Studies in Mössbauer Spectroscopy. Part 11.[1] Antimony-121 Spectra of some Complexes of Palladium(II) and Platinum(II) with Tertiary Stibines †

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Antimony-121 Mössbauer spectra have been obtained for 23 complexes of the type $[MX_2L_2]$ [L = $SbPh_3$, $Sb(C_6H_4Me\text{-}p)_3$, $Sb(C_6H_4Me\text{-}o)_3$, $SbEt_3$, or $Sb(C_6H_{11})_3$; M = Pd or Pt; X = Cl, I, or NO_2], for the five-co-ordinate $[PtI_2L_3]$ (L = $SbMePh_2$ or $SbMe_2Ph$), for $[RhCl_3(SbPh_3)_3]$, and for the free triarylstibines. In each case co-ordination results in a large increase in isomer shift and a decrease in quadrupole coupling constant, as expected for substantial removal of electron density from the lone pair on the antimony atom. In conjunction with far-i.r. data, configurations are assigned to the square-planar complexes, which are *cis* unless the stibine is sterically demanding. The *cis* and *trans* influences of the halides on the electron density on the antimony atom are shown to be opposed.

MÖSSBAUER spectroscopy is of great value in elucidating the effects which the ligands exert on the central atom of a co-ordination complex. The technique also has considerable potential for the examination of the effect which co-ordination has on the ligands, but this has been little exploited. The ^{119}Sn Mössbauer parameters of co-ordinated $SnCl_3$ groups show small changes which appear to be related to the nature and number of other ligands present,[2] and data for a range of complexes have been collated.[3] However, this ligand does not form a very wide range of complexes. The iodide ligand is more versatile, and brief reports of ^{129}I data have appeared recently.[4-10] In a study of the complexes *cis*-$[PtI_2L_2]$ and *trans*-$[PtH(I)L_2]$ the quadrupole coupling constant (q.c.c.) of the iodide ligand reflected the *trans* influence of the other ligands,[5] and for *trans*-$[PtI_2L_2]$ the operation of a large *cis* influence seemed probable,[4] but the ordering of ligands in the two series was opposed. However, it was subsequently shown that the Mössbauer parameters of iodide ligand do not relate directly to the total electron density of the Pt–I bond but only, as might with hindsight be expected, to the distribution of electrons in the valence shell of the iodide itself;[11] this result will also apply to the interpretation of n.q.r. data. Nevertheless, it is clear that the neutral ligands exert a considerable effect on the electron-density distribution in the iodide ligand, and it seemed desirable to confirm these results by the investigation of a neutral ligand. Suitable diversity of co-ordination is found among tertiary stibines, in which the resonance of ^{121}Sb at 37.1 keV may be employed,‡ and we have examined the spectra of several series of complexes. We report here on some unidentate ligands and their palladium(II) and platinum(II) complexes, leaving chelate systems to a later communication. As far as we are aware, the only previous study of this type is of the triphenylstibine derivatives of iron pentacarbonyl.[12]

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† No reprints are available.

‡ Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

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EXPERIMENTAL

The complexes were prepared as described previously.[13] Mössbauer spectra were obtained at P.C.M.U., Harwell, with source ($CaSnO_3$) and absorber immersed in liquid helium. Absorbers contained *ca.* 10 mg cm^{-2} of natural antimony, and were mulled with molten paraffin wax. The complex $[PtI_2(SbMe_2Ph)_3]$, which is particularly prone to dissociation, was mulled with an inert fluorinated grease (Krytox) and did not appear to dissociate. Computer fitting was based on full diagonalization of the Hamiltonian matrix,[14] using the thickness-integral approach described by Shenoy *et al.*[15] embodying Cranshaw's rapid-integration method.[16] Fitting of a single-site 12-line spectrum requires 30—35 s on our CDC7600. Difficulty was experienced in fitting the spectrum of $[Pt(NO_2)_2\{Sb(C_6H_{11})_3\}_2]$ and the values quoted are for the simple sum-of-Lorentzians procedure with asymmetry parameter (η) constrained to zero. In other cases, the simpler approach gave q.c.c. values *ca.* 0.3 mm s^{-1} larger than those from the thickness-integral method. For all the complexes the spectra were poorly resolved and the probable error associated with the small q.c.c. values is *ca.* 0.5 mm s^{-1}. In some cases the programme failed to converge when η was left free, or gave an error comparable to the final η value. In these cases η was constrained to zero.

