THE ACCEPTOR PROPERTIES OF QUADRIPOSITIVE SILICON, GERMANIUM, TIN, AND LEAD

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1. Introduction

It is customary to think of the increased interest in inorganic chemistry during the past decade as stemming largely from the application of physical techniques to compounds of the transition elements. The formidable array of spectroscopic techniques available to the transition-metal chemist is drastically reduced for studies on elements not having partially filled d-shells, and this has led to some neglect of the non-transition elements. However, there have been considerable, although generally less spectacular, advances in the chemistry of these "s- and p-block elements." Broadly speaking, their interest lies in the wide diversity of behaviour which they exhibit and in the very fact that their d-shells are either filled or empty.

One of the objectives in writing this Review has been the correlation of part of the wealth of analytical information available on the stoicheiometry of addition compounds. For example, at least three hundred addition compounds of tin tetrachloride have been described in the literature. However, the main emphasis will be on the need for a physical approach to the stereochemistry and thermodynamic stability of such compounds. In particular, compounds of the type $MX_4,2L$ (where M = Si, Ge, Sn, Pb; X = halogen; L = monodentate ligand) represent a unique series for studying *cis–trans* isomerism and its relation to thermodynamic stability. The ligand, the central atom, and the halogen all allow of considerable variation. A survey of available physical techniques for such studies will indicate the importance of infrared and Raman spectroscopy. With the increased availability of infrared spectrometers capable of detecting fundamental metal–halogen stretching and bending vibrations, the examination of the stereochemistry and stability of co-ordination compounds of the non-transition elements in non-aqueous solutions is greatly facilitated. We start this Review by summarising relevant physical and chemical properties of the title elements and their compounds.

2. Physical Properties

(a) **Electronegativity.**—There is considerable disagreement about the exact sequence of electronegativity values to be assigned to the elements of Group IVB in the quadripositive state. In an excellent review, Pritchard and Skinner[1] have suggested "best values" of 1·8 to 1·9 for silicon, germanium, tin, and lead. However, Allred and Rochow[2] have suggested

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[1] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.
[2] Allred and Rochow, *J. Inorg. Nuclear Chem.*, 1958, **5**, 269; see also Allred, *ibid.*, 1961, **17**, 215.

that germanium is more electronegative than silicon, and, from measurements of proton shifts in Me_4M, have deduced the sequence of electronegativities (M =) Pb> Ge > Sn > Si. Drago[3] has criticised these conclusions and further pointed out that electronegativity differences are probably insignificant for explaining the chemistry of these elements. Most chemists will find it difficult to accept that lead is more electronegative than silicon, particularly when it is remembered that the relationship between quadrupole coupling constants, or proton shifts, and electronegativity contains at least a measure of intuition. In the absence of adequate quantitative calculations[3a] (based, for example, on the Mulliken scale) there do not appear to be any compelling reasons for altering the usually accepted (largely empirical) sequence, Si > Ge > Sn > Pb, the overall change in electronegativity being small. Recent results[4] on electron-release from $-SiMe_3$ and $-GeMe_3$ support the electronegativity sequence Si > Ge, although, remembering that the outer shell of germanium(IV) is $3d^{10}$ compared with the inert-gas configuration of silicon(IV), an inversion of this latter order would not have been surprising.

(b) **Radii.**—The covalent radii (tetrahedral) show a relatively large increase from germanium to tin (1·22—1·40 Å), while the changes from silicon to germanium and from tin to lead are only about 0·05 Å in each case.[5] This behaviour can be understood in terms of the inefficient screening of the nucleus of germanium (relative to silicon) due to the $3d$-shell, and for lead (relative to tin) due to the filled $4f$-shell. The "lanthanide contraction" is still making its effect felt with lead but, equally, it must be remembered that, on traversing the first-row transition series, there is an overall decrease in radius.

(c) **Acceptor Strength of M^{4+}.**—It is difficult to give a quantitative physical measure of the acceptor strength of an ion without reference to specific ligands. The fourth-ionisation potentials of the Group IV elements and a measure of the s–p–d (or d–s–p) separation of the related M^{3+} ions are given in Table 1.[6] For the quadruply-charged ions, the electron affinity

TABLE 1. *Fourth ionisation potentials (equivalent to electron affinities of M^{4+} of the elements of Group IV, and promotion energies for M^{3+} (in ev)).*

Element or 3+ ion	Si	Ge	Sn	Pb	Ti	Zr
Fourth-ionisation potential	45·1	45·5	39·4	42·1	43·2	33·8
$^2S \rightarrow {}^2D$ ($s \rightarrow d$)	19·9	23·6	20·5	22·9	—	—
$^2D \rightarrow {}^2P$ ($d \rightarrow p$)	—	—	—	—	15·8	10·2

[3] Drago, *J, Inorg. Nuclear Chem.*, 1960, **15**, 237.
[3a] See Hinze and Jaffe, *J. Phys. Chem.*, 1963, **67**, 1501.
[4] See, *e.g.*, Bott, Eaborn, Pande, and Swaddle, *J.*, 1962, 1217.
[5] Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1945.
[6] Moore, "Atomic Energy Levels," U.S. Nat. Bur. Standards, Circular No. 467, 1952 (Vol. II); 1958 (Vol. III); Moeller, "Inorganic Chemistry," Wiley, New York, 1952,

might be expected to follow a regular sequence for the series Si, Ti, Zr, Hf, as here all the ions have inert-gas configurations; but it should be noted that the ground states of M^{3+} for the Group IVA elements are $^2D_{3/2}$, while those of the IVB elements $(3+)$ are $^2S_{\frac{1}{2}}$. The poor shielding of germanium is reflected in the value of the fourth-ionisation potential for germanium, which is greater than that for silicon. The fourth-ionisation potentials could also be related to the electronegativity considerations discussed above and would suggest that germanium(IV) should be at least as good an acceptor as titanium(IV). However, inspection of the relevant s–p–d separations in M^{3+} indicates that the promotion energy* $4s \rightarrow 4d$ (covering $4p$) for Ge^{3+} is much greater than the promotion energy $3d \rightarrow 4p$ (covering $4s$) for Ti^{3+}. This is one way of expressing the accepted fact that the hydridisation $(n-1)d^2\,ns\,np^3$ is more readily accomplished than $ns\,np^3\,nd^2$, and reasonably accounts for the greater acceptor properties of the elements of Group IVA relative to the corresponding IVB elements.

3.   Chemical Properties

Chemically, a point of great interest in Group IVB is the discontinuity between carbon on the one hand and silicon, germanium, tin, and lead on the other. The more significant of these differences (which may usually be understood in terms of the availability of d-orbitals, for the elements other than carbon) are summarised in the following paragraphs.

(a)   There is no well-authenticated example of p_π–p_π multiple bonding in Group IV for elements other than carbon. The difference is strikingly shown by contrasting the monomeric carbonates and ketones with the polymeric silicates and "silicones." The work[7] thought to indicate the formation of derivatives of "silicobenzene" has now been differently interpreted,[8] the compound thought[9] to be $Me_2Si:CH\cdot SiMe_3$ is known to be cyclic,[10] and the action of potassium on trichlorophenylgermane leads to intractable polymeric materials[11] rather than species with unsaturated germanium atoms.[12] In the sub-group (titanium, zirconium, and hafnium) multiple bonding is rare.

(b)   Carbon is the only element of Group IV to show a maximum covalency of four. That of quadripositive silicon, germanium, tin, and lead appears to be six, while, in the sub-group, a co-ordination number of eight is by no means unusual for zirconium and hafnium and has recently

* I am indebted to Professor R. S. Nyholm for drawing my attention to this point.

[7] Urry, 133rd American Chemical Society Meeting, San Francisco, 1958, 43L; see also Benkeser and Stanton, *J. Amer. Chem. Soc.*, 1963, **85**, 834.

[8] See Eaborn, "Organosilicon Compounds," Butterworths, London, 1960.

[9] Fritz and Grobe, *Z. anorg. Chem.*, 1961, **311**, 325.

[10] Fritz, Kemmerling, Sonntag, Becher, Ebsworth, and Grobe, *Z. anorg. Chem.*, 1963, **321**, 10; earlier work by Knoth and Lindsey, *J. Org. Chem.*, 1958, **23**, 1392.

[11] Metlesics and Zeiss, *J. Amer. Chem. Soc.*, 1960, **82**, 3321, but see King, *Inorg. Chem.*, 1963, **2**, 199.

[12] Schwarz and Lewinsohn, *Ber.*, 1931, **64**, 2352.

been found for titanium.[13] Compounds such as K_3HSnF_8 are apparently based on six-co-ordinate tin.[14] Where a multiple bond is present, carbon may act as an acceptor without increasing its co-ordination number to greater than four, for example[15] in the zwitterion $^-S_2C\cdot PEt_3{}^+$.

