Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

COORDINATION COMPLEXES OF THE THALLIUM(III) HALIDES AND THEIR BEHAVIOR IN NON-AQUEOUS MEDIA

R. A. WALTON*

Department of Chemistry, Purdue University, Lafayette, Indiana 47907 (U.S.A.)

(Received January 29th, 1970)

CONTENTS

ABBREVIATIONS

py	pyridine	dipyam	di-2-pyridylamine
γ-pic	γ-picoline	ampic	2-aminomethylpyridine
pyz	pyrazine	pyH	pyridinium
quin	quinoline	quinH	quinolinium
bipy	2,2′-bipyridyl	en	ethylenediamine
3,3′-bipy	3,3′-bipyridyl	DMTEA	*N,N′*-dimethyl-(triethylenediamine)
4,4′-bipy	4,4′-bipyridyl	DMSO	dimethylsulphoxide
phen	1,10-phenanthroline	TBP	tri-*n*-butylphosphate
4,7-phen	4,7-phenanthroline		

---

* The author gratefully acknowledges financial support from the Advanced Research Projects Agency through the Purdue University Materials Science Council.

A. INTRODUCTION

Thallium is a classic example of a heavy post-transition group element for which two oxidation states are commonly encountered. The thallic ion (Tl^{3+}) has an electronic configuration terminating $5d^{10}$, while for the thallous ion (Tl^{+}) it is $5d^{10}6s^{2}$. The stability of compounds containing the latter oxidation state (*i.e.* two units below the group oxidation state) was for many years attributed to the so-called "inert-pair" effect, associated with the presumed inertness of the s^2 electron pair. Indeed the standard electrode potentials for the reactions

$$Tl(s) = Tl^{3+}(aq.)+3e(-0.72V)$$

and

$$Tl^{3+}+2e = Tl^{+}(+1.25V)$$

point to the great stability of Tl^{I} over Tl^{III}. However, the marked similarity of the second and third ionization potentials of gallium, indium and thallium give no clue as to the reasons for this trend, since for gallium and indium the higher oxidation state is generally the more stable.

In 1958, Drago pointed out[1] that a decrease in the mean thermochemical bond energies of the Group III trichlorides in the order Ga > In > Tl, could explain the decrease in the stability of this oxidation state as the group is descended. A similar decrease in covalent bond strength is likely for other derivatives of these elements. Thus in spite of the rather forbidding electrode potential data, thallium(III) has an extensive chemistry in both aqueous and non-aqueous media, and in this review we shall consider the stability, reactivity and structure of coordination complexes derived from the thallium(III) halides. These aspects are representative of the interest generally associated with the Lewis acid behavior of the post-transition elements.

It is appropriate for us first to briefly consider some general aspects of thallium chemistry, associated with the stability of its various oxidation states. One of the most commonly encountered classes of thallium compounds is that containing the thallous ion ($r = 1.44$ Å) as in the complex salts Tl_2MoCl_6[2] and Tl_2TiCl_6[3], which have the K_2PtCl_6 structure. The thallous ion chemically resembles the silver(I) and alkali metal ions. This is rather nicely illustrated by the photosensitivity of the thallous halides. Relatively few coordination complexes of thallium(I) are known, although the complex halides $TlX_n^{(n-1)-}$ are among the more important.

The 2+ oxidation state is rare, although it has been postulated as an intermediate in redox reactions involving thallium(III). A Tl^{II} species has also been detected at a dropping mercury electrode when 0.1M potassium nitrate solutions of the complex Tlbipy $(NO_3)_2$ were reduced[5] at low thallium concentrations and pH greater than 5. Very recently Eachus *et al.*[6] have presented ESR evidence that Tl^{2+} is formed by γ-radiation of rigid solutions containing Tl^{3+}. Although phases can be prepared which analyse for the dihalides, these materials are diamagnetic and almost certainly have the ionic structure $Tl^{I}[Tl^{III}X_4]$ (see section C, i). Indeed, simple lattice energy calculations on "$TlCl_2$", show that the authentic dichloride would be unstable with respect to disproportionation[7].

In its highest common oxidation state, thallium forms a variety of compounds other than simple binary halides *etc.*, which are characteristic of the similarities it shows with the other Group III elements, aluminum, gallium and indium. Thus the hydrides $TlCl(AlH_4)_2$[8], $LiTlH_4$[9] and TlH_3[10] are known, and there is an extensive chemistry of organothallium(III) species, especially for alkyl derivatives of the types $RTlX_2$, R_2TlX and R_3Tl*. The latter compounds will not be considered further since two articles have recently been published[11,12], which survey in detail the chemistry of organothallium compounds, including the organothallium halides.

Although in this review we will be principally concerned with coordination complexes of the thallium(III) halides in which the TlX_3 moiety remains intact, it should be remembered that the thallium(III) halides are often convenient starting materials for the preparation of other derivatives of thallium containing no Tl–X bonds. Thus the complex with quinaldic acid $(C_{10}H_6O_2)_3Tl$[13], the tris(diethyldiselenocarbamate) $[(C_2H_5)_2NCSe_2]_3Tl$[14], and $[(CO)_4Co]_3Tl$[15], containing three Co–Tl bonds, are examples of compounds which can be prepared directly from thallium(III) chloride.

Thallium(III) derivatives are also important oxidizing agents for a variety of transition metal ions, and kinetic studies have been carried out on many such systems, including Fe^{II}–Tl^{III} (Refs. 5, 16), Os^{II}–Tl^{III} (Ref. 17), Ru^{II}–Tl^{III} (Ref. 18) and V^{III}–Tl^{III} (Ref. 19). Other thallium(III) compounds, particularly the acetate, are useful reagents in organic chemistry. Thus oxythallation (like oxymercuration) is an important route for the oxidation of olefins such as cyclohexene[20] and norbornadiene[21].

As will be apparent in the following sections, few crystallographic studies have been carried out on coordination compounds of thallium(III), and as far as derivatives of the trihalides are concerned, these have been restricted to the complex halides. The situation is better for alkyl derivatives of thallium(III), where the structural studies on diethyl(salicylaldehydato) thallium(III)[22] and dimethyl-1,10-phenanthroline thallium(III) perchlorate[23] are particularly interesting.

Two articles have recently appeared in this journal which are very relevant to the present review. Firstly, Marcus[24] has reviewed the metal halide complexes (including those of thallium) formed in ion-exchange and solvent-extraction processes, so that these aspects will not be considered here. Also, Carty[25] has made a comparative survey of the vibrational spectra of coordination complexes of

---

* The first cyclopentadienyl derivative of thallium(III) has recently been prepared. Cyclopentadienyldimethylthallium results from the direct reaction of trimethylthallium with cyclopentadiene at room temperature (see A. G. LEE AND G. M. SHELDRICK, *Chem. Commun.*, (1969) 441).

gallium, indium and thallium which is particularly relevant to some of the complexes considered in the present review.

B. THE THALLIUM(III) HALIDES

Of the Group III trihalides, only thallium(III) iodide is unknown. The phase which analyses as the triiodide[26–29], is in reality thallous triiodide $Tl^+I_3^-$ in the solid state[30]; it is isomorphous with the analogous ammonium and caesium salts. Sharpe[28] has rationalized the failure of iodine to oxidize thallous iodide (in a solvent such as methanol)[26] on the basis of the disparity of the thallous-thallic and iodide–iodine standard potentials (−1.23V and −0.53V, respectively). Many years ago Berry *et al.*[26] studied the electronic absorption spectrum of the TlI_3 phase in methanol and concluded that the I_3^- ion is not present in solution; this is of interest in view of the solid state structure. A phase of composition Tl_3I_4 has often been isolated[27–29], but is of unknown structure.

During their studies of the iodination of thallous iodide in dioxan solution, Kul'ba and Mironov[29] isolated a crystalline material $TlI_3 \cdot C_4H_8O_2$ which readily lost iodine in air; the related potassium salt $KI_3 \cdot C_4H_8O_2$ was also isolated. These materials presumably contain weakly held "lattice" dioxan and $TlI_3 \cdot C_4H_8O_2$ is most likely not a coordination complex of thallium(III) iodide (see section D).

Thallium(III) fluoride is prepared by the fluorination of the oxide Tl_2O_3[31,32]; it is immediately decomposed by cold water. Its crystal structure has recently been deduced from powder measurements[33] and it is isomorphous with β-BiF_3.

Several methods are available for the preparation of *anhydrous* thallium(III) chloride. Either the hydrate $TlCl_3 \cdot 4H_2O$[34] may be dehydrated using thionyl chloride or carbonyl chloride[35], or the nitrosyl chloride complex $TlCl_3 \cdot NOCl$[36] can be thermally decomposed under mild conditions to give the trichloride[37]. Alternatively, thallium(III) chloride and bromide can be prepared *in situ* by the halogen oxidation of thallous halide suspended in acetonitrile[38,39]. The resulting trihalides dissolve in acetonitrile, presumably with complex formation[40]. Thallium(III) chloride, like indium(III) and yttrium(III) chlorides, is iso-structural[41] with aluminum(III) chloride and therefore has an ionic layer lattice. No definite structural data appears to be available for the tribromide, although NQR data[42] may be consistent with a related structure. It is interesting to note that whereas gallium(III) chloride, bromide and iodide[43–45] and indium(III) iodide[44–46] have the dimeric Al_2Br_6 type structure, indium(III) bromide[47] might also have a polymeric layer lattice like that of the trichloride.

A series of mixed halide–thiocyanate and –azide derivatives of thallium(III) have been reported[48]. These are of the type TlX_2Y, and are prepared by the halogenation of thallous thiocyanate and azide; they include $TlBr_2(SCN) \cdot 3H_2O$, $TlI_2(SCN)$, and $TlX_2(N_3)$ (X = Cl, Br or I).

Although the oxyhalides TlOCl and TlOBr are known[49] they are the least well characterized of the Group III oxyhalides[50]. Prolonged treatment of thallous chloride with chlorine oxide leads to the formation of some TlOCl and the ozone oxidation of thallous bromide gives TlOBr[50].

C. COMPLEX HALIDES OF THALLIUM(III)

Many of the studies on complex halides of thallium(III) have concerned the stability of species of the type $TlX_n^{(n-3)-}$, where X = Cl, Br or I, and $n = 1$, 2, 3 or 4, in aqueous media[51–58]. It is found that the stability of the TlX_4^- anions lies in the order $I^- > Br^- > Cl^- > F^-$ (Ref. 52), and in this respect thallium(III) behaves as a class (b) acceptor[59]. The behavior of such species in aqueous media will not be considered further except to note that Spiro[60] has carried out a detailed study of the Raman spectra of thallium(III) chloride complexes in aqueous solution, and has confirmed the existence of $TlCl^{2+}$, $TlCl_2^+$, $TlCl_3$ and $TlCl_4^-$ in this medium.

