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Reactions of *cis*-[^{t}BuNTe(μ-N^{t}Bu)]$_2$ with CF_3SO_3Me and M[O_3SCF_3] (M = Ag, Cu): Chelation, Cis → Trans Isomerization, and the Spirocyclic Ligand [^{t}BuNTe(μ-N^{t}Bu)$_2$Te(μ-O)]$_2$

Tristram Chivers,* Masood Parvez, and Gabriele Schatte

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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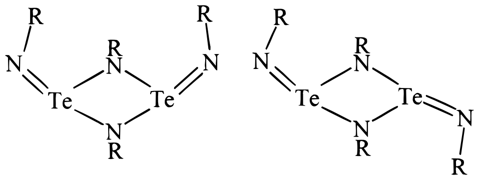
The first investigations of coordination complexes of the tellurium diimide dimer [^{t}BuNTe(μ-N^{t}Bu)]$_2$ (**1a**) are presented. The coinage metals Ag^+ and Cu^+ were chosen to evaluate the ability of **1a** to function as a chelating or bridging ligand. Reaction of **1a** with Ag[O_3SCF_3] in toluene produces [Ag_2L_2][O_3SCF_3]$_2$ (**5**, L = **1a**) or, in the presence of LiCl, [Ag_2L_2(μ-Cl)][O_3SCF_3] (**3**). In **4** the two Ag^+ ions bridge two molecules of *cis*-**1a** and engage in a weak Ag···Ag bonding interaction. In **3** the Cl^- ion bridges two Ag^+ ions, which are each chelated to the terminal N^{t}Bu groups of **1a**. Treatment of **1a** with Cu[O_3SCF_3] in toluene yields {[CuL][CF_3SO_3]}$_n$ (**5**) which, in turn, reacts with **1a** to form [Cu_2L_3][CF_3SO_3]$_2$ (**6**). In **6** the two Cu^+ ions bridge cis and trans forms of **1a**. The hydrolysis products {[^{t}BuNTe(μ-N^{t}Bu)$_2$Te(μ-O)]$_2$[M(H_2N^{t}Bu)]$_2$}[O_3SCF_3]$_2$ (**7a**, M = Ag; **7b**, M = Cu) and [Cu_2L(^{t}BuNH_2)$_2$][O_3SCF_3]$_2$ (**8**) were also structurally characterized. The complexes **7a**,**b** contain the dimer [^{t}BuNTe(μ-N^{t}Bu)$_2$(μ-O)]$_2$ in which one of the terminal N^{t}Bu ligands in **1a** is replaced by an O atom. The central Te_2O_2 ring in this spirocyclic ligand is planar with unsymmetrical oxygen bridging [d(Te−O) = 1.885(7) and 2.170(7) Å in **7b**]. The ligand **1a** in **8** is in the trans conformation. Mono- or dimethylation of **1a** with CF_3SO_3Me was shown to occur at the terminal nitrogens by ^{1}H and ^{125}Te NMR spectroscopy.

Introduction

The chemistry of multiply bonded tellurium−nitrogen (TeN) compounds[1] is poorly developed compared to that of their SN[2a] or SeN[2b,2c] counterparts. In part this is due to the fulminatory nature of binary TeN systems.[1,3] The recent synthesis of the thermally stable tellurium diimide dimer *cis*-[^{t}BuNTe(μ-N^{t}Bu)]$_2$ (**1a**)[4] provides an opportunity for investigations of the reactivity of Te═N double bonds leading to new compounds with interesting properties and novel structures. For example, the reactions of **1** with the nucleophilic reagents Li[HN^{t}Bu] or KO^{t}Bu generate the clusters {Li_2[Te(N^{t}Bu)$_3$]}$_2$[5a] and {K(THF)-[Te(N^{t}Bu)$_2$(O^{t}Bu)]}$_2$,[5b] which contain the anions [Te(N^{t}Bu)$_3$]$^{2-}$ and [Te(N^{t}Bu)$_2$(O^{t}Bu)]$^-$, respectively. Nucleophilic attack at tellurium is anticipated from a consideration of the composition of the lowest unoccupied molecular orbital (LUMO) for the model compound **1b**.[6] By contrast, electrophiles are expected to seek out the site of highest electron density, i.e., the terminal nitrogen atoms.[6] Consistently, the reaction of **1a** with HCl(g) produces the monoprotonated derivative, [^{t}Bu(H)NTe(μ-N^{t}Bu)$_2$TeN^{t}Bu][Cl].[5b]



cis-**1a** (R = ^{t}Bu)
cis-**1b** (R = Me)

trans-**1a** (R = ^{t}Bu)

Wilkinson et al. have investigated the reactions of the manganese (VI) and rhenium (VI) triimide dimers [M′(N^{t}Bu)$_2$-(μ-N^{t}Bu)]$_2$ (M = Mn,[7a] Re[7b]) with a variety of electrophiles including M[O_3SCF_3] (M = Ag, Cu) and observed versatile ligand behavior as well as the formation of the cation radical {[Mn(N^{t}Bu)$_2$(μ-N^{t}Bu)]$_2$}$^{+\bullet}$. These transition−metal complexes are structurally related to **1a**, but they accommodate *two* terminal N^{t}Bu groups at each metal center. By comparison, the existence of both cis and trans isomers of tellurium diimide dimers[8] provides an additional dimension to the coordination chemistry of **1a**. For example, the cis isomer may function as a chelating ligand, whereas the trans isomer could serve as a bridging ligand

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* To whom correspondence should be addressed. Tel: (403) 220-5741. Fax: (403) 289-9488. E-mail: chivers@ucalgary.ca.

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in a coordination polymer. With these possibilities in mind, our initial studies of the coordination complexes of **1a** have focused on the coinage metals.[9] Solubility in organic solvents and the low nucleophilicity of the $[CF_3SO_3]^-$ anion were attractive features of the electrophilic reagents $M[O_3SCF_3]$ (M = Ag, Cu) for this investigation. The products of the reaction of **1a** with MeO_3SCF_3 were also characterized in order to provide spectroscopic benchmarks for complexes formed from **1a** and metal triflates.

Experimental Section

General Procedures and Reagents. $TeCl_4$ (Æsar, 99%), $Ag[AsF_6]$ (Æsar, 98.5%), and *n*-BuLi (Aldrich) were used as received. $^tBuNH_2$ (Aldrich) was predried over KOH and then distilled from CaH_2 onto molecular sieves. MeO_3SCF_3 (Aldrich, 99%) was dried over molecular sieves, and the purity was checked by ^1H NMR: (δ, in C_7D_8) 3.14 (s, CH_3); (δ, in d_8−THF) 3.23 (s, CH_3). The purity of the triflates $Ag[O_3SCF_3]$ and $[Cu(O_3SCF_3)]_2 \cdot C_6H_6$ (Æsar, 99%) was checked by FT−IR spectroscopy and mass spectrometry. $Li[HN^tBu]$ was prepared from anhydrous $^tBuNH_2$ (65 mL, 0.609 mol) and *n*-BuLi (200 mL, 2.5 M solution in hexanes, 0.5 mol) in *n*-hexane (170 mL) at −10 °C,[10] and the purity was ascertained by ^1H NMR spectroscopy (δ 1.37 in C_6D_6). Solvents were dried with the appropriate drying agents and distilled onto molecular sieves before use. All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of argon or under vacuum. All glassware was carefully dried prior to use.

