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New insights into the oxidation of phenoxatellurine with sulfuric acid

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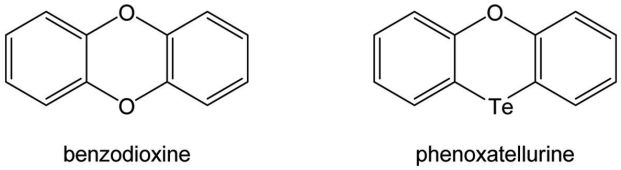
Abstract: The oxidation of phenoxatellurine (PT) with conc. H_2SO_4 was reinvestigated. Two crystalline products, namely $[PT_2][H_3O](SO_4H)_3$ (**1**) and $[PT](SO_4)$ (**2**) were isolated and fully characterized by X-ray crystallography. The structure of **1** features $[PT_2]^{2+}$ dications giving rise to double-decker structures with two parallel PT layers that arise from dimerisation of two radical cations $[PT]^{\cdot+}$. The $[PT_2]^{2+}$ dications and the hydrogensulfate ions are associated via secondary Te···O interations. The oxonium ion and the hydrogensulfate ions are involved in hydrogen bonding. The structure of **2** comprises ion pairs consisting of $[PT]^{2+}$ dications and sulfate ions, which form a 2D coordination polymer. In addition, adjacent sulfate ions in the crystal lattice bind to tellurium atoms via secondary secondary Te···O interations.

Keywords: tellurium; pancake bonding; radical dimer

Phenoxatellurine (PT) is a well-defined dibenzodioxine-type heterocylce (Scheme 1, in which one oxygen atom has been formally replaced by tellurium (Drew, 1926a). Unlike planar dibenzodioxine, PT comprises a butterfly-type structure in the solid-state (Smith et al., 1973). Upon contact with mineral acids, such as sulfuric acid and nitric acids, PT forms intensely colored substances, which remained a curiosity for a long time (Drew, 1926b). There was early suspicion that the color arose from single-electron oxidation of PT (Witzinger, 1929), which was later confirmed by cyclovoltammetry (Cauquis and Maurey-Mey, 1973). However, the exact nature of the colored substances still remained unclear at the time. Very recently, we investigated the single-electron oxidation of PT using nitrosonium salts, $[NO][SbF_6]$ and $[NO][BF_4]$, which produced the well-defined products $[PT_2][SbF_6]_2$ and $[PT_3][BF_4]_2$, respectively, possessing so-called double-decker and triple-decker structures (Mostaghimi et al., 2019). Indeed, the aggregation within these layered structures stemmed from SOMO-SOMO interaction between two radical cations $[PT]^{\cdot+}$, commonly referred to as pancake bonding (Kertesz, 2019), but also from significant London dispersion interactions and non-covalent multi-centre bonding between the tellurium atoms.

In this work we reinvestigated the reaction of PT with sulfuric acid. We were now able to isolate and structurally characterize two compounds, namely, $[PT_2][H_3O][SO_4H]_3$ (**1**) and $[PT][SO_4]$ (**2**), that are closely related to Drew's original work (Drew, 1926b). Following the described procedure, PT was dissolved in concentrated sulfuric acid to give a deep red solution, from which sulfur dioxide evolved. The solution was carefully diluted with water and allowed to stand. After three days, bright red single crystals (**1**) had formed, which were characterized by X-ray crystallography. Accordingly, the composition of the red crystals is $[PT_2][H_3O][SO_4H]_3$ (**1**). Drew's original report suggests that in his case the red crystals were composed of $[PT_2][H_3O]_2[SO_4H]_4(H_2O)$ (denoted **III** in his work). Upon exposure to moist air on porous tile, he also obtained products "free" of sulfuric acid, namely, $[PT_2][SO_4H]_2(H_2O)_3$ (denoted **IV** in his work) and $[PT_2][SO_4H]_2(H_2O)_2$ (denoted **V** in his work), which were intensely blue-violet in colour (Drew, 1926b). We were able to confirm his observation.



Scheme 1: Lewis formulas of benzodioxine and phenoxatellurine.

