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METAL–HALOGEN STRETCHING VIBRATIONS IN COORDINATION COMPLEXES OF GALLIUM, INDIUM AND THALLIUM

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CONTENTS

ABBREVIATIONS

Py = pyridine
γ-pic = γ-picoline
bipy = 2,2′-bipyridyl
terpy = 2,2′,2″-terpyridyl
phen = 1,10-phenanthroline
pyz = pyrazine
pn = 1,3-diamino-propane
dmso = dimethylsulfoxide
diphos = 1,2-bis(diphenylphosphino)ethane.

A. INTRODUCTION

A considerable amount of data has recently been accumulated on metal–halogen stretching vibrations ν(M–X) in coordination complexes of gallium(III), indium(III) and thallium(III) halides. Moreover, in the absence of X-ray structural determinations, the complementary techniques of far-infrared and Raman spectroscopy can be extremely useful in providing stereochemical assignments for

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TABLE 1

ν(Ga-X) VIBRATIONAL FREQUENCIES FOR GALLIUM COMPLEXES

Complex type	*L*	*ν(Ga-X) Frequency or Range (cm^{-1})* X = Cl	X = Br	X = I	*References*
GaX_4^-		346, 386 (R)*	210, 278 (R)	145, 222 (R)	2, 3, 4, 29
		380	275	226	7
		373			19
		372			30
GaX_6^{3-}	X = F				
	464				25
GaX_3L	Me_3N, Et_3N, Py	392–385, 364–357	305–290, 220–216	248, 162	15
	Et_2O	412, 361	308–304, 230	252, 165	15, 16
	Me_2S, Et_2S	409–398, 359–356	303–294, 235–230	248–242, 165–158	15, 16
	tetrahydrofuran	418 358			16
	tetrahydrothiophen	402 355			16
	PR_3(R = H, Me, Ph, *p*-Tolyl, *p*-Anisyl)	394–373, 360–334	292–268, 238–232	246–237, 155–150	7, 17
	$\frac{1}{2}(Ph_2PCH_2CH_2PPh_2)$	394, 390, 354	295, 237	257, 254, 234	7
GaX_3L_2	Me_3N	365			20
		363, 307 (R)			20
	$(CH_3)_2SO$	370			31
$GaX_2L_4^+$	$\frac{1}{2}$(bipy)	301–306	220, 209		28

*(R) = Raman measurement.

TABLE 2

ν(In-X) VIBRATIONAL FREQUENCIES FOR INDIUM COMPLEXES

Complex type	*L*	*ν(In-X) Frequency or Range (cm^{-1})* X = Cl	X = Br	X = I	*References*
InX_4^-		321, 337 (R)	197, 239 (R)	139, 185 (R)	5, 6, 4
InX_5^{2-}		295 (R)			5
		267, 281			19
		272, 282, 295			20
InX_6^{3-}	X = F				
	446	175, 275 (R)			25, 5
		250			12
		193, 277 (R)			12
		248			13
InX_3L_2	Me_3N	290, 323	202, 243	188, 219	21
		290, 325 (R)	201, 241 (R)	161, 180 (R)	21
	Ph_3P	319	233, 244	161, 190	23
	Ph_3PO	342	239	190	23
	$(CH_3)_2SO$			198, 195	23
	Et_2O	317 (R)			24
	$\frac{1}{2}(Ph_2PCH_2CH_2PPh_2)$		219, 232	177, 188	23

TABLE 2 continued

Complex type	*L*	*ν(In-X) Frequency or Range (cm^{-1})*			*References*
		X = Cl	*X = Br*	*X = I*	
InX_3L_3	Py	273, 302	183, 200	138, 146	23
		239, 274			26
	γ-pic	231, 248, 272			26
	3-cyano-py	235, 271, 299			26
	$(CH_3)_2SO$	259, 276, 288	176, 218, 240		23
	½(pyrazine)	260, 287, 310			26
$InX_4L_2^-$	py	255			9
	½(bipy)	239, 252, 265, 282			26
$In_2X_6L_6$*	½(bipy)	229, 249, 268, 281,			26
		301,			26
		251, 270, 284, 300	191, 200, 208	117, 134	27

* For possible structures see Reference 26.

