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Inorganica Chimica Acta 360 (2007) 2653–2660
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Multiple coordination modes of hemilabile 3-dimethylaminopropyl chalcogenolates in platinum(II) complexes: Synthesis, spectroscopy and structures

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Received 28 August 2006; accepted 3 January 2007
Available online 13 January 2007

Abstract

The reactions of *N*,*N*-dimethylaminopropyl chalcogenolates with platinum(II) compounds have been carried out and complexes of the types $[PtCl(ECH_2CH_2CH_2NMe_2)]_2$ (**1**) (E = S (**1a**) and Se (**1b**)), $[Pt(ECH_2CH_2CH_2NMe_2)_2]_n$ (**2**) (E = S (**2a**) and Se (**2b**)), $[(PtCl_2)_2\{(Me_2NCH_2CH_2CH_2E)_2\}]_n$ (**3**), $[PtX(SeCH_2CH_2CH_2NMe_2)]_2$ (**4**) (X = SePh (**4a**) and OAc (**4b**)) and $[PtCl(ECH_2CH_2CH_2NMe_2)(PR_3)]_n$ (**5**) (E = S, Se, Te) have been isolated. These complexes have been characterized by elemental analysis, IR, UV–Vis, NMR (^1H, ^{13}C, ^{31}P, ^{77}Se, ^{195}Pt) spectroscopy and FAB mass spectral data. The structures of $[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1b**) and $[PtCl(SCH_2CH_2CH_2NMe_2)(PPr_3)]_2$ (**5a**) have been established by single crystal X-ray diffraction data. Both the molecules have dimeric structures. In **1b**, two platinum atoms are held together by symmetrically bridging Se atoms of the chelating selenolate groups. In **5a**, two thiolates form a four-membered Pt_2S_2 bridge with dangling NMe_2 groups.

Keywords: Chalcogenolate; N ligands; Platinum(II); NMR; X-ray crystal structure

1. Introduction

The chemistry of aminochalcogenolate ligands, $R_2N(CR'_2)_nE^-$, has been a subject area of considerable research for over the last two decades and has been dominated by thiolate derivatives [1–15]. The complexes containing heavier analogs (Se or Te) have been studied only recently [16–21]. These ligands show versatile coordination chemistry as internal functionalization through N donor provides a way to suppress polymerization of metal chalcogenolates, whereas their hemilability makes them superior catalysts [22,23]. The structures of aminoalkylchalcogenolate metal complexes are greatly influenced by the nature of the metal ion, the number of intervening atoms separating the N and E centers and the substituents on the N atom. Recently we have examined the chemistry of *N*,*N*-dimethylaminopropyl chalcogenolates, $Me_2NCH_2CH_2CH_2E^-$ (E = S, Se, Te), of palladium and have shown the diverse coordination possibilities of the ligand [19–21]. Only a few examples of platinum complexes with *N*,*N*′-dimethylaminopropyl selenolates are reported [19]. To assess the trend with the variation in chalcogen ligand in platinum complexes, we have prepared several platinum(II) complexes with $Me_2NCH_2CH_2CH_2E^-$ (E = S, Se, Te) and compared their chemistry with palladium derivatives.

2. Experimental

The solvents were dried and distilled under a nitrogen atmosphere prior to use. All reactions were carried out in a Schlenk flask under a nitrogen atmosphere. Tellurium and $Me_2NCH_2CH_2CH_2Cl \cdot HCl$ were obtained from commercial sources. Dichalcogenides $(Me_2NCH_2CH_2CH_2E)_2$ (E = S [21,24], Se [19] and Te [21]) were prepared according to the literature methods. Elemental analyses were carried

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doi:10.1016/j.ica.2007.01.002

out by the Radio Chemistry Division of BARC. Melting points were determined in capillary tubes and are uncorrected. ^{1}H, $^{13}C\{^{1}H\}$, $^{77}Se\{^{1}H\}$ and $^{195}Pt\{^{1}H\}$ NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer operating at 300, 75.47, 57.24 and 64.52 MHz, respectively. Chemical shifts are relative to internal chloroform peak at δ 7.26 ppm for ^{1}H and δ 77.0 ppm for $^{13}C\{^{1}H\}$, Me_2Se for $^{77}Se\{^{1}H\}$ and Na_2PtCl_6 for $^{195}Pt\{^{1}H\}$. A 90° pulse was used in every case. A weighting function was applied in $^{13}C\{^{1}H\}$, $^{77}Se\{^{1}H\}$ and $^{195}Pt\{^{1}H\}$ NMR spectra. The IR spectra were recorded as Nujol mulls between CsI plates on a Bomen MB-102 FT-IR spectrometer. UV–Vis absorption spectra were recorded on a Chemito Spectrascan UV 2600 double-beam UV–Vis spectrophotometer using quartz cuvettes with a diameter of 1 cm. Cyclic voltammetry was carried out at a scan rate of 100 mV s^{-1} in CH_2Cl_2/0.1 M Bu_4NPF_6, using a three-electrode configuration (glassy carbon electrode, platinum counter electrode, calomel reference electrode) and an Ecochemie potentiostat 100 with autolab software. The ferrocene/ferrocenium couple served as the external reference. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer at CDRI, Lucknow, India.

