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Cycloaddition reaction of *tert*-butyl isocyanate and a tellurium diimide dimer: extended helical structure of the ureato telluroxide {[OC(μ-NBu^t)$_2$TeO]$_2$(thf)}$_\infty$

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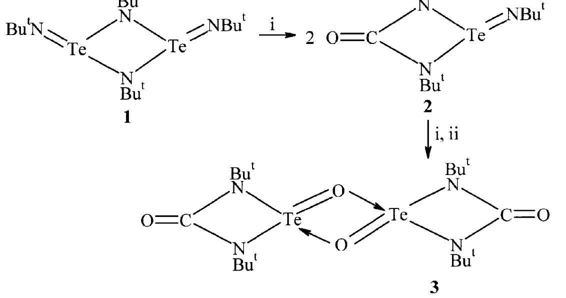
The reaction of Bu^{t}NTe(μ-NBu^t)$_2$TeNBu^t with Bu^{t}NCO in a 1:4 molar ratio in thf produces *N,N′*-bis(*tert*-butyl)ureato telluroxide dimers [OC(μ-NBu^t)$_2$TeO]$_2$, which form an extended helical network *via* weak >C=O···Te interactions.

Reactions of transition-metal imido compounds with heteroallenes have been investigated extensively.[1] The M=NR linkage reacts with isocyanates RNCO *via* cycloaddition of the N=C double bond to give *N,N′*-ureato complexes which, in some cases, can be isolated.[2] The *N,N′*-ureato ligand may also be generated by interaction of oxo complexes of Ru or Os with Bu^{t}NCO, presumably through the formation of an M=NR intermediate.[3] *N,O*-ureato complexes have been implicated in reactions of isocyanates with some transition-metal complexes, but none of the products of C=O cycloaddition to the M = NR bond have been isolated.[4–6] Iminophosphoranes Ph$_3$P=NR normally react with isocyanates by an Aza-Wittig process to generate carbodiimides and Ph$_3$PO.[7] By contrast, sulfur diimides, *e.g.* Bu^{t}N=S=NBu^t undergo exchange reactions with certain isocyanates RNCO (R = R′SO$_2$, R′CO or Ar) to form Bu^{t}NCO and Bu^{t}NSNR.[8] In the context of this divergent behaviour, we have investigated the reactions of the tellurium(IV) diimide dimer Bu^{t}NTe(μ-NBu^t)$_2$TeNBu^t **1**, which contains two highly reactive terminal Te=NBu^t groups,[9] with isocyanates. We describe here, the facile reaction between **1** and Bu^{t}NCO, which yields the *N,N′*-ureato telluroxide **3** *via* the corresponding ureato tellurium imide **2** (Scheme 1). In the solid state **3** forms an extended helical network *via* weak >C=O···Te interactions.

Treatment of the dimer **1** with 2 equiv. of Bu^{t}NCO in toluene at 23 °C produces an extremely moisture-sensitive yellow solid, which was identified as the *N,N′*-ureato tellurium(IV) imide O=C(μ-NBu^t)$_2$Te=NBu^t **2** on the basis of CHN analysis, IR and NMR spectroscopic data.† The ^{1}H NMR spectrum of **2** in C$_6$D$_6$ exhibits two singlets at δ 1.46 and 1.35 in the intensity ratio 1:2. An IR absorption attributed to the CO stretch is observed at 1653 cm^{-1}, and the carbonyl carbon appears in the ^{13}C{^{1}H} NMR spectrum at δ 160.7. Hydrolysis of **2** by atmospheric moisture produces *N,N′*-bis(*tert*-butyl)urea OC[N(H)Bu^t]$_2$ (δ_H 1.24 in d$_8$-thf). Complex **2** can be viewed as the product of the cycloaddition reaction of the monomeric tellurium(IV) diimide Bu^{t}N=Te=NBu^t and Bu^{t}NCO. By contrast, the reaction of **1** with Bu^{t}NCS (1:2 molar ratio) in *n*-hexane at 65 °C produces the cyclic tellurium(II) imide [Te(NBu^t)]$_3$[9a] (95% yield) and no cycloaddition intermediate could be isolated.



Scheme 1 *Reagents and conditions*: i, +2Bu^{t}NCO; ii, −2Bu^{t}NCNBu^t.

