Metal Complexes of Sulphur–Nitrogen Ligands. Synthesis and Characterization of Palladium(II) Complexes of 3-(Mercaptomethyl)piperidine

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The complexes [Pd(HL)X_2] [X = Cl (**1a**) or Br (**1b**)], [$(PdLX)_2$] [X = Cl (**2a**), Br (**2b**), or I (**2c**)], and [Pd_3L_4]Cl_2·$2H_2O$ (**3**), where HL and L denote respectively 3-(mercaptomethyl)piperidine in its zwitterionic and anionic forms, have been prepared and characterized. Complex (**3**) has been shown crystallographically to contain centrosymmetrical trinuclear cations where terminal PdL_2 units, containing *cis*-S_2PdN_2 square-planar metal environments, are bound also in a square-planar fashion to a central palladium atom through bridging mercapto groups. The three planar metal environments exhibit equivalent dihedral angles. Complexes (**2**) exhibit *trans* mercapto-bridged dimeric structures containing S_2PdNX square-planar metal centres. Similar sulphur-bridged dimeric structures, with planar S_2PdX_2 metal environments, are proposed for complexes (**1**). Complexes (**2**) and (**3**) are among the first known chelates of γ-mercaptopiperidines.

Previous reports from our laboratories have dealt with the coordination chemistry of γ-mercaptoamines,[1–3] and we have recently published some results concerning γ-mercaptoalkylpiperidine ligands.[4–7] These were attempts to enhance the chelating ability of one of the ligands previously studied, 4-mercapto-1-methylpiperidine, which behaves as a unidentate ligand.[8–10] In spite of the lower steric requirements of 2- and 3-(mercaptoalkyl)piperidine ligands, no chelate compounds have been found with Ni^{II}, Cu^{I}, Ag^{I}, and Cd^{II}.[6]

In an extension of these studies to the second-row transition metals, and particularly to Pd^{II}, chelate complexes in which 3-(mercaptomethyl)piperidine (HL) behaves as a bidentate ligand have been isolated for the first time.

Experimental

I.r. spectra were recorded on potassium halide or polyethylene (600—180 cm^{-1}) pellets or Nujol mulls using Beckman I.R.-20 A and Perkin-Elmer 850 spectrophotometers. Electronic spectra were recorded on Shimadzu UV 240 (200—800 nm) and Beckman Acta VII (800—2 500 nm) spectrophotometers. Analytical data are given in Table 1. Palladium was determined volumetrically with ethylenediaminetetra-acetate (edta) and C, H, and N with a Perkin-Elmer 240 analyzer.

Table 1. Analytical data for the palladium complexes with required values in parentheses

Complex	Analysis(%) C	H	N	Pd
(**1a**) [Pd(HL)Cl_2]	23.4	4.2	4.3	34.6
	(23.4)	(4.25)	(4.5)	(34.5)
(**1b**) [Pd(HL)Br_2]	18.6	3.4	3.55	26.7
	(18.1)	(3.3)	(3.5)	(26.8)
(**2a**) [$(PdLCl)_2$]	26.75	4.6	5.1	38.7
	(26.5)	(4.45)	(5.15)	(39.1)
(**2b**) [$(PdLBr)_2$]	22.4	3.6	4.5	33.5
	(22.7)	(3.8)	(4.4)	(33.6)
(**2c**) [$(PdLI)_2$]	20.1	3.3	3.9	29.3
	(19.8)	(3.3)	(3.85)	(29.3)
(**3**) [Pd_3L_4]Cl_2·$2H_2O$	30.6	5.5	5.95	33.8
	(30.4)	(5.5)	(5.9)	(33.7)

3-(Mercaptomethyl)piperidine was synthesized following a recently reported method.[11] The racemic mixture was used without separation of the enantiomers.

Preparation of Complexes.—[Pd(HL)Cl_2] (**1a**). The ligand (1.0 mmol) dissolved in water (8 cm^3) with a few drops of methanol was added with stirring to an aqueous solution of $Na_2[PdCl_4]$ (10 cm^3, 1.0 mmol). A red microcrystalline precipitate was collected, washed with water and ethanol, and dried under vacuum.

[Pd(HL)Br_2] (**1b**). An aqueous solution of $Na_2[PdCl_4]$ (10 cm^3, 1.0 mmol) was added with stirring to a hot, saturated KBr solution containing 1.0 mmol of HL in aqueous methanol (19:1 v/v, 20 cm^3). The reaction mixture was stirred at 80—85 °C for 30 min. A dark red microcrystalline precipitate was collected, thoroughly washed with hot water and then with ethanol, and dried under vacuum.

