Selenoether Macrocyclic Chemistry: *trans*-[$RhCl_2$([16]aneSe_4)]BF_4, Synthesis, Single Crystal X-Ray Structure and ^{77}Se NMR Study ([16]aneSe_4 = 1,5,9,13-tetraselenacyclohexadecane)

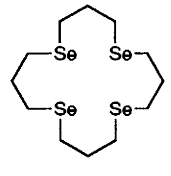
Paul F. Kelly,[a] William Levason,[a] Gillian Reid*[a] and David J. Williams[b]

[a] *Department of Chemistry, University of Southampton, Highfield, Southampton, UK SO9 5NH*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY*

trans-[$RhCl_2$([16]aneSe_4)]$^+$, the first fully characterised example of a platinum metal selenoether macrocyclic complex, has been prepared in high yield; a single crystal X-ray structure determination on this complex is described together with its ^{77}Se NMR and electronic spectroscopic data.

The considerable effort which has been directed towards studying the coordination chemistry of polythio crowns in recent years has established that these macrocyclic ligands exhibit very different coordinating properties from their acyclic counterparts.[1,2] This is principally due to the greater σ-donor effects caused by their cyclic nature, and has facilitated stabilisation of a wide range of metal ions in relatively unusual oxidation states, *e.g.* mononuclear Pd^I, Rh^{II}, Au^{II}, Pt^{IV} *etc.*

The lower electronegativity, and hence greater σ-donating properties, of Se over S suggest that incorporation of selenoether donors (SeR_2) in a macrocyclic arrangement



[16]aneSe$_4$

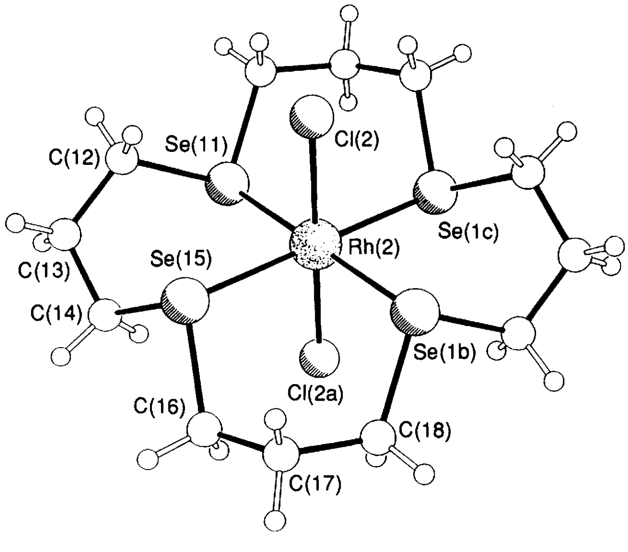


Fig. 1 View of the structure of one molecule of *trans*-[RhCl$_2$([16]aneSe$_4$)]$^+$ with numbering scheme adopted

should yield ligands capable of a rich coordination chemistry. Furthermore, one disadvantage of polythia macrocyclic chemistry is the absence of a suitable NMR-active nucleus with which to monitor structural and conformational behaviour in solution. Thus, full characterisation of these systems has demanded a great many single crystal X-ray structure determinations. Selenoether chemistry is much more attractive in this context owing to the availability of ^{77}Se NMR spectroscopy as a powerful structural probe (^{77}Se I = ½, 7.58%, D_c = 2.98). It is somewhat surprising then that, since the original preparation of macrocyclic selenoether ligands by Pinto *et al.* in 1989,[3] only two reports on the coordination chemistry of this new class of ligands have appeared.[4] We are currently studying in detail the metal ion binding affinities of a series of tetradentate macrocyclic selenoethers including [16]aneSe$_4$ and [14]aneSe$_4$. Many examples of platinum metal complexes involving bidentate selenoether coordination have been reported.[5] However, the only bis-bidentate selenoether complexes known involve Ru^{II}, Ru^{III}, Co^{III}[6] and Rh^{III}.[7]