(i) Tetrahalothallate(III) anions

These are the most commonly encountered complex anions of thallium(III), and are readily formed in aqueous and non-aqueous media from the reaction of the appropriate trihalide or other derivative (*e.g.* the perchlorate $Tl(ClO_4)_3$) with the requisite amount of halide ion. Although thallium(III) iodide does not exist, treatment of other thallium(III) species with a four-fold or greater excess of iodide results in the formation of TlI_4^-.

Although tetrafluorothallates(III), such as $NaTlF_4$ and $LiTlF_4$ are known[61] they do not contain the mononuclear TlF_4^- anions but rather have the CaF_2 type structure.

The most useful general method for the preparation of salts of the $TlCl_4^-$ and $TlBr_4^-$ ions stabilized by organic cations, is that used by Cotton *et al.*[38] in which acetonitrile solutions of the trihalides are treated with an equivalent quantity of the appropriate substituted ammonium or arsonium halide (*e.g.* Me_4N^+, Et_4N^+, Bu_4N^+, Ph_4As^+). The corresponding iodides can be prepared by halide exchange reactions using sodium iodide. An alternative route involves the treatment of a solution of the trihalide in hydrohalic acid with the appropriate organic or metal halide. By this means salts such as (pyH) $TlCl_4$[62] and (quinH) TlX_4[63] have been prepared. Krause and Grosse[64] found that the oxidation of the thallous halides by halogen in the presence of pyridine and an alkyl halide RX (R = Me, Et, Pr or Bu) proceeded with the formation of the alkylpyridinium salts $(C_5H_5NR)TlX_4$.

When aqueous solutions containing the thallous and thallic halides (chloride or bromide) are cooled, the "dihalides" Tl_2X_4 may crystallize[65]. Tl_2X_4 is also prepared by passing chlorine gas over molten thallous chloride, and Tl_2Br_4 from the reaction of thallous bromide with an excess of liquid bromine in a sealed tube at 100° [66]. That these halides have the structure $Tl^I[Tl^{III}X_4]$, containing the tetrahedral TlX_4^- anions is based upon the following evidence. Tl_2Br_4 is iso-structural[67] with Ga_2Cl_4, which is $Ga^I[Ga^{III}Cl_4]$[68]. The thallium nuclear magnetic resonance spectra of molten Tl_2X_4[66] leaves little doubt that both the Tl^I and Tl^{III} states are present. Thallium occurs with two isotopes of mass numbers 203 and 205, each of which has a relatively large magnetic moment and spin of 1/2. The Tl^{205} resonances of molten Tl_2X_4 reveals two peaks, consistent with the presence of Tl^+ and TlX_4^- in the molten state. Finally, Spiro[69] has found that the low frequency vibrational spectrum of Tl_2Br_4 is very similar to that of other derivatives containing the tetrahedral $TlBr_4^-$ anion*.

With the exception of $Tl[TlBr_4]$ there is little direct crystallographic evidence for the structures of the salts so far discussed. Cotton *et al.*[38] have established that $(Ph_4As)TlCl_4$ is isomorphous with the corresponding iron(III) salt[70], and it thus presumably contains the tetrahedral $TlCl_4^-$ anion. Also $(Bu_4N)TlX_4$ ($X = Cl$ or Br) are isomorphous[38] although no single crystal structural data are available. Very recently, a full 3-dimensional X-ray analysis of the pyridine solvate $(pyH)TlI_4 \cdot py$ has been completed[71]. The TlI_4^- anion is a slightly distorted tetrahedron with Tl–I distances ranging from 2.734 to 2.774 Å (with standard deviations of 0.002 Å) and I–Tl–I angles between 106.4° and 112.7°. This complex is prepared from the reaction of the chloro derivative $TlCl_3 \cdot 2py$ (see section D) with sodium iodide in aqueous acetone[71], or by treating an acetonitrile solution of thallium(III) chloride[38,39] with pyridine and an excess of hydroiodic acid[71]. The material which was prepared many years ago by Berry *et al.*[26] and formulated as "$(C_5H_5N)_2HTlI_4$", is almost certainly this same complex.

The most convincing evidence that all those salts so far discussed contain the *tetrahedral* TlX_4^- anions, is provided by the low frequency vibrational spectra of these species[39,69,72–78]. As indicated in Table I, those tetrahalothallates(III) stabilized by thallous and organic cations show vibrational frequencies characteristic of a tetrahedral species[79] and the requisite Raman–IR coincidences, thus ruling out the alternative centrosymmetric square-planar stereochemistry. There remains some doubt in the assignment of either or both of the low frequency bending modes ν_2 and ν_4 for several of the salts listed in Table I, although there is no doubt as to the assignments of the stretching modes ν_1 and ν_3. The usual frequency order $\nu_3 > \nu_1$[79] holds for $TlBr_4^-$ and TlI_4^- but the reverse order is found for all salts containing the $TlCl_4^-$ anion**. For a comparison of the vibra-

---

* Here it may be noted that the vibrational spectra of molten $InCl_2$ is consistent with the structure $In^I[In^{III}Cl_4]$ (see J. H. R. CLARKE AND R. E. HESTER, *Inorg. Chem.*, 8 (1969) 1113 and F. J. J. BRINKMANN AND H. GERDING, *Rec. Trav. Chim. Pays-Bas*, 88 (1969) 275).

** For comparison it is interesting to see that $(Et_4N)InCl_4$, which is known to contain the tetrahedral $InCl_4^-$ anion (J. TROTTER, F. W. B. EINSTEIN AND D. G. TUCK, *Acta Cryst.*, B25 (1969) 603) has $\nu_1 = 318.5$ cm^{-1} and $\nu_3 = 330$ cm^{-1} (F. J. J. BRINKMANN AND H. GERDING, *Rec. Trav. Chim. Pays-Bas*, 88 (1969) 275).

TABLE 1

VIBRATIONAL FREQUENCIES OF THE TETRAHEDRAL TlX_4^- ANIONS (cm^{-1})[a]

Complex	Medium		Assignment					
			$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$	Lattice	Ref.
$[Me_4N]TlCl_4$	Solid	R	312		294			72
	N.M.	IR			302	115 98		75
$[Et_4N]TlCl_4$	Solid	R	312		290			75
	CH_3CN	R	307(p)		295(dp)			77
	N.M.	IR			293	110 93		75
	N.M.	IR			(295) 285	108		73
	Polythene disc	IR			(315) 297	115 (95)	50	77
$[Ph_4As]TlCl_4$	Solid	R	312	60[b]	296	78[b]		72
	N.M.	IR	(306)		296 (278)	88		69
	N.M.	IR			306 292	107 93		75
$[Me_4N]TlBr_4$	N.M.	IR			(207) 199 (186)	102		75
	N.M.	IR			195			76
$[Et_4N]TlBr_4$[c]	Solid	R	192		183			75
	Solid	R	186		196	86		73
	CH_3CN	R	186(p)		203(dp)			77
	N.M.	IR			185 173	78		75
	N.M.	IR			200			73
$[Ph_4As]TlBr_4$	N.M.	IR			196			75
$TlTlBr_4$	Solid	R	182	56	198	74	84, 34	69
	N.M.	IR	(186)		200	~72		69
$CsTlBr_4$	Solid	R	184	58	201	69		69
	N.M.	IR	(186)		205	~74		69
$RbTlBr_4 \cdot H_2O$	Solid	R	180	59	193	59		69
	N.M.	IR	(186)		200	~64		69
$KTlBr_4$	Solid	R	182	58	196	58		69
	N.M.	IR			203	~53		69
$[Et_4N]TlI_4$	Solid	R	130		149			75
	Solid	R	130		154			73
	N.M.	IR			146	60		75
	N.M.	IR			152	72		73
$[Bu_4N]TlI_4$	Solid	R	133		156			69
	N.M.	IR			152	~56		69
$[pyH]TlI_4 \cdot py$	Solid	R	127		(153) 148			71
	N.M.	IR			(152) 147			71
$[Ph_4As]TlI_4$	N.M.	IR			148	~56		75

---

[a] N.M. = Nujol mull; IR = infrared and R = Raman; p = polarized and dp = depolarized.
[b] Adams and Morris (Ref. 75) disagree with these assignments. [c] Note that the assignments of Walton (Ref. 73) and Davies and Long (Ref. 77) differ from those of Adams and Morris (Ref. 75). The latter give $\nu_1 > \nu_3$, whereas in Refs. 73 and 77, $\nu_3 > \nu_1$ which is supported by polarization measurements and is therefore the favored assignment.

tional frequencies of the GaX_4^-, InX_4^- and TlX_4^- anions, reference is made to the recent review by Carty[25].

Vibrational spectroscopy has also proved useful in studying the extraction of the acids $HTlX_4$ (X = Cl or Br) into diisopropyl ether[76], and the nature of the systems TlX_3–LiX in ethanol or water, and TlX_3–HX(aq.) (X = Cl or Br)[77]. Vibrational frequencies characteristic of the TlX_4^- ions were observed for these systems.

In contrast to the complexes so far considered, the alkali metal salts of the $TlBr_4^-$ and TlI_4^- ions present a rather more confusing picture. Ammonium, potassium, rubidium and caesium tetrabromothallates(III) have been prepared by crystallizing aqueous solutions of thallium(III) bromide and the required bromide salt[62,80]; these derivatives may be obtained anhydrous or as mono- or di-hydrates. Watanabe *et al.*[81–83] have briefly reported results of their crystallographic studies on several of these salts; $CsTlBr_4$ and $KTlBr_4 \cdot 2H_2O$ for instance, have been described as containing square-planar $TlBr_4^-$ anions. More recently, the tetraiodothallates(III) $RTlI_4 \cdot 2H_2O$ (R = NH_4, K, Rb or Cs) and $RTlI_4$ (R = NH_4 or K) have been investigated[84] and their X-ray powder patterns found to be very similar to those of $CsTlBr_4$ and $KTlBr_4 \cdot 2H_2O$ *etc.*, indicating isomorphism between these two sets of complexes. Iodine NQR spectra were interpreted accordingly. However, doubt has been cast upon the conclusions of Watanabe *et al.*[81–83] following the work of Spiro[69] who measured the vibrational spectra of $CsTlBr_4$, $RbTlBr_4 \cdot H_2O$ and $KTlBr_4$ (Table 1) and found that these complexes had vibrational spectra characteristic of tetrahedral $TlBr_4^-$. These observations coupled with the structural evidence for $Tl[TlBr_4]$[67] and $(pyH)TlI_4 \cdot py$[71], suggests that a detailed crystallographic investigation of the alkali metal salts would be desirable.

The reaction of nitrosyl chloride with thallium metal or thallous salts in a sealed tube at 100°, or with thallium(III) chloride at −20° affords the complex $TlCl_3 \cdot NOCl$[85]. Complete and rapid exchange of radiochlorine between thallium(III) chloride and liquid nitrosyl chloride is in agreement with the ionic structure $NO^+TlCl_4^-$ (Ref. 86); spectral studies have apparently confirmed this structure[87].