RESULTS AND DISCUSSION

The ^{121}Sb Mössbauer data for the free ligands (Table 1) agree well with earlier measurements and data for other tertiary stibines. The positive isomer shifts (i.s.), relative to other antimony(III) systems,[17] indicate a considerable degree of *s*-orbital participation in the Sb–C bonds, and the large positive q.c.c. values (eQ_g is negative) demonstrate that the lone pair has considerable *p* character and contributes substantially to the electric field gradient (e.f.g.).

The parameters for the palladium(II) and platinum(II) complexes (Table 2) are similar to those for the previously reported Fe–$SbPh_3$ systems.[12] Relative to the free ligands the i.s. values have become more positive (by 2—3 mm s^{-1}) while the q.c.c. values have decreased (by 4—6 mm s^{-1}, 25—35%); representative spectra are shown in Figure 1. These co-ordination shifts are similar for all the ligands and are in the directions expected for delocalization of the lone pair on to the transition metal, provided it is assumed that both the 5*s* and 5*p* orbitals make significant contributions to the lone pair and hence to the metal–antimony bond. In complexes involving bonds between tin and transition metals, both *s* and *p* orbitals are known to participate strongly (ref. 18 and refs. therein). The co-ordination i.s. shift is smaller for the aliphatic than for the aromatic stibines, while the opposite is true of the co-ordination q.c.c. shifts. Both differences are consistent with the higher *s* character expected for Sb–C(aliphatic) bonds and

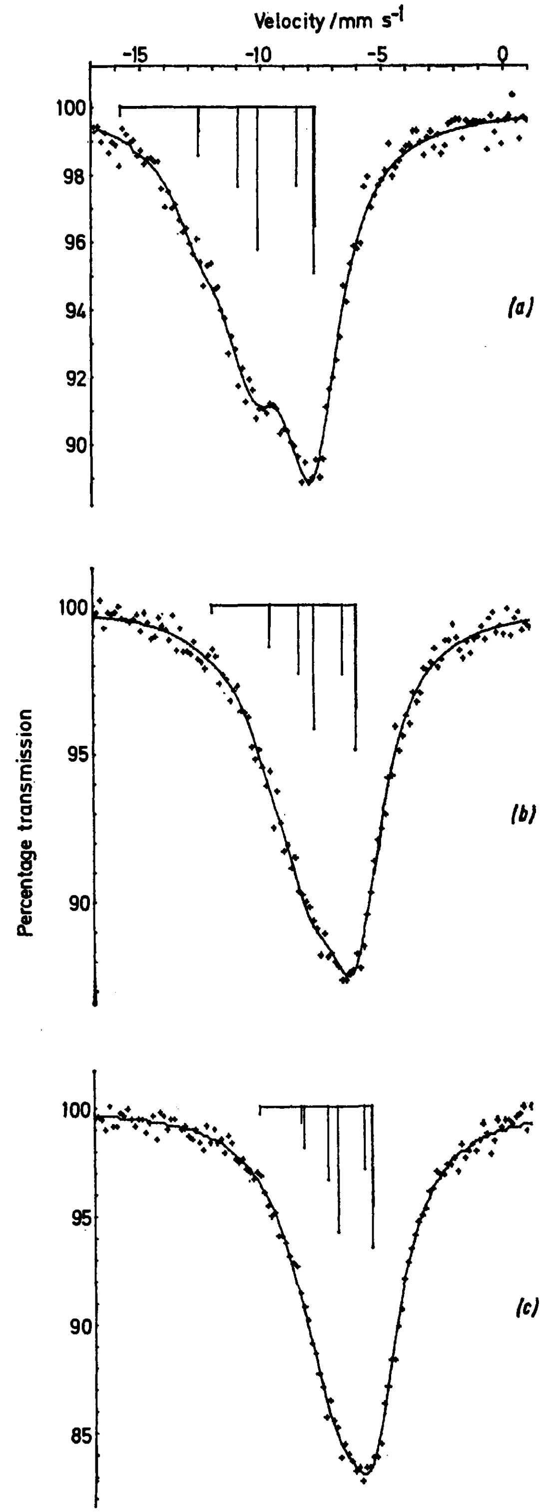

FIGURE 1 Antimony-121 Mössbauer spectra of (*a*) $SbPh_3$, (*b*) $[PdCl_2(SbPh_3)_2]$, and (*c*) $[PtCl_2(SbPh_3)_2]$. The bar spectra show the eight major lines at half the normalized intensities. The full line is the calculated spectrum allowing for thickness effects

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the consequent higher *p* character of the metal–antimony bonds.

