Synthesis and Characterization of Homo- and Hetero-nuclear Mixed Thiolate Phosphine Complexes with Ni^{II}, Pd^{II}, and Pt^{II}. Crystal and Molecular Structure of Bis[μ-(3-dimethylamino-1-propanethiolato)]-bis{[1,2-bis(diphenylphosphino)-ethane]nickel(II)} Tetraphenylborate†

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The following families of complexes have been prepared and characterized: $[M\{S(CH_2)_3NHMe_2\}_2(dppe)][BPh_4]_2$, dppe = $Ph_2PCH_2CH_2PPh_2$, M = Ni, Pd, or Pt; $[M\{S(CH_2)_3NMe_2\}_2(dppe)]$, M = Pd or Pt; $[(dppe)M\{\mu\text{-}S(CH_2)_3NMe_2\}_2M'(dppe)][BPh_4]_2$ (M = M' = Ni, Pd, or Pt; M = Ni, M' = Pd; M = Ni, M' = Pt; M = Pd, M' = Pt); and $[Ni\{Pt[\mu\text{-}S(CH_2)_3NMe_2]_2(dppe)\}_2][BPh_4]_2$. Infrared spectra indicate that within each family the complexes have the same structure. Crystals of the homonuclear nickel dimer are triclinic, space group $P\bar{1}$, with $a = 14.346(1)$, $b = 14.037(1)$, $c = 13.207(1)$ Å, $\alpha = 105.79(1)$, $\beta = 90.81(1)$, and $\gamma = 113.06(1)$°. The crystal structure consists of centrosymmetric binuclear thiolate-bridged cations and anions, well separated. The corresponding homonuclear complexes of Pd^{II} and Pt^{II} are isomorphous. The co-ordination of the metal atoms in the trinuclear complex $[(dppe)Pt(\mu\text{-}SR)_2Ni(\mu\text{-}SR)_2Pt(dppe)]^{2+}$ [R = $(CH_2)_3NMe_2$], has been deduced from $^{31}P\text{-}\{^1H\}$ n.m.r. data. In solution the platinum mononuclear complexes and the nickel dimeric species are the most stable.

Despite the great amount of work devoted nowadays to studying metal thiolate complexes,[1,2] fundamental knowledge of the structures of species with low nuclearity is relatively sparse, even taking into account only those transition metals more frequently studied in co-ordination chemistry. Thus, in the Ni, Pd, and Pt group, the structures of some discrete non-cyclic homoleptic thiolate complexes have been reported for Ni^{II}[3–7] but none for Pd^{II} or Pt^{II}.

A significant feature commonly found in discrete thiolate complexes is the predominance of arenethiolate ligands and/or electron-withdrawing groups in the ligand chains in order to decrease the electron density on the S atom, thus preventing polymer formation. Another successful way to obtain discrete species involves the use of chelating dithiol ligands. In our systematic work on metal complexes of aliphatic γ-mercaptoamine ligands, non-polymeric structures found with Group 10‡ metals are either cyclic, $[Ni_4(\mu\text{-}SC_5H_9NMe)_8]$[8] and $[Ni_6(\mu\text{-}SR)_{12}]$ [R = $(CH_2)_3NMe_2$[9] or $(CH_2)_3\overset{+}{N}HMe_2$[10]], or linear but with the ligands behaving as chelates, $[Ni_3\{S(CH_2)_3NH_2\}_4]^{2+}$,[11] $[\{PdCl[S(CH_2)_3NMe_2]\}_2]$,[12] $[\{PdX(SCH_2C_5H_9NMe)\}_2]$ (X = Cl or Br),[13] $[Pt_2Cl_4(SCH_2C_5H_9NMe)_2]$,[13] $[Pd_3(SCH_2C_5H_9NH)_4]^{2+}$,[12–14] except for the dimer $[\{PdBr_2(\mu\text{-}SCH_2C_5H_9NH_2)\}_2]$[13] where terminal bromine atoms complete the co-ordination around the metal.

In this work we report on the synthesis and the characterization of homo- and hetero-nuclear complexes of Ni, Pd, and Pt with 3-dimethylamino-1-propanethiol behaving as a simple thiol ligand. In all cases the chelating phosphine dppe ($Ph_2PCH_2CH_2PPh_2$) acts as a terminal ligand and limits the nuclearity of the linear complex species. The crystalline nature of the bimetallic complexes has enabled us to determine the molecular structure of the binuclear nickel complex $[\{Ni[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$ and also its isomorphism with those of Pd and Pt.

Mixed thiolate phosphine complexes of Group 10 metals with known structure are limited to the following mononuclear $[Ni(SC_6F_5)_2(dppe)]$[15] and $[Pt(S_2CH_2)(PMe_2Ph)_2]$,[16] binuclear, *cis*-$[\{Pt(SCH_2Ph)(\mu\text{-}SCH_2Ph)(PMePh_2)\}_2]$,[17] and trinuclear, $[Ni_3(S_2C_{10}Cl_6)_3(PPh_3)_3]$,[18] examples. Considering closely related ligands, the mononuclear complexes $[Ni(S_2CNEt_2)(PPh_3)_2]^+$,[19] $[Ni(S_2COEt)_2(PPh_3)]$,[20] *trans*-$[Pd(o\text{-}Ph_2PC_6H_4S)_2]$,[21] and *cis*-$[Pt(SH)_2(PPh_3)_2]$[22] and the binuclear species $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$[23] have to be included.

Experimental

3-Dimethylamino-1-propanethiol was synthesized according to a known procedure,[24] and purified as indicated elsewhere[9] until its purity was superior to 99.5%. The corresponding sodium salt was obtained by evaporating to dryness the methanolic phase formed when a solution of the thiol in diethyl ether and a slight deficiency of the equivalent amount of NaOMe in methanol were mixed, stirred for a while, and then allowed to settle. Metal complexes of formula $[MCl_2(dppe)]$ were prepared by published methods, M = Ni,[25] Pd,[26] or Pt,[27] with minor modifications. The complex $[PtCl_2(dppe)]$ was prepared from $[PtCl_2(cod)]$ (cod = cyclo-octa-1,5-diene)[28] previously. In the following preparations, degassed solvents were used and all manipulations were carried out under an atmosphere of dry nitrogen, except for the synthesis of the starting materials, $[MCl_2(dppe)]$, and while trying to crystallize the complexes.

