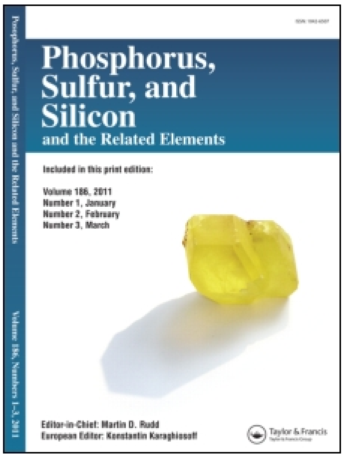

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Chemistry of N,N-Dimethylaminoalkylchalcogenolate Complexes of Palladium(II) and Platinum(II)

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Chemistry of N,N-Dimethylaminoalkylchalcogenolate Complexes of Palladium(II) and Platinum(II)

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Four different series of N,N-dimethylaminoalkylchalcogenolates, viz. $Me_2NCH_2CH_2E^-$, $Me_2NCH(Me)CH_2E^-$, $Me_2NCH_2CH(Me)E^-$, *and* $Me_2NCH_2CH_2CH_2E^-$ *(E = S, Se, Te), (referred as* $E^\cap N$*) have been synthesized and characterized. Their reactions with palladium(II) and platinum(II) precursors have been explored. Complexes of the general formula,* $[MCl(E^\cap N)]_n$, $[MCl(E^\cap N)_2]_n$, $[MCl(E^\cap N)(PR_3)]$, $[M_2Cl_2(\mu\text{-}E^\cap N)_2(PR_3)_2]$, $[M_2(\mu\text{-}E^\cap N)_2(P^\cap P)_2]^{2+}$, *etc. have been isolated. All the complexes have been characterized by elemental analysis, IR, NMR (*^1H, ^{13}C, ^{31}P, ^{77}Se, ^{125}Te, ^{195}Pt*), UV-vis, and FAB mass spectral data. A weak absorption in the electronic spectra of* $[MCl(E^\cap N)(PR_3)]$ *has been attributed to metal mediated ligand-to-ligand charge transfer and showed pronounced chalcogen dependence being red shifted on moving from S → Se → Te. Structures of several complexes have been established by X-ray diffraction analyses. Thermal behavior of some of these complexes has been investigated by TGA.*

Keywords NMR; N,N-dimethylaminoalkylchalcogenolates; palladium; platinum; TGA

INTRODUCTION

The chemistry of metal chalcogenolates continues to be an active area of research. There are several obvious reasons for the sustained interest in metal chalcogenolates. Their emerging applications as single source precursors for low decomposition temperature synthesis of metal chalcogenides has further accelerated work on these complexes. Platinum group metal chalcogenides (M_xE_y; M = Pd or Pt; E = S, Se or Te) find several applications in catalysis and materials sciences.[1] Platinum group metal chalcogenolates have an attractive potential to serve

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as precursors for the preparation of metal chalcogenides.[2,3] The chemistry of platinum group metal chalcogenolates is dominated by metal thiolates which in most of the cases are isolated as non-volatile, insoluble, or sparingly soluble oligomeric species, therefore limiting their utility as molecular precursors. To suppress polymerization sterically, demanding chalcogenolate ligands,[4] strongly coordinating auxiliary ligands (e.g., tertiary phosphines)[5] or internally functionallized ligands[6] have been employed. Aminoalkylchalcogenolates, $R_2N(CR')_nE^-$, represent a family of internally functionalized ligands which contain both hard and soft donor atoms. While the chemistry of mercaptoalkylamines is now fairly well explored,[7–9] heavier analogs containing Se and Te, owing to the current interest in selenium and tellurium containing inorganic materials, have been developed in the author's group and their chemistry of palladium and platinum has been investigated. Some salient feature of this work are described here.

