The Platinum-195 Chemical Shift in some Platinum(0) and Platinum(II) Complexes and its Relationship to their Structure

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The ^{195}Pt chemical shifts (δ_{Pt}) are reported for complexes $[PtL_4]^0$ [L = PMe_2Ph and $P(OMe)_3$], $[PtX_3L]^-$, *cis*- and *trans*-$[PtX_2L_2]$, and $[PtXL_3]^+$ (where L may be PMe_3, $AsMe_3$, $SbMe_3$, SMe_2, $SeMe_2$, or $TeMe_2$, and X may be Cl, Br, or I), $[PtX_3L]^-$ (where L may be NMe_3, $SOMe_2$, or C_2H_4 and X may be Cl or Br), and *cis*-$[PtX_2(SOMe_2)_2]$ (where X may be Cl or Br). The chemical shifts for complexes involving more than one type of halide are used to analyse the effect of halide on δ_{Pt} in different situations. The platinum chemical shift is shown to be relatively insensitive to the substituents on the donor atoms and to be useful in the identification of the nature of platinum complexes. The results for $[PtX_3L]^-$ can be reconciled with the theoretical predictions if the covalency of the metal–ligand bond is taken into account.

THE direct measurement of ^{195}Pt resonances in some platinum complexes by Pidcock *et al.*[1] and von Zelewsky [2] showed that ^{195}Pt chemical shifts, like those of other heavy nuclei, cover a wide range and are sensitive to the ligands present in the co-ordination sphere and even to their arrangement. The relatively low sensitivity of platinum makes direct measurement difficult for all but the most soluble complexes, at least without the use of Fourier transform n.m.r. spectroscopy. However, McFarlane [3] has shown that the use of $^1H\{^{195}Pt\}$ heteronuclear double-resonance methods especially the INDOR technique greatly extends the applicability of ^{195}Pt measurements.

We have been interested in platinum complexes of trimethylphosphine and related ligands containing only methyl groups since the latter greatly simplify the interpretation of the spectra.[4-6] These complexes are particularly suitable for heteronuclear INDOR work as they contain a relatively large number of equivalent protons which are not split by proton–proton coupling. We have already referred to the use of $^1H\{^{195}Pt\}$ INDOR to determine the total spin states of the ^{31}P nuclei in $[Pt(PMe_3)_4]^{2+}$ and evaluation of J_{PtN} in trimethylamine complexes.[7,6] Here we report the ^{195}Pt chemical shifts of a number of types of platinum(II) complexes involving a range of methyl-containing ligands and their relationship to the shifts of complexes of other ligands.

RESULTS

The previous papers reporting ^{195}Pt chemical shifts [1-3,8-11] all use different compounds as the reference zero. Rather than choose one of these or yet another arbitrary complex as standard we prefer to use the standard frequency 21.4 MHz related to the proton resonance of (internal) tetramethylsilane at a frequency of 100 MHz exactly. The observed shifts, δ_{Pt}, lie either side of this and high frequencies are taken as positive

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[1] A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1968, 1970.

[2] A. von Zelewsky, *Helv. Chim. Acta*, 1968, **51**, 803.

[3] W. McFarlane, *Chem. Comm.*, 1968, 393.

[4] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc.* (*A*), 1970, 545.

[5] D. A. Duddell, J. G. Evans, P. L. Goggin, R. J. Goodfellow, A. J. Rest, and J. G. Smith, *J. Chem. Soc.* (*A*), 1969, 2134.

[6] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, J. R. Knight, F. J. S. Reed, and B. F. Taylor, *J.C.S. Dalton*, 1974, 523.

[7] P. L. Goggin, R. J. Goodfellow, J. R. Knight, M. G. Norton, and B. F. Taylor, *J.C.S. Dalton*, 1973, 2220.

[8] R. R. Dean and J. C. Green, *J. Chem. Soc.* (*A*), 1968, 3047.

[9] W. McFarlane and R. F. M. White, *Chem. Comm.*, 1969, 439.

[10] D. W. W. Anderson, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 2370.

[11] W. McFarlane, *J.C.S. Dalton*, 1974, 324.

shifts. Details of the relationship of this scale to those of previous workers are given in the Experimental section. The accuracy of the measurements is mainly dependent on the width of the INDOR band observed which, in turn, depends on whether the individual lines due to PtH coupling are resolved, or one broad envelope has to be measured. The nuclei ^{75}As, ^{121}Sb, ^{123}Sb, and ^{127}I cause relaxation of ^{195}Pt when directly bonded to it.[12] Thus PtH coupling was not resolvable for arsine and stibine complexes but the relaxation due to iodine was insufficient to cause loss of resolution. When only one value of J_{PtH} is involved, *e.g.* complexes containing one or two SMe_2 or PMe_3 ligands, the individual lines due to PtH coupling are resolved but when there is more than one value of J_{PtH} present in the same complex, *e.g.* $[PtCl(PMe_3)_3]^+$ or complexes of PEt_3, frequently only a broad band was obtained. When J_{PtH} is resolved, the errors are less than ± 2 Hz or ± 0.1 p.p.m. but for unresolved spectra are about ten times this. As far as sensitivity is concerned, satisfactory results could be obtained on 0.01M-solutions for the ' resolved ' type of spectra.

The physical conditions (temperature, concentration, and solvent) will affect the value of δ_{Pt} obtained, so we have attempted to get some measure of these effects using *trans*-$[PtCl_2(SMe_2)_2]$ and $[Pr^n_4N][PtCl_3PMe_3]$ which have well resolved INDOR spectra. For the concentration range 0.01—0.2M, there was a non-systematic variation of δ_{Pt} not exceeding ± 1 p.p.m. The relative effect of different solvents on δ_{Pt} was neither the same for the two complexes studied here nor corresponded to the results for *trans*-$[PtCl_2(AsBu^n_3)_2]$ and $[PtH(m\text{-}MeC_6H_4CO_2)(PEt_3)_2]$.[1,8] Clearly the shift cannot correlate with any one property of the solvent. Whilst the effect of solvent cannot be ignored or predicted, it appears that altering the solvent is unlikely to cause a change in shift of greater than 30 p.p.m.

The platinum shift of the two test complexes increased approximately linearly from 210 to 300 K with coefficients 0.25 and 0.5 p.p.m. K^{-1} for the neutral and anionic species respectively (0.1M-solutions in dichloromethane). Whenever possible we have made our measurements on 0.1M-solutions in dichloromethane at *ca.* 300 K but in those cases where other conditions had to be used the effect on the shift should not be greater than 50 p.p.m.

TABLE 1

^{195}Pt Chemical shifts [a] of some complexes *trans*-$[PtX_2L_2]$ (X = Cl, Br, or I)

L =	NMe_3	PMe_3	$AsMe_3$	$SbMe_3$	SMe_2	SMePh	$SeMe_2$	$TeMe_2$
$[PtCl_2L_2]$	2 647	583 [b]	753		1 109	1 148	1 029	
$[PtBr_2L_2]$	2 545	60 [d]	155		634	654	492	
$[PtI_2L_2]$		−1 006	−985	−1 256 [c]	−272	−286	−531	−1 131
$[PtBrClL_2]$	2 598		460		873	904	764	
$[PtClIL_2]$		−208	−122	−216 [c]	392	415	229	
$[PtBrIL_2]$			−430	−598 [c]	158	168	−40	
$\frac{1}{2}[\delta_{Pt}(Cl)-\delta_{Pt}(Br)]$	51	262	299	382	238	269	269	
$\frac{1}{2}[\delta_{Pt}(Br)-\delta_{Pt}(I)]$		533	570	658	453	512		

[a] In p.p.m. to high frequency of 21.4 MHz. [b] At *ca.* 270 K. [c] At *ca.* 240 K. [d] At *ca.* 430 K in nitrobenzene.

