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Synthesis and characterisation of selenoether macrocyclic complexes of Co^{III}, Rh^{III} and Ir^{III}: crystal structures of *trans*-$[CoBr_2([16]aneSe_4)]BPh_4$ and *trans*-$[IrBr_2([16]aneSe_4)]BPh_4$ ($[16]aneSe_4$ = 1,5,9,13- tetraselenacyclohexadecane)

William Levason, Jeffrey J. Quirk and Gillian Reid*

Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK

Reaction of CoX_2 (X = Cl, Br or I) with $[16]aneSe_4$ (1,5,9,13-tetraselenacyclohexadecane) and NH_4PF_6 under a dry oxygen atmosphere yielded the complexes $[CoX_2([16]aneSe_4)]PF_6$. The rhodium(III) and iridium(III) species $[MX_2([16]aneSe_4)]^+$ (M = Rh or Ir, X = Cl or Br) were obtained by reaction of $MX_3{\cdot}3H_2O$ with $[16]aneSe_4$ in refluxing aqueous ethanol, or for $[RhBr_2([16]aneSe_4)]^+$, from $[Rh(H_2O)_6]^{3+}$, LiBr and $[16]aneSe_4$, and isolated by the addition of either $NaBF_4$, NH_4PF_6 or $NaBPh_4$. The compound $[RhCl_2([8]aneSe_2)_2]BF_4$ ($[8]aneSe_2$ = 1,5-diselenacyclooctane) was prepared from $[\{Rh(CO)_2Cl\}_2]$, $[8]aneSe_2$ and HBF_4 in refluxing aqueous acetone. All complexes were characterised by IR, UV/VIS, ^1H and $^{77}Se\text{-}\{^1H\}$ (and ^{59}Co where appropriate) NMR spectroscopies, mass spectrometry and microanalyses. The UV/VIS and ^{59}Co NMR spectroscopy on $[CoX_2([16]aneSe_4)]^+$ showed that for X = Cl and Br only the *trans* dihalide species is present (this is supported by $^{77}Se\text{-}\{^1H\}$ NMR data), whereas a mixture of *cis* and *trans* forms is present where X = I. The $^{77}Se\text{-}\{^1H\}$ NMR spectroscopic studies on $[MX_2([16]aneSe_4)]^+$ (M = Rh or Ir, X = Cl or Br) and $[RhCl_2([8]aneSe_2)_2]^+$ showed the presence of both the *cis* and *trans* forms in dimethylformamide solution, although for $[MCl_2([16]aneSe_4)]^+$ only the *trans* isomer is soluble in $MeNO_2$. The crystal structures of *trans*-$[MBr_2([16]aneSe_4)]BPh_4$ (M = Co or Ir) each show endocyclic co-ordination of the metal to all four Se donor atoms of the macrocycle, with the mutually *trans* bromide ligands completing the distorted octahedron; Co–Br(1) 2.396(1), Co–Se(1) 2.393(1), Co–Se(2) 2.402(1); Ir–Br(1) 2.468(4), Ir–Br(2) 2.483(4), Ir–Se(1) 2.470(3), Ir–Se(2) 2.470(3), Ir–Se(3) 2.461(3), Ir–Se(4) 2.462(3) Å.

In recent years the chemistry of macrocyclic thioethers has attracted considerable interest.[1] In marked contrast to this, selenoether chemistry has been largely restricted to acyclic compounds,[2] with few studies on macrocyclic selenoethers.[3–5] We are interested in developing the chemistry of macrocyclic selenoethers which, owing to their lower electronegativity, ought to be better ligands for transition metals than thioethers. Additionally, ^{77}Se NMR spectroscopy ($I = \frac{1}{2}$, 7.8%) is a convenient probe through which to monitor the behaviour of Se-containing compounds in solution. In this context we have reported the preparation of the square-planar d^8 species $[M([16]aneSe_4)]^{2+}$ (M = Pd or Pt; $[16]aneSe_4$ = 1,5,9,13-tetraselenacyclohexadecane).[4] Treatment of $[Pt([16]aneSe_4)]^{2+}$ with X_2–CCl_4 (X = Cl or Br) yields *trans*-$[PtX_2([16]aneSe_4)]^{2+}$, the first examples of cationic platinum(IV) selenoethers. Platinum-195 and $^{77}Se\text{-}\{^1H\}$ NMR spectroscopic and X-ray crystallographic studies confirmed the Se_4X_2 donor set in these octahedral species, and illustrate the ability of the soft selenoether macrocycle to stabilise the relatively hard platinum(IV) centre.[5] In a preliminary communication we also reported the synthesis and structure of *trans*-$[RhCl_2([16]aneSe_4)]^+$.[6] We now report the preparation and characterisation of the homologous species $[MX_2([16]aneSe_4)]^+$ (M = Co, X = Cl, Br or I; M = Rh or Ir, X = Cl or Br) and $[RhCl_2([8]aneSe_2)_2]BF_4$ ($[8]aneSe_2$ = 1,5-diselenacyclooctane), including their $^{77}Se\text{-}\{^1H\}$ and, where appropriate, ^{59}Co NMR spectroscopic data, together with single-crystal structure determinations on *trans*-$[CoBr_2([16]aneSe_4)]BPh_4$ and *trans*-$[IrBr_2([16]aneSe_4)]BPh_4$.

Results and Discussion

Reaction of anhydrous CoX_2 (X = Cl, Br or I) with $[16]aneSe_4$ in $MeNO_2$ solution in air yields the cobalt(III) selenoether cations $[CoX_2([16]aneSe_4)]^+$, which can be isolated as orange (X = Cl or Br) or purple (X = I) powders by addition of PF_6^- counter ion and diethyl ether. These complexes are stable in the solid state; the chloro and bromo species are also stable in $MeNO_2$ and MeCN solution, whereas $[CoI_2([16]aneSe_4)]PF_6$ decomposes in MeCN solution over the course of a few minutes and in $MeNO_2$ solution over an hour or so. They are insoluble in chlorinated solvents and hydrocarbons. Electrospray mass spectrometry shows that the highest-intensity peaks have the correct isotopic distributions for $[CoX_2([16]aneSe_4)]^+$ (X = Cl, Br or I), while the IR spectra confirm the presence of PF_6^- anion [ν(P–F) 838, δ(F–P–F) 557 cm^{-1}] and $[16]aneSe_4$ ligand. A peak tentatively assigned to ν(Co–Cl) is also seen for X = Cl (379 cm^{-1}), indicative of a *trans*-dihalide arrangement.[7] These results, together with ^1H NMR spectroscopic and microanalytical data, indicate the formulation $[CoX_2([16]aneSe_4)]PF_6$ for the products. Attempts to prepare the cobalt(III) species $[CoX_2([8]aneSe_2)_2]^+$ *via* an analogous route to that described above were unsuccessful. *In situ* reaction mixtures were also monitored by ^{59}Co NMR spectroscopy and showed no evidence for any such species. The only other reported examples of cobalt(III) selenoether complexes are $[CoX_2(MeSeCH_2CH_2SeMe)_2]BPh_4$ (X = Cl, Br or I).[8]

