Synthesis and Characterisation of Palladium(II) Complexes of Mixed Thioether/Oxa Ionophores. Crystal Structures of $[PdCl_2([18]aneS_2O_4)]$, $[Pd([18]aneS_2O_4)_2][PF_6]_2$ ($[18]aneS_2O_4$ = 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane) and $[Pd([18]aneS_3O_3)_2][PF_6]_2$ ($[18]aneS_3O_3$ = 1,4,7-trioxa-10,13,16-trithiacyclooctadecane) †

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The palladium(II) complexes *cis*-$[PdCl_2([18]aneS_2O_4)]$, $[Pd([18]aneS_2O_4)_2][PF_6]_2$ ($[18]aneS_2O_4$ = 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane), $[Pd([18]aneS_3O_3)_2][PF_6]_2$ ($[18]aneS_3O_3$ = 1,4,7-trioxa-10,13,16-trithiacyclooctadecane) and $[PdCl([20]aneS_3O_3)]BPh_4$ ($[20]aneS_3O_3$ = 1,4,7-trioxa-10,14,18-trithiacycloicosane) have been synthesised and characterised. Reaction of $PdCl_2$ with 1 molar equivalent of $[18]aneS_2O_4$ afforded *cis*-$[PdCl_2([18]aneS_2O_4)]$; addition of a second equivalent gave the bis complex cation $[Pd([18]aneS_2O_4)_2]^{2+}$. The crystal structure of *cis*-$[PdCl_2([18]aneS_2O_4)]$ showed the Pd^{II} in a square-planar co-ordination geometry with mutually *cis* Cl^- ligands, Pd–S(1) 2.276(2), Pd–S(4) 2.2786(14), Pd–Cl(1) 2.307(2), Pd–Cl(2) 2.3100(14) Å, Cl(1)–Pd–Cl(2) 92.12(5), Cl(1)–Pd–S(1) 176.33(5), Cl(1)–Pd–S(4) 87.76(5), Cl(2)–Pd–S(1) 91.19(4) Cl(2)–Pd–S(4) 179.24(4) and S(1)–Pd–S(4) 88.96(4)°. The near-planar macrocycle co-ordinates as a bidentate chelating ligand *via* the *exo* oriented S-donor atoms leaving the *endo* oriented O atoms free. The SCH_2CH_2S moiety adopts a *gauche* conformation [S(1)–C(2)–C(3)–S(4) −58.3(4)°] with the ethylene bridge occupying part of the macrocyclic cavity. The crystal structure of $[Pd([18]aneS_2O_4)_2][PF_6]_2$ showed the Pd^{II} occupying a crystallographic inversion centre, with square-planar co-ordination by the $[18]aneS_2O_4$ ionophores through the thioether S donors, Pd–S(1) 2.3217(14), Pd–S(4) 2.3102(13) Å and S(1)–Pd–S(4) 88.71(5)°. The conformation of the macrocycle is very similar to that found in *cis*-$[PdCl_2([18]aneS_2O_4)]$, with the O atoms in *endo* orientations. Reaction of $PdCl_2$ with 2 equivalents of $[18]aneS_3O_3$ afforded $[Pd([18]aneS_3O_3)_2][PF_6]_2$ which has the Pd^{II} occupying a crystallographic inversion centre, with square-planar co-ordination by the $[18]aneS_3O_3$ ligands *via* two of their three thioether S-donor atoms, Pd–S(1) 2.308(2), Pd–S(4) 2.319(2) Å, S(1)–Pd–S(4) 88.33(8)°. The structure exhibits some disorder in the polyether/thioether chain which was modelled in terms of two half-occupied orientations. In one component of the disorder the third S-donor atom of each ligand exhibits a long-range apical interaction with the Pd^{II}, Pd···S(16) 3.290(2) Å. Reaction of $PdCl_2$ with 1 equivalent of $[20]aneS_3O_3$ afforded the monocation $[PdCl([20]aneS_3O_3)]^+$.

Mixed O/S-donor ionophores feature hard and soft binding sites in close proximity within the same macrocyclic cavity. They therefore have the potential to co-ordinate to both hard and soft guest ions or molecules, and should allow for simultaneous co-ordination of two different guests. The concept of simultaneous co-ordination has important implications for the development of responsive macrocyclic complexes, for instance in the area of chemical sensing.[1,2] In addition, mixed S/O ionophores have potential as extractants for heavy metal ions.[3–5] We are interested to establish whether mixed O/S-donor macrocyclic hosts containing transition-metal ions as the responsive centre could be used to co-ordinate to other guest ions or molecules, and report herein initial results of our investigation of palladium(II) complexes with mixed O/S-donor ionophores.

There have been a few reports of complexes between $PdCl_2$ and mixed O/S-donor ionophores, such as $[Pd([15]aneS_2O_3)_2]^{2+}$[6] ($[15]aneS_2O_3$ = 1,4,7-trioxa-10,13-dithiacyclopentadecane), $[Pd([18]aneS_2O_4)_2]^{2+}$[7] ($[18]aneS_2O_4$ = 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane) and *cis*-$[PdX_2(7,16\text{-}[18]aneS_2O_4)]$ (X = Cl[8] or NO_3;[7] 7,16-$[18]aneS_2O_4$ = 1,4,10,13-tetraoxa-7,16-dithiacyclooctadecane). All these complexes show a square-planar co-ordination geometry at the Pd^{II} with the macrocycles adopting *exo* bidentate co-ordination modes. We were interested in establishing the factors which influence *exo* or *endo* co-ordination of platinum-group metal centres to these ionophores.

Results and Discussion

The reaction of $PdCl_2$ with 1 molar equivalent of $[18]aneS_2O_4$[9,10] in refluxing MeOH–water affords a yellow solution from which orange crystals can be isolated upon cooling. The presence of the ligand in the product was confirmed by infrared and ^1H NMR spectroscopy. The FAB mass spectrum shows a low-intensity peak with the correct isotopic distribution assigned to $[^{106}Pd^{35}Cl_2([18]aneS_2O_4) - H]^+$. Two additional strong peaks assigned to fragments $[^{106}Pd^{35}Cl([18]aneS_2O_4)]^+$ and $[^{106}Pd([18]aneS_2O_4)]^+$ are also observed. Analytical data confirmed a 1:1 Pd:$[18]aneS_2O_4$ stoichiometry for the complex. Peaks at 340 and 320 cm^{-1} in the infrared spectrum were assigned to the Pd–Cl stretching

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vibration, ν(Pd–Cl), of a *cis*-dichloro complex.[6] This assignment is complicated by the possible presence of Pd–S vibrations. The single-crystal structure of $[PdCl_2([18]aneS_2O_4)]$ **1** (Fig. 1, Table 1) confirms *cis* binding of Cl^- ions and shows the Pd^{II} adopting the expected square-planar co-ordination geometry. The Pd–S distances, Pd–S(1) 2.276(2) and Pd–S(4) 2.2786(14) Å, are on average 0.039 Å shorter than those in $[Pd([18]aneS_2O_4)_2]^{2+}$ (see below), suggesting that π-back donation from the Pd^{II} ion to the S atoms may be occurring with π donation from the Cl^- to the Pd^{II}. The macrocyclic ligand binds to the Pd^{II} as a bidentate chelate through the two S donors, leaving the O atoms non-interacting but pointing towards the centre of the cavity of the ionophore. The conformation of the macrocycle in this complex is largely unchanged from that of the free macrocycle in the solid state.[10,11] All C–O–C–C torsion angles are *anti* and O–C–C–O arrangements *gauche*.