Instrumentation. ^1H NMR spectra were recorded on Bruker ACE 200 and AM 400 spectrometers, and chemical shifts are reported relative to Me_4Si in $CDCl_3$. ^{125}Te and ^7Li NMR spectra were measured on a Bruker AM 400 spectrometer using a 10-mm broadband probe operating at 126.24 and 155.503 MHz, respectively. The samples were externally referenced to K_2TeO_3 in D_2O and referred to Me_2Te and to 1.0 M LiCl in D_2O, respectively. Line-broadening parameters, used in the exponential multiplication of the free induction decays, were 50 to 0.5 Hz. Mass spectra were obtained with a VG Micromass spectrometer VG7070 (70 eV). Infrared spectra were recorded as Nujol mulls on a Mattson 4030 FT−IR spectrometer in the range 4000−350 cm^{-1}. ESR spectra were measured on solutions sealed in a 5-mm quartz tube by using a Bruker EMX-10/12 spectrometer. Elemental analyses were provided by the Analytical Services Laboratory, Department of Chemistry, University of Calgary and at Canadian Microanalytical Services, Vancouver, BC.

Synthesis of $[^tBuNTe(\mu\text{-}N^tBu)]_2$ (1a). The synthesis of **1a** described in ref 4b was modified as follows. Solid $Li[HN^tBu]$ (11.90 g, 148.6 mmol) was added to a yellow suspension of finely powdered $TeCl_4$ (10 g, 37.1 mmol) in toluene (170 mL) at −78 °C. The yellow-brown reaction mixture was stirred for 12 h at −78 °C and then allowed to reach 23 °C, whereupon the color changed to red-orange. The reaction mixture was stirred for at least 5 h at 23 °C (until the color had changed to dark red, ≤ 24h). The slurry was then filtered through a coarse sintered-glass frit. The dark-red filtrate contained mainly **1a**, varying amounts of $\{Te_2(N^tBu)_4(Li[Te(N^tBu)_2(HN^tBu)])LiCl\}_2$[4b], and a trace of $[Te(N^tBu)]_3$. The solid left on the frit (mainly LiCl) was discarded and the filtrate heated at 70 °C for 19 h to convert $\{Te_2(N^tBu)_4(Li[Te(N^tBu)_2(HN^tBu)])LiCl\}_2$ into $Te_2(N^tBu)_4$ and $\{(Li[Te(N^tBu)_2(HN^tBu)])LiCl\}_2$.[4b] The solvent was removed under vacuum and the brown-red solid residue was extracted with *n*-hexane (ca. 200 mL) to separate **1a** from the less soluble $\{(Li[Te(N^tBu)_2(HN^tBu)])LiCl\}_2$. The solution was filtered by using a fine frit, and the volume of the filtrate was reduced to ca. 10 mL, whereupon a microcrystalline orange solid was formed. The solid was redissolved by warming the concentrated *n*-hexane solution slightly (ca. 35 °C). Orange crystals were obtained upon cooling the *n*-hexane solution to −30 °C for 10 min. The solution above the crystals was transferred via a cannula into another Schlenk vessel and discarded because most of the product had precipitated out. The remaining crystals, still cooled to −30 °C, were washed with cold *n*-pentane (−30 °C) and dried under vacuum to give an orange solid (5.96 g). Anal. Found: C, 34.93; H, 6.70; N, 9.78; Cl, 3.76. Sublimation of the orange solid (87−93 °C, 10^{-3} Torr) produced **1a** as yellow-orange crystals (4.02 g, 67%). Anal. Calcd for $C_8H_{18}N_2Te$: C, 35.61; H, 6.72; N, 10.38. Found: C, 35.11; H, 6.58; N, 9.98; Cl, 0.16. ^1H NMR (in C_6D_6, 25 °C, δ), 1.70, 1.27 (isomer **A**) and 1.61, 1.29 (isomer **B**; ratio, [**A**]:[**B**] = 4:1); (in C_7D_8, 25 °C, δ), 1.65 (s), 1.26 (s) (isomer **A**) and 1.58 (s), 1.28 (s) (isomer **B**; ratio, [**A**]:[**B**] = 4:1); ^{125}Te NMR (in C_7D_8, 25 °C, δ): 1475 ($\upsilon_{1/2} \sim 3000$ Hz).

Reaction of 1a with CF_3SO_3Me. (a) A solution of MeO_3SCF_3 (0.087 g, 0.530 mmol) in toluene (3 mL) was added dropwise to a stirred red solution of **1a** (0.286 g, 0.530 mmol) in toluene (10 mL) cooled to −78 °C, whereupon the color of the solution changed from red to yellow-orange. The reaction mixture was stirred for 0.5 h at −78 °C before warming slowing to 23 °C to give a red-brown solution. After 3 h, the volatile materials were pumped off and the residue was washed with *n*-hexane, leading to the orange-brown solid $[^tBuNTe(\mu\text{-}N^tBu)_2Te^+N(^tBu)(Me)][CF_3SO_3^-]$ (0.334 g, 0.474 mmol; yield: 89%). Anal. Calcd for $C_{18}H_{39}F_3N_4O_3STe_2$: C, 30.72; H, 5.58; N, 7.96. Found: C, 28.92; H, 5.37; N, 7.18. ^1H NMR (in C_7D_8, 298 K): 2.86 (s, CH_3, 3), 1.33 (s, μ-N^{t}C$_4H_9$, 18), 1.31 (s, Te=N^{t}C$_4H_9$, 9), 0.91 (s, Te$^+$N^{t}C$_4H_9$, 9). ^{125}Te NMR (in C_7D_8, 298 K): 1860 (s, Te$^+$N^{t}Bu), 1393 (Te=N^{t}Bu).

(b) The reaction of **1a** with CF_3SO_3Me in toluene was also carried out in a 1:2 molar ratio. The procedures were similar to those described in (a). The product $[^tBu(Me)NTe^+(\mu\text{-}N^tBu)_2Te^+N(Me)(^tBu)][CF_3SO_3]_2$ was obtained as a yellow-green solid (0.352 g, 0.406 mmol, 68%). Anal. Calcd. for $C_{10}H_{21}F_3N_2O_3STe$: C, 27.68; H, 4.88; N, 6.45. Found: C, 27.06; H, 4.85; N, 6.25. ^1H NMR (C_4D_8O): 3.63 (s, CH_3, 6), 1.66 (s, μ-N^{t}C$_4H_9$, 18), 1.60 (s, Te$^+$N^{t}C$_4H_9$). ^{13}C and ^{125}Te NMR spectra could not be obtained because of the very low solubility of the product in organic solvents.