The 1:1 complex $TlCl_3$, PCl_5, first prepared by Groeneveld[88], probably has the ionic structure $PCl_4^+TlCl_4^-$, and would thus resemble structurally the related indium complex $PCl_4^+InCl_4^-$ (Refs. 87, 89).

The $TlCl_4^-$ anion, along with other tetrachlorometallate(III) anions has proved to be particularly useful in stabilizing cationic metal species of the type $M(CH_3CN)_x^{n+}$, such as $[Li(CH_3CN)_4]TlCl_4$, $[Sr(CH_3CN)_8](TlCl_4)_2$ and $[Ni(CH_3CN)_6](TlCl_4)_2$[90,91]. IR spectral studies suggest that the $TlCl_4^-$ ion retains its tetrahedral structure in these complexes.

The Lewis acid behavior or thallium(III) chloride and bromide is further illustrated by their reactions with the trityl halides[92] to form the moisture and air-sensitive derivatives $[(C_6H_5)_3C]TlX_4$; the corresponding iodide can be prepared by adding sodium iodide to an acetonitrile solution of the chloro complex.

The mixed tetrahalothallates(III) $(Et_4N)TlX_{4-n}Y_n$, where Y = Br or I when X = Cl, and Y = I when X = Br, can be isolated as crystalline solids by the reaction of stoichiometric quantities of thallium(III) chloride or $(Et_4N)TlBr_4$ with the appropriate teraethylammonium halide in acetonitrile, according to the eqns.[93]

$$TlCl_3 + nEt_4NX \rightarrow (Et_4N)TlCl_{4-n}X_n + (n-1)\ Et_4NCl$$

or

$$(Et_4N)TlBr_4 + n\ Et_4NI \rightarrow (Et_4N)TlBr_{4-n}I_n + n\ Et_4NBr$$

X-ray powder data[93] and vibrational spectral studies[73] confirm that these complexes are pure phases and not in reality *mixtures* of the component tetrahalothallates(III). IR and Raman spectra[73] are consistent with the species TlX_3Y^-

TABLE 2

VIBRATIONAL FREQUENCIES OF THE THALLIUM–HALOGEN STRETCHING MODES (in cm^{-1}) OF THE TlX_3Y^- AND $TlX_2Y_2^-$ ANIONS OF C_{3v} AND C_{2v} SYMMETRY, RESPECTIVELY[a]

Anion	*Medium*		*Approximate description of mode*			
			A_1(IR, R) *ν(Tl–Y)*		*A_1(IR, R)* *ν(Tl–X)*	*E(IR, R)* *ν_d(Tl–X)*
$TlCl_3Br^-$	N.M.	IR	204			292
	Solid	R	202		307	296
$TlCl_3I^-$	N.M.	IR	165 or 152			283
	Solid	R	164 or 151		302? 291	282
	CH_3CN	R	168 or 153		308? 302	288
$TlBr_3Cl^-$	N.M.	IR	290			200
	Solid	R	293		193 188	~200
TlI_3Cl^-	N.M.	IR	271		136	156
	Solid	R	276		130	152
TlI_3Br^-	N.M.	IR	186			158
	Solid	R	187		138 131	156
	CH_3CN	R	192		137	160
			B_2(IR, R) *ν(Tl–X)*	*A_1(IR, R)* *ν(Tl–X)*	*B_1(IR, R)* *ν(Tl–Y)*	*A_1(IR, R)* *ν(Tl–Y)*
$TlCl_2Br_2^-$	N.M.	IR	... 292	...	204	
	Solid	R	299	291	199	193
$TlCl_2I_2^-$	N.M.	IR	... 280	...	160	137
	Solid	R	290	280	163	140
	CH_3CN	R	... 286	...	165	142
$TlBr_2I_2^-$	N.M.	IR	196		161	144
	Solid	R	196	186	154	144 136
	CH_3CN	R	198	193	159	148 141

[a] N.M. = Nujol mull; IR = infrared and R = Raman.

and $TlX_2Y_2^-$ possessing C_{3v} and C_{2v} symmetries, respectively. Table 2 lists the frequencies of the Tl–X and Tl–Y stretching modes. Although Walton[73] has interpreted the Raman spectra of acetonitrile solutions of these complexes on the basis of the mixed tetrahalothallate(III) anions persisting in solution, Davies and Long[77] suggest from their studies of the solution spectra of $TlCl_3Br^-$ and $TlBr_3Cl^-$, that the solutions consist of mixtures of the $TlCl_4^-$ and $TlBr_4^-$ ions. However, that the latter possibility is unlikely is suggested by measurements of the solution electronic absorption spectra[93]. In all instances the spectra showed a close adherence to Beer's law behavior and the band positions and shapes confirmed that the solutions were not mixtures of the TlX_4^- components. The spectra of $TlCl_4^-$, $TlBr_4^-$ and TlI_4^- are shown in Fig. 1 and that of the $TlCl_3I^-$ ion in Fig. 2. The spectra of $TlBr_4^-$ and TlI_4^- are unchanged in the presence of excess Et_4NX but the 40.8 *kK* band of $TlCl_4^-$ shifts to 39.7 *kK* when a large excess of Et_4NCl is added, indicating the formation of a higher chlorospecies *e.g.* $TlCl_5^{2-}$ (Ref. 93).

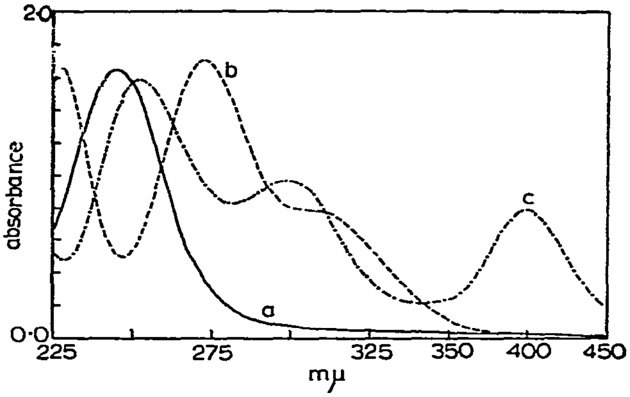

Fig. 1. Electronic absorption spectra of acetonitrile solutions of $(Et_4N)TlX_4$. (a) X = Cl (0.78×10^{-4} g.mol/l); (b) X = Br (0.98×10^{-4} g.mol/l); (c) X = I (6.48×10^{-5} g.mol/l).

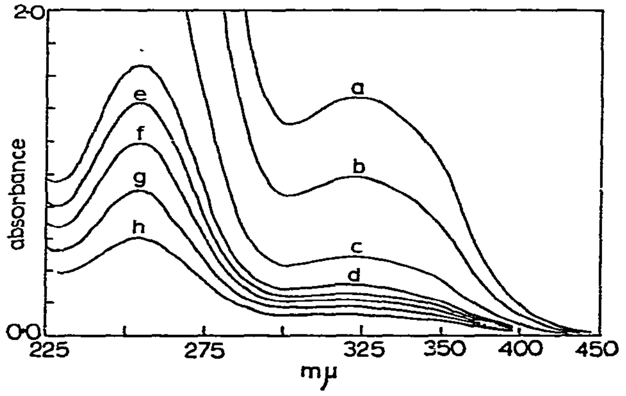

Fig. 2. Electronic absorption spectra of acetonitrile solutions of $(Et_4N)TlCl_3I$. Concentrations of the solutions (in g.mol/l) are as follows: (a) 4.44×10^{-4}; (b) 2.96×10^{-4}; (c) 1.48×10^{-4}; (d) 8.88×10^{-5}; (e) 7.4×10^{-5}; (f) 5.92×10^{-5}; (g) 4.44×10^{-5}; (h) 2.96×10^{-5}.

TlX_4^- are isoelectronic with HgX_4^{2-} and similar electronic absorption spectra are expected. The absorption bands of $TlCl_4^-$ (Fig. 1) are at lower energies than the corresponding absorptions of HgX_4^{2-} (Ref. 94), which is expected in view of the decrease in optical electronegativity[95] for Hg^{II} compared to Tl^{III}. The absorption bands also display the usual bathochromic shift and increase in complexity (owing to spin–orbit coupling effects)[96] characteristic of $X(\pi) \rightarrow M$ electron transfer transitions.

The complex $(Ph_4As)TlBr_2(N_3)_2$ has also been prepared[97,98] but no structural studies have been carried out. Organothallium(III) complex ions of the types $Ph_2TlX_2^-$ (X = Cl, Br or I) and $PhTlX_3^-$ (X = Cl, Br or I) have been stabilized as their Me_4N^+, Et_4N^+ or Ph_4As^+ salts by the direct reaction of Ph_2TlX or $PhTlX_2$ with the appropriate substituted ammonium or arsonium halide[99]. Their formulations were confirmed by vapor pressure measurements using osmometric techniques.

(ii) Pentahalothallate(III) anions

Hydrates such as $Cs_2TlCl_5 \cdot H_2O$[83], $K_2TlCl_5 \cdot 2H_2O$[64] and $SrTlCl_5 \cdot 3H_2O$ (Ref. 100) can be prepared from aqueous media. The caesium salt is isomorphous with $(NH_4)_2InCl_5 \cdot H_2O$ and $(NH_4)_2FeCl_5 \cdot H_2O$[83] and presumably contains the square-pyramidal $TlCl_5^{2-}$ anion, with a water molecule occupying the sixth octahedral position. More recently, anhydrous salts containing substituted ammonium cations have been prepared very easily from organic solvents such as acetonitrile, methylene chloride or methanol. Thus $(Me_4N)_2TlCl_5$[76,101], $(Et_4N)_2TlCl_5$[101] and $(DMTEA)TlX_5$ (X = Cl or Br)[101] have been isolated and $(Et_4N)_2TlCl_5$ shown to be isomorphous with $(Et_4N)_2InCl_5$[102]. The most striking feature of the indium complex is that it contains the square-pyramidal $InCl_5^{2-}$ anion, and is the first example of a non-transition element containing this geometry.

