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# 3-Dimethylaminopropyl chalcogenolate complexes of palladium(II): Syntheses and characterization, including the crystal structures of $[\text{Pd}(\text{OAc})(\text{ECH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2 \cdot \text{H}_2\text{O}$ (E = S, Se) and $[\text{PdCl}(\text{TeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$

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Received 31 August 2005; accepted 16 September 2005

Available online 26 October 2005

## Abstract

The reactions of the sodium salts of 3-dimethylamino-1-propylchalcogenolates, prepared by sodium borohydride reduction of  $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{E})_2$  in methanol, with  $\text{Na}_2\text{PdCl}_4$  yielded homoleptic  $[\text{Pd}(\text{ECH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2]_6$  (**1**) (E = S (**1a**); Se (**1b**); Te (**1c**)). When treated with  $[\text{Pd}(\text{OAc})_2]_3$  or  $\text{Na}_2\text{PdCl}_4$ , compounds **1** readily gave binuclear redistribution products  $[\text{PdX}(\text{ECH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$  where X = OAc (**2**) (E = S (**2a**); Se (**2b**); or Cl (**3**)) (E = S (**3a**); Se (**3b**); Te (**3c**)), respectively. The terminal acetate/chloride ligands in **2b/3b** can be substituted by other ionic ligands like  $\text{PhSe}^-$ . The complexes were characterized by elemental analysis, UV–Vis, IR and NMR spectroscopy. The structures of **2a**, **2b** and **3c** were established by X-ray crystallography. Each molecule has a dimeric structure in which there are two chalcogenolate bridges from the chelating 3-dimethylamino-1-propylchalcogenolate ligands. On pyrolysis, compound **2b** affords  $\text{Pd}_{17}\text{Se}_{15}$ .

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**Keywords:** 3-Dimethylaminopropyl chalcogenolate; Acetate; Palladium(II); Crystal structure; NMR

## 1. Introduction

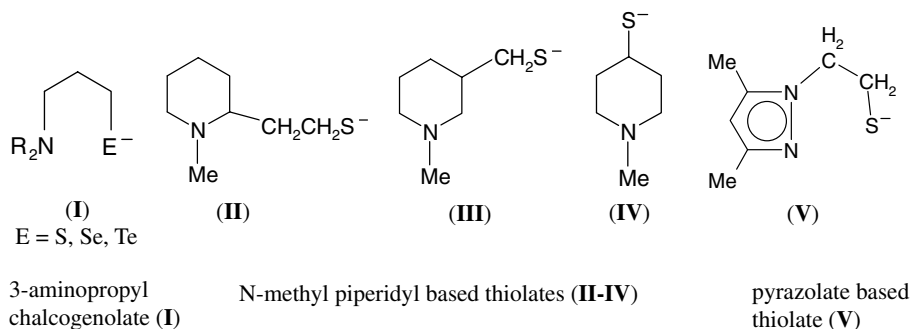
Hemilabile ligands have attracted considerable attention for more than two decades due to their potential applications in catalysis. These ligands contain at least two different types of donor atoms, one of which binds the metal center firmly, while the other donor site is substitutionally labile. Over a period, a wide variety of hemilabile ligands have been designed and synthesized. Among them, internally functionalized thiolates in general and aminoalkylthi-

olates in particular constitute an interesting family of ligands which have not only shown versatile coordination chemistry [1–6], but also exhibited high catalytic activities [6,7]. The structures of their complexes are greatly influenced by the nature of the metal ion, the number of intervening atoms separating the N and S centers, and the substituents on the N atom. Internal functionalization of chalcogenolate ligands assists in suppressing polymerization of the metal complexes and consequently makes them promising candidates as precursor molecules for the synthesis of metal chalcogenides.

The palladium and platinum complexes with thiolates in which S and N are separated with three intervening atoms (e.g., **I** [8–11], **II** [12], **III** [13], **IV** [14,15] and **V** [16])

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Scheme 1.

(Scheme 1) have been investigated. In general, these ligands act as a simple thiolate, however, in  $[MCl(S^{\sim}N)]_2$  ( $M = Pd$  or  $Pt$ ;  $S^{\sim}N = I-V$ ) they function as chelating bridging ligands. The chemistry of the heavier analog of **I** ( $E = Se$ ) has been explored only recently by us [17]. We carried out a reaction between  $[Pd(OAc)_2]_3$  and  $[Pd(SeCH_2CH_2CH_2NMe_2)_2]_6$  [18] with the hope of isolating a new structural motif as the substitution of acetate either in trimeric  $[Pd(OAc)_2]_3$  with ethyl(methylthio)acetate [19] or in tetrameric  $[Pt(OAc)_2]_4$  with diethyldithiophosphate [20] results in the formation of  $[Pd_3(OAc)_3(\mu, \eta^2-MeSCHCOOEt)_3]$  or  $[Pt_4(OAc)_4\{S_2P(OEt)_2\}_4]$ , respectively. Surprisingly, the complex of composition  $[Pd(OAc)(SeCH_2CH_2CH_2NMe_2)]_n$ , isolated from our reaction is dimeric as shown by X-ray crystallography. We have further extended the work with **I**, where  $E = S, Se, Te$ , and the results are summarized herein.

## 2. Experimental

All reactions were carried out under a nitrogen atmosphere using conventional Schlenk techniques. Solvents were dried by standard methods with subsequent distillation under nitrogen. Tellurium and  $Me_2NCH_2CH_2CH_2Cl \cdot HCl$  were obtained from commercial sources. The compound  $(Me_2NCH_2CH_2CH_2Se)_2$  and  $Na_2PdCl_4$  were prepared according to the literature methods [2]. Melting points were determined in capillary tubes and are uncorrected. Elemental analyses were carried out by the Analytical Chemistry Division of B.A.R.C.  $^1H$ ,  $^{13}C\{^1H\}$ ,  $^{77}Se\{^1H\}$  and  $^{125}Te\{^1H\}$  NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer operating at 300, 75.47, 57.24 and 94.86 MHz, respectively. Chemical shifts are relative to the internal chloroform peak at  $\delta$  7.26 ppm for  $^1H$  and  $\delta$  77.0 ppm for  $^{13}C\{^1H\}$ ,  $Me_2Se$  for  $^{77}Se\{^1H\}$  and  $[Te(dtc)_2]$  ( $\delta = 0$  ppm;  $dtc = N,N$ -diethyldithiocarbamate) for  $^{125}Te\{^1H\}$ . A  $90^\circ$  pulse was used in every case. 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. Thermogravimetric analyses (TGA) were carried out on a Setaram 92-16-18 instrument which was calibrated with  $CaC_2O_4 \cdot H_2O$ . The TG curves were recorded at a

heating rate of  $10^\circ C/min$  under a flow of argon. X-ray powder diffraction was measured using  $Cu K\alpha$  radiation. EDAX photographs were taken on a JEOL JSM-T330A instrument.

