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Synthesis and complexation of the mixed tellurium–oxygen macrocycles 1-tellura-4,7-dioxacyclononane, [9]aneO_2Te, and 1,10-ditellura-4,7,13,16-tetraoxacyclooctadecane, [18]aneO_4Te_2 and their selenium analogues

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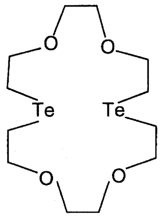
1,10-Ditellura-4,7,13,16-tetraoxacyclooctadecane ([18]aneO_4Te_2) has been synthesised in good yield (50–55%) from Na_2Te and $ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$ in liquid ammonia, and fully characterised by NMR spectroscopy (^1H, $^{13}C\{^1H\}$ and $^{125}Te\{^1H\}$) and mass spectrometry, and by the preparation of the Te(IV) derivatives [18]ane$O_4Te_2Me_2I_2$ and [18]ane$O_4Te_2Cl_4$. A minor by-product (*ca.* 4%) of the preparation is 1-tellura-4,7-dioxacyclononane ([9]aneO_2Te) which has been isolated and similarly characterised. The corresponding reaction of Na_2Se with $ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$ in liquid ammonia is less satisfactory and gives variable yields of 1,10-diselena-4,7,13,16-tetraoxacyclooctadecane ([18]aneO_4Se_2), which is better obtained from the same reagents in ethanol solution under high dilution conditions. [18]aneO_4Se_2 has also been thoroughly characterised spectroscopically. In these reactions the nine-membered ring 1-selena-4,7-dioxacyclononane is generally produced only in trace amounts. A range of complexes of [18]aneO_4Te_2 (L) in which the ligand behaves only as a Te_2 donor has been synthesised, including *cis*-[MX_2L] (M = Pd or Pt, X = Cl or Br), [$RhCl_2L_2$]Y (Y = Cl or PF_6), [CuL_2]BF_4, [AgL_2]BF_4 and [Cu_2L][BF_4]$_2$. The complexes have been characterised by microanalysis, multinuclear NMR spectroscopy (^1H, $^{125}Te\{^1H\}$, ^{195}Pt, ^{63}Cu), ES^+ mass spectrometry, UV/visible and IR spectroscopy as appropriate. Two complexes of [9]aneO_2Te, *cis*-[MCl_2\{[9]aneO_2Te\}$_2$] (M = Pd or Pt) are also reported, together with the selenoether complex [$PtCl_2$\{[18]aneO_4Se_2\}]. The X-ray structures of [MCl_2\{[18]aneO_4Te_2\}] (M = Pt or Pd) and [$PtCl_2$\{[18]aneO_4Se_2\}] all reveal *cis* square planar coordination with no interaction between the metal and the ether oxygens.

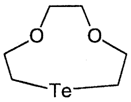
Introduction

We are exploring the synthesis and coordination chemistry of polydentate and macrocyclic ligands containing tellurium. Such ligands have been obtained only relatively recently,[1] much later than sulfur or even selenium analogues, a reflection of the weaker and more reactive Te–C bonds which makes for more challenging syntheses. Our recent contributions to the area include: the complexation of the tripodal $Me(CH_2TeR)_3$ (R = Ph or Me) with a variety of metals in both medium and low oxidation states;[2–4] the synthesis and complexation of the first facultative tritelluroethers $Te(CH_2CH_2CH_2TeR)_2$[5] and of the related $Te(CH_2CH_2CH_2SMe)_2$;[6] the synthesis of the small ring S_2Te macrocycles, [9]aneS_2Te (1-tellura-4,7-dithiacyclononane), [11]aneS_2Te (1-tellura-5,8-dithiacycloundecane) and [12]aneS_2Te (1-tellura-5,9-dithiacyclododecane).[7] Analogues with lighter chalcogens, [9]aneO_3 (1,4,7-trioxacyclononane), [9]aneO_2S (1-thia-4,7-dioxacyclononane) and [9]aneOS_2 (1,4-dithia-7-oxacyclononane), have long been known, although little studied.[8] This is in contrast to [9]aneS_3, which has played a central role in the development of thioether macrocyclic chemistry.[9] The selenium analogue [9]aneO_2Se (1-selena-4,7-dioxacyclononane) has been observed as an unexpected ring contraction product of the reaction of $BrCH_2CH_2OCH_2CH_2OCH_2CH_2Br$, $NCSeCH_2CH_2SeCN$ and $NaBH_4$.[10] The 18-membered ring 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane [18]aneO_4S_2, is well known and a range of metal complexes has been described,[8,11–19] but the selenium analogue 1,10-diselena-4,7,13,16-tetraoxacyclooctadecane, [18]aneO_4Se_2, has been mentioned in only two publications,[10,20] and other Se/O macrocycles have been little studied.[1] Only one Te_3 macrocycle, 1,5,9-tritelluracyclododecane, is known.[21]

Here we report the synthesis of two new Te–O macrocycles 1,10-ditellura-4,7,13,16-tetraoxacyclooctadecane [18]aneO_4Te_2 (**I**) and 1-tellura-4,7-dioxacyclononane [9]aneO_2Te, (**II**) and the characterisation of a range of derivatives and metal complexes involving coordination *via* the Te atoms. More limited studies on the corresponding selenium/oxygen macrocycles are also included.



I



II

Results and discussion

Ligand synthesis

The new macrocycle, [18]aneO_4Te_2, has been obtained in good yield (*ca.* 50–55%) by reaction of Na_2Te with $ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$ in liquid ammonia. The reaction is convenient in that there is no need to use high dilution conditions. Recrystallisation from CH_2Cl_2–Et_2O under nitrogen gave the [18]aneO_4Te_2 as a yellow, slightly air-sensitive solid, which was fully characterised by ^1H, $^{13}C\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectroscopy, the $\delta(^{125}Te)$ of 176 being a particularly useful fingerprint. The EI mass spectrum showed a multiplet at *m*/*z ca.* 488 with the correct isotope pattern for the parent ion. Fig. 1 shows this parent ion and the calculated pattern. It is possible that in the formation of [18]aneO_4Te_2, the Na^+ present may have a templating effect *via* interactions with the ether functions. Electrospray mass spectra obtained from solutions of [18]aneO_4Te_2 and NaCl in CH_2Cl_2–MeCN show a strong multiplet at *m*/*z ca.* 511 corresponding to \{[18]aneO_4Te_2.Na\}$^+$,

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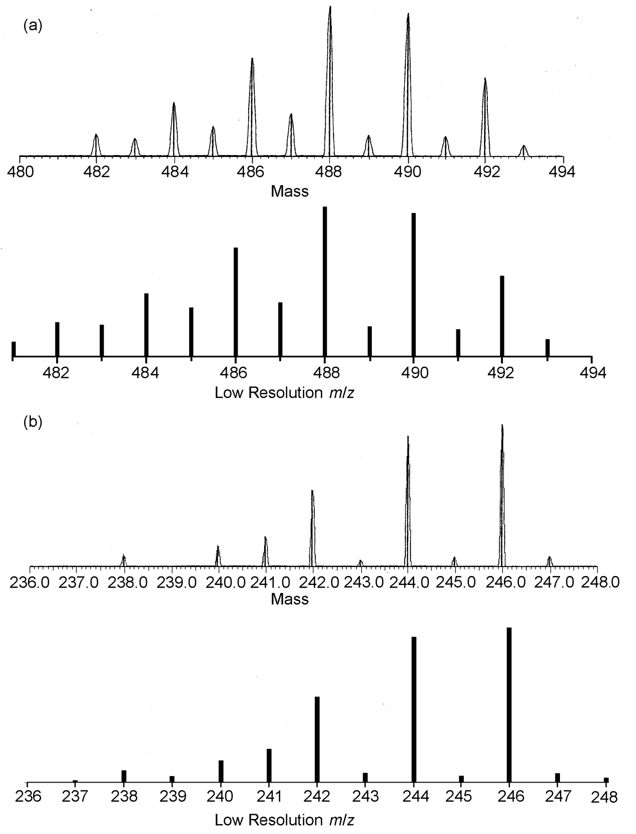

