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THE COORDINATION CHEMISTRY OF THALLIUM(I)

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> 'When we are in possession of a few more local monographs – then, and only then, by grouping their data, by minutely confronting and comparing them, we shall be able to reconsider the subject as a whole, and take a new and decisive step forward To proceed otherwise, would be merely to start, armed with two or three rough and simple ideas, on a kind of rapid excursion It would be in most cases, to pass by everything that is particular, individual, irregular – that is to say, everything, on the whole, that is most interesting '
>
> Lucien Fèbvre
> *'La Terre et L'Evolution Humaine'*

CONTENTS

In 1864, Sir William Crookes wrote [1].

'The position of thallium amongst elementary bodies has given rise to considerable discussion. On the Continent it is generally classed amongst alkali-metals, in England it is, on the other hand, generally regarded as belonging to the silver and lead group.'

Fortunately, this is no longer an issue that needs to be thrashed out between Britain and the members of the Common Market But the effect of the 'heavy-metal-like' properties of thallium on its behaviour as a univalent cation is still of considerable interest. Apart from its intrinsic importance as a problem in inorganic chemistry, there is the possibility that, in the future, it will help to throw some light on a very different problem· that of the interactions of univalent cations (particularly potassium) in biological systems. Not only can the differences between thallium(I) and the alkali metal cations be used to argue the sites of interaction of the alkali metal cations, but thallium(I) can be used as a probe for the alkali metals, whereas the alkali metals have very few properties which can be studied spectroscopically, thallium(I) has many – intense UV absorption, fluorescence, nuclear spin $I = ½$, and temperature-independent paramagnetism

A INTRODUCTION

The first three ionisation potentials of thallium are 142, 472 and 688 kcal/g atom respectively [2] The stability of thallium(I) with respect to thallium(III) is high [2]. The standard oxidation potential of thallium(I) in aqueous solution is [3] $-1\ 25$ V

The thallium(I) ion has the ground state electronic configuration $6s^2$ Such a pair of s electrons beyond a completed shell generally results in a non-spherical charge distribution around the element in solids and this, in turn, results in a lowering of the symmetry of coordination of negative ions around the element. The first excited state of the thallium(I) ion has the configuration $6s^1 6p^1$ and is only 7.4 eV above the $6s^2$ ground state [4]. Extra stabilisation can thus be gained by s–p mixing [5]. As the s atomic orbital is spherically symmetric and a p orbital is not, such stabilisation is only possible for an unsymmetrical distortion of the environment of the ion; a symmetric distortion could only mix the 6*s* electrons with other *s* or with *d* orbitals, but since energy states involving 6*d* and 7*s* orbitals are highly excited, effects of *s*–*s* and *s*–*d* mixing should be unimportant. Thallium(I) derivatives can thus be expected to adopt distorted octahedral or cubic structures. It may require low temperatures to reveal these distortions since at high temperatures the distortions at different sites may be disordered, in which case the crystal, as a whole, will behave as if it were undistorted

TABLE 1

Physical properties of thallium(I) and the alkali metal cations

M	Ionic radii M^+ (Å)	Polarisability [7] M^+ ($Å^3$)	Electronegativity [8] M^+	Electron affinity [9,10]	Enthalpy of hydration [11] (kcal mole^{-1})
Li	0.86	0.03	0.98	0.60	−134
Na	1.12	0.41	0.93	0.35	−107
K	1.44	1.33	0.82	0.30	− 87
Rb	1.58	1.98	0.82	0.27	− 80
Cs	1.84	3.34	0.79	0.23	− 76
Tl	1.54	5.2	1.62	0.32 or 1.21	− 92

The ionic radii of Tl^+ and K^+ are very similar (Table 1). Thallium(I), however, has a considerably greater molecular polarisability This will lead to differences between thallium(I) and the alkali metal cations; to distinguish between those differences arising from this cause and those differences arising from 'partial covalent bonding' is extremely difficult. To some extent polarisation and 'partial covalent bonding' mean the same thing, and 'partial covalent bonding' appears to mean very much more than in reality it does Electronegativities and electron affinities of thallium and the alkali metals are also given in Table 1.

The thallium(I) ion is only very weakly hydrated in solution (Table 1). In view of the very low value for the enthalpy of hydration it is not clear whether one is justified in speaking of a hydrated ion in solution at all, that is, if by hydrated ion one means an ion with a constant hydration number. One might say that the ion is simply stabilised by macroscopic dielectric hydration [12]. Measurements of the self-diffusion of thallium(I) ions in aqueous perchlorate solutions suggest that no water molecules move with the thallium(I) ion [13], although recent measurements of the apparent molar volumes of aqueous thallium(I) perchlorate solutions seem to indicate [165a] the formation of a diaquo complex $[Tl(H_2O)_2]^+$. There is also little evidence for solvation in dimethyl sulphoxide or acetonitrile as solvents [14–16], but there is possibly stronger solvation in dimethylformamide as solvent [17]. The complex $Tl(CH_3CN)_2SbCl_6$, however, could contain the $Tl(CH_3CN)_2^+$ ion [18].

The inability of thallium(I) to form strong complexes is clearly due to the presence of two electrons in the outer *s* orbital which will always be σ-antibonding. Thus the thallium(I) ion shows little tendency to amine formation in solution, and a monoamine complex is formed only at very high amine concentrations in both ammoniacal and ethylenediamine-containing solutions[19,20]. With histamine in aqueous solution, a complex is formed with stability constant[21] ca. 1×10^{-3}. The thallium(I) ion is a very weak acid in aqueous solution with a pK_a of 13.2 at zero ionic strength[22].

B. THALLIUM(I) HALIDES

(i) *Thallium(I) halides in the solid state*

Both thallium(I) chloride and thallium(I) bromide possess a cubic, CsCl-type structure[23], but the crystal structure of thallium(I) fluoride is uncertain. Ketelaar[24] reported a centrosymmetric structure in which thallium was at the centre of a distorted octahedron. Alcock[25] has proposed another structure in which thallium has five nearest-neighbour fluorine atoms (average Tl—F distance 2.58 Å) and two more distant (Tl—F distance 3.53 Å), these later two fluorines occupy *cis* positions in the distorted octahedron around thallium. Possible space groups were $P2_1ma$, $Pm2a$ or $Pmma$. Barlow and Meredith[26], on the other hand, find a space group of either $Pbcm$ or $Pca2_1$, the latter being thought more likely, and propose a structure involving a distorted cubic geometry, similar to that found in thallium(I) methoxide (see p. 321). An infra-red and Raman study[27] is in disagreement with all these structures, but the vibrational spectra contain a number of unexpected features. For example, a strong band was observed in the infra-red spectrum at 475 cm^{-1}, which was assigned "to monomeric TlF which seems to be present in the lattice in small quantities". At 82°C, thallium(I) fluoride is transformed to a tetragonal distortion of the rock salt structure, slightly more dense than the room temperature modification, the structure can be considered to be a compromise between the NaCl-type structure and that of the room temperature modification[26,28,29]. A high pressure phase also appears[29] at 12.6 kbar and 22°C.

Thallium(I) iodide adopts a layer structure in which the thallium(I) has five nearest-neighbour iodine atoms, and two iodines at a greater distance (Fig. 1)[30]. On heating thallium(I) iodide at atmospheric pressure to 170°C, it is transformed from this ortho-

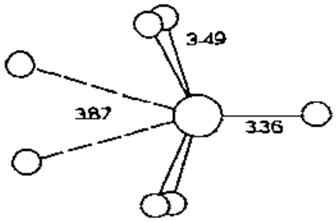


Fig. 1. The environment of thallium in thallium(I) iodide (reproduced from A.G. Lee, *The Chemistry of Thallium*, Elsevier, Amsterdam, 1971).

rhombic structure to a cubic, CsCl-type structure [30], in which the thallium(I) has eight equidistant iodine neighbours located at a distance of 3.64 Å The transformation can also be brought about [31] at room temperature by applying a pressure of about 5 kbar This transformation of thallium(I) iodide is somewhat unusual in that the high temperature phase has the higher density. For a given substance, the phase of lowest density is generally the one of higher entropy and lower symmetry and would be expected to be stable at higher temperatures Thus the alkali halides adopt a NaCl structure at high temperatures and a CsCl structure at low temperatures For thallium(I) iodide, however, the denser and more symmetric form has the higher entropy. Thus, at the transition, the entropy of the cubic phase is 0.75 cal/g.mole °K greater than that of the orthorhombic phase [31] The presence of some ordering effect in the orthorhombic phase is implied by these observations.

Distorted structures of the thallium(I) fluoride and iodide type have been rationalised in terms of s–p mixing on thallium [32] An antisymmetric displacement of anions from an octahedral or cubic field will lead to a mixing of the s and p levels, and the stabilisation due to such mixing will offset the normal forces which hold the octahedron or cube in its regular configuration. If the stabilisation is electrostatic in origin, then it would be expected to be greatest for the fluoride, whereas if it were due to covalent effects it would be expected to be greatest for the heavier halogens A measure of the s–p mixing on thallium in these compounds can be obtained from magnetic susceptibility measurements In the orthorhombic form of thallium(I) iodide, the s–p mixing is about 71% complete on thallium, whereas in the cubic form, it is only about 28% complete [33]. In the cubic thallium(I) chloride and bromide, the s–p mixing has been estimated as 11% and 9% respectively [34] Although these latter two compounds adopt an undistorted CsCl-type structure, they do have very high dielectric constants [35], attributed to the fact that, because s–p mixing will tend to reduce the restoring force opposing ionic displacements, these compounds will be particularly susceptible to atom polarisation by a static electric field [5] Unfortunately, no information about s–p mixing in thallium(I) fluoride is available

Information about the structural transition in thallium(I) iodide can be derived from thallium NMR measurements [36]. At the temperature of the transition, there is a considerable linewidth change, from a second moment of 26 gauss^2 just below the transition temperature to 2.5 gauss^2 just above In the low-temperature form (orthorhombic), the second moment is an order of magnitude greater than that expected for dipolar interactions alone. The linewidth has therefore been attributed to indirect (electron-coupled) spin exchange interactions between the thallium and the iodine The orthorhombic phase can be visualised as a structure intermediate between a hypothetical molecular solid of thallium(I) iodide molecules and a more ionic, cubic CsCl-type structure. In the orthorhombic phase, there is a single short interatomic distance between thallium and iodine, such that the structure could be considered to be made up of Tl–I pairs, and this distance 3 36 Å is intermediate between that of the gaseous thallium(I) iodide molecule (2.81 Å) and the Tl–I distance in the cubic phase (3 64 Å) Thus, although the cubic phase is the more dense, the nearest-neighbour distance is actually greater than in the orthorhombic phase.

The decrease in the magnitude of the Tl–I indirect spin exchange is then what would be expected if rather isolated covalent Tl–I bonds were being weakened in the orthorhombic to cubic phase change Thus, the change in the indirect spin exchange interactions implies a decrease in the 'covalent' bond character between thallium and iodine in the transformation, due to a lengthening of an unusually short thallium–iodine interatomic distance in the transformation to the cubic phase

An estimate of the degree of covalency in the thallium–halogen bonds in the cubic forms of thallium(I) chloride, bromide and iodide can be made from measurements of the ^{205}Tl chemical shift [37,38] Degrees of covalency of 4, 6 and 10% have been estimated in this way for the Tl–Cl, Tl–Br and Tl–I bonds respectively. For these halides there is also a significant discrepancy between the lattice energies calculated from an electrostatic model and those obtained from a Born–Haber cycle (Table 2) The values calculated from the electrostatic model take into account polarisation, quadrupole interactions and the zero-point energy of the crystal.

TABLE 2

Lattice energies of the thallium(I) halides (kcal mole^{-1})

Compound	Calculated from an electrostatic model [11,39]	Obtained from a Born–Haber cycle [11]
Tl–F	196	200
Tl–Cl	169	178
Tl–Br	163	174
Tl–I	157	168

The value of the lattice energy calculated for thallium(I) fluoride is based on the structure of Barlow and Meredith. The calculated lattice energy based on the structure proposed by Alcock [25] is 184 kcal mole^{-1} (ref 11). The increase in the difference between the calculated and Born–Haber cycle lattice energies from thallium(I) fluoride to thallium(I) iodide is in accord with the increasing polarisabilities of the anions It also provides a ready explanation for the fact that thallium(I) fluoride is the only thallium(I) halide which is readily soluble in water

A study of the L_{III} X-ray absorption edge of ^{81}Tl in thallium metal and thallium(I) chloride and bromide has led to the suggestion of a greater covalency for thallium(I) chloride than for thallium(I) bromide; on compound formation there is generally a shift in the absorption edge towards the high energy side of the metal edge, unless the shift is suppressed by covalent character in the bond [40,41]. The shifts (relative to thallium metal) are 0.8 eV for thallium(I) chloride and 6 2 eV for thallium(I) bromide. However, it is thought necessary to take into account changes in hybridisation of the thallium [390], and other data already discussed suggest that changes due to the latter will be most important for thallium(I) bromide. These X-ray absorption edge shifts are, as yet, little understood.

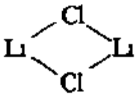
Compressibility data also suggest that thallium(I) chloride may have some 'covalent' character. Thus the pressure–volume data for most of the alkali metal halide crystals can be fitted by a completely ionic model, whereas for thallium(I) chloride there is a definite deviation at high pressure in the direction of smaller compressibility from that predicted from low-pressure data [42]. The compounds are clearly, however, largely ionic Thus the shifts of the optical absorption edges for the cubic phases of the thallium(I) halides with changes in applied pressure are relatively insensitive to the anion involved [43]. In a simple ionic crystal, the valence electrons have been completely transferred from cation to anion, so that the valence band is made up entirely of anion wave functions and the conduction band is made up of cation wave functions. Since the conduction band represents an excited state, it would be expected to be the more sensitive to pressure [43] Thus it would be expected that the shift of the absorption edge with change in applied pressure (i e of the density of the crystal) would be relatively insensitive to the anion if the crystal is largely ionic This can be contrasted with the very considerable sensitivity to anion exhibited by the mercury(I) halides [43]

Extensive studies of ionic conduction and diffusion in the alkali halides with NaCl-type structures have revealed the presence of Schottky defects The ionic transport processes involve jumps of nearest-neighbour ions into single cation and anion vacancies, with the cation usually being more mobile, and therefore tending to dominate the conductivity. In silver(I) chloride and bromide, which also have the NaCl-type structure, the presence of cation Frenkel defects has been proved. Diffusion measurements show that for these crystals the transport processes involving cation vacancies are the same as in the alkali halides, but that those involving interstitial ions occur by a combination of collinear and non-collinear interstitialcy jumps. These differences have been attributed to the larger polarisability of silver [43a] In caesium chloride, bromide and iodide, Schottky defects predominate, and the rate of anion diffusion is comparable to, but somewhat larger than, the cation diffusion rate In thallium(I) chloride, Schottky defects also predominate, but now with highly mobile anion vacancies The smaller cation mobility in Tl–Cl compared with Cs–Cl has been attributed to the greater polarisability of thallium(I), increasing the activation energy for cation movement [43a]

Little is known about the structures of the molten thallium(I) halides, although NMR measurements suggest that the degree of covalency in the Tl–Cl, Tl–Br and Tl–I bonds increases slightly on melting [37,44]. Measurements of the electrical conductivities of fused thallium(I) halides suggest some association, but cannot distinguish the cause [45]. Considerably more is known about the structures of the thallium(I) halides in the vapour phase.

(ii) Thallium(I) halides in the vapour phase

Mass spectrometric analysis of the vapours of the thallium(I) halides shows that for the fluoride [46,47], dimeric species $(TlF)_2$ predominate, with some monomer, trimer and tetramer also present, whereas for the chloride[48] and bromide[49] monomers predominate with a little dimer present, and for the iodide[50] there is less than 1% dimer. The dimer-to-monomer ratio for the thallium(I) fluoride vapour is considerably higher than that for the alkali metal fluorides[46]. Consideration of the experimentally determined entropy of the Tl_2F_2 species led Keneshea and Cubicciotti to suggest that the nature of the chemical bonding for the thallium-containing dimer is quite different from that for the alkali metal halide dimers. The structures of the latter are generally assumed to be rhombohedral (planar) as found for Li_2X_2 by electron diffraction[51,52] and matrix infra-red studies[53]. Theoretical studies indicate that, for an ionic compound, the rhombohedral structure is more stable than the linear dimer[54].



$Li-Cl-Li-Cl$

Keneshea and Cubicciotti[46] proposed a linear symmetrical X—Tl—Tl—X structure for the thallium(I) halide dimers, giving better agreement with the absolute entropy of the Tl_2F_2 dimers.

As additional evidence in favour of a structure with a thallium—thallium bond, the observation of a Tl_2^+ species of medium intensity in the mass spectrum of the fluoride vapour was noted[46], but there is some disagreement over this point. Berkowitz and Walter[55] found that the Tl_2^+ peak intensity was only 0.85% of the Tl_2F^+ peak intensity, whereas Cubicciotti[47] reported that it was 12% of the major dimer peak Tl_2F^+. However, it should also be noted that the mass spectra of a number of dimeric organothallium(III) compounds also show a Tl_2^+ peak[56], although no strong thallium—thallium bond can be postulated to be present in the compounds $(R_2TlX)_2$. The Tl_2^+ ion is presumably formed by some rearrangement process in the mass spectrometer.

The postulated structures for the thallium(I) halide dimers are consistent with the infra-red spectra of Tl_2F_2 and Tl_2Cl_2 trapped in argon and krypton matrices at low temperatures[57]. Two infra-red absorption bands in the spectra were assigned to each dimer, in agreement with a linear, symmetric structure. A simple molecular orbital scheme can easily be constructed for such a molecule. One *sp* hybrid orbital on each thallium is used to form a σ-bonding MO between the thallium and halogen and the other is used to form a σ-bonding MO between the two thallium atoms. The two *p* orbitals remaining on each thallium are used to form a pair of degenerate π MO's. Of the six valence electrons from the two thallium atoms, four are used in the σ-bonding, leaving two which are assigned to the two π-orbitals, giving the molecule a triplet electronic ground state. The extended Hückel MO calculations of Gimarc[58] predict an essentially similar scheme, with a triplet ground state. These calculations also show that for a 20-valence-electron BAAB system, a linear structure has a lower energy than a structure with a *cis* or *trans* geometry.

Arguments based on second-order Jahn—Teller effects also suggest that the linear symmetrical structure will be stable for the thallium(I) halide dimers. Pearson[60] suggests that the alkali halide dimers do not adopt a linear, triplet, structure because the *p* orbitals

TABLE 3

Dissociation of dimeric TlX at 1000°K

Compound	ΔH^0 (dissociation) (kcal.mole^{-1})	ΔS^0 (dissociation) (cal mole^{-1}.°K)	Monomer/dimer ratio	Ref.
TlF	31.0 ± 0.4	27.9 ± 0.5	1.05	46, 59
TlCl	17.0 ± 0.8	18.3 ± 1.2	0.15	48
TlCl	27.7 ± 0.2 [a]	30.2 [a]		61
TlBr	−2 ± 5	2 ± 4	0.07	49

[a] At 1100°K

TABLE 4

Comparison of gaseous and crystalline thallium(I) halides

Compound	Metal–halogen bond lengths (Å)	
	Vapour	Solid CsCl structure
TlF	2.0844 (refs. 62, 63)	
TlCl	2.4848 (refs. 62, 64, 65)	3.32 (ref. 66)
TlBr	2.6181 (ref. 62)	3.44 (ref. 66)
TlI	2.8135 (ref. 62)	3.64 (ref. 66)

on the alkali metals are too high in energy to be of significance in the bonding.

The high stability of the Tl_2F_2 dimer is presumably caused by the electron-withdrawing effect of the highly electronegative fluorine atoms. Data for the dissocation of the dimers Tl_2X_2 are given in Table 3.

The thallium–halogen bond lengths found in the gaseous monomers are considerably less than those found in the crystalline state (Table 4). The decrease in internuclear distance is more than that observed, for example, for the potassium halides. Further, the dipole moments of the thallium(I) halides are considerably smaller than those of the potassium halides: 4.4 debye for TlCl, for example, compared with 10.6 debye for KCl (refs. 66–68). In the gas-phase, monomeric molecule TlX, the Tl^+ is subject to the unsymmetrical field of X^-, so that s–p mixing becomes possible. Such mixing, by concentrating electronic charge in a mixed s–p orbital on the side of the Tl^+ remote from X^-, allows closer approach of Tl^+ and X^-, and the contribution from the lone pair would give a smaller dipole moment for TlX as observed. Any covalent bonding between the thallium(I) and the halide ions will also have an effect on the internuclear distances and dipole moments. The percentage covalent characters of the gaseous halides have been estimated from quadrupole coupling constants to increase from 17% for thallium(I) chloride to 28% for thallium(I) iodide [62,67].

(iii) Thallium(I) halides in aqueous solution

The thallium(I) halides are classical examples of 'incompletely dissociated' 1:1 electrolytes[2]. The association constants for the thallium(I) halides in aqueous solution are considerably higher than those of the alkali halides, the order of association constants in aqueous solution at 25°C is $\mathrm{TlF} < \mathrm{TlCl} < \mathrm{TlBr} < \mathrm{TlI}$. Thus the heat of hydration of the halide ion, decreasing in the order $\mathrm{F} > \mathrm{Cl} > \mathrm{Br} > \mathrm{I}$, is probably the dominating factor, coupled with either an increase, or only a small decrease, in the heat of association of Tl^+ with halide ion from fluoride to iodide.

The association constant of thallium(I) with fluoride ion is very small. Polarographic studies show that the formation constant β_1, defined by

$$\mathrm{Tl}^+ + n\,\mathrm{F}^- \overset{\beta_n}{\rightleftharpoons} \mathrm{TlF}_n{}^{-(1-n)}$$

must be less than 0.4 in a solution of ionic strength 0.1 M, and that, in fact, the association constant is less than that between thallium(I) and perchlorate ion[69]. Similarly, thallium NMR[70] and potentiometric studies using an amalgam electrode[71] or a fluoride ion electrode[72] also failed to detect any complex formation between thallium(I) and fluoride ion. As a consequence, fluoride ion is a more suitable 'non-complexing' ion for maintaining a constant ionic strength than is perchlorate. Using fluoride ion as the 'non-complexing' ion, association constants (β_1) for TlCl of 2.1 and 1.0 were obtained at ionic strengths 1.0 M and 4.0 M respectively[69]. In all previous work, perchlorate ion has been used to maintain ionic strength, although this should not make any considerable difference.

