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Synthesis and structure of 2,8-dimethyl-10,10-dichlorophenoxatellurine

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Abstract: The condensation of 4,4'-dimethyldiphenylether with tellurium tetrachloride yielded 2,8-dimethyl-10,10-dichlorophenoxatellurine (**3**), which was characterized by X-ray diffraction. Unlike the parent phenoxatellurine (**1**) and the 10,10-dichlorophenoxatellurine (**2**) showing butterfly conformations, **3** reveals a planar ring structure.

Keywords: tellurium, phenoxatellurine, diaryltellurium dichloride, secondary bonding

The chemistry of phenoxatellurine (**1**, Scheme 1), a heterocycle formally derived from dibenzodioxine in which one of the two oxygen atoms was replaced by a tellurium atom, has a long history that was covered in a review until 1995 (Gioabă and Gioabă, 1995).

It is assessable by reduction of 10,10-dichlorophenoxatellurine (**2**, Scheme 1)), which can be easily obtained by condensation of diphenylether with tellurium tetrachloride (Drew, 1926). With 2-phenoxyphenyltellurum trichloride an intermediate of this condensation reaction was recently isolated and fully characterized (Toma, et. al., 2016). We recently studied the electronic properties of a charge transfer complex between **1** and [1,2,5]thiadiazolo[3,4-c][1,2,5]thiadiazole (Chulanova et al., 2017) and (re-)investigated the single-electron oxidation of **1** giving rise to the formation of dicationic double- and triple-decker complexes (Mostaghimi et al., 2019a, 2019b). In context of this work, we also studied the condensation reaction of 4,4'-dimethyldiphenylether with tellurium tetrachloride, which afforded 2,8-dimethyl-10,10-dichlorophenoxatellurine (**2**) as slightly yellow crystalline product in 93% yield (Scheme 2).

The ^{125}Te NMR chemical shift of **3** ($\delta = 596.4$ ppm) is nearly identical with that of **2** ($\delta = 594.4$ ppm). The crystal and molecular structure of **3** is shown in Figure 1. The key feature is the crystallographically imposed planarity of the 2,8-dimethylphenoxatellurine scaffold, which is in sharp contrast to the butterfly structures of the unsubstituted phenoxatellurine scaffolds of **1** (Smith et al., 1973), **2** (Korp et. al., 1980), and **2**·1/2 NCMe (Mostaghimi, 2019b).

Like **2** (Korp et al., 1980) and other diaryltellurium dichlorides (Zukerman-Schpector and Haiduc, 2001), the spatial arrangement of the Te atom of **3** is trigonal bipyramidal when bearing in mind the stereochemically active lone pair. In this arrangement, the two crystallographically equivalent Cl atoms occupy the axial positions, whereas the two C atoms and the lone pair are situated in the equatorial positions. Without the lone pair, the structure can be also described as 'see-saw' arrangement. The primary Te–Cl bond length of **3** (2.537(1) Å) is consistent with those of **2** (2.478(3)–2.576(3) Å, Korp et al., 1980) and other diaryltellurium dichlorides (Zukerman-Schpector and Haiduc, 2001). In the crystal lattice, **3** forms a 2D coordination polymer defined by secondary Te...Cl interactions, unlike **2**, which give rise to discrete tetramers with 'cubane' like structures (Korp et al., 1980). The equivalent secondary Te1...Clb contacts of **3** (3.558(1) Å) are again comparable with those of **2** (3.368(4)–2.576(3) Å) and other diaryltellurium dichlorides (Zukerman-Schpector and Haiduc, 2001).

Experimental

Synthesis of **3**

In a dried two necked flask equipped with a condenser and a moist guard 5.55 g (20.6 mmol, 1.00 eq.) tellurium tetrachloride and 4.08 g (20.6 mmol, 1.00 eq.) *p*-tolyl ether are heated slowly over the course of 4 h to 200°C under reflux. After cooling to room temperature the reddish brown solid is mortared into a fine powder and stirred

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Scheme 1: Phenoxatellurine (**1**) and 10,10-dichlorophenoxatellurine (**2**).

Scheme 2: Condensation reaction of 4,4'-dimethyldiphenyl ether with tellurium tetrachloride providing 2,8-dimethyl-10,10-dichlorophenoxatellurine (**3**).

Figure 1: Crystal and molecular structure of **3** showing 30% probability ellipsoid and the essential atomic numbering. Symmetry codes: $a = 1-x, y, 0.5-z$; $b = x, 1-y, -0.5+z$; $c = 1-x, 1-y, 1-z$. Selected bond parameters [Å, °]: Te1-Cl1 2.536(8), Te1...Clb 3.558(1), Te1-C10 2.078(3), Cl1-Te1-Cl1a 178.37(4), C10-Te1-C10a 92.68(2).

in diethyl ether to dissolve unreacted *p*-tolyl ether. The solid is filtered off and the remaining product with traces of elemental tellurium is stirred in acetone and filtered again. Evaporation of the solvent gives 7.53 g (19.1 mmol, 93%) of **3** as a deep red crystalline solid.