Reaction of RhCl$_3$·3H$_2$O with 1 mol of [16]aneSe$_4$ in refluxing aqueous ethanol, followed by addition of an excess of BF$_4^-$, affords the air-stable macrocyclic selenoether complex [RhCl$_2$([16]aneSe$_4$)]BF$_4$ in high yield as a yellow–orange solid. The FAB mass spectrum of the complex shows peaks with the correct isotopic distributions at m/z 659, 624 and 587, corresponding to [^{103}Rh^{35}Cl$_2$([16]aneSe$_4$)]$^+$, [^{103}Rh^{35}Cl([16]aneSe$_4$)]$^+$ and [^{103}Rh([16]aneSe$_4$ − 2H)]$^+$ respectively. Additional fragmentation peaks corresponding to loss of CH$_2$CH$_2$CH$_2$ groups and Se from [Rh([16]aneSe$_4$)]$^+$ are also apparent. This, together with microanalytical and IR data, confirms our formulation for the product. In view of the lack of examples of selenoether macrocyclic complexes and in order to verify the stereochemistry around Rh^{III} and the ligand conformation, we undertook a single crystal X-ray analysis. Single crystals were obtained by slow evaporation from a solution of the complex in MeCN. The single crystal X-ray structure of [RhCl$_2$([16]aneSe$_4$)]BF$_4$† shows (Fig. 1) the cation adopting a *trans*-dichloro octahedral geometry, with the macrocyclic ligand occupying the four equatorial coordination sites in an 'up,up,down,down' or ctct configuration, Rh(2)–Se(11) 2.456(1), Rh(2)–Se(15) 2.461(1), Rh(2)–Cl(2) 2.344(2) Å. This represents the first example of a platinum metal selenoether macrocyclic complex, and only the second example demonstrating endocyclic coordination of a selenoether macrocycle.[4] The stereochemistry observed for [RhCl$_2$([16]aneSe$_4$)]$^+$ is similar to that seen for [RhCl$_2$([16]aneS$_4$)]$^+$ which also exhibits a *trans*-dichloro geometry with the thioether crown occuping the equatorial plane, Rh–S 2.348(3), 2.348(3) Å, Rh–Cl 2.339(2) Å.[8] The longer metal–donor atom bond lengths in the title complex reflect the greater covalent radius of Se (selenoether) over S (thioether) (1.17 *vs.* 1.04 Å). The ^{77}Se NMR spectrum of *trans*-[RhCl$_2$([16]aneSe$_4$)]BF$_4$ measured at 300 K in MeNO$_2$ solutions shows a slightly broadened resonance at +160 ppm relative to neat Me$_2$Se (δ 0). The small shift observed upon coordination to Rh^{III} is consistent with the presence of only six-membered chelate rings in the product. The doublet coupling to ^{103}Rh ($^1J_{\text{Se-Rh}}$), although not very well resolved, is observed to be *ca.* 30 Hz. These data are consistent with the complex retaining its solid-state *trans*-dichloro stereochemistry in solution.[7] Cooling to 243 K does not significantly decrease the linewidth.

The electronic spectrum of *trans*-[RhCl$_2$([16]aneSe$_4$)]BF$_4$ (MeCN solution) exhibits intense bands at λ_{max} 234 nm (ϵ_{mol} = 16 000 mol^{-1} dm^3 cm^{-1}) and 294 (50 500) corresponding to $\pi_{Cl} \rightarrow$ Rh and $\pi_{Se} \rightarrow$ Rh charge-transfer transitions respectively. Additionally, a much weaker d–d band is apparent at λ_{max} 449 nm (ϵ_{mol} = 178 mol^{-1} dm^3 cm^{-1}) corresponding to the $^1A_{1g} \rightarrow {}^1E_g$ transition. The energy of this d–d transition is comparable with those observed for *trans*-[RhCl$_2$(MeSeCH$_2$CH$_2$SeMe)$_2$]$^+$ and *trans*-[RhCl$_2$(PhSeCH$_2$CH$_2$SePh)$_2$]$^+$.[7]

Preliminary cyclic voltammetric studies on *trans*-[RhCl$_2$([16]aneSe$_4$)]BF$_4$ measured in MeCN solution (0.1 mol dm^{-3} Bu$^n_4$NBF$_4$ supporting electrolyte) show an irreversible reduction at $E_{\frac{1}{2}}$ − 1.16 V *vs.* Fc/Fc$^+$ and no redox response in the oxidative range up to +2.0 V.