Preparation of $\{[^tBuNTe(\mu\text{-}N^tBu)]_2[Ag(O_3SCF_3)]\}_2(LiCl)_2$ (2) and $[\{[^tBuNTe(\mu\text{-}N^tBu)]_2Ag\}_2(\mu\text{-}Cl)][O_3SCF_3]$ (3). A solution of $Ag[O_3SCF_3]$ (0.286 g, 1.11 mmol) in toluene (10 mL) was added dropwise to a stirred red solution of unsublimed **1a** (0.6 g, 1.11 mmol) in toluene (10 mL) cooled to −78 °C. The color of the solution changed to orange-red and a precipitate was formed. After 0.5 h at −78 °C, the reaction mixture was warmed slowly to 23 °C and, after 3 h, the solvent was removed under vacuum to give **2** as an orange solid (0.818 g, 0.49 mmol, 88%). Anal. Calcd for $C_{17}H_{36}AgClF_3LiN_4O_3STe_2$: C, 24.34; H, 4.32; N, 6.68; S, 3.82; Cl, 4.22. Found: C, 24.89; H, 4.39; N, 6.64; S, 3.83; Cl, 4.33. ^1H NMR (in CD_2Cl_2, 25 °C, δ), 1.485 (s), 1.480 (s) (ratio, 1:1); (in CD_3CN, 25 °C, δ), 1.444 (s), 1.431 (s). ^7Li NMR (in CD_3CN, 25 °C, δ): 0.197. ^{125}Te NMR (in CD_3CN, 25 °C, δ): 1851.

The complex **3** was obtained by dissolving 50 mg of **2** in CH_3CN (ca. 3 mL) in a two-bulbed reaction vessel equipped with a medium-porosity sintered glass frit. The solution was degassed by using the freeze−thaw technique and then filtered from the precipitate (LiCl and $Li[O_3SCF_3]$) through the frit into the second bulb. The solvent was condensed slowly back into the other bulb by cooling it with tap water (18 °C) until some red needlelike crystals had formed which were used as seeds for growing bigger crystals at −13 °C. Red prismatic crystals suitable for X-ray diffraction were obtained after 2 weeks. Anal. Calcd for $C_{33}H_{72}Ag_2ClF_3N_8O_3STe_4$: C, 26.79; H, 4.90; N, 7.57. Found: C, 26.31; H, 4.41; N, 7.90. ^1H NMR (in CD_3CN, 25 °C, δ): 1.45 [s, C(CH_3)$_3$], 1.43 [s, C(CH_3)$_3$] (ratio, 1:1). ^{125}Te NMR (in CD_3CN, 25 °C, δ): 1851. In a separate experiment, complex **2** (0.140 g) was obtained in quantitative yield from **3** (0.159 g).

Preparation of $\{[^tBuNTe(\mu\text{-}N^tBu)]_2\}_2[Ag(O_3SCF_3)]_2$ (4). $Ag[O_3SCF_3]$ (0.238 g, 0.93 mmol) in toluene (10 mL) was added slowly to a stirred red solution of **1a** (0.6 g, 0.93 mmol) in toluene (10 mL) at −78 °C. The color of the solution changed to orange-red and a precipitate was formed. After 0.5 h at −78 °C, the reaction mixture was warmed slowly to 23 °C and stirred for 3 h. The solvent was removed under vacuum to give **4** as an orange solid (0.673 g, 0.42 mmol, 92%). Anal. Calcd for $C_{17}H_{36}AgF_3N_4O_3STe_2$: C, 25.63; H, 4.55; N, 7.03. Found: C, 25.24; H, 4.13; N, 7.02. ^1H NMR (in CD_3CN, 25

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Table 1. Crystal Parameters and Intensity Data Measurements for {[$Te_2(N^tBu)_4Ag$](μ-Cl)[$Te_2(N^tBu)_4Ag$]}[O_3SCF_3] (**3**), {[$Te_2(\mu\text{-}N^tBu)_2(N^tBu)(O)$]$_2$[$M(H_2N^tBu)$]$_2$}[$O_3SCF_3$]$_2$ (**7a**, M = Ag; **7b**, M = Cu), and {[$Te_2(N^tBu)_4$][$Cu(^tBuNH_2)$]$_2$}[O_3SCF_3]$_2$ (**8**)

	3	**7a**	**7b**	**8**
empirical formula	$C_{33}H_{72}N_8O_3Te_4Ag_2ClF_3S$	$C_{17}H_{38}N_4O_4Te_2AgSF_3$	$C_{17}H_{38}N_4O_4Te_2CuSF_3$	$C_{13}H_{29}N_3O_3TeCuSF_3$
M	1479.6	814.6	770.3	555.6
crystal color, habit	red, needle	yellow, prism	yellow, prism	red, needle
crystal dimensions/mm	0.40 × 0.25 × 0.20	0.48 × 0.40 × 0.34	0.30 × 0.20 × 0.18	0.47 × 0.20 × 0.12
T/°C	−123	−103	−103	−103
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (#2)	$P2_1/a$ (#14)	$P2_1/a$ (#14)	$P2_1$ (#4)
a/Å	16.110(6)	10.086(4)	10.163(1)	10.920(3)
b/Å	16.783(6)	28.305(5)	28.090(7)	18.094(4)
c/Å	10.095(3)	10.491(3)	10.522(3)	11.579(5)
α/deg	92.56(2)			
β/deg	94.76(2)	105.62(3)	106.83(1)	104.27(3)
γ/deg	84.93(2)			
V/Å^3	2707(2)	2884(2)	2875(1)	2217(1)
Z	2	4	4	2
D_c/g cm^{-3}	1.815	1.876	1.780	1.664
F(000)	1424	1576	1504	1104
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69
μ/cm^{-1}	29.68	28.01	28.68	24.10
$2\theta_{max}$	50.1	55.2	50.1	55.1
no. of unique reflcns	6492	6657	5061	5279
no. of obsd reflcns	4045	3833	2496	3132
no. of variables	474	281	301	334
R^a	0.0745	0.0828	0.0450	0.0514
$R_w{}^b$	0.196	0.2444	0.1063	0.1207
goodness of fit	0.988	1.20	1.021	1.005
largest shift/error in final least squares cycle	0.002	0.01	0.08	0.00

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \{[\sum w(F_o{}^2\text{-}F_c{}^2)^2]/[\sum w(F_o{}^2)^2]\}^{1/2}$.

°C, δ): 1.44 [s, C(CH_3)$_3$], 1.40 [s, C(CH_3)$_3$] (ratio, 1:1). ^{13}C NMR (in CD_3CN, 25 °C, δ): 62.46 and 59.88 [C(CH$_3$)$_3$], 37.01 and 36.79 [C(CH$_3$)$_3$].

