
<i>Z</i>	16
<i>D</i> _{calc} (g/cm ³)	2.265
Absorption coefficient (mm ⁻¹)	4.944
<i>F</i> (000)	3728.0
Crystal size (mm)	0.281 × 0.085 × 0.038
2 θ Range for data collection (°)	2.258 – 59.906
Index ranges	−19 ≤ <i>h</i> ≤ 19; −50 ≤ <i>k</i> ≤ 50; −15 ≤ <i>l</i> ≤ 15
Reflections collected	36173
Independent reflections (<i>R</i> _{int} ; <i>R</i> _{sigma})	4070 (0.0399; 0.0214)
Absorption correction	Semi-empirical
Max. and min. transmission	0.834 and 0.337
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	4070/7/235
Goodness-of-fit on F^2	1.086
Final <i>R</i> indices [<i>I</i> > 2 sigma(<i>I</i>)]	<i>R</i> ₁ = 0.0293, <i>wR</i> ₂ = 0.0720
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0300, <i>wR</i> ₂ = 0.0723
Largest diff. peak and hole (eÅ ⁻³)	1.19 and −0.68
Flack parameter	0.001 (3)

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

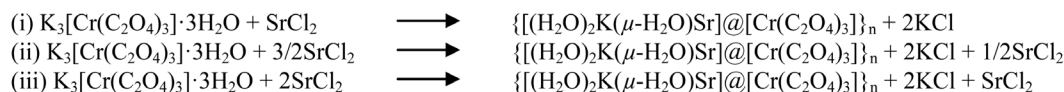
Bond Lengths		Bond Angles	
Sr ⁽¹⁾ –O ⁽²⁾¹	2.625 (4)	O ⁽²⁾¹ –Sr ⁽¹⁾ –O ⁽⁴⁾¹	63.29 (11)
Sr ⁽¹⁾ –O ⁽⁴⁾	2.656 (3)	O ⁽²⁾¹ –Sr ⁽¹⁾ –O ⁽⁴⁾	72.98 (11)
Sr ⁽¹⁾ –O ⁽⁴⁾¹	2.664 (3)	O ⁽⁴⁾ –Sr ⁽¹⁾ –O ⁽⁴⁾¹	115.13 (11)
Sr ⁽¹⁾ –O ⁽⁶⁾²	2.664 (4)	O ⁽²⁾¹ –Sr ⁽¹⁾ –O ⁽⁶⁾²	132.21 (11)
Sr ⁽¹⁾ –O ⁽⁸⁾²	2.688 (3)	O ⁽²⁾¹ –Sr ⁽¹⁾ –O ⁽⁸⁾²	122.97 (11)
Sr ⁽¹⁾ –O ⁽¹⁰⁾³	2.638 (3)	O ⁽²⁾¹ –Sr ⁽¹⁾ –O ⁽¹⁰⁾³	70.95 (12)
Sr ⁽¹⁾ –O ⁽¹²⁾³	2.628 (3)	O ⁽²⁾¹ –Sr ⁽¹⁾ –O ⁽¹²⁾³	69.38 (12)
Sr ⁽¹⁾ –O ⁽¹³⁾	2.653 (4)	O ⁽²⁾¹ –Sr ⁽¹⁾ –O ⁽¹³⁾	126.73 (12)
