Keywords: alkaloids · allenes · natural products · spiro compounds · total synthesis

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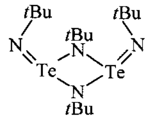
Coinage Metal Complexes of a Tellurium Diimide: *cis*→*trans* Isomerization and Metal–Metal Interactions[**]

Tristram Chivers,[*] Masood Parvez, and Gabriele Schatte

The unique properties of inorganic polymers, especially those with metal atoms in the backbone, provide an incentive for the investigation of novel systems.[1] The versatile ligand behavior of sulfur(IV) diimides encompasses σ(*N*), σ(*N*,*N'*), and, less commonly, σ(*S*) and π(*N*,*S*) bonding modes.[2] The only known complex of a selenium(IV) diimide, $SnCl_4(tBuN{=}Se{=}NtBu)$, displays σ(*N*,*N'*) chelation.[3] Unlike their lighter congeners RN=E=NR (E = S, Se), which adopt monomeric structures with *syn*,*syn* or *syn*,*anti* conformations in the solid state[4, 5] and gas phase,[6] tellurium diimides are dimeric and form *cis* or *trans* isomers in the solid state.[7–9] The *cis* isomer **1** is obtained with an *endo*,*endo* arrangement of terminal *t*Bu groups,[8] whereas in the *trans* isomers **2b** and **2c** the terminal groups occupy *exo* positions with respect to the Te_2N_2 ring.[9] In solution **2b** and **2c** slowly convert into the corresponding *cis* isomers.[9]



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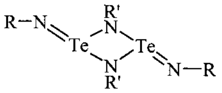

2a, R = R' = *t*Bu
2b, R = PPh_2NSiMe_3, R' = *t*Bu
2c, R = PPh_2NSiMe_3, R' = *t*Oct

As part of our investigations of the coordination chemistry of tellurium diimide dimers the generation of a polymer in which ligands of type **2** are bridged by metal ions seemed especially intriguing. We describe here the synthesis and X-ray structures of **3** and **4**, the first metal complexes of a tellurium diimide dimer. The ligand **1** exhibits remarkably different ligand behavior towards Cu^+ and Ag^+. In particular, Cu^+ promotes *cis*→*trans* isomerization (**1**→**2a**) in the formation of **3**. In contrast, the dinuclear complex **4** with a metal–metal (d^{10}–d^{10}) interaction is produced in the presence of Ag^+.

$[Cu_2L_3](CF_3SO_3)_2$ **3**
$[Ag_2L_2](CF_3SO_3)_2$ **4**
$[Cu_2L](CF_3SO_3)_2$ **5**
$L = tBuN{=}Te(\mu\text{-}NtBu)_2Te{=}NtBu$

Complex **3** was obtained by a two-step process in which **5** was prepared from stoichiometric amounts of copper(I) trifluoromethanesulfonate and **1**.[10] Subsequently, **5** was

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treated with two equivalents of **1** in toluene to give $\mathbf{3}\cdot 2\,C_7H_8$ in excellent yield. An X-ray structure determination of $\mathbf{3}\cdot CH_2Cl_2$[11] revealed a centrosymmetric chain structure in which two Cu^+ ions form linear bridges (N-Cu-N 177.9(8)°) between three dimeric tellurium diimide ligands (Figure 1).

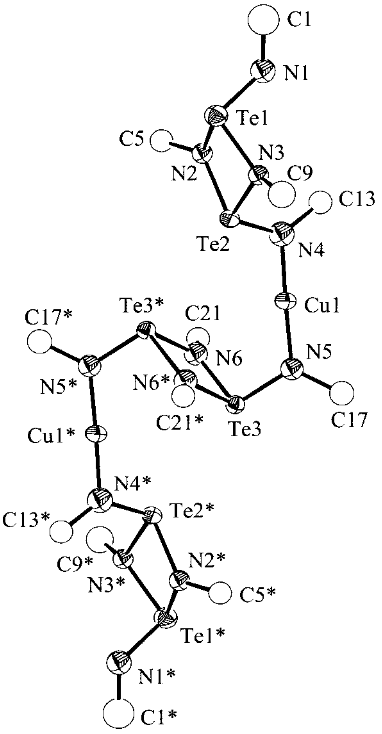

Figure 1. Crystal structure of the cation in **3**. For clarity only the α-carbon atoms of the *t*Bu groups are shown. Selected bond lengths [Å]: Te1–N1 1.87(2), Te1–N2 2.023(18), Te1–N3 2.009(17), Te2–N2 1.997(17), Te2–N3 2.045(18), Te2–N4 1.915(19), Te3–N5 1.868(18), Te3–N6 1.983(19), Te3–N6* 2.025(19), Cu1–N4 1.87(2), Cu1–N5 1.895(19). Symmetry transformation used to generate equivalent atoms (labeled with an asterisk): $x+2, -y, -z+2$.

