ADDITION COMPOUNDS OF GROUP V PENTAHALIDES

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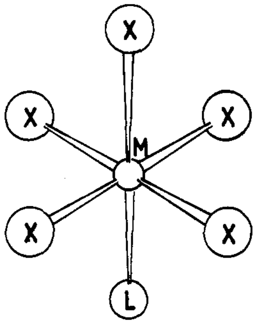
Contents

I. Introduction

The elements phosphorus, arsenic, antimony, and bismuth (which together with nitrogen form group VB) and vanadium, niobium, and tantalum (group VA) form pentahalides with one or more of the halogens. Although phosphorus forms stable pentahalides with fluorine, chlorine, and bromine, and antimony with fluorine and chlorine, only the pentafluoride is known for arsenic, bismuth, and vanadium. Niobium and tantalum form pentahalides with fluorine, chlorine, bromine, and iodine. Molecular compounds formed between these pentahalides and other molecules (organic or inorganic) or ions having the general formula $x[\mathrm{M(Hal)_5}]$–$y[\mathrm{A}]$ (M is a group V element; Hal, halogen; A, any other molecule or ion; x/y, mole ratio $\mathrm{M(Hal)_5/A}$) have been reported in the chemical literature since the middle 19th century, and these compounds form the subject matter of this review. The pentahalides of group V and some aspects of the work in this article have been treated in previous reviews (156, 239, 427, 519), while the book by Lindqvist (333) contains much valuable discussion and hitherto unpublished structure determinations.

Early work dealt primarily with the characterization of the compounds and the determination of the mole ratio $[\mathrm{M(Hal)_5/A}]$ so that much of the literature consists essentially of analytical data. It is only in recent years that the application of a variety of physical techniques has yielded structural information, and it is the purpose of the review to collate and discuss the chemistry of these adducts with reference to structure and stereochemistry of the solid, solution, and gaseous states.

It is intended that the survey of the literature should be complete up to December 1964. The considerable volume of data has been arranged in tabular form for ease of access (see Tables VI–XXIV). All adducts of the type $x[\mathrm{M(Hal)_5}]$–$y[\mathrm{A}]$ are reported even though $\mathrm{M(Hal)_5}$ or A may have no stable existence, *e.g.*, $AsCl_5$–$FeCl_3$. Systems which yield no adduct are tabulated since this information is frequently useful and furthermore difficult to locate, and compounds for which the *only* evidence is an inflection in a titration curve have been marked with an asterisk (*) in the tables.



(a)

$[L_2MX_4]^+[MX_6]^-$

(b)

Figure 1.—Isomerism in MX_5–L.

II. General Discussion

A. PREPARATION

The molecular compounds reported have normally been prepared by mixing the two components either in the presence or absence of a solvent. In the absence of solvent the excess reagent, if volatile, may be pumped off leaving behind the involatile (or less volatile) addition compound. If the components are involatile, the mixture can be treated usually with a suitable solvent to remove the excess of an unreacted component. On mixing the components in a nonpolar solvent one frequently obtains a precipitate of any complexes formed. The solvent $POCl_3$ was used by Groeneveld (169) to prepare a considerable number of adducts between phosphorus pentachloride and other metal halides by mixing hot (~70°) solutions of the components, when the adducts were precipitated. No complications were reported with molecules of solvent being associated with the adducts, although with some systems the adducts contain solvent molecules, *e.g.*, PCl_5–$TaCl_5$–$AsCl_3$ from $AsCl_3$ solution (300), $SbCl_5$–$TiCl_4$–$3POCl_3$ from $POCl_3$ solution (2, 3, 29). On occasion the components are recovered unchanged after mixing indicating no complex formation *under the conditions of the experiment;* yet again, reaction can occur, for example, with niobium pentachloride and 2,2′-bipyridyl which yields $NbCl_4$–2,2′-bipyridyl together with other products (6). "Reaction" here indicates something over and above complex formation. Although the first step may well be the formation of an adduct, it is followed by a reaction to give compounds or a mixture of compounds which do not have the simple formula $x[M(Hal)_5]$–$y[A]$. In the case above there is a change in oxidation state, but this is not necessarily so.

Phase diagrams which provide unequivocal evidence for complex formation and stoichiometry have been investigated for a number of systems and have shown some surprising results. The system BrF_3–SbF_5 shows the solid components of the stoichiometry 3:1, 3:2, 1:1, and 1:3 (145), although only the 1:1 is normally prepared, formulated as $BrF_2^+SbF_6^-$ (*e.g.*, 494). Similarly the system SbF_5–HF shows the presence of SbF_5–5HF (487), and it seems plausible that at least some of these curious stoichiometries are due to fluorine-bridged species while in the last example hydrogen bonding is expected to be important.

Although the compound $SbCl_5$–$POCl_3$ is well established, the phase diagram shows the existence of an incongruently melting $2SbCl_5$–$POCl_3$ as well as the 1:1 adduct (323). No rationalization of these and other reported stoichiometries have been proposed. The ternary system $TiCl_4$–Nb(Ta)Cl_5–$POCl_3$ (354, 522) has been discussed (see section VIIG).

The physical properties of the adducts are varied, but the majority are solids at room temperature. Heat may give rise to a well-defined melting point or decomposition. These compounds are frequently very hygroscopic as indeed are the parent pentahalides, and the use of scrupulously anhydrous conditions is a prerequisite for any investigation of these adducts if reliable results are to be obtained.

B. STOICHIOMETRY

The mole ratio of $M(Hal)_5/A$ shows considerable variation (see Tables VI–XXIV where 1:6, 1:5, 1:3, 2:5, 1:2, 2:3, 1:1, 3:2, 2:1, 3:1, 4:1, 5:1 have been reported), although there is a marked preference for 1:1 adducts particularly among the pentafluorides. A detailed discussion of the groups will be deferred to a later section (section VII), but the various types of behavior associated with the different stoichiometries will be illustrated.

1. 1:1 Adducts ($M(Hal)_5$–A)

With Lewis bases (L:) reacting with the Lewis acid (MX_5, X = halo) the obvious product is that in which a coordinate bond is formed between L: and M by donation of the lone pair of electrons into vacant orbitals of M. M increases its coordination number from 5 to 6 (*i.e.*, trigonal-bipyramidal going to octahedral coordination) as shown in Figure 1a. This behavior has been established by X-ray analysis (see section III) and by ^{19}F n.m.r. spectroscopy (375). In a number of cases the pentahalide is known not to have a trigonal-bipyramidal structure as in the dimeric $NbCl_5$ (567), the tetrameric NbF_5 and TaF_5 (126), and the ionic PCl_5 (90) and PBr_5 (125) (all in the solid state). $SbCl_5$ is monomeric molecular in the solid (398) and gas phase and with a few exceptions (*e.g.*, PBr_5 where dissociation to PBr_3 and Br_2 is essentially complete (218)) the vapors are believed to consist of monomeric trigonal-bipyramidal molecules. The pentahalides are outside the terms of reference and have been described elsewhere, but clearly in some contexts the molecular

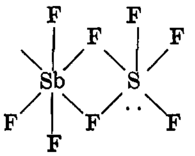


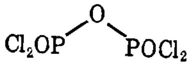
Figure 2.—Possible structure of SbF_5–SF_4.

state is important and must be considered. There does however remain an important alternative ionic formulation where M is six coordinate in both ions (see Figure 1b): the cation $(L_2MX_4)^+$ which is isoelectronic with the compounds of group IV elements (43) is capable of *cis–trans* isomerism. $SbCl_5$–CH_3CN has been formulated as the ionic compound $[SbCl_4$–$2CH_3CN]^+[SbCl_6]^-$ in solution in excess acetonitrile from conductometric (303) and spectroscopic data (47).

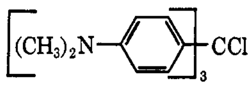
Phosphorus pentachloride in particular is capable of forming complexes with other metal halides which themselves are (in many cases) potential Lewis acids. The compound PCl_5–$AlCl_3$ is an example of this type and should be formulated as $[PCl_4]^+[AlCl_4]^-$ (81, 140) both in the solid state and in solution in nitrobenzene. A fluorine-bridged structure has been put forward to rationalize the ^{19}F n.m.r. spectrum of SbF_5–SF_4 rather than the ionic formulation $SF_3{}^+SbF_6{}^-$. One such structure is shown in Figure 2, although there are a number of other bridged structures (rings and chains) which would be equally acceptable models (409).

2. 2:1 Adducts (2M(Hal)$_5$–A)

This stoichiometry is naturally shown by bifunctional A molecules such as diphenylene-4,4′-tetrazonium fluoride which forms the compound $[N_2C_6H_4$–$C_6H_4N_2]^{2+}$-$[PF_6]_2{}^-$ with phosphorus pentafluoride (320, 479). However, of more interest is $2SbCl_5$–$P_2O_3Cl_4$ (341) for which there exists a number of possible formulations including molecular (the two phosphoryl groups coordinating different $SbCl_5$ molecules) and ionic species, although it has yet to be established that diphosphoryl tetrachloride (I) can act as a chelate ligand. Some of the adducts of 2:1 stoichiometry can be rationalized in terms of respectable ionic species; *e.g.*, $2PCl_5$–$SnCl_4$ can be formulated $[PCl_4]_2{}^+[SnCl_6]^{2-}$ although the supporting physical evidence is slight.



I



II

3. 1:2 Adducts (M(Hal)$_5$–2A)

There seems to be very little evidence at present to support the formulation of these complexes as seven-coordinate species for the B-subgroup elements (P, As, Sb, Bi), although seven- and even eight-coordination has been established unambiguously in the solid state for the A subgroup with the ions $NbF_7{}^{2-}$, $TaF_7{}^{2-}$ (229), $TaF_8{}^{3-}$ (230). The latter was shown to have a square-antiprism stereochemistry, and the first two a distorted trigonal structure with an additional fluorine on a prism face. This latter stereochemistry requires re-examination since $ZrF_7{}^{3-}$, originally thought to have the same stereochemistry as $MF_7{}^{2-}$ (M = Nb, Ta), was later shown to be a pentagonal bipyramid (562). The 1:2 adducts of the A-subgroup halides with Lewis bases seem to have generally been considered as seven-coordinate species (82, 133), while the B-subgroup compounds, *e.g.*, PCl_5–$2(CH_3)_3P$ (240), have been reported without comment as to their nature.

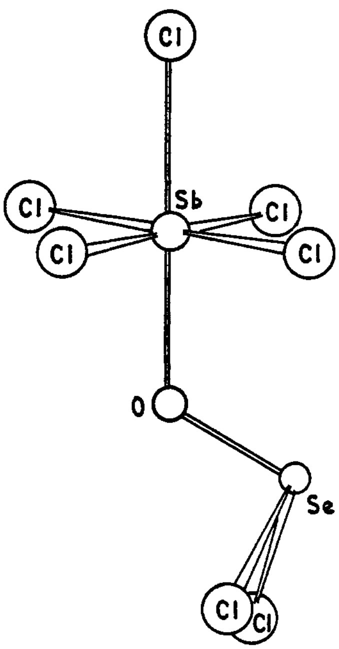


Figure 3.—Structure (schematic) of $SbCl_5$–$SeOCl_2$.

4. Other Stoichiometries

These constitute about 7% of the reported adducts (1:1 ~77%; 1:2, 2:1, ~16%) and include M(Hal)$_5$/A ratios of 1:6, 1:5, 1:3, 2:5, 2:3, 3:2, 3:1, 4:1, and 5:1. Examination of the references given in the tables shows that the compounds have received virtually no serious attention. It must be considered that some may be erroneous owing to reaction or inadequate attention to experimental conditions, but there nevertheless remains a small nucleus of compounds whose stoichiometries have not yet been satisfactorily explained.

III. X-RAY DATA

X-Ray structure determinations have been carried out on the following molecules: $SbCl_5$–$POCl_3$ (335), $SbCl_5$–$PO(CH_3)_3$ (69), $SbCl_5$–$(C_6H_5)_2SO$ (215), $SbCl_5$–$(CH_3)_2SO_2$ (214), $SbCl_5$–$HCON(CH_3)_2$ (66), $SbCl_5$–$SeOCl_2$ (223) (Figure 3), $SbCl_5$–S_4N_4 (387), $SbCl_5$–ICl_3 (525), PCl_5–ICl (568), $NbCl_5$–$POCl_3$ (70), $TaCl_5$–

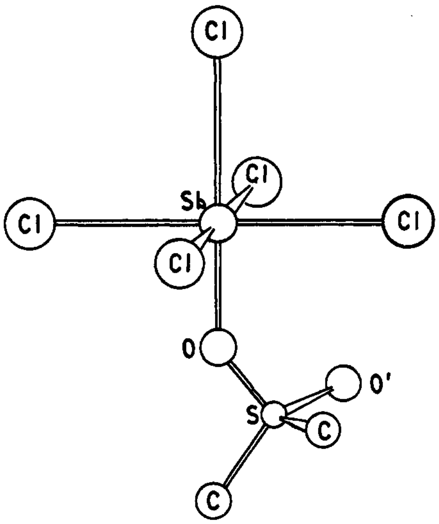


Figure 4.—Structure (schematic) of $SbCl_5$–$(CH_3)_2SO_2$.

TABLE I

BOND LENGTHS IN ADDITION COMPOUNDS AND POLYHALIDE ANIONS OF GROUP V

Compound	Bond lengths, Å.	Ref.
$SbCl_5$–$OPCl_3$	Sb–Cl 2.32–2.35, Sb–O 2.17, O–P 1.47, P–Cl 1.95	70, 334, 335
$SbCl_5$–$OP(CH_3)_3$	Sb–Cl 2.33–2.35, Sb–O 1.94, P–O 1.56, P–C 1.80–1.84	69, 70
$NbCl_5$–$OPCl_3$	Nb–Cl 2.25–2.35, Nb–O 2.16, P–O 1.45, P–Cl 1.94–1.95	70
$SbCl_5$–S_4N_4	SbCl 2.36–2.43, Sb–N 2.17	387
$SbCl_5$–ICl_3	Sb–Cl 2.26–2.44, I–Cl 2.29, 2.33	525
$(ICl_2{}^+SbCl_6{}^-)$	I....Cl 3.00, 2.85	
PCl_5–ICl $(PCl_4{}^+ICl_2{}^-)$	P–Cl (in $PCl_4{}^+$ ion) 1.98, I–Cl (in $ICl_2{}^-$ ion) 2.36	568
PCl_5 $(PCl_4{}^+PCl_6{}^-)$	P–Cl (in $PCl_4{}^+$ ion) 1.98, P–Cl (in $PCl_6{}^-$ ion) 2.07 (av.)	90
PBr_5 $(PBr_4{}^+Br^-)$	P–Br (in $PBr_4{}^+$ ion) 2.13	125
$[PF_6]^-$	P–F 1.73	53, 56–58
$[AsF_6]^-$	As–F 1.85	248, 444
$[SbF_6]^-$	Sb–F 1.88 (78)	52, 59, 78, 470, 471
$[NbF_6]^-$	Nb–F 2.13–2.15	55
$[NbF_7]^{2-}$	Nb–F 1.97 (av.)	229
$[TaF_7]^{2-}$	Ta–F 1.97 (av.)	229
$[TaF_8]^{3-}$	Ta–F 1.98 (av.)	230
$SbCl_5$–$(C_6H_5)_2SO$	Sb–Cl 2.33–2.38, Sb–O 2.16, S–O 1.53, S–C 1.72, 1.81	215
$SbCl_5$–$(CH_3)_2SO_2$	Sb–Cl 2.26–2.37, Sb–O 2.12, O–S 1.53, S–O′ 1.46, S–C 1.60, 1.79	214
$SbCl_5$–$SeOCl_2$	Sb–Cl[a] 2.33–2.36 (2.32–2.36), Sb–O 2.15 (2.04), O–Se 1.63 (1.72), Se–Cl 2.10–2.13 (2.11–2.12)	223

[a] The unit cell contains two independent molecules. The figures in parentheses refer to the second molecule.