Infrared spectra, 4 000—400 cm^{-1}, were recorded on a 1 710 Perkin-Elmer spectrophotometer, electronic spectra (900–200 nm) by using a Kontron Uvikon 860 apparatus. $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were recorded on a Bruker WP80SY spectrometer at 32.43 MHz. Chemical shifts are referenced to external 85%

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

‡ Refers to the 18-group format of the Periodic Table.

H_3PO_4 in D_2O. Elemental analyses were performed with a Carlo-Erba N.A. 1500 or with a Perkin-Elmer 240 analyzer.

$[Ni\{S(CH_2)_3NHMe_2\}_2(dppe)][BPh_4]_2$ (**1**).—A solution of 3-dimethylamino-1-propanethiol (0.17 cm^3, 1.35 mmol) in dichloromethane (15 cm^3) was slowly added with stirring to a suspension of $[NiCl_2(dppe)]$ (0.34 g, 0.64 mmol) in 15 cm^3 of the same solvent. During the addition the initial orange solid dissolved and the reaction mixture became a reddish brown solution. Sodium tetraphenylborate (0.44 g, 1.28 mmol) in sufficient methanol to give a solution was added to the filtrate from the reaction mixture. After some minutes of stirring the solvent was removed, and the residue was extracted with dichloromethane (*ca.* 10 cm^3). This operation was repeated several times with the filtrate of the sodium chloride suspension. The final red-brown foamy solid was treated with diethyl ether overnight and eventually filtered off and dried *in vacuo* (Found: C, 74.65; N, 2.40; S, 4.95. Calc. for $C_{84}H_{90}B_2N_2NiP_2S_2$: C, 75.55; N, 2.20; S, 4.80%).

$[Pd\{S(CH_2)_3NHMe_2\}_2(dppe)][BPh_4]_2$ (**2**).—Analogously, $[PdCl_2(dppe)]$ (0.58 g, 1 mmol) and the thiol (0.26 cm^3, 2.07 mmol) in dichloromethane (40 cm^3) were stirrred for 1 h, during which time the initial pale yellow solid dissolved and the reaction mixture became an orange solution. The filtrate was concentrated to *ca.* 30 cm^3, and sodium tetraphenylborate (0.68 g, 2 mmol) in sufficient methanol to give a solution was added. The solvent was removed and the residue extracted with dichloromethane (15 cm^3). This procedure was repeated several times. Finally, a paste appeared, which was treated with diethyl ether until a bright yellow powder could be filtered off and dried *in vacuo* (Found: C, 72.75; N, 1.90; S, 4.30. Calc. for $C_{84}H_{90}B_2N_2P_2PdS_2$: C, 72.95; N, 2.05; S, 4.65%).

$[Pt\{S(CH_2)_3NHMe_2\}_2(dppe)][BPh_4]_2$ (**3**).—Analogously, $[PtCl_2(dppe)]$ (0.25 g, 0.376 mmol) and the thiol (0.1 cm^3, 0.79 mmol) in dichloromethane (30 cm^3) were stirred for *ca.* 1 h, during which time the white suspension became a pale yellow solution. Sodium tetraphenylborate (0.26 g, 0.76 mmol) in sufficient methanol to give a solution was added to the filtrate from the reaction mixture and stirred for *ca.* 15 min. Then, removal of the solvent and extraction of the residue with dichloromethane was repeated several times. Eventually the pale yellow paste was treated with diethyl ether until it became a powder, which was filtered off and dried *in vacuo* (Found: C, 68.45; N, 2.40; S, 5.15. Calc. for $C_{84}H_{90}B_2N_2P_2PtS_2$: C, 68.55; N, 1.90; S, 4.35%).

$[Pd\{S(CH_2)_3NMe_2\}_2(dppe)]$ (**4**).—A solution of $Na[S(CH_2)_3NMe_2]$ (0.16 g, 1.34 mmol) in methanol (7 cm^3) was added to a suspension of $[PdCl_2(dppe)]$ (0.33 g, 0.58 mmol) in acetonitrile (15 cm^3) and stirred for 28 h, during which time the initial pale yellow suspension became orange. The solvent was removed *in vacuo* and the residue extracted with acetonitrile (*ca.* 10 cm^3). This operation was repeated several times. The resulting paste was treated with diethyl ether and the remaining solid was extracted with dichloromethane. Removal of the solvent *in vacuo* gave a foamy orange solid which was dried *in vacuo* (Found: C, 57.30; N, 3.80; S, 8.85. Calc. for $C_{36}H_{48}N_2P_2PdS_2$: C, 58.30; N, 3.80; S, 8.65%).

$[Pt\{S(CH_2)_3NMe_2\}_2(dppe)]$ (**5**).—A solution of $Na[S(CH_2)_3NMe_2]$ (0.16 g, 1.34 mmol) in methanol (8 cm^3) and a suspension of $[PtCl_2(dppe)]$ (0.39 g, 0.58 mmol) in acetonitrile (*ca.* 10 cm^3) were stirred for 2 d, meanwhile the suspension changed from white to pale yellow. The solvent was removed *in vacuo* and the residue was extracted with acetonitrile (*ca.* 10 cm^3). By repeating this procedure several times, a foamy yellow solid was finally obtained and dried *in vacuo* (Found: C, 51.65; N, 3.60; S, 7.75. Calc. for $C_{36}H_{48}N_2P_2PtS_2$: C, 52.05; N, 3.35; S, 7.70%).

$[\{Ni[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$ (**6**).—Slow evaporation of a solution of (**1**) in dichloromethane under a tetrahydrofuran atmosphere, at room temperature, yielded in *ca.* 1 d large red-brown, block-shaped crystals, which were suitable for *X*-ray analysis. The crystals were separated manually because a very fine white powder probably containing $[Me_2HN(CH_2)_3S]_2[BPh_4]_2$, also separated from the solution. The crystals were washed several times with tetrahydrofuran until the white powder was removed (Found: C, 73.60; N, 1.65; S, 3.05. Calc. for $C_{110}H_{112}B_2N_2Ni_2P_4S_2$: C, 73.80; N, 1.55; S, 3.60%).

