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# A Spectroscopic Investigation of some Complexes of Thallium(I) and Thallium(III) with Nitrogen Donor Ligands

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*Some new vibrational spectroscopic data are given for Tl(chelate)$X_3$ where chelate = 2.2'bipyridyl, 1.10 phenanthroline or di-2-pyridylamine and X = Cl or Br. The new complexes Tl(tripyam)$X_3$ (tripyam = tri-2-pyridylamine, X = Cl or Br) are reported together with a new series of compounds [Tl(chelate)$X_3$. D.M.F.] (chelate = as above or bidentate tri-2-pyridylamine, X = Cl or Br, DMF = dimethyl-formamide). Chemical and spectroscopic reasoning lead to a preference for a polymeric as opposed to a dimeric structure for [Tl(chelate)$X_3$]. New data ($^1$H n.m.r. and i.r.) are reported for [Tl(phen)$_2$]Y (Y = $NO_3^-$ or $ClO_4^-$) and [Tl(bipy)$_2$]$ClO_4$. The stereochemical environment of the thallium(I) cation is considered to be close to ψ tetrahedral.*

## Introduction

A large number of publications have recently been devoted to reports of spectroscopic studies of complexes of the thallium(III) halides.[1] However when the ligand is a molecule such as 2.2'-bipyridyl the structures of the compounds $TlX_3$ chelate remain a matter for speculation, although Walton[2] favours a dimeric or polymeric structure based on six co-ordinate thallium. Although structures such as [Tl(chelate)$_2X_2$][$TlX_4$] or [Tl(chelate)$X_2$]X may be eliminated,[2,3] it is less clear that [Tl(chelate)$_3$][$Tl_2X_9$] need necessarily be inadmissible.[4] In this paper we report some new results for this class of compound together with some observations on the complexes Tl(bipy)$_2$Y and Tl(phen)$_2$Y (bipy = 2,2' bipyridyl, phen 1,10 phenanthroline, Y = $ClO_4^-$, $NO_3^-$) which have been known for many years but not yet investigated in any detail.[4]

## Experimental Section

Infra-red spectra were examined routinely (4000-625 cm$^{-1}$) using a PE 237 grating instrument. Far infra-red spectra were measured for nujol mulls using a PE 225 (650-200 cm$^{-1}$) grating instrument. The compounds were also investigated over the region 400 cm$^{-1}$ - 80 cm$^{-1}$ using a Research and Industrial Instruments Company Fourier spectrometer. Spectra were computed at the University with an Eliot 803 computer.

$^1$H n.m.r. studies were made in dimethyl sulphoxide or methyl cyanide solution using a PE R.10 instrument with T.M.S. as internal reference.

Ultra-violet spectra were obtained by diffuse reflectance (*vs.* Mg.O) with a Unicam SP700 instrument and conductivity data were obtained with a Wayne Kerr bridge for fershly prepared solutions ($\sim 10^{-3}$ *M*).

Raman spectra for two compounds were obtained with a Cary 81 laser instrument (University of Nottingham).

X-ray powder photographs were obtained for Tl(phen)$_2$($NO_3$) and Ag(phen)$_2$($NO_3$) using both copper and silver targets. The silver complex was prepared from stoichiometric proportions of $AgNO_3$ and phen. $H_2O$ in aqueous ethanol.

*Preparations.* The compounds Tl(phen)$X_3$*, Tl(bipy)$X_3$ [5] (X = Cl, Br), Tl(dipyam)$Cl_3$ [3] (dipyam = di-(2-pyridyl)amine) Tl(pyridine)$_2Cl_3$,[5] Tl(bipy)$_2$Y, Tl(phen)$_2$Y (Y = $ClO_4^-$, $NO_3^-$),[6] $Cs_3Tl_2Cl_9$,[7] $Cs_3Tl_2Br_9$ [7] were prepared by the indicated published methods. Physical properties *e.g.* m.p. were in satisfactory agreement with published data and the analytical data (Table I) serve as additional criteria of purity.

*Tri-(2-pyridyl)aminetrichlorothallium(III).* Thallous chloride (.28 g) was suspended in methyl cyanide (10 ml) and oxidised to the soluble thallium(III) chloride with chlorine gas. Excess chlorine was removed by heating and the resulting solution was treated with tri-(2-pyridyl)amine (0.25 g) in ethanol (5 ml). The white crystals which resulted were washed well with ethanol and diethyl ether.