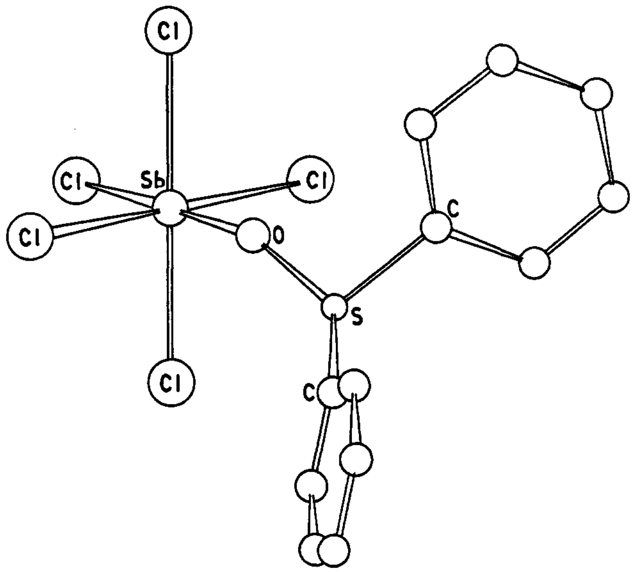


Figure 5.—Structure (schematic) of $SbCl_5$–$(C_6H_5)_2SO$.

$POCl_3$ (65). The adducts of $POCl_3$ and $PO(CH_3)_3$ are molecular solids with coordination from the oxygen atom to the group V element increasing the coordination number to six (Figure 6). A table of bond length in all these adducts and closely related compounds is included (see Table I), and it is not intended to discuss the small variation in bond lengths and angles that occur. It is suffice to state briefly the principal features of the structure. $SbCl_5$–$(C_6H_5)_2SO$ is a molecular solid with coordination from the oxygen (Figure 5) while the one-to-one addition compound between dimethyl sulfone and antimony pentachloride has one coordinated oxygen and one free oxygen atom (Figure 4). $SbCl_5$–S_4N_4 (Figure 8) is a molecular solid with coordination from a nitrogen atom. It is perhaps relevant to mention the recent X-ray structure determination of S_4N_4 (488).

By contrast with the molecular compounds described so far, $SbCl_5$–ICl_3 is an ionic solid containing $[ICl_2]^+$ cations and $[SbCl_6]^-$ anions weakly linked into chains (Figure 7). The only crystallo-

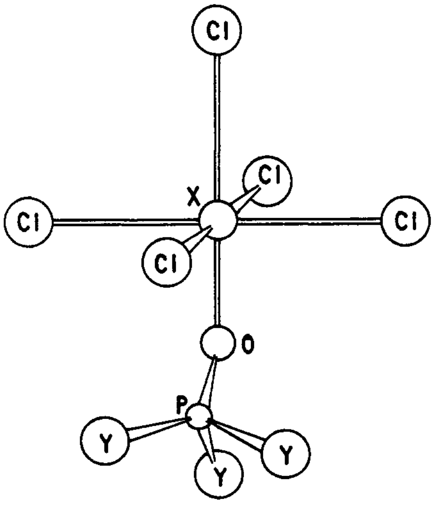


Figure 6.—Structure (schematic) of $SbCl_5$–$POCl_3$, $NbCl_5$–$POCl_3$, and $SbCl_5$–$(CH_3)_3PO$ (X = Nb, Sb; Y = Cl, C).

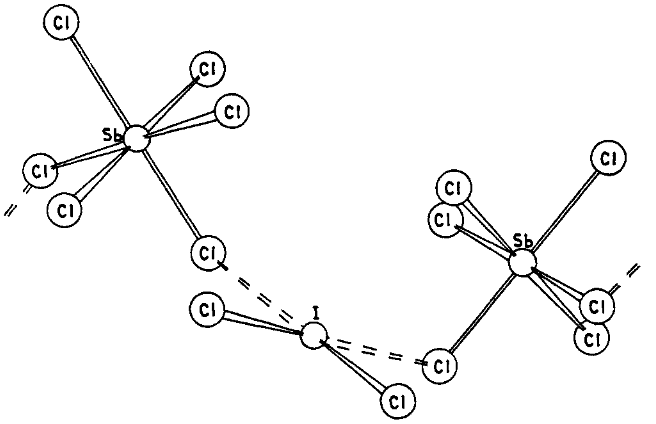


Figure 7.—Partial structure (schematic) of $SbCl_5$–ICl_3.

graphically defined adduct of phosphorus pentachloride, PCl_5–ICl contains the tetrahedral PCl_4^+ and the linear Cl_2^- although the acceptor property of PCl_5 is established by the presence of PCl_4^+ and PCl_6^- ions in

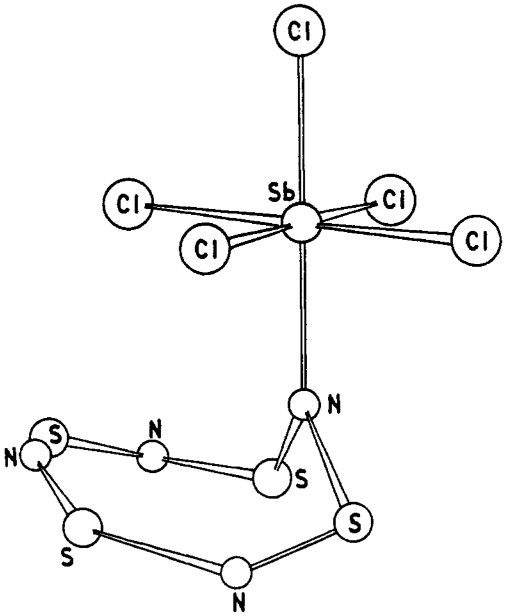


Figure 8.—Structure (schematic) of $SbCl_5$–S_4N_4

TABLE II

FUNDAMENTAL FREQUENCIES OF TETRAHEDRAL $[M(HAL)_4]^+$ IONS (IN CM.$^{-1}$)[a]

Ion(T_d)	$\nu_1(A_1, R)$	$\nu_2(E, R)$	$\nu_3(F_2, IR, R)$	$\nu_4(F_2, IR, R)$	Compound	State	Ref.	Other ref.
PCl_4^+	458	171	658	251	PCl_5	Solid	81	47, 157, 431, 530
$AsCl_4^+$	...	...	...	...	...	...	...	429
$SbCl_4^+$	...	...	...	...	...	...	...	
PBr_4^+	227	72	474	140	PBr_5	Solid	158	

[a] The infrared and Raman spectra of $AsCl_2F_3$ have been reported and interpreted as $AsCl_4^+AsF_6^-$: $AsCl_4^+$, ν_1 422, ν_2 156, ν_3 500, ν_4 187; AsF_6^-, ν_1 682, ν_2 583, ν_3 706, ν_4 402/389, ν_5 372 cm.$^{-1}$. Infrared and Raman frequencies were also reported for $KAsF_6$ (538a). The Raman spectrum of solid $SbCl_4F$ shows the compound to be ionic $[SbCl_4]^+F^-$ with the tetrahedral $[SbCl_4]^+$ ion frequencies of ν_1 353, ν_2 143, ν_3 399, and ν_4 153 cm^{-1} (119a). See also footnote *a*, Table III.

TABLE III

FUNDAMENTAL FREQUENCIES OF OCTAHEDRAL $[M(HAL)_6]^-$ IONS (IN CM.$^{-1}$)[a]

Ion(O_h)	$\nu_1(A_{1g}, R)$	$\nu_2(E_g, R)$	$\nu_3(F_{1u}, IR)$	$\nu_4(F_{1u}, IR)$	$\nu_5(F_{2g}, R)$	Compound	State	Ref.	Other ref.
PF_6^-	735	563			462	KPF_6	Melt	77	106, 321, 403, 429, 430, 489, 491, 550
			840	555		KPF_6	Solid	77	
AsF_6^-	...	...			...				311, 403, 433, 489, 491
			700	400		$KAsF_6$	Solid	430	
SbF_6^-	...	...			...				106, 311, 403, 405, 451
			660	...		$KSbF_6$	Solid	430	
PCl_6^-	360	281			150	PCl_5	Solid	81	47, 157, 428
			449	62		PCl_5	Solid	81	
$SbCl_6^-$	337	277			172	$HSbCl_6$	Soln. in HCl	439	
			336	...		PyH $SbCl_6$	Solid	47	
VF_6^-	...	...			...				
			715	...		KVF_6	Solid	430	
NbF_6^-	683	562			280	$CsNbF_6$	Solid	261	
			580	...		$KNbF_6$	Solid	430	
TaF_6^-	...	...			...				
			580	...		$KTaF_6$	Solid	430	
$NbCl_6^-$	...	...			...				32
			333	...		Et_4NNbCl_6	Solid	1	
$TaCl_6^-$	...	...			...				32
			330	...		Et_4NTaCl_6	Solid	1	

[a] R = Raman active; IR = infrared active. See also footnote *a*, Table II.

solid phosphorus pentachloride (90). The adduct $SbCl_5$–$HCON(CH_3)_2$ has not been described in detail, but coordination to the antimony atom occurs through the oxygen (66) of the keto group rather than the nitrogen.

The octahedral hexafluoroanions MF_6^- have been found by X-ray techniques and PF_6^-, AsF_6^-, SbF_6^-, and NbF_6^- have been characterized (Table I and ref. 262). The detailed structures adopted by the hexafluorides with metal cations have been comprehensively discussed by Kemmitt, *et al.* (262), and interpreted mainly in terms of size effects. The ability of niobium and tantalum to exhibit a coordination number greater than six in the solid state is well established and the NbF_7^{2-}, TaF_7^{2-}, and TaF_8^{3-} ions have been described (see section IIB and Table I).

X-Ray powder photographs have been reported for $AsCl_5$–$AlCl_3$ (309), PCl_5–BCl_3 (431), PCl_5–$AlCl_3$ (431), PCl_5–$GaCl_3$ (431), PCl_5–$TlCl_3$ (431), PCl_5–$NbCl_5$ (298), SbF_5–SF_4 (38), BiF_5–KF (146), PCl_5–VCl_4 (302), SCl_3–AsF_6 (308), $SeCl_3$–AsF_6 (308), $TeCl_3$–AsF_6 (308), PCl_5–$TaCl_5$ (300), and PF_5–PCl_4F (264).

IV. SPECTRA

A. INFRARED AND RAMAN SPECTRA

Vibrational spectra, particularly infrared, have been recorded for a wide variety of compounds in varying degrees of detail and only an outline of the various applications will be discussed.

The tetrahedral $[M(Hal)_4]^+$ and the octahedral $[M(Hal)_6]^-$ ions have been examined in detail, and the assigned fundamental frequencies are shown in Tables II and III. Vibrational frequencies of the $[NbF_7]^{2-}$ ion (261, 430) and the $[TaF_7]^{2-}$ ion (430) have been reported and clearly reveal the absence of discrete $[MF_6]^-$ in the structure in agreement with the X-ray data. The existence of fundamental frequencies for the tetrahedral and octahedral ions, which vary only small amounts from compound to compound has enabled, for example, the $[PCl_4]^+$ ion to be characterized in the compound PCl_5–$AlCl_3$ (81, 431). This approach is applicable to solutions of the adducts and enables changes in stereochemistry between solid and solution states and the presence of dissociative equilibria to be examined.

It is only in recent years that commercial infrared spectrometers working beyond 15 μ have been available, and since for all the halogens, except fluorine, the group V element–halogen stretching vibrations lie beyond this range, these vibrations have not been observed. The vibrations that have been observed in many cases have arisen from the organic ligand, P═O and C≡N stretching vibrations, etc., and conclusions have been drawn from the shifts in frequency relative to the parent donor. Thus the donor atom in the compound $SbCl_5$–$HCON(CH_3)_2$ was considered from infrared data to be the oxygen atom rather than the nitrogen (563), and this was confirmed by subsequent X-ray analysis (66). By a similar argument the coordinating atom in some carboxylic acid and ester complexes of $SbCl_5$ was found to be the keto oxygen atom from the lowering of the C═O stretching vibration (and the increase in the C–O stretching frequency for the esters) (566). In general the correlation of shifts in frequency with *stability* must be considered with suspicion, and these compounds provide no exception. Zackrisson and Aldén showed that for the two compounds $SbCl_5$–$(CH_3)_3PO$ and $SbCl_3$–$(CH_3)_3PO$, although the shifts in the P═O stretching frequency were comparable (*ca.* 100 $cm.^{-1}$ to lower frequencies), the heat of formation of the pentachloride was very much larger than for the trichloride (565).

As a diagnostic tool the infrared spectrum is of course invaluable, and the spectra of coordinated ligands frequently show considerable similarities in a wide variety of compounds. Low site symmetry can broaden and split degenerate fundamentals, but the splitting of the As–F stretching vibration ($\nu_3(F_{1u})$) into a doublet in the compound $[(CH_3)_3Sn][AsF_6]$ was interpreted in terms of lowering of the octahedral symmetry (O_h) to D_{4h} by interaction of two *trans* fluorine atoms with the tin of the trimethyltin grouping (92, 93).

Raman spectroscopy has received less attention than the infrared but nevertheless its utility has been demonstrated. By means of a competitive reaction in 1,2-dichloroethane Kinell, *et al.* (268), were able to show the greater donor strength of $PO(CH_3)_3$ compared with $POCl_3$ toward $SbCl_5$. An equimolar mixture of $SbCl_5$–$POCl_3$, and $PO(CH_3)_3$ in the solvent was shown by Raman spectroscopy to consist of $SbCl_5$–$PO(CH_3)_3$ and free $POCl_3$. Provided complications of reaction between different ligand species is avoided (*e.g.*, the formation of $POCl_2(CH_3)$), the method seems of general applicability. Raman spectroscopy is of course essential to observe the solely Raman active fundamentals (infrared-active combination bands could give this information) and desirable where a vibration is both Raman and infrared active.

The formation of a coordinate bond by donation of a lone pair of electrons merely perturbs the donor molecule, no great changes in stereochemistry are usually required, and the effect on the spectrum appears as small shifts in frequency (with perhaps splitting of bands) and altered intensity. By contrast the acceptor skeleton has to undergo a profound change in stereochemistry, in the present case from trigonal bipyramidal (D_{3h}) to square-pyramidal (C_{4v}) (see Figure 1a). Examination of the element–halogen vibrations (in conjunction with the ligand vibrations) would appear to offer a powerful tool to investigate the stereochemistry of the adducts both in the solid state and in solution.

B. ULTRAVIOLET AND VISIBLE SPECTRA

Apart from the work of Gutmann and his collaborators, only a few visible and ultraviolet measurements have been performed. Popov and co-workers (436, 437) were able to establish that the equilibria present in carbon tetrachloride and acetonitrile solutions of the adducts PCl_5–ICl, and PBr_5–IBr were as follows: (a) in CCl_4

$$\begin{aligned} PCl_5\text{–}ICl &\rightleftharpoons PCl_5 + ICl \\ PBr_5\text{–}IBr &\rightleftharpoons PBr_5 + IBr \\ PBr_5 &\rightleftharpoons PBr_3 + Br_2 \end{aligned}$$

(b) in CH_3CN

$$\begin{aligned} PCl_5\text{–}ICl &\rightleftharpoons PCl_4{}^+ICl_2{}^- \\ PBr_5\text{–}IBr &\rightleftharpoons PBr_4{}^+IBr_2{}^- \end{aligned}$$

Ultraviolet and visible spectra (solution and reflectance) of a number of *p*-dimethylaminobenzenediazonium chloride complexes with metal halides (including $SbCl_5$) have been determined (63). To interpret some of the absorptions, charge-transfer bands in which the diazonium ion is the donor and the metal chloro complex is the acceptor were postulated and given support by elementary calculations. The highly colored and paramagnetic radical salt tritolylaminium hexachloroantimonate $[(p\text{-}CH_3C_6H_4)_3N]^+[SbCl_6]^-$ has been examined both in solution in chloroform and in KBr-pressed disk in the range 240-700 mμ (219). This formed part of a study of the cation (other anions were also used) and the spectra were not interpreted.