RESULTS AND DISCUSSION

Ligand Synthesis

N,N-Dimethylaminoalkyldichalcogenides (**1–4**) were prepared by the reaction routes depicted in Scheme 1.[10–12] Reactions of Me_2NCH_2 $CH(Me)Cl$ results in isomerization giving a mixture of **2** and **3**, the relative ratio of which depends on the nucleophilic character of chalcogen atom. The reaction-4 yields primarily **2** (E = S). A cyclic aziridium species as an intermediate has been attributed in these reactions. All the dichalcogenides **1–4** display only 1 set of resonances, but bis(2-dimethylamino)propyl dichalcogenides exhibit 2 sets of resonances in ^1H and ^{13}C spectra. The ^{77}Se NMR spectrum shows 8 lines (Figure 1) which are assigned to RR/SS and meso forms of **2** and **3**. The intramolecular interactions between Se and N may lead to magnetic non-equivalence of Se atoms in each molecules.

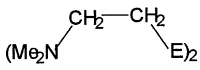
$$2\mathrm{Na} + 2\mathrm{E} \xrightarrow{\mathrm{NH_3}} \mathrm{Na_2E_2} \xrightarrow[\mathrm{-\,2NaCl}]{\mathrm{2Me_2N(CH_2)_nCl}} [\mathrm{Me_2N(CH_2)_nE}]_2 \quad \ldots (1)$$

$$\mathrm{Te} + \mathrm{PhNHNH_2} + \mathrm{Me_2N(CH_2)_nCl} \longrightarrow [\mathrm{Me_2N(CH_2)_nTe}]_2 \quad \ldots (2)$$

$$\mathrm{K_2Te_2} + \mathrm{2Me_2NCH_2CHMeCl} \xrightarrow[\mathrm{-2KCl}]{} [\mathrm{Me_2NCH(Me)CH_2Te}]_2 \quad \ldots (3)$$

$$\begin{tikzcd}
\mathrm{NaOEt} + \mathrm{H_2S} \rightarrow \mathrm{NaSH} \arrow[r, "\mathrm{Me_2NCH_2CH(Me)Cl}"] & \mathrm{Me_2NCH(Me)CH_2SH} \arrow[d, "\frac{1}{4}\mathrm{O_2}"] \\
 & \frac{1}{2}[\mathrm{Me_2NCHMeCH_2S}]_2 \quad \ldots (4)
\end{tikzcd}$$

SCHEME 1



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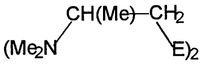

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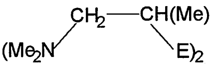

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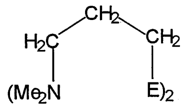

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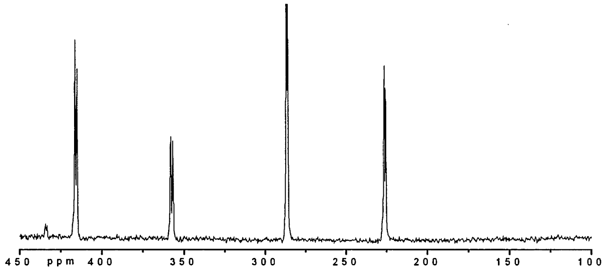


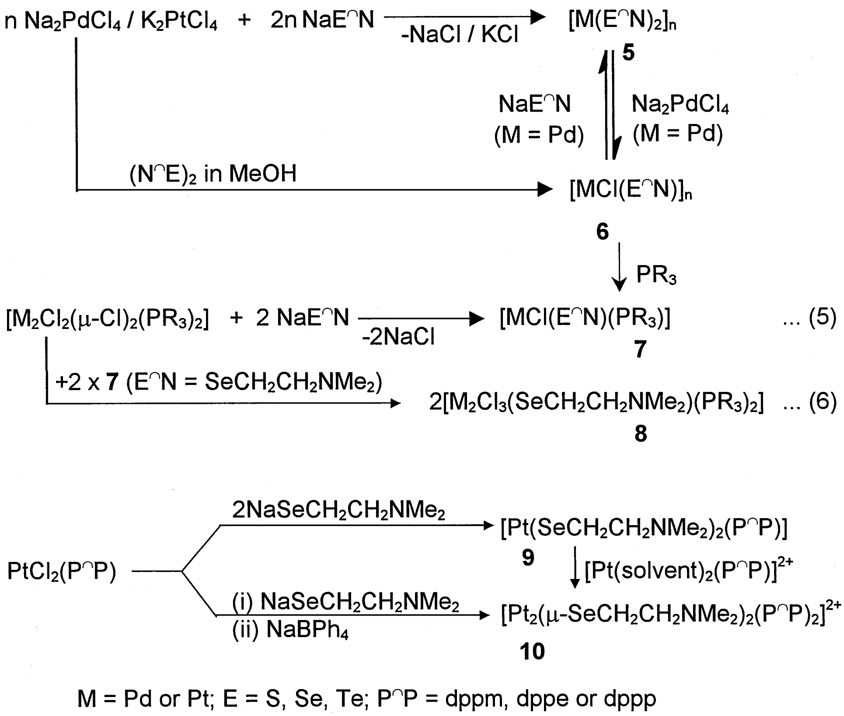
FIGURE 1 ^{77}Se{^{1}H} NMR spectrum of bis(N,N′-dimethylaminopropyl) diselenide in $CDCl_3$.