$[\{Pd[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$ (**7**).—The preceding method but with a solution of complex (**2**) in dichloromethane afforded in *ca.* 2—3 d large yellow, block-shaped crystals, isomorphous with those of (**6**), which also had to be separated manually. The crystals were washed several times with tetrahydrofuran (Found: C, 70.25; H, 5.80; N, 1.50; S, 3.50. Calc. for $C_{110}H_{112}B_2N_2P_4Pd_2S_2$: C, 70.05; H, 5.95; N, 1.50; S, 3.40%).

$[\{Pt[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$ (**8**).—The same procedure as for complexes (**6**) and (**7**) allowed manual separation of yellowish white crystals, isomorphous with those of (**6**), from a dichloromethane solution of (**3**) after *ca.* 1 week. The crystals were washed several times with tetrahydrofuran (Found: C, 64.00; N, 1.65; S, 3.20. Calc. for $C_{110}H_{112}B_2N_2P_4Pt_2S_2$: C, 64.00; N, 1.35; S, 3.10%).

$[(dppe)Ni\{\mu\text{-}S(CH_2)_3NMe_2\}_2Pd(dppe)][BPh_4]_2$ (**9**).—Slow evaporation under a tetrahydrofuran atmosphere of a solution containing equivalent amounts of complexes (**1**) and (**2**) in dichloromethane afforded red-orange crystals, together with a fine white powder. Crystals were separated manually and were washed several times with tetrahydrofuran until the white powder, which also separated from solution, could be removed (Found: C, 70.80; N, 1.75; S, 3.45. Calc. for $C_{110}H_{112}B_2N_2NiP_4PdS_2$: C, 71.85; N, 1.50; S, 3.50%).

$[(dppe)Ni\{\mu\text{-}S(CH_2)_3NMe_2\}_2Pt(dppe)][BPh_4]_2$ (**10**).—Analogously, orange crystals were obtained and washed several times with tetrahydrofuran (Found: C, 67.15; N, 1.50; S, 3.35. Calc. for $C_{110}H_{112}B_2N_2NiP_4PtS_2$: C, 68.55; N, 1.45; S, 3.30%).

$[(dppe)Pt\{\mu\text{-}S(CH_2)_3NMe_2\}_2Pd(dppe)][BPh_4]_2$ (**11**).—A similar procedure afforded bright yellow crystals that were washed several times with tetrahydrofuran (Found: C, 67.70; N, 1.85; S, 3.25. Calc. for $C_{110}H_{112}B_2N_2P_4PdPtS_2$: C, 66.90; N, 1.40; S, 3.25%).

$[Ni\{Pt[\mu\text{-}S(CH_2)_3NMe_2]_2(dppe)\}_2][BPh_4]_2$ (**12**).—Anhydrous $NiCl_2$ [29] (0.13 g, 1 mmol) was added to a stirred solution of complex (**5**) (1.66 g, 2 mmol) in acetonitrile (*ca.* 30 cm^3). The $NiCl_2$ dissolved completely and to the clear solution sodium tetraphenylborate (0.68 g, 2 mmol) in sufficient methanol to give a solution was added and stirring continued for *ca.* 30 min. Then, the solvent was removed and the residue was extracted with acetonitrile (15 cm^3). The filtrate from the acetonitrile suspension was reduced in volume by half. Addition of methanol and cooling to −20 °C produced a brown powder, which was filtered off, washed with cold methanol, and dried *in vacuo* (Found: C, 61.10; N, 2.55; S, 5.45. Calc. for $C_{120}H_{136}B_2N_4NiP_8Pt_2S_4$: C, 61.10; N, 2.35; S, 5.45%).

Table 1. Atomic co-ordinates for complex (**6**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni	0.003 16(6)	0.100 90(6)	0.102 24(6)	C(42)	0.074 0(5)	0.398 1(6)	−0.001 7(5)
S	0.023 95(9)	0.073 55(9)	−0.069 20(9)	C(43)	0.150 5(7)	0.470 5(8)	−0.040 9(8)
P(1)	0.004 92(9)	0.132 60(10)	0.273 70(9)	C(44)	0.249 8(7)	0.504 8(7)	−0.002 4(9)
P(2)	0.006 47(9)	0.263 34(10)	0.129 60(9)	C(45)	0.276 8(7)	0.469 3(6)	0.075 8(8)
C(1)	−0.022 5(5)	0.251 4(4)	0.330 2(4)	C(46)	0.202 3(5)	0.397 5(5)	0.115 4(5)
C(2)	0.027 3(5)	0.333 7(4)	0.272 5(4)	B	0.682 5(4)	0.304 1(5)	0.514 7(5)
C(3)	0.159 4(4)	0.147 5(5)	−0.073 1(5)	C(51)	0.739 4(4)	0.395 7(4)	0.455 9(4)
C(4)	0.231 9(6)	0.126 9(13)	−0.012 3(8)	C(52)	0.683 4(4)	0.416 0(5)	0.382 1(5)
C(5)	0.343 3(6)	0.182 2(9)	−0.030 3(8)	C(53)	0.726 9(5)	0.489 3(6)	0.326 6(6)
N	0.424 3(7)	0.208 4(10)	0.043 2(9)	C(54)	0.832 4(5)	0.546 9(5)	0.341 1(5)
C(6)	0.418 8(9)	0.111 1(14)	0.065 1(13)	C(55)	0.890 9(5)	0.529 0(5)	0.410 9(5)
C(7)	0.442 0(17)	0.289 7(16)	0.136 7(16)	C(56)	0.845 7(4)	0.456 2(4)	0.466 5(5)
C(11)	0.135 6(4)	0.168 5(4)	0.325 7(4)	C(61)	0.613 3(4)	0.189 9(4)	0.422 1(4)
C(12)	0.194 9(5)	0.267 7(5)	0.400 5(5)	C(62)	0.647 2(5)	0.162 3(5)	0.325 4(5)
C(13)	0.296 2(5)	0.292 1(6)	0.435 6(6)	C(63)	0.595 8(7)	0.063 0(7)	0.247 3(6)
C(14)	0.339 0(5)	0.221 1(6)	0.398 4(6)	C(64)	0.506 3(6)	−0.013 2(6)	0.264 7(7)
C(15)	0.280 5(6)	0.121 8(7)	0.324 6(6)	C(65)	0.469 0(5)	0.010 4(5)	0.358 7(6)
C(16)	0.180 3(5)	0.095 8(6)	0.288 1(5)	C(66)	0.520 7(4)	0.110 4(5)	0.435 5(6)
C(21)	−0.079 7(4)	0.027 2(4)	0.323 9(4)	C(71)	0.766 4(4)	0.285 3(4)	0.583 9(4)
C(22)	−0.048 7(5)	−0.041 6(5)	0.358 6(5)	C(72)	0.790 8(5)	0.195 6(5)	0.550 8(5)
C(23)	−0.119 7(7)	−0.128 7(7)	0.383 9(7)	C(73)	0.862 1(6)	0.181 7(7)	0.610 3(6)
C(24)	−0.221 1(6)	−0.146 1(7)	0.378 1(6)	C(74)	0.911 2(5)	0.255 5(6)	0.704 9(5)
C(25)	−0.252 4(6)	−0.078 3(6)	0.345 9(6)	C(75)	0.890 8(5)	0.344 9(6)	0.741 1(6)
C(26)	−0.182 6(5)	0.008 6(5)	0.318 5(5)	C(76)	0.820 2(5)	0.359 8(5)	0.681 3(5)
C(31)	−0.119 9(4)	0.244 7(4)	0.078 3(4)	C(81)	0.609 0(4)	0.340 9(4)	0.597 5(4)
C(32)	−0.180 7(5)	0.283 5(5)	0.141 2(5)	C(82)	0.570 7(5)	0.286 4(5)	0.672 6(5)
C(33)	−0.276 4(5)	0.263 4(7)	0.099 0(7)	C(83)	0.504 4(5)	0.310 4(6)	0.740 1(6)
C(34)	−0.312 9(6)	0.210 2(7)	−0.005 7(7)	C(84)	0.473 7(5)	0.389 9(7)	0.735 4(6)
C(35)	−0.250 6(6)	0.174 8(7)	−0.069 8(6)	C(85)	0.510 2(5)	0.447 6(6)	0.666 5(6)
C(36)	−0.155 4(5)	0.190 4(5)	−0.030 0(5)	C(86)	0.578 0(5)	0.424 8(5)	0.599 4(5)
C(41)	0.100 1(4)	0.359 7(4)	0.076 3(4)				