Theoretical interpretations of ^{195}Pt chemical shifts have been of rather limited success.[1,8] McFarlane and White [9,11] and Anderson *et al.*[10] have suggested that ^{195}Pt chemical shifts can be of practical assistance in the identification of the structures of unknown species. An example of this application is provided by the product formed from $K_2[PtCl_4]$ and aqueous dimethyl sulphoxide for which the formulation $[PtCl_2(SOMe_2)_2]$ was proposed.[9] Since replacing dimethyl sulphide by dimethyl sulphoxide seems to result in a relatively small change in δ_{Pt},[9] the shift of this product (1 532 p.p.m. on our scale) suggested that it was more likely to be related to $[PtCl_3SMe_2]^-$ (δ_{Pt} 1 776 p.p.m.) than *cis*- or *trans*-$[PtCl_2(SMe_2)_2]$ (δ_{Pt} 983 and 1 109 p.p.m. respectively). Accordingly, we have prepared $[Pr^n_4N][PtCl_3SOMe_2]$ and its ^{195}Pt shift (1 534 p.p.m.) confirms that the product of McFarlane and White was $K[PtCl_3SOMe_2]$ not $[PtCl_2(SOMe_2)_2]$.

Such use of the platinum chemical shift would be more general and more reliable if empirical relationships between δ_{Pt} and the nature and configuration of the ligands present could be established. These relationships might also assist theoretical interpretation of the results. A notable example of such an empirical relationship occurs for the chemical shift of ^{119}Sn in tin(IV) tetrahalides.[13] For these, successive replacements of one halide by another result in almost identical changes in the chemical shift which permitted the identification of various mixed halide species such as $SnBrCl_2I$. The only study of this type for ^{195}Pt seems to be the measurement of von Zelewsky [2] of δ_{Pt} of the mixed halogeno-anions formed on equilibration of $[PtCl_6]^{2-}$ with $[PtBr_6]^{2-}$. The changes in δ_{Pt} resulting from successive replacements of chloride by bromide are not quite equal but increase slightly as the number of bromide ions present increases.

In view of the differing *trans*-influences of ligands, we might expect the changes in δ_{Pt} on replacing one halide by another to be affected by the ligand in the *trans*-position but relatively indifferent to the ligands in *cis*-positions. Thus Anderson *et al.*[10] claim that the change in δ_{Pt} on replacing X in a *trans*-[X–Pt–X] grouping by H is independent of the nature of the *cis*-ligands. The mean changes in δ_{Pt} for replacement of one halide by another in *trans*-$[PtX_2L_2]$ are listed according to the

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[12] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, and J. G. Eary, *J.C.S. Dalton*, 1972, 647.

[13] J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 326.

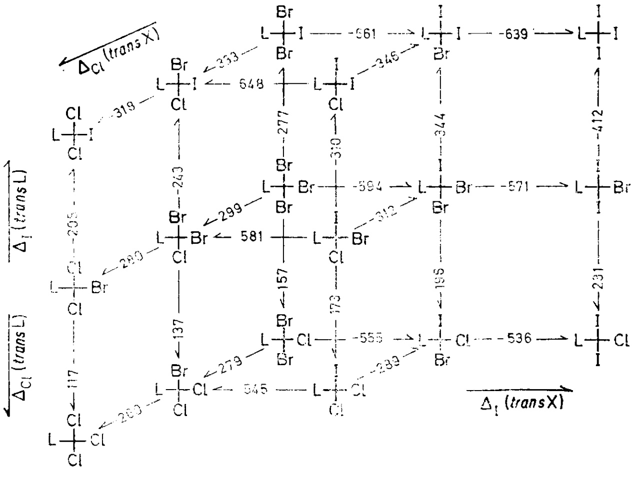
neutral ligand (L) in Table 1. It is clear that the change in ^{195}Pt chemical shift observed depends significantly on the *cis*-ligands for platinum(II). (Anderson *et al.*[10] based their claim on a very limited range of compounds all containing the *trans*-$[Pt(PEt_3)_2]$ unit and even then it does not hold very well for some cases.) To obtain more information on the effect of *cis*- and *trans*-ligands, we have measured the INDOR spectra of mixed halogeno-anions, $[PtX_3L]^-$, formed when mixtures of the single halide species are allowed to equilibrate (Table 2). In some cases, not all the possible species of the type $[PtX_3L]^-$ were observed since, at equilibrium, the concentrations of complexes with iodide *trans* to a neutral ligand of high *trans*-influence can be vanishingly small, particularly if the other two halides are chloride or bromide.

TABLE 2

^{195}Pt Chemical shifts [a] of anions $[PtXYZL]^-$ (X, Y, and Z = Cl, Br, or I)

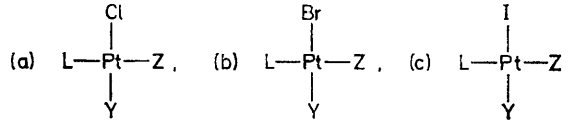
X	Y	Z [c]	L = NMe_3 [d]	PMe_3 [e]	$AsMe_3$ [e]	$SbMe_3$ [d]	SMe_2 [f]	$SeMe_2$ [f]	$TeMe_2$ [f]	$SOMe_2$ [d]	C_2H_4 [d,g]
Cl	Cl	Cl	2 818	1 033	1 360	1 390	1 776	1 764	1 474	1 535	1 748
Cl	Cl	Br	2 265	944 [b]	1 243	1 270	1 632	1 603	1 326	1 416	1 674
Cl	Cl	I			1 038		1 329	1 276	1 045		
Cl	Br	Cl	2 684	782	1 100	1 086	1 546	1 517	1 193	1 304	1 471
Cl	Br	Br	2 467	682 [b]	963	940	1 381	1 336	1 023	1 164	1 378
Cl	Br	I			720		1 043	973	710		
Cl	I	Cl		284 [b]	555	470	1 049	991	613		
Cl	I	Br		153 [b]	382	294	846	770	407		
Cl	I	I			72	−35	440	339	24		
Br	Br	Cl	2 527	520 [b]	821	763	1 305	1 259	896	1 052	1 173
Br	Br	Br	2 282	414	664	605	1 118	1 057	707	892	1 060
Br	Br	I			387	313	743	654	355		
Br	I	Cl		10 [b]	266	140	804	728	312		
Br	I	Br		−141 [b]	70	−60	578	483	80		
Br	I	I		−388 [b]	−274	−418	134	12	−337		
I	I	Cl		−484	−270	−448	336	228	−246		
I	I	Br		−667	−501	−691	73	−56	−515		
I	I	I		−973	−913	−1 109	−440	−596	−995		

[a,b] As in Table 1. [c] Z *trans* to L. [d] $[Pr^n_4N]^+$ salts. [e] $[Ph_4P]^+$ salts. [f] $[Bu^n_4N]^+$ salts. [g] At 280 K in $CDCl_3$.



