Pergamon

0277-5387(95)00128-X

Polyhedron Vol. 14, No. 19, pp. 2753–2758, 1995
Elsevier Science Ltd
Printed in Great Britain
0277-5387/95 $9.50+0.00

SYNTHESIS, SPECTROSCOPIC AND STRUCTURAL CHARACTERIZATION OF Pd^{II} AND Pt^{II} COMPLEXES OF THE CYCLIC DISELENOETHER 1,5-DISELENACYCLOOCTANE, [8]ANESe$_2$*

NEIL R. CHAMPNESS, WILLIAM LEVASON†, JEFFREY J. QUIRK and GILLIAN REID

Department of Chemistry, University of Southampton, Southampton SO17 1BJ, U.K.

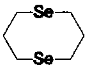
and

CHRISTOPHER S. FRAMPTON

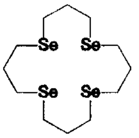
Roche Products Ltd, Welwyn Garden City, Herts AL7 3AY, U.K.

Abstract—The complexes $[M([8]aneSe_2)Cl_2]$ and $[M([8]aneSe_2)_2][PF_6]_2$ [M = Pd or Pt, $[8]aneSe_2 = \overline{Se(CH_2)_3Se(C}H_2)_3]$ have been prepared, and characterized by analysis, UV–vis and multinuclear (^1H, $^{77}Se\{^1H\}$ and ^{195}Pt) NMR spectroscopy and FAB mass spectrometry. The structures of $[Pd([8]aneSe_2)Cl_2]\cdot 0.5MeNO_2$ [Pd—Se = 2.3647(8), 2.3693(8) Å, Pd—Cl = 2.363(2), 2.348(2) Å] and of the related bis(bidentate) diselenoether model complex $[Pt\{MeSe(CH_2)_3SeMe\}_2][PF_6]_2\cdot 2MeCN$ [Pt—Se = 2.414(2), 2.421(2) Å] have been determined by single-crystal X-ray analyses.

There is considerable interest in the coordination chemistry of sulphur, selenium and tellurium ligands.[1,2] We are currently conducting a systematic investigation of metal complexes involving macrocyclic selenoether ligands, and have recently reported elsewhere on complexes of the tetraselenoether, 1,5,9,13,-tetraselenacyclohexadecane, $[16]aneSe_4$ with Rh^{III},[3] Pd^{II} and Pt^{II},[4] and Pt^{IV}.[5] The cyclic diselenoether, 1,5-diselenacyclooctane, $[8]aneSe_2$(I), is generated as a byproduct in the synthesis of $[16]aneSe_4$(II) by reaction of NaSe $(CH_2)_3SeNa$ with $Br(CH_2)_3Br$,[6] and here we report on the synthesis and spectroscopic properties of palladium(II) and platinum(II) complexes of this ligand, and the X-ray structures of *cis*-$[PdCl_2([8]aneSe_2)]\cdot 0.5MeNO_2$ and the related bis(bidentate) Pt^{II} acyclic selenoether complex $[Pt\{MeSe(CH_2)_3SeMe\}_2](PF_6)_2\cdot 2MeCN$.[4] No other complexes of $[8]aneSe_2$ have been reported, but a few complexes of 1,4-diselenacyclohexane $\overline{Se(CH_2)_2Se(C}H_2)_2$ with metal halides were reported many years ago,[7,8] although their structures remain uncertain. The carbonyl complexes $M(CO)_4$(1,4-diselenacyclohexane) (M = Cr, Mo or W), however, contain chelating selenoethers.[9] Complexes of cyclic dithioethers are also known including those of 1,5-dithiacyclooctane.[10]



I



II

EXPERIMENTAL

Physical measurements were made as described previously.[5] The ligand $[8]aneSe_2$ was a by-product

---

*Dedicated to Professor E. W. Abel, on the occasion of his retirement.