Synthesis of Palladium(II) and Platinum(II) Complexes

A variety of palladium(II) and platinum(II) complexes (**5–10**) containing N,N′-dimethylaminoalkylchalcogenolate have been prepared employing reaction routes depicted in Scheme 2. The structure and stereochemistry of these complexes are influenced greatly by the number of carbon atoms between E and N and the nature of the chalcogen atom. The telluorolato complexes often showed reactivity towards halogenated solvents.

The reaction of Na_2PdCl_4/K_2PtCl_4 with $NaE^\cap N$ prepared by sodium borohydride reduction of **2–4** (E = Se), yields homoleptic chalcogenolates of composition $[M(E^\cap N)_2]_n$ (**5**).[12–14] The FAB mass spectrum of $[Pd(SeCH_2CH_2CH_2NMe_2)_2]_6$ (m/z = 2619) and the X-ray structure revealed hexameric structure. The molecule has a hexagonal cyclo-$[PdSe_2]_6$ center in which two palladium atoms are bridged by two selenolate Se atoms while the tertiary amine functions remain uncoordinated.[14]

Treatment of Na_2PdCl_4/K_2PtCl_4 with **1–4** in methanol yields sparingly soluble complexes of empirical composition $[MCl(E^\cap N)]_n$ (**6**). The FAB mass spectrum of M = Pd, $E^\cap N = SeCH_2CH_2NMe_2$ exhibited a peak at m/z 879 indicating its trimeric nature which is unambiguously established by X-ray analysis.[10] This trimeric structure appears to form with the ligand sets **1–3**. However the palladium complex derived from $Me_2NCH_2CH_2CH_2Se^-$ adopts a dimeric structure as shown by FAB mass spectrum (m/z = 614 (molecular ion)][12] and

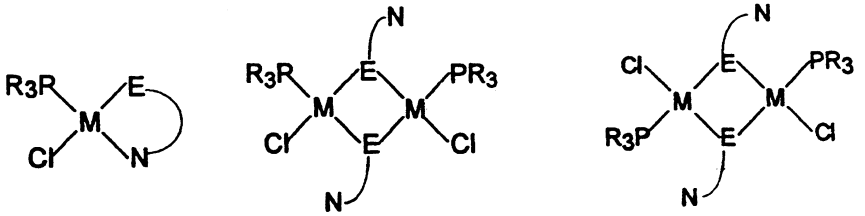


SCHEME 2

X-ray crystallography.[14] The two palladium atoms in this molecule are held together by two symmetrically bridging Se atoms of the chelating selenolate ligands.[14] The hexanuclear compounds **5** (M = Pd; E$^\frown$N = $SeCH_2CH_2CH_2NMe_2$) reacts readily with Na_2PdCl_4 to afford the binuclear complex $[PdCl(SeCH_2CH_2CH_2NMe_2)]_2$. Interconversion of dimeric to hexameric species is quite facile and can be accomplished by treatment of the former with $NaSeCH_2CH_2CH_2NMe_2$.