Fig. 1 The isotope patterns in the EI mass spectrum of the parent ions of (a) [18]aneO$_4$Te$_2$ and (b) [9]aneO$_2$Te and their simulated patterns.

whereas other alkali metal cations fail to give similar ions. We also note that the corresponding cyclisation reactions using the thioether precursors Cl(CH$_2$)$_n$S(CH$_2$)$_n$S(CH$_2$)$_n$Cl (n = 2 or 3), which are not expected to interact significantly with Na$^+$, give the [1 + 1] cyclisation products, and no evidence for higher rings.[7]

Careful examination of the crude products from this synthesis by ^{125}Te{^{1}H} NMR revealed weak resonances at δ 288 and 200 which were lost in the purification. In order to separate these products, the crude reaction mixture was dissolved in CH$_2$Cl$_2$ and adsorbed onto a silica column. Elution with hexane–ethyl acetate gave first a very small amount of yellow oil (δ 288) probably a ditelluride, and then a second fraction, which gave a yellow, air-sensitive solid identified as [9]aneO$_2$Te. The [18]aneO$_4$Te$_2$ does not elute and much was lost on the column, although some could be extracted from the silica with DMF.

The [9]aneO$_2$Te had generally similar ^{1}H and ^{13}C{^{1}H} NMR spectra to those of [18]aneO$_4$Te$_2$ as would be expected, but is readily distinguished by its ^{125}Te{^{1}H} NMR shift of 200 ppm and by its EI mass spectrum (Fig. 1). The yield of the small ring macrocycle is typically *ca.* 4%. The stability of the –TeCH$_2$CH$_2$O– linkage is notable, since –TeCH$_2$CH$_2$Te– units do not form, instead CH$_2$=CH$_2$ is eliminated and ditellurides produced.[22] The six-membered ring 1-tellura-4-oxacyclohexane is also known[23] and we conclude that the strong –CH$_2$–OR bond probably prevents elimination of ethene.

We also explored the similar reaction of Na$_2$Se with ClCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$Cl in liquid ammonia–thf, and found that a mixture of [9]aneO$_2$Se and [18]aneO$_4$Se$_2$ was produced. However, the reaction is much less satisfactory and yields are low. At −78 °C most of the α,ω-dichlorodiether was recovered, and even at the boiling point of ammonia (−33 °C), substantial amounts of ClCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$Cl did not react, and variable yields and ratios of the macrocycles were obtained (together with much polymer) from reactions under apparently similar conditions. It seems likely that reaction of the α,ω-dichlorodiether with the less nucleophilic Se^{2-} is very incomplete at low temperature, and then occurs in an uncontrolled way on warming, resulting in poor yields of the macrocyclic compounds. The reaction was also carried out in ethanol by adding a dilute solution of ClCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$Cl dropwise to a dilute solution of Na$_2$Se in EtOH over 7hr. The mixture was worked up as described in the Experimental section. The crude product examined by ^{77}Se NMR showed moderate amounts of [18]aneO$_4$Se$_2$, some [9]aneO$_2$Se, several resonances in the range δ 123–131 (which we attribute to oligomeric materials), and species with δ 226 and 312 which are probably diselenides. The GC/EI mass spectra confirmed the presence of all these species except the oligomers, which did not pass through the GC. Fractionation *in vacuo* separated the [18]aneO$_4$Se$_2$ from the other products.

The {[18]aneO$_4$Se$_2$–Na}$^+$ system shows similar behaviour to the tellurium analogue with a strong multiplet of *m*/*z ca.* 413 in the ES$^+$ mass spectrum, again suggesting that the sodium ion may have a templating role. As expected, the smaller nine-membered rings do not show association with Na$^+$ in the ES$^+$ mass spectra.

Organo-derivatives

The new telluroether macrocycles were characterised by quaternisation with MeI and, in the case of [18]aneO$_4$Te$_2$, by chlorination. Both reactions occur exclusively at the Te centres. Reaction of [18]aneO$_4$Te$_2$ with excess MeI in refluxing CH$_2$Cl$_2$ produced an orange solid identified by analysis as [18]aneO$_4$Te$_2$Me$_2$I$_2$. The ES$^+$ mass spectra showed a complex ion cluster at *m*/*z ca.* 645 corresponding to [P − I]$^+$ and also an intense feature at *m*/*z ca.* 259 due to the ion [P − 2I]$^{2+}$. The quaternisation is accompanied by substantial high frequency shifts in the ^{1}H and ^{13}C{^{1}H} NMR resonances of the CH$_2$Te groups, and the ^{125}Te{^{1}H} resonance at 506 is typical of an R$_3$TeI group.[22,24] The corresponding data on [9]aneO$_2$TeMeI show similar ^{1}H, ^{13}C{^{1}H} and ^{125}Te{^{1}H} (δ 520) NMR shifts and an ES$^+$ mass spectrum multiplet at *m*/*z ca.* 261. The latter is distinguished from the [P − 2I]$^{2+}$ ion in the spectrum of [18]aneO$_4$Te$_2$Me$_2$I$_2$ by the different isotope pattern and the half-mass separation between ion peaks in the dication.

Chlorination of [18]aneO$_4$Te$_2$ in CH$_2$Cl$_2$ produced the white Te(IV) chloride, [18]aneO$_4$Te$_2$Cl$_4$, which has the characteristic ^{125}Te{^{1}H} chemical shift of 850 ppm.[24] The EI mass spectrum shows a very weak parent ion, but [P − Cl]$^+$ is intense and the identity is confirmed by the characteristic isotope pattern.

The two Se/O macrocycles were identified by comparison of their ^{1}H NMR spectra with literature data,[10,20] by ^{13}C{^{1}H} and ^{77}Se{^{1}H} NMR spectroscopy and EI mass spectrometry (Experimental section). Quaternisation with MeI gave the corresponding Se(IV) compounds which have characteristic NMR shifts,[24] and distinctive ES$^+$ mass spectra.

Metal complexes

Dropwise addition of a dilute MeCN solution of [PtX$_2$(MeCN)$_2$] (X = Cl or Br) or [PdX$_2$(MeCN)$_2$] to a refluxing solution of [18]aneO$_4$Te$_2$ in CH$_2$Cl$_2$/MeCN formed yellow solutions, which on work-up gave complexes of stoichiometry [MX$_2$([18]aneO$_4$Te$_2$)]. These have UV/visible spectra typical of planar MX$_2$Te$_2$ species,[25,26] and exhibit two ν(M–X) vibrations in their far IR spectra, consistent with *cis* isomers. This stereochemistry was confirmed by the X-ray structures (below). The ^{1}H NMR spectra contain overlapping multiplets in the range *ca.* δ 3.0–4.4, showing that the CH$_2$Te resonance in the free ligand (δ 2.8) has shifted to high frequency whilst the CH$_2$O resonances are essentially unchanged, again consistent with [18]aneO$_4$Te$_2$ coordinated through Te. This is confirmed by the ^{125}Te{^{1}H} (and where appropriate ^{195}Pt{^{1}H}) NMR spectra). In CH$_2$Cl$_2$ solution the ^{125}Te{^{1}H} spectrum of [PtCl$_2$([18]aneO$_4$Te$_2$)] has δ = 393 and satellites corresponding to ^1J(^{125}Te–

