DALTON

Structure and reactivity of [{Te(NMe$_2$)$_2$}$_\infty$]; application to the preparation of metalloorganic tellurium(II) compounds †

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Condensation of the highly reactive complex [{Te(NMe$_2$)$_2$}$_\infty$] **1**, prepared by the reaction of TeCl$_4$ and Li[NMe$_2$] (1 : 4 equivalents), with various organic acids has been used as a route to tellurium(II) metalloorganic complexes. The crystal structures of **1** and of Te(SCPh$_3$)$_2$ **2**, formed by the reaction of **1** with Ph$_3$CSH (1 : 2 equivalents), have been determined.

Although there have been a variety of N-bonded complexes of Te^{IV} and Te^{II} characterised in the solid state,[1] very few bis(amido)tellurium(II) compounds have been structurally elucidated.[2] All of the latter have essentially mononuclear structures [containing Te(NR^{1}R^2)$_2$ units] in which steric and electron stabilisation of the tellurium centre is provided by trimethylsilyl substituents. Our studies into heavy p-block metal–nitrogen bonded complexes have recently focused on the applications of the dimethylamidometal reagents as potent bases.[3] The condensation reactions of these reagents with primary amines [NH$_2$R] or lithiated primary amines Li[NHR] has proved to be a highly versatile and general strategy to low-oxidation-state Group 14 (Sn) and 15 metal (Sb, Bi) amido and imido derivatives. However, the extension of this work to Group 16 (Se, Te) had been thwarted by a lack of suitably reactive and readily prepared deprotonation reagents. We here report the synthesis and crystal structure of the polymeric complex [{Te(NMe)$_2$}$_\infty$] **1**. The latter is a highly reactive tellurium(II) reagent and reacts with a range of organic acids (*e.g.* amines, phosphines and thiols). Exemplifying this new approach to metalloorganic tellurium(II) complexes, the synthesis and crystal structure of the monomeric complex Te(SCPh$_3$)$_2$ **2**, produced by the reaction of **1** with Ph$_3$CSH, are reported.

Results and Discussion

Complex **1** was prepared in high yield (up to 74%) by the reaction of TeCl$_4$ with Li[NMe$_2$] (1:4 equivalents) in tetrahydrofuran (thf)–Et$_2$O [equation (1)]. This highly volatile

$$\mathrm{TeCl_4} + 4\mathrm{Li[NMe_2]} \xrightarrow[-78^\circ\mathrm{C}]{\mathrm{thf,Et_2O}} \underset{\mathbf{1}}{\tfrac{1}{\infty}[\{\mathrm{Te(NMe_2)_2}\}_\infty]} \quad (1)$$

complex, which can be sublimed as yellow needles at room temperature and under relatively low pressures (*ca.* 0.1 atm), is highly air- and moisture-sensitive and exposure to air and/or moisture gives rise to black metallic Te. The complex is highly soluble in a variety of organic solvents (*e.g.* hexane, toluene, thf) and is conveniently stored as a standardised solution in hexane at −35 °C. Crystals of **1** for X-ray analysis were obtained from toluene at −35 °C. The mechanism of formation of **1** is not clear. However, in view of its high yield and the absence of disproportionation into metallic Te during its preparation a possible mechanism is that of reductive elimination of Cl$_2$ from [Te(NMe$_2$)$_2$Cl$_2$]. A radical pathway, similar to that proposed by Roesky and co-workers[2b] in the formation of Te[N(SiMe$_3$)$_2$]$_2$ involving initial formation Te(NMe$_2$)$_4$ may also be possible.