2.1. Synthesis

2.1.1. Preparation of $[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1b**)

To a methanolic solution of $NaSeCH_2CH_2CH_2NMe_2$ (prepared from $(Me_2NCH_2CH_2CH_2Se)_2$ (202 mg, 0.61 mmol) and $NaBH_4$ (47 mg, 1.24 mmol) in 15 cm^3 methanol), an aqueous solution of K_2PtCl_4 (507 mg, 1.22 mmol) was added with vigorous stirring which continued for 3 h. The solvents were stripped off in vacuo and the residue was washed with hexane and acetone. The residue was extracted with dichloromethane (3×15 cm^3), filtered through a G-3 filter and the filtrate was passed through a Florisil column. The yellow solution was concentrated to 5 cm^3 and acetone–hexane mixture was added to yield a yellow powder (yield 213 mg, 44%), m.p. >195 °C (dec). *Anal.* Calc. for $C_{10}H_{24}Cl_2N_2Pt_2Se_2$: C, 15.2; H, 3.1; N, 3.5. Found: C, 15.1; H, 3.4; N, 3.5%. UV–Vis (CH_2Cl_2) λ_{max}: 260 (sh), 303 (3820), 331 (2320), 380 (sh). IR ν_{Pt-Cl}: 280 cm^{-1}. ^{1}H NMR in $CDCl_3$ δ: 1.86–1.99 (m); 2.06–2.14 (m); 2.50–2.75 (m), 2.78 (s), 2.83 (s) (NMe_2); 3.00–3.09 (m). $^{13}C\{^{1}H\}$ NMR in $CDCl_3$ δ: 19.4 (s, $–CH_2–$); 27.1 (s, $SeCH_2$, $^{2}J(^{195}Pt–^{13}C)$ 56 Hz); 50.3, 53.6 (each s, NMe_2); 65.3 (s, NCH_2). $^{77}Se\{^{1}H\}$ NMR in $CDCl_3$ δ: −109 ($^{1}J(^{195}Pt–^{77}Se) = 364$ Hz). $^{195}Pt\{^{1}H\}$ NMR in $CDCl_3$ δ: −3209. FAB-MS *m/z*: 791 [M], 755 [M−Cl], 719 [M−($CH_2CH_2NMe_2$)], 670 [M−(Cl+$CH_2CH_2CH_2NMe_2$)]. Cyclic voltammetry (CH_2Cl_2): E_{pa} (ox) 1.10; E_{pc} (red) −2.36.

2.1.2. Preparation of $[PtCl(SCH_2CH_2CH_2NMe_2)]_2$ (**1a**)

Prepared similarly to **1b** from K_2PtCl_4 and $NaSCH_2CH_2CH_2NMe_2$ in 32% yield as a yellow crystalline solid. M.p. >200 °C (dec). *Anal.* Calc. for $C_{10}H_{24}Cl_2N_2Pt_2S_2$: C, 17.2; H, 3.5; N, 4.0. Found: C, 17.1; H, 3.7; N, 4.0%. UV–Vis (CH_2Cl_2) λ_{max}: 288 (2230), 318 (sh), 366 (440) nm. IR ν_{Pt-Cl}: 280 cm^{-1}. ^{1}H NMR in $CDCl_3$ δ: 1.98–2.13 (m); 2.38–2.43 (m); 2.66–2.74 (m), 2.81 (s, J(Pt–H) = 19 Hz), 2.89 (s, J(Pt–H) = 26 Hz), 3.26–3.32 (m). $^{13}C\{^{1}H\}$ NMR in $CDCl_3$ δ: 25.6 (s, $SCH_2–$, $^{2}J(^{195}Pt–^{13}C)$ 40 Hz); 27.1 (s, $–CH_2–$); 51.4, 52.8 (each s, NMe_2); 63.0 (s, $NCH_2–$). $^{195}Pt\{^{1}H\}$ NMR in $CDCl_3$ δ: −2862 (s). Cyclic voltammetry (CH_2Cl_2): E_{pa} (ox) 0.94; E_{pc} (red) −2.46.

2.1.3. Preparation of $[Pt(SCH_2CH_2CH_2NMe_2)_2]_n$ (**2a**)

To a freshly prepared methanolic solution (8 cm^3) of $NaSCH_2CH_2CH_2NMe_2$ (prepared from $(Me_2NCH_2CH_2CH_2S)_2$ (271 mg, 1.15 mmol) and $NaBH_4$ (88 mg, 2.32 mmol)), an aqueous solution (8 cm^3) of K_2PtCl_4 (473 mg, 1.14 mmol) and acetone (10 cm^3) was added with vigorous stirring which continued for 4 h. The solvents were evaporated under reduced pressure. The residue was washed with hexane and extracted with acetone (3×20 cm^3). The yellow solution was filtered, passed through a Florisil column and concentrated to 5 cm^3 under vacuum, and after cooling at −5 °C for 24 h gave a yellow powder in 28% yield (138 mg). M.p. 208 °C (dec). *Anal.* Calc. for $C_{10}H_{24}N_2PtS_2$: C, 27.8; H, 5.6; N, 6.5; S, 14.9. Found: C, 27.0; H, 5.8; N, 6.6; S, 14.0%. UV–Vis (CH_2Cl_2) λ_{max}: 284 (10200), 300 (9800), 380 (sh) nm. ^{1}H NMR in $CDCl_3$ δ: 2.28 (s, NMe_2); 2.34 (br); 2.45 (br), 2.53 (br) ($–CH_2–CH_2–CH_2–$). $^{13}C\{^{1}H\}$ NMR in $CDCl_3$ δ: 31.5 (s, SCH_2); 32.2 (s, $–CH_2–$); 45.4 (s, NMe_2); 58.7 (s, $NCH_2–$). Cyclic voltammetry (CH_2Cl_2): E_{pc} (red) −1.76.

2.1.4. Preparation of $[Pt(SeCH_2CH_2CH_2NMe_2)_2]_n$ (**2b**)

To a freshly prepared methanolic solution (10 cm^3) of $NaSeCH_2CH_2CH_2NMe_2$ (prepared from $(Me_2NCH_2CH_2CH_2Se)_2$ (348 mg, 1.05 mmol) and $NaBH_4$ (81 mg, 2.14 mmol) in methanol), a dichloromethane solution (20 cm^3) of $PtCl_2(PhCN)_2$ (493 mg, 1.04 mmol) was added with vigorous stirring which continued for 4 h whereupon an orange precipitate formed. The solvents were evaporated under reduced pressure and the residue was washed with hexane and ether. The residue was extracted with hot dichloromethane (3×20 cm^3) and filtered. The filtrate was concentrated to 5 cm^3 and hexane was added to give an orange powder (153 mg, 28% yield). M.p. 205 °C (dec). *Anal.* Calc. for $C_{10}H_{24}N_2PtSe_2$: C, 22.9; H, 4.6; N, 5.3. Found: C, 22.0; H, 4.1; N, 4.9%. ^{1}H NMR in $CDCl_3$ δ: 2.22 (s, NMe_2); 2.32–2.38 (br, $–CH_2–CH_2–CH_2–$). $^{13}C\{^{1}H\}$ NMR in $CDCl_3$ δ: 25.5 (s, $SeCH_2$); 32.1 (s, $–CH_2–$); 45.5 (s, NMe_2); 59.6 (s, $NCH_2–$).