Preparation of (a) {[^{t}BuNTe(μ-N^{t}Bu)][Cu(O_3SCF_3)]}$_n$ (5). A solution of [Cu(O_3SCF_3)]$_2$·C_6H_6 (0.186 g, 0.37 mmol) in toluene (10 mL) was added dropwise to a red solution of **1a** (0.20 g, 0.37 mmol) in toluene (10 mL) at −78 °C and stirred for 1 h. A thick, dark-red precipitate was formed (red needles when viewed with a flashlight), and the color of the solution changed to orange-red. The reaction mixture was warmed slowly to 23 °C, and solvent was removed under vacuum to give **5** as a brown-yellow solid (0.326 g, 0.31 mmol; 88%) after washing with *n*-hexane. Anal. Calcd for $C_9H_{18}CuF_3N_2O_3STe$: C, 22.41; H, 3.71; N, 5.81. Found: C, 22.93; H, 3.64; N, 5.53. ^{1}H NMR (in CD_2Cl_2, 25 °C, δ): 1.64−1.47 (m).

Preparation of [{^{t}BuNTe(μ-N^{t}Bu)}$_2$]$_3$[Cu(O_3SCF_3)]$_2$ (6). A solution of **1a** (0.336 g; 0.622 mmol) in toluene (10 mL) was added dropwise to a stirred red slurry of **5** (0.300 g; 0.311 mmol) in toluene (20 mL) cooled to −78 °C. The formation of a red-purple solution containing a dense precipitate of dark-red needles was observed. After 1 h the reaction mixture was warmed slowly to 23 °C and then stirred for 20 h. The volatile materials were pumped off and a dark-purple solid (0.610 g; yield: 96% based on [{^{t}BuNTe(μ-N^{t}Bu)}$_2$]$_3$[Cu(O_3SCF_3)]$_2$) was obtained. Anal. Calcd for $Te_6C_{50}H_{108}N_{12}Cu_2S_2O_6F_6$·$C_7H_8$ [%]: C, 32.06; H, 5.43; N, 7.87. Found: C, 32.91; H, 5.81; N, 7.23. ^{1}H NMR (in CD_2Cl_2, 25 °C, δ): 1.32−1.68 (m), 2.30 (s, CH_3C$_6$H$_5$), 7.0 (m, C$_6$$H_5CH_3$). ^{125}Te NMR (in CD_2Cl_2, 25 °C, δ): 1908 and 1670 (approximate ratio 1:1).

Formation of [^{t}BuNTe(μ-N^{t}Bu)]$_2$[Cu(^{t}BuNH$_2$)]$_2$[O_3SCF_3]$_2$ (8). A solution of [Cu(O_3SCF_3)]$_2$·C_6H_6 (0.14 g, 0.28 mmol) in toluene (10 mL) was added dropwise to a stirred red solution of **1a** (0.30 g, 0.556 mol) in toluene (10 mL) cooled to −78 °C, whereupon the color of the solution changed to dark brown. The reaction mixture warmed slowly to 23 °C after 0.5 h at −78 °C. At 23 °C a rust-brown precipitate was formed. The volatiles were pumped off and the solid washed with *n*-hexane, leading to the rust-brown solid (0.385 g). Recrystallization from CH_2Cl_2 at −10 °C led to very air-sensitive red needles of **8** over a period of 10 days. Anal. Calcd for $C_{13}H_{29}CuF_3N_3O_3STe$: C, 28.10; H, 5.26; N, 7.56. Found: C, 26.90; H, 4.95; N, 6.97. ^{1}H NMR (in CD_2Cl_2, 25 °C, δ): 1.64−1.47 (m). ^{125}Te NMR (in CD_2Cl_2, 25 °C, δ): 1679 and 1403 (ratio, ca. 2:1).

X-ray Crystallography. Crystals of **3**, **7a**, **7b**, and **8** were examined in a drybox under a Wild M3 microscope mounted outside the drybox. A single crystal was then mounted directly from the solutions on a glass fiber coated with epoxy (**3** and **8**), sealed in a glass capillary tube (**7a**), or immersed in a highly viscous oil (Paratone 8277 Exxon) (**7b**). The data were collected on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) at low temperature using ω−2θ scans (2θ_{max} = 50.1 to 55.1°). The structures were determined by direct methods (SIR92)[11] and expanded using Fourier techniques (DIRDIF 94).[12] All data used were corrected for Lorentz and polarization effects. An empirical absorption correction using Ψ scans was applied with maximum and minimum absorption coefficients listed in Table 1.[13] The structures were refined by full-matrix least squares on F^2, using the programs SHELXL93 and SHELXL97,[14] respectively, with all nonhydrogen atoms assigned anisotropic thermal parameters. One of the ^{t}Bu groups in **3** was disordered and the carbon atoms C(17), C(18), C(19), and C(20) were refined isotropically. In addition, the triflate anion was disordered and located over two sites with site occupancy factors of 0.5 each. Both half-anions were included in the refinements as constrained bodies with d_{av}(CF) = 1.32 and d_{av}(SO) = 1.50 Å. In **7a** and **7b**, the carbon atoms of one ^{t}Bu group, which was disordered, were refined isotropically. The C atoms were located over two sites with partial occupancy factors of 0.51 and 0.49.

All hydrogen atoms in the four structures were included at geometrically idealized positions with C−H and N−H 0.95 Å and were not refined. Scattering factors were taken from ref 15, and effects of

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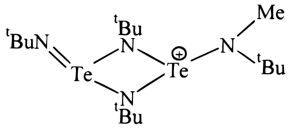
anomalous dispersion were included in F_c using the values given in ref 16. All calculations were performed using the program teXsan.

Results and Discussion

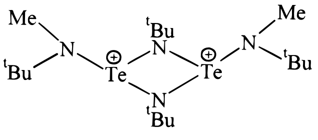
Synthesis and Purification of [^{t}BuNTe(μ-N^{t}Bu)]$_2$ (1a). The reaction of $TeCl_4$ and LiNH^{t}Bu in a 1:4 molar ratio in toluene gives rise to a mixture of several products, including two LiCl complexes (see Experimental Section).[4b] Although a preliminary separation of these products from **1a** can be achieved by extraction with *n*-hexane, we found in this study that a final sublimation is essential to obtain pure **1a**. *If the product is not sublimed, it contains lithium chloride*. From careful inspection of the ^{1}H NMR spectra of samples of unsublimed **1a** from different preparations, it is apparent that LiCl is present as part of the complex $\{Te_2(N^tBu)_4(Li[Te(N^tBu)_2(HN^tBu)])LiCl\}_2$[4b] as well as uncomplexed LiCl (^{7}Li NMR). In previously studied reactions of **1a** with nucleophilic reagents, e.g., Li[HN^{t}Bu][5a] or KO^{t}Bu,[5b] the products were obtained in >90% yields. In those examples the LiCl impurity is inert toward the reagents. However, in reactions of **1a** with electrophiles that react with the Cl^- anion, e.g., Ag^+, the presence of LiCl has to be avoided (vide infra).

