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$\text{Tl}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$: a new crystalline form of thallium(I) oxalate

Abstract: The title compound was prepared by reaction, in aqueous solution, of Tl_2CO_3 and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in a molar ratio of 1:2. Its crystal structure was solved by X-ray diffraction methods. It crystallizes in the monoclinic space group $P2_1/a$ with $Z = 2$ molecules per unit cell. The oxalic acid molecule and the oxalate anion are planar, residing on crystallographic inversion centers, and linked to each other by strong $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds giving rise to a polymeric structure. The Tl(I) ion is in a distorted polyhedral coordination with nine neighboring O atoms, five of oxalate anions and four others of oxalic acid molecules. The FTIR and FT-Raman spectra of the compound were also recorded and are briefly discussed.

Keywords: crystal structure; FTIR spectra; FT-Raman spectra; synthesis; thallium(I) oxalate-oxalic acid.

DOI 10.1515/znb-2014-0257

Received November 25, 2014; accepted January 9, 2015

1 Introduction

As part of our studies of oxalate biominerals [1] and biomineralization processes in plants [1–6], we have performed different studies to attain a wider insight into the general physicochemical properties of metal oxalates (for a recent review cf. [7]).

Interestingly, heavy metal oxalates have so far been scarcely investigated, although crystal data for Ag(I) [8], Hg(II) [9], Cd (II) [10, 11], Sn(II) [12], and Pb(II) [13] oxalates are known, and the vibrational-spectroscopic behavior of

the last two mentioned compounds have recently been investigated [14, 15].

In the case of group 13 metals, structural data for $[\text{In}_2(\text{C}_2\text{O}_4)_3] \cdot 10\text{H}_2\text{O}$ [16], $[\text{In}_2(\text{C}_2\text{O}_4)_3] \cdot 6\text{H}_2\text{O}$ [17], and $\text{Tl}_2\text{C}_2\text{O}_4$ [18, 19] have been reported.

In order to extend the knowledge on thallium(I) oxalates, we have attempted to prepare the thallium(I) hydrogen oxalate, TlHC_2O_4 , mentioned in the older literature [20], but the structural analysis of the generated crystals has now shown, unexpectedly, the formation of a species of composition $\text{Tl}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$. This paper is devoted to the structural and spectroscopic characterization of this new compound.

2 Results and discussion

2.1 Synthesis of the compound

The compound was prepared by reaction of aqueous solutions of thallium(I) carbonate and oxalic acid in a molar ratio of 1:2, under the conditions described in the Experimental section (Section 3).

2.2 Crystal and molecular structure of the compound

An ORTEP [21] plot showing the unit cell content of $\text{Tl}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ is presented in Fig. 1. The corresponding bond distances and angles within the oxalate anion and the oxalic acid molecule are given in Table 1. Both species are positioned at inversion centers, are planar, and show nearly D_{2h} (oxalate) and C_{2h} (oxalic acid) point symmetry.

For the oxalato ion, carboxylic C–O bond distances are 1.24(1) and 1.28(1) Å, the longer one corresponding to the oxygen atoms at the shortest contact with thallium [2.757(7) Å], in correspondence with a delocalized π system. For the oxalic acid, $d(\text{C}-\text{OH}) = 1.29(1)$ Å and $d(\text{C}=\text{O}) = 1.21(1)$ Å, as expected for formally localized single and double C–O bonds. Oxalate and oxalic acid

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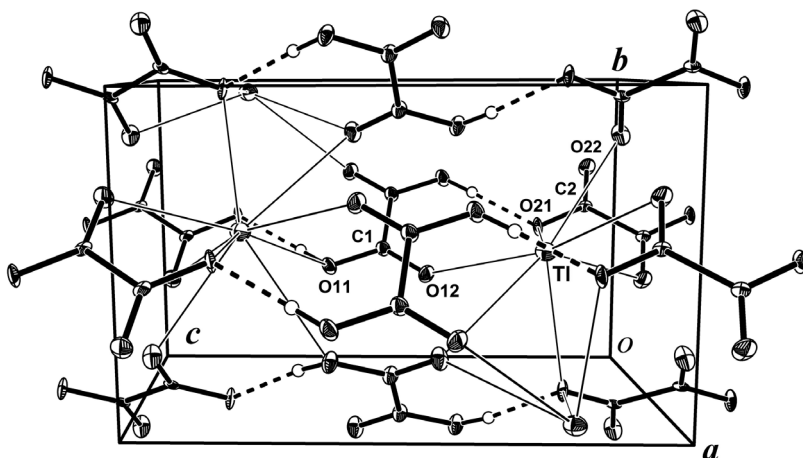


