spin pairing, although in the case of nickel it does not seem to occur extensively.[13]

With the nonmethylated $NH(CH_2CH_2NH_2)_2$ (dien) ligand all the ions from Mn^{2+} to Zn^{2+} form complexes of the type $M(dien)^{2+}$ and $M(dien)_2^{2+}$ in aqueous solution.[14,15]

With the possible exception of the compounds of copper and zinc the others are all octahedral (the first ones through coordination of three molecules of water).[15] Moreover, Bernhard and Barclay isolated the compounds $Co(dien)Cl_2$ and $Co(dien)Br_2$ which are high-spin.[16] For these compounds they postulate a structure either of the type [Co(dien)X]X (with cobalt pseudotetrahedral) or of the type $[Co(dien)_2][CoX_4]$ (with tetrahedrally and octahedrally coordinated cobalt present at the same time).[16] We have now measured the reflectance spectrum of the $Co(dien)Cl_2$ compound, between 5000 and 30,000 cm.$^{-1}$. It shows intense bands in the regions 5000–6000 and 14,000–20,000 cm.$^{-1}$ diagnostic of the $(CoCl_4)^{2-}$ species and one weaker band at 10,500 cm.$^{-1}$ characteristic of the hexamine cobalt(II) species. These data lead to the conclusion that the structure is $[Co(dien)_2][CoX_4]$. Thus it appears clear that a structure which contains six- and four-coordinated cobalt present at the same time is more stable than one with a five-coordinated cobalt when the ligand is dien. The opposite is true when the ligand is dienMe. It is very likely that this is due to the steric requirements of the methyl groups of the ligand dienMe, which cause strong steric hindrance to the coordination of two dienMe molecules to the same metal ion. In fact Stuart models of the ion $[M(dienMe)_2]^{2+}$ cannot be assembled. One must not, however, exclude the fact that a high contribution of lattice energy contributes to the stability of the ionic structure $[Co(dien)_2]$-$[CoX_4]$. Unfortunately the insolubility of these compounds in inert solvents prevents us from ascertaining if this structure is also maintained in the absence of crystal forces.[17]

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(17) NOTE ADDED IN PROOF.—Professor R. S. Nyholm and his co-workers have recently reported [*Nature*, **207**, 72 (1965)] the isolation of high-spin five-coordinated complexes of bivalent transition metals from manganese to zinc (diamagnetic). X-Ray data indicate [P. Pauling, G. B. Robertson, and G. A. Rodley, *ibid.*, **207**, 73 (1965)] that these compounds have a square-pyramidal configuration.

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Coordination Compounds of Thallium(III). II. Some Complexes of Thallium(III) Halides and Their Indium(III) Analogs

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The preparation and characterization of some new complexes of indium(III) and thallium(III) halides are described. Generally, complexes of the types $InCl_3 \cdot 3L$ and $TlX_3 \cdot 2L$ were obtained, although reaction of indium(III) chloride with 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy) in methyl cyanide gave the complexes $InCl_3 \cdot 1.5phen \cdot CH_3CN$ and $InCl_3 \cdot 1.5bipy$, respectively. Conductivity and far-infrared spectral data of the complexes have been used as a guide to their stereochemistry.

Introduction

At present little information is available on the stereochemistry of thallium(III) complexes, and previous studies have been mainly concerned with the preparation and stoichiometry of such complexes. However, conductivity and molecular weight measurements have recently[1–3] been carried out on some complexes of the thallium(III) halides and the tetrahalothallate ions TlX_4^-, where X = Cl, Br, or I. A tetrahedral structure has been definitely established for $TlCl_4^-$ in $(C_6H_5)_4AsTlCl_4$,[1] while both tetrahedral[4] and square-planar[5] crystal structures for $TlBr_4^-$ have been claimed.

As an extension to our earlier studies[1] on complexes of the thallium(III) halides, we have now prepared some further adducts of the type $TlX_3 \cdot 2L$ and their corresponding indium(III) chloride complexes $InCl_3 \cdot 3L$. Conductivity and infrared studies on these and other complexes described previously[1] are now reported.

