

Nickel, Palladium, and Platinum Complexes of the Ditertiary Stibine 1,3-Bis(dimethylstibino)propane

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1,3-Bis(dimethylstibino)propane (dmsp), $\text{Me}_2\text{Sb}[\text{CH}_2]_3\text{SbMe}_2$, and some of its complexes with Ni^{II} , Pd^{II} , and Pt^{II} are reported. The nickel(II) complexes $[\text{Ni}(\text{dmsp})_2\text{X}][\text{ClO}_4]$ ($\text{X} = \text{Cl, Br, or I}$) and $[\text{Ni}(\text{dmsp})_2(\text{OH}_2)][\text{ClO}_4]_2$ have five-co-ordinate square-pyramidal cations, in contrast to the complexes of the corresponding ditertiary arsine which are trigonal bipyramidal. The palladium(II) and platinum(II) complexes $[\text{M}(\text{dmsp})\text{X}_2]$ ($\text{X} = \text{Cl, Br, I, or CNS}$), are planar and the thiocyanates exhibit novel M–NCS co-ordination in solution, the first examples of this in stibine complexes. Antimony-121 Mössbauer spectra have been obtained for some dmsp complexes and for complexes of the related ligand $\text{Ph}_2\text{Sb}[\text{CH}_2]_3\text{SbPh}_2$, and the parameters obtained are discussed in terms of the metal–ligand bond.

THE co-ordination chemistry of diphosphine¹ and diarsine² ligands has been the subject of intensive study over the last 20 years. In marked contrast, few ditertiary stibines are known and their co-ordination chemistry has not been examined to any great extent. Excluding carbonyl complexes, the distibine complexes reported to date are of Pd^{II} , Pt^{II} , and Rh^{III} with 1,3-bis(diphenylstibino)propane,³ bis(diphenylstibino)methane,⁴ and *o*-phenylenebis(diphenylstibine),⁵ none of which bonds to 'harder' metal ions. A preliminary report of the palladium(II) and platinum(II) complexes of *o*-phenylenebis(dimethylstibine) has appeared.⁶ The only nickel(II) complexes containing tertiary stibine co-ordination are the unstable $[\text{Ni}(\text{SbMe}_3)_3\text{X}_2]$ ($\text{X} = \text{Br or I}$)⁷ and complexes of mixed-donor chelates such as *o*- $\text{C}_6\text{H}_4(\text{PPh}_2)(\text{SbPh}_2)$ ⁸ or *o*- $\text{C}_6\text{H}_4(\text{AsMe}_2)(\text{SbMe}_2)$.⁹ Here we report the synthesis of some complexes of 1,3-bis(dimethylstibino)propane and the diarsine analogue, including stable nickel(II) complexes. A preliminary report of this work has appeared.¹⁰

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¹ W. Levason and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1972, **14**, 173.

² E. C. Alyea in 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony Donor Ligands,' ed. C. A. McAuliffe, Macmillan, London, 1973.

³ W. Levason and C. A. McAuliffe, *Inorg. Chem.*, 1974, **13**, 2765.

⁴ W. Levason and C. A. McAuliffe, *J. Co-ordination Chem.*, 1974, **4**, 47.

EXPERIMENTAL

All the synthetic work and manipulations other than recrystallisations were performed under a dry dinitrogen atmosphere. Proton n.m.r. spectra were obtained with Hitachi-Perkin-Elmer R20 and Perkin-Elmer R32 spectrometers. Electronic spectra were recorded with a Beckman

TABLE 1
Analytical data (%) * for ligand derivatives

	C	H	Br
$[\text{Me}_3\text{Sb}(\text{CH}_2)_3\text{SbMe}_3]_2 \cdot 2\text{H}_2\text{O}$	16.4(16.5)	3.4(3.7)	
$[\text{Me}_3\text{As}(\text{CH}_2)_3\text{AsMe}_3]_2$	20.1(19.9)	4.5(4.5)	
$\text{Me}_2\text{Br}_2\text{Sb}[\text{CH}_2]_3\text{SbBr}_2\text{Me}_2$	12.6(12.2)	2.6(2.7)	48.2(48.9)

* Calculated values are given in parentheses.