SCHEME Change in δ_{Pt} on exchanging one halide in $[PtX_3L]^-$ (L = $AsMe_3$)

The Scheme illustrates the changes in δ_{Pt} of $[PtX_3AsMe_3]^-$ that occur for all single halide replacements. It is seen that substitution of Cl *trans* to $AsMe_3$ by Br causes a decrease in δ_{Pt} but that that the magnitude depends on the halides *cis* to it, becoming greater as these become heavier. Indeed these modifying effects due to *cis*-halides are remarkably independent of the neutral ligand. We designate a change in δ_{Pt} resulting from substituting Cl for Br as Δ_{Cl}, and I for Br as Δ_I. Comparing Δ_{Cl} or Δ_I values for the Z position in (a), (b), and (c), the mean values and r.m.s. errors obtained from the data in Table 2 are:



$$\Delta_{Cl}\ (b) - \Delta_{Cl}\ (a) = -21.3 \pm 3.3 \text{ p.p.m}$$

$$\Delta_{I}\ (b) - \Delta_{I}\ (a) = -35.7 \pm 3.0 \text{ p.p.m}$$

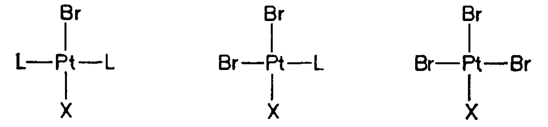
$$\Delta_{Cl}\ (c) - \Delta_{Cl}\ (b) = 37.3 \pm 3.7 \text{ p.p.m}$$

$$\Delta_{I}\ (c) - \Delta_{I}\ (b) = 66.7 \pm 3.0 \text{ p.p.m}$$

If these modifiers for the effect of *cis*-halides are also applied to consideration of platinum shifts of *cis*-$[PtXYL_2]$, X ≠ Y (Table 3), a much better estimate is obtained than from the arithmetic mean of *cis*-$[PtX_2L_2]$ and *cis*-$[PtY_2L_2]$ values (the r.m.s. error over all examples being 7 rather than 39 p.p.m). This suggests that the effect of a *cis*-halide is similar in different types of platinum(II) complex and that adjustment for it is useful (and desirable) when attempting to predict shifts for unknown complexes.

As evidenced in Table 1, Δ_{Cl} and Δ_I are also greatly affected by the nature of the *cis*-neutral ligands. For example, the values of Δ_{Cl} between *trans*-$[PtBr_2L_2]$, *trans*-$[PtBrClL_2]$, and *trans*-$[PtCl_2L_2]$ are less by 252 and 244 p.p.m respectively when L is NMe_3 instead of $AsMe_3$, whereas in *trans*-$[PtX_2BrL]^-$ (X = Cl or Br) the corresponding Δ_{Cl} differences are 114 and 122 p.p.m.; this suggests that the effect is approximately proportional to the number of *cis*-neutral ligands.

To make these observations of general use in estimating changes in δ_{Pt} on halide substitutions, we need a standard value for a given halide replacement and a set of modifying constants to allow for the effects of the *cis*- and *trans*-neighbours. We have chosen bromide as our standard ligand and the standard values of Δ°_{Cl} and Δ°_{I} refer to the changes from $[PtBr_4]^{2-}$ to $[PtBr_3Cl]^{2-}$ and $[PtBr_3I]^{2-}$ respectively. These changes cannot be observed by INDOR but they can be estimated from the sequence



$\Delta_{Cl} = \Delta^{\circ}_{Cl} + 2\delta_L$ $\Delta_{Cl} = \Delta^{\circ}_{Cl} + \delta_L$ $\Delta_{Cl} = \Delta^{\circ}_{Cl}$

TABLE 3

^{195}Pt Chemical shifts [a] of some complexes *cis*-$[PtX_2L_2]$ (X = Cl, Br, or I)

	L = PMe_3	$AsMe_3$	$SbMe_3$	SMe_2	SMePh	$SeMe_2$	$TeMe_2$	$P(OMe)_3$	$SOMe_2$
$[PtCl_2L_2]$	125 [b]	242	−79 [c]	982	1 045	798	164	162	1 056 [b]
$[PtBr_2L_2]$	−103 [b]	−92	−486 [c]	654	675			−66	755
$[PtI_2L_2]$	−595 [b]		−1 283 [c]		−153			−569	
$[PtBrClL_2]$	16 [b]	85	−264 [c]	826	869			57	914
$[PtClIL_2]$			−605 [c]	508	512			−136	
$[PtBrIL_2]$			−852 [c]	309	309			−287	

[a,c] As in Table 1. [b] In CD_3NO_2.

where δ_L represents the deviation of Δ_{Cl} from the standard value as a result of L being present instead of Br. For the ligands NMe_3, $AsMe_3$, SMe_2, and $SeMe_2$, where all the necessary data are available, we get estimates of Δ°_{Cl} of 317, 293, 287, and 286 p.p.m. respectively, giving a mean value of 294 p.p.m. By the same approach, the mean value of Δ°_{I} is −609 p.p.m. Relative to these values, the modifying effects of other neighbours in place of bromide are listed in Table 4. For *cis*-neighbours, heavier donor atoms increase the differences in δ_{Pt} on changing halides, a behaviour akin to the nephelauxetic effect. The effects on Δ_{Cl} and Δ_I caused by a *trans*-halide in different systems are not as constant as those of *cis*-halide, but the values in Table 4 give better predictions than no correction at all. Estimates of the effect of different neutral ligands in place of *trans*-bromide tend to follow their relative *trans*-influences, except that for heavier donor atoms this seems to be partly counter-balanced by a contribution related to their effects when in a *cis*-position. The effects of *trans*-ligands on Δ_{Cl} and Δ_I seem to be somewhat lower in neutral complexes than in anions and we have listed the values separately. The use of Table 4 is illustrated in the following paragraph.

All attempts to prepare *cis*-$[PtBr_2(SMe_2)_2]$ resulted in contamination by another compound surmised to be *cis*-$[PtBr_2SOMe_2SMe_2]$ (δ_{Pt} 673 p.p.m) produced by partial oxidation.[14] The ^{195}Pt chemical shift of *cis*-$[PtCl_2SOMe_2SMe_2]$ has already been reported [9] (980 p.p.m on our scale) from which we can estimate a value for the bromide using the adjustments for the *cis*- and *trans*-ligands according to Table 4. For the first substitution to *cis*-$[PtBrClSOMe_2SMe_2]$ (Br *trans* to $SOMe_2$) the change in δ_{Pt} is −133 [*i.e.* −294 (substitute Br for Cl) + 21 (for *cis* Cl) + 30 (for *cis* SMe_2) + 110 (for *trans* $SOMe_2$)], and for the second substitution to the required product is −178 [*i.e.* −294 + 23 + 93]; this gives a calculated value of 669 p.p.m for *cis*-$[PtBr_2SOMe_2SMe_2]$ which in view of the wide range of platinum shifts is good confirmation of the identity of the compound. We have used similar calculations as checks on the nature of some species which were only formed in solution, *e.g.* *trans*-$[PtClI(SbMe_3)_2]$, *trans*-$[PtBrI(SbMe_3)_2]$, $[PtI(SMe_2)_3][NO_3]$, and $[PtI(SeMe_2)_3][NO_3]$.

TABLE 4

Effects, relative to bromide,[a] of other ligands on the change in δ_{Pt} of platinum(II) complexes when bromide is replaced by chloride (Δ_{Cl}) or iodide (Δ_I).