The complex $[Pd([18]aneS_2O_4)_2][PF_6]_2$ **2** was prepared by following the same procedure as for **1** but with a 1:2 Pd:ligand ratio and addition of an excess of NH_4PF_6. A yellow microcrystalline powder precipitated on cooling. The FAB mass spectrum shows a molecular ion peak (m/z = 843) with the correct isotopic distribution corresponding to $[^{106}Pd([18]aneS_2O_4)_2(PF_6)]^+$. The assignment of the compound was confirmed by IR spectroscopy and microanalytical data. Attempts to prepare the analogous BPh_4^- salt failed due to decomposition upon attempted recrystallisation from Me_2CO, MeCN, $MeNO_2$ or Me_2SO. A similar observation has been made for the analogous complex with $[15]aneS_2O_3$, $[Pd([15]aneS_2O_3)_2][PF_6]_2$,[6] suggesting that the Pd^{II} is exposed and accessible to redox reactions. The analogous dinitrate salt has, however, been reported by Izatt *et al.*[7] Single crystals of **2** suitable for X-ray diffraction studies were obtained by recrystallisation from $MeNO_2$. The single-crystal structure (Fig. 2, Table 2) shows the expected square-planar co-ordination geometry, Pd–S(1) 2.3217(14), Pd–S(4) 2.3102(13) Å, S(1)–Pd–S(4) 88.71(5)°, with the Pd^{II} occupying a crystallographic inversion centre. The conformation of the macrocycle in this complex is again very similar to that of the free

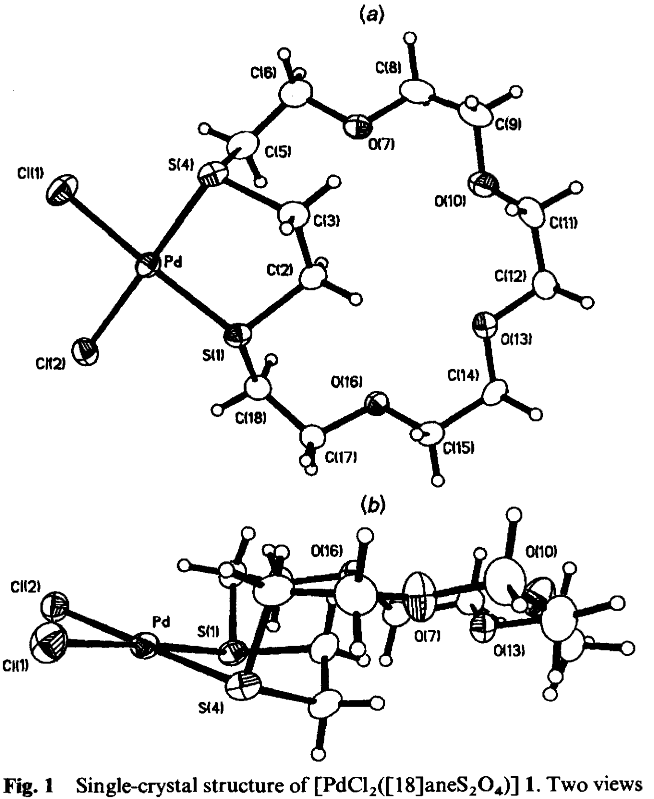

Fig. 1 Single-crystal structure of $[PdCl_2([18]aneS_2O_4)]$ **1**. Two views with the numbering scheme adopted. Thermal ellipsoids enclose 30% probability surfaces and hydrogen atoms are drawn as spheres with arbitrary radii

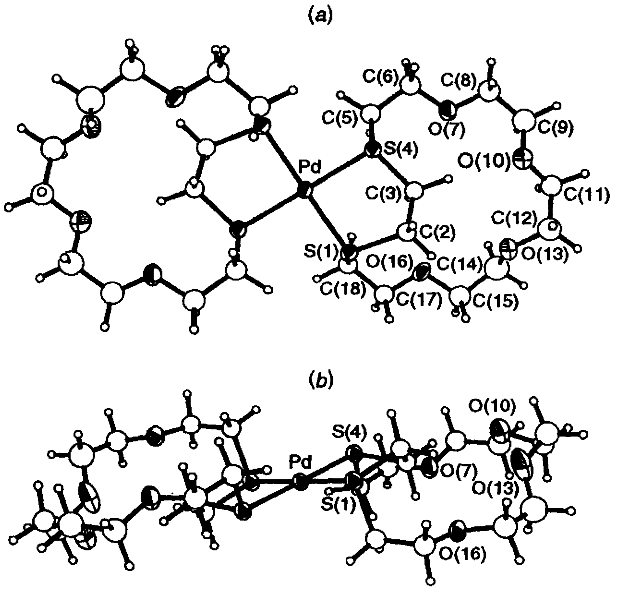

Fig. 2 Single-crystal structure of $[Pd([18]aneS_2O_4)_2]^{2+}$ **2**. Details as in Fig. 1