^{195}Pt) = 862 Hz. The corresponding values for [PtBr$_2$([18]aneO$_4$Te$_2$)] are δ = 390 and ^1J(^{125}Te–^{195}Pt) = 690 Hz, [PdCl$_2$([18]aneO$_4$Te$_2$)] δ = 375 and [PdBr$_2$([18]aneO$_4$Te$_2$)] δ = 370. The one-bond coupling constants are in the range reported for *cis*-PtX$_2$Te$_2$ entities, smaller values being seen in the *trans* isomers.[25,26] We have shown elsewhere[25] that the coordination shifts in the ^{125}Te NMR spectra are sensitive to chelate ring size. Thus, compared to the values in the analogous *cis*-[PtX$_2$(R$_2$Te)$_2$] (preferably where the R-groups are similar to those in the bidentate ligands), five-membered chelate rings have very large positive coordination shifts, whereas six-membered rings have markedly smaller ones, and four-membered rings significantly negative values. In the present case the coordination shifts of *ca*. 200–220 are similar to those in [MX$_2$(Me$_2$Te)$_2$],† which confirms that in the 11-membered rings present in [MX$_2$([18]aneO$_4$Te$_2$)] the chelate ring parameter[25] is close to zero. The ^{195}Pt chemical shifts of −4257 (Cl) or −4756 (Br) are typical of *cis*-PtTe$_2$X$_2$ isomers, whereas values for the corresponding *trans* isomers are typically 400–500 ppm to high frequency.[2] It proved difficult to obtain good quality ^{125}Te or ^{195}Pt NMR spectra from these complexes at ambient temperatures, although spectra were easily obtained from the same solutions at −50 °C. Similar problems were not present in the [9]aneO$_2$Te or the [18]aneO$_4$Se$_2$ complexes. This suggests some dynamic process is present in the [18]aneO$_4$Te$_2$ complexes, which is slowed on cooling; presumably this is reversible chelate ring-opening.

If the reaction of [MX$_2$(MeCN)$_2$] and [18]aneO$_4$Te$_2$ in MeCN was carried out by rapidly mixing the reagents in concentrated solutions, immediate precipitation of yellow or orange–yellow solids occurred. These also had the composition [MX$_2$\{[18]aneO$_4$Te$_2$\}], but were only very slightly soluble in CH$_2$Cl$_2$, the remaining residue being insoluble in chlorocarbons, MeCN or acetone, but dissolved slowly, probably with reaction, in DMSO. The UV/visible spectra of the insoluble compounds were typical of MX$_2$Te$_2$ species, and their IR spectra generally similar to those of the soluble [MX$_2$\{[18]aneO$_4$Te$_2$\}], except for differences in the far-IR metal–halogen region, where they were more complicated. The insolubility has limited full characterisation, but it is highly probable that the syntheses in concentrated solution yields a mixture of *cis*-[MX$_2$\{[18]aneO$_4$Te$_2$\}] (the same species as described above from the high dilution preparations) and varying amounts of oligomeric \{[MX$_2$\{[18]aneO$_4$Te$_2$\}]\}$_n$. When [18]aneO$_4$Te$_2$ behaves as a bidentate Te$_2$ chelating ligand, two 11-membered rings are formed, in which the chelate effect will be minimal, and as in long chain diphosphines[27] (little data are available on long chain Group 16 donor ligands)[1] formation of a mixture of *cis* and *trans* oligomers/polymers is plausible.

The reaction of [9]aneO$_2$Te with [MCl$_2$(MeCN)$_2$] (M = Pd or Pt) in MeCN proceeded straightforwardly to give [MCl$_2$\{[9]aneO$_2$Te\}$_2$]. In both cases the ^{125}Te\{^{1}H\} (and for the latter ^{195}Pt) NMR spectra (CH$_2$Cl$_2$) solution indicated only one isomer. The [PtCl$_2$\{[9]aneO$_2$Te\}$_2$] had δ(^{195}Pt) = −4501 and ^1J(^{125}Te–^{195}Pt) = 975 Hz consistent with a *cis* isomer,[25] and two ν(Pt–Cl) stretches in the far IR spectrum suggest this geometry is present in the solid also. It is not possible to distinguish *cis* and *trans* [PdCl$_2$(R$_2$Te)$_2$] complexes from the ^{125}Te chemical shifts which are quite similar,[25] but the presence of a single δ(^{125}Te\{^{1}H\}) resonance shows only a single isomer is present, and from the two Pd–Cl stretches in the far IR spectrum, it is likely that this too is a *cis* isomer. Few platinum metal complexes of small tellurium rings have been reported: in [PtCl$_2$\{Te(CH$_2$)$_2$O(CH$_2$)$_2$\}$_2$] the geometry is *trans* (from an X-ray structure of the solid),[28] whilst in complexes of Te(CH$_2$)$_4$ (L′) the [PdX$_2$L′$_2$] (X = Cl, Br or I) and [PtX$_2$L′$_2$] (X = Br or I) are *trans*, but [PtCl$_2$L′$_2$] is a mixture of both *cis* and *trans* forms.[29] The [PdCl$_2$L″$_2$] (L″= 1,3-dihydrobenzo[*c*]tellurophene) is *trans*, but the [PtCl$_2$L″$_2$] is *cis*.[30] No clear pattern emerges from the literature data and the differences in isomer stabilities appear small.

Table 1 Selected bond lengths (Å) and angles (°) for *cis*-[PtCl$_2$\{[18]aneO$_4$Se$_2$\}]

Pt(1)–Se(1)	2.391(2)	Se(1)–C(1)	1.96(2)
Pt(1)–Se(2)	2.390(2)	Se(1)–C(12)	1.95(2)
Pt(1)–Cl(1)	2.325(4)	Se(2)–C(6)	1.94(2)
Pt(1)–Cl(2)	2.334(4)	Se(2)–C(7)	1.98(2)
Se(1)–Pt(1)–Se(2)	86.57(6)	Pt(1)–Se(1)–C(1)	105.2(6)
Se(1)–Pt(1)–Cl(1)	91.59(11)	Pt(1)–Se(1)–C(12)	101.3(5)
Se(1)–Pt(1)–Cl(2)	178.30(12)	C(1)–Se(1)–C(12)	96.1(7)
Se(2)–Pt(1)–Cl(1)	177.91(12)	Pt(1)–Se(2)–C(6)	103.1(6)
Se(2)–Pt(1)–Cl(2)	91.74(12)	Pt(1)–Se(2)–C(7)	102.4(5)
Cl(1)–Pt(1)–Cl(2)	90.1(2)	C(6)–Se(2)–C(7)	98.5(8)

One Pt(II) complex of [18]aneO$_4$Se$_2$ was made for comparison purposes; the [PtCl$_2$\{[18]aneO$_4$Se$_2$\}] was similar to the [18]aneO$_4$Te$_2$ analogue, and has corresponding UV/visible, IR and NMR spectra. Notably, the ^{77}Se\{^{1}H\} NMR spectrum contains a single resonance at δ 259 with ^1J(^{195}Pt–^{77}Se) of 550 Hz, with δ(^{195}Pt) −3861, similar to other *cis*-PtCl$_2$Se$_2$ chromophores.[26,31]