TABLE 3

ν(Tl-X) VIBRATIONAL FREQUENCIES FOR TETRAHALOTHALLATES

Complex type	*Cation*	*ν(Tl-X) Frequency (cm^{-1})*		*References*
		$\nu_1(a_1)$	$\nu_3(t_2)$	
$TlCl_4^-$	Ph_4As^+	312 (R)	296 (R)	8
		306	278, 296	8, 11
			292, 306	13
			281, 293, 305	32
	$(C_2H_5)_4N^+$		285, 295	9
		312 (R)	290 (R)	13
			293	13
	$(CH_3)_4N^+$		302	13
	$(C_2H_5)_2N^+H_2$		270, 300	9
$TlCl_3Br^-$	$(C_2H_5)_4N^+$	204	292	9
$TlCl_3I^-$	$(C_2H_5)_4N^+$	164	282, 291, 302	9
	$(C_4H_9)_4N^+$		286	9
$TlBr_4^-$	In acid solution	190 (R)	209 (R)	10
	Tl^+	182 (R)	198 (R)	11
		186	200	11
	Cs^+	184 (R)	201 (R)	11
		186	205	11
$TlBr_4^-$	K^+	182 (R)	196 (R)	11
			203	11
	$(CH_3)_4N^+$		186, 199, 207	13
	$(C_2H_5)_4N^+$	192 (R)	183 (R)	13
			173, 185	13
	Ph_4As^+		196	13
TlI_4^-	$(C_4H_9)_4N^+$	133 (R)	156 (R)	11
			152	11
	$(C_2H_5)_4N^+$	130 (R)	149 (R)	13
			146	13
	Ph_4As^+		148	13

TABLE 4

ν(Tl-X) VIBRATIONAL FREQUENCIES IN THALLIUM COMPLEXES

Complex type	L	ν(Tl-X) Frequency or range (cm^{-1}) X = Cl	X = Br	X = I	References
TlX_6^{3-}		262, 280 (R)	153, 161 (R)		8, 11
		294	190, 195		8, 11
		192, 264 (R)			12
		230			12
TlX_3L	Py			136, 155, 168, 176	9
TlX_3L_2	$(CH_3)_2SO$	298, 309			9
		293, 314 (R)			9
	Py	224, 253, 268			9
		247, 256, 272, 281			32
	½(bipy)	223, 230, 243, 272,			9
		292			9
		231, 249, 279, 290 295			32
	½(phen)	234, 246, 257, 267 292			9
		249, 258, 272, 292, 296, 299			32
TlX_3L_3	γ-pic	235, 255			9
	⅓ (terpy)	248, 285			9
	½ (pyrazine)	229, 274, 290			9
$TlX_2L_3^+$	⅓ (terpy)	270, 277, 308, 318		138, 150, 186	9
$TlX_4L_2^-$	½(bipy)	212, 235, 267	< 200		9
	½(phen)	224, 236, 265			9

complexes containing metal–halogen bonds.[1] The purpose of this review is to summarise the stereochemical information obtained to date from studies of ν(M–X) modes and to discuss the factors affecting ν(M–X) frequencies in gallium, indium and thallium complexes.

Far-infrared and Raman data for ν(M–X) in gallium and indium complexes are tabulated in Tables 1 and 2 respectively. Several detailed studies have recently appeared on the vibrational spectra of tetrahedral halothallate complexes and this data is summarized in Table 3. Results for other thallium(III) species are given in Table 4.

In the following discussion complexes are grouped together according to the coordination number of the metal ion in order to emphasize the dependence of ν(M–X) frequencies on the coordination number and mass of the metal ion as well as on the stereochemistry of the complex.

