Synthesis, structure and reactions of the first tellurium-containing macrocyclic Schiff base

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The condensation of bis(2-formylphenyl) telluride **1** with ethane-1,2-diamine yielded the novel macrocyclic tellurium ligand **2** *via* metal-free dimerisation. Crystals of **2** are triclinic, space group $P\bar{1}$ with $a = 7.956(3)$, $b = 9.885(2)$, $c = 10.068(2)$ Å, $Z = 1$. Hydrogenation of macrocycle **2** provided the corresponding saturated tetraazamacrocycle **3**, protonation of which with HBr afforded **4**. The co-ordination chemistry of **2** has been studied with 'soft' metal ions such as palladium(II) and mercury(II). *N*,*N'*-Bis[(2-chlorotelluranyl)benzylidene]ethane-1,2-diamine has also been characterised by an X-ray diffraction study, with triclinic space group $P\bar{1}$, $a = 7.71(1)$, $b = 7.90(1)$, $c = 8.52(1)$ Å and $Z = 1$.

Supramolecular chemistry, which involves the design and synthesis of polytopic macrocyclic and macrobicyclic ligands containing several recognition sites, is a promising area of considerable current interest. Recently there have been extensive studies on the synthesis and ligating behaviour of macrocyclic Schiff bases containing phenol, pyridine, pyrrole, furan and thiophene units.[1] Very recently the first example of a Schiff-base macrocycle containing a pyridazine unit has been reported.[2]

Most of the work in this area has focussed on the design and synthesis of receptors which are selective for 'hard' metal ions. Recently Beer *et al.*[3] have described the synthesis of several polyazamacrocyclic complexes which incorporate both 'hard' and 'soft' metal ions and contain multiple metallocene redox-active groups. Interest in macrocycles which contain 'hard' and 'soft' donor atoms to complex both 'hard' and 'soft' metal cations derives from their intrinsic potential for (*i*) modulation of the redox properties of a complexed 'soft' transition-metal cation upon co-complexation of a 'hard' cation, (*ii*) allosteric effects and (*iii*) bimetallic activation and catalysis.[4]

Although a few examples of polyazamacrocycles containing 'soft' sulfur[5] or phosphorus[6] and 'hard' nitrogen donor atoms are known, to our knowledge neither selenium nor tellurium has been incorporated into a macrocyclic Schiff base. Some homoleptic selenoether macrocycles, however, have been reported.[7] We report here an easy high yield synthesis, structure and co-ordination of a novel tellurium-containing azamacrocycle (see Scheme 1).

Experimental

Materials and methods

Bis(2-formylphenyl) telluride[8] and [PdCl₂(NCC₆H₅)][9] were prepared by reported procedures. Air-sensitive reactions were carried out under an inert atmosphere. Solvents were purified by standard techniques and were freshly distilled prior to use. Ethane-1,2-diamine (en) (SISCO) was reagent grade and was distilled prior to use. Melting points were recorded in capillary tubes on a Ketan melting point apparatus and are uncorrected. Proton (299.94 MHz), ^{13}C (75.42 MHz) and ^{125}Te (94.75 MHz) NMR spectra were recorded on a Varian VXR 300S spectrometer. Chemical shifts are cited with respect to SiMe₄ as internal standard (^{1}H and ^{13}C) and Te(S₂CNEt₂)₂ as external standard (^{125}Te). Elemental analyses were performed on a Carlo-Erba model 1106 elemental analyser. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 681

spectrometer and as polyethylene pellets on a Bruker IFS 66V FT-IR spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer data system using xenon (6 kV) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. Values are given for the most intense peaks.

Syntheses

Schiff base 2. A solution of bis(2-formylphenyl) telluride **1** (0.2 g, 0.5 mmol) in acetonitrile (100 cm³) was added to a stirred solution of ethane-1,2-diamine (0.5 mmol) in MeCN (100 cm³) over a period of 1 h. The mixture was stirred for 5 h and the precipitated pale yellow powder was filtered off, washed with MeCN and recrystallised from CHCl₃–MeCN (1:1). Yield 0.17 g, 80%, m.p. 255 °C (Found: C, 52.6; H, 3.85; N, 7.55. C₃₂H₂₈N₄Te₂ requires C, 53.10; H, 3.90; N, 7.75%). IR(KBr): $\tilde{v}_{max}$/cm⁻¹ 1647m, 1631s (C=N). NMR (CDCl₃): δ_H 8.6 (s, 4 H, azomethine H), 7.73–7.04 (m, 16 H, aromatic H), 3.82 (br s, 8 H, CH₂); δ_C 165.85 (azomethine C), 138.09, 137.68, 130.79, 129.81, 127.35, 125.82 (aromatic C), 61.29 (CH₂); δ_{Te} −226.5. Mass spectrum (EI): m/z 728 (M^+ for ^{130}Te).

