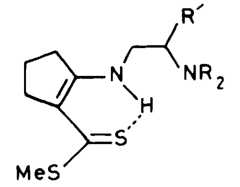
Metal Complexes of Sulphur–Nitrogen Chelating Agents. Part 10.† The Chemistry of Palladium(II) Complexes with some Monoanionic Tridentate Ligands of the Type SNN

Rita Roy, Santosh Kumar Mondal, and Kamalaksha Nag *
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Calcutta 700 032, India

Complexes of the type [PdLX] (X = Cl or Br) have been obtained with the tridentate ligands (HL): methyl 2-(β-aminoethylamino)cyclopent-1-enedithiocarboxylate (HL^1), methyl 2-(β-aminopropylamino)cyclopent-1-enedithiocarboxylate (HL^2), and methyl 2-(β-diethylaminoethylamino)cyclopent-1-enedithiocarboxylate (HL^3). The reactions between [PdLX] and a stoicheiometric amount of silver perchlorate in acetonitrile and 99% methanol lead to the formation of the complexes $[PdL(MeCN)]ClO_4$ and $[PdL(H_2O)]ClO_4$ respectively. The co-ordinated solvents in these compounds can be easily substituted by other nucleophilic bases (B) and the corresponding complexes $[PdL(B)]ClO_4$ are obtained. Due to steric effects complexes of the type [PdL(py)]X (X = Cl, Br, or ClO_4; py = pyridine) cannot be prepared for the ligand HL^3. In dry acetone the reaction between [PdLBr] (L = L^1 or L^2) and silver perchlorate in 2 : 1 molar ratio results in the formation of $[Pd_2L_2Br]ClO_4$. The same reaction in acidic medium (pH 2) affords $[Pd(HL)Br]ClO_4$. However, when the reactants are used in 1 : 1 molar proportion no stable product can be isolated. The heats of dissociation (ΔH) for the reaction $[PdL^1(B)]Cl \longrightarrow [PdL^1Cl] + B$ (B = pyridine, NH_2Et, or $NHEt_2$) have been compared with the analogous nickel(II) complexes, and the results show slightly greater bond strengths of Ni–B.

Despite the phenomenal growth of the chemistry of palladium(II) complexes [1,2] little is known about neutral monohalogen complexes with tridentate ligands. In continuation of our studies [3-8] on sulphur–nitrogen chelating agents we introduce here the potentially tridentate ligands HL: methyl 2-(β-aminoethylamino)cyclopent-1-enedithiocarboxylate (HL^1), methyl 2-(β-aminopropylamino)cyclopent-1-enedithiocarboxylate (HL^2), and methyl 2-(β-diethylaminoethylamino)cyclopent-1-enedithiocarboxylate (HL^3). These ligands are expected to form mononuclear complexes [PdLX] (X = halogen) through deprotonation of the hydrogen-bonded proton. There are two basic objectives for studying these neutral monohalogen complexes. One is to see whether complexes of the type [PdL(B)]X (B = heterocyclic or nucleic acid base; X = Cl^-, ClO_4^-, *etc.*) have any carcinostatic effect, a possibility that is being currently explored in palladium(II) complexes.[9,10] The other motivation stems from the expectation that the removal of the halogenide ion from [PdLX] in a poorly/non-co-ordinating solvent might lead to a co-ordinative unsaturated condition for palladium(II), and under such conditions activation of an alkene, alkyne, or a carbon monoxide molecule may be accomplished through co-ordination.[11] As a step towards this we report here the synthesis and characterisation of complexes of the types [PdLX] (X = Cl or Br), [PdL(B)]X (B = Lewis base; X = Cl, Br, or ClO_4) and $[Pd_2L_2Br]ClO_4$, the reactivities of [PdLX] with $AgClO_4$ in co-ordinating and non-co-ordinating solvents, and the determination of heats of dissociation of some [PdL(B)]Cl complexes to [PdLCl].



