

Research Article

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Synthesis, crystal and molecular structure of *catena*-(bis(μ 1-oxalic acid)- μ 3-hydrogen oxalate-di-aqua-sodium(I))

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Abstract: The crystal and molecular structure of *catena*-(bis(μ -oxalic acid)- μ -hydrogen oxalate-di-aqua-sodium(I)) was detected by X-Ray analysis. The compound crystallizes in the triclinic space group P-1, with a (Å) 6.2378(12); b (Å) 7.1115(14); c (Å) 10.489(2); α (°) 94.65(3); β (°) 100.12(3); γ (°) 97.78(3). The sodium cation in the title compound is eight coordinated and forms a square antiprism. It is surrounded by two molecules of oxalic acid, one hydrogen oxalate anion and one water molecule. Both oxalic acid and hydrogen oxalate anion act as polydentate bridging ligands. Centrosymmetric sodium cations are bounded by hydrogen oxalate anions through a system of H bonds involving the molecules of oxalic acid. In the lattice, the 3D structure stabilized by H bonds is formed.

Supporting information: X-Ray (CIF file)

Keywords: *Catena*-(bis(μ -oxalic acid)- μ -hydrogen oxalate-di-aqua-sodium(I)); crystal structure; molecular structure; synthesis.

1. INTRODUCTION

Crystalline hybrid materials based on organic polyoxo compounds containing oxalic acid, its anionic forms and S-derivatives in the 3D polymeric chains have been a subject of interest of the synthetic chemists over the last two decades [1-4]. This deals with variety of its coordination modes from monodentate to polydentate bridging or chelating metal cations. Oxalic acid can exist in both neutral, mono and dianionic forms which together with the metal ion charge and stoichiometry leads to isolation of neutral or anionic coordination monomers or polymers. Formation of variety of H-bonds plays key role in building of an extended framework architecture through self-assembly process, involving among different interactions, short range and directional bonds [5]. The crystal structures of monovalent cation (hydronium, ammonium, potassium, cesium, thallium and rubidium) oxalates of different composition were detected and refined by different authors [6-14]. The structure of the corresponding sodium salt was not previously described.

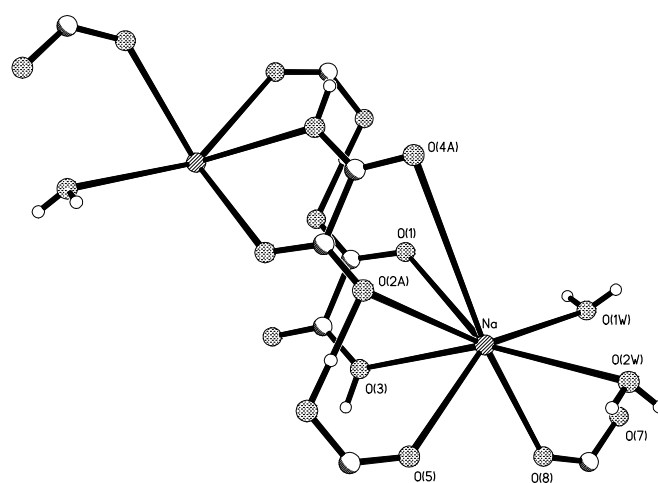


Figure 1. Fragment of the crystal structure of $\{[\text{Na}(\text{HC}_2\text{O}_4)(\text{H}_2\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]\cdot\text{H}_2\text{O}\}_n$, showing the atom numbering.

2. EXPERIMENTAL

All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. Elemental analysis (C, H) was performed on a Flash 2000 instrument. The IR spectrum was recorded with the Bruker Optics FT-IR spectrophotometer in the KBr pellets in the wavenumber interval 4000-400 cm^{-1} .

Synthesis of $\{[\text{Na}(\text{HC}_2\text{O}_4)(\text{H}_2\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]\cdot\text{H}_2\text{O}\}_n$. The title compound was obtained as one of the products in the synthesis of polymeric chromium oxalate. 20 ml of 10^{-1} mol/l aqueous solution of sodium chromate, 20 ml of 10^{-1} mol/l of oxalic acid and 7 ml of 10^{-1} mol/l solution of sodium hydroxide were mixed together and heated on the water bath until the colour changes from yellow to blue. Colourless prismatic crystals appeared in mother-liquor after one week and were separated by filtration. Yield 50%. Anal. Calc. for $\text{C}_6\text{H}_7\text{NaO}_{14}$: C, 22.10; H, 2.16. Found: C, 22.32; H, 2.43 %. IR: 3510, 3444, 3327 cm^{-1} ($\nu(\text{OH}) + \nu(\text{H}_2\text{O})$); 1692 cm^{-1} ($\nu(\text{CO})$); 1553 cm^{-1} ($\nu_{\text{as}}(\text{COO}^-)$); 1415, 1269 cm^{-1} ($\nu_{\text{s}}(\text{COO}^-)$).