Small single crystals of [PtCl$_2$\{[18]aneO$_4$Se$_2$\}] were obtained from CH$_2$Cl$_2$ and the structure of one of these (Table 1, Fig. 2) reveals the *cis* square planar geometry (Se$_2$Cl$_2$) with no interaction between the Pt centre and the ether oxygens. The structures of [PtCl$_2$\{[18]aneO$_4$Te$_2$\}] (Table 2, Fig. 3) and [PdCl$_2$\{[18]aneO$_4$Te$_2$\}] (Table 3, Fig. 4) show very similar planar geometries, with angles at the metal close to 90°. The Cl–M–Cl angles are slightly greater than the Se(Te)–M–Se(Te) angles, though despite the large rings there is no evidence for significant distortion in the chelate rings. The two complexes of [18]aneO$_4$Te$_2$ are isomorphous ($P2_1/n$) but the [PtCl$_2$\{[18]aneO$_4$Se$_2$\}] is isomorphous with the thioether analogues [PdCl$_2$\{[18]aneO$_4$S$_2$\}][19] and [PtCl$_2$\{[18]aneO$_4$S$_2$\}][16] which crystallise in the acentric space group $P2_12_12_1$. The Pt–Se, Pt–Te and Pd–Te (all *trans* Cl) bond lengths are similar to those reported in other systems,[1,26] and the increase as the donor atoms descend Group 16 is in line with the increasing covalent radius of the donor. A comparison of the average d(Pt–Cl) distances in [PtCl$_2$\{[18]aneO$_4$S$_2$\}] (2.32 Å),[16] [PtCl$_2$\{[18]aneO$_4$Se$_2$\}] (2.33 Å) and

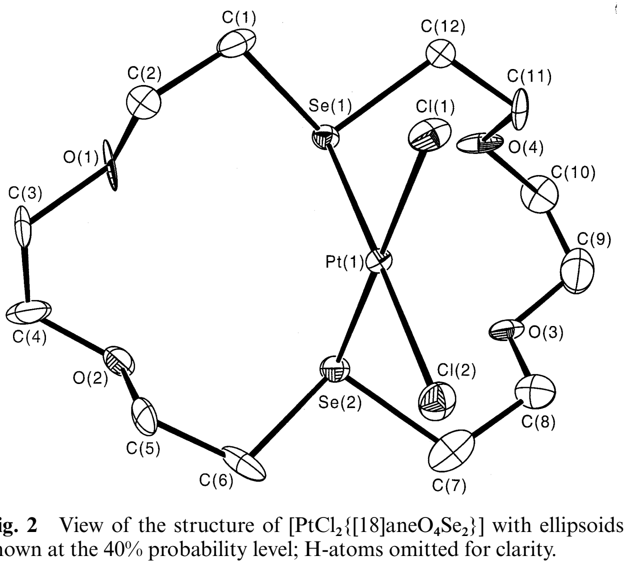

Fig. 2 View of the structure of [PtCl$_2$\{[18]aneO$_4$Se$_2$\}] with ellipsoids shown at the 40% probability level; H-atoms omitted for clarity.

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† Since ^{125}Te NMR shifts are sensitive to substituents at least as far as the γ carbon, and exact comparison with [18]aneO$_4$Te$_2$ would need data on complexes of Te(CH$_2$CH$_2$OR)$_2$ which are not available. Data on Me$_2$Te complexes are used: in practice the ring-size effects are sufficiently large that the trends appear reliable even in the absence of exact ligand analogues.[25]

Table 2 Selected bond lengths (Å) and angles (°) for *cis*-$[PdCl_2\{[18]aneO_4Te_2\}]$

Te(1)–Pd(1)	2.5567(5)	Te(1)–C(1)	2.157(5)
Te(2)–Pd(1)	2.5398(5)	Te(1)–C(12)	2.156(5)
Pd(1)–Cl(1)	2.3474(13)	Te(2)–C(6)	2.144(5)
Pd(1)–Cl(2)	2.3618(12)	Te(2)–C(7)	2.151(5)
Pd(1)–Te(1)–C(1)	100.3(1)	Te(1)–Pd(1)–Te(2)	88.29(2)
Pd(1)–Te(1)–C(12)	105.6(1)	Te(1)–Pd(1)–Cl(1)	89.98(3)
C(1)–Te(1)–C(12)	92.8(2)	Te(1)–Pd(1)–Cl(2)	173.07(3)
Pd(1)–Te(2)–C(6)	100.73(13)	Te(2)–Pd(1)–Cl(1)	175.27(4)
Pd(1)–Te(2)–C(7)	100.09(13)	Te(2)–Pd(1)–Cl(2)	88.84(3)
C(6)–Te(2)–C(7)	96.4(2)	Cl(1)–Pd(1)–Cl(2)	93.35(4)

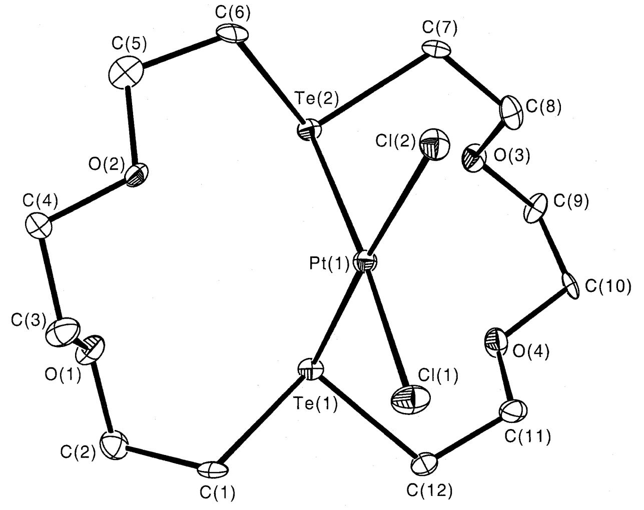

Fig. 3 View of the structure of $[PtCl_2\{[18]aneO_4Te_2\}]$ with ellipsoids shown at the 40% probability level; H-atoms omitted for for clarity.

$[PtCl_2\{[18]aneO_4Te_2\}]$ (2.35 Å) reveals a clear *trans* influence S < Se < Te. It is also informative to compare the corresponding Pd and Pt complexes for a common ligand. For $[18]aneO_4S_2$ and $[18]aneO_4Te_2$ the *d*(M–E) (M = Pd or Pt, E = S or Te) are slightly shorter for M = Pt (2.28, 2.53 Å respectively) than for M = Pd (2.30 and 2.55 Å), whilst the *d*(M–Cl) appear to show the opposite effect, although less clearly, M = Pt (2.32 and 2.35 Å) *vs*. M = Pd (2.31 and 2.35 Å).

The reaction of $RhCl_3 \cdot 3H_2O$ and $[18]aneO_4Te_2$ in EtOH–CH_2Cl_2 gave an orange–yellow complex $[RhCl_2\{[18]aneO_4Te_2\}_2]Cl$, whilst in the presence of NH_4PF_6 the $[RhCl_2\{[18]aneO_4Te_2\}_2]PF_6$ salt was isolated. Both complexes were very poorly soluble in CH_2Cl_2, acetone and MeCN which prevented $^{125}Te\{^1H\}$ NMR studies, but the presence of an ion multiplet in the ES^+ mass spectrum corresponding to $[RhCl_2\{[18]aneO_4Te_2\}_2]^+$ confirms the identity of the cation. The UV/visible spectrum has a d–d band at 28 820 cm^{-1} which suggests a *cis* isomer (*trans* isomers have a markedly lower first d–d transition),[32] and this is supported by the far-IR spectrum, with ν(Rh–Cl) at 335, 324 cm^{-1}, although the assignment of *cis* geometry is made tentatively in the absence of crystallographic or $^{125}Te\{^1H\}$ NMR data.

