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Chromate(III),  $(C_6H_{16}N)[Cr(C_2O_4)_2(H_2O)_2]$ :  
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# A Novel Chromium(III) Hybrid Salt, Triethylammonium *Trans*-Diaquabis(Oxalato- $\kappa^2O^1,O^2$ ) Chromate(III), $(C_6H_{16}N)[Cr(C_2O_4)_2(H_2O)_2]$ : Synthesis, Spectroscopic Studies, Thermal Behavior and Crystal Structure

Pierre R. Ndong<sup>1</sup>, Martin Signé<sup>1</sup>, Patrice T. Kenfack<sup>2\*</sup>, Yves A. Mbiangué<sup>3</sup>, Gouet Bebga<sup>4\*</sup>, Emmanuel Wenger<sup>5</sup>

<sup>1</sup>Department of Inorganic Chemistry, Faculty of Science, University of Yaounde I, Yaounde, Cameroon

<sup>2</sup>Department of Chemistry, Faculty of Science, University of Dschang, Dschang, Cameroon

<sup>3</sup>Department of Chemistry, Higher Teachers' Training College, University of Maroua, Maroua, Cameroon

<sup>4</sup>Department of Chemistry, Higher Teacher Training College, University of Yaounde I, Yaounde, Cameroon

<sup>5</sup>CRM<sup>2</sup>, Université de Lorraine, CNRS, Nancy, France

Email: \*gouetbeb@yahoo.fr, \*pakenfack@gmail.com

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## Abstract

A novel organic-inorganic chromium(III) hybrid salt, triethylammonium *trans*-diaquabis(oxalato- $\kappa^2O^1,O^2$ )chromate(III),  $(C_6H_{16}N)[Cr(C_2O_4)_2(H_2O)_2]$  (**1**), has been synthesized in aqueous solution and characterized by elemental and thermal analyses, FTIR and UV-Vis spectroscopies, and by single crystal X-ray structure determination. Compound **1** crystallizes in the orthorhombic system, *Pbcn* space group with the unit cell parameters  $a = 11.1776(10)$ ,  $b = 7.6105(10)$ ,  $c = 17.5654(2)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 1494.24(3)$  Å<sup>3</sup>,  $Z = 4$  and  $Z' = 1/2$ . The structure of **1** consists of  $[Cr(C_2O_4)_2(H_2O)_2]^-$  mononuclear anions and triethylammonium  $[(C_2H_5)_3NH]^+$  cations. In the anionic unit, the Cr<sup>III</sup> ion is six coordinated, in a distorted octahedral geometry, by four equatorial O atoms of two oxalate anions acting as chelating ligands and two O atoms from *trans*-coordinated water molecules occupying the apical positions with longer metal-oxygen distances. In the solid, O-H ... O and N-H ... O intra and inter molecular hydrogen bonding interactions connect the components into a 3D network. The triethylammonium cations are disordered among two possible orientations with occupancies rates around 50% for C4, N1, C1a, C1b, C4<sup>ii</sup>, N1<sup>ii</sup>, C1a<sup>ii</sup>, C1b<sup>ii</sup> (ii =  $-x + 1$ ,  $y$ ,  $-z + 1/2$ ). The IR spectrum of **1** is

consistent with the presence of the various molecular building constituents. The UV-Vis spectrum shows two absorption bands around 564 and 416 nm which are compatible with an anionic chromium (III) complex in an octahedral environment. Thermal studies carried out in air between 25°C and 700°C confirm the anhydrous character of **1** and show that it is stable up to 210°C.

## Keywords

Hybrid Salt, Chromium(III) Oxalate Complex, Triethylammonium, Static Disorder, Spectroscopy, Crystal Structure, Thermal Study

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## 1. Introduction

In the recent years, the area of organic-inorganic hybrid salts based on bis(oxalato)chromate(III), has become one of intense research activities due to the need for novel solid-state architectures with potential applications as functional materials in various fields such as catalysis, magnetism, medicine, luminescence, conductivity and even materials science and industrial applications [1]-[6].