2.1.5. Reaction of $(Me_2NCH_2CH_2CH_2S)_2$ with K_2PtCl_4 (**3a**)

To a methanolic solution (15 cm^3) of $(Me_2NCH_2CH_2CH_2S)_2$ (152 mg, 0.64 mmol), an aqueous solution (10 cm^3) of K_2PtCl_4 (530 mg, 1.28 mmol) was added with stirring which continued for 4 h, whereupon a pale yellow precipitate formed. The precipitate was filtered through a

G-3 filter, washed thoroughly with H_2O, followed by methanol and acetone, and finally dried under vacuum (yield 317 mg, 65%). M.p. 210 °C (dec). *Anal.* Calc. for $C_{10}H_{24}Cl_4N_2Pt_2S_2$: C, 15.6; H, 3.2; N, 3.6; S, 8.3. Found: C, 13.7; H, 3.0; N, 3.2; S, 10.5%.

Similarly Se (**3b**) [m.p. 188 °C (dec). *Anal.* Calc. for $C_{10}H_{24}Cl_4N_2Pt_2Se_2$: C, 13.9; H, 2.8; N, 3.2. Found: C, 12.6; H, 2.8; N, 3.5%] and Te (**3c**) [m.p. 158 °C (dec). *Anal.* Calc. for $C_{10}H_{24}Cl_4N_2Pt_2Te_2$: C, 12.5; H, 2.5; N, 2.9. Found: C, 11.1; H, 2.3; N, 2.5%] derivatives were prepared.

2.1.6. Preparation of $[Pt(SePh)(SeCH_2CH_2CH_2NMe_2)]_2$ (**4a**)

To a methanolic solution (10 cm^3) of NaSePh (prepared from Ph_2Se_2 (80 mg, 0.26 mmol) and $NaBH_4$ (20 mg, 0.53 mmol) in methanol), a dichloromethane solution (20 cm^3) of $[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$ (200 mg, 0.25 mmol) was added with stirring. The color changed immediately to orange. After 3 h of stirring, the solvents were evaporated in vacuo, and the residue was extracted with toluene (3×15 cm^3) and filtered. The filtrate was concentrated under vacuum to 5 cm^3. To this a mixture of acetone and hexane was added whereupon an orange powder separated (98 mg, 38% yield). M.p. >190 °C (dec). *Anal.* Calc. for $C_{22}H_{34}N_2Pt_2Se_4$: C, 25.6; H, 3.3; N, 2.7. Found: C, 24.9; H, 3.1; N, 3.0%. UV–Vis (CH_2Cl_2) λ_{max}: 354 nm. ^1H NMR in $CDCl_3$ δ: 2.09 (s, with a very broad base) ($SeCH_2CH_2CH_2$); 7.11 (br), 7.85 (br) (Ph). $^{13}C\{^1H\}$ NMR in $CDCl_3$ δ: 24.5 (br, $-CH_2-$); 31.6 (br, $SeCH_2$); 45.4 (s, NMe_2), 59.3 (each s, NCH_2); 123.2 (br); 134.9 (br, Ph).

2.1.7. Preparation of $[Pt(OAc)(SeCH_2CH_2CH_2NMe_2)]_2$ (**4b**)

To a dichloromethane solution (20 cm^3) of $[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$ (170 mg, 0.21 mmol), a methanolic suspension (5 cm^3) of AgOAc (72 mg, 0.43 mmol) was added with vigorous stirring which was continued for 6 h. This was centrifuged to remove AgCl and then filtered through a G-3 funnel. The filtrate was dried under vacuum and the yellowish green solid was recrystallized from CH_2Cl_2–acetone mixture in 45% (81 mg) yield. M.p. >172 °C (dec). *Anal.* Calc. for $C_{14}H_{30}N_2O_4Pt_2Se_2$: C, 20.1; H, 3.6; N, 3.3. Found: C, 19.4; H, 3.3; N, 3.6%. ^1H NMR in $CDCl_3$ δ: 1.99 (s, OAc); 2.66, 2.83 (each s, NMe_2); 2.31 (br); 2.60 (br, m); 3.10 (m) (CH_2-). $^{13}C\{^1H\}$ NMR in $CDCl_3$ δ: 17.6 (s, OAc); 23.6 (s, CH_2); 27.5 (s, $SeCH_2$), 50.8, 53.0 (each s, NMe_2); 65.4 (s, NCH_2); 177.3 (CO).

2.1.8. Preparation of $[PtCl(SCH_2CH_2CH_2NMe_2)(PPr_3)]_2$ (**5a**)

To a dichloromethane solution (20 cm^3) of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PPr_3)_2]$ (180 mg, 0.21 mmol), a methanolic solution of $NaSCH_2CH_2CH_2NMe_2$ (prepared from $(Me_2NCH_2CH_2CH_2S)_2$ (50 mg, 0.21 mmol) and $NaBH_4$ (16 mg, 0.42 mmol)) stirred for 3 h. The solvents were stripped off in vacuo, the residue was washed with hexane and extracted with acetone (3×5 cm^3). The solution was concentrated to 5 cm^3, few drops of hexane were added to yield (120 mg, 56%) an yellow oil. *Anal.* Calc. for $C_{28}H_{66}Cl_2N_2P_2Pt_2S_2$: C, 33.0; H, 6.5; N, 2.8; S, 6.3. Found: C, 32.2; H, 6.4; N, 3.0; S, 6.4%. ^1H NMR in $CDCl_3$ δ: 1.02 (br, P–C–CCH_3); 1.57 (br, PC–CH_2–); 1.79 (br, PCH_2); 2.20, 2.37 (each s, NMe_2); 2.28–2.83 (br, m, $-CH_2CH_2CH_2-$). $^{31}P\{^1H\}$ NMR in $CDCl_3$ δ: 1.1, $^1J(^{195}Pt-^{31}P) = 3184$ Hz. $^{195}Pt\{^1H\}$ NMR in $CDCl_3$ δ: −3802 (d, $^1J(^{195}Pt-^{31}P) = 3206$ Hz). Cyclic voltammetry (CH_2Cl_2): E_{pc} (red) −0.81, −2.37.

