First Chelate Complexes of 4-Mercapto-1-methylpiperidine. Synthesis and Characterization of [{M(μ-SC$_5$H$_9$NMe)X}$_2$] (M = Pd^{II}, X = Cl, Br, or I; M = Pt^{II}, X = Br or I). Crystal and Molecular Structure of [{Pt(μ-SC$_5$H$_9$NMe)Br}$_2$]†

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The reaction of 4-mercapto-1-methylpiperidine in the presence of NEt$_3$ with palladium(II) and platinum(II) halides or treatment of complexes [M(SC$_5$H$_9$NHMe)$_2$][MX$_4$] (M = Pd or Pt; X = Cl, Br, or I) with the same base has led to complexes [{M(μ-SC$_5$H$_9$NMe)X}$_2$] (M = Pd, X = Cl, Br, or I; M = Pt, X = Br or I). When M = Pt and X = Br, crystals are monoclinic, space group $P2_1/a$, with a = 13.236(8), b = 9.280(8), c = 14.823(5) Å, and β = 92.00(4)°. The crystal structure consists of chemically independent dinuclear molecules, where each ligand is terdentate and simultaneously S,N-chelating and μ-S bridging. One bromine atom completes the co-ordination around each platinum. The metal environment is approximately square planar, both S$_2$PtNBr planes generating a dihedral angle of 125.24°. There is no metal–metal bonding. Based on the i.r. and ^{1}H n.m.r. spectra, the same structure is proposed for the remaining complexes.

The recent development of the fundamental chemistry of metal complexes of simple thiolates[1–3] was aimed mainly to provide synthetic analogues of the active sites of metalloproteins,[3–5] among which metallothioneins (low-molecular-weight sulphydryl-rich proteins) constitute a prominent group.[6] However, the known tendency of thiolate ligands to give highly insoluble neutral complexes of polymeric nature has led to new synthetic strategies,[1–4,7–9] most of them in organic media, in order to be able to obtain structural information on metal–thiolate complexes.[1]

Aliphatic γ-mercaptoamine ligands offer important advantages compared to simple thiols. They may behave as such when the amine group is protonated. In this case the complex species may be considered as thiolates, which at the same time are water soluble and even allow solution equilibria studies to be carried out.[10] If the γ-mercaptoamines behave as chelates, additional models of metal binding by metalloproteins can be obtained, because the metal environment in the active sites is not necessarily restricted to sulphur atoms. The recently reported complexation of Hg^{2+} by a heavy-metal receptor protein in the presence of an excess of thiol competitors[11] points out to the usefulness of such models.

The structures of several metal complexes of aliphatic γ-mercaptoamines behaving as simple thiol ligands have already been reported.[12] Furthermore, dinuclear chelate complexes have been fully characterized with Pd^{II} and 3-dimethylamino-1-propanethiol,[13] 2-(mercaptoethyl)-1-methylpiperidine,[14] and 3-(mercaptomethyl)-1-methylpiperidine.[15] Trinuclear chelate complexes of known structure have been reported for Co^{III} (ref. 16) and Ni^{II} (ref. 17) with 3-amino-1-propanethiol and Pd^{II} (refs. 13 and 18) with 3-(mercaptomethyl)piperidine. As an extension of this work we now report the synthesis and structure of the first chelate complexes of 4-mercapto-1-methylpiperidine, which have been obtained with Pd^{II} and Pt^{II}.

Experimental

4-Mercapto-1-methylpiperidine was synthesized according to a previous method.[19] Palladium(II) bromide was obtained from palladium metal by following standard procedures;[20a] the metal was obtained either by refluxing overnight a PdCl$_2$ dispersion in propanol–water (1:1, v/v) or a K$_2$[PdCl$_4$] solution in the same solvent but in a 2:1 ratio. Palladium(II) iodide was synthesized according to known procedures using K$_2$[PdCl$_4$] as starting material.[20b] The compounds PdCl$_2$ and PtCl$_2$ as well as Pt were commercial products; H$_2$PtCl$_6$ and K$_2$[PtCl$_4$] were obtained from Pt according to literature methods.[20c] The rest of the materials as well as solvents were research grade used without further purification. Reactions were carried out in the open air, except for several unsuccessful attempts at synthesizing the complex [{Pt(SC$_5$H$_9$NMe)Cl}$_2$].