The reactions of complex **1** with a range of organic acids [amines, *e.g.* NH$_2$R, (R = Bu^t or Ph$_3$C), NHR$_2$ (R = PhCH$_2$); phosphines, *e.g.* PH$_2$R and PHR$_2$ (R = Ph or C$_6$H$_{11}$) and thiols RSH (R = PhCH$_2$ or Ph$_3$C)] occur smoothly at −78 °C, giving clear orange or orange-red solutions and the formation of NHMe$_2$. Although these solutions are stable at low temperature ($\leqslant$ *ca.* −40 °C), in most cases decomposition, with the deposition of metallic Te, occurs when they are raised to room temperature. So far, the only stable crystalline complexes which have been obtained are those containing bulky thiolate ligands. These observations appear to indicate that a combination of sterically bulky substituents and the presence of soft heteroatomic centres in the organic acid are required to avoid reduction in these reactions. The reaction of **1** with Ph$_3$CSH (1:2 equivalents) produces Te(SCPh$_3$)$_2$ **2** in high yield [equation (2)]. In contrast to **1**, this complex is surprisingly air- and moisture-stable for prolonged periods.

$$\underset{\mathbf{1}}{\tfrac{1}{\infty}[\{\mathrm{Te(NMe_2)_2}\}_\infty]} + 2\mathrm{Ph_3CSH} \xrightarrow[-78^\circ\mathrm{C}]{\text{toluene}} \underset{\mathbf{2}}{\mathrm{Te(SCPh_3)_2}} + 2\mathrm{NHMe_2} \quad (2)$$

The low-temperature (153 K) crystal structures of complexes **1** and **2** were determined. Key bond lengths and angles for both complexes are collected in Table 1. Complex **1** has a polymeric structure [{Te(NMe$_2$)$_2$}$_\infty$] [Fig. 1(*a*)]. There are two crystallographically independent half molecules of **1** [centred at Te(1A) and Te(2B)] and a half molecule of toluene present in the asymmetric unit. The Te(NMe$_2$)$_2$ monomer units are linked together by NMe$_2$ groups, giving a chain of interbonded Te$_2$N$_2$ rings (average N–Te$\cdots$N 77.7, average Te–N$\cdots$Te 101.5°, tellurium centres 0.41 Å out of the idealised Te$_2$N$_2$ ring planes) [Fig. 1(*b*)]. The structural arrangement gives each of the tellurium(II) centres of the polymer almost identical (formally 12e) distorted square-planar geometries (sum of angles about Te 360.1°), with the two lone pairs on each Te^{II} being aligned axially. Despite the bridging of these groups the Te–N bond lengths within each Te(NMe$_2$)$_2$ unit are similar to those

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† *Non-SI unit employed:* atm = 101 325 Pa.

