Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganica Chimica Acta 349 (2003) 104–110

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Synthesis and characterization of 3-dimethylaminopropyl selenolate complexes of palladium(II) and platinum(II)

Sandip Dey[a], Vimal K. Jain[a,*], Axel Knoedler[b], Wolfgang Kaim[b,*]

[a] Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[b] Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Received 20 September 2002; accepted 20 January 2003

Abstract

Bis(3-dimethylaminopropyl)diselenide was prepared by the reaction of Na_2Se_2 with $Me_2NCH_2CH_2CH_2Cl$. 3-Dimethylaminopropylselenolate complexes of palladium and platinum of the formulae $[M(SeCH_2CH_2CH_2NMe_2)Cl]_2$, $[M(SeCH_2CH_2CH_2NMe_2)_2]$ (M = Pd or Pt), $[Pd(OAc)(SeCH_2CH_2CH_2NMe_2)]$, $[PtCl(SeCH_2CH_2CH_2NMe_2)(PR_3)]_2$ ($PR_3 = PMePh_2$ or PPr_3), $[Pt(SeCH_2CH_2CH_2NMe_2)_2(P\text{–}P)]$ (P–P = dppm, dppe or $2PPh_3$) have been synthesized by using either the diselenide or its reduction product from the reaction with $NaBH_4$. All complexes have been characterized by elemental analysis, IR and NMR (^{1}H, ^{13}C, ^{31}P, ^{77}Se, ^{195}Pt) spectroscopy. The stereochemistry of these complexes has been deduced from the NMR spectroscopic data. The structure of $[Pd(SeCH_2CH_2CH_2NMe_2)Cl]_2$ was established by single crystal X-ray diffraction analysis. Each palladium atom in the dimer is surrounded by two μ-Se atoms, a nitrogen atom and a chloride ligand.

Keywords: Crystal structures; Palladium complexes; Platinum complexes; Selenolate ligand

1. Introduction

The chemistry of platinum group metal chalcogenolates has attracted considerable attention for more than two decades [1]. There are several obvious reasons for the sustained interest in this area as these complexes show a wide structural diversity [1] and find several applications in catalysis [2]. More recently, these complexes have been shown to serve as molecular precursors for the synthesis of metal chalcogenides [3–5] for electronic devices [6]. Most of these complexes are non-volatile, insoluble or poorly soluble oligomeric species, thus limiting their utility as precursors for the synthesis of metal chalcogenides. To suppress polymerization we have employed internally functionalized ligands such as $2\text{-}(RC_5H_3N)E^-$ or $Me_2NCH_2CH_2E^-$ (E = Se or Te) [5,7–10]. The latter ligands can be compared with their sulfur analogues ($Me_2NCH_2CH_2S^-$) [11–14]. The coordination behaviour of 2-dimethylaminoethanylchalcogenolate ions ($Me_2NCH_2CH_2E^-$; E = S, Se, Te) is in general very similar, however subtle differences in chemical and physical properties between S and Se/Te complexes have been noticed [5,7–10]. The chemistry of metal complexes derived from mercaptoamines has been investigated in considerable detail [11–25]. Their structure is greatly influenced by the nature of the metal ion, the number of carbon atoms separating the N and S centers and the substituents on the N-atom. For example, α-mercaptoamines (such as 2-mercaptonicotinic acid [15]) and β-mercaptoamines (such as $R_2NCH_2CH_2SH$ where R = H or Me [11–14,16,17]) yield metal chelates whereas γ-mercaptoamines (such as $Me_2CH_2CH_2CH_2SH$ and related derivatives) behave both as simple thiolate ligands (monodentate as well as bridging through sulfur [18–21]) and as chelating ligands, bridging or non-bridging [14,22–25]. These structural variations assisted by the carbon chain length of mercaptoamines have prompted us to examine the chemistry of the heavier homologs of γ-mercaptoamine, i.e., $R_2NCH_2CH_2CH_2E^-$ (E = Se and Te). Herein we report the synthesis of $(Me_2NCH_2CH_2CH_2Se)_2$ and of palladium(II) and

---

* Corresponding authors. Tel.: +91-22-2559-5095; fax: +91-22-551 9613.
E-mail address: jainvk@apsara.barc.ernet.in (V. Jain).

doi:10.1016/S0020-1693(03)00080-X

platinum(II) complexes containing $Me_2NCH_2CH_2CH_2Se^-$. Spectroscopic data and the X-ray structure of $[Pd(SeCH_2CH_2CH_2NMe_2)Cl]_2$ are also reported.

2. Experimental

All reactions were carried out in dry and distilled analytical grade solvents under N_2 using conventional Schlenk technique to prevent oxidation of the selenolate ion. Tertiary phosphines (Strem Chemicals, USA) and $Me_2NCH_2CH_2CH_2Cl \cdot HCl$ were obtained from commercial sources. The Pd and Pt complexes Na_2PdCl_4, K_2PtCl_4, $MCl_2(P–P)$ (P–P = $2PPh_3$, dppm, dppe) and $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ ($PR_3 = PPr_3, PMePh_2, PPh_3$) were prepared according to literature methods [26]. Melting points were determined in capillary tubes and are uncorrected. Microanalysis was performed by the Analytical Chemistry Division of BARC. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{77}Se\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer operating at 300, 75.46, 121.49, 57.24 and 64.52 MHz, respectively. Chemical shifts are relative to internal $CHCl_3$ peak (δ 7.26 ^1H and 77.0 for ^{13}C) and external 85% H_3PO_4 for ^{31}P, Me_2Se for ^{77}Se and Na_2PtCl_6 for ^{195}Pt. UV–Vis absorption spectra were recorded on a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out at 100 mV s^{-1} scan rate in CH_2Cl_2 0.1 M Bu_4NPF_6 using a three electrode configuration (glassy carbon working electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as internal reference.