HL

R = R′ = H (HL^1);
R = H, R′ = Me (HL^2);
R = Et, R′ = H (HL^3)

Experimental

All chemicals were reagent grade and used as received. Solvents were purified by conventional methods. Carbon, hydrogen, and nitrogen analyses were performed by the Microanalytical Services of the Australian Mineral Development Laboratories, Melbourne, and palladium was gravimetrically estimated as the dimethylglyoximate. Infrared spectra were recorded in the range 300—4 000 cm^{-1} as Nujol mulls or in KBr discs, using a Beckman IR-20 spectrophotometer. Proton n.m.r. spectra were recorded at 60 MHz and at 90 MHz using Varian T-60 and EM-390 spectrometers, respectively, with $SiMe_4$ as the internal standard. Electronic spectra were recorded on a Pye-Unicam SP8-150 spectrophotometer. Solution conductivities were measured with a Philips PR-9500 conductivity bridge. Thermogravimetric and differential thermal analyses (d.t.a.) were performed on a Shimadzu DT-30 thermal analysis system. The heats of dissociation were determined by comparing the area under the d.t.a. peak with that obtained for the fusion of In (3.27 kJ mol^{-1}) [12] under identical rate of heating (5 °C min^{-1}) in an atmosphere of nitrogen, and under similar instrumental conditions.

Ligands.—The ligands were obtained by the transamination reactions of methyl 2-aminocyclopent-1-enedithiocarboxylate with 1,2-diaminoethane (for HL^1), 1,2-diaminopropane (for HL^2), and *NN*-diethyl-1,2-diaminoethane (for HL^3) by suitable modification of a procedure described by Bordas *et al.*[13] To methanol solutions (30 cm^3) of methyl 2-aminocyclopent-1-enedithiocarboxylate [5] (3.5 g) the appropriate diamines (4.8 g of 1,2-diaminoethane, 5.9 g of 1,2-diaminopropane, and 7 g of *NN*-diethyl-1,2-diaminoethane) were

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† Part 9 is ref. 8.

Table 1. Analytical and conductivity data for the ligands and palladium(II) complexes

Compound	Analysis (%) [a] C	H	N	Pd	Conductivity [b] (Λ/Ω^{-1} cm^2 mol^{-1})
HL^1	49.8 (50.0)	7.5 (7.4)	13.15 (12.95)		
HL^2	52.3 (52.15)	7.95 (7.8)	12.0 (12.15)		
HL^3	57.15 (57.35)	8.7 (8.8)	10.1 (10.3)		
$[PdL^1Cl]$	30.4 (30.25)	4.5 (4.2)	7.6 (7.85)	29.95 (29.8)	2(nitrobenzene) [c]
$[PdL^2Br]$	29.1 (28.9)	4.1 (4.3)	6.7 (6.8)	25.9 (25.6)	20 (dmso) [c]
$[PdL^3Cl]$	37.65 (37.8)	5.4 (5.55)	6.65 (6.8)	25.85 (25.75)	4 (nitrobenzene) [c]
$[PdL^1(py)]Cl$	38.8 (38.55)	4.7 (4.6)	9.8 (9.65)	24.2 (24.4)	70 (nitromethane),[d] 55 (dmf) [e]
$[PdL^2(H_2O)]ClO_4$	26.3 (26.5)	4.35 (4.2)	6.05 (6.2)	23.4 (23.5)	120 (acetone) [f]
$[PdL^3(MeCN)]ClO_4$	34.3 (34.75)	4.8 (5.0)	8.4 (8.1)	20.3 (20.55)	130 (acetonitrile) [g]
$[PdL^1(py)]ClO_4$	34.0 (33.6)	4.3 (4.0)	8.7 (8.4)	21.4 (21.3)	125 (acetonitrile) [g]
$[Pd_2(L^2)_2Br]ClO_4{\cdot}0.5Me_2CO$	29.0 (29.35)	4.3 (4.2)	6.2 (6.35)	24.1 (24.2)	140 (acetone) [g]
$[Pd(HL^2)Br]ClO_4$	23.25 (23.25)	3.6 (3.5)	5.45 (5.3)	20.55 (20.65)	130 (acetone) [g]