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(2) (a) F. Ya. Kul'ba, V. E. Mironov, C. Ta'ung, and Z. G. Filippova, *Zh. Neorgan. Khim.*, **8**, 672 (1962); (b) F. Ya. Kul'ba, V. E. Mironov, V. I. Sazhina, and T. G. Ogibenina, *ibid.*, **7**, 911 (1963).
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Experimental Section

Preparation of Compounds. **$(C_6H_5)_4AsTlCl_4$, $(C_2H_5)_4NTlCl_4$, $TlCl_3 \cdot 2(CH_3)_2SO$, and $TlCl_3 \cdot 2C_5H_5N$.**—The compounds were prepared following the same procedure as that described earlier.[1]

$(C_2H_5)_4NTlCl_3Br$.—Chlorine was passed briskly through a suspension of thallous chloride (1.2 g.) in methyl cyanide (10 ml.). After 30 min., when all the solid had dissolved the excess chlorine was removed in a fast stream of nitrogen and tetraethylammonium bromide (1.05 g.) added. The solvent was then removed under vacuum, leaving white needles of $(C_2H_5)_4NTlCl_3Br$. The crude product was recrystallized from acetone–alcohol (1:1).

$TlCl_3 \cdot 3\gamma$-pic, $TlCl_3 \cdot 2$morp, $TlBr_3 \cdot 2\gamma$-pic, $TlBr_3 \cdot 2$py, $InCl_3 \cdot 3(CH_3)_2SO$, $InCl_3 \cdot 3\gamma$-pic, $InCl_3 \cdot 3$morp, $InCl_3 \cdot 3$py, $InCl_3 \cdot 3$pyCN, $InCl_3 \cdot 1.5$bipy, and $InCl_3 \cdot 1.5$phen$\cdot CH_3CN$.—These compounds were prepared by the addition of the appropriate ligand to a solution of the trihalide in methyl cyanide. On cooling, the products separated out. They were separated by filtration, washed with methyl cyanide, acetone, and ether, and dried under vacuum.

Electric Conductances.—These were measured on a Philipps P.R. 9500 conductivity bridge. Solvents were of spectroscopic grade and the solutions were all approximately 10^{-3} *M*.

Infrared Spectra.—(1) Spectra in the range 4000–650 cm.$^{-1}$ were recorded on a PE 237 spectrometer equipped with NaCl optics. (2) Spectra in the range 650–265 cm.$^{-1}$ were recorded with a PE 221 double-beam spectrometer equipped with CsBr optics using Nujol mulls between polythene plates.

Results and Discussion

Methyl cyanide is widely used[6] as a solvent for inorganic preparations and provides a route to a variety of new complexes of thallium(III) halides. In this and a previous paper[1] we have found that oxidation of thallium(I) chloride and bromide with halogen in methyl cyanide gives quantitative yields of the appropriate thallium(III) halide in methyl cyanide. Removal of solvent left the hygroscopic halide with some coordinated methyl cyanide which was rapidly lost on pumping. Mixing methyl cyanide solutions of thallium(III) halide and ligand L usually resulted in the precipitation of a complex $TlX_3 \cdot 2L$, where X = Cl or Br and L = pyridine (py), γ-picoline (γ-pic), morpholine (morp), or dimethyl sulfoxide (DMSO). The reaction of thallium(III) chloride with γ-picoline gave only $TlCl_3 \cdot 3\gamma$-pic and there was no evidence for the formation of the expected 1:2 adduct. The DMSO complexes were readily precipitated on adding DMSO to the solid thallium(III) halides.

Attempts to prepare the analogous *p*-toluidine and α-picoline complexes gave sticky noncrystalline products which were not investigated further.