	When in *cis*-position		When in *trans*-position			
			in $[PtX_3L]^-$		in $[PtX_2L_2]$	
Ligand	on Δ_{Cl}	on Δ_I	on Δ_{Cl}	on Δ_I	on Δ_{Cl}	on Δ_I
Cl	−21	+36	−17	+10	−8	−2
I	+36	−66	+10	+28	−2	+39
NMe_3	−117		−55			
PMe_3	−13	+57	−177	+431	−157	+341
$AsMe_3$	+5	+13	−135	+331	−121	
$SbMe_3$	+45	−50	−130	+317	−127	+289
SMe_2	−29	+69	−106	+233	−93	+192
$SeMe_2$	−13	+38	−88	+206		
$TeMe_2$	+24	−16	−101	+258		
$SOMe_2$	−23		−133		−110	
C_2H_4	+22		−180			

[a] When all other ligands are bromide the values are Δ_{Cl} = +294, Δ_I = −609 p.p.m.

Whilst successive replacements of bromide by another halide result in nearly the same change in δ_{Pt} with small modifications due to the incoming halides, the situation for replacement by neutral ligands is quite different. For example, the differences between $[PtBr_3PMe_3]^-$ and $[PtBr_4]^{2-}$ (1 431 p.p.m), between *cis*-$[PtBr_2(PMe_3)_2]$ and $[PtBr_3PMe_3]^-$ (517 p.p.m.), and between $[PtBr(PMe_3)_3]^+$ and *trans*-$[PtBr_2(PMe_3)_2]$ (300 p.p.m.) all relate to substitution of bromide *trans* to bromide by PMe_3. Similar large but non-linear decreases in the change in δ_{Pt} on successive substitutions are found for most of the other neutral ligands used here although the steps are more even for the heavier donors (especially $SbMe_3$). Thus it is not surprising that the mean of the ^{195}Pt chemical shifts of *cis*-$[PtBr_2(SMe_2)_2]$ and *cis*-$[PtBr_2(SOMe_2)_2]$ (705 p.p.m.) does not provide such a good

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[14] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J.C.S. Dalton*, 1974, 576.

prediction of the shift of *cis*-$[PtBr_2SOMe_2SMe_2]$ as the halide replacement approach used above.

TABLE 5

^{195}Pt Chemical shifts [a] of some complexes $[PtXL_3]^+$

	L = PMe_3	$AsMe_3$	$SbMe_3$	SMe_2	$SeMe_2$
$[PtClL_3][NO_3]$	−146	−211	−646 [b]	523 [d]	241
$[PtBrL_3][NO_3]$	−240	−384	−887 [b]	371 [d]	58
$[PtIL_3][NO_3]$	−400	−698 [c]	−1 301 [b]	73 [e]	−307 [e]

[a] and [c] As in Table 1. [b] At *ca.* 190 K. [d] $[BF_4]^-$ Salt instead of $[NO_3]^-$ salt. [e] Formed *in situ* from $[PtI_2L_2]$ + $[AgNO_3L]$.

It is reasonable to expect that where significant changes in the platinum–ligand bond strength do not result, altering the substituent on the donor atom would not result in a very large change in δ_{Pt}. The results for the complexes $[PtCl_3L]^-$, and *cis*- and *trans*-$[PtCl_2L_2]$, where L is various phosphines are given in Table 6.

TABLE 6

The effect of different phosphine ligands on the ^{195}Pt chemical shift [a]

L	$[PtCl_3L]^-$	*cis*-$[PtCl_2L_2]$	*trans*-$[PtCl_2L_2]$
PMe_3	1 033	125	583
PEt_3	993	43	595
$PPr^n{}_3$	1 013	91	
$PBu^n{}_3$	1 009	85	604
PMe_2Ph	1 022	130	
PEt_2Ph		109	569 [b]
$PMePh_2$	1 018	94	
PPh_3	1 020		
$P(OMe)_3$		162	
$P(OEt)_3$		180 [b]	
PF_3	907	58	

[a] As in Table 1. [b] From ref. 11.

Increasing the length of the alkyl chain or replacing it by a phenyl group does not seem to have much effect on δ_{Pt} and even the change to alkoxy or fluoride (*i.e.* phosphite ligands or PF_3) produces surprisingly little effect when compared to equivalent complexes of ligands with a different donor atom (*e.g.* $AsMe_3$). This is also true of various other types of complex (see Table 7 and published results [1,11]). Changes in the platinum–ligand bond probably explain the exceptions. Thus $[Pt(PMe_2Ph)_4]$ seems significantly less stable than $[Pt\{P(OMe)_3\}_4]$, *e.g.* the former decomposes in all but hydrocarbon solvents and shows broad ^{195}Pt satellites due to exchange whereas the latter gives a well resolved spectrum in dichloromethane. The smaller difference between $[Pt\{P(OMe)_3\}_4]^{2+}$ and $[Pt(PMe_3)_4]^{2+}$ may result from significant distortion due to steric strain in the latter [4] (*cf.* $[Ir(PMePh_2)_4][BF_4]$ [15]). Varying the number of hydrogen atoms on a silicon donor does seem to result in quite large differences in δ_{Pt} [10] although the reason is not obvious. It is more to be expected that oxidation of dimethyl sulphide to dimethyl sulphoxide would cause a significant change in the value of δ_{Pt}.

In contrast, the similarity between the platinum shifts of $[Pt_2X_6SMe_2]^{2-}$ and $[PtX_3SMe_2]^-$ (Table 8) suggests that the effect of the alkyl sulphide ligand on δ_{Pt} is essentially indifferent to being co-ordinated to a second platinum atom. The bridging chloride ions in $[Pt_2Cl_4L_2]$ and $[Pt_2Cl_2(PPr^n{}_3)_4]^{2+}$ do seem to result in a somewhat higher platinum chemical shift than in the equivalent terminal complexes ($[PtCl_3L]^-$ and *cis*-$[PtCl_2(PPr^n{}_3)_2]$).

TABLE 7

^{195}Pt chemical shifts [a] of some miscellaneous Pt^0 and Pt^{II} complexes

	δ_{Pt}	Notes
$[Pt(PMe_2Ph)_4]$	−195	In $C_6D_5CD_3$ [b]
$[Pt\{P(OMe)_3\}_4]$	−1 297	*b*
$[Pr^n{}_4N][PtCl_3(oct\text{-}1\text{-}ene)]$	1 815	In $CDCl_3$
cis-$[PtCl_2(SeEt_2)_2]$	745	
trans-$[PtCl_2(SeEt_2)_2]$	1 046	
trans-$[PtBr_2(PEt_3)_2]$	36	*e*
trans-$[PtBr_2(PPr^n{}_3)_2]$	60	
trans-$[PtI_2(PEt_3)_2]$	−1 020	*e*
trans-$[PtBr_2(AsMe_2CH_2SiMe_3)_2]$	176	*c*
cis-$[PtMe_2(PMe_3)_2]$	−22	*f*
cis-$[Pt(C_6F_5)_2(PEt_3)_2]$	−135	*d*
$[PtC_2F_4(PEt_3)_2]$	−251	*b*
$[Pt\{(CF_3)_2CO\}(PEt_3)_2]$	−408	*b*
$[Pt(PMe_3)_4][BF_4]_2$	−358	In H_2O
$[Pt\{P(OMe)_3\}_4]I_2$	−571	*f*
$[Pt_2Cl_4(PBu^n{}_3)_2]$	1 121	In $CDCl_3$
$[Pt_2Cl_2(PPr^n{}_3)_4][BF_4]_2$	278	
$[Pt_3S_2(PMe_3)_6][BF_4]_2$	208	*g*

[a] As in Table 1. [b] Samples from Dr. J. L. Spencer of this Laboratory, [c] Professor E. W. Abel, University of Exeter. [d] Professor F. G. A. Stone of this Laboratory. Other samples were prepared as [e] ref. 4, [f] ref. 17, [g] F. J. S. Reed, Ph.D. Thesis, University of Bristol, 1972.