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However, no single crystals were obtained from any of these intensely blue-violet products. The crystal structure of **1** is shown in Figure 1. Like $[PT_2][SbF_6]_2$ (Mostaghimi et al., 2019), **1** contains $[PT_2]^{2+}$ dications with a layered double-decker structure. The Te-Te bond length of **1** (2.928(1) Å) are slightly larger than those of $[PT_2][SbF_6]_2$ (2.897(1), 2.903(1) Å) having two conformers in the asymmetric unit. The degree of folding of the butterfly-structure can be quantified using the fold angle α between the planes defined by the two phenyl rings and the Te and O atoms. The fold angles α of **1** (3.5°, 21.9°) closely resembles values of one conformer of $[PT_2][SbF_6]_2$ (3.4°, 20.8°). These very similar structural features strongly suggest that the pancake bonding situation including London dispersion and non-covalent Te···Te interactions are also similar (Mostaghimi et al., 2019).

The $[PT_2]^{2+}$ dication is associated with six $[SO_4H]^-$ ions via a total of eight Te···O contacts (2.910(1)-3.465(1) Å, dashed blue lines in Figure 1) that are significantly shorter than the primary Te-O bonds in $[(4\text{-}MeOC_6H_4)_2TeO]_n$ (2.025(2) and 2.100(2) Å) (Beckmann et al., 2003). The $[H_3O]^+$ ion and the $[SO_4H]^-$ ions give rise to rather strong hydrogen bonds, as evidenced by the short O···O donor-acceptor distances (2.535(1)-2.644(1) Å, dashed black lines).

Recrystallization of the red crystals (**1**) from hot water at the air, furnished colorless crystals (**2**), which were also investigated by X-ray crystallography. The composition of the colorless crystals is $[PT][SO_4]$ (**2**), which is apparently the same material Drew obtained by recrystallisation from glacial acid (denoted **VII** in his work). The crystal structure of **2** is shown in Figure 2.

The structure consists of ion pairs alternating $[PT]^{2+}$ dications and sulfate ions that build a 1D coordination polymer. The $[PT]^{2+}$ dication of **2** is almost planar (fold α = 7.7°). The spatial arrangement of the Te atom is defined by two slightly elongated primary Te···O bonds (2.153(4), 2.249(5) Å; dashed black lines in Figure 2) and three secondary Te···O bonds (2.940(4), 2.989(5), 3.099(5) Å; dashed blue lines in Figure 2).

Almost 100 years after the discovery that phenoxatellurine (PT) dissolves in conc. sulfuric acid to give intensively colorful solutions (Drew, 1926b), the nature of one species, namely $[PT_2][H_3O][SO_4H]_3$ (**1**), which is responsible for the red color has been unraveled. A related colorless species, namely $[PT][SO_4]$ (**2**), was also obtained and fully characterized.

X-ray crystallography. Intensity data were collected using a STOE IPDS 2T diffractometer (**1**) and a Bruker Venture D8 diffractometer (**2**) with graphite-monochromated Mo-Kα (0.7107 Å) radiation. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in