[$(PdLCl)_2$] (**2a**). Upon addition of HL (1.0 mmol) dissolved in aqueous methanol (19:1 v/v) to a saturated NaCl aqueous solution containing $Na_2[PdCl_4]$ (1.0 mmol) an orange-red precipitate appeared. The reaction mixture was adjusted to pH 8 with NaOH and then stirred for 30 min. A dark yellow precipitate was filtered off and washed several times with hot water until no chloride was detected in the washings. It was dried *in vacuo* over silica gel.

[$(PdLBr)_2$] (**2b**). The same procedure as above was followed but the $Na_2[PdCl_4]$ solution was saturated with KBr. An orange precipitate was obtained.

[$(PdLI)_2$] (**2c**). An aqueous solution of $Na_2[PdCl_4]$ (1.0 mmol) was added with stirring to a saturated KI aqueous solution containing HL (1.0 mmol) and the stoicheiometric amount of 0.02 mol dm^{-3} NaOH. The mixture was stirred for 30 min. The brown precipitate was collected, thoroughly washed with hot water, and dried under vacuum.

Complexes (**2a**)—(**2c**) are soluble in $CHCl_3$ and CH_2Cl_2.

[Pd_3L_4]Cl_2·$2H_2O$ (**3**). An aqueous solution of $Na_2[PdCl_4]$ (1.0 mmol) was added with stirring to HL (1.3 mmol) dissolved in 3.5 mol dm^{-3} aqueous NH_3. If a small amount of precipitate appeared at this stage it was redissolved by adding some drops of concentrated aqueous NH_3. On standing, yellow crystals appeared within a few days, which were collected and washed with a small amount of ethanol.

The same procedure can be used in the preparation of the corresponding bromide compound.

Table 2. Selected i.r. bands (4 000—250 cm^{-1}) for palladium(II) complexes

(1a)[a]	**(1b)**	**(2a)**	**(2b)**	**(2c)**	**(3)**	Assignment
3 190w	3 180w					$\nu(\overset{+}{N}H_2)$
3 090(sh)	3 080(sh)					
3 050s,br	3 040s,br					
		3 160s	3 160s	3 160s	3 030s	ν(N–H)
1 590m[b]	1 590s[b]					$\delta(H\overset{+}{N}H)$
		490s	490s	490s	482, 492d[c],s	ν(Pd–N)
340m	340m	350m	345m	340m	360, 340m	ν(Pd–S)
		300m, (sh)	300s	300s	300s	Chelate ring
275vs,br		270s				ν(Pd–Cl)

[a] Spectrum recorded within the 4 000—180 cm^{-1} range. [b] Sharp. [c] Doublet.

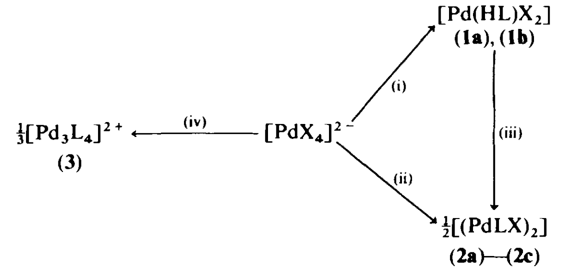
Table 3. Electronic spectra * of palladium(II) complexes

Complex	Solvent				
(**1a**) $[Pd(HL)Cl_2]$	Solid	36.1	, 31.7	, 26.0	, 22.2
(**1b**) $[Pd(HL)Br_2]$	Solid	34.7	, 29.4	, 25.0	, 21.5
(**2a**) $[(PdLCl)_2]$	$CHCl_3$	36.8(18 300),	32.3(6 000),	28.3(4 200),	23.8(800)
(**2b**) $[(PdLBr)_2]$	$CHCl_3$	35.3(19 700),	31.0(6 000),	27.5(4 500),	23.2(800)
(**2c**) $[(PdLI)_2]$	$CHCl_3$	34.0(17 400),	29.4(10 000),	26.3(5 000),	22.7(800)
(3) $[Pd_3L_4]Cl_2 \cdot 2H_2O$	MeOH	39.7(12 000),	35.6(11 000),	29.1(10 400)	

* In 10^3 cm^{-1} with ε/dm^3 mol^{-1} cm^{-1} in parentheses.