The Raman and IR spectra of $(Et_4N)_2MCl_5$ (M = In and Tl) are very similar[101] and for the thallium complex give a good fit with that expected for a square-pyramid. The highest frequency ν(Tl–Cl) mode (ν_1) of $(Et_4N)_2TlCl_5$ is located at 275 cm^{-1} (Ref. 101), about 35 cm^{-1} lower than the ν_1(Tl–Cl) stretching mode of $TlCl_4^-$. The symmetric Tl–Cl stretching modes of $Cs_2TlCl_5 \cdot H_2O$ and $K_2TlCl_5 \cdot 2H_2O$ are at 270 cm^{-1} (Ref. 72), close to that for $(Et_4N)_2TlCl_5$, which indicates that these hydrates contain the square-pyramidal $TlCl_5^{2-}$ anion. Nitromethane solutions of the complexes $(Et_4N)_2MCl_5$ have vibrational spectra very similar to those of the solid-state species although it seems likely that in solution pseudo-octahedral complexes MCl_5S^{2-} are formed[101]. There is also good evidence that significant dissociation to $TlCl_4^-$ occurs in nitromethane solutions of $TlCl_5^{2-}$. Vibrational spectra of the $DMTEA^{2+}$ salts of the $TlCl_5^{2-}$ and $TlBr_5^{2-}$ ions indicate that the latter are highly distorted as a result of crystal packing effects.

Faraglia *et al.*[99] have prepared the complex salts $R_2[Me_2TlX_3]$, where

R = Bu_4N^+ or Ph_4As^+ and X = Cl, Br or I, by a similar procedure to that described already for $Ph_2TlX_2^-$ and $PhTlX_3^-$ (see section C, i). Little is known about the geometry of these anions and a study of their vibrational spectra would be of particular interest.

(iii) Hexahalothallate(III) anions

Fluorocomplexes such as K_3TlF_6[103], Rb_3TlF_6[103] and Cs_2KTlF_6[104] are known and are generally prepared in the fluorination of a mixture of the appropriate alkali metal chloride and thallous chloride.

The most important complex containing the $TlCl_6^{3-}$ ion is orange-red $[Co(NH_3)_6]TlCl_6$, which can be precipitated quantitatively by adding a 2M HCl solution of thallium(III) chloride or an aqueous solution of $K_3TlCl_6 \cdot 2H_2O$ (see later) to one of $Co(NH_3)_6Cl_3$[105]. Wanatabe *et al.*[82] determined its crystal structure and found it to contain octahedral $Co(NH_3)_6^{3+}$ and $TlCl_6^{3-}$ (Tl–Cl = 2.48 Å) in the cubic NaCl arrangement (a = 11.40 Å). The reddish-brown bromide may be prepared similarly[82] and has Tl–Br = 2.58 Å. The vibrational frequencies of the $TlCl_6^{3-}$ anion in this complex have recently been determined by Barrowcliffe *et al.*[106] and are given in Table 3. From a comparison with related data for $TlCl_5^{2-}$ and $TlCl_4^-$ it is seen that the symmetric Tl–Cl stretching frequency decreases in the order $TlCl_4^- > TlCl_5^{2-} > TlCl_6^{3-}$.

TABLE 3

VIBRATIONAL FREQUENCIES OF THE TlX_6^{3-} ANIONS (X = Cl OR Br) in cm^{-1}

$Co(NH_3)_6TlCl_6$	*"$K_3TlCl_6 \cdot 2H_2O$"*	*$Rb_3TlBr_6 \cdot 8/7H_2O$*	*Symmetry*	*Activity*
264	280	161	ν_1 a_{1g}	R
192	262	153	ν_2 e_g	R
230	294	190, (195)[a]	ν_3 f_{1u}	IR
146	246, 222	156, 134	ν_4 f_{1u}	IR
135	155	95	ν_5 f_{2g}	R

[a] Shoulder.

Alkali metal salts such as $K_3TlCl_6 \cdot 2H_2O$[107], $Cs_3TlCl_6 \cdot H_2O$[108] and $Rb_3TlBr_6 \cdot 8/7H_2O$[80,107] crystallize from aqueous media. Hoard and Goldstein[107] carried out an early crystallographic investigation on the above potassium and rubidium salts, and concluded that they contained the octahedral TlX_6^{3-} anions. On the basis of these results, Spiro[69,72] interpreted the low frequency vibrational spectra of these two complexes (Table 3). Band splittings were attributed to the lowered site symmetry, C_i, of the complexes in the crystalline state. It can be seen from Table 3, that the spectral data for the complexes $[Co(NH_3)_6]TlCl_6$ and $K_3TlCl_6 \cdot 2H_2O$ are not in good agreement, and Barrowcliffe *et al.*[106] have suggested that the earlier assignments[75] of the Raman bands of $TlCl_6^{3-}$ was erroneous. They also suggested that the X-ray structure determination of

Hoard and Goldstein[107] was probably in error and that the material they investigated did not contain the $TlCl_6^{3-}$ anion.

The halides Tl_2X_3 ($X = Cl$ or Br) are prepared by crystallizing mixed aqueous solutions of the appropriate thallous and thallic halides[62,109–111]. Other preparative routes are available, including the reaction of thallium metal or Tl_2O_3 with sulphur monochloride[112]. The thallium nuclear resonance spectrum of Tl_2Cl_3 is such that the chemical shifts and band intensities are consistent with the structure Tl_3TlCl_6. There seems little doubt that this is indeed the correct structure. The related indium chloride solid state phase In_2Cl_3, has a vibrational spectrum consistent with the structure In_3InCl_6[87,114,115] although this is not true for the molten state[115].

The complex $Cs_3Tl_2Cl_9$[108,116–118] is a classic example of a compound containing the dinuclear $M_2X_9^{3-}$ species. It is a component of the $TlCl_3$–CsCl–H_2O phase[108] and is readily isolated in the solid state[116–118]. Its crystal structure is known[117,118], and the $Tl_2Cl_9^{3-}$ anion consists of two octahedra fused at a face. Unfortunately, the crystals are extensively twinned, but in spite of this a vibrational analysis has been carried out with the aid of oriented single-crystal Raman measurements[119].

D. COMPLEXES OF THE THALLIUM(III) HALIDES WITH DONOR MOLECULES OF GROUPS V B AND VI B

(i) Nitrogen donors

Complexes of the thallium(III) halides with pyridine, the bipyridyls and the phenanthrolines have been extensively studied for many years. Aspects of their stability and structure will comprise the principal content of this section. However, we shall first briefly consider the Lewis acid behavior of thallium(III) chloride towards phosphorus, arsenic and antimony donor molecules.

The reaction of thallium(III) chloride with triphenylphosphine in diethyl ether[120] or acetonitrile[121], results in reduction to thallous chloride and the recovery of unchanged triphenylphosphine (unstable Ph_3PCi_2 may be a reaction intermediate)[120]. Triphenylarsine[120,121] and tri-*p*-xylyl-arsine[122] and -stibine[122] react similarly, although the ligand oxidation products are stable and can now be isolated. Thus the reaction of thallium(III) chloride with triphenylarsine in the cold affords trace amounts of $PhAsCl_2$, whereas for higher reaction temperatures both Ph_2TlCl and Ph_3AsCl_2 can be isolated in addition to the bulk thallous chloride[120]. This behavior contrasts with the stability of indium(III) and gallium(III) halide complexes of phosphines[123–126], and reflects the decreased stability of the higher oxidation state as the group is descended.

The ammine $TlCl_3 \cdot 3NH_3$ which is prepared by the action of dry gaseous ammonia under pressure on an ether solution of the trichloride[127], decomposes at

170° to a lower ammine and to thallium(I) species at higher temperatures. Thallium(III) iodide is described as forming a *white* ammine of stoichiometry $TlI_3 \cdot 3NH_3$[128]. However, the color of this material and the proposed structure $[Tl(NH_3)_6]TlI_6$[128], are incompatible with the properties of other coordination compounds of this halide with nitrogen donors (see later), and it seems almost certain that this is not such a derivative.

In 1928, Hieber and Sonnekalb[129] described the results of their studies on the thallium(III) chloride–aqueous ethylenediamine systems, from which they isolated products analysing for $TlCl_3 \cdot en \cdot H_2O$, $TlCl_3 \cdot 2en \cdot H_2O$ and $TlCl_3 \cdot 3en \cdot 3H_2O$. Double decomposition of these complexes with potassium bromide or iodide in aqueous alcohol, afforded the derivatives $TlBr_3 \cdot en \cdot H_2O$, $TlBr_3 \cdot 2en$ and $TlI_3 \cdot en$. These workers proposed[129] that the bronze colored $TlI_3 \cdot en$ was monomeric on the basis of a molecular weight measurement in nitrobenzene, but more recent work by Sutton[130], who measured the conductivities of nitrobenzene solutions of $TlBr_3 \cdot en$ and $TlI_3 \cdot en$, led to the suggestion that these two complexes had the ionic structure $(Tl(en)_2X_2)TlX_4$.

The anhydrous derivatives of stoichiometry $TlCl_3 \cdot 3en$ and $TlCl_3 \cdot 2en$ precipitate when stoichiometric quantities of reagents are mixed in absolute methanol[127]. At 153° the 1:3 complex decomposed to $TlCl_3 \cdot 2en$; the thermal stability of the tris(ethylenediamine) complexes of the Group III trichlorides decreases in the order Ga $>$ In $>$ Tl[127]. Addition of an excess of ethylenediamine to acetonitrile solutions of $TlCl_3$, or $TlBr_3$ affords $TlX_3 \cdot 3en$[74]. Since no Tl–Cl stretching frequency was located above 222 cm^{-1} in the low-frequency IR spectrum of $TlCl_3 \cdot 3en$, it was suggested[74] that $TlX_3 \cdot 3en$ have the expected ionic structure $[Tl(en)_3]^{3+}3X^-$. A study of the vibrational frequencies of the coordinated ethylenediamine molecules in $TlX_3 \cdot 3en$ ($X = Cl$, Br or I) apparently confirms[131] these conclusions, but for $TlX_3 \cdot en$ and $TlX_3 \cdot 2en$ ($X = Cl$, Br or I), the relative simplicity of the IR spectra[131] was interpreted in terms of the bridging *trans*-ligand conformation; the 1:1 and 1:2 complexes were therefore considered to be polymers[137]. Thus the structures of $TlX_3 \cdot en$ ($X = Br$ or I) in the solid state may be different from those inferred by Hieber and Sonnekalb[129] and by Sutton[130] from their solution studies.

Electronic absorption spectral measurements on absolute methanol solutions of the 1:1, 1:2 and 1:3 ethylenediamine complexes by Kul'ba *et al.*[132], have not solved the problem of the nature of the solution species. These spectra were compared with those for the salts $LiTlCl_4$, $LiTlBr_4$ and $KTlI_4$*, and while there was good evidence that the TlX_4^- ions were present in solutions of $TlCl_3 \cdot en$ and $TlBr_3 \cdot en$, further conclusions are unjustified until more detailed studies are forthcoming. It seems likely that solution studies are complicated by the presence of competing equilibria in which several thallium halide species are involved.

---

* These spectra were in good agreement with those recorded for acetonitrile solutions of $(Et_4N)TlX_4$ (see Fig. 1).