The rhodium(III) complex $[RhCl_2([8]aneSe_2)_2]BF_4$ was prepared from $[\{Rh(CO)_2Cl\}_2]$, $[8]aneSe_2$ and HBF_4 in aqueous acetone solution, while synthesis of the rhodium(III) and iridium(III) tetraselenoether macrocyclic species $[MX_2([16]aneSe_4)]^+$ used $MX_3{\cdot}3H_2O$ (M = Rh, X = Cl; M = Ir, X = Cl or Br) and $[16]aneSe_4$ in refluxing aqueous ethanol {EtOH–Me_2SO was used for $[IrBr_2([16]aneSe_4)]^+$}. The products were isolated as microcrystalline solids upon addition of a non-co-ordinating counter ion such as PF_6^-, BF_4^- or BPh_4^-. The complex $[RhBr_2([16]aneSe_4)]^+$ was obtained by reaction of $[Rh(H_2O)_6][NO_3]_3$, [16]aneSe_4 and 2 molar equivalents of LiBr, and isolated as an orange solid by the addition of an excess of NH_4PF_6. In each case FAB or electrospray mass spectrometry shows peaks with the correct isotopic distributions for $[MX_2([16]aneSe_4)]^+$, and in certain cases peaks at lower *m*/*z* were also observed, consistent with loss of C_3H_6 from the ligand backbone or loss of X. Infrared spectroscopy confirmed the presence of the selenoether ligand and the counter anion, although ν(M–X) could not be assigned with certainty in the range 200–400 cm^{-1}. Together with ^1H NMR spectroscopic data and microanalyses, these results support the formulae given above for the products.

Electronic spectra

The UV/VIS spectrum of a low-spin d^6 complex with O_h symmetry is expected to show two d–d bands corresponding to the transitions $^1A_{1g}\rightarrow{}^1T_{1g}$ at lower energy and $^1A_{1g}\rightarrow{}^1T_{2g}$ at higher energy. In *trans*-$[CoL_4X_2]^+$ the symmetry is reduced to D_{4h} and the lower-energy transition splits to give $\nu_1 = {}^1A_{1g}\rightarrow{}^1E_g$ and $\nu_2 = {}^1A_{1g}\rightarrow{}^1A_{2g}$. The complex *cis*-$[CoL_4X_2]^+$ has C_{2v} local symmetry, and results in similar splitting. However, the energy gap between ν_1 and ν_2 is typically much smaller than in the *trans* isomer.[9] The UV/VIS spectroscopic data are presented in Table 1. Inspection of the UV/VIS spectra for $[CoX_2([16]aneSe_4)]PF_6$ reveals two d–d bands for X = Cl or Br, suggesting that the chloro and bromo complexes exist as *trans* isomers. The energies of ν_1 and ν_2 are similar to those observed for $[CoX_2(MeSeCH_2CH_2SeMe)_2]^+$ (X = Cl, Br or I).[8] The higher-energy $^1A_{1g}\rightarrow{}^1T_{2g}$ transition is presumably obscured by the more intense charge-transfer transitions in the macrocyclic cations. The UV/VIS spectrum of $[CoI_2([16]aneSe_4)]PF_6$ was recorded by diffuse reflectance owing to the instability of this species in solution. The spectrum shows weak d–d transitions at 13 300 and 12 700 cm^{-1}; however since the ^{59}Co NMR spectrum (see below) of this complex shows two resonances, indicating that it probably exists in solution as a mixture of *cis* and *trans* isomers, further assignment of these bands was not possible. As expected, the $Se(\pi)\rightarrow Co(e_g)$ charge-transfer transition at *ca.* 26 000 cm^{-1} in these species is not very sensitive to the nature of X, while the $X(\pi)\rightarrow Co(e_g)$ transition occurs at 37 310 for X = Cl, 32 470 for X = Br and 19 010 cm^{-1} for X = I.

The ^{77}Se-{^1H} NMR studies show that the rhodium(III) and iridium(III) species are a mixture of *cis* and *trans* isomers in dimethylformamide (dmf) solution. For the rhodium(III) complexes the only d–d transition clearly observed in the UV/VIS spectrum below the higher-energy charge-transfer bands we assign to the $^1A_{1g}\rightarrow{}^1E_g$ transition of the *trans* isomer. This is observed at 23 800 for $[RhCl_2([8]aneSe_2)_2]BF_4$, 22 270 for $[RhCl_2([16]aneSe_4)]BF_4$ and 21 550 cm^{-1} for $[RhBr_2([16]aneSe_4)]PF_6$. This d–d transition occurs at similar energy in *trans*-$[RhCl_2(MeSeCH_2CH_2SeMe)_2]^+$ and *trans*-$[RhCl_2(PhSeCH_2CH_2SePh)_2]^+$.[10] The other absorptions of the *trans* isomer of the macrocyclic rhodium(III) cations and all of the d–d transitions expected for the *cis* isomer are obscured by the charge-transfer bands. The charge-transfer absorptions in these species are not expected to differ significantly between the *cis* and *trans* isomers, and these appear as broad, intense features assigned to $Se(\pi)\rightarrow Rh(e_g)$ at lower energy and $X(\pi)\rightarrow Rh(e_g)$ at higher energy. We observe a shift to higher energy by *ca.* 7000 cm^{-1} upon replacement of Co by Rh in these complexes. For the iridium(III) complexes no significant features were observed below the $\pi\rightarrow\pi^*$ transitions of the BPh_4^- groups.

^{59}Co and ^{77}Se-{^1H} NMR spectra

The ^{59}Co and ^{77}Se-{^1H} NMR data for the compounds are presented in Table 2. Cobalt-59 NMR spectroscopy ($I = \frac{7}{2}$, 100%) has been shown to be a useful technique for the characterisation of cobalt(III) dihalogeno complexes of Group 16 donor ligands, typically showing resonances at around δ 9000, which are broadened due to the quadrupole moment of the ^{59}Co nucleus.[8,11] The chemical shift is sensitive to the donor set around the Co atom and, to a lesser extent, the geometric isomers.[12] Different invertomers have not been observed by ^{59}Co NMR spectroscopy in other cobalt(III) thioether or selenoether complexes,[8,11] probably since the chemical shift differences expected for the different diastereoisomers are smaller than the observed ^{59}Co NMR linewidths. Previous ^{59}Co NMR spectroscopic studies on $[CoX_2([14]aneS_4)]^+$

Table 1 The UV/VIS spectroscopic data[a]

Complex	ν_{max}/cm^{-1} ($\varepsilon_{mol}/dm^3\ mol^{-1}\ cm^{-1}$)	Assignment
$[CoCl_2([16]aneSe_4)]PF_6$	14 620 (314)	$^1A_{1g}\rightarrow{}^1E_g$
	17 360 (285)	$^1A_{1g}\rightarrow{}^1A_{2g}$
	26 600 (25 830)	$Se(\pi)\rightarrow Co(e_g)$
	37 310 (7705)	$Cl(\pi)\rightarrow Co(e_g)$
$[CoBr_2([16]aneSe_4)]PF_6$	14 330 (230)	$^1A_{1g}\rightarrow{}^1E_g$
	16 180 (170)	$^1A_{1g}\rightarrow{}^1A_{2g}$
	25 970 (33 430)	$Se(\pi)\rightarrow Co(e_g)$
	32 470 (19 640)	$Br(\pi)\rightarrow Co(e_g)$
$[CoI_2([16]aneSe_4)]PF_6$[b]	12 700	See text
	13 300	See text
	19 010	$I(\pi)\rightarrow Co(e_g)$
	27 800	$Se(\pi)\rightarrow Co(e_g)$
$[RhCl_2([8]aneSe_2)_2]BF_4$	23 800 (sh *ca.* 2500)	$^1A_{1g}\rightarrow{}^1E_g$
	31 250 (21 700)	$Se(\pi)\rightarrow Rh(e_g)$
	33 330 (sh *ca.* 20 000)	
	43 100 (20 000)	$Cl(\pi)\rightarrow Rh(e_g)$
$[RhCl_2([16]aneSe_4)]PF_6$	22 270 (178)	$^1A_{1g}\rightarrow{}^1E_g$
	34 010 (50 500)	$Se(\pi)\rightarrow Rh(e_g)$
	42 735 (15 960)	$Cl(\pi)\rightarrow Rh(e_g)$
$[RhBr_2([16]aneSe_4)]PF_6$	21 550 (460)	$^1A_{1g}\rightarrow{}^1E_g$
	33 780 (51 050)	$Se(\pi)\rightarrow Rh(e_g)$
	37 880 (28 060)	$Br(\pi)\rightarrow Rh(e_g)$
$[IrCl_2([16]aneSe_4)]BPh_4$	42 200 (sh *ca.* 20 800)	$\pi\rightarrow\pi^*$ (BPh_4^-)
$[IrBr_2([16]aneSe_4)]BPh_4$	41 000 (sh *ca.* 36 300)	$\pi\rightarrow\pi^*$ (BPh_4^-)

[a] Recorded in MeCN solution. [b] Diffuse reflectance.