X-*Ray Data Collection, Structure Determination, and Refinement for* $[\{Ni[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$.—*Crystal data.* $C_{110}H_{112}B_2N_2Ni_2P_4S_2$, $M = 1\,789.2$, triclinic, space group $P\bar{1}$, $a = 14.346(1)$, $b = 14.037(1)$, $c = 13.207(1)$ Å, $\alpha = 105.79(1)$, $\beta = 90.81(1)$, $\gamma = 113.06(1)°$, $U = 2\,332.7(5)$ Å^3, $D_c = 1.274$ g cm^{-3}, $Z = 1$, $F(000) = 944$.

Cell constants were obtained from a least-squares fit using 35 reflections up to $\theta = 45°$. An orange prism-like sample ($0.33 \times 0.20 \times 0.10$ mm) was used for the analysis on a Philips PW1100 diffractometer, with Cu-K_α ($\lambda = 1.5418$ Å) radiation, a graphite monochromator, ω—2θ scans, bisecting geometry, 1×10 detector apertures, scan width 1.40°, and using 1 min per reflection. Good stability of the sample checked every 90 min. 6 766 Unique reflections were measured, of which 5 270 had $I \geqslant 3\sigma(I)$, ($\theta_{max.} = 60°$).

The structure was solved by Patterson and direct difference methods[30,31] and refined by blocked-matrix least-squares procedures for 750 parameters. An empirical absorption correction[32] ($\mu = 19.30$ cm^{-1}) gave minimum and maximum transmission factors of 0.83 and 1.33. All hydrogen atoms were located in difference synthesis except for two of the methyl group C(6). These hydrogen atoms were kept fixed in the final cycle of refinement. An empirical weighting scheme, giving no trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle|F_o|\rangle$ and $\langle\sin\theta/\lambda\rangle$, was introduced. The final shift/error was 0.24 with the maximum peak in the final ΔF of 1.3 e Å^{-3} near the S atom. The maximum thermal parameters were those involving atoms C(6), C(7), and N of the bridging ligand. Because of these high values, a difference synthesis omitting these atoms was computed but no alternative with chemical significance was found. The high thermal parameters were then attributed to the disorder affecting those chains. The final R and R' values were 0.068 and 0.076 respectively. All the calculations were performed on a VAX 11/750 computer. The atomic scattering factors were taken from ref. 33. Table 1 shows the final non-hydrogen co-ordinates, Table 2 the main distances and angles as well as the most relevant geometric parameters for the cation. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

X-*Ray Data Collection for* $[\{M[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$ ($M =$ Pd *or* Pt).—The good quality of the crystals of formula $[\{M[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$, M = Pd^{II} or Pt^{II}, made possible a check of their isomorphism with the nickel(II) compound by determining the unit-cell parameters from 25 reflections and refining them by the full-matrix least-squares method. Measurements were carried out using the same conditions described above. Cell parameters: M = Pd, $a = 14.201$, $b = 14.144$, $c = 13.286$ Å, $\alpha = 105.22$, $\beta = 90.27$, and $\gamma = 113.58°$; M = Pt, $a = 14.191$, $b = 14.186$, $c = 13.284$ Å, $\alpha = 105.05$, $\beta = 90.56$, and $\gamma = 113.59°$. The structure determination for both complexes is now in progress.

Results and Discussion

Structure of $[\{Ni[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$ *and Isomorphous Complexes with* M = Pd *or* Pt.—The crystal structure of $[\{Ni[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$ consists of discrete binuclear cations and tetraphenylborate anions. The cations and anions are well separated. The structure of the anions is unexceptional.

