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Selenoether Macrocyclic Complexes of Platinum(IV): Synthesis and Spectroscopic Studies of $[Pt([16]aneSe_4)X_2][PF_6]_2$ (X = Cl, Br). X-ray Structure of $[Pt([16]aneSe_4)Cl_2][PF_6]_2$

William Levason,* Jeffrey J. Quirk, and Gillian Reid

Department of Chemistry, University of Southampton, Southampton SO9 5NH, U.K.

Christopher S. Frampton

Roche Products Ltd., P.O. Box 8, Welwyn Garden City, Hertfordshire AL7 3AY, U.K.

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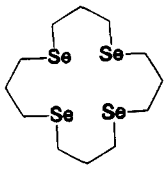
The platinum(IV) complexes $[Pt([16]aneSe_4)X_2][PF_6]_2$ ($[16]aneSe_4$ = 1,5,9,13-tetraselenacyclohexadecane; X = Cl; Br) were obtained by halogen oxidation of $[Pt([16]aneSe_4)][PF_6]_2$ in CCl_4/MeCN and were characterized by analysis and by UV/visible and multinuclear ($^{195}Pt\{^1H\}$, $^{77}Se\{^1H\}$) NMR spectroscopies. The X-ray structure of the chloro complex revealed a *trans* octahedral cation (Pt−Cl = 2.315(2) Å, Pt−Se = 2.4957(7), 2.5015(6) Å) with the ligand in the *up,up,down,down* configuration. Only one invertomer was detected in solution by NMR spectroscopy. Attempts to isolate a Pd(IV) analogue were unsuccessful.

Introduction

In marked contrast to the extensive studies of thioether macrocycle coordination chemistry,[1] very few studies of complexes of macrocyclic selenoethers have been reported.[2] We recently characterized Rh(III),[3] Pd(II) and Pt(II)[4] complexes of $[16]aneSe_4$ (1,5,9,13-tetraselenacyclohexadecane), and Pinto *et al.*[5] have described Cu(II), Cu(I) and Hg(II) complexes. A major aim of our research in this area is to use the superior coordination ability of macrocyclic selenoethers to prepare complexes of metal oxidation states or stereochemistries not found with acyclic analogues. Here we report the first examples of cationic platinum(IV) complexes incorporating selenium donor ligands, $[Pt([16]aneSe_4)X_2][PF_6]_2$ (X = Cl, Br). Although platinum(IV) complexes of selenoethers have been described,[2] they are of the types $[Pt(Me_2Se)X_5]^-$, $[Pt(Me_2Se)_2X_4]$, $[Pt(L\text{-}L)X_4]$, and $[PtMe_3X(L\text{-}L)]$ (L-L = for example $MeSeCH_2CH_2SeMe$ or $o\text{-}C_6H_4(SeMe)_2$)[2,6,7] showing that the platinum(IV) usually prefers to bind sufficient anions to neutralize the charge and cationic species such as $[Pt(L\text{-}L)_2X_2]^{2+}$ do not form.



$[16]aneSe_4$

Experimental Section

Infrared spectra were measured as KBr or CsI disks or as Nujol mulls using a Perkin-Elmer 983 spectrometer over the range 200−4000 cm^{-1}. Mass spectra were run by electron impact or fast-atom bombardment (FAB) using 3-NOBA (3-nitrobenzyl alcohol) as matrix on a VG Analytical 70-250-SE normal-geometry double-focusing mass spectrometer. Solution UV/visible spectra were recorded in 1 cm path length quartz cells using a Perkin-Elmer Lambda19 spectrophotometer. ^1H NMR spectra were recorded using a Bruker AM300 spectrometer. ^{77}Se NMR spectra were recorded using a Bruker AM360 spectrometer operating at 68.68 MHz and are referenced to neat Me_2Se ($\delta = 0$). ^{195}Pt NMR spectra were run using 10 mm diameter tubes containing 10−15% deuterated solvent or a 5 mm insert tube of D_2O as a lock, on a Bruker AM360 spectrometer operating at 77.42 MHz, and are referenced to a solution of Na_2PtCl_6 in H_2O ($\delta = 0$). Microanalyses were performed by the Imperial College microanalytical service.