Thermodynamic data for the association of thallium(I) with chloride and bromide ions are given in Table 5, and compared with data estimated[75] for the potassium halides. The data can be analysed in terms of the following cycle

$$\begin{tikzcd}
\mathrm{MX_g} \arrow[r, "2"] \arrow[d, "1"] & \mathrm{M_g}^+ + \mathrm{X_g}^- \arrow[d, "3"] \\
\mathrm{MX_{aq}} & \mathrm{M_{aq}}^+ + \mathrm{X_{aq}}^- \arrow[l]
\end{tikzcd}$$

Values for ΔH_n° and ΔS_n° for the thallium(I) and potassium halides are given in Table 6.

The values of ΔH_1° and ΔS_1° have been assumed to be the same for the potassium halides as for the thallium(I) halides; this assumption is probably not far wrong, and will not affect the conclusions of the analysis[75]. It is immediately apparent that there are considerable differences for ΔH_2° between the thallium(I) and potassium halides. This can be attributed to the deformation of the thallium(I) ion in a TlX species by s–p mixing of the type already discussed. For the hydration process

$$\mathrm{M_g}^+ + \mathrm{X_g}^- \rightarrow \mathrm{M_{aq}}^+ + \mathrm{X_{aq}}^-$$

ΔH° and ΔS° are very similar for Tl^+ and K^+. This suggests that in the hydrated ion $\mathrm{Tl}^+(\mathrm{H_2O})_m$, the thallium(I) ion is surrounded symmetrically by water molecules, so that

TABLE 5

Thermodynamic data at 25°C for the reaction

$M_{aq}^{+} + X_{aq}^{-} \rightarrow MX_{aq}$

(from refs. 73–75)

MX	ΔG^0 (kcal/mole)	ΔH^0 (kcal/mole)	ΔS^0 (cal/deg.mole)
TlCl	−0.93	−1.43	−1.7
TlBr	−1.2	−2.45	−4.2
KCl	+24.0	+24.1	+0.4
KBr	+20.7	+20.0	−2.2

TABLE 6

Values of ΔH_n^0 and ΔS_n^0 at 25°C (from ref. 75)

	ΔH_n^0 (kcal/mole)		
	ΔH_1^0	ΔH_2^0	ΔH_3^0
TlCl	−27.9	139.5	−166.0
TlBr	−27.3	133.1	−157.9
KCl	(−27.9)	112.8	−164.8
KBr	(−27.3)	109.4	−156.7

	ΔS_n^0 (cal/deg mole)		
	ΔS_1^0	ΔS_2^0	ΔS_3^0
TlCl	−19.2	17.5	−35.0
TlBr	−18.3	17.1	−31.2
KCl	(−19.2)	16.4	−36.0
KBr	(−18.3)	16.1	−32.2

s–p mixing is not possible. However, for the association reaction

$$Tl^+(H_2O)_m + X^-(H_2O)_n \rightarrow Tl^+X^-(H_2O)_x + (m+n-x)\,H_2O$$

there are considerable differences between thallium(I) and potassium. Again, it is possible that in the unsymmetrical field of $Tl^+X^-(H_2O)_x$, *s–p* mixing occurs, the effect of this being to decrease the distance of closest approach of thallium and halide ion, and so to stabilise the molecule[75]. There is quite strong evidence from ultra-violet spectroscopy that the bonding in the associated ions must be largely ionic[76].

An attempt has also been made to explain the association in terms of mutual polarisation, in which each ion in an MX pair will induce in the other a dipole, and the ions are then attracted by the induced charges[77]. This model has, however, been effectively criticised[78].

(iv) Thallium(I) halide complexes

There is considerable evidence for the formation of anionic thallium(I) halide complexes in solutions containing a high concentration of halide ion. By solubility measurements[79–81], studies of molar absorptivities[80,82] and luminescence spectra[83], the species TlX, TlX_2^- and TlX_4^{3-} have been detected in aqueous solutions containing chloride and bromide ions. The interpretation of data at high halide ion concentration is, however, rather difficult, and some authors[71] have claimed the formation of TlX_3^{2-} species, whereas others discount this. On the basis of solubility data, the species TlI, TlI_2^-, TlI_3^{2-} and TlI_4^{3-} have been postulated in solutions containing iodide ions[71,84]. The formation constants reported by Nilsson[71] are given in Table 7. In an aqueous solution of ionic strength 4.0, but with fluoride ion rather than perchlorate as medium, overall formation constants of $TlCl$ and $TlCl_2^-$ are 1.00 and 0.36 respectively[69].

TABLE 7

Association of thallium(I) halides in solution[71], stepwise formation constants in aqueous solution. Ionic strength = 4 M in perchlorate

Complex	K_1	K_2	K_3	K_4
$(TlCl_n)^{1-n}$	0.79	0.2		
$(TlBr_n)^{1-n}$	2.1	0.68	0.35	0.18
$(TlI_n)^{1-n}$	5.0	1.5	1.5	0.42

The complexes are weak, which is only to be expected since in the ground state of Tl^+, the *s*-orbital in any symmetry will be σ-antibonding. The stability constants give an order $F < Cl < Br < I$ for increasing strength of complex formation. In a solution containing two different halide ions, it was found[85] that the stability constant of $TlBrI^-$ was greater than that of $TlBrCl^-$.

The suggestion has been made that, because the absorption spectrum of the thallium(I) ion in these solutions of high halide concentrations is so similar to that of the K(Tl)Cl phosphors (see below), rather than having discrete ion pairs in solution, there is a quasi-crystalline assembly of ions, in which the thallium(I) ion is symmetrically surrounded by six halide ions[86]. As the halide ion concentration decreases, the thallium–halogen interionic distance increases and the interaction decreases, causing the observed changes in the spectra.

In dimethylsulphoxide as solvent, these anionic complexes are considerably more stable than in water[87] (Table 8). Whereas, in water, the iodide complexes are stronger than the chloride, in dimethylsulphoxide the relationships are reversed. This is consistent

TABLE 8

Association of thallium(I) halides in dimethylsulphoxide solution, overall formation constants in dimethylsulphoxide solution [87]

	β_1	β_2	β_3	β
$(TlCl_n)^{1-n}$	180	2300	1460	
$(TlBr_n)^{1-n}$	300	1000	800	
$(TlI_n)^{1-n}$	73	180	230	
$(Tl_2Cl)^+$				1000
$(Tl_2Br)^+$				370
$(Tl_2I)^+$				9
$(Tl_3I)^{2+}$				74

with a higher enthalpy of solvation of iodide ion in dimethylsulphoxide than in water, whereas the reverse is true for the chloride ion. Further, in dimethylsulphoxide, cationic complexes are also present Similar cationic complexes have been proposed to explain the electrical conductivity of thallium(I) chloride in ethylene glycol–water mixtures [88].

Not surprisingly, no solid anionic halide complexes of thallium(I) have been isolated [2]. There is, however, evidence for complexes of the type $K_2[TlBr_3]$ in mixed melts of TlBr and KBr, both from density [89] and conductance [90] measurements Similar complexes have been suggested as being present in thallium-doped alkali halide single-crystal phosphors When a small amount of a thallium(I) halide is added to an aqueous solution of an alkali halide, it emits a blue luminescence accompanied by the appearance of a new absorption band. Both absorption and emission spectra of aqueous solutions of TlCl in KCl indicate that $TlCl_2^-$ is the species responsible, the absorption and emission bands of this complex are at 243 and 430 nm respectively [76]. Solutions of TlF in aqueous KF solutions show no such bands, this being consistent with the lack of complex formation found by other techniques In K(Tl)Cl crystal phosphors there are two main absorption bands at 196 and 247 nm, and two main emission bands at 305 and 475 nm (ref. 76). It was therefore suggested in the early 1930's that complexes similar to $TlCl_2^-$ are present in the crystals [91,92]. The spectra were then analysed in more detail in terms of electronic transitions of a thallium(I) ion substituted into the cubic crystalline field of the alkali halide crystal [2,93], transitions occur from the ground state $6s^2$ to the excited configuration $6s6p$. However, the model is not completely satisfactory, since some of the absorption bands exhibit structure, and show polarisation effects. There are three possible causes for this.

(*i*) An interaction between the optical electrons of the thallium(I) with non-totally symmetric modes of vibration of the anions (the dynamical Jahn–Teller effect).

(*ii*) Preferred bonds formed between the thallium(I) and some of the surrounding anions.

(iii) An 'off-centre' position of the thallium(I) in the crystal

The Jahn–Teller effect is usually the most important, and effectively explains the observed effects in K(Tl)Cl phosphors [94] There is, however, a marked dependence of polarisation effects on the anion involved, and in the Cs(Tl)I phosphor a partially covalent bond with some of the anions was invoked [95]

C. THALLIUM(I) PSEUDOHALIDES

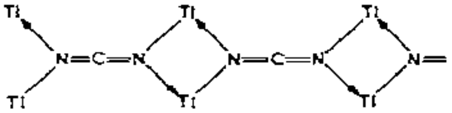
Thallium(I) cyanide adopts a CsCl-type structure [96,97] which is at first sight rather surprising in view of the non-spherical symmetry of the cyanide group Free rotation of the cyanide could account for the structure, but heat capacity measurements suggest hindered rotation [98] A second possibility is that thallium(I) cyanide has only trigonal symmetry, and the TlI ions are distorted by *s–p* mixing just sufficiently to compensate for the non-spherical cyanide ion. The remaining possibility is that the cyanide ions adopt a random orientation, as is possibly the case for the nitrate ion in the cubic form of $TlNO_3$ (see p 307)

There are three phase transitions for thallium(I) cyanide below room temperature, of unknown structure [98]. The ^{205}Tl NMR linewidth at room temperature is consistent with dipolar broadening, but on cooling the absoprtion becomes broad and asymmetric [98]. Whereas the linewidth at room temperature is independent of the magnitude of the applied magnetic field, there is a linear increase in linewidth at 210°K with increasing applied field This has been attributed to a change in the thallium chemical shift tensor at the phase transition, implying the possibility of definite bonds among the ions which change at the phase transition [98] Of the alkali metal cyanides, only caesium cyanide adopts a CsCl-type structure, potassium, sodium and rubidium cyanides adopt a NaCl-type structure [99]

Thallium(I) azide, like potassium azide adopts a tetragonal, distorted CsCl-type structure at room temperature [100] The azide group is linear and symmetrical The thallium–nitrogen distance is rather short compared with the alkali metal azides Tl–N 2 98 Å, K–N 2 96 Å, Rb–N 3 11 Å, and a partially covalent thallium–nitrogen bond is suggested [101] The lattice energy of thallium(I) azide (163 5 kcal/mole) lies between those of NaN_3 and KN_3 (175 and 157 kcal/mole respectively), giving no evidence for extensive covalent bonding (cf AgN_3, lattice energy 204 7 kcal/mole) [102]

At 290°C, thallium(I) azide transforms to an undistorted CsCl-type structure [103], which probably involves random orientation of the anions parallel to the edges of the cubic unit cell

Thallium(I) thiocyanate probably adopts a rhombic unit cell, isomorphous [104] with KNCS Infra-red spectra suggest that the thiocyanate is N-bonded [105] Infra-red spectra show that both TlSCN and TlSeCN are predominantly ionic [106,107] Both thallium(I) cyanate [108] and fulminate [109] crystallise with a body-centred tetragonal lattice, probably isomorphous with the room temperature modification of thallium(I) azide Infra-red spectra again suggest predominantly ionic structures [108,109] The structure of thallium(I) cyanamide is unknown, but measurements of optical and electrical properties suggest a marked degree of covalent bonding to thallium. A polymeric structure has been suggested[110,111], viz



Both potentiometric and polarographic studies give a formation constant of zero for TlCN in aqueous solution[71,112]. A detailed study of the TlCN–KCN–H_2O system failed to find any evidence for complex formation, and Tl^+ ions can replace K^+ ions in solid KCN up to ca. 37 mole % TlCN and still retain the basic KCN structure[97]. In solutions containing Tl^+ and N_3^-, a formation constant of 2.5 has been obtained[74,113] for TlN_3 at 25°C. A number of studies of complex formation between Tl^+ and SCN^- in aqueous solutions containing high concentrations of SCN^- have led to the suggestion of the presence of TlSCN, $Tl(SCN)_2^-$, $Tl(SCN)_3^{2-}$ and $Tl(SCN)_4^{3-}$ (refs. 114, 115), and even $Tl(SCN)_5^{4-}$ and $Tl(SCN)_6^{5-}$ (refs. 116, 117). It has been observed that thiocyanate complexes are more stable than the corresponding complex chlorides, and are similar in stability to the complex bromides[115].

D THALLIUM(I) OXIDE SPECIES

(i) Thallium(I) oxide

Tournoux et al.[118] report that thallium(I) oxide crystallises with a rhombohedral unit cell at room temperature, whereas Sabrowsky[119,120] reports a monoclinic unit cell. The monoclinic unit cell does not correspond to an elementary unit cell[118].

The structure according to Sabrowsky[120] is of the anti-CdI_2 type, in which each thallium has three oxygens as nearest neighbours and each oxygen is surrounded by six thallium atoms in the form of an elongated octahedron. Cs_2O adopts a closely related anti-$CdCl_2$ type structure[121], whereas the other alkali oxides M_2O adopt the quite different anti-fluorite structure[66]. The Cs–O distance of 2.86 Å in Cs_2O can be compared with the sum of ionic radii of 3.24 Å, and the Tl–O distance of 2.51 Å in Tl_2O with the sum of ionic radii of 2.94 Å.

Above 354°C, thallium(I) oxide transforms to a second form[122]. It is appreciably volatile with a vapour pressure of about[123] 1 mm at 580°C. The nature of the gas phase species has attracted some attention. The vaporisation of thallium(I) oxide gives mainly[124] Tl_2O and a little Tl_4O_2. The infra-red spectra of $Tl_2{}^{16}O$ and $Tl_2{}^{18}O$ trapped in a variety of matrices at low temperatures have been reported[125–127]. In all three papers it is agreed that Tl_2O adopts a bent symmetrical structure; there is, however, considerable disagreement about the Tl–O–Tl angle. The strongest band observed in the infrared spectrum is assigned to the antisymmetric ν_3 stretch (Table 9).

The symmetric stretching mode ν_1 is less strong, but has been located by Brom et al.

TABLE 9

Matrix infra-red of thallium(I) oxide, Tl_2O

ν_3 (cm^{-1})	Matrix			Ref
	N_2	Ar at 10°K	Kr at 10°K	
$Tl_2{}^{16}O$	625.3 ± 0.1 [a]			125
	623.2 ± 0.4 [b]	643.3 ± 0.4	634.6 ± 0.3	126
	626.1	643.6		127
$Tl_2{}^{18}O$	591.2 ± 0.1 [a]			125
	590.9 ± 0.4 [b]	609.3 ± 0.5	600 ± 0.3	126

[a] At 10°K

[b] At 15°K.

at 571 cm^{-1} for $Tl_2{}^{16}O$ in an argon matrix on the basis of ^{18}O enrichment and matrix warming studies[126]. Makowiecki et al.[127], however, assign a weak band at 510 cm^{-1} to ν_1, whereas Brom et al.[126] tentatively assign this band to the dimeric species Tl_4O_2. The bending frequency ν_2 should also be infra-red active, but Brom et al.[126] failed to find any evidence for its appearance in any of their spectra. Makowiecki et al.[127] assigned a band at 381.5 cm^{-1} to this mode, whereas the corresponding band observed at 383 cm^{-1} by Brom et al.[126] was assigned to the dimeric species Tl_4O_2. An infra-red study of the heated vapours above Tl_2O_3 (mainly Tl_2O) also shows[128] a strong band at 620 cm^{-1} assigned to ν_3 of Tl_2O, and a weaker band at 480 cm^{-1} assigned to ν_1, which Brom et al.[126] think is more likely to be due to Tl_4O_2.

Unfortunately, the calculated Tl—O—Tl angle is very sensitive to the ν_3 frequency. Hinchchliffe et al.[125] have reported an angle of 131 ± 11° and, using the same data, Brom et al.[126] recalculated the angle as 125°. Using their own data, Brom et al.[126] obtained an angle of 77°.

An approximate force constant calculation[126] with an assumed apex angle of 90° gives Tl—O = 1.86 Å and Tl—Tl = 2.63 Å. Since the single bond covalent radius of thallium is of the order of 1.5 Å, the calculated Tl—Tl distance suggests some strong metal–metal interaction in the Tl_2O molecule. This would also explain the unusually large magnitude of the 'interaction' force constants calculated on the basis of internal coordinates that neglect terminal atom interactions in XY_2 species.

A fairly strong Tl—Tl bond is also suggested by thermodynamic data. The enthalpy of formation of solid Tl_2O from the elements at 298°K has been measured as −40.4 ± 1.4 kcal/mole, from which the enthalpy of formation of gaseous Tl_2O can be calculated[129] to be 1.2 kcal/mole. The enthalpy of atomisation of gaseous Tl_2O is then 145.6 kcal/mole at 298°K. Assuming that the molecule consists of only two Tl—O bonds, a Tl—O bond energy of 72.8 kcal/mole is obtained; this can be compared with dissociation energies of Tl—F 105, Tl—Cl 88.0, Tl—Br 79.2 and Tl—I 64.9 kcal/mole. The bond dissociation energy for Tl—O would be expected to be between those of the fluoride and the chloride, as observed, for example, for the corresponding aluminium derivatives.

The appearance of a relatively strong Tl_2^+ peak in the mass spectrum of Tl_2O has also been taken to indicate the presence of a fairly strong Tl—Tl bond [129], but as already observed, such evidence is suspect.

The alkali oxides M_2O (except Li_2O) vaporise to the gaseous elements.

(ii) Thallium(I) hydroxide

Thallium(I) hydroxide probably adopts [130] a hexagonal structure, of space group $P6_3/m$ (given by Waber and Sturdy as $C6_3/m$, but this is presumably a misprint). In aqueous solution, thallium(I) hydroxide has basic properties similar to those of the alkali hydroxides. The most recent conductivity measurements [131] of the dissociation constant in aqueous solution at 25°C give a value of 3.0. A recent spectrophotometric study gives a value of 4.9 for the stability constant of TlOH at zero ionic strength [132]. At an ionic strength of 3.0 M in perchlorate, the cumulative stability constants for $Tl(OH)_n^{1-n}$ were $\beta_1 = 1.24 \pm 0.15$ and $\beta_2 = 0.16 \pm 0.05$ respectively. These figures include both inner-sphere and outer-sphere complexes, $[Tl(H_2O)_x](OH)_n^{1-n}$ and $[Tl(OH)_n(H_2O)_{x-n}]^{1-n}$, the association constant for the inner sphere complex $[Tl(OH)(H_2O)_{x-1}]$ is estimated as 0.62.

The Raman spectrum of a concentrated aqueous solution of TlOH showed no band attributable to a Tl—O stretch, suggesting that the undisssociated TlOH in solution consisted of ion pairs rather than of covalently bound TlOH molecules [133], a conclusion confirmed by thallium NMR results [70].

(iii) Oxythallate(I) derivatives

Three oxythallate(I) derivatives have been reported: KTlO, RbTlO and Li_5TlO_4. The former two compounds form red monoclinic crystals [134], whose structures may be analogous to KAgO, which is characterised by square $[Ag_4O_4]$ groups [135]. The lithium compound corresponds to $Li_5(vacancy)_2TlO_4$ and is an ordered derivative of the Li_2O-type structure [136].

E THALLIUM(I) SULPHIDE AND SELENIDE

Thallium(I) sulphide adopts a structure similar to that of PbI_2, each thallium being surrounded [137] by six sulphurs at a distance of 2.85 Å. The shortest Tl—Tl distance is 3.62 Å. Thallium(I) selenide is tetragonal (space group C_{4h}^3-P4/n) and has a structure different from that of thallium(I) sulphide [138].

F THALLIUM(I) NITRIDE AND PHOSPHIDE

Thallium(I) nitride, prepared by reaction of thallium(I) nitrate and potassium amide, is of unknown structure ^{282}. Other thallium(I) nitrogen derivatives are discussed in sect. I

Two phases, Tl_3P (ref. 391) and TlP_5 (ref. 392) have been claimed in the thallium–phosphorus system, although more recent work ^{393} has found evidence only for the latter compound. TlP_5 crystallises in the orthorhombic space group, and the compound can be considered ^{393} to be a phosphide of thallium(I). The phosphorus atoms are connected in a two-dimensional network similar to that observed in the monoclinic modification of red phosphorus, known as Hittorf's phosphorus. In this modification of phosphorus, it is possible to discern tubes with pentagonal cross-sections as a very characteristic structural element. Tubes very similar to those in Hittorf's phosphorus can also be seen in the phosphorus arrangement in TlP_5 (Fig. 2). There are two non-equivalent thallium atoms in the structure, both with a very irregular coordination, with two phosphorus atoms at rather short distances of ca. 3.0 Å, and seven additional phosphorus atoms at distances 3.25–3.69 Å. For both thalliums, the short Tl–P distances are to phosphorus atoms within the same phosphorus layer, one of them serving as a bridging atom between different phosphorus tubes, while most of the longer Tl–P contacts are to phosphorus atoms in adjacent layers. It is probable that the Tl–P contacts of ca. 3.0 Å have appreciable covalent character, whilst the others are largely ionic ^{393}.

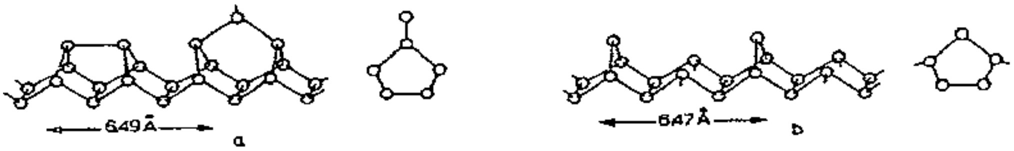


Fig. 2. The phosphorus arrangements in Hittorf's phosphorus (a) and TlP_5 (b) (reproduced, with permission, from O. Olofsson and J. Gullman, ref. 393).

G THALLIUM(I) OXYACID DERIVATIVES

(i) Thallium(I) nitrate

There is now a considerable body of evidence which suggests partial covalent character in thallium(I) nitrate. Details of an infra-red study of matrix isolated thallium(I) and alkali nitrates are given in Table 10.