B. FOUR COORDINATE COMPLEXES

(i) Anionic complexes

Surprisingly little information has been obtained for MX_4^- ions (M = Ga, In; X = Cl, Br, I) although the corresponding tetrahalothallates have been extensively studied. In aqueous solution and in organic extracts from aqueous solution the ions MX_4^- (M = Ga, In) are tetrahedral, both ν(M–X) modes ν_1, and ν_3 being readily identified in the Raman[2–6]. For solid tetrahalogallates ν_3 appears in the far-infrared at similar frequencies to those found in the Raman[7,19]. In nitromethane solutions of several tetrachlorogallates however ν_3 for $GaCl_4^-$ is at 372 cm^{-1}, somewhat lower than in the solid state[7,30]. With cations capable of strong hydrogen bonding to the $GaCl_4^-$ ion, ν_3 may be split into two or three components, suggestive of a lowering[30] of symmetry from Td to C_{3v} or C_{2v}. No solid InX_4^- complexes have yet been investigated.

TlX_4^- species are also tetrahedral both in solution and in the solid state[8–13], an earlier report that $TlBr_4^-$ was square planar[14] having been disproved[11]. For solid TlX_4^- salts considerable splitting of the t_2 mode is observed especially when a cation capable of strong hydrogen bonding is present[9]. Although the presence of three bands in the ν_3 region may indicate complete lifting of the degeneracy of this mode, Spiro[11] has suggested that the highest of these bands may be due to the Raman active a_1 mode. For $TlCl_4^-$ and $TlBr_4^-$, ν_3 varies considerably with cation but no regular trend with increasing cation size is apparent. Some ν(Tl–X) frequencies in C_{3v} ions of the type $TlCl_3X^-$ (X = Br, I) have also been measured[9].

Comparison of the ν_3 frequencies of the MCl_4^- ions as obtained from the Raman ($GaCl_4^-$ 386 cm^{-1}; $InCl_4^-$ 337 cm^{-1}; $TlCl_4^-$ 296 cm^{-1}) shows the marked effect of increasing mass on the ν(M–X) frequency. Similar trends exist for the anionic bromide and iodide species.

(ii) Neutral complexes

Extensive far-infrared studies have been made of gallium complexes of the type GaX_3L[7,15,16,17]. These have monomeric pseudotetrahedral C_{3v} structures in the solid state and in solution in non-polar solvents. Two ν(Ga–X) modes appear in the infrared, one (e) at higher frequency and the other (a_1) at lower frequency than the t_2 mode of the corresponding tetrahedral anion[7,15,17]. ν(Ga–X) varies slightly with the mass of the donor ligand, being highest in complexes with oxygen donors[15,16] and lowest in phosphine complexes[7,17]. This seems unlikely to be due to coupling between metal-donor and metal–halogen vibrations since the effect is in the wrong direction if ν(Ga–O) is above 400 cm^{-1} and ν(Ga–P) below 350 cm^{-1} as expected[7,15,17]. The effect is probably a simple mass effect inasmuch as the heavy atom phosphorus increases the effective mass of the gallium more than the light donor oxygen and hence reduces the ν(Ga–X) frequency. The ratios $\frac{\nu(\text{Ga–Br})}{\nu(\text{Ga–Cl})}$ and $\frac{\nu(\text{Ga–I})}{\nu(\text{Ga–Cl})}$ are approximately constant at 0.75 and 0.63 respectively for these compounds[7,17].

The dimeric compounds Ga_2X_6(diphos) (X = Cl, Br) show two ν(Ga–X) modes, suggesting a structure in which the diphosphine bridges two GaX_3 units, each gallium atom having C_{3v} symmetry[7]. Ga_2I_6(diphos) on the other hand shows three strong bands in the metal–iodine stretching region, one of which resembles the t_2 absorption of GaI_4^-. The ionic structure $[GaI_2(\text{diphos})][GaI_4]$ is suggested[7].