†Author to whom correspondence should be addressed.

of the synthesis of [16]aneSe_4 by the route described by Pinto *et al.*[6] The $^{77}Se\{^1H\}$ NMR spectrum of [8]aneSe_2 in CH_2Cl_2 has $\delta = +137$.

[Pt([8]aneSe_2)Cl_2]

Platinum(II) chloride (0.05 g, 0.19 mmol) and [8]aneSe_2 (0.05 g, 0.21 mmol) were added to degassed MeCN (70 cm^3), and the mixture refluxed for 24 h under N_2. The mixture was cooled, filtered to remove a small amount of platinum metal, concentrated to small volume, and treated with diethyl ether. The resulting white solid produced was dried *in vacuo* (0.043 g, 45%). Found: C, 14.8; H, 2.3. Calc. for $C_6H_{12}Cl_2PtSe_2$: C, 14.2; H, 2.4%. FAB mass spectrum (3-NOBA): $m/z = 473$, calc. for $[^{195}Pt([8]ane^{80}Se_2)^{35}Cl]^+$ 474. NMR data: $^{77}Se\{^1H\}$ in DMF, 298 K, relative to neat external Me_2Se, $\delta = +194$, $^1J(^{77}Se—^{195}Pt) = 680$ Hz; ^{195}Pt in DMF relative to external aqueous $[PtCl_6]^{2-}$ $\delta = -3825$; ^1H in d^6-dmso, 298 K: δ 3.1–2.6 (m, $SeCH_2$), 2.4–2.1 (m, $CH_2CH_2CH_2$). UV–Vis spectrum (DMF): 390 (ε_{mol} 375 $dm^3\ cm^{-1}\ mol^{-1}$), 320 nm (ε_{mol} 1550). IR (nujol mull/cm^{-1}) 1409s, 1287m, 1263m, 1248m, 1209m, 1172m, 1113m, 1042m, 1004m, 962m, 873m, 838m, 768m, 581m, 442w, 303s(Pt—Cl).

[Pd([8]aneSe_2)Cl_2]

Palladium(II) chloride (0.04 g, 0.23 mmol) and [8]aneSe_2 (0.05 g, 0.21 mmol) were refluxed together in degassed MeCN (70 cm^3) for 2.5 h. Removal of the solvent under reduced pressure and washing the residue with diethyl ether left an orange solid (0.066 g, 70%). Found: C, 18.2; H, 2.6; N = 1.3. Calc. for $C_6H_{12}Cl_2PdSe_2 \cdot 1/4MeCN$: C, 18.2; H, 3.0; N, 1.5%. FAB mass spectrum (3-NOBA): $m/z = 385$, calc. for $[^{106}Pd([8]ane^{80}Se_2)^{35}Cl]^+$ 385. NMR data: $^{77}Se\{^1H\}$ in $MeNO_2$ $\delta = +199$; ^1H in d^6-dmso: δ 2.9–2.6 (m, $SeCH_2$), 2.4–2.1 (m, $CH_2CH_2CH_2$). UV–vis spectrum ($MeNO_2$): 400 (ε_{mol} 960), 300 nm (7260). IR (nujol mull/cm^{-1}) 1407s, 1285m, 1262m, 1246m, 1210m, 1170m, 1113m, 1005m, 963m, 884m, 873m, 838m, 829m, 770m, 555w, 444w, 298s(Pd-Cl), 230w.

