Homoleptic Hexathia Complexes of Rhodium. The Synthesis, Electrochemistry, and Single-crystal *X*-Ray Structure of $[RhL_2][PF_6]_3$ (L = 1,4,7-trithiacyclononane)†

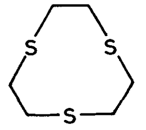
Alexander J. Blake, Robert O. Gould, Alan J. Holder, Timothy I. Hyde, and Martin Schröder *
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Reaction of $[Rh(H_2O)_6]^{3+}$ with 2 molar equivalents of 1,4,7-trithiacyclononane (L) gives the complex cation $[RhL_2]^{3+}$. The single-crystal *X*-ray structure of $[RhL_2][PF_6]_3$ shows a centrosymmetric complex around octahedral Rh^{III} with Rh–S 2.332(2) Å. The crystals are monoclinic, space group *I*2/*m* (alternative setting of *C*2/*m*, no. 12), with a = 11.329(3), b = 9.692(3), c = 14.909(4) Å, β = 101.77(2)°, and Z = 2. Cyclic voltammetry of $[RhL_2][PF_6]_3$ in MeCN (0.1 mol dm^{-3} $NBu^n{}_4PF_6$) at 20 °C at platinum electrodes shows two chemically reversible reductions at $^1E_{\frac{1}{2}} = -0.71$ V, $\Delta E_p = 71$ mV and $^2E_{\frac{1}{2}} = -1.08$ V, $\Delta E_p = 127$ mV *vs.* ferrocene–ferrocenium, which are assigned to Rh^{III}–Rh^{II} and Rh^{II}–Rh^{I} redox couples respectively.

The octahedral bis(macrocycle) complexes $[ML_2]^{x+}$ (L = 1,4,7-trithiacyclononane; M = Fe^{II},[1] Co^{II},[2–5] Co^{III},[5] Ni^{II},[1,2] or Cu^{II} [2,6]) have been reported, and their redox properties related to the electronic and stereochemical characteristics of L. We have extended this work to synthetic, structural, and electrochemical studies on the complexes of L with the platinum group metals.[7,8] The bis(sandwich macrocycle) complexes $[ML_2]^{2+}$ (M = Pd or Pt) have been found to show significant secondary co-ordination to the metal centres to give square-based pyramidal (M = Pt)[9] and distorted octahedral (M = Pd)[10,11] stereochemistries in the solid state. Interestingly, these complexes show reversible oxidations to afford the corresponding mononuclear d^7 derivatives of palladium(III)[11,12] and platinum(III).[9] We have successfully prepared[13] the d^6 species $[ML_2]^{2+}$ (M = Ru^{II} or Os^{II}); the Ru^{II} complex shows a centrosymmetric, octahedral stereochemistry with the Ru^{III} oxidation state being relatively destabilised by the homoleptic hexathia co-ordination. Since homoleptic hexathia ether co-ordination to Pd and Pt had been found to stabilise the corresponding d^7 metal(III) species,[9,11,12] we were intrigued as to the redox activity of the d^6 rhodium(III) system, and whether such a complex could be activated electrochemically to afford an isoelectronic, mononuclear d^7 rhodium(II) species. Preliminary communications of this work have appeared.[8,12]

Results and Discussion

Reaction of $[Rh(H_2O)_6]^{3+}$ with 2 molar equivalents of 1,4,7-trithiacyclononane (L) in water–methanol (1:1 v/v) under reflux afforded the complex cation $[RhL_2]^{3+}$. Addition of NH_4PF_6 gave a pale yellow precipitate which was recrystallised from water to give colourless crystals of $[RhL_2][PF_6]_3$. A single-crystal *X*-ray structure of this compound was undertaken.