No data have yet been reported for neutral indium compounds InX_3L; indeed few of these have been prepared[18]. Four strong bands have been reported in the range 176–130 cm^{-1} for TlI_3(py) but it seems likely that some of these are due to ν(Tl–N)[9].

C. FIVE COORDINATE COMPLEXES

(i) Anionic complexes

The only five coordinate species for which vibrational data exist is the ion $InCl_5^{2-}$. Woodward and Taylor[5] assigned a Raman line at 295 cm^{-1} to ν_1 of the trigonal bipyramidal ion in aqueous solution. For the solid $[(C_2H_5)_4N]_2[InCl_5]$ two strong absorptions between 267 cm^{-1} and 282 cm^{-1} in the infrared are presumably due to the axial ν_3 and equatorial ν_5 stretching modes[19,20]. A shoulder at 295 cm^{-1} [20] may arise either from a lifting of the degeneracy of the $\nu_5(e')$ mode or from the Raman active $\nu_1(a_1')$. This ion is a genuine five coordinate species rather than a halogen bridged dimer as can be seen from a comparison of ν(In–Cl) frequencies in $InCl_4^-$ (337 cm^{-1}), $InCl^{2}{}_{4}^{-}$ (295 cm^{-1}) and $InCl_6^{3-}$ (275 cm^{-1}). The normal decrease in ν(In–Cl) with increasing coordination number is apparent.

It is interesting to note that although the GaF_6^{3-} ion is well known[25], no chloro species higher than $GaCl^-{}_4$ have yet been characterised and whereas the ions $TlCl_6^{3-}$, $TlBr_6^{3-}$ and TlI_4^- are known, no pentahalothallates are known*.

(ii) Neutral complexes

Several five coordinate gallium and indium complexes of the type MX_3L_2 have recently been characterised. For trigonal bipyramidal molecules of this type three structures are possible I–III. The *trans*-isomer I of D_{3h} symmetry has a single infrared active ν(M–X) mode (e′) and two Raman active modes ($a_1'+e'$) whereas both *cis* isomers II and III (C_{2v} and C_s symmetry) have three infrared and Raman active modes ($2a_1+b_2$ or $2a'+a''$). However there are some problems

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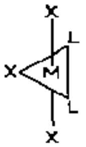
* A brief report of $[(C_2H_5)_4N][TlCl_5]$ has recently appeared. See reference 20.

I



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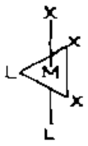

III

in assigning a structure if only infrared or Raman data are available. Thus a molecule with a *trans* structure may give rise to two bands in the infrared due to lifting of the degeneracy of the (e′) mode in the crystal lattice. Also the a_1' Raman active mode may appear weakly in the infrared[21]. Ideally, an assignment should be made using both solid and solution Raman and infrared data. It may also be useful to examine a related compound of known configuration; for example a chelating ligand must give a *cis* configuration if the compound is genuinely five coordinate.

The gallium and indium complexes $MCl_3(Me_3N)_2$ are undoubtedly *trans*[21]. A recent X-ray investigation of $InCl_3(Me_3N)_2$ has confirmed the geometry[22]. A single strong ν(In–Br) mode appears in the infrared of $InBr_3(Me_3N)_2$ suggesting a *trans* configuration but $InI_3(Me_3N)_2$ has a more complex pattern of ν(In–I) bands in the infrared and Raman and may be *cis*[21].

$InCl_3(Ph_3P)_2$, $InX_3(Ph_3PO)_2$ (X = Cl, Br, I) have been assigned *trans* trigonal bipyramidal structures on the basis of a single absorption due to ν(In–X) in the spectra[23]. The Raman spectrum of a melt of $InCl_3\,(Et_2O)_2$ is also consistent with a *trans* structure[24]. *Cis* structures have been assigned to $InX_3(Ph_3P)_2$ (X = Br, I), InX_3(diphos) (X = Br, I) and $InI_3(dmso)_2$ since two or more strong bands due to ν(In–X) were found in the far-infrared[23].