[{Pd(μ-SC$_5$H$_9$NMe)Cl}$_2$] (1).—A solution of 4-mercapto-1-methylpiperidine (0.17 g, 1.3 mmol) in methylene chloride (20 cm^3) containing triethylamine (0.5 cm^3) was added slowly with stirring to a dispersion of PdCl$_2$ (0.23 g, 1.3 mmol) in 10 cm^3 of the same solvent. Stirring was continued overnight and then the slight amount of unreacted PdCl$_2$ was removed by filtration. The solvent was evaporated and the solid residue dissolved in absolute methanol containing three or four drops of triethylamine. The clear solution was then allowed to crystallize overnight in a refrigerator. The first two crops of crystals were identified as NHEt$_3$Cl. Finally, yellow crystals of the palladium complex separated. They were filtered off and washed with cold methanol (Found: C, 26.60; H, 4.50; N, 5.45. Calc. for C$_6$H$_{12}$ClNPdS: C, 26.50; H, 4.45; N, 5.15%).

[{Pd(μ-SC$_5$H$_9$NMe)Br}$_2$] (2).—A solution of 4-mercapto-1-methylpiperidine (0.13 g, 1.0 mmol) in methylene chloride (15 cm^3) containing triethylamine (0.4 cm^3) was added slowly with stirring to a dispersion of PdBr$_2$ (0.26 g, 1.0 mmol) in 10 cm^3 of the same solvent. The solution became reddish brown after the first drops and the reaction mixture was left with stirring overnight. Then, the slight amount of unreacted PdBr$_2$ was filtered off, the solution evaporated to dryness, and the solid residue dissolved in methanol containing a few drops of

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† Bis(μ-1-methylpiperidine-4-thiolato-*N*,μ-*S*)-bis[bromoplatinum(II)].

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triethylamine. The orange crystals that separated from the cold solution were filtered off and washed with cold methanol (Found: C, 22.90; H, 3.80; N, 4.55. Calc. for $C_6H_{12}BrNPdS$: C, 22.75; H, 3.80; N, 4.40%).

[{Pd(μ-SC_5H_9NMe)I}$_2$] (**3**).—A solution of 4-mercapto-1-methylpiperidine (0.44 g, 3.3 mmol) in methylene chloride (45 cm^3) containing triethylamine (1.2 cm^3) was added slowly to a dispersion of PdI_2 (1.05 g, 2.9 mmol) in 30 cm^3 of the same solvent. After stirring for 1 h the filtered solution was evaporated to dryness and the solid residue dissolved in methanol containing several drops of triethylamine. Partial evaporation of the solvent yielded a brown microcrystalline solid that was filtered off, washed with diethyl ether, and dried (Found: C, 20.05; H, 3.25; N, 3.85. Calc. for $C_6H_{12}INPdS$: C, 19.80; H, 3.35; N, 3.85%).

An alternative route consisted of deprotonating the complex [Pd(SC_5H_9NHMe)$_2$][PdI_4],[21] where 4-mercapto-1-methylpiperidine is in zwitterionic form. In this case the addition of an excess of triethylamine to a dispersion of the complex in methylene chloride gave a clear dark coloured solution which once refrigerated yielded a solid with the same composition and aspect as that described above (Found: C, 20.30; H, 3.20; N, 3.90%).

[{Pt(μ-SC_5H_9NMe)Br}$_2$] (**4**).—The complex [Pt(SC_5H_9NHMe)$_2$][$PtBr_4$][21] (0.35 g, 0.36 mmol) was readily dissolved in methylene chloride (20 cm^3) containing triethylamine (3 cm^3). The filtered orange solution was vacuum evaporated until a solid started to separate. A yellow crystalline solid was filtered off, washed with water and diethyl ether, and vacuum dried (Found: C, 18.30; H, 3.00; N, 3.65. Calc. for $C_6H_{12}BrNPtS$: C, 17.80; H, 3.00; N, 3.45%).

Crystals suitable for *X*-ray diffraction were grown from diluted reaction mixtures placed in a refrigerator for several days; they were filtered off, washed with water, which allowed separation from triethylammonium chloride, and finally with diethyl ether. Dissolving the corresponding complex in a solvent containing triethylamine always led either to very thin plates or macles, despite our many attempts in different solvents and at different temperatures.