Before we consider the thallium(III) halide complexes of the bipyridyls and phenanthrolines *etc.*, it is pertinent to mention that a variety of complexes of thallium(III) nitrate and perchlorate with these nitrogen donors are known. From the direct reaction of methanol solutions of the nitrate with 2,2′-bipyridyl, 3,3′-bipyridyl or 1,10-phenanthroline, the complexes $[Tl(bipy)_n](NO_3)_3$, where $n = 2$ or 3[133], $Tl(NO_3)_3 \cdot$ 3,3′-bipy[134], $[Tl(bipy)(phen)](NO_3)_3$[128], $[Tl(phen)_n](NO_3)_3$, where $n = 2$ or 3[135], and $Tl(NO_3)_3 \cdot$ 4,7-phen[136] have been prepared. Replacement reactions with sodium perchlorate, have been used to prepare the related perchlorate derivatives, such as $[Tl(bipy)_n](ClO_4)_3$, where $n = 2$ or 3[133,137], $[Tl(bipy)_2](NO_3)_2(ClO_4)$[137], $[Tl(bipy)(phen)](ClO_4)_3$[128], and $[Tl(phen)_n](ClO_4)_3$, where $n = 2$ or 3[135]. Conductivity measurements on aqueous[133,135] and nitrobenzene[137] solutions of several of these complexes are in keeping with the above formulations if we assume the presence of *ionic* nitrate and perchlorate groups. However, Farver and Nord[137] find good infrared evidence that in the *solid state*, the complexes $[Tl(bipy)_2]Y_3$, where $Y = NO_3$ or ClO_4, contain ionic *and* covalent nitrate and perchlorate groups, and that $[Tl(bipy)_2](NO_3)_2(ClO_4)$ contains coordinated nitrate groups (*i.e.* presumably six coordinate $[Tl(bipy)_2(NO_3)_2]^+$) and an ionic perchlorate. Finally, X-ray powder measurements show that $[Tl(bipy)(phen)](NO_3)_3$ is not in reality a mixture of the *bis*-bipyridyl and phenanthroline derivatives[128].

Many of the above nitrate complexes are useful intermediates in the synthesis of trihalide derivatives of these nitrogen bases. In addition, several react with ethylenediamine to form complexes such as $[Tl(en)_2(phen)](NO_3)_3$ and $[Tl(en)_3](NO_3)_3$[138].

The 2,2′,2″-terpyridyl, bipyridyl, phenanthroline, quinoline, pyridine and pyrazine complexes of the thallium(III) halides which have been prepared and whose existence are reasonably well documented are listed in Table 4, together with some related derivatives. Several methods have been used for their preparation and include the following:

(*A*) addition of the tertiary amine to an acetonitrile solution of thallium(III) chloride or bromide; the latter is prepared by the halogen oxidation of a suspension of the thallous halide;

(*B*) mixing the reagents in water, methanol, ethanol or ether. Using this procedure, the hydrate $TlX_3 \cdot 4H_2O$ can often be used instead of the anhydrous trihalide;

(*C*) reaction of a related nitrate complex (see preceeding section) with an appropriate alkali metal halide;

(*D*) halide exchange, which involves the treatment of a chloride complex with a solution of an alkali metal bromide or iodide*.

---

* It was originally believed[121] that the complex $TlI_3 \cdot$ py was formed when the chlorocomplex $TlCl_3 \cdot$ 2py reacts with aqueous acetone solutions of sodium iodide. It has subsequently been shown[71] that this sample of "$TlI_3 \cdot$ py" was in fact the pyridine solvate $(pyH)TlI_4 \cdot$ py.

TABLE 4

COMPLEXES OF THE THALLIUM(III) HALIDES WITH TERTIARY AMINE DONOR MOLECULES

Complex	*Usual method of preparation*	*References*	*Complex*	*Usual method of preparation*	*References*
$\mathrm{TlCl_3 \cdot bipy}$	A, B	39, 74, 121, 130, 133, 139	$\mathrm{TlBr_3 \cdot 2phen}$	C	135,
$\mathrm{TlCl_3 \cdot 2bipy}$	C	133	$\mathrm{TlBr_3 \cdot 3phen}$	C	135
$\mathrm{[Tl(bipy)_2Cl_2]NO_3}$	C	135	$\mathrm{TlI_3 \cdot phen}$	C, D	121, 130, 135, 142
$\mathrm{TlBr_3 \cdot bipy}$	A, B, C	39, 74, 121, 130, 133, 139	$\mathrm{TlI_3 \cdot 2phen}$	C, D	130, 142
$\mathrm{TlBr_3 \cdot 2bipy}$	A, B, C	133	$\mathrm{TlX_3 \cdot 4,7\text{-}phen}$ ($X = Cl$ or Br)	B	136
$\mathrm{TlI_3 \cdot bipy}$	C, D	121, 130, 133	$\mathrm{TlI_3 \cdot 4,7\text{-}phen}$	[a]	136
$\mathrm{TlI_3 \cdot 2bipy}$	D	130	$\mathrm{TlI_3 \cdot 2(4,7\text{-}phen)}$	[a]	136
$\mathrm{[Tl(bipy)(phen)X_2]\text{-}(NO_3)}$ ($X = Cl$ or Br)	C	128	$\mathrm{TlX_3 \cdot 1/2terpy}$ ($X = Cl$ or Br)	A	121, 141
$\mathrm{TlCl_3 \cdot 3,3'\text{-}bipy}$	B	140	$\mathrm{TlX_3 \cdot terpy}$ ($X = Cl$ or Br)	A	121, 141
$\mathrm{TlCl_3 \cdot 2(3,3'\text{-}bipy)}$	B	140	$\mathrm{TlI_3 \cdot 1/2terpy}$	D	121
$\mathrm{TlX_3 \cdot 3,3'\text{-}bipy}$ ($X = Br$ or I)	D	134	$\mathrm{TlCl_3 \cdot dipyam}$	A	74
$\mathrm{TlX_3 \cdot 2(3,3'\text{-}bipy)}$ ($X = Br$ or I)	D	134	$\mathrm{TlCl_3 \cdot 2quin}$[b]	B	63, 143
$\mathrm{TlCl_3 \cdot 4,4'\text{-}bipy}$	B	140	$\mathrm{TlCl_3 \cdot 2py}$	A, B, C	38, 39, 63, 74, 121, 141
$\mathrm{TlX_3 \cdot (4,4'\text{-}bipy)}$ ($X = Br$ or I)	D	140	$\mathrm{TlCl_3 \cdot 3py}$	A, B, C	62, 63, 141, 143, 144
$\mathrm{TlCl_3 \cdot phen}$	A, B	38, 39, 74, 121, 130, 139	$\mathrm{TlBr_3 \cdot 2py}$[c]	A, C	39, 63, 74, 121
$\mathrm{TlCl_3 \cdot 2phen}$	C	135	$\mathrm{TlI_3 \cdot 2py}$[d]	C	63
$\mathrm{TlCl_3 \cdot 3phen}$	C	135	$\mathrm{TlCl_3 \cdot 3\gamma\text{-}pic}$	A	39, 121, 141
$\mathrm{TlBr_3 \cdot phen}$	A, B	38, 74, 121, 130, 139, 141	$\mathrm{TlCl_3 \cdot 1.5pyz}$	A	121, 145
			$\mathrm{TlCl_3 \cdot ampic}$	B	146
			$\mathrm{TlX_3 \cdot ampic}$ ($X = Br$ or I)	D	146

[a] Prepared by the addition of an alcoholic solution of 4,7-phenanthroline to a similar solution of "$\mathrm{TlI_3}$". [b] Renz (Ref. 148) reported the existence of $\mathrm{TlCl_3 \cdot 3quin}$ but this result was not supported by the more recent work of Kul'ba *et al.* (Ref. 63). [c] $\mathrm{TlBr_3 \cdot 3py}$ is prepared by oxidizing a suspension of thallous bromide in pyridine with pyridinium bromide (Ref. 144). [d] Orange $\mathrm{TlI_3 \cdot 2py}$ was also described as the reaction product when pure "$\mathrm{TlI_3}$" was ground with pyridine (Ref. 26). The early report of $\mathrm{TlI_3 \cdot py}$ by Renz (Ref. 148) has not been confirmed.

The chloride and bromide complexes listed in Table 4 are invariably white to pale yellow in color, whereas the iodides are a deep orange-red. The thermal stability of several of these derivatives decreases in the orders $Cl > Br > I$, phen > 4,7-phen and bipy > 3,3'-bipy; the ease of hydrolysis is also in the sense $Cl > Br > I$. Kul'ba and Makashev[148] have made calorimetric measurements on 2,2'-bipyridyl and 1,10-phenanthroline complexes of the types $\mathrm{TlB^{3+}}$ and $\mathrm{TlB_2{}^{3+}}$, and have concluded that the phenanthroline complexes contain stronger thallium–nitrogen bonds than do the related bipyridyl derivatives. However, in spite of the large number of complexes known, only limited structural information is available.

Conductance and low frequency vibrational spectra measurements have proved to be the most popular means of gleaning structural information, but it is clear that the solid-state and solution structures often are different.

(a) Pyridine, γ-picoline, quinoline and pyrazine complexes

Low frequency IR and Raman studies leave little doubt that the complexes $TlCl_3 \cdot 3py$, $TlCl_3 \cdot 2py$, $TlBr_3 \cdot 2py$ and $TlCl_3 \cdot 3\gamma\text{-pic}$ are non-ionic and six co-ordinate in the solid state[121,141]. The vibrational frequencies are not characteristic of the TlX_4^- ions and none can be attributable to species such as $[Tlpy_2Cl_2]^+$ or $[Tlpy_4Cl_2]^+$, so that ionic solid-state structures $[Tlpy_4Cl_2]TlCl_4$ and $[Tlpy_2Cl_2]Cl$ can be ruled out. $TlCl_3 \cdot 3py$ and $TlCl_3 \cdot 3\gamma\text{-pic}$ like $InCl_3 \cdot 3py$[145,149] probably have *cis*-octahedral structures. The spectrum of $TlCl_3 \cdot 2py$ closely resembles that of $TlCl_3 \cdot 3py$ and reveals marked IR–Raman coincidences; the former complex is most likely a non-centrosymmetric halogen-bridged dimer. Dipole moment studies[143] on benzene solutions of $TlCl_3 \cdot 3py$ and 1,4-dioxan solutions of $TlCl_3 \cdot 2quin$ have been carried out but the results were not interpreted in terms of the stereochemistry of the $[TlCl_3N_2]_x$ moieties.