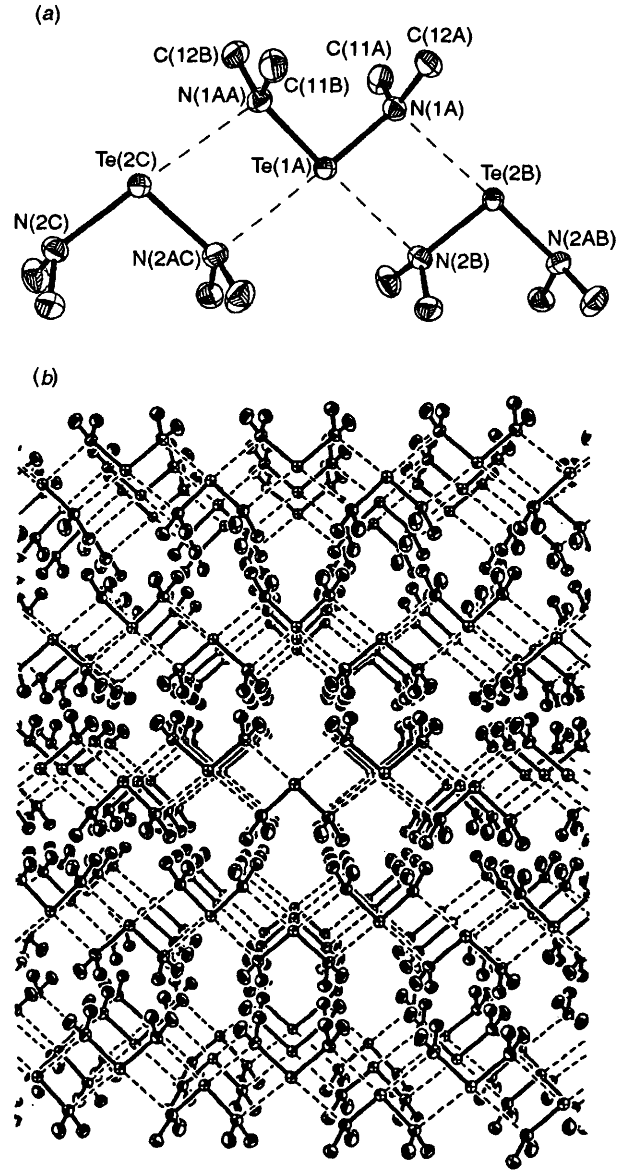

Fig. 1 Crystal structure of complex **1**, (*a*) showing the association of the monomeric units, (*b*) showing the packing of the polymeric strands in the lattice

observed in the previously structurally characterised neutral amidotellurium(II) compounds {Te–N 2.050(2)–2.051(2) in **1** *cf.* average 2.05 Å in Te[N(SiMe$_3$)$_2$]$_2$}.[2b] Although the *intermonomer* Te • • • N bond lengths (average 2.96 Å) are considerably longer than those found within the monomer units, they are markedly shorter than the sum of the van der Waals radii of Te and N (3.70 Å).[4] The relative shortness of these interactions and the orientation of the NMe$_2$ groups, the nitrogen lone pairs of which are directed towards the neighbouring tellurium centres, indicates that these interactions can most aptly be described as weak co-ordinative bonds.

The two structurally characterised neutral amidotellurium(II) complexes Te[N(SiMe$_3$)$_3$]$_2$[2b] and Te[NBu^t(SiMe$_3$)]$_2$[2c] both have essentially monomeric bent structures [N–Te–N *ca.* 106° in both; *cf.* 100.4(1)° in **1**] in which further association *via* intermonomer Te • • • N bonding is precluded by the presence of sterically demanding substituents. It is interesting that in Te[N(SiMe$_3$)$_3$]$_2$ further weak association of the monomeric units is achieved through relatively short Te • • • Te interactions (3.77 Å).[2b] In contrast to the latter, the Te • • • Te distances in **1** are all greater than the predicted van der Waals distance and the structure is held together solely by Te • • • N interactions. In the remarkable tellurium(III) radical cation [Te{N(SiMe$_3$)$_2$}$_2$]$^+$ a similar bent geometry to that of Te[N(SiMe$_3$)$_3$]$_2$ is observed at the Te, now with additional Te • • • F interactions to the AsF$_6^-$ counter anions.[2a] Although association *via* intermolecular Te • • • N interactions is known in a variety of N-bonded complexes of Te^{II} and Te^{IV} (range *ca.* 2.40–3.40 Å),[1] the polymeric structural motif observed for **1** and the consequent co-ordination geometry of the tellurium(II) centres within it are unprecedented structural features in the chemistry of amidotellurium(II) compounds. It is noteworthy also that **1** is the first structurally characterised tellurium(II) amide in which no steric and/or electronic stabilisation of the tellurium(II) centre by SiMe$_3$ substituents is present. However, evidently the association of the monomeric Te(NMe$_2$)$_2$ units of **1** *via* bridging NMe$_2$ groups is comparatively weak judging by cryoscopic molecular-mass measurements of the complex in benzene, which indicate that it largely dissociates into monomers even at relatively high concentration [M_r = 244 ± 1 (n = 1.13 ± 0.01, 0.080 mol dm^{-3}), 206 ± 2 (n = 0.96 ± 0.01, 0.037 mol dm^{-3})].