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(1) A. J. Carty, *Co-ordination Chem. Rev.*, *4*, 29, (1969).

(2) R. A. Walton, *Inorg. Chem.*, *7*, 640, (1968).

(3) W. R. McWhinnie, *J. Chem. Soc.* (*A*), 89, (1966).

(4) W. R. Mchinnie and J. D. Miller, *Adv. Inorg. Radiochem.*, *12*, in press (1969).

(*) If the filtrate from a typical preparation of Tl(phen)$Br_3$ was allowed to stand yellowish crystals of a material of stoichiometry $Tl_2$(phen)$_3Br_6$ were deposited (found C, 30.3, H, 2.0, N, 6.7, calculated for $C_{36}H_{24}Br_6N_6Tl_2$ C, 30.3, H, 1.7, N, 5.9%). Six bands assignable as ν(TlBr) were noted (196, 181, 176, 167, 156, 144 cm$^{-1}$) thus suggesting the formulation *cis*[Tl(phen)$_2Br_2$][Tl(phen)$Br_4$] similar products being well established in iridum chemistry. Attempts to prepare the chloride analogue resulted in materials with analytical data intermediate between those for Tl(bipy)$Cl_3$ and $Tl_2$(bipy)$_3Cl_6$. We are hesitant to discuss the above bromide in more detail in the absence of an authentic specimen of the chloride.

(5) F. A. Cotton, B. F. G. Johnson, and R. M. Wing, *Inorg. Chem.*, *4*, 502, (1965).

(6) F. Ya. Kul'ba, V. E. Mironov and L. A. Anan'eva, *Zh. Neorgan. Khim.*, *8*, 2323 and 2326 (1963).

(7) J. H. Pratt, Z. anorg. Chem., *9*, 19 (1895).

**Table I.** Analytical Data for Complexes of Thallium(I) and Thallium(III)

| Complex | Found C | Found H | Found N | Required C | Required H | Required N | $\Lambda_M$ [a] | ν(CO) |
|---|---|---|---|---|---|---|---|---|
| $Tl(bipy)Cl_3$ | 25.4 | 1.7 | 6.0 | 25.65 | 1.7 | 6.0 | — | — |
| $Tl(bipy)Br_3$ | 20.5 | 1.3 | 4.3 | 20.0 | 1.3 | 4.7 | — | — |
| $Tl(bipy)Cl_3 . DMF$ | 29.0 | 2.8 | 8.0 | 29.0 | 2.8 | 7.8 | 32 | 1640 |
| $Tl(bipy)Br_3 . DMF$ | 20.5 | 1.6 | 6.0 | 23.0 | 2.2 | 6.2 | 38 | 1642 |
| $Tl(phen)Cl_3$ | 29.5 | 1.8 | 5.6 | 29.4 | 1.6 | 5.7 | — | — |
| $Tl(phen)Br_3$ | 23.1 | 1.9 | 4.9 | 23.0 | 1.3 | 4.5 | — | — |
| $Tl(phen)Cl_3 . DMF$ | 30.8 | 2.6 | 7.5 | 31.9 | 2.6 | 7.4 | 26 | 1630 |
| $Tl(phen)Br_3 . DMF$ | 25.8 | 2.5 | 5.7 | 25.8 | 2.2 | 6.0 |  | 1632 |
| $Tl(dipyam)Cl_3$ | 24.6 | 1.9 | 8.9 | 24.9 | 1.9 | 8.7 | — | — |
| $Tl(dipyam)Cl_3 . DMF$ | 27.7 | 2.7 | 10.1 | 28.1 | 2.8 | 10.1 | 31 | 1650 |
| $Tl(tripyam)Cl_3$ | 32.6 | 2.3 | 10.5 | 32.2 | 2.1 | 10.0 | — | — |
| $Tl(tripyam)Br_3$ | 25.0 | 1.9 | 8.0 | 26.0 | 1.7 | 8.1 | — | — |
| $Tl(tripyam)Cl_3 . DMF$ | 34.2 | 3.2 | 11.1 | 34.2 | 3.0 | 11.1 | — | 1640 |
| $Tl(pyridine)_2Cl_3$ | 25.9 | 2.3 | 5.9 | 25.5 | 2.1 | 6.0 | — | — |
| $Tl(bipy)_2ClO_4$ | 39.1 | 2.6 | 9.4 | 39.7 | 2.6 | 9.1 | — | — |
| $Tl(phen)_2ClO_4$ | 43.4 | 2.4 | 8.5 | 43.4 | 2.4 | 8.4 | — | — |
| $Tl(phen)_2NO_3$ | 44.7 | 2.2 | 10.7 | 46.0 | 2.6 | 11.2 | — | — |

[a] $10^{-3}$ *M* in DMF. The small, but not negigible, values of $\Lambda_M$ indicate further solvolysis of the complexes [$Tl(chelate)X_3 . DMF$] in solution.