Table 2 The ^{77}Se and ^{59}Co NMR data

Complex	Isomer	$\delta(^{77}Se)$ ($^{1}J_{RhSe}$/Hz)	$\delta(^{59}Co)$
$[CoCl_2([16]aneSe_4)]PF_6$	*trans*[a]	197	9590
$[CoBr_2([16]aneSe_4)]PF_6$	*trans*[a]	169	9125
$[CoBr_2([16]aneSe_4)]BPh_4$	*trans*[a]	169	9125
$[CoI_2([16]aneSe_4)]PF_6$	*trans* and *cis*[a,b]	Not observed	8436, 8465
$[RhCl_2([8]aneSe_2)_2]BF_4$	*trans*[b,c]	160 (42)	—
	cis[b–d]	156 (36), 181 (43)	—
$[RhCl_2([16]aneSe_4)]PF_6$	*trans*[a]	160 (30)	—
	cis[b–d]	157 (36), 203 (37)	—
$[RhBr_2([16]aneSe_4)]PF_6$	*trans*[a]	141 (32)	—
	cis[b–d]	151 (36), 153 (37)	—
$[IrCl_2([16]aneSe_4)]BPh_4$	*trans*[a]	138	—
$[IrBr_2([16]aneSe_4)]BPh_4$	*trans*[c,e]	123 (major), 128, 134 (minor)	—
	cis[c,d]	124, 152	—

[a] Recorded in $MeNO_2$. [b] Solution contained a mixture of *cis* and *trans* isomers. [c] Recorded in dmf. [d] Downfield signal corresponds to Se *trans* X (X = Cl or Br), upfield signal to Se *trans* Se. [e] Mixture of invertomers.

($[14]aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane) revealed single broad resonances at δ 7384 (X = Cl), 7062 (Br) and 7342 (I), and the latter was assigned as the *trans*-diiodo species in solution, while the dichloro and dibromo species were assigned *cis* octahedral geometries.[11] Both the ^{59}Co and $^{77}Se\text{-}\{^1H\}$ NMR spectra of $[CoCl_2([16]aneSe_4)]PF_6$ and $[CoBr_2([16]aneSe_4)]PF_6$ show a single, fairly broad resonance indicative of the presence of a single isomer in solution. On the basis of the IR and UV/VIS spectroscopic data presented above we assign these cations as the *trans* dihalide isomers. In contrast, $[CoI_2([16]aneSe_4)]PF_6$ shows two resonances of different intensities by ^{59}Co NMR spectroscopy, probably indicating the presence of both the *cis* and *trans* forms for this species (Fig. 1). The ^{59}Co NMR shifts for $[CoX_2([16]aneSe_4)]PF_6$ show the same trend [δ(X = Cl) > δ(Br) > δ(I)], but lie downfield of those for $[CoX_2(MeSeCH_2CH_2SeMe)_2]BPh_4$ (X = Cl, δ 8694, 8645; Br, δ 8310, 8228; I, δ 7689).[8] This downfield shift probably reflects the incorporation of four six-membered chelate rings in the complexes in this study *versus* two five-membered ones in the diselenahexane complexes. Studies on a series of cobalt(III) thioether complexes show similar downfield shifts upon replacement of five- by six-membered chelate rings.[11] Furthermore, the ^{59}Co NMR chemical shifts for the selenoether complexes (involving Se_4X_2 donor sets) lie downfield of those for related cobalt(III) thioether species involving S_4X_2 donor sets,[11] although we must be cautious of drawing further comparisons due to the different ring sizes involved. The $^{77}Se\text{-}\{^1H\}$ NMR resonances for $[CoCl_2([16]aneSe_4)]PF_6$ and $[CoBr_2([16]aneSe_4)]PF_6$ are relatively broad and occur downfield of free [16]aneSe$_4$ (δ 158). The magnitude of the selenium-77 co-ordination shifts ($\delta_{complex} - \delta_{free\ ligand}$) in the present systems are very much smaller than observed for $[CoX_2(MeSeCH_2CH_2SeMe)_2]^+$, which show downfield co-ordination shifts of *ca.* 130 ppm.[8] This is consistent with the presence of six-membered chelate rings in the cyclic systems *vs.* five-membered ones in the diselenoether species. No ^{77}Se NMR spectrum could be observed for the diiodo complex due to its limited stability in solution.

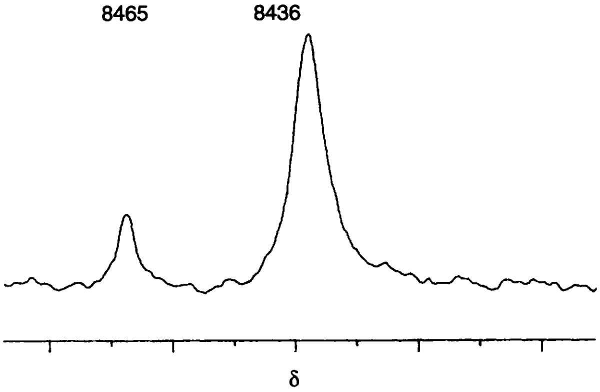

Fig. 1 The ^{59}Co NMR spectrum of $[CoI_2([16]aneSe_4)]PF_6$ at 85.3 MHz in $MeNO_2$–CD_3NO_2, 300 K