(c) Excluding carbonium ions, there is very little evidence for the formation of stable cations R_3M^+ (where R = aryl). Where M = Si, Ge, Sn, or Pb, there are likely to be additional interactions (such as solvation) in the condensed state. Ions of the type $[R_3Si\cdot NR_3]^+$ are most suitably regarded as derivatives of quaternised nitrogen rather than as "siliconium" ions.

(d) Compounds of silicon frequently display stereochemistry distinctly different from that of their carbon analogues. The most quoted example of this behaviour is the near planarity of the NSi_3 skeleton of trisilylamine[16] compared with the pyramidal configuration of trimethylamine.

4. Stoicheiometry of Addition Compounds

(a) **Adducts of the Simple Tetrahalides.**—The main emphasis in this Review will be on the stereochemistry and stability of addition compounds. However, as analytical data are prolific (especially for adducts of tin tetrachloride), it is useful to summarise the observed ratios of acceptor to donor (most frequently 1:2 or 1:1, more rarely 1:4, and occasionally ratios other than these). Table 2 indicates the stoicheiometry of several addition compounds of MX_4 (M = Si, Ge, Sn; X = halogen) with the representative donors pyridine, trimethylamine, acetonitrile, and tetrahydrofuran. This Table is intended to be comprehensive for the bases selected (and where reaction has been reported), although cases where results are clearly invalidated by inadequate experimental techniques, or where compounds are poorly characterised, have been omitted. Because a particular acceptor is not given, it does not necessarily mean that reaction with the appropriate donor does not occur. It may be that the reaction has never been attempted, or that interaction has not been examined over a wide range of experimental conditions. Chelate ligands such as 1,10-phenanthroline have not been extensively studied with these tetrahalides, but the expected 1:1 stoicheiometry is usually found.

The general picture that emerges from Table 2 is that the most frequently occurring ratio is 1:2, presumably to give an octahedrally co-ordinated central atom. The acceptor order indicated is Sn $\gg$ Ge > Si and F > Cl > Br > I. From simple electronegativity considerations or from calculations

[13] See, for example, Clark, Lewis, Nyholm, Pauling, and Robertson, *Nature*, 1961, **192**, 222; Clark, Lewis, and Nyholm, *J.*, 1962, 2461.
[14] Dove, *J.*, 1959, 3722; see, however, Durrant and Durrant, "Introduction to Advanced Inorganic Chemistry," Longmans, London, 1962.
[15] Margulis and Templeton, *J. Amer. Chem. Soc.*, 1961, **83**, 995.
[16] See, for example, Hedberg, *J. Amer. Chem. Soc.*, 1955, **77**, 6491.

TABLE 2.   *The stoicheiometry of certain addition compounds formed between the tetrahalides of Group IVB and certain electron donors.*

Acceptor (A)	Donor (D)	Approx. mole ratio (A:D)	Comments	Ref.
SiF_4	Pyridine	1:2	1:2 does not fume in air (2:3 in ref. 30)	19, 29
$SiCl_4$	,,	1:2	Fully dissociated in gas phase; insoluble; very hygroscopic	18, 22, 23, 26, 29, 50, 51, 52a
$SiBr_4$	,,	1:2	Very hygroscopic	18, 29, 52a
SiI_4	,,	1:4	Very hygroscopic	29, 44, 52a
GeF_4	,,	1:2		19
$GeCl_4$	,,	1:2	*trans*-Octahedral; soluble in benzene and chloroform; easily hydrolysed; monomeric in benzene	31, 46, 50, 51
$GeBr_4$	,,	1:2		46
GeI_4	,,	1:2	No adduct under conditions similar to those in which $GeCl_4$ gives an adduct	45, 52a
SnF_4	,,	1:2	M.p. 180—183°	19, 34
$SnCl_4$	,,	1:2	Insoluble; slow hydrolysis	17, 21, 35, 47
$SnBr_4$	,,	1:2	Insoluble in normal solvents	47
SnI_4	,,	1:2	Insoluble (see also refs. 36 and 47)	33
$PbCl_4$	,,	1:2		52
SiF_4	Trimethylamine	1:1, 1:2	Both sublime at about 63°; soluble in benzene.	20, 25, 43, 43a

Acceptor (A)	Donor (D)	Approx. mole ratio (A:D)	Comments	Refs.
$SiCl_4$	Trimethylamine	1:1	Dissociation pressure 1 mm. at $-66.5°$	24, 25
GeF_4	,,	1:1, 1:2	1:1 has a dissociation pressure of $<$ 0·01 mm. at 0°	25, 48
$GeCl_4$	,,	1:1, 1:2	1:1 has a dissociation pressure of 6·4 mm. at 0°; 1:1 soluble in benzene	48, 51, 25
SnF_4	,,	1:1	Water-soluble (?)	34
$SnCl_4$	,,	1:1, 1:2	Soluble in benzene. 1:2 fairly stable to moisture, reacts with BF_3 to give BF_3,NMe_3; m.p. 171° (decomp)	21, 25
$SnBr_4$	,,	1:2	Stated to be nearly insoluble in water, m.p. 196—198°	27, 28
SnI_4	,,	1:2	Fairly soluble in trimethylamine	27
$SiCl_4$	Acetonitrile	No adduct under conditions similar to those in which $SnCl_4$ gives an adduct		38a, 39, 49
GeF_4	,,	1:1, 1:2	Insoluble in hydrocarbon solvents	48, 32
$GeCl_4$	,,	No adduct under conditions similar to those in which $SnCl_4$ gives an adduct		38, 49
SnF_4	,,	1:2	Sparingly soluble in excess acetonitrile	34
$SnCl_4$	,,	1:2	Soluble in benzene with dissociation; soluble in acetonitrile, m.p. 112—114°	37, 40
$SnBr_4$	,,	1:2		40
SnI_4	,,	No adduct under comparable conditions to those in which $SnBr_4$ gives an adduct		40

Acceptor (A)	Donor (D)	Approx. mole ratio (A:D)	Comments	Refs.
$SiCl_4$	Tetrahydrofuran	No adduct		42
GeF_4	,,	1:2	Decomposes at $-78°$	32
$GeCl_4$	,,	No adduct		42
SnF_4	,,	1:1		34
$SnCl_4$	,,	1:2	Soluble in benzene and tetrahydrofuran	17, 42
$SnBr_4$	,,	1:2	Quite soluble in chloroform, acetone; has odour of tetrahydrofuran	41
SnI_4	,,	Probably no adduct under conditions comparable to those in which $SnBr_4$ gives an adduct		41

[17] Zenchelsky and Segatto, *J. Amer. Chem. Soc.*, 1958, **80**, 4796.
[18] Reynolds, *J.*, 1909, **95**, 512.
[19] Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 1082.
[20] Wilkins and Grant, *J.*, 1953, 927.
[21] Laubengayer and Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 5985.
[22] Hardin, *J.*, 1887, **51**, 40.
[23] Piper and Rochow, *J. Amer. Chem. Soc.*, 1954, **76**, 4318.
[24] Burg, *J. Amer. Chem. Soc.*, 1954, **76**, 2674.
[25] Fergusson, Grant, Hickford, and Wilkins, *J.*, 1959, 99
[26] Wannagat and Vielberg, *Z. anorg. Chem.*, 1957, **291**, 310.
[27] Bannister and Fowles, *J.*, 1959, 310.
[28] Böhme and Boll, *Z. anorg. Chem.*, 1957, **292**, 61.
[29] Wannagat, Schwarz, Voss, and Knauff, *Z. anorg. Chem.*, 1954, **277**, 73.
[30] Comey and Smith, *Amer. Chem. J.*, 1888, **10**, 294.
[31] Abel, *J.*, 1958, 3746.
[32] Aggarwal and Onyszchuk, *Proc. Chem. Soc.*, 1962, 20.
[33] Dimitriou, *Praktika*, 1927, **2**, 496. (*Chem. Abs.*, 1929, **23**, 4904).
[34] Woolf, *J. Inorg. Nuclear Chem.*, 1956, **3**, 285.
[35] Pease and Luder, *J. Amer. Chem. Soc.*, 1953, **75**, 5195.
[36] Cooper and Wardlaw, *J.*, 1930, 1141.
[37] Coerver and Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.