2.1. Synthesis

2.1.1. $(Me_2NCH_2CH_2CH_2Se)_2$

Bis(3-dimethylaminopropyl)diselenide was prepared in an analogous manner to $(Me_2NCH_2CH_2Se)_2$ [5], using $Me_2NCH_2CH_2CH_2Cl$ and Na_2Se_2. The orange–red liquid was fractionally distilled under vacuum. The fraction distilling at 134–140 °C/2 mmHg was collected and was found spectroscopically pure (NMR, Table 1).

2.1.2. $[PdCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1a**)

A methanolic solution (10 cm^3) of Na_2PdCl_4 (1.242 g, 4.22 mmol) was added to a stirred methanolic solution of $(Me_2NCH_2CH_2CH_2Se)_2$ (704 mg, 2.13 mmol). A yellow precipitate formed immediately. The reactants were stirred for 3 h. The yellow precipitate was filtered, washed with MeOH (2×10 cm^{-3}), acetone and Et_2O and finally dried in vacuo (yield 850 mg, 65%). The product was recrystallized from CH_2Cl_2–acetone as orange–red crystals in 38% yield (320 mg). M.p. 205 °C dec. *Anal*. Found: C, 19.3; H, 3.6; N, 5.0. Calc. for $C_{10}H_{24}Cl_2N_2Pd_2Se_2$: C, 19.6; H, 3.9; N, 4.6%.

2.1.3. $[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1b**)

An aqueous solution (10 cm^3) of K_2PtCl_4 (361 mg, 0.87 mmol) was added to a stirred methanolic solution (15 cm^3) of $(Me_2NCH_2CH_2CH_2Se)_2$ (144 mg, 0.44 mmol). Stirring continued for 4 h at room temperature (r.t.) whereupon a pale yellow precipitate formed. The precipitate was filtered, washed thoroughly with water, MeOH, acetone and hexane and dried in vacuo. This was recrystallized from DMF–ether as orange–red crystals in 35% yield (120 mg). M.p. (dec.) 188 °C. *Anal*. Found: C, 12.7; H, 3.6; N, 5.0. Calc. for $C_{10}H_{24}Cl_2N_2Pt_2Se_2$: C, 15.2; H, 3.1; N, 3.5%.

2.1.4. $[Pd(SeCH_2CH_2CH_2NMe_2)_2]$ (**2a**)

To a freshly prepared methanolic solution (8 cm^3) of $NaSeCH_2CH_2CH_2NMe_2$ [prepared from $(Me_2NCH_2CH_2CH_2Se)_2$ (385 mg, 1.17 mmol) and $NaBH_4$ (90 mg, 2.37 mmol)], a solution (25 cm^3) of Na_2PdCl_4 (341 mg, 1.16 mmol) in the same solvent was added with vigorous stirring. The dark brown solution was stirred for 3 h at r.t. The solvent was stripped off in vacuo. The residue was extracted with hexane (3×20 cm^3) and passed through a Florisil column. The volume of the solution was reduced to 8 cm^3. To this a few drops of pentane were added and cooling to −5 °C for several hours gave brownish red needle-shaped crystals which lost crystallinity on drying (yield: 202 mg, 40%). M.p. 102 °C. *Anal*. Found: C, 26.4; H, 5.3; N, 5.3. Calc. for $C_{10}H_{24}N_2PdSe_2$: C, 27.5; H, 5.5; N, 6.4%.

2.1.5. $[Pt(SeCH_2CH_2CH_2NMe_2)_2]_n$ (**2b**)

To a freshly prepared methanolic solution (10 cm^3) of $NaSeCH_2CH_2CH_2NMe_2$ [prepared from $(Me_2NCH_2CH_2CH_2Se)_2$ (241 mg, 0.73 mmol) and $NaBH_4$ (57 mg, 1.50 mmol)] an aq. solution (10 cm^3) of K_2PtCl_4 (300 mg, 0.72 mmol) was added and the mixture was stirred for 4 h. The solvents were stripped off in vacuum and the residue was thoroughly washed with water, MeOH, acetone, ether and finally dried in vacuo (yield: 152 mg, 40%). The dark red product was insoluble in all common organic solvents. M.p. (dec.) 205 °C. *Anal*. Found: C, 20.5; H, 4.4; N, 4.7. Calc. for $C_{10}H_{24}N_2PtSe_2$: C, 22.9; H, 4.6; N, 5.3%.

2.1.6. $[Pd(OAc)(SeCH_2CH_2CH_2NMe_2)]$ (**3**)

To a benzene solution (15 cm^3) of **2a** (73 mg, 0.17 mmol), solid $Pd(OAc)_2$ (39 mg, 0.17 mmol) was added with stirring. To the turbid solution acetone (15 cm^3) was added and the mixture was stirred at r.t. for 2 h. The solvents were evaporated in vacuo and the residue was washed with hexane and extracted with acetone. The solution was passed through a Florisil column, concentrated to 2 cm^3 and cooled at −5 °C for 24 h to yield a yellow solid (44 mg, 40%). M.p. (dec.) 158 °C. *Anal*. Found: C, 24.7; H, 4.9; N, 4.1. Calc. for $C_7H_{15}NO_2PdSe$: C, 25.4; H, 4.6; N, 4.2%.