Gutmann and his co-workers over a period of years have used a number of techniques including ultraviolet and visible spectrophotometry to study nonaqueous ionizing solvent systems (see also section VD). The relative chloride ion acceptor strength of a number of metal halides has been determined in a variety of solvents using $(C_6H_5)_3CCl$ as a source of $[Cl]^-$ ions and measuring the spectrum (340–500 mμ) of the triphenylcarbonium ion. The solvents $C_6H_5POCl_2$ (27), $POCl_3$ (28), $(C_4H_9O)_3PO$ (28), C_6H_5COCl (204), CH_3CN (202) have been examined. The order of relative acceptor strengths is very similar for different solvents but, since the metal halides undoubtedly interact with the solvents to varying extents, the detailed interpretation of the ion-transfer process is complicated. The chloride-donating ability of similar metal halides to the above have also been estimated using ferric chloride as an indicator. The $[FeCl_4]^-$ ion has a characteristic visible spectrum, and by mixing $FeCl_3$ and the metal halides in a suitable solvent the concentration of $FeCl_4{}^-$ can be estimated. The method of continuous variations was used in the experiments to determine the stoichiometry of the adducts formed. The solvents $(C_6H_5)POCl_2$ (24) and $POCl_3$ (25) have been examined. Again the equilibria refer to ion transfer between solvated species, but relative $[Cl]^-$ ion donating ability does not seem to be very dependent on solvent. Antimony pentachloride which is one of the most powerful chloride ion acceptors is a poor $[Cl]^-$ donor, whereas phosphorus pentachloride, one of the poorest acceptors is quite high up the scale of chloride ion donating ability when examined by the Gutmann techniques. The solvent system concept has been extensively developed particularly for phosphoryl chloride and when applied to solutions of $FeCl_3$ in $POCl_3$ (23, 200, 201) interprets the conductivity and existence of $[FeCl_4]^-$ in terms of the equilibria

$$FeCl_3 + POCl_3 \rightleftharpoons [FeCl_3ClPOCl_2] \rightleftharpoons [POCl_2]^+ + [FeCl_4]^-$$

Meek and Drago (360), however, showed the presence of $[FeCl_4]^-$ ions and electrical conductivity in the system $FeCl_3$–$(C_2H_5O)_3PO$ where clearly the solvent system concept is inapplicable, and proposed the equilibrium for the system POY_3–$FeCl_3$ ($Y = Cl$, OC_2H_5).

$$FeCl_3 + Y_3PO \rightleftharpoons [FeCl_3OPY_3] \rightleftharpoons [FeCl_{3-x}(OPY_3)_{1+x}]^{x+} + x[FeCl_4]^-$$

$$x = 1\text{–}3$$

The interpretation of the work of Gutmann and coworkers is manifestly more complicated than was originally thought. Other indicators that have been used to measure relative chloride ion accepting ability include cobalt(II), copper(II), and nickel(II) chlorides in the solvents trimethyl phosphate and acetonitrile. There were small changes in relative acceptor ability in different solvents, but the chloride-accepting sequence $SnCl_4 > SbCl_5 > TiCl_4$ stayed the same (205). A more detailed discussion of these ionic reactions in solvent systems are to be found in other references (124, 195, 197, 333, 360, 505).

The reaction of crystal violet (CV) (II) with antimony pentachloride in the solvents chloroform (39) and phosphoryl chloride (208) has been studied spectroscopically. Gutmann, *et al.* (208), proposed the existence of CV–2$SbCl_5$ and CV–4$SbCl_5$ in solution and invoked coordination of the lone pair of electrons on the nitrogen to the antimony to rationalize the stoichiometries. In chloroform the method of continuous variation showed the adducts CV–2$SbCl_5$, CV–$SbCl_5$, and possibly other species (39).

C. NUCLEAR MAGNETIC RESONANCE SPECTRA

A considerable volume of research work using n.m.r. techniques has been published relevant to this review, and no more than an outline of the principal results can again be given.

The following nuclei have been examined: ^1H (spin $^1/_2$) (401, 403–405, 450); ^{19}F (spin $^1/_2$) (160, 242, 243, 375–377, 380, 381, 403–405, 410, 411, 450); ^{31}P (spin $^1/_2$) (10, 48, 147–149, 231, 258, 393); ^{93}Nb (spin $^9/_2$) (410); ^{121}Sb (spin $^5/_2$) (435).

The use of n.m.r. in inorganic chemistry has been reviewed (381) and mention must be made of Muetterties and co-workers to whom much of the work in this section is attributable. A number of 1:1 adducts between the pentafluorides of phosphorus, arsenic, or antimony and organic donor ligands have been shown on the basis of the ^{19}F n.m.r. spectrum to have the stereochemistry shown in Figure 1a (375, 376, 381). Two types of nonequivalent fluorine atoms were observed: a doublet and a quintuplet with relative intensities of 4:1. Additional spin–spin splitting was observed due to the phosphorus (^{31}P) and arsenic (^{75}As) nuclei. The magnitude of the F–F coupling constants for the phosphorus ($J_{FF} \simeq 55$ c.p.s.) and antimony compounds ($J_{FF} \simeq 100$ c.p.s.) was not sensitive to the nature of the ligands suggesting no important changes in M–F bond lengths or bond angles. For AsF_5–Py, $J_{FF} = 125$ c.p.s. (375).

The hexafluoride anions $[MF_6]^-$ have been well characterized, and the n.m.r. data were shown to be consistent with a regular octahedral stereochemistry. Thus the $[PF_6]^-$ (258, 380, 381, 393, 403), $[AsF_6]^-$ (380, 381, 411), $[SbF_6]^-$ (380, 381, 403–405, 435), $[NbF_6]^-$ (410) ions have been examined. Although $[NbF_7]^{2-}$ is known in the solid state, $[NbF_6]^-$ shows little tendency to interact with fluoride ions in solution (410).

The ^{31}P n.m.r. spectrum of *solid* phosphorus pentachloride was found to consist of two bands attributed to the PCl_4^+ and PCl_6^- ions (−96 and +281 p.p.m. (relative to H_3PO_4)), respectively (10). The $[PCl_6]^-$ ion has also been found in solution in nitromethane in some complex phosphorus–nitrogen compounds, *e.g.*, $[Cl_3P{=}N{-}PCl_3]^+[PCl_6]^-$ prepared by the reaction of PCl_5 with NH_4Cl (48, 147–149) when the chemical shift was found to be +300 p.p.m.

The chlorophosphonium salts $[RPCl_3]^+[AlCl_4]^-$ have been examined by ^{31}P n.m.r. in solution in methylene dichloride (231). The similarity of the spectra of $C_2H_5PCl_4$–$AlCl_3$ and $C_2H_5PCl_4$–$2AlCl_3$ lead to the formulation of the latter as $[C_2H_5PCl_3]^+[Al_2Cl_7]^-$ and *NOT* $[C_2H_5PCl_2]^{2+}[AlCl_4]_2^-$. The nature of the $[Al_2Cl_7]^-$ ion was not established. PCl_4F–$SbCl_5$ was formulated as $[PCl_3F]^+[SbCl_6]^-$ (that is, involving Cl^- transfer rather than F^-) from ^{19}F n.m.r. and infrared spectra and the magnitude of the J_{PF} coupling constant (450).

Olah and his co-workers in a series of publications have elegantly demonstrated the power of n.m.r. spectroscopy (using ^1H and ^{19}F nuclei) in conjunction with other spectroscopic techniques in investigations on the systems RCOF–MF_5 (M = P, As, Sb) (403, 405) and alkyl fluoride–SbF_5 (401). In the former system, ionic species $[RCO]^+[MF_6]^-$, oxygen coordinated compounds $RC(F){=}O{\rightarrow}MF_5$, and dissociative equilibria were established dependent on the nature of R and whether in the solid or solution states. The alkyl fluoride–SbF_5 system showed the presence of stable solvated alkylcarbonium hexafluoroantimonates, while rearrangement of the alkyl group generally occurred to give the more stable secondary or tertiary carbonium ion (401).

D. MISCELLANEOUS SPECTRAL TECHNIQUES

Of the remaining spectroscopic tools only electron spin resonance has found application (272, 273, 343). The best established compound is $SbCl_5$–thianthrene, a colored paramagnetic solid, which has been examined in the solid state and in solution (272, 273, 343). The unpaired electron that gives rise to the e.s.r. spectrum gives rise to paramagnetism, and a more detailed description of this compound is found in section VB. Solid paramagnetic adducts between antimony pentachloride and the sulfur-containing compounds thio-β-naphthol, 2,2′-dinaphthyl disulfide, and dibenzothiophene have been prepared and the e.s.r. spectra of the solids examined (273). The parent organic compounds also yield paramagnetic solutions in concentrated sulfuric acid (228, 273, 346).

V. PHYSICAL TECHNIQUES

A. MOLECULAR WEIGHT

Measurements can be taken both in solution and in the vapor phase. The latter has received little attention but was used to show that the adducts $TaCl_5$–$POCl_3$ and $NbCl_5$–$POCl_3$ are fully dissociated in the vapor (181).

Ebullioscopic and cryoscopic techniques have been used with a variety of solvents to determine molecular weights in solution and have yielded valuable results either on their own or taken as necessary adjuncts to other physical measurements. The phosphorus oxychloride adducts $SbCl_5$–$POCl_3$, $TaCl_5$–$POCl_3$, and $NbCl_5$–$POCl_3$ were shown to be monomeric and undissociated in benzene solution, but in nitrobenzene the degree of dissociation decreased along the series $SbCl_5$–$POCl_3$ > $NbCl_5$–$POCl_3$ > $TaCl_5$–$POCl_3$. (The solutions were nonconductors which eliminated ionic species (521).) The molecular weights of the parent pentahalides in nitrobenzene showed the presence of monomeric species, but at least for antimony pentachloride it seems likely that the species present in solution is $SbCl_5$–$C_6H_5NO_2$ (179, 244). The behavior of the system can probably be expressed by Eq. 1 and 2. Correlation of the degree of dissociation with stability is complicated in the absence of detailed knowledge of Eq. 1.

$$MCl_5 + C_6H_5NO_2 \rightleftharpoons MCl_5\text{–}C_6H_5NO_2 \qquad \text{(Eq. 1)}$$

$$MCl_5 + POCl_3 \rightleftharpoons MCl_5\text{–}POCl_3 \qquad \text{(Eq. 2)}$$

Holmes, *et al.* (244), measured the molecular weights and conductivity of the adducts PCl_5–Py (Py = pyridine) and $SbCl_5$–Py in nitrobenzene and showed them to be monomeric undissociated complexes, an important point in the subsequent discussion of the heats of formation of these and related adducts. Taken with the results of Voitovich (521) on $SbCl_5$–$POCl_3$ discussed above, pyridine is a better donor than phosphoryl chloride toward antimony pentachloride.

Kolditz and Preiss (303) were able to establish the species present in acetonitrile solutions of $SbCl_5$ by measurement of conductivity *and* molecular weight. The equivalent conductance of the solution, Λ_0 = 368 ohm^{-1} cm.^{2} mole^{-1}, indicated the presence of ionic species. The molecular weight determined ebullioscopically corresponds to the molecular weight of $SbCl_5$ thus eliminating equilibria of the type

$$SbCl_5(solv) \rightleftharpoons SbCl_4^+(solv) + Cl^-$$

(when if this equilibrium lay mainly to the right it would give an observed molecular weight ≃ one-half the formula weight). The ionization

$$2SbCl_5(solv) \rightleftharpoons SbCl_4^+(solv) + SbCl_6^-$$

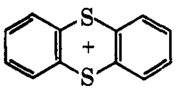
was suggested and subsequently confirmed (47). Kolditz and his co-workers have used molecular weight measurements extensively in their investigations of the ionic and covalent forms of phosphorus and antimony compounds in the solvents AsF_3 (291, 296), $AsCl_3$ (290), and CH_3CN (294, 303).

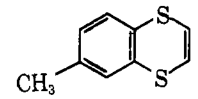
The 1:1 compounds between PCl_5 or PBr_5 and the iodine monohalides have been examined cryoscopically in nitrobenzene and a molecular weight approximately one-half of the calculated molecular weight was found (318, 382). This, together with the conductivity of the solutions, leads to the following ionization being proposed, *e.g.*

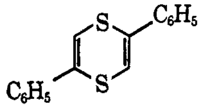
$$PBr_5\text{–}IBr \rightarrow PBr_4^+ + IBr_2^-$$

B. MAGNETIC PROPERTIES

Both diamagnetic and paramagnetic compounds have been investigated, usually by the Gouy method. Surprisingly the 1:1 adduct between $SbCl_5$ and thianthrene (diphenylene disulfide) is a paramagnetic solid (272, 273, 343), although the components are diamagnetic. Thianthrene itself when dissolved in concentrated sulfuric acid gives rise to the paramagnetic ion III which has been characterized by e.s.r. spectroscopy (228, 346). E.s.r. and ultraviolet measurements indicate the same ion to be present in $SbCl_5$–thianthrene while the magnitude of the paramagnetic susceptibility χ_M (897 × 10^{-6}/mole at room temperature) shows the presence of one unpaired electron per formula weight and make the anion diamagnetic (273). Lucken (343) suggests the $[Sb_2Cl_{10}]^{2-}$ ion. The analogous thianthrinium perchlorate has been prepared while 6-methyl-1,4-benzodithiin (IV) and 2,5-diphenyl-1,4-dithiin (V) also yields paramagnetic 1:1 adducts on reaction with $SbCl_5$. It was suggested that the formation of the radical ions is a property of the 1,4-dithiin ring (343). The adduct $SbCl_5$–$(C_6H_5)_2S$ is by contrast diamagnetic (343).


III


IV


V

The reaction of N-methyl-4,4′-dimethoxydiphenylamine with $SbCl_5$ yields a highly colored paramagnetic 1:1 addition compound (259). Spectra (ultraviolet, visible, and infrared) and magnetic measurements at a number of temperatures were taken and the compound was formulated as a radical salt

$$[(p\text{-}CH_3OC_6H_4)_2NCH_3]^+ \cdot {}^1/_2(SbCl_4^- + SbCl_6^-)$$

the anion being formulated as an equimolar mixture of Sb(III) and Sb(V) because of its lack of paramagnetism (*cf.* ref. 343). The compound obeyed the Curie–Weiss law and had a magnetic moment corresponding to one unpaired electron per formula weight. Closely related compounds using other substituted di- and triphenylamines with other anions (*e.g.*, ClO_4^-, $SbCl_6^-$) have been studied (219, 259), and in some cases a temperature-independent paramagnetism has been observed.

The magnetic moment of $PCrCl_8$ (PCl_5–$CrCl_3$) is approximately 3.6 B.M. at room temperature and was investigated over varying temperatures (300–100°K.). The data were put forward as supporting the ionic formulation $PCl_4^+CrCl_4^-$ containing distorted tetrahedral $CrCl_4^-$ ions, although other possibilities were not excluded (345).

A number of complexes formed between *p*-dimethylaminobenzenediazonium chloride and anhydrous chlorides including antimony pentachloride have been prepared and the magnetic susceptibility was measured (62). The results were interpreted as supporting charge-transfer interactions between the metal chloro anion and the diazonium cation.

C. DIPOLE MOMENTS

The dipole moments of only a small number of adducts have been determined and the data are summarized in Table IV. The dipole moment of $SbCl_5$ in carbon tetrachloride is ∼0 D. (499) as expected from a molecule with D_{3h} symmetry, and adduct formation is accompanied by a large increase in dipole due at least in part to the dipolar nature of the co-

TABLE IV
DIPOLE MOMENTS

Compound	Dipole moment, D.	Solvent[a]	Temp., °C.	Ref.
$SbCl_5$–CH_3OH	6.50	a	35	252
CH_3OH	1.67	a	30	351
$SbCl_5$–CH_3CN	7.80	a	35	252
CH_3CN	3.45	a	25	351
$SbCl_5$–C_6H_5CHO	8.65	a	35	252
C_6H_5CHO	2.80	a	25	351
$SbCl_5$–$2C_6H_5CO_2H$	6.44	a	35	252
$C_6H_5CO_2H$	1.65	a	30	351
$SbCl_5$–$2C_6H_5NO_2$	7.61	a	35	252
$C_6H_5NO_2$	3.91	a	30	351
$SbCl_5$–$2C_6H_5COCH_3$	8.66	a	35	252
$C_6H_5COCH_3$	2.96	a	25	351
$SbCl_5$–phenalenone	8.49	b	..	569
Phenalenone	3.89	a	..	569
	3.99	b	..	569

[a] a = benzene, b = dioxane.

ordinate bond. The 1:1 adducts show a much increased dipole over the free ligands. The 1:2 adducts (252) (see Table IV) form an interesting class of compounds, and it was stated, "The linearity of the plot of the dielectric constants of the solutions against the mole fraction of the solute, shows that the compounds are not dissociated in solution." Complete dissociation would presumably give rise to the same effect, and a molecular weight determination in solution would have established the point with more surety. (Details of the preparation and dipole moment measurements have been published (252a). Values of dipole moments reported in Table IV are unchanged, but in addition $SbCl_5$–$C_6H_5CO_2H$ has a dipole moment of 5.26 D. All the 1:2 adducts were found to be dissociated with a molecular weight equal to one-half the formula weight (from cryoscopic measurements in benzene).)

Lack of dissociation for the carboxylic acid adduct would not necessarily mean the presence of seven-coordinate antimony since hydrogen bonding may well be important, but the absence of experimental detail in the preliminary publication makes further comment impossible.