Treatment of $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with two equivalents of NaE$^\frown$N, prepared by reductive cleavage of the E$^\frown$E bond in $(N^\frown E)_2$ with $NaBH_4$ in methanol, gave complexes of the type $[MCl(ECH_2CHR'NMe_2)(PR_3)]$ (**7a**) (R′ = H or Me; E = S, Se, Te) and $[MCl(\mu\text{-}ECH_2CH_2CH_2NMe_2)(PR_3)]_2$ (**7b**) (E = Se or Te). The **7** also can be obtained by the reaction of **6** with phosphine. Structural preferences for complexes of the types **7** are quite evident. The complexes with $ECH_2CHR'NMe_2$ adopt a monomeric structure (**I**) both in the solid state (X-ray crystallography) and in solution (NMR spectroscopy).[10,11,13] However, complexes containing $SCH_2CH_2NMe_2$

and alkylphosphines, small concentration of dimeric species **II** and **III** (Scheme 3) also exist in solution.[15] In contrast, complexes (**7b**) with 3-dimethylaminopropylchalcogenolate (E = Se or Te) are dimeric with chalcogenolate bridge and free NMe_2 group.[12,16]



I
7a

II (*cis*)

III (*trans*)

7b

SCHEME 3

Stereochemistry of these complexes (**7**) has been deduced from NMR (^1H, ^{31}P, ^{77}Se, ^{195}Pt) spectroscopy and X-ray crystallography. The NMe_2 resonance in the ^1H NMR spectra of **7a** shows a doublet due to $^4J(P{-}H)$ couplings (~3 Hz) and $^3J(Pt\text{-}H)$ of ~15 Hz. The magnitude of $^1J(Pt\text{-}P)$ for **7a** is ~3500 Hz while for **7b** it is ~3200 Hz. The ^{77}Se NMR spectra display a triplet due to platinum coupling [$^1J(Pt\cdots Se) = {\sim}130$ Hz] (Figure 2). The ^{195}Pt NMR spectra show a doublet in the region $\delta{-}4100$–4425 ppm. The shielding of ^{195}Pt NMR resonance increases with increasing size of the chalcogen atom (S < Se < Te). The structures of a series of **7a** (Table I) have been established unambiguously by X-ray crystallography. The coordination environment around the metal atom is approximately square planar with the atoms P, Cl, E, and N defining the coordination sphere (Figure 3). The neutral donor atoms (P and N) occupy *trans* positions.

The **7a** are distinctly colored which darkens on going from S to Se through Te. Absorption for platinum complexes appear at higher energies relative to the corresponding palladium derivatives (Table II). Well separated, broad, but relatively weak bands in the visible region have been identified for the origin of the color. These absorptions have been assigned to ligand (E)-to-ligand (PR_3) charge transfer (LLCT) transitions as confirmed by TD-DFT calculations.[11]

The reaction −5 appears to proceed via a binuclear intermediate, $[M_2Cl_3(Se^\frown N)(PR_3)_2]$ (**11**) which after reaction with another mole of $NaSe^\frown N$ affords **7a.**[10,17] The **11** can be isolated by treatment of **7a** with $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ in 2:1 molar ratio. The organoplatinum analog