Table 1

^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{77}Se{^{1}H} and ^{195}Pt{^{1}H} NMR data for 3-(dimethylamino)propaneselenolate complexes of palladium(II) and platinum(II)

Complex	^{1}H δ in ppm	^{13}C{^{1}H} δ in ppm	^{31}P{^{1}H}	^{77}Se{^{1}H} [a]	^{195}Pt{^{1}H} [b]
$(Me_2NCH_2CH_2CH_2Se)_2$	1.90 (m, Se–C–CH_2); 2.20 (s, NMe_2); 2.35 (t, 7.1 Hz, $SeCH_2$); 2.95 (t, 7.1 Hz, NCH_2)	28.2 ($SeCH_2$); 29.2 (s, $SeCH_2CH_2$); 45.4 (s, NMe_2); 59.3 (s, NCH_2)		316	
$[PdCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1a**)	1.93–2.48 (m, NCH_2CH_2); 2.66, 2.74 (each s, NMe_2); 3.46–3.52 (m, $SeCH_2$)	22.6 (s, $^1J(^{77}Se–^{13}C) = 64$ Hz, $SeCH_2$); 27.9 (s, $SeCH_2$–CH_2, ^2J(Se–C) = 35 Hz); 50.0, 52.4 (each s, NMe_2); 65.1 (s, NCH_2)		18	
$[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1b**)					
$[Pd(SeCH_2CH_2CH_2NMe_2)_2]$ (**2a**)	1.93–2.05 (m, SeC–CH_2); 2.21, 2.23 (each s, NMe_2); 2.32–2.56 (m, NCH_2, $SeCH_2$)	20.7, 24.7 (each s, $SeCH_2$); 30.8, 32.6 (each s, SeC–CH_2); 45.5 (s, NMe_2); 59.3, 59.5 (s, NCH_2)		−31 −161	
$[Pd(OAc)(SeCH_2CH_2CH_2Nme_2)]$ (**3**)	1.95, 2.08 (each s); 2.45, 2.67 (each s, NMe_2); 2.90–2.94 (m, $SeCH_2$); 2.61–2.75 (br, m, NCH_2); 2.25 ($NCCH_2$)	19.4, 23.7 (each s, $SeCH_2$); 27.7 (s, SeC–CH_2); 50.0, 51.5 (NMe_2, OAc); 64.4 (NCH_2); 176.7 (C=O)		−32	
trans-$[PtCl(SeCH_2CH_2CH_2NMe_2)(PPr_3)]_2$ [c] (**4a**)	1.05 (t, 7 Hz, PCH_2CH_2*Me*); 1.56–1.85 (m, PCH_2CH_2, NCH_2); 2.24 (s, NMe_2); 2.45 (br, NCH_2); 2.62 (br, m, $SeCH_2$)		−0.1 ^1J(Pt–P) = 3122 Hz		−3960 (d) ^1J(Pt–P) = 3097 Hz
cis-$[PtCl(SeCH_2CH_2CH_2NMe_2)(PMePh_2)]_2$ (**4b**)	1.81 (t, $NCCH_2$); 1.98, 2.25 (each s, NMe_2); 2.03–2.24 (m, PMe, NCH_2CH_2); 2.44, 3.32 (each m, $SeCH_2$); 7.27–7.44 (m), 7.63–7.70 (m) [Ph]		−1.1 ^1J(Pt–P) = 3273 Hz		−4093 (d) [d] ^1J(Pt–P) = 3294 Hz
$[Pt(SeCH_2CH_2CH_2NMe_2)_2(dppm)]$ (**5a**)	2.08 (s, NMe_2, 2.42–2.52 (m, $SeCH_2$); 2.02–2.10 (m, NCH_2); 1.56–1.67 (m, $NCCH_2$–); 4.34 (t, ^2J(P–H) = 10.4, ^3J(Pt–H) = 44 Hz, PCH_2); 7.39–7.49 (m); 7.82–7.90 (m) [Ph]		−52.5 ^1J(Pt–P) = 2401 ; ^2J(Se–P) = 27 Hz		−4235 (t) ^1J(Pt–P) = 2410 Hz
$[Pt(SeCH_2CH_2CH_2NMe_2)_2(dppe)]$ (**5b**)	1.54 (m, NC–CH_2); 1.99–2.40 (m, NCH_2, $SeCH_2$, PCH_2); 2.02 (s, NMe_2); 7.36–7.40 (m); 7.80–7.87 (m) [Ph]		46.6 ^1J(Pt–P) = 2851; ^2J(Se–P) = 32 Hz	55 ^2J(Se–P) = 62 Hz	−4946 (t) ^1J(Pt–P) = 2865 Hz
$[Pt(SeCH_2CH_2CH_2NMe_2)_2(PPh_3)_2]$ (**6**)	1.65 (s, NMe_2); 1.60–1.72 (m, $NCCH_2$); 2.04–2.32 (m, $SeCH_2$, NCH_2); 7.34 (br, PPh_3)		18.4 ^1J(Pt–P) = 2932 Hz	18 ^2J(Se–P) = 17 Hz	−4907 (t) ^1J(Pt–P) = 2938 Hz

[a] ^{77}Se: nuclear spin $I = 1/2$, natural abundance 7.6%.

[b] ^{195}Pt: nuclear spin $I = 1/2$, natural abundance 33.8%. The half line widths of ^{195}Pt signals are 50–100 Hz, hence the variation in the ^1J(Pt–P) coupling constants measured from ^{31}P and ^{195}Pt spectra.