[a] Calculated values are given in parentheses. [b] Solvents used are given in parentheses; dmso = dimethyl sulphoxide. [c] Non-electrolyte [d] 75—95 for 1 : 1 electrolyte. [e] 65—90 for 1 : 1 electrolyte. [f] 100—140 for 1 : 1 electrolyte. [g] 120—160 for 1 : 1 electrolyte. For footnotes *d*—*g* conductivity values are from W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

added. The solutions were allowed to stand at room temperature for 24 h, during which yellow crystalline compounds of *NN'*-ethylenebis(methyl 2-aminocyclopent-1-enedithiocarboxylate) and *NN'*-1,2-propanediylbis(methyl 2-aminocyclopent-1-enedithiocarboxylate) separated out from the first two solutions. These were removed by filtration and the filtrates were slowly diluted with water (120 cm^3) when the products deposited as canary yellow flakes. The compounds were collected by filtration and washed several times with water. The ligand HL^3 was directly crystallised out from the third solution by keeping it in an ice chest overnight. For recrystallisation, the compounds were dissolved in a minimum volume of methanol and then water was slowly added until incipient crystallisation occurred. The solution was then slowly cooled to 0 °C, the crystals deposited were collected and dried *in vacuo*. The yields were 3.6 (HL^1), 3.7 (HL^2) and 4 g (HL^3). The melting points were 92 (HL^1), 94 (HL^2), 52 °C (HL^3). Analytical data of the ligands are shown in Table 1.

$[PdLX]$ ($L = L^1$—L^3; X = Cl *or* Br).—To a methanol solution (40 cm^3) of the ligand (4 mmol) sodium tetrahalogenopalladate (4 mmol) dissolved in methanol (30 cm^3) was added in small portions with stirring. The orange coloured compound formed during mixing was stirred for another 2 h at room temperature. The product was then collected by filtration, washed with benzene (in which the ligands are highly soluble), methanol, and finally with water–methanol (1 : 1). The compounds $[PdL^1X]$ and $[PdL^3X]$ were recrystallised from chloroform. The compounds $[PdL^2X]$ being much less soluble were repeatedly extracted with boiling chloroform.

$[PdL(MeCN)]ClO_4$ ($L = L^1$—L^3).—Silver perchlorate (1.24 g, 6 mmol) was added to solution/dispersion of $[PdLCl]$ (6 mmol) in acetonitrile (50 cm^3) and the mixture was stirred for 4 h. The precipitated silver chloride was removed by filtration and the orange coloured filtrate was concentrated to *ca.* 10 cm^3 in a rotary evaporator. The solution was then filtered and kept in an ice chest for 12 h. The orange crystals formed were collected by filtration and recrystallised from a minimum volume of acetonitrile.

$[PdL(H_2O)]ClO_4$ ($L = L^1$—L^3).—To a suspension of $[PdLCl]$ (4 mmol) in methanol (40 cm^3) silver perchlorate (0.83 g, 4 mmol) was added. The mixture was stirred for 6 h, filtered, and the volume of the filtrate was reduced to 10 cm^3 in a rotary evaporator. This solution was again filtered and the filtrate was then kept in a refrigerator for 6 h. The yellow crystals obtained were recrystallised from methanol–water (80 : 20).

$[Pd_2L_2Br]ClO_4{\cdot}0.5Me_2CO$ ($L = L^1$—L^3).—To a stirred suspension of $[PdLBr]$ (4 mmol) in dry acetone (30 cm^3) silver perchlorate (0.42 g, 2 mmol) was added and stirring was continued for 6 h. It was then filtered. The filtrate was concentrated to 10 cm^3 and light petroleum (b.p. 40—60 °C, 15 cm^3) was slowly added. The product deposited as yellow crystals and was recrystallised from acetone.

$[Pd(HL)Br]ClO_4$ (HL = HL^1 *or* HL^2).—The above reaction was carried out with the addition of two drops of perchloric acid (70%). The solution became deep red and $[Pd(HL)Br]ClO_4$ was isolated as stated above with the addition of light petroleum (b.p. 40—60 °C).

$[PdL(B)]X$ [$L = L^1$ *or* L^2: B = *Pyridine*, *Ethylamine*, *or Diethylamine*; X = Cl *or* Br].—The compound $[PdLX]$ (0.5 g) was suspended in chloroform (10 cm^3) and dry base (5 cm^3) was added. On stirring the mixture for 2 h an orange solution was obtained. This was filtered and the filtrate yielded, on diluting with a large volume of dry diethyl ether, the orange product. The compound was filtered off and washed with n-heptane and diethyl ether.

$[NiL^1(B)]Cl$ (B = *Pyridine*, *Ethylamine*, *or Diethylamine*).—These compounds were obtained in the same way as described above, using $[NiLCl]$.