Protonated Schiff base 3. A suspension of compound **2** (0.3 g, 0.4 mmol) in methanol (50 cm³) was cooled to 0 °C. To this, solid NaBH₄ (excess) was added in small portions and the reaction mixture was stirred for 3 h. Methanol was removed under reduced pressure. To the residue water (50 cm³) was added and the product extracted with dichloromethane. Removal of the solvent and recrystallisation of the residue from CHCl₃–MeCN (1:1) afforded colourless needles of **3** (0.25 g, 83%), m.p. 205–207 °C (Found: C, 52.80; H, 4.9; N, 8.15. C₃₂H₃₆N₄Te₂ requires C, 52.50; H, 4.95; N, 7.65%). IR(KBr): $\tilde{v}_{max}$/cm⁻¹ 3309w, 3212m (NH stretching), 1618s (NH bending). NMR (CDCl₃): δ_H 7.6–6.94 (m, 16 H, aromatic H), 3.9 (s, 8 H, C₆H₄CH_2NH), 2.6 (s, 8 H, NHCH_2), 1.6 (s, NH + H₂O); δ_C 144.28, 138.46, 128.43, 127.37, 126.43, 126.04 (aromatic C), 57.69 (C₆H₄CH_2NH), 48.3 (NHCH_2CH_2); δ_{Te} −312.1. Mass spectrum (EI): m/z 732 (M^+ for ^{128}Te).

Hydrobromide salt of compound 3, 4. The crude reduced Schiff base **3** (0.165 g, 0.23 mmol) was treated with HBr (48%, 5 cm³) and ethanol (50 cm³). The precipitated salt **4** was filtered off, washed with ethanol followed by diethyl ether and recrystallised from water–ethanol (1:1) as colourless crystals (0.2 g, 84%), m.p. 230 °C (decomp.) (Found: C, 35.20; H, 4.20;
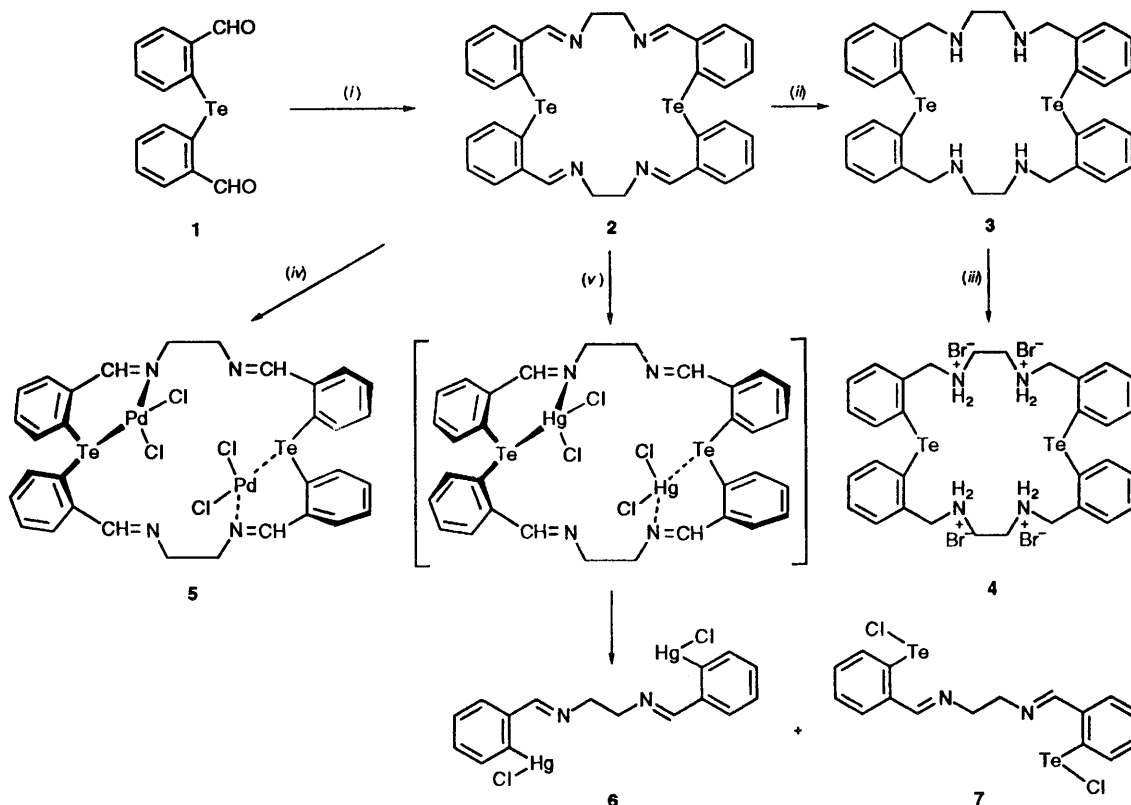
Scheme 1 (*i*) $NH_2CH_2CH_2NH_2$, MeCN, room temperature; (*ii*) $NaBH_4$, MeOH, 0 °C; (*iii*) 48% HBr, EtOH; (*iv*) [$PdCl_2(NCC_6H_5)_2$] (2 molar excess), CH_2Cl_2; (*v*) $HgCl_2$, $CHCl_3$, Me_2CO