Cr ⁽¹⁾ –O ⁽¹⁾	1.978 (3)	O ⁽⁵⁾ –Cr ⁽¹⁾ –O ⁽¹⁾	172.34 (14)
Cr ⁽¹⁾ –O ⁽³⁾	1.973(3)	O ⁽³⁾ –Cr ⁽¹⁾ –O ⁽⁷⁾	96.60 (14)
Cr ⁽¹⁾ –O ⁽⁵⁾	1.976 (4)	O ⁽¹⁾ –Cr ⁽¹⁾ –O ⁽⁵⁾	93.00 (14)
Cr ⁽¹⁾ –O ⁽⁷⁾	1.978 (3)	O ⁽⁹⁾ –Cr ⁽¹⁾ –O ⁽⁷⁾	170.97 (14)
Cr ⁽¹⁾ –O ⁽⁹⁾	1.971 (3)	O ⁽⁹⁾ –Cr ⁽¹⁾ –O ⁽¹⁾	93.39 (15)
Cr ⁽¹⁾ –O ⁽¹¹⁾	1.986 (3)	O ⁽³⁾ –Cr ⁽¹⁾ –O ⁽¹¹⁾	171.42 (14)
K ⁽¹⁾ –O ⁽⁹⁾⁴	2.770 (3)	O ⁽⁹⁾ –K ⁽¹⁾ –O ⁽¹³⁾⁴	86.85 (10)
K ⁽¹⁾ –O ⁽⁹⁾	2.770 (3)	O ⁽⁹⁾ –K ⁽¹⁾ –O ⁽¹⁰⁾	45.09 (9)
K ⁽¹⁾ –O ⁽¹⁰⁾	3.007 (3)	O ⁽¹³⁾ –K ⁽¹⁾ –O ⁽⁹⁾⁴	139.83 (15)
K ⁽¹⁾ –O ⁽¹⁰⁾⁴	3.007 (3)	O ⁽¹³⁾⁴ –K ⁽¹⁾ –O ⁽¹⁰⁾⁴	140.39 (17)
K ⁽¹⁾ –O ⁽¹³⁾⁴	2.876 (4)	O ⁽⁹⁾⁴ –K ⁽¹⁾ –O ⁽¹³⁾⁴	86.85 (10)
K ⁽¹⁾ –O ⁽¹³⁾	2.876 (4)	O ⁽⁹⁾⁴ –K ⁽¹⁾ –O ⁽¹³⁾	115.12 (10)
K ⁽¹⁾ –O ⁽¹⁴⁾⁴	2.889 (8)	O ⁽¹⁴⁾⁴ –K ⁽¹⁾ –O ⁽¹⁰⁾	143.28 (16)
K ⁽¹⁾ –O ⁽¹⁴⁾	2.889 (8)	O ⁽¹³⁾⁴ –K ⁽¹⁾ –O ⁽¹⁴⁾	104.64 (17)
K ⁽²⁾ –O ⁽¹⁾⁵	2.728 (4)	O ⁽¹⁾⁵ –K ⁽²⁾ –O ⁽¹⁵⁾	101.9 (2)
K ⁽²⁾ –O ⁽²⁾⁵	2.892 (4)	O ⁽¹⁵⁾ –K ⁽²⁾ –O ⁽²⁾⁵	120.1 (2)
K ⁽²⁾ –O ⁽⁵⁾	2.810 (4)	O ⁽¹⁵⁾ –K ⁽²⁾ –O ⁽⁵⁾	138.0 (2)
K ⁽²⁾ –O ⁽⁶⁾	2.990 (4)	O ⁽¹⁵⁾ –K ⁽²⁾ –O ⁽⁶⁾	124.5 (2)
K ⁽²⁾ –O ⁽¹⁴⁾⁴	1.922 (8)	O ⁽¹⁴⁾⁴ –K ⁽²⁾ –O ⁽⁵⁾	69.7 (2)
K ⁽²⁾ –O ⁽¹⁴⁾	2.753 (8)	O ⁽¹⁴⁾⁴ –K ⁽²⁾ –O ⁽⁶⁾	112.3 (3)
K ⁽²⁾ –O ⁽¹⁵⁾	2.716 (10)	O ⁽¹⁵⁾ –K ⁽²⁾ –O ⁽¹⁴⁾	77.0 (2)
K ⁽²⁾ –K ⁽²⁾⁴	2.214 (4)		

Symmetry transformations used to generate equivalent atoms: ¹1/4 + X, 5/4 – Y, 1/4 + Z; ²1/4 + X, 5/4 – Y, –3/4 + Z; ³3/4 – X, 1/4 + Y, –1/4 + Z; ⁴1 – X, 1 – Y, +Z; ⁵1/2 + X, +Y, 1/2 + Z.