The crystal structure of complex **2** shows it to be monomeric in the solid state (Fig. 2). The Te–S bond lengths are similar to those in the few previously characterised S-bonded complexes of Te^{II} [2.379(2) Å in **2**; *cf.* 2.36–2.43 Å.[5]] The monomeric nature

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1** and **2***

Complex **1**			
Te(1A)–N(1A)	2.051(2)	Te(1A) • • • N(2B)	2.960(2)
Te(1A)–N(1AA)	2.051(2)	Te(2B) • • • N(1A)	2.959(2)
Te(2B)–N(2B)	2.050(2)	Te(2C) • • • N(1AA)	2.959(2)
Te(2B)–N(AB)	2.050(2)	Te(1A) • • • N(2AC)	2.959(2)
N(1A)–Te(1A)–N(1AA)	100.4(1)	N(1A) • • • Te(2B) • • • N(2B)	77.7(1)
N(1A) • • • Te(1A) • • • N(2B)	77.7(1)	N(1A) • • • Te(2B) • • • N(1AB)	104.3(1)
N(2B) • • • Te(1A) • • • N(2AC)	104.3(1)	N(1AB) • • • Te(2B) • • • N(2AB)	77.7(1)
N(1AA) • • • Te(1A) • • • N(2AC)	77.7(1)	N(1A) • • • Te(2B) • • • N(2AB)	177.4(1)
N(1A) • • • Te(1A) • • • N(2AC)	177.2(1)	N(2B) • • • Te(2B) • • • N(1AB)	177.3(1)
N(1AA) • • • Te(1A) • • • N(2B)	177.2(1)	Te–N • • • Te(average)	101.5
N(2B)–Te(2)–N(2AB)	100.4(1)		
Complex 2			
Te–S(1)	2.379(2)	C(1)–C (aryl) (average)	1.529
S(1)–C(1)	1.918(7)		
S(1)–Te–S(1a)	110.8(1)	C(1)–S(1)–Te	113.7(2)

* Symmetry operations: for **1** 1a $-x-1, y, -z+\frac{3}{2}$; 2a $-x, y, -z+\frac{3}{2}$; for **2** $-x, y, -z+\frac{1}{2}$.

of the complex and the S–Te–S angle reflect the large steric bulk of the attached $SCPh_3$ groups compared to the NMe_2 groups present in **1** [S–Te–S 110.8(1) in **2**; *cf.* 100.4(1)° in **1**]. Previous structural studies of S-bonded compounds of Te^{II} have focused on those containing functionalised thiosulfonate, thiophosphate and thiocarboxylate groups.[5] Despite its structural simplicity, to our knowledge **2** is the first structurally characterised complex containing simple unfunctionalised thiolate ligands. The full characterisation of **2** provides unequivocal proof that reactions of $Te(NMe_2)_2$ with organic acids can be applied as an effective new method in the preparation of metalloorganic tellurium(II) compounds, at least where the organic acids contain bulky substituents and soft heteroatomic centres.

We are continuing to investigate the reactivity and synthetic utility of $Te(NMe_2)_2$. The very high volatility of the complex, which can be sublimed rapidly at 25 °C under reduced pressure, may also be of value in the vapour-phase deposition of thin films, *e.g.* tellurium nitride and mercury telluride.

Experimental

General procedure

The products **1** and **2** and the starting materials $TeCl_4$ and $Li[NMe_2]$ are all air-sensitive. They were handled on a vacuum line using standard inert-atmosphere techniques[6] and under dry O_2-free Ar. The toluene, thf and Et_2O solvents were dried using sodium–benzophenone and were degassed prior to the reactions. Both complexes were isolated and characterised with the aid of an Ar-filled glove-box (Miller-Howe) fitted with an internal Belle Technology O_2 and H_2O recirculation system. Melting points were determined by using a conventional apparatus and sealing samples in capillaries under Ar. Infrared spectra were recorded as Nujol mulls using NaCl windows on a Perkin-Elmer 2400 spectrophotometer. Elemental analyses were performed by first sealing samples under Ar in air-tight aluminium boats (1–2 mg). The C, H and N analyses were carried out using a Perkin-Elmer 240 Elemental Analyser. Proton NMR spectra were recorded on a Bruker WH 400 MHz spectrometer in dry C_6D_6 (using the solvent resonances as the internal reference standard).

