Synthesis and properties of the first series of mixed thioether/telluroether macrocycles

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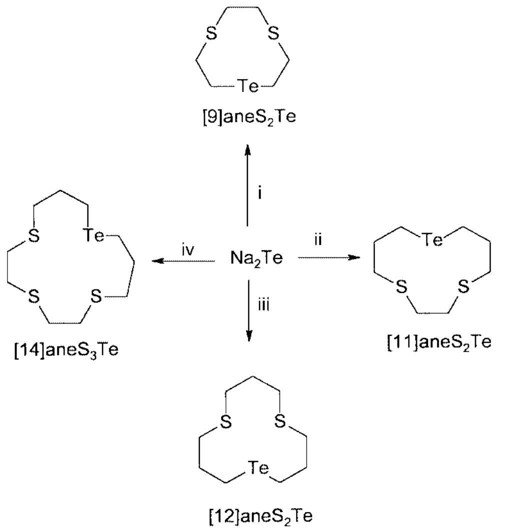
The preparations of the first examples of mixed thioether/telluroether macrocycles, [9]aneS_2Te (1,4-dithia-7-telluracyclononane), [11]aneS_2Te (1,4-dithia-8-telluracycloundecane), [12]aneS_2Te (1,5-dithia-9-telluracyclododecane) and [14]aneS_3Te (1,4,7-trithia-11-telluracyclotetradecane) *via* a 'disguised dilution' method are described, together with the crystal structure of [Ag([11]aneS_2Te)]BF_4 which serves to authenticate the macrocyclic ligand.

In recent years thioether macrocycles have attracted considerable interest in the chemical community. A variety of ring sizes and denticities have been prepared and their metal ion chemistry studied, yielding a diverse range of structures and unexpected electronic and redox responses.[1] The tridentate [9]aneS_3 probably displays the most interesting chemistry, facilitating the stabilisation of a range of unusual oxidation states, including mononuclear Pd(III), Rh(II) and Au(II).[1] We have been conducting comparative studies of the ligating characteristics of acyclic bi- and tri-dentate thio-, seleno- and telluro-ethers to a variety of d- and p-block metal centres and have shown that to low-valent metal centres E→M donation increases in the order $S < Se << Te$.[2] Incorporation of telluroether functions in a macrocyclic environment is expected to significantly enhance their bonding to metal centres and should lead to rich new chemistry. However, while several macrocyclic selenoethers are now known, telluroether crowns are extremely rare[3] and indeed only a handful of multidentate telluroethers have been synthesised.[4] This really reflects the synthetic difficulties which need to be overcome. Thus, since Te–H and Te–C bonds are considerably weaker than those in their lighter Group 16 analogues, the methods used to prepare thioether and selenoether macrocycles are not usually suited to telluroether derivatives. We have therefore begun to develop new synthetic routes to macrocyclic telluroethers and report here the preparations of four new mixed S/Te-donor macrocycles involving different ring sizes and denticities, including [9]aneS_2Te, the direct analogue of [9]aneS_3. The successful incorporation of dimethylene linkages between the S and Te centres is significant since the ditelluroethers $RTe(CH_2)_2TeR$ cannot be isolated, instead undergoing facile elimination of ethene and forming ditellurides.[4] The combination of both S and Te functions within a macrocyclic configuration will permit a direct comparison of their ligating properties to transition metal guests. Silver(I) complexes of the new ligands are also described, together with the crystal structure of [Ag([11]aneS_2Te)]BF_4 which serves to authenticate the macrocyclic ligand.

The synthetic method used for the macrocycles is depicted in Scheme 1.† In a typical preparation a freshly prepared sample of Na_2Te in liquid NH_3 was taken to −78 °C and a THF solution of the appropriate α,ω-dichlorothioalkane species was added dropwise over *ca.* 30 min. Evaporation of the NH_3 followed by subsequent hydrolysis and extraction with CH_2Cl_2 yielded a red oil. The macrocyclic ligands are obtained as light yellow, poorly soluble solids in moderate yields (20–30%) following purification by flash chromatography on silica using ethyl acetate : hexane 1 : 3 or, in the case of [9]aneS_2Te, by recrystallisation from CH_2Cl_2–MeOH. NMR spectroscopic studies and microanalyses are entirely consistent with the formulations, while mass spectrometry confirms the products as [1+1] cyclisation species, showing envelopes of peaks with the correct isotopic distributions associated with the parent ion, together with peaks at lower *m*/*z* consistent with fragments arising from Te–C and S–C bond cleavage. There is no evidence from FAB mass spectrometry for higher macrocycles even in the crude reaction products.