3. Results and Discussion

3.1. Formation of {[$(\text{H}_2\text{O})_2\text{K}(\mu\text{-H}_2\text{O})\text{Sr}@\text{[Cr}(\text{C}_2\text{O}_4)_3\text{]}\}_n$ (**1**)

Our original attempt aimed at synthesizing the heterometallic neutral polynuclear complex, $\{\text{Sr}_3[\text{Cr}^{\text{III}}(\text{C}_2\text{O}_4)_3]_2\} \cdot n\text{H}_2\text{O}$ with the ionic ratio of 3Sr^{II} vs. 2Cr^{III} , analog of the well-documented $\{\text{Ba}_6(\text{H}_2\text{O})_{17}[\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]_4\} \cdot 7\text{H}_2\text{O}$ ($\text{M} = \text{Cr}; \text{Fe}$) compounds [10] [11]. Unexpectedly, the tripotassium tris(oxalato)chromate(III) salt, $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, exchanged only two of its three potassium ions for one strontium(II) ion, yielding the air stable heterometallic neutral trinuclear complex, $\{[(\text{H}_2\text{O})_2\text{K}(\mu\text{-H}_2\text{O})\text{Sr}@\text{[Cr}(\text{C}_2\text{O}_4)_3\text{]}\}_n$ (**1**). The competition between K^+ and Sr^{2+} cations appears as an important point to prevent formation of the expected Sr(II)/Cr(III)-oxalate coordination polymer, in line with the identical coordination number (8) of K^+ and of Sr^{2+} ions in the title compound. Using Ba^{2+} in lieu of Sr^{2+} ions, a total exchange of three potassium cations was observed, demonstrating, therefore, a more pronounced affinity of Ba^{2+} ions to bind tris(oxalato)metalate(III) anions [10] [11]. Efforts were taken to better understand the formation of **1** by carrying out two other syntheses with the $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}:\text{SrCl}_2$ stoichiometric ratios of 1:1 and 1:2. As expected, the same compound **1** was obtained, different only in purity and yield, the maximum yield being 89 % with the 1:1 ratio. From the above results, it is evident that, irrespective to the stoichiometric ratio of reagents, the title compound is readily formed if $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ and SrCl_2 are combined. The possible formation mechanisms producing compound **1** are summarized in Scheme 1.



Scheme 1. The possible formation mechanisms of compound **1**.

3.2. Energy Dispersive X-Ray Analysis

Results from the Energy Dispersive X-ray Spectroscopy (EDX) analyses of **1** are shown in **Figure 1**. It is observed in this EDX spectrum the presence of chemical elements O, K, Sr and Cr, suggesting clearly the success in the preparation of compound **1**.

3.3. Infrared Spectrum

The IR spectrum exhibits weak absorption bands centered at 3449 cm^{-1} and attributable to the well-known $\nu_{\text{O-H}}$ vibrations of the H_2O molecules that are coordinated to the K^+ and Sr^{2+} sites. The band at 1700 cm^{-1} is assigned to $\nu_{\text{C=O}}$ whereas those at 1419 cm^{-1} are attributed to $\nu_{\text{O-C=O}}$ [24]. The sharp peaks at 1277 cm^{-1} and 907 cm^{-1} may be tentatively assigned to the $\nu_{\text{C-O}}$ and $\nu_{\text{C-C}}$ vibrations [24], respectively. Medium to weak bands appearing in the region below 600 cm^{-1} may be attributed to vibrations within the coordination spheres around the metallic centers. These results are, in fact, consistent with the presence of $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ and H_2O in the material concerned.

3.4. UV-Vis Spectrum

The ultraviolet-visible spectrum in aqueous solution showed peaks at 417 and 569 nm attributed to the spin-allowed ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ transitions, respectively, within the octahedral complex anion $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ contained in **1**. It is obvious that the present electronic absorption spectrum is virtually superimposable with that reported [10] [12] [13] [25] since the spectral information thus obtained solely relate to the $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ species.

3.5. 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**. The overall TGA curve consists of two-step weight loss process. The first step between 80°C and 150°C corresponds to a weight loss of 11.4% (calc. 11.3%) which is due to release of the three coordinated water molecules. During the second step, beyond 150°C , a gradual decomposition of the crystal network takes place with formation of a final residue which is proved to be a mixture of SrCrO_4 and K_2CO_3 compounds.