McWhinnie[74] has described the low frequency infrared spectrum of an acetone solution of $TlCl_3 \cdot 2py$ and suggested that the solution species may be $[Tlpy_4Cl_2]TlCl_4$; a molar conductance measurement[74] also indicated the presence of a 1:1 electrolyte, although the concentration of the latter solution was presumably much less than that for which the spectral measurements were recorded. Kul'ba and coworkers[63,150] had previously suggested from limited conductivity studies on acetone solutions of $TlI_3 \cdot 2py$ and nitrobenzene solutions of $TlCl_3 \cdot 2py$ and $TlCl_3 \cdot 3py$, that in solution these molecules do indeed have the structures $[Tlpy_4X_2]TlX_4$ or $[Tlpy_4Cl_2]$ $[Tlpy_2Cl_4]$. More recent concentration range conductivity measurements[121] on acetone and acetonitrile solutions of $TlCl_3 \cdot 2py$ and acetone solutions of $TlCl_3 \cdot 3\gamma\text{-pic}$, reveal behavior characteristic of weak electrolytes, so that while considerable *ionic* dissociation may occur in dilute solution ($\sim 10^{-3}$ M or less) the nature of the more concentrated solutions ($> 10^{-2}$ M) is uncertain.

The pyrazine complex $TlCl_3 \cdot 1\ 1/2pyz$[121] has an infrared spectrum in the 4000–650 cm^{-1} region, which is virtually identical with that of $InCl_3 \cdot 1.5pyz$[149] and characteristic of pyrazine bonded through both nitrogen atoms[151]. A polymeric structure with the central metal atom possessing the local structure MCl_3N_3 seems likely, although vibrational spectral studies[145] do not distinguish between a *cis*- and *trans*-stereochemistry.

The thallium(III) halide complexes of 2-aminomethylpyridine, $TlX_3 \cdot ampic$, form conducting solutions in nitromethane and nitrobenzene[146], but no data is available concerning their solid-state structures.

(b) 2,2′2″-Terpyridyl, bipyridyl and phenanthroline complexes

Studies with these donor molecules have paralleled those described above for the pyridine derivatives of thallium(III). Conductivity measurements on acetonitrile solutions of $TlX_3 \cdot 1/2$ terpy ($X = Cl$ or I)[121], together with low frequency Raman and IR data on these complexes and the related bromide[121,141], indicate that they have the ionic structure $[TlterpyX_2]TlX_4$ in the solid state and solution. The 1:1 complexes $TlX_3 \cdot$ terpy ($X = Cl$ or Br)[121,141] which are also known, probably have a non-ionic octahedral structure, although their vibrational spectra[121,141] provide little evidence favoring this over ionic $[TlX_2 \cdot terpy]X$.

Like the related pyridine derivative, the complexes $TlCl_3 \cdot$ bipy and $TlCl_3 \cdot$ phen most likely have the six coordinate non-centrosymmetric halogen bridged dimeric structures $[(B)Cl_2TlCl_2TlCl_2(B)]$[121,141]. This contrasts with the structure of $GaCl_3 \cdot$ bipy[152], which is ionic [*cis*-$Gabipy_2Cl_2]GaCl_4$, a conclusion which was first suggested from IR studies[152] and later confirmed by a crystallographic investigation[153]. However, the related thallium(III) bromide and iodide complexes $TlX_3 \cdot$ bipy and $TlX_3 \cdot$ phen may, like the above gallium(III) complex, have the ionic structure $[TlB_2X_2]TlX_4$. This is supported by the vibrational spectra of the crystalline complexes[121,141]; a *cis*-stereochemistry for the cations is likely by analogy with *cis*-$Gabipy_2Cl_2^+$ (Refs. 152, 153) and *cis*-$Inbipy_2Cl_2^+$ (Ref. 145). A suggestion by Kul'ba *et al.*[154] that the complexes $[Tlbipy_2X_2]X$, $[Tlphen_2X_2]X$ ($X = Cl$, Br or I), and $[Tlphen_2X_2]NO_3$ ($X = Cl$ or Br) contain the *trans*-octahedral cations, on the basis of the similarity of the low frequency IR spectra of $[Tlbipy_2Cl_2]Cl$ and "*trans*-$[Cobipy_2Cl_2]Cl$", is clearly in error. Only the *cis*-$[Cobipy_2Cl_2]^+$ cations are known and there is good evidence that the *trans*-isomers cannot be isolated in the solid state[155,156].

Conductivity measurements on nitrobenzene solutions of the complexes of stoichiometry $TlX_3 \cdot B$ and $TlX_3 \cdot 2B$ ($B =$ bipy or phen), (many at one concentration only), have been recorded[130,175], and while there seems little doubt that $TlX_3 \cdot 2B$ have the ionic structure $[TlB_2X_2]X$*, disagreement exists in the results for $TlX_3 \cdot B$. Sutton[130] concluded that $TlX_3 \cdot B$ ($B =$ bipy or phen and $X = Cl$, Br or I) had the ionic structure $[TlB_2X_2]TlX_4$ in solution, whereas Kul'ba *et al.*[157] found much lower Λ_m values for several of these complexes (particularly $TlCl_3 \cdot B$), and concluded that an "unambiguous conclusion regarding the number of ions formed by dissociation in nitrobenzene cannot be reached". In another paper, it was suggested[142] that $TlI_3 \cdot$ phen had the structure $[Tlphen_2I_2]TlI_4$.

Concentration range conductance studies on acetonitrile solutions of

---

* This is presumably also the solid-state structure. Also, conductance measurements are in keeping with ionic structures for $[Tlphen_2Cl_2]NO_3$ and $[Tlbipy_2Cl_2]NO_3$ (Ref. 135).

$TlCl_3 \cdot$ bipy and $TlI_3 \cdot$ bipy[121] indicate that like $TlCl_3 \cdot 2$py and $TlCl_3 \cdot 3\gamma$-pic (see above), these systems behave like weak electrolytes; assuming an ionic formulation $[Tlbipy_2X_2]TlX_4$ at concentrations of $\sim 10^{-3}$ M, Λ_m values of ~ 80 $ohm^{-1}cm^2$ are still well below that of typical 1:1 electrolytes in this solvent (~ 130 $ohm^{-1}cm^2$)[158].

In the thallium(III) complexes of 3,3′-bipyridyl, 4,4′-bipyridyl and 4,7-phenanthroline (Table 4), prepared by Kul'ba *et al.*[134,136,140], the bidentate nitrogen donor molecules clearly cannot chelate, although the Russian workers have often assumed to the contrary. Thus they attributed the lower thermal stability of the 3,3′-bipyridyl complexes compared to their 2,2′-bipyridyl analogs, to the reduced stability of the seven membered rings formed in the former derivatives. In reality, the solid-state structures are presumably polymeric. Low-frequency vibrational spectra studies have not been reported, but conductivity measurements[157] point to considerable ionic dissociation occurring in nitrobenzene.

As has been mentioned already, acetonitrile solutions of thallium(III) chloride and bromide[38,39] have been used as reagents for the preparation of coordination complexes of these trihalides. Reedijk and Groeneveld[40] have recently isolated the complex $TlCl_3 \cdot 2MeCN$, and find that it forms a non-conducting solution in acetonitrile and has a Raman spectrum (in this same solvent) with bands at 315 and 250 cm^{-1}. It was suggested[40] that this complex does not contain the $TlCl_4^-$ ion. In view of the apparent simplicity of the Raman spectrum and the relatively high frequency of the ν(Tl–Cl) mode at 315 cm^{-1}, this molecule may have a fairly high symmetry structure, possibly *trans*-trigonal bipyramidal. Alternatively, perhaps a further molecule of acetonitrile coordinates in solution to give $TlCl_3 \cdot 3MeCN$. The above conductance results conflict with those of Berry *et al.*[26] and Sheka and Pechenaya[159], who observed high conductance values and postulated the presence of ionic species in solution. In view of the sensitivity of this system to moisture it is possible that the differing results which were observed[26,159] could be due to varying degrees of hydrolysis.

The ternary phase $TlCl_3$–$SbCl_5$–MeCN has been investigated[160] and $TlCl_3 \cdot SbCl_5 \cdot 6MeCN$ isolated, but few details of its structure are known although it may contain the $TlCl_2^+$ species (presumably solvated).

(ii) Oxygen donors

Few systems have been investigated in sufficient detail to warrant other than a cursory survey.

As expected, solvolysis occurs with phenols such as the α- and β-naphthols to form the naphthoxy derivatives $(C_{10}H_7O)_3Tl$[161]. On the other hand, pyrogallol, pyrocatechol and hydroquinone reduce the trihalides to the thallous state, the hydroquinone being oxidized to quinone in the process[161].

Electronic absorption bands characteristic of the $TlCl_4^-$ and $TlBr_4^-$ ions are observed in the spectra of methanolic solutions of the trihalides. This was interpreted[132] in terms of a dissociation

$$2TlX_3 \rightleftharpoons TlX_2^+(\text{solvent}) + TlX_4^-$$

The same dissocation was postulated to explain the conductance of methanol solutions of thallium(III) chloride[159]. However, like the related acetonitrile solutions, it is likely that these systems are also susceptible to hydrolysis.

Thallium(III) chloride dissolves in diethylether to yield the etherate $TlCl_3 \cdot Et_2O$[62], and by the slow evaporation of a solution of the trichloride in 1,4-dioxan, crystals of $TlCl_3 \cdot 2C_4H_8O_2$[143] have been isolated. Dipole moment measurements on solutions of thallium(III) chloride in dioxan and ether and $TlCl_3 \cdot 2C_4H_8O_2$ in benzene[143] have been made but not interpreted in terms of specific structures for these species.

From their study of the extraction of thallium(III) by tri-*n*-butylphosphate-(TBP) from aqueous chloride–sulphate solutions, Chuchalin *et al.*[163] suggested that the trichloride enters the organic phase as $TlCl_3 \cdot 2TBP$. This species is described[164] as being monomeric in benzene and non-ionic in nitrobenzene, and as having a dipole moment of 3.6D and ν(Tl–Cl) at 315 cm^{-1}. Its most probable structure was considered[164] to be a distorted trigonal-bipyramid in which TBP coordination is via the oxygen atom of the P=O group.

As with the TBP reaction, thallium(III) chloride reacts with dimethylsulphoxide and triphenylphosphine oxide to form $TlCl_3 \cdot 2DMSO$ and $TlCl_3 \cdot 2Ph_3PO$, respectively[38], for which conductance measurements in acetonitrile indicate only slight ionic dissociation. The IR spectra of these complexes are characteristic of oxygen-bonded donor molecules[38]. Both complexes appeared to be monomers in sulfolane[38] and the Raman spectrum of $TlCl_3 \cdot 2DMSO$ has been interpreted[121] in terms of a *trans*-trigonal-bipyramidal structure. The highest frequency ν(Tl–Cl) mode is at 314 cm^{-1}, similar to that quoted for $TlCl_3 \cdot 2TBP$. The behavior of $TlCl_3 \cdot 2DMSO$ in acetone[121] illustrates the difficulty sometimes encountered in inferring the structures of solid-state species from the results of solution measurements. Such freshly prepared solutions ($\sim 10^{-3}$ M) initially have a low conductance but within a minute or so of their preparation, these values increase rapidly. Clearly reaction with the solvent occurs, and this is further borne out by molecular weight measurements in this solvent[121].

