Pyridine-base Complexes of the Tetrachlorophosphonium Ion

By **Keith B. Dillon,* Roger N. Reeve,** and **Thomas C. Waddington,** Chemistry Department, University of Durham, South Road, Durham DH1 3LE

Complex formation between the tetrachlorophosphonium ion, usually in the form of $[PCl_4][SbCl_6]$, and some pyridine bases has been investigated in solution by means of ^{31}P n.m.r. spectroscopy. Bidentate pyridines L′ form stable 1 : 1 ionic complexes $[PCl_4L'][SbCl_6]$. Sufficiently basic and sterically unhindered unidentate pyridines L form 2 : 1 complexes $[PCl_4L_2][SbCl_6]$, but these take part in a solution equilibrium with the molecular species $PCl_5 \cdot L$ and $SbCl_5 \cdot L$. Unusual behaviour was observed with 3-cyano- and 2-cyano-pyridine, the latter probably forming both ionic and molecular complexes co-ordinated *via* the cyano-group. 2-Substituted methylpyridines undergo halogenation, with simultaneous formation of PCl_3. Very weak or sterically hindered bases other than 2-cyanopyridine appear not to take part in complex formation. Several of the complexes have been isolated as solids, in which state they are comparatively stable, sometimes showing remarkable resistance to hydrolysis. The structures have been confirmed by analysis and ^{31}P n.m.r., i.r., and ^{35}Cl n.q.r. spectroscopy. A *cis* configuration is suggested for some of the $[PCl_4L_2]^+$ ions from the n.q.r. data, although the structure of the pyridine complex itself remains uncertain.

THE acceptor properties of tetrachlorophosphonium ion, $[PCl_4]^+$, towards Lewis bases were demonstrated by Beattie *et al.*[1] using the salt $[PCl_4][SbCl_6]$. From i.r. spectroscopy in acetonitrile solution they deduced the formation of complexes $[PCl_4L_2][SbCl_6]$ [L = pyridine (py), tetrahydrofuran (thf), or tetrahydrothiophene], but were unable to isolate these as solids. The pyridine complex was originally thought to have a *cis* configuration, but later work showed that the data were insufficient to confirm the stereochemistry.[2] No evidence for 1 : 1 complexes was found. More stable derivatives have been isolated by using bidentate pyridines such as 1,10-phenanthroline(phen), which forms the complex $[PCl_4(phen)][SbCl_6]$. This species has a similar i.r. spectrum between 660 and 250 cm^{-1} to that of $[PCl_4(phen)]Cl$,[1,3] apart from the extra band due to $[SbCl_6]^-$, thus showing that similar phosphorus-containing moieties are present. Indeed, phosphorus(v) chloride itself forms ionic complexes with the bidentate pyridines phen and 2,2′-bipyridyl (bipy), of the types $[PCl_4L'][PCl_6]$, $[PCl_4L']Cl$, or mixtures of these, although the stable species in concentrated solution is the 2 : 1 adduct.[1,3,4] This behaviour is in contrast to that of unidentate pyridines which give molecular adducts $PCl_5 \cdot L$ with PCl_5.[4] Mixtures of PCl_5, $AlCl_3$ (or $FeCl_3$), and py have also been used to effect Walden-inversion chlorinations of organic compounds, and intermediates such as $[PCl_4(py)][AlCl_4]$ and $[PCl_4(py)_2]Cl$ were postulated although direct physical evidence was lacking.[5]

In a recent paper[4] we described the formation of complexes between a variety of pyridine bases and PCl_5, and discussed the factors affecting complex formation. This work has been extended to derivatives of $[PCl_4]^+$, using the known ionic adducts $[PCl_4][SbCl_6]$[6] and occasionally $[PCl_4][AlCl_4]$[7] as the source of $[PCl_4]^+$ ions. Solution investigations have been carried out mainly by use of ^{31}P n.m.r. spectroscopy. Several of the complexes have been isolated as solids and further characterised by elemental analysis and i.r., ^{31}P n.m.r., and ^{35}Cl n.q.r. spectroscopy.

EXPERIMENTAL

All the manipulations, including sample preparation, were carried out either *in vacuo* or under an inert atmosphere of dry nitrogen. Chemicals of the best available commercial grade were used without further purification, except for some of the bases which were purified as described previously,[4] and aluminium chloride which was resublimed before use. The complex $[PCl_4][SbCl_6]$ was prepared from PCl_5 and antimony(v) chloride by the method of Schmidpeter and Brecht,[8] while $[PCl_4][AlCl_4]$ was prepared from PCl_5 and aluminium(III) chloride, following the procedure of Petro and Shore.[9] The adduct $SbCl_5 \cdot py$ was also prepared by a literature[10] method.

Phosphorus-31 n.m.r. spectra were recorded at 307.2 K on a Perkin-Elmer R10 spectrometer at 24.29 MHz, with a Digiac signal-averaging accessory and sample tubes of 8.4-mm outside diameter. Chemical shifts were measured relative to external P_4O_6, but are expressed relative to 85% phosphoric acid, with the upfield direction taken as positive. Infrared spectra of solids were recorded as Nujol mulls in the range 250—4 000 cm^{-1} on a Perkin-Elmer 457 instrument. Caesium iodide plates for the region below 650 cm^{-1} were protected with Polythene discs to prevent attack by chlorine-containing compounds. Chlorine-35 n.q.r. spectra were obtained at 77 K on a mid-range (5—55 MHz) Decca spectrometer, using Zeeman modulation. Sideband suppression was used where necessary to clarify the positions of line centres. Resonance frequencies were determined to ±10 kHz by interpolation between the spectrometer frequency markers, which were calibrated by means of a frequency counter (Advance Instruments T.C. 16). Techniques used for elemental analysis of C, H, N, P, and halogens have been described previously.[4] In general, the results for phosphorus and halogens were considered to be more reliable, although even here problems were sometimes encountered, particularly when two halogens were present in the same compound. (The automatic analyses for C, H, and N often gave unusual ratios for carbon : hydrogen and/or carbon : nitrogen, which

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[1] I. R. Beattie, K. Livingston, and M. Webster, *J. Chem. Soc.*, 1965, 7421.