3.6. Crystal Structure

The molecular structure of **1** has been determined by X-ray study, which shows that it crystallizes in orthorhombic chiral space group $\text{Fdd}2$ with three-dimensional arrangement. As depicted in **Figure 3**, the asymmetric unit of **1** consists of one cationic motif-formally $[(\text{H}_2\text{O})_2\text{K}(\mu\text{-H}_2\text{O})\text{Sr}]^{3+}$, and one anionic $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ entity. The anionic building stone, $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$, functions as a metalloligand or else, as an interconnecting bridge. Hence, this interconnecting bridge interconnects, across its O atoms, the independent sites K, Sr1 and Cr1 into a three-dimensional polymeric lattice network.

Two independent K centers (K1 and K2) are eight-coordinate both by H_2O and oxalate ligands and are present 50% in the asymmetric unit. Atom K1 is coordinated to two water molecules (OW13 and OW14). Atom K2 is coordinated to two water molecules (OW14 and OW15). The water molecules OW13 and OW14 bridge the K1 and Sr1 centers and the K1 and K2 centers, respectively. The water molecule OW15 belongs solely to the K2 center. A molecular drawing of compound **1** with complete coordination spheres of the metal atoms is shown in **Figure 4** and selected geometrical parameters are presented in **Table 2**. As can be seen from **Figure 4**, the eighth coordination of the K2 center is completed by an unusual short K2 - K2⁴ metallic bond of $2.214(4)\text{ \AA}$. All the K-O bond lengths fit well within the range of previous results [26].

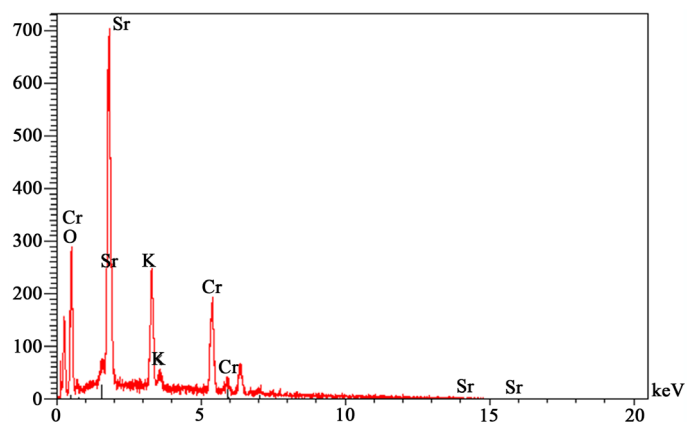


Figure 1. EDX analysis of compound **1** showing the nature of its different chemical elements.

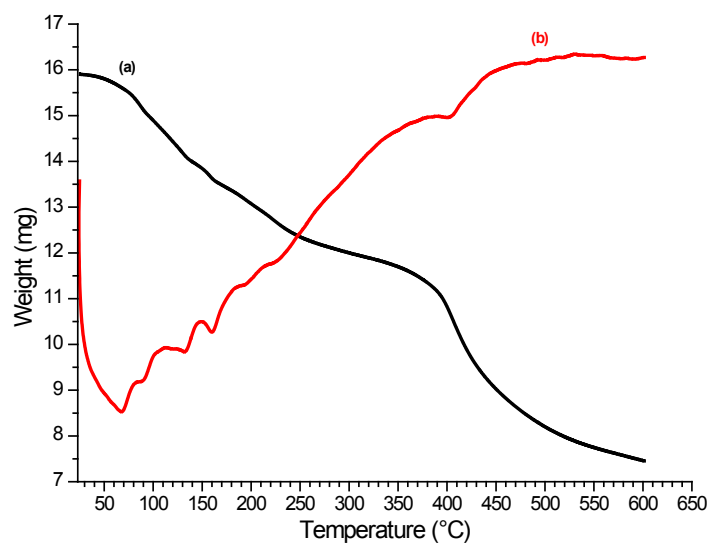


Figure 2. TGA (curve (a)) and DTA (curve (b)) of compound **1**.