### 2.1. Synthesis

#### 2.1.1. Preparation of bis[3-(*N,N*-dimethylamino)propyl]-disulfide, $[(Me_2NCH_2CH_2CH_2S)_2]$

Bis(3-dimethylaminopropyl)disulfide was prepared in an analogous manner to  $(Me_2NCH_2CH_2CH_2Se)_2$  [2], using  $Me_2NCH_2CH_2CH_2Cl$  (40.41 g, 332 mmol) and  $Na_2S_2$  (18.30 g, 166 mmol). The liquid was distilled in vacuo ( $160^\circ C/2$  mm Hg) to give a pale-yellow liquid (22 g, 56% yield). Spectroscopic data are given in Table 1.

#### 2.1.2. Preparation of bis[3-(*N,N*-dimethylamino)propyl]-ditelluride, $[(Me_2NCH_2CH_2CH_2Te)_2]$

The title compound was prepared from  $K_2Te_2$  (37.96 g, 114 mmol) and  $Me_2NCH_2CH_2CH_2Cl$  (27.63 g, 227 mmol) in a manner similar to the preparation of  $(Me_2NCH_2CH_2CH_2Se)_2$  [2], in 58% yield (28 g) as a dark red oil. This oil on attempted distillation under vacuum led to excessive decomposition (formation of  $Te$  metal). Therefore, the crude dark red oil was extracted with hexane and cooled at  $-5^\circ C$  overnight. A white insoluble part separated in variable yields and was not characterized. The hexane solution was passed through a Florisil column and the solvent was evaporated under vacuum to give a red liquid (18 g, 37% yield) which was found to be spectroscopically pure (Table 1).

#### 2.1.3. Preparation of $[Pd(SCH_2CH_2CH_2NMe_2)_2]_6$

To a methanolic solution ( $10\text{ cm}^3$ ) of  $NaSCH_2CH_2CH_2NMe_2$  (prepared by  $NaBH_4$  (104 mg, 2.74 mmol), reduction of  $(Me_2NCH_2CH_2CH_2S)_2$  (318 mg, 1.34 mmol) in methanol), a solution of  $Na_2PdCl_4$  (395 mg, 1.34 mmol) in methanol was added which was followed by addition of  $20\text{ cm}^3$  of acetone. The mixture was stirred for 4 h at room temperature. The solvents were evaporated under vacuum and the residue was extracted with hexane ( $3 \times 25\text{ cm}^3$ ). The brown solution was filtered through a G-3 filter. The filtrate was concentrated to  $15\text{ cm}^3$  and was passed through a Florisil column. Few drops of

Table 1

Spectroscopic data for 3-dimethylaminopropyl chalcogenolate ( $E^{\ominus}N = Me_2NCH_2CH_2CH_2E$ ;  $E = S, Se, Te$ ) complexes of palladium(II)

Complex	NMR $\delta$ in ppm in $CDCl_3$			UV–Vis <sup>a</sup>	IR in $cm^{-1}$
	$^1H$	$^{13}C\{^1H\}$	$^{77}Se\{^1H\}/^{125}Te\{^1H\}$		
$(Me_2NCH_2CH_2CH_2S)_2$	1.85 (m, C–CH <sub>2</sub> –C); 2.22 (s, NMe <sub>2</sub> ); 2.35 (t, 7 Hz, NCH <sub>2</sub> –); 2.72 (t, 7 Hz, SCH <sub>2</sub> )	27.2 (s, C–CH <sub>2</sub> –); 36.8 (s, –CH <sub>2</sub> –); 45.3 (s, NMe <sub>2</sub> ); 58.2 (s, NCH <sub>2</sub> )		282 (180)	
$(Me_2NCH_2CH_2CH_2Se)_2$	1.90 (m, C–CH <sub>2</sub> –C); 2.20 (s, NMe <sub>2</sub> ); 2.35 (t, 7 Hz, NCH <sub>2</sub> ); 2.95 (t, 7 Hz, SeCH <sub>2</sub> )	28.2 (SeCH <sub>2</sub> ); 29.2 (s, C–CH <sub>2</sub> ); 45.4 (s, NMe <sub>2</sub> ); 59.3 (s, NCH <sub>2</sub> )	316	301 (770)	
$(Me_2NCH_2CH_2CH_2Te)_2$	1.87 (m, C–CH <sub>2</sub> –C); 2.22 (s, NMe <sub>2</sub> ); 2.40 (t, 6.6 Hz, NCH <sub>2</sub> –); 3.21 (t, 7.0 Hz, TeCH <sub>2</sub> )	2.4 (s, TeCH <sub>2</sub> –); 30.5 (s, –CH <sub>2</sub> –); 45.6 (s, NMe <sub>2</sub> ); 61.2 (s, NCH <sub>2</sub> )	–653 <sup>b</sup>	355 (586)	
$[Pd(OAc)_2]_3$	1.98 (s, CH <sub>3</sub> )	22.7 (s, CH <sub>3</sub> ); 188.5 (s, C=O)		398 (255)	1601, 1564
$[Pd(S^{\ominus}N)_2]_6$	2.21 (br, –CH <sub>2</sub> –); 2.26 (s, NMe <sub>2</sub> ); 2.33, 2.40 (each br, NCH <sub>2</sub> /SCH <sub>2</sub> )	30.7 (s, CH <sub>2</sub> ); 33.0 (s, SCH <sub>2</sub> ); 45.5 (s, NMe <sub>2</sub> ); 58.8 (s, NCH <sub>2</sub> )		258, 380	
$[Pd(Se^{\ominus}N)_2]_6$	1.93–2.05 (m, SeC–CH <sub>2</sub> ); 2.21, 2.23 (each s, NMe <sub>2</sub> ); 2.32–2.56 (m, NCH <sub>2</sub> , SeCH <sub>2</sub> )	20.7, 24.7 (each s, SeCH <sub>2</sub> ); 30.8, 32.6 (each s, SeC–CH <sub>2</sub> ); 45.5 (s, NMe <sub>2</sub> ); 59.3, 59.5 (s, NCH <sub>2</sub> )	–31, –161	298 (13800), 338 (9900), 440 (5000)	
$[Pd(Te^{\ominus}N)_2]_6$	decompose			316 (4450), 454 (4500)	
$[PdCl(S^{\ominus}N)]_2$	2.32 (m, CH <sub>2</sub> ); 2.46 (t, 5 Hz, NCH <sub>2</sub> ); 2.75, 2.72 (each s, NMe <sub>2</sub> ); 3.12 (m, SCH <sub>2</sub> )	26.8 (s, SCH <sub>2</sub> ); 28.7 (s, SCH <sub>2</sub> CH <sub>2</sub> ); 50.8, 52.1 (each s, NMe <sub>2</sub> ); 63.1 (s, NCH <sub>2</sub> )		285 (11400), 325 (sh), 368 (2100)	291
$[PdCl(Se^{\ominus}N)]_2$	1.93–2.48 (m, NCH <sub>2</sub> CH <sub>2</sub> ); 2.66, 2.74 (each s, NMe <sub>2</sub> ); 3.46–3.52 (m, SeCH <sub>2</sub> )	22.6 (s, $^1J(^{77}Se-^{13}C) = 64$ Hz, SeCH <sub>2</sub> ); 27.9 (s, SeCH <sub>2</sub> –CH <sub>2</sub> , $^2J(Se-C) = 35$ Hz); 50.0, 52.4 (each s, NMe <sub>2</sub> ); 65.1 (s, NCH <sub>2</sub> )	18	298 (10000), 335 (sh), 370 (sh)	
$[PdCl(Te^{\ominus}N)]_2$				324, 390	
$[Pd(OAc)(S^{\ominus}N)]_2^d$	1.97 (OAc); 2.47, 2.70 (each s, NMe <sub>2</sub> ); 2.26 (m, CCH <sub>2</sub> ); 2.76 (m, NCH <sub>2</sub> ); 2.95 (t, SCH <sub>2</sub> )	23.9 (s, OAc); 26.7, 27.0 (each s, –CH <sub>2</sub> –/SCH <sub>2</sub> ); 50.8 (s, NMe <sub>2</sub> ); 63.1 (s, NCH <sub>2</sub> ); 177.0 (C=O)		278 (12200), 351 (2300), 430 (sh)	1580
$[Pd(OAc)(Se^{\ominus}N)]_2^d$	1.95 (s, OAc); 2.45, 2.67 (each s, NMe <sub>2</sub> ); 2.90–2.94 (m, SeCH <sub>2</sub> ); 2.61–2.75 (br, m, NCH <sub>2</sub> ); 2.25 (NCCH <sub>2</sub> )	19.4 (CH <sub>2</sub> ); 23.7 (OAc); 27.7 (s, SeCH <sub>2</sub> ); 50.0, 51.5 (NMe <sub>2</sub> ); 64.4 (NCH <sub>2</sub> ); 176.7 (C=O)	–32	287 (19000), 291 (19000), 373 (sh), 442 (sh)	1613
$[Pd(SePh)(Se^{\ominus}N)]_n^c$	2.15 (with a very broad base); 7.10 (br); 7.94 (br)	24.8 (br, –CH <sub>2</sub> –); 32.6 (br, SeCH <sub>2</sub> ); 45.7 (s, NMe <sub>2</sub> ); 59.6 (s, NCH <sub>2</sub> ); 126.8, 128.2, 131.2 (C-1); 135.9 [Ph]		299 (11600), 363 (sh), 419 (13200)	