Results and Discussion

Synthesis.—The preparative reactions are indicated in Scheme 1. Reaction (iii) may be considered as a non-reversible acid–base reaction in which amine groups, upon deprotonation, become co-ordinated to metal atoms, as it will be demonstrated later. No appreciable reaction is observed on treating complexes (**2a**)—(**2c**) with diluted acids. Reactions similar to (iii) but reversible have been shown to occur between cationic and neutral complexes of γ-mercaptoamines,[3,10] the reaction proceeding in both directions without significant rearrangement of their common sulphur-bridged polymeric structures. Owing to the non-reversibility of reaction (iii), frameworks different from the latter may be expected in our case.



Scheme 1. (i) X = Cl or Br, HL; (ii) X = I, L^-; (iii) X = Cl or Br, NaOH, pH 8.0; (iv) X = Cl or Br, $\frac{4}{3}$ L^-, 3.5 mol dm^{-3} NH_3

I.r. Spectra.—Table 2 lists the principal i.r. bands. Complexes (**1a**) and (**1b**) are shown to contain protonated amine groups and thus the ligands are in zwitterionic form (HL), co-ordinating only through the sulphur atom. The frequencies of the $\nu(\overset{+}{N}H_2)$ bands are indicative of weak hydrogen-bonding interactions[12] suggesting that the halide anions are not free but involved in metal co-ordination.

A relevant feature of the complexes with the ligand in its anionic form, (**2a**)—(**2c**) and (**3**), is the shift of ν(N–H) from 3 280 cm^{-1} for the free ligand to 3 160 cm^{-1} for (**2a**)—(**2c**) and 3 030 cm^{-1} for (**3**) showing that co-ordination *via* nitrogen is taking place.[13] Owing to the non-sensitivity of ν(N–H) in complexes (**2a**)—(**2c**) towards the corresponding halide, the N–H groups are not appreciably involved in hydrogen-bond formation suggesting that halide anions are co-ordinated to the palladium atoms. This is not the case for the complex (3), where the much larger shift of ν(N–H) indicates, besides N-co-ordination, strong hydrogen-bonding interactions which point to a counter-cation behaviour of the chloride anions.[13,14]

Assignments of the metal–ligand vibrations (Table 2) confirm the chelating behaviour of the ligand in complexes (**2a**)—(**2c**) and (3) as well as the existence of Pd–Cl bonds in (**1a**) and (**2a**). While ν(Pd–S)[15–17] and ν(Pd–N)[18–20] are in good agreement with other data reported, ν(Pd–Cl) appears at rather lower frequencies than is usual.[19,20]

Electronic Spectra.—The electronic spectra of the complexes (Table 3), displaying a common pattern and showing no bands above 500 nm, are indicative of square-planar palladium(II) environments.[21] Strong ligand-to-metal charge-transfer (l.m.c.t.) absorptions appearing above 25 000 cm^{-1} overlap the spin-allowed *d–d* bands and make difficult the determination of the latter. Thus we have been able to estimate no band other than ν_1(22 200, 21 500, 23 800, 23 200, and 22 700 cm^{-1}) corresponding to complexes (**1a**), (**1b**), and (**2a**)—(**2c**).

The orders of decreasing energy, X = Cl > Br > I, (**2a**) > (**1a**), and (**2b**) > (**1b**), displayed by the *d–d* bands and also by the charge-transfer transitions of complexes (**1a**), (**1b**), and (**2a**)—(**2c**) reflect the spectrochemical series as well as the optical electronegativity of X,[22,23] and provide additional support for the co-ordination of the halide anions in these compounds. Moreover, the highest energy c.t. absorptions observed for complex (3) account for the absence of Pd–Cl bonds.

Complexes with the Ligand in Anionic Form.—The structure of $[Pd_3L_4]Cl_2 \cdot 2H_2O$ (3). The crystal structure of this compound has recently been published[5] but only a general description was given. The numbering system employed is depicted in Figure 1.