When a solution of **1** in *n*-hexane is added to a solution of Bu^{t}NCO in thf (1:4 molar ratio) a white solid identified by X-ray crystallography‡ as {[OC(μ-NBu^t)$_2$TeO]$_2$(thf)}$_\infty$ (**3**·thf)$_\infty$ is obtained in essentially quantitative yield.† The carbodiimide Bu^{t}N=C=NBu^t was detected as a by-product of this reaction by ^{1}H NMR (δ_H 1.17). This observation implies that an unstable tellurium(IV) complex involving both *N,N′* and *N,O*-bound ureato ligands is an intermediate in the formation of **3**. As indicated in Fig. 1 the asymmetric unit in **3** is *N,N′*-bis(*tert*-butyl)ureato telluroxide [*d*(Te=O) = 1.9040(17) Å] which, in common with other telluroxides, dimerizes *via* O→Te [2.0723(18) Å] interactions, *cf. d*(TeO) = 1.885(7) and 2.170(7) Å in metal complexes of the related dimer [Bu^{t}NTe(μ-NBu^t)$_2$(μ-O)]$_2$.[10] The ureato ligands in **3** adopt a *cis* arrangement with respect to the Te$_2$O$_2$ ring which is essentially planar (torsion angle −2.6°). The CNTeN rings are slightly puckered (torsion angle −7.2°). In the parent urea OC(NHBu^t)$_2$[11] and in ureato complexes of Ru and Os[3] the NCN unit is symmetrical [|*d*(CN)| = 1.352 and 1.380 Å, respectively]. By contrast, the CN bonds in **3** are unsymmetrical [*d*(CN) = 1.345(4) and 1.420(3) Å] as are the TeN bonds [*d*(TeN) = 2.034(2) and 2.087(2) Å]. The C=O bond length is 1.227(3) Å, *cf.* 1.252(3) Å in OC(NHBu^t)$_2$[11] and 1.22–1.26 Å in ureato complexes of Ru[3], Os[3] and W.[12] Complex **3** is readily hydrolyzed by traces of moisture to give the urea OC[N(H)Bu^t]$_2$ and TeO$_2$.

The presence of a two-fold screw axis (2$_1$) at the centre and corners of the unit cell and a four-fold (4$_1$) axis at the mid-points of the cell axes results in two different channels parallel to the *ab* plane involving weak >C=O···Te contacts [3.020(2) Å, *cf.* sum of van der Waals radii for Te and O = 3.58 Å][13] as depicted in Fig. 2. The first type involves a lantern-shaped arrangement of four dimers. Two disordered thf molecules located in the middle of the lantern also engage in weak Te···O interactions [2.961(6) Å]. The second type of >C=O···Te interaction involves only one Te atom of four dimeric units and gives rise

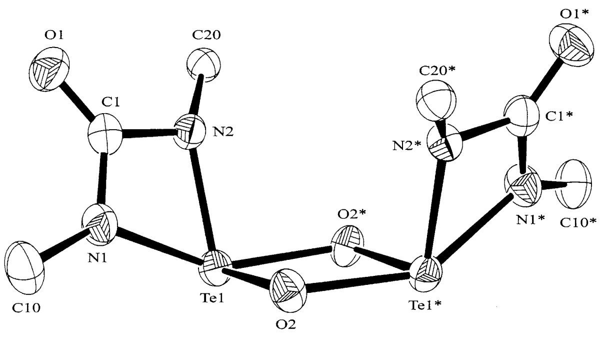


Fig. 1 The structure of [OC(μ-NBu^t)$_2$TeO]$_2$ **3** with the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond angles (°): Te(1)–O(2)–Te(1)* 102.84(8), O(2)–Te(1)–O(2)* 77.10(8), O(2)–Te(1)–N(2) 104.52(9), O(2)*–Te(1)–N(2) 92.08(8), O(2)–Te(1)–N(1) 88.71(9), O(2)*–Te(1)–N(1) 148.18(9), N(1)–Te(1)–N(2) 63.88(9), Te(1)–N(1)–C(1) 95.79(17), Te(1)–N(2)–C(1) 95.76(17), N(1)–C(1)–N(2) 104.0(2). Symmetry transformation used to generate equivalent atoms marked with an asterisk: *y*, *x*, −*z*.

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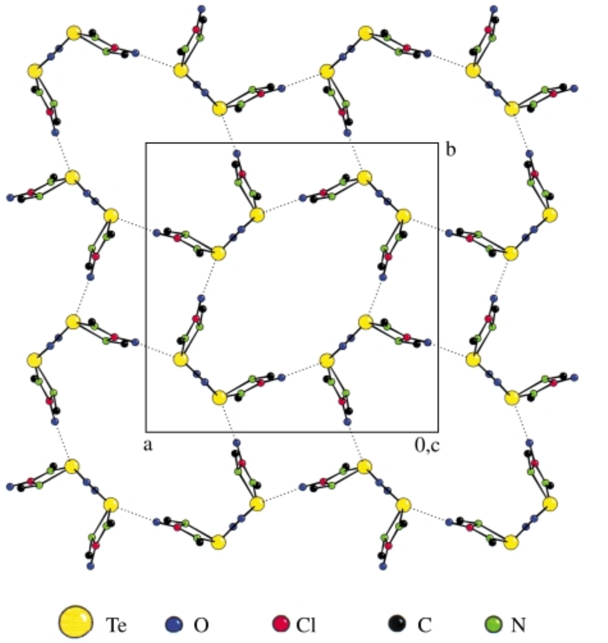

Fig. 2 Unit cell of $\{[\mathrm{OC}(\mu\text{-}\mathrm{NBu^t})_2\mathrm{TeO}]_2(\mathrm{thf})\}_\infty$ viewed down the *c*-axis. Disordered thf molecules are omitted.

to a square-shaped arrangement. In both of these structural motifs one of the $>$C=O···Te interactions links dimeric units in adjacent planes of the unit cell to give a helical arrangement, which is apparent when viewed down the *c* axis. The Te···Te distance in both cases is 12.4867(8) Å, *i.e.* the length of the *c* axis. Although weak intermolecular E···Te (E = O, N, S) interactions are a well known feature of tellurium complexes,[14] an extended network involving carbonyl–tellurium contacts is unique.