L

The structure of the $[RhL_2]^{3+}$ cation is shown in Figure 1. Bond lengths, bond angles, and torsion angles are given in Table 1, grouped together to show the almost exact S_6 symmetry. The sulphur atoms form a very slightly distorted octahedron about the rhodium centre, with each sulphur being 3.263(2) Å from the two others within its own molecule and 3.332(3) Å from two in the other ligand. As this is significantly less than the normal van der Waals diameter (3.70 Å) of sulphur,[14] it is not surprising that the Rh^{III}–S distances in $[RhL_2]^{3+}$ [2.332(2) Å] are very close to the Ru^{II}–S distances in $[RuL_2]^{2+}$ [2.335(2) Å].[13] The conformation of the co-ordinated trithia macrocycles in $[RhL_2]^{3+}$ may therefore be regarded as 'close' or endodentate because of the close proximity of the sulphur atoms, as opposed to the more 'open' conformations observed for $[PdL_2]^{2+}$ [10,11] and *cis*-$[PdX_2L]$ (X = Cl[15] or Br[10]). Two types of carbon atom may be distinguished in this 'close' conformation; C(3), C(6), and C(9) may be called axial as they extend further above the plane of the sulphur atoms than do C(2), C(5), and C(8) which can be regarded as equatorial. This endodentate conformation is not very different from that of the free ligand[16] whose bond distances and angles are included in Table 2. The major differences are in two of the torsional angles; for L the S ··· S separation is 3.451(2) Å.

The ^1H n.m.r. spectrum of $[RhL_2][PF_6]_3$ in CD_3CN at 293 K shows a complex ABCD multiplet centred at δ 3.77 for the methylene protons of the co-ordinated macrocycles (Figure 2). This is similar to the ^1H n.m.r. spectral data for $[CoL_2]^{3+}$,[5] $[PdL_2]^{2+}$,[11] and for $[PtL'_2]^{4+}$ [17] (L′ = 1,4,7-triazacyclononane) and is characteristic of a rigid, non-fluxional system in solution. Fast-atom-bombardment mass spectroscopy shows peaks at *m*/*z* 752, 607, and 461 corresponding to $[RhL_2(PF_6)_2]^+$ (*m*/*z* 753), $[RhL_2(PF_6)]^+$ (*m*/*z* 608), and $[RhL_2]^+$ (*m*/*z* 463) respectively. The electronic spectrum of $[RhL_2]^{3+}$ shows an absorbance at $\lambda_{max.}$ = 270 nm (ε = 30 600 dm^3 mol^{-1} cm^{-1}) assigned to a ligand-to-metal charge-transfer transition.

Cyclic voltammetry of $[RhL_2][PF_6]_3$ in MeCN (0.1 mol dm^{-3} $NBu^n{}_4PF_6$) at platinum electrodes shows two chemically reversible reductions at $^1E_{\frac{1}{2}} = -0.71$ V, $\Delta E_p = 71$ mV and $^2E_{\frac{1}{2}} = -1.08$ V, $\Delta E_p = 127$ mV *vs.* ferrocene–ferrocenium at

---

† Bis(1,4,7-trithiacyclononane-$S^1S^4S^7$)rhodium(III) tris(hexafluorophosphate).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Selected bond lengths (Å), angles and torsion angles (°) for $[RhL_2][PF_6]_3$, S(4) and S(7) being related by symmetry

Rh–S(1)	2.331 6(14)	Rh–S(4)	2.333 5(12)	Rh–S(7)	2.333 5(12)
S(1)–C(2)	1.788(12)	S(4)–C(5)	1.813(13)	S(7)–C(8)	1.796(12)
S(1)–C(9)	1.870(14)	S(4)–C(3)	1.859(14)	S(7)–C(6)	1.856(13)
C(2)–C(3)	1.527(18)	C(5)–C(6)	1.532(18)	C(8)–C(9)	1.503(18)
S(1)–Rh–S(4)	88.78(5)	S(1)–Rh–S(7)	88.78(5)	S(4)–Rh–S(7)	88.84(4)
Rh–S(1)–C(2)	102.9(4)	Rh–S(4)–C(5)	102.5(4)	Rh–S(7)–C(8)	102.8(4)
Rh–S(1)–C(9)	103.0(4)	Rh–S(4)–C(3)	103.9(4)	Rh–S(7)–C(6)	104.4(4)
C(2)–S(1)–C(9)	100.7(6)	C(3)–S(4)–C(5)	101.1(6)	C(6)–S(7)–C(8)	101.1(6)
S(1)–C(2)–C(3)	113.9(8)	S(4)–C(5)–C(6)	113.5(9)	S(7)–C(8)–C(9)	112.8(9)
S(4)–C(3)–C(2)	112.4(9)	S(7)–C(6)–C(5)	112.2(9)	S(1)–C(9)–C(8)	113.0(9)
S(1)–C(2)	63.9(10)	S(4)–C(5)	64.4(10)	S(7)–C(8)	64.4(10)
S(1)–C(9)	−136.1(9)	S(4)–C(3)	−134.3(9)	S(7)–C(6)	−134.7(9)
C(2)–C(3)	48.4(11)	C(5)–C(6)	48.5(11)	C(8)–C(9)	50.3(11)