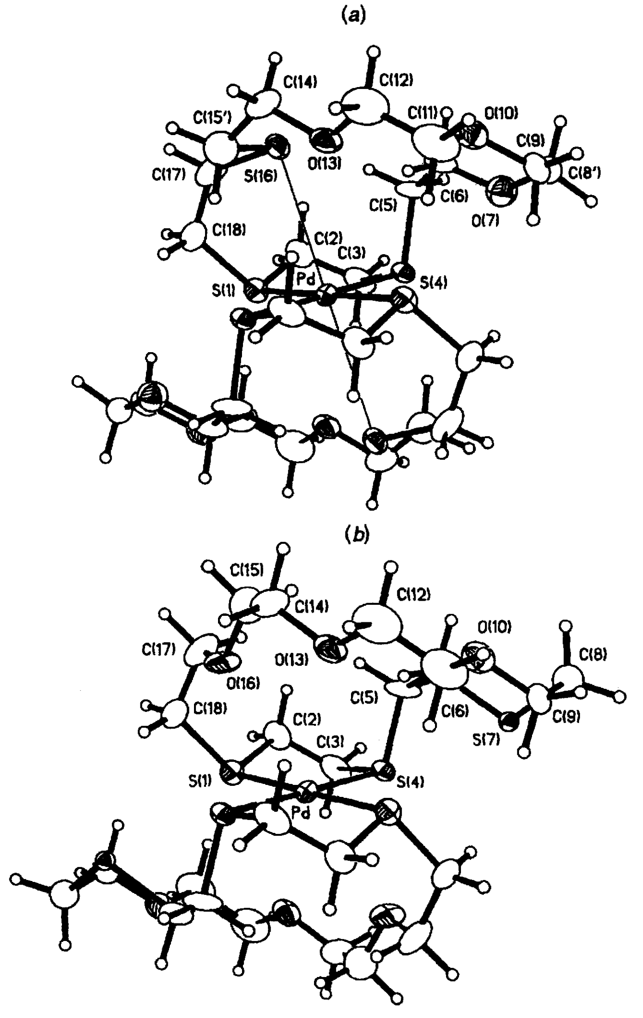

Fig. 3 Single-crystal structure of $[Pd([18]aneS_3O_3)_2]^{2+}$ **3**. Two views illustrating the disorder with the numbering scheme adopted. Other details as in Fig. 1

Table 1 Bond lengths (Å), angles (°) and torsion angles (°) with estimated standard deviations (e.s.d.s) in parentheses for [PdCl$_2$([18]aneS$_2$O$_4$)] **1**

Pd-S(1)	2.276(2)	O(7)-C(8)	1.411(8)
Pd-S(4)	2.2786(14)	O(7')-C(8)	1.50(3)
Pd-Cl(1)	2.307(2)	C(8)-C(9)	1.421(9)
Pd-Cl(2)	2.3100(14)	C(9)-O(10)	1.430(7)
S(1)-C(2)	1.819(5)	O(10)-C(11)	1.400(6)
S(1)-C(18)	1.820(5)	C(11)-C(12)	1.486(7)
C(2)-C(3)	1.503(7)	C(12)-O(13)	1.421(6)
C(3)-S(4)	1.816(5)	O(13)-C(14)	1.420(6)
S(4)-C(5)	1.823(5)	C(14)-C(15)	1.498(7)
C(5)-C(6)	1.495(8)	C(15)-O(16)	1.423(6)
C(6)-O(7)	1.426(8)	O(16)-C(17)	1.426(6)
C(6)-O(7')	1.46(3)	C(17)-C(18)	1.496(7)
Cl(1)-Pd-Cl(2)	92.12(5)	C(8)-O(7)-C(6)	115.4(5)
S(1)-Pd-S(4)	88.96(4)	C(6)-O(7')-C(8)	109(2)
S(1)-Pd-Cl(1)	176.33(5)	O(7)-C(8)-C(9)	110.6(5)
S(4)-Pd-Cl(1)	87.76(5)	C(9)-C(8)-O(7')	107.9(12)
S(1)-Pd-Cl(2)	91.19(4)	C(8)-C(9)-O(10)	112.3(5)
S(4)-Pd-Cl(2)	179.24(4)	C(11)-O(10)-C(9)	111.6(4)
C(18)-S(1)-Pd	111.3(2)	O(10)-C(11)-C(12)	111.2(4)
C(2)-S(1)-Pd	101.8(2)	O(13)-C(12)-C(11)	109.9(4)
C(3)-S(4)-Pd	102.5(2)	C(14)-O(13)-C(12)	111.9(4)
C(5)-S(4)-Pd	101.5(2)	O(13)-C(14)-C(15)	109.1(4)
C(3)-C(2)-S(1)	107.4(4)	O(16)-C(15)-C(14)	108.0(4)
C(2)-C(3)-S(4)	111.8(3)	C(15)-O(16)-C(17)	113.8(4)
C(3)-S(4)-C(5)	103.6(2)	O(16)-C(17)-C(18)	109.0(4)
C(6)-C(5)-S(4)	113.6(4)	C(17)-C(18)-S(1)	111.6(3)
O(7)-C(6)-C(5)	104.7(4)	C(2)-S(1)-C(18)	103.0(2)
O(7')-C(6)-C(5)	128(2)		
C(18)-S(1)-C(2)-C(3)	164.3(3)	O(7')-C(8)-C(9)-O(10)	95(2)
S(1)-C(2)-C(3)-S(4)	-58.3(4)	C(8)-C(9)-O(10)-C(11)	-163.5(5)
C(2)-C(3)-S(4)-C(5)	-67.9(4)	C(9)-O(10)-C(11)-C(12)	-174.0(5)
C(3)-S(4)-C(5)-C(6)	-64.6(4)	O(10)-C(11)-C(12)-O(13)	-72.3(5)
S(4)-C(5)-C(6)-O(7)	77.6(6)	C(11)-C(12)-O(13)-C(14)	176.9(4)
S(4)-C(5)-C(6)-O(7')	40(2)	C(12)-O(13)-C(14)-C(15)	179.6(4)
C(5)-C(6)-O(7)-C(8)	165.2(6)	O(13)-C(14)-C(15)-O(16)	65.7(5)
C(5)-C(6)-O(7')-C(8)	118(2)	C(14)-C(15)-O(16)-C(17)	-179.8(4)
C(6)-O(7)-C(8)-C(9)	154.2(6)	C(15)-O(16)-C(17)-C(18)	148.0(4)
C(6)-O(7')-C(8)-C(9)	-155(2)	O(16)-C(17)-C(18)-S(1)	-76.1(5)
O(7)-C(8)-C(9)-O(10)	53.4(8)	C(2)-S(1)-C(18)-C(17)	75.3(4)

macrocycle and in **1**. The co-ordination geometry at the Pd^{II} in the dinitrate compound is square planar with Pd–S distances of 2.304(3)–2.308(3) Å and S–Pd–S angles close to 90 and 180°.[7]

The results for complexes **1** and **2** confirm that enlargement of the macrocyclic cavity on going from [15]aneS$_2$O$_3$ to [18]aneS$_2$O$_4$ does not of itself yield *endo* co-ordination of Pd^{II}. It seems more likely that the hard O-donor environment within the macrocyclic cavity renders in-cavity co-ordination to Pd^{II} unfavourable. We therefore investigated the binding of related ionophores [18]aneS$_3$O$_3$ (1,4,7-trioxa-10,13,16-trithiacyclooctadecane) and the larger macrocycle [20]aneS$_3$O$_3$ (1,4,7-trioxa-10,14,18-trithiacycloicosane) in order to ascertain whether *endo* co-ordination to Pd^{II} is observed.

Reaction of [18]aneS$_3$O$_3$[12] with PdCl$_2$ in refluxing MeOH–water yielded a dark orange resin after addition of NH$_4$PF$_6$ and removal of the solvent. Purification was achieved by repeated recrystallisation from Me$_2$CO although this diminished the yield drastically. The FAB mass spectrum of the product shows peaks with the correct isotopic distribution corresponding to [^{106}Pd([18]aneS$_3$O$_3$)$_2$(PF$_6$)]$^+$ and [^{106}Pd([18]aneS$_3$O$_3$)]$^+$. Analytical data were in good agreement with a 1:2 Pd:[18]aneS$_3$O$_3$ stoichiometry.

