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Tribromo(3,5-dimethyl-2-nitrophenyl-κ2C1,O)tellurium(IV),
bromo(3,5-dimethyl-2-nitrophenyl-κ2C1,O)tellurium(II) and
bromo(3,5-dimethyl-2-nitrosophenyl-κ2C1,O)tellurium(II)

Prabodhika R. Mallikaratchy
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Thomas Junk

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**Organic Compounds**

Tribromo(3,5-dimethyl-2-nitrophenyl-κ²C¹,O)tellurium(IV), bromo(3,5-dimethyl-2-nitrophenyl-κ²C¹,O)tellurium(II) and bromo(3,5-dimethyl-2-nitrosophenyl-κ²C¹,O)tellurium(II)

Prabodhika Mallikaratchya, Richard E. Norman, Frank R. Fronczek and Thomas Junk

*Chemistry Department, CNSB-210, University of Louisiana at Monroe, LA 71209, USA,* and *Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA*

Correspondence e-mail: junk@ulm.edu

All three title compounds, prepared from bis(3,5-dimethyl-2-nitrophenyl)ditellurium, exhibit high degrees of intramolecular Te—O coordination. Their Te—O distances increase in the order $C_6H_6BrNOTe < C_6H_6BrNO_2Te < C_6H_6Br_2NO_2Te$, with distances of 2.165 (3), 2.306 (1) and 2.423 (6) Å, respectively, indicating that $C_6H_6BrNOTe$ may be more aptly described as 1-bromo-4,6-dimethyl-2,1,3-benzoxatellurazole.

**Comment**

Intramolecularly coordinated organotellurium compounds commonly exhibit properties that are significantly different from those of their non-coordinated counterparts. Moieties through which a Lewis basic atom intramolecularly coordinates to tellurium include azo, imino, carbonyl and amino functionalities (Detty & O’Regan, 1994). This coordination can stabilize otherwise unstable low-valent organotellurium halides and pseudohalides (Cobbledick et al., 1979; Detty et al., 1989; Sadekov et al., 1990; Menon et al., 1996), as well as telluronium cations (Fujihara et al., 1995). Intramolecular coordination by nitroso and nitro moieties has not been documented in much detail because of limited access to these classes of organotellurium compounds. Thus, the only published procedure for the preparation of an ortho-nitrosubstituted diphenylditellurium compound (Wiriyachitra et al., 1979) was found to be challenging. The few reported examples of NO and NO$_2$ coordination include dioxatellurapentalenes (Perrier & Vialle, 1971) and 1-nitroso-2-naphthyltellurium monohalides found in the patent literature (Gunther & Lok, 1986; Przyklek-Elling et al., 1987). It appears highly probable that bromo(2-nitrophenyl)tellurium(II) and tribromo(2-nitrophenyl)tellurium(IV) (Wiriyachitra et al., 1979) also feature strong intramolecular Te—O coordination, but no structural information has been made available for these compounds to date. Compounds carrying ortho nitro, nitroso and amino functionalities are of interest as potential precursors to compounds featuring coordinatively stabilized telluronium cations and as intermediates to organotellurium heterocycles (Junk & Irgolic, 1988).

Recent advances in the synthesis of substituted diarylditelluriums by selective ortho nitration, as well as from boronic acid precursors (Clark et al., 2002), have provided easier access to compounds such as bis(3,5-dimethyl-2-nitrophenyl)ditellurium, which is employed in this study. Bis(3,5-dimethyl-2-nitrophenyl)ditellurium was prepared by nitration of bis(3,5-dimethylphenyl)ditellurium to 3,5-dimethyl-2-nitrobenzenetellurinic acid nitrate, followed by reduction (see first Scheme below).

Treatment of bis(3,5-dimethyl-2-nitrophenyl)ditellurium with stoichiometric amounts of bromine produced tribromo-(3,5-dimethyl-2-nitrophenyl-κ²C,O)tellurium(IV), (I), bromo-(3,5-dimethyl-2-nitrophenyl-κ²C,O)tellurium(II), (II), and bromo(3,5-dimethyl-2-nitrosophenyl-κ²C,O)tellurium(II), (III), which may be described as heterocyclic (a substituted benzoxatellurazole).