As previously observed,[4] the ^{1}H NMR spectrum of *pure* **1a** in toluene exhibits two well-separated pairs of resonances, corresponding to terminal and bridging N^{t}Bu groups, with relative intensities of ca. 4:1. The ^{13}C NMR spectra of **1a** also exhibit two sets of resonance corresponding to major and minor components of a mixture of two species. Since trans isomers of tellurium diimide dimers have been structurally characterized and shown to isomerize in solution,[8] the coexistence of cis and trans isomers of **1a** is a possible explanation of these solution NMR data. However, no indication of the interconversion of these two species is observed in the ^{1}H NMR spectra up to 100 °C in toluene. Regardless of the explanation of these observations, both species behave in a similar manner with a variety of reagents to give high yields of products.[5] Furthermore, the possible existence of a trans isomer as well as a cis isomer of **1a** may lead to unusual coordination chemistry including the formation of metal-bridged polymers of the trans-ligand.

Methylation of [^{t}BuNTe(μ-N^{t}Bu)]$_2$ (1a). As a prelude to our investigation of the ligand behavior of **1a** toward M^+ centers (M = Ag, Cu) we have spectroscopically characterized mono- and dimethylated derivatives of **1a**. The reaction of **1a** with methyl trifluoromethanesulfonate in toluene was carried out in both 1:1 and 1:2 molar ratios to give the monomethylated and dimethylated derivatives [**1a**·Me]$^+$ and [**1a**·Me$_2$]$^+$, respectively, which were characterized by ^{1}H NMR spectroscopy.



[**1a**·Me]$^+$



[**1a**·Me$_2$]$^{2+}$

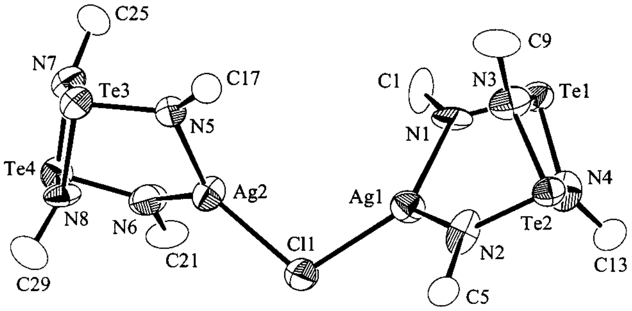
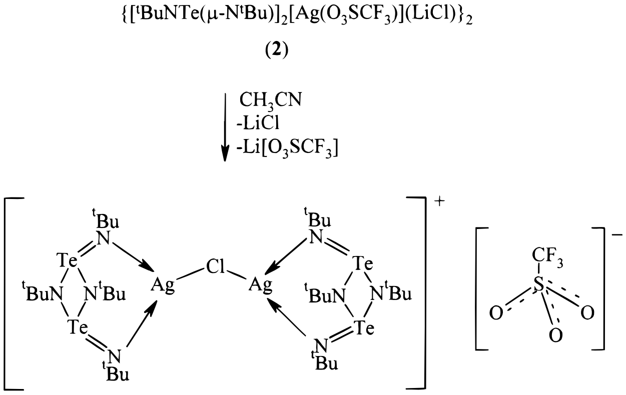


Figure 1. ORTEP diagram for the cation in **3**. For clarity, only the α-carbon atoms of ^{t}Bu groups are shown.

Scheme 1



(**3**)

The ^{1}H NMR spectrum of [**1a**·Me]$^+$ in toluene at 298 K shows the expected three resonances for N^{t}Bu groups at δ 1.33, 1.31, and 0.91, with relative intensities of 2:1:1, in addition to the resonances for the Me group at δ 2.86. By contrast, the monoprotonated derivative [**1a**·H]$^+$ is a highly fluxional species, and only one resonance at δ 1.63 is observed for the N^{t}Bu groups at 298 K.[4b] The expected three resonances for [**1a**·H]$^+$ are observed at 190 K in C_7D_8. The ^{125}Te NMR spectrum of [**1a**·Me]$^+$ in C_7D_8 at 298 K shows two singlets at δ 1393 and 1860 (cf. δ 1475 for **1a**). The low-field resonance is tentatively assigned to the Te atom attached to the methylated N^{t}Bu group.

Although **1a** cannot be diprotonated by HCl(g), dimethylation occurs readily with 2 equiv of CF_3SO_3Me. The ^{1}H NMR spectrum of [**1a**·Me$_2$]$^{2+}$ in d_8-THF shows two equally intense resonances at δ 1.66 and 1.60 for the bridging and terminal N^{t}Bu groups, respectively. Further NMR spectroscopic characterization was not possible because of the poor solubility of [**1a**·Me$_2$]$^{2+}$ in organic solvents. The dimethylated product [**1a**·Me$_2$]$^{2+}$ begins to convert into [**1a**·Me]$^+$ in solution after 1 day (25 °C) and then deposits elemental tellurium.

Synthesis and X-ray Structure of [^{t}BuNTe(μ-N^{t}Bu)]$_2$Ag(μ-Cl)Ag[^{t}BuNTe(μ-N^{t}Bu)]$_2$[O$_3$SCF$_3$] (3). Initial investigations of the reaction of **1a** with Ag[O$_3$SCF$_3$] were carried out using *unsublimed* **1a**. This reaction produced $\{[^tBuNTe(\mu\text{-}N^tBu)]_2[Ag(O_3SCF_3)]\}_2(LiCl)_2$ (**2**), which was identified on the basis of elemental analyses (C, H, N, S, and Cl) and by ^{1}H, ^{7}Li, and ^{125}Te NMR spectra. Dissolution of **2** in acetonitrile precipitated a mixture of LiCl and Li[O$_3$SCF$_3$] and, subsequently, red crystals of complex **3**, which exhibited two equally intense resonances at δ 1.45 and 1.43 ppm in the ^{1}H NMR spectrum (Scheme 1).

The structure of **3** was determined by X-ray crystallography. An ORTEP drawing is depicted in Figure 1, and selected bond distances and angles are summarized in Table 2. The structure consists of a cation in which the ligand **1a** is chelated via the two terminal N^{t}Bu groups to Ag^+. Two of these moieties are linked through the Ag^+ ions by a bridging Cl^- anion and the net +1 charge is balanced by a noninteracting triflate ion. Within the limited accuracy of the data caused by the disorder in one

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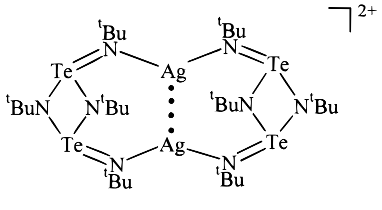
Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for **3**