In the crystal structure of [Pd([18]aneS$_3$O$_3$)$_2$][PF$_6$]$_2$ **3** (Fig. 3, Table 3) the Pd^{II} occupies a crystallographic inversion centre: each asymmetric unit therefore contains one macrocycle co-ordinated to the metal. As seen for **2**, **3** exhibits a square-planar co-ordination geometry at the Pd^{II}, Pd–S$_{eq}$ 2.308(2) and 2.319(2) Å, S(1)–Pd–S(4) 88.33(8)°, even though each [18]aneS$_3$O$_3$ macrocycle contains an additional S donor compared to [18]aneS$_2$O$_4$. The structure of **3** shows some disorder which may result from the two additional S donors. Since only two of the three S donors per ligand co-ordinate to the Pd^{II}, there is a 50:50 statistical probability of finding the third S atom on the 'left'- or 'right'-hand side of the molecule. This disorder affects not only the third S but also an O atom and part of the linking methylene group. The disorder was successfully modelled with site occupancies of 0.5 for each distinct orientation. The position of the S atom in relation to the Pd^{II} is, however, different in each of the disordered sites. Fig. 3(*a*) and 3(*b*) illustrate that S(16) [Pd $\cdots$ S(16)$_{ap}$ 3.290(2) Å], in contrast to its equivalent S(7) [Pd $\cdots$ S(7) 4.374(2) Å], participates in a long-range apical interaction with the Pd^{II}. None of the O atoms interacts with the Pd^{II}.

Complexation of Pd^{II} by [12]aneS$_4$ (1,4,7,10-tetrathiacyclododecane), [14]aneS$_4$ (1,4,8,11-tetrathiacyclotetradecane) and [16]aneS$_4$ (1,5,9,13-tetrathiacyclohexadecane) confirms a complementarity between the metal ion and soft thioether S donors. The Pd^{II} in [Pd([12]aneS$_4$)]$^{2+}$ is displaced out of the S$_4$ best-fit plane by 0.3116 Å, but the displacement becomes smaller on going from [Pd([12]aneS$_4$)]$^{2+}$ to [Pd([14]aneS$_4$)]$^{2+}$ to [Pd([16]aneS$_4$)]$^{2+}$.[13] Related long-range apical interactions to Pd^{II} have been observed in [Pd([9]aneS$_3$)$_2$]$^{2+}$,[14] [Pd([9]aneS$_3$)X$_2$] (X = Cl or Br),[15] [Pd([9]aneS$_3$)L$_2$]$^{2+}$ {L = PPh$_3$, $\frac{1}{2}$bipy (2,2'-bipyridine), $\frac{1}{2}$phen (1,10-phenanthroline);[16] [9]aneS$_3$ = 1,4,7-trithiacyclononane} and [Pd([18]aneS$_6$)]$^{2+}$ ([18]aneS$_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane).[17]

Table 2 Bond lengths (Å), angles (°) and torsion angles (°) with e.s.d.s in parentheses for $[Pd([18]aneS_2O_4)_2][PF_6]_2$ **2**

Pd–S(1)	2.3217(14)	O(10)–C(11)	1.431(5)
Pd–S(4)	2.3102(13)	O(10)–C(11′)	1.426(9)
S(1)–C(2)	1.819(5)	C(11)–C(12)	1.520(5)
S(1)–C(18)	1.813(5)	C(11′)–C(12′)	1.521(11)
C(2)–C(3)	1.498(7)	C(12)–O(13)	1.429(5)
C(3)–S(4)	1.825(5)	C(12′)–O(13)	1.560(9)
S(4)–C(5)	1.816(5)	O(13)–C(14)	1.401(8)
C(5)–C(6)	1.508(8)	C(14)–C(15)	1.464(9)
C(6)–O(7)	1.413(7)	C(15)–O(16)	1.431(7)
O(7)–C(8)	1.400(7)	O(16)–C(17)	1.391(7)
C(8)–C(9)	1.481(9)	C(17)–C(18)	1.517(7)
C(9)–O(10)	1.428(7)		
S(1)–Pd–S(4)	88.71(5)	C(9)–O(10)–C(11′)	126.3(5)
Pd–S(1)–C(2)	101.16(16)	O(10)–C(11)–C(12)	104.0(3)
Pd–S(1)–C(18)	102.85(17)	O(10)–C(11′)–C(12′)	107.2(6)
Pd–S(4)–C(3)	102.53(16)	C(11)–C(12)–O(13)	110.5(3)
Pd–S(4)–C(5)	109.74(18)	O(13)–C(12′)–C(11′)	97.9(6)
S(1)–C(2)–C(3)	112.4(3)	C(12)–O(13)–C(14)	128.9(4)
C(2)–C(3)–S(4)	108.2(3)	C(12′)–O(13)–C(14)	92.4(5)
C(3)–S(4)–C(5)	103.9(2)	O(13)–C(14)–C(15)	110.7(5)
S(4)–C(5)–C(6)	110.4(4)	C(14)–C(15)–O(16)	108.2(5)
C(5)–C(6)–O(7)	107.4(4)	C(15)–O(16)–C(17)	114.0(4)
C(6)–O(7)–C(8)	114.5(4)	O(16)–C(17)–C(18)	107.6(4)
O(7)–C(8)–C(9)	108.6(5)	C(17)–C(18)–S(1)	112.7(4)
C(8)–C(9)–O(10)	108.8(5)	C(18)–S(1)–C(2)	104.5(2)
C(9)–O(10)–C(11)	100.9(4)		
S(1)–C(2)–C(3)–S(4)	59.5(4)	O(10)–C(11′)–C(12′)–O(13)	−83.3(6)
C(2)–C(3)–S(4)–C(5)	−158.7(3)	C(11)–C(12)–O(13)–C(14)	77.6(3)
C(3)–S(4)–C(5)–C(6)	−77.5(4)	C(11′)–C(12′)–O(13)–C(14)	172.4(5)
S(4)–C(5)–C(6)–O(7)	67.6(5)	C(12)–O(13)–C(14)–C(15)	160.6(4)
C(5)–C(6)–O(7)–C(8)	−161.5(4)	C(12′)–O(13)–C(14)–C(15)	−175.1(5)
C(6)–O(7)–C(8)–C(9)	−178.1(5)	O(13)–C(14)–C(15)–O(16)	68.8(6)
O(7)–C(8)–C(9)–O(10)	−63.8(6)	C(14)–C(15)–O(16)–C(17)	−176.9(5)
C(8)–C(9)–O(10)–C(11)	169.0(4)	C(15)–O(16)–C(17)–C(18)	169.5(4)
C(8)–C(9)–O(10)–C(11′)	−168.3(5)	O(16)–C(17)–C(18)–S(1)	−80.9(4)
C(9)–O(10)–C(11)–C(12)	−176.4(3)	C(17)–C(18)–S(1)–C(2)	56.4(4)
C(9)–O(10)–C(11′)–C(12′)	−87.5(7)	C(18)–S(1)–C(2)–C(3)	64.2(4)
O(10)–C(11)–C(12)–O(13)	75.7(3)		