Removal of *s*-electron density from antimony would give a dramatic increase in i.s. owing to the large negative value of $\delta R/R$ for ^{121}Sb.[17] In this respect, formation of the co-ordinate bond may be regarded as a formal oxidation, and the i.s. increases towards the values found for organoantimony(V) compounds. The majority of such compounds involve five-co-ordinate antimony atoms with trigonal-bipyramidal configurations which invalidates comparison with the present systems. The best analogy is with $[SbPh_4][ClO_4]$ which is believed to

TABLE 1

Antimony-121 Mössbauer parameters for the ligands (4.2 K) [a]

Ligand	$\delta(CaSnO_3)$ mm s^{-1}	e^2qQ/h mm s^{-1}	η [b]	Γ mm s^{-1}	t effective thickness	χ^2 degrees of freedom
$SbPh_3$	−9.35(3)	+16.2(3)	0.06(14)	2.62(6)	0.05(1)	1.02
c	−9.69	+17.5	0			
d	−9.11	+17.0	0			
$Sb(C_6H_4Me\text{-}o)_3$	−9.77(3)	+17.4(3)	0.16(7)	2.90(6)	0.60(6)	0.91
$Sb(C_6H_4Me\text{-}m)_3$ [e]	−9.52(4)	+16.8(3)	0	2.64(13)	0.54(1)	0.96
$Sb(C_6H_4Me\text{-}p)_3$ [e]	−9.37(4)	+17.0(3)	0	2.40(10)	0.34(2)	1.09
$Sb(C_6H_4Cl\text{-}p)_3$ [f]	−9.3	0				
$Sb(C_6H_4OMe\text{-}p)_3$	−9.0	0				
$Ph_2Sb[CH_2]_4SbPh_2$ [d]	−9.0	+16.9	0			
$SbMe_3$ [d]	−8.72	+16.3	0			

[a] Figures in parentheses are the standard errors of the fitting procedure. [b] An entry of 0 signifies that η was constrained to zero (see Experimental section). [c] Ref. 19. [d] T. B. Brill, G. E. Parris, G. G. Long, and L. H. Bowen, *Inorg. Chem.*, 1973, **12**, 1888. The i.s. of InSb relative to $CaSnO_3$ has been taken as +8.5 mm s^{-1} (G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 59). [e] Minor components were also present with $\delta = -4.75$ mm s^{-1} and $e^2qQ/h = +18.7$ mm s^{-1} $[Sb(C_6H_4Me\text{-}m)_3]$, and $\delta = -4.81$ mm s^{-1} and $e^2qQ/h = +19.1$ mm s^{-1} $[Sb(C_6H_4Me\text{-}p)_3]$. [f] S. E. Gukasyan and V. S. Shpinel, *Phys. Stat. Solidi*, 1968, **29**, 49. These spectra were fitted as single Lorentzians.

TABLE 2

Antimony-121 Mössbauer parameters for the complexes (4.2 K)