TABLE 8

^{195}Pt chemical shifts [a] of some dimeric complexes

	X = Cl	Br	I
$[Pt_2X_4(PMe_3)_2]$	1 123	548	−764
$[Pt_2X_4(AsMe_3)_2]$	1 499	832	−679
$[Pt_2X_4(SbMe_3)_2]$		761	−853
$[Pt_2X_4(SMe_2)_2]$			−294 [b] −262
$[Pt_2X_5SMe_2]^-$	2 336 [c]	1 583 [c]	
$[Pt_2X_6SMe_2]^{2-}$	1 776 [c]	1 146 [d]	

[a] As in Table 1. [b] Two isomers see ref. 14. [c] $[Pr^n{}_4N]^+$ salt. [d] $[Bu^n{}_4N]^+$ salt.

This differential is greater for the heavier halides which would agree with the effect of bridging halide on δ_{Pt} being less than for a terminal halide. We have suggested that four-membered rings involving dimethyl sulphide necessitate strain of the angles at sulphur [14] and this could account for the much more positive shift of $[Pt_2X_5SMe_2]^-$ compared to $[Pt_2X_6SMe_2]^{2-}$ or $[PtX_3SMe_2]^-$.

On the basis that different organic substituents on the donor atom should not have large effects on δ_{Pt}, three of the platinum shifts reported by McFarlane [11] seemed anomalous. Thus, the value for *cis*-$[PtCl_2(SeEt_2)_2]$ (1 022 p.p.m. on our scale) seemed too far from that for *cis*-$[PtCl_2(SeMe_2)_2]$ whilst comparison of those for the *cis*- and *trans*-isomers of $[PtClI(SMePh)_2]$ (420 and 517 p.p.m. respectively) with those for the analogous dimethyl sulphide complexes suggested that they had been assigned to the wrong isomers. We have prepared $[PtCl_2(SeEt_2)_2]$ and examined the n.m.r. spectra of a

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[15] G. R. Clark, C. A. Reed, W. R. Roper, B. W. Skelton, and T. N. Waters, *Chem. Comm.*, 1971, 758.

concentrated solution. The methyl resonances consisted of two triplets in the ratios *ca.* 4 : 1 but the methylene region was much more complicated since the CH_2 groups are prochiral. However, lines due to the ^{195}Pt species were identified for the two isomers and these gave platinum shifts of 1 046 and 745 p.p.m. The former, for the more abundant complex, agrees with McFarlane's value for the *trans*-isomer whilst the latter compares well with the value for *cis*-$[PtCl_2(SeMe_2)_2]$.

The proton spectrum of a mixture of $[PtCl_2(SMePh)_2]$ and $[PtI_2(SMePh)_2]$ showed, in addition to the resonances of the individual starting materials, a strong peak (τ 7.21, $^3J_{PtH}$ 44.2 Hz) and two much weaker peaks (τ 7.35, $^3J_{PtH}$ 45.4; τ 7.02, $^3J_{PtH}$ 48.6 Hz) all with ^{195}Pt satellites. The latter two gave the same ^{195}Pt resonance (512 p.p.m.) and must, therefore, be due to the *cis*-isomer of $[PtClI(SMePh)_2]$ whilst the strong peak (δ_{Pt} 415 p.p.m.) must be due to the *trans*-isomer, *i.e.* McFarlane's values had been assigned to the wrong isomers. We have measured the platinum shift of the other complexes of the type $[PtX_2(SMePh)_2]$ (X = Cl, Br, or I) including the mixed bromo-iodo-system and *cis*-$[PtI_2(SMePh)_2]$ (as a weak feature in a solution consisting mainly of the *trans*-isomer) which were not reported by McFarlane. The proton resonances of *cis*-$[PtBrI(SMePh)_2]$ were very weak resulting in a rather inaccurate value for δ_{Pt} ($\pm$10 p.p.m.). The results are given in Tables 1 and 2 and agree reasonably well with those previously reported.[11]

DISCUSSION

The main contribution to the shielding of a heavy-metal nucleus such as ^{195}Pt should be the paramagnetic term defined by Ramsey.[16] This has been evaluated for

$$\sigma_P = -\tfrac{16}{3}\beta^2 \langle r^{-3}\rangle C_{a_{1g}}{}^2[2C_{a_{2g}}{}^2\Delta E_A{}^{-1} + C_{e_g}{}^2\Delta E_E{}^{-1}] \quad (1)$$

d^8 platinum complexes of D_{4h} symmetry by Dean and Green [8] who obtain the expression (1) † where

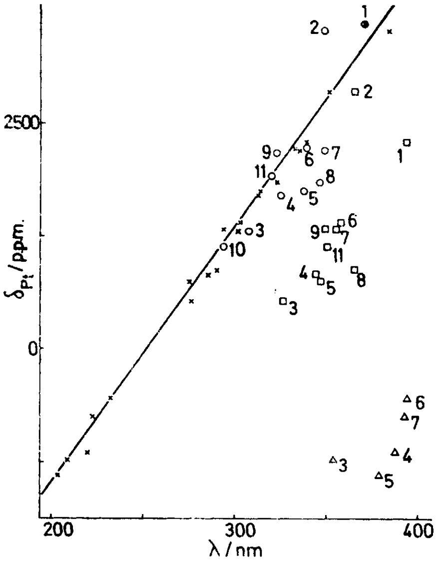
$$\Delta E_A = E(^1A_{2g}) - E(^1A_{1g})$$
$$\Delta E_E = E(^1E_g) - E(^1A_{1g})$$

and $C_{a_{1g}}$, $C_{a_{2g}}$, and C_{e_g} are the coefficients of the platinum *d* orbitals in the molecular orbitals. If we make the approximation that $C_{a_{1g}} \approx C_{e_g}$, then the observed shifts should follow equation (2) where λ is the weighted mean of the reciprocal transition energies, *i.e.* 1/3 ($2E_A{}^{-1} + E_E{}^{-1}$), *c* allows for the arbitrary zero used for our shifts,

$$\delta_{Pt} = m\lambda + c \quad (2)$$

and we have taken account of the sign convention. Although the anions $[PtX_3L]^-$ do not have D_{4h} symmetry, their electronic spectra can usually be assigned [17,18] on the same basis as $[PtX_4]^{2-}$ so it does not seem unreasonable to expect equation (1) to hold approximately for these also. Details of the electronic spectra of some of these anions, additional to those of references 17 and 18, are given in Table 9.