2.1.9. Preparation of $[PtCl(SeCH_2CH_2CH_2NMe_2)(PPr_3)]_2$ (**5b**)

Compound **5b** prepared according to the literature method [19]. ^1H NMR in $CDCl_3$: 1.05 (t, 7 Hz, PCH_2CH_2Me); 1.56–1.85 (m, PCH_2CH_2, NCH_2); 2.24(s, NMe_2); 2.45 (br, NCH_2); 2.62 (br, m, $SeCH_2$). $^{31}P\{^1H\}$ NMR in $CDCl_3$: −0.1, ^1J(Pt–P) = 3122 Hz. $^{195}Pt\{^1H\}$ NMR in $CDCl_3$: −3960 (d), ^1J(Pt–P) = 3097 Hz.

2.1.10. Preparation of $[PtCl(TeCH_2CH_2CH_2NMe_2)(PEt_3)]_2$ (**5c1**)

To a freshly prepared methanolic solution of $NaTeCH_2CH_2CH_2NMe_2$ (prepared from $(Me_2NCH_2CH_2CH_2Te)_2$ (100 mg, 0.23 mmol) and $NaBH_4$ (18 mg, 0.48 mmol)), an acetone suspension of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ (179 mg, 0.23 mmol) was added with stirring which continued for 4 h at room temperature. The solvents were evaporated under vacuum. The residue was extracted with hexane (3×8 cm^3) followed by acetone (3×8 cm^3). The extracts were separately dried under vacuum and studied by NMR spectroscopy.

Hexane soluble part: ^1H NMR in $CDCl_3$: 1.09–1.25 (m, PCH_2Me); 1.78–2.14 (m, PCH_2); 2.18 (s, minor); 2.20 (d, 3.8 Hz, NMe_2, major); 2.23–2.43 (m); 2.63–2.65 (m). $^{31}P\{^1H\}$: 4.6 (s, ^1J(Pt–P) = 3030 Hz, minor); 7.5 (s, ^1J(Pt–P) = 3046 Hz, major) (other small peaks were also present). *Anal.* Calc. for $C_{22}H_{54}Cl_2N_2P_2Pt_2Te_2$: C, 23.5; H, 4.8; N, 2.5%.

Acetone fraction contained mainly ~90% *cis*-$[PtCl_2(PEt_3)_2]$, $^{31}P\{^1H\}$ NMR: 9.8 (^1J(Pt–P) = 3492 Hz); $^{195}Pt\{^1H\}$ NMR: −4475 (t, ^1J(Pt–P) = 3496 Hz). $^{31}P\{^1H\}$ NMR: 8.1 (^1J(Pt–P) = 3054 Hz); $^{195}Pt\{^1H\}$ NMR: −4735 (d, ^1J(Pt–P) = 3065 Hz) (minor).

2.1.11. Preparation of $[PtCl(TeCH_2CH_2CH_2NMe_2)(PMePh_2)]_2$ (**5c2**)

To a methanolic solution of $NaTeCH_2CH_2CH_2NMe_2$ (prepared from $(Me_2NCH_2CH_2CH_2Te)_2$ (78 mg, 0.18 mmol) and $NaBH_4$ (15 mg, 0.40 mmol) in methanol) was added an acetone suspension (15 cm^3) of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PMePh_2)_2]$ (167 mg, 0.18 mmol) with vigorous stirring which continued for 4 h. The solvents were removed in vacuo. The residue was washed with hexane (2 cm^3) and extracted with acetone (3×8 cm^3) and filtered. The filtrate

Table 1
Crystallographic and structure refinement data for **1b** and **5a**

Compound	**1b**	**5a**
Chemical formula	$C_{10}H_{24}Cl_2N_2Pt_2Se_2$	$C_{28}H_{66}Cl_2N_2P_2Pt_2S_2$
Formula weight	791.32	1017.96
Crystal size (mm)	$0.71 \times 0.33 \times 0.18$	$0.28 \times 0.24 \times 0.10$
Temperature (K)	103(2)	103(2)
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
Unit cell dimensions		
a (Å)	10.3406(19)	21.896(3)
b (Å)	8.6477(15)	11.5656(14)
c (Å)	19.141(3)	15.9619(19)
β (°)	97.809(2)	106.588(2)
V (Å^3)	1695.7(5)	3874.0(8)
D_{calc} (g cm^{-3})	3.100	1.745
Z	8	8
μ (mm^{-1})/F(000)	21.075/1424	7.563/2000
θ Range for data collection (°)	2.13–28.27	1.94–30.87
Limiting indices	$-11 \leqslant h \leqslant 13$, $-11 \leqslant k \leqslant 11$, $-25 \leqslant l \leqslant 25$	$-31 \leqslant h \leqslant 28$, $-16 \leqslant k \leqslant 15$, $-22 \leqslant l \leqslant 22$
Goodness-of-fit on F^2	1.064	1.123
Absorption correction	SADABS	SADABS
Reflections collected/ unique	16000/4161	20802/5532
Data/restraints/ parameters	4161/6/167	5532/0/177
Final R_1, wR_2 indices	0.0413, 0.1119	0.0573, 0.1199
R_1, wR_2 (all data)	0.0451, 0.1142	0.0708, 0.1269
Largest difference in peak and hole (e Å^{-3})	3.569 and −3.723	5.895 and −4.797
Computer programs used	SHELXTL-5.1 [31]	SHELXTL-5.1 [31]