[2] I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc. (A)*, 1968, 2772.

[3] M. Webster and M. J. Deveney, *J. Chem. Soc. (A)*, 1968, 2166.

[4] K. B. Dillon, R. N. Reeve, and T. C. Waddington, *J.C.S. Dalton*, 1977, 1410.

[5] W. Hückel and H. Pietrok, *Annalen*, 1939, **540**, 250.

[6] I. R. Beattie and M. Webster, *J. Chem. Soc.*, 1963, 38.

[7] J. R. Van Wazer, personal communication in ref. 8.

[8] A. Schmidpeter and H. Brecht, *Angew. Chem.*, 1967, **79**, 535.

[9] V. P. Petro and S. G. Shore, *J. Chem. Soc.*, 1964, 336.

[10] J. C. Hutton and H. W. Webb, *J. Chem. Soc.*, 1931, 1518.

could not be explained on the basis of likely impurities from the reagents, solvents, or derivatives thereof.)

Solid complexes (except for the 3,5-dichloropyridine adduct) were prepared by direct addition of the pyridine, if liquid, or a solution of the pyridine in the minimum volume of solvent, to a solution of the tetrachlorophosphonium salt in the minimum quantity of the same solvent The latter was chosen, by trial if necessary, so that the product crystallised out as soon as the components were mixed, thus avoiding any decomposition of the complex in solution (Discussion section). The complex $[PCl_4(bipy)][SbCl_6]$ did not crystallise immediately from any of the solvents attempted; this complex, which is much more stable than those of unidentate pyridines, was obtained by evaporating a nitrobenzene solution under reduced pressure. The 3,5-dichloropyridine adduct was obtained by adding small quantities of solid $[PCl_4][SbCl_6]$, with stirring, to a solution of the ligand in the minimum volume of solvent, until there was a sudden thickening of the solid remaining. Details of the solvents used are given in Table 1. The products were rapidly isolated, washed with methylene chloride and low-boiling light petroleum, and excess of liquid removed by pumping where necessary. Lack of contamination by adducts of the type $PCl_5{\cdot}py$ or $SbCl_5{\cdot}py$ was confirmed by the absence of their characteristic i.r. bands.[4] Elemental analyses are given in Table 1.

TABLE 1

Analytical data (%) for $[PCl_4L_2][SbCl_6]$ (L = unidentate pyridine), or $[PCl_4L'][SbCl_6]$ (L′ = bidentate pyridine)

		Found						Calc.					
L or L′	Solvent	C	H	N	P	Cl	X[a]	C	H	N	P	Cl	X[a]
py	$EtNO_2$	17.25	1.20	5.10	4.35	53.4		18.05	1.50	4.20	4.65	53.3	
3,5Me_2-py	$PhNO_2$	23.6	2.85	3.75	4.10	48.9		23.3	2.50	3.90	4.30	49.1	
3Me-py	$PhNO_2$	19.95	2.65	4.50	4.35	50.9		20.8	2.05	4.05	4.45	51.1	
3Cl-py	$EtNO_2$	16.35	1.10	4.15	4.05	58.8		16.35	1.10	3.80	4.20	57.9	
3Br-py	$EtNO_2$	14.4	1.20	3.40	3.75	42.7	19.7	14.6	1.00	3.40	3.75	43.1	19.4
3I-py	$MeNO_2$	13.15	0.90	3.40	3.15	37.8	29.1	13.1	0.90	3.05	3.40	38.6	27.7
4CN-py	$EtNO_2$	17.8	1.00	7.95	4.05	49.6		20.15	1.15	7.85	4.35	49.6	
4CN-py[b]	$PhNO_2$	30.6	1.85	8.75	3.25	37.2		29.95	1.90	8.75	3.20	36.9	
3,5Cl_2-py	$PhNO_2$	15.65	1.10	4.40	3.50	60.4		14.95	0.75	3.50	3.85	61.8	
phen	$PhNO_2$	20.65	1.30	3.90	4.45	51.7		20.95	1.20	4.10	4.50	51.6	
bipy	$PhNO_2$	18.0	1.20	4.15	4.30	53.0		18.1	1.20	4.20	4.65	53.4	
py[c]	$PhNO_2$	23.6	1.85	6.60	5.80	55.5		24.05	2.00	5.60	6.20	56.7	

[a] X = Br or I. [b] Complex is $[PCl_4L_2][SbCl_6]{\cdot}2PhNO_2$. [c] Complex is $[PCl_4L_2][AlCl_4]$.