The plot of δ_{Pt} *vs.* λ is shown in the Figure. Taking all the points, it is clear that no line of sensible slope can be drawn through them. However, considering the points for each halide separately, these (especially those for $[PtCl_3L]^-$ and $[PtBr_3L]^-$) do lie approximately on three lines of different slope. The mean line for $[PtCl_3L]^-$ results in a value of 5.2 a.u. for $\langle r^{-3}\rangle$ if $C_{a_{1g}}$, $C_{a_{2g}}$, and C_{e_g} are set to unity. Whilst this is less than the value calculated by Carlson *et al.*[19] (14.0 a.u.) from a relativistic Hartree–Fock–Slater treatment of platinum(0), it suggests a relationship between δ_{Pt} and the electronic spectra exists along the lines of equation (1).



Plot of ^{195}Pt chemical shift *vs.* mean reciprocal transition energy, $\lambda = 1/3\ (2\Delta E_A{}^{-1} + \Delta E_E{}^{-1})$ for $[PtX_3L]^-$, X = Cl(○), Br(□), or I(△); L = X^- (1), NMe_3 (2), PMe_3 (3), $AsMe_3$ (4), $SbMe_3$ (5), SMe_2 (6), $SeMe_2$ (7), $TeMe_2$ (8), C_2H_4 (9), PF_3 (10), or $SOMe_2$ (11) and points replotted (×) *vs.* $\frac{1}{4}\lambda\Sigma k$

In keeping with the relative positions of the lines for chlorides, bromides, and iodides, the points for ligands with heavy donor atoms ($SbMe_3$ and $TeMe_2$) lie below these lines whilst points for light donor atoms or ' hard ' ligands (NMe_3, C_2H_4, and $SOMe_2$) lie above the lines, *i.e.* *m* in equation (2) varies with the type of ligand. Since the term $\langle r^{-3}\rangle$ should be dominated by the contribution at small radius it is unlikely to be greatly affected by the ligands, leaving as the most likely cause the coefficients $C_{a_{1g}}$, $C_{a_{2g}}$, and C_{e_g} (smaller for the heavier donor atoms as the metal–ligand bond is more covalent). We have attempted to take account of these differences by including a constant for each ligand as in equation (3).

$$\sigma = \tfrac{1}{4}m(k_1 + k_2 + k_3 + k_4)\lambda + c \quad (3)$$

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† In ref. 8, *h* was inadvertently written instead of *ħ*.

[16] N. F. Ramsey, *Phys. Rev.*, 1950, **78**, 699.

[17] P. L. Goggin, J. R. Knight, L. Sindellari, and L. M. Venanzi, *Inorg. Chim. Acta*, 1971, **5**, 62.

[18] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J.C.S. Dalton*, 1972, 1298.

[19] T. A. Carlson, C. C. Lu, T. C. Tucker, C. W. Nestor, jun., and F. B. Malik, ' Eigenvalues, Radial Expectation Values and Potentials for Free Atoms from Z = 2 to 126 as Calculated from Relativistic Hartree–Fock–Slater Atomic Wave Functions,' Oak Ridge National Laboratory, 1970.

It seems that the effect is much the same for neutral ligands of the same period but rather different for the halide of that period, especially for the case of $SbMe_3$ and $TeMe_2$ compared to iodide. Accordingly, we have used six coefficients, one for the neutral ligands of each period and one each for bromide and iodide, chloride being arbitrarily fixed as unity. Adjustment of these constants results in a good approximation to a straight line (4) where λ is in nm. The ρ value for the 21 complexes

$$\sigma = (23.67 \pm 0.36)(\tfrac{1}{4}\lambda\Sigma k) - (5\,906 \pm 106) \quad (4)$$

considered was 0.998 and the points for σ are plotted against $\frac{1}{4}\lambda\Sigma k$ in the Figure. The coefficients, k, were 1.25_5 for NMe_3, 0.82 for PMe_3 and SMe_2, 0.74 for $AsMe_3$ and $SeMe_2$, 0.62 for $SbMe_3$ and $TeMe_2$, 0.83_5 for bromide, and 0.50_5 for iodide compared to chloride equal to 1.00. The constant, −5 906 p.p.m., represents the shift of ^{195}Pt on our scale when there is no paramagnetic term.

TABLE 9

Visible and ultraviolet spectra of $[PtX_3L]^-$ (X = Cl, Br, or I) [a]

$[Bu^n_4N][PtCl_3SeMe_2]$			27.2 (180) [d]	31.9 (280) [e]	
$[Bu^n_4N][PtCl_3TeMe_2]$		23.5sh [c]	27.3 (440)	32.7 (1 400)	
$[Bu^n_4N][PtCl_3PF_3]$		28.1sh	31.7 (650)	39.7 (2 200)	
$[Pr^n_4N][PtCl_3SOMe_2]$		25.6sh	30.0 (310)	34.1sh	40.7 (7 000)
$[Pr^n_4N][PtCl_3C_2H_4]$		23.3 (19)	29.9 (270)	33.2 (1 000)	38.0 (3 100), 40.3 (3 200)
$[Pr^n_4N][PtBr_3AsMe_3]$	20.2sh [b]	24.2 (130)	27.5 (570)	32.6sh	36.0 (5 300), 37.8sh, 41.0 (7 100)
$[Pr^n_4N][PtBr_3SMe_2]$		22.6sh	26.3 (410)	32.1 (2 150)	37.0 (7 500)
$[Bu^n_4N][PtBr_3SeMe_2]$			26.5 (280)	31.9 (2 000)	35.7 (6 400)
$[Bu^n_4N][PtBr_3TeMe_2]$			25.9 (660)	30.9 (5 000)	34.1 (9 500), 37.7 (8 300)
$[Pr^n_4N][PtBr_3SOMe_2]$			27.3sh	31.4 (2 000)	35.8 (3 300)
$[Pr^n_4N][PtBr_3C_2H_4]$				32.5 (3 500)	36.5 (4 650)
$[Pr^n_4N][PtI_3PMe_3]$		24.4sh	27.0 (3 200)	31.0 (3 800)	33.2 (4 500), 35.7sh
$[Hx_4N][PtI_3AsMe_3]$			25.6 (3 500)	29.4 (3 700)	32.9sh
$[Pr^n_4N][PtI_3SbMe_3]$			25.2 (4 300)	28.8 (4 700)	33.3sh, 37.7 (11 000)
$[Bu^n_4N][PtI_3SMe_2]$			24.2 (3 000)	28.1 (2 200)	31.3 (6 300), 36.4sh
$[Bu^n_4N][PtI_3SeMe_2]$			24.2 (2 500)	28.8 (2 400)	31.7 (7 400), 35.7sh

[a] Positions of maxima (× 10^{-3} cm^{-1}), intensities (l mol^{-1} cm^{-1}) in parentheses. [b] Transitions related to $^1A_{1g} \longrightarrow {}^3A_{2g}$, [c] $^1A_{1g} \longrightarrow {}^3E_g$, [d] $^1A_{1g} \longrightarrow {}^1A_{2g}$ and [e] $^1A_{1g} \longrightarrow {}^1E_g$ of $[PtX_4]^{2-}$.

It seems unlikely that covalency of metal–ligand bond would reduce the platinum d-orbital contribution to less than 50%, *i.e.* the resultant of the covalency terms in equation (1) should lie between 0.25 and unity. Applying these criteria and including the values of k derived for trimethylamine and iodide, suggests that $\langle r^{-3}\rangle$ lies in the range 6.4—10.2 a.u. This is below the published value [19] which may be a consequence of the approximations involved in the application of equation (1) to these systems.