Two features of the ligand geometries are noteworthy. First, coordination to Cu^+ engenders *cis* → *trans* isomerization of the central ligand. Second, the exocyclic *t*Bu groups of the terminal ligands adopt an *endo,exo* arrangement, presumably as a result of facile rotation about the dipolar $Te^+{-}N^-{-}t$Bu bonds that involve the uncoordinated nitrogen atoms.[13]

Coordination of the tellurium diimide ligand to Cu^+ likely involves the HOMO − 2 orbital, an in-plane σ lone pair on the exocyclic nitrogen atoms, rather than the HOMO, which is a π-type orbital located primarily on the exocyclic nitrogen atoms.[9] Accordingly, the exocyclic Te–N bond lengths of the coordinated N atoms are not significantly longer than that involving the uncoordinated N atoms. However, the mean bridging Te–N distance of 2.014(18) Å in **3** is somewhat shorter than that of 2.081(8) Å in **1**.[8] Isomerization imposes planarity on the central Te_2N_2 ring of **2**, whereas the terminal Te_2N_2 rings retain the puckered conformation of the free ligands (the N-Te-N-Te torsion angles are −14.4(7) and 14.6(4)°, respectively; cf. 19.8(5)° in **1b**).[8] There are no interactions between the cation of **3** and the $CF_3SO_3^-$ anions. The Cu–N bond lengths are comparable to those reported for $[(t\mathrm{BuN})\mathrm{Re}(\mu\text{-N}t\mathrm{Bu})_2]_2(\mu\text{-N}t\mathrm{Bu})_2[\mathrm{Cu}(O_3SCF_3)]_2$ (1.860(7) and 1.871(7) Å).[14]

The silver(I) complex **4** was obtained in almost quantitative yield from the reaction of equimolar amounts of silver trifluoromethanesulfonate and **1** in toluene. Both the ^1H and ^{13}C NMR spectra of **4** in CD_3CN exhibit equally intense signals for bridging and terminal N*t*Bu groups. The simplicity of these spectra compared to the ^1H NMR spectrum of **3**, which exhibits multiple signals for N*t*Bu groups, implies a significantly different structure for **4**.

An X-ray structure determination of **4**[15] showed that the Ag^+ ions in this complex bridge two tellurium diimide dimers (Figure 2). The two ligands **1** retain their *cis* configurations, but the exocyclic *t*Bu groups are both in *exo* positions to accommodate chelation to the Ag_2^{2+} moiety. The Te_2N_2 rings are rotated by 90° with respect to each other to give a helical structure with no interactions between the dication and the $CF_3SO_3^-$ anions. In contrast, the related rhenium ligand $(t\mathrm{BuN})_2\mathrm{Re}(\mu\text{-N}t\mathrm{Bu})_2\mathrm{Re}(\mathrm{N}t\mathrm{Bu})_2$ chelates a single Ag^+ ion and the $CF_3SO_3^-$ anions bridge two Ag^+ ions in a dimeric structure.[14] The most significant feature of the structure of **4** is the Ag⋯Ag distance of 2.888(2) Å. The existence of metal–metal bonding in d^{10}–d^{10} systems in which the two metals are closer than the interatomic distances in copper or silver metal is controversial.[16, 17] Ionic complexes of Ag^+ with neutral ligands provide the most appropriate comparison for **4**, for example, $d(\mathrm{Ag}\cdots\mathrm{Ag}) = 2.9501(8)$ Å in $[Ag_2(PPh_2CH_2SPh)_2][ClO_4]_2$[17] and 3.033(1) Å in $[\mathrm{Ag}(\mu\text{-L})(O_3SCF_3)]_2$ (L = 1-[(diphenylphosphanyl)methyl]-4-(2-pyridyl)piperazine).[18] Recent ab initio calculations at the MP2/II level on the model system $[Ag_2(H_2PCH_2SH)_2]^{2+}$ indicate the presence of a metallophilic attraction as a correlation effect.[17] In **4** the geometrical parameters are strongly indicative of a Ag⋯Ag bonding interaction. First, the mean N-Ag-N angle of 163.3(5)° deviates substantially from the linear geometry found for Cu^+ in **3**. Secondly, the N-Te-μ-N bond angles of the complexed ligand (av 99.1(5),

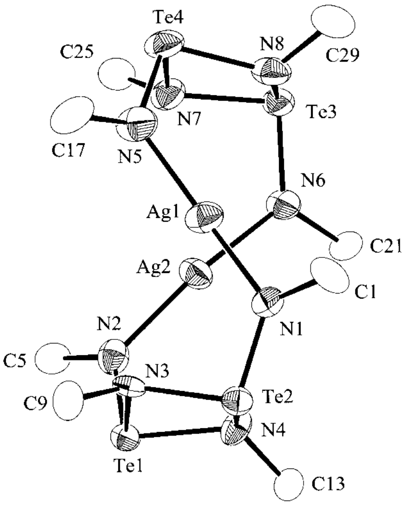

Figure 2. Crystal structure of the cation in **4**. For clarity only the α-carbon atoms of the *t*Bu groups are shown. Mean bond lengths [Å] and angles [°]: $Te{-}N_{exo}$ 1.898(12), $Te{-}N_{endo}$ 2.036(12), Ag–N 2.132(12); N-Ag-Ag 94.0(3)–101.8(3) (av 98.2(3)), Te-N-Ag 122.6–125.0(5) (av 123.9(6)).