Detailed interpretation of the dipole moment data is in general complicated by the coordinate bond *not* lying in the same direction as the dipole moment, while dissociation into the components must be a possibility, particularly with the less powerful donors or acceptors. The results do, however, establish a pattern of behavior. The dipole moment of $SbCl_5$–$CH_3CO_2C_2H_5$ has been reported as 6.89 D., but no details were given (420).

D. CONDUCTIVITY AND POTENTIOMETRY

Conductivity measurements have been extensively used in experimental investigations, frequently to confirm or deny ionic formulations for the addition compounds; thus $NbCl_5$–C_2H_5CN (and $TaCl_5$–C_2H_5CN) is virtually a nonconductor in ethyl cyanide ($\Lambda_0 < 5$ ohm^{-1} cm.^{2} mole^{-1}) and was appropriately formulated as $CH_3CN \rightarrow NbCl_5$ (135), while the antimony analog $SbCl_5$–CH_3CN was found to be an extremely good conductor in acetonitrile ($\Lambda_0 = 368$ ohm^{-1} cm.^{2} mole^{-1}) and from this and other data was formulated as $[SbCl_4\text{–}2CH_3CN]^+[SbCl_6]^-$ (303). The magnitude of the extrapolated Λ_0 has been noted (47) and seems remarkably large compared with other uni-univalent electrolytes in acetonitrile (129). The rise in conductivity with time enables the change from molecular $CH_3CN \rightarrow SbCl_5$ to ionic $[SbCl_4\text{–}2CH_3CN]^+$-$[SbCl_6]^-$ to be followed (300). Many examples of this type of investigation have been reported in the literature and will not be discussed further.

In conjunction with conductivity measurements some workers have used ion-transport measurements to establish the nature of the species present in solution. Migration of Al to the anode and P to the cathode on electrolysis of PCl_5–$AlCl_3$ in nitrobenzene supported the $PCl_4^+AlCl_4^-$ formulation (140), subsequently confirmed by infrared spectroscopy (81). Conductivity measurements have been carried out using a variety of nonaqueous ionizing solvents (for reviews of properties and acid–base behavior in nonaqueous solvents, see ref. 124, 195, 197, 360, 505), and frequently such solvents provide convenient media for preparative reactions where more conventional solvents would be unsuitable.

Gutmann and his collaborators over a period of years have carried out investigations into nonaqueous solvent systems and interpreted the results in terms of a halide ion transfer process (although as pointed out in section IVB, this is not the complete story (360)). In addition to the spectroscopic techniques used to determine relative chloride donor–acceptor abilities of halides (see section IVB), a considerable number of titrations have been performed in nonaqueous solvents using both conductivity and potentiometry to follow the course of the titration. "Breaks" (changes in slope) in the curves of mole ratio of the two titrants *vs.* conductivity or e.m.f. are said to be associated with neutralization reactions and give the stoichiometry of the compounds formed. Electrodes used for potentiometric work include Ag–AgCl (for $AsCl_3$ solutions) (9) and Mo (for $POCl_3$ solutions (210, 211) and for $SOCl_2$ solutions (504)).

During the course of some titrations precipitation occurred, and analysis has confirmed the stoichiometry indicated by the titration curve, although in some cases molecules of solvent have been found in the complex; such molecules may well be essential in the complex (rather than loosely bonded solvates), *e.g.*, $SbCl_5$–$TiCl_4$–$2POCl_3$ (210) (*cf.* section VIIE). In many cases "breaks" in the curve are associated with unusual stoichiometries, and, where solid species have not been isolated and their chemical integrity established, the precise interpretation of such mole ratios must remain in doubt. (Mole ratios characterized only by an inflection in a titration curve are marked with an asterisk (*) in the tables.)

In addition to $[(CH_3)_4N][SbCl_6]$ the potentiometric titration of tetramethylammonium chloride *vs.* $SbCl_5$ in sulfuryl chloride gave evidence for $SbCl_5$–$2(CH_3)_4NCl$ (formulated $[(CH_3)_4N]_2{}^+[SbCl_7]^{2-}$) (193). Similarly titration of PCl_5 against $SbCl_5$ in the same solvent gave breaks corresponding to PCl_5–$SbCl_5$ and $2PCl_5$–$SbCl_5$ stoichiometries. The former is well known but the latter, formulated as $(PCl_4)_2{}^+(SbCl_7)^{2-}$, is probably better left as the species $2PCl_5$–$SbCl_5$–nSO_2Cl_2 (193). Radiochlorine exchange experiments between $SbCl_6^-$ and radiochloride ions in the solvent acetonitrile tends to rule out $SbCl_7{}^{2-}$ species (305). Spandau and Brunneck (504) found that $(C_2H_5)_4NCl$ potentiometrically titrated against $SbCl_5$ in thionyl chloride only gave evidence for a 1:1 complex, but pyridine (and some other nitrogen bases) gave inflections at Py/$SbCl_5$ mole ratios of 1:1, 2:1, 3:1 ?, and 4:1. Such titration experiments have been carried out in $POCl_3$ (22, 189, 190, 192, 194, 207, 210, 211); SO_2Cl_2 (193); $SOCl_2$ (192, 504); $AsCl_3$ (9, 187, 188, 191, 192); ICl (183, 186, 188); SO_2 (253); BrF_3 (557); C_6H_5COCl (213); $C_6H_5POCl_2$ (30, 31); $CH_3CO_2C_2H_5$ (421).

VI. THERMOCHEMISTRY

Although free energy data are the final requirement in complete thermodynamic calculation of stability, measurements have been confined to changes in enthalpy. Stone (509) has reviewed the energetics of complex formation for the group III adducts and much of this is applicable in the present context. It has been argued that heats of reaction can give some idea of the strength of donor–acceptor interaction (333), and certainly among closely related molecules, where the change in entropy is likely to be fairly constant, the heat of reaction will parallel the free energy change. The relevant thermochemical cycle is shown in Scheme I for a ligand (L) reacting with a pentahalide (MX_5) to form a 1:1 adduct (g = gas; l = liquid; s = solid; soln. = solution).

The published data has been tabulated (see Table V). A knowledge of the final state of the reactants is *vital* in any discussion of enthalpies of formation, and Holmes, *et al.* (244), were able to show for the pyridine and substituted pyridine adducts in Table V that the species present in solution were undissociated molecular addition compounds.

SCHEME I

$$\begin{tikzcd}
MX_5(g) + L(g) \arrow[r, "\Delta H_1"] \arrow[dr, "\Delta H_2"'] & MX_5,\ L(g) \\
MX_5(s) + L(g) \arrow[r, "\Delta H_6"'] & MX_5,\ L(s) \\
MX_5(\text{soln.}) + L(\text{soln.}) \arrow[r, "\Delta H_3"'] \arrow[ur, "\Delta H"'] & MX_5,\ L(\text{soln.}) \\
MX_5(l) + L(\text{soln.}) \arrow[u, "\Delta H\text{soln.}"'] \arrow[ur, "\Delta H_4"'] &
\end{tikzcd}$$

The so-called "relative donor strengths," which are of course relative heats of reaction, have been obtained for a number of donor sequences usually with antimony pentachloride as the acceptor. Provided that small differences in the enthalpy of formation are neglected the general trends are probably correct and reflect the trends in stability. The following order of donor strengths (ΔH_3) toward $SbCl_5$ in the solvent ethylene chloride have been found.

(a) $[(CH_3)_2N]_2CO > CH_3CON(CH_3)_2 = HCON(CH_3)_2 \gg (CH_3)_2CO$ (563)

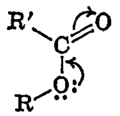
(b) $Ph_2SeO > (CH_3O)_2SeO$
$(CH_3)_3PO > (CH_3O)_3PO$
$(CH_3)_2SO > (CH_3O)_2SO$
$(CH_3)_2CO \approx CH_3CO_2C_2H_5$
$(CH_3)_2SO_2 > CH_3(CH_3O)SO_2$ (337)

(c) 1. $Ph_2SeO = Ph_3AsO > (CH_3)_3PO > (CH_3)_2SO$
2. $(C_2H_5)_2S > (CH_3)_2CO = CH_3CO_2C_2H_5 = (C_2H_5)_2CO = (C_2H_5)_2O$
3. $(CH_3)_2SO_2 > Ph_2SO_2 = POCl_3 = SeOCl_2 > SOCl_2$
$1 \gg 2 \gg 3$ (340)

(d) $C_4H_8S > C_4H_8O$
$POCl_3 \gg PSCl_3$ (564)

Using pyridine as a reference base Holmes, *et al.* (from the enthalpy change ΔH_4), determined the Lewis acid strength of a number of halides and found $BBr_3 > BCl_3 \sim SbCl_5 > PCl_3F_2 > BF_3 \gtrsim PCl_4F > PCl_5$ (244) (see Table V).

The small changes in enthalpies of reaction that are observed among closely related ketone and ester donors have been interpreted in terms of inductive and delocalization (mesomeric) effects. The keto oxygen atom in the esters being assumed to be the donor atom (supported by infrared data (566)), the ether oxygen atom can delocalize its lone pair of electrons and increase the electron density on the keto oxygen (VI) and hence its donor strength (406, 408).



VI

Detailed thermodynamic data are likely to be extremely complicated both to obtain and interpret, but a number of useful semiempirical correlations can be

TABLE V

HEATS OF REACTION

Acceptor	Donor	Enthalpy of formation ($-\Delta H$), kcal./mole	Enthalpy measured	Ref.	Solvent
$SbCl_5$	$(CH_3)_2N(CH_3)CO$	27.80 ± 0.08	ΔH_3	407	Ethylene chloride
$SbCl_5$	$((CH_3)_2N)_2CO$	29.64 ± 0.03	ΔH_3	407	Ethylene chloride
$SbCl_5$	$CH_3COC_2H_5$	17.43 ± 0.03	ΔH_3	406	Ethylene chloride
$SbCl_5$	$CH_3CO(i\text{-}C_3H_7)$	17.07 ± 0.03	ΔH_3	406	Ethylene chloride
$SbCl_5$	$CH_3CO(t\text{-}C_4H_9)$	16.95 ± 0.03	ΔH_3	406	Ethylene chloride
$SbCl_5$	$C_2H_5CO_2C_2H_5$	16.82 ± 0.03	ΔH_3	406	Ethylene chloride
$SbCl_5$	$(CH_3)_2CHCO_2C_2H_5$	16.44 ± 0.05	ΔH_3	406	Ethylene chloride
$SbCl_5$	$t\text{-}C_4H_9CO_2C_2H_5$	12.93 ± 0.03	ΔH_3	406	Ethylene chloride
$SbCl_5$	CH_3OH	24.1	ΔH_2	279	...
$SbCl_5$	C_2H_5OH	15.6	ΔH_2	279	...
$SbCl_5$	$i\text{-}C_3H_7OH$	11.6	ΔH_2	279	...
$SbCl_5$	H_2O	17.8	ΔH_2	279	...
$SbCl_5$	C_6H_5CHO	21.0	ΔH_5	123	CCl_4 + trace quinol
$SbCl_5$	CH_3Cl	8.92	ΔH_6	80	...
$SbCl_5$	C_5H_5N	28.3 ± 0.4	ΔH_3	244	$C_6H_5NO_2$
		38.7 ± 0.8	ΔH_4	244	$C_6H_5NO_2$
$SbCl_5$	3-Methylpyridine	36.6 ± 1.0	ΔH_4	244	$C_6H_5NO_2$
$SbCl_5$	4-Methylpyridine	41.4 ± 1.0	ΔH_4	244	$C_6H_5NO_2$
$SbCl_5$	4-Ethylpyridine	41.1 ± 0.9	ΔH_4	244	$C_6H_5NO_2$
$SbCl_5$	4-Isopropylpyridine	40.5 ± 0.9	ΔH_4	244	$C_6H_5NO_2$
PCl_5	Pyridine	22.0 ± 0.2	ΔH_3	244	$C_6H_5NO_2$
PCl_4F	Pyridine	27.0 ± 0.2	ΔH_3	244	$C_6H_5NO_2$
PCl_3F_2	Pyridine	35.3 ± 0.3	ΔH_3	244	$C_6H_5NO_2$
$SbCl_5$	$(CH_3)_2CO$	17.03 ± 0.04	ΔH_3	408	Ethylene chloride
$SbCl_5$	$MeO(CH_3)CO$	16.38 ± 0.03	ΔH_3	408	Ethylene chloride
$SbCl_5$	$EtO(CH_3)CO$	17.08 ± 0.05	ΔH_3	408	Ethylene chloride
$SbCl_5$	$i\text{-}PrO(CH_3)CO$	17.53 ± 0.05	ΔH_3	408	Ethylene chloride
$SbCl_5$	$EtO(Pr)CO$	16.76 ± 0.05	ΔH_3	408	Ethylene chloride
$SbCl_5$	$(MeO)_2CO$	15.17 ± 0.03	ΔH_3	408	Ethylene chloride
$SbCl_5$	$(EtO)_2CO$	15.98 ± 0.05	ΔH_3	408	Ethylene chloride
NbF_5[a]	NH_3	7.87	ΔH_2	85	...
NbF_5[a]	Pyridine	22.96	ΔH_2	85	...
NbF_5	NOF	20.5	ΔH_2	91	...
VF_5	NOF	18.00	ΔH_2	91	...
VF_5	NO_2F	13.75	ΔH_2	91	...
AsF_5	SF_4	31.0 ± 0.8	ΔH_2	38	...
$TaCl_5$	KCl	22.0 ± 0.8	c	574	...
PF_5	Me_2O	25.4	ΔH_2	168	...
PF_5	$(n\text{-}Pr)_2O$	10.8	b	168	...
PF_5	$(n\text{-}Bu)_2O$	12.1	b	168	...
PF_5	$(i\text{-}Pr)_2O$	14.0	d	168	...
PF_5	Me_2S	24.6	ΔH_2	168	...
PF_5	Et_2S	10.7	b	168	...
PF_5	Me_2Se	20.2	ΔH_2	168	...
SbF_5	BrF_3	27.8	ΔH_2	110 (*cf.* 109)	...

[a] Stoichiometry NbF_5–2Ligand. [b] Measured from the system $PF_5L(l) \rightarrow PF_5(g) + L(l)$. [c] $TaCl_5\text{–}KCl(s) \rightarrow TaCl_5(g) + KCl(s)$. [d] $PF_5\text{–}L(s) \rightarrow PF_5(g) + L(l)$.

obtained from the measured enthalpies of reaction if sufficient caution and detail in experiment is exercised. The limited amount of data available suggest that the complexes are dissociated in the gas phase, making ΔH_1 experimentally inaccessible. It has been suggested that the heat of formation in an inert solvent (ΔH_3) would closely parallel the heat of formation in the gas phase (ΔH_1) (408) and in the absence of conflicting experimental evidence seems a reasonable assumption. In nitrobenzene (certainly not an inert solvent) the heat of solution of $SbCl_5$ is 10.4 ± 0.4 kcal./mole (244) enabling ΔH_4 to be calculated from the experimentally found ΔH_3.

The heat of reaction of pyridine with $SbCl_5$ in the solvent acetonitrile is -11.0 kcal./mole (209), but comparison with the data using nitrobenzene as solvent is meaningless without a knowledge of the species present in solution (*cf.* section IIB). The heats of formation of some metal hexachloroniobates and -tantalates have been measured (500).