<sup>a</sup> Wavelengths  $\lambda_{max}$  at the absorption maxima in nm, molar extinction coefficients in  $M^{-1} cm^{-1}$ .<sup>b</sup> Recorded in acetone- $d_6$ .<sup>c</sup> Spectra show broad resonances.<sup>d</sup> A broad peak appears at 1.69 due to coordinated water molecule, another peak appeared at 2.10 and could not be assigned.

pentane were added to yield (286 mg, 62%) a pasty solid at  $-5^{\circ}\text{C}$ . Analogous Se and Te complexes were prepared similarly. Only prolonged cooling could give a crystalline product. The tellurium complex decomposed on standing and hence satisfactory analysis could not be done.

#### 2.1.4. Preparation of $[\text{PdCl}(\text{TeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$

To a stirred methanolic solution ( $20\text{ cm}^3$ ) of  $\text{Na}_2\text{PdCl}_4$  (731 mg, 2.48 mmol) was added a methanolic solution of  $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Te})_2$  (531 mg, 1.24 mmol). A brownish yellow precipitate formed immediately. The reaction mixture was stirred for 3 h. The solvent was evaporated under vacuum and the residue was washed with hexane and methanol ( $25\text{ cm}^3$ ). The residue was extracted with acetonitrile, filtered and dried under vacuum, to give an orange solid (238 mg, 27%). Analytical data are given in Table 2.

#### 2.1.5. Preparation of $[\text{Pd}(\text{OAc})(\text{SCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2 \cdot \text{H}_2\text{O}$

An acetone solution ( $5\text{ cm}^3$ ) of  $[\text{Pd}(\text{OAc})_2]_3$  (144 mg, 0.214 mmol) was added to a toluene solution ( $10\text{ cm}^3$ ) of  $[\text{Pd}(\text{SCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2]_6$  (153 mg, 0.074 mmol). The reddish reaction mixture was stirred for 4 h. The solvents were stripped off in vacuum. The residue was washed with hexane and extracted with toluene ( $3 \times 8\text{ cm}^3$ ). The red solution was filtered and concentrated to  $2\text{ cm}^3$ . Few drops of acetone and hexane were added and cooled at  $-5^{\circ}\text{C}$  to yield a yellow crystalline product (166 mg, 56%). Single crystals were obtained from the supernatant at  $-5^{\circ}\text{C}$  after 2 days.  $[\text{Pd}(\text{OAc})(\text{SeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$  was prepared in an analogous manner.

#### 2.1.6. Preparation of $[\text{Pd}(\text{SePh})(\text{SeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_n$

A dichloromethane solution ( $20\text{ cm}^3$ ) of  $[\text{PdCl}(\text{SeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$  (104 mg, 0.34 mmol) was added to a freshly prepared methanolic solution ( $5\text{ cm}^3$ ) of  $\text{NaSePh}$  (prepared by  $\text{NaBH}_4$  (28 mg, 0.74 mmol) and reduction of  $\text{Ph}_2\text{Se}_2$  (108 mg, 0.34 mmol) in methanol). The color of the reaction mixture immediately changed to dark chocolate. The reactants were stirred for 3 h. The solvents were stripped off in vacuo, the residue was washed with hexane and the residue was extracted with toluene ( $3 \times 10\text{ cm}^3$ ). The solution

was concentrated to  $5\text{ cm}^3$  and a few drops of hexane were added to yield (64 mg, 44%) a chocolate colored powder.