Preparation of $[Pt([16]aneSe_4)Cl_2][PF_6]_2$. To a solution of $[Pt([16]aneSe_4)][PF_6]_2$ (0.050 g, 0.51 mmol) in 1 cm^3 of MeCN was added a saturated solution of Cl_2 in CCl_4 (5 drops) to give a yellow precipitate. After 10 min of stirring, the solid was collected by filtration, washed with Et_2O and dried *in vacuo* (yield 0.031 g, 57%). Anal. Calcd for $[Pt([16]aneSe_4)Cl_2][PF_6]_2$ ($C_{12}H_{24}Cl_2F_{12}P_2PtSe_4$): C, 13.8; H, 2.3. Found: C, 13.6; H, 2.2. FAB mass spectrum (3-NOBA matrix), *m/z*: found M^+ 894, 752, 715; calculated for $[^{195}Pt([16]aneSe_4)Cl_2PF_6]^+$ M^+ = 895, $[^{195}Pt([16]aneSe_4)Cl_2]^+$ M^+ = 751, $[^{195}Pt([16]aneSe_4)Cl]^+$ M^+ = 716. UV/visible spectrum (MeCN): ν = 32 300 cm^{-1} (ϵ = 20 740 $dm^3\ mol^{-1}\ cm^{-1}$), 40 720 cm^{-1} (ϵ = 14 000 $dm^3\ mol^{-1}$, cm^{-1}). ν(Pt−Cl) (Nujol mull) = 357 cm^{-1}. $^{195}Pt\{^1H\}$ NMR spectrum (77.4 MHz/CD_3CN relative to $[PtCl_6]^{2-}$ in D_2O): $\delta = -3079$, $w_{1/2}$ = 200 Hz. $^{77}Se\{^1H\}$ NMR spectrum (68.68 MHz, CD_3CN relative to Me_2Se): $\delta = +268$.

Preparation of $[Pt([16]aneSe_4)Br_2][PF_6]_2$. To a solution of $[Pt([16]aneSe_4)][PF_6]_2$ (0.050 g, 0.51 mmol) in MeCN (1 cm^3) was added dropwise a solution of Br_2 in CCl_4 until precipitation of the orange product was complete. After 10 min of stirring, the solid was collected by filtration, washed with Et_2O and dried *in vacuo* (yield 0.045g, 73%). Anal. Calcd for $[Pt([16]aneSe_4)Br_2][PF_6]_2$ ($C_{12}H_{24}Br_2F_{12}P_2PtSe_4$): C, 12.7; H, 2.1. Found: C, 12.3; H, 2.0. FAB mass spectrum (3-NOBA matrix), *m/z*: found M^+ 839, 758; calculated for $[^{195}Pt([16]aneSe_4)Br_2]^+$ M^+ = 839, $[^{195}Pt([16]aneSe_4)Br]^+$ M^+ = 760. UV/visible spectrum (MeCN): ν = 32 360 cm^{-1} (ϵ = 32 540 $dm^3\ mol^{-1}\ cm^{-1}$), 37 540 cm^{-1} (ϵ = 35 860 $dm^3\ mol^{-1}$, cm^{-1}). $^{195}Pt\{^1H\}$ NMR spectrum (CD_3CN): $\delta = -3785$. $^{77}Se\{^1H\}$ NMR spectrum (CD_3CN): $\delta = +232$.

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Table 1. Crystal Data for *trans*-$[PtCl_2([16]aneSe_4)][PF_6]_2$

formula	$[C_{12}H_{24}Cl_2Se_4Pt][PF_6]_2$
mol wt	1040.1
color, morphology	yellow plate
crystal size/mm^3	0.24 × 0.11 × 0.4
crystal system	triclinic
a/Å	10.523(4)
b/Å	11.013(4)
c/Å	6.104(3)
α/deg	90.38(4)
β/deg	96.33(4)
γ/deg	63.19(2)
V/Å^3	626.7(4)
space group	$P\bar{1}$
Z	1
D_{calc}/g·cm^{-3}	2.755
λ/Å	0.710 73 (Mo)
μ/cm^{-1}	118.38
F(000)	482
transm factors: max, min	0.9984, 0.3370
no. of unique data	2730
no. of obsd data with $F > 5\sigma(F)$	2563
scan type	$\omega-2\theta$
$2\theta_{max}$/deg	54.0
final $\Delta\varrho$/(e Å^{-3})	2.15
final Δ/σ	0.00
R	0.033
R_w	0.038
temp/K	120