Up to now, there has been a significant interest in the synthesis and characterization of bis(oxalato)chromate(III) compounds through a synthetic strategy based on supramolecular chemistry and self-assembly processes of two different components. Thus, to investigate new supramolecular architectures containing molecular building blocks  $[M(C_2O_4)_3]^{3-}$  or  $[Cr(C_2O_4)_2(H_2O)_2]^-$  ( $M = Cr, Fe$ ), a lot of work has been devoted to the study of their combination with different organic cations ( $OrgH^+$ ). In this context, heterocyclic aromatic amines (pyridine, pyrazole, imidazole, etc.) rings are often used as organic cations, by protonating their imine groups, leading to 3D hybrid (oxalato)metalate(III) salts with the general formula  $(OrgH)_3[M(C_2O_4)_3] \cdot nH_2O$  ( $M = Cr, Fe; n \geq 0$ ) [7] [8] [9] or  $A[Cr(C_2O_4)_2(H_2O)_2] \cdot nB$  with  $A = OrgH^+$ ;  $B = H_2O$  or urea,  $CO(NH_2)_2$ ;  $n \geq 0$  [10] [11] [12] [13] [14].

To the best of our knowledge, it appears that in this family of compounds, (oxalato)metalate(III) hybrid salts involving protonated acyclic aliphatic amines chains (linear or branched) as organic cations are still poorly characterized in terms of their solid-state structures and properties [14]. We have been investigating this class of salts not only with a view of producing new materials, but also to unravel the subtle structural features that characterize these solids.

In this direction, our investigation has thus been focused on the synthesis and characterization of new bis(oxalato)chromate(III) species of general formula  $A[Cr(C_2O_4)_2(H_2O)_2] \cdot nB$  ( $A = OrgH^+$ ;  $B = H_2O$  or  $CO(NH_2)_2$ ;  $n \geq 0$ ) [10] [11] [14]. By using triethylammonium as organic cation, we have isolated a new hybrid salt:  $(C_6H_{15}NH)[Cr(C_2O_4)_2(H_2O)_2]$  and we herein report its synthesis and structural characterization as well as its spectroscopic and thermal properties.

## 2. Experimental

### 2.1. Materials and Physical Measurements

Reagents were obtained from Prolabo (oxalic acid, hydrochloric acid and triethylamine) and Riedel-de Haën (chromium(III) trichloride hexahydrate) and used as such without further purification. Elemental analyses for carbon, hydrogen and nitrogen were performed using a Thermo Scientific FLASH 2000 Analyzer. The FTIR spectrum ( $4000 - 400 \text{ cm}^{-1}$ ) of the solid sample was performed with an Alpha-P spectrophotometer using KBr pellets. The UV-Vis spectrum was recorded on an Aqualytic spectrophotometer in water solution in the range 200 - 800 nm. Thermal analyses (TG, DSC and DTG) were carried out on a STA PT-1000 Linseis Thermogravimetric Analyser under air in the temperature range  $25^\circ\text{C} - 700^\circ\text{C}$ , with a heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$ . Single-crystal X-ray measurements were performed using Bruker D8 Quest diffractometer with Mo  $k\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ).