was concentrated to 5 cm^3 and hexane (1 cm^3) was added and cooled at −5 °C for 24 h whereupon pale yellow crystals separated (yield: 111 mg, 48%) (m.p. 172 °C). *Anal.* Calc. for $C_{36}H_{50}Cl_2N_2P_2Pt_2Te_2$: C, 33.5; H, 3.9; N, 2.2. Found: C, 33.9; H, 3.9; N, 2.1%. ^{1}H NMR in $CDCl_3$: 2.15 (d, 11 Hz, PMe_2); 2.03, 2.17, 2.26 (each s); 1.82–2.34 (broad+multiplets); 7.28–7.71 (m, Ph). $^{31}P\{^1H\}$ NMR: 0.1 (s, ^1J(Pt–P) = 3110 Hz), −0.9 (s, ^1J(Pt–P) = 3075 Hz) (each 1:1); −1.7 (s, ^1J(Pt–P) = 3100 Hz, small). $^{195}Pt\{^1H\}$ NMR: −4754 (d, ^1J(Pt–P) = 3129 Hz), −4809 (d, ^1J(Pt–P) = 3084 Hz) (each 1:1); −4789 (d, ^1J(Pt–P) = 3058 Hz, minor) ppm. *cis*-$[PtCl_2(PMePh_2)_2]$ −0.2; ^1J(Pt–P) = 3614 Hz.

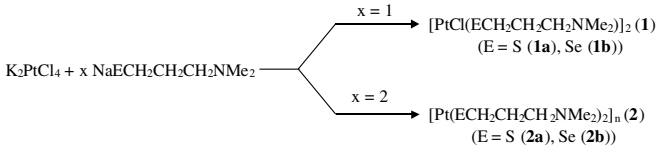
2.2. X-ray crystallography

The unit cell parameters and the intensity data for yellow single crystals of $[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1b**) and $[PtCl(SCH_2CH_2CH_2NMe_2)(PPr_3)]_2$ (**5a**) were collected at −170 °C on a Bruker Smart 1K CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), employing the ω scan technique. The intensity data were corrected for Lorentz, polarization and absorption effects [25]. The structure was solved and refined with SHELX program [26]. The non-hydrogen atoms were refined anisotropically. Selected crystallographic data are given in Table 1.

3. Results and discussion

3.1. Synthesis and NMR spectroscopic data

The reactions of $NaECH_2CH_2CH_2NMe_2$ with K_2PtCl_4 in 1:1 and 2:1 stoichiometry gave yellow-orange complexes of compositions $[PtCl(ECH_2CH_2CH_2NMe_2)]_2$ (**1**) (E = S (**1a**); Se (**1b**)) and $[Pt(ECH_2CH_2CH_2NMe_2)_2]_n$ (**2**) (E = S (**2a**); Se (**2b**)), respectively, as a sparingly soluble powder. Similar reactions with $NaTeCH_2CH_2CH_2NMe_2$, however, gave brown insoluble solid which was not characterized further. The reaction of Na_2PdCl_4 with $(Me_2NCH_2CH_2CH_2E)_2$ in methanol affords dimeric $[PdCl(ECH_2CH_2CH_2NMe_2)]_2$, which has been unambiguously characterized by X-ray crystallography [18,20]. The reaction of K_2PtCl_4 with $(Me_2NCH_2CH_2CH_2Se)_2$ gave an insoluble complex which was thought to be $[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1b**), although microanalytical data were slightly different from the expected composition [18]. When this reaction was extended to other dichalcogenides (E = S or Te), insoluble products were formed which gave microanalysis slightly lower than that expected for **1**. The analytical data are, however, closer to the composition, $[Pt_2Cl_4\{(Me_2NCH_2CH_2CH_2E)_2\}]$ (**3**). These complexes are soluble in coordinating solvents, like DMSO and pyridine, with which they react. The $^{195}Pt\{^1H\}$ NMR spectra of DMSO solutions of **3a** and **3b** exhibited major signals due to the *cis* and *trans* $[PtCl_2(DMSO)_2]$ (δ −2964, −3455 ppm) and several small peaks in the regions −2858, −2900, −3250 and −3500 (**3a**); −3600 and −3800 ppm (**3b**), respectively. The peaks at −2858 (in **3a**) and −3193 (in **3b**) ppm may be due to **1a** and **1b** and the slight difference in chemical shift may be due to solvent effects. A similar $^{195}Pt\{^1H\}$ NMR spectrum was observed when a DMSO solution of $[PtCl_2(DMSO)_2]$ was treated with $(Me_2NCH_2CH_2CH_2Se)_2$. These complexes also dissolved readily in pyridine to give deep colored solutions from which a colorless product was isolated. This colorless product has been characterized as $[PtCl(py)_3]Cl$ (m.p. >260 (d)) from microanalysis (*Anal.* Calc.: C, 35.8; H, 3.0; N, 8.3. Found: C, 37.6; H, 3.7; N, 8.8%.) and ^{1}H NMR spectra. From these data it appears that these complexes **3** contain dichalcogenide ligand coordinated to platinum through chalcogen/nitrogen donors.



The FAB mass spectrum of **1b** displayed a multiplet at m/z 791 suggesting a dimeric formulation of **1**. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **1** displayed two signals for the methyl groups of NMe_2, suggesting that they are anisochronous. The $^{13}C\{^1H\}$ signals for NCH_2 and ECH_2 in **1b**

are deshielded as compared to the corresponding resonances for **1a**. The $^{195}Pt\{^1H\}$ spectra (Fig. 1) showed a single resonance, suggesting that there is only one type of platinum center. The $^{77}Se\{^1H\}$ NMR spectrum of **1b** displayed a single resonance at −104 ppm with ^1J(Pt–Se) of 364 Hz (Fig. 2). The ^1J(Pt–Se) in platinum(II) selenolate complexes has been reported in the range of 100–385 Hz [17,27]. The ^1H NMR spectra of **2** showed multiplets for CH_2 proton resonances and a singlet for NMe_2 protons. The $^{13}C\{^1H\}$ NMR spectra displayed a single resonance for the methylene and methyl carbons of chalcogenolate groups.

