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Synthesis and characterisation of transition-metal complexes involving cyclic diselenoether ligands

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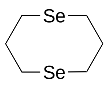
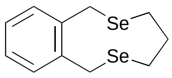
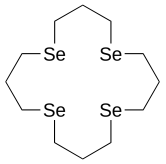
Treatment of $NCSe(CH_2)_3SeCN$ with o-$C_6H_4(CH_2Br)_2$ in Na–NH_3–tetrahydrofuran yielded L^2 (3*H*-1,4,5,7-tetrahydro-2,6-benzodiselenonine) in greater than 80% yield. This cyclic diselenoether has been fully characterised spectroscopically and structurally. Reaction of $[Cu(MeCN)_4]Y$ ($Y = BF_4$ or PF_6) or $AgBF_4$ with 2 molar equivalents of L^1 (1,5-diselenacyclooctane) or L^2 afforded the mononuclear species $[M(L)_2]Y$ (M = Cu, $Y = BF_4$ or PF_6; M = Ag, $Y = BF_4$). These compounds have been characterised by IR and ^1H NMR spectroscopy, mass spectrometry and microanalysis. Crystal structure determinations on $[Cu(L^2)_2]BF_4$, $[Ag(L^1)_2]BF_4$ and $[Ag(L^2)_2]BF_4$ confirmed the discrete molecular nature of these products, giving distorted tetrahedral cations in each case. These structures are compared to the structures of related species involving acyclic bidentate thio-, seleno- and telluroethers. The preparation of the tetraselenoether macrocyclic complex $[Ag([16]aneSe_4)]BF_4$ ($[16]aneSe_4$ = 1,5,9,13-tetraselenacyclohexadecane) has also been determined. Compounds L^1 and L^2 reacted with 2 molar equivalents of [AuCl(tht)] (tht = tetrahydrothiophene) to yield $[(AuCl)_2L^1]$ or $[(AuCl)_2L^2]$ respectively as white solids. These neutral compounds are thought to involve linear Se–Au–Cl fragments. Compound L^2 reacted with 1 molar equivalent of MCl_2 (M = Pd or Pt) in refluxing MeCN to give *cis*-$[MCl_2(L^2)]$. Unusual low-frequency co-ordination shifts [δ(free ligand) $-$ δ(complex)] were revealed by ^{77}Se-$\{^1H\}$ NMR spectroscopy in each case. This is in contrast to *cis*-$[MCl_2(L^1)]$ which display high-frequency co-ordination shifts. The ^{195}Pt NMR spectroscopic data on *cis*-$[PtCl_2(L^2)]$ are consistent with an Se_2Cl_2 donor set at Pt^{II}. The crystal structure of *cis*-$[PdCl_2(L^2)]$ shows a distorted square-planar arrangement, with *d*(Pd–Se) slightly longer than in *cis*-$[PdCl_2(L^1)]$.

As part of a study of Group 16 donor ligand chemistry, we have recently reported the co-ordination chemistry of a series of bidentate ligands, $RE(CH_2)_nER$ and o-$C_6H_4(ER)_2$ (E = S or Se; n = 1, 2 or 3; E = Te; n = 1 or 3), with the Group 11 metals.[1–4] The combination of variable-temperature ^1H, ^{77}Se-$\{^1H\}$, ^{125}Te-$\{^1H\}$ and ^{109}Ag NMR spectroscopies and X-ray crystallography has shown that subtle ligand variations can have a dramatic influence upon the structures of the compounds produced, generating simple mononuclear bis(chelate) species, *e.g.* $[Ag\{MeSe(CH_2)_2SeMe\}_2]^+$, linear chain polymers, *e.g.* $[Ag_n\{MeS(CH_2)_3SMe\}_n]^{n+}$ involving a new binding mode for $MeS(CH_2)_3SMe$, and extended three-dimensional networks, *e.g.* $[Ag_n\{PhSe(CH_2)_3SePh\}_{2n}]^{n+}$, and, in the case of the methylene-bridged ligands, highly unusual 'zeolite-like' structures involving large channels which host PF_6^- or BF_4^- anions, *e.g.* $[Cu_n(MeSeCH_2SeMe)_{2n}]^{n+}$. In tandem with this, we have also been investigating the co-ordination chemistry of cyclic selenoethers, including $[16]aneSe_4$ (1,5,9,13-tetraselenacyclohexadecane) and $[8]aneSe_2$ (L^1, 1,5-diselenacyclooctane), and have reported the preparation and characterisation of a number of complexes of these ligands with the platinum-group metals, including for example *trans*-$[PtX_2([16]aneSe_4)]^{2+}$ (X = Cl or Br), the first examples of platinum(IV) species involving an Se_4X_2 donor set.[5–10] More recently we have also begun to investigate the chemistry of these ligands with hard chromium(III) centres.[11] Pinto and co-workers[12] have reported the structure of the three-dimensional copper(I) polymeric species $[Cu_n([16]aneSe_4)_n]^{n+}$,[12] in which one Se donor atom from four different $[16]aneSe_4$ molecules is ligated to Cu^I, affording a pseudo-tetrahedral arrangement at each metal centre within the network, Cu–Se 2.42–2.52 Å. The copper(II) species $[Cu([16]aneSe_4)][CF_3SO_3]_2$ has also been reported, the structure of which shows square-planar Se_4 co-ordination, with two weakly interacting axial $CF_3SO_3^-$ anions, Cu–Se 2.4593(6), 2.4554(6), Cu $\cdots$ O 2.464(5) Å.[13] In view of the wide range of structural motifs observed for compounds of Cu^I and Ag^I involving bidentate acyclic selenoethers and the polymeric structure reported for $[Cu_n([16]aneSe_4)_n]^{n+}$, we have undertaken a study on complexes of the cyclic diselenoethers L^1 and L^2 (3*H*-1,4,5,7-tetrahydro-2,6-benzodiselenonine) with Cu^I, Ag^I and Au^I. There have been very few reported examples of cyclic diselenoether complexes with transition-metal ions, examples include $[M(CO)_4L]$ (M = Cr, Mo or W; L = 1,4-diselenacyclohexane),[14] $[Ru(\eta^6\text{-}C_6H_6)L(EtCN)]^{2+}$ (L = 2,11-diselena[3.3]orthocyclophane)],[15] *cis*-$[PdCl_2(L^1)]$,[9] *trans*-$[RhCl_2(L^1)_2]^+$ [8] and *cis*-$[RuCl_2(L^1)_2]$.[10] Kumagai and Akabori[16] have reported a preparation for L^2 previously, together with mercury(II) complexes of it, however little spectroscopic data on these species were presented. These are the only complexes of L^2 of which we are aware. Compound L^2 also allows us to determine the effects on the co-ordination chemistry of varying the interdonor linkages in these cyclic systems.


L^1


L^2


$[16]aneSe_4$

We report here an improved synthesis and full spectroscopic and X-ray structural characterisation of L^2, together with the preparation and spectroscopic characterisation of $[M(L^1)_2]Y$ (M = Cu, $Y = PF_6$; M = Ag, $Y = BF_4$), $[M(L^2)_2]BF_4$, $[Ag([16]aneSe_4)]BF_4$, $[(AuCl)_2(L^1)]$ and $[(AuCl)_2(L^2)]$. The preparations of *cis*-$[M'Cl_2(L^2)]$ (M′ = Pd or Pt) are also included, together with single-crystal structure determinations on $[Ag(L^1)_2]BF_4$, $[Ag(L^2)_2]BF_4$, $[Cu(L^2)_2]BF_4$ and *cis*-$[PdCl_2(L^2)]$.