If the coefficients k do relate to the orbital coefficients $C_{a_{1g}}$, $C_{a_{2g}}$, and C_{e_g} of equation (1), then they give an indication of the covalency of the platinum–ligand bond. Using the values of k for the halides, separate values can be calculated for the neutral ligands which imply that the apparent covalency increases in the order $NMe_3 \ll Cl^- < C_2H_4 < SOMe_2 \approx Br^- \approx SMe_2 \approx PMe_3 < SeMe_2 < AsMe_3 < SbMe_3 < TeMe_2 < I^-$. The suggestion of particularly high covalency in the Pt–I bond is in keeping with the low i.r. intensity of Pt–I stretching vibrations and their high Raman intensity.[4]

It follows as a consequence of the competing effects of covalency and changes in electronic excitation energies, that simple generalisations on the relationship between structure and platinum shift cannot be universal. Thus McFarlane's statement [11] that *trans*-isomers give resonances to lower field of their related *cis*-isomers does not hold for $[PtI_2(PMe_3)_2]$. Here, although ΔE is undoubtedly less for the *trans*-isomer from their relative colours, this is outweighed by greater covalency in the *trans*-isomer. Nonetheless, there are surprisingly few exceptions to the rule that equilibria favour the complexes with the more negative value of δ_{Pt}, *i.e.* in general more negative shifts indicate stronger bonds.

In principle, platinum(0) complexes should possess no paramagnetic contribution to the platinum shift which would therefore be in the region of −5 900 p.p.m. The few values we have obtained (Table 7) suggest that there is some paramagnetic contribution, *i.e.* the electronic configuration is not simply $5d^{10}$.

The ability to predict the change in δ_{Pt} when halides are exchanged, together with the relative insensitivity of δ_{Pt} to the substituents on the donor atoms, should make the platinum shift valuable for the identification of the nature of complexes. When combined with data on the electronic transitions, it seems that some measure of the covalency of the metal–ligand bonds may be obtained.

EXPERIMENTAL

The INDOR measurements were performed as previously described.[7] Normally the peak maximum of a ^{195}Pt satellite was monitored whilst the region of ^{195}Pt resonances was scanned with the second radio frequency at low power, *i.e.* equivalent to a ' tickling ' experiment. However, for trimethylstibine complexes where the satellites are very broad because of relaxation of the ^{195}Pt nuclei by the quadrupolar antimony nuclei (*cf.* ref. 12), better sensitivity and narrower lines were obtained by observing the main proton resonance and using a much higher power level for the ^{195}Pt frequency, *i.e.* equivalent to a decoupling experiment. The latter method was also used for one or two trimethylarsine complexes where the proton resonance was particularly weak.

Where previous results are given in terms of the ^{195}Pt frequency when tetramethylsilane resonates at 100 MHz,[8-11] conversion into the scale used here is trivial. However this does not apply to the direct measurements of Pidcock *et al.*[1] and von Zelewsky.[2] We have measured the platinum shift by INDOR of two of the complexes used by Pidcock *et al.*, *cis*-$[PtCl_2(PBu^n{}_3)_2]$ and $[Pt_2Cl_4(PBu^n{}_3)_2]$. Taking the mean of the values for these two (78 and 1 121 p.p.m. in deuteriochloroform respectively), the shift on our scale of the compounds reported by Pidcock *et al.* is found to be $[32\,974 - (\nu_r - \nu_8)]/12.815$, *i.e.* the reference complex, $[PtCl_2(4\text{-n-pentylpyridine})_2]$ has $\delta_{Pt} = 2\,573$ p.p.m. The result reported for $H_2[PtCl_6]$ is then found to be 4 535 p.p.m. on the present scale and von Zelewsky's [2] results for other platinum halogen-anions may be converted accordingly.

For measurements on mixed halogeno-species formed *in situ* by mixing solutions of single halide species, it is necessary to identify the proton resonances of the various complexes. The peaks due to the single halide species were first identified by comparison with the results when they were examined alone. The remaining resonances were assigned to mixed halide complexes following our previous observation [5] that increasing the atomic number of a halide in a *cis*-position causes a relatively large downfield shift whilst increasing the atomic number of a halide in the *trans*-position usually results in a smaller upfield shift; *e.g.* for $[PtClBr(SMe_2)_2]$, the ^1H resonance of the *trans*-isomer occurs at τ 7.25, approximately midway between those of the respective *trans*-dibromo- and dichloro-complexes [20] whilst for the *cis*-isomer, the resonance of the sulphide ***trans*** to Cl occurs 2 Hz to high frequency of that of *cis*-$[PtBr_2(SMe_2)_2]$ and that of the sulphide ***trans*** to Br occurs 2 Hz to low frequency of *cis*-$[PtCl_2(SMe_2)_2]$. For the anions $[PtX_3L]^-$, binary mixtures were examined before attempting to assign peaks in the ternary mixture required for $[PtBrClIL]^-$. The values of δ_{Pt} for the set of halogeno-complexes provided a further check on the assignments.

Visible/u.v. spectra were recorded as in reference 18.

We have previously described the preparation of most of the complexes of trimethylamine,[18] trimethylphosphine, trimethylarsine, and triethylphosphine,[4] trimethyl phosphite,[21] dimethyl sulphide, and methyl phenyl sulphide [14,20] examined here. Details for the derivatives of dimethyl selenide, dimethyl telluride, and trifluorophosphine will be reported in future publications. Characterising data for the compounds described below are in Table 10.

TABLE 10

Characterising data of the complexes

	Colour	M.p. (θ_c/°C)	Analysis (%) * C	H	N
$[PtCl_2(SbMe_3)_2]$	White	174—177 †	12.0 (12.0)	3.0 (3.0)	
$[PtBr_2(SbMe_3)_2]$	Pale yellow	174—176 †	10.75 (10.45)	2.8 (2.6)	
$[PtI_2(SbMe_3)_2]$	Yellow	162—164 †	9.25 (9.2)	2.5 (2.3)	
$[Pt_2Br_4(SbMe_3)_2]$	Buff	124—126 †	7.05 (6.9)	1.8 (1.75) ‡	
$[Pt_2I_4(SbMe_3)_2]$	Deep orange	150—151 †	5.5 (5.85)	1.4 (1.45)	
$[Pr^n{}_4N][PtCl_3SbMe_3]$	Yellow-orange	119—122	28.0 (27.5)	5.4 (5.7)	2.05 (2.15) §
$[Pr^n{}_4N][PtBr_3SbMe_3]$	Orange	129—131 †	23.25 (22.85)	4.65 (4.7)	1.7 (1.8)
$[Pr^n{}_4N][PtI_3SbMe_3]$	Deep orange	129	19.45 (19.4)	4.3 (4.0)	1.3 (1.5)
$[PtCl(SbMe_3)_3][NO_3]$	White	144—155 †	13.65 (13.6)	3.35 (3.4)	1.95 (1.75)
$[PtBr(SbMe_3)_3][NO_3]$	White	153 †	13.3 (12.9)	3.15 (3.2)	1.45 (1.65)
$[PtI(SbMe_3)_3][NO_3]$	White	175—185 †	12.4 (12.2)	3.2 (3.1)	1.55 (1.6)
$[AgNO_3SbMe_3]$	White	103—106 †	10.8 (10.65)	2.85 (2.65)	
$[Pr^n{}_4N][PtCl_3SOMe_2]$	Yellow	146—148	29.65 (29.8)	6.0 (6.0)	2.4 (2.4)
$[Pr^n{}_4N][PtBr_3SOMe_2]$	Orange	152—153	24.15 (23.9)	4.85 (4.8)	1.9 (2.0)
$[PtBr_2(SOMe_2)_2]$	Lime-green	196—201 †	9.55 (9.4)	2.3 (2.4)	
$[Pr^n{}_4N][PtCl_3C_2H_4]$	Yellow	140	31.9 (32.6)	6.0 (6.3)	2.7 (2.55)
$[Pr^n{}_4N][PtBr_3C_2H_4]$	Orange	133	30.85 (30.7)	5.7 (5.7)	2.2 (2.0)
$[Pr^n{}_4N][PtCl_3C_8H_{16}]$	Yellow	87—88	38.55 (40.05)	7.35 (7.4)	2.1 (2.35)
$[Pt_2Cl_2(PPr^n{}_3)_4][BF_4]_2$	White	213—215	33.9 (34.0)	6.6 (6.3)	
$[Bu^n{}_4N][PtI_3SMe_2]$	Deep orange	104—105 †	24.5 (24.55)	4.9 (4.8)	1.6 (1.6)