[Pt(SC_5H_9NHMe)$_2$][PtI_4] (**5**).—The salt $K_2[PtCl_4]$ (0.45 g, 1.08 mmol) was dissolved in 5 cm^3 of a saturated solution of sodium iodide in water at room temperature. The solution became nearly black and stirring was continued for 0.5 h. Then, 4-mercapto-1-methylpiperidine (0.15 g, 1.15 mmol) in water (10 cm^3) with 10% (v/v) methanol was added. An orange-brown precipitate appeared immediately. Stirring was continued for 45 min. This solid (0.60 g, 95% yield) was filtered off, washed with water and ethanol, and vacuum dried (Found: C, 12.75; H, 2.35; N, 2.45. Calc. for $C_6H_{13}I_2NPtS$: C, 12.40; H, 2.25; N, 2.40%).

[{Pt(μ-SC_5H_9NMe)I}$_2$] (**6**).—Complex (**5**) (0.575 g, 0.49 mmol) was dissolved in methylene chloride (20 cm^3) containing triethylamine (3 cm^3). The filtered solution was allowed to evaporate until an orange crystalline solid separated (30 min). The solid was filtered off and washed with water and diethyl ether (Found: C, 15.75; H, 2.65; N, 3.10. Calc. for $C_6H_{12}INPtS$: C, 15.95; H, 2.65; N, 3.10%). Subsequent solids obtained from the mother-liquor always gave mixtures of complex (**6**) with [Pt(SC_5H_9NMe)$_2$] and [Pt(SC_5H_9NHMe)$_2$]$^{2+}$, presumably both of them of polymeric nature.[21]

Complex (**6**) was also synthesized by adding a solution of 4-mercapto-1-methylpiperidine (0.066 g, 0.45 mmol) in methylene chloride (15 cm^3) containing triethylamine (0.5 cm^3) to a suspension of platinum(II) iodide (0.19 g, 0.42 mmol) in methylene chloride (6 cm^3). Stirring was continued for 5 h. Then methanol was added to the filtered solution until some solid separated. It was left in a refrigerator overnight, when the crystalline orange solid was filtered off, washed with diethyl ether, and vacuum dried. The solid thus recovered was of comparable formula to that of complex (**6**) (Found: C, 15.80; H, 2.60; N, 3.05%).

[Pt(SC_5H_9NHMe)$_2$][$PtCl_6$]·$2H_2O$ (**7**).—Dropwise addition of a concentrated H_2PtCl_6 aqueous solution (15% Pt w/w) to a dispersion of [Pt(SC_5H_9NMe)$_2$][21] (0.18 g, 0.375 mmol) in water–methanol (1:1, 100 cm^3) was carried out until a slight excess of the reactant H_2PtCl_6 was present. Stirring was continued for 30 min. At this time not only the solution had became orange but also the initially yellow solid had changed to this colour. Vacuum filtration of the reaction mixture was very slow, as usual with these polymeric compounds. The orange solid was washed with ethanol and diethyl ether and then dried *in vacuo* (Found: C, 15.55; N, 3.20; S, 6.85. Calc. for $C_6H_{15}Cl_3NOPtS$: C, 16.00; N, 3.10; S, 7.10%).

Analyses.—Microanalyses were performed either with a Carlo Erba NA-1500 or with a Perkin-Elmer 240 analyzer.

Physical Measurements.—Infrared spectra were recorded from 4000 to 600 cm^{-1} in KBr on a Perkin-Elmer 1710 spectrophotometer, proton n.m.r. spectra on a Varian XL-200 spectrometer in $CDCl_3$ solution.

X-Ray Data Collection, Structure Determination, and Refinement for [{Pt(μ-SC_5H_9NMe)Br}$_2$].—*Crystal data*. $C_6H_{12}BrNPtS$, $M = 810.5$, monoclinic, $a = 13.236(8)$, $b = 9.280(8)$, $c = 14.823(5)$ Å, $\beta = 92.00(4)°$, $U = 1\,819$ Å^3, $Z = 4$, $D_c = 2.96$ g cm^{-3}, $F(000) = 1\,472$, space group $P2_1/a$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 20$ mm^{-1}, room temperature.