The X-ray diffraction data were collected at 100(2) K with an Xcalibur diffractometer using Mo radiation ($\lambda = 0.71073 \text{ \AA}$) and ω scans were used for the data collection. The lattice parameters were determined using reflections in the range $2.91 < \theta < 29.06^\circ$. The structure was solved with direct methods using SHELXTL [15]. The refinement of the structure was performed by the full-matrix least square method on F2 for all the data with anisotropic thermal parameters for non-hydrogen atoms. All the hydrogen atoms were added using a riding model. CCDC reference number 1002737. The supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The crystallography details for the structures determination of the compound are presented in Table 1.

Table 1. Crystallographic data and structure refinement parameters for $\{[\text{Na}(\text{HC}_2\text{O}_4)(\text{H}_2\text{C}_2\text{O}_4)2\text{H}_2\text{O}]\cdot\text{H}_2\text{O}\}_n$

Empirical formula	$\text{C}_4\text{H}_6\text{NaO}_{10}$
Formula weight	237.08 g/mol
Crystal color	Colorless
Temperature	100(2) K
Wavelength	0.71073 \AA
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	$a(\text{\AA}) 6.2378(12);$ $b(\text{\AA}) 7.1115(14);$ $c(\text{\AA}) 10.489(2);$ $\alpha(^{\circ}) 94.65(3);$ $\beta(^{\circ}) 100.12(3);$ $\gamma(^{\circ}) 97.78(3)$
Volume	$451.22(15) \text{ \AA}^3$
Z, calculated density	2, $1.745 \text{ Mg}\cdot\text{m}^{-3}$
Absorption coefficient	0.218 mm^{-1}
$F(000)$	1096
Crystal size	$0.40 \times 0.35 \times 0.30 \text{ mm}$
Theta range for data collection	2.91 to 29.98 deg.
Limiting indices	$-6 \leq h \leq 8, -9 \leq k \leq 7, -14 \leq l \leq 14$
Reflections collected/unique	2420/2082 [R(int) = 0.0210]
Completeness to theta = 29.98	100%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2420/0/136
Goodness-of-fit on F2	1.077
Final R indices [$I > 2 \text{ sigma}(I)$]	R1 = 0.0563, wR2 = 0.1523
R indices (all data)	R1 = 0.0651, wR2 = 0.1605
Largest diff. peak and hole	$0.944 \text{ e}\cdot\text{\AA}^{-3}$ and $-0.411 \text{ e}\cdot\text{\AA}^{-3}$

3. RESULTS AND DISCUSSION

In the detected structure, the sodium cation in the title compound $\{[\text{Na}(\text{HC}_2\text{O}_4)(\text{H}_2\text{C}_2\text{O}_4)2\text{H}_2\text{O}]\cdot\text{H}_2\text{O}\}_n$ is eight coordinated and forms a square antiprism. It is surrounded by two molecules of oxalic acid, one hydrogen oxalate anion and one water molecule. (Fig. 1). The distances Na-O lie in the interval 2.882(2) - 2.970(2) \AA (Table 2). Both oxalic acid and hydrogen oxalate anion act as polydentate bridging ligands. The hydrogen oxalate ion chelates a Na cation through O1 and O3, and bridges the

Table 2. Selected bond lengths (\AA) and angles (deg) in $\{[\text{Na}(\text{HC}_2\text{O}_4)(\text{H}_2\text{C}_2\text{O}_4)2\text{H}_2\text{O}]\cdot\text{H}_2\text{O}\}_n$