Table 2. Co-ordinates (Å) for the ideal bound ligand L

Atom	x	y	z
S(1)	2.2917	0.0000	0.0000
C(2)	1.6465	0.6759	−1.5657
H(21)	1.6677	−0.1089	−2.3074
H(22)	2.2924	1.4834	−1.8774
C(3)	0.2330	1.2067	−1.4777
H(31)	−0.4502	0.3730	−1.4108
H(32)	0.0177	1.7780	−2.3686
S(4)	0.0000	2.2917	0.0000
C(5)	−1.5657	1.6465	0.6759
H(51)	−2.3074	1.6677	−0.1089
H(52)	−1.8774	2.2924	1.4834
C(6)	−1.4777	0.2330	1.2067
H(61)	−1.4108	−0.4502	0.3730
H(62)	−2.3686	0.0177	1.7780
S(7)	0.0000	0.0000	2.2917
C(8)	0.6759	−1.5657	1.6465
H(81)	−0.1089	−2.3074	1.6677
H(82)	1.4834	−1.8774	2.2924
C(9)	1.2067	1.4777	0.2330
H(91)	0.3730	−1.4108	−0.4502
H(92)	1.7780	−2.3686	0.0177

These co-ordinates give the following bond lengths (Å), angles and torsion angles (°) (values for the free ligand from ref. 16 are given in parentheses):

Bonds: S(1)–C(2) 1.823 (1.824), C(2)–C(3) 1.512 (1.510), and C(3)–S(4) 1.848 (1.820).

Angles: S(1)–C(2)–C(3) 114.2 (113.0), C(2)–C(3)–S(4) 111.7 (117.1), and C(3)–S(4)–C(5) 101.3 (102.8).

Torsion angles S(1)–C(2) 66.5 (55.0), C(2)–C(3) 47.0 (58.6), and C(3)–S(4) −133.5 (−131.1).

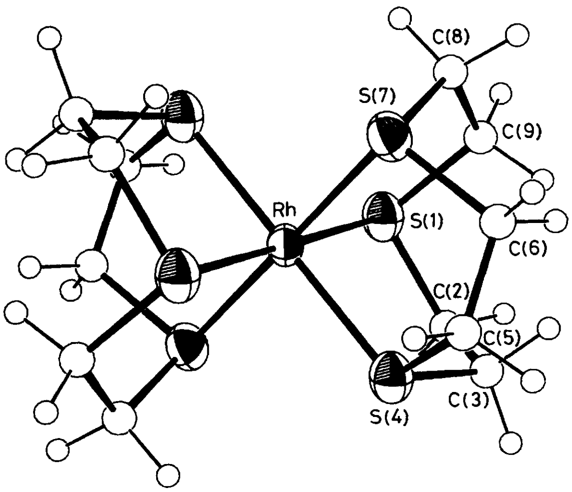


Figure 1. Single-crystal *X*-ray structure of $[RhL_2][PF_6]_3$ with the numbering scheme adopted