Complex	$\delta(CaSnO_3)$ mm s^{-1}	e^2qQ/h mm s^{-1}	η [a]	Γ mm s^{-1}	t effective thickness	χ^2 degrees of freedom
$[PdCl_2(SbPh_3)_2]$	−7.31(2)	+12.0(3)	0	2.75(6)	0.53(1)	0.87
$[PdI_2(SbPh_3)_2]$	−7.23(2)	+10.7(3)	0	2.76(7)	0.62(1)	1.18
$[Pd(NO_2)_2(SbPh_3)_2]$	−7.04(2)	+9.6(3)	0	2.75(6)	0.65(1)	1.27
$[PtCl_2(SbPh_3)_2]$	−6.44(1)	+9.5(2)	0.22(10)	2.63(5)	0.67(1)	0.89
$[PtI_2(SbPh_3)_2]$	−6.78(2)	+9.6(3)	0	2.70(8)	0.46(1)	0.98
$[Pt(NO_2)_2(SbPh_3)_2]$	−6.73(2)	+9.3(3)	0	2.88(6)	0.63(1)	1.09
$[RhCl_3(SbPh_3)_3]$	−7.14(2)	+10.7(3)	0	2.83(7)	0.58(1)	1.07
b	−6.87(5) −8.09(12)	+11.1(5) +13.3(7)	0 0	2.66(2)		1.07
c, *d*	−6.83(5) −8.32(15)	+10.3(4) +12.8(8)	0 0	2.67(25) 2.30(56)		1.07
$[Fe(CO)_4(SbPh_3)]$ [e]	−6.62	+9.0	0			
$[Fe(CO)_3(SbPh_3)_2]$ [e]	−6.65	+10.9	0			
$[Fe(\eta\text{-}C_5H_5)(CO)_2(SbPh_3)][PF_6]$	−6.7	+9.5	0			
$[SbPh_4][ClO_4]$ [f]	−5.9	0.0				
$[PtCl_2\{Sb(C_6H_4Me\text{-}p)_3\}_2]$	−6.48(2)	+10.0(3)	0.20(12)	2.71(6)	0.66(1)	1.10
$[PtI_2\{Sb(C_6H_4Me\text{-}p)_3\}_2]$	−6.91(3)	+10.8(4)	0.27(12)	2.60(8)	0.58(1)	1.04
$[Pt(NO_2)_2\{Sb(C_6H_4Me\text{-}p)_3\}_2]$	−6.75(2)	−9.3(3)	0.26(11)	2.70(6)	0.92(1)	1.17
$[PdCl_2\{Sb(C_6H_4Me\text{-}o)_3\}_2]$	−7.40(2)	+10.6(2)	0.26(8)	2.79(5)	0.93(1)	1.08
$[PdI_2\{Sb(C_6H_4Me\text{-}o)_3\}_2]$	−7.24(4)	+9.6(6)	0	2.67(13)	0.42(1)	1.04
$[Pd(NO_2)_2\{Sb(C_6H_4Me\text{-}o)_3\}_2]$	−7.24(1)	+9.8(2)	0.26(10)	2.85(5)	0.85(1)	1.14
$[PtCl_2\{Sb(C_6H_4Me\text{-}o)_3\}_2]$	−7.09(1)	+10.8(2)	0	2.80(5)	0.87(1)	0.85
$[PtI_2\{Sb(C_6H_4Me\text{-}o)_3\}_2]$	−7.00(2)	+11.0(2)	0	2.83(6)	0.86(1)	0.91
$[Pt(NO_2)_2\{Sb(C_6H_4Me\text{-}o)_3\}_2]$	−6.84(1)	+9.4(2)	0.31(8)	2.73(5)	0.94(1)	1.05
$[PtCl_2\{Sb(C_6H_{11})_3\}_2]$	−7.65(2)	+8.2(4)	0.37(18)	2.78(9)	0.67(1)	1.59
$[PtI_2\{Sb(C_6H_{11})_3\}_2]$	−7.55(2)	+9.3(3)	0.24(13)	2.71(6)	0.83(1)	1.01
$[Pt(NO_2)_2\{Sb(C_6H_{11})_3\}_2]$ [c]	−7.53(2)	+8.3(2)	0	3.05(10)		0.99
$[PtCl_2(SbEt_3)_2]$	−6.66(2)	+8.0(3)	0	2.74(7)	0.63(1)	1.07
$[PtI_2(SbEt_3)_2]$	−7.08(2)	+9.0(3)	0	2.62(8)	0.57(1)	1.08
$[Pt(NO_2)_2(SbEt_3)_2]$	−7.00(2)	+7.3(4)	0	2.64(8)	0.57(1)	1.00
$[PtI_2(SbMePh_2)_2]$	−6.94(3)	+11.2(3)	0	2.77(8)	0.57(1)	1.07
$[PtI_2(SbMe_2Ph)_2]$	−6.94(3)	+11.1(3)	0	2.79(8)	0.58(1)	1.07
$[PtI_2(SbMePh_2)_3]$	−6.56(3)	+9.5(4)	0	2.88(10)	0.66(1)	1.12
b	−6.34(11) −7.33(22)	+10.7(9) +10.9(10)	0 0	2.67(3)		1.15
$[PtI_2(SbMe_2Ph)_3]$	−6.47(3)	+8.6(5)	0	2.87(10)	0.74(1)	1.16
b	−6.22(11) −7.37(21)	+9.1(1) +11.6(11)	0 0	2.65(3)		1.17
c, *g*	−6.23(6) −7.34(15)	+9.0(5) +11.4(9)	0 0	2.80(36) 1.92(48)		1.18