Acquisition of $^{77}Se\text{-}\{^1H\}$ NMR spectroscopic data for the rhodium(III) and iridium(III) selenoether complexes was hindered by their limited solubilities, however the data are given in Table 2. We have previously shown that in $MeNO_2$ solution we observe *trans*-$[RhCl_2([16]aneSe_4)]BF_4$ only, with δ 160 and $^{1}J_{RhSe}$ *ca.* 30 Hz.[6] Table 2 shows that in dmf solution, however, both the *trans* and *cis* forms are present. Confirmation that all of the Se donor atoms are co-ordinated in these rhodium(III) cations comes from the doublet couplings to ^{103}Rh ($I = \frac{1}{2}$, 100%) which are observed on each resonance (Fig. 2). Similarly, mixtures of the *cis* and *trans* forms are observed for $[RhCl_2([8]aneSe_2)_2]^+$ and $[RhBr_2([16]aneSe_4)]^+$. For each of the complexes, in the *cis* isomer the downfield doublet is assigned to Se *trans* to halide, with Se *trans* to Se occurring close to the doublet resonance for the *trans*-dihalide isomer. Similar chemical shift ranges have been observed previously for Se *trans* to Cl and Se *trans* to Se on Rh^{III} in selenoether complexes.[10,13] We believe that the observation of both *cis* and *trans* isomers in dmf solution *vs.* *trans* only in $MeNO_2$ solution is probably simply a consequence of the different solubilities of these isomers in the two solvents, rather than due to any *cis–trans* isomerisation processes occurring in these low-spin d^6 systems. The *cis* isomer is less soluble than the *trans* form in $MeNO_2$ solution, and we were able to obtain samples containing *trans*:*cis* ratios of 9:1 or better by careful recrystallisation from $MeNO_2$. There is little difference in the Rh–Se coupling constants for these two arrangements, with $^{1}J_{RhSe}$ lying in the range 30–42 Hz for the compounds in this study. The ^{77}Se NMR chemical shifts for the iridium(III) complexes occur upfield of those for the rhodium(III) complexes, giving the usual trend in $\delta(^{77}Se)$, with the cobalt(III) species at highest frequency and the iridium(III) species at lowest frequency. The ^{77}Se NMR spectrum of $[IrCl_2([16]aneSe_4)]BPh_4$ shows only one singlet resonance, showing that only the *trans*-dichloro species is present in $MeNO_2$ solution. In contrast, both *cis*- and *trans*-$[IrBr_2([16]aneSe_4)]BPh_4$ are present in dmf solution. Again this probably reflects the different solubilities of the *cis* and *trans* forms. For *cis*-$[IrBr_2([16]aneSe_4)]^+$ the downfield resonance at δ 152 is assigned to Se *trans* to Br, with Se *trans* to Se occurring at δ 124. Importantly, while we have been able to detect both geometric isomers in several of these [16]aneSe$_4$

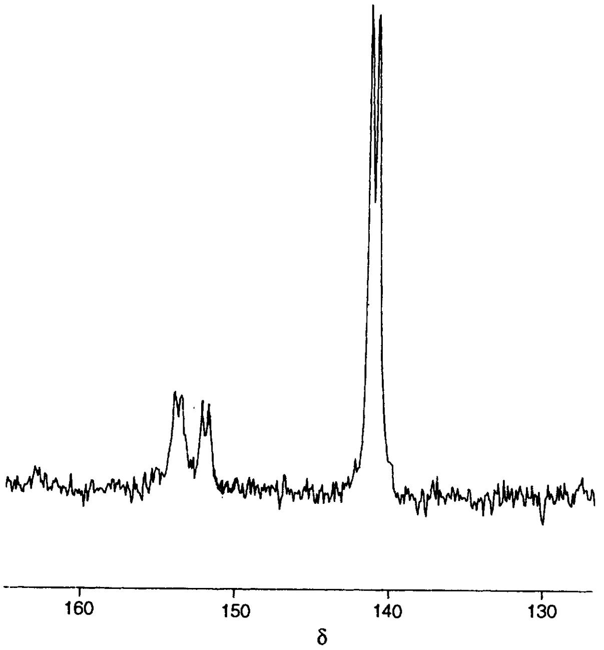

Fig. 2 The ^{77}Se-{^{1}H} NMR spectrum of [RhBr$_2$([16]aneSe$_4$)]PF$_6$ at 66.68 MHz in Me$_2$NHCO–(CD$_3$)$_2$NDCO, 300 K

complexes in solution by ^{77}Se NMR spectroscopy, in the case of the corresponding thioether species [RhCl$_2$([16]aneSe$_4$)]$^+$ X-ray crystallography confirmed the *trans*-dichloro form in the solid state, but it is unlikely that small amounts of other isomers would be detectable in solution due to the absence of suitably sensitive spectroscopic techniques.

X-Ray crystallography

In our earlier communication we reported the crystal structure of the centrosymmetric cation [RhCl$_2$([16]aneSe$_4$)]$^+$ which shows a *trans*-dichloro arrangement with the macrocyclic Se donors occupying the equatorial co-ordination sites and the non-bonded selenium lone pairs adopting an up, up, down, down configuration, Rh–Se 2.456(1), 2.461(1), Rh–Cl 2.344(2) Å.[6] The same configuration is seen in the corresponding thioether macrocyclic complex *trans*-[RhCl$_2$([16]aneS$_4$)]$^+$ [Rh–Cl 2.339(2), Rh–S 2.348(3), 2.348(3) Å], although the smaller-ring thioether complex [RhCl$_2$([14]aneS$_4$)]$^+$ occurs in the *cis*-dichloro form in the solid state [Rh–Cl 2.3836(12), Rh–S 2.2870(12), 2.3275(12) Å].[14] Since there are very few examples of cobalt or iridium selenoethers (the iridium species all have Se$_2$X$_4$ donor sets),[8,15–17] and none has been structurally characterised, we undertook single-crystal X-ray analyses on [CoBr$_2$([16]aneSe$_4$)]BPh$_4$ and [IrBr$_2$([16]aneSe$_4$)]BPh$_4$.

Orange rhomb-shaped crystals of [CoBr$_2$([16]aneSe$_4$)]BPh$_4$ were obtained from MeNO$_2$ solution. The structure shows (Fig. 3, Table 3) a centrosymmetric cation involving *trans*-bromo ligands with the macrocyclic Se donors equatorially bound to the Co^{III}, Co–Br(1) 2.396(1), Co–Se(1) 2.393(1), Co–Se(2) 2.402(1) Å. The *cis* angles subtended at Co are in the ranges 86.88(5)–93.12(5)°, while the inversion centre at Co defines the Br(1)–Co–Br(1*), Se(1)–Co–Se(1*) and Se(2)–Co–Se(2*) angles to be precisely 180°. Thus we have confirmed that the *trans*-dibromo arrangement identified in solution by ^{59}Co and ^{77}Se NMR and UV/VIS spectroscopy is retained in the solid state.

Small, weakly diffracting crystals of [IrBr$_2$([16]aneSe$_4$)]BPh$_4$ were obtained by slow evaporation from a solution of both the *cis*- and, *trans*-dibromo forms of the complex in MeNO$_2$. The structure shows (Fig. 4, Table 4) the iridium(III) ion occupying the macrocyclic cavity and bound through all four Se donors, with two mutually *trans*-bromide ligands completing the distorted-octahedral geometry, Ir–Br(1) 2.468(4), Ir–Br(2) 2.483(4), Ir–Se(1) 2.470(3), Ir–Se(2) 2.470(3), Ir–Se(3) 2.461(3), Ir–Se(4) 2.462(3) Å. The angles around Ir^{III} lie in the ranges 85.5(1)–94.1(1) and 178.6(1)–179.2(1)°, deviating only slightly from those expected for a regular octahedral geometry. The configuration adopted by the non-bonded selenium lone pairs in the complexes of Co^{III} and Ir^{III} is the same as that for the rhodium(III) analogue discussed above. These are the first structural characterisations of cobalt or iridium selenoether complexes.