N, 5.10. $C_{32}H_{36}N_4Te_2 \cdot 4HBr \cdot 2H_2O$ requires C, 35.20; H, 4.05; N, 5.15%). NMR [$(CD_3)_2SO$]: δ_H 9.37 (s, 8 H, NH_2^+), 7.2–7.0 (m, 16 H, aromatic H), 4.57 (s, 4 H, $C_6H_4CH_2NH_2$), 3.8 (s, 8 H, CH_2NH_2); δ_C 141.25, 136.68, 130.76, 127.91, 123.39 (aromatic C), 55.65 [$CH_2(C_6H_4)NH_2^+$], 42.9 [$CH_2(NH_2)CH_2$]; δ_{Te} −301.

Reaction of compound 2 with [$PdCl_2(NCC_6H_5)$]. To a dichloromethane solution of compound **2** (0.15 g, 0.2 mmol), [$PdCl_2(NCC_6H_5)$] (0.1588 g, 0.4 mmol) in dichloromethane was added dropwise and stirred for 0.5 h. The precipitated yellow product (**5**) was filtered off, washed with dichloromethane and dried. Yield 0.21 g, 94%, m.p. 212 °C (decomp.) (Found: C, 33.65; H, 2.95; N, 5.05. $C_{32}H_{28}Cl_4N_4Pd_2Te_2 \cdot 3H_2O$ requires C, 33.95; H, 3.05; N, 4.95%). IR(KBr): $\tilde{v}_{max}/cm^{-1}$ (polyethylene) 1633.6s (C=N), 441.8s, 392.5m, 343.4m, 319.9vs, 282.8m, 236s. NMR [$(CD_3)_2SO$]: δ_H 9.18 (s, 2 H, azomethine H), 9.06 (s, 2 H, azomethine H), 8.05–7.03 (m, 16 H, aromatic H), 4.49, 4.45 (d, 2 H, CH_2), 4.23, 4.2, 4.16 (m, 4 H, CH_2), 3.91, 3.88 (d, 2 H, CH_2); δ_C 170.09, 163.04 (co-ordinated and unco-ordinated azomethine C), 138.63, 138, 136.58, 135.52, 135.44, 133.37, 132.98, 131.82, 130.58, 120.59, 119.44 (aromatic C), 63.73, 57.86 (CH_2); δ_{Te} −77.5. Mass spectrum: m/z 867 (**2** + PdCl, 100%), 832 (**2** + Pd, 80%). Conductivity (Λ_M) 46 S cm^2 mol^{-1}.

Reaction of compound 2 with $HgCl_2$. Mercury(II) chloride (0.11 g, 0.04 mmol) in acetone (2 cm^3) was added to a solution of compound **2** (0.15 g, 0.02 mmol) in chloroform (20 cm^3). The mixture was stirred for 0.5 h. The resulting yellow precipitate was filtered off and dried *in vacuo*. An additional amount of precipitate was obtained by the addition of hexane (20 cm^3) to the filtrate. The combined product was recrystallised from acetonitrile. The white powdery product which precipitated first was characterised as **6** and the yellowish crystalline precipitate obtained from the filtrate on standing was characterised as **7**. Compound **6** (0.06 g, 41%), m.p. 254 °C (Found: C, 27.2; H, 1.80; N, 4.25. $C_{16}H_{14}Cl_2Hg_2N_2$ requires C,