RESULTS AND DISCUSSION

(*a*) *Solution Investigations.*—The behaviour of a number of uni- and bi-dentate pyridines towards $[PCl_4][SbCl_6]$ in solution was studied by ^{31}P n.m.r. spectroscopy, in an attempt to obtain information about the stabilities of cationic complexes $[PCl_4L_2]^+$ (or $[PCl_4L]^+$) relative to those of the molecular species $PCl_5{\cdot}py$,[4] and to compare if possible the acceptor properties of PCl_5 and $[PCl_4]^+$. In view of the reported existence of relatively stable ionic derivatives $[PCl_4L']^+$ (L′ = a bidentate pyridine),[1,3,4] these species were studied initially. Solutions containing 1 : 1 molar ratios of $[PCl_4][SbCl_6]$ and either 2,2′-bipyridyl or 1,10-phenanthroline in nitrobenzene were prepared, and showed single ^{31}P n.m.r. peaks at 191.5 and 190.5 p.p.m. respectively. These values are in excellent agreement with previous data for the cations $[PCl_4(bipy)]^+$ and $[PCl_4(phen)]^+$,[4] and confirm that no other phosphorus-containing species are present. Very similar shifts of 190.4 and 189.6 p.p.m. were obtained when 1.5 : 1 and 2 : 1 molar ratios of bipy to $[PCl_4][SbCl_6]$ were used, indicating that no more of the base co-ordinates when it is present in excess. The solutions showed no signs of further reaction over a period of months, in contrast to the complexes of unidentate pyridines described below.

Nitrobenzene solutions of unidentate pyridines and $[PCl_4][SbCl_6]$ in a 2 : 1 molar ratio were prepared; the ^{31}P n.m.r. results are shown in Table 2, in the order of the pK_a values of their conjugate acids.[11,12] The data for various groups of pyridines are discussed separately.

TABLE 2

Phosphorus-31 n.m.r. data for 2 : 1 molar ratios of pyridines to $[PCl_4][SbCl_6]$ in $PhNO_2$

Pyridine	pK_a[11,12]	$\delta(^{31}P)$/p.p.m.
2,4,6Me_3-py	7.4	−218.5
3,5Me_2-py	6.2	Adduct insoluble
2Me-py	5.9	−218.1
3Me-py	5.6	Adduct insoluble
py	5.2	180.8, 229.6
3I-py	3.3	188.0, 231.6
3F-py	3.0	184.0, 225.0
3Br-py	2.9	184.9, 229.7
3Cl-py	2.8	182.5, 226.3
4CN-py	1.9	Adduct insoluble
3CN-py	1.4	−6.0, −3.6
Pyrazine	0.8	180.7, 224.2
3,5Cl_2-py	0.7	−86.4
2Br-py	0.8	−87.1
2Cl-py	0.6	−86.7
2CN-py	−0.3	18.0, 107.3, 173.4
2F-py	−0.4	−86.4

Pyridine and 3-*substituted pyridines*, 3X-py (X = F, Cl, Br, *or* I). These solutions required several hours in the spectrometer before stability was achieved, and then showed two peaks of six-co-ordinate phosphorus, in the ranges 180—188 and 225—232 p.p.m. (Table 2). The resonance at higher field is readily assigned to the molecular species $PCl_5{\cdot}L$,[4,13] while by analogy with the

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[11] D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965.

[12] K. Schofield, 'Heteroaromatic Nitrogen Compounds,' Butterworths, London, 1967.

[13] H. P. Latscha, *Z. Naturforsch.*, 1968, **B23**, 139.

shifts for complexes of bidentate pyridines $[PCl_4L']^+$ the lower-field signal is ascribed to $[PCl_4L_2]^+$. The results suggest that the complex $[PCl_4L_2][SbCl_6]$ is initially formed, but then reacts further to give the molecular species $PCl_5{\cdot}L$ and (presumably) $SbCl_5{\cdot}L$.[10,14] This hypothesis was supported by detailed observation of the 3-iodopyridine system, where the solution was concentrated enough for the resonances to be visible on a single scan. Immediately after preparation the sample showed a single peak only, at 188.1 p.p.m., assigned to the cationic complex. An additional peak at *ca.* 230 p.p.m. became apparent after a few hours, and grew in intensity relative to the signal at lower field. Even after several months, however, the reaction had proceeded no further than the two species being present in approximately equal proportions, suggesting that equilibrium (1) is

$$[PCl_4L_2][SbCl_6] \rightleftharpoons PCl_5{\cdot}L + SbCl_5{\cdot}L \qquad (1)$$

established. Similar behaviour was observed for the other ligands in this group.

This equilibrium was confirmed for the pyridine system by preparing an approximately equimolar mixture of $PCl_5{\cdot}py$ and $SbCl_5{\cdot}py$ [10] in nitrobenzene and allowing it to equilibrate. After 1 d the ^{31}P n.m.r. spectrum showed two lines of similar intensity at 181.7 and 232.0 p.p.m. The position of equilibrium can thus be approached from either direction. (Solutions of similar $PCl_5{\cdot}py$ complexes alone in nitrobenzene are indefinitely stable.[4]) Hence the reported instability of $[PCl_4(py)_2][SbCl_6]$ solutions in acetonitrile [1] may have been due to insufficient time having been allowed for the establishment of equilibrium, although reaction of one or more of the components with this solvent is also possible.[15]

Slightly different results were obtained for the system $[PCl_4][AlCl_4]$–pyridine (1 : 2). After a few hours, only the resonance due to $[PCl_4(py)_2]^+$ at 182.2 p.p.m. was apparent, but an additional weaker peak was visible after 1 d at 230.4 p.p.m. The former peak decreased in intensity relative to the latter with time, and had disappeared after *ca.* 10 weeks. In this case reaction (2)

$$[PCl_4(py)_2][AlCl_4] \longrightarrow PCl_5{\cdot}py + AlCl_3{\cdot}py \qquad (2)$$

appears to go to completion, and the position of equilibrium seems to be anion-dependent. Freshly mixed solutions of the reagents used by Hückel and Pietrok [5] to effect organic chlorinations would thus have contained the complex $[PCl_4(py)_2][AlCl_4]$, together with low concentrations of $PCl_5{\cdot}py$ and $AlCl_3{\cdot}py$.

