Short Communication

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Synthesis and structure of diarylhalotelluronium hexahalotellurates $[(8\text{-}Me_2NC_{10}H_6)_2TeX]_2TeX_6$ (X=Cl, Br)

Abstract: The title compounds $[(8\text{-}Me_2NC_{10}H_6)_2TeX]_2TeX_6$ (**1**, X=Cl; **2**, X=Br) were obtained by the oxidation of $(8\text{-}Me_2NC_{10}H_6)_2Te$ with SO_2Cl_2 and Br_2 and the subsequent addition of $TeCl_4$ and $TeBr_4$, respectively, and were characterized by X-ray crystallography and multinuclear NMR spectroscopy. Due to the intramolecularly coordinating 8-dimethylaminonaphthyl substituents, **1** and **2** comprise loosely associated ion pairs of distorted trigonal bipyramidal $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ cations and octahedral TeX_6^{2-} anions (X=Cl, Br).

Keywords: ^{125}Te NMR spectroscopy; secondary bonds; structure determination; tellurium.

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Recently, we reported on a series of diaryltelluronium compounds $[(8\text{-}Me_2NC_{10}H_6)_2TeX]Y$ (X=Cl, Br, I, OH; Y=Cl, Br, I, I_3, PF_6, O_3SCF_3) in which two intramolecularly coordinating 8-dimethylaminonaphthyl substituents gave rise to cationic structures (Beckmann et al., 2012, 2013).

The zwitterionic diaryltelluronium acetimidate, $(8\text{-}Me_2NC_{10}H_6)_2TeNC(O)CH_3$, obtained by an unexpected oxygen transfer from the diaryltellurium oxide, $(8\text{-}Me_2NC_{10}H_6)_2TeO$, to acetonitrile belongs to the same structure type (Mallow et al., 2014). In the context of this work, we also isolated the title compounds $[(8\text{-}Me_2NC_{10}H_6)_2TeX]_2TeX_6$ (**1**, X=Cl; **2**, X=Br), at first in small crops from halogenation reactions of impure $(8\text{-}Me_2NC_{10}H_6)_2Te$ containing small amounts of elemental tellurium. After their structural elucidation, the same products were deliberately prepared in good yields by the reaction of analytically pure $(8\text{-}Me_2NC_{10}H_6)_2Te$ with SO_2Cl_2 and Br_2, respectively, followed by the immediate addition of $TeCl_4$ and $TeBr_4$, respectively (Scheme 1). The last two apparently abstract chloride and bromide ions from the initially formed diarylhalotelluronium halides $[(8\text{-}Me_2NC_{10}H_6)_2TeX]X$ (X=Cl, Br) (Beckmann et al., 2013).

The title compounds $[(8\text{-}Me_2NC_{10}H_6)_2TeX]_2TeX_6$ (**1**, X=Cl; **2**, X=Br) were obtained as yellow and brown single crystals that were substantially more stable than the initial oxidation products $[(8\text{-}Me_2NC_{10}H_6)_2TeX]X$ (X=Cl, Br) (Beckmann et al., 2013). The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. Selected bond parameters were collected and are shown in the caption of the figures, and crystal and refinement data are listed in Table 1. The spatial arrangement of the Te atoms of the cations can be described in two ways. Taking into account the first coordination sphere only, it is a distorted trigonal bipyramidal setting in which C10, C20 and N2 occupy the equatorial positions, whereas N1 and Cl1 or Br1 are situated in the axial positions.

The Te1-Cl1 bond length of **1** [2.429(2) Å] and the Te1-Br1 bond length of **2** [2.594(2) Å] are slightly shorter than those of Ph_2TeCl_2 [2.506(2) Å] (Alcock and Harrison, 1982) and Ph_2TeBr_2 [2.6818(6) Å] (Beckmann et al., 2004).