27.20; H, 2.00; N, 3.95%). IR(KBr): $\tilde{v}_{max}/cm^{-1}$ 1643vs (C=N). NMR [$(CD_3)_2SO$]: δ_H 8.6 (s, 2 H, azomethine H), 7.5–7.2 (m, 8 H, aromatic H), 4.2 (s, 4 H, CH_2); δ_C 165.5 (azomethine C), 147.9, 139.7, 137.92, 132.9, 132.4, 128.7 (aromatic C), 59.63 (CH_2). Compound **7** (0.07 g, 60%), m.p. 270 °C (lit.,[10] 288–290 °C) (Found: C, 34.65; H, 2.45; N, 5.1. $C_{16}H_{14}Cl_2N_2Te_2$ requires C, 34.30; H, 2.50; N, 5.0%). IR(KBr): $\tilde{v}_{max}/cm^{-1}$ 1581m (C=N). NMR [$(CD_3)_2SO$]: δ_H 9.75 (s, 2 H, azomethine H), 8.44–7.5 (m, 8 H, aromatic H), 4.61 (s, 4 H, CH_2); δ_C 167.53 (azomethine C), 141.2, 135.9, 133.4, 132.7, 131.95, 127.07 (aromatic C), 57.18 (CH_2); δ_{Te} 498.7.

Crystal-structure determination of compounds 2 and 7

Diffraction quality single crystals of compound **2** were obtained by allowing a saturated chloroform–acetonitrile (1 : 1) solution to evaporate slowly at room temperature. Yellow crystals of compound **7** were obtained by slow evaporation of the filtrate obtained from the reaction of compound **2** with $HgCl_2$.

Data collection, structure solution and refinement. All diffraction measurements were performed at room temperature (295 K) on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å) employing the ω–2θ scan technique. The unit cell was determined from 25 randomly selected reflections using the automatic search, index and least-squares routines. The data were corrected for Lorentz and polarisation effects. An empirical absorption correction was applied to the data by measuring the intensities of eight reflections with χ near 90° for different ψ values (0 < ψ < 360°, every 10°) and using the EAC program from the Enraf-Nonius Package.[11] The maximum and minimum transmission factors are 0.99 and 0.78 for **2** and 0.99 and 0.82 for **7** respectively. The structure was solved by the routine heavy-atom method (using SHELXS 86)[12] and Fourier methods and refined by full-matrix least squares with the non-hydrogen atoms anisotropic and the hydrogen atoms (located from the difference map) with the fixed isotropic thermal parameters of 0.07 Å^2 using the SHELX 76 program.[13] The

Table 1 Crystal data and refinement datails for compounds **2** and **7**

	2	**7**
Formula	$C_{32}H_{28}N_4Te_2$	$C_{16}H_{14}Cl_2N_2Te_2$
M	724.05	560.24
Crystal, habit	Pale yellow, needles	Yellow, needles
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a/\text{Å}$	7.956(3)	7.71(1)
$b/\text{Å}$	9.885(2)	7.90(1)
$c/\text{Å}$	10.068(2)	8.52(1)
$\alpha/°$	102.88(2)	67.34(7)
$\beta/°$	96.99(2)	68.10(8)
$\gamma/°$	107.95(2)	88.56(9)
$U/\text{Å}^3$	718.71	439.81
Z	1	1
$D_c/\text{g cm}^{-3}$	1.67	2.11
$F(000)$	352	262
μ/cm^{-1}	19.1	35.86
θ Limit/°	$2 < \theta < 25$	$2 < \theta < 25$
Total no. of reflections collected	2681	1669
No. of reflections with $I > 3\sigma(I)$	2333	1542 [with $I > 2.5\sigma(I)$]
No. of parameters refined	214	100
R	0.052	0.054
R'	0.071	0.072
Residual $\rho_{max}/\text{e Å}^{-3}$	2.1	1.8
(near tellurium/Å)	≈ 0.99	0.97
Maximum (Δ/σ)	0.4	0.8

weighting scheme employed was of the form $w = K/[\sigma^2(F_o) + g(F_o)^2]$ where K and g refined to 1.00 and 0.0054 at convergence for **2** and 3.03 and 0.0014 for **7** respectively.

The scattering factors for tellurium (corrected for f' and f'') were taken from ref. 14, while those for the remaining atoms were as incorporated in the SHELX 76 program. All calculations were carried out on an ND-500 computer. The relevent crystal data along with the refinement details are given in Table 1.