### 2.2. Synthesis

In a stirred mixture of water/ethanol (Sigma-Aldrich) (30 mL) in the ratio 1:2, was dissolved commercial triethylamine ( $\text{C}_2\text{H}_5)_3\text{N}$  (10 mmol; 1.01 g), hydrochloric acid (0.05 M; 2 mL) and successive small portions of oxalic acid  $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  (20 mmol; 2.54 g): Solution A.  $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$  (10 mmol; 2.70 g) was dissolved in 40 mL of water (solution B) and added dropwise in solution A. The resultant violet solution was stirred at room temperature for 2 hours, then filtered and the filtrate was allowed to evaporate at room temperature. Violet prismatic crystals suitable for X-ray diffraction were formed within three weeks. Yield: 73% based on  $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ . *Anal. Calc.* for  $\text{C}_{10}\text{H}_{20}\text{NCrO}_{10}$  Mw = 366.23: C, 32.77; H, 5.46; N, 3.82%. Found: C, 32.23; H, 4.88; N, 3.82%. IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3153 m ( $\nu_{\text{N-H}}$ ), 3009 m ( $\nu_{\text{O-H}}$ ), 1647s ( $\nu_{\text{asyC=O}}$ ), 1394s ( $\nu_{\text{C-C}}$ ), 1257 m ( $\nu_{\text{syC-N}}$ ), 1182 m ( $\nu_{\text{syC-O}}$ ), 901 - 806 w ( $\delta_{\text{C=O}}$ ), 463 w (Cr-O). UV-Vis ( $\text{H}_2\text{O}$  solution, nm): 416, 564.

### 2.3. X-Ray Crystallography

A prismatic violet crystal of the material with dimensions  $0.17 \times 0.14 \times 0.06 \text{ mm}^3$  was selected and mounted on a glass fiber. Diffraction data were obtained at 293 K on a Bruker D8 Quest APEX-III CCD area detector Photon III diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The X-ray intensities were corrected using multi-scan method applied by SADABS [15]. The crystal structure was solved by direct method of SHELXS-97 [16] and refined by full-matrix least-square techniques on  $F^2$  using the SHELXL-2014 program package [17]. A structural disorder was found on the cationic part of this compound (triethylammonium ion) both at 293 and at 100 K but the structure was well modeled at 293 K, with all non-hydrogen atoms refined anisotropically. The positions of all the hydrogen atoms were assigned from the electron density map generated by Fourier difference apart from those of one ethyl group (hydrogen atoms of C2) which were ideally introduced. These atoms were refined freely but three restrains

were used for H3B and H1 bonded respectively to C3 and N1 to keep the normal N-H and C-H bond lengths and avoid the short contact between H1 and C4 in one of its disordered position. All these hydrogen atoms were included as riding atoms with isotropic displacement parameters

$(U_{iso} H = 1.2U_{eq} C = 1.2U_{eq} N = 1.5U_{eq} O_w)$ . DIAMOND program [18] was used to deal with the processed crystallographic data and artwork representations. Details of the structure determination and final refinements are summarized in **Table 1** and selected bond lengths (Å) and angles (°) around the central chromium (III) ion are listed in **Table 2**.

**Table 1.** Crystal data and structure refinement details for 1.

CCDC N°	1981174
Empirical formula	C <sub>10</sub> H <sub>20</sub> CrNO <sub>10</sub>
Formula weight	366.27
Temperature (K)	293 (2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Pbcn</i>
Unit cell dimensions	<i>a</i> = 11.1776 (10) (Å)
	<i>b</i> = 7.6105 (10) (Å)
	<i>c</i> = 17.5654 (2) (Å)
	$\alpha = 90.0^\circ$ $\beta = 90.0^\circ$ $\gamma = 90.0^\circ$
Volume (Å <sup>3</sup> )	1494.24 (3)
<i>Z</i> , <i>Z'</i>	4, 1/2
Density (calculated) mg/m <sup>3</sup>	1.628
Absorption coefficient (mm <sup>-1</sup> )	0.817
<i>F</i> (000)	764
Crystal size (mm <sup>3</sup> )	0.172 × 0.144 × 0.055
Theta range for data collection (°)	2.319 - 28.714
Index ranges	-15 ≤ <i>h</i> ≤ 15, -9 ≤ <i>k</i> ≤ 10, -23 ≤ <i>l</i> ≤ 23
Reflections collected	26,559
Independent reflections	1936 (R(int) = 0.029)
Completeness to theta = 25.242°	100.0%
Refinement method	Full-matrix least squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	1936/3/151
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.100
Final R indices [ <i>I</i> > 2 sigma( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0275, <i>wR</i> <sub>2</sub> = 0.0810
R indices (all data)	<i>R</i> <sub>1</sub> = 0.0325, <i>wR</i> <sub>2</sub> = 0.0862
Extinction coefficient	0.0059 (8)
Largest diff. peak and hole (e/Å <sup>3</sup> )	0.386 and -0.487