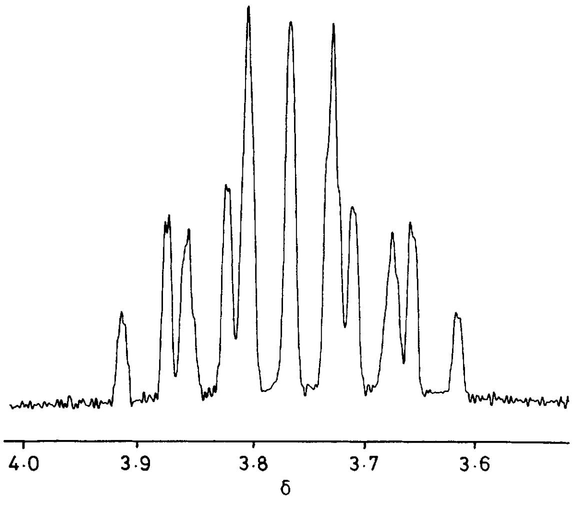


Figure 2. Proton n.m.r. spectrum (CD_3NO_2, 293 K, 200 MHz) of $[RhL_2][PF_6]_3$

20 °C at a scan rate of 100 mV s^{-1} (Figure 3). The isoelectronic and isostructural cation $[CoL_2]^{3+}$ likewise shows two reversible reductions in MeCN at ${}^1E_{\frac{1}{2}} = -0.013$ V and ${}^2E_{\frac{1}{2}} = -0.86$ V *vs.* ferrocene–ferrocenium assigned to Co^{III}–Co^{II} and Co^{II}–Co^{I} redox couples respectively.[1] This suggested that similar redox processes might be occurring in the rhodium system and that the generation of both Rh^{II} and Rh^{I} was possible utilising hexathia co-ordination. Controlled-potential electrolysis of $[RhL_2]^{3+}$ at −0.8 V at a platinum gauze in MeCN afforded a reduced product ($\lambda_{max.} = 268$ nm, $\varepsilon = 22\,300$ dm^3 mol^{-1} cm^{-1}), the e.s.r. spectrum of which (measured as a frozen glass at 77 K) can be tentatively assigned to the formation of a paramagnetic rhodium(II) species $[RhL_2]^{2+}$ ($g_1 = 2.089$, $g_2 = 2.082$, $g_3 = 2.010$). It should be noted however that similar g values have also been reported for rhodium(III) superoxy species.[18,19] The reactivity of $[RhL_2]^{2+}$ with O_2 and related species is currently under investigation. The complex $[RhL_2]^{2+}$ is significantly less stable in solution than the corresponding d^7 species $[PdL_2]^{3+}$ and $[PtL_2]^{3+}$. This might be expected in view of the smaller formal charge in the rhodium(II) species, and the availability of the rhodium(I) oxidation state with tetrathia co-ordination.[20] Controlled-potential electrolysis of the complex at −1.2 V leads to the loss of the e.s.r. signal with the formation presumably of the highly air- and water-sensitive

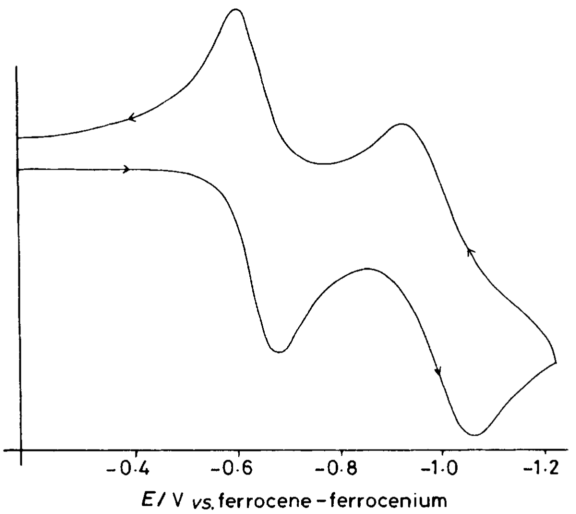
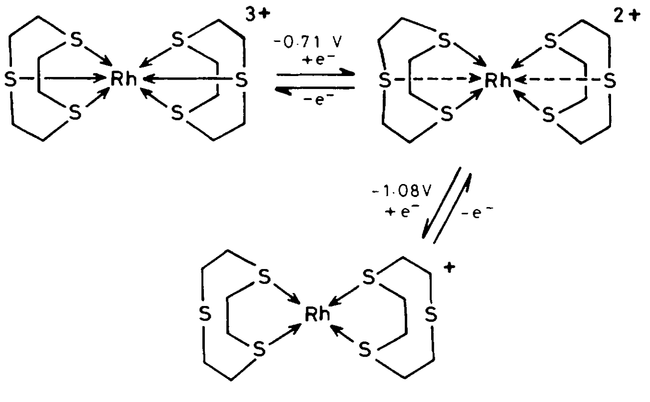


Figure 3. Cyclic voltammogram of $[RhL_2][PF_6]_3$ in MeCN (0.1 mol dm^{-3} $NBu^n_4PF_6$) at platinum electrodes. Scan rate = 100 mV s^{-1}, T = 293 K



Scheme.