Results and Discussion

The compound $NCSe(CH_2)_3SeCN$ was added to a solution of Na in tetrahydrofuran (thf)–liquid NH_3, generating $NaSe(CH_2)_3SeNa$ *in situ*. Dropwise addition of α,α′-dibromo-*o*-

Table 1 Selected bond lengths (Å) and angles (°) for compound L^2

Se(1)–C(1)	1.95(1)	Se(1)–C(11)	1.980(10)
Se(2)–C(3)	1.952(9)	Se(2)–C(4)	1.97(1)
Se(3)–C(12)	1.957(9)	Se(3)–C(22)	1.985(10)
Se(4)–C(14)	1.96(1)	Se(4)–C(15)	1.96(1)
C(1)–C(2)	1.51(1)	C(2)–C(3)	1.52(1)
C(4)–C(5)	1.51(1)	C(5)–C(6)	1.40(1)
C(5)–C(10)	1.42(1)	C(6)–C(7)	1.38(1)
C(7)–C(8)	1.38(1)	C(8)–C(9)	1.37(1)
C(9)–C(10)	1.40(1)	C(10)–C(11)	1.49(1)
C(12)–C(13)	1.52(1)	C(13)–C(14)	1.52(1)
C(15)–C(16)	1.50(1)	C(16)–C(17)	1.39(1)
C(16)–C(21)	1.41(1)	C(17)–C(18)	1.37(1)
C(18)–C(19)	1.39(1)	C(19)–C(20)	1.37(1)
C(20)–C(21)	1.39(1)	C(21)–C(22)	1.49(1)
C(1)–Se(1)–C(11)	100.8(4)	C(3)–Se(2)–C(4)	102.6(4)
C(12)–Se(3)–C(22)	101.5(4)	C(14)–Se(4)–C(15)	101.9(4)
Se(1)–C(1)–C(2)	114.5(7)	C(1)–C(2)–C(3)	115.2(9)
Se(2)–C(3)–C(2)	114.9(7)	Se(2)–C(4)–C(5)	113.9(7)
C(4)–C(5)–C(6)	117.9(9)	C(4)–C(5)–C(10)	123.3(10)
C(6)–C(5)–C(10)	118.8(9)	C(5)–C(6)–C(7)	121.1(9)
C(6)–C(7)–C(8)	120(1)	C(7)–C(8)–C(9)	119.7(10)
C(8)–C(9)–C(10)	122.1(9)	C(5)–C(10)–C(9)	118.0(9)
C(5)–C(10)–C(11)	122.0(9)	C(9)–C(10)–C(11)	119.9(9)
Se(1)–C(11)–C(10)	115.0(6)	Se(3)–C(12)–C(13)	114.1(7)
C(12)–C(13)–C(14)	114.6(8)	Se(4)–C(14)–C(13)	114.2(7)
Se(4)–C(15)–C(16)	115.7(6)	C(15)–C(16)–C(17)	118.2(9)
C(15)–C(16)–C(21)	122.5(9)	C(17)–C(16)–C(21)	119.3(9)
C(16)–C(17)–C(18)	122.1(9)	C(17)–C(18)–C(19)	119.4(9)
C(18)–C(19)–C(20)	118.5(10)	C(19)–C(20)–C(21)	123.9(10)
C(16)–C(21)–C(20)	116.6(9)	C(16)–C(21)–C(22)	123.9(9)
C(20)–C(21)–C(22)	119.5(8)	Se(3)–C(22)–C(21)	111.9(6)

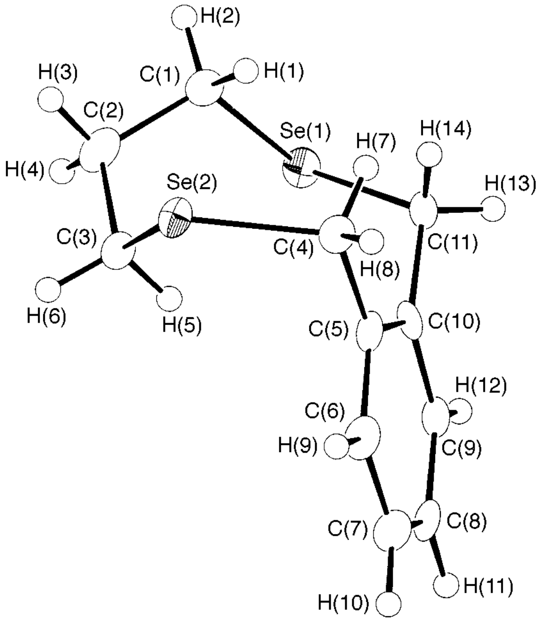


Fig. 1 View of the structure of one of the independent molecules of compound L^2 in the asymmetric unit with the numbering scheme adopted (the other molecule is essentially indistinguishable). Ellipsoids are shown at 40% probability

xylene gave L^2 which was isolated in greater than 80% yield following purification by column chromatography [δ(^{77}Se) +296]. Electron impact (EI) mass spectrum: found $m/z = 306$, calculated $m/z = 306$]. Surprisingly, a ^{77}Se-{^{1}H} NMR spectrum of the crude reaction mixture following evaporation of the NH_3 revealed only trace amounts of other Se-containing species. This contrasts with the reaction of $NCSe(CH_2)_3SeCN$ and $Br(CH_2)_3Br$ with Na in thf–liquid NH_3, which gives L^1 (17%), [16]aneSe_4 (40%), [24]aneSe_6 (15%) (1,5,9,13,17,21-hexaselenacyclotetracosane) and higher polymers, and suggests that the α,α′-dibromo-*o*-xylene sets up the correct geometry for ring closure *via* a [1 + 1] cyclisation process. The crystal structure of the product from this reaction confirms (Fig. 1, Table 1) the formation of the [1 + 1] cyclisation product, L^2, with the Se atom lone pairs pointing out of the ring, presumably to minimise the repulsion. The angles around the Se atoms are in the range 100.8(4)–102.6(4)°.

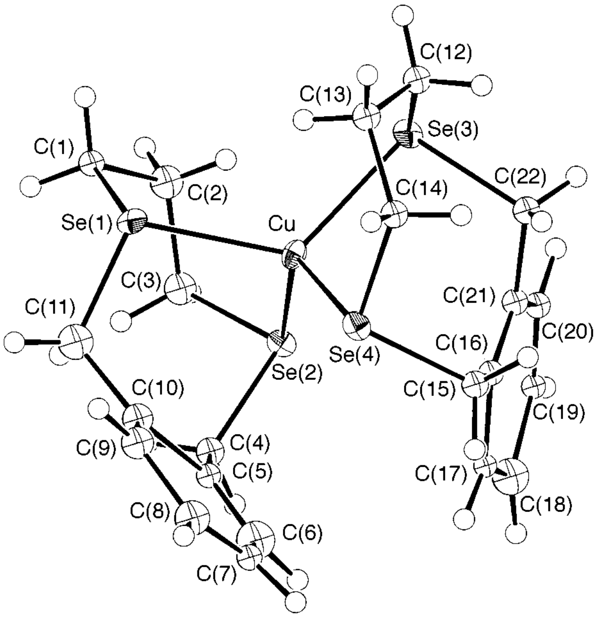


Fig. 2 View of the structure of $[Cu(L^2)_2]^+$ with the numbering scheme adopted. Ellipsoids as in Fig. 1

Reaction of $[Cu(MeCN)_4]Y$ ($Y = BF_4$ or PF_6) with 2 molar equivalents of L ($L = L^1$ or L^2) in degassed acetone at room temperature for 12 h gave colourless solutions. Addition of diethyl ether afforded $[Cu(L)_2]Y$ as cream or white solids. Electrospray mass spectra showed peaks with the correct isotopic pattern at $m/z = 549$ and 673 respectively for L^1 and L^2, corresponding to $[Cu(L)_2]^+$. Infrared spectroscopy was not very informative, revealing only the presence of L and either BF_4^- or PF_6^- counter ion as appropriate. Significantly however, there was no evidence for co-ordinated MeCN in the IR spectra. The formulations $[Cu(L)_2]Y$ were confirmed by ^{1}H NMR spectroscopy and microanalytical measurements and a single crystal structure of $[Cu(L^2)_2]BF_4$. The structure shows (Fig. 2, Table 2) a discrete copper(I) monomer, with two chelating L^2 ligands generating a distorted tetrahedral stereochemistry, Cu–Se 2.409(5), 2.403(6), 2.405(5) and 2.436(6) Å. These distances compare well with *d*(Cu–Se) observed in other copper(I) selenoether complexes, *e.g.* $[Cu_n([16]aneSe_4)_n]^{n+}$ Cu–Se 2.42–2.52 Å,[12] $[Cu\{o\text{-}C_6H_4(SeMe)_2\}_2]^+$ Cu–Se 2.379(2), 2.419(2) Å.[3] The Se–Cu–Se angles lie in the range 98.6(2)–122.39(7)°, with those involved in the chelate rings at the lower end of this range. The six-membered chelate rings in the $[Cu(L^2)_2]^+$ cation both adopt a boat arrangement.