#### 2.1.7. Reaction between $\text{NaTeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ and $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PEt}_3)_2]$

To a methanolic solution ( $10\text{ cm}^3$ ) of  $\text{NaTeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$  (prepared from  $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Te})_2$  (124 mg, 0.29 mmol) and  $\text{NaBH}_4$  (22 mg, 0.58 mmol) in methanol), an acetone ( $10\text{ cm}^3$ ) suspension of  $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PEt}_3)_2]$  (170 mg, 0.29 mmol) was added with vigorous stirring which was continued for 4 h. The solvents were evaporated in vacuo and the residue was extracted with hexane ( $3 \times 10\text{ cm}^3$ ), followed by extraction with acetone ( $3 \times 8\text{ cm}^3$ ). Both hexane and acetone fractions were passed through a Florisil column and the yellow solution was dried under vacuum to give a yellow solid. M.p.  $130^{\circ}\text{C}$ . Anal. Calc. for  $\text{C}_{12}\text{H}_{30}\text{Cl}_2\text{P}_2\text{Pd}$ : C, 34.8; H, 7.3. Found: C, 33.6; H, 7.2; N,  $<0.2\%$ .  $^1\text{H}$  NMR in acetone- $d_6$   $\delta$ : 1.18 (m, PC- $\text{CH}_3$ ); 1.84–1.88 (m, PCH $_2$ ),  $^{31}\text{P}\{^1\text{H}\}$  in acetone- $d_6$   $\delta$ : 18.6 ppm. Similarly, the reaction of  $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PPh}_3)_2]$  with  $\text{NaTeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$  was carried out and a mixture of products formed from which  $\text{PdCl}_2(\text{PPh}_3)_2$  was isolated [Anal.: Calc. for  $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{P}_2\text{Pd}$ : C, 61.6; H, 4.3. Found C, 60.2; H, 4.7; N, 0.4%.  $^{31}\text{P}\{^1\text{H}\}$  in acetone- $d_6$   $\delta$ : 23.7 ppm].

#### 2.2. X-ray crystallography

X-ray data on single crystals of  $[\text{Pd}(\text{OAc})(\text{SCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2 \cdot \text{H}_2\text{O}$  (**2a** ·  $\text{H}_2\text{O}$ ),  $[\text{Pd}(\text{OAc})(\text{SeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2 \cdot \text{H}_2\text{O}$  (**2b** ·  $\text{H}_2\text{O}$ ) and  $[\text{PdCl}(\text{TeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$  (**3c**) were collected using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ), employing the  $\omega$ – $2\theta$  scan technique. Crystal data are given in Table 3 [21–24]. The unit cell parameters were determined from 25 reflections measured by random search routine and indexed by the method of short vectors followed by least-squares refinement. The intensity data were corrected for Lorentz, polarization and absorption effects [25]. The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$ . The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were introduced using the appropriate riding model.

Table 2

Physical and analytical data for 3-dimethylaminopropyl chalcogenolate ( $\text{E}^-\text{N} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{E}$ ; E = S, Se, Te) complexes of palladium(II)

Complex	Recrystallization solvent (% yield)	Color/m.p. ( $^{\circ}\text{C}$ )	% Analysis Found (Calcd.)		
			C	H	N
$[\text{Pd}(\text{S}^-\text{N})_2]_6^a$	hexane (62)	brown/paste	34.7 (35.0)	7.1 (7.1)	7.9 (8.2)
$[\text{Pd}(\text{Se}^-\text{N})_2]_6$	hexane–pentane (40)	brown–red/102	26.4 (27.5)	5.3 (5.5)	5.3 (6.4)
$[\text{Pd}(\text{Te}^-\text{N})_2]_6$	hexane (28)	brown/paste	17.7 (22.5)	3.8 (4.5)	3.8 (5.2)
$[\text{PdCl}(\text{S}^-\text{N})]_2$	dichloromethane (21)	orange–red/180 (d)	22.8 (23.1)	4.4 (4.7)	5.5 (5.4)
$[\text{PdCl}(\text{Se}^-\text{N})]_2$	dichloromethane–acetone (38)	orange–red/205 (d)	19.3 (19.6)	3.6 (3.9)	5.0 (4.6)
$[\text{PdCl}(\text{Te}^-\text{N})]_2$	acetonitrile (27)	red/106	16.5 (16.9)	3.6 (3.4)	4.2 (3.9)
$[\text{Pd}(\text{OAc})(\text{S}^-\text{N})]_2 \cdot \text{H}_2\text{O}$	acetone–hexane (56)	brown/160 (d)	28.3 (28.7)	6.1 (5.5)	4.7 (4.8)
$[\text{Pd}(\text{OAc})(\text{Se}^-\text{N})]_2 \cdot \text{H}_2\text{O}$	toluene–hexane (51)	orange–red/156 (d)	24.7 (24.8)	4.9 (4.7)	4.1 (4.1)
$[\text{Pd}(\text{SePh})(\text{Se}^-\text{N})]_n$	toluene–hexane (44)	red/96 (d)	30.9 (30.9)	4.9 (4.0)	3.1 (3.3)

<sup>a</sup> S: Found 18.0; Calc. 18.7.

Table 3  
Crystallographic and structure refinement data for **2a** · H<sub>2</sub>O, **2b** · H<sub>2</sub>O and **3c**