**Table II.** $^1H$ n.m.r. Spectrum of $Tl(phen)_2^+$ in DMSO

|  | Chemical shifts (Hz) from TMS |  |  |  |
|---|---|---|---|---|
|  | 2 and 9 | 3 and 8 | 4 and 7 | 5 and 6 |
| $Tl(phen)_2NO_3$ | 551 | 472 | 514 | 483 |
| $Tl(phen)_2ClO_4$ | 552 | 471 | 516 | 483 |

|  | Measured Coupling Constants (Hz) |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  | $J_{2.4}$ | $J_{2.3}$ | $J_{3.4}$ | $J_{3.2}$ | $J_{4.3}$ | $J_{4.2}$ |
| $Tl(phen)_2NO_3$ | 1.8 | 4.4 | 8.4 | 2.0 | 8.5 | 3.5 |
| $Tl(phen)_2ClO_4$ | 1.8 | 4.3 | 8.4 | 2.0 | 8.4 | 3.6 |
| Free 1,10 phenanthroline | 1.8 | 4.3 | 8.1 |  |  |  |

$^1H$ n.m.r. Spectrum of $Tl(tripyam)Br_3$ in $CH_3CN$

|  | Chemical shifts (Hz) from TMS |  |  |  |
|---|---|---|---|---|
| Protons | 2 | 3 | 4 | 5 |
| $Tl(tripyam)Br_3$ | 521 | 451 | 486 | 415 |
| tri—(2—pyridyl)amine | 426 (a) |  | 465 (b) | 504 (c) |

*Tri-(2-pyridyl)aminetribromothallium(III).* A similar procedure to that above was employed except that the resulting solution of thallic bromide was treated with tri-(2-pyridyl)-amine dissolved in methyl cyanide. The product was recrystallised from ethanol-acetone (1: 1).

*Preparation of Complexes with Dimethyl formamide.* [Tl(chelate) . DMF . $X_3$]. In a typical experiment $Tl(bipy)Cl_3$ (0.5 g) was added to a small amount of pure dry dimethyl formamide. The mixture was warmed until the complex dissolved. The solution was then cooled on an ice bath when fine white crystals separated. The complex was washed with ethanol, then diethyl ether and dried *in vacuo.*

$Tl(phen)Cl_3DMF$, $Tl(dipyam)Cl_3DMF$, $Tl(tripyam)Cl_3DMF$ were prepared by the same method but $Tl(bipy)Br_3 . DMF$ required the addition of ether to the cold DMF solution to induce precipitation.

## Results

Some $^1H$ n.m.r. data and infra-red spectra are tabulated in Tables II and III respectively. We have noted that for three complexes $Tl(pyridine)_2Cl_3$, $Tl(bipy)Cl_3$ and $Tl(phen)Cl_3$ band positions of thallium chlorine stretching vibrations recently reported by Walton[2] are not in particularly good agreement with those reported by McWhinnie.[3] We have therefore carefully measured these spectra on two instruments and find our results to be in better agreement with those of McWhinnie, except that some slight shoulders are not reproduced.

## Discussion

The infra-red spectra of $Tl(chelate)X_3$ confirm the previously held views[2,3] that the compounds have similar solid state structures.

The solution behaviour of $Tl(chelate)X_3$ is not simple[2] $Tl(bipy)X_3$ behaves as a weak electrolyte in methyl cyanide and acetone solutions thus making an ionic structure unlikely for the solid state, however a formulation such as [$Tl(bipy)_3$][$Tl_2X_9$][4] does not appear to have been considered. This structure