There is now sufficient information available on indium complexes of this type to enable ranges for ν(In–X) to be specified. These are: ν(In–Cl) 290–342 cm^{-1}; ν(In–Br) 201–244 cm^{-1}; ν(In–I) 161–219 cm^{-1}. These results suggest that the 219 cm^{-1} infrared absorption assigned by Beattie[21] to ν(In–I) in $InI_3(Me_3N)_2$ may have a different origin since the absorption is well within the range for ν(In–Br) and it is unlikely that ν(In–I) in a five coordinate complex would appear near ν(Ga–I) in a four coordinate species[7]. It is also interesting to note that all of the chloride complexes investigated appear to be *trans* isomers.

Using the average values for ν(In–X) in each case, the ratios $\frac{\nu(\text{In–Br})}{\nu(\text{In–Cl})}$ and $\frac{\nu(\text{In–I})}{\nu(\text{In–Cl})}$ are 0.71 and 0.60 respectively, considerably less than for the four coordinate gallium complexes.

A full vibrational analysis of $TlCl_3\,(dmso)_2$ suggests a trans D_{3h} configuration although ν(Tl–Cl) appears as a closely spaced doublet at 300 cm^{-1} in the infrared[9]. The compound of stoichiometry $TlCl_3(py)_2$ is unlikely to have a monomeric five coordinate structure since ν(Tl–Cl) occurs in the range 224–268 cm^{-1} where octahedral complexes absorb. Walton[9] suggests a halogen bridged octahedral dimer in the solid state. McWhinnie[32] proposes that in acetone solution the compound exists as the ionic dimer $[TlCl_2(py)_4][TlCl_4]$, ν_3 for $TlCl_4^-$ being readily identified as a strong band at 295 cm^{-1}. TlX_3(bipy) and TlX_3(phen) absorb in the same spectral region as $TlCl_3(py)_2$ and may have similar halogen bridged structures[9]. TlI_3(bipy) on the other hand has only two halogen sensitive bands at 156 cm^{-1} and 140 cm^{-1} and may therefore have a *cis* trigonal bipyramidal structure[9].

D. SIX COORDINATE COMPLEXES

(i) *Anionic complexes*

Only for the fluorides are all three MX_6^{3-} ions known[25]; ν(M–F) shows the usual decrease with mass increase[25].

The $InCl_6^{3-}$ ion has been identified in aqueous solution[5] and in the complexes $[Co(NH_3)_6][InCl_6]$ and $[Co(pn)_3][InCl_6]$[12,13]. Spiro[11] concludes from a detailed examination of the Raman and infrared spectra of $K_3TlCl_6\frac{8}{7}H_2O$ that ν_3 for $TlCl_6^{3-}$ is at 294 cm^{-1}, a value which is difficult to reconcile with the ν_3 frequency of 296 cm^{-1} in $[Ph_4As][TlCl_4]$[11] or with the lower value of ν_3 for the $InCl_6^{3-}$ ion[12,13]. Beattie and co-workers[12] however find ν_3 for $TlCl_6^{3-}$ at 230 cm^{-1} in $[Co(NH_3)_6][TlCl_6]$ so presumably Spiro's compound does not contain the hexachlorothallate ion.

The infrared and Raman spectra of $Rb_3TlBr_6\frac{8}{7}H_2O$ agree with the presence of the $TlBr_6^{3-}$ ion[11]. However the value of ν_3 (195 cm^{-1}) is rather high in this case since $\frac{\nu(\text{Tl–Br})}{\nu(\text{Tl–Cl})} = 0.85$ if Beattie's[12] value for ν_3 of $TlCl_6^{3-}$ is used. This ratio rarely exceed 0.74 for ions of this type[1]. A reinvestigation of both of Spiro's compounds is needed to resolve these anomalies. No other hexahalometallates of this group have been investigated.