An undistorted nitrate ion has D_{3h} symmetry and the $\nu_3(e)$ and $\nu_4(e)$ modes are degenerate. The extent of the splitting of these degenerate modes in any particular compound is related to the distortion of the anion. For the alkali metal nitrates, cation polarisation of the anion in a monomer causes differences in the force constants K_1 and K_2 and hence a splitting of ν_3.

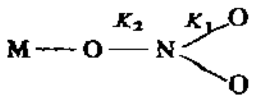


TABLE 10

Infra-red spectra of metal nitrates in argon matrices[139]

Modes	$LiNO_3$	$NaNO_3$	KNO_3	$RbNO_3$	$TlNO_3$
ν_1	1017	1023	1031	1033	1020
ν_2	823	825	830	1830	
ν_3(a)	1275	1283	1291	1293	1252
ν_3(b)	1515	1484	1462	1456	1495

Values for the cation polarising power have been estimated from the expression

$$P = (Z/r)(5Z^{1.27}/r^{1/2}I)$$

where r is the ionic radius, Z is the cation charge and I is the ionisation potential. It can then be shown[139] that cation polarisation of the anion is the dominant source of the anion distortion in the alkali nitrate monomers. This cannot be the case for thallium(I) nitrate, however, since the polarising power of thallium(I) is roughly equal to that of the potassium ion, and the ν_3 splitting is 1.5 times greater for the $TlNO_3$ monomer. It was therefore suggested[139] that the covalent contribution to anion distortion is of the same order of magnitude as that from cation polarisation of the anion.

Infra-red and Raman studies[140–143] of solid thallium(I) nitrate are also consistent with a basically D_{3h} symmetry for the nitrate group, so that the compound is more an ionic nitrate $Tl^+NO_3^-$ than a 'nitrato' compound Tl–O–NO_2.

At room temperature, thallium(I) nitrate adopts an orthorhombic structure, which transforms at 79°C to a hexagonal form which in turn changes to a cubic form at 144.6°C (refs. 144–150). All three polymorphs are based on the same subshell[149]. Thermodynamic data for these transitions are given in Table 11.

TABLE 11

Parameters for thermal transitions in thallium(I) nitrate[151]

Transition	Transition temp (°C)	ΔS (cal/deg.mole)	ΔV% (% vol. change)
Orthorhombic to hexagonal	75	0.7	0.4
Hexagonal to cubic	143	2.18	1.4

For the hexagonal to cubic transition, ΔS is remarkably close to $R \ln 3$ (= 2.19). Since, owing to the close relationship between these two phases (they are both related to the CsCl type) there are good grounds for believing that the vibrational entropy is virtually unaltered at the transition, it seems that this difference must be a difference in configurational entropy[151,152]. The suggestion of free rotation of the nitrate group (for example, in the plane of the oxygen atoms) in the cubic phase can then be ruled out, since completely free rotation would mean an entropy contribution [151], of some 25 cal/deg mole. The configurational entropy of the hexagonal phase is probably zero, and it has been shown [151] that anion disorder in the cubic phase could lead to a configurational entropy of R ln 3. The source of the anion disorder is not yet certain. From considerations of the entropy change at the transition it has been concluded that the disorder was dominated by the nitrate ion being slightly displaced from the C_3 axis in the direction of the N—O bond [151]. It has also been suggested, however, that the disorder arises from rotational randomisation in which the C_3 axis is maintained [152] The Raman spectrum of this phase is in agreement with the structure being that of a disordered solid [143].

It seems probable that disorder of the nitrate ions is accompanied by positional disorder of the thallium(I) ions. At the phase change from hexagonal to cubic there is a very large increase in electrical conductivity whereas at the orthorhombic-to-hexagonal phase change there are only very small changes [148] The slight electrical conduction of the orthorhombic and hexagonal phases is probably due to the mobility of defect ions At a thermal transformation some change in this ionic conductance is to be expected, and there could possibly be a large increase in defect ion mobility at the hexagonal-to-cubic phase change as a consequence of an increase in interstitial space accompanying the change of structure However, there is a large change in the ^{205}Tl NMR linewidth associated with this transformation [153]. In thallium(I) nitrate, the ^{205}Tl linewidth is about 0.1 G near the melting point It remains unchanged on cooling to 143°C, the temperature of the transition to the hexagonal form, when there is a large and sudden increase to ca 1 5 G. There is probably also a further, small increase in linewidth on cooling through the hexagonal—orthorhombic transformation at 75°C The sharp lines observed in the cubic phase are consistent with ready diffusion of thallium(I) ions in this structure

The hexagonal phase of $TlNO_3$ is not stable at room temperature and goes over to an orthorhombic form below about 79°C This transition probably involves no orientational disorder. Neither rubidium nor caesium nitrates, which have the same high temperature phases as thallium(I) nitrate, have a low temperature phase of this type, and the deviation from a symmetrical ion arrangement could well be connected with the ability of thallium(I) to undergo asymmetric distortion

There is some evidence for partial covalent character in the thallium—oxygen bond The lattice energy of thallium(I) nitrate (ca 165 kcal/mole) is greater than might have been expected by comparison with the alkali nitrates [154,155]. The vapour pressure of thallium(I) nitrate is twenty times higher than the alkali nitrates but between ten and twenty times lower than that of the 'nitrato' derivatives of copper, zinc, mercury and indium [156]. Other data also suggest that thallium(I) nitrate is an intermediate between nitrates like the alkali nitrates and nitrato derivatives. It has a high electrical conductivity in the fused state; at 600°C, $\Lambda = 39\ 2$ ohm^{-1}.cm^2 (ref. 157). The ultra-violet spectrum of solid thallium(I) nitrate at 20°C is similar to that of solid rubidium nitrate, both showing a band at 32,000 cm^{-1}, characteristic of the nitrate ion However, the spectrum of rubidium nitrate undergoes relatively little change on fusion, whereas that of thallium(I) nitrate changes more markedly [158,159]. A small amount of covalent bonding in fused thallium(I) nitrate has been postulated to account for the heat of mixing of thallium(I) nitrate with fused alkali nitrates[160] and for the excess volumes of fused thallium(I) nitrate–alkali nitrate mixtures[161]. The definite and significant chemical shift in the ^{205}Tl NMR resonance frequency on fusion has been attributed to an increase in the vibrational overlap of the anion–cation wave functions in the molten state, i.e. the ion-pairing is attributed to an increase in the partial covalency of the anion–cation contact pair[162]. Electrical conductivity and viscosity measurements also indicate anion–cation interactions[157]. Raman spectra of molten thallium(I) nitrate are also interpreted in terms of pronounced nearest-neighbour interactions, although the data have also been interpreted in terms of short-range, quasi-crystalline, order, without postulating any specific association[163]

The mass spectrum of the vapour over molten thallium(I) nitrate shows the presence of mainly monomeric species with some dimeric[164], in agreement with vapour pressure measurements[156]

In aqueous solution, association between thallium(I) and nitrate ions is weak[114]. In 3 M perchlorate at 25°C, the stability constant K_1 is 2 15 (ref 74) and in 1 M fluoride it is 0.65 (ref 69). Conductance measurements[165] give a value of 3.2 at 25°C. No evidence has been found for higher complexes in solution. Measurements of the apparent molar volumes of solutions of thallium(I) nitrate in aqueous solutions containing excess sodium nitrate suggest that an inner-sphere complex $[Tl(H_2O)(NO_3)]$ is formed, but the stability constant determined in this way is about 1/5 of the value determined by thermodynamic methods. It is suggested that only about 20% of the nitrate ions associated with thallium(I) are in the inner coordination sphere, the remaining fraction consisting of ion pairs[165a] Although no compound formation was detected in the $NaNO_3$–$TlNO_3$ or $CsNO_3$–$TlNO_3$ systems[166,167], a compound $LiNO_3.2TlNO_3$ of unknown structure has been found in the $LiNO_3$–$TlNO_3$ system[168] Crystals of $TlNO_3.2HNO_3$ have been obtained[169] from saturated nitric acid solution, and are suggested to be $Tl[(HNO_3)_2NO_3]$

(ii) Thallium(I) carboxylates

Thallium(I) salts of a wide range of carboxylic acids have been isolated[2]. With dicarboxylic acids, both normal and acid salts can be prepared, and with hydroxycarboxylic acids, both the normal salt and the hydroxy derivative can be prepared. Thus, whereas only a dipotassium salt of tartaric acid can be isolated, both dithallium(I) and tetrathallium(I) derivatives have been reported[170]. A number of derivatives of sugars have been reported, but sugars with reducing properties led to formation of thallium metal Most of these derivatives are obtained as anhydrous salts, investigation of the thallium(I) formate– and thallium(I) acetate–water systems[171,172] gave no evidence for hydrate formation The tartaric acid derivative $C_2H_2(OH)_2(COOTl)_2$ can, however, be isolated as the hemihydrate[170], and is thus one of the very few known thallium(I) derivatives with water of crystallisation; another such[170] is the thallium(I) salt of 2-methylpyridine-3,4,6-tricarboxylic acid, $CH_3C_5HN(COOTl)_3.H_2O$.

The structures of the thallium(I) carboxylates are unknown. In the infra-red spectrum of thallium(I) formate, the symmetric OCO stretch and asymmetric OCO deformations appear as doublets, in the alkali formates these bands appear as singlets. A difference in structure was therefore suggested [173]. The spectra of thallium(I) acetate and the alkali acetates also show characteristic differences [174]. Interestingly, the shift of the L_{III} X-ray absorption edge of ^{81}Tl in thallium(I) acetate relative to thallium metal is very large (15.4 eV). The origins of these shifts are little understood, and the suggestion [40,41] of thallium–thallium bonding must be taken as unproven at the present time.

Thallium(I) acetate is incompletely dissociated in solution and, from conductivity measurements, the association constant $K_1 = 0.78$ at zero ionic strength has been obtained [175]. The stability constant of the malonate complex ($\log K_1 = 0.54$ at ionic strength 0.15) [176] is considerably larger and the oxalate complex is even more stable [177] ($\log K_1 = 2.03$). This considerable increase in stability of the small dicarboxylate complexes as compared with acetate indicates chelation. The oxalate ion would form a five-membered ring complex and be more stable than the six-membered malonate complex. Succinate could only form a seven-membered ring, and thus complexing is weaker [176].

The ultra-violet spectrum of thallium(I) oxalate in aqueous solution is indicative of a structure in which the bonds from thallium(I) to the carboxyl groups have some covalent character (unlike in the alkali oxalates)[178].

The complex with citrate may well be more stable than those with the dicarboxylic acids, but the correct value for the stability constant is uncertain. A spectrophotometric study [176] gives a value of $\log K = 1.36$ at ionic strength 0.15 and 25°C, whereas an ion exchange study [179] gave a value of $\log K = 1.04$ in a 0.1 M solution at 25°C and a conductivity study gave a value of $\log K = 2.82$ in a medium of unreported ionic strength [180]. A higher value for citrate would suggest the possibility that thallium(I) bonds to all three of its carboxylate groups. A conductivity study [180] also suggests that the stability constant of the 1:1 thallium(I) tartrate complex is less than that of the citrate ($\log K = 1.39$).

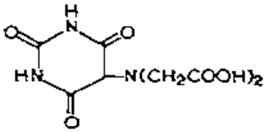
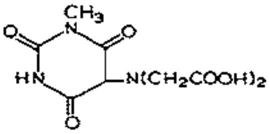
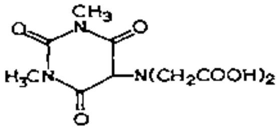
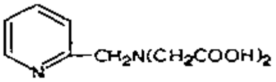
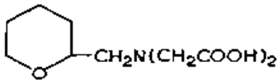
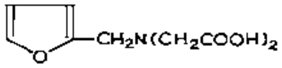
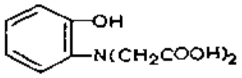
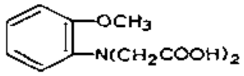
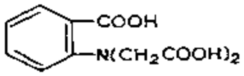
Very few association constants have been measured for the corresponding alkali carboxylates [183], but, using a cation-sensitive glass electrode, values for alkali citrates of $\log K_1 = 0.83$ for lithium and $\log K_1 = 0.59$ for potassium have been obtained [181] in 0.1 M perchlorate at 25°C.

The complexes formed with nitrilotriacetic acid ($\log K_1 = 4.42$ at ionic strength 0.15) [176] and ethylenediaminetetraacetic acid ($\log K_1 = 6.55$ at ionic strength 0.1) [182] are even stronger. It is noticeable that the nitrilotriacetic acid complex is considerably stronger than the citrate, although both have three carboxylate groups, this suggests strong binding of thallium(I) to nitrogen-containing ligands. Association of thallium(I) with diethylenetriaminepentaacetic acid is weaker than with ethylenediaminetetraacetic acid: stability constants of $\log K = 5.45$ at ionic strength 0.4 (ref. 184) and $\log K = 5.97$ at ionic strength 0.1 (ref. 185) have been obtained. The binding of both sodium and potassium to ethylenediaminetetraacetic acid is very considerably weaker (Table 12).

The position of the ν(C=O) stretch in the solid tetrathallium(I) complex of ethylenediaminetetraacetic acid is closer to that suggested for ionic bonding than to that for

TABLE 12

Stability constants for alkali metal and thallium(I) derivatives in aqueous solution ($\mu = 0.1\ M$) at 20°C

Carboxylic acid	log K_{ML} Li	Na	K	Tl^{I}
Ethylenediaminetetraacetic acid	2.79[a]	1.66[a]	0[b]	6.47[b]
 I	4.90[b]	2.72[b]	1.23[b]	5.99[b]
	4.86[c]	2.67[c]	1.11[c]	5.79[c]
	4.91[c]	2.53[c]	0.94[c]	5.73[c]
	1.71[d]	0.85[d]		3.84[d]
	1.74[e]	0.85[e]		4.06[e]
				3.11[e]
	2.20[c,f]	1.0[c,g]		2.34[c]
	4.79[c,g]			
	2.05[c]	0.89[c]		2.93[c]

[a] Ref. 114, [b] ref 182; [c] ref 186; [d] ref 187; [e] ref 188; [f] acid salt; [g] neutral salt

TABLE 13

Thermodynamic data for the reaction of uramildiacetic acid with univalent metal ions [182]

Metal	$-\Delta H$	$-\Delta S$
Li	7 0	1 ± 5
Na	8.7	18 ± 2
K	11 8	35 ± 2
Tl^I	15 4	25 ± 4

covalent bonding, despite the large formation constant found in solution [178]

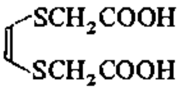
The high stability constants found with uramildiacetic acid, I, are surprising (Table 12) Thermodynamic data are given in Table 13. The most striking observation is that all the metal complexes are stabilised by a negative enthalpy change and that the entropy changes are invariably opposed to complex formation. Although the stabilisation by the favourable enthalpy change increases in the order $Li^+ < Na^+ < K^+$, the opposing entropy effect increases in the same order but more rapidly, thus leading to the reversal of the order of the stabilities The stability of many 1 . 1 metal complexes is due to a favourable (positive) net entropy change resulting from the circumstances that the entropy increase due to the liberation of water from the hydrated cation and the hydrated ligand on complex formation exceeds the concomitant loss in configurational entropy of the ligand and that due to the reduction in the number of reacting molecules. It is then significant that the net entropy change with complexes of uramildiacetic acid is almost zero for the strongly hydrated lithium ion and that unfavourable values of ΔS are most negative for the largest and least hydrated ions. The greater stability of the thallium(I) derivatives could again be due to the presence of nitrogen in these derivatives.

It has been observed [189] that the association constant of thallium(I) and salicylic acid ($\log K_1 = 3\ 90$) is greater than that of thallium(I) and thiosalicylic acid ($\log K_1 = 3\ 66$) and similarly that the association constant of thallium(I) with lactic acid is greater than that with thiolactic acid [190]. Thus thallium(I) is behaving as a 'class a' metal in these complexes

Stability constants for thallium(I) with α-alanine and β-alanine have been measured [191] as $\log K_1 = 1\ 49$ and $\log K_1 = 1.04$ respectively at 28°C.

A study of the thallium NMR spectra of aqueous solutions of the acetate and citrate suggest that the association is due to electrostatic rather than to covalent forces [70,192] The proton NMR spectra of aqueous solutions of thallium(I) ethylenediaminetetraacetic acid and nitrilotriacetic acid have been observed [176]. The fact that the protons on the carbon attached directly to the nitrogen in EDTA have about the same shift on complexing with thallium(I) as those near the carboxylate group has been taken as evidence that the nitrogen is also bound to thallium(I), as deduced from stability data.

Although the stability constant for the thallium(I) complex of *S,S'*-1,2-*cis*-dimercapto-ethylenediacetic acid



is high ($\log K_1$ = 3.28 in 0.1 *M* KCl at 20°C), the proton NMR spectrum suggests that there is essentially no covalent thallium–sulphur interaction present[194]. The proton NMR spectrum of this compound, as with those discussed above, shows no Tl···H coupling, thallium(I)–proton coupling has, as yet, only been observed for one compound, a thallium(I) cryptate (see sect. O (iv)). The stability constants for association of thallium(I) and β-mercaptopropionic acid, $HSCH_2CH_2COOH$, is also high ($\log K_1$ = 2.78 at 20°C, with ΔH° = −3.34 kcal/mole and ΔS° = +2.01 cal/deg mole at 30°C)[195]

The structure of thallium(I) carbonate is unknown, but it is interesting that whereas rubidium carbonate melts at 873°C (ref. 193), thallium(I) carbonate melts at 270°C (ref. 196)

(iii) Acids of the Group V elements

Thallium(I) nitrite adopts a CsCl-type structure[197], which presumably implies disorder of the nitrite ions rather than the free rotation originally suggested. There is no compound formation between thallium(I) nitrite and sodium, potassium, rubidium or caesium nitrites, but with lithium nitrite a compound $TlNO_2 \cdot 3LiNO_2$ is formed[198,199]. Association between thallium(I) and nitrite ion in aqueous solution is slightly stronger than with the nitrate ion, $\log K_1$ = 0.81 at 25°C in aqueous solution corrected to zero ionic strength[200]. Addition of thallium(I) ions to solid alkali metal nitrites causes a red luminescence, and this was attributed to a weak interaction between the thallium and nitrogen atoms[76]

Reaction of thallium(I) hydroxide with nitroethane produces a thallium(I) salt[201,202] whose infra-red spectrum[203] suggests the structure $CH_3CH{=}NO.OTl$. Derivatives are also formed with nitromethane and 1,3,5-trinitrobenzene, but these are explosive[201,203]

A large number of thallium(I) phosphates have been prepared[2], but the structure of only one of them has been determined. Thallium(I) metaphosphate is tetrameric in the solid state, $[Tl(PO_3)]_4$, and contains cyclic $P_4O_{12}{}^{4-}$ anions[204]. There are two types of thallium(I) in the unit cell. One of these has two pairs of thallium–oxygen distances less than 3 Å (2.70 and 2.74 Å) whereas the other forms only one such pair (2.85 Å).

The stability constants of a number of thallium(I) phosphates have been determined (Table 14). Pyrophosphate forms the most stable complex, probably owing to a chelation effect giving a six-membered ring complex. Pyrophosphite ($H_2P_2O_5{}^{2-}$) cannot form such a chelated ring, and binds less strongly than pyrophosphate[205]. Phosphate and protonated pyrophosphate form complexes of about the same stability. Comparison of the data for protonated phosphate and ribose phosphate suggests that the ribose does not have any appreciable effect on the stability constant. Comparison of the ADP and protonated pyrophosphate stability constants then shows that the purine base of ADP has a marked destabilising effect. Phosphorus NMR spectra[176] suggest that in both the pyrophosphate

TABLE 14

Stability constants of thallium(I) phosphates in aqueous solution at 25°C, ionic strength = 0.15 *M* (ref. 176)

Ligand	$\log K_1$
HPO_4^{2-}	0.73 ± 0.1
Ribose phosphate^{2-}	0.87 ± 0.15
ADP^{3-}	1.32 ± 0.1
ATP^{4-}	1.99 ± 0.1
$HP_2O_7^{3-}$	2.34 ± 0.1
PO_4^{3-}	2.41 ± 0.1
$P_2O_7^{4-}$	3.05 ± 0.04

and ADP there is chelation, causing appreciable chemical shifts for both phosphorus nuclei In ATP, there are shifts for all three phosphates, and it has been suggested [176] that thallium(I) is binding to the oxygens of all three phosphorus atoms. This is consistent with a structure for thallium(I) ATP with a direct bridge across the $\beta\gamma$ position and a slightly longer bridge to the α position [176] The binding to three oxygens would explain the five-fold increase in stability of the ATP complex compared with the ADP.

Comparison with the alkali metal derivatives is difficult because of the lack of data for the latter However, stability constants of pyrophosphate and ATP with the alkali metals are generally [114,183] a factor of ten weaker than those of thallium(I).

(iv) Acids of the Group VI elements

The room temperature modification of thallium(I) sulphate is isostructural with the room temperature form of potassium sulphate [206–208]. On heating to about 500°C, it is transformed to a hexagonal form analogous to the high temperature modification of potassium sulphate [207,209]. In the hexagonal, high-temperature, form it has been suggested that there is disorientation of the sulphate groups rather than free rotation [206].

Thallium(I) sulphate vaporises to give mainly [210] the monomeric species, with a little Tl_2O, SO_2 and O_2. The vaporisation products of metal sulphates depend on the relative energies of the metal–sulphate, metal–metal and metal–oxygen bonds. Silver sulphate vaporises to give solid silver, SO_2 and O_2, owing to strong intermetallic bonds in silver metal. Sodium sulphate vaporises to gaseous sodium, SO_2 and O_2 Rubidium and caesium sulphates form the corresponding M_2SO_4 vapour molecules to some extent, indicating the increasing stability of the metal–sulphate bond for the heavier alkali metals [210].

The stability constants β for complex formation between thallium(I) and sulphate ions in aqueous solution have been determined [211] as $Tl(SO_4)^-$, $\beta_1 = 0.33$ and $Tl(SO_4)_2^{3-}$, $\beta_2 = 0.13$. The Raman spectra [212] of these aqueous solutions suggest outer sphere complexes of the type $Tl(H_2O)_n^+SO_4^{2-}$ The ultra-violet spectrum of thallium(I) sulphate in concentrated sulphuric acid and $NaHSO_4$–$KHSO_4$ glasses shows a thallium(I) $^1S_0 \rightarrow {}^3P_1$ transition closer to that observed in the 'free' ion than to that in, for example, the chloro complexes, implying predominantly ionic binding [213].