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.

Results and Discussion

The tellurium macrocycle **2** was easily isolated *via* simple condensation of bis(2-formylphenyl) telluride (**1**) and ethane-1,2-diamine without recourse to metal-ion template or high dilution reaction (Scheme 1). Secondary intramolecular Te · · · N co-ordination (see below) plays an important role in the formation of the macrocycle by reducing the unfavourable lone pair–lone pair interaction between nitrogen atoms in the ring. The yield of the reaction was found to be highly dependent on the purity of the solvent. The ligand is fairly soluble in $CHCl_3$ and CH_2Cl_2 but insoluble in polar solvents such as MeOH and $(CH_3)_2SO$; it could be recrystallised from $CHCl_3$–MeCN (1:1). Reduction of compound **2** was attempted to generate the tetramine derivative **3**, which would be superior to its Schiff-base parent in chemical stability and flexibility. Reduction with $LiAlH_4$ was unsuccessful and the reduction with $NaBH_4$ in ethanol gave many products (by TLC). However, reduction with $NaBH_4$ in methanol at 0 °C afforded **3** in better yield. The colourless needles of **3** were obtained by slow evaporation of a $CHCl_3$–MeCN solution. The protonated derivative **4** was obtained in very good yield by treatment of **3** with 48% hydrobromic acid and was recrystallised from water–ethanol (1:1) as colourless needles.

These compounds were characterised by elemental analysis, IR, NMR (^{1}H, ^{13}C and ^{125}Te) and mass spectroscopic studies. The ν(C=N) vibrational frequency of the macrocycle **2** was observed at 1647 and 1631 cm^{-1} and its mass spectrum showed

an intense molecular ion peak at m/z 728 (for ^{128}Te). Both ^{1}H and ^{13}C NMR spectra of compounds **2**, **3** and **4** show resonances corresponding to one quarter of the molecule suggesting very symmetric structures for the macrocycles. Although all four nitrogen atoms are not equivalent (see below) in the solid state, the very symmetric NMR spectra are probably due to a fast (on the NMR time-scale) Te · · · N(1), Te · · · N(2) bond scrambling. This leads to a dynamic equilibrium between the two topomeric 10-Te-3* structures which apparently takes place *via* a 12-Te-4 tellurane intermediate as reported by Minkin *et al.*[15] This conclusion is further supported by the observation of a single signal in the ^{125}Te NMR spectrum of compound **2** at δ −226.5. In its ^{1}H NMR spectrum the CH_2 protons appear as a broad singlet. In the case of compound **3**, the disappearance of the ν(C=N) absorption in the IR and δ(CH=N) in the ^{1}H NMR spectra confirmed the reduction of the CH=N bond. The NH proton was observed at δ 1.6 together with the water peak of $CDCl_3$.

The addition of 2 equivalents of $[PdCl_2(NCC_6H_5)_2]$ to a dichloromethane solution of compound **2** resulted in immediate precipitation of a yellow powdery complex **5**, in almost quantitative yield. This was slightly soluble in dimethylformamide and completely soluble in Me_2SO. This complex was found to be a non-electrolyte in Me_2SO. The ^{1}H NMR spectrum of compound **5** showed two peaks in equal intensity for the azomethine protons and the ^{13}C spectrum also exhibited two signals each for the azomethine and the methylene carbons suggesting co-ordination through only two imine nitrogens. The ^{125}Te NMR spectrum exhibited a single signal in the deshielded region (δ −77.5) compared with that in the parent **2** (δ −226.5) confirming co-ordination of Te to Pd and the presence of identical environments around both tellurium atoms. Although the elemental analysis and NMR studies suggest the formation of the 2:1 complex **5**, unfortunately, the FAB mass spectrum did not show the corresponding molecular ion peak. The highest peaks corresponded to $[2 + PdCl]^+$ $\{m/z$ 867(100%)$\}$ and $[2 + Pd]^+$ $\{m/z$ 832$\}$ respectively, suggesting that the macrocycle is intact in the complex. In addition the spectrum clearly shows fragmentation peaks due to the loss of

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* The first number indicates the total electrons in the valence shell of Te, the second the atoms bonded to Te.