The terminal chloride in **1b** can be replaced with other anionic ligands, viz., OAc, SePh. Thus the reaction of **1b** with NaSePh or AgOAc gave $[Pt(SePh)(SeCH_2CH_2CH_2NMe_2)]_n$ (**4a**) or $[Pt(OAc)(SeCH_2CH_2CH_2NMe_2)]_n$ (**4b**), respectively. The NMR (^1H and ^{13}C) data of **4b** can be compared with $[Pd(OAc)(SeCH_2CH_2CH_2NMe_2)]_2$, suggesting that **4b** may have binuclear selenolate bridged structure similar to the palladium complex [21]. The ^1H NMR spectrum of **4a**, however, showed broad resonances.

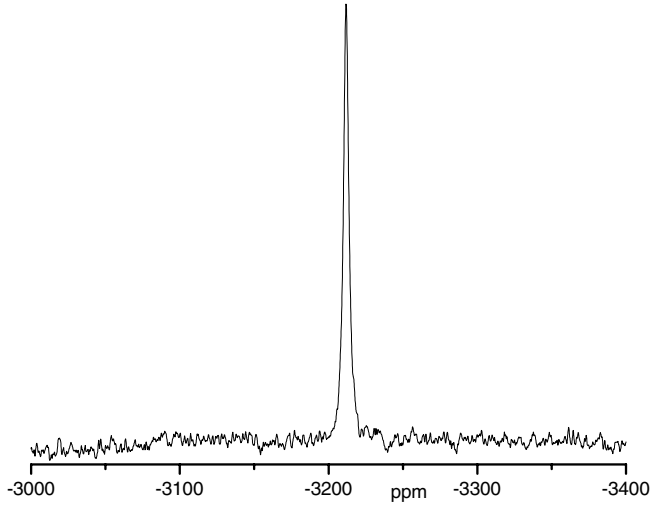


Fig. 1. $^{195}Pt\{^1H\}$ NMR spectrum of $[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$ in $CDCl_3$.

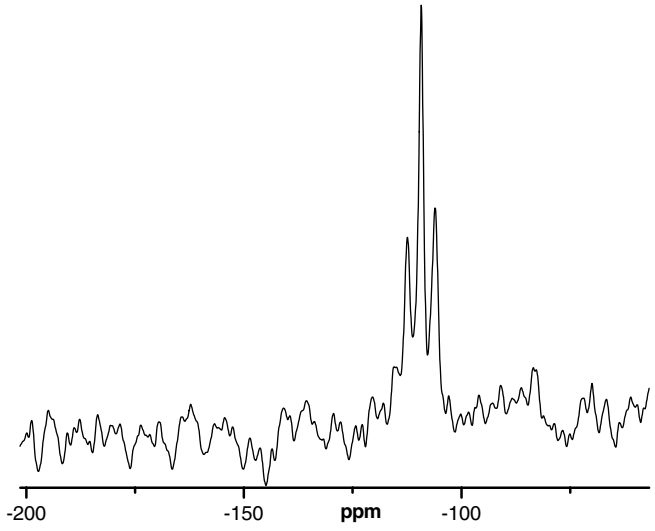
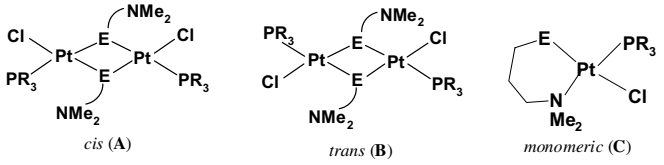


Fig. 2. $^{77}Se\{^1H\}$ NMR spectrum of $[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$ in $CDCl_3$.

Treatment of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with two equivalents of $NaECH_2CH_2CH_2NMe_2$ gave complexes of the general composition $[Pt_2Cl_2(\mu\text{-}ECH_2CH_2CH_2NMe_2)_2(PR_3)_2]$, which are formed as either *cis* (E = S; $PR_3 = PPr_3$) or a mixture of *cis* and *trans* (E = Se or Te) isomers. The tellurolate derivatives tend to disproportionate slowly to $PtCl_2(PR_3)_2$ in solution and the latter could be isolated by recrystallization. In contrast to the platinum complexes, similar reactions of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with $NaSeCH_2CH_2CH_2NMe_2$ gave a mixture of products from which $[PdCl(SeCH_2CH_2CH_2NMe_2)]_2$ was isolated [21].

The ^1H NMR spectrum of **5a** showed two NMe_2 signals, suggesting that the complex has sym-*cis* configuration. The $^{31}P\{^1H\}$ NMR spectra of **5a** and **5b** displayed a singlet with platinum coupling. The magnitude of ^1J(Pt–P) can be compared with that of $[Pt_2Cl_2(\mu\text{-}ER')_2(PR_3)_2]$ (E = S or Se), therefore, a dimeric chalcogenolato-bridged structure may be suggested (**A** and **B**; E = S or Se) (see later, X-ray crystallography) [28,29]. The ^{31}P spectra of **5c1**, **5c2**, however, displayed three resonances. These resonances can be attributed for *cis*- (**A**, E = Te) and *trans*- (**B**, E = Te) isomers. The third resonance can be assigned to a monomeric species (**C**, E = Te) $[PtCl(TeCH_2CH_2CH_2NMe_2)(PR_3)]$. The $^{195}Pt\{^1H\}$ NMR spectrum of $[PtCl(TeCH_2CH_2CH_2NMe_2)(PMePh_2)]_n$ (**5c2**) (Fig. 3) also displayed three doublets (δ ^{195}Pt = −4754; −4809; −4789 ppm) due to phosphorous coupling. A small doublet at δ −4789 ppm may be attributed to the monomeric species. The former two doublets appearing in approximately 1:1 ratio may be assigned to the *cis* and *trans* isomers. The ^{195}Pt resonance gets shielded while ^1J(Pt–P) decreases on increasing the size of the chalcogen atom, −3802 (*cis*, **5a**, S, ^1J(Pt–P) = 3206 Hz); −4065 (*cis*, **5b**, Se, ^1J(Pt–P) = 3155 Hz); −4735 (*cis*, **5c1**, Te, ^1J(Pt–P) = 3065 Hz). The decreasing magnitude of ^1J(Pt–P) with increasing size of chalcogen atom reflects their increasing *trans* influence of the chalcogenolate ligand [27]. This is manifested from facile disproportionation of tellurolate derivative in solution.