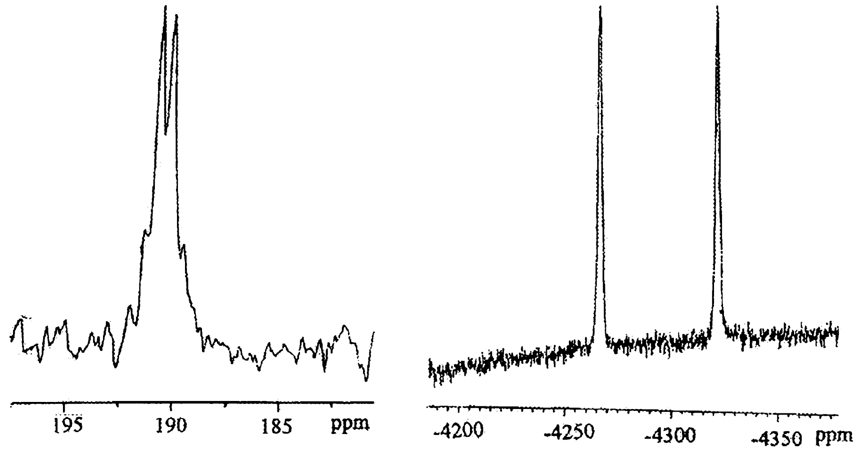


FIGURE 2 ^{77}Se (left) [δ 190.6 (d) ppm, ^{1}J (^{195}Pt-^{77}Se) = 104 Hz, ^{2}J (^{77}Se-^{31}P) = 30 Hz], ^{195}Pt (right) [δ -4293 (d) ppm, ^{1}J (^{195}Pt-^{31}P) = 3555 Hz] NMR spectra of $[PtCl(SeCH_2CH_2NMe_2)(PMePh_2)]$ in $CDCl_3$.

of **11**, $[Pt_2Ph_2(Cl)(SeCH_2CH_2NMe_2)(PBu_3)_2]$ (**11a**) (**IV**)[14] (Scheme 4) indeed has been isolated as one of the product from the reaction between $[Pt_2Ph_2(\mu\text{-}Cl)_2(PBu_3)_2]$ and $NaSeCH_2CH_2NMe_2$. The ^{31}P and ^{195}Pt NMR spectra of **11** and **11a** show two separate resonances as expected. The structure of **11a** consists of two distorted square planar platinum atoms which are held together by bridging selenolate ligand.

TABLE I Some Bond Lengths and Angles for $[MCl(E^{\cap}N)(PR_3)]$ Complexes

	Bond lengths (Å)				
Complex	M-E	M-N	M-Cl	LE-M-N (degree)	Ref.
$[PdCl(SCH_2CH_2NMe_2)(PPh_3)]$	2.2600(6)	2.1520(15)	2.3755(6)	86.86(5)	13
$[PdCl(SCH_2CHMeNMe_2)(PmePh_2)]$	2.2560(10)	2.172(2)	2.3676(10)	87.33(7)	11
$[PtCl(SCH_2CHMeNMe_2)(PMe_2Ph)]$	2.235(2)	2.130(3)	2.403(3)	88.6(2)	11
$[PdCl(SeCH_2CH_2NMe_2)(PPh_3)]$	2.3710(6)	2.160(3)	2.3823(10)	87.33(9)	8
$[PtCl(SeCH_2CH_2NMe_2)(PPh_3)]$	2.3773(7)	2.161(5)	2.3788(15)	87.02(14)	15
$[PtCl(SeCH_2CH_2NMe_2)(PEt_3)]$	2.3563(10)	2.160(7)	2.356(2)	86.3(2)	9
$[PdCl(SeCH_2CHMeNMe_2)(PMePh_2)]$	2.323(3)	2.149(18)	2.332(6)	84.0(5)	11
$[PtCl(SeCH_2CHMeNMe_2)(PMe_2Ph)]$	2.3860(11)	2.220(8)	2.348(3)	86.6(2)	11
$[PdCl(TeCH_2CH_2NMe_2)(PR_3)]$	2.5095(8)	2.172(3)	2.3740(12)	87.85(9)	9
$[PdCl(TeCH_2CH_2NMe_2)(PMePh_2)]$	2.5156(6)	2.143(4)	2.3929(14)	86.61(13)	9
$[PtCl(TeCH_2CH_2NMe_2)(PMePh_2)]$	2.5261(5)	2.182(4)	2.3780(14)	87.32(11)	9

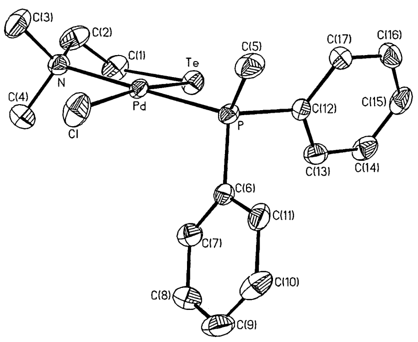
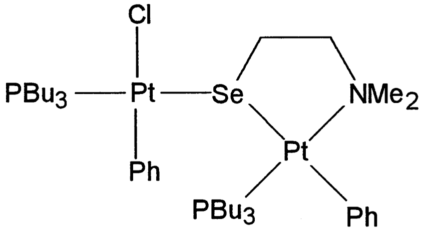


FIGURE 3 Molecular structure of [PdCl($TeCH_2CH_2NMe_2$)($PMePh_2$)].