Complex formation between thiosulphate and thallium(I) has been studied in aqueous solution, and Nilsson [214] found evidence for $[TlS_2O_3]^-$ ($\log K_1 = 0.86$), $[Tl(S_2O_3)_2]^{3-}$ ($\log K_2 = -0.14$), $[Tl(S_2O_3)_3]^{5-}$ ($\log K_3 = -0.54$) and $[Tl_m(S_2O_3)_{m+2}]^{(m+4)-}$ ($m > 2$).

The structures of thallium(I) and potassium trithionates, $M_2S_3O_6$, have been reported to be different [215]. Thallium(I) selenate adopts the same structure as the room temperature modification of thallium(I) sulphate [216].

(v) Acids of the Group VII elements

Both thallium(I) chlorate and bromate crystallise with the space group C_{3v}^5, thallium(I) bromate has the same structure [217,218] as $KBrO_3$. The structures are a simple rhombohedral distortion of the NaCl-type structure, and the three oxygen atoms of any ClO_3 or BrO_3 ion are equidistant from the thallium atom on the same axis. The infra-red spectrum of $TlBrO_3$ shows a Br—O stretching vibration at some 40–50 cm^{-1} lower than in $NaBrO_3$, together with a weak splitting of the degenerate BrO_3 deformations, suggesting interaction of the thallium(I) with the three BrO_3 oxygens [219]. Solubility measurements [220] show that thallium(I) bromate is associated in solution, and at 30°C in solutions of ionic strength less than 0.1 M, $K_1 = 1.9 \pm 0.5$.

The association constant of thallium(I) and perchlorate ion in aqueous solutions of ionic strength 1.0 M in fluoride has been obtained as 0.32 by polarographic studies [69]. Conductivity measurements suggest an association constant close to unity in aqueous solution [221], whilst in acetonitrile, the association constant is 32 (ref. 222), compared with an association constant of 14 for thallium(I) and BF_4^- ions in acetonitrile. If the ion pairing were electrostatic in origin, the smaller BF_4^- ion might be expected to associate most, a specific interaction between thallium(I) and perchlorate was therefore suggested [222]. The Raman spectrum of an aqueous solution of $TlClO_4$ contains a large number of very low frequency absorptions not assignable to the ClO_4^- ion, so that the presence of some sort of complex was suggested [223]. The ultra-violet spectra [224] of aqueous solutions of thallium(I) perchlorate, however, show no changes with concentration up to 0.02 M, but it is known that ion-pairing may sometimes have no effect on the ultra-violet spectra of free ions. Measurements of apparent molar volumes of thallium(I) perchlorate solutions in water give no evidence of inner coordination sphere complex formation [165a].

(vi) Acids of the transition metals

Thallium(I) chromate has three polymorphic modifications the room temperature modification is isomorphous with thallium(I) sulphate [225,226]. Thallium(I) trichromate adopts a structure, analogous to potassium trichromate [227], consisting of CrO_6 octahedra and CrO_4 tetrahedra, the polyhedra being arranged in layers by sharing corners, and the layers being held together by thallium(I) ions which have ten nearest oxygen neighbours. The structure of $Tl^ITl^{III}(CrO_4)_2$ is related [228]; the thallium(I) ions occupy sites with eleven nearest-neighbour oxygen atoms at distances of ca. 3 Å, and four more at 4 2–4 5 Å.

Thallium(I) pertechnetate and perrhenate both crystallise in an orthorhombic system and have a high-temperature, tetragonal modification of the closely related scheelite-type structure[229–231]. Infra-red and Raman spectra confirm a basic T_d symmetry for the ReO_4^- and TcO_4^- ions in these crystals[232,233] The thioperrhenate $TlReO_3S$ probably has the $BaSO_4$-type structure[234]. The structure of the phosphotungstate $Tl_3PW_{12}O_{40}$ is analogous to the corresponding caesium salt[235].

Base-exchange experiments with ammonium ions led to the suggestion that the thallium(I) ion is more tenaciously held in $Tl_3PMo_{12}O_{40}$ than the other univalent cations This has been attributed to distortion of the anion structure by polarisation; the cations in these compounds are fitted between the 'outer sphere' formed by the twelve linked MoO_6 octahedra and the PO_4 group in the centre[236–238] The effects of thallium(I) on oxide glasses are discussed in sect Q

(vii) Sulphur and selenium analogues

The structures of $Tl^I[Tl^{III}S_2]$ and $Tl^I[Tl^{III}Se_2]$ are analogous The thallium(III) ion is surrounded by four sulphur or selenium atoms in a tetrahedron (Tl–S = 2 60 Å, Tl–Se = 2.68 Å) and the thallium(I) has eight sulphur or selenium nearest neighbours (Tl–S = 3 32 Å, Tl–Se = 3 42 Å)[239,240] The structure of TlTe is completely different[241], it is a substitution variant of the structure of W_5Si_3. In Tl_3VS_4 the vanadium is surrounded by four sulphurs at 2 3 Å and each thallium is surrounded by four sulphurs at 3.1 Å and four at 3.7 Å (ref. 242)

H THALLIUM(I) METAL DERIVATIVES

A very large number of thallium(I) metal derivatives have been prepared, they are listed elsewhere[2] Most of the halides $TlMX_n$ adopt structures very similar to the corresponding potassium salts, and the coordination numbers of thallium are very high (usually between eight and twelve) In this thallium(I) is more like the alkali metals than like silver, for many silver compounds, the structure distorts to bring the silver close to just a few of the surrounding MX_n groups Presumably, because of its smaller polarisability, this does not happen for thallium(I) Thus, for example, the isomer shift in the Mossbauer spectrum of $TlFeCl_4$ is consistent with a tetrahedral $FeCl_4^-$ ion and a largely ionic interaction with the thallium(I) ion[243,244]

There is strong evidence for a thallium(I)–metal interaction in thallium(I) hexacyanoferrate(III), $Tl_3Fe(CN)_6$ Since it is isomorphous with $K_3Fe(CN)_6$ with only slightly different unit-cell dimensions, and since thallium(I) can be substituted in $K_3Fe(CN)_6$ in all proportions, it can be assumed that thallium(I) ions occupy the same sites as potassium ions[245]. The unit cell of $K_3Fe(CN)_6$ contains two types of potassium. one type is surrounded by an irregular octahedron of nitrogen atoms, two at 2 87, two at 3 02 and two at 3 14 Å, and the other type has a roughly trigonal-prismatic coordination, with two nitrogens at 2 57 and four at 2.77 Å Infra-red spectra show little effect on the absorption frequencies of the cyanide ion when K^+ is replaced by Tl^+, so that the $Fe(CN)_6^{3-}$ ion cannot be very different in the potassium and thallium(I) salts. However, the quadrupole splitting of the Mossbauer spectrum of $Tl_3Fe(CN)_6$ is considerably greater than that of $K_3Fe(CN)_6$, indicative of a significant Tl^I—$Fe(CN)_6^{3-}$ interaction The thallium NMR chemical shift observed for solid $Tl_3Fe(CN)_6$ was considerably greater than that observed for other thallium(I) compounds This could not be attributed solely to the presence of a paramagnetic Fe^{III} ion since the thallium chemical shift in $TlFe(SO_4)_2$ $12H_2O$ is considerably less It was concluded that the shift was due to unpaired electron density on thallium, transmitted from Fe^{III} through the cyanide groups.

The absorption spectrum of solid $Tl_3Fe(CN)_6$ shows a band at 21,200 cm^{-1}, absent in $K_3Fe(CN)_6$ There is also an increase both in the intensity and the bandwidth of the lowest energy internal charge transfer band of $Fe(CN)_6^{3-}$. The most interesting feature of the spectrum, however, is the polarisation of the 21,200 cm^{-1} band in the plane perpendicular to the *c* axis of the crystal. It is the thallium with trigonal nitrogen coordination which, together with the iron atoms of the $Fe(CN)_6^{3-}$, define this plane, and hence it is from the set of more closely coordinated thallium atoms that the electron migrates to $Fe(CN)_6^{3-}$ during the intermolecular charge transfer process [245,246].

The electrical conductivity of solid $Tl_3Fe(CN)_6$ is unusually high, and cannot be attributed to ion migration [247]. Rather, electron transfer from thallium(I) to iron(III) can occur, with formation of thallium(II), and the conduction is best considered as a series of 'hops' from one localised site to another. As neither $Tl_3Co(CN)_6$ nor $Tl_4Fe(CN)_6$ contain both a reducible and an oxidisable ion, this mechanism for electrical conduction is no longer available, and they both have low conductivities in the solid state. Further, there are no charge-transfer absorptions in their visible and ultra-violet spectra [245]

The new bands appearing in the thallium(I) salts of $[OsCl_6]^{2-}$, $[OsBr_6]^{2-}$ and $[IrCl_6]^{2-}$ have also been attributed to charge transfer from thallium to the metal [246,248,249]

Thallium NMR spectra of aqueous solutions of $Tl_3Fe(CN)_6$ show [192] that association occurs with an association constant of about 70. It was also noted that the thallium chemical shift was very similar to that with a diamagnetic ion of similar charge. Any appreciable covalency in the ion pair would lead to some unpairing of the thallium(I) electrons due to the paramagnetic $Fe(CN)_6^{3-}$ ion, causing a considerable shift of the thallium resonance to lower applied field, as observed in the solid. Further, the charge-transfer band found at 21,200 cm^{-1} in the solid is absent in aqueous solution This suggests that there can be no significant covalent bonding in the ion pairs.

Strong association also occurs between thallium(I) and ferrocyanide ion in aqueous solution, association constants of $\log\beta = 0\ 82$ in 3 *M* perchlorate solution at 25°C and $\log\beta = 3$ at zero ionic strength have been reported [73,224,250].

The infra-red spectra of $M_3[Cr(NCS)_6]$ show a slight increase in ν_{CN} from the potassium salt to the thallium(I) salt, a weak interaction between the isothiocyanate and thallium(I) has been suggested [251].

No thallium(I) derivative of cobalt(II) cyanide has been isolated, but such a species has been observed in solution [252] Aqueous solutions of thallium(I) nitrate react very rapidly with solutions containing the pentacyanocobaltate(II) ion to give a new complex, characterised by an intense charge-transfer band at 389 nm The complex is diamagnetic since it gives no ESR signal, and has been formulated as $[(CN)_5Co{-}Tl{-}Co(CN)_5]^{5-}$

A thallium–gold interaction has been suggested [253] in $TlAu(CN)_2$. The compound is yellow, whereas the alkali metal derivatives are colourless, and it is also insoluble in water, whereas the alkali metal derivatives are soluble The infra-red and Raman spectra give no sign of an interaction between thallium and the cyanide groups. Rather, the spectra are consistent with a T-shaped molecule, with a weak Tl–Au bond and a linear or nearly linear $Au(CN)_2$ group

The alums $TlM^{III}(SO_4)_2 . 12H_2O$ (M = Al,Cr) [254,255] adopt the α-alum structure, in which the next nearest neighbours of the thallium(I) are six water molecules The anhydrous sulphates and selenates $TlM^{III}(SO_4)_2$ and $TlM^{III}(SeO_4)_2$ [M = Al, Ga, Cr, Fe] adopt the $KAl(SO_4)_2$ structure, in which each thallium is surrounded by twelve oxygen atoms [256,257]. The anhydrous double sulphates $Tl_2M^{II}{}_2(SO_4)_3$ adopt the $K_2Mg_2(SO_4)_3$ structure [256,258] The sulphates, selenates and chromates $Tl_2M(XO_4)_2$ [X = S, Se, Cr, M = Sr. Pb, X = Cr, M = Ba] adopt a structure of the $Sr_3(PO_4)_2$ type, in which the thallium has ten oxygen atoms as nearest neighbours [259–262] In thallium(I) voltaite, $\{Tl_2(Cd_5,Fe)Fe_2[SO_4]_{12}.12H_2O\}$ [Al $6H_2O$], thallium is surrounded by twelve sulphate oxygens [263].

Little is known about thallium(I)–metal carbonyl derivatives $TlCo(CO)_4$ has been prepared by the reaction of a mixture of thallium and cobalt metals with carbon monoxide [264], although in the reaction [265] between a thallium(I) salt and $NaCo(CO)_4$, $TlCo(CO)_4$ is formed as a yellow compound which readily redistributes to thallium metal and $Tl[Co(CO)_4]_3$ The thallium(I) derivatives $Tl[MoC_5H_5(CO)_3]$ and $Tl[WC_5H_5(CO)_3]$ are more stable, however, and can be prepared by the reaction of a thallium(I) salt and the appropriate sodium salt in aqueous solution, the former compound is yellow and the latter orange-yellow, in contrast to the colourless sodium salts [265] The tungsten carbonyl $Tl[WC_5H_5(CO)_3]$ has also been prepared [266] from $C_5H_5W(CO)_3H$ The chromium carbonyl $Tl[(C_5H_4CHPh)_2Cr(CO)_3]$ is almost certainly largely ionic [267] Reaction of $[Fe(CO)_4]^{2-}$ with thallium(I) hydroxide produces a compound [268] $Tl_2Fe_3(CO)_{12}$, which, on the basis of infra-red evidence, does not seem to contain bridging carbonyl groups [265]

I ORGANOTHALLIUM(I) DERIVATIVES

Cyclopentadienyl thallium(I) is precipitated when cyclopentadiene is added to an aqueous solution of thallium(I) hydroxide [269]

$$TlOH + C_5H_6 \rightarrow C_5H_5Tl + H_2O$$

A number of methyl and higher alkylcyclopentadienyls, hydropentalenide and isodicyclopentadienide derivatives have similarly been prepared, but in general these products are, unlike TlC_5H_5, air-sensitive[270–274]

The microwave spectrum of TlC_5H_5 in the vapour phase has been interpreted[275,276,276a] in terms of a symmetric top model with a planar C_5H_5 ring, the distance from the thallium to the centre of the ring being 2 4 Å, and the thallium–carbon distance 2 70 Å. This distance is relatively short when compared with the sum of the van der Waals radius of carbon and the ionic radius of thallium(I), which is about 3.1 Å. It has therefore been suggested that there is appreciable covalent bonding in the molecule in the gas phase, and it has been shown that metal orbital–ring orbital overlap is substantial, even when pure *p* metal orbitals are used – *sp* hybridisation would increase the overlap, but at the expense of the 6*s*–6*p* promotional energy[277]

In the solid state, TlC_5H_5 consists[278] of an infinite lattice containing zig-zag chains of $-Tl-C_5H_5-Tl$ The thallium–carbon bond distance in the solid is very probably greater than that in the gas phase, and considerable ionic character seems likely The NMR spectra of a variety of cyclopentadienyl thallium(I) derivatives suggest that they are largely ionic in solution, and no $^{203}Tl \cdots H$ or $^{205}Tl \cdots H$ couplings are seen[271]

The standard free energy of formation of TlC_5H_5 has been measured[279] at 298°K as ΔG^0(formation) = 42 3 ± 0 5 kcal/mole.

The only other thallium(I) organo derivative to have been isolated[280] is the derivative of tris(methylsulphonyl)methane, $TlC(SO_3Me)_3$, which is presumably largely ionic. The stability of these derivatives is presumably associated with the stability of the respective anions. Although monoalkyl- and monoaryl-thallium(I) derivatives have been postulated as reaction intermediates, they have never been isolated[2,281]

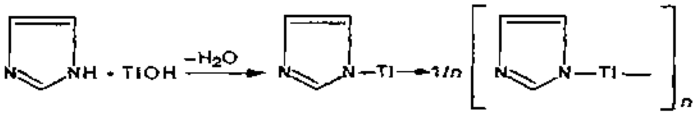
J THALLIUM(I) NITROGEN DERIVATIVES

Thallium(I) nitride has been prepared by the reaction between thallium(I) nitrate and potassium amide in liquid ammonia[282].

$$3\ TlNO_3 + 3\ KNH_2 \rightarrow Tl_3N + 3\ KNO_3 + 2\ NH_3$$

With an excess of potassium amide, a yellow crystalline compound is formed which could be either $TlNK_2$ $4NH_3$ or $TlNH_2$ $2KNH_2$ $2NH_3$ On warming to room temperature, the compound loses ammonia to give $TlNK_2.2NH_3$, which on heating to 100°C in turn loses ammonia to give[282] $TlNK_2.1\frac{1}{3}NH_3$. Thallium(I) nitride is very sensitive to shock, and reacts explosively with water to give thallium(I) hydroxide No evidence has been found[282] for the formation of $TlNH_2$ or Tl_2NH. No simple organoamine derivatives of thallium(I) of the type $TlNR_2$ have been reported, although the thallium(I) salt of hexanitrodiphenylamine has been prepared by reaction with thallium(I) carbonate[283] Thallium(I) acetamide, benzene sulphonamide and *p*-toluene sulphonamide have been prepared from thallium(I) nitride in liquid ammonia[284] Thallium(I) benzamide has been prepared from thallium(I) hydroxide and benzamide in water[1] This is unusual in that most compounds containing a thallium–nitrogen bond are very moisture-sensitive

Thallium(I) urate and thallium(I) phthalimide [285], and imidazolyl thallium(I), benzimidazolyl thallium(I) and triazolyl thallium(I) [286] can also be prepared in aqueous solution, viz



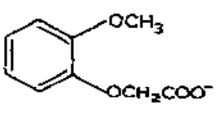
The infra-red and Raman spectra of imidazolyl thallium(I) are consistent with a polymeric structure rather than an anionic structure as adopted by the sodium salt of imidazole [286]. Both the ultra-violet and the NMR spectra indicate that imidazolylthallium(I) is incompletely dissociated in aqueous solution [286] The stabilisation of imidazolylthallium(I) is clearly associated with the additional nitrogen atom in the heterocyclic ring in the three position to the –NH group, thus there is no reaction between pyrrole and thallium(I) hydroxide in aqueous solution [287]

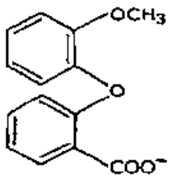
A number of thallium(I) Schiff base derivatives (N-substituted salicylaldimines) have been prepared [288] Infra-red spectra of the solids suggest bonding via the phenolic oxygen and imine nitrogen atoms. A structure analogous to that adopted by thallium(I) acetylacetonate (see sect. M) has been suggested [288]

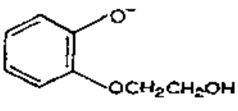
No further structural or chemical information is available on thallium(I) nitrogen derivatives. A list of these derivatives has been given elsewhere [2]

K THALLIUM(I) ALKOXIDES AND PHENOXIDES

Thallium(I) alkoxides and phenoxides can readily be prepared from thallium(I) hydroxide or thallium(I) ethoxide and the corresponding alcohol or phenol In contrast to thallium(I) methoxide, which is a white solid decomposing without melting at 120°C, thallium(I) ethoxide is an oily liquid, decomposing before it can be vaporised The alkoxides are soluble in, or miscible with, most organic solvents The methoxide, ethoxide, *t*-butoxide, amyl oxide and trimethylsilyl oxide are tetrameric in benzene in about *N*/20 solution, and somewhat less associated in more dilute solutions [291–293]. In more concentrated solutions, thallium(I) ethoxide seems to undergo some further polymerisation [291]. Thallium(I) phenoxide is trimeric at about *N*/50 in benzene, which is the limit of its solubility Thallium(I) ethoxide is also tetrameric in boiling ethanol, whereas thallium(I) methoxide is monomeric in boiling methanol [291]. The thallium(I) derivatives of the following three ligands have also been shown to be either tetrameric or polymeric in solution [295]







Thallium(I) phenoxide derivatives have very low ionic conductances in acetone solution, suggesting that there is little ionisation [17].

The ligand π—π^* transitions in solutions of a number of metal phenoxides in 2,4-dimethoxyethane and dimethylformamide have been shown to be sensitive to the metal [17] The perturbation of the molecular energy levels of the anion by the cationic field is the primary influence determining the observed spectral shifts in these associated anions, the role of the solvent is secondary. For the alkali metal phenoxides, there exists a primary cation effect in which a blue shift results from an increased cationic field (i e. Cs^+ to Li^+), which means that excitation results in net movement of negative charge away from the centre of positive charge. This indicates a stronger interaction of the cation with the ground state than with the excited state. Thallium(I) has been shown to exert a greater cationic field than might have been expected from its ionic radius [17]. This is consistent with a greater covalent character for the thallium—oxygen bond than for the corresponding alkali metal—oxygen bond In valence-bond language, the metal phenoxides may be described by a wave function containing contributions from covalent and ionic structures

$$\psi_{\text{ROM}} = a\,\psi_{\text{cov}}(\text{ROM}) + b\,\psi_{\text{ionic}}(\text{RO}^-\text{M}^+)$$

Presumably in the ground state a is large, whereas in the electronic excited state b is of greater importance Thus an increase in covalent character of the ground state should increase the electronic transition energy and produce a red shift. The experimental results thus suggest that the thallium—oxygen bond is more covalent than the corresponding alkali metal—oxygen bond [17]. The results obtained also suggest that the degree of covalent bonding decreases with decreasing pK_A of the phenoxides [17]. Unlike the alkali metal phenoxides, the thallium(I) phenoxides are incompletely dissociated in aqueous solution [17]

A partial single-crystal X-ray structure determination of thallium(I) methoxide shows the presence of tetrameric molecules $[TlOCH_3]_4$ in which the thallium atoms are at the corners of regular tetrahedra [294]. The average intramolecular thallium—thallium distance is 3 48 Å. The positions of the methoxy groups could not be determined, but the most likely structure was thought to be a distorted cube in which the oxygen atoms occupy the corners of a tetrahedron smaller than that occupied by the thallium atoms (Fig 3)

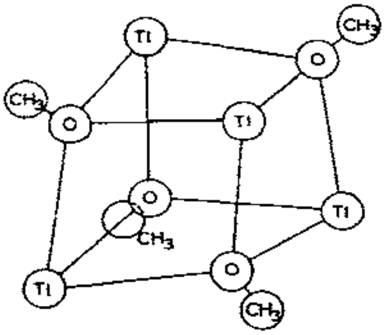


Fig 3 The thallium(I) methoxide tetramer (reproduced from *The Chemistry of Thallium*, Elsevier, Amsterdam, 1971).