Table 2 Fractional atomic coordinates ($\times 10^4$) of non-hydrogen atoms of compound **2** with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Te(1)	1496(1)	3112(0)	4761(0)
C(1)	−627(8)	1471(6)	3200(6)
C(2)	−621(9)	1297(7)	1783(7)
C(3)	−2018(11)	232(9)	776(8)
C(4)	−3463(10)	−705(8)	1145(8)
C(5)	−3480(10)	−572(8)	2543(9)
C(6)	−2084(9)	527(7)	3575(7)
N(1)	−1026(8)	1645(6)	5996(6)
C(8)	−1063(10)	1648(8)	7438(8)
C(9)	3297(9)	3601(7)	3350(7)
C(10)	4624(10)	2946(8)	3370(8)
C(11)	5893(10)	3212(8)	2532(9)
C(12)	5895(9)	4140(8)	1725(8)
C(13)	4648(10)	4851(8)	1738(8)
C(14)	3354(8)	4598(6)	2538(6)
C(15)	1927(9)	5288(7)	2414(7)
N(2)	2066(8)	6263(6)	1786(6)
C(16)	581(10)	6822(8)	1645(8)

Table 3 Selected bond lengths (Å) and angles (°) for compound **2** with e.s.d.s in parentheses

Te(1)–C(1)	2.117(6)	C(9)–C(10)	1.398(10)
Te(1)–C(9)	2.163(7)	C(9)–C(14)	1.409(9)
C(1)–C(2)	1.400(9)	C(10)–C(11)	1.393(11)
C(1)–C(6)	1.398(9)	C(11)–C(12)	1.354(12)
C(2)–C(3)	1.379(10)	C(12)–C(13)	1.381(11)
C(3)–C(4)	1.385(12)	C(13)–C(14)	1.380(10)
C(4)–C(5)	1.387(12)	C(14)–C(15)	1.500(9)
C(5)–C(6)	1.401(10)	C(15)–N(2)	1.251(8)
C(6)–C(7)	1.470(10)	N(2)–C(16)	1.455(9)
C(7)–N(1)	1.250(9)	N(1)–C(8)	1.455(9)
C(8)–C(16)	1.488(12)		
Te(1)–C(1)–C(2)	121.7(5)	C(7)–N(1)–C(8)	119.5(6)
Te(1)–C(1)–C(6)	120.0(5)	C(9)–C(10)–C(11)	120.1(7)
C(1)–Te(1)–C(9)	94.6(2)	C(10)–C(9)–C(14)	118.4(6)
Te(1)–C(9)–C(10)	114.9(5)	C(9)–C(14)–C(13)	119.8(6)
Te(1)–C(9)–C(14)	126.5(5)	C(9)–C(14)–C(15)	121.3(6)
C(1)–C(2)–C(3)	121.2(7)	C(10)–C(11)–C(12)	120.7(7)
C(2)–C(1)–C(6)	118.3(6)	C(11)–C(12)–C(13)	120.2(7)
C(1)–C(6)–C(5)	120.0(5)	C(12)–C(13)–C(14)	120.8(7)
C(1)–C(6)–C(7)	121.6(5)	C(13)–C(14)–C(15)	118.7(6)
C(2)–C(3)–C(4)	120.6(7)	C(14)–C(15)–N(2)	120.9(6)
C(3)–C(4)–C(5)	119.2(6)	C(4)–C(5)–C(6)	120.6(7)
C(5)–C(6)–C(7)	118.3(6)	C(6)–C(7)–N(1)	120.7(6)
N(1)–C(8)–C(16)	111.6(5)		