Table 2

Bond Lengths (Å)			
Pt(1)−Se(1)	2.5015(6)	Se(1)−C(1)	1.972(7)
Pt(1)−Se(2)	2.4957(7)	Se(2)−C(4)	1.970(6)
Pt(1)−Cl(1)	2.315(2)	Se(1)−C(2)	1.971(6)
C(1)−C(6)	1.522(8)	Se(2)−C(5)	1.964(7)
C(3)−C(4)	1.513(9)	C(5)−C(6)	1.522(8)
C(2)−C(3)	1.531(9)		
Bond Angles (deg)			
Se(1)−Pt(1)−Cl(1)	87.36(4)	Se(1)−Pt(1)−Se(2)	88.42(2)
Se(2)−Pt(1)−Cl(1)	87.70(4)	Pt(1)−Se(1)−C(1)	106.0(2)
Pt(1)−Se(1)−C(2)	100.5(2)	C(1)−Se(1)−C(2)	93.8(3)
Pt(1)−Se(2)−C(4)	100.6(2)	Pt(1)−Se(2)−C(5)	104.3(2)
C(4)−Se(2)−C(5)	95.0(3)	Se(1)−C(2)−C(3)	111.2(5)
C(2)−C(3)−C(4)	115.6(5)	Se(2)−C(4)−C(3)	111.3(5)
Se(2)−C(5)−C(6)	113.8(5)	C(1)−C(6)−C(5)	115.2(5)
Se(1)−C(1)−C(6)	115.5(5)		
Torsion Angles (deg)			
Se(1)−C(1)−C(6)−C(5)	73.7(7)	Se(1)−C(2)−C(3)−C(4)	−43.3(7)
Se(2)−C(4)−C(3)−C(2)	−48.4(7)	Se(2)−C(5)−C(6)−C(1)	77.6(6)
C(1)−Se(1)−C(2)−C(3)	−169.9(4)	C(2)−Se(1)−C(1)−C(6)	−167.0(5)
C(3)−C(4)−Se(2)−C(5)	−170.7(4)	C(4)−Se(2)−C(5)−C(6)	−174.0(4)

X-ray Structure Analysis. Crystals of *trans*-$[PtCl_2([16]aneSe_4)][PF_6]_2$ were obtained by slow diffusion of Et_2O into a solution of the complex in MeCN. The crystal selected was coated in silicone oil and mounted on a glass fiber. The accurate unit cell parameters were obtained by a least-squares analysis of 25 centered reflections. Data were collected on a Rigaku AFC7R four-circle diffractometer using graphite monochromated Mo Kα radiation. A summary of the crystallographic data and data collection and refinement parameters is given in Table 1.

A Patterson synthesis located the Pt atom on a crystallographic inversion center at (0.5, 0.5, 0.5).[8] Successive full-matrix least-squares cycles and difference Fourier analysis[9] revealed all other non-H atoms for a half $[PtCl_2([16]aneSe_4)]^{2+}$ cation and one PF_6^- anion in the asymmetric unit. Anisotropic thermal parameters were refined for all non-H atoms. H atoms were placed in fixed, calculated positions. Selected bond lengths, angles and torsion angles are given in Table 2.