The corresponding silver(I) complexes $[Ag(L)_2]BF_4$ were obtained by reaction of $AgBF_4$ with 2 molar equivalents of L in degassed acetone. These reactions were conducted in foil-wrapped vessels due to the sensitivity of the compounds to light. Electrospray mass spectra on the products showed $m/z = 593$ and 717, corresponding to $[Ag(L^1)_2]^+$ and $[Ag(L^2)_2]^+$ respectively. To enable a comparison with the copper(I) species above, and with the silver(I) complexes involving acyclic bidentate thio-, seleno- and telluro-ether ligands,[1–4] single-crystal structure determinations were undertaken on $[Ag(L^1)_2]BF_4$ and $[Ag(L^2)_2]BF_4$. The structure of the former shows (Fig. 3, Table 3) a distorted tetrahedral silver(I) monomer with two bidentate L^1 ligands, Ag–Se 2.636(4), 2.668(4), 2.639(4) and 2.695(4) Å. The Se–Ag–Se angles involved in the six-membered chelate rings are Se(1)–Ag–Se(2) 90.0(1) and Se(3)–Ag–Se(4)

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu(L^2)_2]^+$

Se(1)–Cu	2.409(5)	Se(1)–C(1)	1.96(2)	C(5)–C(10)	1.53(2)	C(6)–C(7)	1.40(3)
Se(1)–C(11)	1.93(2)	Se(2)–Cu	2.403(6)	C(7)–C(8)	1.24(2)	C(8)–C(9)	1.45(3)
Se(2)–C(3)	1.95(2)	Se(2)–C(4)	1.95(2)	C(9)–C(10)	1.39(3)	C(10)–C(11)	1.53(3)
Se(3)–Cu	2.405(5)	Se(3)–C(12)	2.00(2)	C(12)–C(13)	1.33(2)	C(13)–C(14)	1.54(2)
Se(3)–C(22)	2.02(2)	Se(4)–Cu	2.436(6)	C(15)–C(16)	1.54(2)	C(16)–C(17)	1.50(2)
Se(4)–C(14)	1.97(2)	Se(4)–C(15)	2.01(2)	C(16)–C(21)	1.30(2)	C(17)–C(18)	1.40(2)
C(1)–C(2)	1.72(2)	C(2)–C(3)	1.60(3)	C(18)–C(19)	1.55(2)	C(19)–C(20)	1.34(2)
C(4)–C(5)	1.49(2)	C(5)–C(6)	1.30(3)	C(20)–C(21)	1.40(2)	C(21)–C(22)	1.49(3)
Cu–Se(1)–C(1)	104.0(5)	Cu–Se(1)–C(11)	102.1(6)	C(6)–C(5)–C(10)	119(1)	C(5)–C(6)–C(7)	121(1)
C(1)–Se(1)–C(11)	100.9(8)	Cu–Se(2)–C(3)	106.7(6)	C(6)–C(7)–C(8)	126(1)	C(7)–C(8)–C(9)	116(1)
Cu–Se(2)–C(4)	103.7(6)	C(3)–Se(2)–C(4)	93.8(8)	C(8)–C(9)–C(10)	123(1)	C(5)–C(10)–C(9)	113(1)
Cu–Se(3)–C(12)	102.6(5)	Cu–Se(3)–C(22)	100.1(5)	C(5)–C(10)–C(11)	124(1)	C(9)–C(10)–C(11)	121(1)
C(12)–Se(3)–C(22)	96.6(7)	Cu–Se(4)–C(14)	100.3(5)	Se(1)–C(11)–C(10)	112(1)	Se(3)–C(12)–C(13)	119(1)
Cu(1)–Se(4)–C(15)	102.8(5)	C(14)–Se(4)–C(15)	106.1(7)	C(12)–C(13)–C(14)	116(1)	Se(4)–C(14)–C(13)	120(1)
Se(1)–Cu–Se(2)	99.1(2)	Se(1)–Cu–Se(3)	122.39(7)	Se(4)–C(15)–C(16)	113(1)	C(15)–C(16)–C(17)	109(1)
Se(1)–Cu–Se(4)	108.5(2)	Se(2)–Cu–Se(3)	109.6(2)	C(15)–C(16)–C(21)	132(1)	C(17)–C(16)–C(21)	117(1)
Se(2)–Cu–Se(4)	120.28(7)	Se(3)–Cu–Se(4)	98.6(2)	C(16)–C(17)–C(18)	122(1)	C(17)–C(18)–C(19)	112(1)
Se(1)–C(1)–C(2)	113(1)	C(1)–C(2)–C(3)	115(1)	C(18)–C(19)–C(20)	121(1)	C(19)–C(20)–C(21)	120(1)
Se(2)–C(3)–C(2)	109(1)	Se(2)–C(4)–C(5)	117(1)	C(16)–C(21)–C(20)	124(1)	C(16)–C(21)–C(22)	118(1)
C(4)–C(5)–C(6)	126(1)	C(4)–C(5)–C(10)	113(1)	C(20)–C(21)–C(22)	117(1)	Se(3)–C(22)–C(21)	111(1)

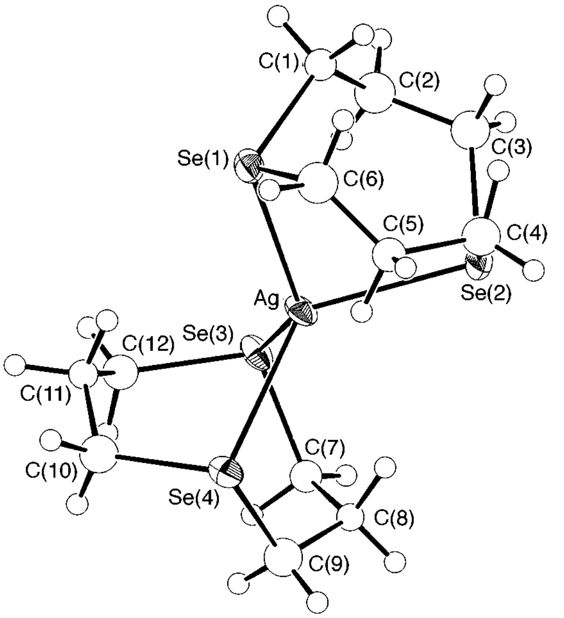


Fig. 3 View of the structure of $[Ag(L^1)_2]^+$ with the numbering scheme adopted. Ellipsoids as in Fig. 1

89.30(9)°, while the other Se–Ag–Se angles lie in the range 113.9(1)–128.5(2)°. The L^1 ligands adopt a boat–boat conformation. This is in contrast to the chair–boat conformation observed in the solid state for *cis*-$[PdCl_2(L^1)]$.[9] The only other silver(I) complex of an acyclic diselenoether incorporating a trimethylene backbone is $[Ag_n\{PhSe(CH_2)_3SePh\}_{2n}]^{n+}$, and the polymeric structure of this cation is clearly very different from the discrete molecular structure observed for $[Ag(L^1)_2]^+$. The structure of $[Ag(L^2)_2]^+$ shows (Fig. 4, Table 4) a very similar arrangement to that in the copper(I) analogue above, with two chelating L^2 ligands co-ordinated tetrahedrally to Ag^I, Ag–Se 2.658(1) and 2.679(2) Å. The Ag–Se bond lengths observed in these cyclic diselenoether complexes are longer than *d*(Cu–Se) in $[Cu(L^2)_2]^+$ above, in accord with the increased radius of Ag^I over Cu^I. Similar Ag–Se distances have been observed in other silver(I)–selenoether species, *e.g.* $[AgL_2]^+$ (L = 1,3,5-triselenacyclohexane) Ag–Se 2.78(1)–3.05(1) Å[17] and $[Ag\{MeSe(CH_2)_2SeMe\}_2]^+$ Ag–Se 2.626(2), 2.638(1), 2.634(2) and 2.610(1) Å.[2]

We have also isolated a silver(I) complex incorporating the tetraselena crown [16]aneSe_4. Reaction of $AgBF_4$ with 1 molar equivalent of [16]aneSe_4 in degassed acetone for 1 h at room temperature yielded a colourless solution. Concentrating this solution and addition of diethyl ether afforded a white solid. The IR spectrum showed peaks due to BF_4^- anion and co-ordinated [16]aneSe_4, while the electrospray mass spectrum (MeCN solution) showed peaks with the correct isotopic pattern at $m/z = 593$ and 549, corresponding to $[Ag([16]aneSe_4)]^+$ and $[Ag([16]aneSe_4 - C_3H_6)]^+$ respectively (Fig. 5). The IR spectroscopic and microanalytical data are also consistent with the formulation $[Ag([16]aneSe_4)]BF_4$. Given the polymeric structure reported for the copper(I) analogue, $[Cu([16]aneSe_4)]^+$,[12] and the very poor solubility shown by this silver(I) species in organic solvents, it seems likely that this may also adopt a polymeric arrangement in the solid state.