^1H NMR (600 MHz, CDCl_3): δ = 7.67 (s, 2H, $\text{C}_{\text{Ar}}\text{-H}$), 7.49 (d, $^3J_{\text{H-H}} = 8.45$ Hz, 2H, $\text{C}_{\text{Ar}}\text{-H}$), 7.39 (dd, $^3J_{\text{H-H}} = 8.45$ Hz, $^4J_{\text{H-H}} = 2.00$ Hz, 2H, $\text{C}_{\text{Ar}}\text{-H}$), 2.41 (s, 6H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ = 148.65 (s, $\text{C}_{\text{Ar}}\text{-O}$), 135.55 (s, C_{Ar}), 135.23 (s, C_{Ar}), 135.23 (s, C_{Ar}), 132.28 (s, C_{Ar}), 119.87 (s, C_{Ar}), 115.72 (s, $\text{C}_{\text{Ar}}\text{-Te}$), 20.53 (s, CH_3) ppm. ^{125}Te NMR (190 MHz, CD_2Cl_2): δ = 596.40 (s) ppm. EI-MS (70 eV, 200°C, direct injection) m/z (rel. Int.) = 367 (7) $[\text{M}]^+$, 361 (17) $[\text{M-Cl}]^+$, 326 (57)

Table 1: Crystal data and structure refinement of **3**

Formula	$\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{OTe}$
Formula weight, g mol^{-1}	394.74
Crystal system	monoclinic
Crystal size, mm	$0.08 \times 0.06 \times 0.04$
Space group	$C2/c$
a , Å	18.6738(7)
b , Å	10.0086(3)
c , Å	7.7964(3)
α , °	90.00
β , °	97.676(1)
γ , °	90.00
V , Å ³	1444.08(9)
Z	4
ρ_{calcd} , Mg m^{-3}	1.816
T , K	100
μ (Mo $K\alpha$), mm^{-1}	1.966
$F(000)$	760
θ range, deg	2.31 to 35.03
Index ranges	$-30 \leq h \leq 30$ $-16 \leq k \leq 16$ $-12 \leq l \leq 12$
No. of reflns collected	22659
Completeness to θ_{max}	98.4%
No. indep. Reflns	3181
No. obsd reflns with $(I > 2\sigma(I))$	2788
No. refined params	84
GooF (F^2)	1.113
R_1 (F) ($I > 2\sigma(I)$)	0.0267
wR_2 (F^2) (all data)	0.0808
$(\Delta/\sigma)_{\text{max}}$	< 0.001
Largest diff peak/hole, e Å^{-3}	0.898/−1.479

$[\text{M-2Cl}]^+$, 196 (100) $[\text{M-Te}]^+$. UV/Vis (CH_2Cl_2): λ_{max} 275 nm, 305 nm, 386 nm, 518 nm.

HRMS ESI ($\text{CH}_2\text{Cl}_2/\text{MeCN}$ 1:10 + 1% water): $[\text{M-2Cl+OH}]^+$ calculated for $\text{C}_{14}\text{H}_{13}\text{O}_2\text{Te}$, m/z = 342.99723; found, 342.99711. No signal was found without the addition of water.

Decomp. point: 263°C

X-ray crystallography

Intensity data of **3** was collected on a Bruker Venture D8 diffractometer with graphite-monochromated Mo- $K\alpha$ (0.7107 Å) radiation. The structure was solved by direct methods and difference Fourier synthesis with subsequent Full-matrix least-squares refinements on F^2 , using all data (Farrugia, 1999). 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. Crystal and refinement data are collected in Table 1. Figures were

created using DIAMOND (Brandenburg and Putz, 2006). Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC number 1976524. 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>).

Conflict of interest: One of the authors (Jens Beckmann) is a member of the Editorial Board of Main Group Metal Chemistry.

References

- Brandenburg K., Putz H., DIAMOND V3.1d, Crystal Impact GbR, 2006.
- Chulanova E.A., Pritchina E.A., Malaspina L.A., Grabowsky S., Mostaghimi F., Beckmann J., et al., New Charge-Transfer Complexes with 1,2,5-Thiadiazoles as Both Electron Acceptors and Donors Featuring an Unprecedented Addition Reaction. *Chem. Eur. J.*, 2017, 23, 852-864.
- Drew H.D.K., Cyclic organo-metallic compounds. Part I. Compounds of tellurium. *J. Chem. Soc.*, 1926, 129, 223-231.
- Farrugia L.J., WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystal.*, 1999, 32, 837-838.
- Gioabă A.N., Gioabă A.A., Chemistry of phenoxatellurin. *Roum. Chem. Q. Rev.*, 1995, 3, 303-327.
- Korp J.D., Bernal I., Turley J.C., Martin G.E., Crystal and Molecular Structure of Phenoxatellurin 10,10-Dichloride. *Inorg. Chem.*, 1980, 19, 2556-2560.
- Mostaghimi F., Bolsinger J., Lork E., Beckmann J., New insights into the oxidation of phenoxatellurine with sulfuric acid. *Main Group Met. Chem.*, 2019a, 42, 150-152.
- Mostaghimi F., Lork E., Hong I., Roemmele T.L., Boéré R., Mebs S., Beckmann J., The reaction of phenoxatellurine with single-electron oxidizers revisited. *New. J. Chem.*, 2019b, 43, 12754-12766.
- Smith M.R., Mangion M.M., Zingaro R.A., Meyer E.A., The crystal structure of phenoxatellurine, C₁₂H₈OTe. *J. Heterocycl. Chem.*, 1973, 10, 527-531.
- Toma A.M., Nicorără A., Silvestru A., Rüffer T., Lang H., Mehning M., Bis(2-phenoxyphenyl)dichalcogenides and their chemical reactivity. *J. Organomet. Chem.*, 2016, 810, 33-39.
- Zukerman-Schpector J., Haiduc I., Diorganotellurium(IV) dihalides and secondary bonding: revisiting the coordination polyhedral. *Phosphorus Sulfur*, 2001, 171, 73-112.