Acta MIV spectrometer and vibrational spectra (Nujol and hexachlorobutadiene mulls) with a Perkin-Elmer 621 spectrometer. Antimony-121 Mössbauer spectra were obtained at P.C.M.U., Harwell. Analytical data for the derivatives of the ligands are given in Table 1 and of the complexes in Table 2.

⁵ W. Levason, C. A. McAuliffe, and S. G. Murray, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 849.

⁶ E. Shewchuk and S. B. Wild, *J. Organometallic Chem.*, 1974, **71**, C1.

⁷ M. F. Ludman-Obier, M. Dartinguenave, and Y. Dartinguenave, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 147.

⁸ W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, 1974, **11**, 33.

⁹ B. R. Cook, C. A. McAuliffe, and D. W. Meek, *Inorg. Chem.*, 1971, **10**, 2676.

¹⁰ R. J. Dickinson, W. Levason, C. A. McAuliffe, and R. V. Parish, *J.C.S. Chem. Comm.*, 1975, 272.

Preparations.—1,3-Bis(dimethylstibino)propane, $\text{Me}_2\text{Sb}[\text{CH}_2]_3\text{SbMe}_2$ (dmsp). Bromodimethylstibine¹¹ (23.2 g, 0.1 mol) was added dropwise to a stirred solution of sodium (4.6 g, 0.2 mol) in liquid ammonia (400 cm³) cooled to -78°C . When the addition was complete the solution was allowed to warm to -33°C and stirred at that temperature for 3 h. Cautious dropwise addition of 1,3-dibromopropane (10.1 g, 0.05 mol) rapidly discharged the deep red colour and the addition was stopped when the colour of the solution became pale fawn. The ammonia was boiled off, deoxygenated water (100 cm³) was added dropwise, and the mixture stirred with diethyl ether (200 cm³). The ether layer

in chloroform until a permanent orange colouration was obtained. The resulting white precipitate was filtered off, rinsed with chloroform (10 cm³) and ethanol (10 cm³), and dried *in vacuo* over K[OH] pellets to remove bromine. Yield 0.71 g (74%).

Bis[1,3-bis(dimethylstibino)propane]chloronickel(II) perchlorate, $[\text{Ni}(\text{dmsp})_2\text{Cl}][\text{ClO}_4]$. Nickel(II) chloride hexahydrate (0.24 g, 1.0 mmol) and nickel(II) perchlorate hexahydrate (0.37 g, 1.0 mmol) were dissolved in warm n-butanol (20 cm³) and dmsp (1.4 g, 4.0 mmol) was syringed into the rapidly stirred solution. After 30 min the complex was precipitated by the dropwise addition of diethyl ether