	<b>2a</b> · H <sub>2</sub> O	<b>2b</b> · H <sub>2</sub> O	<b>3c</b>
Chemical formula	C <sub>14</sub> H <sub>32</sub> N <sub>2</sub> O <sub>5</sub> Pd <sub>2</sub> S <sub>2</sub>	C <sub>14</sub> H <sub>32</sub> N <sub>2</sub> O <sub>5</sub> Pd <sub>2</sub> Se <sub>2</sub>	C <sub>10</sub> H <sub>24</sub> Cl <sub>2</sub> N <sub>2</sub> PdTe <sub>2</sub>
Diffractionmeter model	Nonius CAD4	Rigaku AFC-6S	Siemens P4
Formula weight	585.34	679.14	711.21
Crystal size (mm <sup>3</sup> )	0.2 × 0.2 × 0.1	0.56 × 0.35 × 0.10	0.35 × 0.30 × 0.10
Temperature (K)	293(2)	103(2)	173(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n
<i>Unit cell dimensions</i>			
<i>a</i> (Å)	12.5451(13)	12.522(3)	10.765(2)
<i>b</i> (Å)	12.1990(13)	12.304(3)	8.6628(17)
<i>c</i> (Å)	15.649(3)	15.465(3)	19.491(4)
β (°)	111.293(13)	113.23(2)	98.05(3)
Volume (Å <sup>3</sup> )	2231.4(5)	2189.5(8)	1799.8(6)
Density calcd. (g cm <sup>−3</sup> )	1.742	2.060	2.625
Z	4	4	4
μ (mm <sup>−1</sup> )/F(000)	1.822/1176	4.992/1320	
θ for data collection (°)	2.18 to 24.98	2.19 to 28.32	2.11 to 27.02
Limiting indices	−14 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 14, −1 ≤ <i>l</i> ≤ 18	−14 ≤ <i>h</i> ≤ 16, −14 ≤ <i>k</i> ≤ 16, −20 ≤ <i>l</i> ≤ 20	−13 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 11, 0 ≤ <i>l</i> ≤ 24
Goodness of fit on F <sup>2</sup>	1.132	1.027	1.091
Absorption correction	ψ scan	semi-empirical from equivalents	empirical, XABS2
Reflections collected/unique	3922/2772	16407/5355	3900/3186
Data/restraints/parameters	2772/2/235	5355/3/232	3186/0/167
Final R <sub>1</sub> , wR <sub>2</sub> indices	0.0377, 0.1094	0.0302, 0.0734	0.0509, 0.1216
R <sub>1</sub> , wR <sub>2</sub> (all data)	0.0721, 0.1270	0.0383, 0.0769	0.0678, 0.1333
Computer programs used	SHELXS 86 [21], SHELXL 97 [22]	TEXSAN [23]	SHELXTL-5.1 [24]

### 3. Results and discussion

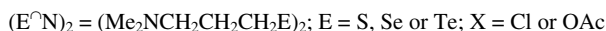
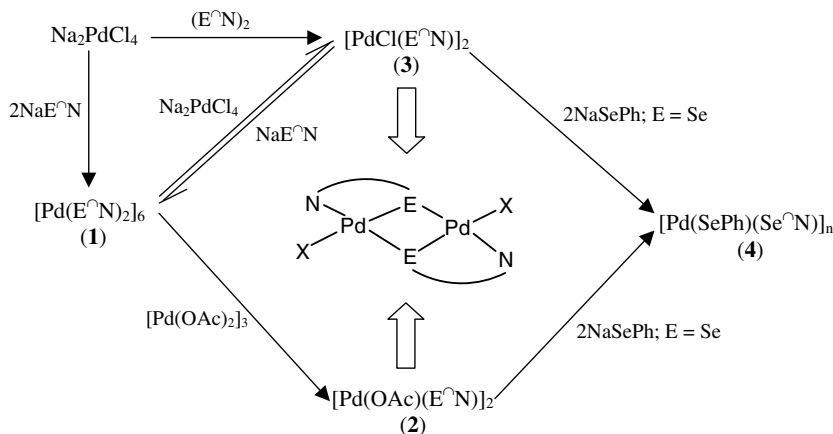
#### 3.1. Synthesis and spectroscopy

Bis(3-dimethylamino-1-propyl)dichalcogenides (Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>E) (E = S or Te) were prepared by the reaction of Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl with Na<sub>2</sub>S<sub>2</sub> or K<sub>2</sub>Te<sub>2</sub> in a manner similar to the synthesis of (Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Se)<sub>2</sub> [17]. The disulfide and diselenide could be distilled under vacuum as yellow and orange-red liquids, respectively, whereas the ditelluride, a dark red oil, decomposed on attempted distillation. The NMR spectra (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) displayed the expected resonances (Table 1). The <sup>77</sup>Se{<sup>1</sup>H} and <sup>125</sup>Te{<sup>1</sup>H} NMR spectra exhibited only a single signal. These signals appeared within the range reported for R<sub>2</sub>E<sub>2</sub> (E = Se or Te) [26].

Synthetic routes for palladium(II) 3-dimethylamino-1-propylchalcogenolates are illustrated in Scheme 2. The homoleptic palladium complexes, [Pd(ECH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]<sub>n</sub> (**1**) (E = S (**1a**); Se (**1b**) or Te (**1c**)), have been prepared by the reaction of Na<sub>2</sub>PdCl<sub>4</sub> with two equivalents of NaECH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> in methanol–acetone. Compound **1b** has been reported to have hexameric structure (from FAB mass spectrometry and X-ray crystallography) [11,17]. The spectroscopic data of **1a** and **1c** are similar to those of **1b**, suggesting that all these complexes have a hexameric structure. Compound **1c** tends to decompose when left in solution, and hence no satisfactory microanalyses and NMR spectra could be obtained.

When treating complex **1** with Pd(OAc)<sub>2</sub> or Na<sub>2</sub>PdCl<sub>4</sub>, the formation of redistribution products [Pd(OAc)(ECH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]<sub>n</sub> (**2**) (E = S (**2a**) or Se (**2b**)) and [PdCl(ECH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (**3**) (E = S (**3a**); Se (**3b**) or Te (**3c**)), respectively, was observed. Compounds **3** can also be obtained by the reaction of Na<sub>2</sub>PdCl<sub>4</sub> with (Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>E)<sub>2</sub> in methanol as sparingly soluble powders. Compounds **3a** [11] and **3b** [17] have been reported earlier and their dimeric structures have been established by X-ray crystallography. Like **1c**, **2c** and **3c** decompose in solution, most and rapidly in chlorinated solvents (e.g., CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>). The tellurolate complexes of palladium and platinum are also known to decompose in halogenated solvents [27]. Compound **3c**, however, could be stored in the solid state for several days without any apparent decomposition and hence could be characterized crystallographically. The reactions of **2b** and **3b** with Na-SePh gave [Pd(SePh)(SeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]<sub>n</sub> (**4**). The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **2** and **3** displayed the expected resonances and peak multiplicities. The methyl groups on NMe<sub>2</sub> are anisochronous as two separate resonances are observed both in the <sup>1</sup>H and <sup>13</sup>C NMR spectra. One of the methyl resonances of the NMe<sub>2</sub> group in the <sup>1</sup>H NMR spectra is considerably shielded (~2.45 ppm) for the acetato complexes (**2**) as compared to its position for the corresponding chloro complexes (**3**) (~2.70 ppm) (Table 1). This may be attributed to the anisotropic effect of the carbonyl group on the methyl protons which lie below the C=O group, according to the X-ray structural result.





Interconversion of palladium chalcogenolates

Scheme 2.

