1358. *The Stereochemistry of Some Addition Compounds of the PCl_4^+ Ion*

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The compound $[PCl_4 phen]^+[SbCl_6]^-$ (where phen = 1,10-phenanthroline) is characterised and used to define the position of the " P–Cl stretching vibrations " of six-co-ordinate adducts of the PCl_4^+ ion, in the infrared and Raman spectra. From a study of the infrared spectra of solutions of $PCl_4^+SbCl_6^-$ in acetonitrile on the addition of tetrahydrofuran, tetrahydrothiophen, and pyridine the formation of 1 : 2 adducts, stable to dissociation in solution, is inferred. The tetrahydrofuran and tetrahydrothiophen adducts adopt a *trans* stereochemistry while the pyridine adduct is assigned a *cis* formulation. The stereochemistries are discussed in the light of related data on co-ordination compounds of Group IV tetrahalides.

WE have previously drawn attention [1] to the value of vibrational spectroscopy in studying the stereochemistry of co-ordination compounds of the non-transition elements, particularly where information is required on the compounds in solution. Although Group IV tetrahalides form many 1 : 2 adducts which represent an interesting series for study, unfortunately in many cases these compounds are stable only in the solid state. This is particularly true for adducts of silicon and germanium,[1b] where the low atomic weight of the central atom may simplify the interpretation of the vibrational spectra for the lighter halogens. The species PCl_4^+ is well characterised,[2] and the evidence for $AsCl_4^+$, although not conclusive,* is strong.[3] (It may be noted here that the formulation of the compound PCl_5AsCl_5 as $AsCl_4^+PCl_6^-$ involves the assumption that PCl_4^+ is at least comparable in acceptor power with $AsCl_4^+$). In the case of $SbCl_4^+$, an extremely powerful acceptor, the existence of the free ion is not proved.† Thus, the suggestion [4] that the compound SbF_3Cl_2 can exist in the ionic form $SbCl_4^+SbF_6^-$ has been questioned,[5] whilst more recently [6] it has been proposed that polymerisation may occur *via* fluorine bridging. Certainly polymerisation and/or ionisation must occur to some extent to explain the physical properties of this compound. In a similar way the compound [7] formulated as $SbCl_4^+F^-$ may be a polymer.†

As is to be expected, adducts of $M'Cl_4^-$ (M′ = Al, Ga, or In) appear to be appreciably less stable [8] than the corresponding addition compounds of MCl_4 (M = Si, Ge, or Sn). Similarly, for the species $M''Cl_4^+$ (M″ = P, As, or Sb) we expect much better acceptor properties than for their isoelectronic counterparts MCl_4. However, although several hundred

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* *Note added in proof.*—The Raman and infrared spectra of the compound AsF_3Cl_2 indicates that it is to be formulated as $AsCl_4^+AsF_6^-$ (K. Dehnicke and J. Weidlein, *Z. anorg. Chem.*, 1965, **337**, 113).

† *Note added in proof.*—The Raman spectrum of $SbCl_4F$ strongly suggests that the solid is correctly formulated as $SbCl_4^+F^-$ (K. Dehnicke and J. Weidlein, *Ber.*, 1965, **98**, 1087).

[1] (*a*) I. R. Beattie and L. Rule, *J.*, 1964, 3267; (*b*) I. R. Beattie, *Quart. Rev.*, 1963, **17**, 382; (*c*) I. R. Beattie, T. Gilson, M. Webster, and G. P. McQuillan, *J.*, 1964, 238; (*d*) I. R. Beattie and M. Webster, *J.*, 1963, 4285.

[2] D. Clark, H. M. Powell, and (independently) A. F. Wells, *J.*, 1942, 642.

[3] See, *e.g.*, L. Kolditz and W. Schmidt, *Z. anorg. Chem.*, 1958, **296**, 188, and references therein.

[4] L. Kolditz and W. von der Lieth, *Z. anorg. Chem.*, 1961, **310**, 236.

[5] K. Dehnicke and J. Weidlein, *Z. anorg. Chem.*, 1963, **323**, 267.

[6] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 1298.

[7] L. Kolditz, *Z. anorg. Chem.*, 1957, **289**, 128.