The related bromide complexes $TlBr_3 \cdot 2DMSO$ and $TlBr_3 \cdot 2Ph_3PO$ have also been prepared[38,39], but no structural information is available although appreciable dissociation is detected in solutions of $TlBr_3 \cdot 2DMSO$ in several polar solvents[38]. The reaction of sodium iodide with $TlX_3 \cdot 2Ph_3PO$ (X = Cl or Br) in aqueous acetone affords the 1:3 complex $TlI_3 \cdot 3Ph_3PO$[38]. This may be an authentic six coordinate derivative of thallium(III) iodide; conductance data in acetonitrile and nitromethane[38] are consistent with the ionic dimer $[Tl(Ph_3PO)_4I_2]$-$[Tl(Ph_3PO)_2I_4]$. Like most metal halides thallium(III) chloride reacts with $POCl_3$, product being $TlCl_3 \cdot 2POCl_3$[165], which contains oxygen bonded $POCl_3$ molecules and has ν(Tl–Cl) assigned to bands at 304 and 292 cm^{-1}.

E. CONCLUDING REMARKS

In the preceding sections, the reactions of the thallium(III) halides with halide ions, and nitrogen and oxygen donor molecules have been surveyed. In spite of the large number of complex species isolated little unambiguous structural data are available, especially for the nitrogen and oxygen donor complexes. Clearly crystallographic studies on several of these derivatives would clarify these structural details and serve as a basis for making a meaningful comparison with related gallium(III) and indium(III) systems. The nature of many of these complexes in solution remains very much of a mystery. Some impetus for solving these remaining problems stems from the realization that thallium(III) derivatives can be useful oxidants for the synthesis of new compounds. Many may well prove to be selective in their reactivity, but their utilization is at present frustrated by the confusion which surrounds their solution properties. By way of illustrating their use, it is interesting to note that recent work has revealed the oxidizing properties of bromobis(pentafluorophenyl)thallium(III), and its use in preparing pentafluorophenyl derivatives of transition and non-transition metals by reaction with the metals themselves[166], or a metal halide or other derivative[167]. Thallium(III) derivatives will continue to find use in synthetic organic chemistry and as oxidants in kinetic studies.

REFERENCES

1 R. S. Drago, *J. Phys. Chem.*, 62 (1958) 353.
2 A. J. Edwards, R. D. Peacock and A. Said, *J. Chem. Soc.*, (1962) 4643.
3 K. F. Guenther, *Inorg. Chem.*, 3 (1964) 923.
4 See for example, K. G. Ashurst and W. C. E. Higginson, *J. Chem. Soc.*, (1953) 3044.
5 O. Farver and G. Nord, *Chem. Commun.*, (1967) 736.
6 R. S. Eachus, M. C. R. Symons and J. K. Yandell, *Chem. Commun.*, (1969) 979.
7 D. A. Johnson, *Some Thermodynamic Aspects of Inorganic Chemistry*, Cambridge University Press, London–New York, 1968, p. 32.
8 E. Wiberg and M. Schmidt, *Z. Naturforsch.*, 6b (1951) 334.
9 E. Wiberg, O. Dittmann and M. Schmidt, *Z. Naturforsch.*, 12b (1957) 60.
10 E. Wiberg, O. Dittmann, H. Noth and M. Schmidt, *Z. Naturforsch.*, 12b (1957) 61.
11 K. Yasuda and R. Okawara, *Organometal. Chem. Rev.*, 2 (1967) 255.
12 A. N. Nesmeyanov and R. A. Sokolik, *Organic Compounds of Boron, Aluminum, Gallium, Indium and Thallium*, The World Publishing Co., New York, 1967.
13 M. B. Koromantzou and G. A. Pneumaticakis, *Chem. Ind.*, (1967) 1089.
14 K. A. Jensen and V. Krishnan, *Acta Chem. Scand.*, 21 (1967) 2904.
15 D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 5 (1966) 1586.
16 O. L. Forcheimer and R. P. Epple, *J. Amer. Chem. Soc.*, 74 (1952) 5772.
17 D. H. Irvine, *J. Chem. Soc.*, (1957) 1841.

18 J. D. Miller and R. H. Prince, *J. Chem. Soc. (A)*, (1966) 1048.
19 N. A. Naugherty, *J. Amer. Chem. Soc.*, 87 (1965) 5026.
20 J. B. Lee and M. J. Price, *Tetrahedron*, 20 (1964) 1017.
21 K. C. Pande and S. Winstein, *Tetrahedron Lett.*, (1964) 3393.
22 G. H. W. Milburn and M. R. Truter, *J. Chem. Soc. (A)*, (1967) 648.
23 T. L. Blundell and H. M. Powell, *Chem. Commun.*, (1967) 54.
24 Y. Marcus, *Coord. Chem. Rev.*, 2 (1967) 195.
25 A. J. Carty, *Coord. Chem. Rev.*, 4 (1969) 29.
26 A. J. Berry, T. M. Lowry and R. R. Goldstein, *J. Chem. Soc.*, (1928) 1748.
27 H. W. Foote and M. Fleischer, *J. Phys. Chem.*, 44 (1940) 647.
28 A. G. Sharpe, *J. Chem. Soc.*, (1952) 2165.
29 F. Ya. Kul'ba and V. E. Mironov, *Zhur. Neorg. Khim.*, 2 (1957) 244.
30 A. C. Hazell, *Acta Cryst.*, 16 (1963) 71.
31 O. Hannebohn and W. Klemm, *Z. Anorg. Chem.*, 229 (1936) 337.
32 G. Brauer, *Handbook of Preparative Inorganic Chemistry*, Vol. I, Academic Press, New York, 1963, p. 230.
33 C. Hebecker and R. Hoppe, *Naturwissenschaften*, 53 (1966) 104.
34 Ref. 32, p. 870.
35 H. Hecht, *Z. Anorg. Chem.*, 254 (1947) 37.
36 J. R. Partington and A. L. Whynes, *J. Chem. Soc.*, (1948) 1952.
37 W. L. Groeneveld and A. P. Zuur, *Inorg. Nucl. Chem. Letters*, 3 (1967) 229.
38 F. A. Cotton, B. F. G. Johnson and R. M. Wing, *Inorg. Chem.*, 4 (1965) 502.
39 B. F. G. Johnson and R. A. Walton, *Inorg. Chem.*, 5 (1966) 49.
40 J. Reedijk and W. L. Groeneveld, *Rec. Trav. Chim. Pays-Bas*, 87 (1968) 552.
41 D. H. Templeton and G. F. Carter, *J. Phys. Chem.*, 58 (1954) 940.
42 E. A. C. Lucken, *Nuclear Quadrupole Coupling Constants*, Academic Press, London and New York, 1969, p. 259–272.
43 S. C. Wallwork and I. J. Worrall, *J. Chem. Soc.*, (1965) 1816.
44 J. D. Forrester, A. Zalkin and D. H. Templeton, *Inorg. Chem.*, 3 (1964) 63.
45 I. R. Beattie, T. Gilson and G. A. Ozin, *J. Chem. Soc. (A)*, (1968) 813.
46 D. M. Adams and R. G. Churchill, *J. Chem. Soc. (A)*, (1968) 2140.
47 N. N. Greenwood, D. J. Prince and B. P. Straughton, *J. Chem. Soc. (A)*, (1968) 1694.
48 S. S. Batsanov and N. R. Serebryanaya, *Chem. Abstr.*, 55 (1961) 12126i.
49 S. Kaufmann and K. Dehnicke, *Z. Anorg. Chem.*, 347 (1966) 318.
50 B. Siegel, *Inorg. Chim. Acta Rev.*, 2 (1968) 137.
51 D. Peschanski and S. Valladas-Dubois, *Bull. Soc. Chim. France*, (1956) 1170.
52 S. Ahrland, *Acta Chem. Scand.*, 10 (1956) 723.
53 S. Ahrland, I. Grenthe, L. Johansson and B. Noren, *Acta Chem. Scand.*, 17 (1963) 1567.
54 I. Leden and T. Ryhl, *Acta Chem. Scand.*, 18 (1964) 1196.
55 S. Ahrland and L. Johansson, *Acta Chem. Scand.*, 18 (1964) 2125.
56 M. J. M. Woods, P. K. Gallagher, Z. Z. Hugus and E. L. King, *Inorg. Chem.*, 3 (1964) 1313.
57 F. Ya. Kul'ba, V. E. Mironov and I. F. Marvin, *Zhur. Fiz. Khim.*, 39 (1965) 2595.
58 L. Johansson, *Acta Chem. Scand.*, 20 (1966) 2156.
59 S. Ahrland, J. Chatt and N. R. Davis, *Quart. Rev.*, 12 (1958) 265.
60 T. G. Spiro, *Inorg. Chem.*, 4 (1965) 731.
61 R. Hoppe and C. Hebecker, *Z. Anorg. Chem.*, 335 (1965) 85.
62 R. J. Meyer, *Z. Anorg. Chem.*, 24 (1900) 321.
63 F. Ya. Kul'ba, V. E. Mironov, V. I. Sazhina and T. G. Ogibenina, *Russ. J. Inorg. Chem.*, 8 (1963) 468.
64 W. Krause and A. Grosse, *Ber.*, 59 (1926) 1712.
65 Ref. 32, pp. 872 and 875.
66 T. J. Rowland and J. P. Bromberg, *J. Chem. Phys.*, 29 (1958) 626.
67 A. C. Hazell, *J. Chem. Soc.*, (1963) 3459.
68 G. Garton and H. M. Powell, *J. Inorg. Nucl. Chem.*, 4 (1957) 84.
69 T. G. Spiro, *Inorg. Chem.*, 6 (1967) 569.