3- *and* 4-CN-py. The solvated complex $[PCl_4(4CN\text{-}py)_2][SbCl_6]{\cdot}2PhNO_2$ precipitated immediately when nitrobenzene solutions of $[PCl_4][SbCl_6]$ and 4-cyanopyridine were mixed, and no solution spectra could be obtained. The 2 : 1 mixture of 3-cyanopyridine and $[PCl_4][SbCl_6]$ showed no ^{31}P n.m.r. signals due to six-co-ordinate species. Reproducible resonances of similar intensity were found at −6.0 and −3.6 p.p.m.; unfortunately these peaks lie close to the region of hydrolysis products such as PCl_3O.[16] The i.r. spectrum of 3CN-py showed the absence of water as an impurity. however, and no hydrolysis difficulties were encountered with PCl_5–3CN-py [4] which is equally moisture-sensitive. The signals may arise from a five-co-ordinate ionic adduct $[PCl_4(3CN\text{-}py)]^+$, for which various isomers are possible; the ligand could occupy an axial or equatorial site in a trigonal bipyramid, although the latter seems more probable since the most electronegative groups tend to occupy the axial positions. Co-ordination *via* either the pyridine nitrogen or the cyano-group is also feasible, but the former mode is usually preferred because of the greater nucleophilic character of the ring nitrogen.[17,18] There is no obvious reason why this ligand should form a different type of complex from other pyridines of similar basicity. Nevertheless it is noteworthy that 2-cyanopyridine behaves differently from 2-halogenopyridines towards both $[PCl_4][SbCl_6]$ and PCl_5,[4] and the cyano-group may be involved in co-ordination.

Pyrazine. This weakly basic pyridine initially showed a similar spectroscopic pattern to the 3-halogenopyridines, with two signals present due to $[PCl_4L_2]^+$ and $PCl_5{\cdot}L$. The peak for the cationic complex was very broad, however, possibly because of an exchange process, and disappeared over a period of days leaving the molecular species in solution. The latter is evidently more stable relative to the cationic complex in the pyrazine system than in those discussed earlier.

3,5-*Dichloropyridine.* Although this base is comparable in strength with pyrazine, the solution showed a single peak at −86.4 p.p.m., readily assigned to unco-ordinated $[PCl_4]^+$.[8] (The salt $[PCl_4][SbCl_6]$ gave a ^{31}P chemical shift of −85.8 p.p.m. in nitrobenzene.) No peak due to a six-co-ordinate species was apparent even after 240 scans. This ligand has been shown to co-ordinate to some extent with PCl_5, even when they are present in equimolar proportions,[4] and provides the best evidence that PCl_5 is a rather better acceptor than $[PCl_4]^+$. (Steric effects are not expected to be important in these systems because of the positions of the ring substituents.) The difference in acceptor properties may be due to the extra orbital-hybridisation energy needed for co-ordination by $[PCl_4]^+$, since any increase in co-ordination number requires *d*-orbital participation. A five-co-ordinate acceptor such as PCl_5 must already be utilising 3*d* orbitals for bonding, and the rearrangement from five- to six-co-ordination may thus be energetically more favourable than a change from four- to five- (or six-)co-ordination. Despite its failure to form in solution, the solid complex $[PCl_4L_2][SbCl_6]$ was isolated (Experimental and solid-state sections) by adding small portions of $[PCl_4][SbCl_6]$ to an excess of the ligand in nitrobenzene solution.

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[14] M. Webster, *Chem. Rev.*, 1966, **66**, 87.

[15] H. P. Latscha, W. Weber, and M. Becke-Goehring, *Z. anorg. Chem.*, 1969, **367**, 40.

[16] V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 227.

[17] S. C. Chan and F. T. Wong, *Austral. J. Chem.*, 1971, **24**, 1519.

[18] S. C. Jain, *J. Inorg. Nuclear Chem.*, 1973, **35**, 505.

2-*Substituted pyridines*, 2X-py (X = F, Cl, *or* Br). No complex formation was observed for 2 : 1 mixtures of these weak bases with $[PCl_4][SbCl_6]$, as shown by the chemical shifts which correspond to free $[PCl_4]^+$ (Table 2). This parallels their behaviour towards PCl_5,[4] where little (if any) co-ordination takes place in solutions containing 1 : 1 molar ratios of reagents. Attempts were made to dissolve $[PCl_4][SbCl_6]$ in neat 2-chloropyridine, but any possible ionic derivatives were too insoluble to give solution spectra, and no peaks due to six-co-ordinate species were visible after spectrum accumulation.

2-*Cyanopyridine*. Three peaks upfield from $[PCl_4]^+$ were found in this system (Table 2), even though the base is weaker than 2-bromo- or 2-chloro-pyridine. The resonance at highest field has a very similar shift (173.4 p.p.m.) to that of the PCl_5–2CN-py complex (171.3 p.p.m.) which was considered to be co-ordinated *via* the cyano-group,[4] and is assigned to the molecular species. The formation of transition-metal complexes bonded in this way has been ascribed to favourable steric factors,[17,19] despite the greater nucleophilic character of the ring nitrogen which does co-ordinate in some cases.[20] The other two peaks may be assigned to $[PCl_4(2CN\text{-}py)_2]^+$ (107.3 p.p.m.) and $[PCl_4(2CN\text{-}py)]^+$ (18.0 p.p.m.), the former almost certainly co-ordinated through the cyano-groups in view of the shift difference from other $[PCl_4L_2]^+$ species.