(ii) *Neutral complexes*

For MX_3L_3 species *cis* (C_{3v}) or *trans* (C_{2v}) isomers are possible. The latter should exhibit three infrared active ν(M–X) modes ($2a_1+b_1$) and the former two ν(M–X) (a_1+e). Conflicting data have been reported[23,26] for $InCl_3(py)_3$. Walton[26] finds ν(In–Cl) at 274 cm^{-1} and 239 cm^{-1} and assigns a *cis* configuration whereas Adams and co-workers[23] also suggest a *cis* structure but assign ν(In–Cl) to strong bands at 302 cm^{-1}, 273 cm^{-1} and ν(In–N) to the 239 cm^{-1} absorption. Walton (refs. 9, 26) has indicated that in *cis* MX_3L_3 complexes ν(M–X) appears *ca.* 30 cm^{-1} lower than in the *trans* compounds. He concludes[26] that $InCl_3$ (γ-pic)$_3$ and $InCl_3(dmso)_3$ have *cis* octahedral structures whereas $InCl_3$(terpy) and

$InCl_3(pyz)_{1.5}$ have *trans* configurations. Other workers[23] find three strong ν(In–X) absorptions for $InX_3(dmso)_3$ (X = Cl, Br) and suggest *trans* structures.

Some of these ambiguities may arise because in complexes of nitrogen donor ligands, ν(In–N) modes appear in the same spectral region as ν(In–X)[23,27]. Thus it is possible that many of the observed bands are not due to pure metal–halogen vibrations but arise from ν(In–X) coupled with ν(In–N). The use of deuterated ligands may help to resolve some of these apparent anomalies but more detailed work will be necessary before the structures of these complexes can be unequivocally established.

Similar problems arise in the case of the thallium complexes TlX_3L_3. Assignments for ν(Tl–X) in $TlCl_3(pyz)_{1.5}$ and $TlCl_3(\gamma\text{-pic})_3$ agree with *trans* and *cis* configurations respectively (Table 4) but the analogous bromide and iodide complexes were not prepared to establish that thallium–nitrogen vibrations do not occur in the same spectral region[9]. In $TlCl_3$(terpy) only two ν(Tl–Cl) absorptions were found; nevertheless a *trans* structure was preferred[9].

Although many of the results described in this section need corroborating, the trends are sufficiently clear for ν(M–Cl) ranges to be given. These are ν(In–Cl) 312–239 cm^{-1}; ν(Tl–Cl) 290–224 cm^{-1}.

(iii) Other six coordinate complexes

The compounds $InX_3(bipy)_{1.5}$[26,27] are interesting in view of the structural possibilities IV–VI.

$[In(bipy)_3][InX_6]$ $[In(bipy)_2X_2][In(bipy)X_4]$ $In_2(bipy)_3X_6$
IV V VI

IV can be ruled out completely on the basis of the far-infrared spectra since only one ν(In–X) mode is expected for the $InX_6{}^{3-}$ ion whereas at least two modes are found[26,27]. On the basis of the similarity of the spectra of $[Ph_4As][InCl_4(bipy)]$ and $InCl_3(bipy)_{1.5}$ Walton assigns an ionic dimer structure V to the chloride complex with the highest band (301 cm^{-1}) being assigned to the cation $[InCl_2(bipy)_2]^+$ and the four lower absorptions to the four modes $(2a_1+b_1+b_2)$ expected for the C_{2v} cation $[InCl_4(bipy)]^-$. However the lowest absorption is due to ν(In–N) since it also appears in the bromide and iodide spectra[27], and only three ν(In–Br) and two (In–I) absorptions appear in $InBr_3(bipy)_{1.5}$, and $InI_3(bipy)_{1.5}$ respectively[27]. Thus the spectral data cannot be unequivocally interpreted in terms of structure V and the non-ionic, bipyridyl bridged structure VI may be correct. An X-ray determination will be needed to solve this problem. Some assignments have been given for ions of the type $MCl_4L_2{}^-$ [L = ½(2,2'-bipyridyl), ½(1.10-phenanthroline), pyridine]. $[Ph_4As]$ $[InCl_4(py)_2]$ has a single strong band at 255 cm^{-1} assigned to ν(In–Cl) of trans $[InCl_4(py)_2]^-$[9]. $[Ph_4As]$ $[InCl_4(bipy)]$ has already been mentioned in connection with $InCl_3(bipy)_{1.5}$; for $[(C_2H_5)_4N]$ $[TlCl_4L_2]$ three strong ν(Tl–Cl) bands are observed in the infrared, consistent with a *cis* configuration for the anions[9].