[c] When the solution is left for a day isomerization takes place to give a mixture of *cis* and *trans* isomers. δ ^{31}P = −0.1 [^1J(Pt–P) = 3120 Hz]; −1.0 [^1J(Pt–P) = 3155 Hz]. ^{195}Pt NMR δ: −3963(d) [^1J(Pt–P) = 3116, ^2J(Pt–Pt) = 1060 Hz]; −4065(d) [^1J(Pt–P) = 3155; ^2J(Pt–Pt) = 972 Hz].

[d] ^2J(Pt–Pt) = 953 Hz.

2.1.7. [PtCl(SeCH$_2$CH$_2$CH$_2$NMe$_2$)(PMePh$_2$)] (4b)

To a freshly prepared methanolic solution (10 cm^3) of NaSeCH$_2$CH$_2$CH$_2$NMe$_2$ [prepared from (Me$_2$NCH$_2$CH$_2$CH$_2$Se)$_2$ (72 mg, 0.22 mmol) and NaBH$_4$ (17 mg, 0.45 mmol)] was added an acetone (20 cm^3) suspension of [Pt$_2$Cl$_2$(μ-Cl)$_2$(PMePh$_2$)$_2$] (196 mg, 0.21 mmol) with stirring under a nitrogen atmosphere. The pale yellow reaction mixture was stirred for 4 h. The solvents were stripped off in vacuum and the residue was washed with hexane and was extracted with CH$_2$Cl$_2$ (6 × 3 cm^3). The solution was passed through a Florisil column and the volume of the solution reduced to 5 cm^3. After adding a few drops of hexane, the solution was kept in the freezer (−5 °C) to yield pale yellow fibrous crystals in 48% yield (120 mg). M.p. 126 °C. *Anal*. Found: C, 35.8; H, 4.2; N, 2.8. Calc. for C$_{18}$H$_{25}$ClNPPtSe: C, 36.3; H, 4.2; N, 2.4%.

2.1.8. [PtCl(SeCH$_2$CH$_2$CH$_2$NMe$_2$)(PPr$_3$)] (4a)

Prepared in a manner similar to **4b** and recrystallized from hexane in 45% yield, m.p. 118 °C. *Anal*. Found: C, 30.7; H, 5.9; N, 2.4. Calc. for C$_{14}$H$_{33}$ClNPPtSe: C, 30.2; H, 6.0; N, 2.5%.

2.1.9. [Pt(SeCH$_2$CH$_2$CH$_2$NMe$_2$)$_2$(dppm)] (5a)

Prepared from PtCl$_2$dppm and 2NaSeCH$_2$CH$_2$CH$_2$NMe$_2$ and recrystallized from toluene–hexane in 45% yield, m.p. 184 °C. *Anal*. Found: C, 42.4; H, 3.9; N, 2.4. Calc. for C$_{35}$H$_{46}$N$_2$P$_2$PtSe$_2$: C, 46.2; H, 5.1; N, 3.1%.

2.1.10. [Pt(SeCH$_2$CH$_2$CH$_2$NMe$_2$)$_2$(dppe)] (5b)

Prepared from PtCl$_2$dppe and 2NaSeCH$_2$CH$_2$CH$_2$NMe$_2$ and recrystallized from acetone–hexane in 60% yield. *Anal*. Found: C, 46.1; H, 5.0; N, 2.8. Calc. for C$_{36}$H$_{48}$N$_2$P$_2$PtSe$_2$: C, 46.8; H, 5.2; N, 3.0%.

2.1.11. [Pt(SeCH$_2$CH$_2$CH$_2$NMe$_2$)$_2$(PPh$_3$)$_2$] (6)

Prepared from PtCl$_2$(PPh$_3$)$_2$ and 2NaSeCH$_2$CH$_2$CH$_2$NMe$_2$ and recrystallized from toluene–pentane in 55% yield. *Anal*. Found: C, 52.3; H, 5.3; N, 2.5. Calc. for C$_{46}$H$_{54}$N$_2$P$_2$PtSe$_2$: C, 52.6; H, 5.2; N, 2.7%.

2.2. Crystallography

X-ray data of an orange–yellow crystal of [PdCl(SeCH$_2$CH$_2$CH$_2$NMe$_2$)]$_2$ (**1a**) were collected on a Siemens P3 diffractometer using graphite monochromated Mo Kα radiation and employing the $\omega-2\theta$ scan technique. The unit cell parameters (Table 2) were determined from 25 reflections measured by a random search routine. The intensity data were corrected for Lp and absorption effects (ψ scans). The structure was solved by direct methods (program SHELXTL-5.1 [27]). The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were introduced using the appropriate riding model.

Table 2
Crystallographic and structure refinement data for [PdCl(SeCH$_2$CH$_2$CH$_2$NMe$_2$)]$_2$ (**1a**)