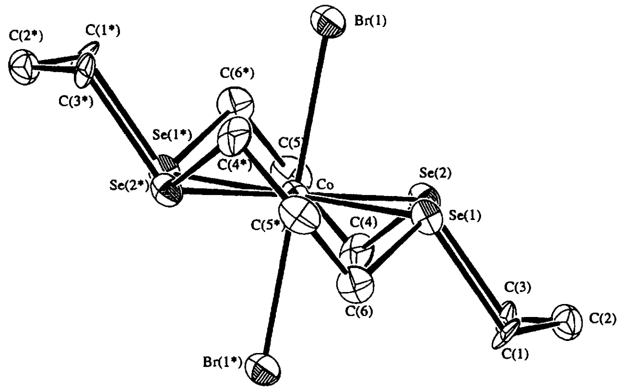

Fig. 3 View of the structure of the *trans*-[CoBr$_2$([16]aneSe$_4$)]$^+$ cation with the numbering scheme adopted [asterisked atoms are related by a crystallographic inversion centre (0, 0, 0)]. Ellipsoids are drawn at 40% probability

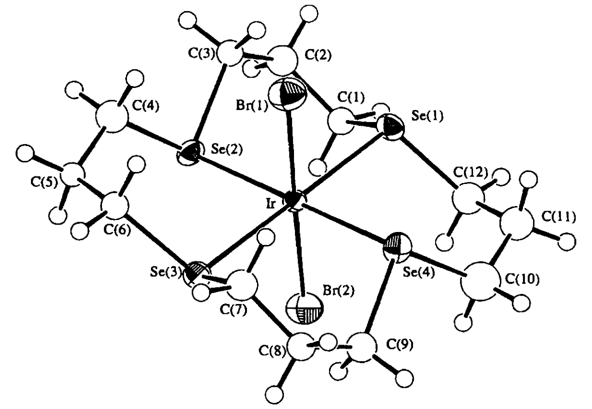

Fig. 4 View of the structure of the *trans*-[IrBr$_2$([16]aneSe$_4$)]$^+$ cation with the numbering scheme adopted. Ellipsoids are drawn at 40% probability

In only a few cases crystal structure data are available for complexes of Co^{III}, Rh^{III} and Ir^{III} involving a particular set of ligands, enabling comparisons of the M–L bond lengths. For example, the low-spin species [M(H$_2$O)$_6$]$^{3+}$ show d(Co–O) = 1.873(5), d(Rh–O) = 2.016(3), d(Ir–O) = 2.041(3),[18,19] and for [M(NO$_2$)$_6$]$^{3-}$ d(Co–N) = 1.9516(7), d(Rh–N) = 2.056(3), d(Ir–N) = 2.060(8) Å.[20–22] Thus, the differences in d(M–L) for these ions follow very closely the differences in ionic radii for Co^{III} (0.545), Rh^{III} (0.66) and Ir^{III} (0.68 Å).[23] Comparison of the M–Se bond lengths for the series [MX$_2$([16]aneSe$_4$)]$^+$ (M = Co, Rh or Ir) shows that while Rh–Se are not significantly different from Ir–Se, the Co–Se bond lengths are shorter by approximately 0.06 Å; this is less than the differences between d(Rh–L) and d(Co–L) for the hexaaqua and hexanitro species.

It is worth noting that in contrast to the cobalt(III) tetraselenoether macrocyclic complexes described here, we have been unable to synthesise [CoX$_2$([8]aneSe$_2$)$_2$]$^+$. This presumably reflects the enhanced stability imparted by the macrocycle, H, 3.2%). FAB mass spectrum: m/z = 659, 589; calc. for $[\mathrm{Rh^{35}Cl_2([8]ane^{80}Se_2)_2}]^+$ m/z = 661, $[\mathrm{Rh([8]ane^{80}Se_2)_2}]^+$ 591. ^{1}H NMR [$(\mathrm{CD_3})_2\mathrm{CO}$, 300 K]: δ 2.2–3.4 (m, $\mathrm{CH_2}$). IR (CsI disc): 2985m, 2955m, 1443m, 1419m, 1287w, 1266w, 1235m, 1048vs (br), 958w, 877m, 826w, 806w, 768m, 731m, 667w, 594w, 554w, 521m and 305w cm^{-1}.

[RhCl$_2$([16]aneSe$_4$)]BF$_4$. The compound [16]aneSe$_4$ (79 mg, 16 mmol) was added to EtOH (100 cm^3) and the solution was brought to reflux; $\mathrm{RhCl_3 \cdot 3H_2O}$ (51 mg, 0.16 mmol) in water (10 cm^3) was added dropwise over 0.5 h and the mixture refluxed for 1 h to give an orange solution. An excess of $\mathrm{NaBF_4}$ was then added and the solution concentrated to *ca.* 5 cm^3 *in vacuo*, prior to treatment with diethyl ether which afforded an orange solid. Yield 94 mg, 78% (Found: C, 19.3; H, 2.9. $\mathrm{C_{12}H_{24}BCl_2F_4RhSe_4}$ requires C, 19.4; H, 3.2%). FAB mass spectrum: m/z = 659, 624, 587; calc. for $[\mathrm{Rh^{35}Cl_2([16]ane^{80}Se_4)}]^+$ m/z = 661, $[\mathrm{Rh^{35}Cl([16]ane^{80}Se_4)}]^+$ 626, $[\mathrm{Rh([16]ane^{80}Se_4)}]^+$ 591. ^{1}H NMR ($\mathrm{CD_3CN}$, 300 K): δ 2.8–3.4 (16 H, m, $\mathrm{SeCH_2}$) and 2.5–2.6 (8 H, m, $\mathrm{CH_2C}H_2\mathrm{CH_2}$). IR (CsI disc): 2980w, 2923m, 1430m, 1292w, 1251w, 1218w, 1107m, 1048vs (br), 986w, 795w, 744m, 520m, 347w, 312w and 223w cm^{-1}.

[RhBr$_2$([16]aneSe$_4$)]PF$_6$. The complex $[\mathrm{Rh(H_2O)_6}][\mathrm{NO_3}]_3$ (2.2 cm^3, 0.048 mol dm^{-3}) was added to ethanol (70 cm^3); [16]aneSe$_4$ (50 mg, 0.1 mmol) and LiBr (18 mg, 0.2 mmol) were added and this mixture was refluxed for 3 h and then stirred at room temperature for 16 h to give a brown solution. The salt $\mathrm{NH_4PF_6}$ (40 mg, 0.24 mmol) was added and the solution concentrated to *ca.* 2 cm^3 *in vacuo.* Diethyl ether was then added to afford a light brown solid, which was filtered off and dried *in vacuo.* Yield 76 mg, 82% (Found: C, 16.0; H, 2.3. $\mathrm{C_{12}H_{24}Br_2F_6PRhSe_4}$ requires C, 16.1; H, 2.7%). FAB mass spectrum: m/z = 746, 704, 666; calc. for $[\mathrm{Rh^{79}Br_2([16]ane^{80}Se_4)}]^+$ m/z = 749, $[\mathrm{Rh^{79}Br_2([16]ane^{80}Se_4 - C_3H_6)}]^+$ 707, $[\mathrm{Rh^{79}Br([16]ane^{80}Se_4)}]^+$ 670. ^{1}H NMR ($\mathrm{CD_3CN}$, 300 K): δ 2.9–3.1 (16 H, m, $\mathrm{SeCH_2}$) and 2.4–2.6 (8 H, m, $\mathrm{CH_2C}H_2\mathrm{CH_2}$). IR (Nujol): 1215w, 1153w, 1075w, 1042w, 973w, 844vs, 796m and 557vs cm^{-1}.