Methylpyridines. The 2-substituted bases 2,4,6-trimethyl- and 2-methyl-pyridine react similarly with $[PCl_4][SbCl_6]$ and PCl_5,[4] forming PCl_3 in solution which is readily identified from its ^{31}P chemical shift.[16] This behaviour is attributed to ready chlorination of the methyl groups.[4] 3,5-Dimethyl- and 3-methyl-pyridine formed adducts of the normal 2 : 1 type, but these were insoluble in nitrobenzene and no solution data could be obtained.

With the exception of the 3-cyano- and 2-cyano-pyridine systems discussed above, there was no clear evidence for the formation of 1 : 1 complexes, $[PCl_4L]^+$, by unidentate pyridines. Such species are difficult to detect unambiguously by ^{31}P n.m.r., since a shift intermediate between $[PCl_4]^+$ and molecular PCl_5 (80 p.p.m.)[16] is expected, and this includes the region of likely hydrolysis products such as PCl_3O or $P_2Cl_4O_3$.[16] For this reason the mixtures were prepared in a 2 : 1 molar ratio, as described. Small peaks in the hydrolysis-product area were found occasionally, but were never major constituents of the spectra. An attempt to record the spectrum of a 1 : 1 mixture of $[PCl_4][SbCl_6]$ and 3I-py in nitrobenzene gave no ^{31}P n.m.r. signals even after 150 scans, and it was concluded that these were broadened beyond recognition by exchange between the various species present, which could include $[PCl_4L]^+$.

In the octahedral complexes $[PCl_4L_2]^+$, *cis* or *trans* isomers are possible, but only one signal was apparent even though distinct signals from isomeric forms have been observed for related species.[21] A single resonance could arise either from a preferred conformation for the complexes in solution, or from a rapid exchange between the isomeric forms. The configuration of the solid $[PCl_4L_2]^+$ complexes is discussed subsequently.

(*b*) *Solid-state Studies*.—Several of the complexes were isolated as solids in an endeavour to confirm and extend the structural deductions from the solution data. The adducts of bidentate pyridines analysed as 1 : 1 species (Table 1) and those of unidentate pyridines as 2 : 1 complexes, in agreement with the suggested formulations. The solid-state ^{31}P n.m.r. spectra were recorded,[22] and showed broad but well defined resonances between 175 and 195 p.p.m. (Table 3), indicating six-co-ordinate phosphorus. Spectrometer drift, which led to sloping baselines, caused larger error limits than usual for the 3-iodopyridine complex, and made it impossible to determine a reproducible value for the 3-bromopyridine analogue. No signals were detected from $[PCl_4(3,5Cl_2\text{-}py)_2][SbCl_6]$, possibly because of extreme broadness. The complex $[PCl_4(4CN\text{-}py)_2][SbCl_6]\cdot 2PhNO_2$ did not stabilise in the spectrometer, apparently because slow dissociation of the solid to the molecular adducts $PCl_5\cdot L$ and $SbCl_5\cdot L$ was taking place. The shifts agree well with the solution data, and show that the complexes have the structure $[PCl_4L_2][SbCl_6]$ for unidentate pyridines and $[PCl_4L'][SbCl_6]$ for bidentate pyridines, rather than alternatives such as $[SbCl_4L_2][PCl_6]$, where a ^{31}P n.m.r. shift of *ca.* 300 p.p.m. would be expected,[23] or 1 : 1 mixtures of the molecular species $PCl_5\cdot L$[4] and $SbCl_5\cdot L$.

TABLE 3

Phosphorus-31 chemical shifts for solid complexes $[PCl_4L_2]$-$[SbCl_6]$ (L = unidentate pyridine) or $[PCl_4L'][SbCl_6]$ (L′ = bidentate pyridine)

L or L′	$\delta(^{31}P)$/p.p.m.
$3,5Me_2$-py	176.4 ± 3.6
3Me-py	187.3 ± 5.7
py	188.2 ± 3.8
phen	184.6 ± 2.2
bipy	191.2 ± 3.3
3I-py	189.5 ± 12
3Cl-py	184.0 ± 6.5
4CN-py	182.9 ± 2.2

Further confirmation is provided by the i.r. spectra (Nujol mulls) in the range 250—660 cm^{-1} (Table 4). The complexes have some intense bands at <660 cm^{-1} which are not present in the spectra of either the starting materials or the $PCl_5\cdot L$ adducts,[4] while the $[PCl_4]^+$ absorption at 654 cm^{-1} is absent. Each of the hexachloroantimonates has a strong band between 350 and 335 cm^{-1}, attributed to $[SbCl_6]^-$.[6] The presence of unco-ordinated nitrobenzene in the complex $[PCl_4(4CN\text{-}py)_2][SbCl_6]\cdot 2PhNO_2$ was shown by the appearance

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[19] I. Piljac and T. Reynolds, *Inorg. Chim. Acta*, 1969, **3**, 49.

[20] F. Farha and R. T. Iwamoto, *Inorg. Chem.*, 1965, **4**, 844.

[21] K. B. Dillon, R. N. Reeve, and T. C. Waddington, in preparation.