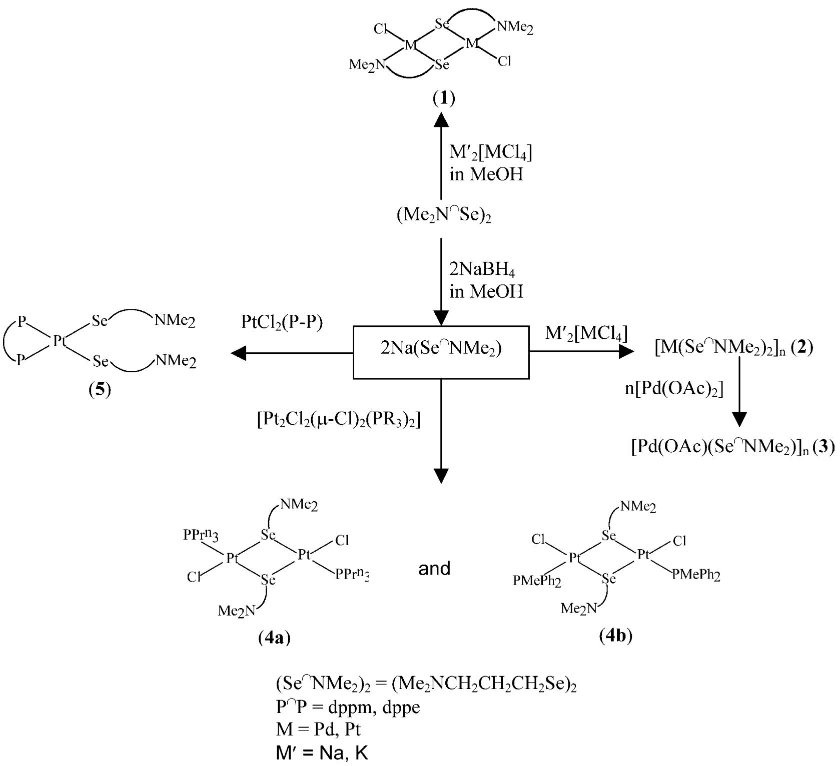
Chemical formula	C$_{10}$H$_{24}$Cl$_2$N$_2$Pd$_2$Se$_2$
Formula weight	613.93
Temperature (K)	173(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	10.395(2)
b (Å)	8.6978(17)
c (Å)	19.160(4)
β (°)	98.18(3)
Volume (Å^3)	1714.7(6)
Z	4
D_{calc} (g cm^{-1})	2.378
Crystal size (mm)	0.3 × 0.25 × 0.2
Absorption correction	Ψ scan
Reflections collected/unique	4359/4139
Data/restraints/parameters	4139/0/164
Final R_1, ωR_2 indices	0.0356, 0.0797
R_1, ωR_2 (all data)	0.0491, 0.0860
Largest difference peak and hole (e Å^3)	1.310 and −1.297

3. Results and discussion

Synthetic routes to 3-dimethylaminopropylselenolate complexes of palladium(II) and platinum(II) are given in Scheme 1. In a few cases the analytical data were unsatisfactory. Poor solubility of **1b** and **2b** in non-coordinating solvents and dissociation in coordinating solvents rendered their purification difficult while slow air oxidation of the phosphine/selenolate in **5a** gave variable analyses.

The reaction of Na$_2$PdCl$_4$ with (Me$_2$NCH$_2$CH$_2$CH$_2$Se)$_2$ in methanol yields an orange–yellow precipitate which, after recrystallization from CH$_2$Cl$_2$–acetone, gave microcrystals of the empirical composition [PdCl(SeCH$_2$CH$_2$CH$_2$NMe$_2$)]$_n$ (**1a**). The IR spectrum of **1a** exhibited a band at 291 cm^{-1}, attributable to νPd–Cl. The structure of the complex has been unambiguously established by X-ray diffraction, **1a** is dimeric. The structure is similar to that of γ-mercaptoamine complexes of palladium(II) and platinum(II), e.g. [PdCl(SCH$_2$CH$_2$CH$_2$NMe$_2$)]$_2$ [24], [PdCl{SCH$_2$CH$_2$(2-N(Me)C$_5$H$_7$)}]$_2$ [23] or [PtBr(SC$_4$H$_8$NMe-4)]$_2$ [25].

Treatment of Na$_2$PdCl$_4$ with 2 equiv. of NaSeCH$_2$CH$_2$CH$_2$NMe$_2$ yields a hexane-soluble brown product of the composition [Pd(SeCH$_2$CH$_2$CH$_2$NMe$_2$)$_2$] (**2a**). However, a similar reaction with K$_2$PtCl$_4$ gave an insoluble red product **2b**. These complexes may appear to be bis-chelates. However, the corresponding [Pd(SeCH(Me)CH$_2$NMe$_2$)$_2$]$_6$ was shown to be hexameric by



Scheme 1.

X-ray crystallography [28]. A similar hexameric structure has been reported for the nickel thiolato complex $[Ni(SCH_2CH_2CH_2NMe_2)_2]_6$ [19]. In both cases oligomerization takes place via the chalcogen bridges while the NMe_2 groups remain free. It is possible that **2a** may have a similar hexameric structure in the solid. The FAB mass spectrum of **2a** displayed a multiplet at m/z 2619 with an isotopic pattern attributable to the hexamer. The $^{13}C\{^1H\}$ NMR spectrum of the complex, however, exhibited two singlets each for three methylene carbons. This suggests that lower oligomeric species (such as dimeric) may be present in $CDCl_3$ solution. When **2a** is treated with $Pd(OAc)_2$, a redistribution product $[Pd(OAc)(SeCH_2CH_2CH_2NMe_2)]$ is formed ($\nu C{=}O$ 1613 cm^{-1}).

The reaction of $[PtCl_2(P{-}P)]$ ($P{-}P$ = dppm or dppe) with 2 equiv. of $NaSeCH_2CH_2CH_2NMe_2$ gave mononuclear $[Pt(SeCH_2CH_2CH_2NMe_2)_2(P{-}P)]$ as yellow crystalline solids. The $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ (nuclear spin $I = 1/2$ with a natural abundance of 33.8%) data are similar to those reported for several organochalcogenolates of platinum(II) [7,29]. These complexes have been assigned a *cis* configuration.