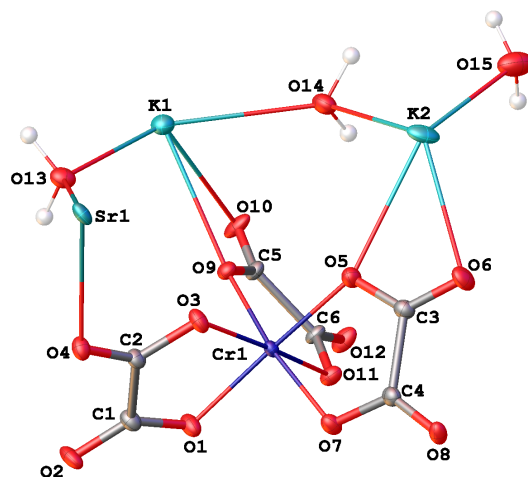


Figure 3. A molecular drawing of the asymmetric unit of compound **1** shown with 50% probability ellipsoids. Atoms K1 and K2 are present 50% of the time.

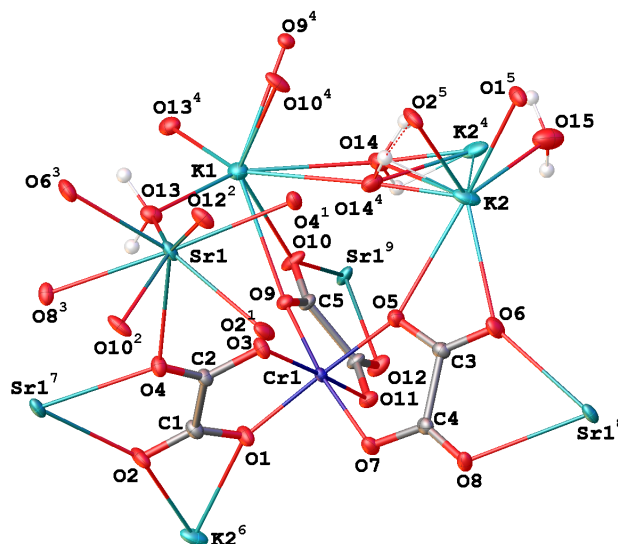


Figure 4. A molecular drawing of compound **1** shown with 50% probability ellipsoids. The coordination spheres of the metal atoms are completed. Atoms K1 and K2 are present 50% of the time. Symmetry codes: \$11/4 + X, 5/4 - Y, 1/4 + Z, \$23/4 - X, 1/4 + Y, -1/4 + Z, \$31/4 + X, 5/4 - Y, -3/4 + Z, \$41 - X, 1 - Y, +Z, \$51/2 + X, +Y, 1/2 + Z, \$6-1/2 + X, +Y, -1/2 + Z, \$7-1/4 + X, 5/4 - Y, -1/4 + Z, \$8-1/4 + X, 5/4 - Y, 3/4 + Z, \$93/4 - X, -1/4 + Y, 1/4 + Z.

The Sr1 site experiences also eight-coordinate coordination sphere, involving one chelation via the “external” O atoms (O6,O8) and to six monodentate linkages, *i.e.* one across an O atom of water molecule (OW13) and five across “external” O atoms (O2, O4, O4¹, O10, O12). Taking into account the coordination of aqua ligands to K and Sr centers, the cationic motif in the asymmetric unit of **1** can be formulated [(OW15)K₂_{1/2}(μ-OW14)K₁_{1/2}(μ-OW13)Sr1]³⁺ or simply [(H₂O)₂K(μ-H₂O)Sr]³⁺.

The Cr1 center is exclusively coordinated by oxalates to produce the well-established helical coordination geometry of [Cr(C₂O₄)₃]³⁻ ions. This coordination to chromium occurs across the six “internal” O atoms (O1, O3, O5, O7, O9, O11), giving rise to Cr1-O bond lengths ranging from 1.971 (3) to 1.983 (6) Å and O-Cr1-O bond angles ranging from 82.18 (14) to 172.34 (14). These bond lengths and bond angles are in good agreement with those found in other tris(oxalato)metalate(III) complexes [10]–[15] [26].