[a] An entry of 0 signifies that η was constrained to zero. [b] Constrained sum-of-Lorentzians fit. [c] Sum-of-Lorentzians fit. [d] Intensity ratio 2.8 : 1. [e] Ref. 12. [f] W. R. Cullen, D. J. Patmore, J. R. Sams, and J. C. Scott, *Inorg. Chem.*, 1974, **13**, 649. [g] Intensity ratio 2.3 : 1.

contain tetrahedral $[SbPh_4]^+$ cations.[19] In this cation, which in the present context may be regarded formally as being derived by co-ordination of $SbPh_3$ to Ph^+, the i.s. is more positive than for any of the complexes, as would be expected from the high covalent character of the Sb–C bond.

The decrease in q.c.c. presumably represents loss of *p*-electron density to the metal and the closer approach to regular tetrahedral hybridization. The shapes of the spectra clearly indicate that the coupling constants, although small, are all positive, *i.e.* that V_{zz} is negative. These data therefore also indicate that the metal atoms act as less effective acceptors than the Ph^+ group. The involvement of both orbitals in complementary fashion is demonstrated by the excellent linear relation between i.s. and q.c.c. shown by the triphenylstibine complexes, which extrapolates to the value for the free ligand (Figure 2). Similar relations are found for iodine compounds but not normally for tin derivatives, although both are isoelectronic with the stibine complexes.

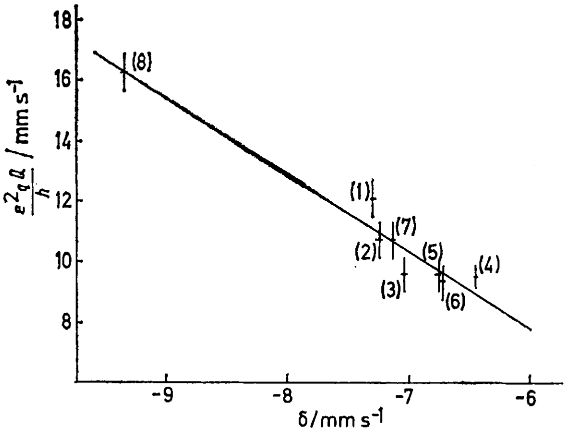

FIGURE 2 Plot of q.c.c. against i.s. for triphenylstibine complexes. The best least-squares line is drawn through points (1)—(7) only. Compounds: $[PdX_2(SbPh_3)_2]$ [X = Cl (1), I (2), or NO_2 (3)]; $[PtX_2(SbPh_3)_2]$ [X = Cl (4), I (5), or NO_2 (6)]; $[RhCl_3(SbPh_3)_3]$ (7); $SbPh_3$ (8)

The effect of metal-to-antimony π bonding, involving the $5d_{xz}$ and $5d_{yz}$ orbitals of antimony ($5p_x$ and $5p_y$ are primarily involved in σ bonding), would be to decrease the *s*-electron density at the antimony nucleus, increasing further the i.s., and to increase V_{zz}, offsetting the decrease in q.c.c. While the effect of synergistic enhancement of σ donation cannot be assessed, the change in i.s. is a measure of $(\sigma + \pi)$ effects and that in q.c.c. a measure of $(\pi - \sigma)$. However, it is unlikely that π bonding will be of great importance in the compounds studied here, and our interpretation is based solely on changes in the σ system. It should also be re-emphasized that the Mössbauer parameters give information about the changes in electron distribution on the antimony atom only, and cannot be directly related to the nature of the metal–antimony bond as a whole. Nevertheless, it is possible to interpret the present data in terms of the configurations of the complexes and the ability of the various MX_2 groups to accept electron density from the antimony.

(*i*) It is clear that Pd^{II} is a less effective acceptor than Pt^{II}. For the triphenylstibine complexes the co-ordination i.s. and q.c.c. shifts are considerably less for all the palladium complexes and for $[RhCl_3(SbPh_3)_3]$ than for any of the platinum complexes, and the same is true for the co-ordination i.s. shifts of the tris(*o*-tolyl)stibine complexes of palladium. Since tertiary stibines are 'soft' bases, this result is in accord with the generally accepted softer-acid character of platinum.