TABLE VI

ADDITION COMPOUNDS OF PF_5

Other molecule (X)	Ratio PF_6/X	Ref.
C_5H_5N	1:1	376, 556
C_6H_5CHO	1:1	556
CH_3CN	1:1	556
$O(C_2H_4)_2O$	1:1	556
$CH_3COC_2H_5$	1:1	556
$C_2H_5COOCH_3$	1:1	556
$[(CH_3)_2CH]_2CO$	1:1	556
$(CH_2)_5CO$	?	556
$(CH_3)_3N$	1:1	168, 376
$(CH_3)_2NCHO$	1:1	376
$(CH_3)_2NCHS$	1:1	376
$(CH_3)_2CNOH$	1:1	376
$(CH_3)_2SO$	1:1	376
$(C_2H_5)_2O$	1:1	376
$(CH_2)_4O$	1:1	376
$(CH_2)_5O$	1:1	376
$C_5N_{10}O$[a]	1:1	376
NO_2F	1:1	18, 106, 225, 316, 400. 558, 561
N_2O_4	2:1	376, 513
ClO_2F	1:1	463
SF_4	Interaction	409
MF	1:1	53, 56–58, 77, 98, 99, 320, 430, 443, 479, 507
$(C_5H_5)Fe(CO)_3F$	1:1	270
$(C_7H_9)Fe(CO)_3F$	1:1	270
$(C_8H_9)Fe(CO)_3F$	1:1	270
PBr_4F[b]	1:1	296
NOF[c]	1:1	320, 479, 490, 551
$(CH_3)_4NF$	1:1	129, 479
$N_2C_6H_4C_6H_4N_2F_2$	2:1[d]	320, 479
PCl_4F[e]	1:1	264, 265, 289, 292
$(n\text{-}C_4H_9)_4NF$	1:1	129
$(C_6H_5)_4AsF$[f]	1:1	4
RCOF[g]	1:1	400, 403
$O_2^+F^-$	1:1	503, 561
XeF	1:1	100
$XC_6H_4N_2F$[h]	1:1	76
$(CH_3)_2NH$[i]	1:1	72
HNF_2[j]	1:1	112
NF_3	...	112
N_2F_4	...	112
CH_3NF_2[k]	1:1	112
CH_3PF_4	1:1	377
$(CH_3)_2PF_3$	1:1	377
$(CH_3)_2O$	1:1	168
$(C_2H_5)_2O$	1:1	168
$(n\text{-}C_3H_7)_2O$	1:1	168
$(n\text{-}C_4H_9)_2O$	1:1	168
$(i\text{-}C_3H_7)_2O$	1:1	168
$(CH_3)_2S$	1:1	168
$(C_2H_5)_2S$	1:1	168
$(CH_3)_2Se$	1:1	168
$C_6N_3OCH_3$[l]	...	168
$C_6H_5OC_2H_5$[m]	...	168
$(C_2H_5)_3N$	1:1	168
$(t\text{-}C_4H_9)OC_2H_5$	Reaction	168

[a] $C_5H_{10}O$ = 2-methyltetrahydrofuran. [b] $PBr_4^+PF_6^-$. [c] $\nu(NO) = 2358$ cm.$^{-1}$. [d] Diphenylene 4,4′-tetrazonium hexafluorophosphate. [e] $PCl_4^+PF_6^-$. [f] Used for gravimetric determination of PF_6^- ion. [g] R = CH_3, C_2H_5, C_6H_5, $(CH_3)_3C$, $(C_2H_5)_3C$, $(C_6H_5)_3C$. [h] X = p-CH_3, p-Cl, p-NO_2, m-NO_2. [i] At 100° loses HF → Me_2NPF_4. [j] Decomposes to N_2F_2, HF, PF_5. [k] Decomposes to HCN, HF, PF_5. [l] At 0° and −35.8°. [m] At 0°.

VII. DISCUSSION OF VARIOUS GROUPS OF ACCEPTORS

There seems little value in discussing all the observed addition compounds shown in Tables VI to XXIV, and in the following sections only some of the better established or more unusual compounds will be presented. Readers with an interest in specific compounds will no doubt wish to refer to the original literature.

A. PF_5, AsF_5, SbF_5, BiF_5 (TABLES VI, IX, XI, AND XIV)

Nearly all the reported adducts of phosphorus and arsenic pentafluoride have 1:1 stoichiometry presumably based on a six-coordinate group V atom. The formation of octahedral $[MF_6]^-$ ions has been established by X-ray analysis for phosphorus, arsenic, and antimony (see Table I), and the stability of these ions has led a number of authors to give ionic formulations to some adducts. With organic ligands such as pyridine the ^{19}F n.m.r. data for PF_5, AsF_5, and SbF_5 show the molecule to have the stereochemistry shown in Figure 1a (375, 376, 381). Seel and Detmer (476, 478) examined the 1:1 adducts between SF_4, SOF_4, ClF_3, IF_7, BrF_3, and AsF_5 or SbF_5 and from detailed infrared and conductivity data on *some* of the compounds formulated them all as ionic solids containing the hexafluoride ion of arsenic or antimony. The situation is not simple since SF_4 and SiF_4 (a powerful fluoride ion acceptor) shows no interaction and the ^{19}F n.m.r. spectrum of the system sulfur tetrafluoride–antimony pentafluoride led to the 1:1 adduct SF_4–SbF_5 being formulated as containing fluorine bridges (409). One structure is shown in Figure 2, but other species are possible.

The compounds $[MCl_3][AsF_6]$ (M = S, Se, Te) have been prepared (307, 308) and studied conductiometrically in acetonitrile. The Λ_0 value (161 (S), 187 (Se), 205 (Te) ohm^{-1} cm.^{2} mole^{-1}) is in the region for a uni-univalent electrolyte supporting the ionic formulation (in solution).

The stoichiometric ratios exhibited by antimony pentafluoride are more varied than the pentafluorides of phosphorus, arsenic, or bismuth (only 1:1 is observed). The phase diagram for the system SbF_5–

TABLE VII

ADDITION COMPOUNDS OF PCl_5

Other molecule (X)	Ratio PCl_5/X	Ref.
$(C_2H_5)_2O$	3:2	322
$(CH_3)_3P$[a]	. . .	240
	1:2[b]	240
$(CH_3)_3N$	Reaction	240
$(C_2H_5)_3N$[c]	Reaction	46, 240, 516
C_5H_5N	1:1	46, 236, 244
Isoquinoline	1:5	399
$(C_2H_5)_4NCl$	1:1	30, 31, 210, 299, 504
BF_3	1:1	528–530
BCl_3	1:1	167, 169–171, 177, 235, 238, 355, 431, 528, 530, 532, 573
	1:2	528, 529
BBr_3	1:2	512
B_2Cl_4	2:1	232
$AlCl_3$	1:1[d]	40, 41, 81, 140, 144, 157, 169–171, 174, 178, 235, 367, 431, 476, 534, 543
$GaCl_3$	1:1[e]	165, 166, 235, 237, 431
$TlCl_3$	1:1	169–171, 177, 431
$FeCl_3$	1:1	24, 25, 30, 31, 40, 41, 114, 115, 140, 154, 169–171, 204, 534
	1:2	34
$CrCl_3$	1:1	114, 115, 169–172, 175, 345
$AuCl_3$	1:1	169–171, 332
$AsCl_5$	1:1	114, 185, 239, 309
$SbCl_5$	1:1	30, 31, 47, 114, 115, 169–172, 175, 186, 193, 210, 291, 450, 535
	2:1*	193
$MoCl_5$	1:1	114, 115, 169–172, 175, 502
WCl_6	1:1	114, 115, 169–172, 175
$SnCl_4$	1:1	40, 41, 79, 84, 169–172, 175, 177, 537
	2:1	79, 169–172, 175, 177
$TiCl_4$	1:1	34, 159, 169–172, 175, 177, 188, 426, 517, 537, 538
	2:1*[h]	171, 426
VCl_4	1:1	169–172, 175, 302
	2:1	192
	3:1	192
$ZrCl_4$	. . .	359, 501
	2:1	169–171, 207
	2:3	180
	1:1[i]	207, 391
	1:2	14, 137, 207, 391
$SeCl_4$	1:1	40, 41, 169–171, 326, 363
$TeCl_4$	1:1	169–172, 175, 177, 191
	1:2	191, 363
	2:1	170–172, 175, 177, 191
$PtCl_4$	2:1	40, 41, 169–171
PCl_5	1:1[j]	10, 47, 90, 157, 530
CCl_4	2:1	312
$AsCl_3$	2:5	290
$SbCl_3$	1:2 (2:4)	290
$(CF_3)_3SbCl_2$	. . .	116
$TaCl_5$	1:1	181, 300
$TaCl_5$–$AsCl_3$	1:1:1	300
$NbCl_5$	1:1	181, 298
ICl	1:1	40, 41, 141, 142, 318, 174, 436, 568
IBr	1:1	382
$NbCl_5$–$AsCl_3$	1:1:1	298
UCl_5	1:1	416
CH_3CN	. . .	47, 425
$POCl_3$	. . .	189, 520
C_7H_7Cl	1:2	75
$PNCl_2$	1:1	176
$PNCl_2$	1:n[k]	344
SO_3	1:1	529, 530
$(C_6H_5)_3PO$	Reaction	152
C_5H_5N–$POCl_3$	1:1:1	194
$(C_2H_5)_3PO$	Reaction	101
Phenalenone	1:1	571
$GeCl_4$	. . .	527
	1:1*	171
	2:1*	171
MCl	. . .	188
	1:1*	183, 188
$(CH_3)_4NCl$	1:1	143, 188
PCl_4Br	1:1[m]	297
Br_2	1:5	434
PCl_4F	1:1[n]	265
R_2NPCl_4	1:1[o]	366
$ZnCl_2$	1:1	169–172, 175
$HgCl_2$	1:1	169–172, 175
$BiCl_3$	3:1	169–171
$SbCl_3$	3:1?	169, 171
CrO_2Cl_2	1:1	172, 173, 175
$MgCl_2$	. . .	170, 172, 175
$CdCl_2$	1:1	170–172, 175
$InCl_3$	. . .	431
$[(p\text{-}CH_3C_6H_4)_2N]_2$	1:1	544
$(C_6H_5)_3CCl$	1:1*[p]	204
	1:4*[q]	202
$SiCl_4$	. . .	392
$(CH_3)_3As$	Reaction	241
$(CH_3)_3Sb$	Reaction	241
$SbCl_5$–ophen	1:1:1[r]	44
$SeOCl_2$	Reaction[s]	325
$(CH_3)_2NNO$	1:1	468

[a] 0–100°. At 100°; also in C_6H_5Br. [c] Reference 516 reports 1:1 and 1:2.5. [d] M.p. 343°. [e] M.p. 368–371°. [f] M.p. 332°. [g] M.p. 120°. [h] Conductivity titration in $POCl_3$. Breaks at 1:1 and 2:1 (171). [i] M.p. 365°. [j] $PCl_4^+PCl_6^-$. [k] n normally > 10. [l] Conductivity titration in $POCl_3$. [m] Formulated as $PCl_4^+PCl_5Br^-$. [n] Formulated as $PCl_4^+PCl_5F^-$. [o] R = CH_3, C_2H_5, i-C_4H_9. [p] Soluble in C_6H_5COCl. [q] Solution in MeCN. [r] Formulated as $[PCl_4(ophen)]^+[SbCl_6]^-$. ophen = 1,10-phenanthroline. [s] Gives $POCl_3$ + $SeCl_4$.

TABLE VIII

ADDITION COMPOUNDS OF PBr_5

Other molecule (X)	PBr_5/X	Ref.
CCl_4	1:2	312, 436
IBr	1:1	142, 184, 317, 318, 436
$SnBr_4$	1:1	217
	1:2	217
MeCN	...	217
$C_6H_5NO_2$	...	217
ICl	1:1	382
BBr_3	1:1	511

TABLE IX

ADDITION COMPOUNDS OF AsF_5

Other molecule (X)	AsF_5/X	Ref.
SF_4	1:1	36–38, 478
SeF_4	1:1	36–38, 478
TeF_4	1:1	36
SCl_3F	$1:1^a$	307, 308
$SeCl_3F$	$1:1^b$	307, 308
$TeCl_3F$	$1:1^c$	307, 308
SOF_4	1:1	476, 478
ClF_3	1:1	87, 402, 478
BrF_3	1:1	402
IF_7	1:1	476–478
ClO_2	1:1	464
Cl_2O	$1:1^d$	465
ClO	1:1	465
ClO_2F	1:1	462–464
NO_2	1:1	20, 465
NO_2F	1:1	18, 225, 316, 400, 464, 558, 561
NOF	1:1	452, 456, 464, 474
MF	1:1	17; 99, 121, 304, 311, 430, 433, 444
$AsCl_4F$	$1:1^e$	122, 288
C_5H_5N	1:1	375
$RCOF^f$	1:1	400, 403
IO_2F	$1:1^g$	21, 433, 466
KrF_2	Adduct (V, unstable)	485
$(CH_3)_3SnF$	1:1	92, 93
XeF_6	1:1	484
$O_2^+F^-$	1:1	561
$C_6H_5N_2F$	1:1	304
cis-N_2F_2	1:1	575

[a] SCl_3AsF_6. [b] $SeCl_3AsF_6$. [c] $TeCl_3AsF_6$. [d] Decomposes at −50° to $ClO–AsF_5$ and Cl_2. [e] $AsCl_4^+AsF_6^-$ proposed. [f] R = CH_3, C_2H_5, C_6H_5, $(CH_3)_3C$, $(C_2H_5)_3C$, $(C_6H_5)_3C$. [g] $IO_2^+AsF_6^-$ proposed from infrared analysis.

BrF_3 shows the presence of four compounds (145) but the 1:1 is best characterized and has been formulated as an ionic solid $[BrF_2]^+[SbF_6]^-$ following conductance data for SbF_5 in bromine trifluoride (557). The nature of the compounds $SbF_5–3BrF_3$, $2SbF_5–3BrF_3$, and $3SbF_5–BrF_3$ is not clear. Adducts between xenon difluoride and antimony and tantalum pentafluoride have been reported and the compounds $XeF_2–2SbF_5$ and $XeF_2–2TaF_5$ (127) isolated. The analogous krypton compound $KrF_2–2SbF_5$ (485) is known. An unstable compound between KrF_2 and AsF_5 has been reported (485) and $XePF_6$ (and possibly $XeSbF_6$) prepared (100). It has been suggested on the basis of the diamagnetism and the volatility of $XeF_2–2MF_5$ (M = Sb, Ta) that the bonding involves fluorine bridges

$$F_5M–F–Xe–F–MF_5 \quad (127)$$

TABLE X

ADDITION COMPOUNDS OF $AsCl_5$

Other molecule (X)	$AsCl_5/X$	Ref.	Comments
$AlCl_3$	1:1	239, 309	Condy.[a] of $AlCl_3–AsCl_3–Cl_2$, m.p. 80° (dec.) (309)
$GaCl_3$	1:1	239, 309	Condy. of $GaCl_3–AsCl_3–Cl_2$, m.p. ~5° (309)
$FeCl_3$	1:1	239, 309	Condy. of $FeCl_3–AsCl_3–Cl_2$ (309)
$AuCl_3$	1:1	239, 309	Condy. of $AuCl_3–AsCl_3–Cl_2$ (309)
PCl_5	1:1	114, 185, 239, 309	
$SbCl_5$	1:1	185, 239, 309	
$TaCl_5$	1:1	309	Condy. of $TaCl_5–AsCl_3–Cl_2$
KCl	...	185	
Me_4NCl	...	185	
$(CH_3)_3PO$	1:1	338, 339	Orange crystals decomp. ~50°
$(C_2H_5)_3N$	1:1	516	
$SiCl_4$	...	309	Condy.[a] of $SiCl_4–AsCl_3–Cl_2$
$TiCl_4$	...	309	Condy. of $TiCl_4–AsCl_3–Cl_2$
$SnCl_4$	...	309	Condy. of $SnCl_4–AsCl_3–Cl_2$

[a] Conductivity.

The complexes formed between nitrosyl fluoride (NOF) or nitryl fluoride (NO_2F) and the pentafluorides of P, As, or Sb have been shown from infrared measurements to contain the nitrosonium ion (NO^+) or the linear nitronium ion (NO_2^+) in the solid state (106, 490).

The compounds formed between BiF_5 and metal fluorides MF (M = Li, Na, K, Ag) probably contain BiF_6^- ion (146), and the bromine trifluoride adduct with BiF_5 has been formulated as $[BrF_2]^+[BiF_6]^-$ (203).

Phosphorus pentafluoride has been reported as a conductor in acetonitrile (425). Acyl and alkyl fluoride complexes have been discussed in section IVC. The compound $PF_5–(CH_3)_2NH$ when heated at 100° decomposes to HF and dimethylaminotetrafluorophosphorane (72).