$[PdL(py)]ClO_4$ ($L = L^1$ *or* L^2).—Pyridine (5 cm^3) was added to a solution of $[PdL(MeCN)]ClO_4$ (0.5 g) in acetonitrile (10 cm^3). The solution was filtered after stirring for 1 h and the yellow compound was isolated from the filtrate by addition of dry diethyl ether.

$[PdL(NH_3)]ClO_4$ ($L = L^1$—L^3).—Dry ammonia gas was bubbled through an acetonitrile solution (15 cm^3) of $[PdL(MeCN)]ClO_4$ (0.5 g) for 5 min. The colour of the solution changed from orange to yellow. The compound was isolated by the addition of dry diethyl ether.

Results and Discussion

Synthesis and Properties.—Sodium tetrahalogenopalladates(II) cause ready deprotonation of the ligands, and the monohalogen complexes, $[PdLX]$, are obtained in good yields (*ca.* 75%). The solubility of the complexes in common organic

Table 2. Selected i.r. data for the palladium(II) complexes

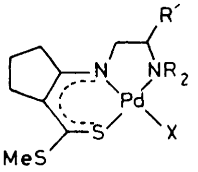
Complex	$\nu_{asym}(NH)/cm^{-1}$	$\nu_{sym}(NH)/cm^{-1}$	$\delta(NH_2)/cm^{-1}$	$\nu(C\cdots C)/cm^{-1}$	$\nu(C\cdots N) + \nu(C\cdots C)/cm^{-1}$
[PdL^{1}Cl]	3 260m	3 200m 3 120w	1 565s		1 465s
[PdL^{2}Cl]	3 260w	3 200w 3 120w	1 575s		1 460s
[PdL^{2}Br]	3 240w	3 190w 3 110m	1 570s		1 455s
[PdL^{3}Cl]				1 570m	1 455s
[PdL^1(py)]ClO$_4$	3 260m	3 190w 3 120w	1 595m	1 560s	1 440s
[PdL^1(NH$_3$)]ClO$_4$	3 310m	3 200w 3 260m	1 610m	1 570s	1 450s
[PdL^2(MeCN)]ClO$_4$	3 260w	3 210w 3 110w	1 590w	1 565s	1 450s
[Pd$_2$(L^2)$_2$Br]ClO$_4$·0.5Me$_2$CO *	3 240m	3 180m 3 100m	1 600m	1 570m	1 450s
[Pd(HL^2)Br]ClO$_4$	3 260m	3 220m 3 130m	1 610s	1 580s	1 455s

* $\nu(C{=}O)$ at 1 700 cm^{-1}.

solvents is [PdL^{3}X] > [PdL^{1}X] > [PdL^{2}X]. The compounds [PdL^{1}X] and [PdL^{2}X], but not [PdL^{3}X], react with pyridine (py) to form [PdL(py)]X. In acetonitrile medium all [PdLX] compounds react quantitatively with silver perchlorate resulting in the formation of complexes of composition [PdL(MeCN)]ClO$_4$. The same reaction in methanol (containing *ca.* 1% water) medium leads to the formation of the compounds [PdL(H$_2$O)]ClO$_4$. Facile nucleophilic substitution of water and acetonitrile molecules in these complexes can be accomplished by Lewis bases like ammonia, ethylamine, and diethylamine. Similar reaction with pyridine leads to the isolation of the complexes [PdL(py)]ClO$_4$ (L = L^1 or L^2). The absence of formation of the compounds [PdL^3(py)]X (X = Cl, Br, or ClO$_4$) clearly indicates that due to the steric effect of the terminal *NN*-diethyl moiety of HL^3 a relatively big molecule like pyridine cannot approach the metal centre. In dry acetone medium the reaction of a [PdLX] compound with a stoicheiometric amount of silver perchlorate afforded a deep red solution from which an intractable viscous material that eluded crystallisation was obtained. If the ratio of [PdLBr] (L = L^1 or L^2) to silver perchlorate is maintained at 2 : 1, the product obtained is a dimeric complex of composition [Pd$_2$L$_2$Br]ClO$_4$. These compounds on boiling with methanol-water (9 : 1) disproportionate to [PdLBr] and [PdL(H$_2$O)]ClO$_4$. Again the reaction between [PdLBr] (L = L^1 or L^2) and silver perchlorate in a 2 : 1 molar ratio in acetone under acidic conditions (pH *ca.* 2) leads to the formation of a protonated complex [Pd(HL)Br]ClO$_4$ in which the ligand is apparently in the neutral form. This type of compound can be deprotonated to [PdLBr] by treating it with the desired amount of methanolic potassium hydroxide. The analytical data of some of the representative compounds along with their conductivity values are summarised in Table 1.