**Table 2.** Selected bond lengths (Å) and bond angles (°) of **1**.

Selected bond lengths (Å)			
Cr1-O4 <sup>i</sup>	1.9630 (9)	Cr1-O1	1.9729 (9)
Cr1-O4	1.9630 (9)	Cr1-O1W	2.0041 (11)
Cr1-O1 <sup>i</sup>	1.9728 (9)	Cr1-O1W <sup>i</sup>	2.0041 (11)
Selected bond angles (°)			
O4 <sup>i</sup> -Cr1-O4	180.00	O1 <sup>i</sup> -Cr1-O1W	89.45 (4)
O4 <sup>i</sup> -Cr1-O1 <sup>i</sup>	82.05 (4)	O1-Cr1-O1W	90.55 (4)
O4-Cr1-O1 <sup>i</sup>	97.95 (4)	O4 <sup>i</sup> -Cr1-O1W <sup>i</sup>	89.91 (4)
O4 <sup>i</sup> -Cr1-O1	97.95 (4)	O4-Cr1-O1W <sup>i</sup>	90.09 (4)
O4-Cr1-O1	82.05 (4)	O1 <sup>i</sup> -Cr1-O1W <sup>i</sup>	90.55 (4)
O1 <sup>i</sup> -Cr1-O1	180.00 (2)	O1-Cr1-O1W <sup>i</sup>	89.45 (4)
O4 <sup>i</sup> -Cr1-O1W	90.09 (4)	O1W-Cr1-O1W <sup>i</sup>	180.0
O4-Cr1-O1W	89.91 (4)		

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

### 3. Results and Discussion

#### 3.1. Formation of $(C_6H_{16}N)[Cr(C_2O_4)_2(H_2O)_2]$ (**1**)

The combination of triethylamine ( $C_2H_5$ )<sub>3</sub>N with hydrochloric acid and oxalic acid in aqueous solution generates in situ  $(C_6H_{16}N)_2C_2O_4$  which reacts with  $CrCl_3 \cdot 6H_2O$  in water to give, by evaporation of the resulting solution at room temperature after three weeks, the title compound  $(C_6H_{16}N)[Cr(C_2O_4)_2(H_2O)_2]$  (**1**) as violet prismatic crystals. **1** is thermally stable up to 210 °C.