TABLE 2
Analytical data and spectroscopic properties of the complexes

Complex	Colour	Analysis (%) ^a		$\frac{\Lambda}{S}$ $\text{cm}^2 \text{mol}^{-1}$	I.r. spectra (cm ⁻¹) (Nujol mull)	Electronic spectra (10 ³ cm ⁻¹)	
		C	H			solution ^c	reflectance
$[\text{Ni}(\text{dmap})_2\text{Cl}][\text{ClO}_4]$	Dark blue	24.0(23.3)	5.1(5.1)	98	1 080, 620 $[\text{ClO}_4]^-$	17.5 (700) ^d	18.1
$[\text{Ni}(\text{dmap})_2\text{Br}][\text{ClO}_4]$	Dark blue	22.6(22.7)	4.9(4.9)	100	1 080, 620 $[\text{ClO}_4]^-$	16.9 (1 010), 27.7 (5 530) ^d	17.4
$[\text{Ni}(\text{dmap})_2\text{I}][\text{ClO}_4]$	Dark blue	21.2(21.3)	4.5(4.7)	101	1 080, 620 $[\text{ClO}_4]^-$	16.7 (2 285), 26.5 (2 020) ^d	16.0
$[\text{Ni}(\text{dmap})_2][\text{ClO}_4]_2$	Orange-brown	22.0(21.8)	4.6(4.8)	186	1 080, 622 $[\text{ClO}_4]^-$	18.5 (660), 22.0(sh) ^e	22.3
$[\text{Ni}(\text{dmsp})_2\text{Cl}][\text{ClO}_4]$	Purple	19.0(18.4)	4.1(4.1)	110	1 080, 620 $[\text{ClO}_4]^-$	20.5 ^{d,f}	19.6
$[\text{Ni}(\text{dmsp})_2\text{Br}][\text{ClO}_4]$	Purple	17.9(17.7)	3.9(4.2)	106	1 080, 620 $[\text{ClO}_4]^-$	20.6 (636) ^e	19.6
$[\text{Ni}(\text{dmsp})_2\text{I}][\text{ClO}_4]$	Purple	17.2(17.0)	3.6(3.8)	108	1 080, 620 $[\text{ClO}_4]^-$	18.9 (553) ^e	19.4
$[\text{Ni}(\text{dmsp})_2(\text{OH}_2)][\text{ClO}_4]_2$	Purple	17.4(17.5)	3.8(4.0)	166	1 080, 620 $[\text{ClO}_4]^-$; 3 300, 1 630 (H_2O)	18.1 (1 180), 25.6 (2 220) ^e	18.4, 23.5
$[\text{Co}(\text{dmsp})_2]_2[\text{CoI}_4]$	Brown	14.5(15.2)	3.1(3.9)	insoluble		19.1 (854) ^e	19.3
						5.8, 16.5, 19.8, 25.0 ^{d,f}	5.8, 16.4(sh 19), 23.0, 25.8(sh)
$[\text{Pd}(\text{dmsp})\text{Cl}_2]$	Yellow	16.4(16.2)	3.5(3.6)	<1	292, 270 Pd-Cl	27.0 (3 720) ^d	24.6
$[\text{Pd}(\text{dmsp})\text{Br}_2]$	Brown	13.7(13.8)	3.0(3.2)	<1	220 Pd-Br	23.3(sh) (886), 26.3 (6 540) ^d	23.4
$[\text{Pd}(\text{dmsp})\text{I}_2]$	Dark brown	11.9(12.0)	2.5(2.7)	<1		23.3 (19 875) ^d	22.6
$[\text{Pd}(\text{dmsp})(\text{SCN})_2]$	Brown	19.8(19.8)	3.2(3.0)	<1	2 105, 2 115 $\nu(\text{CN})$ ^g	25.0 (2 700) ^d	23.0
$[\text{Pt}(\text{dmsp})\text{Cl}_2]$	Yellow	13.9(13.9)	3.0(3.0)	<1	295, 273 Pt-Cl	28.2(sh) (753), 32.1 (3 786) ^d	26.5
$[\text{Pt}(\text{dmsp})\text{Br}_2]$	Yellow	12.2(12.1)	2.6(2.5)	<1	230 Pt-Br	ca. 27.5(sh) (820), 31.8 (2 680) ^d	24.0
$[\text{Pt}(\text{dmsp})\text{I}_2] \cdot \text{EtOH}$	Orange	13.0(13.3)	2.7(2.7)	<1	3 250 $\nu(\text{OH})$	23.8 (656) ^d	23.3
$[\text{Pd}(\text{dmsp})(\text{SCN})_2]$	Yellow-green	16.4(16.5)	2.8(3.1)	ca. 1	2 100, 2 095(sh) $\nu(\text{CN})$ ^h	ca. 28.1(sh) (770), 30.3(sh), (ca. 1 000) ^d	24.8

^a Calculated values are given in parentheses. ^b ca. 10^{-3} mol dm⁻³ MeNO₂. ^c Absorption coefficients ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) are given in parentheses. ^d In CH₂Cl₂. ^e In MeNO₂. ^f Only slightly soluble. ^g In CH₂Cl₂; $\nu(\text{CN})$ at 2 100 and 2 065 cm⁻¹. ^h In CH₂Cl₂; $\nu(\text{CN})$ at 2 100 and 2 060 cm⁻¹.

was separated, dried over anhydrous sodium sulphate, and distilled to yield 1,3-bis(dimethylstibino)propane (7.8 g, ca. 45%), b.p. 65°C (0.5 mmHg),* as a colourless very air-sensitive liquid: ¹H n.m.r. spectrum (neat liquid) τ 8.65(m, 6 H, CH₂) and 8.8(s, 12 H, CH₃).