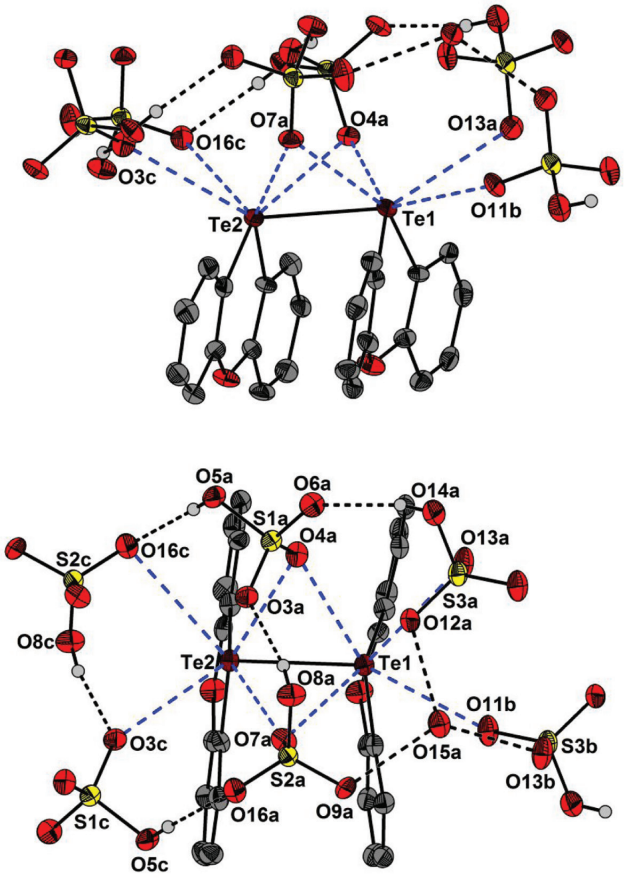

Figure 1: Crystal structure of **1** (from two perspectives) showing 30% probability ellipsoids and the atomic numbering. The dashed black and blue lines show secondary Te···O contacts and hydrogen bonds, respectively.

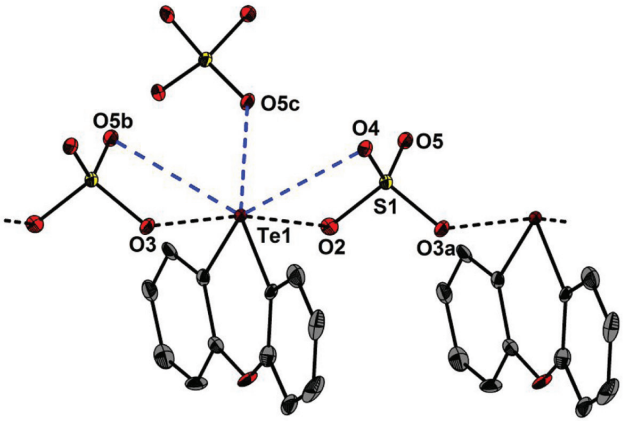

Figure 2: Crystal structure of **2** showing 30% probability ellipsoids and the atomic numbering. The dashed black and blue lines show slightly elongated primary Te···O bonds and secondary Te···O contacts, respectively.

Table 1: Crystal data and structure refinement of **1** and **2**.

	1	**2**
Formula	$C_{24}H_{22}O_{15}S_3Te_2$	$C_{12}H_8O_5STe$
Formula weight, g mol^{-1}	901.80	391.84
Crystal system	triclinic	monoclinic
Crystal size, mm	0.5 × 0.5 × 0.5	0.08 × 0.07 × 0.04
Space group	$P\bar{1}$	$P2_1/n$
a, Å	10.997(2)	8.414(2)
b, Å	12.523(2)	6.224(1)
c, Å	12.689(2)	22.629(6)
α, °	66.41(1)	90
β, °	78.10(1)	96.175(9)
γ, °	65.83(1)	90
V, Å^3	1459.1(4)	1178.18(5)
Z	2	4
ρ_{calcd}, Mg m^{-3}	2.053	2.715
μ (Mo *Kα*), mm^{-1}	2.288	2.209
F(000)	876	752
θ range, deg	1.75 to 29.26	2.50 to 27.50
Index ranges	−15 ≤ h ≤ 15	−10 ≤ h ≤ 10
	−17 ≤ k ≤ 15	−7 ≤ k ≤ 8
	−17 ≤ l ≤ 17	−29 ≤ l ≤ 29
No. of reflns collected	16726	28767
Completeness to θ_{max}	97.9%	97.3%
No. indep. Reflns	7776	2640
No. obsd reflns with ($I>2\sigma(I)$)	4479	1816
No. refined params	406	127
GooF (F^2)	0.943	1.048
R_1 (F) ($I > 2\sigma(I)$)	0.0608	0.0535
wR_2 (F^2) (all data)	0.1759	0.0788
Largest diff peak/ hole, e Å^{-3}	1.007 / −3.305	1.631 / −1.398
CCDC number	1915290	1915291

the program WinGX 2002 (Farrugia, 1999). Full-matrix least-squares refinements on F^2, using all data. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model and were refined isotropically. The hydrogen atoms attached to the oxygen atoms (expect O15) of **1** were located during the last refinement cycle and refined isotropically. Crystal and refinement data are collected in Table 1. Figures were created using DIAMOND (Brandenburg and Putz, 2006). Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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