A well formed plate-like orange crystal (0.31 × 0.23 × 0.12 mm) was mounted on an Enraf-Nonius CAD4 diffractometer. Intensity data were collected in the range $1 \leqslant \theta \leqslant 25°$ using the flat ψ mode for minimizing absorption effects. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using MULTAN 11/84[22] and refined by full-matrix least-squares techniques with SHELX 76.[23] Only Pt, Br, N, and S atoms were allowed to refine with anisotropic thermal parameters; C atoms were refined isotropically. The refinement procedure converged to $R = 0.078$ and $R' = 0.076$ where $w = [\sigma^2(F_o) + 0.007\,273|F_o|^2]^{-1}$ using 2 137 observed reflections $[I \geqslant 3\sigma(I)]$. The four highest peaks in the final Fourier difference synthesis were at distances of between 0.95 and 1.01 Å from platinum atoms. Atomic co-ordinates are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results and Discussion

Synthesis.—The two different synthetic routes indicated in the Scheme, have been followed to obtain complexes of formula [{M(SC_5H_9NMe)X}$_2$] (M = Pd, X = Cl, Br, or I; M = Pt, X = Br or I). The choice of the route in each particular case has been mainly determined by the availability of the metal-containing starting material. The synthesis of [{Pt(SC_5H_9NMe)Cl}$_2$] has not been achieved despite different changes in the procedures indicated in the Scheme. Thus, the bases sodium methoxide, potassium t-butoxide, and n-tributylamine were tested as well as using bis(benzonitrile)dichloroplatinum(II) and potassium tetrachloroplatinate(II) as starting materials. In most

Table 1. Fractional atomic co-ordinates (× 10^4) for non-H atoms of [{Pt(μ-SC_5H_9NMe)Br}$_2$]*

Atom	*X/a*	*Y/b*	*Z/c*
Pt(1)	201(1)	366(1)	6 468(1)
Pt(2)	−1 148(1)	−895(1)	7 982(1)
Br(1)	699(3)	2 897(3)	6 248(3)
Br(2)	−805(3)	−3 066(4)	8 908(3)
S(1)	−1 340(5)	957(8)	7 000(6)
S(2)	−447(5)	−1 865(7)	6 728(6)
N(1)	1 567(18)	−646(23)	6 097(15)
N(2)	−1 795(18)	419(25)	9 018(20)
C(11)	707(23)	−2 973(36)	6 962(23)
C(12)	1 165(23)	−3 286(40)	6 084(23)
C(13)	1 400(27)	−1 992(44)	5 549(26)
C(14)	2 247(27)	338(47)	5 586(26)
C(15)	1 464(21)	−2 051(35)	7 563(20)
C(16)	2 133(22)	−1 083(37)	6 927(21)
C(21)	−1 302(22)	2 515(38)	7 786(22)
C(22)	−2 342(23)	2 692(39)	8 139(22)
C(23)	−2 695(23)	1 258(39)	8 593(23)
C(24)	−2 175(26)	−457(40)	9 768(25)
C(25)	−503(26)	2 326(42)	8 530(25)
C(26)	−947(25)	1 420(46)	9 299(25)

* Numbers in parentheses are errors in the last significant digit(s). See Figure for atom-labelling scheme.