$[RhL_2]^+$ cation. The complexation of Rh^I by tetrathia macrocycles has been reported previously;[20] in $[RhL_2]^+$ it is likely that the Rh^I is co-ordinated by two macrocyclic ligands in a square plane with the two remaining thia donors interacting only weakly with the electron-rich metal centre. The complex $[RhL_2]^+$ appears to be a very strong reducing agent, and solutions of this cation may be generated by reaction of $[\{RhCl(C_2H_4)_4\}_2]$ with 4 equivalents of L. Cyclic voltammetric studies on $[RhL_2]^+$ show the same electrochemical response as $[RhL_2]^{3+}$, confirming the chemical reversibility of the system (Scheme).

As in the generation of the analogous d^7 palladium(III)[11,12] and platinum(III)[9] species, the ability of the trithia crowns stereochemically and conformationally to respond to the variations of the metal oxidation state is thought to be critical in the stabilisation of the Rh^{III}–Rh^{II}–Rh^I conversions. The mononuclear rhodium(II) centre is likely to be isostructural with the isoelectronic palladium(III) complex $[PdL_2]^{3+}$,[12] which shows a tetragonally distorted octahedral stereochemistry due to the expected Jahn–Teller distortion imposed by the d^7 metal ion. Few examples of mononuclear, paramagnetic rhodium(II) complexes have been reported[19,21–24] with many of these being based on porphyrin species.[19,22] Interestingly, the value of the Rh^{III}–Rh^{II} redox couple for $[RhL_2]^{3+}$, $^1E_{\frac{1}{2}} = -0.71$ V *vs.* ferrocene–ferrocenium, contrasts with the vaue of -1.8 V *vs.* Ag–Ag$^+$ for the hexa-aza cryptand complex $[Rh(sep)]^{3+}$ (sep = sepulchrate, 1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]icosane).[23] Further reduction of $[RhL_2]^{2+}$ affords a square-planar rhodium(I) species *via* elongation or cleavage of two apical Rh–S bonds; this would explain the large peak–peak separation ($^2\Delta E_p$ = 127 mV) observed for the Rh^{II}–Rh^I couple when compared with the Rh^{III}–Rh^{II} couple ($^1\Delta E_p$ = 71 mV). The degree of apical interaction(s) between the thioether donors and the metal centre in $[RhL_2]^+$ is however unclear at present.

Current work is aimed at the elucidation of the stereochemical and electronic changes underlying these, and related, redox processes. Certainly the potentials at which these redox couples occur are consistent with metal-based processes for the bis(macrocycle) complexes of Rh, Ni, Pd, and Pt. However, the exact degree of electronic participation and interaction between the thia macrocycles and these various metal centres is still unclear. Full spectroelectrochemical studies on $[ML_2]^{x+}$ (M = Ru, Os, Rh, Ir, Pd, or Pt) are in progress.

Experimental

Infrared spectra were measured over the range 200—4 000 cm^{-1} as Nujol mulls, KBr and CsI discs using a Perkin-Elmer 598 spectrometer, u.v.–visible spectra in quartz cells using a Pye Unicam SP8-400 spectrophotometer. Microanalyses were performed by the Edinburgh University Chemistry Department microanalytical service. E.s.r. spectra were recorded as solids or as frozen glasses down to 77 K using a Bruker ER200D *X*-band spectrometer. Electrochemical measurements were performed on a Bruker E310 Universal Modular Polarograph. All readings were taken using a three-electrode potentiostatic system in acetonitrile containing 0.1 mol dm^{-3} $NBu^n_4PF_6$ as supporting electrolyte. Cyclic voltammetric measurements were carried out using a double platinum electrode and a Ag–AgCl reference electrode. All potentials are quoted *versus* ferrocene–ferrocenium. Mass spectra were run by electron impact on a Kratos MS 902 and by fast-atom bombardment on a Kratos MS 50 TC spectrometer. Proton n.m.r. spectra were run at 80 and 200 MHz on Bruker WP80 and WP200 spectrometers.