groups from the macrocyclic framework. Attempts to obtain suitable single crystals of the complex for X-ray crystallography were frustrated by its poor solubility in most solvents and instability in solvents such as Me_2SO.
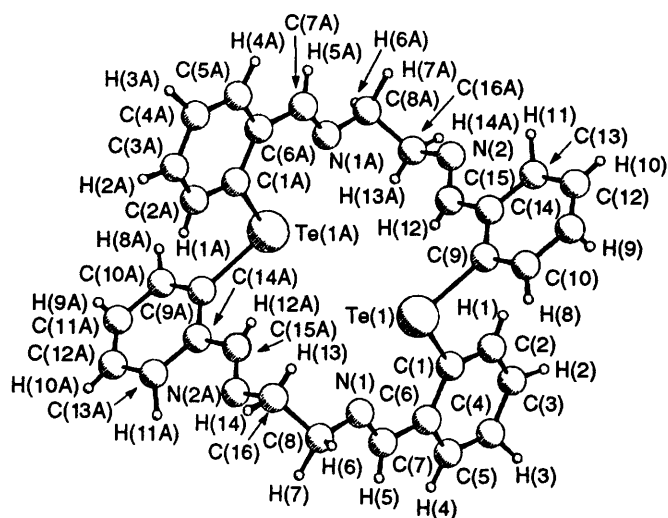
The complexation behaviour of compound **2** was further studied with another 'soft' Lewis acid, $HgCl_2$. Stirring **2** at room temperature in chloroform with 2 equivalents of $HgCl_2$ in acetone led to a facile ring cleavage affording a yellow precipitate. Recrystallisation of the crude product from acetonitrile gave a white flaky material which was characterised as the bis(organomercury) Lewis acid **6**, and more soluble yellow crystals of the bis(organotellurenyl chloride) **7**[10] were obtained from the mother-liquor. The interesting dismutation reaction probably proceeds through the formation of a weakly associated addition complex followed by the migration of groups. A similar observation has been made by Mbogo and co-workers,[16] where the reaction of (p-ethoxyphenyl)[2-(2-pyridyl)phenyl]tellurium with $HgCl_2$ leads to 'reverse transmetallation', however, the cleavage products were isolated as a complex salt. These two compounds were characterised by elemental analysis, IR and NMR spectroscopy. The very low C=N stretching frequency (1581 cm^{-1}) displayed by compound **7** and the deshielded azomethine resonance at δ 9.75 indicated a strong Te $\cdots$ N interaction (see below). The ^{125}Te NMR spectrum exhibited a single resonance at δ 498.7 in the deshielded region compared to that of **2**. In **6** the weak Hg $\cdots$ N co-ordination, as indicated by IR and ^{1}H NMR spectroscopy, is comparable to that of the Te $\cdots$ N interaction observed in **2**.

Crystal structure of compound 2

The molecular structure of **2** with atom numbering is presented in Fig. 1,[17] the positional parameters in Table 2 and selected bond lengths and angles in Table 3. The crystal structure consists of discrete molecules of **2** and the unit cell contains one macrocyclic molecule. The structure confirms the 2 + 2 dipodal condensation of bis(2-formylphenyl) telluride and ethane-1,2-diamine and the formation of the novel 22-membered heterocycle. The molecule lies across a crystallographic inversion centre and therefore has an imposed C_i symmetry. Two opposite aromatic rings in the macrocycle are coplanar. The Te(1)–C(1) distance, 2.117(6) Å, is in excellent agreement with the sum of the Pauling single bond covalent radii for tellurium (1.37 Å) and the sp^2-hybridised carbon (0.74 Å).[18] However, the Te(1)–C(9) bond is slightly longer (0.05 Å) than the sum of the relevant covalent radii, although comparable bond lengths have been observed for bis[2-(4-

Fig. 1 Molecular structure of compound **2**

methoxyphenyl)iminomethylphenyl] telluride [2.128(4) and 2.162(4) Å] and bis(2-isopropyliminomethylphenyl) telluride [2.125(2) and 2.163(2) Å].[15] The Te(1) $\cdots$ N(1) distance of 2.701(6) Å is shorter than that in 1,6-bis(o-butyltelluranylphenyl)-2,5-diazahexa-1,5-diene (2.773 Å)[19] and close to that in bis[2-(4-methoxyphenyl)iminomethylphenyl)] telluride [2.702(3) Å].[15] Although there is an equal chance of N(1) or N(2) co-ordinating to the Te(1) atom, the N(2) atom is not co-ordinated to Te(1) and lies 0.49 Å below the C(1)–Te(1)–C(9) mean plane with the Te(1) $\cdots$ N(2) distance being 4.74 Å. Thus the solid-state geometry of the molecule indicates the presence of only one attractive interaction per tellurium atom, i.e. it corresponds to the structure of 10-Te-3 tellurane. The bond configuration at the tellurium atom is T-shaped with the transannular Te $\cdots$ Te distance (4.979 Å) longer than the sum of the van der Waals radii (4.4 Å). That the tellurium macrocycle is puckered is inferred from the C(1)–Te(1)–C(9)–C(10) torsion angle [100.5(4)°]. This is further confirmed from the interplanar angle between the two phenyl rings bonded to the same tellurium atom which measures 99°. Atom Te(1A) lies 4.76 Å away from the mean plane through Te(1)–C(1)–C(9).
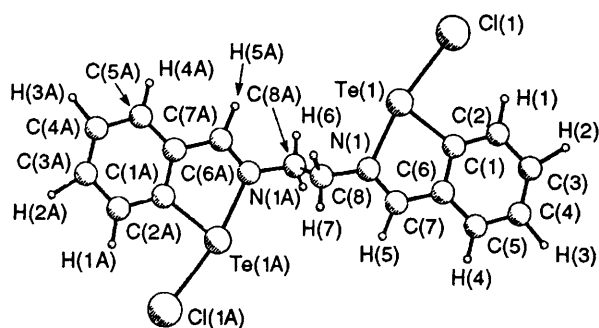
Fig. 2 Molecular structure of compound **7**