[Pt([8]aneSe_2)$_2$][PF_6]$_2$

$PtCl_2$ (0.037 g, 0.14 mmol), [8]aneSe_2 (0.065 g, 0.27 mmol) and $TlPF_6$ (0.093 g, 0.27 mmol) were refluxed together in degassed MeCN (75 cm^3) for 3 h and then heated at 50°C for 16 h. The TlCl was removed by filtration, the filtrate concentrated, and the white product isolated by addition of diethyl ether (0.07 g, 52%). Found: C, 14.2; H, 2.7. Calc. for $C_{12}H_{24}F_{12}P_2PtSe_4$: C, 14.65; H, 2.5. FAB mass spectrum (3-NOBA): $m/z = 825$, calc. for $[^{195}Pt([8]ane^{80}Se_2)_2PF_6]^+$ 828; 679 calc. for $[^{195}Pt([8]ane^{80}Se_2)_2]^+$ 683. NMR data: $^{77}Se\{^1H\}$ in MeCN $\delta = 168$ $^1J(^{77}Se—^{195}Pt) = 317$ Hz, ^{195}Pt $\delta = -4606$. UV–vis spectrum (MeCN): 279 (12,800), 231 nm (14,470). IR (nujol mull/cm^{-1}) 1375s, 1270m, 1222m, 1153m, 1029m, 1008m, 967m, 882m, 842s, 768m, 638w, 558s.

[Pd([8]aneSe_2)$_2$][PF_6]$_2$

A mixture of [8]aneSe_2 (0.05 g, 0.21 mmol), $PdCl_2$ (0.021 g, 0.12 mmol) and $TlPF_6$ (0.072 g, 0.21 mmol) were refluxed together in degassed MeCN (75 cm^3). After 12 h the yellow solution was filtered to remove TlCl, concentrated to 5 cm^3 and diethyl ether added to afford the yellow complex (0.07 g, 67%). Found: C, 16.1; H, 3.0. Calc. for $C_{12}H_{24}F_{12}P_2PdSe_4$: C, 16.4; H, 2.7. FAB mass spectrum (3-NOBA): $m/z = 737$ calc. for $[^{106}Pd([8]ane^{80}Se_2)_2PF_6]^+$ 739; 591 calc. for $[^{106}Pd([8]ane^{80}Se_2)_2]^+$ 594. NMR data, $^{77}Se\{^1H\}$ in MeCN $\delta = +164$. UV–vis spectrum (MeCN): 350 (10,620), 279nm (13,890). IR (nujol mull/cm^{-1}) 1375s, 1267m, 1221m, 1073m, 1007m, 967m, 879m, 838s, 772m, 557s, 471m, 312w.

Single-crystal structure determination on [Pd([8]aneSe_2)Cl_2]·0.5$MeNO_2$

Orange needles of suitable quality for a single-crystal X-ray determination were obtained from vapour diffusion of diethyl ether into a solution of the complex in $MeNO_2$. The selected crystal (0.20 × 0.15 × 0.30 mm) was coated with silicone oil and mounted on a glass fibre.

Crystal data. $C_6H_{12}Cl_2Se_2Pd \cdot 0.5CH_3NO_2$, $M = 449.9$, orthorhombic, space group *Fdd*2, $a = 24.396(7)$, $b = 27.450(4)$, $c = 7.103(4)$ Å, $U = 4756$ Å^3 [from 2θ values of 25 reflections measured at $\pm\omega$ ($24.9 \leqslant 2\theta \leqslant 39.7°$, $\lambda = 0.71069$ Å)], $Z = 16$, $D_{calc} = 2.513\ g\ cm^{-3}$, $T = 123$ K, $\mu = 80.22\ cm^{-1}$, $F(000) = 3392$.

Data collection and processing. Rigaku AFC7R four-circle diffractometer, using graphite-monochromated Mo-K_α X-radiation, $T = 123$ K, ω–2θ scans with ω scan width = $(1.42 + 0.35\tan\theta)°$, 1468 data collected ($2\theta_{max} = 54°$; h 0–30, k 0–34, l 0–9) giving 1318 reflections with $F \geqslant 5\sigma(F)$ for use in all calculations. No significant crystal decay or movement was observed. As there were no identifiable faces, the data were corrected for Lorentz and polarization effects and absorption empirically using ψ-scans (max. and min. transmission factors = 0.9949 and 0.8044, respectively).