The reaction of $[Cu(MeCN)_4]BF_4$ with 2.2 mol. equivalents of $[18]aneO_4Te_2$ in MeCN produced orange–brown $[Cu\{[18]aneO_4Te_2\}_2]BF_4$. The ES^+ mass spectrum (MeCN solution) shows ions corresponding to $[Cu\{[18]aneO_4Te_2\}_n]^+$ (n = 2 or 1). The ^1H NMR spectrum shows a broad CH_2Te resonance at δ 2.9, a high frequency shift from that in the free ligand (δ 2.78), but the CH_2O resonances are unshifted from those of the free ligand. The $^{125}Te\{^1H\}$ NMR spectrum shows a broad resonance at δ 166 which corresponds to a coordination shift of −10; small low frequency coordination shifts are normal for Cu(I) telluroethers.[33] Addition of varying amounts of $[18]aneO_4Te_2$ to the NMR solution resulted in single $^{125}Te\{^1H\}$ resonances with shifts which varied with the temperature and with added ligand, showing evidence for fast exchange between the solution species. The pure complex does not exhibit a ^{63}Cu NMR spectrum, but in the presence of excess $[18]aneO_4Te_2$, the solution showed a broad ^{63}Cu NMR resonance at δ −59 ($w_{1/2}$ = 11 000 Hz) attributable to the tetrahedral $[Cu\{[18]aneO_4Te_2\}_2]^+$ ($CuTe_4$) in which the quadrupolar relaxation of the ^{63}Cu nucleus has slowed significantly.[33] Using an excess of $[Cu(MeCN)_4]BF_4$ in the preparation resulted in a yellow complex of composition $[Cu_2\{[18]aneO_4Te_2\}][BF_4]_2$, on the basis of microanalysis, which was insoluble in chlorocarbons or MeCN and is presumably oligomeric.

Table 3 Selected bond lengths (Å) and angles (°) for *cis*-$[PtCl_2\{[18]aneO_4Te_2\}]$

Pt(1)–Te(1)	2.5357(6)	Te(1)–C(1)	2.164(9)
Pt(1)–Te(2)	2.5322(6)	Te(1)–C(12)	2.159(8)
Pt(1)–Cl(1)	2.344(2)	Te(2)–C(6)	2.156(9)
Pt(1)–Cl(2)	2.356(2)	Te(2)–C(7)	2.161(9)
Te(1)–Pt(1)–Te(2)	88.81(2)	Pt(1)–Te(1)–C(1)	105.5(2)
Te(1)–Pt(1)–Cl(1)	90.87(6)	Pt(1)–Te(1)–C(12)	101.7(2)
Te(1)–Pt(1)–Cl(2)	174.96(6)	C(1)–Te(1)–C(12)	93.0(3)
Te(2)–Pt(1)–Cl(1)	176.12(6)	Pt(1)–Te(2)–C(6)	101.2(3)
Te(2)–Pt(1)–Cl(2)	89.68(5)	Pt(1)–Te(2)–C(7)	100.6(2)
Cl(1)–Pt(1)–Cl(2)	90.97(7)	C(6)–Te(2)–C(7)	95.5(3)

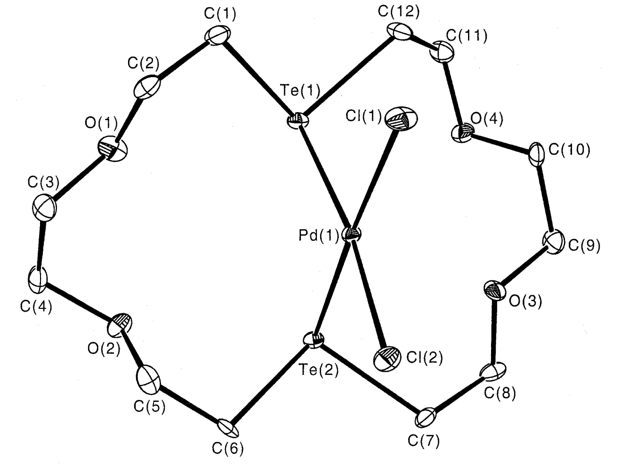

Fig. 4 View of the structure of $[PdCl_2\{[18]aneO_4Te_2\}]$ with ellipsoids shown at the 40% probability level; H-atoms omitted for for clarity.

The reaction of $AgBF_4$ with $[18]aneO_4Te_2$ in a 1 : 2 molar ratio in MeCN gave a pale orange, light-sensitive solid of composition $[Ag\{[18]aneO_4Te_2\}_2]BF_4$. This was generally similar in properties to the copper(I) complex, although less stable. The broad ^1H and $^{125}Te\{^1H\}$ NMR resonances observed from CD_2Cl_2 solutions of the complex at room temperature suggest fast dissociation/exchange. Again the $^{125}Te\{^1H\}$ coordination shift was negative, consistent with reports on other Ag(I) telluroethers.[34] As for the analogous copper system, it proved possible to isolate a complex with a 2 : 1 $AgBF_4$: $[18]aneO_4Te_2$ stoichiometry, but this was insoluble in common solvents and was not further studied.

Experimental

Physical measurements were made as described previously.[2–5] All preparations were carried out under dinitrogen.

Preparations:

[9]aneO$_2$Te and [18]aneO$_4$Te$_2$

Sodium (1.48 g, 0.064 mol) was added over a few min to liquid ammonia (600 cm^3) at −78 °C, followed by freshly ground tellurium powder (3.28 g, 0.026 mol). The mixture was allowed to warm until a white precipitate of Na_2Te was observed, and then re-cooled to −78 °C. A solution of $ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$ (4.81 g, 0.026 mol) in dry THF (100 cm^3) was added dropwise over a period of 30 min to the stirred solution, and then the mixture allowed to warm slowly to room temperature overnight. The yellow–orange mixture was hydrolysed with water (200 cm^3) extracted with CH_2Cl_2 (2 × 200 cm^3) and the organic extracts combined, dried ($MgSO_4$) and filtered to produce a clear orange solution. The solvent was removed to give a pale orange solid which was recrystallised from CH_2Cl_2–Et_2O at −18 °C. Yield 3.39 g, 54%. This was identified as [18]aneO_4Te_2: mp 49 °C. ^{1}H NMR ($CDCl_3$): δ 2.80 (t) [8H] CH_2Te, 3.57 (s) [8H] OCH_2CH_2O, 3.85 (t) [8H] $TeCH_2CH_2O$. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 2.6 CH_2Te, 70.0, 73.4 CH_2O. $^{125}Te\{^1H\}$ NMR (CH_2Cl_2): δ 176. EI mass spectrum: *m*/*z* 488; calc. for $[C_{12}H_{24}O_4{}^{128}Te_2]^+$, $[C_{12}H_{24}O_4{}^{126}Te^{130}Te]^+$ 488.

Isolation of [9]aneO_2Te. Examination of the crude solid obtained above by $^{125}Te\{^1H\}$ NMR revealed very weak resonances at δ 288 and 200, which were lost upon recrystallisation. In an alternative work up, the crude product was dissolved in CH_2Cl_2 and adsorbed onto a silica column and eluted with 3 : 1 hexane–ethyl acetate. The first fraction contained a small amount of orange oil [δ ^{125}Te (CH_2Cl_2) = 288]. The remaining fractions had identical $^{125}Te\{^1H\}$ NMR spectra and were combined and the solvent removed to give a yellow solid (0.31 g, *ca.* 4% based on Te) identified as [9]aneO_2Te: mp 70–72 °C. ^{1}H NMR ($CDCl_3$): δ 2.85 (t) [4H] CH_2Te, 3.65 (s) [4H] OCH_2CH_2O, 3.8 (t) [4H] $TeCH_2CH_2O$. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 2.2 CH_2Te, 70.3, 74.0 CH_2O. $^{125}Te\{^1H\}$ NMR (CH_2Cl_2): δ 200. EI mass spectrum: *m*/*z* 246; calc. for $[C_6H_{12}O_2{}^{130}Te]^+$ 246.