(*ii*) On the basis of i.r. data and other reasonable inferences we have previously suggested that the complexes have *cis* configurations unless the steric requirements of the stibine force *trans* geometry.[13] Thus, the $[PtCl_2L_2]$ complexes of L = $SbEt_3$, $SbPh_3$, $Sb(C_6H_4Me\text{-}p)_3$, and $Sb(C_6H_4Me\text{-}m)_3$ are *cis*, while those of $Sb(C_6H_{11})_3$ and $Sb(C_6H_4Me\text{-}o)_3$ are *trans*. This would be consistent with Tolman's calculation of cone angles for the corresponding phosphines.[20] It seems likely that the corresponding bromo-, iodo-, and nitro-complexes are analogous, and this has been confirmed for *cis*-$[PtI_2(SbPh_3)_2]$ and *cis*-$[Pt(NO_2)_2(SbPh_3)_2]$.[13,21] The palladium complexes are similarly thought to have *cis* configurations except possibly for $[Pd(NO_2)_2(SbPh_3)_2]$ and $[PdCl_2\{Sb(C_6H_4Me\text{-}o)_3\}_2]$.[13,22] Some but not all of the conclusions are confirmed by the Mössbauer data.

In view of the high error associated with the small q.c.c. values of the complexes, it is rarely possible to distinguish differences between or trends within the data for the individual series $[PtX_2L_2]$. Thus, the values for L = $SbPh_3$ and $Sb(C_6H_4Me\text{-}p)_3$ are indistinguishable for all X, whereas for L = $Sb(C_6H_4Me\text{-}o)_3$ and possibly for $SbEt_3$ the values for X = Cl and I are indistinguishable but that for X = NO_2 may be significantly lower. If the triphenylstibine complexes and $[PtCl_2\{Sb(C_6H_4Me\text{-}p)_3\}_2]$ have *cis* geometry the q.c.c. values must be relatively insensitive to small changes in the nature of the *trans* ligand, and *cis* configurations may be assigned to the other tris(*p*-tolyl)stibine complexes. The complex $[Pt(NO_2)_2\{Sb(C_6H_4Me\text{-}o)_3\}_2]$ and possibly $[Pt(NO_2)_2(SbEt_3)_2]$ presumably have different configurations from the corresponding halogeno-complexes but on the basis of the q.c.c. data alone no confident assignment can be made. If the configurations of the chloro-complexes are those indicated by i.r. spectroscopy, $[PtX_2\{Sb(C_6H_4Me\text{-}o)_3\}_2]$ (X = Cl or I) and $[Pt(NO_2)_2(SbEt_3)_2]$ would now be assigned *trans* geometry and the other members of these series would be *cis*.

The i.s. values are much better defined and more confident assignments may be made from them. For *cis*-$[PtX_2(SbPh_3)_2]$ the i.s. decreases smoothly for X = Cl > NO_2 > I (Figure 3). The same trend is found for

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[20] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

[21] J. L. Burmeister and R. C. Tummer, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1973.

[22] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 1953, 70.

$[PtX_2\{Sb(C_6H_4Me\text{-}p)_3\}_2]$ and for $[PtX_2(SbEt_3)_2]$, suggesting that all nine complexes have *cis* configurations. {This would imply that the q.c.c. of $[Pt(NO_2)_2(SbEt_3)_2]$ was not significantly different from those of the corresponding chloro- and iodo-complexes.} When $L = Sb(C_6H_4Me\text{-}o)_3$ and $Sb(C_6H_{11})_3$ a different trend in i.s. is found, $Cl < I \lesssim NO_2$, suggesting different configurations. If the chloro-complexes have the *trans* configuration indicated by the i.r. data, the iodo-complex must also be *trans*. Since the trends in i.s. and q.c.c. are different, the nitro-complex presumably has the alternative *cis* geometry. If these assignments are correct the isomer-shift trend for change of halide from chloride to iodide is different for the two configurations.

For $[PdX_2(SbPh_3)_2]$ the trends in both parameters are the same as for $[PtX_2L_2]$ [$L = Sb(C_6H_4Me\text{-}o)_3$ or $Sb(C_6H_{11})_3$], suggesting that the configurations are analogous, *i.e.* *trans* for X = Cl or I and probably *cis* for X = NO_2. This reverses the previous assignments for X = Cl.[13,21] On the basis of the slight increase in i.s., Cl < I, and the indistinguishability of q.c.c., $[PdX_2\{Sb(C_6H_4Me\text{-}o)_3\}_2]$ (X = Cl or I) must be assigned *trans* geometry in accord with the i.r. data for X = Cl.[13] The parameters for the nitro-complex are very similar and probably indicate similar geometry; we tentatively assign a *trans* configuration to this complex.