The packing diagram of compound **1** viewed down the crystallographic *c*-axis is shown in Figure 5. The bulk structure of **1** is consolidated by coulombic interactions between the ionic motifs and a three-dimensional network of hydrogen bonding of the type O-H···O, with O···O distances ranging from 2.626 (14) to 2.898 (8) Å (Table 3). It should be noted that, to the best of our knowledge, compound **1** constitutes the first chiral, non-hydrated representative of oxalate-based coordination polymers with general formula {M(I)/M(II)/M^{III}(C₂O₄)₃} · nH₂O.

4. Conclusion

We have isolated from aqueous solution at room temperature, a novel trinuclear heterometallic complex of composition {[(H₂O)₂K(μ-H₂O)Sr]@[Cr(C₂O₄)₃]}_n (**1**), via a metathesis reaction of K₃[Cr(C₂O₄)₃] · 3H₂O with SrCl₂. The bulk structure of **1** is a chiral, 3-D metal-organic framework held together by intermetallic linkages across oxalate and aqua oxygen bridging with extensive hydrogen-bonding interactions stabilizing the crystal packing. Thermal analysis of **1** reveals that it is stable up to *ca.* 80°C. Preliminary observations from our laboratory suggest that a well conceived and systematically conducted preparative procedure may be applied generally to fabricate a whole range of homologous members of this promising family of chiral, 3-D metal(I)/metal(II)/metal(III)-oxalate polymers.

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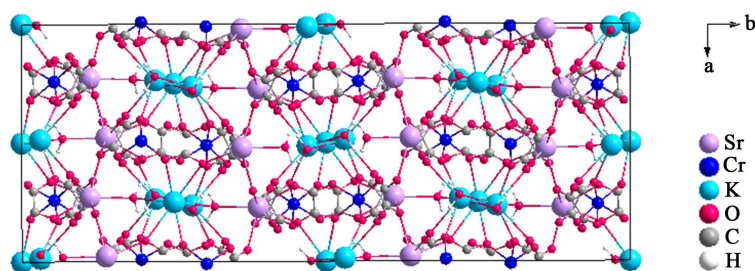


Figure 5. Packing diagram of compound **1** viewed down *c*-axis highlighting the chiral three-dimensional network.

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)
O ⁽¹³⁾ -H ^(13A) ...O ⁽¹²⁾¹	0.9583 (15)	1.803 (19)	2.727 (5)	161 (5)
O ⁽¹⁴⁾ -H ^(14A) ...O ⁽⁵⁾²	0.96	1.95	2.799 (8)	146.6
O ⁽¹⁴⁾ -H ^(14B) ...O ⁽²⁾³	0.96	1.95	2.898 (8)	171.8
O ⁽¹⁵⁾ -H ^(15A) ...O ⁽⁶⁾²	0.96	1.90	2.830 (9)	165.0
O ⁽¹⁵⁾ -H ^(15B) ...O ⁽¹⁾³	0.96	1.82	2.722 (9)	156.1

Symmetry transformations used to generate equivalent atoms (D: donor; A: acceptor): ¹1/2 - X, 1 - Y, -1/2 + Z; ²1 - X, 1 - Y, +Z; ³1/2 - X, 1 - Y, 1/2 + Z.

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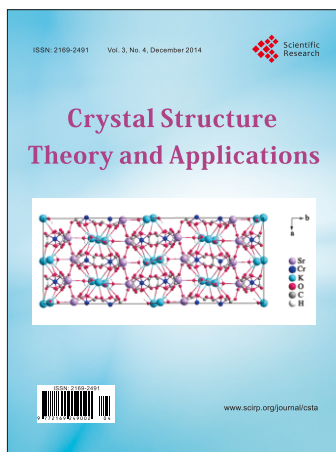
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Supplementary Material

Detailed crystallographic data in CIF format for this paper were deposited with the Cambridge Crystallographic Data Centre (CCDC-1021676). The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk].



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