There are two molecules of (I), of nearly identical geometry, in the asymmetric unit (Fig. 1). There appears to be a non-crystallographic center of symmetry between the two independent molecules (at about $x = 0.105, y = 0.248$ and $z = \frac{1}{2}$). Similar centers appear in more than 65% of $Pca_2_1$ structures in which $Z$ is greater than 4 (Marsh et al., 1998) and often result in unusual correlations between corresponding atoms in the two molecules. Since the average values of equivalent bond distances are apparently unaffected by this pseudo-symmetry (Marsh et al., 1998), we discuss the average case. The geometry about the Te atom is square pyramidal, with the basal plane defined by three Br atoms and an O atom. A C atom is in the axial position, and a stereochemical lone pair is...
located trans to this C atom. The Te atom sits ‘below’ the basal plane, which is consistent with the principles of VSEPR (valence-shell electron-pair repulsion) theory. The Te—Br distance for the Br atom trans to atom O1 is significantly shorter than the other Te—Br distances [2.5047 (12) Å versus 2.6540 (11) and 2.6754 (11) Å; Table 1]. The Te1—C1 bond distance [2.132 (7) Å] is in good agreement with those reported for non-coordinated aryl—Te bonds, e.g. in catena-μ-bromo-dibromo(phenyl)tellurium(IV) [2.140 (8) Å; Alcock & Harrison, 1982a]. The O1—Te1—C1 angle is constrained to 71.8 (2)° by the five-membered ring. These structural features are similar to those reported for trichloro(2-phenylazo-phenyl-C,N)tellurium(IV), in which there is coordination of tellurium by the N atom of the azo group (Ahmed et al., 1985a). There is a short intermolecular contact in (I) between atoms O2A and N1B, which is reminiscent of the perpendicular motif found for carbonyl—carbonyl interactions (Allen et al., 1998).

Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level.

Figure 2
The molecular structure of (II), with displacement ellipsoids drawn at the 50% probability level.

Figure 3
The molecular structure of (III), with displacement ellipsoids drawn at the 50% probability level.

The geometries of (II) and (III) are ‘T-shaped’ about the Te atom, with the O—Te—Br angles being distinctly non-linear [168.80 (14) and 169.57 (9)°, respectively; Tables 2 and 3, and Figs. 2 and 3] and the bromide ion displaced towards the phenyl ring, which geometry is again consistent with VSEPR theory and the presence of two stereochemical lone pairs of electrons on the TeII centers. The N—O distance in (III) [1.315 (5) Å] is significantly longer than the analogous distance in (II) [1.268 (8) Å], which is in turn significantly longer than the other (non-coordinated) N—O distance of 1.208 (8) Å. The Te—C distance of 2.098 (6) Å in (II) is the same as that found in bromo(2-phenylazo-phenyl-C,N)tellurium(IV) [2.092 (8) Å; Majeed et al., 1997], while the Te—C distance is shortened to 2.038 (4) Å in (III).

The Te—O bond distances of 2.307 (6) Å in (II) and 2.165 (3) Å in (III) are shorter than the Te—O distance of 2.423 (6) Å for (I) and are comparable to Te—O distances observed for amides [e.g. 2.237 (8) Å for bromo(2-amido-phenyl-C,O)tellurium(II); Dupont et al., 1979], for carboxylates [e.g. 2.167 (4) Å for acetato(2-phenylazo-phenyl-C,N)tellurium(II); Ahmed et al., 1985b] and for nitrates [e.g. 2.171 (3) Å for diphenyltellurium(IV) dinitrate; Alcock & Harrison, 1982b].

The relative ease with which (I) was reduced to (III) is indicative of the high stability of ortho-nitroso-stabilized aryltellurium subhalides. In practice, exposure of the tellurium(IV) compound to a variety of ketones and alcohols resulted in gradual color changes indicative of reduction.