[8] I. R. Beattie and P. Cocking, unpublished observations.

addition compounds of Group IV tetrahalides have been described [1b] we know [9] of no well-characterised adducts of PCl_4^+ or $AsCl_4^+$ with neutral donor molecules. For the very strong acceptor $SbCl_4^+$ there is evidence [10] for the ion $[SbCl_4(MeCN)_2]^+$, but we have not been able to find reports of other compounds of this type in the literature. From previous work we know that the adduct PCl_5,py (py = pyridine) is stable in solution in benzene [11] and in nitrobenzene.[12] Similarly, the acceptor properties of PCl_4^+ are evidenced by the formation of PCl_6^- in solution in acetonitrile [10] and by the stability of the PCl_5 molecule in carbon disulphide solution. (No co-ordination compounds of silicon tetrachloride with the chloride ion have been characterised.) Ions of the type $[MCl_4L_2]^+$ (where L is a neutral monodentate ligand) are thus likely to be stable in solution, and offer a better chance of studying stereochemistry under equilibrium conditions than do the less stable and frequently insoluble adducts of the Group IV tetrahalides. The main disadvantage (that of having to use ionising solvents which are therefore co-ordinating solvents) is largely offset by the fact that the ions under study have reached their normal [13] covalency maximum of six, although solvation effects may still be important.[14]

The compound $PCl_5,SbCl_5$ (formulated [10] as $PCl_4^+SbCl_6^-$) serves as a readily prepared source of PCl_4^+, the $SbCl_6^-$ ion having infrared (i.r.)-active vibrations occurring at appreciably longer wavelengths than those to be expected for the group of three i.r.-active "P–Cl stretching" frequencies of *cis*-$[PCl_4L_2]^+$ or the corresponding single stretching frequency of *trans*-$[PCl_4L_2]^+$. Further, the $SbCl_6^-$ ion is unlikely to interact with donors added to solutions of $PCl_4^+SbCl_6^-$ in solvents such as acetonitrile, as it is known [15] that radiochloride ions exchange extremely slowly with $SbCl_6^-$ in this solvent, except in the presence of antimony trichloride, for example. Similarly, we find that pyridinium hexachloroantimonate(V) is unaffected by the addition of pyridine.

The vibrational spectra of some co-ordination compounds of the PCl_4^+ ion, and related spectra (infrared 660—270 cm.$^{-1}$, Raman $\Delta\nu = \sim 450$ to ~ 200 cm.$^{-1}$)

Compound	State	Frequency (cm.$^{-1}$)
$PCl_4^+SbCl_6^-$	In MeCN [a]	657s (PCl_4^+), ~590vw,[i] 374s,[e] 343s [c]
$PCl_4^+SbCl_6^-$	In MeCN + phen [a]	658vvw, 617w,[d] 592w,[i] 543m, 505s, 490s, 463s, 450s, 406w,[d] 376s,[e] 345s,[c] ~278?
$[PCl_4\,phen]^+SbCl_6^-$	Mull [a]	564vvw, 534s, 506s, 468sbr, 445m, 334m,[c] 277m
$[PCl_4\,phen]^+SbCl_6^-$	In $MeNO_2$ [b]	3405,[c] 290m [c]
$PCl_4^+SbCl_6^-$	In MeCN + py [a]	621m, 568m, 517w,[f] 499s, 488s, 445s, 372s,[e] 340s [c]
$PCl_4^+SbCl_6^-$	In MeCN + THT [a,g]	592w,[i] 488s, 374s,[e] 345s [c]
$PCl_4^+SbCl_6^-$	In MeCN + THF [a,h]	590s,[i] 483s, 376s,[e] 345s [c]
$SbCl_5$,py [j]	In MeCN [a]	377s,[e] 358m
py	In MeCN [a]	602m, 403s, 375s [e]
phen	In MeCN [a]	614m, 405m, 373s [e]
THT [g]	In MeCN [a]	517m, 467w, 374s [e]
THT [h]	In MeCN [a]	654m, 372s [e]

[a] Infrared; [b] Raman; [c] $SbCl_6^-$; [d] phen; [e] MeCN; [f] Impurity; [g] THT = tetrahydrothiophen; [h] THF = tetrahydrofuran; [i] $POCl_3$ impurity; [j] $SbCl_5$,py has only a low solubility in acetonitrile.

(N.B. The i.r. spectrum of $POCl_3$ in acetonitrile appears to be unaffected by the addition of pyridine.)

When solid 1,10-phenanthroline is added to a solution of $PCl_4^+SbCl_6^-$ in acetonitrile, the 1,10-phenanthroline initially dissolves, but subsequently a pale yellow precipitate of the 1 : 1 adduct $[PCl_4\,phen]^+[SbCl_6]^-$ (phen = 1,10-phenanthroline) appears. The i.r. spectrum of this compound is given in the Table, and by analogy [1c] with $[SiCl_4\,phen]$ it is apparent that ν_3 of PCl_4^+ at about 650 cm.$^{-1}$ has been replaced by a group of frequencies

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[9] M. Webster, *Chem. Rev.*, in the press.

[10] I. R. Beattie and M. Webster, *J.*, 1963, 38.

[11] I. R. Beattie and M. Webster, *J.*, 1961, 1730.