Structure solution and refinement. The structure was solved by direct methods[11] and developed by using iterative cycles of full-matrix least-squares refinement and difference Fourier syntheses which located all non-H atoms.[12] During refinement a half occupied $MeNO_2$ solvent molecule was identified per Pd^{II} molecule. All non-H atoms were refined anisotropically, while H atoms were located in the difference map, included but not refined. H atoms on the solvent molecule were not located and therefore were omitted from the refinement. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses. At final convergence R, $R_w = 0.019$, 0.022 respectively, $S = 1.60$ for 118 refined parameters. The final ΔF synthesis showed no peaks above 0.52 or below -0.87 e Å^{-3} and the maximum $\Delta/\sigma = 0.00$. Selected bond lengths, angles and torsion angles are given in Table 1. Fractional atomic coordinates are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and observed and calculated structure factors.

Single crystal structure determination on $[Pt\{MeSe(CH_2)_3SeMe\}_2](PF_6)_2\cdot 2MeCN$

This complex was prepared as described previously.[4] Colourless prisms of suitable quality for a single crystal X-ray determination were obtained from vapour diffusion of diethyl ether into a solution of the complex in MeCN. The selected crystal ($0.25\times0.25\times0.10$ mm) was coated with mineral oil and mounted on a glass fibre.

Crystal data. $C_{10}H_{24}Se_4Pt\cdot P_2F_{12}\cdot 2CH_3CN$, $M = 1027.3$, triclinic, space group $P\bar{1}$, $a = 8.732(2)$, $b = 10.882(3)$, $c = 8.326(3)$ Å, $\alpha = 95.50(3)$, $\beta = 98.46(3)$, $\gamma = 111.86(2)°$, $U = 716.4$ Å^3 [from 2θ values of 25 reflections measured at $\pm\omega$ ($25.9 \leqslant 2\theta \leqslant 31.8°$, $\lambda = 0.71073$ Å)], $Z = 1$, $D_{calc} = 2.381$ g cm^{-3}, $T = 240$ K, $\mu = 101.57$ cm^{-1}, $F(000) = 480$.

Data collection and processing. Rigaku AFC7S four-circle diffractometer, using graphite-monochromated Mo-K_α X-radiation, $T = 240$ K, ω–2θ scans with ω scan width $= (1.05 + 0.35\tan\theta)°$, 2696 data collected, 2517 unique ($R_{int} = 0.065$; ($2\theta_{max} = 50°$, h 0–10, k-13–13, l-10–10) giving 1997 reflections with $F \geqslant 6\sigma(F)$ for use in all calculations. No significant crystal decay or movement was observed.

Structure solution and refinement. The structure was solved by Patterson methods which located the Pt atom position on a crystallographic inversion centre,[13] and developed by using iterative cycles of full-matrix least-squares refinement and difference Fourier syntheses which located all non-H atoms in one half $[Pt\{MeSe(CH_2)_3SeMe\}_2]^{2+}$ cation and one PF_6^- anion.[12] During refinement one fully occupied MeCN solvent molecule was identified per half Pt^{II} cation. Since there were no identifiable faces on the crystal, at isotropic convergence the data were corrected for absorption empirically using DIFABS[14] (max. and min. transmission factors = 1.000 and 0.555, respectively). All non-H atoms were then refined anisotropically, while H

Table 1. Selected bond lengths (Å) and angles (°) for $[PdCl_2([8]aneSe_2)]\cdot 0.5MeNO_2$