70 B. Zaslow and R. E. Rundle, *J. Phys. Chem.*, 61 (1957) 490.
71 M. G. B. Drew, D. F. Lewis and R. A. Walton, *Inorg. Nucl. Chem. Letters*, in the press.
72 T. G. Spiro, *Inorg. Chem.*, 4 (1965) 1290.
73 R. A. Walton, *Inorg. Chem.*, 7 (1968) 1927.
74 W. R. McWhinnie, *J. Chem. Soc. (A)*, (1966) 889.
75 D. M. Adams and D. M. Morris, *J. Chem. Soc. (A)*, (1968) 694.
76 M. J. Taylor, *J. Chem. Soc. (A)*, (1966) 1780.
77 J. E. D. Davies and D. A. Long, *J. Chem. Soc. (A)*, (1968) 2050.
78 M. Delwaulle, *Compt. Rend.*, 238 (1954) 2522.
79 D. M. Adams, *Metal–Ligand and Related Vibrations*, Arnold, New York, 1968, p. 56–59.
80 J. H. Pratt, *Amer. J. Sci.*, 149 (1895) 397.
81 T. Wanatabe, Y. Sarto, R. Shino and M. Atoji, *Abstracts, First Congress of the International Union of Crystallography*, 1948, p. 30; *Struct. Rept.*, 11 (1947–1948), 393.
82 T. Wanatabe, M. Atoji and C. Okazaki, *Acta Cryst.*, 3 (1950) 405.
83 T. Wanatabe and M. Atoji, *J. Amer. Chem. Soc.*, 72 (1950) 3819.
84 H. Kashiwagi, D. Nakamura and M. Kubo, *J. Phys. Chem.*, 71 (1967) 4443.
85 J. R. Partington and A. L. Whynes, *J. Chem. Soc.*, (1948) 1952.
86 J. Lewis and D. B. Sowerby, *J. Chem. Soc.*, (1963) 1305.
87 Unpublished observations quoted by F. J. J. Brinkmann and H. Gerding, *Rec. Trav. Chim. Pays-Bas*, 88 (1969) 275.
88 W. L. Groeneveld, *Rec. Trav. Chim. Pays-Bas*, 71 (1952) 1152.
89 F. J. J. Brinkmann and H. Gerding, *Inorg. Nucl. Chem. Letters*, 5 (1969) 119.
90 J. Reedijk and W. L. Groeneveld, *Rec. Trav. Chim. Pays-Bas*, 87 (1968) 513.
91 J. Reedijk, *Rec. Trav. Chim. Pays-Bas*, 88 (1969) 86.
92 G. Thiele, K. H. Kilian, W. Weigel and K. Brodersen, *Z. Naturforsch.*, 22b (1967) 1217.
93 R. W. Matthews and R. A. Walton, *J. Chem. Soc. (A)*, (1968) 1639.
94 C. K. Jørgensen, *Advan. Chem. Phys.*, 5 (1963) 33.
95 C. K. Jørgensen, in B. G. Wybourne (Ed.), *Chemical Applications of Spectroscopy*, Interscience, N.Y., in the press.
96 C. K. Jørgensen, *Mol. Phys.*, 2 (1959) 309.
97 W. Beck, E. Schuierer, P. Poellmann and W. P. Fehlhammer, *Z. Naturforsch.*, 21b (1966) 811.
98 W. Beck, W. P. Fehlhammer, P. Poellmann, E. Schuierer and K. Feldl, *Chem. Ber.*, 100 (1967) 2335.
99 G. Faraglia, L. R. Fiorani, B. C. L. Pepe and R. Barbieri, *Inorg. Nucl. Chem. Letters*, 2 (1966) 277; *J. Organometal. Chem.*, 10 (1967) 363.
100 Paz de Tiedra de Tiedra, *Acta Salmanticensia Ser. Cienc.*, 3 (1) (1961) 53; *Chem. Abstr.*, 57 (1962) 12093*c*.
101 D. F. Shriver and I. Wharf, *Inorg. Chem.*, 8 (1969) 2167.
102 D. S. Brown, F. W. B. Einstein and D. G. Tuck, *Inorg. Chem.*, 8 (1969) 14.
103 H. Bode and E. Voss, *Z. Anorg. Chem.*, 290 (1957) 1.
104 R. Hoppe and S. Schneider, *Z. Anorg. Chem.*, 361 (1968) 113.
105 C. Spacu and A. Pop, *Z. Anal. Chem.*, 120 (1940) 322.
106 T. Barrowcliffe, I. R. Beattie, P. Day and K. Livingston, *J. Chem. Soc. (A)*, (1967) 1810.
107 J. L. Hoard and L. Goldstein, *J. Chem. Phys.*, 3 (1935) 645.
108 G. Malquori, *Gazz. Chim. Ital.*, 56 (1926) 37.
109 Ref. 32, pp. 873 and 875.
110 A. S. Cushman, *Amer. Chem. J.*, 24 (1900) 222.
111 A. Benrath, *Z. Anorg. Chem.*, 93 (1915) 161; *ibid.*, 136 (1924) 358.
112 H. Funk, K. H. Berndt and G. Henze, *Chem. Abstr.*, 54 (1960) 12860*g*.
113 R. Freeman, R. P. H. Gaser and R. E. Richards, *Mol. Phys.*, 2 (1959) 301.
114 A. W. Atkinson, J. R. Chadwick and E. Kinsella, *J. Inorg. Nucl. Chem.*, 30 (1968) 401.
115 J. H. R. Clarke and R. E. Hester, *Inorg. Chem.*, 8 (1969) 1113.
116 J. H. Pratt, *Z. Anorg. Chem.*, 9 (1895) 23.
117 J. L. Hoard and L. Goldstein, *J. Chem. Phys.*, 3 (1935) 199.

118 H. M. Powell and A. F. Wells, *J. Chem. Soc.*, (1935) 1008.
119 I. R. Beattie, T. R. Gilson and G. A. Ozin, *J. Chem. Soc. (A)*, (1968) 2765.
120 A. E. Goddard and D. Goddard, *J. Chem. Soc.*, 121 (1922) 482.
121 R. A. Walton, *Inorg. Chem.*, 7 (1968) 640.
122 A. E. Goddard, *J. Chem. Soc.*, 123 (1923) 1161.
123 A. J. Carty and D. G. Tuck, *J. Chem. Soc. (A)*, (1966) 1081.
124 M. V. Veidis and G. J. Palenik, *Chem. Commun.*, (1969) 586.
125 I. R. Beattie and G. A. Ozin, *J. Chem. Soc. (A)*, (1968) 2373.
126 A. J. Carty, *Can. J. Chem.*, 45 (1967) 345; 3187.
127 A. P. Kochetkova and V. G. Tronev, *Zhur. Neorg. Khim.*, 2 (1957) 2043.
128 F. Ya. Kul'ba, Yu. A. Makashev and V. E. Mironov, *Russ. J. Inorg. Chem.*, 6 (1961) 758.
129 W. Hieber and F. Sonnekalb, *Ber.*, 61B (1928) 555.
130 G. J. Sutton, *Aust. J. Chem.*, 11 (1958) 120.
131 F. Ya. Kul'ba, A. V. Barsukov and Yu. S. Varshavskii, *Russ. J. Inorg. Chem.*, 13 (1968) 237.
132 F. Ya. Kul'ba, V. E. Mironov, A. V. Barsukov and B. I. Lobov, *Russ. J. Inorg. Chem.*, 14 (1969) 73.
133 F. Ya. Kul'ba and V. E. Mironov, *Russ. J. Inorg. Chem.*, 4 (1959) 346.
134 F. Ya. Kul'ba, V. E. Mironov, L. P. Rozhanovskaya and O. A. Skuratov, *Russ. J. Inorg. Chem.*, 9 (1964) 883.
135 F. Ya. Kul'ba and V. E. Mironov, *Russ. J. Inorg. Chem.*, 4 (1959) 627.
136 F. Ya. Kul'ba, V. E. Mironov and Chin-Yang Ts'ung, *Russ. J. Inorg. Chem.*, 8 (1963) 961.
137 O. Farver and G. Nord, *Acta Chem. Scand.*, 20 (1966) 1429.
138 F. Ya. Kul'ba, V. E. Mironov and V. Zderadichkova, *Russ. J. Inorg. Chem.*, 9 (1964) 1016.
139 G. J. Sutton, *Aust. J. Sci. Res.*, A4 (1951) 654.
140 F. Ya. Kul'ba, V. E. Mironov and L. P. Rozhanovskaya, *Russ. J. Inorg. Chem.*, 7 (1962) 1202.
141 R. A. Walton, *J. Inorg. Nucl. Chem.*, 32 (1970) 2875.
142 F. Ya. Kul'ba, V. E. Mironov, L. A. Anan'eva, O. S. Andreeva and L. P. Rozhanovskaya, *Russ. J. Inorg. Chem.*, 8 (1963) 727.
143 I. A. Sheka, *J. Gen. Chem. USSR*, 26 (1956) 25.
144 R. K. Abbott, *Iowa State Coll. J. Sci.*, 18 (1943) 3; *Chem. Abs.*, 38 (1944) 62.
145 R. A. Walton, *J. Chem. Soc. (A)*, (1969) 61.
146 G. J. Sutton, *Aust. J. Chem.*, 16 (1963) 1134.
147 C. Renz, *Ber.*, 35 (1902) 1110.
148 F. Ya. Kul'ba and Yu. A. Makashev, *Russ. J. Inorg. Chem.*, 7 (1962) 661.
149 R. A. Walton, *J. Chem. Soc. (A)*, (1967) 1485.
150 F. Ya. Kul'ba, V. E. Mironov and O. S. Andreeva, *Russ. J. Inorg. Chem.*, 8 (1963) 1217.
151 A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, (1962) 1235.
152 A. J. Carty, *Can. J. Chem.*, 46 (1968) 3779.
153 R. Restivo and G. J. Palenik, *Chem. Commun.*, (1969) 867.
154 F. Ya. Kul'ba, N. G. Yaroslavskii, L. V. Konovalov, A. V. Barsukov and V. E. Mironov, *Russ. J. Inorg. Chem.*, 13 (1968) 79.
155 J. G. Gibson and E. D. McKenzie, *J. Chem. Soc. (A)*, (1969) 2637.
156 D. M. Palade, *Russ. J. Inorg. Chem.*, 14 (1969) 754.
157 F. Ya. Kul'ba, V. E. Mironov, Chin-Yang Ts'ung and Z. G. Filippova, *Russ. J. Inorg. Chem.*, 8 (1963) 341.
158 R. A. Walton, *Quart. Rev.*, 19 (1965) 126.
159 Z. A. Sheka and E. I. Pechenaya, *Ukrain. Khim. Zhur.*, 21 (1955) 149.
160 A. P. Zuur, J. J. Van Houte and W. L. Groeneveld, *Rec. Trav. Chim. Pays-Bas*, 87 (1968) 755.
161 N. N. Mel'nikov and G. P. Gracheva, *J. Gen. Chem. USSR*, 7 (1937) 467.
162 I. A. Sheka, *J. Gen. Chem. USSR*, 25 (1955) 2283.
163 L. K. Chuchalin, I. A. Kuzin, K. F. Obzherina, T. T. Omarov and L. S. Chuchalina, *Russ. J. Inorg. Chem.*, 12 (1967) 622.

164 L. K. CHUCHALIN, B. I. PESHCHEVITSKII, I. A. KUZIN, Z. A. GRANKINA AND E. V. DULEPOV, *J. Struct. Chem.*, 9 (1968) 158.
165 E. W. WARTENBERG AND J. GOUBEAU, *Z. Anorg. Chem.*, 329 (1964) 269.
166 G. B. DEACON AND J. C. PARROTT, *J. Organometal. Chem.*, 17 (1969) P17.
167 R. S. NYHOLM AND P. ROYO, *Chem. Commun*, (1969) 421.