**Table III.** For Infra-red Spectra (400-80 cm$^{-1}$) of some Shallium Complexes

| Complex | ν(TlX) | δ(TlX) | Other bands |
|---|---|---|---|
| $TlCl_3$ . bipy | 295 (s), 278 (s)<br>250 (s), 233 (s)<br>229 (sh) | 123 (s), 110 (s)<br>87 (s) | 362 (m), 169 (m)<br>153 (m), 136 (m) |
| $TlBr_3$ . bipy | 204 (s), 198 (s)<br>187 (s), 181 (sh) | | 228 (m), 218 (m)<br>162 (m), 151 (m) 139 (m) |
| $TlCl_3$ . bipy . DMF | 296 (m), 284 (s)<br>265 (s), 251 (s)<br>232 (m) | | |
| $TlBr_3$ . bipy . DMF | 199 (s.b), 187 (s) | | 356 (w), 228 (m), 217 (m)<br>162 (w-m), 151 (m) 140 (m) |
| $TlCl_3$ . phen | 295 (s), 273 (s)<br>260 (s), 249 (s) | 120 (s), 104 (sh)<br>97 (s) | 384 (m), 166 (s) |
| Raman shifts | 292 (s), 272 (w)<br>256 (w) | 128 (s), 104 (s)<br>89 (s) | |
| $TlBr_3$ . phen | 204 (s), 190 (s)<br>170 (s), 159 (s) | | 383 (m), 287 (m)<br>240 (m), 107 (m) |
| $TlCl_3$ . phen . DMF | 282 (s), 263 (m)<br>254 (s) | 118 (m), 88 (m) | 385 (s), 345 (m)<br>295 (sh), 170 (m) |
| $TlCl_3$ . 2py | 270 (s), 256 (s),<br>222 (m) | 145 (s), 125 (s)<br>97 (s) | 184 (s), 172 (b) |
| $TlBr_3$, phen . DMF | 193 (s), 180 (s)<br>169 (s) | | 360 (m), 340 (m), 292 (m)<br>240 (w), 137 (m), 104 (w) |
| Raman shifts | 191 (s), 183 (s),<br>167 (s) | | 296 (w), 134 (m), 109 (m) |
| $TlCl_3$ . dipyam | 287 (s), 266 (s)<br>257 (s), 240 (s) | 137 (s), 116 (s) [a]<br>99 (s) | 389 (w), 373 (w), 346 (m),<br>340 (sh), 205 (w), 188 (w) |
| $TlCl_3$ . dipyam . DMF | 279 (s), 253 (s)<br>243 (s) | 130 (w), 115 (s.b) [a] | 386 (m), 372 (s), 360 (s)<br>348 (m), 336 (m), 320 (b)<br>214 (m), 185 (m), 102 (sh) |
| $TlCl_3$ . tripyam | 302 (s), 276 (s)<br>252 (s) | 116-85 (s)<br>poor resolution | 394 (m), 374 (w), 366 (m)<br>224 (m), 207 (w), 160 (m) |
| $TlBr_3$ . tripyam | 207 (s), 199 (s)<br>193 (s) | | 386 (m), 374 (m), 356 (m)<br>341 (m), 244 (m), 223 (m)<br>181 (s) |
| $TlCl_3$ . dipyam . DMF | 277 (s), 261 (s),<br>250 (s) | 122 (s), 116 (s),<br>101 (s) | 383 (m), 366 (m), 355 (m)<br>310 (m), 211 (m), 207 (m)<br>134 (s) |
| $[Tl(phen)_2](NO_3)$ | — | — | 249 (m), 245 (m), 239 (m)<br>119 (m) |
| $[Tl(bipy)_2](ClO_4)$ | — | — | 339 (m), 186 (composite)<br>125 (b) |

[a] Tentative in absence of bromo-complex

could be compatible with the infra-red data (which eliminate cationic species with thallium-chlorine bonds) and also since the solution behaviour of both $[Tl(bipy)_3]^{3+}$ [8] and $[Tl_2Cl_9]^{3-}$ [9] are not simple it follows that the behaviour of solutions of such a complex should be complicated. The ultra-violet spectrum (35.5, 42.0, 49.0 kK) of $Tl(bipy)Cl_3$ is not compatible with that of a species containing $M(bipy)_3^{3+}$ since such an ion would be expected to absorb between 31.0 and 33.0 kK.[4,10] In addition the position of the thallium-chlorine stretching vibrations do not correspond well with those of $Cs_3Tl_2Cl_9$ (Table III) which have been discussed in detail by Beattie *et al.*[11] Thus this ionic structure may be discounted for $Tl(bipy)Cl_3$ and, by analogy, for $Tl(chelate)X_3$.