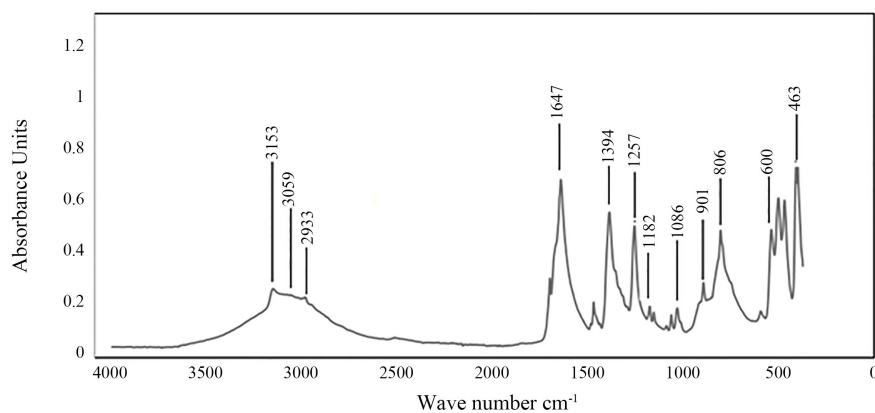
#### 3.2. Characterization of **1**

The FTIR spectrum of **1** (Figure 1) exhibits weak absorption bands centered at 3153  $cm^{-1}$  attributed to  $\nu_{N-H}$  of triethylammonium cations. The sharp bands observed at 3009  $cm^{-1}$  can be assigned to the well-known  $\nu_{O-H}$  vibrations of the  $H_2O$  coordinated to the  $Cr^{III}$  sites [19]. The strong band appearing at 1647  $cm^{-1}$  corresponds to  $\nu_{C=O}$  [20] [21] and the medium-size band at 1453  $cm^{-1}$  can be assigned to the symmetric stretching absorption of the carboxylate groups of the oxalato ligand [22]. Strong to medium well-resolved bands appearing at 1394  $cm^{-1}$ , 1257  $cm^{-1}$ , 1182  $cm^{-1}$  could be attributed to  $\nu_{C-N}$ ,  $\nu_{C-O}$  and  $\nu_{C-C}$  respectively [23] [24] [25]. The pattern of the  $\delta_{O-C=O}$ : 901 - 806  $cm^{-1}$  vibrations support the presence of chelating oxalate in the structure of **1** [24] [25]. Medium to weak bands observed in the region 600 - 463  $cm^{-1}$  may be attributed to  $\nu_{Cr-O}$  vibrations within the coordination spheres around the metallic centers [26] [27]. These results are consistent with the presence of triethylammonium cation,  $[(C_2H_5)_3NH]^+$  and  $[Cr(C_2O_4)_2(H_2O)_2]^-$  complex anion in **1**.

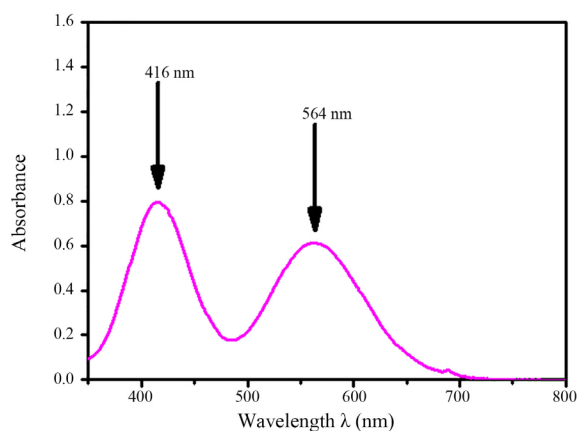
The UV-Vis spectrum of **1** (Figure 2) reveals two absorption bands at 416 nm (24,038  $cm^{-1}$ ) and 564 nm (17,730  $cm^{-1}$ ) which correspond respectively to  ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$  and  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  *d-d* transitions within the octahedral complex anions  $[Cr(C_2O_4)_2(H_2O)_2]^-$  contained in **1** [11] [28] [29]. Obviously, the present electronic

absorption spectrum is virtually superimposable with that reported since the spectral information thus obtained solely relates to the  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$  species. This assignment is in agreement with the X-ray structural results.