This structure can be contrasted with those adopted by the alkali metal methoxides. Potassium, rubidium and caesium methoxides adopt layer structures with the methyl groups on both sides of each layer, with the cations in the central part, each cation being surrounded by five oxygen atoms in a tetragonal-pyramidal array [296,297]. Lithium methoxide adopts a layer structure of the type ABCBAABCBA. ., where A = Me, B = O and C = Li, in which the lithium is surrounded by a distorted tetrahedron of oxygen atoms [298].

Examination of the ^{203}Tl and ^{205}Tl NMR spectra of pure liquid thallium(I) ethoxide confirms a tetrameric structure [299]. The observed spectra are complex, which indicates the presence of ^{203}Tl$\cdots$^{205}Tl coupling (J = 2560 Hz) since there is no Tl$\cdots$H coupling in the proton NMR spectrum of the compound. From considerations of the relative neutral abundance of the two thallium isotopes it is possible to calculate the relative amounts of the various tetrameric molecules containing different combinations of the isotopes and to show that if the calculated NMR spectra arising from the various forms of such a molecule were superimposed, the observed ^{203}Tl and ^{205}Tl spectra would be obtained. The lack of Tl$\cdots$H coupling in the proton spectrum is somewhat surprising. This coupling would be expected to be much less than the very large ^{203}Tl$\cdots$^{205}Tl coupling. One possible explanation, therefore, is exchange of methoxide groups either between tetramers, or between tetramers and lower polymers, at such a rate as to collapse the smaller Tl$\cdots$H coupling but not the greater ^{203}Tl$\cdots$^{205}Tl coupling

The low-frequency vibrational spectra of thallium(I) ethoxide and *n*-propoxide are in agreement with tetrameric structures [300]. Force field calculations suggest an appreciable thallium–thallium interaction [300]. As long as the valence interactions are limited to thallium–oxygen and carbon–oxygen bonds there is poor agreement between experimental and calculated frequencies for vibrations of the skeleton The inclusion of thallium–thallium interactions, however, leads to a very close fit of the data. It is possible to get agreement with the experimental data using alternative force fields, but none of these alternatives provides a chemically satisfactory account of the cage deformation frequencies [301]. Although the force field with a large thallium–thallium force constant is the only one that seems to give a natural explanation of the frequencies, the calculated force constants would predict much more intense spectral lines than are in fact observed. Calculations based on spectral intensities suggest that the electron density involved in the thallium–thallium bond is of the order of 5 to 10% of that associated with a normal covalent bond. This is consistent with the relatively large Tl–Tl distance (3 84 Å) in $[\mathrm{TlOMe}]_4$ (cf. Tl–Tl distance of 3 4 Å in thallium metal).

A bonding scheme can readily be constructed to allow for weak thallium–thallium bonding in the alkoxide [300]. If hybridisation of the s and p_z orbitals on thallium occurs (z is taken to be the direction on each thallium towards the centre of the cage) then the resulting hybrids would be favourably orientated for mutual overlap These hybrids can form a bonding set of four molecular orbitals inside the Tl_4 cage, in which the eight thallium valence electrons can be delocalised, with a corresponding antibonding set outside the cage. The thallium p_x and p_y orbitals are then available for bonding with the alkoxide oxygens. Eight bonding molecular orbitals are then available for sixteen of the alkoxide electrons, and one filled orbital on each oxygen is left non-bonding.

The mass spectrum of thallium(I) phenoxide shows the presence of both monomeric and dimeric species in the gas phase [17].

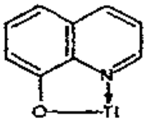
Although the thallium(I) alkoxides are, in general, rapidly hydrolysed by water, thallium(I) phenoxide derivatives can be prepared from thallium(I) hydroxide and the appropriate phenol in aqueous solution. A number of thallium(I) derivatives of polyhydric alcohols can also be prepared in aqueous solution Di-, tri- and tetra-thallium(I) derivatives of ethylene glycol, glycerol and erythritol, respectively, have been so prepared [302]. So far as is known, all hydroxyl hydrogen atoms in a straight chain compound can be substituted by thallium(I) When, however, the compound contains a pyranose, furanose or an attached benzene ring, substitution may be incomplete. Thus methyl arabinoside gives a trithallium(I) derivative, as does methyl glucoside. Sucrose, with eight OH groups and salicin with five, give tetrathallium(I) sucrose and trithallium(I) salicin It is only in rings containing an oxygen atom that incomplete substitution has been observed Inositol, in which all six OH groups are secondary, forms hexathallium(I) inositol. These polymeric polythallium(I) derivatives are generally insoluble in organic solvents [302] Only a monothallium(I) derivative of 1,2-dihydroxybenzene could be isolated [303].

A number of fluoroalkoxide derivatives of thallium(I) have been prepared from thallium(I) hydroxide, but the structures and properties of these compounds have not yet been reported [304]

Conductance measurements suggest that thallium(I) salicylaldehyde is largely undissociated in acetone solution [17]. The mass spectrum shows no peaks corresponding to loss of the —CHO radical, although such a peak is prominent in the mass spectra of aromatic aldehydes. This is perhaps indicative of chelation [17].

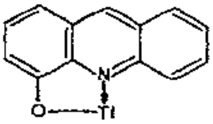
L QUINOLINATES AND SIMILAR DERIVATIVES

The ultra-violet spectrum of thallium(I) 8-hydroxyquinolinate is suggestive of chelation [17].

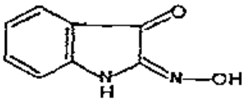


The infra-red spectrum is also suggestive of a chelated structure for the thallium(I) derivative in the solid state, in contrast to largely ionic structures for the alkali metal derivatives [17]. Chloroform solutions of thallium(I) 8-hydroxyquinolinate are very light-sensitive; photochemical decomposition is accompanied by a change in colour from clear yellow through cloudy red, brown, green and bright blue to pale yellow with deposition of a white solid [305]. The nature of these transitions has not yet been established.

The complex formed between thallium(I) and 8-mercaptoquinoline is very considerably stronger than that with 8-hydroxyquinoline [306]. A complex has also been reported between 1-hydroxyacridine and thallium(I) [307], viz

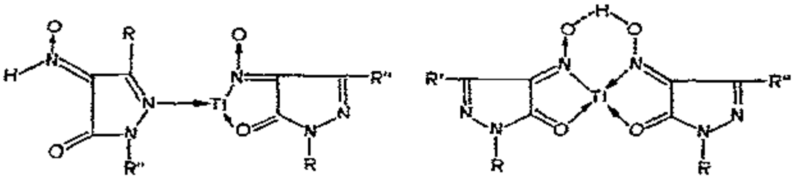


In the thallium(I) derivative of 2-isatoxime

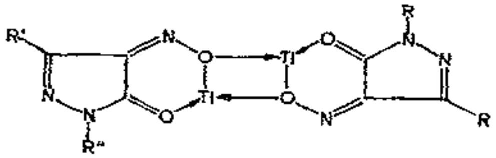


it is probably the –N–OH group that is acting as an acid, and coordination with either the carbonyl or the –NH group is possible [308]

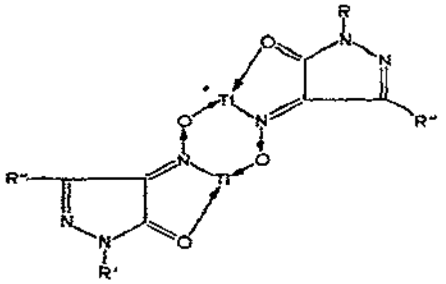
Thallium(I) derivatives of 4-isonitrosopyrazolone and its derivatives have been prepared in aqueous solution, the product depending on the pH of the solution [289,290]. In acid media (pH 3–4), salts of the type HTlPz are formed, which could contain three- or four-coordinate thallium



At pH 5–7.5, derivatives of the type TlPz are formed, which could be either monomeric or dimeric of the two types

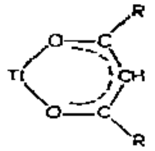


or



M. THALLIUM(I) β-DIKETONE DERIVATIVES

Thallium(I) derivatives of enolisable β-diketones have been prepared from thallium(I) ethoxide or thallium(I) carbonate and the β-diketone. Both thallium(I) hexafluoroacetonate and thallium(I) dibenzoylmethane are monomeric in benzene solution, and their dipole moments are consistent with chelated structures with only moderately polar thallium–oxygen bonds [309].



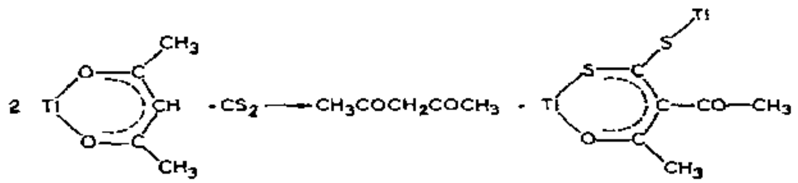
Thallium(I) ethylacetoacetate, however, is dimeric in benzene solution [291]. A single NMR vinyl CH signal is observed for a number of acetylacetonate derivatives in solution [310–312]. No spin–spin coupling was observed with ^{203}Tl or ^{205}Tl, although metal–proton coupling is known for the tin and platinum derivatives [312,313]

The crystal structure of thallium(I) acetylacetonate shows the presence of 1.1 complexes, with Tl–O distances of 2 43 and 2 54 Å, with each thallium atom bonded to oxygen atoms of neighbouring molecules in such a way that molecules are linked indefinitely along the *a* and *c* axes, but not along the *b* axis [314] Infra-red spectra support a chelated structure; the complexes show no carbonyl band, but a C=C stretching vibration appears [315–318] at 1630–1650 cm^{-1} Infra-red spectra of a variety of other thallium(I) derivatives of β-diketones and of monothiodibenzoylmethane are also consistent with a chelated structure [319,320].

The ultra-violet spectra of thallium(I) and alkali metal acetylacetonates again indicate a greater covalency for the thallium–oxygen bond than for the alkali metal–oxygen bonds, and indicate incomplete dissociation for thallium(I) acetylacetonate in aqueous solution [17].

The mass spectrum of thallium(I) acetylacetonate shows the presence of both monomeric and dimeric species in the vapour phase [17].

With carbon disulphide there is an unusual reaction in which acetylacetone and the dithallium(I) salt of 1-acetyl-2-methyl-2-hydroxydithioacrylic acid are formed [321,322].



N. THALLIUM(I) SULPHUR DERIVATIVES

A number of thallium(I) derivatives of thiols have been prepared from thallium(I) hydroxide in aqueous solution, but no details of structures or reactivities have yet been reported [2]. More is known about thallium(I) derivatives of dialkyldithiocarbamates. The structure of thallium(I) dipropyldithiocarbamate can be considered as built up of dimers $[(C_3H_7)_2NCS_2Tl]_2$ (Fig. 4) [323], linked together by thallium—sulphur interactions into chains running parallel to the *a* axis. The central part of the dimer consists of thallium and sulphur atoms in the form of a distorted octahedron. The sulphur atoms of this octahedron form a tetragon which is not far from being planar. The two thallium atoms in the dimer are crystallographically non-equivalent. The four Tl_2–S distances range from 2.91 to 3.29 Å, whereas three of the Tl_1—S distances are short (2.88—3.12 Å) but the fourth is considerably longer (4.37 Å). There is also a difference in the way that the two thallium atoms are linked to the sulphur atoms of adjacent dimers, the two sulphur atoms which are linked in this way to Tl_2 are situated in different dithiocarbamate ligands, while the corresponding sulphur atoms linked to Tl_1 belong to the same ligand.

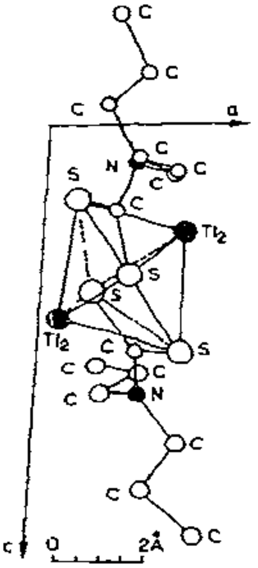


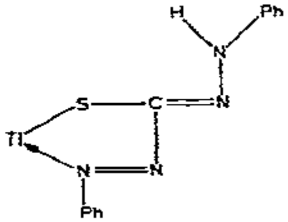
Fig. 4. The dimeric units of thallium(I) dipropyldithiocarbamate (reproduced by permission from L. Nilson and R. Hesse, ref. 323)

It is probable that whereas some of these thallium—sulphur bonds are largely ionic, others are appreciably covalent. The sum of the ionic radii for thallium(I) and sulphur is 3.38 Å, and can be compared with the thallium(I)—sulphur distances of 3.32 and 3.43 Å respectively found in $Tl_2S.Tl_2S_3$ (ref. 324) and $TlNO_3.4SC(NH_3)_2$ (ref. 325). The three shortest Tl—S distances found for each thallium (2.88, 3.02 and 3.12 Å for Tl_1 and 2.91, 3.11 and 3.12 Å for Tl_2) then probably correspond to essentially covalent bonds, and the other Tl—S distances to largely ionic bonds The Tl—Tl distance within a dimeric unit is 3.98 Å, slightly longer than the distance of 3.84 Å found in the TlOMe tetramer

Thallium(I) dipropyldithiocarbamate also exists as a dimer in benzene solution [326]. The dithiophosphinate $TlSSPPh_2$ has been found [327] to be associated in benzene solution, with $n = 1.6$, and is probably a mixture of monomer and dimer. The thallium(I) dialkyldithiophosphates $TlS_2P(OMe)_2$ and $TlS_2P(OEt)_2$ are dimeric in chloroform solution [328].

O. DITHIZONATES AND SIMILAR DERIVATIVES

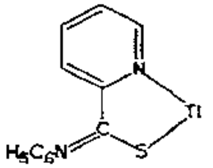
The structure of the primary dithizonate of thallium(I), Tl[PhN=NCSN.NHPh] could involve chelation of two nitrogens or nitrogen and sulphur. The similarity of the infra-red spectrum of the thallium(I) derivative to that of the copper(II) derivative (whose crystal structure shows the presence of N,S chelation) led to the suggestion of structure I for the thallium(I) derivative [329,330].



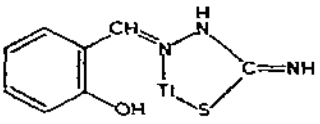
I

The compound is red in the solid state. On irradiation of a chloroform solution with a low-pressure mercury arc, the colour changes irreversibly from orange-red to red-violet; the nature of these changes is unknown [329].

Nitrogen, sulphur chelation has been suggested [331] in the thallium(I) derivative of thiopicolinanilide, II, and salicylaldehyde thiosemicarbazone [332], III

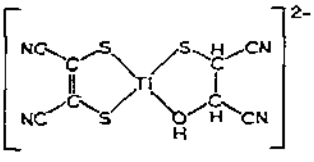


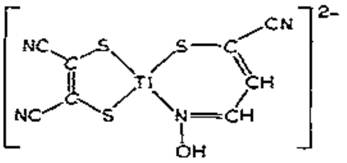
II

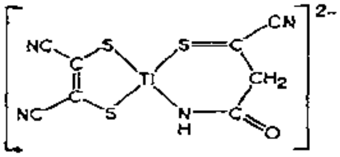


III

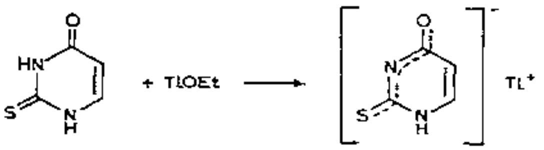
The thallium(III) derivative of dicyanoethylene-1,2-dithiolate (mnt) reacts with sodium chloride solution to give black crystals of a uni-bivalent electrolyte, $K_2[(mnt)Tl(C_4H_3N_2OS)]$. Three possible structures were drawn [333] for this compound, all involving thallium(I).







The position of coordination of thallium(I) in its 2-thiouracil salt is unclear [341]



P COMPLEXES OF THALLIUM(I)

(i) Nitrogen complexes

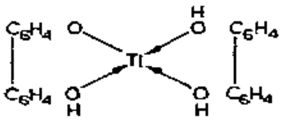
Weak complexes are formed with ammonia and ethylenediamine in aqueous solution, with stability constants of 0.1 and 0.25 respectively [19] Although no solid complexes could be isolated with ethylenediamine or pyridine [287], with 1,10-phenanthroline, $Tl(phen)_2NO_3$ and $Tl(phen)_2ClO_4$ can be prepared [334,335]. The electrical conductivity of $Tl(phen)_2NO_3$ corresponds to that of a binary electrolyte [335]. Reaction of $Tl(phen)_2NO_3$ with sodium chloride produces $Tl(phen)_2Cl$, but with sodium bromide and iodide, the major products are thallium(I) bromide and iodide respectively. Bis(1,10-phenanthroline)thallium(I) iodide can be prepared [336] by the action of heat on the thallium(III) derivative $Tl(phen)_2I_3$ The corresponding bipyridyl derivative $Tl(dipy)_2I$ has also been prepared by the reduction of $Tl(dipy)_2I_3$ with sodium sulphite [336]

The infra-red spectra [337] of these derivatives are too complex to yield any useful information. The NMR spectra of solutions of the $[Tl(phen)_2]^+$ ion show no Tl···H coupling, and show that the two halves of the phenanthroline ligand are equivalent magnetically on the NMR time scale[338]. Exchange of ligands between the ions would seem to be very likely. The infra-red spectrum of the complex with *p,p'*-diamino-2,3-diphenylbutane, $Tl(DPB)_3ClO_4$, shows bands due to a free ClO_4^- ion [339].

(ii) Oxygen complexes

A number of complexes of the alkali metals of the type ML HL and ML.HL′ have been reported, where HL includes the β-diketones, salicylaldehyde, *o*-nitrophenol, 8-hydroxyquinoline, *o*-aminobenzoic acid, 2,4-dinitrophenol, *o*-nitrobenzoic acid and isonitrosoacetophenone [342–345]. The isonitrosoacetophenone derivative $K^+[PhC(O)CH{=}NOHON{=}CHC(O)Ph]^-$ has been shown to be an acid salt rather than a complex [346]. The crystal structure of the complex formed between isonitrosoacetophenone and potassium *o*-nitrophenoxide, however, shows it to be a complex in which the potassium is surrounded by seven oxygen atoms and one oxime-nitrogen atom [347].

Thallium(I) does not readily form derivatives of this type. With salicylaldehyde, a derivative TlL.HL has been prepared [17]. No solid derivatives of this type have been isolated with other ligands, although the observation that thallium(I) diphenol is soluble in chloroform solutions containing diphenol suggest that a compound of the type



might be formed [348].

(iii) Thiourea complexes

A wide variety of thiourea complexes of thallium(I) has been prepared With singly charged anions, derivatives of the type TlX.4TU (TU = thiourea) are formed. With doubly charged anions, the same cation thiourea ratio can be retained [325] as in $Tl_2SO_4.8TU$. With triply charged cations this is no longer so [340]; thallium(I) orthophosphate forms a complex $Tl_3PO_4.6TU$.

The arrangement of sulphur atoms about thallium in $TlNO_3.4TU$ is shown in Fig. 5. The thallium atom environment is almost that of a tetragonal prism, but slightly distorted towards an antiprism. The eight sulphur atoms are equidistant [325] at 3.43 Å. This distance is very similar to the thallium(I)–sulphur distance [324] in $Tl^{I}(Tl^{III}S_2)$ of 3.3 Å and hence the thiourea complex must be largely ionic, and the major cohesive interactions in the crystal are ion–dipole interactions The structures of a number of other thiourea complexes have been determined and all involve a very similar thallium(I) environment, they have been discussed at length elsewhere [2,349]. The alkali metal halide thiourea complexes MX 4TU (M = K, Rb, Cs; X = Br, I) are isomorphous [325] with $TlClO_4.4TU$.

It can readily be seen that, on the basis of maximum repulsion, eight ligand ions around a central ion will ideally lie at the corners of an Archimedean antiprism. For a thiourea complex MX.4TU whose structure is determined largely by electrostatic forces, the cations would then be regularly spaced in linear chains where they are each surrounded by eight sulphur atoms at the corners of a cubically distorted and slightly elongated antiprism

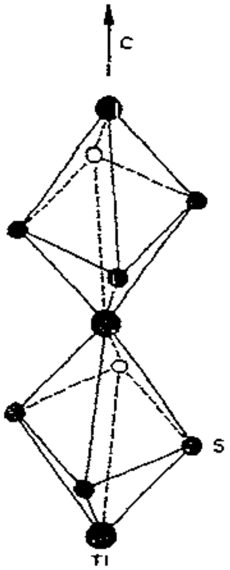


Fig 5 Arrangement of sulphur atoms about thallium in $TlNO_3$ 4TU (reproduced by permission from J C A Boeyens and F H. Herbstein, ref 325)

centred on the cation. The elongation occurs because cation–cation separations are on the average longer than the distance between interstitial positions between antiprismatically close-packed sulphur atoms, and the cubic distortion is necessary to simultaneously optimise the cation–sulphur and sulphur–sulphur distances [349]

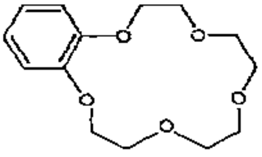
Assuming that the free ions in the complexes MX.4TU have unit charges, and the sulphur atoms and $-NH_2$ groups have charges determined by the dipole moment of thiourea polarised in the field of the free ions, a lattice energy of 179 kcal/mole can be calculated [350]. Since the electrostatic attraction between four moles of thiourea amounts to approximately 17 kcal, it follows that thiourea will form solid complexes of the above type with compounds of lattice energy less than about 162 kcal/mole. This satisfactorily explains the data for the alkali halide complexes Whereas KBr with a lattice energy of 158 kcal/mole forms a complex, NaBr with a lattice energy of 172 kcal/mole does not [349]. The fact that all the thallium(I) halides form complexes is therefore anomalous (see lattice energies in Table 2). There are two factors which could well contribute to an increased stability of the thiourea complexes for thallium(I) The first is a greater polarisation of the thiourea by the thallium(I) than by other univalent ions, and the second is a degree of covalent bonding in the Tl–S bond. As has already been mentioned, however, the Tl–S bond length is relatively long, so the latter factor must be relatively small.

It is possible that thiourea complexes are also formed in aqueous solution, although the thallium(I) halides are virtually insoluble in water, they dissolve in aqueous thiourea [325].

(iv) Cryptates and polyether derivatives

The binding of thallium(I) to a number of macrocyclic ligands has been reported, but it is obvious that this is a field in which much more work must be done before any detailed picture can be given.