1,4,7-Trithiacyclononane (L) was prepared by the literature method.[25]

Synthesis of $[RhL_2][PF_6]_3$.—The salt $RhCl_3 \cdot 3H_2O$ (0.08 g, 0.305 mmol) was refluxed in water (20 cm^3) with $AgNO_3$ (0.232 g, 1.37 mmol) for 2 h. The solution was allowed to cool to room temperature and the AgCl removed by filtration. To this solution was added L (0.109 g, 0.607 mmol) in methanol (20 cm^3) and the mixture refluxed for 24 h. Addition of an excess of NH_4PF_6 gave a pale yellow precipitate which was washed with hot methanol and recrystallised from water. Yield = 0.136 g, 50% (Found: C, 16.2; H, 2.7. Calc. for $[RhL_2][PF_6]_3$: C, 16.0; H, 2.7%). Infrared spectrum: 2 985, 2 984, 1 444, 1 411, 1 300, 1 289, 1 270, 1 248, 1 178, 1 134, and 840 cm^{-1}. ^{1}H N.m.r. spectrum (80 MHz, CD_3NO_2, 293 K): δ 3.77 (CH_2, ABCD). Electronic spectrum (MeCN): $\lambda_{max.}$ = 270 nm (ε = 30 600 dm^3 mol^{-1} cm^{-1}). Fast atom-bombardment mass spectrum (glycerol–dimethylformamide): *m/z* 752 {calc. for $[RhL_2(PF_6)_2]^+$, 753}, 607 {calc. for $[RhL_2(PF_6)]^+$, 608}, and 461 (calc. for $[RhL_2]^+$, 463).

Crystal Structure Determination of $[RhL_2][PF_6]_3$.—Crystals of $[RhL_2][PF_6]_3$ were grown from aqueous solution and a plate of dimensions 0.9 × 0.4 × 0.1 mm was selected for data collection on a Stoe-Siemens AED2 four-circle diffractometer.

Crystal data. $C_{12}H_{24}F_{18}P_3RhS_6$, M = 898.3, monoclinic, space group *I2/m* (alternative setting of *C2/m*, no. 12), a = 11.329(3), b = 9.692(3), c = 14.909(4) Å, β = 101.77(2)°, U = 1 603 Å^3, Z = 2, D_c = 1.861 g cm^{-3}, $F(000)$ = 888, μ(Mo-K_α) = 11.57 cm^{-1}.

Table 3. Fractional atomic co-ordinates for $[RhL_2][PF_6]_3$ with standard deviations

Atom	x	y	z	$U_{eq}/\text{Å}^2$	Multiplicity	Occupancy
Rh	0.0	0.0	0.0	0.032 5(6)	0.25	1.0
S(1)	0.205 25(15)	0.0	0.065 64(12)	0.044 2(11)	0.5	1.0
S(4)	0.036 87(11)	0.168 52(13)	−0.102 65(8)	0.044 3(9)	1.0	1.0
C(2)	0.256 0(9)	0.159 9(12)	0.027 1(8)	0.043 3(25)	1.0	0.5
C(3)	0.203 2(11)	0.192 0(15)	−0.073 3(9)	0.054(3)	1.0	0.5
C(5)	0.019 4(13)	0.073 4(12)	−0.209 3(7)	0.049(3)	1.0	0.5
C(6)	0.078 1(13)	−0.069 6(13)	−0.198 3(7)	0.050(3)	1.0	0.5
C(8)	0.181 2(10)	−0.235 8(14)	−0.047 4(9)	0.050(3)	1.0	0.5
C(9)	0.268 9(11)	−0.124 8(14)	−0.007 6(10)	0.054(3)	1.0	0.5
P(1)	0.447 79(17)	0.0	−0.224 03(13)	0.046 4(12)	0.5	1.0
F(1)	0.548 6(4)	0.115 4(4)	−0.216 3(3)	0.077 0(25)	1.0	1.0
F(2)	0.432 7(5)	0.0	−0.331 8(4)	0.076(4)	0.5	1.0
F(3)	0.464 5(6)	0.0	−0.115 2(4)	0.089(4)	0.5	1.0
F(4)	0.347 9(4)	0.115 8(5)	−0.232 1(3)	0.089(3)	1.0	1.0
P(2)	0.0	0.0	0.5	0.053 9(18)	0.25	1.0
F(5)	0.008 8(14)	0.127 4(11)	0.559 3(8)	0.177(11)	1.0	0.667
F(6)	0.117 9(14)	0.0	0.568 2(14)	0.177(15)	0.5	0.667
F(7)	0.099 0(20)	0.0	0.448 5(18)	0.239(24)	0.5	0.667
O(1)	0.438(4)	0.0	0.476(3)	0.223(16)	0.5	0.5
O(2)	0.247(3)	0.205(3)	0.278 6(17)	0.201(9)	1.0	0.5
O(3)	0.265(5)	0.0	0.342(3)	0.247(19)	0.5	0.5