The complexes of the type [PdLX] are non-electrolytes, while all of the complexes containing perchlorate ion are 1 : 1 electrolytes. The conductivity values of [PdL(py)]X (X = Cl or Br) in nitromethane lie slightly below the threshold of 1 : 1 electrolytes, and these values are somewhat low for 1 : 1 electrolytes in dimethylformamide (dmf). This indicates that in polar solvents dissociation of [PdL(py)]X complexes occurs: [PdL(py)]X $\rightleftharpoons$ [PdLX] + py. The conductivity measurements showed that the equilibrium can be shifted completely to the left by the addition of excess of pyridine. The above dissociation, however, does not take place when the accompanying anion is perchlorate.

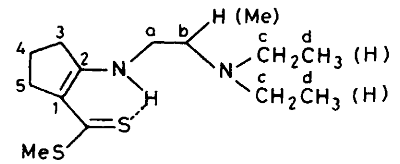
Infrared Spectra.—Some i.r. frequencies that are diagnostic of metal–ligand bonding are set out in Table 2 for representative compounds. The band assignments have been made in accordance with our previous studies.[3,5,7] The symmetric and antisymmetric NH stretches in the complexes are shifted to lower frequencies relative to the ligands (HL^1 and HL^2) by 80—100 cm^{-1}. Considerable delocalisation of the double bonds in the chelate ring (below) is evident since



$C\cdots C$ and $C\cdots N$ stretchings are observed at lower energies. The $C\cdots S$ stretching frequency could not be located with certainty in the complexes as mixing of C=C, C=N, and C=S vibrations occurs in the region 1 300—900 cm^{-1}.[14–16] All perchlorate ion containing complexes show a strong broad band centred at 1 100 cm^{-1}, a weak band at 920 cm^{-1}, and a sharp band at 620 cm^{-1}, the features typical of ionic perchlorates.[17] In the region 600—300 cm^{-1} few new bands which are absent in the ligands are observed in the complexes. There are two vibrations in the complexes [PdLX] at 550 ± 10 and 500 ± 10 cm^{-1} which appear to be due to Pd–N stretches; the latter probably arises due to bonding with the terminal nitrogen atom.[18–20] Another band appearing at 380 cm^{-1} appears to be due to Pd–S stretching.[21–23] Finally, the Pd–Cl stretch appears in the expected region, 330 ± 10 cm^{-1}.[1,24–26] The Pd–Br vibration which normally appears at *ca.* 275 cm^{-1} [1,24–26] was not observed up to 300 cm^{-1}.

Proton N.M.R. Spectra.—The chemical shifts observed in the ^{1}H n.m.r. spectra of the ligands and complexes are compared in Table 3. It may be noted that the decreasing order of hydrogen bonding in the ligands is HL^1 > HL^2 > HL^3. Due to complex formation, a profound shift at lower field occurs for the NH$_2$ protons. Similar deshielding is observed for the c-CH$_2$ and d-CH$_3$ resonances. As a consequence of delocalisation of the double bonds in the chelate ring shielding of the 3,4,5-CH$_2$ protons of the cyclopentene moiety and of a-CH$_2$

Table 3. Hydrogen-1 n.m.r. data for the ligands[a] and some palladium(II) complexes