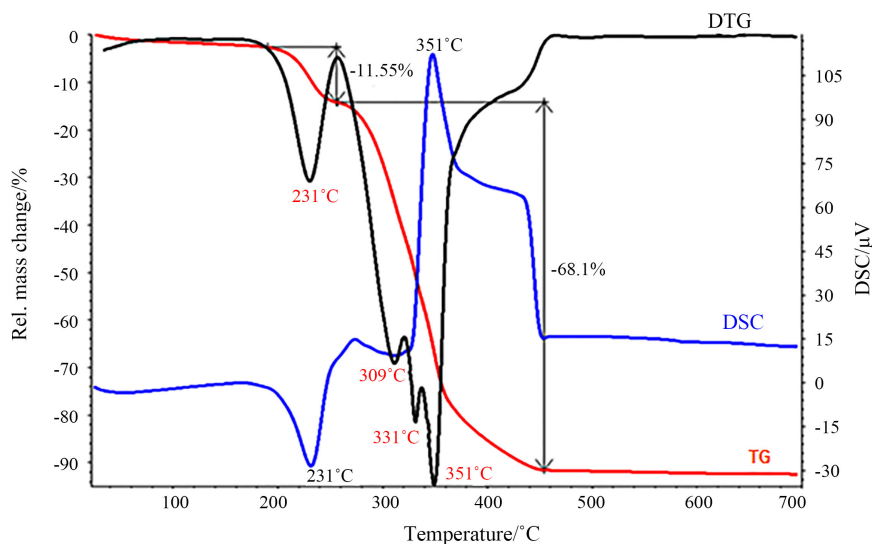
The thermal behavior of **1** was performed by thermogravimetric (TG), differential thermal gravimetric (DTG) and differential scanning calorimetry (DSC) analyses under air, in the temperature ranging from 25 °C to 700 °C, with a heating rate of 10 °C·min<sup>-1</sup>. The curves obtained are shown in **Figure 3**. The thermograms exhibit no mass loss up to 210 °C, thus confirming that the water molecules in **1** are bonded to chromium ion. The overall weight loss amounts to 79.65% and is based on the stoichiometry of the starting material  $(\text{C}_6\text{H}_{16}\text{N})[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$  (formula weight: 336.23 gmol<sup>-1</sup>). In the temperature range 210 °C - 240 °C, the TG trace shows a 11.55% loss in weight (endothermic peak at 231 °C), suggesting that **1** loses two water molecules in one step which is consistent with the calculated weight loss of 10.0%. The result is in agreement with the structure which contains two coordinated water molecules. In addition, the salt loses weight between 240 °C - 445 °C, which is attributed to the decomposition of the oxalate groups and the organic part of the material, the final residue being  $\text{Cr}_2\text{O}_3$  [24] [30]. But no clear plateaus were reached in these stages and the total weight loss is equal to 68.1%.



**Figure 1.** Infrared absorption spectrum of **1**.



**Figure 2.** Electronic absorption spectrum of **1**.



**Figure 3.** TG curve (red), DSC curve (blue) and DTG curve (black) of **1**.

### 3.3. Crystal Structure Description of **1**

The unit cell of **1** contains four formula units, each of which is formed by one  $(\text{C}_6\text{H}_{15}\text{NH})^+$  triethylammonium cation and the paramagnetic  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$  mononuclear complex anion in *trans*-aqua configuration (**Figure 4**).

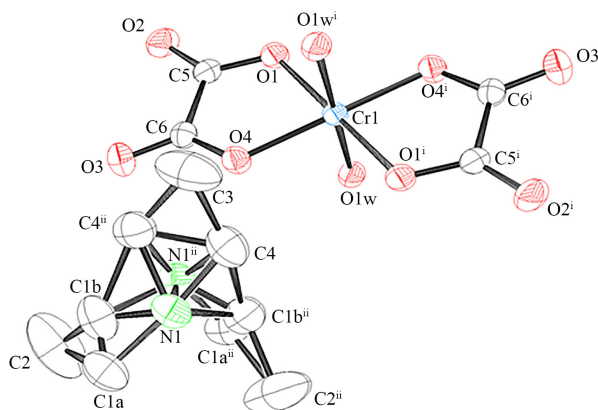
The  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$  anionic molecular building block shows a slightly distorted (4 + 2) octahedral coordination of the central metal ( $\text{Cr}^{\text{III}}$ ) by four equatorial O atoms (O1, O1<sup>i</sup>, O4, O4<sup>i</sup>,  $i = -x + 1, -y + 1, -z + 1$ ) of two coplanar oxalate and two axial O atoms (O1w, O1w<sup>i</sup>) of aqua ligands. The four Cr-O(ox) distances that range from 1.9630(9) to 1.9729(9) Å are somewhat slightly shorter than Cr-O(water) ones: 2.0041(11) Å (**Table 2**) but comparable to those reported hitherto in similar compounds [11] [14] [26].