1,3-Bis(dimethylarsino)propane, $\text{Me}_2\text{As}[\text{CH}_2]_3\text{AsMe}_2$ (dmap). This compound was prepared from sodium (9.2 g, 0.4 mol), iododimethylarsine (50.0 g, 0.2 mol), and 1,3-dibromopropane (20.1 g, 0.1 mol) in tetrahydrofuran (thf) (400 cm³) by an analogous method to that described by Feltham *et al.*¹² for *o*-phenylenebis(dimethylarsine). The product (16.5 g, 66%) was purified by distillation, b.p. $98-100^\circ\text{C}$ (12 mmHg), and was a colourless air-sensitive liquid: ¹H n.m.r. spectrum (neat liquid) τ 8.45(m, 6 H, CH₂) and 9.0(s, 12 H, CH₃).

Ligand dimethiodides. Each ligand (1.0 g) was heated under reflux with a five-fold excess of iodomethane in ethanol and the products were recrystallised from acetone. The quaternary stibine was obtained as a dihydrate in the form of white crystals, m.p. $218-220^\circ\text{C}$, Λ (10^{-3} mol dm⁻³, MeNO₂) = 168 S cm² mol⁻¹: ¹H n.m.r. spectrum in (D₃C)₂SO τ 7.5(m, 6 H, CH₂) and 8.35(s, 18 H, CH₃). The quaternary arsine was an anhydrous white solid, m.p. $258-260^\circ\text{C}$, Λ (10^{-3} mol dm⁻³, MeNO₂) = 174 S cm² mol⁻¹: ¹H n.m.r. spectrum in (D₃C)₂SO τ 7.5(m, 6 H, CH₂), and 8.0(s, 18 H, CH₃).

1,3-Bis(dibromodimethylstibino)propane, $\text{Me}_2\text{Br}_2\text{Sb}[\text{CH}_2]_3\text{SbBr}_2\text{Me}_2$. 1,3-Bis(dimethylstibino)propane (0.5 g) in chloroform (10 cm³) was treated dropwise with bromine

* Throughout this paper: 1 mmHg \approx 13.6 \times 9.8 Pa.

¹¹ G. T. Morgan and G. R. Davies, *Proc. Roy. Soc.*, 1926, **A110**, 523.

(20 cm³) to the rapidly stirred solution. The resulting purple powder was filtered off, washed with n-butanol and diethyl ether, and dried *in vacuo*, yield 53%. The product was analytically pure, but recrystallisation could be effected from nitromethane when necessary.

The complexes $[\text{Ni}(\text{dmsp})_2\text{X}][\text{ClO}_4]$ (X = Br or I) and $[\text{Ni}(\text{dmap})_2\text{X}][\text{ClO}_4]$ (X = Cl, Br, or I) were prepared analogously in yields of >60%. The corresponding reaction of dmsp, CoL₂·6H₂O, and Co[ClO₄]₂·6H₂O gave an insoluble brown material, thought to be $[\text{Co}(\text{dmsp})_2\text{I}_2][\text{CoI}_4]$.

Aquabis[1,3-bis(dimethylstibino)propane]nickel(II) perchlorate, $[\text{Ni}(\text{dmsp})_2(\text{OH}_2)][\text{ClO}_4]_2$. Nickel(II) perchlorate hexahydrate (0.72 g, 2.0 mmol) in n-butanol (20 cm³) was treated with dmsp (1.4 g, 4.0 mmol). The resulting purple solution was stirred for 1 h and then treated dropwise with diethyl ether (15 cm³) to precipitate the purple product, yield 85%.

The orange complex $[\text{Ni}(\text{dmap})_2][\text{ClO}_4]_2$ was prepared similarly and recrystallised from dichloromethane.

[1,3-Bis(dimethylstibino)propane]dichloropalladium(II), $[\text{Pd}(\text{dmsp})\text{Cl}_2]$. Sodium tetrachloropalladate(II) (0.3 g, 1.0 mmol) in ethanol (10 cm³) was treated with dmsp (0.4 g, 1.15 mmol) in dichloromethane (10 cm³). The mixture was stirred for 1 h and evaporated to dryness, after which the residue was taken up in dichloromethane-ethanol (10 : 1), filtered, and allowed to crystallise to give yellow crystals, yield 65%.