Te1−N1	1.83(2)	Te1−N4	2.02(2)
Te1−N3	2.04(2)	Te2−N2	1.86(2)
Te2−N3	2.01(2)	Te2−N4	2.07(2)
Te3−N5	1.87(2)	Te3−N7	2.02(2)
Te3−N8	2.04(1)	Te4−N6	1.89(2)
Te4−N8	2.02(2)	Te4−N7	2.02(2)
Ag1−N1	2.31(2)	Ag1−N2	2.35(1)
Ag1−C11	2.525(6)	Ag2−N6	2.28(2)
Ag2−N5	2.35(2)	Ag2−C11	2.487(6)
N1−Te1−N4	96.4(7)	N1−Te1−N3	95.1(9)
N4−Te1−N3	76.7(7)	N2−Te2−N3	92.6(8)
N2−Te2−N4	98.8(7)	N3−Te2−N4	76.2(7)
N5−Te3−N7	103.6(7)	N5−Te3−N8	96.2(7)
N7−Te3−N8	75.7(7)	N6−Te4−N8	93.8(8)
N6−Te4−N7	102.7(8)	N8−Te4−N7	76.3(6)
N1−Ag1−N2	116.5(7)	N1−Ag1−C11	127.9(6)
N2−Ag1−C11	115.5(5)	N6−Ag2−N5	114.6(6)
N6−Ag2−C11	120.5(5)	N5−Ag2−C11	124.7(4)
Ag1−C11−Ag2	107.3(2)	C1−N1−Te1	124.7(13)
C1−N1−Ag1	124.9(14)	Te1−N1−Ag1	109.5(9)
C5−N2−Te2	125.7(13)	C5−N2−Ag1	122.3(13)
Te2−N2−Ag1	107.8(8)	C9−N3−Te2	126.2(13)
C9−N3−Te1	124.0(13)	Te2−N3−Te1	103.8(8)
C13−N4−Te1	126.9(15)	C13−N4−Te2	125.8(15)
Te1−N4−Te2	102.4(8)	C17−N5−Te3	124.6(13)
C17−N5−Ag2	126.1(13)	Te3−N5−Ag2	106.6(7)
C21−N6−Te4	121.1(15)	C21−N6−Ag2	128.3(14)
Te4−N6−Ag2	108.9(9)	C25−N7−Te4	124.7(13)
C25−N7−Te3	127.0(13)	Te4−N7−Te3	104.2(8)
C29−N8−Te4	125.7(13)	C29−N8−Te3	123.8(13)
Te4−N8−Te3	103.7(7)		

of ^{t}Bu groups and in the $CF_3SO_3^-$ anion, the Te−N bond distances in **3** are similar to those found in **1a**.[4a] For example, the average terminal Te−N distance in **3** is 1.845(15) Å (cf. 1.876(10) Å in **1a**). The bridging Te−N bond lengths, which are in the range 2.01−2.07(2) Å, may be compared to the mean value of 2.081(8) Å for the corresponding bonds in **1a**.[4a] The mean Ag−N distance is 2.32(3) Å (cf. 2.336(22) Å for [AgL$_4$][O$_3$SCF$_3$] (L = thiadiazacyclononane)[17] and 2.336(19) Å for [AgCl(piperidine)$_2$]$_n$). There is a very slight asymmetry in the Ag−Cl−Ag bridging unit {d(Ag−Cl) = 2.525(6) and 2.487(6), cf. 2.524(3), 2.667(3) Å in [AgCl(piperidine)$_2$]$_n$[18]}.

The bond angles found in the four-membered Te$_2$N$_2$ ring of the Te$_2$(N^{t}Bu)$_4$ unit in **3** are similar to those reported for **1a**.[4a] However, the N−Te−N angles involving one of the terminal nitrogen atoms are significantly different from those found in **1a** as a result of chelation to Ag$^+$. They are in the range of 92.6(8)−96.2(7)° (cf. 113.1(5)° in **1a**).[4a] The N−Ag−N angles of 114.6(6)° and 116.5(7)° are comparable to those found in {[(^{t}BuN)Re(μ-N^{t}Bu)]$_2$(μ-N^{t}Bu)$_2$Ag(μ-O$_3$SCF$_3$)}$_2$ [120.0(3)°].[7b]

Preparation and Structure of {[Te(μ-N^{t}Bu)]$_2$(μ-N^{t}Bu)$_2$Ag(O$_3$SCF$_3$)}$_2$ (4). When sublimed (LiCl-free) **1a** was used for the reaction with Ag[O$_3$SCF$_3$], an orange complex **4** was obtained. The ^{1}H NMR spectrum of **4** exhibits two equally intense resonances at δ 1.44 and 1.40 ppm and closely resembles that of **3** (vide supra). However, an X-ray structural determination revealed a novel structure in which the two tellurium diimide ligands **1a** in cis conformations are bridged by two Ag$^+$ ions. The structure of **4** has been discussed in a preliminary communication, and detailed comments on the structural parameters are unwarranted.[8] It is pertinent to point out, however, that the geometrical arrangement suggests a weak Ag···Ag bonding interaction.



4 (cation only)

Ag$^+$ salts are good one-electron oxidants. For example, the Te(II) derivative Te[N(SiMe$_3$)$_2$]$_2$ is readily oxidized by Ag[AsF$_6$] to the corresponding cation radical Te[N(SiMe$_3$)$_2$]$_2^{+\bullet}$, which was characterized by ESR spectroscopy.[19] However, no evidence for the formation of the cation radical **1a**$^{\bullet +}$ was obtained when an aliquot taken directly from a mixture of **1a** and Ag[AsF$_6$] (1:1 molar ratio) in toluene/CH$_2$Cl$_2$ at −85 °C was examined by ESR spectroscopy.

Synthesis of {[^{t}BuNTe(μ-N^{t}Bu)][Cu(O$_3$SCF$_3$)$_2$]}$_n$ (5) and {Cu$_2$[^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu]$_3$}[O$_3$SCF$_3$]$_2$ (6). The reaction of **1a** with [Cu(O$_3$SCF$_3$)]$_2$·C$_6$H$_6$ in a 1:1 molar ratio produced the complex **5** in high yield. In contrast to the ^{1}H NMR spectrum of the Ag$^+$ complex **4**, which exhibits two equally intense resonances attributable to bridging and terminal N^{t}Bu groups, the ^{1}H NMR spectrum of **5** in CD$_2$Cl$_2$ exhibits multiple resonances in the N^{t}Bu region.

Attempts to crystallize this product have not been successful. However, the treatment of **5** with 2 equiv of **1a** in toluene leads to the formation of [Cu$_2$L$_3$][CF$_3$SO$_3$]$_2$ (**6**). Details of the structure of **6** have been reported in the preliminary communication.[8] Of special significance is the observation that coordination to Cu$^+$ promotes cis → trans isomerization of the central ligand in **6**, while the terminal ligands retain their cis conformations. Complex **6** represents a fragment of a metal-bridged polymer with alternating *cis*- and *trans*-**1a** as ligands (Chart 1).

X-ray Structures of {[^{t}BuNTe(μ-N^{t}Bu)$_2$Te(μ-O)]$_2$[M(H$_2$N^{t}Bu)]$_2$}[O$_3$SCF$_3$] (7a, M = Ag; 7b, M = Cu) and [^{t}BuNTe(μ-N^{t}Bu)]$_2$[Cu(^{t}BuNH$_2$)]$_2$[O$_3$SCF$_3$]$_2$ (8). Coordination to transition metals enhances the hydrolytic sensitivity of sulfur diimides.[20] In this work, the transition-metal complexes of **1a** were found to be even more moisture-sensitive than the ligand itself, and several hydrolysis products were isolated during crystallization attempts and structurally characterized by X-ray crystallography.