The reactions of  $[Pd_2Cl_2(\mu-Cl)_2(PR_3)_2]$  with  $NaECHR'-CH_2NMe_2$  ( $R' = H$  or  $Me$ ) have been reported to yield  $[PdCl(ECHR'CH_2NMe_2)(PR_3)]$  ( $E = S, Se, Te$ ) [1–3]. To assess whether 3-dimethylamino-1-propylchalcogenolate can be used in a similar manner, the reactions of  $NaECH_2CH_2CH_2NMe_2$  ( $E = Se, Te$ ) with  $[Pd_2Cl_2(\mu-Cl)_2(PR_3)_2]$  were carried out. In each case, a mixture of products was formed as revealed by  $^{31}P$  NMR spectroscopy. From the reaction of  $[Pd_2Cl_2(\mu-Cl)_2(PMePh_2)_2]$  with  $NaSeCH_2CH_2CH_2NMe_2$  (**3b**) could be separated [17]. The reaction of  $NaTeCH_2CH_2CH_2NMe_2$  with  $[Pd_2Cl_2(\mu-Cl)_2(PR_3)_2]$  ( $PR_3 = PEt_3, PPh_3$ ) gave a mixture of products and from this mixture at least  $PdCl_2(PR_3)_2$  ( $R = Et$  or  $Ph$ ) could be isolated and characterized by microanalysis and NMR ( $^1H$  and  $^{31}P$ ) spectral data.

### 3.2. Electronic spectra

The absorption spectra of the complexes display long wavelength bands in dichloromethane (Table 1). These absorptions can be assigned as charge transfer transitions from electron-rich chalcogenolate ligand centers to unoccupied metal orbitals (LMCT). The absorptions of the complexes  $[Pd(ECH_2CH_2CH_2NMe_2)_2]_6$  are intense and red-shifted in comparison to the corresponding complexes  $[PdCl(ECH_2CH_2CH_2NMe_2)_2]$ . The absorptions of the acetato complexes **2** are considerably red-shifted in comparison to corresponding chloro derivatives **3**.

### 3.3. Crystal structures of $[Pd(OAc)(ECH_2CH_2CH_2NMe_2)]_2 \cdot H_2O$ ( $E = S$ or $Se$ )

The structures of  $[Pd(OAc)(ECH_2CH_2CH_2NMe_2)]_2$  ( $E = S$  or  $Se$ ), which crystallized with one molecule of water, were confirmed by single crystal X-ray diffraction methods. The ORTEP plots with atomic numbering

scheme are shown in Figs. 1 and 2 and the selected bond lengths and angles are given in Tables 4 and 5.

The two structures are isomorphous and can be compared with those of  $[PdCl(ECH_2CH_2CH_2NMe_2)]_2$  ( $E = S$  [11] and  $Se$  [17]) and  $[PdCl(SC_8H_{16}N)]_2$  [12]. The two distorted square planar palladium atoms in each molecule are held together by asymmetric chalcogenolato-bridges. Each palladium atom is surrounded by one oxygen atom of  $OAc^-$ , one nitrogen and two chalcogen atoms. The acetate groups are in *anti* position. One water molecule is hydrogen bonded to the carbonyl oxygen atom of the acetate group. The six-membered chelate rings ( $PdECCCN$ ) are in boat conformation, while the four-membered “ $Pd_2E_2$ ” ring is non-planar.

Although the  $Pd-E$  distances *trans* to  $N$  are longer than those *trans* to the acetate linkages, they are well within the range reported for several complexes [11,12,16,17]. In contrast, the  $Pd-E$  distances in  $[PdCl(ECH_2CH_2CH_2NMe_2)]_2$  are essentially similar [11,12,17]. The  $Pd-O$  distances in

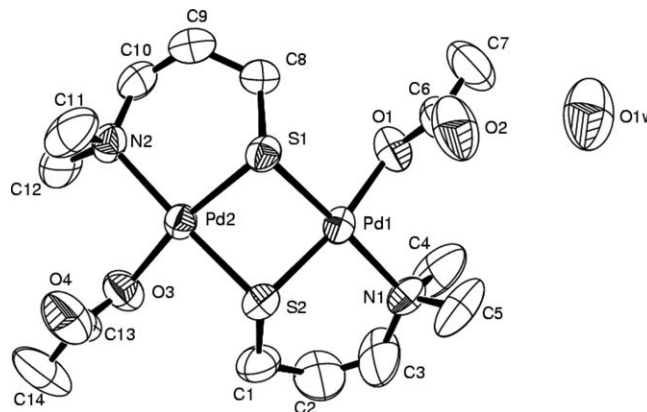


Fig. 1. Molecular structure of  $[Pd(OAc)(SCH_2CH_2CH_2NMe_2)]_2 \cdot H_2O$  with atomic numbering scheme.

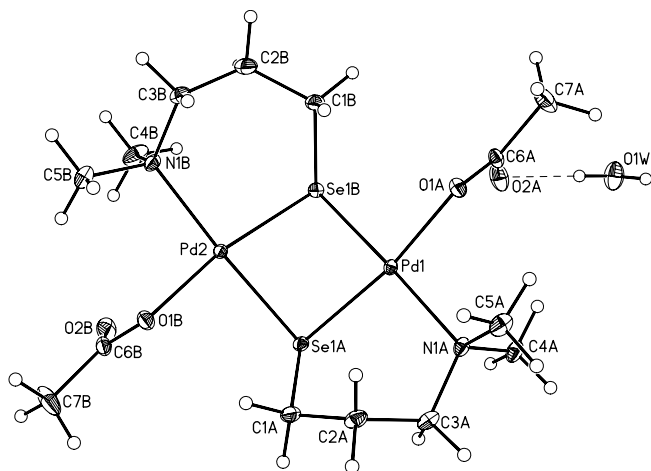


Fig. 2. Molecular structure of  $[\text{Pd}(\text{OAc})(\text{SeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2] \cdot \text{H}_2\text{O}$  with atomic numbering scheme.