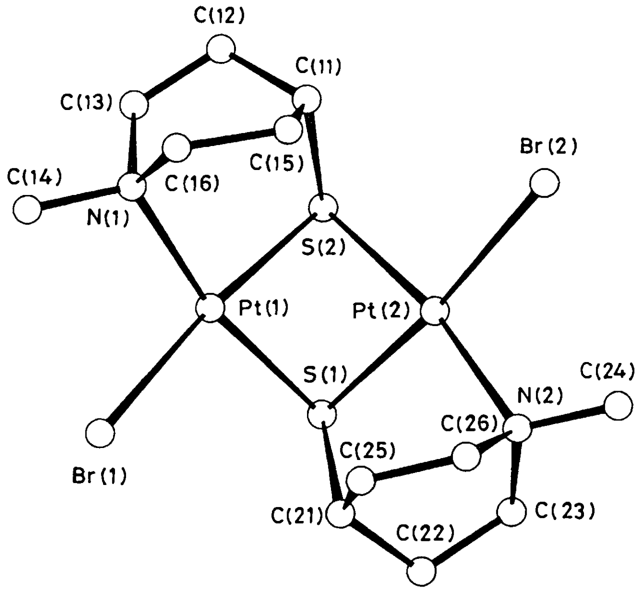
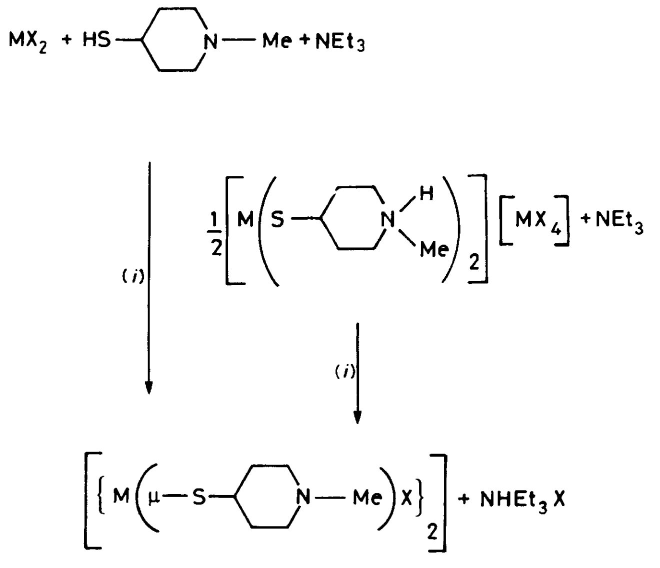


Figure. Structure of the molecule [{Pt(μ-SC_5H_9NMe)Br}$_2$] with the atom numbering scheme



Scheme. (*i*) CH_2Cl_2

cases the complex ($Pt(SC_5H_9NMe)_2$]^{21} is the final product. The high stability of [$M^{II}(SC_5H_9NMe)_2$] complexes, regardless of whether M = Pd or Pt,^{21} together with the fact that complex (**1**) is easily obtained and is as stable in the solid state as the other members of the family [(**2**)—(**4**) and (**6**)], make it difficult to find an explanation for the difficulties encountered in the synthesis of the platinum analogue. However, it should be noted that whilst the average yield of the palladium complexes is about 50%, in the case of platinum it is lower and even for complex (**6**) the maximum yield was 15%. Despite the low yield, the synthesis was reproducible by both methods.

Complexes (**1**)—(**4**) and (**6**) are all crystalline products very soluble either in methylene chloride or acetone. However, their stability in solution requires the presence of a base such as triethylamine in order to avoid protonation of the ligand and thus breakage of the M–N bond, which then leads to formation of [$M(SC_5H_9NHMe)_2]^{2+}$ species. Even though contamination of the chelates by triethylammonium chloride can easily be overcome by washing with water or methanol, contamination by sulphur-bridged polymeric species, [$M(SR)_2$] or [$M(SRH)_2]^{2+}$, never allowed a good isolation of pure chelate complexes.

Complex (**7**) belongs to a previously reported family of formula [$M(SRH)_2]^{2+}$.^{21} It is practically insoluble in all usual solvents such as water, methanol, ethanol, methylene chloride, chloroform, acetonitrile, dimethyl sulphoxide, and dimethylformamide and thus structure determination is no easier than that of its parent complexes, [$M(SR)_2$].

Description of the Structure of [{Pt(μ-SC_5H_9NMe)Br}$_2$] (**4**).—The crystal structure consists of dinuclear neutral molecules with no chemical interaction between them. The Figure displays the structure of the only crystallographically independent molecule, geometrical parameters for which are summarized in Table 2. The molecule, which is devoid of an inversion centre, comprises two platinum atoms linked by two bridging sulphur atoms. Both aminothiolate ligands also co-ordinate through nitrogen to Pt(1) and Pt(2), respectively, and thus behave as chelates. Two terminal *trans*-oriented bromine atoms complete the co-ordination around Pt(1) and Pt(2).