The cation $[\{Ni[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2]^{2+}$ is centrosymmetric, Figure 1, and can be described as formed by three central rings: P(1)–C(1)–C(2)–P(2)–Ni, Ni–S–Ni′–S′, and Ni′–P(1′)–C(1′)–C(2′)–P(2′), which are practically coplanar, Figure 2, the bridging ligands departing in opposite directions along the normal to the Ni_2S_2 plane and thus having an *anti* conformation. The idealized symmetry of the cation is C_{2h} but

Table 2. Selected geometrical parameters (distances in Å, angles in °) for $[\{Ni[\mu-S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$

Ni–S	2.236(1)	Ni–P(1)	2.184(1)
Ni–S′	2.237(2)	Ni–P(2)	2.191(2)
Ni–Ni′	3.310(1)	S–S′	3.009(2)
P(2)–Ni–S′	172.0(1)	P(1)–N–S′	95.0(1)
P(1)–Ni–P(2)	85.8(1)	S–Ni–S′	84.6(1)
S–Ni–P(2)	95.8(1)	S–Ni–P(1)	172.2(1)
Ni–S–Ni′	95.5(1)	Ni–S–C(3)	106.6(2)
Ni′–S–C(3)	106.5(2)		

Plane 1: S, Ni, S′, Ni′
Plane 2: Ni, P(1), P(2)
Plane 3: C(11)—C(16)
Plane 4: C(21)—C(26)
Plane 5: C(31)—C(36)
Plane 6: C(41)—C(46)
Plane 7: S, C(3), C(4), C(5), N

Plane 1/Plane 2	11.6(1)	Plane 1/Plane 3	96.4(2)
Plane 1/Plane 4	78.6(2)	Plane 1/Plane 5	101.3(2)
Plane 1/Plane 6	96.0(2)	Plane 1/Plane 7	90.5(2)

(′ means the -*x*, -*y*, -*z* symmetry related atom)

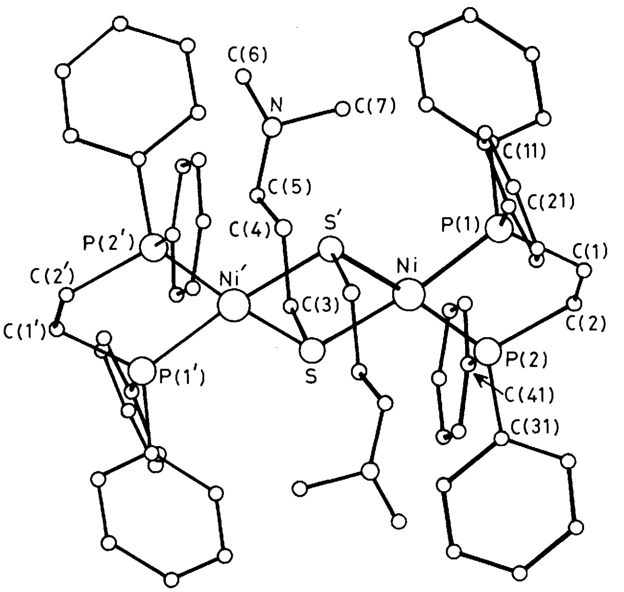

Figure 1. Structure of the $[\{Ni[\mu-S(CH_2)_3NMe_2](dppe)\}_2]^{2+}$ cation together with the atom-labelling scheme. Hydrogen atoms have been omitted. Primed and unprimed atoms are related by a centre of symmetry

that of the core, that is, omitting the aliphatic hydrocarbon chains and the aromatic rings is D_{2h}.

Deviations from the ideal plane defined by the three rings mentioned are of two different types. First, the plane Ni–S–Ni′–S′ is a perfect plane as the crystallographic inversion centre coincides with the centre of the Ni_2S_2 ring. However the plane Ni–P(1)–P(2), and its symmetry-related Ni′–P(1′)–P(2′), form a dihedral angle of 11.6(1)° with the Ni_2S_2 plane, as indicated in Table 2 and Figure 2. The second deviation refers to the position of C(1) and C(2), and symmetry-related atoms, in relation to the plane Ni–P(1)–P(2). Both carbon atoms are out of that plane but along opposite directions. Thus, C(1) is 0.397 Å below the plane while C(2) is 0.244 Å above it, each NiP_2C_2 ring adopting a half-chair conformation.

The *anti* conformation of the bridging units as well as the orientation of the phenyl groups with respect to the plane defined by the three central rings can be expressed by the angle formed by the S–C(3) vector, and those of P(1)–C(11), P(1)–C(21), P(2)–C(31), P(2)–C(41), with the normal to the Ni_2S_2 plane. These values are, respectively, 5.2(2), 62.4(1), 7.3(1), 12.8(1), and 58.2(1)°.

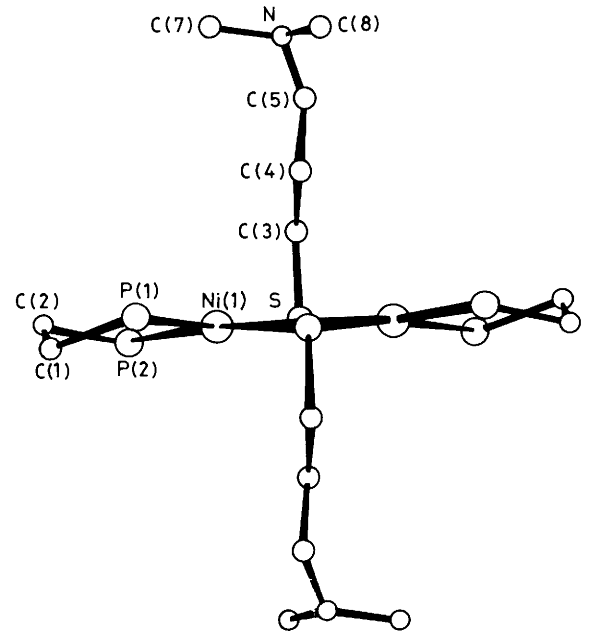

Figure 2. *anti* Conformation of bridging thiolate ligands in the Ni_2S_2 ring and the idealized plane defined by the three central rings in the cation $[\{Ni[\mu-S(CH_2)_3NMe_2](dppe)\}_2]^{2+}$, even though NiP_2C_2 cycles adopt a half-chair conformation. The dihedral angle formed by Ni_2S_2 perfect plane and that defined by Ni–P(1)–P(2) or by its symmetry-related Ni′–P(1′)–P(2′) is 11.6(1)°

The co-ordination around the Ni is essentially square planar as indicated by the angles P(1)–Ni–P(2) 85.8(1)°, S–Ni–P(2) 95.8(1)°, S–Ni–S′ 84.6(1)°, and P(1)–Ni–S′ 95.0(1)°. The substituents linked to the bridging sulphur atom give rise to a distorted tetrahedral co-ordination around it. The angles Ni–S–Ni′, Ni–S–C(3), and Ni′–S–C(3) are, respectively, 95.5(1), 106.6(2), and 106.5(2)°.