Fig. 1: View of the unit cell content of $\text{Tl}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ showing the labeling of the non-H atoms and their displacement ellipsoids at the 30 % probability level. Metal-oxygen short contacts up to 3.250 Å are indicated by thin lines and hydrogen bonds by dashed lines.

C–C bond lengths are equal within experimental accuracy [1.54(2) and 1.55(2) Å]. Bond lengths and angles are in general agreement with values reported for the acid in $\alpha\text{-H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ [22] and for the OOC-COO^- anion in $\text{Tl}_2\text{C}_2\text{O}_4$ [18] and $\text{Na}_2\text{C}_2\text{O}_4$ [23, 24].

Each OH moiety of the oxalic acid molecule in crystals of $\text{Tl}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ forms a strong O–H \cdots O hydrogen bond with one oxygen atom of a neighboring oxalato anion [$d(\text{O}\cdots\text{O}) = 2.561(9)$ Å, $\angle(\text{O-H}\cdots\text{O}) = 165(11)^\circ$], giving rise to a nearly planar polymeric structure that extends along the crystallographic *c* axis (see Fig. 1).

Up to a coordination sphere of 3.250 Å in radius, the thallium ion is in an irregular 9-fold environment, conformed by five oxygen atoms of neighboring oxalate ions (Tl–O distances from 2.757 to 3.181 Å) and by four other oxygen atoms of oxalic acid molecules (Tl–O distances in the 3.111–3.250 Å range). Besides, direct consequences related to the expected activity of the $6s^2$ lone electron pair of Tl(I) [19] are not clearly visible, although part of the distortion of the coordination polyhedron around the metal center is surely originated by this effect (cf. also [18, 19]).

Table 1: Bond lengths (Å) and angles (deg) within oxalate anions and oxalic acid molecules^a.

C(1)–O(12)	1.22(1)	O(12)–C(1)–O(11)	122.5(8)
C(1)–O(11)	1.29(1)	O(12)–C(1)–C(1)#1	119.9(10)
C(1)–C(1)#1	1.55(2)	O(11)–C(1)–C(1)#1	117.6(9)
C(2)–O(22)	1.24(1)	O(22)–C(2)–O(21)	125.3(8)
C(2)–O(21)	1.28(1)	O(22)–C(2)–C(2)#2	120.2(10)
C(2)–C(2)#2	1.54(2)	O(21)–C(2)–C(2)#2	114.5(9)

^aSymmetry transformations used to generate equivalent atoms: #1 $-x, -y + 1, -z + 1$; #2 $-x, -y + 1, -z$.

2.3 Vibrational spectra

The FTIR spectrum of the compound presents a very complex pattern. A first qualitative overview of this spectrum clearly confirms the presence of bands related to oxalic acid and to the oxalate anion. The corresponding Raman spectrum looks much simpler, presenting only a reduced number of bands, most of them related to the anionic species.

The FTIR spectrum, in the spectral range between 3000 and 400 cm^{-1} , is shown in Fig. 2 and the proposed assignments, for both the FTIR and FT-Raman spectra, are presented in Table 2. These assignments, based on previous studies of oxalic acid [25–28] and on some of our investigations of different crystalline metal oxalates [15, 29], are briefly commented on as follows. The stretching vibration of the OH groups is found as a relatively strong