(E^N = $Me_2NCH_2CH_2CH_2E$; E = S, Se, Te)

3.2. Electronic spectra and electrochemistry

Absorption spectra and cyclovoltammetric peak potentials of a few complexes have been recorded in dichloromethane. These absorptions can be assigned as charge

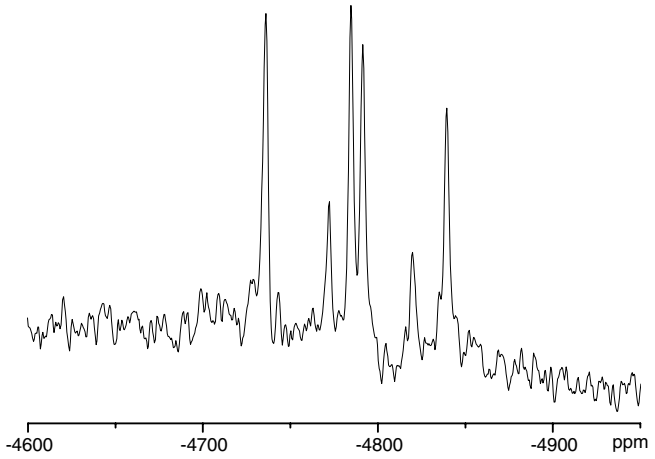


Fig. 3. $^{195}Pt\{^{1}H\}$ NMR spectrum of $[PtCl(TeCH_2CH_2CH_2NMe_2)(PMePh_2)]_n$ ($n = 1$ or 2) in $CDCl_3$.

Table 2
Selected bond lengths (Å) and angles (°) for $[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1b**)

Pt(1)–Se(1)	2.3915(8)	Pt(2)–Se(1)	2.3992(8)
Pt(1)–Se(2)	2.3938(8)	Pt(2)–Se(2)	2.3812(8)
Pt(1)–Cl(1)	2.3348(19)	Pt(2)–Cl(2)	2.3570(19)
Pt(1)–N(2)	2.134(6)	Pt(2)–N(1)	2.136(6)
Se(1)–C(21)	1.956(8)	Se(2)–C(11)	1.982(8)
N(2)–C(23)	1.499(10)	N(1)–C(13)	1.490(10)
Se(1)–Pt(1)–Se(2)	80.13(3)	Se(2)–Pt(2)–Se(1)	80.22(3)
N(2)–Pt(1)–Se(1)	96.19(18)	N(1)–Pt(2)–Se(2)	95.34(17)
Cl(1)–Pt(1)–Se(1)	171.93(5)	Cl(2)–Pt(2)–Se(2)	172.30(5)
N(2)–Pt(1)–Se(2)	175.92(18)	N(1)–Pt(2)–Se(1)	173.78(18)
Cl(1)–Pt(1)–Se(2)	91.84(5)	Cl(2)–Pt(2)–Se(1)	92.38(5)
N(2)–Pt(1)–Cl(1)	91.82(18)	N(1)–Pt(2)–Cl(2)	91.87(18)
Pt(1)–Se(1)–Pt(2)	91.20(3)	Pt(2)–Se(2)–Pt(1)	91.58(3)
Pt(1)–Se(1)–C(21)	103.8(2)	Pt(2)–Se(2)–C(11)	105.7(2)
Pt(2)–Se(1)–C(21)	107.7(2)	Pt(1)–Se(2)–C(11)	109.3(2)

transfer transitions from electron-rich chalcogenolate ligand centers to unoccupied metal orbitals (LMCT). The absorptions of the complexes $[Pt(ECH_2CH_2CH_2NMe_2)_2]_n$ are intense and red-shifted in comparison to the corresponding complexes $[PtCl(ECH_2CH_2CH_2NMe_2)]_2$. According to cyclic voltammetry in CH_2Cl_2/0.1 M Bu_4NPF_6, the chelating bridging chalcogenolates in Pt(II) complexes **1** are oxidized irreversibly. The anodic peak potentials >0.9 V for **1a** and **1b** show that they are hard to oxidize, but in case of thiolate compound **1a** rather facile oxidation takes place in comparison to selenolate derivative **1b**. The smaller reduction potential (−1.76 V) of hexameric $[Pt(SCH_2CH_2CH_2NMe_2)_2]_6$ (**2a**) compared to dimeric $[PtCl(SCH_2CH_2CH_2NMe_2)]_2$ (**1a**) may be explained due to increased orbital interaction of the metal based LUMO which shifts to lower energy in the case of **2a**.

3.3. Crystal structures of *1b* and *5a*

The structure of $[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1b**) was confirmed by single crystal X-ray diffraction methods. The ORTEP plot with atomic numbering scheme is shown in Fig. 4 and the selected bond lengths and angles are given in Table 2. The structure of the title complex **1b** is isomorphous to those of the corresponding palladium derivatives, $[PdCl(ECH_2CH_2CH_2NMe_2)]_2$ (E = S, Se or Te) [19,21]. The molecule comprises of two distorted square planar platinum atoms bridged together by two selenolate groups of symmetrically chelated $SeCH_2CH_2CH_2NMe_2$ ligands. The coordination environment around each platinum atom is defined by two Se, one N and one Cl atoms. The two chloride ligands are mutually *trans*. The four-membered Pt_2Se_2 ring is non-planar. The various bond lengths and angles in the "$PtClNSe_2$" fragments are comparable. The two Pt–Se distances trans to N and trans to Cl are essentially similar. The Pt–Cl [17,18,30], Pt–N [17,18,30], Pt–Se [17,18,30] and Se–C [21] distances are well within the range reported earlier. The Se–Pt–Se angles (80°) have reduced considerably from the ideal value of 90°, consequently other angles have opened up.