Although the pyridine complexes $TlX_3 \cdot 2$py, where X = Cl or Br, have been reported before by Russian workers,[2b] we have found the method described above more convenient since the readily available thallium(I) halides can be used. The preparation of $TlCl_3 \cdot 2$py from aqueous medium has also been described.[1]

A rather unexpected feature of the reaction of γ-picoline with thallium(III) chloride is the formation of $TlCl_3 \cdot 3\gamma$-pic. Although complexes of stoichiometry $TlX_3 \cdot 2L$ are usually formed, the phosphine oxide complex $TlI_3 \cdot 3(C_6H_5)_3PO$ is known[1] and shows no tendency to lose the "extra" molecule of triphenylphosphine oxide. There is no obvious explanation for these differing stoichiometries, although the further molecule of ligand (phosphine oxide or γ-picoline) may simply be present in the lattice as a "molecule of crystallization."

Complexes of indium(III) halides of the type $InX_3 \cdot 3L$ have previously been reported with pyridine, γ-picoline,[7] and a variety of oxygen[8] and sulfur[9] donor molecules. Sutton[10] has also prepared several ionic 2-picolylamine and ethylenediamine complexes, $[InL_3]X_3$ and $[InL_2X_2]X$, in which the indium has a coordination number of six. The tris-bipyridyl and 1,10-phenanthroline complexes of indium(III) are also known.[11]

As with thallium(III) chloride no methyl cyanide complex of indium(III) chloride could be isolated on evaporating a solution of indium(III) chloride in methyl cyanide. This is in contrast to the aluminum[12] and gallium[13] halides, which form well-defined complexes in the absence of moisture.

We have found that the reaction of several nitrogen ligands with methyl cyanide solutions of indium(III) chloride gives crystalline complexes of the type $InCl_3 \cdot 3L$ with pyridine, γ-picoline, 4-cyanopyridine, and morpholine, and of the type $InCl_3 \cdot 1.5L$ with 2,2′-bipyridyl and 1,10-phenanthroline. In the case of the 1,10-phenanthroline reaction the complex crystallized with a molecule of methyl cyanide, as shown by a characteristic sharp absorption at *ca.* 2240 cm.$^{-1}$ in the infrared spectrum.[6] The DMSO complex $InCl_3 \cdot 3$DMSO was formed on shaking a suspension of indium(III) chloride in DMSO.

Washing the 4-cyanopyridine complex with acetone resulted in the loss of one molecule of ligand and the formation of the 1:2 complex. No such behavior was observed with the other complexes of indium(III) chloride, and the loss of a molecule of ligand is not readily understood.

As a guide to the structure and stereochemistry of the complexes reported in this paper, we have measured their conductivity and infrared spectra. These results are now discussed.

Conductivity.—With the exception of $TlCl_3 \cdot 2$DMSO and $InCl_3 \cdot 3$pyCN, all the complexes were virtually insoluble in nonpolar solvents such as benzene, pentane, chloroform, etc. The thallium(III) bromide complexes appeared to be insoluble in all polar and nonpolar solvents tried and in several instances tended to decompose to leave a brown residue.

Most of the complexes, however, were sufficiently soluble in suitable solvents for conductivity measurements to be carried out (Table II). Significant conductivity values were observed in the solvents used, although the values of Λ_M calculated for the monomeric formulations were less than those usually found for 1:1

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TABLE I
ANALYTICAL DATA FOR INDIUM AND THALLIUM(III) HALIDE COMPOUNDS[a]

Compound	C, % Found	C, % Calcd.	H, % Calcd.	H, % Found	N, % Found	N, % Calcd.	X, % Calcd.	X, % Found
$InCl_3\cdot1.5$bipy	39.2	39.6	2.9	2.7	9.1	9.2	...	...
$InCl_3\cdot1.5$phen$\cdot CH_3CN$	44.9	45.1	2.8	2.8	10.4	10.6	...	...
$InCl_3\cdot2$pyCN	33.1	33.6	2.4	1.9	12.8	13.1	...	...
$InCl_3\cdot3$pyCN	40.3	40.5	2.4	2.3	15.6	15.8	...	...
$InCl_3\cdot3$py	40.5	39.3	3.5	3.3	9.0	9.2	...	...
$InCl_3\cdot3\gamma$-pic	43.5	43.2	4.1	4.2	8.6	8.4	21.2	21.3
$InCl_3\cdot3$morp	29.2	29.9	5.6	5.6	8.6	8.7	...	...
$InCl_3\cdot3$DMSO	16.3	15.8	4.1	4.0	21.8[b]	21.1[b]	24.0	23.4
$TlCl_3\cdot3\gamma$-pic	36.8	36.6	3.7	3.6	7.3	7.1	18.0	18.1
$TlCl_3\cdot2$morp	19.8	19.6	4.3	3.7	5.8	5.7	21.7	21.8
$TlBr_3\cdot2\gamma$-pic	22.7	22.9	1.8	2.2	4.6	4.4	38.0	38.1
$TlBr_3\cdot2$py	20.0	19.9	2.5	1.7	4.9	4.7	38.9	39.8
$TlBr_3\cdot2$DMSO	7.5	8.0	1.3	2.0	10.1[b]	10.8[b]	38.1	40.0