The complexes $[\text{Pd}(\text{dmsp})\text{X}_2]$ (X = Br, I, or CNS) were prepared similarly in the presence of a five-fold excess of the

¹² R. D. Feltham, A. Kasenally, and R. S. Nyholm, *J. Organometallic Chem.*, 1967, **7**, 285.

appropriate lithium salt. The corresponding platinum complexes (60–85% yield) were prepared from potassium tetrachloroplatinate(II), lithium salt, and the ligand in an aqueous ethanol-dichloromethane mixture, and subsequently recrystallised from dichloromethane-ethanol.

RESULTS AND DISCUSSION

The new ligand 1,3-bis(dimethylstibino)propane, dm_{sp}, was obtained as a colourless extremely air-sensitive oil, which was characterised by ¹H n.m.r. and mass spectroscopy.¹³ Bromine converts it to the white air- and moisture-stable tetrabromide, Me₂Br₂Sb-[CH₂]₃SbBr₂Me₂, and treatment with iodomethane yields the dimethiodide derivative, [Me₃Sb(CH₂)₃SbMe₃-I₂·2H₂O (Table 1). The corresponding diarsine, 1,3-bis(dimethylarsino)propane, dmap, was prepared for comparison and similarly characterised by its ¹H n.m.r. and mass spectrum¹³ and as the dimethiodide (Table 1).

The distibine reacts with 'NiX(ClO₄)'¹⁴ (mol ratio dm_{sp} : NiX₂ : Ni(ClO₄)₂ = 4 : 1 : 1) in n-butanol to yield the diamagnetic purple complexes [Ni(dm_{sp})₂X]-[ClO₄] (X = Cl, Br, or I), which are poorly soluble in alcohols and halogenoalkane solvents but dissolve readily in nitromethane. The solids are stable in air for several weeks and are thus the first examples of stable complexes containing Ni^{II}-SbR₃ co-ordination where such co-ordination is not 'encouraged' by the presence of phosphorus or arsenic donors in the ligand. The stability of these complexes contrasts with that of [Ni(SbMe₃)₃X₂],⁷ which are decomposed by most donor solvents and by dioxygen. In 10⁻³ mol dm⁻³ nitromethane solution the complexes are 1 : 1 electrolytes (Table 2) and their electronic spectra exhibit one broad absorption in the range 18 000–21 000 cm⁻¹, consistent with the presence of five-co-ordinate, essentially square-pyramidal, cations.^{8,15} The electronic spectra of the solids are generally similar and the i.r. spectra are consistent with the presence of unco-ordinated perchlorate ions.¹⁶ Thus, in both the solid state and in solution, square-pyramidal [NiSb₄X]⁺ chromophores are present. Attempts to prepare corresponding complexes with X = NCS or NO₃ did not yield pure products.

The reaction of Ni(ClO₄)₂·6H₂O with dm_{sp} yields a diamagnetic purple complex [Ni(dm_{sp})₂(OH₂)]-[ClO₄]₂, the i.r. spectrum of which confirms the presence of water and of ionic perchlorate.¹⁶ In solution this complex is a 1 : 2 electrolyte and its electronic spectrum in both the solid state and in solution is consistent with a five-co-ordinate square-pyramidal nickel(II) ion.^{8,15}

The corresponding complexes of 1,3-bis(dimethylarsino)propane, [Ni(dmap)₂X]-[ClO₄] (X = Cl, Br, or I), are dark blue crystalline materials, the i.r. spectra of which once again give evidence of ionic perchlorate

groups; in solution the complexes function as 1 : 1 electrolytes consistent with five-co-ordination for the nickel atom, [NiAs₄X]⁺. However, the electronic spectra, both of the solids and of solutions in dichloromethane, exhibit one broad asymmetric absorption at 16 000–18 000 cm⁻¹, assignable to trigonal-bipyramidal geometry,^{15,17} in contrast to the square-pyramidal structures deduced for the dm_{sp} analogues. It is interesting to recall that the diphosphine analogue, 1,3-bis(dimethylphosphino)propane, gives complexes of both geometries: [Ni(dm_{pp})₂X]⁺ being trigonal bipyramidal for X = Br and I and distorted square pyramidal for X = Cl or NCS.¹⁸ Examination of the literature^{12,19} shows that bidentate group 5B donor ligands with two-carbon backbones generally produce square-pyramidal [NiL₂X]⁺ entities, whilst from the data above the longer C₃ case the factors which favour one geometry or the other are unclear.^{19,20} Indeed, in view of the considerable distortion from ideal geometry often present, it is sometimes difficult to decide on the best description of the structure, and from this viewpoint it is surprising that for Ni^{II} the electronic spectra show marked differences.