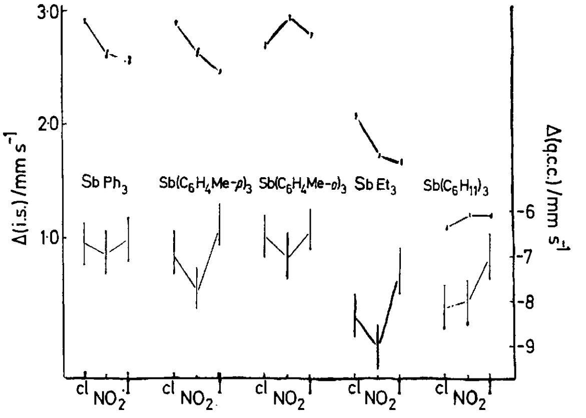

FIGURE 3 Co-ordination i.s. (upper) and q.c.c. (lower) shifts for the complexes $[PtX_2L_2]$. The values for free $SbMe_3$ were taken as approximations to those for $SbEt_3$ and $Sb(C_6H_{11})_3$

If these assignments are correct, *trans* complexes have more negative i.s. and larger q.c.c. than the corresponding *cis* isomers (but see below).

(*iii*) It may reasonably be presumed that $[PtI_2L_2]$ ($L = SbMePh_2$ or $SbMe_2Ph$) are *cis* like the other $[PtI_2L_2]$ complexes of non-sterically demanding stibines, although the co-ordination q.c.c. shift is rather small (using the value for $Ph_2Sb[CH_2]_4SbPh_2$ as an approximation to that for $SbMePh_2$). The corresponding tris(ligand) complexes give very different spectra, showing a slight decrease in i.s. and a substantial decrease in q.c.c. In neither case can signals attributable to the free ligand be discerned, and the spectra can be satisfactorily fitted for a single antimony site. The linewidths are comparable to those of the other complexes, although at the upper end of the range, and the χ^2 values are only slightly higher.

If, on this basis, it is assumed that the three ligands are equivalent, and that the platinum atom is five-coordinate, the stereochemistry must be trigonal bipyramidal with the stibines in the equatorial plane. The change from *cis* planar to trigonal apparently results in increased donation by the stibines to the platinum. This could be the case if the axial Pt–I bonds were relatively weak and the equatorial bonds, with their higher Pt *s* character, were stronger.

On the other hand, a recent determination of the crystal structure of $[PdCl_2(PMePh_2)_3]$ shows a slightly distorted square-pyramidal geometry, with the phosphines in the plane, and these ligands and the Pd–P bonds are clearly non-equivalent.[23] Accordingly, attempts were made to fit the spectra of the tris(stibine) complexes as the superposition of two spectra. Using the thickness-integral program no convincing solutions could be obtained with a range of starting parameters. The program either failed to converge or reduced the thickness and width of one of the components to very small values. Sum-of-Lorentzian fits were more successful, and parameters for two sites could be obtained with reduced linewidths, although the χ^2 values were the same as for the single-site fits. For both tris(stibine) complexes the integrated intensities of the two components were *ca.* 3 : 1. Slightly better fits (in the sense that the fitting errors were smaller) were obtained by constraining the linewidths to be the same for the two components and the intensity ratio to be 2 : 1. For the methyldiphenylstibine complex the two apparent components have different i.s. values but indistinguishable q.c.c., while for the dimethylphenylstibine complex the two sets of parameters are perhaps just significantly different. If this analysis is accepted the more intense spectrum should correspond to the pair of *trans* stibines and the weaker to the unique *cis* ligand. The parameters of the minor component are indeed similar to those of the *cis*-bis(ligand) complex, but the major component shows a less negative i.s. and a smaller q.c.c. This trend is the reverse of that suggested from the analysis of the data for the planar complexes in (*ii*) above but, in view of the lack of improvement in χ^2 and the larger errors of the two-site fit, this conclusion should be treated with caution.

(*iv*) The complex $[RhCl_3(SbPh_3)_3]$ has previously been assigned the *mer* configuration on the basis of dipole-moment data.[24] The far-i.r. spectrum confirms this structure, there being a band at 332 cm⁻¹ clearly due to the stretching of a pair of mutually-*trans* Rh–Cl bonds. Another band, expected at lower frequency, is presumably obscured by ligand absorptions. The two-site computer fit to the Mössbauer spectrum was similar to those for the tris(ligand)platinum complexes, *i.e.* no improvement in χ^2 over the single-site fit and larger

[23] W. J. Louw, D. J. A. de Waal, and G. J. Kruger, *J.C.S. Dalton*, 1976, 2364.