We have synthesised two new complexes of thallium(III) with the potentially vicinal terdentate ligand tri-(2-pyridyl)amine. The infra-red spectrum (4000-400 cm$^{-1}$) is characteristic of a complex of terdentate tri-(2-pyridyl)amine[12] however the thallium chlorine stretching region is richer than anticipated for a complex of $C_{3v}$ symmetry. We therefore examined the $^1H$ n.m.r. spectrum of $Tl(tripyam)Br_3$ which was sufficiently soluble in methyl cyanide for this purpose. The spectrum (Table II) can only be reconciled with the presence of the terdentate base, we therefore conclude that the observation of three bands assignable as ν(TlX) arise from the splitting of the degenerate E mode in $C_{3v}$ symmetry by crystal field effects.

These conclusions become a little tentative in view of the low, but not negligible, conductivity of $Tl(tripyam)Cl_3$ in both methyl cyanide ($\Lambda_M = 65$) and nitromethane ($\Lambda_M = 33$) which indicate some degree of solvolysis. However it does not seem to be possible to reconcile the stoichiometry and terdentate co-ordination of tri-2-pyridylamine with other than a monomeric structure unless a co-ordination number higher than six is invoked for thallium.

Recrystallisation of $[Tl(tripyam)Cl_3]$ from dimethylformamide (DMF) affords $[Tl(tripyam)Cl_3 . DMF]$, a complex of bidentate tri-2-pyridylamine according

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(8) O. Farver and G. M. Nord, *Acta Chem. Scand.*, *20*, 1429, (1966).
(9) T. G. Spiro, *Inorg. Chem.*, *4*, 731, (1965).
(10) B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nuclear Chem.*, *23*, 207 (1961).
(11) I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc. (A)*, 2765 (1965).
(12) W. R. McWhinnie, G. C. Kulasingam, and J. C. Draper, *J. Chem. Soc. (A)*, 1199 (1966).

to the infra-red data.[12] The DMF is co-ordinated as shown by the shift of ν(CO) (Table I) and also by the considerable differences between [Tl(tripyam)Cl$_3$] and [Tl(tripyam)Cl$_3$ . DMF] in the ν(TlCl) region of the spectrum. Similar DMF complexes may be obtained for [Tl(chelate)X$_3$] (chelate = bipy, phen, dipyam). All the DMF complexes have very similar infra-red spectra in the ν(TlX) region and it is tempting to deduce from this that all have similar structures, the choice being between Figures 1a and 1b.

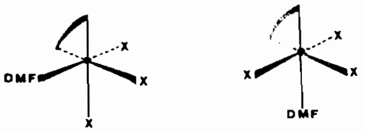


Figure 1.

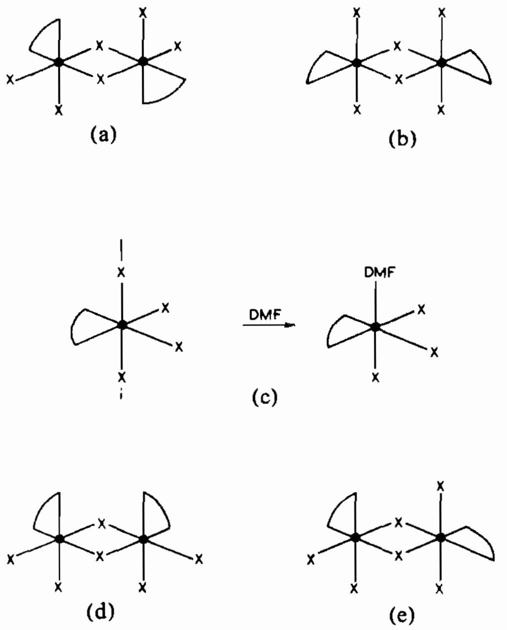
In the case of [Tl(phen)Br$_3$ . DMF] it was possible to obtain Raman data. The co-incidence of each i.r. and Raman band below 400 cm$^{-1}$ indicates the low symmetry of the complex, a result compatible with either 1a or 1b. If the local symmetry of the TlX$_3$ unit were to determine the spectrum in the ν(TlX) region 1b (local symmetry $C_{2v}$) would be favoured over 1a (local symmetry $C_{3v}$) however we see no justification for such arguments and consider that the spectroscopic data are unable to differentiate the possible structures.