Complex **7a** was obtained from the attempted recrystallization of **3** from CH$_2$Cl$_2$/THF over a period of 6 weeks. An ORTEP drawing of the cation in **7a** is displayed in Figure 2. The corresponding Cu$^+$ complex **7b** was obtained during attempts to crystallize **6**. An ORTEP diagram of **7b** is depicted in Figure 3, and selected bond distances and bond angles are compared with those for **7a** in Table 3. The cation in **7a**,**b** is derived from **1a** by the formal replacement of one terminal N^{t}Bu group by an oxo ligand (eq 1). The exocyclic Te═O bond thus formed is stabilized by dimerization to give a Te$_2$O$_2$ ring, while the remaining terminal N^{t}Bu groups coordinate to M$^+$ ions, which are also linked to a ^{t}BuNH$_2$ molecule formed by the hydrolysis of **1a**.

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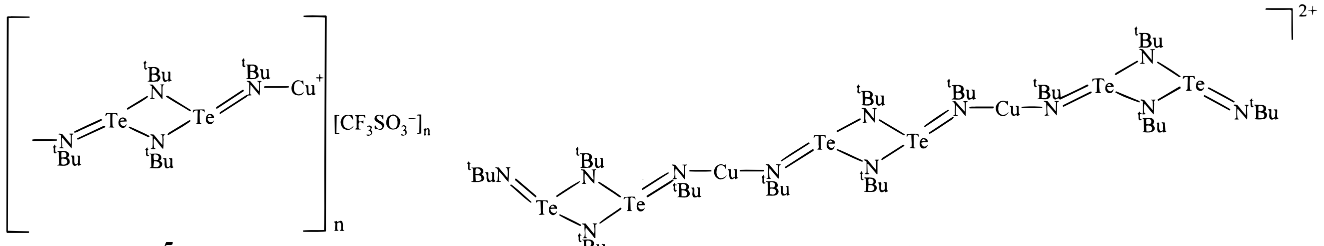
Chart 1



5

6 (cation only)

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for **7a**^{a} (M = Ag$^+$) and **7b** (M = Cu$^+$)

	7a	7b		7a	7b
Te1−O4	1.890(14)	1.885(7)	Te2−N2	2.05(2)	2.035(9)
Te1−O4*	2.151(13)	2.170(7)	Te2−N3	1.94(2)	1.901(10)
Te1−N1	2.07(2)	2.108(8)	M−N3	2.09(2)	1.850(9)
Te1−N2	2.00(2)	2.015(8)	M−N4	2.14(2)	1.887(10)
Te2−N1	2.00(2)	1.998(8)			
O4−Te1−N2	106.8(7)	107.2(3)	C1−N1−Te2	121.1(13)	120.3(6)
O4−Te1−N1	89.3(6)	88.6(3)	C1−N1−Te1	125.6(13)	123.2(7)
N2−Te1−N1	75.4(7)	75.1(3)	Te2−N1−Te1	102.6(7)	101.4(4)
O4−Te1−O4*	75.2(6)	75.6(3)	C5−N2−Te1	129.4(14)	126.8(8)
N2−Te1−O4*	91.7(6)	92.2(3)	C5−N2−Te2	121.3(13)	123.2(7)
N1−Te1−O4*	156.2(6)	156.1(3)	Te1−N2−Te2	103.0(7)	103.2(4)
N3−Te2−N1	97.7(8)	96.9(4)	C9−N3−Te2	121.3(15)	120.1(8)
N3−Te2−N2	99.4(8)	100.7(4)	C9−N3−M	127.0(15)	125.8(8)
N1−Te2−N2	75.9(6)	77.0(3)	Te2−N3−M	111.2(8)	113.9(5)
N3−M−N4	172.6(9)	176.7(4)	C13−N4−M	120.1(8)	120.6(8)
Te1−O4−Te1*	104.8(6)	104.4(3)			

^{a} Symmetry operation for starred atoms: $2 - x, -y, 2 - z$.

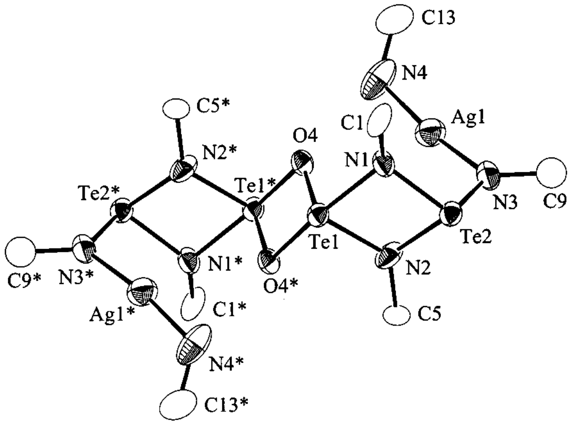


Figure 2. ORTEP diagram for the cation in **7a**. For clarity, only the α-carbon atoms of ^{t}Bu groups are shown.

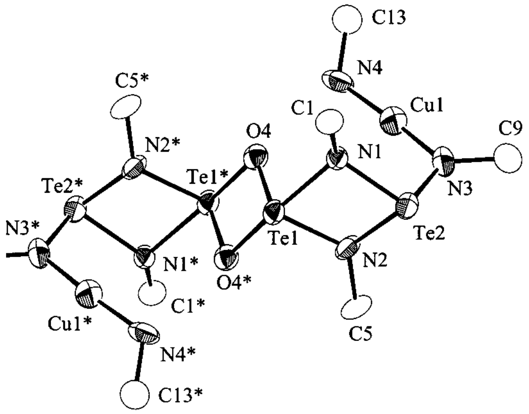


Figure 3. ORTEP diagram for the cation in **7b**.

The complexes **7a** and **7b** are isostructural, but the quality of the data for **7b** is superior. Consequently, quantitative comparisons with related structures will be made using the metrical parameters for **7b**. Distinct TeO bond distances [1.885(7) and 2.170(7) Å] are apparent in the planar, centrosymmetric bridge in **7b** [cf. (2,4,6-$Ph_3C_6H_2$)Te(μ-O)X] [X = Br, 1.898(4) and 2.084(5) Å; X = I, 1.914(2) and 2.086(2) Å[21] and 1.88(2) Å and 1.93(2) Å in β-TeO_2[22]]. The predicted Te−O single- and double-bond values are 2.12 and 1.89 Å, respectively.[23] Thus, the Te_2O_2 unit in **7a**,**b** can be viewed to involve two Te═O bonds and two dative bonds ═O→Te. By contrast, the TeO distances in $(Ph_2TeO)_2$ are 1.890 and 2.554 Å, indicating much weaker interactions between monomeric Ph_2-Te═O molecules.[24] The bridging Te−N distances in **7b** are in the range 1.998(8)−2.108(8) Å; however, the terminal Te−N bond length of 1.94(2) Å is significantly longer than the value of 1.86(2) Å found for the chelated complex **3**.