A number of displacement reactions have been studied, some of which are given below.

$$IF_7–AsF_5 + KF \rightarrow KAsF_6 + IF_7 \quad (477)$$

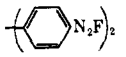
$$IF_7–3SbF_5 + 3KF \rightarrow 3KSbF_6 + IF_7 \quad (477)$$

$$IF_7 \rightarrow IF_5 + F_2 \quad (477)$$

$$SF_4–SbF_5 + KF \rightarrow KSbF_6 + SF_4 \quad (476)$$

TABLE XI

ADDITION COMPOUNDS OF SbF_5

Other molecule (X)	SbF_5/X	Ref.
AsF_5	1:1	379, 559
SbF_3	1:2	559
	1:5	559
SF_4	1:1	36–38, 409, 478
SeF_4	1:1	36–38
TeF_4	1:1	36
SOF_4	1:1	478
ClF_3	1:1	402, 476, 478
BrF_3	1:3	145
	2:3	145
	1:1[a]	109, 110, 145, 402, 464, 494, 495, 554, 555, 557
	3:1	145
BrF_5	2:1	467
Xanthone	1:1?	104
$O_2^+F^-$	1:1	561
IF_5	1:1	375, 552, 559
IF_7	3:1	477, 478
ClO_2	1:1	464
NO_2F	1:1	18, 106, 225, 400, 483, 558
NO_2	1:1	20
SO_2	1:1	20
IO_2F	1:3[b] or 1:1	19
	0.8:1	21
ClO_2F	1:1	463, 464, 555
$(CH_3)_2PF_3$	1:1	377
$C_2H_5PF_4$	1:1	377
S	2:1	20
	1:1	454
Se	2:1	20
Te	5:1	20
HCl	1:1[c]	295
HF	1:5	487
N_2F_4	2:1	451
	3:2?	451
NOF	1:1[d]	35, 451, 452, 456, 474, 490
KrF_2	2:1	485
XeF_2	2:1[e]	127, 233
XeF_6	1:1	155
	1:2	155
	2:1	155
XeF	1:1	100
MF (K)	1:1	35, 59, 97, 98, 248, 306, 311, 319, 430, 451
(Tl)		471
(Na)		97, 267, 311, 319, 451, 470
(Cs)		311, 471
(NH_4)		319, 471
(Rb)		311, 319, 471
(Ag)		52, 97
$(CH_3)_3SnF$	1:1	92, 93
$SbCl_4F$	1:1[f]	222, 301
$AsCl_4F$	1:1[g]	310
C_5H_5N	1:1	375
$(CH_3)_3N$	1:1	375
$(CH_3)_2SO$	1:1	375
$(CH_3)_2NCHO$	1:1	375
$[(CH_3)_2N]_2CO$	1:1	375
Br_2	2:1	454
I_2	2:1	454
	4:1	454
	2:1	319
NOCl	1:1	531
SO_3	1:1	160
RCOF[h]	1:1	400, 403, 405
RF[i]	1:1	401

[a] Reference 110 corrects error in calculation of ref. 109. [b] Analysis given for 1:3 but text refers to 1:1. [c] At −75° (exchange occurs at higher temp.). [d] $NO^+SbF_6^-$; $\nu(NO) = 2350$ cm.$^{-1}$. [e] M.p. 63°. [f] $SbCl_4^+SbF_6^-$ proposed (301); see, however, ref. 119 and 378. [g] $AsCl_4^+SbF_6^-$ proposed. [h] R = CH_3, C_2H_5, C_6H_5, $(CH_3)_3C$, $(C_2H_5)_3C$, $(C_6H_5)_3C$. [i] R = alkyl.

The driving force for such reactions is probably the volatility of the IF_7 (or SF_4) and thus says nothing about relative stability. Similarly the reactions

$$SF_4\text{–}MF_5 + SeF_4 \rightarrow SeF_4\text{–}MF_5 + SF_4 \ (M = As, Sb) \quad (37, 38)$$

$$SeF_4\text{–}AsF_5 + SbF_5 \rightarrow SeF_4\text{–}SbF_5 + AsF_5 \quad (38)$$

have been observed.

There is no evidence that the pentafluorides under discussion can have a coordination number greater than six.

B. PCl_5, R_nPCl_{5-n}, PF_nCl_{5-n} (TABLES VII AND XXIV)

The reported stoichiometries for molecular addition compounds of phosphorus pentachloride show much variety but with a preference for 1:1 and 2:1 ($2PCl_5$–A) mole ratios. The PCl_5 molecule can both lose a chloride ion (in the presence of a Cl^- acceptor) to give PCl_4^+ ions or act as an electron pair acceptor, for example, in the PCl_6^- ion, and *solid* phosphorus pentachloride is found to consist of PCl_4^+ and PCl_6^- ions (90). With oxygen donors only the compounds $3PCl_5$–$2(C_2H_5)_2O$ (322) and PCl_5–phenalenone (571) have been reported, while with OH containing molecules reaction occurs with the elimination of HCl (286). With nitrogen donors complexes are nearly as scarce; trimethylamine (240) and triethylamine (46, 240) react and acetonitrile does not form a complex with PCl_5 (47, 425), although earlier work by Trost suggests the compounds PCl_5–$(C_2H_5)_3N$ and PCl_5–$2.5(C_2H_5)_3N$ (516). Pyridine with PCl_5 (46, 236, 244), PCl_4F, and PCl_3F_2 (242–244) forms 1:1 adducts (see section VI) while with dichlorotrifluorophosphorane the adduct $2PCl_2F_3$–3Py was isolated (242). (Chlo-

TABLE XII

ADDITION COMPOUNDS OF $SbCl_5$

Other molecule (X)	$SbCl_5$/X	Ref.
$(CH_3)_4NCl$	1:1	9, 22, 49, 187, 188, 193, 211, 253
	1:2*	193, 479
$(C_2H_5)_4NCl$	1:1	30, 31, 211, 504
C_5H_5N	1:1	49, 209, 236, 244, 247, 395, 504, 533
	1:2*	504
	1:3*?	504
	1:4*	504
	2:3	247
C_5H_5NO	1:1	227
$(CH_3)_3N$	1:1	61, 240
$(C_2H_5)_3N$	1:1	61, 240, 504, 516
NH_3	1:6	364
S_4N_4	1:1	118, 387, 388, 549
C_6H_5CN	1:1	276
ClCN	1:1	7, 285, 553
CH_3CN	1:1	47, 221, 252, 300, 303
$POCl_3$	1:1	2, 5, 9, 22, 67, 68, 190, 206, 208, 268, 269, 323, 334, 335, 340, 358, 397, 506, 535, 564
$POCl_3$	2:1	323
$PO(CH_3)_3$	1:1[a]	67–69, 268, 337–340, 565
$PO(C_6H_5)_3$	1:1[b]	338–340
$PSCl_3$	1:1	256, 564
$P_2O_3Cl_4$	2:1[c]	341, 342
$TiCl_4$–$POCl_3$	1:1:3	2, 3, 29
$TiCl_4$–$POCl_3$	1:1:2	210
BCl_3	. . .	235
	1:1*[d]	30
$FeCl_3$	. . .	210
PCl_5	1:1	30, 31, 47, 114, 115, 169–172, 175, 186, 193, 210, 291, 450, 535
	1:2*	193
$(CH_3)_3PCl_2$	1:1	113
$(CH_3)_3P$	1:2	240
	1:1	240
$(CH_3)_3As$	Reaction	241
$(CH_3)_3Sb$	Reaction	241
$(CH_3)SbCl_4$	Complex	113
$AsCl_5$	1:1	185, 309
$AsCl_3$	1:1	187
	. . .	5
$ZrCl_4$	1:2	207
CH_3OH	1:1	252, 279, 546, 547
$(CH_3)_2O$	1:1	277, 546
$(C_2H_5)_2O$	1:1[e]	277, 280, 340, 361, 362, 546, 547
$(CH_2)_4O$	1:1	564
C_2H_5OH	1:1	279, 394, 547
	1:2*	394
$(CH_3)_2CHOH$	1:1	279
H_2O	1:1	11, 12, 279
$O(C_2H_4)_2O$	2:1	362
CH_3CHO	1:1	282, 449
C_6H_5CHO	1:1	123, 252, 282, 449
$(CH_3)_2CO$	1:1	282, 337, 340, 408, 449, 563
$(C_2H_5)_2CO$	1:1	340
$C_6H_5CO_2C_2H_5$	1:1	449
$CH_3CO_2C_2H_5$	1:1	340, 394, 408, 420, 566
	2:1*	420
	1:2*	394
$HCO_2C_2H_5$	1:1	395, 566
$C_8H_{12}O_4$[f]	2:1	226
$C_8H_{12}O_4$[g]	2:1	226
$C_{12}H_{14}O_4$[h]	2:1	226
$C_7H_8O_2$[i]	1:1	103, 362
C_6H_5COCl	2:3	449
	1:1	362, 403, 418
CH_3CONH_2	2:3	449
CH_3COCl	1:1	362, 394, 403, 420, 423, 472
$C_6H_5NO_2$	2:3	449
	1:1	179, 244, 353
	1:2	252, 353
CH_3CO_2R	1:1	283, 408
$(CH_3)_2NCON(CH_3)_2$	1:1	407, 563
$HCON(CH_3)_2$	1:1	15, 66, 227, 563
$CH_3CON(CH_3)_2$	1:1	66, 407, 563
$SO_2(CH_3)_2$	1:1	68, 214, 336, 337, 340
$SO(C_6H_5)_2$	1:1	67, 68, 215, 216, 336
$SO_2(C_6H_5)_2$	1:1	336, 340
$SOCl_2$	1:1	336, 340, 506
SO_2Cl_2	1:1	336
$(CH_3)_2S$	1:1	60, 274, 275
R_2SO_2	1:1	281
$(CH_2)_4S$	1:1	275, 564
$(C_2H_5)_2S$	1:1	275, 340
$(C_6H_5)_2S$	1:1	343
R_2S	1:1	274
$SO(CH_3)_2$	1:1	336, 337, 340
$(p\text{-}(CH_3)_2NC_6H_4)_2NC_6H_5$	1:1	352
NOCl	1:1	16, 224, 327–329, 442, 450, 472, 473, 475, 479, 480, 482, 490, 492, 510, 540
NO	2:1	51, 64
NO_2Cl	1:1	481

TABLE XII (*Continued*)

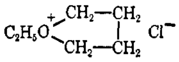
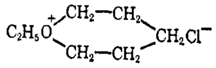
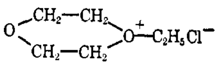
Other molecule (X)	$SbCl_5/X$	Ref.
$VOCl_3$	...	199
	1:1	170
ClO_2	1:1	399
ICl	1:2	139, 164, 457
	1:3	139, 164, 457
$C_6H_5N_2Cl$	1:1	386, 440
SCl_4	1:1	170–172, 175, 356, 417, 445, 453, 455, 535
$SeCl_4$	1:1	169–172, 175, 356, 535
$TeCl_4$	1:2	191
	1:1	169–172, 175, 191, 324, 356
$(C_6H_5)_3AsO$	1:1	340, 432
$(C_6H_5)_2SeO$	1:1	337, 340
$SeOCl_2$	1:1	5, 68, 223, 340, 536, 537
	1:2	548
ICl_3	1:1	525, 526
CH_3CO_2H	1:1	283, 284, 447, 518, 566
	1:2	518
HCO_2H	1:1	284, 395, 566
$C_{25}H_{30}N_3Cl^k$	1:1*	39
	2:1*	39, 198, 208
	4:1*	198, 208
Thianthrene	1:1	272, 273, 343
CH_3Cl	1:1	80, 385
$AlCl_3$–$POCl_3$	3:1:6	26
	1:1:3	196
	1:1:2	190
$C_9H_8S_2{}^l$	1:1	343
$C_{16}H_{12}S_2{}^m$	1:1	343
$ZrCl_4$–$POCl_3$	1:1:2	207
$AlCl_3$	1:1	210
	2:1*^{n}	30
$NaCl$	1:1	313
KCl	1:1	183, 212, 254, 255, 459, 539
$RbCl$	1:1	170, 171, 173
$C_6H_5COCH_3$	1:2	252
	1:1	282
$C_6H_5CO_2H$	1:2	252
$(CH_3)_2CO_3$	1:1	408
$(C_2H_5)_3CO_3$	1:1	408
$CH_3CO_2CH_3$	1:1	284, 408
$CH_3CO_2C_3H_7$	1:1	408
$C_3H_7CO_2C_2H_5$	1:1	394, 395, 408
$(C_6H_{11})_3PCl_2$	1:1	249
$(C_6H_5)_3PCl_2$	1:1	249, 450
PBr_3Cl_2	1:1	450
$C_6H_5OPCl_4$	1:1	450
$[(C_2H_5)_2N]_3PCl_2$	1:1	450
$[(C_2H_5)_2N]PCl_4$	1:1	450
$(C_6H_5)_2PCl_3$	1:1	450
$(C_6H_5)PCl_4$	1:1	450
$AuCl_3$	1:1	498
$C_2H_5CO_2H$	1:1	395, 518
	1:2	518
$C_3H_7CO_2H$	1:1	518
	1:2	518
$C_9H_7N^o$	1:1*	504
	1:2*	504
	1:3*	504
$(C_6H_5)_2NH$	1:1*	504
	1:2*	504
	1:3*	504
$(C_6H_5)N(C_2H_5)_2$	1:1*	504
	1:2*	504
	1:3*	504
$(CH_3)_3O^+Cl^-$	1:1	278, 361
$(C_2H_5)_3O^+Cl^-$	1:1	227, 361, 278
$(C_3H_7)_3O^+Cl^-$	1:1	278
$(C_4H_9)_3O^+Cl^-$	1:1	278
	1:1	361
	1:1	361
	1:1	361
$TiCl_4$	...	384, 171
	1:1*^{p}	30, 31
p-$(CH_3)_2NC_6H_4N_2Cl$	1:1^q	62, 63, 257
$C_6H_{10}O^r$	1:1	282, 506
C_9H_7N–$C_6H_5COCl^s$	1:1:1	419
RNH_3Cl	1:1	182
$RR'NH_2Cl$	1:1	182
$RR'R''NHCl$	1:1	182, 280
$RR'R''R'''NCl$	1:1	182
$(Aryl)N_2Cl$	1:1	260, 386, 440
$(CO_2H)_2$	2:1	449
	Reaction	11, 12
$C_2H_4(CO_2H)_2$	2:1	449
$(C_6H_5)_2CO$	2:1	365
	1:1	282
$C_{10}H_6O_2{}^t$	2:1	365
$C_{14}H_8O_2{}^u$	2:1	365
$(C_6H_5)CH{=}CHCO_2C_2H_5$	2:3	446
$(C_6H_5)CH{=}CHCO_2H$	2:3	446
$CH_3COCH_2COCH_3$	1:1	448
$(C_6H_5)COCH_2COCH_3$	1:1	448
$(CH_3CO)_2O$	2:5	424
	1:1	420
$(CH_3)_2SH^+Cl^-$	1:1	275
$(CH_3)_3S^+Cl^-$	1:1	227, 275
$(C_2H_5)_2S^+HCl^-$	1:1	275
$(i\text{-}C_3H_7)_2S$	1:1	275
$(i\text{-}C_3H_7)_2S^+HCl^-$	1:1	275
$(CH_2)_4S^+HCl^-$	1:1	275
$(C_6H_5)_2S^+HCl^-$	1:1	275
$(C_6H_5)_3CCl$	1:1	27, 28, 42, 161, 202, 204, 234
$HCO_2(CH_3)$	1:1	284
HCO_2CH_3–HCl	1:2:1	284
CH_3CO_2H–HCl	1:1:1	284
CH_3CO_2H–HCl	1:2:1	284

TABLE XII (*Continued*)