Formal replacement of two ethylene bridges in $[18]aneS_3O_3$ by trimethylene bridges gives $[20]aneS_3O_3$. We anticipated that this compound might adopt tridentate co-ordination towards Pd^{II} without causing a strained geometry, although all S–Pd–S chelating angles in compounds **1**–**3** are somewhat less than the ideal angle of 90°. Reaction of $PdCl_2$ with $[20]aneS_3O_3$ in refluxing MeOH–water and addition of $NaBPh_4$ afforded an orange microcrystalline solid which could be recrystallised from Me_2CO without decomposition. The BPh_4^- salts of other palladium(II) complexes with mixed O/S-donor ionophores deteriorate rapidly in solution.[6] The enhanced stability of $[PdCl([20]aneS_3O_3)]BPh_4$ **4** suggests a more enclosed and protected environment for the Pd^{II}. Microanalytical results and mass spectrometric studies confirmed the formulation of **4** as a monocationic 1 : 1 Pd : $[20]aneS_3O_3$ complex with possible *endo* co-ordinated Pd^{II} in the macrocyclic cavity. We anticipate that the Pd^{II} binds to one Cl and three S donors consistent with the orange colour (an S_4 donor set gives yellow materials). Unfortunately we have been unable to isolate single crystals of **4** suitable for X-ray diffraction studies: we would like to establish the structure to confirm *endo* co-ordination of the $PdCl^+$ fragment.

These results show that it is possible to design mixed O/S-donor ionophores to co-ordinate *exo* as well as *endo* to Pd^{II}. The trimethylene-bridged S_3 moiety could be a key element in the design of potentially stable palladium(II) macrocyclic hosts containing S/O ionophores. Current work is aimed at the investigation of metal complexes with the related large-ring ionophores.

Experimental

Infrared spectra were measured as KBr discs or between KBr plates using Perkin-Elmer 598 and FT-1600 spectrometers over the range 400–4000 cm^{-1}, electronic spectra in quartz cells using a Perkin-Elmer Lambda 9 spectrophotometer. Microanalyses were performed by the Edinburgh University Chemistry Department microanalytical service. Mass spectra were run by fast-atom bombardment on a Kratos MS50TC spectrometer, ^1H and ^{13}C NMR spectra on Bruker WP200, AC250 and WH360 instruments. The compounds $[18]aneS_2O_4$ and $[18]aneS_3O_3$ were prepared following the methods reported by Bradshaw and co-workers.[9,10,12]

$[PdCl_2([18]aneS_2O_4)]$ **1**.—Treatment of $PdCl_2$ (40 mg, 0.226 mmol) with $[18]aneS_2O_4$ (67 mg, 0.226 mmol) in refluxing MeOH–water (1 : 1 v/v, 35 cm^3) for 2 h under dinitrogen afforded a bright yellow solution. The reaction mixture was filtered while hot and the orange crystals which precipitated upon cooling were isolated, dried and characterised (yield: 55 mg, 50%) (Found: C, 30.2; H, 5.15. Calc. for $C_{12}H_{24}Cl_2O_4PdS_2$: C, 30.4; H, 5.10%). Fast-atom bombardment mass spectrum (3-nitrobenzyl alcohol matrix): *m*/*z* 437 and 402; calc. for $[^{106}Pd^{35}Cl([18]aneS_2O_4)]^+$ 439, $[^{106}Pd([18]aneS_2O_4)]^+$ 402. ^1H NMR (CD_3NO_2, 298 K, 200.13 MHz): δ 3.00–4.25 (m, CH_2, 24 H). Infrared spectrum (KBr disc): 2960m, 2900m, 1480m, 1440m, 1420m, 1400m, 1360m, 1350m, 1340m, 1290m, 1250m, 1180w, 1105s, 1020w, 940m, 920m, 840m, 340w and 320w cm^{-1}.

Table 3 Bond lengths (Å), angles (°) and torsion angles (°) with e.s.d.s in parentheses for $[Pd([18]aneS_3O_3)_2][PF_6]_2$ **3**

Pd–S(1)	2.308(2)	C(9)–O(10)	1.427(12)
Pd–S(4)	2.319(2)	O(10)–C(11)	1.424(13)
S(1)–C(2)	1.828(9)	C(11)–C(12)	1.486(17)
C(2)–C(3)	1.492(13)	C(12)–O(13)	1.416(14)
C(3)–S(4)	1.821(10)	O(13)–C(14)	1.434(13)
S(4)–C(5)	1.832(10)	C(14)–C(15)	1.52(2)
C(5)–C(6)	1.480(13)	C(14)–C(15′)	1.52(2)
C(6)–S(7)	1.828(10)	C(15)–O(16)	1.42(2)
C(6)–O(7)	1.421(16)	C(15′)–S(16)	1.830(15)
S(7)–C(8)	1.830(14)	O(16)–C(17)	1.420(15)
O(7)–C(8′)	1.42(2)	S(16)–C(17)	1.830(10)
C(8)–C(9)	1.520(16)	C(17)–C(18)	1.523(14)
C(8′)–C(9)	1.52(2)	C(18)–S(1)	1.826(11)
S(1)–Pd–S(4)	88.33(8)	C(8′)–C(9)–O(10)	105.5(9)
Pd–S(1)–C(18)	110.3(3)	C(9)–O(10)–C(11)	114.8(8)
Pd–S(1)–C(2)	102.9(3)	O(10)–C(11)–C(12)	108.6(9)
Pd–S(4)–C(3)	101.2(3)	C(11)–C(12)–O(13)	108.6(10)
Pd–S(4)–C(5)	105.9(3)	C(12)–O(13)–C(14)	110.7(8)
S(1)–C(2)–C(3)	107.4(6)	O(13)–C(14)–C(15)	110.2(10)
C(2)–C(3)–S(4)	112.4(7)	O(13)–C(14)–C(15′)	108.2(9)
C(3)–S(4)–C(5)	100.4(4)	C(14)–C(15)–O(16)	124.0(13)
S(4)–C(5)–C(6)	114.1(7)	C(14)–C(15′)–S(16)	96.4(9)
C(5)–C(6)–S(7)	106.0(6)	C(15)–O(16)–C(17)	114.9(11)
C(5)–C(6)–O(7)	108.8(9)	C(15′)–S(16)–C(17)	88.9(6)
C(6)–S(7)–C(8)	104.4(6)	O(16)–C(17)–C(18)	101.8(8)
C(6)–O(7)–C(8′)	122.8(11)	S(16)–C(17)–C(18)	125.8(7)
S(7)–C(8)–C(9)	101.0(8)	C(17)–C(18)–S(1)	116.9(7)
O(7)–C(8′)–C(9)	125.5(13)	C(18)–S(1)–C(2)	103.3(5)
C(8)–C(9)–O(10)	110.7(8)		
S(1)–C(2)–C(3)–S(4)	−60.0(7)	O(10)–C(11)–C(12)–O(13)	64.8(11)
C(2)–C(3)–S(4)–C(5)	−65.7(7)	C(11)–C(12)–O(13)–C(14)	−173.9(9)
C(3)–S(4)–C(5)–C(6)	169.5(7)	C(12)–O(13)–C(14)–C(15)	150.4(10)
S(4)–C(5)–C(6)–S(7)	55.3(8)	C(12)–O(13)–C(14)–C(15′)	−167.7(9)
S(4)–C(5)–C(6)–O(7)	57.6(10)	O(13)–C(14)–C(15)–O(16)	65.0(17)
C(5)–C(6)–S(7)–C(8)	161.9(7)	O(13)–C(14)–C(15′)–S(16)	−67.5(9)
C(5)–C(6)–O(7)–C(8′)	172.6(12)	C(14)–C(15)–O(16)–C(17)	173.7(12)
C(6)–S(7)–C(8)–C(9)	79.0(8)	C(14)–C(15′)–S(16)–C(17)	−160.9(8)
C(6)–O(7)–C(8′)–C(9)	61(2)	C(15)–O(16)–C(17)–C(18)	−175.2(11)
S(7)–C(8)–C(9)–O(10)	−78.6(9)	C(15′)–S(16)–C(17)–C(18)	−87.3(9)
O(7)–C(8′)–C(9)–O(10)	−51.0(16)	O(16)–C(17)–C(18)–S(1)	−76.3(9)
C(8)–C(9)–O(10)–C(11)	−177.4(9)	S(16)–C(17)–C(18)–S(1)	−40.4(11)
C(8′)–C(9)–O(10)–C(11)	161.9(9)	C(17)–C(18)–S(1)–C(2)	−55.3(8)
C(9)–O(10)–C(11)–C(12)	−176.7(8)	C(18)–S(1)–C(2)–C(3)	159.9(6)