In summary, the presence of *two* Te=NBu^t linkages in **1** presents a unique opportunity for the study of double cycloadditions with heteroallenes. The reaction of **1** with Bu^{t}NCO generates a *N*,*N′*-ureato ligand *and* converts a tellurium imide (TeNBu^t) to a telluroxide (TeO) linkage, presumably *via* an unstable *N*,*O*-ureato complex. Thus it combines features of the reactions of both transition-metal imides and iminophosphoranes with isocyanates.

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Notes and references

† *Experimental procedure*: all manipulations were performed under an inert atmosphere of dry argon using standard Schlenk techniques. All solvents were dried prior to use.

2: a colourless solution of Bu^{t}NCO (0.120 mL, 1.112 mmol) in toluene (10 mL) was added to an orange solution of **1**[9c] (0.30 g, 0.556 mmol) in toluene (5 mL) at room temperature. The addition of a small amount of Bu^{t}NCNBu^t prevents the formation of **3**. A yellow precipitate of **2** was formed after 3 min. The pale orange solution was stirred for 2 h, cooled to −10 °C and then the supernatant was decanted *via* cannula. The solid product was washed with cold *n*-pentane (3 mL) to give **2** (0.185 g, 0.501 mmol, 45%) as a yellow solid. ^{1}H NMR (400.13 MHz, $\mathrm{C_6D_6}$, 25 °C) δ 1.46 (9 H), 1.35 (18 H). ^{13}C NMR (100.62 MHz, $\mathrm{C_6D_6}$, 25 °C) δ 160.70 (CO), 64.17 [$C(\mathrm{CH_3})_3$], 54.83 [$C(\mathrm{CH_3})_3$], 34.69 [$\mathrm{C}(C\mathrm{H_3})_3$], 31.86 [$\mathrm{C}(C\mathrm{H_3})_3$]. ^{125}Te NMR (126.20 MHz, $\mathrm{C_6D_6}$, 25 °C) δ 1225. IR:1653 [ν(CO)] cm^{-1}.

3: an orange solution of **1** (0.30 g, 0.556 mmol) in *n*-hexane (10 mL) was added to a colourless solution of Bu^{t}NCO (0.257 mL, 2.223 mmol) in thf (10 mL) at 23 °C. The pale yellow solution was stirred for 1.5 h and then volatile materials were removed under vacuum and **3**·2 thf (0.423 g, 0.549 mmol, 99%) was obtained as a white solid. Colourless crystals of **3**·thf suitable for X-ray diffraction were obtained after two days at 23 °C by layering an orange–red solution of **3** in *n*-hexane (3 mL) over a solution of Bu^{t}NCO in thf (3 mL). ^{1}H NMR (400.13 MHz, $\mathrm{C_6D_6}$, 25 °C) δ 3.55 (thf), 1.45 (Bu^t, 18H), 1.41 (thf). ^{13}C NMR (100.62 MHz, $\mathrm{C_6D_6}$, 25 °C) δ 160.39 (CO), 68.15 (thf), 54.97 [$C(\mathrm{CH_3})_3$], 31.27 [$\mathrm{C}(C\mathrm{H_3})_3$], 26.15 (thf). ^{125}Te NMR (126.20 MHz, $\mathrm{C_6D_6}$, 25 °C) δ 1090. IR: 1669 [ν(CO)], 663 [ν(TeO)] cm^{-1}.

‡ *Crystal data* for $(\mathbf{3}\cdot\mathrm{thf})_\infty$: $\mathrm{C_{22}H_{44}N_4O_5Te_2}$, M = 699.81, tetragonal, space group $P4_12_12$ (no. 92), a = b = 15.5941(7), c = 12.4867(8) Å, V = 3036.5(3) Å^3, Z = 4, D_c = 1.531 g cm^{-3}, μ(Mo-Kα) = 19.55 cm^{-1}. Crystal dimensions 0.26 × 0.23 × 0.15 mm. Data were collected on a Bruker AXS P4/RA/SMART 1000 CCD diffractometer with graphite-monochromated Mo-Ka radiation using ϕ and ω scans. The structure was solved using direct methods (SIR-97) and refined by full-matrix least squares on F^2 (SHELXL-97). The thf molecule was disordered around the two-fold screw axis with partial occupancy factors of 0.5. Of the 2593 unique reflections 2410 had $I \geqslant 2.00\sigma(I)$. The final agreement factors were R_1 = 0.0164 and wR_2 = 0.041.

CCDC 182/1728. See http://www.rsc.org/suppdata/cc/b0/b004137h/ for crystallographic files in .cif format.

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