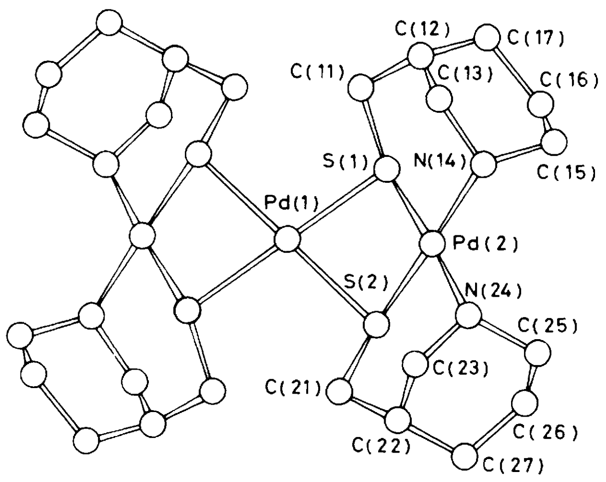


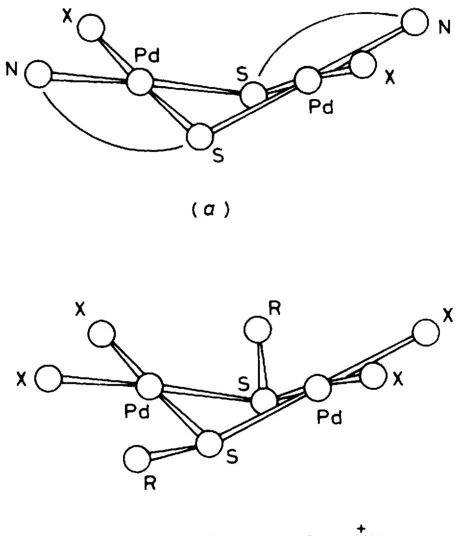
Figure 1. A view of the structure of $[Pd_3L_4]^{2+}$, with the atom numbering scheme

The structure consists of discrete trinuclear $[Pd_3L_4]^{2+}$ cations, chloride anions, and water molecules. The shortest N–Cl distances (3.24, 3.15 Å) account for significant N–H $\cdots$ Cl hydrogen bonding[14] as was indicated by the i.r. spectrum.

Even though the cation closely approaches C_{2h} symmetry, this is actually C_i. The crystallographically imposed inversion centre, which is located at the central palladium atom, causes the cation to contain both enantiomers of the ligands. Two of these, respectively *d* and *l*, co-ordinate each terminal palladium atom giving rise to *cis*-S_2PdN_2 environments. The central palladium atom is held to the terminal moieties through bridging sulphur atoms of the mercapto groups, the five atoms of the PdS_4 environment lying rigorously on a plane due to the inversion centre at the metal atom. Both this plane and the also planar S_2PdN_2 units (largest deviation from mean plane 0.025 Å) determine dihedral angles of 133° thus imposing folding of the four-membered PdS_2Pd rings along the S–S axis. These rings have the *syn-endo* bridged conformation.*[,24] While the two crystallographically independent piperidine rings exhibit a regular chair conformation, the two six-membered chelate rings have a slightly distorted one.

Fackler[24] has discussed the relationships between some structural parameters of these mercapto-bridged rings and their influence on M–M interactions. According to his work, the large values of the Pd–Pd distance [3.217(1)Å] and of the dihedral folding (133.0°) preclude any M–M interaction in our complex. Due to the fact that the S–S distance [2.982(6)Å] is shorter than the normal S–S van der Waals non-bonding distance (3.2 Å), significant bonding forces may be associated with it.[24] The values of these parameters lie between those found in some dimeric palladium complexes of γ-mercaptoamines[5,7] and in the complex $[\{Pd(SBu^t)(S_2CSBu^t)\}_2]$.[24]

Both types of palladium environments display significant deviations from the square geometry. This is revealed by the S(1)–Pd(1)–S(2) angle of 80.0° as well as the mean value of the N–Pd–S angles (95.2°), which are 14.0 and 6.8° respectively larger than S–Pd(2)–S and N–Pd–N. Both Pd–S distances [mean 2.319(5) and 2.291(11) Å, respectively for Pd(1) and Pd(2)] and Pd–N [mean 2.098(17) Å] are in good agreement with other reported data (2.28—2.38 Å for Pd–S[5,7,24–27] and 2.02—2.18 Å for Pd–N[5,7,28–30]). The planar PdS_4 environment of an analogous PdNi heterometallic complex[27] exhibits exactly the same S–Pd–S angles (80, 100°) but slightly larger Pd–S bond lengths (2.34 Å).