[IrCl$_2$([16]aneSe$_4$)]BPh$_4$. The compounds [16]aneSe$_4$ (120 mg, 0.24 mmol) and $\mathrm{NaBPh_4}$ (120 mg, 0.35 mmol) were added to deoxygenated ethanol (200 cm^3) and heated to reflux; $\mathrm{IrCl_3 \cdot 3H_2O}$ (85 mg, 0.24 mmol) in water (20 cm^3) was then added dropwise over 0.5 h. The reaction mixture was refluxed for 16 h and then stirred at room temperature for 8 h to give a yellow solution and precipitate. The solution was concentrated *in vacuo* to *ca.* 15 cm^3 and a yellow solid was filtered off. It was dissolved in $\mathrm{MeNO_2}$, filtered to remove any insoluble material, and the filtrate concentrated *in vacuo* to *ca.* 2 cm^3 and treated with diethyl ether to afford a cream solid. Yield 25 mg, 10% (Found: C, 39.9; H, 3.7. $\mathrm{C_{36}H_{44}BCl_2IrSe_4}$ requires C, 40.5; H, 4.1%). FAB mass spectrum: m/z = 749; calc. for $[\mathrm{^{193}Ir^{35}Cl_2([16]ane^{80}Se_4)}]^+$ m/z = 751. ^{1}H NMR ($\mathrm{CD_3NO_2}$, 300 K): δ 6.8–7.3 (20 H, m, Ph) and 2.4–3.6 (24 H, m, $\mathrm{CH_2}$). IR (CsI disc): 3051m, 2981m, 2927w, 1576w, 1477m, 1426m, 1400w, 1257w, 1219m, 1122w, 1031m, 987w, 843m, 802w, 734s, 706s, 612m, 471w and 298w cm^{-1}.

[IrBr$_2$([16]aneSe$_4$)]BPh$_4$. The compounds [16]aneSe$_4$ (125 mg, 0.26 mmol) and $\mathrm{NaBPh_4}$ (125 mg, 0.36 mmol) were added to deoxygenated ethanol (200 cm^3) and heated to reflux; $\mathrm{IrBr_3 \cdot 3H_2O}$ (125 mg, 0.26 mmol) in $\mathrm{Me_2SO}$ (25 cm^3) was then added dropwise over 0.5 h and the solution was refluxed for 20 h and then stirred at room temperature for 6 h to produce a yellow solution. Removal of the ethanol *in vacuo* and treatment with diethyl ether produced a yellow-brown solid which was filtered off and discarded. The $\mathrm{Me_2SO}$ was then removed by distillation. The resulting solid was recrystallised from $\mathrm{MeNO_2}$ (2 cm^3) and diethyl ether to afford a cream precipitate. Yield 40 mg, 14% (Found: C, 37.1; H, 3.5. $\mathrm{C_{36}H_{44}BBr_2IrSe_4}$ requires C, 37.3; H, 3.8%). ES$^+$ mass spectrum: m/z = 837, 793; calc. for $[\mathrm{^{193}Ir^{79}Br_2([16]ane^{80}Se_4)}]^+$ m/z = 839, $[\mathrm{^{193}Ir^{79}Br_2([16]ane^{80}Se_4 - C_3H_6)}]^+$ 797. ^{1}H NMR ($\mathrm{CD_3NO_2}$, 300 K): δ 6.8–7.3 (20 H, m, Ph) and 2.5–3.4 (24 H, m, $\mathrm{CH_2}$). IR (CsI disc): 3050m, 2981m, 2727w, 1576m, 1477m, 1425m, 1401w, 1338w, 1291w, 1274w, 1254m, 1217w, 1137m, 1066w, 1031w, 986w, 889w, 841m, 800w, 736s, 705s, 612m, 469w and 434w cm^{-1}.

X-Ray crystallography

Small crystals of [CoBr$_2$([16]aneSe$_4$)]BPh$_4$ and [IrBr$_2$([16]aneSe$_4$)]BPh$_4$ were obtained by slow evaporation from a solution of the appropriate complex in $\mathrm{MeNO_2}$. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Cryostreams low-temperature attachment operating at 150 K, using graphite-monochromated Mo-Kα X-radiation ($\lambda_{\max}$ = 0.71073 Å), ω–2θ scans. No significant crystal decay or movement was observed. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses.

***trans*-[CoBr$_2$([16]aneSe$_4$)]BPh$_4$.** An orange rhomb-shaped crystal (0.45 × 0.15 × 0.05 mm) was coated with mineral oil and mounted on a glass fibre.

Crystal data. $\mathrm{C_{36}H_{44}BBr_2CoSe_4}$, M = 1022.1, monoclinic, space group $C2/c$, a = 11.595(4), b = 20.688(5), c = 15.199(5) Å, β = 92.70(3)°, U = 3641(1) Å^3, Z = 4, D_c = 1.864 g cm^{-3}, μ = 6.696 mm^{-1}, F(000) = 1992.

Data collection and processing. ω Scan width = (1.26 + 0.35tan θ)°, 3482 data collected, 3305 unique (R_{int} = 0.062 based on F^2) ($2\theta_{\max}$ 50°, h 0–13, k 0–24, l −17 to 18) giving 1958 reflections with $F \geqslant 5\sigma(F)$ for use in all calculations.

Structure solution and refinement. The structure was solved by direct methods[24] and developed by using iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses which located all non-H atoms in an ordered half [CoBr$_2$([16]aneSe$_4$)]$^+$ cation and half $\mathrm{BPh_4}^-$ anion in the asymmetric unit.[25] The Co atom occupies a crystallographic inversion centre (0, 0, 0), while the B atom of the anion occupies a crystallographic two-fold site (0, y, 0.25). As there were no identifiable faces, with the model at isotropic convergence, the raw data were corrected for absorption using DIFABS[26] (maximum and minimum transmission factors = 1.000, 0.510). All non-H atoms were then refined anisotropically, while H atoms were placed in fixed, calculated positions. At final convergence R, R' = 0.058, 0.071 respectively, S = 1.98 for 201 refined parameters. The final ΔF synthesis showed no peaks above 1.14 or below −1.42 e Å^{-3} (both < 1 Å from the Br atom) and the maximum Δ/σ = 0.01.

***trans*-[IrBr$_2$([16]aneSe$_4$)]BPh$_4$.** A yellow irregular crystalline fragment (0.24 × 0.20 × 0.12 mm) was coated with mineral oil and mounted on a glass fibre.

Crystal data. $\mathrm{C_{36}H_{44}BBr_2IrSe_4}$, M = 1155.4, monoclinic, space group $P2_1/c$, a = 13.396(5), b = 10.594(8), c = 26.256(4) Å, β = 102.15(2)°, U = 3642(2) Å^3, Z = 4, D_c = 2.107 g cm^{-3}, μ = 9.809 mm^{-1}, F(000) = 2192.

Data collection and processing. ω Scan width = (0.94 + 0.35tan θ)°, 7106 data collected, 6783 unique (R_{int} = 0.117 based on F^2) ($2\theta_{\max}$ 50°, h 0–15, k 0–12, l −30 to 30) giving 2128 reflections with $F \geqslant 4\sigma(F)$ for use in all calculations. As there were no identifiable faces the data for each crystal were corrected for absorption using ψ scans (maximum and minimum transmission factors = 1.000, 0.807).