* Calculated values in parentheses. † With decomposition. ‡ Br = 30.25 (30.65). § Cl = 16.0 (16.25).

cis-$[PtCl_2(SbMe_3)_2]$.—Trimethylstibine (4.9 g) was added, as slowly as possible under nitrogen, to a filtered stirred solution of potassium tetrachloroplatinate(II) (6.3 g) in water (20 ml). After ½ h the mixture was evaporated to dryness on a rotary evaporator. The residue was extracted with dichloromethane (3 × 100 ml) and the extract reduced in volume; ether was added to aid the crystallisation of the white product, which was washed with ether and dried *in vacuo*; yield 56%.

cis-$[PtBr_2(SbMe_3)_2]$.—Platinum(II) bromide (0.65 g) was stirred overnight under nitrogen with a solution of sodium bromide (0.4 g) in water (15 ml). The filtered solution was treated with trimethylstibine (0.7 g) as in the case of the chloride; yield 46%.

cis-$[PtI_2(SbMe_3)_2]$.—Potassium tetrachloroplatinate(II) (1.0 g) was dissolved in water and the solution filtered. Potassium iodide (2.0 g) was added and the solution stirred (¼ h). The solution was treated with trimethylstibine (0.8 g) as above; yield 58%.

$[Pt_2Br_4(SbMe_3)_2]$.—Sodium bromide (1.0 g) and potassium tetrachloroplatinate(II) (0.6 g) were dissolved in water (10 ml) and the solution was warmed (10 min). The solution was filtered and added to a solution of $[PtBr_2(SbMe_3)_2]$ (1.0 g) in acetone (30 ml) and the mixture stirred for 24 h; it was then warmed with animal charcoal, filtered, and evaporated to dryness. The residue was then treated as in the case of $[PtCl_2(SbMe_3)_2]$ to give an orange-brown solid; yield 15%. $[Pt_2I_4(SbMe_3)_2]$ was prepared from the corresponding bromide by exchange with a four-fold excess of sodium iodide in acetone (10 min). The reaction mixture was evaporated to dryness, extracted with dichloromethane,

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[20] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, F. J. S. Reed, J. G. Smith, and K. M. Thomas, *J.C.S. Dalton*, 1972, **1904**.

[21] R. J. Goodfellow and B. F. Taylor, *J.C.S. Dalton*, 1974, **1676**.

and the dark brown product precipitated by addition of pentane.

The salts $[Pr^n_4N][PtX_3SbMe_3]$ (X = Br or I) were prepared by stirring $[Pt_2X_4(SbMe_3)_2]$ with exactly 2 mole-equivalents of $[Pr^n_4N]X$ in dichloromethane for 10 min and the products were crystallised by addition of ether; yields *ca.* 90%.

$[Pr^n_4N][PtCl_3SbMe_3]$ was prepared by passing trimethylstibine in a stream of nitrogen (generated by warming $SbMe_3Br_2$ with zinc dust and a drop of water) through a solution of $[Pr^n_4N]_2[Pt_2Cl_6]$ [18] in dimethylformamide. When the initial orange colour of the solution had turned pale yellow, ether was added to precipitate the salt which was then recrystallised from dichloromethane by addition of ether; yield 65%.

$[AgNO_3SbMe_3]$.—This complex was prepared by the reaction of an aqueous slurry of powdered $AgNO_3$ with trimethylstibine in ether, as previously described for $[AgNO_3PMe_3]$.[22] Reaction of $[AgNO_3SbMe_3]$ with $[PtX_2(SbMe_3)_2]$ (X = Cl, Br, or I) in 1 : 1 mol ratio, by stirring (30 min) in dichloromethane, filtering, and adding ether gave crystalline $[PtX(SbMe_3)_3][NO_3]$; yields *ca.* 80%.

$[Pr^n_4N][PtX_3SOMe_2]$ (X = Cl *or* Br).—These anionic complexes were prepared in the same manner as $[Pr^n_4N][PtCl_3NMe_3]$ and recrystallised from acetone on slow addition of ether; yields 35% (X = Cl) and 60% (X = Br).

$[PtBr_2(SOMe_2)_2]$.—Platinum(II) bromide and an excess of dimethyl sulphoxide were maintained at 140 °C for 3/4 h in an oil-bath by which time nearly all the solid had dissolved. On cooling the filtered solution, the product was slowly deposited and was then recrystallised from hot dichloromethane; yield 25%. The analogous chloride was prepared by the method of Price *et al.*[23]

$[Pr^n_4N][PtCl_3C_2H_4]$. This complex was prepared by stirring $[Pr^n_4N]_2[Pt_2Cl_6]$ (2.0 g) suspended and partly dissolved in nitromethane (30 ml), under an ethylene atmosphere in a large flask (1 l) until all the solid had dissolved to give a pale yellow solution (3 days). The solution was filtered and the product crystallised by the addition of ether; yield 68%. The corresponding bromide was prepared similarly; yield 90%.

$[Pr^n_4N][PtCl_3(\text{oct-1-ene})]$. This complex was prepared by stirring an equivalent quantity of oct-1-ene with $[Pr^n_4N]_2[Pt_2Cl_6]$ in nitromethane for 24 h. The precipitate produced by the addition of ether to the filtered solution was recrystallised from acetone–ether.

Solutions of $[Pr^n_4N][PtCl_3PR_3]$ (R = Pr^n, Bu^n, *etc.*—see Table 6) were made up from equivalent amounts of $[Pr^n_4N]Cl$ and $[Pt_2Cl_4(PR_3)_2]$. The other phosphine complexes in this Table were prepared by the usual methods.

$[Pt_2Cl_2(PPr^n_3)_4][BF_4]_2$. This complex was prepared by stirring *cis*-$[PtCl_2(PPr^n_3)_2]$ with an exactly equivalent quantity of $Ag[BF_4]$ in acetone (30 min). The solution was filtered and the white product precipitated by slow addition of ether; yield 92%.

$[Bu^n_4N][PtI_3SMe_2]$ was prepared from $[Bu^n_4N]_2[Pt_2I_6]$ by the method described in ref. 18. The product is indefinitely stable, in contrast to the corresponding $[Pr^n_4N]^+$ salt which tends to lose dimethyl sulphide on crystallisation.[20]

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