The geometry at the Te atoms of the Te_2O_2 ring is distorted TBP with lone pairs on Te in a trans orientation with respect to each other. Thus the equatorial bond angle (O4−Te1−N2) is 107.2(3)° and the axial bond angle (N1−Te1−O4*) is 156.1(3)°. The bond angles in the Te_2O_2 ring [104.4(3)° at O and 75.6(3)° at Te] are similar to those reported for the corresponding bond angles in [(2,4,6-$Ph_3C_6H_2$)Te(μ-O)X]$_2$ (X = Br, I),[21] β-TeO_2,[22] and $(Ph_2TeO)_2$.[24] The geometry at the Ag^+ ions is close to linear [∠ N3−Ag1−N4 = 176.3(4)°].

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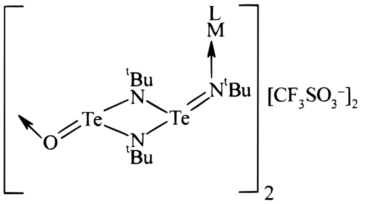
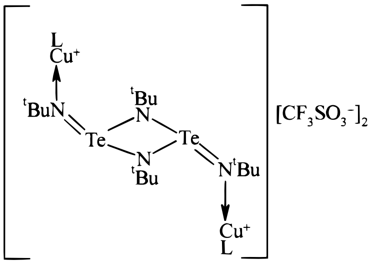


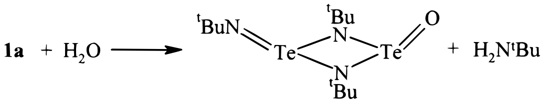
7a (M = Ag$^+$, L = ^{t}BuNH$_2$)
7b (M = Cu$^+$, L = ^{t}BuNH$_2$)



8 (L = ^{t}BuNH$_2$)

The complex [^{t}BuNTe(μ-N^{t}Bu)]$_2$[Cu(^{t}BuNH$_2$)]$_2$[CF$_3$SO$_3$]$_2$ (**8**) was isolated from a reaction of **1a** with [Cu(O$_3$SCF$_3$)]$_2$·C$_6$H$_6$ in a 2:1 molar ratio. The structure of **8** was determined by X-ray crystallography. As shown in Figure 4, it consists of {[^{t}BuNTe(μ-N^{t}Bu)]$_2$[Cu(^{t}BuNH$_2$)]$_2$}$^{2+}$ cations and two noninteracting CF$_3$SO$_3^-$ anions. As in the central portion of complex **6** (Figure 3), the terminal N^{t}Bu groups of the trans isomer of **1a** each coordinate to a Cu$^+$ center. Each Cu$^+$ ion is also attached to a ^{t}BuNH$_2$ ligand. Selected bond distances and bond angles for complex **8** are summarized in Table 4. The mean exocyclic Te–N distance is 1.931(14) Å, significantly longer than the value of 1.845(15) Å observed for the chelated complex **3**. The endocyclic Te–N bond lengths are in the range 2.004(14)–2.117(14) Å with a mean value of 2.05 Å (cf. 2.081(1) Å for **1a**).[4a] The two-coordinate N–Cu–N geometry is close to linear [177.5(8)° and 178.9(7)°], with Cu–N distances in the range 1.831(14)–1.91(2) Å (cf. 1.860(7) and 1.871(7) Å in [(^{t}BuN)Re(μ-N^{t}Bu)$_2$]$_2$(μ-N^{t}Bu)$_2$[Cu(O$_3$SCF$_3$)]$_2$).[7b]

The formation of the complexes **7a**, **7b**, and **8** from attempted crystallizations of Ag$^+$ and Cu$^+$ complexes of **1a** over periods ranging from 10 days to 6 weeks is presumably the result of the metal-promoted partial hydrolysis of **1a** according to eq 1. However, the attempted generation of the dimer [^{t}BuNTe(μ-N^{t}Bu)$_2$Te(μ-O)]$_2$ by controlled hydrolysis of **1a** with a deficiency of water produced only TeO$_2$ and unreacted **1a** regardless of the stoichiometry. Thus it appears that the M$^+$ ions play a key role in stabilizing this novel spirocyclic ligand.



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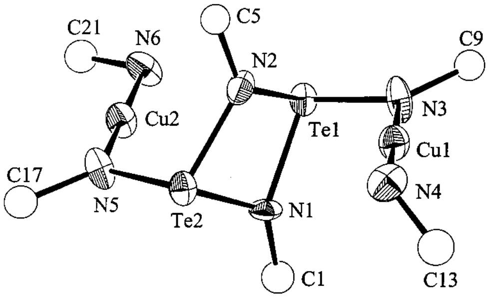

Figure 4. ORTEP diagram for the cation in **8**. For clarity, only the α-carbon atoms of ^{t}Bu groups are shown.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for **8**

Te1–N1	2.117(14)	Te1–N2	2.029(14)
Te2–N5	1.943(14)	Te1–N3	1.919(12)
Te2–N2	2.06(2)	Te2–N1	2.004(14)
Cu1–N4	1.91(2)	Cu1–N3	1.89(2)
Cu2–N6	1.89(2)	Cu2–N5	1.831(14)
C1–N1–Te2	128.4(11)	C1–N1–Te1	127.2(11)
Te2–N1–Te1	101.0(6)	C5–N2–Te1	128.1(12)
C5–N2–Te2	123.7(11)	Te1–N2–Te2	102.2(6)
C9–N3–Cu1	124.4(10)	C9–N3–Te1	122.8(11)
Cu1–N3–Te1	112.7(7)	C13–N4–Cu1	119.1(12)
C17–N5–Cu2	123.4(11)	C17–N5–Te2	118.4(11)
Cu2–N5–Te2	117.8(7)	C21–N6–Cu2	118.1(12)
N3–Te1–N2	95.6(5)	N3–Te1–N1	99.4(7)
N2–Te1–N1	75.2(6)	N3–Te1–Te2	109.4(5)
N5–Te2–N1	101.5(5)	N5–Te2–N2	101.1(6)
N1–Te2–N2	77.1(5)	N5–Te2–Te1	94.3(4)
N3–Cu1–N4	177.5(8)	N5–Cu2–N6	178.9(7)

Conclusion

Investigations of the first transition-metal complexes of a tellurium diimide dimer have confirmed the anticipated versatility of this novel type of ligand. Both chelating and bridging functions have been ascertained in complexes with coinage metals. The ability of Cu$^+$ to promote cis → trans isomerization is especially noteworthy and suggests that further investigations of the coordination chemistry of **1a** will be fruitful. The modification of the reactivity of **1a** upon complexation to a metal, as exemplified by the formation of the novel spirocyclic ligand [^{t}BuNTe(μ-N^{t}Bu)$_2$Te(μ-O)]$_2$, suggests that reactions of the metal-coordinated ligand may lead to new chemistry.

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Supporting Information Available: The four X-ray crystallographic files, in CIF format, are available on the Internet only. This material is available free of charge via the Internet at http://pubs.acs.org.

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