Table 3 Selected bond lengths (Å) and angles (°) for $[Ag(L^1)_2]^+$

Ag–Se(1)	2.636(4)	Ag–Se(2)	2.668(4)
Ag–Se(3)	2.639(4)	Ag–Se(4)	2.695(4)
Se(1)–C(1)	2.04(3)	Se(1)–C(6)	1.86(4)
Se(2)–C(3)	2.06(3)	Se(2)–C(4)	1.85(3)
Se(3)–C(7)	1.93(3)	Se(3)–C(12)	1.98(3)
Se(4)–C(9)	1.95(3)	Se(4)–C(10)	2.02(3)
C(1)–C(2)	1.48(4)	C(2)–C(3)	1.51(5)
C(4)–C(5)	1.58(4)	C(5)–C(6)	1.47(5)
C(7)–C(8)	1.50(4)	C(8)–C(9)	1.50(4)
C(10)–C(11)	1.51(4)	C(11)–C(12)	1.41(4)
Se(1)–Ag–Se(2)	90.0(1)	Se(1)–Ag–Se(3)	128.5(2)
Se(1)–Ag–Se(4)	113.9(1)	Se(2)–Ag–Se(3)	114.5(1)
Se(2)–Ag–Se(4)	124.6(2)	Se(3)–Ag–Se(4)	89.30(9)
Ag–Se(1)–C(1)	99.2(8)	Ag–Se(1)–C(6)	101(1)
C(1)–Se(1)–C(6)	103(1)	Ag–Se(2)–C(3)	97.7(10)
Ag–Se(2)–C(4)	101(1)	C(3)–Se(2)–C(4)	100(1)
Ag–Se(3)–C(7)	102.3(8)	Ag–Se(3)–C(12)	100.2(10)
C(7)–Se(3)–C(12)	103(1)	Ag–Se(4)–C(9)	100(1)
Ag–Se(4)–C(10)	97.3(9)	C(9)–Se(4)–C(10)	100(1)
Se(1)–C(1)–C(2)	117(2)	C(1)–C(2)–C(3)	114(2)
Se(2)–C(3)–C(2)	117(2)	Se(2)–C(4)–C(5)	117(2)
C(4)–C(5)–C(6)	118(2)	Se(1)–C(6)–C(5)	118(2)
Se(3)–C(7)–C(8)	116(1)	C(7)–C(8)–C(9)	114(2)
Se(4)–C(9)–C(8)	117(2)	Se(4)–C(10)–C(11)	119(2)
C(10)–C(11)–C(12)	123(2)	Se(3)–C(12)–C(11)	117(2)

Gold complexes involving thio-, seleno- and telluro-ether ligands have been limited mainly to examples involving macrocyclic thioethers, *e.g.* $[Au([9]aneS_3)_2]^{+/2+/3+}$ ([9]aneS_3 = 1,4,7-trithiacyclononane),[18] $[AuCl([9]aneS_3)]$[19] and $[Au_2([15]aneS_5)_2]^{2+}$ ([15]aneS_5 = 1,4,7,10,13-pentathiacyclopentadecane),[20] and a few examples involving mono- and bi-dentate thioethers, such as $[AuX(SR_2)]$, [AuX(tht)] (tht = tetrahydrothiophene)[21] and $[(AuCl)_2\{\mu\text{-}RS(CH_2)_nSR\}]$ (R = Me, Et or Ph; *n* = 2 or 3).[22] The only well characterised examples of gold–selenoether complexes are $[AuCl(Ph_2Se)]$ and $[AuCl_3(Ph_2Se)]$ prepared by

Table 4 Selected bond lengths (Å) and angles (°) for $[Ag(L^2)_2]^+$

Ag–Se(1)	2.658(1)	Ag–Se(1)	2.658(1)
Ag–Se(2)	2.679(2)	Ag–Se(2)	2.679(2)
Se(1)–C(1)	1.90(1)	Se(1)–C(11)	2.03(1)
Se(2)–C(3)	1.91(1)	Se(2)–C(4)	2.03(1)
C(2)–C(3)	1.56(2)	C(1)–C(2)	1.53(2)
C(5)–C(6)	1.39(2)	C(4)–C(5)	1.50(2)
C(6)–C(7)	1.36(2)	C(5)–C(10)	1.39(2)
C(8)–C(9)	1.41(2)	C(7)–C(8)	1.36(2)
C(10)–C(11)	1.47(2)	C(9)–C(10)	1.41(2)
Se(1)–Ag–Se(1)	133.03(8)	Se(1)–Ag–Se(2)	93.20(5)
Se(1)–Ag–Se(2)	111.26(4)	Se(1)–Ag–Se(2)	111.26(4)
Se(1)–Ag–Se(2)	93.20(5)	Se(2)–Ag–Se(2)	116.66(8)
Ag–Se(1)–C(1)	103.1(4)	Ag–Se(1)–C(11)	101.1(3)
C(1)–Se(1)–C(11)	101.6(6)	Ag–Se(2)–C(3)	100.7(4)
Ag–Se(2)–C(4)	97.9(4)	C(3)–Se(2)–C(4)	101.4(6)
Se(1)–C(1)–C(2)	115.4(9)	C(1)–C(2)–C(3)	116(1)
Se(2)–C(3)–C(2)	118.5(9)	Se(2)–C(4)–C(5)	112.1(9)
C(4)–C(5)–C(6)	118(1)	C(4)–C(5)–C(10)	122(1)
C(6)–C(5)–C(10)	119(1)	C(5)–C(6)–C(7)	122(1)
C(6)–C(7)–C(8)	119(1)	C(7)–C(8)–C(9)	119(1)
C(8)–C(9)–C(10)	120(1)	C(5)–C(10)–C(9)	117(1)
C(5)–C(10)–C(11)	123(1)	C(9)–C(10)–C(11)	118(1)
Se(1)–C(11)–C(10)	112.3(9)		

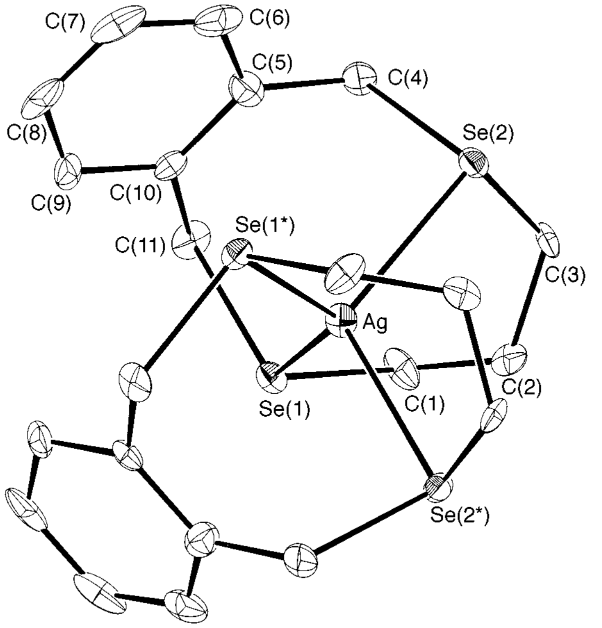


Fig. 4 View of the structure of $[Ag(L^2)_2]^+$ with the numbering scheme adopted. Atoms marked * are related by a crystallographic two-fold operation. Ellipsoids as in Fig. 1