The co-ordination geometry around each platinum is approximately square planar, the angles around the metal being within the range 79.3—98.8°, and the deviations of the atoms from the best plane defined by the platinum and its four donor atoms do not exceed 0.041 Å. The interplanar dihedral angle is 125.24°, which is significantly smaller than those found in dinuclear palladium complexes with other chelating γ-mercaptoamine ligands, as indicated in Table 3. Chelated platinum complexes of this family of ligands as well as of 4-mercapto-1-methylpiperidine are reported here for the first time.

The average Pt–S bond length is 2.28(1) Å and the average Pt–N is 2.14(2) Å. Since it is generally found that chemically equivalent Pt–X and Pd–X bond lengths are within 0.01 Å of each other, the values found for Pt–S and Pt–N in the present compound can be compared with those reported for palladium chelates of 3-dimethylamino-1-propanethiol^{13} and 2-(mercaptoethyl)-1-methylpiperidine.^{14} As shown in Table 3, the M–S and M–N (M = Pd or Pt) values are in very good agreement. However, significant differences appear when comparing other geometric parameters in these three complexes. In the case of platinum the metal–metal distance [3.141(2) Å] is the shortest of the three whilst that of S • • • S [2.91(1) Å] lies in between those reported for the palladium complexes. Also, both Pt–S–Pt angles are smaller than the Pd–S–Pd angles. The observed Pt • • • Pt distance, which does not imply metal–metal bonding, can only be attributed to the relatively small interplanar dihedral angle, already mentioned, which is probably determined by the particular geometric constraints of the 4-mercapto-1-methylpiperidine ligand. The greater flexibility of the other aliphatic γ-mercaptoamines must account for the greater dihedral angles and consequently for the greater palladium–palladium distances and Pd–S–Pd angles. The fact that dinuclear complexes of Ni^{II}, Pd^{II}, and Pt^{II} with nonchelating S-bridging 3-dimethylamino-1-propanethiol have a dihedral angle of 180°[24] corroborates the importance of ligand structural requirements for the geometry of the M_2S_2 core.

Table 2. Interatomic distances (Å) and angles (°) for [{Pt(μ-SC_5H_9NMe)Br}$_2$] with estimated standard deviations in parentheses

Pt(2) • • • Pt(1)	3.141(2)	C(16)–N(1)	1.474(39)
Br(1)–Pt(1)	2.464(3)	C(12)–C(11)	1.484(45)
S(1)–Pt(1)	2.279(7)	C(15)–C(11)	1.571(43)
S(2)–Pt(1)	2.279(7)	C(13)–C(12)	1.478(51)
N(1)–Pt(1)	2.127(21)	C(16)–C(15)	1.593(42)
Br(2)–Pt(2)	2.471(4)	C(23)–N(2)	1.539(39)
S(1)–Pt(2)	2.261(8)	C(24)–N(2)	1.479(44)
S(2)–Pt(2)	2.290(8)	C(26)–N(2)	1.505(44)
N(2)–Pt(2)	2.162(26)	C(22)–C(21)	1.498(42)
C(21)–S(1)	1.856(35)	C(25)–C(21)	1.511(45)
C(11)–S(2)	1.863(32)	C(23)–C(22)	1.570(48)
C(13)–N(1)	1.501(45)	C(26)–C(25)	1.548(50)
C(14)–N(1)	1.505(43)		
Br(1)–Pt(1)–Pt(2)	127.7(1)	C(13)–N(1)–Pt(1)	113.3(19)
S(1)–Pt(1)–Pt(2)	46.0(2)	C(14)–N(1)–Pt(1)	113.0(19)
S(1)–Pt(1)–Br(1)	93.6(2)	C(14)–N(1)–C(13)	108.2(25)
S(2)–Pt(1)–Pt(2)	46.7(2)	C(16)–N(1)–Pt(1)	108.5(17)
S(2)–Pt(1)–Br(1)	172.9(2)	C(16)–N(1)–C(13)	106.5(24)
S(2)–Pt(1)–S(1)	79.3(3)	C(16)–N(1)–C(14)	106.9(24)
N(1)–Pt(1)–Pt(2)	122.0(6)	C(12)–C(11)–S(2)	107.6(23)
N(1)–Pt(1)–Br(1)	98.8(6)	C(15)–C(11)–S(2)	108.0(22)
N(1)–Pt(1)–S(1)	167.1(6)	C(15)–C(11)–C(12)	109.4(26)
N(1)–Pt(1)–S(2)	88.3(6)	C(13)–C(12)–C(11)	114.3(32)
Br(2)–Pt(2)–Pt(1)	127.1(1)	C(12)–C(13)–N(1)	114.5(30)
S(1)–Pt(2)–Pt(1)	46.5(2)	C(16)–C(15)–C(11)	109.2(25)
S(1)–Pt(2)–Br(2)	172.7(2)	C(15)–C(16)–N(1)	111.8(23)
S(2)–Pt(2)–Pt(1)	46.4(2)	C(23)–N(2)–Pt(2)	108.3(19)
S(2)–Pt(2)–Br(2)	93.4(2)	C(24)–N(2)–Pt(2)	112.2(19)
S(2)–Pt(2)–S(1)	79.4(3)	C(24)–N(2)–C(23)	107.9(24)
N(2)–Pt(2)–Pt(1)	123.1(7)	C(26)–N(2)–Pt(2)	103.5(19)
N(2)–Pt(2)–Br(2)	97.7(7)	C(26)–N(2)–C(23)	111.1(24)
N(2)–Pt(2)–S(1)	89.4(7)	C(26)–N(2)–C(24)	113.6(27)
N(2)–Pt(2)–S(2)	168.6(7)	C(22)–C(21)–S(1)	107.4(23)
Pt(2)–S(1)–Pt(1)	87.6(2)	C(25)–C(21)–S(1)	111.8(24)
C(21)–S(1)–Pt(1)	113.5(10)	C(25)–C(21)–C(22)	112.7(29)
C(21)–S(1)–Pt(2)	100.8(11)	C(23)–C(22)–C(21)	110.3(28)
Pt(2)–S(2)–Pt(1)	86.9(3)	C(22)–C(23)–N(2)	111.5(24)
C(11)–S(2)–Pt(1)	102.8(10)	C(26)–C(25)–C(21)	109.0(29)
C(11)–S(2)–Pt(2)	114.7(11)	C(25)–C(26)–N(2)	115.5(30)