The reaction of $[PtCl_2(PPh_3)_2]$ with 2 equiv. of $NaSeCH_2CH_2CH_2NMe_2$ afforded $[Pt(SeCH_2CH_2CH_2NMe_2)_2(PPh_3)_2]$. A freshly prepared $CDCl_3$ solution of the complex exhibited singlet and triplet signals in the $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra, respectively. The ^{31}P and ^{195}Pt chemical shifts and the magnitude of $^1J(Pt{-}P)$ are similar to $[Pt(SePh)_2(PPh_3)_2]$ [29,30] suggesting the formation of *trans*-$[M(SeCH_2CH_2CH_2NMe_2)_2(PPh_3)_2]$.

Treatment of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ ($PR_3 = PPr^n_3$, $PMePh_2$) with 2 equiv. of $NaSeCH_2CH_2CH_2NMe_2$ resulted in the formation of $[PtCl(SeCH_2CH_2CH_2NMe_2)(PR_3)]$. These complexes show a single resonance in the ^{31}P NMR spectra with ^{195}Pt satellites and a doublet in the ^{195}Pt NMR spectra due to coupling with one phosphorus nucleus. Although the NMR data of these complexes are very similar to recently reported mononuclear complexes, $[MCl(ECH_2CH_2NMe_2)(PR_3)]$ (M = Pd or Pt; E = S, Se, Te) [5,7,8,31], the magnitude of $^1J(Pt{-}P)$ for the former series is significantly reduced and shows a phosphine dependence. The magnitude of $^1J(Pt{-}P)$ ($\sim$3400 Hz) for $[PtCl(ECH_2CH_2NMe_2)(PR_3)]$ shows little dependence either on the phosphine ligand or on the nature of the chalcogen atom (S, Se, Te). The magnitude of $^1J(Pt{-}P)$ for the present series of complexes can be compared with that of $[Pt_2Cl_2(\mu\text{-}SeR')_2(PR_3)_2]$ (R' = Et, Bz, Ph) [32], therefore, these complexes may be assigned a dimeric structure with selenolate bridges. This is further substantiated by the presence of $^2J(Pt{-}Pt)$ coupling in the ^{195}Pt NMR spectra. Complex **4a** is formed as a *sym–trans* isomer which slowly isomerizes to a mixture of *sym–cis/trans* isomers as revealed by NMR spectroscopy. Compound **4b** is isolated as *sym–cis* isomer.

In contrast to the reactions of $NaSeCH_2CH_2CH_2NMe_2$ with chloro-bridged platinum complexes, the similar reaction with $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMePh_2)_2]$ after

Table 3
UV–Vis absorption [a] and electrochemical data of complexes in CH_2Cl_2 and 0.1 M Bu_4NPF_6/CH_2Cl_2 [b], respectively

Complex	λ_{max} (ε)	E_{pa} [b]
$[PdCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1a**)	298 (10 000), 335 (sh), 370 (sh)	1.17
$[Pd(SeCH_2CH_2CH_2NMe_2)_2]$ (**2a**)	298 (13 800), 338 (9900), 440 (5000)	
$[PtCl(\mu\text{-}SeCH_2CH_2CH_2NMe_2)(PPr^n_3)]_2$ (**4a**)	251 (6700), 271 (7000), 290 (6400)	0.59
$[PtCl(\mu\text{-}SeCH_2CH_2CH_2NMe_2)(PMePh_2)]_2$ (**4b**)	249 (12 500), 270 (11 500), 286 (9300), 315 (4470)	0.58
$[Pt(SeCH_2CH_2CH_2NMe_2)_2(dppm)]$ (**5a**)	266 (29 000), 369 (1700)	0.47

[a] Wavelengths λ_{max} at the absorption maxima in nm, molar extinction coefficients in M^{-1} cm^{-1}.

[b] From cyclic voltammetry at 100 mV s^{-1} scan rate, E_{pa} anodic peak potentials in V vs. $FeCp_2/FeCp_2^+$.

recrystallization afforded **1a**. The reaction mixture showed several peaks in the ^{31}P NMR spectrum.

3.1. Absorption spectra and electrochemistry

Absorption spectra and cyclovoltammetric peak potentials of a few complexes have been recorded in dichloromethane and are summarized in Table 3. The long-wavelength transitions of the complexes have their origin in the electron-rich selenolate groups, the unoccupied target orbital is typically associated with the metal [8]. Very weak features of the triorganophosphine-containing compounds have been attributed to selenolate-to-phosphine charge transfer transitions [7,8]. Aggregation, and thereby increased orbital interaction, shifts these transitions to lower energies as is evident from a comparison between dimeric **1a** and presumably hexameric **2a**. Typically, the palladium compounds display absorptions at lower energies than the platinum analogues [7,8]. The peak potentials for irreversible oxidation reflect the donor capacity of triorganophosphine co-ligands.