Data collection and processing. Of the 1 088 independent data measured to $\theta = 22.5°$, solution and refinement[26] were based on 1 007 data with $I \geqslant 3\sigma(I)$. With the Rh atom fixed at the origin (site symmetry C_{2h}), all S and P atoms could be located in positions compatible with the space group $I2/m$. This requires the cation and one PF_6^- ion to have C_{2h} symmetry, while a second anion has imposed C_s symmetry. The symmetry imposed on a ligand is thus C_s, but the carbon atoms are disordered, and refinement gives unrealistic bond lengths and thermal parameters. A set of macrocycle co-ordinates based on those from the related ruthenium(II) cation $[RuL_2]^{2+}$ [13] was idealised to give strict C_3 symmetry, co-ordinates for which are given in Table 2. These co-ordinates were fitted to the observed sulphur positions, so that the crystal symmetry superimposed the macrocycle on its mirror image, with the sulphur atoms being common to both. This model refined well with no constraints on the carbon atom positions, but with S(1) constrained to lie in the mirror plane at $y = 0$ and S(4) constrained to be related to S(7) by that plane. One of the PF_6^- ions is partly disordered, and was refined with partial site occupancy for some F atoms. Some partial occupancy of solvent (water) was also apparent, and was refined as oxygen. In the final cycles of refinement, all atoms heavier than oxygen were refined anisotropically, with a weighting scheme $w^{-1} = \sigma^2(F) + 0.0045|F^2|$. Hydrogen atoms were included in idealised positions (C–H 1.08 Å) on all carbon atoms.[24] At convergence, $R = 0.042$, $R' = 0.072$, and $S = 0.83$, for 115 refined parameters. In the last cycle no shift exceeded 0.1 of an estimated standard deviation (e.s.d.) except for some shifts in the disordered solvent of up to 0.4 of an e.s.d. No peak or trough exceeded ± 0.8 e Å^{-3} in a final difference electron-density synthesis. Illustrations were prepared using ORTEP,[27] molecular geometry calculations utilised CALC,[28] and scattering factor data were taken from ref. 29. Fractional co-ordinates are given in Table 3.

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

Acknowledgements

We thank the S.E.R.C. and BP Chemicals for a C.A.S.E. Award (to T. I. H.) and the S.E.R.C. for support. We are grateful to Dr. Barrie Raynor for helpful discussions.

References

1 K. Wieghardt, H-J. Küppers, and J. Weiss, *Inorg. Chem.*, 1985, **24**, 3067.

2 R. S. Glass, W. N. Setzer, C. A. Ogle, and G. S. Wilson, *Inorg. Chem.*, 1983, **22**, 266.

3 G. S. Wilson, D. D. Swanson, and R. S. Glass, *Inorg. Chem.*, 1986, **25**, 3827.

4 J. R. Hartman and S. R. Cooper, *J. Am. Chem. Soc.*, 1986, **108**, 1208.

5 H. J. Küppers, A. Neves, C. Pomp, D. Ventur, K. Wieghardt, B. Nuber, and J. Weiss, *Inorg. Chem.*, 1986, **25**, 2400.

6 J. R. Hartman and S. R. Cooper, *J. Am. Chem. Soc.*, 1986, **108**, 1202.

7 M. Schröder, *Pure Appl. Chem.*, 1988, **60**, 517.

8 Presented at the 4th International Symposium on Inclusion Phenomena, University of Lancaster, July 1986; M. N. Bell, A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, A. J. Lavery, G. Reid, and M. Schröder, *J. Inclusion Phenomena*, 1987, **5**, 169.