Scheme 1 *Reagents and conditions*: i, $Cl(CH_2)_2S(CH_2)_2S(CH_2)_2Cl$, THF/$NH_3$(liq); ii, $Cl(CH_2)_3S(CH_2)_2S(CH_2)_3Cl$, THF/$NH_3$(liq); iii, $Cl(CH_2)_3S(CH_2)_3S(CH_2)_3Cl$, THF/$NH_3$(liq); iv, $Cl(CH_2)_3S(CH_2)_2S(CH_2)_2S(CH_2)_3Cl$, THF/$NH_3$(liq); $T = -78$ °C, reagents added dropwise over 30 min.

The macrocycles (L) react readily with one mol. equiv. of $Ag[CF_3SO_3]$ in CH_2Cl_2 at r.t. for one hour to yield light yellow, very poorly soluble, powdered species of formula $[AgL][CF_3SO_3]$. Electrospray mass spectrometry (MeCN) shows major peaks associated with $[AgL]^+$ for all four complexes (as well as $[AgL_2]^+$ for L = [9]aneS_2Te, [11]aneS_2Te and [12]aneS_2Te). Crystals of the analogous tetrafluoroborate salt, [Ag([11]aneS_2Te)]BF_4, were obtained from $MeNO_2$–MeOH–Et_2O solution and a crystal structure‡ of this species established unequivocally the macrocyclic configuration. The cation assumes a one-dimensional polymeric structure [Fig. 1(a) and 1(b)] in which Ag centres are bridged by [11]aneS_2Te ligands, with a silver(I) ion coordinated to each macrocyclic donor atom. The Ag(I) ions adopt a distorted trigonal planar coordination environment. The Ag–Te bond distance [2.674(1) Å] is slightly shorter than those observed in $[Ag\{MeTe(CH_2)_3TeMe\}_2]BF_4$ [d(Ag–Te) = 2.785(2)–2.837(2) Å],[5] while the Ag–S distances [2.521(3), 2.634(3) Å] are comparable to those observed for $[Ag\{PhS(CH_2)_3SPh\}_2]BF_4$ [d(Ag–S) = 2.573(3)–2.623(3) Å][6] (both of which also adopt infinite structures).

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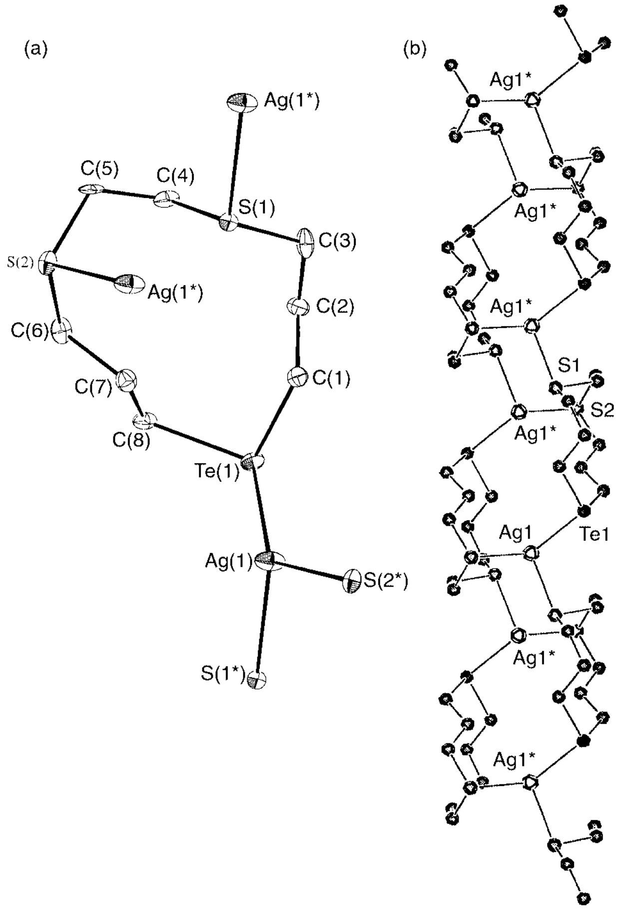

Fig. 1 (*a*) View of the asymmetric unit of $[Ag([11]aneS_2Te)]^+$, together with nearest symmetry-related atoms. H atoms are omitted for clarity and ellipsoids are shown at the 40% probability level. Selected bond lengths (Å) and angles (°): Ag(1)–S(1*) 2.634(3), Ag(1)–S(2*) 2.521(3), Ag(1)–Te(1) 2.674(1); S(1*)–Ag(1)–S(2*) 106.7(1), S(1*)–Ag(1)–Te(1) 107.46(7), S(2*)–Ag(1)–Te(1) 135.67(9). (b) View of a portion of the one-dimensional lattice adopted by $[Ag([11]aneS_2Te)]BF_4$.