There are as yet insufficient data available to allow a valid comparison of the frequency range for MX_3L_3 and $MX_4L_2^-$ but it is obvious that ν(M–Cl) vibrations in these species occur within the same general range 305–230 cm^{-1} (Tables 3 and 4).

Recent work[28] has clearly demonstrated that $GaCl_3(bipy)$ has the structure $[GaCl_2(bipy)_2]$ $[GaCl_4]$ rather than a five coordinate monomer structure. Thus four bands were found between 400 cm^{-1} and 200 cm^{-1}; a strong band at 374 cm^{-1} arises from the t_2 mode of $GaCl_4^-$ while a strong absorption at 305 cm^{-1} was assigned to the ν(Ga–Cl) (e_u) mode expected for a *trans* octahedral $[GaCl_2(bipy)_2]^+$ cation[28]. The remaining two bands are due to ν(Ga–N). Reaction of $GaCl_3(bipy)$ with sodium tetrafluoroborate gave $[GaCl_2(bipy)_2]BF_4$ which had an identical spectrum to $GaCl_3(bipy)$ except that the 374 cm^{-1} absorption was missing, thus providing confirmation of the proposed structure. $GaBr_3(bipy)_2$ by similar reasoning was found to have the structure $[GaBr_2(bipy)_2]Br$ with a *cis* cation[28]. The values for ν(Ga–X) in these compounds are the first reported results for octahedral chloro and bromo gallium(III) complexes.

Some interesting comparisons can now be made of the effect of coordination number on ν(M–Cl) for gallium indium and thallium complexes. Thus comparing $GaCl_3(Me_3N)$[15], $GaCl_3(Me_3N)_2$[21] and $[GaCl_2(bipy)_2]^+$[28], the highest ν(Ga–Cl) frequency in the infrared falls from 392 cm^{-1} to 365 cm^{-1} to 305 cm^{-1} as the coordination number changes from four to six. Similarly comparing $InCl_3(Me_3N)_2$ (ref. 21) and $InCl_3(py)_3$[23], ν(In–Cl) falls 21 cm^{-1} for a unit increase in coordination number. For thallium ν(Tl–Cl) drops from 309 cm^{-1} to 255 cm^{-1} on changing from $TlCl_3$ $(dmso)_2$[9] to $TlCl_3(\gamma\text{-pic})_3$[9]. One other feature is abundantly clear on surveying Tables 2 and 4. Many of the regions of ν(M–X) absorption for indium and thallium complexes of the same coordination number overlap. This is particularly evident for complexes of the type MX_3L_3. If comparisons are to be made, they are most relevant when compounds of the same stoichiometry having the same ligands are compared.

Finally, it is worth noting that no single crystal X-ray data have yet been reported for a gallium(III), indium(III) or thallium(III) halide complex. Without such data, some of the structural assignments mentioned above, are necessarily tentative. Nevertheless it is possible to obtain a composite picture of the structural features of a given compound type provided sufficient information is available on ν(M–X). There can be little doubt for example that the structures of the GaX_3L species deduced from far-infrared results are predominantly correct or that complexes of the type $InCl_3L_2$ are *trans* five coordinate monomers.

Further unequivocal assignments will doubtless be possible when more ν(M–X) data is available.

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