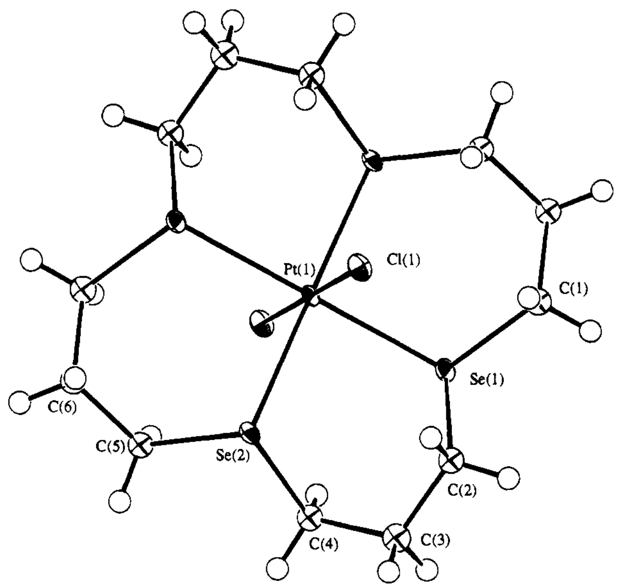

Figure 1. View of the X-ray structure of $[PtCl_2([16]aneSe_4)]^{2+}$ with numbering scheme adopted.

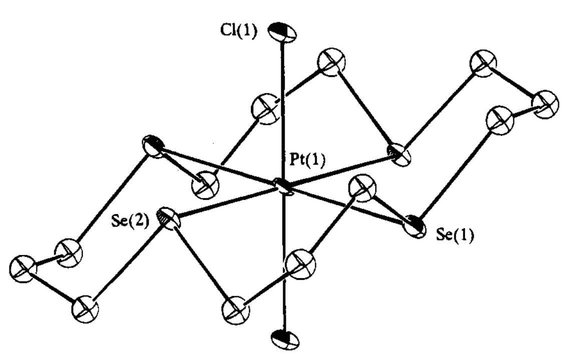

Figure 2. Edge view of the structure of $[PtCl_2([16]aneSe_4)]^{2+}$ showing the *up,up,down,down* configuration.

Results and Discussion

Addition of a solution of the appropriate halogen in CCl_4 to the colorless $[Pt([16]aneSe_4)][PF_6]_2$[4] in MeCN resulted in the precipitation of yellow $[Pt([16]aneSe_4)Cl_2][PF_6]_2$ and orange $[Pt([16]aneSe_4)Br_2][PF_6]_2$, identified by analysis and from the characteristic fragment ions in the FAB mass spectra (Experimental Section). The $^{77}Se\{^1H\}$ NMR spectra revealed a single resonance in each complex indicative of a *trans* geometry, and this was confirmed by an X-ray study of the dichloride.

The structure of $[PtCl_2([16]aneSe_4)][PF_6]_2$ shows (Figure 1) the Pt atom occupying a crystallographic inversion center, giving a *trans*-dichloro arrangement, with the four Se donor atoms coordinated equatorially, Pt−Se(1) = 2.5015(6), Pt−Se(2) = 2.4957(7), Pt−Cl = 2.315(2) Å. The ligand is in an *up,up,down,down* configuration (Figure 2). This is the only configuration which has been observed to date for endocyclic complexes of $[16]aneSe_4$ in the solid state. The lengthening of the Pt−Se bond lengths in the platinum(IV) cation *trans*-$[PtCl_2([16]aneSe_4)]^{2+}$ by approximately 0.08 Å compared to those in the Pt^{II} species $[Pt([16]aneSe_4)]^{2+}$ is consistent with the increased coordination number in the former. These values can also be compared with the $Pt^{IV}-Se_{trans-Cl}$ distances in $[Pt\{o\text{-}C_6H_4(SeMe)_2\}Cl_4]$[6] of 2.432(2) and 2.441(1) Å. The $Pt^{IV}-Cl$ distances in the macrocycle complex may be similarly compared with those in $[Pt([14]aneN_4)Cl_2]Cl_2{\cdot}HCl{\cdot}H_2O$[10] ($[14]aneN_4$ =

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(8) SAPI91: Hai-Fu, F. *Structure Analysis Programs with Intelligent Control*; Rigaku Corp.: Tokyo, 1991.

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(10) Waknine, D.; Heeg, M. J.; Endicott, J. F.; Ochrymowycz, L. A. *Inorg. Chem.* **1991**, *30*, 3691.

1,4,8,11-tetraazacyclotetradecane) (2.307(4) Å) and [Pt{*o*-C_6H_4-$(SeMe)_2$}Cl_4][6] (2.299(4), 2.328(3) Å).