[38] Udovenko and Fialkov, *Zhur. neorg. Khim.*, 1957, **2**, 2126.
[38a] Harold, *J. Amer. Chem. Soc.*, 1898, **20**, 13.
[39] Alikberov, Shklover, Syromyatnikova, and Shcherbakova, *Russ. J. Phys. Chem.*, 1960, **34**, 443.
[40] Pfeiffer and Halperin, *Z. anorg. Chem.*, 1914, **87**, 335.
[41] Sisler, Schilling, and Groves, *J. Amer. Chem. Soc.*, 1951, **73**, 426.
[42] Sisler, Batey, Pfahler, and Mattair, *J. Amer. Chem. Soc.*, 1948, **70**, 3821.
[43] Miller, *Nature*, 1946, **158**, 950.
[43a] Schnell, *Monatsh.*, 1962, **93**, 1136.
[44] Muetterties, *J. Inorg. Nuclear Chem.*, 1960, **15**, 182.
[45] Dennis and Hance, *J. Amer. Chem. Soc.*, 1922, **44**, 2854.
[46] Lebedev and Troney, *Russ. J. Inorg. Chem.*, 1960, **5**, 837.
[47] Pfeiffer, *Z. anorg. Chem.*, 1911, **71**, 97.
[48] Barnard, *Diss. Abs.*, 1954, **14**, 1913.
[49] Devin and Perrot, *Compt. rend.*, 1958, **246**, 772.
[50] Hulme, Leigh, and Beattie, *J.*, 1960, 366.
[51] Beattie and Leigh, *J. Inorg. Nuclear Chem.*, 1961, **23**, 55.
[52] Matthews, *J. Amer. Chem. Soc.*, 1898, **20**, 834.
[52a] Beattie, Gilson, Webster and (in part) McQuillan, *J.*, in the press.

of d-orbital contraction[53] we should expect the fluorides to be the best acceptors. The situation is not, however, comparable to that found in the boron trihalides, for which the acceptor order appears to be Br $\approx$ Cl > F. In the reaction,

$$BX_3 + L \to BX_3,L$$
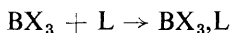
it is usually accepted that the free trihalide has appreciable $p_\pi-p_\pi$ bonding between the boron and the halogen. Virtually no π-bonding is to be expected in the adduct BX_3,L, so that, if the order of π-bonding in BX_3 is F > Cl > Br, the apparent inversion of the acceptor order is explicable.[54] In the case of the reaction,

$$MX_4 + 2L \to MX_4,2L$$

although there is likely to be appreciable $d_\pi-p_\pi$ bonding in the free tetrahalide, π-bond formation is still easily accomplished in the adduct $MX_4,2L$, particularly for a *cis*-configuration. With regard to the effect of the central atom (Sn $\gg$ Ge > Si) there is clearly a size effect operative.

Donors other than those mentioned in Table 2 have been much less extensively studied but support the general picture outlined above. Phosphoryl chloride gives an adduct with tin tetrachloride but does not react with the corresponding silicon or germanium compound.[55-59] Trialkyl phosphines form stable addition compounds with tin tetrachloride and tin tetrabromide, the chloride giving the more stable adduct. With tin tetraiodide no compound could be isolated.[60] One of the few anomalies found during the compilation of Table 2 was the supposed adduct $SiBr_4,2MeCN$.[18] We have not been able to prepare this compound from silicon tetrabromide and acetonitrile under anhydrous conditions.[61]

Occasionally, when a potential ligand is added to the acceptor, the result is a reaction rather than simple adduct formation, or the adduct undergoes subsequent reaction, for example with the excess of ligand. This is not, however, prevalent for fluorides; for example, the compound $SiF_4,2NH_3$ is well characterised.[62] In the case of the other halides, ease of reaction (as opposed to adduct formation) appears to decrease from silicon to tin. Silicon tetrachloride is easily hydrolysed or ammonolysed. With tin tetrachloride, the diammoniate has been reported[63] and, although the nature of the compound[64] $SnCl_4,5H_2O$ has yet to be fully elucidated, tin

[53] Craig and Zauli, *J. Chem. Phys.*, 1962, **37**, 609.
[54] Cotton and Leto, *J. Chem. Phys.*, 1959, **30**, 993.
[55] Markov, Voitovich, and Barabanova, *Russ. J. Inorg. Chem.*, 1961, **6**, 616.
[56] Sheldon and Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 4775.
[57] Sheldon and Tyree, *J. Amer. Chem. Soc.*, 1959, **81**, 2290.
[58] Payne, *Rec. Trav. chim.*, 1956, **75**, 620.
[59] Garner and Sugden, *J.*, 1929, 1298.
[60] Allison and Mann, *J.*, 1949, 2915.
[61] Beattie and Gilson, unpublished observations.
[62] Miller and Sisler, *J. Amer. Chem. Soc.*, 1955, **77**, 4998.
[63] Bannister and Fowles, *J.*, 1958, 751.
[64] See, for example, Maine and Walsh, *J. Inorg. Nuclear Chem.*, 1961, **19**, 156.

tetrachloride is less readily hydrolysed than silicon tetrachloride. It is interesting in this connection that germanium tetrachloride can be prepared by the action of hydrochloric acid on germanium dioxide.[65] The action of alcohols such as ethanol on these tetrachlorides shows[66] a reactivity order Si $\gg$ Sn $>$ Ge.

With donors not having an N–H or O–H grouping, the problem of reactivity is less obvious but may still be dominating. Dimethyl sulphoxide forms a simple addition compound with tin tetrachloride,[67] but if dimethyl sulphoxide is mixed with silicon tetrachloride, the following reaction occurs:[68]

$$SiCl_4 + 2Me_2SO \rightarrow 2Me_2S \cdot CH_2Cl + SiO_2 + 2HCl$$

It has recently been suggested that certain 1:4 addition compounds of silicon tetrachloride with electron donors such as pyridine N-oxide and triphenylphosphine oxide are examples of eight-co-ordinate silicon.[69] However the addition compound $SiBr_4,4Ph_3PO$ yields conducting solutions in propionitrile and has an infrared spectrum almost identical with that of $SiBr_2(ClO_4)_2,4Ph_3PO$ apart from the bands due to perchlorate. It appears that these compounds may contain the ion $[Si(Ph_3PO)_4]^{4+}$, which is stable in solution in propionitrile.[69a] Similarly the infrared spectrum of the adduct $SiI_4,4py$ has been interpreted[52a] on the basis of an ionic formulation cis-$[SiI_2 py_4]^{2+}$ $2I^-$, while tin and germanium tetraiodide with terpyridyl give 1:1 adducts which yield conducting solutions in nitrobenzene.[69b] The other tin tetrahalides with terpyridyl give 3:2 adducts[69b] which can be interpreted in terms of an ionic formulation (including SnX_6^{2-}). Silicon tetrachloride and germanium tetrachloride or bromide do not react with terpyridyl.[51,69b] In this connection it is interesting that the powerful donor o-phenylenebisdimethylarsine, which gives a 1:1 and a 1:2 (eight-co-ordinate) adduct with titanium tetrachloride, yields only a 1:1 adduct with tin tetrachloride and no adduct with silicon or germanium tetrachloride.[13]

   (b) **Adducts of Compounds Other than Simple Tetrahalides.**—Replacement of part or all of the halogen in the tetrahalides by other electronegative groups (including other halogens) leaves the central atom as a good acceptor. Thus, compounds such as $SiCl_2F_2,NMe_3$,[25] $Si(ClO_4)_4,2MeCN$ (cf. $SiCl_4$),[70] $Si(NO_3)_4,2py$,[71] $Si(SO_3F)_4,2MeCN$,[72] and $Sn(NO_3)_4,6Et_3N$[28]

[65] Foster and Williston, *Inorg. Synth.*, 1946, **2**, 112.
[66] Bradley, Caldwell, and Wardlaw, *J.*, 1957, 3039.
[67] Cotton and Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986.
[68] Lappert and Smith, *J.*, 1961, 3224.
[69] Issleib and Reingold, *Z. anorg. Chem.*, 1962, **314**, 113.
[69a] Beattie and Webster, unpublished work.
[69b] Wilkins, private communication.
[70] Schmeisser, *Angew. Chem.*, 1955, **67**, 493.
[71] Beattie and Leigh, *J.*, 1961, 4249.
[72] Hayek, Czaloun, and Krismer, *Monatsh.*, 1956, **87**, 741.