[22] K. B. Dillon and T. C. Waddington, *Spectrochim. Acta*, 1971, **A27**, 1381.

[23] K. B. Dillon, R. J. Lynch, R. N. Reeve, and T. C. Waddington, *J. Inorg. Nuclear Chem.*, 1974, **36**, 815.

of its characteristic i.r. bands,[24,25] no marked frequency shifts being observed.

TABLE 4

Infrared bands (cm^{-1}) for complexes $[PCl_4L_2][SbCl_6]$ (L = unidentate pyridine) or $[PCl_4L'][SbCl_6]$ (L′ = bidentate pyridine) as Nujol mulls in the range 250—660 cm^{-1}

L or L′	
3,5Me$_2$-py	542s, 538(sh), 468s, 438s, 412s, 365(sh), 348s, 340(sh), 302w
3Me-py	581w, 530s, 469s, 396s, 346s, 302w, 276w
py	612w, 536s, 447s, 410s, 340s, 265w
py [a]	610w, 535(sh), 528s, 496s,[b] 450m, 410m, 325w
phen	572w, 539s, 528m, 512s, 481s, 474(sh), 452m, 358(sh), 342s, 332s, 302w, 278w
bipy	658m, 512s, 502s, 461s, 417w, 393w, 342s, 306w, 280w, 258m
3I-py	618w, 579w, 541s, 518s, 463s, 398s, 358m, 341s, 331(sh), 278w
3Br-py	590w, 547s, 527s, 472s, 403s, 372m, 360m, 338s
3Cl-py	590w, 545s, 527s, 472s, 434m, 400s, 366s, 358m, 338s
4CN-py	570s, 554m, 521m, 507s, 420w, 390s, 360m, 340s
4CN-py [c]	610w, 572s, 556m, 520m, 508s, 472w, 424w, 398s, 348s, 330w
3,5Cl$_2$-py	588w, 545s, 508w, 478s, 456w, 424m, 388s, 342s, 302w

[a] $[PCl_4(py)_2][AlCl_4]$. [b] $[AlCl_4]^-$. [c] $[PCl_4(4CN\text{-}py)_2][SbCl_6]\cdot 2PhNO_2$.

The phenanthroline complex $[PCl_4(phen)][SbCl_6]$ was described in the literature as a pale yellow solid when isolated from acetonitrile solution,[1] but the product obtained in the present work was a white crystalline material. The i.r. frequencies correspond only approximately with the previous values,[1] but are in very good agreement with those reported for $[PCl_4(phen)][PCl_6]$,[4] except for bands attributable mainly to the anions. The frequencies for $[PCl_4(bipy)][SbCl_6]$, a pale yellow solid, are also identical, apart from anion bands, to those for $[PCl_4(bipy)][PCl_6]$,[4] showing that the same cations are present.

TABLE 5

Infrared bands (cm^{-1}) for $[PCl_4(py)_2][SbCl_6]$ solutions in the range 300—660 cm^{-1}

Solvent										
MeCN		598s [a]	532s		489w	458(sh)	452w	408m	371m [b]	347m
$PhNO_2$ (initial)	612w [c]	595w [a]	527s [c]	*ca.* 500(sh)	489(sh)	457(sh)	449m	400s [c]		345s
(after 20 min)	612w [c]	594w [a]	528s [c]	502m	489m		448m	398s [c]		344s
$PCl_5\cdot py$ in $PhNO_2$			534m [d]	502s	488s		448s	398s [d]		

[a] PCl_3O. [b] MeCN. [c] Partly $PhNO_2$. [d] $PhNO_2$.

The i.r. spectrum of $[PCl_4(py)_2][SbCl_6]$ in acetonitrile has been reported,[1] but bears little resemblance to the data in Table 4. The strong bands at 536 and 410 cm^{-1} were not present, while vibrations at 568m, 499s, and 488s cm^{-1} were found.[1] In order to resolve this discrepancy, the solid was dissolved in acetonitrile and its i.r. spectrum run immediately after dissolution (Table 5). The frequencies are very similar to those for the solid, with the addition of bands due either to solvent or PCl_3O impurity. Solution spectra were also recorded in nitrobenzene, which is less suitable for i.r. work because it has absorptions at 612w, 535w, 422vw, and 392s cm^{-1}.[24] The initial spectrum in this solvent (Table 5) was again similar to that in acetonitrile, with the addition of a shoulder at *ca.* 500 cm^{-1}. The band at *ca.* 530 cm^{-1} was much more intense than in $PhNO_2$ alone, suggesting the presence of a strong absorption from the complex. The two absorptions between 510 and 470 cm^{-1} increased rapidly in intensity over 20 min (Table 5). These may be assigned to $PCl_5\cdot py$, since bands at 502 and 488 cm^{-1} were observed for $PCl_5\cdot py$ in nitrobenzene (this work), and values of 495 and 483 cm^{-1} in benzene have been reported.[2] The solution behaviour deduced from the n.m.r. data is thus supported by the i.r. results. The bands given [1] for $[PCl_4(py)_2][SbCl_6]$ in acetonitrile at 499 and 488 cm^{-1} thus probably arise from $PCl_5\cdot py$, but the assignment of the line seen by Beattie *et al.* at 568 cm^{-1} is not clear.