The bulk of the material ([18]aneO_4Te_2) did not elute, although some could be re-extracted from the silica by stirring overnight in *N*,*N*-dimethylformamide. However, substantial amounts of the 18-membered ring compound were lost in this process.

[9]aneO_2Se and [18]aneO_4Se_2

Method 1. A solution of Na_2Se in liquid ammonia (600 cm^3) was generated from sodium (1.72 g, 0.075 mol) and freshly ground selenium powder (2.36 g, 0.03 mol). A solution of $ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$ (5.60 g, 0.03 mol) in dry THF (100 cm^3) was added over a period of approximately 2 h, at the boiling point of the ammonia (−33 °C), to give a pale cream mixture. This was then allowed to warm to room temperature overnight, gently refluxed for 30 min and then hydrolysed with water (200 cm^3). The mixture was extracted with CH_2Cl_2 (2 × 200 cm^3) and the extracts combined and dried over $MgSO_4$. Filtration and removal of the solvent gave a yellow oil (4.46 g). Kugelröhr distillation (0.2 mmHg) gave low boiling selenium free fractions, and at 200 °C a yellow oil, leaving an involatile red–brown solid. This oil contained highly variable amounts of [9]aneO_2Se and [18]aneO_4Se_2 (by $^{77}Se\{^1H\}$ NMR). In some cases only traces of [9]aneO_2Se were present, while in others [9]aneO_2Se dominated. If separation proved necessary, it was achieved by careful sublimation of the oil *in vacuo* onto a liquid nitrogen cold finger which separated [9]aneO_2Se as a yellow oil and the less volatile residue was [18]aneO_4Se_2.

[9]aneO_2Se. ^{1}H NMR ($CDCl_3$): δ 2.90 (t) [4H] CH_2Se, 3.65 (s) [4H], 4.10 (t) [4H] CH_2O. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.3 CH_2Se, 72.5, 75.5 CH_2O. $^{77}Se\{^1H\}$ NMR (CH_2Cl_2): δ 204. EI mass spectrum: *m*/*z* 196; calc. for $[C_6H_{12}O_2{}^{80}Se]^+$ 196.

[18]aneO_4Se_2. ^{1}H NMR ($CDCl_3$): δ 2.78 (t) [8H] CH_2Se, 3.59 (s) [8H] CH_2O, 3.73 (t) [8H] $SeCH_2CH_2O$. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.5 CH_2Se, 71.3, 71.5 CH_2O. $^{77}Se\{^1H\}$ NMR (CH_2Cl_2): δ 144. EI mass spectrum: *m*/*z* 392; calc. for $[C_{12}H_{24}O_4{}^{80}Se_2]^+$ 392.

Method 2. Sodium (1.72 g, 0.075 mol) and freshly ground selenium powder (2.36 g, 0.03 mol) were added to liquid NH_3 (300 cm^3) in a 2 l flask, and the mixture left to warm to room temperature overnight to form Na_2Se. This was redissolved in dry EtOH (1 l.) and $Cl(CH_2)_2O(CH_2)_2O(CH_2)_2Cl$ (5.60 g, 0.03 mol) in EtOH (1 l.) added slowly dropwise to the solution at room temperature over the course of 7 h. The mixture was then stirred overnight at room temperature and refluxed for 1 h before allowing it to cool. It was hydrolysed with water (100 cm^3), filtered, and the solvent removed. The residue was extracted with CH_2Cl_2 (2 × *ca.* 60 cm^3). The extracts were combined, dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to produce a viscous yellow oil. Yield 5 g. This was then recrystallised (CH_2Cl_2–hexane) to produce crude solid [18]aneO_4Se_2 (1 g). The mother-liquor was evaporated and the residue Kugelröhr distilled to produce four fractions. Fraction 1 distilled at ≤125 °C (2 mmHg) and was [9]aneO_2Se ($\delta^{77}Se\{^1H\}$ = 203), yield 0.25 g. Fractions 2 and 3 both distilled at ≤ 200 °C (2 mmHg); fraction 2 was largely diselenide ($\delta^{77}Se\{^1H\}$ = 227), yield 0.09 g, while fraction 3 ($\delta^{77}Se\{^1H\}$ = 144) was [18]aneO_4Se_2 yield 0.050 g. A red–brown residue remained.

[18]ane$O_4Te_2Me_2I_2$

Iodomethane (1 cm^3) was added to a solution of [18]aneO_4Te_2 (0.08 g, 0.15 mmol) in CH_2Cl_2 (40 cm^3) and the mixture gently refluxed for 30 min. The volume was reduced (10 cm^3) and added to ice-cold Et_2O to produce a pale yellow solid which, when dried *in vacuo*, quickly turned into a waxy orange solid. Yield 0.13 g, 83% (Found: C, 20.8; H, 3.7. Calc. for $C_{14}H_{30}I_2O_4Te_2{\cdot}CH_2Cl_2$: C, 20.4; H, 3.6%). ^{1}H NMR (d^6-DMSO): δ 2.3 (s) [3H] MeTe, 3.2 (m) [4H] CH_2Te, 3.6, 3.9 (m) [8H] CH_2O, 5.4 (s) [H] CH_2Cl_2. $^{13}C\{^1H\}$ NMR (DMSO): δ 4.3 MeTe, 25.9 CH_2Te, 57.0 CH_2Cl_2, 66.2, 69.9 CH_2O. $^{125}Te\{^1H\}$ (DMSO): δ 506. ES^+ mass spectrum: *m*/*z* 645; calc. for $[C_{14}H_{30}O_4{}^{126}Te^{130}TeI]^+$ and $[C_{14}H_{30}O_4{}^{128}Te_2I]^+$ 645.

[9]aneO_2TeMeI

[9]aneO_2Te (0.08 g, 0.33 mmol) was dissolved in CH_2Cl_2 (40 cm^3), MeI (1 cm^3) added and the mixture refluxed for 1 h. The resulting pale yellow solution was concentrated and the product precipitated by diethyl ether. The solid was filtered off and dried *in vacuo*. Yield 0.096 g, 75% (Found: C, 21.6; H, 3.7. Calc. for $C_7H_{15}IO_2Te$: C, 21.8; H, 3.9%). ^{1}H NMR (d^6-DMSO): δ 2.3 (s) [3H] MeTe, 3.25 (m) [4H] CH_2Te, 3.60, 3.85 (m) [8H] CH_2O. $^{13}C\{^1H\}$ NMR (DMSO): δ 2.0 MeTe, 24.9 CH_2Te, 64.5, 68.4 CH_2O. $^{125}Te\{^1H\}$ (DMSO): δ 520. ES^+ mass spectrum: *m*/*z* 261; calc. for $[C_7H_{15}O_2{}^{130}Te]^+$ 261.

[18]ane$O_4Te_2Cl_4$

Chlorine was bubbled through a solution of [18]aneO_4Te_2 (0.10 g, 0.20 mmol) in CH_2Cl_2 (40 cm^3) for 1 min. The reaction was stirred at room temperature for 30 min, reduced in volume (5 cm^3) and the product precipitated with ice-cold Et_2O. The precipitate was filtered and dried *in vacuo* to give a white solid (0.13 g, 99%). The solid darkened on storage (Found: C, 21.0; H, 3.4. Calc. for $C_{12}H_{24}Cl_4O_4Te_2.CH_2Cl_2$: C, 21.8; H, 3.6%). ^{1}H NMR ($CDCl_3$): δ 4.2 (m) [H] CH_2Te, 3.6–3.8 (m) [4H] CH_2O. 5.4 CH_2Cl_2. $^{13}C\{^1H\}$ NMR (CH_2Cl_2): δ 15.5 CH_2Te, 65.4, 66.0 CH_2O. $^{125}Te\{^1H\}$ (CH_2Cl_2): δ 850. ES^+ mass spectrum: *m*/*z* = 595; calc. for $[C_{12}H_{24}{}^{35}Cl_2{}^{37}ClO_4{}^{126}Te^{130}Te]^+$ and $[C_{12}H_{24}{}^{35}Cl_2{}^{37}ClO_4{}^{128}Te_2]^+$ 595.