---

† *Crystal data* for C$_{12}$H$_{24}$Cl$_2$RhSe$_4^+$·BF$_4^-$, M = 744.8, triclinic, space group $P\bar{1}$, a = 8.157(3), b = 8.196(4), c = 15.515(6) Å, α = 88.60(3), β = 87.17(2), γ = 86.03(2)°, V = 1033.3(8) Å^3, Z = 2, D_c = 2.394 g cm^{-3}, μ(Mo-Kα) = 8.159 mm^{-1}. An orange coloured block (0.217 × 0.550 × 0.700 mm) was mounted on a Siemens P4/PC four-circle diffractometer. Data collection at 293 K using Mo-Kα X-radiation (λ = 0.71073 Å), ω scans, gave 3649 unique reflections of which 3052 with $F > 4\sigma(F)$ were used in all calculations. The structure was solved using direct methods. Iterative cycles of least-squares refinement and difference Fourier synthesis revealed the positions of all non-H atoms for the two independent half-cations (each of which lies across a crystallographic inversion centre) and the one BF$_4^-$ anion in the asymmetric unit. The structure was refined by full-matrix least-squares using absorption-corrected data, with anisotropic thermal parameters for all fully-occupied non-H atoms; H atoms were included in fixed, calculated positions. One of the two crystallographically independent cations is partially disordered. The disorder takes the form of a 'flipping' up and down of alternate Se atoms around the ring, the positions of the carbon atoms remaining essentially unchanged. This results in a tilting of the Cl–Rh–Cl axis with respect to the carbon skeleton. The overall gross conformation does not differ from that of the other cation. In view of the greater accuracy of atomic positions for the ordered cation [involving Rh(2)], only this molecule is discussed in the main text. At final convergence, R = 0.0383, R_w = 0.0417, S = 1.34 for 237 parameters and the final ΔF synthesis showed no $\Delta\rho$ outwith the range 0.80 to −0.64 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

We have recently prepared and fully characterised the related platinum metal complexes of [16]aneSe_4, $[M([16]aneSe_4)]^{2+}$, M = Pd, Pt. Single crystal X-ray structure analyses on each of these show the expected square-planar tetraselena coordination around the metal centre, with the macrocyclic adopting the same 'up,up,down,down' conformation as observed for the title complex. However, in contrast to $[RhCl_2([16]aneSe_4)]^+$, ^{77}Se and ^{195}Pt NMR studies on $[M([16]aneSe_4)]^{2+}$ provide evidence for a mixture of invertomers in solution at 298 K.[9]

These results confirm that high-yield syntheses of platinum metal selenoether macrocyclic complexes involving endocyclic coordination are readily achieved. Work to investigate the effects of varying the metal oxidation state and the macrocyclic ring-size is underway.

We thank Johnson-Matthey plc for generous loans of platinum metal salts.

Received, 22nd July 1993; Com. 3/04380K

References

1 M. Schröder, *Pure Appl. Chem.*, 1988, **60**, 517; A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1; G. Reid and M. Schröder, *Chem. Soc. Rev.*, 1990, **19**, 239.
2 S. R. Cooper, *Acc. Chem. Res.*, 1988, **21**, 141; S. R. Cooper and S. C. Rawle, *Structure Bonding* (*Berlin*), 1990, **72**, 1.
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.
4 R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J-H. Gu and B. M. Pinto, *J. Organomet. Chem.*, 1991, **411**, 147; 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.
5 For examples see E. G. Hope and W. Levason, *Coord. Chem. Rev.*, 1993, **122**, 109, and references cited therein.
6 N. R. Champness, W. Levason, D. Pletcher and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1992, 3243; J. L. Brown, T. Kemmitt and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1990, 1513.
7 D. J. Gulliver, E. G. Hope, W. Levason, S. G. Murray and G. L. Marshall, *J. Chem. Soc., Dalton Trans.*, 1985, 1265.
8 A. J. Blake, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1989, 1675.
9 P. F. Kelly, W. Levason, G. Reid, A. M. Z. Slawin and D. J. Williams, unpublished work.