Complexes have been prepared [350a] between thallium(I) and crown ethers such as benzo-15-crown-5, IV



IV

Stability constants of the complexes between the cryptate V and thallium(I) and the alkali metal chlorides are given in Table 15.

V

The crystal structures of the alkali metal derivatives of V show that the metal is in a central position, surrounded by the two nitrogens and six oxygens [352,353]. For the alkali metal derivatives there is a good correlation between the ionic radius and the stability constant. The estimated cavity size of the cryptate can be measured by the radius of the sphere which may be included without distorting the ligand, and has a value of 1.4 Å. The low stability constant of the sodium complex arises from the fact that the ion is somewhat too small for effective coordination whilst the low stability constant of caesium can be attributed to its large size [351]. The high stability constants observed for thallium(I) and

TABLE 15

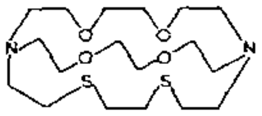
Stability constants in water (ca. 10^{-3} M in ligand) for complexing between metal ions and cryptate, V, with chloride ion [351]

Ion	log K
Li^+	< 2.0
Na^+	3.90
K^+	5.40
Rb^+	4.35
Cs^+	< 2.0
Tl^+	6.30
Ag^+	9.60

silver(I) clearly show that other effects are also important besides considerations of radius ratios It would clearly be of considerable interest to know how much of this high stability constant for thallium(I) is due to the presence of nitrogen in the cryptate V, and to know the stability constants with a series of polyether derivatives

Shifts in the proton NMR spectra of the CH_2 groups occur as a metal salt is added to a solution of V in chloroform or water, and in this way it has been shown [354] that complex formation is complete when the metal-to-ligand ratio is 1.1. With metal-to-ligand ratios of 1 2, signals due to both the complexed and the free form of the cryptate can be observed at low temperatures, but as the temperature is raised, the rate of exchange of metal between one complex and another becomes fast on the NMR time scale and only one broad set of resonances is seen. The rate of exchange for the alkali metals is faster in water than in chloroform, for thallium(I) the opposite is true [354] For thallium(I) the rate of exchange was sensitive to the anion present, exchange is faster for the thallium(I) nitrate cryptate than for the sparingly soluble thallium(I) chloride cryptate The reason for this is not clear. Interestingly, this molecule shows the presence of Tl ··· H coupling at low temperatures (below 40°C for the chloride and below −6°C for the nitrate), with $J(\mathrm{Tl} \cdots \mathrm{CH_2N})$ ca 14 Hz and $J(\mathrm{Tl} \cdots \mathrm{CH_2C})$ ca 12 Hz This is the only thallium(I) derivative for which thallium–proton coupling has been observed, it strongly suggests that the lack of coupling in other species is due to rapid exchange of thallium(I) between ligands

A thallium(I) derivative of the ligand VI has also been prepared [355].



VI

The structure of this derivative is unknown NMR spectra of the alkali metal derivatives show that only hydrogens on the CH_2 groups attached to nitrogen were affected by complex formation, whereas for the silver and lead derivatives, the resonances of the $S{-}CH_2$ groups were also shifted

These derivatives are all closely related to a number of antibiotics of the valinomycin and nigericin group Compounds of the valinomycin group are highly selective for potassium and have the property of increasing the cation permeability of artificial lipid membranes and induce the transport of alkali metal ions into intact mitochondria Compounds of the nigericin group have the property of interfering with the uptake of alkali metal cations into mitochondria when uptake is induced by antibiotics of the valinomycin group. Studies of the interaction between these compounds and thallium(I) have yet to be reported.

Q THALLIUM(I) IN GLASSES AND ION-SELECTIVE GLASS ELECTRODES

A number of thallium(I) germanate [356], aluminogermanate [396], borate [357,358] and silicate [359,360] glasses have been studied Pure GeO_2 glasses possess a structure consisting of corner-shared GeO_4 tetrahedra that form randomly arranged, three-dimensional polymeric networks. The addition of an alkali oxide or Tl_2O to molten GeO_2 causes a sudden elimination of the network via the formation of significant concentrations of GeO_6 octahedra [356].

The alkali germanate glasses are colourless at all concentrations For thallium(I) glasses, however, there is a marked concentration dependence, up to ca 10 mole % Tl_2O, the glasses are colourless, at 15 mole % Tl_2O the glass is green, and the colour gradually deepens in intensity and the wavelength of the transmitted light (colour) shifts to longer wavelengths until it is yellow at 36 mole % Tl_2O With Ag^+ ions in GeO_4 glasses, at a given ionic concentration, the colours are more intense and are shifted to longer wavelength than with thallium(I)

Due to the stronger polarising power of thallium(I) than of the alkali ions, an anion such as O^{2-} or O^- near to a thallium(I) will act as if it were encountering a larger positive charge than if it were near to a potassium ion, for example Consequently, the anion near the thallium(I) will be more distorted Conversely, because of the greater polarisability of thallium(I), the thallium(I) is in turn more easily polarised by the anion than is a potassium ion. Large polarisation effects can cause intense charge-transfer bands in which an electron is transferred from the anion (O^{2-} or O^- in the glass) to the cation in short-lived excited states

The sudden appearance of colour in these thallium(I) glasses would suggest a sudden structural change, and one might guess that this would consist of a shortening of the thallium—oxygen bond. There is indeed strong evidence for this from studies of the thallium NMR spectra of borate glasses [358]. The thallium(I) borate glasses are also systems in which the network-forming species, boron, changes coordination with added thallium(I) The NMR studies led to two conclusions (*i*) low Tl_2O content glasses (0—25 mole % Tl_2O) have ionic thallium bonding (diamagnetic chemical shift with small anisotropy), (*ii*) higher Tl_2O content glasses (> 35 mole % Tl_2O) have covalently bound thallium (paramagnetic chemical shift with large anisotropy)

It was also found that there was an abrupt increase of the dipolar width and a sudden ^{203}Tl NMR broadening relative to ^{205}Tl at 0 25 mole fraction Tl_2O This was associated with a substantial molecular orbital overlap between the thallium atoms (covalency) [358] At this composition the BO_4/BO_3 ratio was reported [358] as 0 4. The onset of colour at 15 mole % Tl_2O in germanate glasses occurs [356] at a GeO_6/GeO_4 ratio of ca. 0 3

The concepts just considered for thallium(I) incorporated into glasses also apply for thallium(I) in ion-selective glasses When a thin membrane of glass is interposed between two solutions, an electric potential difference is observed across the glass, which depends on the ions present in the solutions in a simple and reproducible manner Depending on the exact composition of the glass, the response may be mainly to H^+ or to one of the alkali cations or to NH_4^+, Ag^+ or Tl^+, or to some polyvalent ion. By varying the composition of the glass (usually an $SiO_2-Al_2O_3-Na_2O$ mixture) a variety of selectivity preferences for the monovalent cations can be generated [361].

The observed selectivities are attributed to the different attractive forces, mainly Coulombic, exerted on different cations by water on the one hand and by membrane negative charges on the other The glass electrodes specific for these cations are ion exchangers in which the negatively charged site for cation exchange is $[AlOSi]^-$. The cation preferred by the negative site will be that cation which experiences the greatest decrease in free energy when its nearest neighbour becomes that site rather than water. Thus the relative affinities of the site for two different cations n and m will be governed by the free energy difference

$$\Delta F_{n,site} - \Delta F_{m,site} - \Delta F_{n,water} + \Delta F_{m,water}$$

where $\Delta F_{n,water}$ and $\Delta F_{m,water}$ are the free energies of hydration and $\Delta F_{n,site}$ and $\Delta F_{m,site}$ are the free energies of interaction between the cation and the negative site. In the case that the site has a very high electric field strength, so that the cation negative site ΔF's and their differences are much higher than the hydration energies and their differences, then affinities will be controlled by the term

$$\Delta F_{n,site} - \Delta F_{m,site}$$

Since the smallest cation will have the greatest ΔF, the affinity order will decrease with increasing ionic radius and the sequence $Li > Na > K > Rb > Cs$ is obtained for the alkali cations. If, on the other hand, the site has a very low electric field strength, cation–site ΔF's will be smaller than the hydration energies, and then cation selectivity will be governed by

$$\Delta F_{n,water} - \Delta F_{m,water}$$

In this case, the smallest cation, which has the highest free energy of hydration, will have the most unfavourable value of $\Delta F_{ion,site} - \Delta F_{ion,water}$ so that affinity will decrease with decreasing ionic radius and the alkali ion sequence $Cs > Rb > K > Na > Li$ will be observed As the site strength is varied continuously from a very low to a very high value, the observed series of cation sequences is obtained [361].

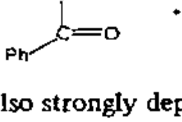
In order to reproduce these cation sequencies in a semi-theoretical manner, values of $\Delta F_{ion,site}$ have been calculated in one of two ways, both using the metal halides as examples of anionic sites with different field strengths [361] The first method was to apply Coulomb's law to a system of a negatively charged sphere of variable radius and a positively charged sphere of radius equal to the cation radius This method neglects all non-Coulombic forces. In the second method, $\Delta F_{ion,site}$ for halide-type sites of different field strengths was equated with the experimentally determined free energies of formation of the metal halides Both methods yield curves of $(\Delta F_{ion,site} - \Delta F_{ion,water})$ as a function of the site field strength or the radius of the halide ion, for the metal cations For the alkali metal cations, both methods yield similar curves, which are similar to those obtained experimentally For silver(I), the observed curve is intermediate between that calculated for the thermochemical model and that calculated for the purely electrostatic model, showing that polarisation effects are important for silver(I) For thallium(I), two different curves for $(\Delta F_{\mathrm{Tl,site}} - \Delta F_{\mathrm{Tl,water}})$ are also obtained from the two models, but now the agreement with the electrostatic model is much better than with the thermochemical model, so that polarisation effects for thallium(I) are relatively unimportant in these oxide sites [361].

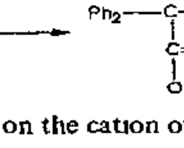
R CATALYSIS OF ORGANIC REACTIONS

The rate of hydrolysis of a number of organic compounds in water has been found to be slower when thallium(I) hydroxide is the base than when it is sodium hydroxide, but a number of cases have also been found where the reverse is true. Thus the rate of depolymerisation of diacetone alcohol,

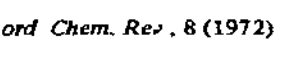
$$CH_3\ COCH_2.CMe_3\ OH \xrightarrow{OH^-} 2\ Me_2CO$$

which shows specific hydroxyl ion catalysis, is slower with thallium(I) hydroxide than with sodium hydroxide [362]. This was attributed to incomplete dissociation of thallium(I) hydroxide. The kinetics of the base-catalysed hydrolysis of ethyl acetate have also been measured, and the second-order rate constant for this reaction was found to be the same with thallium(I) hydroxide as with sodium hydroxide [363] However, in the alkaline hydrolysis of a number of half-esters of dicarboxylic acids, a much more marked effect was observed [364] It was found that the alkali metal cations only had a small, negative salt effect on the rate of alkaline hydrolysis of the half-esters of adipic and sebacic acids. Thallium(I) ions, however, had a marked catalytic effect on the hydrolysis of the half-esters of oxalic and malonic acids The catalytic effect was attributed to chelate formation between the transition state of the hydrolysis and the thallium(I) ion, resulting in a stabilisation of the transition state

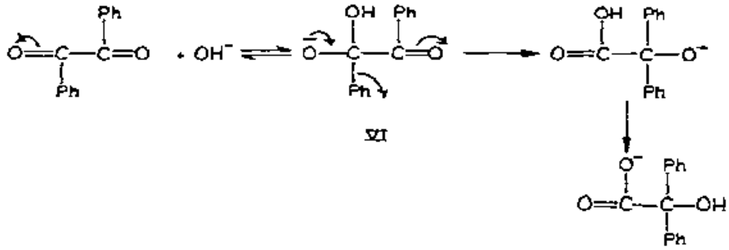




It has also been found that the benzil rearrangement caused by bases



is also strongly dependent on the cation of the base [365] Here again, thallium(I) is much more effective than the alkali metal cations (Table 16). This can be attributed to a stabilisation of the transition state VI by coordination of thallium(I).



XI

Undoubtedly, many other hydrolysis and rearrangement reactions of this type will be found to be sensitive to catalysis by thallium(I).

TABLE 16

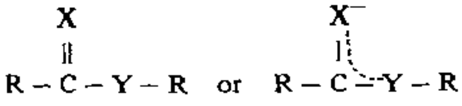
Half-life period (min) of the rearrangement of 0.01 *M* 2,2'-dichlorobenzil with bases of 0.01 *N* initial concentrations[365] in 1:1 dioxane/water at 60.5°C

Base	Half-life
KOH	472
NaOH	461
LiOH	459
CsOH	453
TlOH	5.7

5 ACTIVATION OF ENZYMES

A number of enzymes have been found which require potassium ions for activity. As a general rule, it has been found that such enzymes are also activated by rubidium, but are little activated by sodium and even less by lithium. It has also been found that the molar concentration of potassium and rubidium required for maximum activity is high, having an activation constant K_A near 0.01 *M* in most cases[366]. The mode of action of the alkali metal cations is not yet completely clear. It has been suggested[369] that the role of the monovalent cation is to maintain a specific protein conformation necessary for optimum catalytic efficiency[366]. The alternative suggestion has also been made that the monovalent cation exerts its role by forming a complex between enzyme and substrate (thus see ref. 367).

It has been noted[367] that the intermediates for one of the substrates in monovalent-cation-activated enzyme-catalysed reactions have the structure



$$\overset{\displaystyle X}{\overset{\|}{R-C-Y-R}} \quad \text{or} \quad R-\overset{X^-}{C}\cdots Y-R$$

X = O, N or C, Y = O, N

Thus the following types of reaction have been found to show such catalysis

(*a*) Phosphoryl transfer

(*i*) phosphorylation of $-C(=O)-OH$

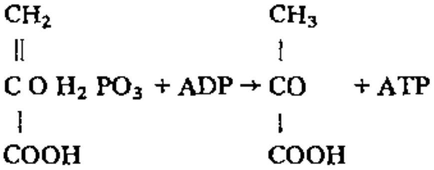
(*ii*) phosphorylation of $-C(=CH_2)-OH$

(*iii*) phosphorylation of $-C(=N-R)-OH$

(*b*) Elimination reactions (such as those with trytophanase and threonine dehydrase)

Thallium(I) has been found to substitute for alkali metal cations in a number of these systems The comparison with the organic reactions catalysed by thallium(I) and discussed in the previous section is obvious.

The enzyme that has received most attention is pyruvate kinase This enzyme is activated by Mg^{2+} and also requires a monovalent cation. It catalyses the reaction between phosphoenol pyruvate and ADP



$$\begin{array}{llll} CH_2 & & CH_3 & \\ \| & & | & \\ C\,O\,H_2\,PO_3 + ADP & \rightarrow & CO & + ATP \\ | & & | & \\ COOH & & COOH & \end{array}$$

Rabbit muscle pyruvate kinase (ATP pyruvate phosphotransferase. EC 2 7 1.40) is a four-subunit glycolytic enzyme [368,369] of molecular weight 237,000 daltons The enzyme has an absolute requirement for a monovalent cation as well as a divalent cation, the latter probably being involved in enzyme–substrate bridge formation [370]

Thallium(I) has been found to stimulate the pyruvate kinase reaction in a manner similar to that observed for potassium [371] The relative maximum activities for various monovalent cations are given in Table 17. The most striking feature is that the apparent affinity of thallium(I) for the enzyme is a factor of about 50 greater than that of potassium. Further, the thallium(I) binding becomes slightly stronger with increasing divalent ion concentration up to the concentration of maximum activation, and then the apparent affinity decreases A marked inhibition of the reaction is seen at thallium(I) concentrations greater than 10 m*M* This also depends on the concentration of the divalent ion, the higher the divalent ion concentration, the less the inhibition at high thallium(I) concentrations. Since both a divalent and a monovalent cation are required for activation, this suggests a mutual competition between the two ions, with an inactive enzyme resulting from the binding of thallium(I) to the bivalent site An alternative explanation, however, could be thallium(I) binding to one of the substrates, this would cause an inhibition either by reducing the free substrate concentration or by the formation of a thallium(I)–substrate complex which could act as a competitive inhibitor of the enzyme Addition of ADP to the enzyme which already had an inhibiting level of thallium(I) caused a further reduction in the reaction velocity. This suggests competitive inhibition by the thallium(I)–ADP complex (thallium(I) is known to complex ADP, see p 314), either at the thallium(I) site or at the substrate (ADP) site

The number of binding sites for thallium(I) in the enzyme has been found to be four.

TABLE 17

Relative activation of pyruvate kinase reaction by monovalent cations (Cl^- as anion. $[Mg^{2+}]$ 8 m*M*)[371]

Cations	$\dfrac{V_{max}(\text{cation})^a}{V_{max}(K^+)}$	Optimum cation concn (m*M*)
Li^+	0.02	100
Na^+	0.08	100
K^+	1.00	100
Rb^+	0.65	100
Cs^+	0.09	100
NH_4^+	0.81	50
Tl^+	0.61	3

[a] V_{max} is the maximum initial velocity of the reaction.

Again, four binding sites for PEP (ref. 371) and for Mn^{2+} (which also activates the enzyme)[371,372] have been found, and four reactive lysyl ε-amino groups have been implicated[371] in the binding of ADP. The conclusion is obvious that a unitary relationship exists between the substrates, monovalent and divalent activators and the number of enzyme subunits.

A thallium NMR study has been reported for the binding of thallium(I) to pyruvate kinase. The ^{205}Tl line of a 0.10 *M* thallium(I) nitrate solution is broadened from 7 Hz to 16.5 Hz on addition of 4.38×10^{-5} *M* enzyme. Addition of Mn^{2+} (4.7×10^{-4} *M*) causes a further broadening to 30.5 Hz. This additional broadening is probably due to dipolar interactions of the thallium(I) with the unpaired electronic spin of Mn^{2+} (the addition of diamagnetic Mg^{2+} causes no broadening), and implies that the thallium(I) and Mn^{2+} are relatively close in the enzyme.[373]

A number of other enzymes have been shown to be activated by thallium(I). Details are given in Table 18. Thallium(I) activates[371] yeast pyruvate kinase with a half-maximum activation at ca. 0.5 m*M* $[Tl^+]$ ($V_{max}^{[Tl^+]}/V_{max}^{[K^+]}$ in $[NO_3^-] = 1.0$, in $[Cl^-] = 0.8$). Thallium(I) activation of both the acetylphosphatase and the *p*-nitrophenylphosphatase of beef brain microsomes has been demonstrated, with an affinity 9–10 times that of potassium.[374,375] AMP deaminase is known not to require K^+ (or Tl^+) for activity, rather, the monovalent cation acts as an allosteric activator.

The reaction sequence of the ($Na^+ + K^+$)-dependent ATPase appears to involve a Na^+-dependent phosphorylation of the enzyme followed by a K^+-dependent dephosphorylation.[380] The enzyme is particularly important since it has been associated with the active transport of Na^+ and K^+. Several models for the mode of action of the enzyme have been proposed, incorporating either two sets of ion-specific sites or interconversion of specificity for one set of sites. ATP has been shown[380a] to bind to a single site on kidney cell ATPase. This binding is inhibited by K^+ with antagonism of this inhibition by Na^+. Thus addition of Na^+ to the ATPase causes binding of ATP and addition of K^+ drives off the ATP from the binding site. Further addition of Na^+ reverses the action of the K^+ and allows the ATP to return to the binding site. The ATP can be driven off with other monovalent ions, and the sequence of apparent ion affinity found[380a] is

TABLE 18

Effect of thallium(I) and other monovalent cations on enzyme activation

Enzyme	Order of efficiency (K_m)	Ref
Rabbit muscle pyruvate kinase	$Tl^+ > K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$	371
Yeast pyruvate kinase	$Tl^+ > K^+$	371
Beef brain phosphatases	$Tl^+ > K^+ > Rb^+ > Cs^+ > NH_4^+ > Na^+ > Li^+$	374,375
Diol-dehydratase (B_{12})	$Tl^+ > NH_4^+ > K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$	376
Muscle AMP deaminase	$Tl^+ > K^+$	371
E coli homoserine dehydrogenase I	Activated by Tl^+	371
Na/K ATPases (K-function)	$Tl^+ > K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$	377–379,380a
Aminoacyl transferases	$NH_4^+ > Tl^+$	381

$Rb^+ = K^+ > Tl^+ > NH_4^+ > Cs^+$. For the dephosphorylation step in ATPase, the sequence of apparent affinities found [380a] is $Tl^+ > Rb^+ > K^+ > Cs^+ > NH_4^+ > Li^+$, and the thallium(I) has an affinity ca. 10 times greater than potassium for the K^+ site [377].

In the transfer of amino acids from aminoacyl sRNA to polypeptides, the aminoacyl transferase is most activated by ammonium ions, with potassium somewhat less effective and Na^+, Rb^+ and Tl^+ much less active, lithium and caesium ions were found to be the least active [381]. The mechanism of this reaction is, as yet, little understood.

T THALLIUM(I) IN OTHER BIOLOGICAL SYSTEMS

Alkali cations are involved in at least three roles in biological systems. The first is in neutralising ionic charge, and maintaining conformations in macromolecules. The second is in the activation of enzymes The third is in maintaining a membrane potential (by accumulation of potassium ions and rejection of sodium ions), which allows nerves and muscle to function.

Thallium(I) activation of isolated enzymes has been dealt with in the previous section It has also been found that thallium(I) can be concentrated within an erythrocyte membrane instead of potassium [382] Thallium(I) will also activate the frog sartorius muscle fibre at external thallium(I) concentration of the order of 74 μM, higher concentrations lead to irreversible damage [383] Thallium(I) will also start the beating of a frog *Rana esculenta* heart which has been stopped by washing with potassium-free water [384].

Thallium(I) has been found to substitute for potassium in the stabilisation of ribosomes [385] The binding of thallium(I) to whole casein has been studied at pH 7.0, and it has been found that there are 16.7 independent binding sites per 10^5 g casein [386]

Thallium(I) is toxic to living species, and causes degeneration in a great many tissues. It has been suggested that thallium(I) combines with mitochondrial SH groups, and so interferes with oxidative phosphorylation [387] The effect of thallium(I) on the development of the eggs of ***Paracentrotus lividus*** has been studied [388,389] Clearly, in such whole-body studies, there will be very many points at which thallium(I) could interfere with the normal processes and give rise to toxic manifestations.