Other molecule (X)	SbCl/X	Ref.	Other molecule (X)	$SbCl_5$/X	Ref.
$C_3H_7CO_2CH_3$–HCl	1:1:1	284	$C_2H_5CO_2H$–C_5H_5N	1:1:1	395
$C_3H_7CO_2CH_3$–HCl	1:2:1	284	$C_3H_7CO_2H$–C_5H_5N	1:1:1	395
HCHO	1:1	282	CH_3OH–C_5H_5N	1:1:1	395
HCHO–HCl	1:1:1	282	C_3H_7OH–C_5H_5N	1:1:1	395
i-C_4H_9CHO	1:1	282	C_4H_9OH–C_5H_5N	1:1:1	395
$(CH_3)_3CCHO$	1:1	282	$C_5H_{11}OH$-C_5H_5N	1:1:1	395
Cl_3CCHO	1:1	282	$CH_3CO_2C_2H_5$–C_5H_5N	1:1:1	395
$C_6H_4O_2$[v]	1:1	282	$C_2H_5CO_2C_2H_5$–C_5H_5N	1:1:1	395
	2:1	282	$C_3H_7CO_2C_2H_5$–C_5H_5N	1:1:1	395
$H_2CO^+CH_3Cl^-$	1:1	282	$ClCH_2CO_2C_2H_5$–C_5H_5N	1:1:1	395
C_2H_5CHO	1:1	282	$HCO_2C_2H_5$–C_5H_5N	1:1:1	395
(*p*-$CH_3C_6H_4)_3N$[w]	1:1	544	Acridine[y]	1:1	50
[*p*-$(CH_3C_6H_4)N$—$]_2$	1:1	544	BrCN	1:1	7
(*p*-$CH_3COC_6H_4)_2NH$	1:1	545	ICN	1:1	7
$SnCl_4$[x]	1:1*	30, 31	PCl_5	1:1	256
HCN	1:3	285	$(CH_3)_2NNO$	1:1	162, 468
	1:1	8	NO_2	3:2	51
(*p*-$(CH_3)_2NC_6H_4)_2NH$	1:1	352	$\left[\begin{smallmatrix}Cl\\H\end{smallmatrix}>C—NH_2\right]^+Cl^-$	1:1	8
C_2H_5CN	1:1	45, 221	$\left[\begin{smallmatrix}C_2H_5O\\H\end{smallmatrix}>C—NH_2\right]^+Cl^-$	1:1	8
$C_5H_{11}CN$	1:1	221	4-Methylpyridine	Adduct[z]	105
Cl_3CCN	1:1	120	C_7H_7Cl	1:1 [aa]	42, 234
$C_6H_5CH{=}CHCHO$	1:1	446	$C_{13}H_7OBr$[bb]	1:1	570
(*p*-$CH_3OC_6H_4)_2NCH_3$	1:1	259	SO_3	1:1	330
$CH_3COC_2H_5$	1:1	406		1:2	330
$(CH_3)_2CHCOCH_3$	1:1	406		Reaction	13
$(CH_3)_3CCOCH_3$	1:1	406	CCl_3SCl	1:1	383
$C_2H_5CO_2C_2H_5$	1:1	395, 406		1:2	383
$(CH_3)_2CHCO_2C_2H_5$	1:1	406	CH_2N_2	1:1	163
$(CH_3)_3CCO_2C_2H_5$	1:1	406	$R'COO^+R_2Cl^-$	1:1[cc]	280
$CH_3CO_2C(CH_3)_3$	Reaction	406	$PSCl_3$–C_5H_5N	1:1:1	422
Phenalenone	1:1	569, 572	$PSCl_3$–C_9H_7N[dd]	1:1:1	422
C_2H_5COCl	1:1	403	$PSCl_3$–C_6H_7N[ee]	1:1:1	422
C_3H_7OH	1:1	395	$C_{22}H_{18}O_4$[ff]	1:1	458
C_4H_9OH	1:1	395	$C_{22}H_{16}O_3$[gg]	1:1	458
$C_5H_{11}OH$	1:1	395			
HCO_2H–C_5H_5N	1:1:1	395			
CH_3CO_2H–C_5H_5N	1:1:1	395			

[a] M.p. 176–177°. [b] M.p. 196–197°. [c] M.p. 107–109°. [d] Potentiometric titration in C_6H_5POCl. [e] M.p. 68–69°. [f] $C_8H_{12}O_4$ = diethyl fumarate. [g] $C_8H_{12}O_4$ = diethyl maleate. [h] $C_{12}H_{14}O_4$ = diethyl terephthalate. [i] $C_7H_8O_2$ = 2,6-dimethyl-γ-pyrone. [j] Reference 224 reports 2:5. [k] $C_{25}H_{30}N_3Cl$ = crystal violet = (*p*-$(CH_3)_2NC_6H_4)_3)CCl$. [l] $C_9H_8S_2$ = 6-methyl-1,4-benzodithiin. [m] $C_{16}H_{12}S_2$ = 2,5-diphenyl-1,4-benzodithiin. [n] Solvent $C_6H_5POCl_2$. [o] C_9H_7N = quinoline. [p] Solution in $(C_6H_5)POCl_2$. [q] M.p. 136.5°. [r] $C_6H_{10}O$ = cyclohexanone. [s] C_9H_7N = quinoline. [t] $C_{10}H_6O_2$ = 1,4-naphthoquinone. [u] $C_{14}H_8O_2$ = 9,10-anthraquinone. [v] $C_6H_4O_2$ = *p*-benzoquinone. [w] See, however, ref. 219. [x] Solution in $(C_6H_5)POCl_2$. [y] Break in conductometric and potentiometric titrations in $C_6H_5NO_2$; also isolated and analyzed. [z] M.p. 103–105°. [aa] $[C_7H_7]^+[SbCl_6]^-$. [bb] $C_{13}H_7OBr$ = 2-bromophenalenone. [cc] Formulated as $R'COO^+R_2SbCl_6^-$. [dd] C_9H_7N = quinoline. [ee] C_6H_7N = 3-methylpyridine. [ff] $C_{22}H_{18}O_4$ = phenolphthalein dimethyl ether. [gg] $C_{22}H_{16}O_3$ = 3′,6′-dimethylfluoran.

TABLE XIII

ADDITION COMPOUNDS OF $SbBr_5$

Other molecule (X)	$SbBr_5$/X	Ref.
$(C_2H_5)_2O$	1:1	357, 438

TABLE XIV

ADDITION COMPOUNDS OF BiF_5

Other molecule (X)	BiF_5/X	Ref.
BrF_3	1:1	203
MF	1:1	146, 203

TABLE XV

ADDITION COMPOUNDS OF VF_5

Other molecule (X)	VF_5/X	Ref.
NOF	1:1	91, 474, 493
NO_2F	1:1	91
SbF_5	...	91
BF_3	...	91
ClO_2F	1:1[a]	91
C_5H_5N	Reaction	85
NH_3	Reaction	85
$NH_2CH_2CH_2NH_2$	Reaction	85
MF	1:1	130, 262
SO_2	Reaction	91

[a] Stable at low temperature.

TABLE XVI

ADDITION COMPOUNDS OF NbF_5

Other molecule (X)	NbF_5/X	Ref.
BrF_3	1:1	203
BF_3	. . .	91
C_5H_5N	1:2	85, 91
NH_3	1:2	85
MF	1:1	54, 55, 91, 203, 262, 410
	1:2	229, 508
NO_2F	1:1	91
NOF	1:1	91
o-$C_6H_4(AsMe_2)_2$	1:1	95
$(CH_3)_2O$	1:1	131, 132
	1:2	131, 132
$(C_2H_5)_2O$	1:1	131, 132
$(CH_2)_4O$	Reaction	132
$(CH_3)_2S$	1:1	131, 132
	1:2	132
$(C_2H_5)_2S$	1:1	131, 132
$(CH_2)_4S$	1:2	132
$HCON(CH_3)_2$	Reaction	410
SF_4	1:0.54	263
SO_2	1:2.1	91

TABLE XVII

ADDITION COMPOUNDS OF $NbCl_5$

Other molecule (X)	$NbCl_5$/X	Ref.
$(CH_3)_3N$	1:2	150
C_5H_5N	Reaction[a]	6, 349
$POCl_3$	1:1	68, 70, 89, 181, 354, 389, 461, 496, 497, 521, 522, 524
$PSCl_3$	. . .	256, 390
$(C_2H_5)_2O$	1:1	71, 111, 108, 131
$(CH_2)_4O$	Reaction	131
$(CH_2)_5O$	1:1	136
$(CH_3)_2S$	1:1	131, 133
$(C_2H_5)_2S$	1:1	108, 131, 133
$(CH_2)_4S$	1:2	131, 133
$(CH_2)_4S$	1:1[b]	136
$(CH_2)_5S$	1:1	136
$(CH_3)_2SO$	Reaction	131
$(C_2H_5)_4NCl$	1:1	211, 213
LiCl	. . .	245, 246
MCl	1:1	32, 86, 245, 246, 370, 372–374, 412, 413, 415, 500, 515, 574
$(CH_3)_4NCl$	1:1	32, 211
o-$C_6H_4(AsMe_2)_2$	Reaction[c]	94
o-$C_6H_4(AsMe_2)_2$	1:1	95
PCl_5	1:1	181, 298
PCl_3	. . .	181
SCl_4	1:1	153
S_2Cl_4	. . .	523
$(n\text{-}C_3H_7)_2O$	1:1	108
$(CH_3)_2O$	1:1	108
$(n\text{-}C_3H_7)_2S$	1:1	108
$(C_2H_5)_3N$	1:1	71
HCN	1:1	71
$(C_2H_5)_3N$–HCN	1:1:1	71
4-Methylpyridine	Reaction[d]	6
2,2′-Bipyridyl	Reaction	6
Acridine	1:1*[e]	50
	1:3*[e]	50
$(CH_3)_2SO$	Reaction	107
$(C_6H_5)_2SO$	Reaction	107
CH_3CN	1:1	135, 266
C_2H_5CN	1:1	135
n-C_3H_7CN	1:1	135
$TiCl_4$–$POCl_3$	1:1:3	354, 522
$(C_6H_5)_3CCl$	1:1*	202
$ZrCl_4$	. . .	370
$AlCl_3$	. . .	371
$(C_6H_5)_4AsCl$	1:1	266
$C_4H_8O_2$[f]	1:1	136
C_4H_8OS[g]	1:1	136

[a] $NbCl_4$–$2Py^+$.... 1:2 adduct could not be prepared. [c] $NbCl_4$–$2(o\text{-}C_6H_4(AsMe_2)_2)$. [d] $NbCl_4$–2-(4-methylpyridine) +.... [e] Titration in $C_6H_5NO_2$. [f] $C_4H_8O_2$ = 1,4-dioxane. [g] C_4H_8OS = 1,4-thioxane.

rinated pyridines were obtained from heating pyridine with PCl_5 (486).) The compounds of PCl_5 with other Lewis acids, themselves potential chloride ion acceptors, have been shown by a variety of techniques to contain the PCl_4^+ ion. PCl_5–$FeCl_3$ is a conductor in acetonitrile and nitrobenzene, and ion-transport experiments show the cation to contain phosphorus and the anion iron (140). Infrared spectroscopy has shown the presence of PCl_4^+ and $SbCl_6^-$ ions in the solid state and in acetonitrile solution for the compound $SbCl_5$–PCl_5 (47) and the ionic nature of the following has been established by infrared and Raman techniques: $PCl_4^+AlCl_4^-$ (81, 431); $PCl_4^+BCl_4^-$ (431, 530); $PCl_4^+GaCl_4^-$ (431); $PCl_4^+TlCl_4^-$ (431); PCl_4^+-SO_3Cl^- (530); $PCl_4^+BF_3Cl^-$ (530). The recent discovery of the $SnCl_5^-$ ion (74) suggests the ionic formulation $PCl_4^+SnCl_5^-$ for the compound PCl_5–$SnCl_4$.

$RPCl_4$, R_2PCl_3, and R_3PCl_2 compounds will react with aluminium trichloride to give 1:1 (and sometimes 1:2, see section IVC) adducts formulated as containing the substituted phosphonium ions $RPCl_3^+$, $R_2PCl_2^+$, and R_3PCl^+, respectively.

Phosphorus pentachloride reacts with N-H bonds with the elimination of HCl (287) and with ammonia gives poorly characterized P-N compounds (138).

C. PBr_5 (TABLE VIII)

Very few addition compounds of phosphorus pentabromide have been reported and in none does the molecule appear to be acting as an acceptor. The 1:1 complex with iodine monobromide (see section IVB) dissociates in nonionizing solvents and ionizes in acetonitrile to give PBr_4^+ and IBr_2^- ions (436, 437). The $[PBr_4]^+$ and Br^- ions are found in solid PBr_5 (125) and presumably the adduct PBr_5–BBr_3 (511) is to be formulated $PBr_4^+BBr_4^-$. Bromination of PBr_3 in carbon tetrachloride yields PBr_5–$2CCl_4$ which is assumed to be a solvate. Harris and Payne (217), in order to explain their conductance data on phosphorus pentabromide in acetonitrile, proposed the existence of PBr_4^+ and PBr_6^- ions in solution. Kolditz and

TABLE XVIII
ADDITION COMPOUNDS OF $NbBr_5$

Other molecule (X)	$NbBr_5/X$	Ref.
$(C_2H_5)_2O$	1:1	131
$(CH_2)_4O$	Reaction	131
$C_4H_8O_2$[a]	1:1	136
$(CH_3)_2S$	1:1	131, 133
$(C_2H_5)_2S$	1:1	131, 133
$(CH_2)_4S$	1:2	131, 133
$(CH_2)_4S$	1:1[b]	136
$(CH_2)_5S$	1:1	136
C_4H_8OS[c]	1:1	136
HCN	1:1	71
CH_3CN	1:1	135, 266
C_2H_5CN	1:1	135
n-C_3H_7CN	1:1	135
C_5H_5N	Reaction	6, 348, 349
4-Methylpyridine	Reaction	6
$(CH_3)_3N$	1:2	83
o-$C_6H_4(AsMe_2)_2$	1:1	95
	Reaction	94

[a] $C_4H_8O_2$ = 1,4-dioxane. 1:2 adduct could not be prepared. [c] C_4H_8OS = 1,4-thioxane.

TABLE XIX
ADDITION COMPOUNDS OF NbI_5

Other molecule (X)	NbI_5/X	Ref.
C_5H_5N	Reaction	348
$(CH_3)_2SO$	Reaction	107
o-$C_6H_4(AsMe_2)_2$	Reaction	94

TABLE XX
ADDITION COMPOUNDS OF TaF_5

Other molecule (X)	TaF_5/X	Ref.
BrF_3	1:1	203
C_5H_5N	1:2	91
NOF	1:1	91
ClO_2F	Interaction	555
XeF_2	2:1[a]	127, 233
$(CH_3)_2O$	1:1	131, 132
	1:2	131, 132
$(C_2H_5)_2O$	1:1	131, 132
$(CH_3)_2S$	1:1	131, 132
	1:2	132
$(C_2H_5)_2S$	1:1	131, 132
$(CH_2)_4S$	1:2	132
$(CH_2)_4O$	Reaction	132
MF	1:1	33, 54, 55, 91, 203, 261, 262
	1:2	33, 88, 128, 229, 261
	1:3	128, 230
SF_4	1:0.39	263
SO_3	1:2.6	91

[a] M.p. 81°.

co-workers prepared $[PBr_4][PF_6]$ (296) and $[PBr_4]^+F^-$ (which exists in covalent and ionic forms) (294). Bromination of PBr_2F in CCl_4 gives the compound PBr_4F–$2CCl_4$ (294) (*cf.* PBr_5–$2CCl_4$ above).

TABLE XXI
ADDITION COMPOUNDS OF $TaCl_5$

Other molecule (X)	$TaCl_5/X$	Ref.
$POCl_3$	1:1	65, 89, 181, 354, 389, 460, 461, 496, 497, 521, 522, 524
$PSCl_3$	. . .	256, 390
CH_3CN	1:1[a]	135, 266, 300
PCl_3	. . .	181
PCl_5	1:1	181, 300
PCl_5–$AsCl_3$	1:1:1	300
SCl_4	1:1	153
S_2Cl_2	. . .	523
$(C_2H_5)_4NCl$	1:1	211, 213
$(CH_3)_4NCl$	1:1	32, 211
C_5H_5N	1:1	194, 348, 349
	Reaction[b]	6
	1:2	331
$(CH_3)_2S$	1:1	131, 133
	1:2	133
$(C_2H_5)_2S$	1:1	108, 131, 133
$(CH_2)_5S$	1:1	136
$(CH_2)_4S$	1:1[c]	136
	1:2	131, 133
$(CH_2)_4O$	Reaction	131
$(CH_2)_5O$	1:1	136
$(C_2H_5)_2O$	1:1	108, 111, 131
$(CH_3)_2O$	1:1	108
$(n$-$C_3H_7)_2O$	1:1	108
MCl	1:1	32, 86, 245, 246, 372, 373, 374, 414, 415, 500, 515, 574
4-Methylpyridine	Reaction	6
2,2′-Bipyridyl	Reaction	6
Acridine	1:1*[d]	50
	1:2*[d]	50
$(CH_3)_2SO$	Reaction	107
C_2H_5CN	1:1	135
n-C_3H_7CN	1:1	135
$SnCl_2$	2:1	369
$TiCl_4$–$POCl_3$	1:1:3	354, 522
$(CH_3)_3N$	1:2	82
$(C_2H_5)_3N$	1:1	82
$AlCl_3$	. . .	371
o-$C_6H_4(AsMe_2)_2$	1:1	95
$C_4H_8O_2$[e]	1:1	136
C_4H_8OS[f]	1:1	136

[a] M.p. 202°. $TaCl_4$–2(pyridine) + ... [c] 1:2 adduct could not be prepared. [d] Titration in $C_6H_5NO_2$. [e] $C_4H_8O_2$ = 1,4-dioxane. [f] C_4H_8OS = 1,4-thioxane.