The complex [Ni(dmap)₂][ClO₄]₂ contains only ionic perchlorate groups in the solid state; the electronic spectrum (maximum at 22 300 cm⁻¹) is consistent with a four-co-ordinate planar cation.^{8,9} However, in nitromethane the electronic spectrum exhibits a new absorption at 18 500 cm⁻¹ which strongly suggests that a five-co-ordinate species is present. Since the complex is a 1 : 2 electrolyte in this solvent the fifth ligand cannot be perchlorate, and we thus believe that this cation is [Ni(dmap)₂(O₂NMe)]²⁺. In dichloromethane the complex is very slightly soluble and exhibits a weak absorption at 20 500 cm⁻¹, again pointing to the presence of a five-co-ordinate species, in this case possibly [Ni(dmap)₂(OCIO₃)]⁺. Somewhat similar behaviour has been observed previously with the nickel(II) perchlorate complex of *cis*-Ph₂AsCH:CHAsMe₂.²¹

All attempts to obtain 1 : 1 complexes of dm_{sp} with nickel(II) halides failed, even when a considerable excess of NiX₂ was used. A comparison of the nickel(II) complexes of the three ligands dm_{pp}, dmap, and dm_{sp} confirms the previously observed trend⁸ in promoting five-co-ordination, P < As < Sb.

The reaction of dm_{sp} with 'CoI(ClO₄)' in n-butanol yields a very slightly soluble brown powder which contains no perchlorate groups (i.r. evidence). The electronic spectrum is consistent with a [Co(dm_{sp})₂I]₂-[CoI₄] species, and the analytical data are approximately consistent with this stoichiometry. Due to its insolubility, the complex could not be purified and

¹³ W. Levason, C. A. McAuliffe, S. G. Murray, and R. D. Sedgwick, *J. Organometallic Chem.*, 1976, **105**, 195.

¹⁴ T. D. Dubois and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 1395.

¹⁵ J. R. Preer and H. B. Gray, *J. Amer. Chem. Soc.*, 1970, **92**, 7306.

¹⁶ S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 1965, **4**, 1091.

¹⁷ G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1965, 1293.

¹⁸ J. C. Cloyd and D. W. Meek, *Inorg. Chim. Acta*, 1972, **6**, 480.

¹⁹ R. Morassi, I. Bertini, and L. Sacconi, *Co-ordination Chem. Rev.*, 1973, **11**, 343.

²⁰ J. S. Wood, *Prog. Inorg. Chem.*, 1972, **16**, 227.

²¹ K. K. Chow, W. Levason, and C. A. McAuliffe, *Inorg. Chim. Acta*, 1976, **16**, 173.

attempts to isolate other cobalt(II) complexes were unsuccessful. The greater 'hardness' of Co^{II} compared with Ni^{II} would be expected to make isolation of stibine complexes of the former more difficult, but it appears that the differences between these two metal ions are particularly pronounced with very soft ligands.²²

The reaction of dmsp with the appropriate tetrahalogeno-palladate(II) or -platinate(II) yields the complexes [M(dmsp)X₂] (M = Pd or Pt; X = Cl, Br, I, or SCN). The i.r. and electronic spectra of these complexes are consistent with *cis*-planar stereochemistry³ (Table 2). In the solid state the thiocyanate complexes are formulated as containing M-SCN linkages on the basis of the high energy of $\nu(\text{CN})^*$ and the spectrochemical series derived from the electronic-reflectance spectra (Cl > Br > SCN > I).^{23,24} The occurrence of S-bonding in these complexes is expected in view of the similar mode of co-ordination found in the complexes of Ph₂Sb[CH₂]₃-SbPh₂³ and *o*-C₆H₄(SbPh₂)₂.⁵ Both thiocyanato-complexes are poorly soluble in dichloromethane in which they exhibit two widely separated $\nu(\text{CN})$ vibrations, consistent with both M-SCN and M-NCS linkages, and in support of this the electronic spectra of the solutions exhibit the spectrochemical series Cl > NCS > Br > I.^{24,†} These appear to be the first examples of isothiocyanate co-ordination to these two metals in stibine complexes.^{23,25} Although dichloromethane is one of Burmeister's class B solvents²⁶ which tends to promote S → N isomerism, the occurrence of NCS co-ordination with antimony ligands is not readily rationalised on either steric or electronic grounds and is a further illustration that the control of the mode of thiocyanate co-ordination to Pd^{II} and Pt^{II} is still incompletely understood.^{23,25}