$[Pd([18]aneS_2O_4)_2][PF_6]_2$ **2**.—Palladium(II) chloride (30 mg, 0.169 mmol) was added to a solution of $[18]aneS_2O_4$ (100 mg, 0.338 mmol) in MeOH–water (35 cm^3, 1 : 1 v/v). The reaction mixture was refluxed for 2 h under N_2 yielding a bright yellow solution to which an excess of NH_4PF_6 was added. A yellow precipitate formed upon cooling to −25 °C: this was isolated, recrystallised from $MeNO_2$ and dried (yield: 105 mg, 63%) (Found: C, 29.1; H, 4.90. Calc. for $C_{24}H_{48}F_{12}O_8P_2PdS_4$: C, 29.1; H, 4.90%). Fast-atom bombardment mass spectrum: *m/z* 843, 697 and 402; calc. for $[^{106}Pd([18]aneS_2O_4)_2(PF_6)]^+$ 843, $[^{106}Pd([18]aneS_2O_4)_2]^+$ 698, $[^{106}Pd([18]aneS_2O_4)]^+$ 404. Infrared spectrum (KBr disc): 3655w, 3510w, 2995m, 2955m, 2900s, 1955w, 1630w, 1475m, 1400m, 1355s, 1290m, 1245m, 1195w, 1120vs, 1095s, 1040m, 935m, 920m, 835vs and 560s cm^{-1}.

$[Pd([18]aneS_3O_3)_2][PF_6]_2$ **3**.—Method as above but using $PdCl_2$ (89 mg, 0.5 mmol) and $[18]aneS_3O_3$ (312 mg, 1.0 mmol) in MeCN–MeOH (20 cm^3, 9 : 1 v/v). Removal of the solvent *in vacuo* yielded an orange residue which was repeatedly recrystallised from MeCN and dried (Found: C, 28.6; H, 4.90. Calc. for $C_{24}H_{48}F_{12}O_6P_2PdS_6$: C, 28.2; H, 4.75%). Fast-atom bombardment mass spectrum: *m/z* 877, 729 and 418; calc. for $[^{106}Pd([18]aneS_3O_3)_2(PF_6)]^+$ 875, $[^{106}Pd([18]aneS_3O_3)_2]^+$ 730, $[^{106}Pd([18]aneS_3O_3)]^+$ 418. Electronic spectrum (MeCN): λ_{max} = 295 nm (ε_{max} 18 000 dm^3 mol^{-1} cm^{-1}).

$[20]aneS_3O_3$.—Commercial EtOH (1 dm^3) was placed in a round-bottom flask (2 dm^3) equipped with a gas inlet, a coiled condenser and a mechanical stirrer. Sodium metal (28 g, 1.2 mol) was slowly added to the stirred EtOH under a stream of N_2 and the clear solution was heated to 70 °C. 4-Thiaheptane-1,7-dithiol (3.64 g, 0.02 mol) and 1,11-dibromo-3,6,9-trioxaundecane (6.36 g, 0.02 mol) in EtOH–$HCONMe_2$ (250 cm^3, 4 : 1 v/v) were added slowly over a period of 48 h. The progress of the reaction was monitored by the appearance of some cloudiness due to precipitation of NaBr. The cold reaction mixture was then carefully neutralised with diluted hydrochloric acid and the solvents were removed *in vacuo*. The remaining NaCl/NaBr slurry was extracted with CH_2Cl_2 (3 × 50 cm^3) and with hexane (3 × 50 cm^3). The solvents were removed leaving the macrocycle as a light yellow oil. ^1H NMR spectrum ($CDCl_3$, 298 K, 250.13 MHz); δ 1.7–1.8 (qnt, CH_2, 4 H), 2.45–2.65 (m, CH_2S, 12 H) and 3.4–3.7 (m, CH_2O, 12 H). IR spectrum (film between KBr plates): 2915s, 2865s, 1445m, 1350m, 1295m, 1250m, 1115vs, 800w, 670w and 570w cm^{-1}.