Structure solution and refinement. The structure was solved by heavy-atom methods[27] and developed by using iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses which located all non-H atoms in an ordered

Table 3 Selected bond lengths (Å) and angles for *trans*-[CoBr$_2$([16]aneSe$_4$)]$^+$

Br(1)–Co	2.396(1)	Se(1)–Co	2.393(1)
Se(1)–C(1)	1.95(1)	Se(1)–C(6)	1.98(1)
Se(2)–Co	2.402(1)	Se(2)–C(3)	1.96(1)
Se(2)–C(4)	1.94(1)	C(1)–C(2)	1.53(2)
C(2)–C(3)	1.53(2)	C(4)–C(5)	1.54(2)
C(5)–C(6)	1.48(2)		
Co–Se(1)–C(1)	109.1(4)	Co–Se(1)–C(6)	102.9(4)
C(1)–Se(1)–C(6)	94.0(6)	Co–Se(2)–C(3)	109.0(4)
Co–Se(2)–C(4)	104.6(4)	C(3)–Se(2)–C (4)	92.8(6)
Se(1)–Co–Se(2)	87.65(5)	Br(1)–Co–Se(1)	86.88(5)
C(1)–C(2)–C(3)	116(1)	Br(1)–Co–Se(2)	87.25(4)
Se(2)–C(4)–C(5)	112.3(9)	Se(1)–C(1)–C (2)	114.1(8)
Se(1)–C(6)–C(5)	112.7(9)	Se(2)–C(3)–C (2)	115.0(9)
		C(4)–C(5)C(6)	116(1)

Table 4 Selected bond lengths (Å) and angles for *trans*-[IrBr$_2$([16]aneSe$_4$)]$^+$

Ir–Br(1)	2.468(4)	Ir–Br(2)	2.483(4)
Ir–Se(1)	2.470(3)	Ir–Se(2)	2.470(3)
Ir–Se(3)	2.461(3)	Ir–Se(4)	2.462(3)
Se(1)–C(1)	1.98(3)	Se(1)–C(12)	1.93(3)
Se(2)–C(3)	1.99(2)	Se(2)–C(4)	1.91(3)
Se(3)–C(6)	1.96(3)	Se(3)–C(7)	1.94(3)
Se(4)–C(9)	1.94(3)	Se(4)–C(10)	1.92(3)
C(1)–C(2)	1.49(4)	C(2)–C(3)	1.46(3)
C(4)–C(5)	1.53(3)	C(5)–C(6)	1.44(3)
C(7)–C(8)	1.50(3)	C(8)–C(9)	1.53(3)
C(10)–C(11)	1.51(4)	C(11)–C(12)	1.55(4)
Br(1)–Ir–Br(2)	178.8(1)	Br(1)–Ir–Se(1)	86.8(1)
Br(1)–Ir–Se(2)	93.7(1)	Br(1)–Ir–Se(3)	94.1(1)
Br(1)–Ir–Se(4)	85.5(1)	Br(2)–Ir–Se(1)	92.3(1)
Br(2)–Ir–Se(2)	87.0(1)	Br(2)–Ir–Se(3)	86.9(1)
Br(2)–Ir–Se(4)	93.7(1)	Se(1)–Ir–Se(2)	90.5(1)
Se(1)–Ir–Se(3)	178.6(1)	Se(1)–Ir–Se(4)	89.8(1)
Se(2)–Ir–Se(3)	88.3(1)	Se(2)–Ir–Se(4)	179.2(1)
Se(3)–Ir–Se(4)	91.4(1)	Ir–Se(1)–C(1)	101.5(8)
Ir–Se(1)–C(12)	104.8(9)	C(1)–Se(1)–C(12)	95(1)
Ir–Se(2)–C(3)	102.5(7)	Ir–Se(2)–C(4)	106.7(8)
C(3)–Se(2)–C(4)	96(1)	Ir–Se(3)–C(6)	107.0(7)
Ir–Se(3)–C(7)	102.7(8)	C(6)–Se(3)–C(7)	96(1)
Ir–Se(4)–C(9)	103.2(8)	Ir–Se(4)–C(10)	107(1)
C(9)–Se(4)–C(10)	95(1)	Se(1)–C(1)–C(2)	112(1)
C(1)–C(2)–C(3)	116(2)	Se(2)–C(3)–C(2)	110(1)
Se(2)–C(4)–C(5)	116(1)	C(4)–C(5)–C(6)	118(2)
Se(3)–C(6)–C(5)	115(1)	Se(3)–C(7)–C(8)	113(1)
C(7)–C(8)–C(9)	115(2)	Se(4)–C(9)–C(8)	113(1)
Se(4)–C(10)–C(11)	116(2)	C(10)–C(11)–C(12)	116(2)
Se(1)–C(12)–C(11)	111(2)		

and suggests that selenoether crowns may open up a new and rich area of co-ordination chemistry.

Experimental

Infrared spectra were measured as KBr or CsI discs or as Nujol mulls using a Perkin-Elmer 983 spectrometer over the range 200–4000 cm^{-1}, UV/VIS spectra in solution using 1 cm path length quartz cells, or in the solid state by diffuse reflectance using samples diluted with BaSO$_4$, using a Perkin-Elmer Lambda 19 spectrophotometer. Mass spectra were run 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. Proton NMR spectra were recorded using a Bruker AM300 or AM360 spectrometer operating at 300 or 360 MHz respectively, ^{77}Se-{^{1}H} and ^{59}Co NMR spectra using a Bruker AM360 spectrometer operating at 66.68 and 85.3 MHz respectively and referenced to neat Me$_2$Se [δ(^{77}Se) 0] or aqueous [Co(CN)$_6$]$^{3-}$ [δ(^{59}Co) 0]. Microanalyses were performed by the Imperial College microanalytical service.

Syntheses

The compounds [8]aneSe$_2$ and [16]aneSe$_4$ were prepared by the literature procedure.[3] Complexes were prepared under a nitrogen atmosphere unless otherwise stated, and stored in sealed containers in a desiccator. Anhydrous cobalt halide starting materials were dried *in vacuo* at 150 °C for 3 h.

[CoCl$_2$([16]aneSe$_4$)]PF$_6$. The compound [16]aneSe$_4$ (65 mg, 0.13 mmol), anhydrous CoCl$_2$ (17 mg, 0.13 mmol) and NH$_4$PF$_6$ (24 mg, 0.14 mmol) were added to dry deoxygenated nitromethane (20 cm^3). The mixture was stirred for 0.5 h under N$_2$ to produce a green solution. A drying tube (CaCl$_2$) was then fitted and the mixture stirred under dry air for 40 h, becoming brown. The solution was concentrated *in vacuo* to *ca.* 2 cm^3 and treated with diethyl ether to afford an orange-brown solid which was filtered off and dried *in vacuo*. Yield 44 mg 43% (Found: C, 19.3; H, 3.1. C$_{12}$H$_{24}$Cl$_2$CoF$_6$PSe$_4$ requires C, 19.0; H, 3.2%). ES$^+$ mass spectrum: m/z = 614; calc. for [Co^{35}Cl$_2$([16]ane^{80}Se$_4$)]$^+$ m/z = 617. ^{1}H NMR (CD$_3$CN, 300 K): δ 2.3–3.0 (m, CH$_2$). IR (CsI disc): 2919m, 2843w, 1440m, 1430m, 1360m, 1285w, 1272m, 1255w, 1165w, 1096w, 985w, 888w, 832vs, 790m, 741m, 630w, 557s, 436w, 379m and 295w cm^{-1}.

[CoBr$_2$([16]aneSe$_4$)]PF$_6$. Method as above, using [16]aneSe$_4$ (71 mg, 0.14 mmol), anhydrous CoBr$_2$ (32 mg, 0.14 mmol) and NH$_4$PF$_6$ (25 mg, 0.15 mmol). Yield 49 mg, 40% of orange-brown solid (Found: C, 16.8; H, 2.5. C$_{12}$H$_{24}$Br$_2$CoF$_6$PSe$_4$ requires C, 17.0; H, 2.8%). ES$^+$ mass spectrum: m/z = 704; calc. for [Co^{79}Br$_2$([16]ane^{80}Se$_4$)]$^+$ m/z = 705. ^{1}H NMR (CD$_3$CN, 300 MHz): δ 2.4–3.2 (m, CH$_2$). IR (CsI disc): 2980w, 2917m, 1428m, 1402m, 1289w, 1277w, 1250w, 1214w, 1135w, 1076m, 983w, 835vw, 794m, 742m, 629w, 557vs, 435w and 294w cm^{-1}.