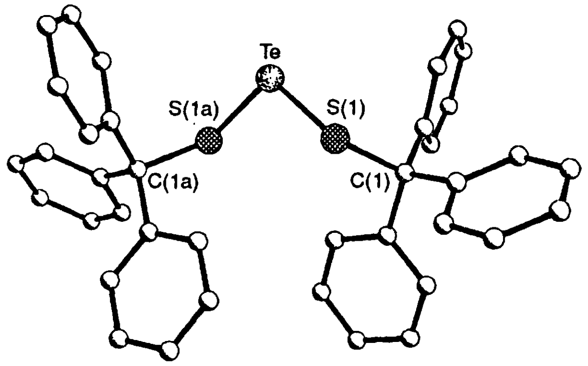

Fig. 2 Crystal structure of monomer molecules of complex **2**

Preparations

Complex 1. A solution of $Li[NMe_2]$ (4.08 g, 80 mmol) in thf (60 cm^3) was added to a suspension of $TeCl_4$ (5.39 g, 20 mmol) in Et_2O (20 cm^3) at −78 °C. An immediate bright yellow colouration was observed. The reaction mixture was kept at −78 °C (20 min) before being stirred at room temperature (1 h). The solvent was gently removed *in vacuo* and complex **1** was obtained as highly air- and moisture-sensitive yellow crystalline needles by distillation (80 °C, 0.1 atm), in highest yields of 3.20 g (74%); m.p. *ca.* 35 °C to a yellow oil. NMR (25 °C, C_6D_6): ^1H (400.13 MHz), δ 3.46 (s, Me_2N); ^{13}C (100.61 MHz), δ 57.30 (q, Me_2N) (Found: C, 23.0; H, 5.6; N, 13.9. Calc. for $C_4H_{12}N_2Te$: C, 22.3; H, 5.6; N, 13.0%). X-Ray-quality crystals were grown at −35 °C from a toluene solution of **1**.

Complex 2. The compound Ph_3CSH (0.553 g, 2.0 mmol) was added to a solution of $Te(NMe_2)_2$ (0.216 g, 0.1 mmol) in toluene (10 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature and a solution changed from yellow to orange, with the precipitation of an orange solid. The solid was dissolved by gentle heating and storage at room temperature gave orange cubic crystals of complex **2** in 90% yield (0.61g); decomp. > 145 °C to black solid. ^1H NMR (25 °C, C_6D_6, 400.13 MHz): δ 7.54–7.49 (m) and 7.13–6.98 (m) (30 H, aryl CH). IR (Nujol), $\tilde{\nu}_{max}/cm^{-1}$ 3060m (C–H aryl), 1592m (C$\overset{...}{-}$C aryl); other absorptions at 1183s, 1082s, 1032s, 758s, 729s, 698s and 660s (Found: C, 67.1; H, 4.5. Calc. for $C_{38}H_{30}S_2Te$: C, 67.2; H, 4.4%).

Table 2 Crystal data and structure solutions for complexes **1** and **2**[a]

Empirical formula	$C_4H_{12}N_2Te{\cdot}0.5\,C_6H_6$[a]	$C_{38}H_{30}S_2Te$
M	169.87	678.34
Crystal size/mm	0.6 × 0.5 × 0.4	0.2 × 0.3 × 0.3
a/Å	7.779(1)	11.713(4)
b/Å	24.868(8)	14.936(6)
c/Å	11.439(3)	17.401(5)
β/°	109.88(1)	96.08(4)
U/Å^3	2081.0(9)	3027(2)
Z	8	4
D_c/Mg m^{-3}	1.627	1.488
θ range/°	3.28–25.00	4.01–22.53
μ/mm^{-1}	1.147	1.488
Reflections collected	2147	2174
Maximum, minimum transmission	0.959, 0.741	0.823, 0.743
Independent reflections	1842	1946
Parameters	154	186
$R1$ [$F > 4\sigma(F)$]	0.018	0.046
$wR2$ (all data)	0.053	0.116
Final difference peak and hole/e Å^{-3}	0.419, −0.485	1.422, −1.861