[12] R. R. Holmes, W. Gallagher, and R. P. Carter, *Inorg. Chem.*, 1963, **2**, 437.

[13] See, however, E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, 1964, **86**, 5132.

[14] See, *e.g.*, J. Chatt and R. G. Wilkins, *J.*, 1956, 525.

[15] L. Kolditz and W. Röhnsch, *Z. anorg. Chem.*, 1962, **318**, 17.

around 500 cm.$^{-1}$. As with the silicon tetrachloride adduct it is difficult to assign the " M–Cl stretching " vibrations unambiguously, but they lie within the range 534—445 cm.$^{-1}$, comparable with the range 475—425 cm.$^{-1}$ found for the adduct [$SiCl_4$ phen]. The rather higher frequency found for the P–Cl vibrations is not unexpected in view of the formal positive charge on the phosphorus (ν_3 of $SiCl_4$ is [16] at 620 cm.$^{-1}$ while ν_3 of PCl_4^+ is at [10,17] 650 cm.$^{-1}$). The solution spectra are clearly directly comparable with the solid-state spectra and require no further comment than to note that the ion [PCl_4 phen]$^+$ is stable in solution.

It has recently been suggested [17a] that for adducts of the type *cis*-[$SnCl_4L_2$] only one strong band will be observed in the Raman spectrum in the region of the " Sn–Cl stretching " vibrations. Although this observation appears to be confirmed by studies [18] on *cis*-[SiX_4 py_2] (X = Cl or Br) all these cases rely on initial assignment of the stereochemistry using spectroscopic techniques. We have not yet been able to obtain Raman spectra of known chelate adducts of Group IV tetrahalides. The Raman spectrum of [PCl_4phen]$^+$ as a solution in nitromethane is reported in Table 1, but only two strong bands are apparent, at 340 and 200 cm.$^{-1}$. The supposed *cis*-adduct [$SiCl_4$ py_2] shows one strong Raman band at 326 cm.$^{-1}$ (ν_1 of $SiCl_4$ is [16] at 424 cm.$^{-1}$ while ν_1 of PCl_4^+ is[17] at 459 cm.$^{-1}$). Thus it is probable that the main Raman band of [PCl_4 phen]$^+$ lies under the $SiCl_6^-$ band at 340 cm.$^{-1}$.

In the case of the other adducts described in this Paper, *reaction* rather than simple addition became a complication, although by working quickly we found it possible to obtain reliable spectra. Pyridine added directly to solid $PCl_4^+SbCl_6^-$ led to a black coloration turning to dark red. However, when pyridine was added to a solution of $PCl_4^+SbCl_6^-$ in acetonitrile, the resultant spectrum gave clear evidence for the formation of *cis*-[PCl_4 py_2]$^+$ with " P–Cl stretching " vibrations covering the range 568—445 cm.$^{-1}$ (cf.[1c] [$SiCl_4$ py_2] 482—382 cm.$^{-1}$). One of the bands lying within the above range must be a pyridine out-of-plane deformation vibration. As the adduct $SbCl_5$,py shows [10] ligand pyridine at 438 cm.$^{-1}$, following trends [1c] in Group IV we would expect ligand pyridine in *cis*-[PCl_4 py_2]$^+$ to lie above 440 cm.$^{-1}$, and probably in the region of 490 cm.$^{-1}$. It is clearly important in this case to show that other species (such as the five-co-ordinate adduct [PCl_4 py]$^+$) are absent. The i.r. spectrum of a solution containing sufficient pyridine to just form a 1 : 2 adduct showed no trace of the free pyridine band at 403 cm.$^{-1}$. Similarly, formulation as $SbCl_5$,py + PCl_5,py appears to be excluded by the band at 340 cm.$^{-1}$.

A similar experiment involving the addition of tetrahydrothiophen to a solution of $PCl_4^+SbCl_6^-$ in acetonitrile yielded the unambiguous result of one strong band in the 500-cm.$^{-1}$ region of the i.r. spectrum at 488 cm.$^{-1}$. Thus we may assign a *trans*-configuration to [PCl_4 (tetrahydrothiophen)$_2$]$^+$ with some confidence. In the case of the equivalent experiment using tetrahydrofuran, reaction was very rapid, leading to the production of phosphoryl chloride. Again, by working rapidly, it was possible to show the presence of a strong i.r. band at 483 cm.$^{-1}$, presumably arising from the adduct *trans*-[PCl_4 (tetrahydrofuran)$_2$]$^+$. Although we attempted to obtain solid compounds from the pyridine, tetrahydrothiophen, and tetrahydrofuran experiments, in no case were we successful, and indeed we found that pyridine or tetrahydrothiophen mixed with acetonitrile and $PCl_4^+SbCl_6^-$ in an all-glass vacuum system rapidly led to brownish solutions, which later deposited dark solids.