The average Pt–S and Pt–N distances in complex (**4**) also agree well with those reported for the $[Pt_6(SCH_2CH_2NH_2)_8]^{4+}$ cation,[25] 2.30(2) and 2.085(10) Å respectively. Although the two structures are very different and thus further comparisons are difficult, in both cases the mercaptoamine ligands behave simultaneously as chelates and as bridging ligands. The average value found for Pt–Br in complex (**4**), 2.467(5) Å, agrees with that reported for sulphur-bridged dinuclear platinum and palladium complexes with terminal bromine atoms.[26]

Both piperidine rings exhibit a twist-boat conformation as evidenced by the lack or parallelism between the straight lines defined by C(12)–C(13) and C(15)–C(16) in one ring and by C(22)–C(23) and C(25)–C(26) in the other. The same conformation is found in both six-membered rings defined by Pt(1)–S(2)–C(11)–C(12)–C(13)–N(1) and Pt(1)–S(2)–C(11)–C(15)–C(16)–N(1) and also in the corresponding rings involving Pt(2) and S(1) atoms. The angle between the lines C(12)–C(13) and C(15)–C(16) (24.95°), Pt(1)–S(2) and C(12)–C(13) (24.40°), and Pt(1)–S(2) and C(15)–C(16) (35.10°) is a measure of the deviation of the corresponding ring from the ideal boat form. Values for the second piperidine ring are, respectively, 24.16, 27.36, and 32.05°. Despite the fact that no chelate complexes of 4-mercapto-1-methylpiperidine had been reported to date, it is now evident that metal bond formation together with the chelate effect can compensate for the higher energy of the twist-boat over the chair form in the piperidine ring. This energy is about 10 kcal mol^{-1} (41.84 kJ mol^{-1}) per ring.

The minimum distance found between molecules in the unit cell is 3.491 Å [C(13) • • • C(14′)], which indicates that the only forces acting on the chemical species are van der Waals interactions.