Pd(1)—Se(1)	2.3647(8)	Pd(1)—Se(2)	2.3693(8)
Pd(1)—Cl(1)	2.363(2)	Pd(1)—Cl(2)	2.348(2)
Se(1)—C(1)	1.964(6)	Se(1)—C(6)	1.957(6)
Se(2)—C(3)	1.963(6)	Se(2)—C(4)	1.985(7)
C(1)—C(2)	1.516(8)	C(2)—C(3)	1.515(8)
C(4)—C(5)	1.510(9)	C(5)—C(6)	1.543(8)
Se(1)—Pd(1)—Se(2)	91.76(3)	Se(1)—Pd(1)—Cl(1)	87.03(5)
Se(1)—Pd(1)—Cl(2)	175.56(5)	Se(2)—Pd(1)—Cl(1)	172.85(5)
Se(2)—Pd(1)—Cl(2)	87.20(4)	Cl(1)—Pd(1)—Cl(2)	94.53(6)
Pd(1)—Se(1)—C(1)	104.6(2)	Pd(1)—Se(1)—C(6)	105.9(2)
C(1)—Se(1)—C(6)	101.4(3)	Pd(1)—Se(2)—C(3)	107.4(2)
Pd(1)—Se(2)—C(4)	104.9(2)	C(3)—Se(2)—C(4)	99.2(3)
C(1)—C(2)—C(3)	115.0(5)	Se(2)—C(3)—C(2)	117.3(4)
Se(2)—C(4)—C(5)	116.1(4)	C(4)—C(5)—C(6)	116.0(5)
Se(1)—C(6)—C(5)	115.6(4)	Se(1)—C(1)—C(2)	117.0(4)
C(1)—Se(1)—C(6)—C(5)	-104.5(5)	C(2)—C(1)—Se(1)—C(6)	41.5(5)
C(2)—C(3)—Se(2)—C(4)	-47.3(5)	C(3)—Se(2)—C(4)—C(5)	106.3(5)
Se(2)—C(3)—C(2)—C(1)	-66.6(6)	Se(2)—C(4)—C(5)—C(6)	-69.6(7)
Se(1)—C(1)—C(2)—C(3)	71.3(6)	Se(1)—C(6)—C(5)—C(4)	69.9(6)

Table 2. Fractional atomic coordinates for $[Pd([8]aneSe_2)Cl_2]\cdot 0.5MeNO_2$

	x	*y*	*z*
Pd(1)	0.27236(2)	0.57405(2)	−0.1722
Se(1)	0.22545(2)	0.53294(2)	0.0720(1)
Se(2)	0.19527(2)	0.62392(2)	−0.2355(1)
Cl(1)	0.35157(6)	0.53097(5)	−0.0775(2)
Cl(2)	0.31499(6)	0.61129(5)	−0.4314(3)
O(1)	0.2261(2)	0.2815(2)	0.325(1)
N(1)	0.2500	0.2500	0.242(1)
C(1)	0.1568(3)	0.5108(2)	−0.0442(9)
C(2)	0.1156(3)	0.5497(2)	−0.0984(9)
C(3)	0.1318(3)	0.5807(2)	−0.2658(9)
C(4)	0.1762(3)	0.6537(2)	0.0106(10)
C(5)	0.2092(3)	0.6366(2)	0.1779(9)
C(6)	0.1988(3)	0.5837(2)	0.2423(9)
C(7)	0.2500	0.2500	0.034(2)

atoms were placed in fixed calculated positions. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses. At final convergence R, $R_w = 0.063$, 0.059 respectively, $S = 3.59$ for 160 refined parameters. The final ΔF synthesis showed the maximum peak and trough of 2.01 and −2.74 e Å^{-3}, respectively, to be within 1 Å of the Pt atom (no other significant electron density was unassigned) and the maximum $\Delta/\sigma = 0.00$. Selected bond lengths, angles and torsion angles are given in Table 3. Fractional atomic coordinates are listed in Table 4.

RESULTS AND DISCUSSION

The reaction of the appropriate MCl_2 (M = Pd or Pt) with $[8]aneSe_2$ in MeCN afforded the poorly soluble $[M([8]aneSe_2)Cl_2]$ complexes. The spectroscopic data (Experimental section) are consistent with *cis*-planar Se_2Cl_2 donor sets, and may be compared with similar data on the acyclic diselenoether complexes $[M\{MeSe(CH_2)_3SeMe\}Cl_2]$.[15] The most notable difference is that the latter complexes exist as both *meso* and DL enantiomers which interconvert by pyramidal inversion at selenium,[1] whereas in the $[8]aneSe_2$ complexes the higher symmetry of the coordinated ligand excludes the occurrence of enantiomers. (Interconversion of the chelate ring conformations is likely to be a low-energy process, and due to the poor solubility of the complexes was not investigated.) The coordination shifts in the ^{77}Se NMR spectra of the $[M([8]aneSe_2)Cl_2]$ complexes are +57 (Pt) and +62 ppm