[24] W. E. Hill and C. A. McAuliffe, *Inorg. Chem.*, 1974, **13**, 1524.

errors. Again the larger component had the less negative i.s. and smaller q.c.c.

Conclusions.—The ^{121}Sb Mössbauer parameters of co-ordinated tertiary stibines are a good deal less sensitive to small changes in the nature of the acceptor group than for ^{129}I.[4,5] This is presumably due to the buffering effect of the three organic substituents which remain constant, *i.e.* the electron distribution in only one bond of four is being directly influenced. A better analogy is found with complexes containing tin-donor ligands, *e.g.* $[SnCl_3]^-$, where the parameters are sensitive to gross changes in the acceptor,[2,3,17] *e.g.* a change in metal atom or the replacement of a carbonyl ligand by a tertiary phosphine. Some sensitivity to smaller changes is also seen, *e.g.* in the series $[Rh(C_7H_8)L(SnCl_3)]$ (L = PPh_3, $AsPh_3$, $SbPh_3$, or C_7H_8), or between $[PtCl_2(SnCl_3)_2]^{2-}$ and $[Pt(SnCl_3)_5]^{3-}$. In all these cases the quadrupole splitting is a more sensitive parameter than the i.s., whereas for ^{121}Sb the reverse is true, reflecting the differences in nuclear parameters for the two isotopes:[17] $\delta R/R = ca.\ 3.5 \times 10^{-4}$ (^{119}Sn), $ca.\ 1.5 \times 10^{-3}$ (^{121}Sb); $eQ_{ex}(^{119}Sn) = -0.08$ b, $eQ_g(^{121}Sb) = -0.26$ b. Small changes in the q.c.c. for the stibine complexes are obscured by the lack of resolution attendant on the large natural linewidth and the complexity of the spectra.

TABLE 3

Probable configurations of the complexes $[PtX_2L_2]$ *

X	L $SbPh_3$	$Sb(C_6H_4Me\text{-}p)_3$	$Sb(C_6H_4Me\text{-}o)_3$	$SbEt_3$	$Sb(C_6H_{11})_3$
Cl	*cis* (*trans*)	*cis*	*trans* (*trans*)	*cis*	*trans*
I	*cis* (*trans*)	*cis*	*trans* (*trans*)	*cis*	*trans*
NO_2	*cis* (*cis?*)	*cis*	*cis?* (*trans?*)	*cis*	*cis?*

* Configurations in parentheses refer to the corresponding palladium complex.

In all the present cases, co-ordination results in large changes in the parameters in directions consistent with removal of charge density from the antimony atom by donation to the metal. If the stereochemical assignments given above are correct (summarized in Table 3), the extent of donation in complexes *cis*-$[PtX_2L_2]$ increases in the order X = I < NO_2 < Cl, while for the *trans* complexes the reverse sequence applies, X = Cl > I (> NO_2?; the configurations of the nitro-complexes cannot be confidently assigned). The differences between parameters for corresponding *trans*-chloro- and -iodo-complexes [*i.e.* i.s.(X = Cl) − i.s.(X = I)] is smaller than, and of opposite sign to, that for the *cis* complexes. The differences in q.c.c. values mostly show a similar change of sign, but are small or insignificant relative to the probable errors. For the *trans* complexes the sequence (*i.e.* the apparent *cis* influence of the halides) is the reverse of the normal *trans*-influence series, but it should be reiterated that only the charge density on the antimony atom is being monitored and not the properties of the metal–antimony bond as a whole. For the *cis* complexes the co-ordination shifts represent a combination of *cis* and *trans* influences in which it seems that the *trans* influence must predominate since the co-ordination shifts are larger. However, the data for X = NO_2 are out of place for the conventional *trans*-influence series, which may represent the working of the *cis* influence. The effect of the other ligands on donation by the antimony thus follows the same trends as previously found for iodide ligands.[4,5] However, in view of the analysis of data for the complexes of higher co-ordination number and the uncertainty of the stereochemical assignments, these conclusions should be treated with some caution. In a later paper we shall present data for chelate complexes in which the stereochemistry is better defined.

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