A comparison of some geometric parameters of Ni_2S_2 rings in thiolate-bridged binuclear nickel(II) complexes is given in Table 3. The following main features can be deduced from the values and references given there. (*a*) There is a great similarity between the geometry of the $[Ni_2(SEt)_6]^{2-}$ anion and that of the $[\{Ni[S(CH_2)_3NMe_2](dppe)\}_2]^{2+}$ cation, which indicates that the substitution of the terminal thiol ligands by the chelating diphosphine does not appreciably affect the geometry of the core of the binuclear homoleptic thiolate complex. (*b*) Complexes (**I**)—(**VII**) in Table 3 can be divided in two sets. The one formed by compounds (**I**)—(**V**), inclusive, where the dihedral angle along the S ··· S axis varies from 82.3 to 145.2°, and that formed by complexes (**VI**) and (**VII**) exclusively, where the Ni_2S_2 ring plane is perfect and the bridging units of both complexes have an *anti* conformation. (*c*) The planarity of the Ni_2S_2 ring in complexes (**VI**) and (**VII**) causes the Ni–Ni distances and $Ni–S_b–Ni$ angles to be greater than those of the other set of complexes while the S ··· S distance is *ca.* 0.2 Å longer. The Ni–Ni distance in complexes (**VI**) and (**VII**), 3.3 Å, excludes any metal–metal interaction. However, taking into account that the Ni_2S_2 cores of complexes (**I**) and (**VI**) have the same bridging units, $Ni_2(\mu-SEt)_2$, but different geometries (Φ = 110.2 and 180° respectively), and that complexes (**VI**) and (**VII**) have different bridging units, $Ni_2(\mu-SEt)_2$ and $Ni_2[\mu-S(CH_2)_3NMe_2]_2$ respectively, but the same geometry (180°), it seems likely that the bite angle of the terminal ligands [(**I**), (**II**)], or bridging ligands with structural contraints [(**III**)—(**V**)], are the main factors determining possible Ni–Ni interactions and/

Table 3. Relevant geometric parameters (distances in Å, angles in °) in Ni_2S_2 rings of thiolate-bridged binuclear nickel(II) complexes

Complex	Ni–S_b[a]	Ni–Ni	Ni–S_b–Ni	S_b–Ni–S_b	Φ[b]	Ref.
(I) $[Ni_2(SEt)_2(S_2CSEt)_2]$	2.183	2.763	78.4(1)	81.6(1)	110.2	*c*
(II) $[Ni_2(SCH_2Ph)_2(S_2CSCH_2Ph)_2]$	2.188	2.795	79.5	81.7	114.3	*d*
(III) $[Ni_2(SCH_2CH_2SCH_2CH_2S)_2]$	2.182	2.733(5)	76.7(2)	82.5(2)	82.3	*e*
(IV) $[Ni_2(C_5H_4NCH_2CH_2NHCH_2CH_2S)_2][ClO_4]_2$	2.177(1)	2.739(1)	77.94(5)	79.61(6)	110	*f*
(V) $[Ni_2\{SCH(CH_2CH_2NH_2)_2\}_2]Br_2$	2.174(2)	3.134(2)	92.2(1)	81.36(9)	145.2	*g*
(VI) $[NMe_4]_2[Ni_2(SEt)_6]$	2.220	3.356	98.2(1)	81.8(1)	180	3
(VII) $[\{Ni[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$	2.237(2)	3.310(1)	95.5(1)	84.6(1)	180	This work

[a] S_b denotes a bridging sulphur atom. [b] Dihedral angle between S_b–Ni–S_b' and S_b–Ni′–S_b' planes. [c] A. C. Villa, A. G. Manfredotti, M. Nardelli, and C. Pelizzi, *Chem. Commun.*, 1970, 1322. [d] J. P. Fackler, jun., and Wm. J. Zegarski, *J. Am. Chem. Soc.*, 1973, **95**, 8566. [e] D. J. Baker, D. C. Goodall, and D. S. Moss, *Chem. Commun.*, 1969, 325. [f] T. B. Vance, jun., L. G. Warner, and K. Seff, *Inorg. Chem.*, 1977, **16**, 2106. [g] M. Mikuriga, S. Kida, and I. Murase, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1180.

Table 4. Bond distances Ni–P and angles P–Ni–P in some Ni^{II}-dppe complexes with square-planar co-ordination around the nickel atom

Complex	d(Ni–P)/Å	P–Ni–P/°	Ref.
$[NiCl_2(dppe)]$	2.157(2) 2.145(2)	86.96(6)	*a*
$[Ni(NO_2)_2(dppe)]$	2.178(3) 2.182(4)	86.3(1)	*b*
$[Ni(SC_6F_5)_2(dppe)]$	2.182(3) 2.193(3)	85.7(1)	15
$[\{Ni[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2]^{2+}$	2.184(1) 2.191(2)	85.8(1)	This work

[a] A. L. Spek, B. P. van Eijch, R. J. F. Jans, and G. van Koten, *Acta Crystallogr., Sect. C*, 1987, **43**, 1878. [b] J. Kriege-Simondsen and R. D. Feltham, *Inorg. Chim. Acta*, 1983, **71**, 185.

or the dihedral angle between NiS_bS_b' and $Ni'S_bS_b'$ planes. Other hypotheses[34] have referrred to the pyramidal stereochemistry about the three-co-ordinate bridging sulphur atom and to the S $\cdots$ S distances in the bridge as the determining factors for Ni $\cdots$ Ni interactions.

The two Ni–P distances found in the NiP_2C_2 rings of the cation $[\{Ni[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2]^{2+}$ together with those of other nickel(II) complexes are given in Table 4. The distances for this cation agree well with those reported for $[Ni(SC_6F_5)_2(dppe)]$,[15] and with the average value, d_{mean}(Ni–P) = 2.22(5) Å, calculated from 104 compounds having P–Ni–S fragments.[35]

The unit cell of the isomorphous complexes $[\{M[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$, M = Ni, Pd, or Pt, includes one cation and two anions, and 234 atoms.