3.2. Crystal structure analysis of $[PdCl(SeCH_2CH_2CH_2NMe_2)]_2$ (1a)

The molecular structure of **1a** is shown in Fig. 1, selected bond lengths and angles are summarized in Table 4. The structure contains two distorted square planar palladium atoms which are held together by two symmetrically bridging Se atoms of the chelating selenolate ligands. The two chloride ligands are mutually *trans*. Each palladium atom is surrounded by Cl, N and two Se atoms. The various bond lengths and angles in the '$PdClNSe_2$' fragments are comparable. The Pd···Pd distance at 3.413(1) Å is significantly longer than expected for any direct Pd···Pd bonding interac-

Table 4
Selected bond lengths (Å) and angles (°) for $[PdCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1a**)

Bond lengths			
Pd(1)–Se(1)	2.3858(7)	Pd(2)–Cl(2)	2.3445(14)
Pd(1)–Se(2)	2.4037(7)	Pd(1)–N(1)	2.148(4)
Pd(2)–Se(1)	2.3954(9)	Pd(2)–N(2)	2.141(4)
Pd(2)–Se(2)	2.3965(7)	Se(1)–C(1)	1.973(5)
Pd(1)–Cl(1)	2.3677(15)	Se(2)–C(6)	1.981(6)
Bond angles			
Se(1)–Pd(1)–Se(2)	79.67(2)	Se(1)–Pd(2)–Se(2)	79.62(3)
Se(1)–Pd(1)–Cl(1)	171.22(4)	Se(2)–Pd(2)–Cl(2)	170.84(4)
Se(1)–Pd(1)–N(1)	94.78(12)	Se(2)–Pd(2)–N(2)	95.56(12)
Se(2)–Pd(1)–N(1)	172.49(12)	Se(1)–Pd(2)–N(2)	174.31(11)
Se(2)–Pd(1)–Cl(1)	91.98(4)	Se(1)–Pd(2)–Cl(2)	91.35(4)
N(1)–Pd(1)–Cl(1)	93.29(13)	N(2)–Pd(2)–Cl(2)	93.37(12)
Pd(1)–Se(1)–Pd(2)	91.11(3)	Pd(1)–Se(2)–Pd(2)	90.64(3)

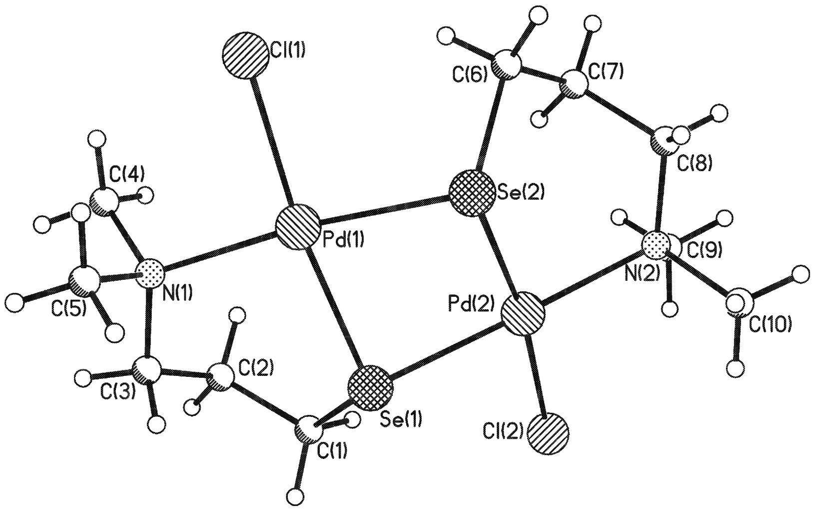


Fig. 1. View of $[PdCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1a**) with crystallographic numbering scheme.

tion. The Pd···Pd separation is considerably greater than that of thiolato-bridged analogues (3.144(2)–3.374 (1) Å [23–25]) due to the larger size of bridging selenium. An even smaller Pd···Pd separation of 2.9726 (7) Å was found in the related (and isostructural) phosphinothiolato complex [PdCl(SCH$_2$CH$_2$CH$_2$PPh$_2$)]$_2$ [33]. Like in the latter compound, the six-membered chelate rings ('PdSeCCCN' in **1a**) are puckered in a boat-type conformation while the four-membered 'Pd$_2$Se$_2$' ring is non-planar with a hinge angle of 136.2°, showing an *anti* configuration. The Pd–Se distances *trans* to N and *trans* to Cl are essentially similar and are well within the range expected for chelated selenolate ligands in palladium [5,8] and analogous platinum complexes [7]. Also, the Pd–Cl and Pd–N distances are well within the ranges reported for similar derivatives [5,7,8]. The former is longer by about 0.14 Å while the latter is shorter by 0.07 Å relative to the values reported for the sulfur analogue [PdCl(SCH$_2$CH$_2$CH$_2$NMe$_2$)]$_2$ [24]. The Se–Pd–Se angle is small and, in consequence, the other right angles have opened up to 95.56(12)°.

In summary, the chemistry of the 3-dimethylaminopropylselenolate ligand differs considerably from that of its lower homologue Me$_2$NCH$_2$CH$_2$Se$^-$. The γ-aminoselenolate ligand can bind palladium and platinum as a simple selenolate or as metal–metal bridging selenolate, in N,Se-chelating or chelating-bridging modes.

4. Supplementary material

The material is available from the authors on request.

Acknowledgements

We thank Drs. J.P. Mittal and P. Raj for encouragement of this work and Dr. Axel Klein for helpful discussions. We are also grateful to Dr. M. Sudershanan, Head, Analytical Chemistry Division, BARC for providing microanalyses of complexes. Support for this work under the Indo-German Bilateral Program from the BMBF (Project No. IND 99/060) is gratefully acknowledged.