(from aqueous solution) are well established. Replacement of only one halogen in a tetrahalide by an alkyl or aryl group vastly alters the acceptor power of the central atom. Thus, silicon tetrachloride and pyridine react at room temperature to form a stable $1:2$ adduct of low volatility. Only a very unstable compound is formed with methyltrichlorosilane; with dimethyldichlorosilane and trimethylchlorosilane there is no apparent reaction under comparable conditions.[51] It is difficult to attribute this behaviour to steric effects. However, it has recently been shown[53] that the effects of hydrogen, carbon, fluorine, and chlorine in their perturbing power on the $3d$-orbitals of second-row elements fall in the order $F > Cl > C \gg H$. The first three are closer than would be expected on the basis of electronegativity alone, while hydrogen is relatively ineffective. Thus, we might expect a fall in acceptor power on substituting one chlorine in silicon tetrachloride by a methyl group. In addition to rendering the $3d$-orbitals more accessible for subsequent bonding, the substituents on the central atom must also be able to assist in delocalisation of the charge consequent on formation of a co-ordinate bond from the ligand. Chlorine is likely to be much more able to accommodate changes in its bonding to silicon (for example) than is methyl under comparable conditions. With tin(IV), the fall off on substituting halogen by alkyl or aryl is much less spectacular but still evident. A recent review[73] tabulates the co-ordination compounds of organotin halides with electron donors, so that this information is not repeated here. Frequently the stoicheiometry of these compounds can be interpreted in terms of a co-ordination number of six and it has been pointed out that the stability of six-co-ordinate anions of tin falls as the number of electronegative halogen substituents decreases,[74] giving the series $SnCl_6^{2-} > RSnCl_5^{2-} > R_2SnCl_4^{2-} > R_3SnCl_3^{2-}$. No addition compounds of MR_4 have ever been reported.[75] Trialkyltin halides such as trimethyltin chloride tend to give $1:1$ addition compounds with bases such as pyridine, but will not react with chelate donors such as 1,10-phenanthroline under comparable conditions.[76] This is in contrast with the other alkyltin halides which, like the tetrahalides, tend to give $1:1$ addition compounds with chelate ligands.[76,77]

The effect of the replacement of halogen in a tetrahalide by hydrogen is less easy to understand, as silane (like MR_4) forms no adducts, whereas Aylett[78] has interpreted earlier work[24] on the interaction of trimethylamine with SiH_xCl_{4-x} in terms of the unexpected stability sequence, $SiH_3Cl > SiH_2Cl_2 > SiHCl_3 > SiCl_4$. The very low volatility of H_3SiI,NMe_3 has been taken[25] to suggest a constitution different from those of apparently

[73] Ingham, Rosenberg, and Gilman, *Chem. Rev.*, 1960, **60**, 459.
[74] Seyferth and Grim, *J. Amer. Chem. Soc.*, 1961, **83**, 1610.
[75] See, for example, Kocheshkov, *Uchenuie Zapiski* (*Wiss. Ber. Moskau Staats-Univ.*), 1934, **3**, 297 (*Chem. Abs.*, 1936, **30**, 8184).
[76] Beattie and McQuillan, *J.*, 1963, 1519.
[77] Alleston and Davies, *Chem. and Ind.*, 1961, 551.
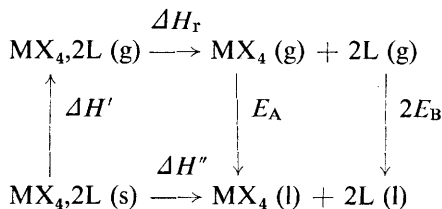[78] Aylett, *J. Inorg. Nuclear Chem.*, 1960, **15**, 87.

related compounds. Steric factors are clearly important in the complexes involving hydrogen linked to silicon.

5.   Use of the Term "Stability"

A note of caution should be observed here. All the discussion so far has centred on solid addition compounds. The observations on "stability" thus refer to the presence, at a particular temperature, of a solid compound for which the partial pressures of both of its constituents in the vapour phase in equilibrium with the solid are lower than the vapour pressures of the pure constituents. This statement ignores the possibility of complicating factors such as the formation of solid solutions. If we measure the vapour pressure above a solid $MX_4,2L$ as a function of temperature, then, in the simplest case, we obtain an approximate value for the enthalpy change in the reaction:

$$MX_4,2L \text{ (s)} \rightarrow MX_4 \text{ (g)} + 2L \text{ (g)}$$

(assuming that the compound is fully dissociated in the gas phase). A simple cycle indicates that ΔH for the above reaction includes a term due to the lattice energy.

$$
\begin{array}{ccc}
& \Delta H_r & \\
MX_4,2L \text{ (g)} & \longrightarrow & MX_4 \text{ (g)} + 2L \text{ (g)} \\
\uparrow \Delta H' & \downarrow E_A & \downarrow 2E_B \\
& \Delta H'' & \\
MX_4,2L \text{ (s)} & \longrightarrow & MX_4 \text{ (l)} + 2L \text{ (l)}
\end{array}
$$

From the above cycle:

$$\Delta H_r = - E_A - 2E_B + \Delta H'' - \Delta H'$$

Although the latent heats of evaporation of the acceptor (E_A) and of the ligand (E_B) are usually known, to calculate ΔH_r from $\Delta H''$ requires a knowledge of $\Delta H'$ the lattice energy term. Brown and Pearsall[79] state "of two addition compounds of *closely similar structure* and molecular weight, the less stable exhibits the higher saturation pressure" (my italics). A recent discussion by Bradley on molecular weight and volatility is of interest here.[80] Conclusions regarding the stability of co-ordination compounds, based on vapour pressure measurements on the solids are open to doubt and can only be of qualitative interest in the absence of adequate structural evidence.

[79] Brown and Pearsall, *J. Amer. Chem. Soc.*, 1945, **67**, 1765.
[80] Bradley, *Nature*, 1954, **174**, 323.

6. Stereochemistry

(a) **Mole Ratio, Acceptor: Donor, 1:1 (Monodentate.)**—There is only one compound in this class for which the stereochemistry is known. Me_3SnCl,py is an example of five-co-ordinate tin, the three methyl groups lying in the equatorial plane, with the pyridine and the chlorine axially.[81] An interesting related compound is the dimer of tetramethyl-1,3-bistrimethylsiloxydistannoxane with a nearly square Sn—O—Sn—O grouping.[82] The compound is unique in that it contains four- and five-co-ordinate tin and provides an example of oxygen donation to tin bound to two organic groups. As in the case of alkoxide polymers, the formation of "autocomplexes" involves synchronous donation and acceptance, rather than the simple acceptance of a lone pair of electrons, and accounts for the unusual stability of polymers of this type. Another example of a co-ordination number of five in the group may arise in the triptychsiloxazolidines[83] [e.g., $HSi(O \cdot CH_2 \cdot CH_2)_3N$].

A plausible explanation of 1:1 stoicheiometry would be the formation of salts, for example as quaternary ammonium compounds. This type of reaction is apparently rather rare for compounds of the elements of Group IV other than carbon, possibly because of a kinetic effect. Trimethylsilyl chloride and trimethylamine do not react when mixed at room temperature,[51] and trimethylsilyl chloride and pyridine can be heated under reflux without reaction.[61] However, methyl iodide and NN-dimethyl-(trimethylsilyl)amine react slowly at room temperature to give a 1:1 adduct,[84] involatile in vacuo at room temperature and unchanged after 18 hours at 110°. Similarly, although silylamines react readily with hydrogen chloride to yield chlorosilanes, it is possible[85] to obtain hydro-chlorides such as $Me_2N \cdot SiCl_3$,HCl analogous to the supposed $[Me_3Si \cdot NMe_3]^+I^-$. Silyl iodide, unlike trimethylsilyl chloride, forms with trimethylamine a 1:1 addition compound which yields conducting solutions in acetonitrile.[86] This adduct has therefore been formulated as an ammonium derivative.

The formation of compounds such as $[R_3ML]^+X^-$, where L is an electron-pair donor, is related to the ease of formation of the ion R_3M^+ in solvating solvents. It is well established that triphenylsilyl chloride does not ionise in solvents of high dielectric constant, such as nitrobenzene, even in the presence of powerful chloride acceptors.[87] This has been discussed in terms of the stabilisation of the molecular form of triphenylsilyl chloride by "resonance contributions" analogous to those usually

[81] Beattie, McQuillan, and Hulme, Chem. and Ind., 1962, 1429; Hulme, J., 1963, 1524.
[82] Okawara, Proc. Chem. Soc., 1961, 383.
[83] Frye, Vogel, and Hall, J. Amer. Chem. Soc., 1961, 83, 996.
[84] Ebsworth and Emeléus, J., 1958, 2150.
[85] Cass and Coates, J., 1952, 2347.
[86] Aylett, Emeléus, and Maddock, J. Inorg. Nuclear Chem., 1955, 1, 187.
[87] Thomas and Rochow, J. Inorg. Nuclear Chem., 1957, 4, 205.

used to explain the stability of the triphenylcarbonium ion.[88] The accessibility of R_3Si^+ and R_3C^+, where R is alkyl, may be comparable.[89] There is clear evidence for the ionisation of alkyltin halides in ionising solvents in the presence of a suitable Lewis base,[90] or where the solvent is also a donor. Thus, Prince[91] writes equilibria of the type:

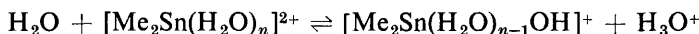$$R_3SnCl + S: \rightleftharpoons R_3SnS^+ + Cl^-$$
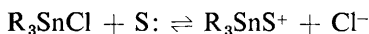
where S: is the donor solvent. Similarly, in solution in sulphuric acid,[92] trimethyltin sulphate is ionised, giving four particles for every molecule of $(Me_3Sn)_2SO_4$:

$$(Me_3Sn)_2SO_4 + H_2SO_4 = 2Me_3Sn^+ + 2HSO_4^-$$
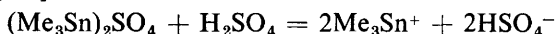
It is not known whether the ions are solvated. In aqueous solution the situation is complicated by hydrolysis and the formation of polynuclear species.[93] Dimethyltin chloride, when dissolved in water, yields strongly conducting solutions, interpreted in terms of the dissociation:[94]

$$Me_2SnCl_2 + nH_2O \rightleftharpoons [Me_2Sn(H_2O)_n]^{2+} + 2Cl^-$$

and the hydrolysis:

$$H_2O + [Me_2Sn(H_2O)_n]^{2+} \rightleftharpoons [Me_2Sn(H_2O)_{n-1}OH]^+ + H_3O^+$$