These results fit into a general picture of steric effects determining stereochemistry, and in many ways parallel earlier work on $SnCl_4L_2$ species. It is particularly interesting that tetrahydrofuran, which gives no adduct with silicon tetrachloride,[19] forms a *trans*-adduct

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[16] G. Herzberg, " Infrared and Raman Spectra," Van Nostrand, New York, 1945.

[17] G. L. Carlson, *Spectrochim. Acta,* 1963, **19**, 1291.

[17a] I. R. Beattie and L. Rule, *J.*, 1965, 2995.

[18] I. R. Beattie and T. Gilson, unpublished observations.

[19] H. H. Sisler, H. H. Batey, B. Pfahler, and R. Mattair, *J. Amer. Chem. Soc.*, 1948, **70**, 3821.

with PCl_4^+, stable in solution. The *trans*-assignment with the small donor atom oxygen probably reflects the steric hindrance of the $>CH_2$ groups, and suggests that the differences observed [20] between oxygen and sulphur donor ability to (presumably) planar $TiCl_3$ and (presumably) C_{2v} $TiCl_4$ may be a demonstration of such steric effects influenced by the increase in bond length on going from O–C to S–C.

EXPERIMENTAL

Pyridinium hexachloroantimonate(V) and $PCl_5,SbCl_5$ were prepared as described previously.[10] Tetrahydrofuran, tetrahydrothiophen, pyridine, 1,10-phenanthroline, and acetonitrile were purified and dried as before.[1a] In the case of the adducts of tetrahydrofuran, tetrahydrothiophen, and pyridine, the ligand was added to a solution of $PCl_4^+SbCl_6^-$ in acetonitrile, giving a slight excess of ligand above the ratio 1 : 2 (PCl_4^+ : ligand). I.r. spectra were then run in polyethylene cells.[21] For the 1,10-phenanthroline adduct a slight excess of 1,10-phenanthroline above the mole ratio 1 : 1 was added to a solution of $PCl_4^+SbCl_6^-$ in acetonitrile. The solid initially dissolved, but slowly reprecipitated small crystals of *adduct* $[PCl_4\,phen]^+[SbCl_6]^-$ (chloride by alkaline hydrolysis and potentiometric titration with silver nitrate solution) (Found: Cl, 51·3. $C_{12}H_8Cl_{10}N_2PSb$ requires Cl, 51·6%). After removal of the crystalline material (centrifuge), the residual solution was examined in a polyethylene cell to obtain the spectrum of this compound in solution. All attempts to obtain solid compounds for ligands other than 1,10-phenanthroline failed. Similarly, an attempt to study these reactions using $PCl_4^+ClO_4^-$ or $PCl_4^+NO_3^-$ failed, due to the apparent instability of these compounds, leading to the production of phosphoryl chloride. (Phosphorus pentachloride was dissolved in acetonitrile, and to this solution was added the stoicheiometric quantity of silver perchlorate or silver nitrate in acetonitrile. In both cases reaction was shown by the production of a yellowish colour, the lack of PCl_4^+ bands of any appreciable intensity in the i.r. spectrum, but the presence of strong phosphoryl chloride bands.)

I.r. spectra were taken on a Perkin-Elmer 221 spectrometer equipped with rock salt–grating–cæsium bromide optics. Raman spectra were run on a Cary 81 instrument using mercury blue and mercury green excitation (5461 Å). To use the green line requires little modification of the instrument. The usual circulated filter solution, a mixture of *o*-nitrotoluene, propan-2-ol, and Methyl Violet, was replaced by propan-2-ol alone. A cylindrical gelatin filter (Wratten No. 12) was then slid inside the filter jacket. Spectra may thus be readily run over the range to $\Delta\nu = 900$ cm.$^{-1}$ (when the mercury yellow doublet starts to interfere). There is unfortunately a mercury line at $\Delta\nu = 291$ cm.$^{-1}$ which is troublesome at high gain, but is useful for calibration at low gain. A rather more sophisticated arrangement has been described by Noack and Jones,[22] who attempt to remove the yellow doublet by using a saturated neodymium chloride solution in a static filter jacket. It is interesting that the compound $[PCl_4\,phen]^+[SbCl_6]^-$ does not hydrolyse readily, and we attempted to take the Raman spectrum of a pressed disc. This failed, however, and we were able only to obtain the spectrum of a solution in nitromethane.

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[20] K. Baker and G. W. A. Fowles, *Proc. Chem. Soc.*, 1964, 362.
[21] I. R. Beattie and M. Webster, *J.*, 1965, 3672.
[22] K. Noack and R. N. Jones, *Z. Elektrochem.*, 1960, **64**, 707.