Experimental
All of the title compounds were prepared from bis(3,5-dimethyl-phenyl)ditellurium, accessible via the Haller–Irgolic method (Haller & Irgolic, 1972). This compound was converted to bis(3,5-dimethyl-2-nitrophenyl)ditellurium by nitration and subsequent reduction (Nair, 2002). For the preparation of (I), bis(3,5-dimethyl-2-nitrophenyl)ditellurium (1.0 g, 1.8 mmol) was dissolved in carbon tetrachloride (30 ml). A solution of bromine (10% w/w) in carbon tetrachloride was added slowly, and a gradual darkening to magenta was observed, followed by a sharp color change to yellow. Addition of
bromine was discontinued and the product was crystallized by open-air evaporation. In contrast to non-coordinated aryltellurium trihalides, this compound was found to be insensitive to moisture (yield quantitative; m.p. 467–469 K). 1H NMR (CDCl3, p.p.m.): 2.58 (3H), 2.80 (3H), 7.51 (1H), 8.41 (1H); 13C NMR (CDCl3, p.p.m.): 22.5, 22.7, 129.5, 136.0, 137.5, 138.1, 140.8, 151.4.

For the preparation of (II), bis(3,5-dimethyl-2-nitrophosphoryl)-ditellurium (1.0 g, 1.8 mmol) was dissolved in carbon tetrachloride (30 ml). One third of the previously prepared ditellurium solution was converted to a solution of the tribromide by addition of bromine as above. Subsequently, the tribromide solution was combined with the remaining two parts of the bis(3,5-dimethyl-2-nitrophosphoryl)-ditellurium solution. Equilibration to the desired monobromide occurred rapidly. The crude product was collected by open-air evaporation of the solvent and recrystallized from cyclohexane (brown–red needles; yield 1.06 g, 82%; m.p. 380–381 K). 1H NMR (CDCl3, p.p.m.): 2.43 (3H), 2.79 (3H), 7.19 (1H), 8.15 (1H); 13C NMR (CDCl3, p.p.m.): 21.9, 23.0, 131.8, 133.2, 134.1, 140.5, 144.3, 146.8. Well-formed crystals were obtained by slow open-air evaporation of a solution in dichloromethane.

For the preparation of (III), a stirred solution of (I) (0.2 g, 0.4 mmol) in acetone (20 ml) and 2-propanol (20 ml) was heated to reflux for 24 h. A color change from yellow to blue was noticed. The blue solid remaining after open-air evaporation under the hood was taken up in carbon tetrachloride, and the well-formed purple crystals remaining after open-air evaporation were collected (yield 42 mg, 32%; m.p. 430–431 K). 1H NMR (CDCl3, p.p.m.): 2.36 (3H), 2.99 (3H), 7.26 (1H), 8.35 (1H); 13C NMR (CDCl3, p.p.m.): 18.9, 23.3, 132.4, 133.7, 138.1, 146.2, 149.1, 154.41.

### Compound (I)

**Crystal data**

C₈H₈Br₃NO₂Te, C₈H₈BrNO₂Te and C₈H₈BrNOTe organic compounds

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<th>Value</th>
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<td>Orthorhombic, Pca2₁</td>
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<tr>
<td>a, Å</td>
<td>7.371 (2)</td>
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<tr>
<td>b, Å</td>
<td>12.139 (5)</td>
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<td>c, Å</td>
<td>28.274 (11)</td>
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<tr>
<td>V, Å³</td>
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<tr>
<td>Z</td>
<td>8</td>
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<tr>
<td>Dₐ</td>
<td>2.717 Mg m⁻³</td>
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**Data collection**

Nonius KappaCCD diffractometer

with an Oxford Cryosystems Cryostream cooler

ω scans with ϕ offsets

Absorption correction: multi-scan

(HKL SCALEPACK:
Otwinowski & Minor, 1997)

T min = 0.108, T max = 0.170

28 416 measured reflections

**Refinement**

Refinement on F²

R(F²) = 0.035

wR(F²) = 0.087

S = 1.01

3800 reflections with I > 2σ(I)