The hydrated Me_2Sn^{2+} ion is retained by an ion-exchange column and can be eluted with acids to yield the corresponding salts.[95] Similarly, triethyltin bromide has been reported to behave as a typical 1:1 electrolyte in water.[96]

The partial resolution of MeEtPrSnI from aqueous solution by conversion into the camphor sulphonate, followed by reconversion into the iodide, is recorded in the literature.[97] This has (reasonably) been taken to indicate that the ion $R^1R^2R^3Sn^+$ is monosolvated in aqueous solution, leading to an approximately tetrahedral arrangement.[98] Accumulated evidence on the tendency of tin linked to three alkyl groups to obtain a co-ordination number of five,[99] plus recent experiments yielding the nuclear magnetic resonance spectrum of trimethyltin chloride in aqueous solution,[100] suggests that hydrated triorganotin ions contain the planar

[88] Beattie and Gilson, *Nature*, 1962, **193**, 1041.
[89] Sommer and Baughman, *J. Amer. Chem. Soc.*, 1961, **83**, 3346.
[90] Kraus and Greer, *J. Amer. Chem. Soc.*, 1923, **45**, 2946.
[91] Prince, *J.*, 1959, 1783.
[92] Gillespie and Robinson, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 414.
[93] Tobias, Ogrins, and Nevett, *Inorg. Chem.*, 1962, **1**, 638.
[94] Rochow and Seyferth, *J. Amer. Chem. Soc.*, 1953, **75**, 2877.
[95] Gingold, Rochow, Seyferth, Smith, and West, *J. Amer. Chem. Soc.*, 1952, **74**, 6306.
[96] Dennison, Thesis, London, 1954.
[97] See, for example, Pope and Peachey, *Proc. Chem. Soc.*, 1900, **16**, 116.
[98] Coates, "Organometallic Compounds," Metheun, London, 1960.
[99] See, for example, Luijten, Janssen, and van der Kerk, *Rec. trav. chim.*, 1962, **81**, 202.
[100] Holmes and Kaesz, *J. Amer. Chem. Soc.*, 1961, **83**, 3903.

SnC_3 group and that the supposed resolution was not effected. This is borne out by Raman data on aqueous solutions of trimethyl-lead nitrate and perchlorate, which indicate the presence of planar PbC_3 units.[101]

In the solid state, the existence of discrete organotin ions has been inferred from the infrared spectra of the corresponding carboxylates,[102] but this approach has been criticised.[103]

An examination of Table 2 shows that adducts of trimethylamine *or* adducts of fluoride acceptors tend to give 1:1 stoicheiometry. In the case of trimethylamine addition compounds, where steric requirements are likely to be important, the stereochemistry of the ligand is such as to encourage a co-ordination number of five rather than six. By contrast, in the case of adducts with MF_4, halogen bridging is an attractive suggestion. The only *X*-ray evidence for halogen bridging in Group IVB is that found in the tetrafluorides of tin and lead[104] and in the recently determined structure of trimethyltin fluoride.[104a]

(b) **Mole Ratio, Acceptor:Donor, 1:2 (monodentate), 1:1 (bidentate).**— The model to be expected here is that based on an octahedral distribution about the central atom with the added possibility of *cis–trans* isomerism for non-chelate ligands. Considering the adduct MX_4L_2, and representing L by a single atom, we have to decide between *cis*- (I) and *trans*-isomers (II). Where X is much larger than L, the main repulsions will be between X and X. L will have to fit in as best it can. Initially it may appear that a
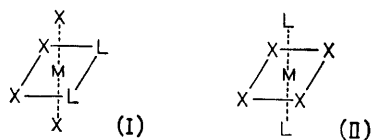
trans-adduct is favoured if only X–X repulsions are considered [and all bond angles are 90°, as indicated in (I) and (II)]. However, if the *cis*-adduct is distorted so that the MX_4 residue becomes more like the original tetrahalide, then, on the basis of X–X repulsions only, a *cis*-adduct becomes stereochemically probable. This is illustrated in the Figure, which shows the nitrogen (radius taken as 0·7 Å) of acetonitrile co-ordinated to two faces of undistorted tetrahedral tin tetrachloride (tin and chlorine radii taken as 1·2 Å to allow crudely for the ionic nature of the Sn–Cl link). The pointed acetonitrile molecules can thus fit into the tetrahedron (causing distortion) and effectively make a *cis*-adduct. Had we used

[101] Goggin, Thesis, Oxford, 1960.
[102] Okawara, Webster, and Rochow, *J. Amer. Chem. Soc.*, 1960, **82**, 3287; see also Kriegsmann and Pischtschan, *Z. anorg. Chem.*, 1961, **308**, 212.
[103] Beattie and Gilson, *J.*, 1961, 2585; see also Okawara, Hathaway, and Webster, *Proc. Chem. Soc.*, 1963, 13; Janssen, Luijten,and van der Kerk, *Rev. Trav. chim.*, 1963, **82**, 90.
[104] Hoppe and Dähne, *Naturwiss.*, 1962, **49**, 254.
[104a] Clark, O'Brien, and Trotter, *Proc. Chem. Soc.* 1963, 85.

a large ligand atom (or a sterically hindered ligand) we would predict a
change over to a *trans*-adduct, as L–X repulsions would then be of major
importance. Introducing d_π–p_π bonding, the *cis*-adduct is apparently
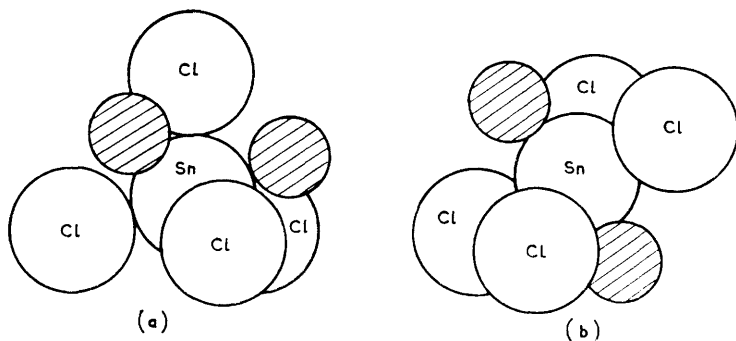
Co-ordination of the nitrogen of acetonitrile to tin tetrachloride to yield the 1:2 *adduct:*
(a) cis, (b) trans.

favoured if we assume that π-bonding from X to M is more important than π-
bonding involving L. It is interesting to notice here that two faces of the
tetrahedron in Fig. (a) are still unoccupied, but if further co-ordination
occurs we obtain an eight-co-ordinate adduct, rather like that found for
$TiCl_4(o\text{-phenylenebisdimethylarsine})_2$.[13]
    The examination of the stereochemistry of MX_4L_2 at equilibrium in

TABLE 3. *Probable stereochemistry of* $MX_4,2L$ *adducts.*

Compound	Stereochemistry	Technique	Ref.
$SnF_4 2A$	*cis*	n.m.r. [19]F	19
$SnCl_4,2MeCN$	*cis*	i.r. (Sn–Cl)	105a
$SnCl_4,2EtCN$	*cis*	i.r. (Sn–Cl)	105a
$SnCl_4,2Me_2CO$	*cis*	i.r. (Sn–Cl)	105b
$SnCl_4,2POCl_3$	*cis*	X-ray	106
$GeCl_4,2$ pyridine	*trans*	i.r. (Ge–Cl) and X-ray	50, 105a
$SiCl_4,2$ pyridine	*cis*	i.r. (Si–Cl)	52a
$SiBr_4,2$ pyridine	*cis*	i.r. (Si–Br)	52a
$Me_2SnCl_4{}^{2-}$	*trans*	i.r. (Sn–C)	76
$SnCl_4,2(CH_2)_4O$	*trans*	i.r. (Sn–Cl)	105b
$SnCl_4,2(CH_2)_4S$	*trans*	i.r. (Sn–Cl)	105b
$SnCl_4,2Et_2S$	*trans*	i.r. (Sn–Cl)	105b
$SnCl_4,2Et_2O$	*trans*	i.r. (Sn–Cl)	105b
$SnCl_4,2NMe_3$	*trans*	i.r. (Sn–Cl)	105b

A = various donors (not clearly specified).