The two platinum square planes are inclined to each other through a Pt-Se-Pt angle of 111.69(5)°.[17]



IV

SCHEME 4

The reaction of $PtCl_2$(P-P) with two equivalents of $NaSeCH_2CH_2NMe_2$ affords *cis*-[Pt($SeCH_2CH_2NMe_2$)$_2$(P-P)] (**9**) (P-P = dppm, dppe or dppp), but similar reaction with one equivalent of $NaSeCH_2CH_2NMe_2$ in the presence of $NaBPh_4$ yields cationic binuclear complexes, [Pt_2($SeCH_2CH_2NMe_2$)$_2$(P-P)$_2$][BPh_4]$_2$ (**10**). These complexes have been characterized by ^{31}P, ^{77}Se, and ^{195}Pt (Figure 4) NMR spectroscopy.[17]

TABLE II UV/vis Absorption Data for Some [MCl($E^\frown N$)(PR_3)]

Complex	$\lambda_{max}(\varepsilon)$ (nm)
[PdCl($SCH_2CH_2NMe_2$)(PPh_3)]	260 (27100), 341 (2940), 484 (80)
[PdCl($SeCH_2CH_2NMe_2$)(PPh_3)]	344 (1980), 514 (80)
[PdCl($TeCH_2CH_2NMe_2$)(PPh_3)]	224 (32000), 269 (21650), 367 (sh), 623 (150)
[PtCl($SCH_2CH_2NMe_2$)($PMePh_2$)]	288 (2040), 393 (90)
[PtCl($SeCH_2CH_2NMe_2$)($PMePh_2$)]	266 (sh), 273 (sh), 293 (sh), 418
[PtCl($TeCH_2CH_2NMe_2$)($PMePh_2$)]	243 (17200), 270 (sh), 300 (sh), 460 (140)

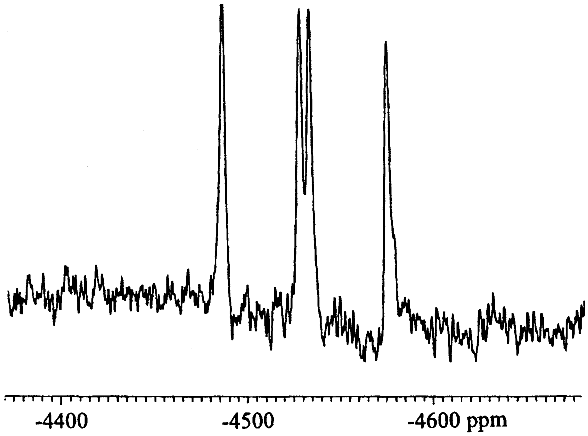


FIGURE 4 ^{195}Pt{^{1}H} NMR spectrum of [$Pt_2(SeCH_2CH_2NMe_2)_2(dppp)_2$] [$BPh_4$]$_2$ in $CDCl_3$ [δ-3534 (d,d)^{1}J (^{195}Pt-^{31}P) = 2706 Hz].

THERMAL STUDIES

To evaluate suitability of these complexes as molecular precursors thermal behavior of some of the palladium complexes with thiolate and selenolate ligands has been studied by TGA. The thiolato derivatives generally yields Pd_4S while selenolate compounds lead to the formation of $Pd_{17}Se_{15}$ as characterized by XRD and EDAX.

CONCLUSION

It is evident from this work that N,N-dialkylaminoalkylchalcogenolates show versatile coordination chemistry. Complexes with varying nuclearity and structural motifs can be designed and isolated. The availability of a number of NMR active nuclei (^{31}P, ^{77}Se, ^{125}Te, ^{195}Pt) in these complexes provides an important diagnostic tool to study structural aspects in solution. These molecules also can be employed as precursors to prepare single-phase palladium chalcogenides at relatively low temperatures.

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