Synthesis of the Complexes.—Despite the straightforward synthetic methods followed to obtain the mononuclear complexes **(1)**—**(5)**, the great solubility of these compounds in all common organic solvents has made practically impossible a good way of purification. Addition of diethyl ether to organic solutions often led to sticky pastes. The lability of these complexes, especially those of Ni^{II}, the ease of oxidation of dppe to the corresponding oxides, and of the thiol to the disulphide, and the difficulties encountered when analyzing even crystals suitable for *X*-ray diffraction, explain some of our analytical data.

Different attempts to deprotonate compounds **(1)**—**(3)** with organic bases always led to the corresponding binuclear species **(6)**—**(8)** instead of the mononuclear complexes **(4)** and **(5)**. These have been synthesized by a direct route but the nickel complex was always contaminated with some dppe oxide and is not reported here.

The degree of purity of all these complexes can be checked either by the $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy and also by i.r. spectroscopy. These data together with some comments on the lability of the mononuclear complexes are given later.

Infrared Data.—The i.r. spectra of the solid complexes **(1)**—**(12)** indicate that the members of each family either have the same structure or are very similar, because the corresponding spectra are practically identical. The most relevant region in all cases is 3 100—2 300 cm^{-1} where aromatic and aliphatic ν(C–H) and $\nu(R_3\overset{+}{N}\text{–}H)$ vibrations appear. Despite the fact that there are aliphatic C–H bonds in the thiol as well as in dppe, this region allows one to determine unambiguously whether the ligand is in its zwitterionic or anionic form. Infrared spectra of 3-dimethylamino-1-propanethiol behaving as a simple R-SH thiol, as a zwitterion, or as a chelate have already been discussed.[10] The knowledge of the structure of the binuclear nickel cation just described has also been very useful in interpreting i.r. spectra.

By comparing the 3 100—2 300 cm^{-1} region for all the complexes a very good correlation has been found between the ratio of the intensities of absorptions at *ca.* 3 050 cm^{-1} (aromatic C–H stretchings), *ca.* 2 980, and *ca.* 2 770 cm^{-1} (aliphatic C–H stretchings) with the empirical formula of the complex. Where the amine group is protonated the correlation also works well, but the broad band centred at 2 670 cm^{-1} has to be considered instead of that at 2 770 cm^{-1}. Applying this correlation, we could predict before elemental analyses that the number of aromatic rings per thiol ligand in the trinuclear complex $[Ni\{Pt[\mu\text{-}S(CH_2)_3NMe_2]_2(dppe)\}_2][BPh_4]_2$ had to be approximately 4. In this case the intensities of the bands followed the ratio: $I_{3\,050} \approx I_{2\,767} > I_{2\,980}$ or $I_{3\,050}$ practically equal to $I_{2\,767}$, both being somewhat more intense than the band at 2 980 cm^{-1}.

The appearance of bands at 1 182 and 1 123 cm^{-1}, assigned to ν(P=O) stretchings, is indicative of the presence of dppe oxide and thus can reflect the degree of purity of the complexes.

Electronic Spectra.—The electronic spectra of complexes **(1)**—**(12)** in the visible region have all been measured as solutions in dichloromethane. All the nickel(II) complexes show bands at wavelengths shorter than 520 nm and, within each family, bands for the complexes of Pd^{II} and Pt^{II} appear at higher energies than those of Ni^{II}. These data indicate that the co-ordination around these metals is neither octahedral nor tetrahedral, in accord with the structure found for the dimeric nickel complex and the isomorphous complexes of Pd and Pt. The higher-energy bands usually appeared as shoulders on intense π–π^* transitions in the u.v. region, and this led to imprecise measurement of the absorption coefficients. Attempts to resolve the bands by the fourth-derivative curve method have not been successful for most heavy metals. However all our data (wavelengths, molar absorption coefficients) agree well with values already reported for similar complexes with square-planar co-ordination around the metal atom.[36,37]

Table 5. $^{31}P-\{^1H\}$ n.m.r. data for mixed-ligand thiolate phosphine complexes of Ni^{II}, Pd^{II}, and Pt^{II} where R = $(CH_2)_3NMe_2$

Empirical formula	Metal	Solvent[a]	δ/p.p.m.	^1J(Pt–P)/Hz
$[MCl_2(dppe)]$				
	Ni	CH_2Cl_2	57.55	
	Ni	dmso	61.17	
	Pd	CH_2Cl_2	65.10	
	Pt	CH_2Cl_2	41.73	*b*
	Pt	dmso	43.53	3 606.2
$[M(HSR)_2(dppe)]^{2+}$				
	Ni (**1**)	CH_2Cl_2	59.13	
	Ni (**1**)	dmso	56.74	
	Pd (**2**)	dmso	55.53	
	Pt (**3**)	dmso	47.54(t)[c]	2 804.6
$[M(SR)_2(dppe)]$				
	Pd (**4**)	dmso	53.44	
	Pt (**5**)	CH_2Cl_2	46.91(t)	2 789.6
$[(dppe)M(\mu-SR)_2M'(dppe)]^{2+}$				
M = M′	Ni (**6**)	dmso	61.10	
	Pd (**7**)	dmso	63.42	
	Pt (**8**)	$CHCl_3$	46.65(t)	3 045.6
M ≠ M′	Ni, Pd (**9**)	dmso	57.05, 63.17	
	Ni, Pt (**10**)	dmso	47.49, 62.10(t)	2 074.9
	Pd, Pt (**11**)	dmso	64.06, 49.48(t)	3 031.0
$[Ni\{Pt(SR)_2(dppe)\}_2]^{2+}$	(**12**)	MeCN	46.84(t)	3 084.4

[a] dmso = Dimethyl sulphoxide. [b] The signal-to-noise ratio in the spectrum does not allow ^1J(Pt-P) to be determined. [c] t = Triplet.