[CoBr$_2$([16]aneSe$_4$)]BPh$_4$. Method as above, using [16]aneSe$_4$ (105 mg, 0.22 mmol), CoBr$_2$ (48 mg, 0.22 mmol) and NaBPh$_4$ (75 mg, 0.22 mmol). Yield 82 mg, 37% of orange solid (Found: C, 41.6; H, 4.2. C$_{36}$H$_{44}$BBr$_2$CoSe$_4$ requires C, 42.2; H, 4.3%). ES$^+$ mass spectrum: m/z = 705; calc. for [Co^{79}Br$_2$([16]ane^{80}Se$_4$)]$^+$ m/z = 705. IR (CsI disc): 3051m, 3030w, 3009w, 2979m, 2925w, 1575m, 1478m, 1427m, 1399w, 1289w, 1274w, 1251m, 1227w, 1214w, 1153w, 1130w, 1116w, 1065w, 1030w, 984w, 886w, 860w, 840m, 796m, 737s, 705s, 610m, 503w, 473w, 436w and 295w cm^{-1}.

[CoI$_2$([16]aneSe$_4$)]PF$_6$. Method as above, using [16]aneSe$_4$ (62 mg, 0.13 mmol), CoI$_2$ (40 mg, 0.13 mmol) and NH$_4$PF$_6$ (21 mg, 0.13 mmol). Yield 46 mg, 38% of purple solid (Found: C, 15.0; H, 2.3. C$_{12}$H$_{24}$CoF$_6$I$_2$PSe$_4$ requires C, 15.2; H, 2.5%). ES$^+$ mass spectrum: m/z = 798, 671; calc. for [CoI$_2$([16]ane^{80}Se$_4$)]$^+$ m/z = 801, [CoI([16]ane^{80}Se$_4$)]$^+$ 674. ^{1}H NMR (CD$_3$NO$_2$, 300 K): δ 2.1–3.5 (m, CH$_2$). IR (CsI disc): 2963w, 2915m, 1426m, 1357w, 1288w, 1248w, 1213w, 1164w, 1113w, 982w, 835vs, 794m, 739m, 557vs, 435w and 298w cm^{-1}.

[RhCl$_2$([8]aneSe$_2$)$_2$]BF$_4$. The compound [8]aneSe$_2$ (160 mg, 0.66 mmol) was added to acetone (5 cm^3); [{Rh(CO)$_2$Cl}$_2$] (65 mg, 0.16 mmol) and 40% aqueous HBF$_4$ (1 cm^3) were quickly added and this mixture was refluxed for 0.5 h. Addition of water (10 cm^3) and removal of a brown solid by filtration produced an orange solution which was concentrated to *ca.* 2 cm^3 *in vacuo*. Acetone (3 cm^3) was then added and the solution treated with diethyl ether to afford an orange solid. Yield 85 mg, 67% (Found: C, 19.1; H, 2.9. C$_{12}$H$_{24}$BCl$_2$F$_4$RhSe$_4$ requires C, 19.3;

$[IrBr_2([16]aneSe_4)]^+$ cation and BPh_4^- anion in the asymmetric unit.[25] The Ir, Br and Se atoms were refined anisotropically, while H atoms were placed in fixed, calculated positions. At final convergence R, $R' = 0.054$, 0.052 respectively, $S = 1.54$ for 212 refined parameters. The final ΔF synthesis showed no peaks above 1.50 or below -1.35 e Å^{-3} (both < 1 Å from the Ir atom) and the maximum $\Delta/\sigma = 0.02$.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/176.

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References

1 A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1; S. R. Cooper and S. R. Rawle, *Struct. Bonding (Berlin)*, 1990, **71**, 1.
2 E. G. Hope and W. Levason, *Coord. Chem. Rev.*, 1993, **122**, 109.
3 R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J.-H. Gu, B. D. Johnston and B. M. Pinto, *J. Am. Chem. Soc.*, 1989, **111**, 6582; R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J.-H. Gu, B. M. Pinto and X.-M. Zhou, *J. Am. Chem. Soc.*, 1990, **112**, 3706; R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J.-H. Gu and B. M. Pinto, *J. Organomet. Chem.*, 1991, **411**, 147; I. Cordova-Reyes, E. VandenHoven, A. Mohammed and B. M. Pinto, *Can. J. Chem.*, 1995, **73**, 113.
4 N. R. Champness, P. F. Kelly, W. Levason, G. Reid, A. M. Z. Slawin and D. J. Williams, *Inorg. Chem.*, 1995, **34**, 651.
5 W. Levason, J. J. Quirk, G. Reid and C. S. Frampton, *Inorg. Chem.*, 1994, **33**, 6120.
6 P. F. Kelly, W. Levason, G. Reid and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1993, 1716.
7 J. Lewis, R. S. Nyholm and G. A. Rodley, *J. Chem. Soc.*, 1965, 1483.
8 J. L. Brown, T. Kemmitt and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1990, 1513.
9 A. P. B. Lever, *Inorganic Electronic Spectroscopy*, 2nd edn., Elsevier, Amsterdam, 1984.
10 D. J. Gulliver, E. G. Hope, W. Levason, S. G. Murray and G. L. Marshall, *J. Chem. Soc., Dalton Trans.*, 1985, 1265.
11 K. Travis and D. H. Busch, *Inorg. Chem.*, 1974, **13**, 2591; J. J. Jenkinson, W. Levason, R. J. Perry and M. D. Spicer, *J. Chem. Soc., Dalton Trans.*, 1989, 453.
12 See, *Transition Metal Nuclear Magnetic Resonance Spectroscopy*, ed. P. S. Pregosin, Elsevier, Amsterdam, 1991; H. C. Jewiss, W. Levason and M. Webster, *Inorg. Chem.*, 1986, **25**, 1997; H. C. Jewiss, W. Levason, M. D. Spicer and M. Webster, *Inorg. Chem.*, 1987, **26**, 2102.
13 E. G. Hope, W. Levason, S. G. Murray and G. L. Marshall, *J. Chem. Soc., Dalton Trans.*, 1985, 2185.
14 A. J. Blake, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1989, 1675.
15 R. A. Cipriano, W. Levason, D. Pletcher, N. A. Powell and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1987, 1901.
16 E. G. Hope, W. Levason, M. Webster and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1986, 1003.
17 R. A. Cipriano, L. R. Hanton, W. Levason, D. Pletcher, N. A. Powell and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1988, 2483.
18 J. K. Beattie, S. P. Best, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 2105.
19 R. S. Armstrong, J. K. Beattie, S. P. Best, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 1973.
20 S. Ohba, K. Toriuma and Y. Saito, *Acta Crystallogr., Sect. B*, 1978, **34**, 3535.
21 S. A. Gromilov, V. I. Alekseev, I. A. Baidina and S. P. Khranenko, *Russ. J. Inorg. Chem.*, 1992, **37**, 306.
22 S. A. Gromilov, I. A. Baidina, V. I. Alekseev, A. B. Venediktov and S. P. Khranenko, *Russ. J. Inorg. Chem.*, 1990, **35**, 3.
23 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984.
24 G. M. Sheldrick, SHELXS 86, Program for crystal structure solution, University of Göttingen, 1986.
25 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1995.
26 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
27 PATTY: The DIRDIF program system, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, Technical report of the Crystallography Laboratory, University of Nijmegen, 1992.

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