9 A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, M. O. Odulate, A. J. Lavery, and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1987, 118.

10 K. Wieghardt, H-J Küppers, E. Raabe, and C. Krüger, *Angew. Chem.*, 1986, **98**, 1136; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1101.

11 A. J. Blake, A. J. Holder, T. I. Hyde, Y. V. Roberts, A. J. Lavery, and M. Schröder, *J. Organomet. Chem.*, 1987, **323**, 261.

12 A. J. Blake, A. J. Holder, T. I. Hyde, and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1987, 987.

13 M. N. Bell, A. J. Blake, H-J. Küppers, M. Schröder, and K. Wieghardt, *Angew. Chem.*, 1987, **99**, 253; *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 250.

14 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260.

15 A. J. Blake, A. J. Holder, Y. V. Roberts, and M. Schröder, *Acta Crystallogr., Sect. C*, 1988, **44**, 360.

16 R. S. Glass, G. S. Wilson, and W. N. Setzer, *J. Am. Chem. Soc.*, 1980, **102**, 5068; W. N. Setzer, B. R. Coleman, G. S. Wilson, and R. S. Glass, *Tetrahedron*, 1981, **37**, 2743.

17 K. Wieghardt, M. Köppen, W. Swiridoff, and J. Weiss, *J. Chem. Soc., Dalton Trans.*, 1983, 1869.

18 J. B. Raynor, R. D. Gillard, and J. D. Pedrosa de Jesus, *J. Chem. Soc., Dalton Trans.*, 1982, 1165.

19 B. B. Wayland and A. R. Newman, *J. Am. Chem. Soc.*, 1979, **101**, 6472.

20 W. D. Lemke, K. E. Travis, N. E. Takvoryan, and D. H. Busch, *Adv. Chem. Ser.*, 1977, **50**, 358; T. Yoshida, Y. Ueda, T. Adachi, K. Yamamoto, and T. Higuchi, *J. Chem. Soc., Chem. Commun.*, 1985, 1137.

21 For a review see, T. R. Felthouse, *Prog. Inorg. Chem.*, 1982, **29**, 74.

22 B. B. Wayland and A. R. Newman, *Inorg. Chem.*, 1981, **20**, 3093; K. M. Kadish, C-L. Yao, J. E. Anderson, and P. Cocolios, *ibid.*, 1985, **24**, 4515; J. E. Anderson, C-L. Yao, and K. M. Kadish, *ibid.*, 1986, **25**, 718; *J. Am. Chem. Soc.*, 1987, **109**, 1106.

23 J. MacB. Harrowfield, A. J. Herit, P. A. Lay, A. M. Sargeson, A. M. Bond, W. A. Mulac, and J. C. Sullivan, *J. Am. Chem. Soc.*, 1983, **105**, 5503.

24 E. Billig, S. I. Shupack, J. H. Waters, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, 1964, **86**, 926; M. A. Bennett and R. A. Longstaff, *ibid.*, 1969, **91**, 6266; C. Masters and B. L. Shaw, *J. Chem. Soc. A*, 1971, 3679; B. R. James, F. T. T. Ng, and E. Ochiai, *Can. J. Chem.*, 1972, **50**, 590; G. Valentini, G. Braca, G. Sbrana, and A. Colligiani, *Inorg. Chim. Acta*, 1983, **69**, 221; N. V. Vugman and W. O. Franco, *J. Chem. Phys.*, 1983, **78**, 2099; N. V. Vugman and N. M. Pinhal, *Mol. Phys.*, 1983, **49**, 1315; N. G. Connelly and G. Garcia, *J. Chem. Soc., Chem. Commun.*, 1987, 246.

25 D. Sellmann and L. Zapf, *Angew. Chem.*, 1984, **96**, 799; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 807; D. Sellmann and L. Zapf, *J. Organomet. Chem.*, 1985, **289**, 57.

26 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

27 P. D. Mallinson and K. W. Muir, ORTEP II, interactive version, *J. Appl. Crystallogr.*, 1985, **18**, 51.

28 R. O. Gould and P. Taylor, CALC, Fortran 77 version, University of Edinburgh, 1985.

29 D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.

Received 15*th June* 1987; *Paper* 7/1058