Thallium(I) has been shown [394] to have a very high affinity for the potassium-specific binding sites in *Chlorella* and readily competes with potassium for binding sites on macromolecular substances in barley root tissues [395] Thallium(I) is readily absorbed into the protoplasm, but vacuolar accumulation is slow and tends to stagnate, and this latter feature is the only difference between the absorption of thallium(I) and potassium or rubidium Thus thallium(I) seems to block the systems that mediate its transport into the vacuoles The process by which ions are released to the vacuole appears to be much more discriminating with respect to the nature of the ion than the process of binding to protoplasmic or carrier sites The nature of the vacuolar release is unknown, and could be an enzymatic breakdown of either a chemical or a physical nature of the ion—carrier complex.

U SPECTROSCOPIC PROBES FOR THALLIUM

Potentially the most useful spectroscopic property of thallium is its nuclear spin. It has two isotopes both with nuclear spin $I = \frac{1}{2}$, the most abundant being ^{205}Tl, with a natural abundance of 70.48%. It has a high relative sensitivity for NMR (19.2% of that for protons). Relatively few thallium NMR studies have been performed. Table 19 lists the ^{205}Tl chemical shifts defined as

$$\delta = \frac{\nu_{\text{ref}} - \nu_{\text{cpd}}}{\nu_{\text{ref}}} \times 10^6$$

for a number of solids Clearly, the chemical shift range of thallium(I) is large. The chemical shift in a number of aqueous solutions of thallium(I) has been found to be very sensitive to the anion concentration [70]. At low anion concentrations, the chemical shift varies non-linearly with anion concentration, but at higher anion concentrations, the variation becomes linear Again, the shifts are large For example, for a 0 3 M solution of thallium(I) hydroxide containing 6 M KOH, the chemical shift δ is −1400, and with acetate as the anion at the same concentration, δ is ca −400 (ref. 70) At low concentrations, the shifts have been attributed to ion pair formation, and at higher anion concentrations, the shifts have been attributed to the effect of ions on the hydration atmosphere of the ion pair. The change in the magnetic shielding is probably due mainly to a change in the temperature-independent paramagnetism induced in the electrons of the thallium atom [70]. This term is most effective when chemical interactions are strongest, and so it appears that these interactions are most important for hydroxide ions and very small with, for example, fluoride ions

The linewidth observed [373] for a 0 1 M solution of thallium(I) nitrate is 7 Hz, which compares well with that calculated from the T_1 value obtained by progressive saturation, assuming that $T_1 = T_2$

These large chemical shifts can, in principle, be used as a very sensitive probe for the environment of thallium. Further, a very large ^{203}Tl ··· ^{205}Tl coupling constant ($J = 2560$ Hz) has been observed in thallium(I) ethoxide, the only polymeric thallium(I) compound to have been studied [299] by thallium NMR. The detection of dimerisation and

TABLE 19

^{205}Tl chemical shifts δ (p p m.) [397]

Compound	δ (p p.m.)[a]
Thallium(I) perchlorate	+370
Thallium(I) nitrate	−280
Thallium(I) chloride	−610
Thallium(I) sulphate	− 90
Thallium(I) formate	−1110
Thallium(I) carbonate	−1120
Thallium(I) fluoride	− 790
Thallium(I) bromide	−1080
Thallium(I) iodide	−2330
K_3TlCl_6	−2230
$Zn(TlCl_4)_2$	−2970
0 3 M aq soln $TlNO_3$ (ref)	0 0

[a] Positive values, more shielded than reference

polymerisation in thallium(I) compounds should, therefore, be readily performed by NMR.

The only thallium NMR study of thallium(I) in a biological system has been a study of the binding of thallium(I) to pyruvate kinase (sect R)

The temperature-independent paramagnetism of thallium(I) also causes large chemical shifts in the resonances of other nuclei present in ligands bound to thallium(I) Thus proton shifts of −0 2 p p.m. have been observed in ethylenediaminetetraacetic acid on binding to thallium(I), and shifts of up to −2 2 p p m. have been observed [376] in phosphorus resonances on binding of phosphates to thallium(I)

The position of the intense absorption band due to the thallium(I) $7s \rightarrow 7p$ (triplet) excitation can also, in principle, be used to study the binding of thallium(I). This band shifts from 215 nm in the aquated cation to 246 nm on binding to ethylenediaminetetraacetate, for example [376] However, no clear pattern emerges from consideration of the shifts with a number of different ligands.

The fluorescence of thallium(I) is also of potential use, but, unfortunately, most ligands appear to quench the fluorescence [398].

REFERENCES

1 W Crookes, *J. Chem Soc* , (1864) 112
2 A G Lee, *The Chemistry of Thallium*, Elsevier, Amsterdam, 1971
3 W M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd edn , Prentice-Hall, New York, 1952
4 C E Moore, *Atomic Energy Levels*, Nat. Bur Stand , Washington, 1958.
5 L E Orgel, *J. Chem. Soc* , (1959) 3815
6 M.F C Ladd, *Theor. Chim Acta*, 12 (1968) 333.

7 J R. Tessman, A H Kahn and W. Shockley, *Phys Rev* , 92 (1953) 890

8 A L. Allred, *J Inorg Nucl Chem* , 17 (1961) 215

9 R.J. Zollweg, *J Chem Phys* , 50 (1969) 4251

10 P Politzer, *Trans Faraday Soc* , 64 (1968) 2241

11 M F C Ladd and W H. Lee, *Trans Faraday Soc* , 66 (1970) 2767.

12 C K Jorgensen, *Inorganic Complexes*, Academic Press, New York, 1963

13 A. Gosman and J. Sedlacek, *Radiochim Acta*, 11 (1969) 112

14 R Takahashi, *Rev Polarogr* , 9 (1961) 116

15 J Courtot-Coupez, A Laouenan and M Le Demezet, *C R Acad Sci* , *Ser. C*, 267 (1968) 1475.

16 J F Coetzee and J.J. Campion, *J Amer Chem Soc* , 89 (1967) 2513.

17 A G. Lee, *J Chem Soc A*, (1971) 2007

18 J Reedijk, A.P. Zuur and W.C. Groeneveld, *Rec. Trav Chim Pays-Bas*, 86 (1967) 1127

19 P. Job, *Ann Chim (Paris)*, 9 (1928) 113

20 J Bjerrum, *Metal Amine Formation in Aqueous Solution*, Haase, Copenhagen, 1957.

21 S Halem, *Helv Chim Acta*, 43 (1960) 1431

22 R P Bell and M H Panckhurst, *J Chem Soc* , (1956) 2836

23 R.W G. Wyckoff, *Crystal Structures*, Vol 1, Interscience, New York, 1963

24 J A A. Ketelaar, *Z Kristallogr , Kristallogeometrie, Kristallphys , Kristallchem* , 92 (1935) 30

25 N W. Alcock, *Acta Crystallogr , Sect A*, 25 (1969) S101.

26 M Barlow and C C. Meredith, *Z Kristallogr , Kristallgeometrie, Kristallphys , Kristallchem* , 130 (1969) 304

27 A Ruoff and J Weidlein, *Z Anorg Allg Chem* , 370 (1969) 113

28 C Caranoni, R Favier, L Capella and A. Tranquard, *C R Acad Sci , Ser C*, 270 (1970) 1795

29 C W F T Pistorius and J B Clark, *Phys Rev* , 173 (1968) 692

30 L Helmholz, *Z Kristallogr , Kristallgeometrie, Kristallphys , Kristallchem* , 95 (1936) 129

31 G.A Samara, L C Walters and D A Northrop, *J Phys Chem Solids*, 28 (1967) 1875.

32 J D. Dunitz and L E Orgel, *Advan Inorg Chem Radiochem.*, 2 (1960) 45

33 E A Boudreaux, *Coord Chem. Rev* , 2 (1967) 117

34 E A Boudreaux, L D Dureau and H B Jonassen, *Mol Phys* , 6 (1963) 377

35 G A Samara, *Phys Rev* , 165 (1968) 959

36 R W Vaughan and D H Anderson, *J Chem Phys* , 52 (1970) 5287

37 S Hafner, *J Phys. Chem Solids*, 27 (1966) 1881

38 Y Saito, *J Phys Soc. Jap* , 21 (1966) 1072

39 C S N Murthy and Y.V G S. Murti, *Proc Phys Soc , London (Solid State Phys)*, 3 (1970) L22

40 B K. Agarwal and L P Verma, *Proc Phys Soc , London (Solid State Phys)*, 2 (1969) 104

41 B.K Agarwal and L.P Verma, *Proc Phys Soc , London (Solid State Phys)*, 3 (1970) 535

42 H G. Drickamer, R W Lynch, R L Clendenen and E A Perez-Albuerne, *Solid State Phys* , Vol. 19 , Academic Press, New York, 1966

43 J C Zahner and H G Drickamer, *Phys Chem Solids*, 11 (1959) 92

43a R.J. Friauf, *Z Naturforsch. A*, 26 (1971) 1210

44 T J Rowland and J P Bromberg, *J Chem Phys* , 29 (1958) 626

45 L F Grantham and S.J Yosim, *J Chem Phys* , 45 (1966) 1192

46 F.J. Keneshea and D. Cubicciotti, *J. Phys Chem* , 69 (1965) 3910

47 D. Cubicciotti, *High Temp Sci.*, 2 (1970) 65

48 D. Cubicciotti, *J Phys Chem* , 68 (1964) 1528

49 D Cubicciotti, *J Phys Chem* , 68 (1964) 3835.

50 D Cubicciotti, *J Phys Chem* , 69 (1965) 1410.

51 S H. Bauer, T Ino and R F Porter, *J Chem Phys* , 33 (1960) 685

52 S H Bauer and R F Porter, in M Blander (Ed), *Molten Salt Chemistry*, Interscience, New York, 1964

53 A Snelson, *J Chem Phys* , 46 (1967) 3652.

54 P A Kollman, J.F Liebman and L C Allen, *J Amer Chem Soc* , 92 (1970) 1142

55 J. Berkowitz and T A Walter, *J Chem Phys* , 49 (1968) 1184

56 A G. Lee, *Int J Mass Spectrom. Ion Phys*, 3 (1969) 239.
57 J M Brom and H F Franzen, *J Chem Phys*, 54 (1971) 2874
58 B M. Gimarc, *J Amer Chem. Soc*, 92 (1970) 266
59 F.J. Keneshea and D. Cubicciotti, *J Phys Chem*, 71 (1967) 1958
60 R G. Pearson, *J Chem. Phys*, 52 (1970) 2167
61 O N Komshilova and O G Polyachenok, *Zh Fiz. Khim*, 43 (1969) 2676
62 A H Barrett and M Mandel, *Phys Rev*, 109 (1958) 1572, see also R H Hammerle, J T Dickinson, R G Van Ausdal, D.A Stephenson and J C Zorn, *J. Chem. Phys*, 50 (1969) 2086
63 R K Ritchie and H. Lew, *Can J Chem*, 43 (1965) 1701
64 R F Barrow, *Proc Phys Soc, London, Sect A*, 70 (1957) 622
65 H W de Wijn, *Physica (Utrecht)*, 31 (1965) 1193
66 A F Wells, *Structural Inorganic Chemistry*, 3rd edn, Oxford University Press, London, 1962
67 B P Dailey and C H Townes, *J Chem Phys*, 23 (1955) 118.
68 R D Carlson, C A Lee and B P Fabricand, *Phys Rev*, 85 (1952) 784
69 A M Bond, *J Phys Chem*, 74 (1970) 331
70 R Freeman, R P H Gasser, R E Richards and D H Wheeler, *Mol Phys*, 2 (1959) 75
71 R O Nilsson, *Ark Kemi*, 10 (1957) 363
72 A M Bond and T A O'Donnell, *J Electroanal Chem Interfacial Electrochem* 26 (1970) 137
73 R P Bell and J H B George, *Trans Faraday Soc*, 49 (1953) 619
74 V S K Nair and G H Nancollas, *J Chem Soc*, (1957) 318
75 M H Panckhurst, *Aust J Chem*, 15 (1962) 194.
76 S Makishima, T Tomotsu, M Hirata, S Hayakawa, K Hasegawa, R Kambe and S Shionoya, in H K. Kallman and G M Spruch (Eds), *Luminescence of Organic and Inorganic Materials*, Wiley, New York, 1962
77 A D'Aprano and R M Fuoss, *J Amer Chem Soc.*, 91 (1969) 279.
78 M H Panckhurst, *J Phys Chem*, 73 (1969) 2097
79 K H. Hu and A B Scott, *J Amer Chem Soc*, 77 (1955) 1380
80 A B. Scott, R G. Dartau and S Sapsoonthorn, *Inorg Chem*, 1 (1962) 313
81 F.Ya Kul'ba, V E Mironov, V A. Fedorov and V.A Baevskii *Zhr. Neorg Khim*, 8 (1963) 1945
82 A B Scott and K H Hu, *J Chem Phys*, 23 (1955) 1830
83 R E Curtice and A B Scott, *Inorg Chem*, 3 (1964) 1383
84 F.Ya. Kul'ba and V E Mironov, *Zh Neorg Khim*, 5 (1960) 1898
85 Yu D Fridman, R.I Sorochan and N V. Dolgashova, *Zh Neorg Khim*, 7 (1962) 2127
86 R C Woodford, *J Chem Soc A* (1970) 651
87 D C Luehrs, *J Inorg Nucl Chem*, 31 (1969) 3517
88 A B Garrett and S J Vellenga, *J Amer Chem Soc*, 67 (1945) 225
89 E R. Buckle, P.E. Tsaoussoglou and A R. Ubbelohde, *Trans Faraday Soc*, 60 (1964) 684
90 E R Buckle and P E Tsaoussoglou, *Trans Faraday Soc*, 60 (1964) 2144
91 H Fromherz, *Z Phys*, 68 (1931) 233
92 R Hilsch, *Proc Phys Soc, London*, 49 (extra part) (1937) 40
93 F Seitz, *J Chem Phys*, 6 (1938) 150
94 A M Lemos, M C Stauber and J F Marion, *Phys Rev B* 2 (1970) 4161
95 S G. Zazubovich, *Phys Status Solidi*, 38 (1970) 119
96 M. Strada, *Atti Accad Naz Lincei, Mem Cl Sci Fis., Mat Natur., Sez 3a* [7] 19 (1934) 809
97 R A. Penneman and E Staritzky, *J Inorg Nucl Chem*, 6 (1958) 112
98 T Matsuo, M Sugisaki, H Suga and S Seki, *Bull Chem Soc Jap*, 42 (1969) 1271
99 M Sugisaki, T. Matsuo, H Suga and S Seki, *Bull Chem Soc Jap*, 41 (1968) 1747
100 B H Krause, *Z. Kristallogr., Kristallgeometrie, Kristallphys, Kristallchem*, 115 (1961) 413
101 P Gray, *Quart Rev, Chem. Soc*, 17 (1963) 441
102 B L Evans, A D Yoffe and P Gray, *Chem Rev*, 59 (1959) 515
103 C W F T Pistorius, *J Chem Phys*, 51 (1969) 2604
104 W. Bussem, P Gunther and R. Tubin, *Z. Phys Chem, Abt B*, 24 (1934) 1
105 S J Patel, *J Inorg Nucl Chem*, 32 (1970) 3708
106 A Tramer, *J Chim Phys*, 59 (1962) 232

107 Yu Ya Kharitonov and V V Skopenko, *Zh Neorg Khim*, 10 (1965) 1803.
108 T C Waddington, *J Chem Soc*, (1959) 2499
109 Z Iqbal and A D Yoffe, *Proc Roy Soc*, *Ser A*, 302 (1967) 35
110 S K Deb and A D Yoffe, *Trans Faraday Soc*, 55 (1959) 106.
111 M J Sole and A D Yoffe, *Proc Roy Soc*, *Ser A*, 277 (1964) 498
112 I M Kolthoff and C S Miller, *J Amer Chem Soc*, 62 (1940) 2171
113 D Banerjea and I P Singh, *J Indian Chem Soc*, 39 (1962) 353
114 L.G Sillen and A E Martell, Stability constants of metal–ion complexes, *Chem Soc*, *Spec Publ*, *No 17*, 1964.
115 F Ya Kul'ba, V E Mironov and G Mrnyakova, *Zh Neorg Khim*, 10 (1965) 1393
116 C -P Chang and L -S Liu, *K'o Hseuh T'ung Pao*, (1964) 435, *Chem Abstr*, 61 (1964) 12699
117 K -H Hsu and H -G Tsiang, *Hua Hsueh Hseuh Pao*, 24 (1958) 277, *Chem Abstr* 53 (1959) 11060
118 M Tournoux, R Marchand and M Bouchama, *C R Acad Sci*, *Ser C*, 270 (1970) 1007
119 H Sabrowsky, *Naturwissenschaften*, 56 (1969) 414
120 H. Sabrowsky, *Z Anorg Allg Chem*, 381 (1971) 266.
121 K -R Tsai, P M Harris and E N Lassettre, *J Phys Chem*, 60 (1956) 338
122 M. Touboul and R Boaziz, *C R Acad Sci*, *Ser C*, 270 (1970) 1235
123 R N Mulford, *AEC Rep No LA-1373*, 1952
124 D Cubicciotti, *AEC Rep No SRIA-10669* 1969
125 A J Hinchchliffe and J S Ogden, *Chem Commun* (1969) 1053.
126 J M Brom, T. Devore and H F Franzen, *J Chem Phys*, 54 (1971) 2742
127 D M Makowiecki, D A Lynch and K D Carlson, *J Phys Chem*, 75 (1971) 1963
128 V F. Shevel kov, N A Klyuev and A A Mal'tsev, *Vestn Mosk Univ*, *Khim*, 24 (1969) 32, *Chem Abstr*, 72 (1970) 84510
129 D Cubicciotti, *High Temp Sci*, 1 (1969) 11
130 J T Waber and G E Sturdy, *J Electrochem Soc* 101 (1954) 583.
131 W T Lindsay, *J Phys Chem*, 66 (1962) 1341
132 F Ya Kul'ba, Yu B Yakolev and E A Kopylov, *Zh Neorg Khim*, 15 (1970) 2112
133 J H B George, J A Rolfe and L A Woodward, *Trans Faraday Soc*, 49 (1953) 375
134 H Sabrowsky, *Z Anorg Allg Chem*, 365 (1969) 146
135 H Sabrowsky and R Hoppe, *Z Anorg Allg Chem*, 358 (1968) 241
136 R Hoppe and P Panek, *Z Anorg Allg Chem*, 381 (1971) 129
137 J A A. Ketelaar and E W Gorter, *Z Kristallogr*, *Kristallgeometrie, Kristallphys*, *Kristallchem*, 101 (1939) 367
138 M M Stasova and B K Vainshtein, *Kristallografiya*, 3 (1958) 141
139 D Smith, D.W. James and J P Devlin, *J Chem Phys*, 54 (1971) 4437
140 G J Janz and D W. James, *J Chem Phys*, 35 (1961) 739
141 J R. Ferraro, *J Mol Spectrosc.*, 4 (1960) 99
142 M H Brooker and D E Irish, *Can J Chem*, 48 (1970) 1183
143 D W James and J P Devlin, *Aust J Chem*, 24 (1971) 743
144 C. Finbak and O Hassel, *Z Phys Chem*, *Abt B*, 35 (1937) 25
145 R M Hinde and E A Kellett, *Acta Crystallogr*, 10 (1957) 383
146 S.W Kennedy and J H Patterson, *Z Kristallogr*, *Kristallgeometrie*, *Kristallphys*, 116 (1961) 143
147 J H Patterson, *Microsc Cryst Front*, 13 (1962) 291
148 R N. Brown and A C McLaren, *Acta Crystallogr*, 15 (1962) 977
149 S W Kennedy and J H Patterson, *Proc Roy Soc*, *Ser A*, 283 (1965) 498
150 E. Rapoport and C W F T Pistorius, *J Chem Phys*, 44 (1966) 1514
151 D M. Newns and L A K Staveley, *Chem Rev*, 66 (1966) 267
152 A C McLaren, *Rev Pure Appl Chem*, 12 (1962) 54
153 P C Bury and A C McLaren, *Phys Status Solidi*, 31 (1969) K 5
154 M F C Ladd and W H Lee, *Progr. Solid State Chem*, 1 (1964) 37
155 M F C Ladd and W H. Lee, *Progr Solid State Chem*, 2 (1965) 378