[a] Analytical data are the results of microanalyses by A. Bernhardt, Germany. [b] Sulfur analyses.

TABLE II
CONDUCTIVITY VALUES FOR INDIUM(III) AND THALLIUM(III) COMPOUNDS Λ_M (OHM^{-1} CM.^{2})[a]

	$C_6H_5NO_2$	CH_3NO_2	CH_3CN
$TlCl_3$	...	...	75 (6.76)
	...	...	50 (1.35)
$TlCl_3\cdot3\gamma$-pic	...	68 (1.41)	...
$TlCl_3\cdot2$py[b]	...	...	97[c]
$InCl_3$	...	...	27 (4.26)
$InCl_3\cdot1.5$bipy	...	28 (0.88)	...
$InCl_3\cdot1.5$phen$\cdot CH_3CN$	...	28 (1.24)	...
$InCl_3\cdot3\gamma$-pic	9 (1.28)	...	...
$InCl_3\cdot3$pyCN	...	46 (0.79)	49 (1.24)
$InCl_3\cdot3$py	11 (1.15)	...	...
$InCl_3\cdot3$DMSO	...	33 (0.89)	...

[a] Concentrations in parentheses ($\times10^{-3}$ M). [b] Conductivity values of $TlI_3\cdot2$py in acetone at concentrations in the range 0.64×10^{-3} to 10.24×10^{-3} M lay in the range 90–130 ohm^{-1} cm.^{2}. [c] F. A. Cotton, B. F. G. Johnson, and R. M. Wing, *Inorg. Chem.*, **4**, 502 (1965).

electrolytes.[6,14] Methyl cyanide solutions of thallium(III) chloride in particular have appreciable molar conductivities and this points to the possible formation of a species such as $[TlCl_2(CH_3CN)_4]TlCl_4$. This species can evidently only be stable in solution since removal of solvent leaves unchanged halide.

For the complexes of thallium(III) halides with monodentate ligands the picture is rather less clear-cut. Thus, although the complexes $TlCl_3\cdot2$DMSO, $TlCl_3\cdot2(C_6H_5)_3PO$, and $TlBr_3\cdot2(C_6H_5)_3PO$ are believed[1] to be nonionic, they have significant conductivities in methyl cyanide (*ca.* 20–44 ohm^{-1} cm.^{2}) and this may arise from an anionic dissociation of the type

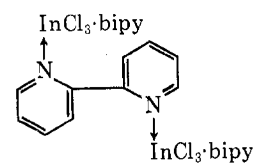
$$TlX_3\cdot2L + CH_3CN \rightleftharpoons TlX_2(CH_3CN)\cdot2L^+ + X^-$$

Such behavior is often observed in polar solvents.

The general insolubility of $TlBr_3\cdot2$py, $TlBr_3\cdot2\gamma$-pic, and $TlBr_3\cdot2$DMSO in polar solvents also suggests a nonionic structure; a dimeric structure with halogen bridging is very likely.

The conductivity values for the indium(III) chloride complexes are somewhat low for both monomer and dimer ionic formulations. In the latter case, the possibilities $[InX_2L_4]^+[InX_4L_2]^-$ and $[InL_6]^{3+}[InCl_6]^{3-}$ arise. The $InCl_6^{3-}$ species, however, does not appear to be stable although $InCl_4^-$ and $InCl_5^{2-}$ are known.[15,16] In view of the low values we tend to favor the nonionic six-coordinate species $InCl_3\cdot3L$, for L = pyridine, γ-picoline, 4-cyanopyridine, or DMSO.