direct reaction of Ph_2Se with AuCl or Au_2Cl_6 respectively. Crystallographic studies on these species show that the Au^I–Se bond length is 0.07 Å shorter than the Au^{III}–Se bond length, consistent with the gold(I)–selenoether interaction being substantially stronger.[23] Treatment of [AuCl(tht)] with 0.5 molar equivalent of L ($L = L^1$ or L^2) in degassed acetone affords $[(AuCl)_2(L)]$ as white solids. The IR spectra of these species show peaks due to co-ordinated L, and a terminal Au–Cl stretching vibration at 330 and 328 cm^{-1} for L^1 and L^2 respectively. Proton NMR spectroscopy and microanalyses are consistent with the formulation $[(AuCl)_2(L)]$ for the products. Unfortunately, despite repeated attempts, we have been unable to obtain crystals suitable for a single-crystal structure determination. However, analogy with the neutral 1:2 ligand:Au complexes, $[(AuCl)_2\{\mu\text{-}RS(CH_2)_nSR\}]$ (R = Me, Et or Ph; $n = 2$ or 3),[22] would suggest linear co-ordination of an AuCl fragment to each Se donor of L^1 and L^2 in these compounds.

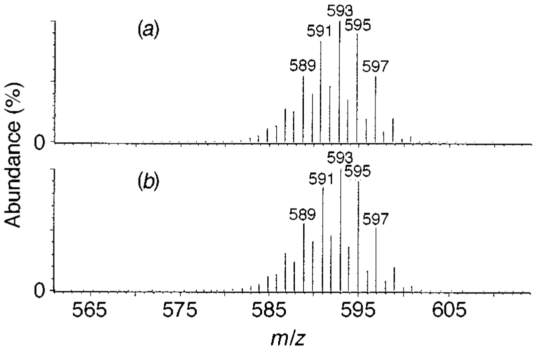


Fig. 5 Observed (*a*) and calculated (*b*) electrospray mass spectrum of $[Ag([16]aneSe_4)]^+$

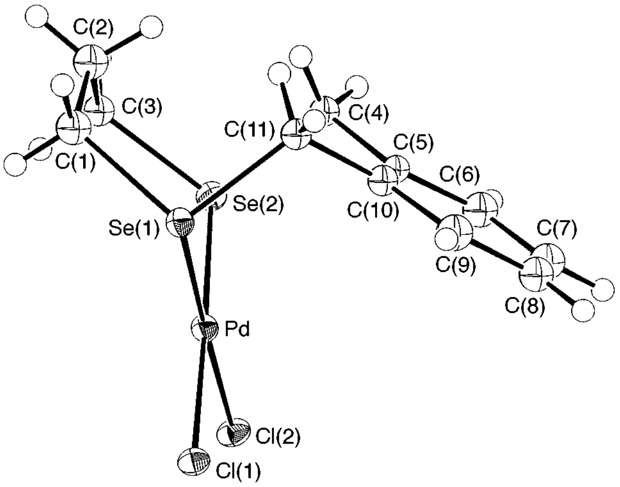


Fig. 6 View of the structure of *cis*-$[PdCl_2(L^2)]$ with the numbering scheme adopted. Ellipsoids as in Fig. 1

We have previously reported the preparation and spectroscopic characterisation of the complexes *cis*-$[MCl_2(L^1)]$ (M = Pd or Pt), together with the crystal structure of *cis*-$[PdCl_2(L^1)]$, which gave d(Pd–Cl) = 2.363(2) and 2.348(2) and d(Pd–Se) = 2.3647(8) and 2.3693(8) Å.[9] Compound L^1 adopts a chair–boat conformation in this complex. Reaction of MCl_2 (M = Pd or Pt) with 1 molar equivalent of L^2 in refluxing MeCN affords the neutral species $[MCl_2(L^2)]$ as orange (Pd) or yellow (Pt) solids. These compounds are very poorly soluble {less so than $[MCl_2(L^1)]$} in most organic solvents, and only sparingly soluble in dimethyl sulfoxide (dmso). The IR spectrum of $[PtCl_2(L^2)]$ shows peaks at 317 and 305 cm^{-1}, indicative of a terminal *cis*-$PtCl_2$ unit. For $[PdCl_2(L^2)]$ a broad peak is observed at 314 cm^{-1}, and it seems likely that the two ν(Pd–Cl) stretching vibrations expected for a *cis*-$PdCl_2$ unit are overlapping in this case. Attempts to obtain FAB or electrospray mass spectra for these materials proved unsuccessful, probably due to their very low solubilities. This was also evident in our attempts to obtain NMR spectra, and hence long accumulation times were required. The $^{77}Se\text{-}\{^1H\}$ NMR spectra were obtained for both compounds in dmso solution, and showed singlets at δ +249 and +244 for Pd and Pt respectively. The resonance for the platinum species was broad ($w_{\frac{1}{2}}$ *ca.* 400 Hz) and hence the ^{195}Pt satellites were not resolved. In contrast to many other d-block complexes with selenoether ligands which typically show high-frequency co-ordination shifts,[24] these compounds show shifts to low frequency upon co-ordination to Pd^{II} or Pt^{II} [free L^2: δ(^{77}Se) +296]. For example, $[MCl_2(L^1)]$ show shifts to high frequency of +62 and +57 ppm for M = Pd and Pt respectively, relative to free L^1 [δ(^{77}Se) +137]. The ^{195}Pt NMR spectrum of *cis*-$[PtCl_2(L^2)]$ shows a single resonance at δ −3672, consistent with an Se_2Cl_2 donor set at Pt^{II}. This is a similar shift to that of *cis*-$[PtCl_2(L^1)]$ which gave δ(^{195}Pt) −3825, and

Table 5 Selected bond lengths (Å) and angles (°) for *cis*-[$PdCl_2(L^2)$]

Pd–Se(1)	2.381(2)	Pd–Se(2)	2.380(2)
Pd–Cl(1)	2.348(4)	Pd–Cl(2)	2.343(4)
Se(1)–C(1)	1.98(2)	Se(1)–C(11)	1.97(2)
Se(2)–C(3)	1.94(2)	Se(2)–C(4)	1.98(2)
C(1)–C(2)	1.50(2)	C(2)–C(3)	1.50(2)
C(4)–C(5)	1.49(2)	C(5)–C(6)	1.40(2)
C(5)–C(10)	1.41(2)	C(6)–C(7)	1.37(2)
C(7)–C(8)	1.39(2)	C(8)–C(9)	1.37(2)
C(9)–C(10)	1.40(2)	C(10)–C(11)	1.51(2)
Se(1)–Pd–Se(2)	94.34(7)	Se(1)–Pd–Cl(1)	87.1(1)
Se(1)–Pd–Cl(2)	178.4(1)	Se(2)–Pd–Cl(1)	177.9(1)
Se(2)–Pd–Cl(2)	85.9(1)	Cl(1)–Pd–Cl(2)	92.8(1)
Pd–Se(1)–C(1)	106.5(4)	Pd–Se(1)–C(11)	105.0(4)
C(1)–Se(1)–C(11)	100.5(7)	Pd–Se(2)–C(3)	106.3(4)
Pd–Se(2)–C(4)	106.4(4)	C(3)–Se(2)–C(4)	101.5(7)
Se(1)–C(1)–C(2)	118(1)	C(1)–C(2)–C(3)	117(1)
Se(2)–C(3)–C(2)	120(1)	Se(2)–C(4)–C(5)	110(1)
C(4)–C(5)–C(6)	119(1)	C(4)–C(5)–C(10)	121(1)
C(6)–C(5)–C(10)	119(1)	C(5)–C(6)–C(7)	119(1)
C(6)–C(7)–C(8)	122(1)	C(7)–C(8)–C(9)	117(1)
C(8)–C(9)–C(10)	122(1)	C(5)–C(10)–C(9)	118(1)
C(5)–C(10)–C(11)	121(1)	C(9)–C(10)–C(11)	120(1)
Se(1)–C(11)–C(10)	111(1)		

significantly to high frequency of the homoleptic tetraselena species [$Pt(L^1)_2$]$^{2+}$ which gave δ(^{195}Pt) −4606.[9]

In order to ascertain that these are discrete molecular species, and to confirm the M–Se ligation, we undertook a single-crystal structure determination on *cis*-[$PdCl_2(L^2)$]. Single crystals were obtained from a solution of the compound in dmso. The crystal structure does indeed confirm that this is a mononuclear species, and shows (Fig. 6, Table 5) the expected *cis*-dichloro arrangement, with one chelating L^2 ligand completing the distorted square-planar geometry, Pd–Cl 2.348(4) and 2.343(4), Pd–Se 2.381(2) and 2.380(2) Å. In this species the six-membered chelate ring is in a chair conformation, and the Se(1)–Pd–Se(2) angle is 94.34(7)°. While the Pd–Cl distances are very similar, the Pd–Se bond lengths are slightly longer than in *cis*-[$PdCl_2(L^1)$], possibly due to the increased steric effect of the *o*-xylyl linkage.