156 B. Cleaver and B C J. Neil, *Trans Faraday Soc* , 65 (1969) 703
157 A Timidei and G J Janz, *Trans. Faraday Soc* , 64 (1968) 202
158 B Cleaver, E Rhodes and A R Ubbelohde, *Discuss Faraday Soc* , 32 (1962) 22
159 B. Cleaver, E Rhodes and A R. Ubbelohde, *Proc. Roy Soc., Ser A*, 276 (1963) 437
160 O J. Kleppa and L S Hersh, *J Chem Phys* , 36 (1962) 544
161 B. Cleaver and B C L Neil, *Trans Faraday Soc* , 65 (1969) 2860
162 S Hafner and N H Nachtrieb, *J Chem Phys* , 40 (1964) 2891
163 J H R Clarke, *Chem Phys Lett* , 4 (1969) 39
164 D Cubicciotti, *High Temp Sci* , 2 (1970) 131
165 A D'Aprano and R M Fuoss, *J Phys Chem* , 72 (1968) 4710
165a V Jedinakova and J Celeda, *Collect Czech Chem Commun* , 36 (1971) 3071
166 P Franzosini and C Sinistri, *Ric Sci , Parte 2 Sez A*, 3 (1963) 439
167 P I Protsenko and V V Rubleva, *Zh Obshch Khim.*, 25 (1955) 238
168 C Sinistri and P Franzosini, *Ric Sci , Parte 2, Sez A*, 3 (1963) 419
169 M A. Yakimov, V Ya Mishin and L F Golova, *Zh Neorg Khim* , 8 (1963) 1470
170 G H Cristie and R C Menzies, *J Chem Soc* , (1925) 2369
171 M J Boinon, C Caranoni, R Favier, A. Sebaoun and A Tranquard, *C R Acad Sci , Ser C*, 271 (1970) 724
172 C Caranoni, M J Boinon, R Favier, L Capella and A Tranquard, *C R Acad Sci., Ser C*, 271 (1970) 673
173 J D Donaldson, J F Knifton and S D Ross, *Spectrochim Acta*, 20 (1964) 847
174 J D Donaldson, J F. Knifton and S D Ross, *Spectrochim Acta*, 21 (1965) 275
175 R A Robinson and C W Davies, *J Chem Soc* , (1937) 574
176 J P Manners, K G Morallee and R J P Williams, *J Inorg Nucl Chem* , 33 (1971) 2085
177 R Abegg and J F Spencer, *Z Anorg Allg Chem* , 46 (1905) 406.
178 A G Lee, *J. Chem Soc A*, (1971) 2007
179 J A Schufle and C D Agostine *J Phys Chem.* 60 (1956) 1623.
180 K N Sahu and A K Bhattacharya, *J Indian Chem Soc* , 42 (1965) 247
181 G A Rechnitz and S B. Zamochnik, *Talanta*, 11 (1964) 1061
182 H Irving and J J R F da Silva, *J Chem Soc* , (1963) 448
183 L G Sillen, Stability constants of metal–ion complexes, *Suppl No 1, Part 1, Chem Soc Spec Publ , No 25*, 1971
184 M Kodama, T Noda and M Murata, *Bull Chem Soc Jap* , 41 (1968) 354
185 G Anderegg and E Bottari, *Helv Chim Acta*, 50 (1967) 2341
186 J J R F. da Silva, *Rev Port Quim* , 7 (1965) 88
187 H Irving and J J R F da Silva, *J Chem Soc* , (1963) 945
188 H Irving and J J R F da Silva, *J Chem Soc* , (1963) 1144
189 M V. Reddy and A K Bhattacharya, *J Inorg Nucl Chem* , 32 (1970) 2321
190 M V Reddy and A K Bhattacharya, *Indian J Chem* , 7 (1969) 282
191 K N Sahu and A K Bhattacharya, *J Indian Chem Soc* , 46 (1969) 325
192 R P H Gasser and R E Richards, *Mol Phys* , 2 (1959) 357
193 A Reisman, *J Amer Chem Soc* , 80 (1958) 3558
194 H Schuenzel, E Hoyer, G Klose and W Schroth, *Z Chem* , 7 (1967) 464
195 R S Saxena, K C Gupta and M L Mittal, *Monatsh Chem* , 99 (1968) 1779
196 A Tranquard, G Lacassagne, M. Boinon, L Capella and R Cohn-Adad, *C R Acad Sci* , 264 (1967) 1111
197 L. Cavalca, M Nardelli and I W Bassi, *Gazz Chim. Ital* , 85 (1955) 153
198 P I Protsenko and N A Brykova, *Zh Neorg Khim* , 10 (1965) 1220
199 L Cavalca, M Nardelli and A Braibanti, *Gazz Chim Ital* , 85 (1955) 1544
200 M Nardelli, A Braibanti and I Chierici, *Gazz Chim Ital* , 87 (1957) 510
201 H Gilman and R K. Abbott, *J Amer Chem Soc* , 71 (1949) 659
202 L P McHatton and M J Soulal, *J Chem Soc* , (1953) 4095
203 A G Lee, *Spectrochim Acta*, in press
204 J K Fawcett, V Kocman, S C. Nyburg and R J O'Brien, *Chem Commun* , (1970) 1213

205 D Grant and D S Payne, *J Inorg Nucl Chem* , 26 (1964) 1985.
206 H F Fischmeister, *Monatsh Chem.*, 93 (1962) 420
207 G Pannetier and M. Gaultier, *Bull Soc Chim Fr* , (1966) 188
208 G Pannetier and M. Gaultier, *C R Acad Sci , Ser C*, 263 (1966) 132
209 A J Majumdar and R Roy, *J Phys Chem* , 69 (1965) 1684.
210 D Cubicciotti, *High Temp Sci*, 2 (1970) 389
211 F Ya Kul'ba, Yu B Yakovlev and V E. Mironov, *Zh Neorg Khim* , 10 (1965) 2044
212 R E Hester and R A Plane, *Inorg Chem* , 3 (1964) 769
213 J.A Duffy, S.M Forbes and M D Ingram, *J Chem. Soc A*, (1970) 451.
214 R O Nilsson, *Ark Kemi*, 12 (1958) 371
215 J A A Ketelaar and J K Sanders, *J Chem Phys* , 4 (1936) 621
216 G Gattow, *Naturwissenschaften*, 47 (1960) 442
217 P Smith and S M Carrera, *An Real Soc. Espan Fis Quim. Ser A* 47 (1951) 89
218 L. Rivoir and M. Abbad, *An Real Soc Espan Fis Quim., Ser A*, 44 (1948) 5
219 K H Khoo and J D Murray, *J Inorg Nucl Chem* , 31 (1969) 2437
220 K H Khoo, *J Inorg Nucl Chem* , 30 (1968) 2425
221 R.A. Robinson and C W. Davies, *J Chem Soc* , (1937) 574
222 H L Yeager and B Kratochvil, *J Phys Chem.*, 74 (1970) 963
223 M M Jones, E A Jones, D F Harmon and R T Semmes, *J Amer Chem Soc* , 83 (1961) 2038
224 M H. Panckhurst and K G Woolmington, *Proc Roy Soc., Ser A*, 244 (1958) 124
225 N I Bashilova, *Zh Neorg Khim* , 9 (1964) 106
226 M Abbad and L Rivoir, *An Real Soc Espan Fis Quim* , 43 (1947) 831
227 K A Wilhelmi, *Chem Commun* , (1966) 437
228 P A. Koz'min and M. Surazhskaya, *Zh Strukt Khim* , 9 (1968) 917
229 C Keller and B Kanellakopulos, *Radiochim Acta*, 1 (1963) 107
230 J Beintema, *Z Kristallogr , Kristallgeometrie, Kristallphys , Kristalchem* , 97 (1937) 300
231 B Kanellakopulos, *J Inorg Nucl Chem* , 28 (1966) 813
232 A Muller and B Krebs, *Z Naturforsch A*, 20 (1965) 967
233 K Ulbricht and H Kriegsmann, *Z Chem* , 6 (1966) 232
234 A Muller and B Krebs, *Z Anorg Allg Chem* , 342 (1966) 182
235 J A Santos, *Proc Roy. Soc , Ser A*, 150 (1935) 309
236 W P Thistlethwaite and W T Wilson, *J Inorg Nucl Chem.*, 24 (1962) 1559
237 J van R Smit, J J Jacobs and W Robb, *J Inorg Nucl Chem* , 12 (1959) 95
238 B C Purkayastha amd S Sen, *J. Indian Chem. Soc* , 42 (1965) 601
239 H. Hahn and W Klingler, *Z. Anorg. Allg Chem* , 260 (1949) 110
240 J A A Ketelaar, W H. t'Hart, M. Moerel and D Polder, *Z Kristallogr , Kristallgeometrie, Kristallphys , Kristallchem* , 101 (1939) 396
241 K. Burkhardt and K. Schubert, *J Less-Common Metals*, 18 (1969) 426
242 C. Crevecoeur, *Acta Crystallogr* , 17 (1964) 757
243 E R Jones, M E Hendricks, S L Finklea, L Cathy, T Auel and E L Amma, *J Chem Phys* , 52 (1970) 1922
244 K Tempelhoff, H.-H Emons and W. Meisel, *Z Anorg Allg Chem* , 372 (1970) 1
245 D. Herbison-Evans, P B P Phipps and R J P Williams, *J. Chem Soc* , (1965) 6170
246 P Day, *Inorg Chim Acta Rev.*, 3 (1969) 81
247 P S Braterman, P B P Phipps and R J P Williams, *J Chem Soc.*, (1965) 6164.
248 C K Jorgensen, *Acta Chem Scand* , 17 (1963) 1034
249 C K Jorgensen, *Mol Phys* , 4 (1961) 235.
250 I F Mavrin, F Ya Kul'ba and V.E. Mironov, *Zh Fiz. Khim* , 41 (1967) 1659
251 J R Wasson and C Trapp, *J Inorg Nucl. Chem* , 30 (1968) 2437
252 E C.C. Crouch and J.M. Pratt, *Chem Commun.* (1969) 1243
253 H Stammreich, B M Chadwick and S G Frankiss, *J Mol Struct* , 1 (1968) 191
254 A H C Ledsham and H Steeple, *Acta Crystallogr., Sect B*, 25 (1969) 398.
255 H Lipson, *Proc. Roy. Soc , Ser A*, 151 (1935) 347.
256 W. Franke and G. Henning, *Acta Crystallogr* , 19 (1965) 870.

257 W. Franke, *Acta Crystallogr*, 20 (1966) 920.

258 A. Zemann and J. Zemann, *Acta Crystallogr*, 10 (1957) 409

259 H. Schwarz, *Z Anorg Allg Chem*, 344 (1966) 41

260 C K. Moller, *Acta Chem Scand*, 8 (1954) 81

261 H Schwarz, *Z. Anorg Allg. Chem*, 344 (1966) 214

262 H. Schwarz, *Z Anorg Allg Chem* 345 (1966) 230

263 K Mereiter, *Naturwissenschaften*, 57 (1970) 670

264 W. Hieber and U Teller, *Z Anorg Allg Chem*, 249 (1942) 43.

265 A.T.T. Hsieh and M.J Mays, personal communication

266 *Brit Pat No. 827,374*, 1960, *Chem Abstr*, 55 (1961) 3612

267 R L Cooper, E O Fischer and W Semmlinger, *J Organometal Chem*, 9 (1967) 333.

268 W. Hieber, J Gruber and F Lux, *Z Anorg Allg Chem*, 300 (1959) 275

269 F A Cotton and L T Reynolds, *J Amer. Chem Soc*, 80 (1958) 269.

270 L T Reynolds and G Wilkinson, *J Inorg Nucl Chem*, 9 (1959) 86

271 H P Fritz and F H Kohler, *J Organometal Chem*, 30 (1971) 177

272 A N Nesmeyanov, R B Materikova, E I Fedin, N S Kochetkova, P V Petrovskii, L A Fedorov and E V. Leonova, *Dokl Akad Nauk SSSR*, 177 (1967) 586

273 T J Katz and J.J. Mrowca, *J Amer Chem Soc*, 89 (1967) 1105

274 T Chivers, *Organometal Chem Rev*, 6 (1970) 1

275 J K Tyler, A.P Cox and J Sheridan, *Nature*, 183 (1959) 1182

276 C Roberts, H P Cox and M J. Whittle, *J Mol Spectrosc.*, 35 (1970) 476.

276a M J. Whittle, P A Cox and C Roberts, *Chem Phys Lett*, 9 (1971) 42

277 S Shibata, L S Bartell and R M Gavin, *J Chem Phys*, 41 (1964) 717

278 E. Frasson, E Menegus and C Panattoni, *Nature*, 199 (1963) 1087

279 H Hull and A G Turnbull, *Inorg Chem*, 6 (1967) 2020

280 H.J Backer, *Rec Trav Chim Pays-Bas*, 65 (1946) 53.

281 A G Lee, in E I Becker and M Tsutsui (Eds), *Organometallic Reactions*, Vol 5, Wiley-Interscience, New York, to be published

282 E C Franklin, *J Phys Chem*, 16 (1912) 682

283 Langhans, *Z Ges Schiess-Sprengstoff*, 31 (1936) 359

284 E C Franklin, *J Amer Chem Soc*, 37 (1951) 2279

285 K Freudenberg and G Uthemann, *Chem. Ber*, 52 (1919) 1509

286 A.G. Lee, *J. Chem Soc A*, (1971) 880

287 A G. Lee, unpublished observations

288 R J Cozens, K S Murray and B O West, *Aust J Chem*, 23 (1970) 683

289 O L Brady and M D Porter, *J Chem Soc*, (1933) 840

290 V Hovorka and L Sucha, *Collect Czech Chem. Commun*, 25 (1960) 1790.

291 N V Sidgwick and L E Sutton, *J Chem Soc*, (1930) 1461

292 H Schmidbaur, M Bergfeld and F Schindler, *Z Anorg Allg Chem*, 363 (1968) 73

293 D C Bradley, *J Chem Soc*, (1958) 4780.

294 L F Dahl, G L Davis, D L. Wampler and R West, *J Inorg Nucl Chem*, 24 (1962) 357

295 R S Nyholm and M L Tobe, *U S Clearinghouse Fed Sci Tech Inform*, 1967, AD 663164

296 E Weiss, *Helv Chim Acta*, 46 (1963) 2051

297 E Weiss and H Alsdorf, *Z Anorg Allg. Chem*, 372 (1970) 206

298 P.J. Wheatley, *J Chem Soc*, (1960) 4270

299 W G Schneider and A D Buckingham, *Discuss Faraday Soc*, 34 (1962) 147

300 V A Maroni and T G Spiro, *Inorg Chem*, 7 (1968) 193.

301 P A Bulliner and T G Spiro, *Spectrochim. Acta, Part A*, 26 (1970) 1641

302 R.C Menzies, *J Chem Soc*, (1947) 1378

303 O S Tomar and P K. Bhattacharya, *J Indian Chem Soc*, 43 (1966) 250

304 J S Skelcey, J E Rumminger and K O. Groves, *U S Pat No 3,494,946 Chem. Abstr*, 72 (1971) 110787

305 T Moeller and A.J Cohen, *J Amer Chem Soc*, 72 (1950) 3546

306 J Bankovskii, L. Cera and A. Ievins, *Latv. PSR Zinat Akad. Vestis, Kim Ser*, (1966) 601, *Chem. Abstr*, 66 (1967) 119460
307 D.H. Freeman and F Lions, *J Proc. Roy. Soc. N S. W*, 74 (1941) 520.
308 V. Hovorka and L Divis, *Collect Czech Chem. Commun*, 14 (1949) 116
309 C Z Moore and W H Nelson, *Inorg Chem*, 8 (1969) 143
310 J A S. Smith and E.J. Wilkins, *J Chem Soc. A*, (1966) 1749
311 Y Kawasaki, T Tanaka and R Okawara, *Bull Chem Soc Jap*, 40 (1967) 1562.
312 J C Hammel, J A S Smith and E J Wilkins, *J Chem Soc A*, (1969) 1461
313 F Bonati, *Organometal Chem. Rev*, 1 (1966) 379
314 N.C. Webb, from E C. Taylor, G.H Hawks and A McKillop, *J. Amer. Chem. Soc*, 90 (1968) 2421
315 E. Uhlig, *Z Anorg Allg Chem*, 326 (1963) 89
316 R. Mecke and F. Funck, *Z Elektrochem*, 60 (1956) 1124
317 R West and R. Riley, *J Inorg Nucl Chem*, 5 (1958) 295.
318 Y Kawasaki, T Tanaka and R Okawara, *Spectrochim Acta*, 22 (1966) 1571
319 E Uhlig, *Z Anorg Allg Chem*, 326 (1963) 89
320 E Uhlemann and P Thomas, *Z Anorg Allg. Chem.*, 356 (1967) 71
321 F Feigl and E Bacher, *Monatsh Chem*, 49 (1928) 401
322 E. Uhlig and E Uebel, *Z Anorg Allg Chem*, 337 (1965) 98
323 L. Nilson and R Hesse, *Acta Chem. Scand* 23 (1969) 1951
324 H Hahn and W Klingler, *Z Anorg Allg Chem*, 260 (1949) 110
325 J C A Boeyens and F H. Herbstein, *Inorg Chem*, 6 (1967) 1408
326 S. Akerstrom, *Acta Chem Scand*, 18 (1964) 824.
327 F. Bonati, S Cenini and R Ugo, *J Organometal Chem*, 9 (1967) 395
328 F. Bonati and G Minghetti, *Inorg Chim Acta*, 3 (1969) 161.
329 L S Meriwether, E C. Breitner and C L Sloan, *J Amer Chem Soc.*, 87 (1965) 4441
330 A Janowski and T Ganko, *Bull Acad Pol Sci, Ser. Sci Chim*, 16 (1968) 223
331 G. Bahr and E Scholz, *Z Anorg Allg Chem*, 299 (1959) 281.
332 V Hovorka and Z Holzbecher, *Collect. Czech Chem Commun*, 15 (1950) 267
333 G Hunter and B C. Williams, *J Chem Soc A*, (1971) 2554
334 P Pfeiffer and B Werdelmann, *Z Anorg Allg. Chem*, 261 (1950) 197.
335 F.Ya Kul'ba, V E Mironov and L A Anan'eva, *Zh Neorg Khim*, 8 (1963) 2326
336 G J. Sutton, *Aust J Sci Res., Ser. A*, 4 (1951) 654
337 A.A Schilt and R C Taylor, *J Inorg Nucl Chem*, 9 (1959) 211
338 J R Hudman, M Patel and W R McWhinnie, *Inorg Chim. Acta*, 4 (1970) 161
339 G T. Cochran, J F. Allen and N.P Marullo, *Inorg Chim Acta*, 1 (1967) 109
340 G Pfrepper, *Z Anorg Allg Chem*, 347 (1966) 160
341 G T Rogers and T L V Ulbricht, *J Chem Soc C*, (1971) 2995
342 N V. Sidgwick and F.M Brewer, *J Chem Soc.*, (1925) 2379.
343 F.M Brewer, *J Chem Soc.*, (1931) 361.
344 A K Banerjee, A.J. Layton, R S Nyholm and M R Truter, *J Chem Soc A*, (1969) 2536
345 A K Banerjee, A.J Layton, R S. Nyholm and M.R. Truter, *J. Chem. Soc A*, (1970) 292
346 M A. Bush, H Luth and M R Truter, *J Chem. Soc A*, (1971) 740
347 M A. Bush and M R. Truter, *J. Chem Soc A*, (1971) 745
348 O.L Brady and E D Hughes, *J. Chem Soc*, (1933) 1227.
349 J.C A Boeyens, *Acta Crystallogr, Sect. B*, 26 (1970) 1251
350 J C A. Boeyens and G. Gafner, *J. Chem Phys*, 49 (1968) 2435
351 J M. Lehn and J.P. Sauvage, *Chem. Commun.*, (1971) 440
352 B. Metz, D Moras and R Weiss, *Chem Commun.*, (1970) 217
353 B. Metz, D. Moras and R Weiss, *Chem. Commun*, (1971) 444
354 J.M. Lehn, J.P Sauvage and B Dietrich, *J Amer. Chem Soc*, 92 (1970) 2916.
355 B. Dietrich, J M. Lehn and J.P. Sauvage, *Chem. Commun*, (1970) 1055.
356 E F. Riebling, *J Chem. Phys.*, 55 (1971) 804

357 R.K. Momu and N H. Nachtrieb, *J. Phys Chem* , 72 (1968) 3416.
358 J.F. Bauger and P.J Bray, *Phys. Chem. Glasses,* 10 (1969) 77
359 K Otto and M E Milberg, *J Amer Ceram Soc* , 50 (1967) 513
360 M E Milberg and C R Peters, *Phys Chem Glasses,* 10 (1969) 46
361 G Eisenman, *Advan Anal Chem Instrum.,* 4 (1965) 213.
362 R P. Bell and J E. Prue, *J Chem. Soc* , (1949) 362.
363 J. Murto, *Suom. Kemistilehti B,* 34 (1961) 26.
364 J I Hoppe and J.E Prue, *J Chem Soc* , (1957) 1775
365 E Pfeil, G Geissler, W. Jacquemin and F Zomker, *Chem Ber* , 89 (1956) 1210
366 H.J Evans and G.J Sorger, *Ann Rev Plant Physiol* , 17 (1966) 47
367 C.H. Suelter, *Science,* 168 (1970) 789.
368 M A Steinmetz and E W C Beal, *Biochemistry,* 5 (1966) 1399
369 G.L. Cottam, P F Hollenberg and M.J Coon, *J. Biol. Chem.,* 244 (1969) 1481.
370 A S Mildvan and M. Cohn, *J Biol Chem* , 241 (1966) 1178
371 F.J. Kayne, *Arch Biochem Biophys* , 143 (1971) 232
372 G L Cottam and A.J Mildvan, *J. Biol Chem* , 245 (1970) 6539
373 F.J. Kayne and J Reuben, *J. Amer Chem. Soc* , 92 (1970) 220
374 C E Inturrisi, *Biochem. Biophys Acta,* 173 (1969) 567
375 C E Inturrisi, *Biochem Biophys Acta,* 178 (1969) 630
376 R.J.P. Williams, *Quart Rev , Chem Soc* , 24 (1970) 331
377 J S Britten and M. Blank, *Biochem. Biophys Acta* 159 (1968) 160
378 P J. Gehring and P B Hammond, *J Pharmacol Exp Ther* , 155 (1967) 187
379 J D Robinson, *Arch Biochem Biophys* , 139 (1970) 17
380 R W. Albers, *Ann. Rev Biochem* , 36 (1967) 727
380a C. Hegyvary and R L Post, *J. Biol Chem* , 246 (1971) 5234.
381 H Levine, M R Trindle and K Moldave, *Nature,* 211 (1966) 1302
382 P.J. Gehring and P B Hammond, *J Pharmacol Exp Ther* , 145 (1964) 215.
383 L.J. Mullins and R D Moore, *J Gen. Physiol* , 43 (1960) 759
384 I Rusznyak, L Gyorgy, S Ormai and T. Millner, *Experientia,* 24 (1968) 809
385 P H. Naslund and T Hultin, *Biochim Biophys Acta,* 204 (1970) 237
386 N R. Sundararajan and R McL Whitney, *J Dairy Sci* , 52 (1969) 1445
387 M M Herman and K G Bensch, *Toxicol Appl Pharmacol* , 10 (1967) 199
388 R Lallier, *C R Acad Sci , Ser. D,* 267 (1968) 962.
389 R Lallier, *C R Soc Biol* , 163 (1969) 598
390 A K. Dey and B.K Agarwal, *Lett. Nuovo Cimento Soc Ital Fis* , (2) 1 (1971) 803
391 E. Montignie, *Bull Soc. Chim Fr* , 4 (1937) 295
392 H Puff, H Spender and H. Gotta, *Naturwissenschaften,* 53 (1966) 405
393 O Olofsson and J. Gullman, *Acta Chem Scand* , 25 (1971) 1327
394 D. Cohen, *J Gen Physiol* , 45 (1962) 959
395 G G.J. Bange and F. Van Iren, *Acta Bot Neer* , 19 (1970) 646
396 E F Riebling, *J Chem Phys.,* 55 (1971) 3921.
397 R Freeman, R.P H Gasser and R.E Richards, *Mol Phys* , 2 (1959) 301
398 G Steffen and K Sommermeyer, *Biophysik,* 5 (1968) 192.