Compound	Chemical shifts (δ/p.p.m.)[b]
HL^1 [c]	1.13br (NH_2); 1.92m (4-CH_2); 2.52s (SCH_3); 2.83m (b-CH_2 + 3,5-CH_2);[d] 3.33q (a-CH_2); 12.7br (N–H ··· S)
HL^2 [c]	1.07br (NH_2); 1.20m (b-CH_3); 1.88m (4-CH_2); 2.52s (SCH_3); 2.75m (b-CH + 3,5-CH_2);[d] 3.19q (a-CH_2); 11.0br (N–H ··· S)
HL^3 [c]	1.06t (d-CH_3); 1.83m (4-CH_2 + b-CH_2);[d] 2.52s (SCH_3); 2.70m (c-CH_2 + 3,5-CH_2);[d] 3.33q (a-CH_2); 9.7br (N–H ··· S)
$[PdL^1Cl]$ [e]	1.80m (4-CH_2); 2.10m (a-CH_2); 2.50s (SCH_3); 2.67m (3,5-CH_2); 3.57t (b-CH_2); 4.93br (NH_2)
$[PdL^2Cl]$ [e]	1.19d (b-CH_3); 1.87m (4-CH_2); 2.52s (SCH_3); 2.64m (3,5-CH_2 + a-CH_2);[d] 3.59m (b-CH); 4.92br (NH_2)
$[PdL^3Cl]$ [c]	1.38t (d-CH_3); 1.83m (4-CH_2); 2.53s (SCH_3); 2.62m (3,5-CH_2 + a-CH_2);[d] 3.05m (c-CH_2); 3.63t (b-CH_2)
$[PdL^1(py)]ClO_4$ [c]	1.87m (4-CH_2); 2.52s (SCH_3); 2.6—3.8;[d] 5.43br (NH_2); 7.72 (2 H), 8.12 (1 H), 9.12 (2 H), (py)
$[PdL^1(NH_3)]ClO_4$	1.87m (4-CH_2); 2.55s (SCH_3); 2.6—3.8;[f] 5.0br (NH_2 + NH_3)[d]
$[PdL^1(H_2O)]ClO_4$ [e]	1.87m (4-CH_2); 2.58s (SCH_3); 2.4—3.3;[f] 5.48br (NH_2); 4.9br (H_2O)
$[PdL^3(MeCN)]ClO_4$ [e]	1.38t (d-CH_3); 1.88m (4-CH_2); 2.05s (MeCN); 2.60s (SCH_3); 2.4—3.2;[f] 3.73t (b-CH_2)
$[PdL^2(py)]Cl$ [e]	1.18d (b-CH_3); 1.85m (4-CH_2); 2.52s (SCH_3); 2.5—3.5;[f] 4.95br (NH_2); 7.40 (2 H), 7.82 (1 H), 8.85 (2 H), (py)

[a] See above for numbering of carbon atoms. [b] s = Singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. [c] In $CDCl_3$. [d] Overlapping multiplets with the indicated centre of gravity. [e] In $[^2H_6]$dmso. [f] Several overlapping resonances.

protons take place to some extent. In $[PdL^2(py)]ClO_4$ relatively large downfield shifts of the pyridine resonances show strong bonding with the metal ion. However, it may be noted that in dmso solution considerable dissociation of $[PdL^2(py)]Cl$ has taken place.

Electronic Spectra.—The electronic spectral features of the complexes are summarised in Table 4. The broad shoulder appearing at about 21 000 cm^{-1} appears to be due to a $^1A_{1g} \longrightarrow {}^1A_{2g}$ ($d_{xy} \longrightarrow d_{x^2-y^2}$) transition. The higher energy bands are due to charge transfer(s) and internal ligand transitions. The crystal-field separation energies of the complexes calculated from the relationship[27] $\Delta_1 = E(v) + 35F_4$ [$F_4 = 60$ cm^{-1} for palladium(II)] vary in the range 21 500—24 000 cm^{-1}.

Thermal Analysis.—Both $[PdL^1Cl]$ and $[NiL^1Cl]$ are thermally stable compounds and do not decompose below 250 °C. Complexes of the type $[ML^1(B)]Cl$ (B = py, NH_2Et, or $NHEt_2$) undergo thermal dissociation in the temperature range 110—190 °C and quantitative liberation of the base molecules takes place (see below). The heats of decomposition

Table 4. Electronic spectral data for the palladium(II) complexes

Complex	Solvent	$\lambda_{max.}/cm^{-1}$ (ε/dm^3 mol^{-1} cm^{-1})
$[PdL^1Cl]$	$MeNO_2$	21 300 (355); 25 000 (6 050)
$[PdL^2Cl]$	dmso	21 200 (380); 25 000 (6 000); 30 100 (2 900)
$[PdL^2Br]$	dmso	21 280 (400); 25 000 (6 000); 30 300 (2 900)
$[PdL^3Cl]$	$CHCl_3$	21 050 (370); 24 100 (7 600); 25 000 (5 400); 29 000 (3 100); 32 500 (10 000); 36 800 (12 050)
$[PdL^3Br]$	$CHCl_3$	20 800 (260); 24 100 (7 600); 25 000 (5 400); 32 600 (10 700); 36 200 (11 800)
$[PdL^1(MeCN)]ClO_4$	MeCN	21 460 (210); 25 500 (8 100); 33 560 (11 500)
$[PdL^3(MeCN)]ClO_4$	MeCN	21 900 (325); 25 380 (7 050); 33 780 (11 300); 38 760 (34 800)
$[PdL^1(py)]ClO_4$	MeCN	2 540 (9 200), 33 560