These results show that L^1 and L^2 are effective ligands for a variety of metal centres, and comparisons with our previous work on complexes of Cu^I and Ag^I of acyclic bidentate selenoethers further support the conclusion that subtle variations in the framework of bidentate selenoethers, particularly interdonor linkage, substituent and cyclic *vs.* acyclic arrangement, dramatically influence the structures adopted in the solid state.

Experimental

Infrared spectra were measured as KBr of CsI discs or as Nujol mulls using a Perkin-Elmer 983G spectrometer over the range 200–4000 cm^{-1}, mass spectra by fast-atom bombardment (FAB) using 3-nitrobenzyl alcohol as matrix on a VG Analytical 70-250-SE normal geometry double-focusing mass spectrometer or by positive electrospray (ES) using a VG Biotech Platform and UV/VIS spectra in solution using 1 cm path length quartz cells using a Perkin-Elmer Lambda 19 UV/visible spectrophotometer. Proton NMR spectra were recorded using a Bruker AM300 spectrometer operating at 300 MHz, ^{77}Se-{^{1}H} and ^{195}Pt NMR spectra using a Bruker AM360 spectrometer operating at 68.68 and 77.8 MHz respectively and referenced to neat Me_2Se [δ(^{77}Se) 0] or aqueous [$PtCl_6$]$^{2-}$ [δ(^{195}Pt) 0]. Spectra were recorded using 10 mm outside diameter tubes containing *ca.* 10% deuteriated solvent. Microanalyses were performed by the Imperial College microanalytical service. The compounds [$Cu(MeCN)_4$]Y (Y = BF_4 or PF_6),[25] [AuCl(tht)][21] and L^1 (ref. 26) were prepared by the literature methods.

Syntheses

L^2. To a stirred solution of 1,3-bis(selenocyanato)propane (4 g, 16 mmol) in liquid ammonia (600 cm^3) and anhydrous thf (200 cm^3) was added Na metal (1.5 g, 64 mmol) in small pieces under nitrogen until a colourless, homogeneous solution was obtained. At this point, a solution of α,α′-dibromo-*o*-xylene (4.2 g, 16 mmol) in anhydrous thf (100 cm^3) was added dropwise over 6 h. The ammonia was allowed to evaporate overnight, and the reaction mixture diluted with water (100 cm^3) before concentrating to *ca.* 150 cm^3 *in vacuo.* The aqueous phase was extracted with dichloromethane (3 × 200 cm^3) and the combined organic extracts washed with water (100 cm^3), dried over $MgSO_4$, and concentrated *in vacuo* to yield a light yellow crystalline solid. Purification by silica gel chromatography [hexane–ethyl acetate (20 : 1)] afforded L^2 as colourless crystals (4.07 g, 83%). EI mass spectrum: found *m/z* = 306, 202; calculated for L *m/z* = 306, [L^2 − *o*-$C_6H_4(CH_2)_2$] 202. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.1–7.3 (m, *o*-C_6H_4, 4 H), 3.8 [s, *o*-$C_6H_4(CH_2Se)_2$, 4 H], 2.65 (m, $SeCH_2CH_2$, 4 H) and 2.0 (m, $CH_2CH_2CH_2$, 2 H). ^{13}C-{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 139.0, 130.2, 127.6 (*o*-C_6H_4, each 2C), 34.1 ($CH_2CH_2CH_2$, 1C), 25.2 ($SeCH_2$, 2C, $^1J_{SeC}$ = 62) and 24.0 ($SeCH_2$, 2C, $^1J_{SeC}$ = 68 Hz). ^{77}Se-{^{1}H} NMR (68.68 MHz, $CDCl_3$): δ 296. IR (KBr disc): 3065w, 3050w, 3035w, 2961w, 2923w, 2885w, 2827w, 1483s, 1446s, 1411s, 1340m, 1280s, 1259m, 1219m, 1189m, 1113m, 1099m, 1072m, 1039m, 946w, 869w, 860m, 820m, 803m, 760s, 746s, 614s, 606s, 593m, 580m, 446w and 394w cm^{-1}.

[$Cu(L^1)_2$]PF_6. The compound [$Cu(MeCN)_4$]PF_6 (77 mg, 0.21 mmol) was added to L^1 (100 mg, 0.41 mmol) in Me_2CO (10 cm^3) under N_2. The reaction mixture was stirred at room temperature for 1.5 h, giving a colourless solution. Addition of deoxygenated diethyl ether (100 cm^3) afforded a white precipitate which was filtered off, recrystallised from Me_2CO and dried *in vacuo.* Yield = 74 mg, 52% (Found: C, 20.8; H, 3.3. Calc. for $C_{12}H_{24}CuF_6PSe_4$: C, 20.7; H, 3.5%). Electrospray mass spectrum (MeCN): found *m/z* = 549; calculated for [$Cu(L^1)_2$]$^+$ *m/z* = 551 (^{63}Cu, ^{80}Se). ^{1}H NMR [$(CD_3)_2CO$, 300 K]: δ 3.1–3.3 ($SeCH_2$, 4 H) and 2.3 ($CH_2CH_2CH_2$, 2 H). IR (Nujol): 1295w, 1250w, 1222w, 1152w, 1050w, 1001w, 960w, 876w, 838s and 556s cm^{-1}.

[$Cu(L^2)_2$]BF_4. The compound L^2 (50 mg, 0.16 mmol) was stirred in a solution of [$Cu(MeCN)_4$]BF_4 (26 mg, 0.08 mmol) in deoxygenated acetone (10 cm^3, 273 K) under an atmosphere of N_2 for 2 h. The solvent volume was reduced to *ca.* 1 cm^3 *in vacuo* and deoxygenated diethyl ether was added (30 cm^3). The resulting cream solid was filtered off, recrystallised from CH_2Cl_2 and dried *in vacuo.* Yield = 37 mg, 60% (Found: C, 31.0; H, 2.5. Calc. for $C_{22}H_{28}BCuF_4Se_4 \cdot 2CH_2Cl_2$: C, 31.0; H, 3.0%). Electrospray mass spectrum: found *m/z* = 673; calculated for [$Cu(L^2)_2$]$^+$ *m/z* = 675 (^{63}Cu, ^{80}Se). ^{1}H NMR spectrum (CD_3CN, 300 K): δ 7.1–7.3 (*o*-C_6H_4, 4 H), 4.2 [*o*-$C_6H_4(CH_2Se)$, 4 H], 2.6 ($SeCH_2CH_2$, 4 H) and 2.1 ($CH_2CH_2CH_2$, 2 H). IR (CsI disc): 3046w, 2923w, 2957w, 2977w, 1482w, 1445m, 1404m, 1395m, 1370w, 1339w, 1280w, 1256m, 1219w, 1189s, 860w, 824m, 774m and 609m cm^{-1}.