Table 4

Selected bond lengths (Å) and angles (°) for  $[\text{Pd}(\text{OAc})(\text{SCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2] \cdot \text{H}_2\text{O}$

Pd(1)–S(1)	2.292(2)	Pd(2)–O(3)	2.066(6)
Pd(1)–S(2)	2.268(2)	Pd(1)–N(1)	2.129(7)
Pd(2)–S(1)	2.263(2)	Pd(2)–N(2)	2.131(7)
Pd(2)–S(2)	2.291(2)	S(1)–C(8)	1.840(9)
Pd(1)–O(1)	2.061(6)	S(2)–C(1)	1.822(10)
C(6)–O(2)	1.220(13)	C(13)–O(4)	1.225(14)
C(6)–O(1)	1.268(11)	C(13)–O(3)	1.264(13)
C(6)–C(7)	1.488(16)	C(13)–C(14)	1.522(15)
S(1)–Pd(1)–S(2)	79.47(8)	S(1)–Pd(2)–S(2)	79.59(8)
S(1)–Pd(1)–O(1)	93.7(2)	S(2)–Pd(2)–O(3)	91.76(19)
S(1)–Pd(1)–N(1)	172.69(19)	S(2)–Pd(2)–N(2)	172.4(2)
S(2)–Pd(1)–N(1)	95.9(2)	S(1)–Pd(2)–N(2)	95.3(2)
S(2)–Pd(1)–O(1)	169.23(19)	S(1)–Pd(2)–O(3)	168.9(2)
N(1)–Pd(1)–O(1)	91.7(3)	N(2)–Pd(2)–O(3)	94.0(3)
Pd(1)–S(1)–Pd(2)	88.16(7)	Pd(1)–S(2)–Pd(2)	88.08(8)
C(6)–O(1)–Pd(1)	121.1(7)	C(13)–O(3)–Pd(2)	117.6(8)
O(2)–C(6)–O(1)	124.1(11)	O(4)–C(13)–O(3)	124.1(10)
O(2)–C(6)–C(7)	120.8(11)	O(4)–C(13)–C(14)	121.6(11)
O(1)–C(6)–C(7)	115.1(11)	O(3)–C(13)–C(14)	114.3(12)
Pd(1)–N(1)–C(3)	116.2(7)	Pd(2)–N(2)–C(10)	115.3(5)
Pd(1)–N(1)–C(4)	112.6(6)	Pd(2)–N(2)–C(11)	106.5(6)
Pd(1)–N(1)–C(5)	105.6(6)	Pd(2)–N(2)–C(12)	109.9(6)
Pd(1)–S(2)–C(1)	107.1(4)	Pd(2)–S(1)–C(8)	106.2(3)
Pd(1)–S(1)–C(8)	108.4(3)	Pd(2)–S(2)–C(1)	109.4(3)

Pd(1)···Pd(2) 3.1689(9).

the two molecules are slightly longer than those reported in  $[\text{Pd}(\text{OAc})_2]_3$  (Pd–O = 1.973–2.014(9) Å) [28] and  $[\text{Pd}(\text{8-hydroxyquinolate})_2]$  (2.02(2) Å) [29], owing to the strong *trans* influence of the chalcogen ligand *trans* to the acetate group. The Pd···Pd separation in acetato complexes (for S: 3.1689(9) Å; Se: 3.289(9) Å) is significantly reduced in comparison to the corresponding chloro analogs (for S: 3.305(1) Å [11]; Se: 3.413(1) Å [17]). The E–Pd–E and Pd–E–Pd angles in the acetato complexes are ~8° and 86–88°, respectively. The corresponding angles in the chloro derivatives have been reported to be 80° and 90–93°, respectively [11,17].

Table 5

Selected bond lengths (Å) and angles (°) for  $[\text{Pd}(\text{OAc})(\text{SeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2] \cdot \text{H}_2\text{O}$

Pd(1)–O(1A)	2.053(3)	Pd(2)–O(1B)	2.078(3)
Pd(1)–N(1A)	2.129(3)	Pd(2)–N(1B)	2.141(3)
Pd(1)–Se(1A)	2.3776(8)	Pd(2)–Se(1B)	2.3742(6)
Pd(1)–Se(1B)	2.3952(6)	Pd(2)–Se(1A)	2.4025(5)
O(1A)–C(6A)	1.255(4)	Se(1A)–C(1A)	1.974(4)
O(2A)–C(6A)	1.260(5)	Se(1B)–C(1B)	1.966(4)
O(1B)–C(6B)	1.292(5)	O(1W)–H(1W1)	0.842(19)
O(2B)–C(6B)	1.232(6)	O(1W)–H(1W2)	0.847(19)
O(1A)–Pd(1)–N(1A)	90.19(11)	O(1B)–Pd(2)–N(1B)	94.76(12)
O(1A)–Pd(1)–Se(1A)	170.18(8)	O(1B)–Pd(2)–Se(1B)	169.07(8)
N(1A)–Pd(1)–Se(1A)	96.41(8)	N(1B)–Pd(2)–Se(1B)	94.57(9)
O(1A)–Pd(1)–Se(1B)	93.80(8)	O(1B)–Pd(2)–Se(1A)	91.01(8)
N(1A)–Pd(1)–Se(1B)	174.02(8)	N(1B)–Pd(2)–Se(1A)	172.84(9)
Se(1A)–Pd(1)–Se(1B)	80.221(17)	Se(1B)–Pd(2)–Se(1A)	80.14(2)
C(1A)–Se(1A)–Pd(1)	103.47(13)	C(1B)–Se(1B)–Pd(2)	102.19(13)
C(1A)–Se(1A)–Pd(2)	106.43(12)	C(1B)–Se(1B)–Pd(1)	105.03(12)
Pd(1)–Se(1A)–Pd(2)	86.97(2)	Pd(2)–Se(1B)–Pd(1)	87.21(2)
C(6A)–O(1A)–Pd(1)	121.1(2)	H(1W1)–O(1W)–H(1W2)	105(3)
C(6B)–O(1B)–Pd(2)	114.6(3)		
O(1A)–C(6A)–O(2A)	124.3(4)	O(1B)–C(6B)–O(2B)	123.9(4)
O(1A)–C(6A)–C(7A)	115.4(4)	O(1B)–C(6B)–O(7B)	114.5(4)
O(2A)–C(6A)–O(7A)	120.1(4)	O(2B)–C(6B)–O(7B)	121.6(4)
Pd(1)–N(1A)–C(3A)	114.9(2)	Pd(2)–N(1B)–C(3B)	116.0(2)
Pd(1)–N(1A)–C(4A)	104.1(2)	Pd(2)–N(1B)–C(4B)	106.2(2)
Pd(1)–N(1A)–C(5A)	111.9(2)	Pd(2)–N(1B)–C(5B)	109.7(3)

### 3.4. Crystal structure of $[\text{PdCl}(\text{TeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2]$

The molecular structure of **3c** is shown in Fig. 3, it is comparable to those of  $[\text{PdCl}(\text{ECH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2]$  (E = S or Se). Two distorted square planar palladium atoms in the molecule are held together by two telluroate bridges of the chelating  $\text{TeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$  ligands. The coordination environment around each palladium atom is defined by two Te atoms, N and Cl. The two chloride ligands are mutually *trans*. The four-membered  $\text{Pd}_2\text{Te}_2$  ring is non-planar. The Pd–Te distances *trans* to N and *trans* to Cl are essentially similar. The Pd–Cl [17,30], Pd–N [17,30] and Pd–Te [2,30] distances (Table 6) are well within the range reported for palladium(II) derivatives.