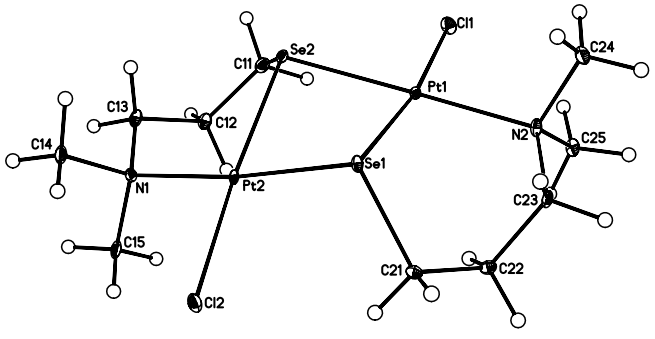


Fig. 4. Molecular structure of $[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$ (**1b**) with atomic numbering scheme.

The molecular structure of $[PtCl(SCH_2CH_2CH_2NMe_2)(PPr_3)]_2$ (**5a**), established by the X-ray diffraction method, is illustrated in Fig. 5. Selected bond lengths and bond angles are given in Table 3. The molecule is a centrosymmetric dimer comprising two distorted square planar platinum atoms bridged together by thiolate groups. The molecule has a sym-*trans* configuration with a planar four-membered "Pt_2S_2" ring, the bridging $SCH_2CH_2CH_2NMe_2$ groups adopt an *anti* configuration with respect to each other. Owing to high *trans* influence of phosphine ligand, the Pt–S distances *trans* to P are longer than the one *trans* to Pt–Cl. Various other bond angles around each platinum atom are as expected for $[Pt_2Cl_2(\mu\text{-}ER)_2(PR_3)_2]$ (E = S or Se) [27,31].

In conclusion, the chemistry of platinum(II) *N*,*N*-dimethylaminopropylchalcogenolates differs markedly from the corresponding palladium derivatives both in terms of stability and lability. While the platinum complexes of type **5** are readily isolated, the reactions to isolate palladium counterparts of **5** lead to the formation of a mixture of products. Different bonding modes, viz., chelating, chelating bridging, bridging of *N*,*N*-dimethylaminopropyl chalcogenolates, have been demonstrated.

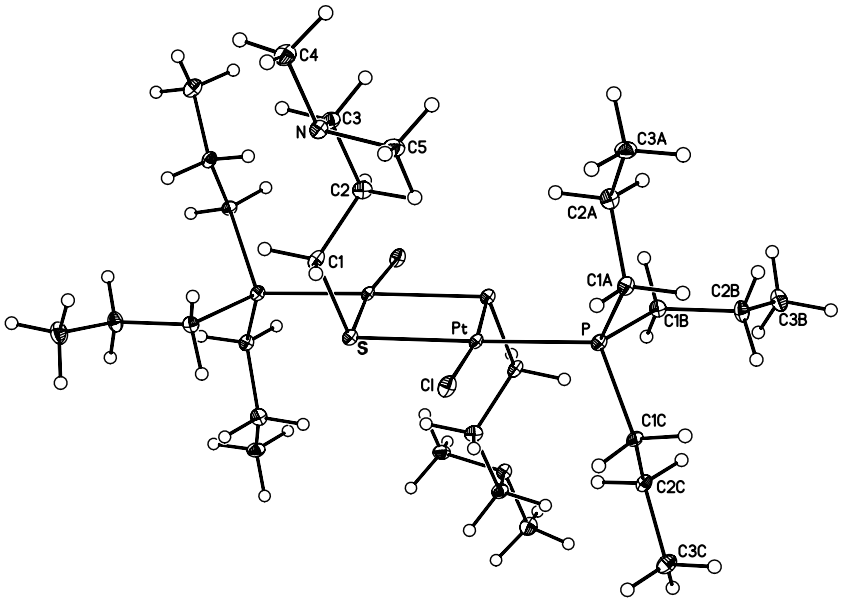


Fig. 5. Molecular structure of $[PtCl(SCH_2CH_2CH_2NMe_2)(PPr_3)]_2$ (**5a**) with atomic numbering scheme.

Table 3
Selected bond lengths (Å) and angles (°) for $[PtCl(SCH_2CH_2CH_2NMe_2)(PPr_3)]_2$ (**5a**)

Pt–P	2.264(2)	C(2)–C(3)	1.520(13)
Pt–S	2.383(2)	N–C(4)	1.466(12)
Pt–S#1	2.310(2)	N–C(5)	1.469(13)
Pt–Cl	2.355(2)	N–C(3)	1.470(12)
S–Pt#1	2.310(2)	P–C(1A)	1.831(9)
S–C(1)	1.845(9)	P–C(1B)	1.822(9)
C(1)–C(2)	1.519(13)	P–C(1C)	1.860(9)
P–Pt–S#1	97.19(8)	C(1)–S–Pt#1	106.7(3)
P–Pt–Cl	89.36(8)	C(1)–S–Pt	100.6(3)
S#1–Pt–Cl	172.98(8)	Pt#1–S–Pt	97.00(8)
P–Pt–S	178.55(9)	Pt–P–C(1A)	112.8(3)
S#1–Pt–S	83.00(8)	Pt–P–C(1B)	116.9(3)
Cl–Pt–S	90.39(7)	Pt–P–C(1C)	112.2(3)

Acknowledgments

We thank Drs. T. Mukherjee and S.K. Kulshreshtha for encouragement of this work. We are grateful to Dr. V.K. Manchanda, Head, Radiochemistry Division, BARC, for providing microanalyses of the complexes. We are also thankful to CDRI, Lucknow, for recording the FAB mass spectra.

Appendix A. Supplementary material

CCDC 616504 and 616503 contain the supplementary crystallographic data for ($[PtCl(SeCH_2CH_2CH_2NMe_2)]_2$) and ($[PtCl(SCH_2CH_2CH_2NMe_2)(PPr_3)]_2$). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.01.002.

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