Table 4 Fractional atomic coordinates ($\times 10^4$) for non-hydrogen atoms of compound **7** with e.s.d.s in parentheses

Atom	x	y	z
Te(1)	2028(1)	1159(1)	298(1)
Cl(1)	2539(4)	2024(4)	−3126(3)
N(1)	2256(10)	658(8)	2918(8)
C(1)	4677(10)	2564(10)	−553(9)
C(2)	5932(12)	3577(11)	−2369(10)
C(3)	7672(12)	4426(12)	−2688(12)
C(4)	8200(12)	4269(12)	−1267(13)
C(5)	6953(13)	3280(12)	530(12)
C(6)	5189(11)	2456(10)	889(10)
C(7)	3821(12)	1395(10)	2725(10)
C(8)	834(11)	−512(11)	4722(9)

Table 5 Selected bond lengths (Å) and angles (°) for compound **7** with e.s.d.s in parentheses

Te(1)–C(1)	2.079(8)	Te(1)–Cl(1)	2.597(3)
Te(1) ⋯ N(1)	2.185(8)	C(1)–C(2)	1.392(8)
C(1)–C(6)	1.396(13)	C(2)–C(3)	1.398(14)
C(3)–C(4)	1.377(17)	C(4)–C(5)	1.377(10)
C(5)–C(6)	1.396(13)	C(6)–C(7)	1.437(8)
C(7)–N(1)	1.279(12)	C(8)–N(1)	1.455(7)
Cl(1)–Te(1) ⋯ N(1)	167.4(2)	C(1)–Te(1)–Cl(1)	90.5(2)
C(1)–Te(1)–N(1)	77.2(3)	C(7)–N(1)–C(8)	122.3(8)
C(6)–C(7)–N(1)	118.8(8)	C(7)–C(6)–C(1)	115.6(8)
C(6)–C(1)–Te(1)	114.6(4)	C(6)–C(1)–C(2)	118.7(8)
C(1)–C(2)–C(3)	119.0(9)	C(2)–C(3)–C(4)	122.2(7)
C(3)–C(4)–C(5)	118.8(9)	C(4)–C(5)–C(6)	120.1(10)
C(5)–C(6)–C(7)	123.3(9)		

Crystal structure of compound 7

The molecular structure of **7** with atom numbering is shown in Fig. 2, the positional parameters in Table 4 and selected bond lengths and angles in Table 5. It is centrosymmetric and like the parent macrocycle **2**, only half the molecule represents the asymmetric unit and has only one molecule per unit cell. The most characteristic feature of the molecule is a very strong attractive intramolecular N ⋯ Te interaction, with the distance between these two atoms being one of the shortest [2.185(8) Å] reported in the literature.[20] This is, however, slightly higher than the sum of the Pauling's covalent radii for tellurium and nitrogen (2.07 Å).[18] Owing to this interaction the molecule has a T-form configuration of bonds at the tellurium atom, which is typical for 10-Te-3 tellurane. The angle N ⋯ Te–Cl is 167.4(2)° and as in the analogous compounds studied earlier,[21] is less than the ideal value of 180°. This arises from the steric influence of the unshared electron pair, occupying an equatorial position in the trigonal-bipyramidal environment of the tellurium atom. The tellurium atom lies 0.058(4) Å above the plane containing the N(1), C(1) and Cl(1) atoms. The five-membered ring is almost planar as evident from the sum of the endocyclic torsional angles. The Te(1)–C(1) distance of 2.079(8) Å is less than the sum of the Pauling covalent radii and can be compared to that of 2-[(4-tolyliminomethyl)phenyl]tellurium

acetate [2.087(7) Å].[15] The Te(1)–Cl(1) distance of 2.597(3) Å is significantly longer than the sum of the single bond covalent radii (2.36 Å), but is comparable with axial Te–Cl bonds in other trigonal-bipyramidal structures.[15]

Acknowledgements

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