### 3.5. Thermal studies

These studies were conducted to assess whether these complexes can be used as precursors for the synthesis of palladium chalcogenides, which can find applications in catalysis and in the electronics industry [31]. Thus, the thermal behavior of  $[\text{Pd}(\text{OAc})(\text{SeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2] \cdot \text{H}_2\text{O}$  (**2b**) was investigated. The TG curve (Fig. 4) showed a three step decomposition with a total weight loss of 47.7%, which corresponds to  $\text{Pd}_{17}\text{Se}_{15}$  (calcd. weight loss 48.1%). In the first step of decomposition at 130 °C, the coordinated water molecule is liberated. The second step of decomposition at 175 °C leads to the formation of PdSe (from weight loss 45.6%; calcd. 45.4%), which finally loses some selenium at 260 °C to give the single phase of  $\text{Pd}_{17}\text{Se}_{15}$ . The latter is also obtained when a bulk quantity of **2b** is heated at 300 °C



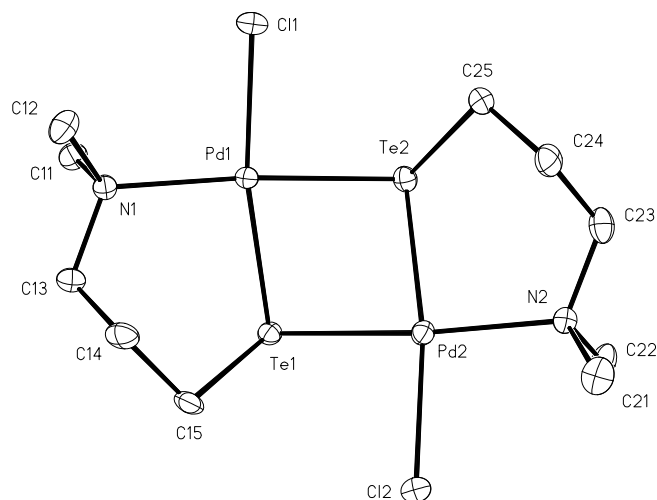


Fig. 3. Molecular structure of  $[\text{PdCl}(\text{TeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2]_2$  with atomic numbering scheme.

Table 6  
Selected bond lengths (Å) and angles (°) for  $[\text{PdCl}(\text{TeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2]_2$

Pd(1)–Te(1)	2.5532(9)	Pd(2)–Te(2)	2.5395(10)
Pd(1)–Te(2)	2.5467(11)	Pd(2)–Te(1)	2.5520(10)
Pd(1)–Cl(1)	2.361(2)	Pd(2)–Cl(2)	2.386(3)
Pd(1)–N(1)	2.174(8)	Pd(2)–N(2)	2.177(8)
Te(1)–C(15)	2.173(10)	Te(2)–C(25)	2.166(10)
Te(1)–Pd(1)–Te(2)	79.36(3)	Te(1)–Pd(2)–Te(2)	79.52(3)
Te(1)–Pd(1)–Cl(1)	169.64(7)	Te(2)–Pd(2)–Cl(2)	170.43(7)
Te(2)–Pd(1)–Cl(1)	90.29(7)	Te(1)–Pd(2)–Cl(2)	90.95(7)
Te(1)–Pd(1)–N(1)	96.0(2)	Te(2)–Pd(2)–N(2)	94.8(2)
Te(2)–Pd(1)–N(1)	175.2(2)	Te(1)–Pd(2)–N(2)	173.4(2)
Cl(1)–Pd(1)–N(1)	94.3(2)	Cl(2)–Pd(2)–N(2)	94.6(2)
Pd(1)–Te(1)–Pd(2)	90.06(3)	Pd(2)–Te(2)–Pd(1)	90.49(3)
Pd(1)–Te(1)–C(15)	98.6(3)	Pd(1)–Te(2)–C(25)	107.8(3)
Pd(2)–Te(1)–C(15)	103.3(3)	Pd(2)–Te(2)–C(25)	100.8(3)

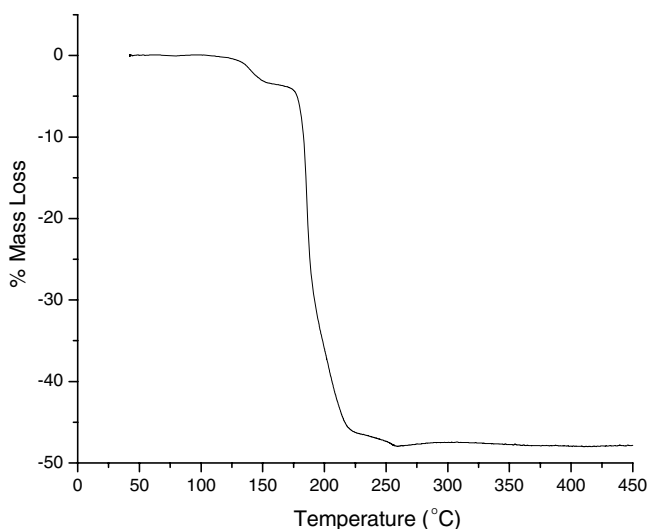


Fig. 4. Thermogravimetric curve of  $[\text{Pd}(\text{OAc})(\text{SeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2] \cdot \text{H}_2\text{O}$ .

under flowing argon atmosphere. The XRD pattern of the residue confirms the formation of  $\text{Pd}_{17}\text{Se}_{15}$  [32].

In conclusion, the chemistry of the 3-dimethylamino-1-propylchalcogenolate ligands differs considerably from that of 2-aminoalkylchalcogenolates, both in terms of coordination behavior and chemical reactivity. The acetato derivatives show promising potential as low temperature decomposition precursors for the synthesis of palladium chalcogenides.

#### 4. Supplementary material

CCDC Nos. 268184 ( $[\text{Pd}(\text{OAc})(\text{SeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2] \cdot \text{H}_2\text{O}$ ), 277357 ( $[\text{Pd}(\text{OAc})(\text{SCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2] \cdot \text{H}_2\text{O}$ ) and 277356 ( $[\text{PdCl}(\text{TeCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_2]$ ) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44 1223/336 033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

#### Acknowledgments

We thank Drs. T. Mukherjee and S.K. Kulshreshtha for encouragement of this work. We are also grateful to Dr. M. Sudershanan, Head, Analytical Chemistry Division, BARC for providing microanalyses of the complexes.

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