Although the bipyridyl complex could have either of the two ionic structures suggested above, it could also be nonionic with a bridging bipyridyl molecule.



Such structures have recently been proposed for the analogous nonionic bipyridyl complexes of titanium(III) halides.[17] In the case of the 1,10-phenantholine complex, a simple nonionic structure is not obvious and the molecule of methyl cyanide may well be present as a coordinated ligand rather than as a molecule of crystallization. We find no evidence for the tris-bipyridyl and 1,10-phenantholine complexes which have previously been reported.[11]

Infrared Spectra.—The infrared spectra of the above complexes were measured between 4000 and 265 cm.$^{-1}$. It is convenient to discuss the results obtained in the regions 4000–400 and 400–265 cm.$^{-1}$, respectively. In the former region, only bands associated with the ligand vibrations were observed, whereas below 400 cm.$^{-1}$ metal–ligand vibrations are expected.

(a) **4000–400 Cm.$^{-1}$.**—The pyridine and γ-picoline complexes $InCl_3\cdot3$py, $InCl_3\cdot3\gamma$-pic, and $TlCl_3\cdot3\gamma$-pic had infrared spectra typical of coordinated ligand and were in fact very similar to the analogous titanium(III) bromide complexes $TiBr_3\cdot3$py and $TiBr_3\cdot3\gamma$-pic.[17b]

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Table III
Far-Infrared Spectra of Indium(III) and Thallium(III) Compounds (400–265 cm.$^{-1}$)

Compound	Ligand vibrations	ν(M–X)	ν(M–L)
$InCl_3 \cdot 3DMSO$	347 w, 339 w, 315 w	285 br	442 m
$InCl_3 \cdot 3py$	. . .	300 w, 292 sh, 284 s, br, 272 s, br	<200
$InCl_3 \cdot 3\gamma$-pic	. . .	306 w, 292 sh, 282 s, br, *ca.* 272 s, br	<200
$InCl_3 \cdot 3pyCN$	. . .	306 sh, *ca.* 290 sh	<200
$InCl_3 \cdot 1.5bipy$	. . .	306 sh, *ca.* 294 sh, 284 s, br	<200
$InCl_3 \cdot 1.5phen \cdot CH_3CN$	. . .	306 sh, *ca.* 294 sh, *ca.* 283 s, br	
$TlCl_3 \cdot 2DMSO$	331 m, *ca.* 304 w	. . .	405 ms
$TlBr_3 \cdot 2DMSO$	331 m, *ca.* 303 w	. . .	405 ms
$TlCl_3 \cdot 2py$	. . .	*ca.* 283 sh, 274 s, br	<200
$TlBr_3 \cdot 2py$	. . .	. . .	<200
$TlCl_3 \cdot 3\gamma$-pic	. . .	*ca.* 283 w, *ca.* 263, s, br	<200
$TlBr_3 \cdot 2\gamma$-pic	. . .	. . .	<200
$(C_2H_5)_4NTlCl_4$	. . .	305 sh, *ca.* 292 s, br, 283 s, br	. . .
$(C_2H_5)_4NTlCl_3Br$	. . .	306 sh, 294 s, br, 274 sh	. . .
$(C_6H_5)_4AsTlCl_4$	351 ms, 344 ms	307 s, *ca.* 294 s, br, 284 sh	. . .
$(C_6H_5)_4AsCl$	362 s, 345 s	. . .	. . .