Table 3. Selected bond lengths (Å) and angles (°) for $[Pt\{MeSe(CH_2)_3SeMe\}_2]^{2+}$

Pt(1)—Se(1)	2.414(2)	Pt(1)—Se(2)	2.421(2)
Se(1)—C(1)	1.96(2)	Se(1)—C(2)	1.93(2)
Se(2)—C(4)	1.95(2)	Se(2)—C(5)	1.91(1)
N(1)—C(6)	1.13(2)	C(2)—C(3)	1.55(2)
C(3)—C(4)	1.53(2)	C(6)—C(7)	1.43(2)
Pt(1)—Se(1)—C(1)	105.9(5)	Pt(1)—Se(1)—C(2)	107.3(5)
C(1)—Se(1)—C(2)	99.8(8)	Pt(1)—Se(2)—C(4)	105.2(5)
Pt(1)—Se(2)—C(5)	109.8(5)	C(4)—Se(2)—C(5)	95.1(8)
Se(1)—Pt(1)—Se(2)	89.09(6)	Se(1)—C(2)—C(3)	117(1)
C(2)—C(3)—C(4)	114(1)	Se(2)—C(4)—C(3)	114(1)
N(1)—C(6)—C(7)	178(2)		
Se(1)—C(2)—C(3)—C(4)	−67(1)	Se(2)—C(4)—C(3)—C(2)	−71(1)
C(1)—Se(1)—C(2)—C(3)	−47(1)	C(3)—C(4)—Se(2)—C(5)	176(1)

Table 4. Fractional Atomic coordinates for [Pt{MeSe(CH$_2$)$_3$SeMe}$_2$](PF$_6$)$_2$·2MeCN

	x	*y*	*z*
Pt(1)	0.0000	0.0000	0.0000
Se(1)	0.1870(2)	−0.0742(2)	−0.1301(2)
Se(2)	0.2028(2)	0.0792(2)	0.2574(2)
P(1)	0.7260(7)	0.3001(5)	0.7103(7)
F(1)	0.832(2)	0.434(1)	0.821(2)
F(2)	0.639(2)	0.239(1)	0.855(2)
F(3)	0.586(2)	0.347(2)	0.659(2)
F(4)	0.619(2)	0.160(1)	0.600(2)
F(5)	0.808(2)	0.356(1)	0.564(2)
F(6)	0.859(2)	0.245(2)	0.765(3)
N(1)	0.293(2)	0.293(2)	0.922(3)
C(1)	0.211(2)	0.010(2)	−0.328(2)
C(2)	0.061(2)	−0.259(2)	−0.231(2)
C(3)	−0.094(2)	−0.291(2)	−0.370(2)
C(4)	0.241(2)	0.267(2)	0.315(2)
C(5)	0.424(2)	0.114(2)	0.216(2)
C(6)	0.289(2)	0.383(2)	0.869(3)
C(7)	0.288(3)	0.501(2)	0.807(3)

(Pd); such small values being characteristic of six-membered chelate rings.[15]

In order to establish the geometry of the complex formed from reaction of PdCl$_2$ with one molar equivalent of [8]aneSe$_2$, a single-crystal X-ray study was undertaken. Orange needles of [Pd([8]aneSe$_2$)Cl$_2$]·0.5MeNO$_2$ suitable for single-crystal X-ray analysis were obtained from vapour diffusion of diethyl ether into a solution of the complex in MeNO$_2$. The structure determination shows (Fig. 1, Tables 1 and 2) the Pd^{II} ion ligated to both Se donors of the bidentate [8]aneSe$_2$ ligand and two *cis*-chloro ligands, giving discrete molecules of [Pd([8]aneSe$_2$)Cl$_2$], Pd—Se(1) = 2.3647(8), Pd—Se(2) = 2.3693(8) Å, Pd—Cl(1) = 2.363(2), Pd—Cl(2) = 2.348(2) Å. The [8]aneSe$_2$ ligand adopts the chair–boat conformation also observed in the corresponding 1,5-dithiacyclooctane complex.[10] Similar lengths have been observed for the Pd—Se and Pd—Cl bonds in the related species *cis*-[Pd(Pr^{i}SeCH$_2$CH$_2$SePr^i)Cl$_2$], Pd—Se = 2.40(1), 2.36(1) Å, Pd—Cl = 2.31(2), 2.32(2) Å.[16]