The axial Te1-N1 bond lengths of **1** [2.435(5) Å] and **2** [2.381(7) Å] are shorter than the equatorial Te1-N2 bond lengths of **1** [2.694(4) Å] and **2** [2.81(1) Å], thus contradicting Bent's (1961) rule. Overall, these parameters are very similar to those of $[(8\text{-}Me_2NC_{10}H_6)_2TeX]X$ (X=Cl, Br) (Beckmann et al., 2013). Besides the first coordination sphere, there is a secondary contact arising from ion pairing. The related Te1···Cl2 [3.291(2) Å] and Te1···Br2 [3.570(2) Å] bond distances of **1** and **2** are slightly longer than those of $[(8\text{-}Me_2NC_{10}H_6)_2TeX]X$ [X=Cl: 3.173(1) Å; X=Br: 3.411(4) Å] (Beckmann et al., 2013). Thus, considering also the second coordination sphere, the spatial arrangement of the Te

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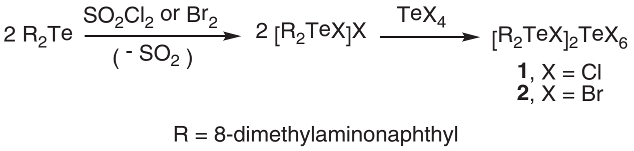

Scheme 1 Synthesis of compounds **1** and **2**.

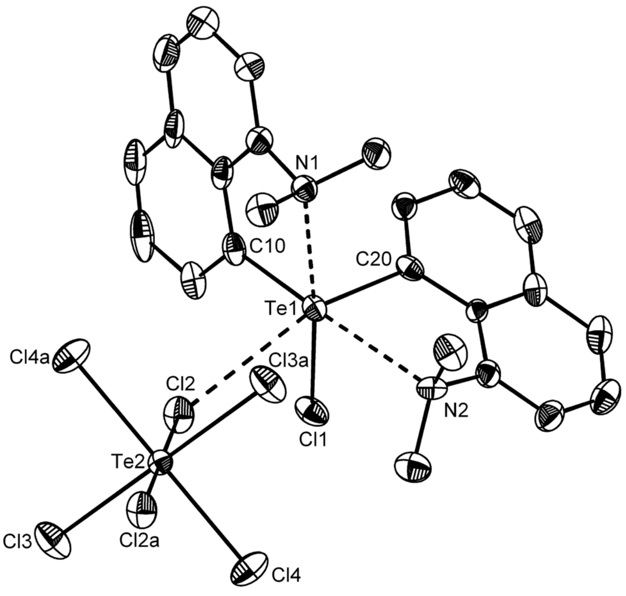

Figure 1 Molecular structure of $[(8\text{-}Me_2NC_{10}H_6)_2TeCl]_2TeCl_6$ (**1**) showing 30% probability ellipsoids and the crystallographic numbering scheme.
Selected bond parameters (Å, °): Te1-Cl1 2.429(2), Te1-C20 2.118(5), Te1-C10 2.132(6), Te1-N1 2.435(5), Te1-N2 2.694(4), Cl1-Te1-C10 91.2(2), Te2-Cl2 2.527(2), Te2-Cl3 2.533(2), Te2-Cl4 2.529(2), Cl1-Te1-C20 88.41(14), C10-Te1-C20 97.2(2); ion contact: Te1···Cl2 3.291(2).