[18]ane$O_4Se_2Me_2I_2$

[18]aneO_4Se_2 (0.07 g, 0.018 mmol) was gently refluxed with excess iodomethane (1 cm^3) in CH_2Cl_2 (30 cm^3) for 1 h, then concentrated and pipetted into ice-cold Et_2O, producing a precipitate that was filtered off, and dried *in vacuo* to give a yellow solid. Yield 0.05 g, 43% (Found: C, 25.3; H, 4.3. Calc. for $C_{14}H_{30}I_2O_4Se_2$: C, 24.9; H, 4.1%). ^{1}H NMR (d^6-DMSO):

Table 4 Crystallographic parameters

Complex	[PtCl$_2${[18]aneO$_4$Se$_2$}]	[PdCl$_2${[18]aneO$_4$Te$_2$}]	[PtCl$_2${[18]aneO$_4$Te$_2$}]
Formula	$C_{12}H_{24}Cl_2O_4PtSe_2$	$C_{12}H_{24}Cl_2O_4PdTe_2$	$C_{12}H_{24}Cl_2O_4PtTe_2$
M	656.24	664.83	753.52
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1$/n
a/Å	9.1685(2)	10.5109(3)	10.5179(3)
b/Å	9.5824(2)	15.9002(5)	15.9441(5)
c/Å	20.5134(5)	10.9837(3)	11.0394(3)
β/°	90	96.8439(11)	96.440(2)
U/Å^3	1802.10(6)	1822.58(8)	1839.61(8)
Z	4	4	4
μ(Mo-Kα)/mm^{-1}	12.102	4.460	11.007
Unique reflections	3165	4281	4369
Obs. reflections with $[I_o > 2\sigma(I_o)]$	3055	3811	3517
$R\ [I_o > 2\sigma(I_o)]$	0.0555	0.0370	0.0464
R_w	0.0650	0.0470	0.0500

$R = \Sigma(|F_{obs}|_i - |F_{calc}|_i)/\Sigma|F_{obs}|_i$; $R_w = (\Sigma[w_i(|F_{obs}|_i - |F_{calc}|_i)^2/\Sigma w_i|F_{obs}|_i^2)^{1/2}$.

δ 2.90 [6H] Me, 3.78 (t) [8H] CH_2Se, 3.59 (s) [8H] CH_2O, 3.80 (t) [8H] $SeCH_2CH_2O$. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.2 Me, 24.6 CH_2Se, 65.5, 70.1 CH_2O. $^{77}Se\{^1H\}$ NMR (CH_2Cl_2): δ 318. ES$^+$ mass spectrum: m/z 549, 211; calc. for $[C_{14}H_{30}IO_4{}^{80}Se_2]^+$ 549, $[C_{14}H_{30}O_4{}^{80}Se_2]^{2+}$ 211.

[9]aneO$_2$SeMeI

The preparation was carried out similarly to that above. ^{1}H NMR (d^6-DMSO): δ 2.90 [3H] Me, 3.65 (t) [4H] CH_2Se, 3.55 (s) [4H] CH_2O, 3.70 (t) [4H] $SeCH_2CH_2O$. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.6 Me, 43.4 CH_2Se, 70.8, 71.6 CH_2O. $^{77}Se\{^1H\}$ NMR (CH_2Cl_2): δ 354. ES$^+$ mass spectrum: m/z 211; calc. for $[C_7H_{15}IO_2{}^{80}Se]^+$ 211.

[PtCl$_2${[18]aneO$_4$Te$_2$}]

$PtCl_2$ (0.04 g, 0.15 mmol) was dissolved in refluxing MeCN (40 cm^3), the solution cooled and filtered. It was then added dropwise to a gently refluxing solution of [18]aneO$_4$Te$_2$ (0.075 g, 0.15 mmol) in CH_2Cl_2 (25 cm^3)–MeCN (100 cm^3) over *ca.* 30 min. The solution was refluxed for 1 h, cooled and stirred overnight. It was filtered through Celite, concentrated to *ca.* 10 cm^3 and the product precipitated by slow addition of Et_2O (5 cm^3). The yellow solid was filtered off and dried *in vacuo*. Yield 0.097 g, 76% (Found: C, 19.5; H, 3.0. Calc. for $C_{12}H_{24}Cl_2O_4PtTe_2$: C, 19.3; H, 3.2%). ν(Pt–Cl)/cm^{-1}: 308, 291. UV/vis (CH_2Cl_2) $\tilde{\nu}_{max}$/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 34435 (4770), 25560 (965). ^{1}H NMR ($CDCl_3$): δ 3.0–4.4 (m). ^{195}Pt NMR (CH_2Cl_2 223 K): δ −4257. $^{125}Te\{^1H\}$ NMR (CH_2Cl_2): δ 393 ($^1J(^{195}Pt–^{125}Te)$ = 862 Hz).

[PtBr$_2${[18]aneO$_4$Te$_2$}]

This was obtained similarly to the above using $PtBr_2$. Yield 70% (Found: C, 17.3; H, 2.6. Calc. for $C_{12}H_{24}Br_2O_4PtTe_2$: C, 17.1; H, 2.9%). ν(Pt–Br)/cm^{-1}: 223. UV/vis (CH_2Cl_2) $\tilde{\nu}_{max}$/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 36075 (7310), 30980 (2670). ^{1}H NMR ($CDCl_3$): δ 3.0–4.4(m). ^{195}Pt NMR (CH_2Cl_2, 223 K): δ −4756. $^{125}Te\{^1H\}$ NMR (CH_2Cl_2, 223 K): δ 390 ($^1J(^{195}Pt–^{125}Te)$ = 690 Hz);

[PdCl$_2${[18]aneO$_4$Te$_2$}]

Prepared similarly using $PdCl_2$. Yield 80% (Found: C, 23.3; H, 3.2. Calc. for $C_{12}H_{24}Cl_2O_4PdTe_2\cdot1/2Et_2O$: C, 24.1; H, 4.1%). ν(Pd–Cl)/cm^{-1}: 311, 301. UV/vis (CH_2Cl_2) $\tilde{\nu}_{max}$/cm^{-1}(ε_{mol}/dm^3 mol^{-1} cm^{-1}): 30600 (3900), 25640 (1775). ^{1}H NMR ($CDCl_3$): δ 3.0–4.5 (m). $^{125}Te\{^1H\}$ NMR (CH_2Cl_2, 223 K): δ 375.

[PdBr$_2${[18]aneO$_4$Te$_2$}]

Prepared similarly. Orange solid, yield 36% (Found: C, 18.1; H, 3.4; calc. for $C_{12}H_{24}Br_2O_4PdTe_2\cdot CH_2Cl_2$: C, 18.6; H, 3.1%. ^{1}H NMR ($CDCl_3$): δ 3.2–4.1 (m), 5.4 (s) CH_2Cl_2. $^{125}Te\{^1H\}$ NMR (CH_2Cl_2): δ 373. ν(Pd–Br)/cm^{-1}: 243, 221. UV/vis (CH_2Cl_2) $\tilde{\nu}_{max}$/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 24630 (4200), 28900 (7350).