In the case of the morpholine complexes $InCl_3 \cdot 3$morp and $TlCl_3 \cdot 2$morp the ligand asymmetric C–O–C stretching vibration was observed as a strong band at 1095 cm.$^{-1}$ identical with that in the free ligand.[18] The N–H stretching vibration, at 3320 cm.$^{-1}$ in morpholine, was lowered to 3150 cm.$^{-1}$ in the complexes, suggesting that the ligand was nitrogen- rather than oxygen-bonded. The bipyridyl and 1,10-phenanthroline complexes $InCl_3 \cdot 1.5$bipy and $InCl_3 \cdot 1.5phen \cdot CH_3CN$ had bands split in the 1650–1500 and 900–700 cm.$^{-1}$ regions, typical of coordinated bipyridyl and 1,10-phenanthroline.[19,20]

With $InCl_3 \cdot 3$pyCN a weak sharp band at 2240 cm.$^{-1}$ was presumably associated with the C≡N stretching vibration of 4-cyanopyridine and appeared to be little changed from the free ligand. The known instability of nitrile complexes of indium and thallium suggests that in this complex the ligand is bonded *via* the nitrogen atom of the pyridine ring rather than through the C≡N group.

The dimethyl sulfoxide complexes $InCl_3 \cdot 3DMSO$ and $TlBr_3 \cdot 2DMSO$ show a characteristic decrease[21] in the S=O stretching frequency compared with free dimethyl sulfoxide (at 1102 cm.$^{-1}$ in the liquid).[22] In $InCl_3 \cdot 3DMSO$ $\nu_{S=O}$ occurred as a triplet centered at about 950 cm.$^{-1}$ (962, 950, and 932 cm.$^{-1}$), whereas in $TlBr_3 \cdot 2DMSO$ it was observed as a single strong band at 930 cm.$^{-1}$ (compared with $TlCl_3 \cdot 2DMSO$ at 930 cm.$^{-1}$).

(b) **400–265 Cm.$^{-1}$.**—The infrared absorption bands of a number of the complexes in this region are listed in Table III and typical spectra are shown in Figures 1 and 2.

Delwaulle[23] reported four Raman bands consistent with tetrahedral $TlBr_4^-$. Very recently the Raman spectra of several thallium(III) species have been

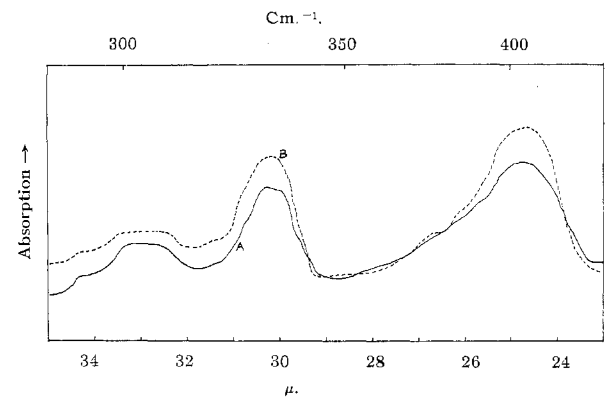

Figure 1.—Far-infrared spectra of (A) $TlCl_3 \cdot 2DMSO$ and (B) $TlBr_3 \cdot 2DMSO$.

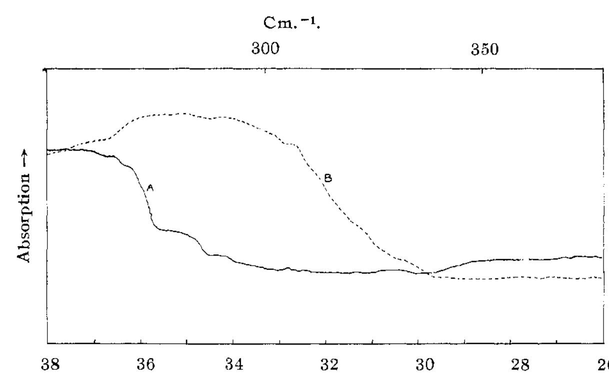

Figure 2.—Far-infrared spectra of (A) $TlCl_3 \cdot 2py$ and (B) $(C_2H_5)_4NTlCl_4$.

determined[24] in aqueous solution, and it was concluded that the structure of the ion $TlCl_4^-$ could be either tetrahedral or square-planar.