[$Ag(L^1)_2$]BF_4. The compound $AgBF_4$ (32 mg, 0.16 mmol) in Me_2CO (5 cm^3) was added to L^1 (78 mg, 32 mmol) in CH_2Cl_2 solution (10 cm^3) under N_2. Stirring for 1 h in a foil-wrapped flask gave a colourless solution, to which deoxygenated diethyl ether (100 cm^3) was added, giving a white precipitate. The solid was filtered off, recrystallised from MeCN and dried *in vacuo.* Yield = 61 mg, 56% (Found: C, 20.7; H, 2.7. Calc. for $C_{12}H_{24}AgBF_4Se_4 \cdot CH_2Cl_2$: C, 20.4; H, 3.1%). Electrospray mass spectrum (MeCN): found *m/z* = 593; calculated for [$Ag(L^1)_2$]$^+$ *m/z* = 595 (^{107}Ag, ^{80}Se). ^{1}H NMR (CD_3CN, 300 K): δ 3.1–3.3

($SeCH_2$, 4 H) and 2.5 ($CH_2CH_2CH_2$, 2 H). IR (Nujol): 1292w, 1222w, 1050s, 879w and 519m cm^{-1}.

[Ag(L^2)$_2$]BF_4. The compound L^2 (50 mg, 0.16 mmol) was stirred in a solution of $AgBF_4$ (31 mg, 0.08 mmol) in deoxygenated Me_2CO (10 cm^3, foil-wrapped flask) under an atmosphere of N_2 for 2 h. The solution was reduced to *ca.* 1 cm^3 and deoxygenated diethyl ether was added (30 cm^3). The resulting white solid was filtered off, recrystallised from CH_2Cl_2 and dried *in vacuo.* Yield = 34 mg, 60% (Found: C, 31.1; H, 2.8. Calc. for $C_{22}H_{28}AgBF_4Se_4 \cdot CH_2Cl_2$: C, 31.1; H, 3.4%). Electrospray mass spectrum: found $m/z = 412$, 717; calculated for $[Ag(L^2)]^+$ $m/z = 413$, $[Ag(L^2)_2]^+$ $m/z = 719$ (^{107}Ag, ^{80}Se). ^1H NMR (CD_3CN, 300 K): δ 7.2–7.3 (*o*-C_6H_4, 4 H), 4.2 [*o*-$C_6H_4(CH_2Se)$, 4 H], 2.8 ($SeCH_2CH_2$, 4 H) and 2.1 ($CH_2CH_2CH_2$, 2 H). IR (CsI disc): 3051w, 2932w, 2877w, 1704w, 1629w, 1487m, 1444m, 1424m, 1406m, 1381w, 1344w, 1283m, 1256m, 1222w, 1182w, 1164w, 1086 (br), 1049 (br), 885w, 861w, 836w, 825w, 808w, 774w, 608m, 598 (sh), 542w, 521w and 447w cm^{-1}.

[(AuCl)$_2$$L^1$]. The compound L^1 (50 mg, 0.26 mmol) was added to a solution of [AuCl(tht)] (133 mg, 0.41 mmol) in degassed MeCN (20 cm^3) in the dark (*i.e.* in a foil-wrapped flask) at 0 °C for 1 h. During this time a white precipitate formed, which was filtered off, washed with degassed MeCN and dried *in vacuo.* Yield = 56 mg, 30% (Found: C, 10.4; H, 2.0. Calc. for $C_6H_{12}Au_2Cl_2Se_2$: C, 10.2; H, 1.7%). ^1H NMR (CD_3CN, 300 K): δ 2.9–2.6 ($SeCH_2$, 4 H) and 1.7 ($CH_2CH_2CH_2$, 2 H). IR (CsI disc): 3051w, 2956w, 2921w, 1426m, 1412m, 1360m, 1286w, 1217m, 1123m, 987w, 931w, 806w, 617m and 330w cm^{-1}.

[(AuCl)$_2$$L^2$]. The compound L^2 (50 mg, 0.16 mmol) was stirred in a solution of [AuCl(tht)] (105 mg, 0.33 mmol) in deoxygenated Me_2CO (10 cm^3, foil-wrapped apparatus) under an atmosphere of N_2 at 0 °C for 1 h during which time a white precipitate formed. Special care was taken not to expose the reaction mixture to light. The required solid was filtered off and washed with degassed Me_2CO (1 cm^3 × 2) and dried *in vacuo.* Yield = 41 mg, 31% (Found: C, 17.0; H, 1.9. Calc. for $C_{11}H_{14}Au_2Cl_2Se_2$: C, 17.2; H, 1.8%). ^1H NMR [$(CD_3)_2CO$, 300 K]: δ 7.4–7.7 (*o*-C_6H_4, 4 H), 4.3 [*o*-$C_6H_4(CH_2Se)_2$, 4 H], 3.1 ($SeCH_2CH_2$) and 2.1 ($CH_2CH_2CH_2$, 2 H). IR (CsI disc): 3010w, 2961w, 2928w, 1486w, 1448w, 1406w, 1356w, 1221m, 1114s, 769m, 613w and 328w cm^{-1}.

[Ag([16]aneSe$_4$)]BF_4. The compound $AgBF_4$ (36 mg, 0.18 mmol) in Me_2CO (5 cm^3) was added to [16]aneSe$_4$ (85 mg, 18 mmol) in CH_2Cl_2 solution (10 cm^3) under N_2. Stirring for 1 h in a foil-wrapped flask gave a colourless solution, to which deoxygenated diethyl ether (100 cm^3) was added, giving a white precipitate. The solid was filtered off, washed with diethyl ether and dried *in vacuo.* Yield = 81 mg, 66% (Found: C, 20.9; H, 3.3. Calc. for $C_{12}H_{24}AgBF_4Se_4$: C, 21.1; H, 3.5%). Electrospray mass spectrum (MeCN): found $m/z = 595$, 549; calculated for $[^{107}Ag([16]ane^{80}Se_4)]^+$ $m/z = 593$, $[^{107}Ag([16]ane^{80}Se_4 - C_3H_6)]^+$ $m/z = 553$. IR (Nujol): 1289w, 1222w, 1203w, 1045s and 519m cm^{-1}.

***cis*-[PdCl$_2$(L^2)].** The compound $PdCl_2$ (29 mg, 0.16 mmol) was added to a solution of L^2 (50 mg, 0.16 mmol) in degassed MeCN solution (20 cm^3). Refluxing this mixture for 10 h afforded an orange precipitate. After concentrating the solution, the solid was filtered off, washed with diethyl ether and dried *in vacuo.* Yield = 63 mg, 80% (Found: C, 27.0; H, 3.2. Calc. for $C_{11}H_{14}Cl_2PdSe_2$: C, 27.4; H, 2.9%). ^1H NMR [$(CD_3)_2SO$, 300 K]: δ 7.3–7.5 (*o*-C_6H_4, 4 H), 4.4 [*o*-$C_6H_4(CH_2Se)_2$, 4 H], 2.6 ($SeCH_2CH_2$, 4 H) and 2.1 ($CH_2CH_2CH_2$, 2 H). ^{77}Se-{^1H} NMR [68.68 MHz, Me_2SO–$(CD_3)_2SO$, 300 K]: δ +249. IR (Nujol mull): ν(Pd−Cl) 314 (br) cm^{-1}.

***cis*-[PtCl$_2$(L^2)].** Method as for *cis*-[PdCl$_2$(L^2)] above, but using $PtCl_2$ (43 mg, 0.16 mmol) and L^2 (50 mg, 0.16 mmol), giving a yellow solid. Yield = 65 mg, 72% (Found: C, 23.5; H, 2.6. Calc. for $C_{11}H_{14}Cl_2PtSe_2$: C, 23.1; H, 2.5%). ^1H NMR spectrum [$(CD_3)_2SO$, 300 K]: δ 7.3–7.5 (*o*-C_6H_4, 4 H), 4.4 [*o*-$C_6H_4(CH_2Se)_2$, 4 H], 3.6 ($SeCH_2CH_2$, 4 H) and 2.1 ($CH_2CH_2CH_2$, 2 H). ^{77}Se-{^1H} NMR [68.68 MHz, Me_2SO–$(CD_3)_2SO$, 300 K]: δ +244. ^{195}Pt NMR [77.8 MHz, $(CD_3)_2SO$, 300 K]: δ −3672. IR (Nujol mull): ν(Pt−Cl) 317m and 305w cm^{-1}.