range 95.9(5)–102.0(5)°) are significantly smaller than those of the free ligand **1** (av 113.4(5)°).[8] The mean Ag–N bond length of 2.132(12) Å in **4** is somewhat shorter than those of related Ag^+ complexes (2.274(7)–2.457(8) Å).[14, 18]

In summary, the profound differences in the ligand behavior of **1** towards different coinage metals heralds a fascinating and unpredictable coordination chemistry for tellurium diimide dimers. The initial complexation of **1** to Cu^+ causes *cis* → *trans* isomerization of the ligand.[10] Complex **3** can be viewed as a fragment of a metal-bridged polymer with alternating *cis* and *trans* ligands **1** and **2a**. The 1:1 complex $\{[CuL]CF_3SO_3\}_n$, the stoichiometric equivalent of **4**, may have a polymeric structure, but efforts to obtain crystals of this material have so far been unsuccessful.

Experimental Section

3: Complex **5** was obtained in 97% yield as a yellow-brown solid from the reaction of equimolar amounts of $Cu_2(CF_3SO_3)_2 \cdot C_6H_6$ and freshly sublimed **1** in toluene (satisfactory CHN analysis). A solution of **1** (0.34 g, 0.62 mmol) in toluene (10 mL) was added dropwise to a stirred slurry of **5** (0.30 g, 0.31 mmol) in toluene (10 mL) at −78 °C. After 20 h at 23 °C removal of solvent gave $\mathbf{3} \cdot 2\,C_7H_8$ (0.61 g, 0.31 mmol, 88%) as a dark red solid. ^1H NMR (200 MHz, CD_2Cl_2, 23 °C): $\delta = 1.32–1.68$ (m).

4: A solution of $AgCF_3SO_3$ (0.24 g, 0.93 mmol) in toluene (10 mL) was added slowly to a solution of freshly sublimed **1** (0.60 g, 0.93 g) in toluene (10 mL) at −78 °C. After 3 h at 23 °C, the solvent was removed to give **4** (0.67 g, 0.42 mmol, 92%) as an orange solid. Satisfactory CHN analysis; ^1H NMR (200 MHz, CD_3CN, 23 °C): $\delta = 1.44$ (s, 9H, $C(CH_3)_3$), 1.40 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (400 MHz, CD_3CN, 23 °C): $\delta = 62.46$, 59.88 ($C(CH_3)_3$), 37.01, 36.79 ($C(CH_3)_3$).

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[11] a) Dark red prisms of $\mathbf{3} \cdot CH_2Cl_2$ were obtained from a solution in CH_2Cl_2/*n*-hexane after 24 h by using a reported procedure.[12] Crystal data for $\mathbf{3} \cdot CH_2Cl_2$: $C_{52}H_{112}N_{12}O_6S_2Te_6Cu_2F_6Cl_4$, $M_r = 2214.14$, monoclinic, space group $P2_1/c$, $a = 14.007(4)$, $b = 17.646(4)$, $c = 17.383(4)$ Å, $\beta = 103.07(2)°$, $V = 4185(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.757\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 27.96\ cm^{-1}$, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $T = -103\,°C$, $F(000) = 2160$. Data were collected on a Rigaku AFC6S diffractometer on a crystal coated with Paratone 8277 oil and mounted on a glass fiber (crystal dimensions 0.32 × 0.31 × 0.31 mm). Of the 8003 reflections collected, 7331 were unique ($R_{int} = 0.084$). The structure was solved by direct methods (SIR92) and expanded by Fourier techniques. The *t*Bu groups were disordered due to high thermal motions, and the C–N and C–C distances were therefore constrained during the refinements. The final cycle of full-matrix least-squares refinement with F^2 coefficients (SHELXL97) was based on 2043 observed reflections ($I > 2.00\,\sigma(I)$) and 265 parameters and led to $R = 0.0702$ and $R_w = 0.1685$. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-113882 and -113883. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[15] Crystals of **4** were obtained from a solution in CH_3CN at −15 °C (four weeks).: Crystal data for **4**: $C_{34}H_{72}N_8O_6Ag_2F_6S_2Te_4$, $M_r = 1593.24$, monoclinic, space group $P2_1/n$ (no. 14), $a = 20.342(4)$, $b = 11.409(5)$, $c = 24.512(5)$ Å, $\beta = 106.26(2)°$, $V = 5461(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.938\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 29.48\ cm^{-1}$, $\lambda\ (Mo_{K\alpha}) = 0.71069$ Å, $T = -103\,°C$, $F\ (000) = 3072$. Data were collected on a Rigaku AFC6S diffractometer on a yellow plate (0.35 × 0.40 × 0.13 mm) coated with Paratone 8277 oil and mounted on a glass fiber. Of the 9674 unique reflections collected, 5204 had $I > 2.00\,\sigma(I)$. The structure was solved by direct methods (SIR92), completed by Fourier synthesis (DIRDIF94), and refined on F^2 by full-matrix least-squares procedures: $R = 0.0497$, $R_w = 0.1273$.[11b]

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