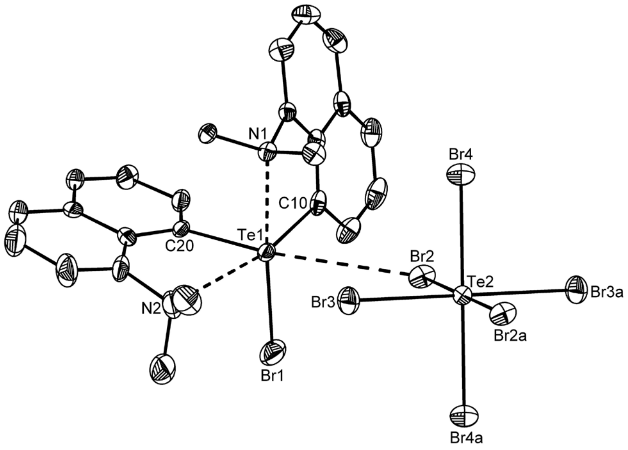

Figure 2 Molecular structure of $[(8\text{-}Me_2NC_{10}H_6)_2TeBr]_2TeBr_6$ (**2**) showing 30% probability ellipsoids and the crystallographic numbering scheme.
Selected bond parameters (Å, °): Te1-Br1 2.594(2), Te1-C10 2.14(1), Te1-C20 2.138(9), Te1-N1 2.381(7), Te1-N2 2.81(1), Te2-Br2 2.694(1), Te2-Br3 2.687(1), Te2-Br4 2.690(2), Br1-Te1-C10 92.9(3), Br1-Te1-C20 92.5(2), C10-Te1-C20 94.3(3); ion contact: Te1···Br2 3.570(2).

atoms of the cations can be regarded as strongly distorted octahedral. In the counterions, TeX_6^{2-} of **1** (X=Cl) and **2** (X=Br), the Te atoms adopt only slightly distorted octahedral arrangements. The average Te2-Cl bond lengths of **1** [2.530(2) Å] and the average Te-Br bond lengths of **2** [2.690(2) Å] closely resemble those of known hexahalotellurate ions, $[Me_2SO)_2H]_2[TeCl_6]$ [2.537(1) Å] (Pietikäinen et al., 2002), $[Ph_3Te]_2[TeCl_6]$ [2.545(1) Å] (Närhi et al., 2004) and $[PhMe_2Te]_2[TeBr_6]$ [2.71(2) Å] (Santos dos Santos et al., 2007).

Like $[(8\text{-}Me_2NC_{10}H_6)_2TeX]X$ (X=Cl, Br) (Beckmann et al., 2013), $[(8\text{-}Me_2NC_{10}H_6)_2TeX]_2TeX_6$ (**1**, X=Cl; **2**, X=Br) are best soluble in polar solvents such as acetonitrile, where they undergo electrolytic dissociation. The ^{125}Te NMR spectra (CDCN) of **1** and **2** show two signals at δ=1201.0 and 1471.6 ppm and δ=1190.9 and 1365.6 ppm in integral ratios of 2:1, which are unambiguously assigned to the $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ cations and TeX_6^{2-} anions, respectively (X=Cl, Br). The ^{1}H NMR spectra (CDCN) of **1** and **2** show four signals in the aliphatic range, demonstrating that the two 8-dimethylaminonaphthyl groups are magnetically inequivalent, which is consistent with the idea that the spatial arrangement of the cations in the solid state is retained in solution.

Experimental

General

Bis(8-dimethylaminonaphthyl)telluride was prepared according to literature procedure (Beckmann et al., 2012). The ^{1}H, ^{13}C and ^{125}Te NMR spectra were recorded using the Jeol GX 270 and Varian 300 Unity Plus spectrometers and were referenced to $SiMe_4$ (^{1}H, ^{13}C) and Me_2Te (^{125}Te). Microanalyses were obtained from a Vario EL elemental analyzer.

Synthesis of $[(8\text{-}Me_2NC_{10}H_6)_2TeCl]_2TeCl_6$ (1)

To a solution of bis(8-dimethylaminonaphtyl)telluride (520 mg, 1.11 mmol) in dry tetrahydrofuran (THF) (20 mL), sulfuryl chloride (150 mg, 1.11 mmol) was added and stirred for 15 min. Then a solution of tellurium tetrachloride (299 mg, 1.11 mmol) in THF (10 mL) was added. Directly after the addition, a yellow powder precipitated, which was collected by filtration. The crude product was dissolved in acetonitrile (40 mL), and slow evaporation of the solvent yielded yellow crystals of **1** [450 mg, 0.33 mmol, 55%; Mp. 224–229°C (dec.)].