Reaction of Na₂[PdCl₄] with a large excess of dmsp with or without addition of Li[ClO₄] or Na[BPh₄] yields only the 1:1 complex [Pd(dmsp)Cl₂]. The reluctance of dmsp to promote five-co-ordination to Pd^{II} is unexpected, both in view of its great tendency to generate [Ni(dmsp)₂X]⁺ ions and the ability of other stibine ligands to yield five-co-ordinate complexes.²⁵ The failure to prepare [Pd(dmsp)₂X]⁺ cannot be due to steric factors since there is clearly no problem in accommodating the same ligand environment about the smaller Ni²⁺ ion. In the cases of phenyl-substituted ditertiary stibines we believe that the inability of the ligands to compete with halide ions for co-ordination positions on the metal may be the major electronic factor precluding isolation of [PdL₂X]X, but in view of the much stronger

* Observation of $\nu(\text{CS})$ and $\delta(\text{SCN})$ is prevented by ligand absorptions.

† In view of the poor solubility, integrated-intensity measurements were not obtained.

²² W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, 1975, **14**, 127.

²³ A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 231.

²⁴ D. W. Meek, P. Nicpon, and V. I. Meek, *J. Amer. Chem. Soc.*, 1970, **92**, 5351.

σ -donor power of dmsp this mechanism is unlikely to be operating here.

We have obtained the ¹²¹Sb Mössbauer spectra of dmsp and the Ph₂Sb[CH₂]₃SbPh₂ analogue,³ and of some complexes of both ligands (Table 3). Unfortunately,

TABLE 3
Antimony-121 Mössbauer data at 4.2 K

	$\delta(\text{CaSnO}_3)$ mm s ⁻¹	e^2qQ mm s ⁻¹	Γ mm s ⁻¹	η^a	χ^2^b
dmsp ^c	-9.21(12)	16.6(8)	2.1(3)	0	1.12
[Pd(dmsp)Cl ₂]	-6.72(7)	10.7(6)	2.5(3)	0.29(1)	1.09
[Pd(dmsp)I ₂]	-7.00(3)	10.2(8)	2.7(6)	0.27(1)	1.27
[Pt(dmsp)I ₂]	-6.50(5)	8.9(3)	2.7(1)	0.36(1)	1.20
dmsp	-9.24(8)	15.3(6)	2.8(1)	0.42(1)	1.07
[Ni(dmsp) ₂ (OH ₂)]- [ClO ₄] ₂	-6.98(3)	9.2(2)	2.6(1)	0.29(1)	1.03

^a $\eta = 0$ signifies that η was constrained to zero.²⁸ ^b Degrees of freedom. ^c dmsp = Ph₂Sb[CH₂]₃SbPh₂.

due to considerable delays between the preparation of the dmsp complexes and the running of the spectra, some slight decomposition-oxidation had occurred and a few of the spectra revealed contamination by organo-antimony(V) species or Sb₂O₃. Whilst spectra of the complexes were obtainable, this slight contamination did have the effect of making the parameters less well defined in some cases than for the complexes of unidentate stibines studied earlier.²⁷ The ligand parameters are similar to those reported²⁸ for Ph₂Sb[CH₂]₄-SbPh₂ [$\delta(\text{CaSnO}_3) = -9.0$ mm s⁻¹, $e^2qQ/h = 16.9$ mm s⁻¹] and display the large positive quadrupole-coupling constant expected for tertiary stibines having a stereochemically active lone pair.

The parameters of the complexes clearly display the effects of donation of the lone pair to the metal, *viz.* an increase in isomer shift and a decrease in quadrupole-coupling constant. As observed previously, these parameter changes are greater for co-ordination to Pt^{II} than Pd^{II}. The differences between the two palladium complexes, although small, are consistent with the trends found for *cis* complexes. The spectrum of the nickel complex shows no evidence for more than one type of co-ordinated antimony; the linewidth is normal and the χ^2 value is good. This is consistent with the configuration suggested above.

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