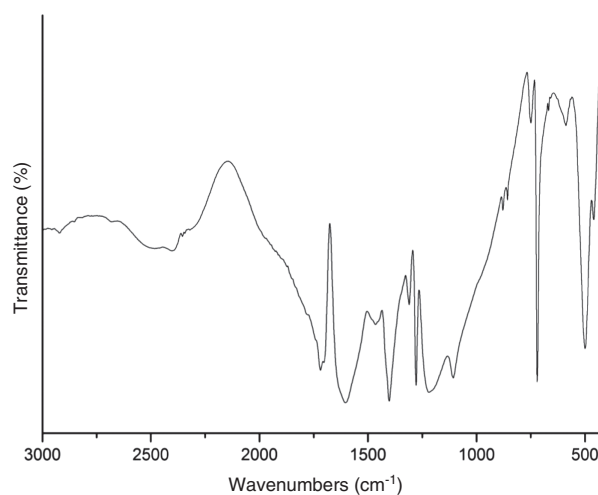


Fig. 2: FTIR spectrum of $\text{Tl}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ in the spectral range between 3000 and 400 cm^{-1} .

Table 2: Assignment of the vibrational spectra of $\text{Tl}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ (band positions in cm^{-1})^a.

FTIR	FT-Raman	Assignments
2441 s, br, 2400 s		$\nu(\text{O}-\text{H})$
2000 sh, 1723 vs	1727 vs	$\nu(\text{C}=\text{O})$
1602 vs	1579 m	$\nu_{\text{as}}(\text{C}-\text{O})$ anion
1464 w		$\nu(\text{C}-\text{O})$
	1444 vs	$\nu_{\text{s}}(\text{C}-\text{O})$ anion
1403 vs		$\nu(\text{C}-\text{O}) + \delta(\text{C}-\text{OH})$
	1393 w, 1363 w	$\nu(\text{C}-\text{O}) + \delta(\text{C}-\text{OH})$
1314 m, 1281 vs		$\nu_{\text{as}}(\text{C}-\text{O})$ anion
1223 vs, 1107 s	1231 w	$\delta(\text{C}-\text{OH}) + \nu(\text{C}-\text{O})$
881 w, 858 w	879 m, 859 m	$\nu(\text{C}-\text{C})$ anion
	844 w, 818 vw	$\nu(\text{C}-\text{C})$
754 m		$\delta(\text{O}-\text{C}-\text{O})$ anion
718 vs		$\tau(\text{OH})$
590 m	590 vw, 539 vw	$\rho(\text{O}-\text{C}-\text{O})$ anion
502 vs	485 w	$\delta(\text{C}=\text{O})$
461 w	476 sh, 460 w	$\gamma(\text{C}=\text{O})$
	428 m	$\delta(\text{OCO})$

^avs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

and broad doublet centered at about 2400 cm^{-1} . The position of this band is clearly in agreement with the presence of the strong hydrogen bonds [30, 31] determined in the structural analysis (see above). The band broadening is usually related to anharmonicity effects in the $\text{O}-\text{H}\cdots\text{O}$ motions in the crystal [28, 32].

The antisymmetric (C–O) stretching of the anion appears as two well-identifiable groups of bands in the FTIR spectrum, whereas the corresponding symmetric mode is the strongest line in the Raman spectrum.

The $\nu(\text{C}-\text{C})$ stretching of the acid was only seen as a relatively weak doublet in the Raman spectrum, whereas the corresponding mode for the anion could be identified in both spectra and at somewhat higher energies.

The $\nu(\text{C}-\text{O})$ and $\delta(\text{C}-\text{OH})$ vibrations of the acid appear coupled in different spectral ranges, a fact also observed in the case of the free acid.

Probably, some of the lower frequency modes, observed below 700 cm^{-1} , are not totally pure vibrations and are surely coupled with each other to a certain extent.

3 Experimental section

3.1 Materials and measurements

Thallium(I) carbonate and oxalic acid dihydrate were supplied by Merck (Darmstadt, Germany), analytical

grade, and were used as purchased. Elemental analysis of the obtained compound was performed with a Carlo Erba (Milano, Italy) model EA 1108 elemental analyzer. The infrared absorption spectra were recorded on a FTIR Bruker (Billerica, MA, USA) EQUINOX-55 spectrophotometer in the spectral range between 4000 and 400 cm^{-1} , using the KBr pellet technique. Raman spectra were obtained with a Perkin Elmer (Waltham, MA, USA) FT-Raman RFs 110/s spectrometer, using the 1064 nm line of a solid state Nd: YAG laser for excitation.