X-Ray crystallography

For each compound the selected crystal was coated with mineral oil, mounted on a glass fibre using silicone grease as adhesive, and immediately placed in a stream of cold nitrogen gas. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Systems Cryostream low-temperature attachment, with graphite-monochromated Mo-Kα X-radiation ($\lambda_{max} = 0.710\ 73$ Å), $T = 150$ K, ω–2θ scans. The intensities of three standard reflections were monitored every 150. No significant crystal decay or movement was observed {except for [Ag([8]aneSe$_2$)$_2$]BF_4, see below}. As there were no identifiable faces the raw data were corrected for absorption using ψ scans {except for *cis*-[PdCl$_2$(L^2)], see below}. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses in each case and all refinements were based on *F*. Crystallographic data are presented in Table 6.

L^2. Single crystals of compound L^2 were obtained from a solution in $CHCl_3$. The structure was solved by direct methods using SHELXS 86[27] and expanded using iterative cycles of full-matrix least squares and Fourier-difference syntheses which located all of the remaining non-H atoms for two independent molecules in the asymmetric unit.[28] All non-H atoms were refined anisotropically and H atoms were included in fixed, calculated positions with d(C−H) = 0.95 Å.

[Cu(L^2)$_2$]BF_4. Crystals suitable for single-crystal X-ray analysis were obtained by vapour diffusion of diethyl ether into a solution of the complex in MeCN. Analysis of the systematic absences indicated the space group to be either *C*2/*c* or *Cc*. The structure was initially solved in *C*2/*c* since the intensity statistics suggested a centric space group. Structure solution used heavy-atom methods,[29] and all other non-H atoms were then located by iterative cycles of full-matrix least-squares refinements and Fourier-difference syntheses.[28] This gave one half cation in the asymmetric unit, but the BF_4^- anion appeared to be very badly disordered and would not refine. The space group was then changed to *Cc*, and this gave a complete cation and an ordered BF_4^- anion in the asymmetric unit. The Cu, Se and F atoms were refined anisotropically (the low data : parameters ratio meant that the C and B atoms were refined isotropically). The choice of enantiomorph was confirmed by refining the Flack parameter.[30] Hydrogen atoms were included in fixed, calculated positions with d(C−H) = 0.95 Å.

[Ag(L^1)$_2$]BF_4. Single crystals of this compound were obtained by vapour diffusion of Et_2O into a solution in CH_2Cl_2. During data collection the intensities of the standard reflections decreased by 6.5%, hence a linear decay correction was applied to the raw data to account for this. The data set was rather weak probably reflecting rather poor crystal quality. The systematic absences indicated the space group to be either $P4_1$ or $P4_3$. The structure was solved in the former using heavy-atom methods[29] and developed by using iterative cycles of full-matrix least-squares refinements and Fourier-difference syntheses.[28] This gave one complete $[Ag(L^1)_2]^+$ cation and a BF_4^- anion in the asymmetric unit. The choice of space group was confirmed by refining the Flack parameter.[30] Some disorder was identified in the BF_4^- anion. This was modelled quite successfully by using two fully occupied F atoms [F(1) and F(3)] and four 50% occupied

Table 6 Crystallographic data

	L^2	$[Ag(L^1)_2BF_4$	$[Cu(L^2)_2]BF_4$	$[Ag(L^2)_2]BF_4$	*cis*-$[PdCl_2(L^2)]$
Formula	$C_{11}H_{14}Se_2$	$C_{12}H_{24}AgBF_4Se_4$	$C_{22}H_{28}BCuF_4Se_4$	$C_{22}H_{28}AgBF_4Se_4$	$C_{11}H_{14}Cl_2PdSe_2$
M	304.15	678.83	758.65	802.97	481.46
Colour, morphology	Colourless, column	Colourless, column	Colourless, column	Colourless, block	Yellow, block
Crystal dimensions/mm	0.70 × 0.10 × 0.08	0.30 × 0.15 × 0.10	0.60 × 0.45 × 0.20	0.60 × 0.55 × 0.40	0.25 × 0.25 × 0.25
Crystal system	Monoclinic	Tetragonal	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P4_1$	Cc	$Fdd2$	$P2_1/c$
a/Å	5.304(5)	10.198(3)	15.341(7)	15.92(1)	12.584(5)
b/Å	15.472(8)	10.198	11.844(5)	26.087(5)	7.895(6)
c/Å	26.600(8)	18.618(3)	14.953(7)	11.985(6)	13.666(4)
β/°	90.66(8)	—	114.56(4)	—	98.70(3)
U/Å^3	2182(2)	1936(1)	2471(2)	4977(4)	1342(1)
Z	8	4	4	8	4
F(000)	1184	1280	1464	3072	912
D_c/g cm^{-3}	1.851	2.329	2.039	2.143	2.383
μ(Mo-Kα)/cm^{-1}	66.60	85.86	68.17	66.99	71.10
Transmission factors (maximum, minimum)	1.000, 0.555	1.000, 0.480	1.000, 0.619	1.000, 0.299	1.000, 0.469
No. unique observed reflections	4011	1971	2300	1226	2555
R_{int} (based on F^2)	0.064	—	0.085	—	0.089
Unique observed reflections with $[I_o > n\sigma(I_o)]$	1929 (n = 2.5)	1126 (n = 2)	1683 (n = 2.5)	1072 (n = 2.5)	1295 (n = 2.5)
No. parameters	235	132	173	144	90
Goodness of fit	1.32	1.51	2.99	1.71	1.85
$R(F_o)$	0.038	0.052	0.047	0.042	0.050
$R'(F_o)$	0.041	0.057	0.058	0.055	0.059
Maximum, minimum residual peaks/e Å^{-3}	0.62, −0.59	1.51, −1.27	1.43, −1.54	1.60, −1.93	0.96, −1.24

$R = \Sigma(|F_o|_i - |F_c|_i)/\Sigma|F_o|_i$, $R' = [\Sigma w_i(|F_o|_i - |F_c|_i)^2/\Sigma w_i|F_o|_i^2]^{\frac{1}{2}}$, goodness of fit $= [\Sigma(|F_o|_i - |F_c|_i)/\sigma_i]/(n - m) \approx 1$.

F atoms. Atoms F(1) and F(3) also showed slightly higher than expected thermal parameters, but attempts to split their occupancies were not successful. The Ag, Se and fully occupied F atoms were refined anisotropically. The other non-H atoms were refined isotropically due to the limited data : parameter ratio resulting from the weak data set. Hydrogen atoms were included in fixed, calculated positions with d(C–H) = 0.95 Å.

$[Ag(L^2)_2]BF_4$. Crystals suitable for single-crystal X-ray analysis were obtained by vapour diffusion of diethyl ether into a solution of the complex in MeCN. The structure was solved by heavy-atom methods,[29] which revealed the Ag atom occupying a crystallographic two-fold site. The other non-H atoms of one half-cation and a half BF_4^- anion (with the B atom occupying a crystallographic two-fold site) were then located by iterative cycles of full-matrix least-squares refinements and Fourier-difference syntheses.[28] The BF_4^- anion showed some disorder which was satisfactorily modelled by using partial F atom occupancies, such that the B atom had four 50% occupied F atoms around it (related to another four by the two-fold operation). The Cu, Se, C and B atoms were refined anisotropically, while the partially occupied F atoms were refined isotropically. Hydrogen atoms were included in fixed, calculated positions with d(C–H) = 0.95 Å.

***cis*-$[PdCl_2(L^2)]$.** Suitable crystals were obtained from a solution of the complex in dimethyl sulfoxide. The structure was solved by direct methods using SHELXS 86[27] and developed by iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses which located all non-H atoms in the asymmetric unit.[28] At isotropic convergence an empirical absorption correction was applied to the raw data using DIFABS[31] since the initial ψ-scans did not give a satisfactory correction. The Pd, Cl and Se atoms were refined anisotropically and H atoms were included in fixed, calculated positions with d(C–H) = 0.95 Å.

CCDC reference number 186/637.

Acknowledgements

We thank the Leverhulme Trust (S. M. S.) and the EPSRC (J. J. Q. and D. G. B.) for support, and the latter for provision of the diffractometer. We also thank Johnson-Matthey plc for generous loans of $KAuCl_4$, $PdCl_2$ and $PtCl_2$.

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Received 27th May 1997; *Paper* 7/03636A