In solution in CD_3CN only one invertomer is present in each complex, demonstrated by the single $^{195}Pt\{^1H\}$ resonances,[11] probably with the same *up,up,down,down* form of the ligand present in the solid dichloride complex. This contrasts with the behavior of the platinum(II) precursor, for which several invertomers have been identified in solution,[4] but is similar to the case of *trans*-[Rh([16]aneSe_4)Cl_2]PF_6.[3] The $^{195}Pt\{^1H\}$ chemical shifts of −3079 ppm (Cl) and −3785 ppm (Br) are substantially to high frequency of those for the Pt(II) analogue (−4568, −4676 ppm). Comparison can also be made with the Pt(IV) complexes $[PtCl_6]^{2-}$ (0 ppm), *trans*-$[Pt(Me_2Se)_2Cl_4]$ (−1787 ppm), $[Pt(MeSeCH_2CH_2CH_2SeMe)Cl_4]$ (−2070, −2078 ppm) and $[Pt(MeSeCH_2CH_2CH_2SeMe)Br_4]$ (−2902, −2908 ppm),[6] which show a progressive shift to low frequency upon replacement of halide ligands by selenium and between chloride and bromide analogues. The values observed in [Pt([16]aneSe_4)X_2][PF_6]$_2$ are thus further strong support for their formulation as Pt(IV) complexes with Se_4X_2 donor sets. The $^{77}Se\{^1H\}$ spectra, in addition to confirming the presence of a single invertomer, show a substantial positive shift (X = Cl, $\delta = +268$; X = Br, $\delta = +232$) from the values observed for [Pt([16]aneSe_4)][PF_6]$_2$ (δ = 187, 147),[4] the usual effect of oxidation at the metal center.[6] The UV/visible spectra of both complexes in MeCN show a major feature at *ca.* 32 500 cm^{-1} which is tentatively assigned as the charge transfer transition $\pi(Se) \rightarrow d_{z^2}(Pt)$, while the second transitions to higher energy which vary with the X group are probably $\pi(X) \rightarrow d_{z^2}(Pt)$.

The palladium(II) complex[4] [Pd([16]aneSe_4)][PF_6]$_2$ was not oxidized by treatment with Cl_2/CCl_4, but dissolved in a mixture of concentrated HCl and HNO_3 at 0 °C to give an orange solution, from which 70% $HClO_4$ precipitated an orange-brown solid. This material decomposed during drying in vacuum and therefore could not be characterized, but it is likely that this was the Pd(IV) complex of [16]aneSe_4. The only isolated palladium(IV) selenoether complexes are $[Pd(Me_2Se)X_5]^-$ (X = Cl, Br).[12]

The ability of the macrocycle [16]aneSe_4 to produce cationic platinum(IV) complexes with Se_4X_2 donor sets contrasts with the formation of only $PtSeX_5$ or $PtSe_2X_4$ species with acyclic ligands. Cationic platinum(IV) species $[Pt(L\text{-}L)_2X_2]^{2+}$ are obtainable only with a limited range of strong σ-donor neutral ligands, including[13] bis(primary amines), *o*-$C_6H_4(PMe_2)_2$, and $Me_2PCH_2CH_2PMe_2$, which suggests that [16]aneSe_4 has similar coordinating abilities, and thus may afford complexes unprecedented in acyclic selenoether chemistry. Further studies to test this hypothesis are underway.

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Supplementary Material Available: Tables of complete atomic coordinates, anisotropic thermal parameters, bond lengths, bond angles, and torsion angles (6 pages). Ordering information is given on any current masthead page.

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[11] Previous studies have revealed that pyramidal inversion in thioether and selenoether complexes is a higher energy process in Pt(IV) than in analogous Pt(II) complexes: Abel, E. W.; Bhargava, S. K.; Orrell, K. G. *Prog. Inorg. Chem.* **1984**, *32*, 1. Thus the possibility that the single resonance is due to fast inversion in [Pt([16]aneSe_4)X_2][PF_6]$_2$ can be safely excluded.

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