D. $AsCl_5$ (TABLE X)

Although the compound arsenic pentachloride has no stable existence (see Dasent (117) for a review on the $AsCl_3$–Cl_2 and $AsBr_3$–Br_2 systems), the valency state V can be stabilized by complex formation. Passing chlorine into a suspension of aluminium trichloride in arsenic trichloride gave a large increase in conductivity and a compound $AlAsCl_8$ formulated as $[AsCl_4]^+$-$[AlCl_4]^-$ was isolated (309). Similar results were obtained with other chloride ion acceptors, *e.g.*, $[AsCl_4]^+[GaCl_4]^-$ and $[AsCl_4]^+[TaCl_6]^-$ (309). Two

TABLE XXII

ADDITION COMPOUNDS OF $TaBr_5$

Other molecule (X)	$TaBr_5/X$	Ref.
C_5H_5N	1:1	348, 349
	Reaction	6
$(C_2H_5)_2O$	1:1	111, 131
$(CH_3)_2S$	1:1	131, 133
$(C_2H_5)_2S$	1:1	131, 133
$(CH_2)_5S$	1:1	136
$(CH_2)_4S$	1:1[a]	136
$(CH_2)_4S$	1:2	131, 133
$(CH_2)_4O$	Reaction	131
$(CH_3)_3N$	. . . ?[b]	83
$(CH_3)_2SO$	Reaction	107
$(C_6H_5)_2SO$	Reaction	107
o-$C_6H_4(AsMe_2)_2$	1:1	95
CH_3CN	1:1	266
C_4H_8OS[c]	1:1	136
$C_4H_8O_2$[d]	1:1	136

[a] 1:2 adduct could not be prepared. [b] Possibly due to surface coating. [c] C_4H_8OS = 1,4-thioxane. [d] $C_4H_8O_2$ = 1,4-dioxane.

TABLE XXIII

ADDITION COMPOUNDS OF TaI_5

Other molecule (X)	TaI_5/X	Ref.
$(C_2H_5)_2O$	. . .	131
$(C_2H_5)_2S$	Complex	131
	1:1	133
C_5H_5N	Reaction	347, 348
$(CH_2)_4S$	1:2	133

TABLE XXIV

ADDITION COMPOUNDS OF M(V)

Group V molecule (A)	Other molecule (X)	A/X	Ref.
$(CF_3)_3SbCl_2$	C_5H_5N	1:1	116
$(C_6H_5)SbCl_4$	$C_6H_5N_2Cl$	1:1	73, 440
$ArSbCl_4$	ArN_2Cl	1:1	260, 441
$(Ar)_2SbCl_3$	ArN_2Cl	1:1	260
$(C_6H_5)SbCl_4$	C_5H_6NCl[a]	1:1	386
$(C_6H_5)_2SbCl_3$	H_2O	1:1	73
PCl_3F_2	C_5H_5N	1:1	242–244
PCl_4F	C_5H_5N	1:1	242–244
PCl_2F_3	C_5H_5N	2:3	242
$(C_6H_{11})_3PBr_2$	$SbBr_3$	1:1	249
$(C_6H_{11})_3PBr_2$	$HgBr_2$	1:1	249
$(C_6H_{11})_3PI_2$	HgI_2	1:1	249
		1:3	249
$ArPCl_4$	$AlCl_3$	1:1	560
$RPCl_4$	$(CH_3)_2SO$	Reaction	410
$C_6H_5SbCl_4$	NH_4Cl	1:1	514
$SbCl_2F_3$	CH_3CN[b]	1:1	293
$RPCl_4$[c]	$AlCl_3$	1:1	96, 134, 231, 271
		1:2	134, 231
R_2PCl_3	$AlCl_3$	1:1	134
		1:2	134
R_3PCl_2	$AlCl_3$	1:1	251
PBr_4F	CCl_4	1:2	294
$SbCl_3(OC_2H_5)_2$	C_5H_5N	1:1	421
R_2PBr_3	Br_2	1:1	314, 315
$C_6H_5PF_4$	C_5H_5N	1:1	377
$C_6H_5PF_4$	$(CH_3)_2NCOCH_3$	1:1	377
$C_6H_5PF_4$	CH_3CN	. . .	377
$C_6H_5PF_4$	$(CH_3)_2SO$	Reaction	377
$(CH_3)_2PF_3$	BF_3	1:1	377
$(CH_3)_2PF_3$	SbF_5	1:1	377
$(CH_3)_2PF_3$	PF_5	1:1	377
CH_3PF_4	$(CH_3)_2SO$	Reaction	377
CH_3PF_4	PF_5	1:1	377
$C_6H_5PF_4$	NOF	1:1[e]	469
$C_6H_5PF_4$	NO_2F	Reaction	469
$C_6H_5PF_4$	R_1R_2NH	Reaction	469
$C_6H_5PF_4$	RNH_2	Reaction	469
$NbCl_4(CN)$	$(C_2H_5)_2O$	1:1	71
$(C_6H_{11})PI_4$	HgI_2	1:1	250
$(C_6H_{11})_2PI_3$	HgI_2	2:1	250

[a] C_5H_6NCl = pyridine hydrochloride. [b] Formulated as $[SbCl_4–2CH_3CN]^+SbF_6^-$. [c] R = alkyl, cyclohexyl, or CCl_3. [d] One product is $[CH_3PF_5]^-$ ion. [e] $NO^+[PF_5C_6H_5]^-$.

principal ionic formulations exist for $PCl_5–AsCl_5$ (185), namely, $AsCl_4^+PCl_6^-$ and $PCl_4^+AsCl_6^-$, of which the former must be considered the more probable (both ions (or derivatives thereof) having been characterized),[1] but the point has not yet been unambiguously established. $AsCl_3–Cl_2$ mixtures with trimethylphosphine oxide gave the compound $AsCl_5–(CH_3)_3PO$[1] in which arsenic pentachloride is apparently acting as an *acceptor* (338). Nyholm (396) has argued from promotion energy data of the free atom that the instability of $AsCl_5$ is a reflection of the large energy required to uncouple the s-pair and the higher energy of the 4d orbitals relative to the 4s and 4p. On this basis $AsCl_4^+$ might be expected. The existence of $AsCl_5–(CH_3)_3PO$ would suggest that under some conditions d orbitals may be used. Kolditz and his coworkers have made other derivatives of the $AsCl_4^+$ cation, $[AsCl_4][AsF_6]$ (288) and $[AsCl_4][SbF_6]$ (310), while organic derivatives of the $AsCl_4^+$ ion have been characterized by X-ray analysis, $[As(CH_3)_4]^+$ (102) and $[As(C_6H_5)_4]^+$ (368). Five-covalent arsenic is known in the compound $(C_6H_5)_5As$ (541) when the molecule has a trigonal-bipyramidal configuration (neglecting the symmetry of the phenyl groups) (*cf.* $(C_6H_5)_5Sb$, section VIIE). Infrared spectroscopy showed the presence of AsH_4^+ ions in the system $AsH_3–HX$ (X = Br, I, but *not* Cl) at low temperatures, but gave no evidence for SbH_4^+ ions in the system $SbH_3–HX$ (220).

E. $SbCl_5$, $SbBr_5$, R_nSbCl_{5-n}, R_nSbF_{5-n}, SbF_nCl_{5-n} (TABLES XII, XIII, AND XXIV)

Antimony pentachloride has been the most extensively studied of all the compounds under review and much of the chemistry has been discussed in earlier sections (II, III, VC, VI). Lewis acid–base behavior

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(1) The compound $[(C_2H_5)_4N]^+[AsCl_6]^-$ has been prepared from the $(C_2H_5)_4NCl–AsCl_3–Cl_2$ system and contains the previously unknown $[AsCl_6]^-$ ion. $AsCl_5–2(C_6H_5)_3PO$ was also prepared and investigated, and possible structures were discussed (468a).

is observed with a wide variety of organic donors with coordination from nitrogen, phosphorus, oxygen, and sulfur atoms, and the majority of adducts conform to 1:1 stoichiometry.

Both $TiCl_4$–$SbCl_5$–$3POCl_3$ (2, 3, 29) and $TiCl_4$–$SbCl_5$–$2POCl_3$ (210) have been isolated from mixtures of the components although the phase diagram for $TiCl_4$–$SbCl_5$ shows no compound formation (384). The 1:1:3 adduct conducts in ethylene chloride and was formulated as $[TiCl_3\text{–}3POCl_3]^+[SbCl_6]^-$. Other ternary compounds reported include $ZrCl_4$–$SbCl_5$–$2POCl_3$ (207), $AlCl_3$–$3SbCl_5$–$6POCl_3$ (26), $AlCl_3$–$SbCl_5$–$3POCl_3$ (196), $AlCl_3$–$SbCl_5$–$2POCl_3$ (190), for which ionic formulations have been proposed. Phase diagrams for the systems $SnCl_4$–$SbCl_5$–$POCl_3$ and $AsCl_3$–$SbCl_5$–$POCl_3$ show *no* ternary compound formation (2, 3).

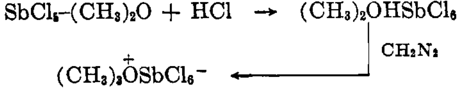
Adducts of the type $SbCl_5$–$2RCO_2H$ seem to be well established in addition to the 1:1 adducts, and although conclusive evidence is lacking it seems plausible that the increased acidity of the proton on complex formation is responsible. This proton can then presumably strongly hydrogen bond to a second acid molecule or proton transfer could occur of the type

$$SbCl_5\text{–}RCO_2H + RCO_2H \rightleftharpoons [SbCl_5RCO_2]^-[RCO_2H_2]^+ \quad (518)$$

The system is further complicated by reaction to give $SbCl_4O_2CR$ and HCl.

The ionic and covalent form of $SbCl_5$–CH_3CN have already been discussed (see section IIB and VA). The related adduct SbF_3Cl_2–CH_3CN has been formulated as $[SbCl_4\text{–}2CH_3CN]^+[SbF_6]^-$ (293). From conductivity and molecular weight experiments SbF_3Cl_2 probably exists as $[SbCl_4][SbF_6]$ in arsenic trifluoride solution and both ionic (solid) and covalent (liquid) forms were proposed for the pure compound (301). Subsequent work suggested that the solid was not ionic (119) and recently Muetterties, *et al.* (378), pointed out that the physical properties suggested a polymer and proposed that fluorine-bridged structures exist in the liquid from ^{19}F n.m.r. spectra (*cf.* SbF_5 which is a fluorine-bridged polymeric liquid).

A considerable number of organic derivatives of the hexachloroantimony(V) anion have been prepared by Klages and co-workers (274–284) by reaction of an antimony pentachloride adduct with HCl. For example



$$SbCl_5\text{–}(CH_3)_2O + HCl \rightarrow (CH_3)_2\overset{+}{O}HSbCl_6^- \xrightarrow{CH_2N_2} (CH_3)_3\overset{+}{O}SbCl_6^-$$

The reaction can be carried out with a variety of ligands.

Only one adduct of (the unknown) $SbBr_5$ has been reported, namely $SbBr_5$–$(C_2H_5)_2O$, prepared by the bromination of Sb in ether (357, 438) (compare section VIID).

Substitution of one or two chlorine atoms by phenyl groups in $SbCl_5$ still leaves the molecule with acceptor properties, but no systematic studies have been performed. Pentaphenylantimony is extraordinary in containing discrete square-pyramidal molecules in the solid state (542).

The mixed hexahalogeno anion $[SbF_4Cl_2]^-$ has been prepared by Kolditz, *et al.*, by the reaction of SbF_5 with NaCl in liquid sulfur dioxide (310); $Na[SbF_6]$ is the other reaction product.

F. VF_5, NbF_5, TaF_5
(TABLES XV, XVI, AND XX)

The pentafluorides of vanadium, niobium, and tantalum show marked acceptor properties and hexafluorides are known for all the elements, but only niobium and tantalum exhibit a coordination number greater than six. A coordination number of seven has been formed for niobium in $[NbF_7]^{2-}$, and seven and eight for tantalum in $[TaF_7]^{2-}$ and $[TaF_8]^{3-}$ (see section III). The potential fluoride ion donors nitryl fluoride and nitrosyl fluoride form 1:1 adducts which were formulated as the ionic $[NO_2]^+[MF_6]^-$ and $[NO]^+[MF_6]^-$, respectively (91). The behavior toward pyridine shows marked variation; thus VF_5 reacts to form VF_4–Py (85), while NbF_5 and TaF_5 yields NbF_5–2Py (TaF_5–2Py) (91). With ammonia again both reduction and complex formation are observed; VF_5 gives the compound VF_4–NH_3 (plus other products), while NbF_5 gives the 1:2 adduct NbF_5–$2NH_3$ (85). Toward ethers and thioethers, NbF_5 and TaF_5 form mainly conventional 1:1 adducts (132), and in addition dimethyl ether was observed to form MF_5–$2(CH_3)_2O$ (132). The compound $2TaF_5$–XeF_2 has been discussed (section VIIA).

G. $NbCl_5$, $NbBr_5$, NbI_5, $TaCl_5$, $TaBr_5$, TaI_5
(TABLES XVII, XVIII, XIX, XXI, XXII, AND XXIII)

Adduct formation is observed for oxygen, nitrogen, and sulfur donors with the pentachlorides and -bromides exhibiting the stoichiometry $M(Hal)_5/A$ of 1:1 and 1:2.

The behavior toward pyridine shows considerable complexity and is dependent of the experimental conditions. $NbCl_5$ and $NbBr_5$ react with the formation of NbX_4–2Py (X = Cl or Br) (6, 348) though under some conditions mixtures of NbX_5–Py and NbX_4–2Py were obtained (349), the latter predominating. With $TaCl_5$ both complex formation of $TaCl_5$–Py (348, 349) and $TaCl_5$–2Py (331) and reaction to $TaCl_4$–2Py (6) have been reported. Tantalum pentabromide has been reported as forming a 1:1 pyridine complex (348, 349) and as reacting to $TaBr_4$–2Py (6). Reaction of the tetrahalides with pyridine yields MX_4–2Py (347, 350). The oxidation products of the reactions have been studied and a mechanism has been proposed

(349). Niobium and tantalum pentaiodides are again reduced to M(IV) according to the equation (347–349)

$$2MI_5 + 5Py \rightarrow 2MI_4\text{–}2Py + PyI_2 \ (M = Nb, Ta)$$

Donors related to pyridine (*e.g.*, γ-picoline) also react to give paramagnetic M(IV) compounds. The formation of $TaCl_5\text{–}2(CH_3)_3N$, but only the 1:1 adduct $TaCl_5\text{–}(C_2H_5)_3N$, has been interpreted as due to the greater steric requirements of the ethyl derivative (82). Ammonia and primary and secondary amines react with the pentahalides under discussion eliminating HCl and forming complex metal amino halides (82, 83, 150, 151). The ternary compounds $TiCl_4\text{–}MCl_5\text{–}3POCl_3$ (M = Nb, Ta) (354, 522) have been established by phase studies but no structural data are available (*cf.* $TiCl_4\text{–}SbCl_5\text{–}3POCl_3$ (2), section VIIE). The adducts formed by the pentachlorides with PCl_5 are presumably ionic $PCl_4^+ \, MCl_6^-$ (M = Nb, Ta).

VIII. CONCLUDING REMARKS

Space precludes a detailed discussion of the various ligands that have been used, and indeed it would be largely repetitious. Although much data have been accumulated, some surprising gaps remain. For example, many of the fundamental frequencies for the octahedral anions $M(Hal)_6^-$ are not yet known (see Table III). Although a number of X-ray structure determinations have been carried out, there remains many compounds (often involving pentafluorides) where ambiguity between bridged and ionic structures exist, *e.g.*, $AsF_5\text{–}SF_4$; and it seems probable that the solid-state structures would give valuable information. The more unusual stoichiometries, *e.g.*, $SbCl_5\text{–}2RCO_2H$ and $PCl_5\text{–}2(CH_3)_3P$, have received scant attention and surely deserve more.

The isomerism discovered by Kolditz for the compound $SbCl_5\text{–}CH_3CN([SbCl_4\text{–}2CH_3CN]^+[SbCl_6]^-)$ potentially gives rise to a whole range of compounds derived from the $SbCl_4^+$ ion (compare the extensive coordination chemistry of the isoelectronic $SnCl_4$ (43), and by analogy the $AsCl_4^+$ and PCl_4^+ ions (the ion $[PCl_4\text{–}ophen]^+$ isoelectronic with $SiCl_4\text{–}ophen$ has been prepared (44); ophen = 1,10-phenanthroline). The above few examples chosen from the review that seem to offer promise are naturally subjective and reflect the authors interests—readers will no doubt make their own choice.

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