For tetrahedral MX_4^{n-} Clark and Dunn[25] have observed that the ratio ν(M–Br)/ν(M–Cl) is *ca.* 0.77 for first-row transition metals. Applying this ratio to the nontransition metal ions GaX_4^- and InX_4^-, values of 0.72 and 0.69 are obtained,[26,27] respectively. The Ra-

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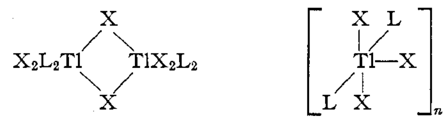
man spectrum[23] of $TlBr_4^-$ has shown that the Raman- and infrared-active thallium–bromide stretching vibration $\nu_3(F_2)$ occurs at 209 cm.$^{-1}$, so that for $TlCl_4^-$, assuming ν(Tl–Br)/ν(Tl–Cl) *ca.* 0.7, the triply-degenerate ν_3 vibration should occur at about 300 cm.$^{-1}$. For the salts $(C_2H_5)_4NTlCl_4$ and $(C_6H_5)_4AsTlCl_4$ we observed a very broad band centered at about (292 cm.$^{-1}$) which appeared to be resolved into at least a triplet. This splitting in the solid state is not unexpected if the symmetry in the crystal is much lower than T_d. The mixed halide ion $TlCl_3Br^-$ has a very similar spectrum to $TlCl_4^-$. On changing from $TlCl_4^-$ to $TlCl_3Br^-$ the symmetry is lowered from T_d to C_{3v} and hence $F_2 \rightarrow A_1 + E$. Any further lowering in symmetry should result in a splitting of the E mode. For $(C_2H_5)_4NTlCl_3Br$ we observed a shoulder and a very broad band envelope, which was probably at least a doublet. The similarity of the spectra of $TlCl_4^-$ and $TlCl_3Br^-$ is consistent with a low site symmetry in each case. This characteristic splitting of ν_3 is also observed with other tetrahedral species, *e.g.*, $TiCl_4$ and $TiCl_3Br$.[28]

The dimethyl sulfoxide complexes $TlCl_3 \cdot 2DMSO$ and $TlBr_3 \cdot 2DMSO$ had a strong band 400 cm.$^{-1}$ which we have assigned to the thallium–oxygen stretching vibration. This is not unreasonable since this band is present in both chloride and bromide. Weak bands at 331 and 304 cm.$^{-1}$ are assigned to the vibrations ν_{23} and ν_{12} which occur[22] in the free ligand at 333 and 308 cm.$^{-1}$. The latter band is only observed in the Raman spectrum of dimethyl sulfoxide but clearly becomes infrared-active on coordination. There was no evidence for the ν(Tl–X) modes.

Only in the case of the thallium(III) chloride–pyridine and γ-picoline complexes was γ(Tl–X) observed above 265 cm.$^{-1}$. For the analogous bromide complexes γ(Tl–Br) probably occurs below 200 cm.$^{-1}$ and vibrations associated with ν(Tl–N) expected[29] in the region 270–200 cm.$^{-1}$ are clearly not observed here.

Clearly the absence of bands associated with ν(Tl–X) modes for the dimethyl sulfoxide complexes $TlX_3 \cdot 2DMSO$ suggests that these compounds have a different structure from the analogous pyridine and α-picoline complexes. The former complexes have been suggested[1] to be examples of the five-coordinate thallium(III) and an investigation of the Raman spectra of these complexes is now in progress[30] in an attempt to resolve this ambiguity. The absence of bands associated with the TlX_4^- ion would suggest that structures of the type $[TlL_4X_2][TlX_4]$ are not present. We are unable to distinguish between polymeric structures of the types I and II. The dimethyl sulfoxide



I II

complexes $TlX_3 \cdot 2DMSO$ may, of course, be of types I or II rather than five-coordinate monomers. The general insolubility of the bromide complexes provides evidence for this.

The spectra of the indium(III) chloride complexes are very similar and all show a generally broad complex band below *ca.* 300 cm.$^{-1}$. Its proximity to the limit of the range of our measurements precludes a more detailed analysis. The absence of a band at 337 cm.$^{-1}$ associated with $InCl_4^-$ excludes this ion from any formulation. The most likely structure is octahedral, monomeric $InCl_3 \cdot 3L$.

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