As in many compounds of the triethylammonium cation  $(\text{C}_6\text{H}_{16}\text{N})^+$ , the structure of the latter is disordered. Indeed, many entries were found in the CSD [31] with this specification. In **1**, the nitrogen atom (N1) of this cation as well as the C4 atom are disordered over two positions around the  $2_{[1/2, y, 1/4]}$ -fold axis with 50% of occupancies. C3 atom bonded to C4 to build one of the ethyl groups of this cation lies on this 2-fold axis and thus is constrained to vibrate along particular directions but its equivalent isotropic displacement parameters ( $U_{\text{eq}}$ ) is comparable to those of C2 and C2<sup>ii</sup> ( $ii = -x + 1, y, -z + 1/2$ ) atoms (**Figure 4**). Indeed, the two other ethyl groups of the cation are symmetrically equivalent owing the axis indicated above. The carbon atom of the  $\text{CH}_2$  group in these ethyl chains are also disordered over two positions (C1a and C1b) with occupancies of 53% and 47% respectively. This compound thus shows two static disorders. The first one (around two symmetrically equivalent positions) is related to one of the ethyl group and the nitrogen atom while the second one (related to two crystallographic independent positions) is observed for the two other ethyl groups of the cation. This behavior was observed in more than 10 triethylammonium compounds in the CSD. Some of these compounds are reported in the following

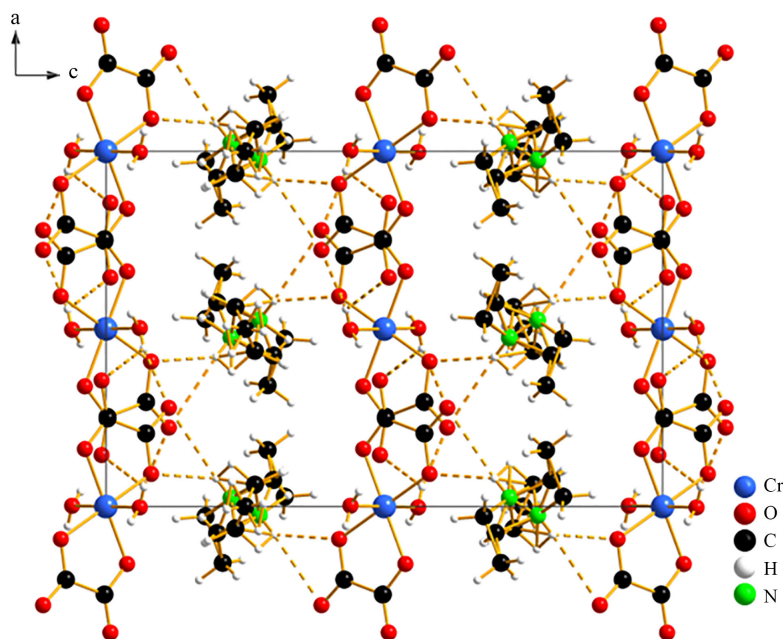


papers: [32] [33] [34].

Both ions  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$  and  $(\text{C}_6\text{H}_{16}\text{N})^+$  are connected such to build alternate pseudo corrugated layers running along [001] (**Figure 5**). The cohesion of the structure is ensured by O-H ... O (intra, within anions) and N-H ... O (inter, between anions and cations) hydrogen bonds [length  $d(\text{D} \dots \text{A})$  and angle,  $(\text{D}-\text{H} \dots \text{A})$  vary from 2.7074(15) to 3.500(3) Å and 122(2) to 178(3)°, respectively] interactions leading to a 3D supramolecular framework (**Table 3**). The coordinated water molecules ( $\text{O1w}$  and  $\text{O1w}^i$ ) act as donors, forming an anions-anions interaction type (dashed lines, **Figure 5**).