(*a*)

(*b*) $R = C_6H_{11}\overset{+}{N}H_2$

Figure 2. Structures proposed for (*a*) $[(PdLX)_2]$ (X = Cl, Br, or I) **(2a)**—**(2c)** and (*b*) $[Pd(HL)X_2]$ (X = Cl or Br) **(1a)** and **(1b)**

cis-S_2PdN_2 Environments give rise to the splitting of ν(Pd–N) (482, 492 cm^{-1}).[19]

$[(PdLX)_2]$ (X = Cl, Br, *or* I) **(2a)**—**(2c)**. The stoicheiometry and spectral properties of these compounds, which indicate co-ordination *via* N, S, and X, together with a strong tendency of the mercapto groups to behave as bridging ligands,[31,32] lead to the assumption of a sulphur-bridged dimeric structure containing square-planar palladium environments. Besides the experimental solubilities, the presence of an unique band attributable to ν(Pd–N) in the i.r. spectra of all these complexes as well as the sole ν(Pd–Cl) in that of complex **(2a)** point to a *trans* configuration[19] [splitting of ν(Pd–N) was observed for complex (3)]. Similarly to complex (3), these structures are expected to be bent about the sulphur bridge [Figure 2(*a*)].[24] Only the *trans* isomer has been analyzed crystallographically in related complexes.[5,7] A strong *trans* effect has been associated with sulphur ligands.[32,33] The low frequency of ν(Pd–Cl) for complex **(2a)** might be due to the *trans* effect of one of the bridging mercapto groups on the chlorine atom.

Complexes with the Ligand in Zwitterionic Form, $[Pd(HL)X_2]$ (X = Cl *or* Br) **(1a)** *and* **(1b)**.—Two structural possibilities may be derived from the stoicheiometry and available spectral data, both containing square-planar palladium environments. A sulphur-bridged polymeric structure $[\{Pd(HL)_2\}_n]^{2n+}$ with $[PdX_4]^{2-}$ as counter cation has already been suggested for some palladium complexes of 4-mercapto-1-methylpiperidine.[10] A molecular dimeric structure $[\{Pd(HL)X_2\}_2]$, similar to that proposed for complexes **(2a)**—**(2c)**, may also be considered.

A lower frequency for ν_6 corresponding to $[PdCl_4]^{2-}$ than in its usual range (336—327 cm^{-1})[34,35] would be expected in the presence of a polymeric cation such as $[\{Pd(HL)_2\}_n]^{2n+}$. The large shift of 60 cm^{-1} that would be required to reach the frequency of 275 cm^{-1} observed for complex **(1a)** makes it unlikely that this band can be associated with ν_6.[19] In this connection, shifts up to only 15 cm^{-1} have been found for ν_3 of $[CoX_4]^{2-}$ in $[\{Co(HL)_2\}_n][(CoX_4)_n]$, polymeric complexes of Co^{II} with 3-(mercaptomethyl)-1-methylpiperidine.[36] Furthermore, there is no absorption around 193 cm^{-1} (ν_7 of $[PdCl_4]^{2-}$) or around 260 cm^{-1} (ν_6 of $[PdBr_4]^{2-}$)[19] for complex **(1b)**.

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* Mis-stated as *syn-exo* in ref. 5.

Therefore, the i.r. data do not support an ionic polymeric structure for complexes (**1a**) and (**1b**). The behaviour of the reaction (iii), already mentioned, also casts some doubt on this assumption.

Both arguments allow us to postulate the existence of dimeric structures in complexes (**1a**) and (**1b**) with planar X_2PdS_2 metal environments which probably determine a dihedral angle about the S bridge [Figure 2(*b*)].[24] The two i.r. -allowed ν(Pd–Cl)[19] due to the *cis*-Cl_2PdS_2 units in complex (**1a**) would be obscured by the broad and very strong absorption centered at 275 cm^{-1}. As in complex (**2a**), the *trans* effect of the bridging mercapto groups would account for the low value of this frequency. A similar structure but with tetrahedral metal centres has been crystallographically demonstrated in the complex [{Zn(HL)-Cl_2}$_2$] where HL is 4-mercapto-1-methylpiperidine.[8]

Conclusions

By reacting 3-(mercaptomethyl)piperidine with $[PdX_4]^{2-}$ salts we have been able to prepare complexes with the ligand in its zwitterionic form and trinuclear and dinuclear S,N-chelates. These are among the first known chelate compounds containing γ-mercaptopiperidine ligands.[7]

Corresponding reactions of 2- and 3-(mercaptoalkyl)-piperidines as well as of 3-(dimethylamino)propane-1-thiol with nickel(II) salts led to polymeric compounds where metal co-ordination was achieved only through sulphur atoms.[3,6] The higher stability of Pd^{II}–X compared with Ni^{II}–X bonds, the greater size of palladium(II) ion, and, in our case, the softening of the nitrogen atom in the piperidine ring[37] seem to account for this different behaviour.

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