$$[ML(B)]X\ (s) \longrightarrow [MLX]\ (s) + B\ (g)$$

(ΔH) determined by d.t.a. consist of two enthalpy terms, namely the heat of dissociation ($\Delta H_{dissoc.}$) of the complexes and the heat of vaporisation ($\Delta H_{vap.}$) of the Lewis bases. In Table 5 relevant thermal analysis data for palladium(II) and nickel(II) complexes are compared. Although the heat of vaporisation of pyridine (35.15 kJ mol^{-1}) is available,[28] unfortunately the values for ethylamine and diethylamine are not. The ΔH values, therefore, do not give information about the heat of dissociation (which in effect is the heat of formation) of the complexes. Nevertheless, nickel(II) and palladium(II) complexes with the same Lewis base can be compared to give their relative stabilities. The values of ΔH_{Ni}—ΔH_{Pd} in Table 5 indicate that in all three cases the nickel(II) complexes are more stable. This would mean relatively greater bond strengths of Ni–B and identical geometry for all of the complexes.

Conclusions

The present study shows that the palladium(II) complexes [PdLX] and [PdL(B)]X (X = Cl, Br, or ClO_4) are quite stable. The reaction between stoicheiometric amounts of [PdLX] (X = Cl or Br) and silver perchlorate in methanol and acetonitrile demonstrates that the solvent molecules readily become co-ordinated under co-ordinatively unsaturated conditions. The two types of complexes obtained, namely $[Pd_2L_2Br]ClO_4$ and $[Pd(HL)Br]ClO_4$, in acetone show the difference in reactivity patterns of [PdLX] with silver perchlorate (2 : 1 molar ratio) with change in acidity of the medium. The most likely bonding involved in $[Pd(HL)Br]ClO_4$ is shown below; $[Pd_2L_2Br]ClO_4$ appears to be a monohalogen-bridged dimeric palladium(II) complex.

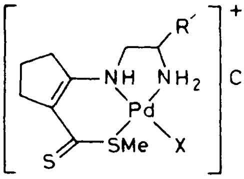
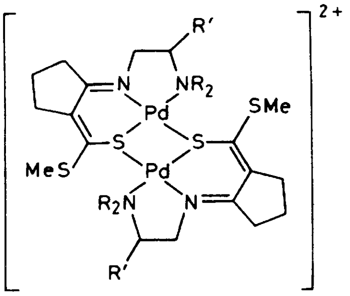


Table 5. Thermal analysis data for some palladium(II) and nickel(II) complexes

Complex	Temperature range for decomposition (°C)	% Weight loss Observed	% Weight loss Calculated	ΔH/ kJ mol^{-1}	$(\Delta H_{Ni} - \Delta H_{Pd})$/ kJ mol^{-1}
$[NiL^1(py)Cl]$	115—190	20.7	20.4	52	3
$[PdL^1(py)Cl]$	130—185	18.4	18.1	49	
$[NiL^1(NH_2Et)Cl]$	110—185	12.3	12.7	37	5
$[PdL^1(NH_2Et)Cl]$	110—180	11.2	10.8	32	
$[NiL^1(NHEt_2)Cl]$	110—160	18.6	19.1	41	4
$[PdL^1(NHEt_2)Cl]$	110—160	16.2	16.5	37	



In dry acetone where the solvent co-ordination is no longer feasible one would expect to find the formation of the dimeric species $[Pd_2L_2][ClO_4]_2$ (above). Indeed, $[Ni_2L_2][ClO_4]_2$ has been isolated;[29] however, the lack of formation of the palladium(II) analogue indicates that some deviation from the planar configuration that would be required due to thiolo-bridge formation in the above structure is not allowed by crystal field effects. This would offer an opportunity for the formation of the species $[PdLL']ClO_4$ (L' = CO, alkene, alkyne, *etc.*) which will be the subject matter of future reports.

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