NaO1	2.895(2)	O8NaO1	124.54(6)
NaO1W	2.969(2)	O8NaO5	80.11(5)
NaO3	2.928(2)	O1NaO5	115.40(6)
NaO4A	2.903(2)	O8NaO4	122.74(6)
NaO5	2.900(2)	O1NaO4	84.89(5)
NaO8	2.881(2)	O5NaO4	134.80(6)
NaO2A	3.157(2)	O8NaO3	92.41(6)
NaO2W	3.030(2)	O1NaO3	53.91(5)
O1C1	1.241(3)	O5NaO3	68.32(6)
O2C1	1.265(3)	O4NaO3	137.60(6)
O3C2	1.299(3)	O8NaO1W	67.24(5)
O4C2	1.221(3)	O1NaO1W	86.65(6)
O5C3	1.218(3)	O5NaO1W	147.24(6)
O6C3	1.291(3)	O4NaO1W	67.22(5)
O7C4	1.295(3)	O3NaO1W	114.09(6)
O8C4	1.222(3)		
C1C2	1.552(3)		
C3C4	1.554(4)		

NaB cation through an O4 atom. The two oxalic acid molecules act as m-bridging ligands (Fig. 1). One of them is tridentate with two O atoms chelating one sodium atom and the other bridging another Na atom. The other molecule of oxalic acid is bidentate chelating. The centrosymmetric sodium cations are bounded by hydrogen oxalate anions through a system of H bonds involving the molecules of oxalic acid (Table 3). The bond lengths of two molecules of oxalic acid are C3O5 1.218(3) \AA ; C3O6 1.292(3) \AA ; C4O8 1.221(3) \AA ; C4O7 1.294(3) \AA . The C4O7 distance corresponds to singular bond. The H atom at O7 could not be detected. It might be delocalized between O7 atom and the O1W atom of the lattice water molecule to form a hydronium cation as it was detected by Kherfi et al. [5]. O7O1W distance is 2.459(3) \AA , which may also indicate the existence of an H bond between the oxalic acid and the lattice water molecule.

The structure involves 10 distinct hydrogen bonds between O atoms: they range in length (OO) from 2.709 to 3.342 Å, and the OHO angle from 118.44 to 173.55 deg. In the lattice, the 3D structure stabilized by H bonds is formed (Table 3).

The determined crystal structure of the substance correlates with the FT IR spectrum where the absorption of a lattice water

molecule (3510 cm^{-1}), as well as stretching of coordinated H_2O molecule and OH group of the hydrogen oxalate ion (3444 , 3327 cm^{-1}) are found. The vibration of a C=O group in hydrogen oxalate 1692 cm^{-1} may overlap with $d(\text{H}_2\text{O})$. The absorption at 1553 cm^{-1} and $1415/1269\text{ cm}^{-1}$ is due to asymmetric and symmetric vibrations of the COO^- groups respectively.

Table 3. Hydrogen bonds in $\{[\text{Na}(\text{HC}_2\text{O}_4)(\text{H}_2\text{C}_2\text{O}_4)2\text{H}_2\text{O}]\cdot\text{H}_2\text{O}\}_n$ (Å and deg.)

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O1W-H1W1	0.772	1.958	166.60	2.715	O4 [-x+1, -y+1, -z+1]
O1W-H1W1	0.772	2.602	118.44	3.046	O2 [-x+1, -y+1, -z+1]
O1W-H1W2	0.757	1.964	167.98	2.709	O1 [-x+1, -y+2, -z+1]
O2W-H2W1	0.815	1.994	163.17	2.784	O8 [-x+1, -y+2, -z+2]
O2W-H2W1	0.815	2.362	118.68	2.844	O7 [x-1, y, z]
O2W-H2W2	0.825	2.065	156.26	2.840	O5 [-x+1, -y+2, -z+2]
O2W-H2W2	0.825	2.340	124.87	2.892	O6 [x+1, y+1, z]
O3-H3	0.859	1.652	169.95	2.503	O2W [x, y-1, z]
O6-H6	1.045	1.446	173.55	2.487	O2 [-x, -y+1, -z+1]
O6-H6	1.045	2.644	123.95	3.342	O1 [-x, -y+1, -z+1]

4. CONCLUSION

A polymeric bis(μ -oxalic acid)- μ -hydrogen oxalate-di-aqua-sodium(I) was isolated as one of the products in the synthesis of polymeric chromium oxalate, and its crystal and molecular structure was determined by the X ray analysis on single crystals. The sodium cation is found to be eight coordinated and forms a square antiprism. Two molecules of oxalic acid and one hydrogen oxalate anion act as polydentate bridging ligands. One water molecule is also included in coordination. The 3D lattice is stabilized by a system of hydrogen bonds.

Acknowledgements

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