Rw(F²) = 0.104

3933 reflections

121 parameters

H-atoms constrained

w = 1/[σ²(F²) + (0.0333P)²]

where P = (F² + 2Fc²)/3

(Δσ/σ)max < 0.001

ΔFₚ = 2.77 e Å⁻³

ΔFₘ = -2.44 e Å⁻³

Extinction correction: SHELLX97

Extinction coefficient: 0.0062(17)

### Table 1

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<th>Selected geometric parameters (Å, °) for (I)</th>
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<td>Te₁A—Cl₁A</td>
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<td>Te₂A—Br₂A</td>
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<td>Te₄A—Br₄A</td>
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<td>O₁A—N₁A</td>
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<td>O₂A—N₂A</td>
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<td>N₁A—C₂A</td>
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<td>C₂A—Cl₂A</td>
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<td>O₁A—Te₁A—Br₃A</td>
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<td>Te₁A—Br₁A—Br₂A</td>
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<td>Te₂A—Br₄A—Br₂A</td>
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<td>N₁A—O₁A—Te₁A</td>
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<td>C₈A—Cl₈A—Te₈A</td>
<td>121.1 (6)</td>
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<tr>
<td>C₂A—Cl₂A—Te₂A</td>
<td>118.9 (5)</td>
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</table>

### Compound (II)

**Crystal data**

C₈H₄BrNO₂Te, C₈H₄BrNO₂Te and C₈H₄BrNOTe

Mᵣ = 357.66

Monoclinic, P2₁/a

a = 14.175 (4) Å

b = 9.582 (2) Å

c = 15.433 (4) Å

β = 95.70 (2)°

V = 2085.8 (9) Å³

Z = 8

*Mo* Kα radiation

Cell parameters from 25 reflections

θ = 2.9°

μ = 6.65 mm⁻¹

T = 298 K

Parallelepiped, brown-red

0.35 × 0.22 × 0.20 mm

**Data collection**

Enraf-Nonius CAD-4
diffractometer

θ/2θ scans

Absorption correction: ϕ scan (North et al., 1968)

T min = 0.020, T max = 0.266

7028 measured reflections

2393 independent reflections

1325 reflections with I > 2σ(I)

**Refinement**

Refinement on F²

R(F²) > 2σ(F²) = 0.043

wR(F²) = 0.104

S = 1.10

2393 reflections

121 parameters

H-atoms constrained

w = 1/[σ²(F²) + (0.0117P)²]

where P = (F² + 2Fc²)/3

(Δσ/σ)max = 0.003

ΔFₚ = 0.95 e Å⁻³

ΔFₘ = -0.81 e Å⁻³

Extinction correction: SHELLX97

Extinction coefficient: 0.000270

**Table 2**

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<th>Selected geometric parameters (Å, °) for (II)</th>
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<tr>
<td>Te—Cl</td>
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<td>Te—O₁</td>
<td>2.507 (6)</td>
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<td>Te—Br</td>
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<td>C₁—Te—O₁</td>
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<td>C₁—Te—Br</td>
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<td>O₁—Te—Br</td>
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<td>N—O₁—Te</td>
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<td>O₂—N—O₁</td>
<td>120.6 (7)</td>
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<td>O₂—N—C₂</td>
<td>122.4 (7)</td>
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Table 3
Selected geometric parameters (Å, °) for (III).

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<th>O1—N1</th>
<th>Te1—O1</th>
<th>N1—C2</th>
<th>Te1—Br1</th>
<th>N1—O1—C1</th>
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<tr>
<td>2.038 (4)</td>
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<td>1.315 (5)</td>
<td>2.165 (3)</td>
<td>1.348 (5)</td>
<td>2.6401 (16)</td>
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<tr>
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<td>Cl—Te1—Br1</td>
<td>92.76 (11)</td>
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<tr>
<td>O1—Te1—Br1</td>
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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1028). Services for accessing these data are described at the back of the journal.

References