Table 4 Experimental data for single-crystal structure determinations of $[PdCl_2([18]aneS_2O_4)]$ **1**, $[Pd([18]aneS_2O_4)_2][PF_6]_2$ **2** and $[Pd([18]aneS_3O_3)_2][PF_6]_2$ **3**[a]

	1	**2**	**3**
Formula	$C_{12}H_{24}Cl_2O_4PdS_2$	$C_{24}H_{48}F_{12}O_8P_2PdS_4$	$C_{24}H_{48}F_{12}O_6P_2PdS_6$
M	473.7	989.25	1021.7
Crystal size/mm	0.20 × 0.40 × 1.00	0.12 × 0.19 × 0.82	0.12 × 0.23 × 0.35
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$ (alt. $P2_1/c$, no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	8.714(2)	7.7395(15)	8.421(8)
b/Å	10.915(3)	11.618(2)	10.478(8)
c/Å	18.787(8)	11.882(2)	11.243(11)
α/°	90	102.171(12)	76.01(7)
β/°	92.04(3)	95.518(15)	87.10(8)
γ/°	90	103.673(15)	84.61(7)
U/Å^3	1785.00	1002.76	958.00
Z	4	1	1
D_c/g cm^{-3}	1.762	1.638	1.770
μ/mm^{-1}	1.562	0.828	0.967
F(000)	960	504	520
T/K	295	298	150[b]
h,k,l Ranges	−9 to 9, 0–11, 0–20	−8 to 8, −12 to 12, 0–12	−10 to 9, −10 to 11, 0–12
Measured reflections	2496	2632	2490
Independent reflections	2344	2632	2336
Observed reflections $[F \geqslant 4\sigma(F)]$	2073	2306	2050
Full-matrix least-squares refinement on program	F^2 (SHELXL 93)	F (SHELX 76)	F (SHELX 76)
Parameters refined	196	210	241
SHELX 76[c] R,R',S	—	0.045, 0.059, 1.22	0.063, 0.083, 1.10
m In weighting scheme	—	0.000 193	0.000 121
SHELXL 93[d] $R1,wR2,S$	0.046, 0.112, 1.07		
m,n In weighting scheme	0.0848, 1.06		
$(\Delta/\sigma)_{max}$	0.020	0.100	0.002
$\Delta\sigma_{max,min}$/e Å^{-3}	+1.60, −0.59	+0.65, −0.60	+1.26, −1.11

[a] Details in common: Stoë Stadi-4 four-circle diffractometer, ω–2θ scan mode, graphite monochromated Mo-Kα radiation (λ = 0.710 73 Å); $2\theta_{max}$ 45°. [b] Oxford Cryosystems low-temperature device (ref. 20). [c] Ref. 18. Weighting scheme $w^{-1} = \sigma^2(F) + mF^2$, S (goodness of fit) $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$. [d] Ref. 19. Weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (mP)^2 + nP]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$, $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{\frac{1}{2}}$ (N_o = no. of observations; N_p = no. of parameters).

Table 5 Fractional atomic coordinates with e.s.d.s in parentheses for $[PdCl_2([18]aneS_2O_4)]$ **1**

Atom	*x*	*y*	*z*
Pd	0.5328(1)	0.1059(1)	0.2660(1)
Cl(1)	0.3982(2)	0.807(2)	0.1590(1)
Cl(2)	0.4433(1)	0.3037(1)	0.2785(1)
S(1)	0.6765(1)	0.1216(1)	0.3691(1)
C(2)	0.7035(5)	−0.0384(4)	0.3935(3)
C(3)	0.7558(5)	−0.1048(4)	0.3285(3)
S(4)	0.6181(1)	−0.901(1)	0.2542(1)
C(5)	0.4528(5)	−0.1774(5)	0.2826(3)
C(6)	0.4844(7)	−0.3113(5)	0.2917(3)
O(7)	0.5675(7)	−0.3204(4)	0.3582(3)
O(7′)	0.622(3)	−0.369(3)	0.323(2)
C(8)	0.5786(8)	−0.4395(5)	0.3873(4)
C(9)	0.7116(8)	−0.4501(5)	0.4328(4)
O(10)	0.7188(4)	−0.3569(3)	0.4863(2)
C(11)	0.8664(6)	−0.3468(5)	0.5177(3)
C(12)	0.8689(6)	−0.2593(4)	0.5783(3)
O(13)	0.8538(4)	−0.1375(3)	0.5523(2)
C(14)	0.8475(5)	−0.0509(5)	0.6085(2)
C(15)	0.8328(5)	0.0753(4)	0.5776(3)
O(16)	0.6882(4)	0.0832(3)	0.5403(2)
C(17)	0.6596(6)	0.1994(4)	0.5078(3)
C(18)	0.5635(5)	0.1813(4)	0.4411(2)

$[PdCl([20]aneS_3O_3)]BPh_4$ **4**.—Palladium(II) chloride (89 mg, 0.5 mmol) and $[20]aneS_3O_3$ (170 mg, 0.5 mmol) were heated in MeOH–water (5:1 v/v, 12 cm^3) for 2 h under N_2. Addition of an excess of $NaBPh_4$ to the cold reaction mixture, removal of the solvent and successive recrystallisation from Me_2CO yielded an orange microcrystalline product (yield: 60 mg, 15%) (Found: C, 56.60; H, 5.90. Calc. for $C_{38}H_{48}BClO_3PdS_3$: C, 56.95; H, 6.05%). Fast-atom bombardment mass spectrum: m/z 483; calc. for $[^{106}Pd^{35}Cl([20]aneS_3O_3)]^+$ 483. ^1H NMR [$(CD_3)_2CO$, 297 K, 250.13 MHz]: δ 1.9 (m, $SCH_2CH_2CH_2S$, 4 H), 2.7 (m, SCH_2, 12 H), 3.6 (m, OCH_2, 12 H) and 6.7–7.8 [m, $B(C_6H_5)_4^-$, 20 H]. Infrared spectrum (KBr disc): 3053m, 2982w, 2920m, 1720w, 1657w, 1579m, 1478m, 1426m, 1351w, 1262m, 1183w, 1110s, 1032m, 904w, 842m, 735vs, 708vs, 620m, 558w and 464w cm^{-1}.

Single-crystal Structure Determinations.—Details of the crystal data, data collection and processing and structure analysis are given in Table 4. All three structures were solved from Patterson syntheses (SHELX 76[18]) and developed by iterative cycles of least-squares refinement and Fourier-difference syntheses. Hydrogen atoms were included in fixed, calculated positions. Final atomic coordinates appear in Tables 5–7. Illustrations were generated using SHELXTL-PC,[21] and molecular geometry calculations utilised CALC[22] and SHELXTL-PC.

$[PdCl_2([18]aneS_2O_4)]$ **1**. During refinement atom O(7) was found to be disordered over two positions with site occupancies for O(7) and O(7′) of 0.88 and 0.12 respectively. All non-hydrogen atoms apart from O(7′) were refined with anisotropic thermal parameters. Hydrogen atoms were included in fixed calculated positions with $U_{iso}(H) = 1.2U_{eq}(C)$.