[105a] Beattie, McQuillan, Rule, and Webster, *J.*, 1963, 1514.
[105b] Beattie and Rule, *J.*, in the press.
[106] Branden, *Acta. Chem. Scand.*, 1963, **17**, 759.

solution is most conveniently carried out using infrared and Raman spectroscopy. The symmetry of the MX_4 residue in MX_4L_2 is lower for a *cis*-adduct (C_{2v}) than for a *trans*-adduct (D_{4h}), leading to the prediction[69a] that the infrared spectrum of the *cis*-adduct should be more complex (three fundamentals) than that of the *trans*-adduct (one fundamental) in the region of the M–X stretching vibrations. The spectra of adducts containing supposedly chelate ligands, such as 1,10-phenanthroline and 2,2′-bipyridyl, supports these conclusions which enable the assignment of stereochemistry to be made, in the absence of complicating factors such as crystal field effects. Table 3 summarises the results of such an investigation and includes certain other stereochemical assignments made on the basis of reliable physical studies. It should be noted that recent Raman work on addition compounds of tin tetrachloride does not agree with the *cis* infrared assignment for the acetonitrile and propionitrile adducts.[107]

Generally, the picture emerging from Table 3 is that small ligands tend to give *cis*-adducts, while ligands which are sterically hindered (in a fairly symmetrical fashion) tend to give *trans*-adducts. Where a strongly co-ordinating ligand such as the methide ion, Me:⁻ is used, the adduct is perhaps best considered as a co-ordination compound of linear $SnMe_2^{2+}$ (analogous to linear $HgMe_2$) with chloride ions. A strongly co-ordinating ligand could also have the effect of reducing d_π–p_π-bonding between the halogen and the tin, so that one factor favouring a *cis*-configuration is lost. In the case of tin tetrafluoride where F–F repulsions in the adduct are not likely to be of major importance, it is necessary to invoke fairly strong π-bonding to account for the stereochemical observations.[19] The position of the M–F vibrations has been invoked to assign an octahedral configuration to certain adducts of silicon tetrafluoride,[108] and ligand vibrations have been used to assign stereochemistry in a rather less satisfactory manner. The splitting of the frequency associated with the S–O bond in dimethyl sulphoxide adducts of tin tetrachloride[68] and tin tetrafluoride[109] and of the phosphoryl absorption in $SnCl_4,2POCl_3$[56] suggests a *cis*-configuration for these molecules, although other explanations are possible. Similarly, the lack of splitting in $SnCl_4,2EtOAc$[110] (single sharp carbonyl band), $SiF_4,2Me_2SO$, and $GeF_4,2Me_2SO$ (both with a single sulphinyl band)[109] has been taken to indicate a *trans*-formulation. However, assignment is difficult even under ideal conditions. The coupling between two ligand molecules via the central atom of an adduct will depend on the force-constant of the metal–ligand bond and on the mass of the central atom. If the coupling is weak, the splitting for a *cis*-adduct may not be observed. Conversely, splitting in the solid state cannot be considered to be conclusive evidence for a *cis*-adduct and, in solution, "splitting" may be

[107] Brune and Zeil, *Z. phys. Chem.* (*Frankfurt*), 1962, **32**, 384.
[108] Gutmann and Utvary, *Monatsh.*, 1959, **90**, 706.
[109] Muetterties, "Advances in the Chemistry of the Co-ordination Compounds," ed. Kirschner, Macmillan, New York, 1962.
[110] Lappert, *J.*, 1962, 542.

due to dissociation to other species. The compound $SnCl_4,2MeCN$ is a *cis* octahedral co-ordination compound, as shown by its infrared spectrum in the Sn–Cl stretching region.[105a] In the rock-salt region, however, apparently only one C–N frequency is observed.[37] It is interesting that splitting of a band close to that found for the phosphoryl group in phosphoryl chloride can be observed in the Raman spectrum of tin tetrachloride dissolved in phosphoryl chloride.[111]

The only *X*-ray data available for 1:2 addition compounds are those on $MX_6{}^{2-}$ ($[SnCl_6]^{2-}$, for example, may be regarded as a 1:2 adduct of $SnCl_4$ and Cl^-) plus the determinations on *cis*-$[SnCl_4(SeOCl_2)_2]$,[112] *cis*-$[SnCl_4(POCl_3)_2]$,[106] and *trans*-$[Ge\ py_2Cl_4]$.[50] The crystal structure of *cis*-$[SnCl_4(SeOCl_2)_2]$ is complicated by additional interactions within the crystal above those indicated by the molecular formulation, and attributed to the acceptor properties of selenyl chloride. The configuration of the $MX_6{}^{2-}$ ions is octahedral and the occurrence of $SiF_6{}^{2-}$, $GeF_6{}^{2-}$, $GeCl_6{}^{2-}$, $SnF_6{}^{2-}$, $SnCl_6{}^{2-}$, $SnBr_6{}^{2-}$, and $SnI_6{}^{2-}$ reinforces the earlier comments on acceptor properties, $Sn \gg Ge > Si$ and $F > Cl > Br > I$. The hexahydroxotin(IV) ion is also octahedral.[113]

Nuclear magnetic resonance spectroscopy has been applied to the study of the stereochemistry of adducts of tin tetrafluoride. The ^{19}F spectrum of tin tetrafluoride in certain ligands, from about $+15°$ down to the freezing point of the ligand, consists of two peaks further of equal intensity, each split into triplets.[19] This behaviour is to be expected for a *cis*-adduct where there are two pairs of fluorines in different environments. On warming these solutions, the fine structure is lost with simultaneous broadening of the peaks and eventual collapse to a single resonance. Where a single peak is observed (as predicted for a *trans*-adduct and observed for germanium tetrafluoride and silicon tetrafluoride in various ligands) the results are inconclusive, as the single peak may be due to an exchange process.

The number of soluble silicon or germanium tetrahalide co-ordination compounds is extremely small, so that nearly all the dipole-moment work has been carried out on tin compounds, particularly on adducts of tin tetrachloride. There have been two main approaches to this problem, *viz.*, solution of the acceptor in the (non-polar) ligand and solution of the adduct in an inert solvent.

The electric moments of silicon tetrachloride (0 D),[114] germanium tetrachloride (0·67 D)[114], and tin tetrachloride (3·82[114] and 5·10 D[115]) in dioxan have been interpreted in terms of an increased tendency to form complexes on passing from silicon to tin. However, the formation of a six-co-ordinate *trans*-adduct could result in a moment, ranging from zero to quite a large

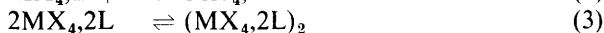[111] Kinell, Lindqvist, and Zackrisson, *Acta Chem. Scand.*, 1959, **13**, 1159.
[112] Hermodsson, *Acta Cryst.*, 1960, **13**, 656.
[113] Björlung, *Arkiv Kem. Mineral Geol.*, 1941, **15***B*, No. 2.
[114] Lane, McCusker, and Curran, *J. Amer. Chem. Soc.*, 1942, **64**, 2076.
[115] Osipov and Kletenik, *Russ. J. Inorg. Chem.*, 1959, **4**, 672.

value (depending on the alignment of the ligands), while a five-co-ordinate entity of almost any shape would be expected to have a large moment. A further difficulty in the interpretation of such data is the possibility that the adducts may have a high atom-polarisation. There is a considerable amount of Russian work on measurements of the dipole moment of various MX_4 adducts, in inert solvents. This has been criticised by Brown and Kubota,[116] dipole moments having been computed on the arbitrary assumption that stoicheiometric quantities of donor and acceptor, when present in solution, react quantitatively to give the required addition compound. It is essential that dipole-moment studies should be supported by ancillary measurements. Ulich, Hertel, and Nespital[117] have examined the molecular weight and dipole moment of $1:2$ adducts of tin tetrachloride with benzonitrile, propionitrile, acetone, acetophenone, and benzaldehyde. These authors realised that, for $1:2$ adducts, there was a possibility of *cis-trans* isomerism and interpreted their data in terms of the equilibria (1)—(3). It was observed

$$MX_4 + L \rightleftharpoons MX_4,L \qquad (1)$$
$$MX_4,L + L \rightleftharpoons MX_4,2L \qquad (2)$$
$$2MX_4,2L \rightleftharpoons (MX_4,2L)_2 \qquad (3)$$

that all compounds dissociate on dissolution in benzene, and for nitrile adducts a co-ordination number of five appeared to be rather stable. The system, tin tetrachloride–benzonitrile in benzene, has been reinvestigated in detail,[116] using infrared data to supplement the dipole-moment measurements. The results obtained agreed qualitatively with those of the earlier workers but the inclusion of equilibrium (3) was found to be unnecessary. It is noteworthy that in the only case where the equilibria have been extensively studied, the dipole moment of the $1:2$ adduct could not be determined. That of the $1:1$ adduct was in the region of 8.4 D. In several cases, although authors appear to be aware of the possibility of dissociation, it is not clear whether quantitative allowance has been made for the effects of this dissociation.[118] There is also the added difficulty that *cis-* and *trans-* isomers may co-exist in one solution.