In principle, deduction of the configuration of the $[PCl_4(py)_2]^+$ species is possible from vibrational spectroscopy, since a *trans*-octahedral species should show only one major P–Cl absorption in its i.r. spectrum at high frequency (>350 cm^{-1}), while a *cis* complex should show three.[26] Some of these bands may nevertheless coincide if the P–N force constant has a particular value.[2,26] Complications may also arise from the possible presence of a P–N stretching vibration in the P–Cl region, and from splitting of degenerate P–Cl bands for a *trans* complex, as discussed in detail for the isoelectronic compound $SiCl_4\cdot 2py$.[2] Beattie and his co-workers were unable to assign a configuration to the silicon compound which is known to be *trans* from *X*-ray crystallography,[27] even from a full normal-co-ordinate analysis based on complete i.r. and Raman data.[2] The original deduction [1] of a *cis* configuration for $[PCl_4(py)_2]^+$ could not thus be substantiated,[2] and this conclusion is not affected by amending the frequencies to those reported here. The i.r. spectra of the complexes of substituted pyridines are even more difficult to interpret, since extra ligand modes are usually present in this region. More extensive vibrational-spectroscopic studies were therefore not attempted. It is perhaps significant, in view of the n.q.r. results discussed below, that the i.r. spectrum of $[PCl_4(py)_2]^+$ appears to be simpler than those of other complexes with the same ring symmetry.

The ^{35}Cl n.q.r. spectra of the complexes should in theory resolve the problem of stereochemistry if all the

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resonances can be observed, since a single group of lines is expected for a *trans* structure and two separate groups for a *cis* structure. As the phosphorus atom is a poor transmitter of inductive effects,[28,29] however, the frequency difference in the *cis* complexes is not expected to be large.

The ^{35}Cl frequencies measured for the cationic complexes are given in Table 6. In addition, signals between 23 and 25.5 MHz were observed for these compounds, with the exception of the 4-cyano- and 3-methyl-pyridine adducts, assignable either to $[SbCl_6]^-$ (refs. 29—31) or to ^{37}Cl signals from the cations. A resonance at 37.18 MHz was also found for the 3-chloropyridine complex, due to the ring chlorines. No signals were detected for complexes of 3,5Cl$_2$-py, 3,5Me$_2$-py, or bipy.

TABLE 6

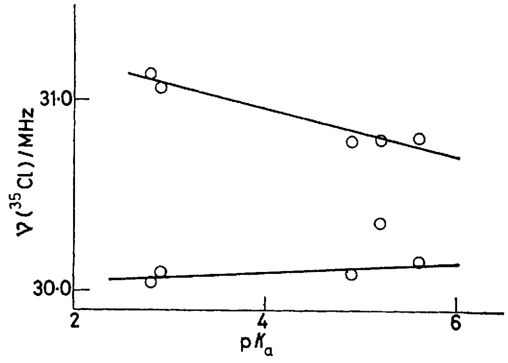
Chlorine-35 n.q.r. frequencies for $[PCl_4L_2]^+$ or $[PCl_4L']^+$ ions at 77 K

L or L′	$\nu(^{35}Cl)$/MHz	Signal : noise ratio
3Me-py	30.15	4 : 1
	30.80	3.5 : 1
py	30.35	6 : 1
	30.79	5 : 1
phen	29.97	2 : 1
	30.09	3 : 1
	30.22	3.5 : 1
	30.48	3.5 : 1
	30.80	4 : 1
	31.07	3 : 1
3Br-py	29.98	2 : 1
	30.20	2 : 1
	30.92	2 : 1
	31.22	3 : 1
3Cl-py	30.045	4 : 1
	31.13	4.5 : 1
4CN-py *	31.11	2 : 1

* $[PCl_4(4CN\text{-}py)_2][SbCl_6]\cdot 2PhNO_2$.

Where resonances were observed, two or more lines were present from chlorines bound to phosphorus for all the complexes except $[PCl_4(4CN\text{-}py)_2][SbCl_6]\cdot 2PhNO_2$, and here the signal-to-noise ratio was so low that other lines could easily have been missed. Where the multiplicity is greater than two, the frequencies can be separated into two distinct groups (Table 6). The frequency difference between the groups of lines ranges from 0.44 to 1.1 MHz, and, although comparable with crystallographic splittings at the lower end of these values, appears to be significantly larger at the upper end. Indeed, if the average frequencies for both groups of lines are plotted against pK_a,[11,12] a good linear correlation is found (Figure) for all the complexes except $[PCl_4(py)_2]^+$. Included in the graph are the results for $[PCl_4(phen)]^+$ which must have a *cis* configuration from geometrical considerations. A linear relation between frequency and change in donor strength of the base is not unexpected, provided the geometry remains constant, since the degree of ionic character in the P–Cl bonds should be affected. Hence a *cis* configuration for the other complexes which obey this relation may reasonably be deduced.

For $[PCl_4(py)_2]^+$ the higher-frequency resonance lies on the line in the Figure but the lower-frequency peak is *ca.* 0.2 MHz higher than expected. This anomaly could arise from a different (*i.e. trans*) configuration for the complex, with the separation of 0.44 MHz representing a crystallographic splitting. There is no obvious reason for pyridine to form a different isomer, but the isoelectronic species $SiCl_4\cdot 2py$ is known to have a *trans* structure in the solid state,[27] as does $GeCl_4\cdot 2py$.[2,32] A *cis* structure has been suggested for the bis complexes of 2-, 3-, and 4-methylpyridine with $GeCl_4$,[33] as for $[PCl_4(3Me\text{-}py)_2]^+$ in the present work, but no direct evidence was given to support this deduction.