[PtCl$_2${[18]aneO$_4$Se$_2$}]

Made as described for [PtCl$_2${[18]aneO$_4$Te$_2$}], but using [18]aneO$_4$Se$_2$. Isolated as a very pale yellow powder, yield 70% (Found: C, 21.3; H, 3.5, N, 1.8. Calc. for $C_{12}H_{24}Cl_2O_4PtSe_2$: C, 21.9; H, 3.5%). ν(Pt–Cl)/cm^{-1}: 322, 304 cm^{-1}. UV/vis (CH_2Cl_2) $\tilde{\nu}_{max}$/cm^{-1}(ε_{mol}/dm^3 mol^{-1} cm^{-1}): 30640 (880). ^{1}H NMR ($CDCl_3$): δ 3.0–4.4 (m). ^{195}Pt NMR (CH_2Cl_2): δ −3861. $^{77}Se\{^1H\}$ NMR (CH_2Cl_2): 259 ($^1J(^{195}Pt–^{77}Se)$ = 550 Hz).

[PtCl$_2${[9]aneO$_2$Te}$_2$]

$PtCl_2$ (0.05 g, 0.17 mmol) was dissolved in boiling MeCN (100 cm^3) and [9]aneO$_2$Te (0.09 g, 0.35 mmol) in CH_2Cl_2 (80 cm^3)-MeCN (20 cm^3) added slowly. The solution was cooled and stirred overnight. It was then filtered and the filtrate concentrated (10 cm^3) and Et_2O (5 cm^3) added to produce a greenish–yellow precipitate. This was filtered off and dried *in vacuo*. Yield 0.08 g, 62% (Found: C, 19.8; H, 3.0. Calc. for $C_{12}H_{24}Cl_2O_4PtTe_2$: C, 19.3; H, 3.2%). ν(Pt–Cl)/cm^{-1}: 311, 290. UV/vis (CH_2Cl_2) $\tilde{\nu}_{max}$/cm^{-1}(ε_{mol}/dm^3 mol^{-1} cm^{-1}): 37940 (10885), 29205 (368). ^{1}H NMR ($CDCl_3$): δ 3.0–4.4 (m). ^{195}Pt NMR (CH_2Cl_2): δ −4501. $^{125}Te\{^1H\}$ NMR (CH_2Cl_2): δ 394 ($^1J(^{195}Pt–^{125}Te)$ = 975 Hz).

[PdCl$_2${[9]aneO$_2$Te}$_2$]

Made similarly from $PdCl_2$ and [9]aneO$_2$Te in MeCN. Yield 65% (Found: C, 21.9; H, 3.3. Calc. for $C_{12}H_{24}Cl_2O_4PdTe_2$: C, 21.7; H, 3.6%). ν(Pd–Cl)/cm^{-1}: 305, 283. UV/vis (CH_2Cl_2) $\tilde{\nu}_{max}$/cm^{-1}(ε_{mol}/dm^3 mol^{-1} cm^{-1}): 30490 (7810), 26710 (1862). ^{1}H NMR ($CDCl_3$): δ 2.9–4.3 (m). $^{125}Te\{^1H\}$ NMR (CH_2Cl_2): δ 387.

[RhCl$_2${[18]aneO$_4$Te$_2$}$_2$]Cl

A solution of [18]aneO$_4$Te$_2$ (0.10 g, 0.2 mmol) in CH_2Cl_2 (20 cm^3) was added to a solution of $RhCl_3\cdot3H_2O$ (0.027 g, 0.1 mmol) in EtOH (100 cm^3) and the mixture stirred at room temperature overnight before concentrating to *ca.* 10 cm^3. Diethyl ether was added dropwise to form an orange precipitate, which was filtered off and dried *in vacuo*. Yield 0.06 g, 48% (Found: C, 24.5; H, 3.8; calc. for $C_{24}H_{48}Cl_3O_8RhTe_4$: C, 24.3; H, 4.1%). ^{1}H NMR ($CDCl_3$): δ 3.0–4.5 (m). ν(Rh–Cl)/cm^{-1}: 335, 324. UV/vis (CH_2Cl_2) $\tilde{\nu}_{max}$/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 28820 (880). ES$^+$ mass spectrum m/z 1154; calc. for $[C_{24}H_{48}{}^{35}Cl_2O_8Rh^{130}Te_4]^+$ 1158.

The corresponding PF_6^- salt was made using a similar reaction in the presence of $[NH_4][PF_6]$ (0.1 mmol) and was spectroscopically very similar.

$[Cu\{[18]aneO_4Te_2\}_2]BF_4$

$[Cu(MeCN)_4]BF_4$ (0.043 g, 0.14 mmol) was added to a solution of $[18]aneO_4Te_2$ (0.15 g, 0.31 mmol) in CH_2Cl_2 (10 cm^3) and the mixture stirred at room temperature overnight. The mixture was then concentrated to *ca*. 5 cm^3 and precipitated by addition of Et_2O. The precipitate was filtered off and dried *in vacuo* to produce an orange–brown waxy solid. Yield 0.13 g, 85% (Found: C, 25.3; H, 4.3; calc. for $C_{24}H_{48}BCuF_4O_8Te_4$: C, 25.6; H, 4.3%). ^1H NMR ($CDCl_3$): δ 2.9 (t) [H] CH_2Te, 3.6 (s), 3.8 (t) [4H] CH_2O. $^{125}Te\{^1H\}$ NMR (CH_2Cl_2): δ 166. ^{63}Cu NMR (with excess $[18]aneO_4Te_2$ added): δ −59. IR (CsI disk)/cm^{-1}: 1080vs br, 524m. ES^+ mass spectrum: *m*/*z* 1039; calc. for $[C_{24}H_{48}{}^{63}CuO_8{}^{130}Te_4]^+$ 1047.

$[Ag\{[18]aneO_4Te_2\}_2]BF_4$

A solution of $AgBF_4$ (0.027 g, 0.15 mmol) was added to a solution of $[18]aneO_4Te_2$ (0.15 g, 0.31 mmol in CH_2Cl_2 (10 cm^3) and the mixture stirred at room temperature in a foil-wrapped flask for 2 h. The solution was concentrated to *ca*. 5 cm^3 and pipetted into Et_2O to give an pale orange solid. Yield 0.115 g, 72% (Found: C, 25.3; H, 4.3; calc. for: $C_{24}H_{48}AgBF_4O_8Te_4$: C, 24.6; H, 4.1%). ^1H NMR ($CDCl_3$): δ 2.95 (m) [H] CH_2Te, 3.55 (m), 3.85 (m) [4H] CH_2O. $^{125}Te\{^1H\}$ NMR (CH_2Cl_2): δ 140 ($w_{1/2}$ = 1500 Hz). IR (CsI disk)/cm^{-1}: 1086vs, 526m. ES^+ mass spectrum: *m*/*z* 1085; calc. for $[C_{24}H_{48}{}^{109}AgO_8{}^{130}Te_4]^+$ 1093.

X-Ray crystallography

Details of the crystallographic parameters are given in Table 4. Crystals of $[PtCl_2\{[18]aneO_4Se_2\}]$ and $[PdCl_2\{[18]aneO_4Te_2\}]$ were grown by slow evaporation from a solution of the complex in CH_2Cl_2, while crystals of $[PtCl_2\{[18]aneO_4Te_2\}]$ were from slow evaporation from a solution in MeOH. Data collection used a Nonius CCD diffractometer equipped with an Oxford Systems open-flow cryostat operating at 120 K, using graphite-monochromated Mo–Kα X-radiation (λ = 0.71073 Å). Structure solution and refinement were generally routine,[35–38] although the quality of the data for the two telluroether complexes were better than for the selenoether derivative.

CCDC reference numbers 207103–207105.

See http://www.rsc.org/suppdata/dt/b3/b303365c/ for crystallographic data in CIF or other electronic format.

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