Although resolution of a chelate adduct such as *cis*-$MX_2Y_2A_2$ (where X and Y are different halogens and A_2 is the chelate ligand) would constitute proof of configuration, no examples of such behaviour are known or likely to be found. However, the partial resolution of the trisoxalato-germanium(IV) ion through the quinine and strychnine salts has been reported.[119] The authors of this paper commented (1953) that this was the first recorded resolution of a six-co-ordinate "outer orbital" complex of a quadripositive ion. The compound $[Si(acac)_3]^+HCl_2^-$ (where Hacac = acetylacetone) was resolved through the dibenzoyl tartrate.[120]

[116] Brown and Kubota, *J. Amer. Chem. Soc.*, 1961, **83**, 331, and references therein.
[117] Ulich, Hertel, and Nespital, *Z. phys. Chem.*, 1932, **B17**, 21.
[118] See, for example, Gold'shtein, Gur'yanova, and Kocheshkov, *Proc. Akad. Sci.*, (*U.S.S.R.*), 1961, **138**, 566.
[119] Moeller and Nielsen, *J. Amer. Chem. Soc.*, 1953, **75**, 5106.
[120] Dhar, Doron, and Kirschner, *J. Amer. Chem. Soc.*, 1959, **81**, 6372.

7. Acceptor Strength

(a) d_π–p_π-**Bonding.**—There is a formidable array of evidence that silicon is capable of forming π-bonds to ligands by the use of d-type orbitals. Particularly striking examples suggesting the existence of d_π–p_π bonding are the near planarity of the NSi_3 skeleton of trisilylamine,[16] the apparent coplanarity of the three nitrogen valencies in tetramethyl-NN'-bistrimethylsilylcyclodisilazane,[121] the wide Si–O–Si angle in siloxane,[122] and the apparent colinearity of the heavy atoms in silyl isothiocyanate.[123] Similarly, "bond-shortening" in the tetrahalides of silicon can be explained in terms of "back-donation," although other suggestions have been advanced.[5,124] The "radius sum" in silicon tetrafluoride is 1·89 Å, where the observed distance[5] Si–F is 1·54 Å. The C–F distance in carbon tetrafluoride[125] is also "anomalously short."

Eaborn[8] has discussed d_π–p_π-bonding in organosilicon compounds in some detail, so that only more recent references are here noted. Thus, d_π–p_π-bonding may be invoked to explain the relative basicities, $Me_3N >$ $Me_2N{\cdot}SiH_3 > MeN(SiH_3)_2 > N(SiH_3)_3$, towards the reference acceptor trimethylaluminium[126] (although steric effects must be of some importance here), the sequence of basicities, ethers > alkoxysilanes > siloxanes, towards phenol for hydrogen-bond formation,[127] and the colour of α-silyl ketones.[128]

A point of more general interest concerns the relative abilities of silicon, germanium, tin, and lead to form d_π–p_π-bonds. Microwave studies[129] suggest that silicon forms π-bonds more efficiently than germanium in compounds of the type MH_3X (where M = Si or Ge, and X = F, Cl or Br). Studies on hydrogen-bond formation with ether and phenol, using the compounds Ph_3MOH (M = Si, Ge, Sn, Pb), suggest that π-bonding from oxygen to M is greatest where M is silicon, weaker where M is germanium, and negligible where M is tin or lead.[130] Similarly, the electron spin resonance spectra of phenyltrimethyl-silane and -germane anions suggest that silicon in $-SiMe_3$ is more able to delocalise aromatic π-electrons than germanium in $-GeMe_3$.[130a] By contrast, studies of the strengths

[121] Wheatley, *J.*, 1962, 1721.

[122] See, for example, McKean, Taylor, and Woodward, *Proc. Chem. Soc.*, 1959, 321, and references therein.

[123] Ebsworth, Mould, Taylor, Wilkinson, and Woodward, *Trans. Faraday Soc.*, 1962, **58**, 1070, see also Linnett, *Nature*, 1963, **199**, 168.

[124] Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 2140.

[125] For an interesting account of double-bonding in CF_4, see Williams, *Trans. Faraday Soc.*, 1961, **57**, 2089.

[126] Manasevit, *U.S. Dept. Com., office Tech. Serv., PB Rept.*, 143, 572, 1959 (*Chem. Abs.*, 1961, **55**, 17333).

[127] West, Whatley and Lake, *J. Amer. Chem. Soc.*, 1961, **83**, 761.

[128] Harnish and West, *Inorg. Chem.*, 1963, **2**, 1082.

[129] See, for example, Sharbaugh, Pritchard, Thomas, Mays, and Dailey, *Phys. Rev.*, 1950, **79**, 189; Dailey, Mays, and Townes, *Phys. Rev.*, 1949, **76**, 136; Griffiths and McAfee, *Proc. Chem. Soc.*, 1961, 456.

[130] West, Baney, and Powell, *J. Amer. Chem. Soc.*, 1960, **82**, 6269.

[130a] Bedford, Bolton, Carrington, and Prince, *Trans. Faraday Soc.*, 1963, **59**, 53.

of the acids $p\text{-}R_3M\cdot C_6H_4\cdot CO_2H$ (M = Si, Ge, Sn) have been taken to indicate that $d_\pi\text{-}p_\pi$-bonding from the aromatic system to M is independent of the nature of M[131] (in agreement with theoretical predictions that $d_\pi\text{-}p_\pi$-bonding should not depend greatly on the relative sizes of the orbitals concerned, particularly where the d-orbitals are much more diffuse than the p-orbital).[132]

(b) σ-**Bonding Involving d-Type Orbitals.**—It appears that co-ordination compounds of MX_4 with electron donors are almost fully dissociated in the gas phase. In the absence of techniques capable of measuring the small amount of adduct present in the vapour, the best that can be obtained is a measure of the equilibria present in solution in an inert solvent. However, the co-ordination compounds under review are frequently insoluble at normal temperatures in all solvents with which they do not react. The more powerful donors such as pyridine, dimethyl sulphoxide, and pyridine N-oxide appear to yield (where formed) insoluble adducts with MCl_4 (M = Si, Ge, Sn). With weaker donors, such as acetonitrile, tetrahydro-furan, and diethyl sulphide, the adducts with tin tetrachloride will dis-solve in solvents such as benzene, frequently with extensive dissociation. There is very little evidence of complex formation by these ligands with silicon and germanium tetrachlorides under comparable conditions.

In the reaction:

$$MX_4 \text{ (soln.)} + nL \text{ (soln.)} \rightleftharpoons MX_4,nL \text{ (soln.)} \qquad (4)$$

if the amount of adduct formed is small, it will normally be necessary to determine MX_4,nL, as the concentration of MX_4 and L will be significantly altered by unavoidable hydrolysis. It is not easy to devise a simple tech-nique which will quantitatively measure the low concentration of an adduct, particularly where elevated temperatures are necessary to obtain adequate solubilities. Ultraviolet spectroscopy will quantitatively measure MX_4,nL for certain suitable ligands, and, with adequate precaution, may be useful as a general technique. The accuracy of determination using infrared spectro-scopy or nuclear magnetic resonance spectroscopy is lower, but these tech-niques are capable of supplying semi-quantitative information. Although competitive reactions, involving MX_4 and MY_4 (where X and Y are both halogens) and a ligand, may appear to be useful to study the relative acceptor strengths of MX_4 and MY_4, rapid equilibration may occur between the two acceptors to yield species such as MX_2Y_2.[133]

There have been very few quantitative studies along the lines indicated above. Job's method of continuous variations has been applied to the systems tin tetrachloride–4-aminoazobenzene, in 1,2-dichloroethane (A_3B_2 adduct) and tin tetrachloride–tribenzylamine in 1,2-dichloroethane
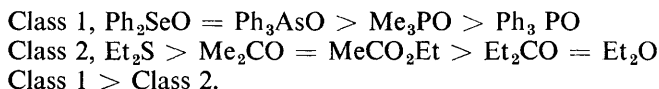
[131] Chatt and Williams, *J.*, 1954, 4403.

[132] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

[133] See, for example, Burke, and Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 326; also Delwaull, Buisset, and Delhaye, *J. Amer. Chem. Soc.*, 1952, **74**, 5768.

(AB adduct),[134] using the ultraviolet spectra of the species as the physical property. More recently, Satchell and Wardell[135] have examined the interaction of tin tetrachloride with nitroanilines and ring-substituted nitroanilines in o-dichlorobenzene. The results show the presence of 1:1 adducts in solution whose stabilities, in the absence of steric effects, are generally in the same order as the base strength of the ligands in aqueous solution. It is interesting that the only isolable solids had 1:2 stoicheiometry. A detailed study of the system tin tetrachloride–benzonitrile in benzene, using infrared spectroscopy, also indicated the presence of a fairly stable 1:1 adduct.[116]

There have likewise been few systematic studies of the enthalpy change in reactions such as (4). Where $n = 2$, the enthalpy change appears to be[17,136] of the order of -20 kcal. mole^{-1}. Lindqvist and Zackrisson[137] have studied the relative strengths of various donors to tin tetrachloride in solution by taking two equal volumes of a solution of tin tetrachloride, pouring a solution of a different donor into each, and noting which gave out the greater heat. The qualitative order so formed was:

Class 1, $Ph_2SeO = Ph_3AsO > Me_3PO > Ph_3\,PO$
Class 2, $Et_2S > Me_2CO = MeCO_2Et > Et_2CO = Et_2O$
Class 1 > Class 2.