Table 6. Selected literature $^{31}P-\{^1H\}$ n.m.r. data for some thiolate phosphine complexes[a]

Complex	Solvent	δ(P)/p.p.m.	^1J(Pt–P)/Hz	Ref.
$[PtCl_2(dppe)]$	CH_2Cl_2	47.8	2 370	*b*
$[PtCl_2(dppe)]$	$CDCl_3$	41.0	3 617	*c*
$[PtCl_2(dppm)]$	$C_2D_2Cl_4$	69.70	3 088	27
$[Pt(SPh)_2(dppe)]$	CH_2Cl_2	92.7	3 047	*d*
$[Pt(SCH_2Ph)_2(dppe)]$	$CDCl_3$	47.2	2 798	*e*
$[Pt(SC_6H_4Me-4)_2]$	$CDCl_3$	45.6	2 896	*e*
$[(dppe)M(\mu-SMe)_2PtXMe_3]$				
M = Pt, X = Cl	CD_2Cl_2	43.2	—	*f*
M = Pd, X = Cl	CD_2Cl_2	52.6	—	*f*
cis-$[\{PtCl(\mu-SEt)(PBu^t_3)\}_2]$	$CDCl_3$	61.0	3 157	*g*
cis-$[Pt(SMe)_2(PPh_3)_2]$	CD_2Cl_2	25.5	2 862	22
$[Pd_2(\mu-SEt)_2Cl_2(PBu^n_3)_2]$	$CDCl_3$	15.9	—	*h*
$[PdPt(\mu-SEt)_2Cl_2(PPr^n_3)_2]$	$CDCl_3$	13.4 1.4	 3 144	 *h*

[a] Chemical shift of dppe oxide in toluene and $CHCl_3$ solutions is 31.25 p.p.m. [b] E. G. Hope, W. Levason, and N. A. Powell, *Inorg. Chim. Acta*, 1986, **115**, 187. [c] I. M. Al-Najjar, *Inorg. Chim. Acta*, 1987, **128**, 93. [d] C. Eaborn, K. J. Odell, and A. Pidcock, *J. Organomet. Chem.*, 1979, **170**, 105. [e] R. D. Lai and A. Shaver, *Inorg. Chem.*, 1981, **20**, 477. [f] E. W. Abel, N. A. Cooley, K. Kite, K. G. Orrell, V. Sik, M. B. Hursthouse, and H. M. Dawes, *Polyhedron*, 1987, **6**, 1261. [g] H. C. Clark, V. K. Jain, and G. S. Rao, *J. Organomet. Chem.*, 1985, **279**, 181. [h] V. K. Jain, *Inorg. Chim. Acta*, 1987, **133**, 261.

$^{31}P-\{^1H\}$ *N.M.R. Studies.*—The room-temperature $^{31}P-\{^1H\}$ n.m.r. spectral data for freshly prepared solutions of the complexes obtained in this work and for the compounds used as starting materials are collected in Table 5. For the homonuclear complexes containing nickel or palladium, (**1**), (**2**), (**4**), (**6**), and (**7**), only one singlet is observed in agreement with the magnetic equivalence of the phosphorus atoms in these complexes under our experimental conditions, that is with proton decoupling. The spectrum of the heteronuclear dimer (**9**) shows two singlets of the same intensity, one corresponding to phosphorus atoms linked to Ni, the other to the two phosphorus atoms linked to Pd. The spectra of the platinum-containing complexes (**3**), (**5**), (**8**) and (**12**) consist only of a 1:4:1 triplet, as expected for $^{31}P-^{195}Pt$ coupling. The fact that no other signal appears in the spectrum of the trinuclear species (**12**) clearly indicates that the nickel atom is not linked to phosphorus atoms and thus the core of this complex is of the type $[(dppe)Pt(\mu-SR)_2Ni(\mu-SR)_2Pt(dppe)]$. Spectra of complexes (**10**) and (**11**) consist of a singlet and a triplet in very good agreement with their expected geometry.

Our experience with mixed thiol-phosphine complexes of Group 10 metals had led us to the conclusion that mononuclear nickel(II) complexes were very unstable toward oxidation and dimerization, compared to those of Pd and Pt. N.m.r. results have confirmed these observations and also allowed us to establish that the order of increasing stability of mononuclear complexes is Ni < Pd < Pt. Thus, the ^{31}P n.m.r. spectra of compound (**1**) and the unreported $[Ni\{\mu\text{-}S(CH_2)_3NMe_2\}(dppe)]$ show the presence of dppe oxide (*ca.* 31 p.p.m.) as well as the nickel dimer (*ca.* 61 p.p.m.). The spectrum of complex (**2**), but not that of (**4**), shows only dimer formation, (**7**) (*ca.* 63 p.p.m.). The spectra of compounds (**3**), (**5**), and (**8**) have no other signals than those given in Table 5, indicating that those species are retained as such in solution. The coupling constants $^1J(P\text{-}Pt)$ found, given in Table 5, agree well with those reported for similar platinum compounds, which confirms the diamagnetic behaviour of our complexes and thus the square-planar co-ordination around the metal atom. Reported ^{31}P n.m.r. data are given in Table 6.

Conclusions

The empirical formula as well as the physical and spectral data for $[M\{S(CH_2)_3NHMe_2\}_2(dppe)]^{2+}$, M = Ni, Pd, or Pt, and $[M\{S(CH_2)_3NMe_2\}_2(dppe)]$, M = Pd or Pt, suggest that within each family the complexes have practically the same structure which should consist of discrete mononuclear species with square-planar co-ordination around the metal atoms. The stability of those species in solution increases according to Ni < Pd < Pt.

Homo- and hetero-nuclear complexes of formula $[(dppe)M\{\mu\text{-}S(CH_2)_3NMe_2\}_2M'(dppe)][BPh_4]_2$ (M = M′ = Pd or Pt; M = Ni, M′ = Pd; M = Ni, M′ = Pt; M = Pd, M′ = Pt) very likely have the same structure as that found for M = M′ = Ni by *X*-ray diffraction, consisting of centrosymmetric binuclear S-bridged cations and tetrahedral BPh_4 anions. The molecular structure of the cation is very similar to that found for $[Ni_2(\mu\text{-}SEt)_6]^{2-}$. The stability of the homo-nuclear dimeric complexes in solution follows the order Pt < Pd < Ni.

$^{31}P\text{-}\{^1H\}$ N.m.r. data indicate that in the trinuclear complex $[Ni\{Pt[\mu\text{-}S(CH_2)_3NMe_2]_2(dppe)\}_2][BPh_4]_2$ the nickel atom is co-ordinated only to sulphur atoms, the core of the complex being $[(dppe)Pt(\mu\text{-}SR)_2Ni(\mu\text{-}SR)_2Pt(dppe)]$.

The $^1J(Pt\text{-}P)$ coupling constants for all the platinum complexes agree well with literature data.

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