^1H *N.M.R. Data.*—The ^1H n.m.r. spectra of the complexes of formula [{M(μ-SC_5H_9NMe)X}$_2$] [(**1**)—(**4**) and (**6**)] are all very similar. Although signals corresponding to all piperidinic protons appear as overlapped peaks, a singlet assigned to the methyl group can easily be distinguished in all cases. However, the chemical shift of this singlet moves to lower fields, if compared with the free ligand, HSC_5H_9NMe (δ 2.18), depending mainly on the halogen co-ordinated to the metal atom. Thus for X = Cl, Br, and I, δ = 2.73, 2.85, and 3.13 for the palladium complexes (**1**)—(**3**) respectively, and for X = Br

Table 3. Comparison of the most relevant geometrical parameters of dinuclear γ-mercaptoamine chelates of Pd^{II} and Pt^{II}[a]

	[{Pd[μ-$S(CH_2)_3NMe_2$]Cl}$_2$][13]	[{Pd[μ-$S(CH_2)_2C_5H_9NMe$]Cl}$_2$][14]	[{Pt(μ-SC_5H_9NMe)Br}$_2$][b]
M–S (mean)/Å	2.279(6)	2.283(2)	2.28(1)
M–N (mean)/Å	2.160	2.180	2.14(2)
M • • • M/Å	3.305(1)	3.374(1)	3.141(2)
S • • • S/Å	2.929(4)	2.859(3)	2.91(1)
M–S–M (mean)/°	92.9	95.2	87.2(5)
Conformation of M_2S_2 ring	*syn–endo*[c]	*syn–endo*	*syn–endo*
Dihedral angle between MS_2NX planes	154.4(2)	142.8(1)	125.24

[a] The error in the last significant digit is given in parentheses, when reported. [b] This work. [c] Mis-stated as *syn–exo* in ref. 13.

and I, $\delta = 3.07$ and 3.32 for those of platinum, (**4**) and (**6**). This together with the fact that the singlet corresponding to the methyl group appears in the range 2.20—2.25 for complexes where 4-mercapto-1-methylpiperidine is in anionic form and co-ordinating through the sulphur atom exclusively, leads to the conclusion that the ligand behaves as a chelate in complexes (**1**)—(**3**) and (**6**) analogously as it has been shown in the molecular structure of complex (**4**). Reported ^1H n.m.r. data for $[\{Pd[\mu-S(CH_2)_2C_5H_9NMe]Cl\}_2]$[14] are in accord with the observed displacement of the resonance of the methyl group when the ligand behaves as a chelate.

Infrared Data.—The i.r. spectra of the crystalline complexes (**1**)—(**4**) and (**6**) are practically identical from 4 000 to 600 cm^{-1}. The ν(C–H) stretching region indicates unambiguously that 4-mercapto-1-methylpiperidine behaves as a chelating ligand, as in this case only a broad band centred at *ca.* 2 900 cm^{-1} appears between 3 000 and 2 500 cm^{-1}. By comparing these spectra with those of complexes with known structure where the ligand co-ordinates through the sulphur atom exclusively[12b] and also with palladium(II) chelate complexes of other γ-mercaptoamine ligands,[13,14] one can conclude that (*a*) the weak absorption at 3 020 cm^{-1} assigned to $\nu(CH_3-\overset{+}{N})$ and (*b*) the disappearance of the strong bands at 2 790 and 1 380 cm^{-1} assigned to $\nu(CH_3-\overline{N})$[27] and $\delta(CH_3-\overline{N})$[28] respectively, together with the characteristic band at 2 900 cm^{-1}, indicated above, are good evidence for the chelating behaviour of 4-mercapto-1-methylpiperidine.

Conclusions

Two different synthetic routes have led to the first metal complexes in which 4-mercapto-1-methylpiperidine behaves as a chelating agent. The complexes have the general formula $[\{M(SC_5H_9NMe)X\}_2]$ with either M = Pd and X = Cl, Br, or I or M = Pt and X = Br or I. The i.r. and ^1H n.m.r. spectra of the five complexes compare very well. Furthermore, the 3 000—2 800 cm^{-1} region of the i.r. spectra and the chemical shift of the methyl group indicate that the nitrogen atom participates in co-ordination. The molecular structure of the complexes must be very close to that found for M = Pt and X = Br by single-crystal *X*-ray diffraction, which consists of dinuclear neutral S-bridged molecules.

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