Cioff and Zenchelsky[137a] examined the interaction of tin tetrachloride with cyclic ethers and interpreted their results (tetrahydrofuran $>$ tetrahydropyran $>$ 4-methyltetrahydropyran $>$ 2-methyltetrahydrofuran $>$ 2,5-dimethyltetrahydrofuran) in terms of steric factors.

Cryoscopic and ebullioscopic determinations of molecular weight are important ancillary experiments to the majority of studies in solution. In most cases a co-ordination number of six is indicated, showing dissociation to a five-co-ordinate adduct on dilution. Stannic isopropoxide forms a solvate which is nearly dimeric $[Sn_2(OPr^i{}_8)(Pr^iOH)_2]$ in boiling isopropanol,[138] $SnCl_4,2Et_2O$ shows extensive dissociation in benzene,[21] dimethyl sulphoxide adducts of silicon tetrafluoride and tin tetrafluoride in tetrahydrofuran have been reported to yield cryoscopic molecular weights of 265 and 344, respectively,[19] in good agreement with those calculated for a co-ordination number of six, while the 1:1 adduct of tin tetrachloride with diethyloxalate is apparently dimeric in benzene.[139]

A superficially attractive method of studying the "stability" of co-ordination compounds depends on shifts in the frequency of infrared active vibrations of the ligand on complex formation. Its attraction lies

[134] Shuba and Zenchelsky, *J. Amer. Chem. Soc.*, 1960, **82**, 4136.
[135] Satchell and Wardell, *Proc. Chem. Soc.*, 1963, 82.
[136] Hieber and Reindl, *Z. Elektrochem.*, 1940, **46**, 559.
[137] Lindqvist and Zackrisson, *Acta Chem. Scand.*, 1960, **14**, 453.
[137a] Cioff and Zenchelsky, *J. Phys. Chem.*, 1963, **67**, 357.
[138] Bradley and Holloway, *Canad. J. Chem.*, 1962, **40**, 1176.
[139] Sumarakova, Nevskaya, and Yarmukhamedova, *J. Gen. Chem. (U.S.S.R.)*, 1960, **30**, 1696.

in the fact that measurements can be made rapidly and it is applicable in the solid state. For example, on co-ordination of acetonitrile with several acceptors, the "C–N stretching frequency" is shifted to a higher frequency than that found for the free ligand. The shift of the C–N frequency on co-ordination could be taken as a measure of the stability of the adduct. However, it is known that the frequency of the cyanide vibration in complexes involving this ion is relatively insensitive to changes in the metal-carbon bond frequency.[140] Further, although the enthalpies of formation of $SbCl_5,Me_3PO$ and $SbCl_3,Me_3PO$ are very different, the P–O stretching frequencies in the two compounds occur at similar positions on their infrared spectra.[141] Similarly, the stretching force constants of the M–O bond in PO_4^{3-}, SO_4^{2-}, and ClO_4^- follow the erratic order 9·05, 9·07, 8·24 md/Å, respectively.[142] The effect of co-ordination on the carbonyl frequency of ethyl acetate has been interpreted in terms of the stability of the adducts with $SiCl_4$, $GeCl_4$, $SnCl_4$, and $SnBr_4$.[110] Similarly, the *position* of the totally symmetric Sn–Cl stretching vibration of $MCl_4,2L$ (symmetry taken as D_{4h}) has been interpreted in terms of the *strength* of the M–L bond, although the assignment of stereochemistry is in doubt.[105a,107]

8. Summary and Conclusions

(a) The formation of co-ordination compounds by the tetrahalides of silicon, germanium, and tin appears to follow the sequence Sn $\gg$ Ge $>$ Si and F $>$ Cl $>$ Br $>$ I. The majority of the observations refer to 1:2 addition compounds with monodentate ligands and can be understood in terms of a co-ordination number of six. Where a 1:1 adduct is formed with a monodentate ligand this may be rationalised through halogen bridging (most probable for fluoride adducts) or a co-ordination number of five. It appears that, for this class of compound, a co-ordination number of five is by no means rare in solution.

Nearly all stability-constant observations refer to aqueous solutions, where it is usually found $K_1 > K_2 > K_N$. This is the sequence to be expected when it is remembered that the reaction observed is essentially the displacement of water from the co-ordination sphere by the new ligand. In non-aqueous non-co-ordinating solvents the tetrahalide commences with tetrahedral symmetry and finishes as a trigonal bipyramidal or octahedral adduct. There is thus a "reorganisation" energy involved which renders the prediction of the relative stability of 1:1 and 1:2 adducts difficult. Similarly, the "reorganisation" energy will be less favourable for sp^3d^2 hybridisation (involving d-orbitals of the same principal quantum number as the s- and p-orbitals) than for d^2sp^3 hybridisation, where inner d-orbitals are used.

[140] Cotton, "Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience, London, 1960, see also Beattie and Gilson, *J.*, in the press.
[141] Zackrisson and Alden, *Acta Chem. Scand.*, 1960, **14**, 994.
[142] See Cruickshank, *J.*, 1961, 5486.

(b) The occurrence of *cis–trans*-isomers of the 1:2 adducts may be conveniently discussed from the point of view of steric effects and d_π–p_π-bonding. For tin tetrafluoride, π-bonding appears to be of major importance. Steric factors can possibly account for the sequence: *cis*-SiCl$_4$py$_2$, *trans*-GeCl$_4$py$_2$, *trans*-SnCl$_4$py$_2$. Compounds such as *trans*-Me$_2$SnCl$_4{}^{2-}$ are best regarded as adducts of linear Me$_2$Sn^{2+} with chloride ions.

(c) There is a lack of reliable thermochemical data for reactions of the type:

$$MX_4 + nL \rightleftharpoons MX_4L_n$$
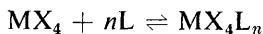
in solution. This is largely due to the insolubility of many of the co-ordination compounds, plus the insolubility of tin tetrafluoride in non-co-ordinating solvents. Nevertheless, for the other tin tetrahalides, this last difficulty does not occur and many of the less stable co-ordination compounds are soluble in inert solvents. There is a wide field available for the study of the thermochemical and stereochemical properties of the 1:1 and 1:2 adducts of these tetrahalides in non-aqueous solutions. It is likely that infrared and Raman spectroscopy will play an important role in such studies.

(d) A considerable amount of published work in Group (IV) is suspect owing to the presence of water in the systems. The statement, "20 p.p.m. of water by weight (0·002%) in a solvent means a water molarity of about M/1000," should constantly be borne in mind (we have assumed the specific gravity of the solvent to be 1). In the characterisation of an adduct, extreme care is necessary to ensure that the analytical figures do not refer to a hydrolysis product. The compound SiI$_4$,4py has been reported by several groups of workers and represents a true adduct. Inspection

TABLE 4. *Analytical data for the adduct SiI$_4$,4py and its hydrolysis product (figures represent weight %).*

	C	H	N	I	Si	Ref.
SiI$_4$,4py (theory)	28·2	2·4	6·6	59·6	3·2	—
SiI$_4$,4py (found)	27·4	2·5	6·6	60·6	3·2	29
SiI$_4$,4py (found)	27·9	3·2	5·9	57·2	—	44
4(py,HI) + SiO$_2$	27·0	2·7	6·3	57·1	3·2	—

of Table 4 indicates how difficult it is to differentiate the hydrolysis products from an adduct solely by analysis. Infrared spectroscopy in the rock-salt region would, however, immediately show whether co-ordinated pyridine, or pyridinium ion, was present. In certain cases, compounds that are apparently stable to hydrolysis may, on the addition of bases such as pyridine, undergo rapid hydrolysis. Thus, reactions intended to yield addition compounds of organotin halides may, when carried out in wet solvents, lead to compounds of the type R$_4$Sn$_2$X$_2$O.[143]

Where physical measurements are subsequently carried out in dilute

[143] Alleston and Davies, *Chem. and Ind.*, 1961, 949.

solution, care is even more necessary. Such examples occur in conductance experiments or ultraviolet spectroscopic measurements. Frequently, titrations of reactive halides with Lewis bases such as pyridine yield conductance curves showing remarkable resemblances to those found in the titration of pyridine with hydrogen halide,[144] while, at 10^{-4}M, only 2 p.p.m. of water makes the mole ratio of compound to water $1:1$.

[144] Beattie and Leigh, *J.*, 1962, 4726.