Studies on the coordination chemistry and associated reaction chemistry of these and other related macrocycles are in progress.

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Notes and references

† Satisfactory analytical data were obtained for all new compounds. *Selected spectroscopic data*: for **[9]aneS₂Te**: ^1H NMR: δ 2.84 (s, 4H, SCH_2CH_2S), 2.93 (t, 4H, $SC\mathit{H}_2CH_2Te$), 3.06 (t, 4H, $TeCH_2$). $^{13}C\{^1H\}$ NMR: δ 38.9 (CH_2S), 32.9 (CH_2S), 2.9 (CH_2Te). $^{125}Te\{^1H\}$ NMR: δ 345. FAB-MS: *m/z* 278, 204; calc. for $[C_6H_{12}S_2{}^{130}Te]^+$ 278, $[C_3H_6S^{130}Te]^+$ 204. For **[11]aneS₂Te**: ^1H NMR: δ 2.74 (s, 4H, SCH_2CH_2S), 2.73 (t, 4H, $SC\mathit{H}_2CH_2CH_2Te$), 2.67 (t, 4H, $TeCH_2$), 2.05 (*q*, 4H, $CH_2C\mathit{H}_2CH_2$). $^{13}C\{^1H\}$ NMR: δ 34.7 ($CH_2\mathit{C}H_2CH_2$), 32.9 (CH_2S), 32.6 (CH_2S), 2.2 (CH_2Te). $^{125}Te\{^1H\}$ NMR: δ 234. FAB-MS: *m/z* 306, 204; calc. for $[C_8H_{16}S_2{}^{130}Te]^+$ 306, $[C_3H_6S^{130}Te]^+$ 204. For **[12]aneS₂Te**: ^1H NMR: δ 2.78 (t, 4H, SCH_2), 2.73 (t, 4H, SCH_2), 2.66 (t, 4H, $TeCH_2$), 2.06 (q, 4H, $SCH_2C\mathit{H}_2CH_2Te$), 1.86 (q, 2H, $SCH_2C\mathit{H}_2CH_2S$). $^{13}C\{^1H\}$ NMR: δ 33.5 ($SCH_2\mathit{C}H_2CH_2Te$), 30.1 (CH_2S), 29.0 (CH_2S), 27.7 ($SCH_2\mathit{C}H_2CH_2S$), 1.0 (CH_2Te). $^{125}Te\{^1H\}$ NMR: δ 217. FAB-MS: *m/z* 320, 246, 204; calc. for $[C_9H_{18}S_2{}^{130}Te]^+$ 320, $[C_6H_{12}S^{130}Te]^+$ 246, $[C_3H_6S^{130}Te]^+$ 204. For **[14]aneS₃Te**: ^1H NMR: δ 2.78 (m, 8H, SCH_2), 2.73 (t, 4H, SCH_2), 2.62 (t, 4H, $TeCH_2$), 2.09 (q, 4H, $CH_2C\mathit{H}_2CH_2$). $^{13}C\{^1H\}$ NMR: δ 36.1 ($CH_2\mathit{C}H_2CH_2$), 34.5, 34.9, 35.7 (CH_2S), 4.7 (CH_2Te). $^{125}Te\{^1H\}$ NMR: δ 254. FAB-MS: *m/z* = 366, 264; calc. for $[C_{10}H_{20}S_3{}^{130}Te]^+$ 366, $[C_5H_{10}S_2{}^{130}Te]^+$ 264.

‡ *Crystal data* for $[Ag([11]aneS_2Te)]BF_4$: M = 498.61, monoclinic, space group $P2_1/n$, a = 8.885(2), b = 17.329(3), c = 9.018(2) Å, β = 93.48(2)°, V = 1386.0(4) Å^3, Z = 4, D_c = 2.389 g cm^{-3}, μ(Mo-Kα) = 38.34 cm^{-1}. Rigaku AFC7S four-circle diffractometer, T = 150 K, Mo-Kα X-radiation (λ = 0.71073 Å), 2548 unique reflections, 2022 reflections with $I > 2\sigma(I)$. Structure solution and refinement were routine.[7,8] R = 0.038, R_w = 0.071.

CCDC 151895. See http://www.rsc.org/suppdata/cc/b0/b008370o/ for crystallographic data in .cif or other electronic format.

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