3.2 Synthesis of the compound

A solution of 0.50 g (4 mmol) of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ dissolved in 20 mL of distilled water was heated to boiling; 0.94 g (2 mmol) of solid Tl_2CO_3 was added in small portions under continuous stirring, and after completion of the addition, the solution was boiled and stirred for a

Table 3: Crystal data and structure refinement results for $\text{Tl}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$.

Empirical formula	$\text{C}_4\text{H}_2\text{O}_8\text{Tl}_2$
Formula weight	586.80
Crystal dimension, mm^3	$0.12 \times 0.06 \times 0.06$
Temperature, K	297(2)
Crystal system	Monoclinic
Space group	$P2_1/a$
a , Å	6.2891(4)
b , Å	6.3974(4)
c , Å	10.3618(6)
β , deg	94.526(6)
Volume, Å ³	415.60(4)
Z	2
Calculated density, g cm^{-3}	4.69
Absorption coefficient, mm^{-1}	38.7
$F(000)$, e	504
θ range for data collection, deg	3.75–26.00
Index ranges	$-7 \leq h \leq 7$; $-4 \leq k \leq 7$; $-12 \leq l \leq 9$
Reflections collected	1498
Independent reflections/ R_{int}	810/0.0304
Observed reflect. [$I > 2\sigma(I)$]	710
Max. and min. transmission	0.212/0.086
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	810/1/69
Goodness-of-fit on F^2	1.010
Final indices $R1/wR2$ [$I > 2\sigma(I)$]	0.0292/0.0603
Final indices $R1/wR2$ (all data)	0.0344/0.0633
Largest peak/hole, e Å^{-3}	1.10/−1.84

further 10 min. The precipitated solid was separated by filtration, washed several times with hot water and left to dry in air. The product was re-crystallized from water. The very small and thin colorless plates were separated and dried in air (yield: ca. 75%). The purity of the salt was confirmed by elemental analysis. – Analysis: $C_4H_2O_8Tl_2$ (586.80): calcd. C 8.18, H 0.34; found C 8.14, H 0.38.

Single crystals adequate for structural X-ray diffraction studies were selected from the crystalline mass employing a microscope.

The X-ray diffraction measurements were performed on an Oxford Xcalibur, Eos, Gemini CCD diffractometer with graphite-monochromatized MoK_α ($\lambda = 0.71073 \text{ \AA}$) radiation employing a very small single crystal of about $4.3 \times 10^{-4} \text{ mm}^3$ in volume to reduce absorption distortive effects (linear absorption coefficient $\mu = 38.7 \text{ mm}^{-1}$). X-ray diffraction intensities were collected (ω scans with ϑ and κ offsets), integrated and scaled with the CRYALISPRO [33] suite of programs. The unit cell parameters were obtained by least-squares refinement (based on the angular settings for all collected reflections with intensities larger than seven times the standard deviation of measurement errors) using CRYALISPRO. Data were corrected for extinction and empirically for absorption employing the multi-scan method implemented in CRYALISPRO. The structure was solved by Direct Methods with SHELXS-97 of the SHELX package [34] and the molecular model refined with SHELXL-97 of the same suite of programs [34]. The oxalic acid hydrogen atom was located in a Fourier difference map phased on the heavier atoms and refined at its found position with isotropic displacement parameters and the O–H distance restrained to a target value of 0.86(1) \AA . Crystal data, data collection procedure, structure determination methods and refinement results are summarized in Table 3.

CCDC 1033750 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments: This work was supported by the Universidad Nacional de La Plata, by CONICET (PIP 1529), and by ANPCyT (PME06 2804 and PICT 06 2315) of Argentina. O.E.P., G. A. E., and A.C.G-B. are Research Fellows of CONICET. The authors are also indebted to Prof. Aida Ben Altabef (Universidad Nacional de Tucumán) for the measurement of the Raman spectra.

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