$\nu(^{35}Cl)$ as a function of pK_a for some pyridine complexes of $[PCl_4]^+$

An alternative method of interpreting n.q.r. spectra also fails to resolve this problem unambiguously. Maksyutin *et al.*[34] suggested that for some tin tetrachloride adducts of (mainly) oxygen donors the average of all the ^{35}Cl n.q.r. frequencies for *cis* and *trans* isomers should be different. Hence, if the average frequencies for the presumed *cis* complexes as a function of pK_a lie on a straight line, the frequency for the pyridine complex is expected to deviate from this line if it has a *trans* structure. An approximately linear relation was found for the other complexes, having a gradient of $-0.048\,4 \pm 0.014\,2$ MHz per pK_a unit, corresponding to an estimated standard deviation (e.s.d.) of $\pm 0.034\,8$ MHz. The average frequency for the pyridine complex is higher than the value calculated from this relation by 0.105 MHz, *ca.* 3 e.s.d.s. This difference may be significant, but the range of values is so small that firm conclusions

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cannot be drawn. The difference between phosphorus and tin is due to the much better transmission characteristics of Sn, which cause a bigger change in frequency with structural variation. This is readily seen by comparing the changes in ^{35}Cl n.q.r. frequency in the series $[PR_nCl_{4-n}]^+$ and SnR_nCl_{4-n} (R = Ph or Me).[31,35]

The Figure shows that a change in basicity of the *pyridine* affects the higher-frequency n.q.r. line(s) more than those at lower frequency. In $SnCl_4$ complexes, the resonance at higher frequency was assigned to chlorines *trans* to the ligand.[33] This may well hold in $[PCl_4]^+$ complexes also, since a larger effect of basicity on chlorines *trans* to the ligands seems reasonable.

The average frequency for $[PCl_4]^+$ in $[PCl_4][SbCl_6]$ is 32.37 MHz at 77 K,[30] while that for an isolated chlorine atom is 54.87 MHz. If the Townes–Dailey relation[36] is applied, on the assumption of no chlorine *sp* hybridisation and no π character in the P–Cl bond, the residual charge on each chlorine in $[PCl_4]^+$ is calculated as 0.41e. When a similar treatment is applied to the n.q.r. frequencies for the ion $[PCl_4(3Cl\text{-}py)_2]^+$ the frequency of 30.045 MHz corresponds to a charge of 0.452e and that of 31.13 MHz to a charge of 0.433e. The total charge on the chlorines in $[PCl_4L_2]^+$ is then 1.77e, compared with 1.64e in $[PCl_4]^+$. Co-ordination thus results in a net charge transfer to the chlorines of 0.13e. The ring chlorines increase in frequency from 35.24 (ref. 35) to 37.18 MHz on co-ordination, corresponding to a decrease in charge of 0.035 3e. These data agree with the concept of acceptor–donor complexes, where positive charge is transferred from the acceptor to the donor molecules. The true charge transfer on complexing will, if anything, be even larger than calculated, since the neglect of π bonding in $[PCl_4]^+$ is not justified.[29,37]

The complexes are much more stable in the solid than in solution. Their i.r. spectra, with the exception of the 4-cyano- and 3-iodo-pyridine derivatives, remained unchanged for a long time {at least 11 months for $[PCl_4(py)_2][SbCl_6]$}. The 4-cyanopyridine complex and its bis(nitrobenzene) solvate, initially white, became brown over a period of weeks at room temperature, and new peaks appeared in their i.r. spectra which were attributed to formation of $PCl_5{\cdot}L$ and $SbCl_5{\cdot}L$. This behaviour may be correlated with the instability of $[PCl_4(4CN\text{-}py)_2][SbCl_6]{\cdot}2PhNO_2$ at the n.m.r. operating temperature of 307.2 K. The 3-chloro- and 3-bromo-pyridine complexes, initially white, also became fawn after some weeks, but without change in their i.r. spectra.

The solid complexes are also markedly stable to hydrolysis. The pyridine, 3-bromopyridine, and phenanthroline complexes showed no change in their i.r. spectra after overnight exposure to the atmosphere, apart from a change in intensity of two minor peaks at 1 534 and 1 418 cm^{-1} in the case of the phenanthroline derivative. The pyridine and phenanthroline complexes likewise showed no sign of decomposition on addition of water. This stability is due partly to co-ordinative saturation of both cation and anion, which makes an S_N2-type attack difficult, and partly to the insolubility of the complex. The nature of the anion is clearly important also, since $[PCl_4(phen)][PCl_6]$ is much more readily attacked[4] than the $[SbCl_6]^-$ salt, even though it is appreciably more resistant to hydrolysis than $[PCl_4][PCl_6]$ itself.

We conclude that unidentate pyridines which are sufficiently basic and unhindered form ionic 2 : 1 adducts $[PCl_4L_2][SbCl_6]$ with $[PCl_4][SbCl_6]$, which then take part in a solution equilibrium with the molecular species $PCl_5{\cdot}L$ and $SbCl_5{\cdot}L$. Bidentate pyridines also form ionic derivatives $[PCl_4L'][SbCl_6]$, which are stable in solution. Unusual behaviour was found with 3-cyano- and 2-cyano-pyridine as ligands, the latter probably co-ordinating *via* the cyano-group. 2-Substituted methylpyridines undergo halogenation, with formation of PCl_3. The solid complexes are comparatively stable, and some of them show remarkable resistance to hydrolysis. A *cis* configuration is suggested for the octahedral species $[PCl_4L_2]^+$ on the basis of ^{35}Cl n.q.r. data, although some uncertainty remains in the case of the complex $[PCl_4(py)_2]^+$.

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