References

[1] (a) I.G. Dance, Polyhedron 5 (1986) 1037;
(b) P.J. Blower, J.R. Dilworth, Coord. Chem. Rev. 76 (1987) 121;
(c) J. Arnold, Prog. Inorg. Chem. 43 (1995) 353.
[2] (a) L.Y. Chiang, J.W. Swirczewski, R. Kastrup, C.S. Hsu, R.B. Upasani, J. Am. Chem. Soc. 113 (1991) 6574;
(b) K. Osakada, Y. Ozawa, K. Yamamoto, J. Chem. Soc., Dalton Trans. (1991) 759;
(c) W.D. Jones, M.R. Chim, J. Am. Chem. Soc. 116 (1994) 198;
(d) J.R. Dilworth, N. Wheatley, Coord. Chem. Rev. 119 (2000) 89;
(e) J. Real, M. Pages, A. Polo, J.F. Pinella, A. Alvarez-Larena, Chem. Commun. (1999) 277;
(f) V.K. Jain, G.S. Rao, Inorg. Chiem. Acta 127 (1987) 161.
[3] S. Narayan, V.K. Jain, K. Panneerselvam, T.H. Lu, S.F. Tung, Polyhedron 18 (1999) 1253.
[4] A. Singhal, V.K. Jain, R. Misra, B. Varghese, J. Mater. Chem. (2000) 1121.
[5] S. Dey, V.K. Jain, S. Chaudhury, A. Knoedler, F. Lissner, W. Kaim, J. Chem. Soc., Dalton Trans. (2001) 723.
[6] (a) Y. Tonomura, J. Handa, Mitsubishi Paper Mills Ltd., Jpn Pat (1991) 03126035 (Chem. Abst. 115 (1991) 218921);
(b) T. Oota, K. Yoshioka, T. Akyama, S. Mori, Jap. Pat. (1995) 7205548 (Chem. Abst. 123 (1995) 325855).
[7] S. Dey, V.K. Jain, A. Knoedler, W. Kaim, S. Zalis, Eur. J. Inorg. Chem. (2001) 2965.
[8] S. Dey, V.K. Jain, A. Knodler, A. Klein, W. Kaim, S. Zalis, Inorg. Chem. 41 (2002) 2864.
[9] S. Narayan, V.K. Jain, B. Varghese, J. Chem. Soc., Dalton Trans. (1998) 2359.
[10] S. Dey, V.K. Jain, J. Singh, V. Trehan, K.K. Bhasin, B. Varghese, unpublished results.
[11] C.W. Schläpfer, K. Nakamoto, Inorg. Chiem. Acta 6 (1972) 177.
[12] D. Gibson, S.J. Lippard, Inorg. Chem. 25 (1986) 219.
[13] I. Casals, P. Gonzalez-Duarte, W. Clegg, C. Foces-Foces, F.H. Cano, M. Martinez-Ripoll, M. Gomez, X. Solans, J. Chem. Soc., Dalton Trans. (1991) 2511.
[14] M. Capdevila, W. Clegg, P. Gonzalez-Duarte, I. Mira, J. Chem. Soc., Dalton Trans. (1992) 173.
[15] S. Marchal, V. Moreno, G. Aullon, S. Alvarez, M. Quiros, M. Font-Bardia, X. Solans, Polyhedron 18 (1999) 3675.
[16] D.C. Jicha, D.H. Busch, Inorg. Chem. 1 (1962) 872.
[17] J. Suades, X. Solans, M. Font-Altaba, Polyhedron 3 (1984) 1227.
[18] M. Capdevila, P. Gonzalez-Duarte, C. Foces-Foces, F.H. Cano, M. Martinez-Ripoll, J. Chem. Soc., Dalton Trans. (1990) 143.
[19] M. Capdevila, P. Gonzalez-Duarte, J. Sola, C. Foces-Foces, F.H. Cano, M. Martinez-Ripoll, Polyhedron 8 (1989) 1253.
[20] H. Barrera, J.C. Bayon, J. Suades, C. Germain, J.P. Declerq, Polyhedron 3 (1984) 969.
[21] M. Capdevila, W. Clegg, P. Gonzalez-Duarte, B. Harris, I. Mira, J. Sola, I.C. Taylor, J. Chem. Soc., Dalton Trans. (1992) 2817.
[22] J. Sola, R. Yanez, J. Chem. Soc., Dalton Trans. (1986) 2021.
[23] H. Barrera, J.M. Vinas, M. Font-Altaba, X. Solans, Polyhedron 4 (1985) 2027.
[24] X. Solans, M. Font-Altaba, J.L. Brianso, J. Sola, J. Suades, H. Barrera, Acta Crystallogr., C 39 (1983) 1653.
[25] J.A. Ayllon, P. Gonzalez-Duarte, C. Miravitlles, E. Molins, J. Chem. Soc., Dalton Trans. (1990) 1793.
[26] F.R. Hartley, The Chemistry of Platinum and Palladium, Wiley, New York, 1973.
[27] SHELXTL-5.1, Bruker Analytical X-ray Systems, Madison, WI, 1998.
[28] S. Dey, V.K. Jain, A. Klein, W. Kaim, unpublished results.
[29] A. Singhal, V.K. Jain, B. Varghese, E.R.T. Tiekink, Inorg. Chim. Acta 285 (1999) 190.
[30] V.K. Jain, S. Kannan, E.R.T. Tiekink, J. Chem. Res. (M) (1994) 501.
[31] S. Dey, V.K. Jain, A. Knoedler, W. Kaim, unpublished results.
[32] (a) V.K. Jain, S. Kannan, J. Organomet. Chem. 405 (1991) 265;
(b) V.K. Jain, S. Kannan, R.J. Butcher, J.P. Jasinski, Polyhedron 14 (1995) 3641;
(c) S. Dey, V.K. Jain, B. Verghese, J. Organomet. Chem. 623 (2001) 48.
[33] N. Brugat, A. Polo, A. Alvarez-Larena, J.F. Piniella, J. Real, Inorg. Chem. 38 (1999) 4829.