[a] Details in common: 153(2) K; Mo-Kα radiation (λ = 0.710 73 Å); monoclinic, space group $C2/c$; $wR1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$.[9] [b] Half a disordered toluene molecule is present in the asymmetric unit. This was included as a benzene molecule in the refinement because the methyl group could not be located.

Table 3 Atomic coordinates (× 10^4) for complex **1**

Atom	x	y	z
Te(1)	−5000	8649(1)	7500
N(1)	−3088(3)	8121(1)	7308(2)
C(11)	−3485(4)	7860(1)	6104(3)
C(12)	−2279(4)	7745(1)	8328(3)
Te(2)	0	8851(1)	7500
N(2)	−2101(3)	9379(1)	7312(2)
C(21)	−2909(4)	9643(1)	6110(3)
C(22)	−1892(4)	9755(1)	8326(3)
C(1)	−4878(22)	6263(5)	8723(8)
C(2)	−6773(24)	6267(5)	8371(12)
C(3)	−7838(11)	6232(4)	7121(16)
C(4)	−7008(22)	6193(5)	6223(7)
C(5)	−5113(24)	6190(5)	6575(14)
C(6)	−4048(11)	6224(4)	7825(17)
C(1′)	−5770(25)	6297(5)	8768(7)
C(2′)	−7478(16)	6254(4)	7849(16)
C(3′)	−7619(15)	6219(5)	6607(12)
C(4′)	−6051(27)	6228(5)	6284(8)
C(5′)	−4342(18)	6272(4)	7202(17)
C(6′)	−4204(14)	6306(5)	8444(13)

Table 4 Atomic coordinates (× 10^4) for complex 2

Atom	x	y	z
Te	0	533(1)	2500
S(1)	565(2)	1437(1)	3600(1)
C(1)	−701(6)	1896(5)	4096(4)
C(10)	−1071(6)	2803(5)	3749(4)
C(11)	−1253(9)	2903(6)	2962(5)
C(12)	−1640(9)	3715(6)	2639(5)
C(13)	−1827(7)	4446(6)	3093(5)
C(14)	−1663(7)	4338(5)	3878(5)
C(15)	−1288(6)	3523(5)	4208(4)
C(20)	−1664(6)	1212(5)	4040(4)
C(21)	−1455(7)	319(5)	4277(4)
C(22)	−2324(7)	−297(5)	4282(4)
C(23)	−3443(7)	−46(6)	4039(5)
C(24)	−3662(6)	815(5)	3777(5)
C(25)	−2784(6)	1443(5)	3784(4)
C(30)	−131(6)	2019(5)	4930(4)
C(31)	849(6)	2563(5)	5065(4)
C(32)	1356(7)	2739(5)	5804(5)
C(33)	903(7)	2358(5)	6435(4)
C(34)	−54(7)	1823(5)	6310(4)
C(35)	−556(6)	1645(5)	5577(4)

X-Ray crystallography

Crystals of complexes **1** and **2** were mounted directly from solution at room temperature under Ar using a perfluorocarbon oil which protects them from atmospheric moisture and oxygen (Riedel-de Haën). The oil 'freezes' at reduced temperatures and holds the crystal static in the X-ray beam.[7] Data were collected on a Stoe AED diffractometer, and a semiempirical absorption correction based on ψ scans was employed. The structures were solved by direct methods (SHELXTL PLUS)[8] and refined by full-matrix least squares on F^2 (SHELXL 93),[9] hydrogen atoms were fixed geometrically. Details of the structure solutions and refinements are listed in Table 2, while final atomic coordinates are presented in Tables 3 and 4.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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