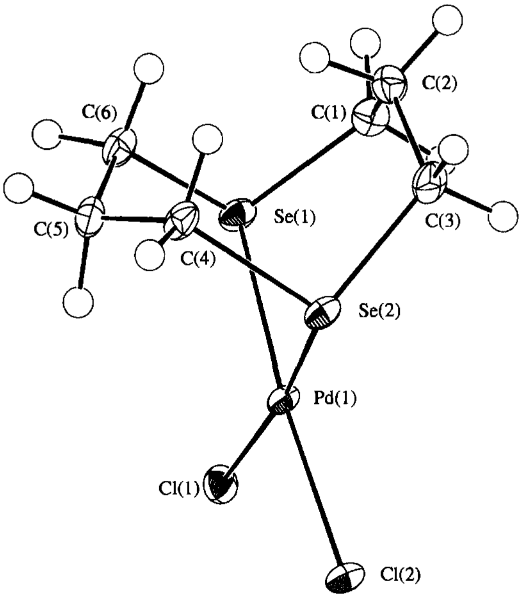


Fig. 1. View of the structure of [Pd([8]aneSe$_2$)Cl$_2$] with numbering scheme adopted.

The reaction of 2 molar equivalents of [8]aneSe$_2$ with MCl$_2$ and TlPF$_6$ in MeCN produced the *bis* (ligand) complexes [M([8]aneSe$_2$)$_2$][PF$_6$]$_2$ in moderate yield after filtration of the precipitated TlCl. These complexes were identified by major fragments in their FAB mass spectra corresponding to [M([8]aneSe$_2$)$_2$(PF$_6$)]$^+$ and [M([8]aneSe$_2$)$_2$]$^+$. Again due to the high symmetry of the coordinated diselenoether, only one isomer of each complex is possible, confirmed by single δ(^{77}Se) resonances, in these cases with even smaller coordination shifts than in the chlorides [+31 (Pt) and +27ppm (Pd)] consistent with the high *trans* influence of selenium. The ^{195}Pt NMR spectrum of [Pt([8]aneSe$_2$)](PF$_6$)$_2$ also shows a single resonance at δ −4606, very similar to the chemical shifts observed for [Pt([16]aneSe$_4$)]$^{2+}$. As expected, the ^{195}Pt NMR shifts for those [PtSe$_4$]$^{2+}$ cores are significantly

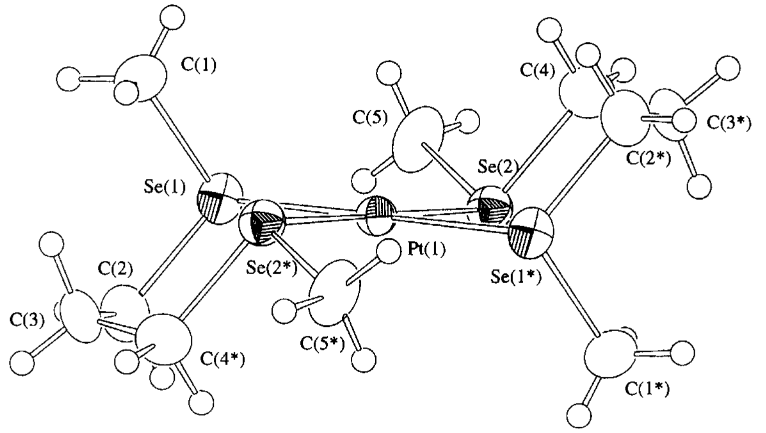


Fig. 2. View of the structure of $[Pt\{MeSe(CH_2)_3SeMe\}_2]^{2+}$ with numbering scheme adopted.

upfield compared with that for the $[PtSe_2Cl_2]$ core in $[Pt([8]aneSe_2)Cl_2]$, δ −3825.