**Figure 4.** Molecular components of **1** with the atom numbering scheme (The hydrogen atoms have been omitted for the sake of clarity). (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + 1, y, -z + 1/2$ .



**Figure 5.** Interconnection of the constituents of **1** into a 3D network showing positive and negative alternate pseudo corrugated layers running along the [100]. Hydrogen bonds are highlighted with dashed lines.

**Table 3.** Hydrogen bond lengths (Å) and bond angles (°) of **1**.

<i>D-H ... A</i>	<i>D-H</i>	<i>H ... A</i>	<i>D ... A</i>	<i>D-H-A</i>
O(1W)-H(1WA) ... O(2)#3	0.72 (3)	2.58 (3)	3.0304 (17)	122 (2)
O(1W)-H(1WA) ... O(3)#3	0.72 (3)	2.05 (3)	2.7499 (14)	165 (3)
O(1W)-H(1WB) ... O(2)#4	0.77 (3)	1.94 (3)	2.7074 (15)	178 (3)
N(1)-H(1) ... O(3)#2	0.985 (18)	2.53 (2)	3.500 (3)	168 (3)
N(1)-H(1) ... O(4)#2	0.985 (18)	2.11 (3)	2.899 (3)	136 (3)

Symmetry transformations used to generate equivalent atoms: #1  $-x+1, -y+1, -z+1$ ; #2  $-x+1, y, -z+1/2$ ; #3  $x-1/2, -y+1/2, -z+1$ ; #4  $-x+3/2, y-1/2, z$ .

For the oxalate groups, the peripheral carboxylate oxygen atoms O3 and O4 are the only acceptors. The  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$  and  $(\text{C}_6\text{H}_{16}\text{N})^+$  are connected via N-H ... O (inter) hydrogen bonds that link the amino N1-H1 group ( $d_{\text{N1...O3}} = 3.500(3)$  Å,  $d_{\text{N1...O4}} = 2.899(3)$  Å) to the free O3 and O4 oxalato O atoms, forming a cations-anions interaction type by connecting the positive and the negative layers (dashed lines, **Figure 5**). The low number of hydrogen bonds between the two ions involved in **1** ( $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$  and  $(\text{C}_6\text{H}_{15}\text{NH})^+$ ) can explain the static disorders observed in the triethylammonium ion of this compound.

All these interactions link the alternate pseudo corrugated layers together, forming a three-dimensional network and reinforcing the cohesion of the ionic structure.

## 4. Conclusions

Single crystals of the new salt  $(\text{C}_6\text{H}_{16}\text{N})[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$  were grown from an aqueous solution at ambient temperature. The crystal structure of **1** has been characterized by single crystal X-ray structure determination and confirmed by elemental analysis, by FTIR and UV-Vis spectroscopies and TG-DSC-DTG techniques. The crystal structure of **1** reveals that the triethylammonium cations are disordered among two possible orientations. A 3D network was shown to be generated by intra O-H ... O and inter N-H ... O hydrogen-bonding interactions involving the organic cation and the complex anion. FTIR data and the thermal analysis have allowed to check the absence of solvate water in **1** as well as the nature of connections to the network of these molecular bricks, confirming the result of the structural study.

In our research group, the replacement of organic cations in these hybrid salts by small positive charged species such as hydronium ( $\text{H}_3\text{O}^+$ ) cations, compensating the negative charge of the anionic complex is under way. Such systems, no doubt, could be well-adapted models to monitor the exploration of the concept of protonic charge transport processes in the solid state [35] [36] [37].

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## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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### Supplementary Material

Detailed crystallographic data in CIF format for this paper were deposited with the Cambridge Crystallographic Data Centre (CCDC-1981174). The data can be obtained free of charge at <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).