$[Pd([18]aneS_2O_4)_2][PF_6]_2$ **2**. Both the macrocycle and the PF_6^- counter anion exhibited disorder. In the former, disorder affecting C(11) and C(12) was successfully modelled by allowing two positions for each atom. The disorder in the PF_6^-

Table 6 Fractional atomic coordinates with e.s.d.s in parentheses for $[Pd([18]aneS_2O_4)_2][PF_6]_2$ **2**

Atom	*x*	*y*	*z*
Pd	0.5	0.5	0.5
S(1)	0.404 64(17)	0.547 78(13)	0.679 32(11)
C(2)	0.538 2(6)	0.479 0(4)	0.766 2(4)
C(3)	0.546 8(6)	0.355 5(4)	0.701 5(4)
S(4)	0.646 48(16)	0.372 20(12)	0.570 82(11)
C(5)	0.572 4(6)	0.220 0(5)	0.475 0(5)
C(6)	0.682 1(7)	0.139 3(5)	0.512 1(5)
O(7)	0.638 7(5)	0.120 9(4)	0.620 9(3)
C(8)	0.764 5(7)	0.080 3(5)	0.684 1(5)
C(9)	0.698 9(7)	0.061 0(6)	0.793 4(6)
O(10)	0.690 7(4)	0.175 5(3)	0.862 7(3)
C(11)	0.593 3(4)	0.136 5(3)	0.950 4(3)
C(11′)	0.664 9(9)	0.200 2(7)	0.981 8(7)
C(12)	0.568 1(4)	0.253 6(3)	1.023 8(3)
C(12′)	0.462 9(9)	0.169 6(7)	0.983 1(7)
O(13)	0.431 1(4)	0.292 2(3)	0.964 2(3)
C(14)	0.243 8(8)	0.247 1(6)	0.951 1(6)
C(15)	0.153 6(7)	0.336 1(5)	0.920 3(5)
O(16)	0.181 2(5)	0.345 3(4)	0.804 8(3)
C(17)	0.109 4(6)	0.432 0(5)	0.766 8(5)
C(18)	0.178 8(6)	0.447 8(5)	0.654 5(4)
P	1.021 4(2)	0.228 47(15)	0.278 81(14)
F(1)	1.017 8(6)	0.310 8(5)	0.187 9(4)
F(2)	1.008 8(7)	0.133 6(5)	0.356 3(5)
F(3)	0.801 2(6)	0.193 4(6)	0.251 5(5)
F(4)	1.235 1(6)	0.243 9(6)	0.281 7(6)
F(5)	0.981 5(8)	0.124 4(6)	0.153 6(6)
F(6)	1.052 3(9)	0.337 5(7)	0.386 8(7)
F(7)	0.075 9(9)	0.192 6(9)	0.402 0(9)
F(8)	0.124 4(10)	0.371 8(9)	0.351 6(9)
F(9)	−0.045 5(9)	0.310 0(8)	0.388 6(8)
F(10)	−0.158 7(9)	0.242 7(7)	0.302 1(8)
F(11)	0.226 6(10)	0.297 3(10)	0.339 8(10)
F(12)	−0.064 7(10)	0.101 7(10)	0.268 9(10)
F(13)	0.189 6(10)	0.198 2(9)	0.234 6(9)
F(14)	0.059 4(10)	0.136 6(8)	0.185 0(8)
F(15)	−0.013 7(10)	0.099 2(9)	0.201 6(9)
F(16)	0.066 8(10)	0.341 5(10)	0.236 3(10)

Table 7 Fractional atomic coordinates with e.s.d.s in parentheses for $[Pd([18]aneS_3O_3)_2][PF_6]_2$ **3**

Atom	*x*	*y*	*z*
Pd	0.5	0.5	0.5
S(1)	0.497 2(3)	0.286 9(2)	0.618 4(2)
C(2)	0.697 3(11)	0.213 8(8)	0.591 1(9)
C(3)	0.812 3(11)	0.311 0(9)	0.599 6(8)
S(4)	0.776 0(2)	0.467 3(2)	0.487 29(19)
C(5)	0.822 9(13)	0.414 2(9)	0.344 9(8)
C(6)	0.777 2(11)	0.515 2(7)	0.232 5(8)
S(7)	0.874 8(6)	0.662 1(5)	0.238 7(4)
C(8)	0.871 6(12)	0.762 1(18)	0.080 8(8)
O(7)	0.854 9(18)	0.630 8(9)	0.229 3(14)
C(8′)	0.850 5(14)	0.740 7(15)	0.126 5(16)
C(9)	0.700 7(10)	0.823 9(9)	0.074 7(10)
O(10)	0.593 8(8)	0.732 1(6)	0.058 5(6)
C(11)	0.431 1(14)	0.783 1(11)	0.046 3(10)
C(12)	0.333 6(13)	0.674 9(13)	0.037 5(11)
O(13)	0.341 6(8)	0.577 8(8)	0.149 7(6)
C(14)	0.263 2(12)	0.464 7(11)	0.141 6(10)
C(15)	0.340(3)	0.341 0(15)	0.226 2(9)
O(16)	0.337 3(16)	0.317 9(9)	0.356 1(10)
C(15′)	0.243 4(7)	0.378 4(19)	0.270 3(12)
S(16)	0.455 9(6)	0.330 0(5)	0.294 9(4)
C(17)	0.401 7(14)	0.190 5(7)	0.418 2(7)
C(18)	0.367 9(12)	0.193 6(9)	0.551 9(10)
P	1.048 2(3)	0.914 9(2)	−0.251 2(2)
F(1)	1.054 4(7)	1.066 4(5)	−0.320 7(6)
F(2)	0.999 6(9)	0.878 4(6)	−0.373 7(5)
F(3)	1.043 1(7)	0.763 2(5)	−0.181 6(5)
F(4)	0.864 5(7)	0.941 5(6)	−0.217 6(6)
F(5)	1.231 6(7)	0.885 7(6)	−0.285 0(7)
F(6)	1.096 3(8)	0.945 9(6)	−0.127 1(6)

anion was modelled by one major PF_6^- component (site occupancy 0.6) and a minor component comprising the symmetrically distributed F atoms. With hindsight this disorder might have been avoided (or at least simplified) by carrying out the data collection at low temperature. All non-hydrogen atoms apart from C(11), C(11′), C(12), C(12′) and F(6)–F(16) were refined with anisotropic thermal parameters. Hydrogen atoms were refined in fixed calculated positions with fixed thermal parameters $U_{iso}(H) = 0.08$ Å^2.

$[Pd([18]aneS_3O_3)_2][PF_6]_2$ **3**. The disorder affecting atoms O(7), S(7), O(16) and S(16) is described in the Results and Discussion section. It was successfully modelled over two equally occupied orientations including C(8)/C(8′) and C(15)/C(15′). It was necessary to restrain the C–C, C–O and C–S bond lengths in the two affected moieties to 1.52, 1.42 and 1.83 Å respectively. At isotropic convergence, final corrections (minimum 0.842, maximum 1.162) for absorption were made using DIFABS.[23] All non-hydrogen atoms apart from O(7), S(7), C(8), C(8′), C(15) and C(15′) were refined with anisotropic thermal parameters. Hydrogen atoms were included in fixed calculated positions with a common thermal parameter which was allowed to refine freely to $U_{iso}(H) = 0.068$ Å^2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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