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

	1·2 MeCN	**2·2 CHCl$_3$**
Formula	$C_{52}H_{54}Cl_8N_6Te_3$	$C_{50}H_{50}Br_8Cl_6N_4Te_3$
Formula weight, g/mol	1429.41	1941.72
Crystal system	Triclinic	Triclinic
Crystal size, mm	0.15×0.10×0.04	0.15×0.10×0.05
Space group	*P*-1	*P*-1
a, Å	9.177(4)	8.299(5)
b, Å	11.095(4)	11.832(5)
c, Å	14.215(4)	16.083(5)
α, °	86.75(4)	82.640(5)
β, °	80.96(4)	88.065(5)
γ, °	81.26(4)	81.127(5)
V, Å^3	1411.9(12)	1547.3(12)
Z	1	1
ρ_{calcd}, Mg/m^3	1.681	2.084
T, K	150	150
μ (Mo Kα), mm^{-1}	1.959	6.866
F(000)	700	916
θ range, °	2.50–25.25	2.30–26.00
Index ranges	$-11 \leq h \leq 11$	$-8 \leq h \leq 10$
	$-13 \leq k \leq 13$	$-14 \leq k \leq 14$
	$-17 \leq l \leq 16$	$-19 \leq l \leq 19$
No. of reflections collected	10,940	13,418
Completeness to θ_{max}	99.1%	99.6%
No. of independent reflections	5047	6046
No. of observed reflections with [$I > 2\sigma(I)$]	2431	3496
No. of refined parameters	313	322
GooF (F^2)	0.854	0.868
R_1 (F) [$I > 2\sigma(I)$]	0.0350	0.0526
wR_2 (F^2) (all data)	0.0551	0.1101
$(\Delta/\sigma)_{max}$	<0.01	<0.01
Largest difference peak/hole, e/Å^{-3}	0.497/-0.525	1.069/-1.106
CCDC	999867	999868

GooF, goodness of fit.

^{1}H NMR (CDCN): δ=8.80 (d, 1H); 8.46 (d, 1H); 8.16 (m, 2H); 8.07 (t, 1H); 7.97 (m, 2H), 7.78 (m, 3H), 7.28 (t, 1H;), 7.01 (d, 1H) ($C_{10}H_6$), 3.24 (s, 3H); 3.08 (s, 3H); 3.04 (s, 3H), 2.38 (s, 3H). ^{125}Te NMR (CDCN): δ=1201.0 (2Te), 1471.6 (1Te). Anal. Calcd. for $C_{48}H_{48}N_4Cl_8Te_3$ (1347.35): C 42.79, H 3.59; N 4.16. Found: C 43.06, H 3.45; N 3.98.

Synthesis of $[(8\text{-}Me_2NC_{10}H_6)_2TeBr]_2TeBr_6$ (2)

To a solution of bis(8-dimethylaminonaphtyl)telluride (468 mg, 1.00 mmol) in dry THF (10 mL), dibromine (160 mg, 1.00 mmol) was added and stirred for 15 min. Then a solution of tellurium tetrabromide (447 mg, 1.00 mmol) in THF (10 mL) was added. Directly after the addition, an orange brown powder precipitated, which was collected by filtration. The crude product was dissolved in hot CHCl$_3$ (40 mL). Slow evaporation of the solvent yielded brown crystals of **2** [610 mg, 0.36 mmol, 67%; Mp. 200–210°C (dec.)].

^{1}H NMR (CDCN, -35°C): δ=8.88 (d, 1H); 8.48 (d, 1H); 8.18 (m, 2H); 8.04 (t, 1H); 7.97 (m, 2H), 7.86–7.72 (m, 3H), 7.26 (t, 1H;), 7.02 (d, 1H) ($C_{10}H_6$), 3.20 (s, 3H); 3.13 (s, 3H); 3.03 (s, 3H), 2.40 (s, 3H). ^{125}Te NMR (CDCN): δ=1190.9 (2Te), 1365.6 (1Te). Anal. Calcd. for $C_{48}H_{48}N_4Br_8Te_3$ (1702.95): C 33.85, H 2.84; N 3.29 Found: C 33.65, H 2.55; N 3.13.

X-ray crystallography

The intensity data of **1** and **2** were collected on a STOE IPDS 2T area detector 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 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 four hydrogen atoms attached to the oxygen atoms 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 the DIAMOND software (Brandenburg and Putz, 2006). Crystallographic data (excluding structure factors) 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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