In an attempt to obtain a single-crystal X-ray structural data on the one of the *bis*([8]aneSe$_2$) complexes, colourless single crystals of $[Pt([8]aneSe_2)_2](PF_6)_2$ were obtained by diffusion of Et_2O into a solution of the complex in MeCN. However, severe disorder problems prevented full refinement of the data, although the square planar *bis*([8]aneSe$_2$) chelation at Pt^{II} was established beyond doubt.

In parallel with our work on macrocyclic selenoether complexes of the platinum metals we reported the characterization of the acyclic *bis* (bidentate) M^{II} complexes (M = Pd, Pt).[4] We have now obtained X-ray structural data for one of these model systems, $[Pt\{MeSe(CH_2)_3SeMe\}_2](PF_6)_2 \cdot 2MeCN$, to enable comparison with the cyclic selenoether complexes. The structure shows (Fig. 2, Tables 3 and 4) the Pt^{II} atom occupying a crystallographic inversion centre and coordinated to a square planar array of four Se donor atoms, Pt—Se(1) = 2.414(2), Pt—Se(2) = 2.421(2) Å. These bond lengths are strictly in accord with those observed in the tetraselenoether macrocyclic species $[Pt([16]aneSe_4)]^{2+}$ [Pt—Se = 2.420(3), 2.417(3) Å].[4] The angles around the central Pt atom in $[Pt\{MeSe(CH_2)_3SeMe\}_2]^{2+}$ do not deviate significantly from 90 or 180° reflecting the good match of the six-membered chelate rings formed by the diselenoether and the *cis*-angles required for the square planar geometry. Notably, in the solid-state the coordinated diselenoether ligands both adopt the DL configuration, thus the overall stereochemistry is very similar to that determined previously for $[Pt([16]aneSe_4)]^{2+}$.[4]

Acknowledgements—We thank the EPSRC for support (J.J.Q.) and Johnson Matthey plc for loans of $PtCl_2$ and $PdCl_2$. We also thank the EPSRC for a grant to purchase the diffractometer.

REFERENCES

1. E. W. Abel, K. G. Orrell and S. K. Bhargava, *Prog. Inorg. Chem.* 1984, **32**, 1.
2. E. G. Hope and W. Levason, *Coord. Chem. Rev.* 1993, **122**, 109.
3. P. F. Kelly, W. Levason, G. Reid and D. J. Williams, *J. Chem. Soc., Chem. Commun.* 1993, 1716.
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. 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.
7. E. S. Gould and W. Burlant, *J. Am. Chem. Soc.* 1956, **78**, 5825.
8. P. J. Hendra and N. Sadasivan, *J. Chem. Soc.* 1965, 2063.
9. G. Hunter and R. C. Massey, *J. Chem. Soc., Dalton Trans.* 1974, 1873.
10. C. Drexler, H. Paulus and H. Elias, *Inorg. Chem.* 1991, **30**, 1297.
11. G. M. Sheldrick, SHELXS-86, program for crystal structure solution, *Acta Cryst.* 1990, **A46**, 467.
12. TeXsan: Crystal Structure Analysis Package. Molecular Structure Corporation (1992).
13. P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, PATTY: The DIRDIF Program System. University of Nijmegen, The Netherlands (1992).
14. N. Walker and D. Stuart, DIFABS: an empirical absorption correction program, *Acta Cryst.* 1983, **A39**, 158.
15. D. J. Gulliver, E. G. Hope, W. Levason, S. G. Murray and G. L. Marshall, *J. Chem. Soc., Dalton Trans.* 1985, 1265.
16. H. J. Whitfield, *J. Chem. Soc. A* 1970, 113.