It is known that terdentate tri-2-pyridylamine may « open out » to become bidentate, another ligand entering the co-ordination sphere to maintain constant the co-ordination number at the metal ion.[12] Assuming no rearrangement of other ligands within the primary co-ordination sphere to occur during the reaction:

$$[\text{Tl(tripyam)Cl}_3] + \text{DMF} \longrightarrow [\text{Tl(tripyam)Cl}_3\,.\,\text{DMF}]$$

then 1a is the most likely structure for [Tl(tripyam)-Cl$_3$ . DMF] and by the similarity of i.r. spectra, for [Tl(chelate)X$_3$ . DMF]. An alternative view would be that the DMF adds to the complex to increase the co-ordination number at thallium since the highest frequency ν(TlCl) band shifts downwards on complex formation. However this shift merely reflects a lower effective positive charge ion the thallium ion in the DMF complex which may equally well arise from the different ligand environments in the six co-ordinate species we propose above. Also the data for the tri-2-pyridylamine complexes do not lend themselves to this interpretation and it is the similarity of the DMF complexes with [Tl(tripyam)Cl$_3$DMF] upon which the above arguments are based. We can then argue that the *cis* TlX$_3$ configuration might also be characteristic of [Tl(chelate)X$_3$], the DMF complexes probably arising by splitting of halogen bridges. Figure 2 represent some possible dimeric and one possible polymeric structure for Tl(chelate)X$_3$.

Since we were able to isolate only a single product from each reaction with DMF and since co-incidences in the i.r. and Raman for [Tl(phen)Cl$_3$] would appear to eliminate a centrosymmetric structure *e.g.* 2a or 2b, we reach the conclusion that only structure 2c provides a self consistent interpretation of the data in this paper. This conclusion rests upon a number of obvious assumptions and it is our view that these structural problems will only be finally solved by a single crystal X-ray study for a representative compound.



(a) (b) (c) (d) (e)

Figure 2.

Walton[2] in a careful conductivity study of freshly prepared acetone solutions of Tl(pyridine)$_2$Cl$_3$ concluded that the material showed behaviour expected for a weak electrolyte. This would seem to conflict with an earlier suggestion by McWhinnie[3] that infra-red bands characteristic of TlCl$_4^-$ could be observed for such solutions. We have now remeasured the infra-red spectra of 2% and 5% solutions of the complex in dry acetone and are able to confirm the presence of a band in the region associated with $\nu_3$ of TlCl$_4^-$. Our new data obtained interferometrically are 306 (sh), 301, 298 (sh) cm$^{-1}$; the two sets of data are not incompatible since our solutions are many times more concentrated than those used for the conductivity measurements and also they are probably « aged » compared with those of Walton. In our view a polymeric Tl(pyridine)$_2$Cl$_3$ breaks down in acetone solution, probably initially to Tl(pyridine)$_n$-(acetone)$_{3-n}$Cl$_3$, with TlCl$_4^-$ being one of the possible ultimate products.

One recent paper[13] suggested assignments of ν(TlN) at 290 cm$^{-1}$ for [Tl(phen)X$_3$] (x = Cl, Br). We are unable to accept this suggestion and we are hesitant

[13] F. Ya. Kul'ba, N. G. Yaraslavskii, L. V. Konovalov, A. V. Barsukov, and V. E. Mironov, *Russ. J. Inorg. Chem.*, *13*, 79 (1968).

to attempt assignments of bands other than thallium-halogen modes for the compounds we consider here, although the consistency with which unassigned bands appear in the region of 160 cm$^{-1}$ for the phenanthroline and bipyridyl complexes is suggestive; Walton has made a similar point respect to terpyridyl complexes.[2]

*Thallium(I) Complexes.* The ions $[Tl(phen)_2]^+$ and $[Tl(bipy)_2]^+$ have been known for many years yet little is known of their detailed stereochemistry, in particular the stereochemical role (if any) of the 6s electrons is not defined. We have been unable to observe any reaction between the thallium(I) salts and neutral Lewis acids such as $SbCl_5$ and $BF_3$; to the extent that such observations are meaningful low Lewis basicity is indicated for the two cations.

Recently Miller and Prince[14] indicated that $^1H$ n.m.r. spectroscopy could differentiate six-co-ordinate *cis* and *trans* bis phenanthroline complexes, a simple extension of these arguments is relevant here since the three most likely structures for $[Tl(phen)_2]^+$ are given in Figure 3.

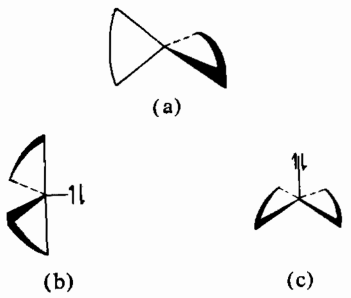


Figure 3.

We believe that 3(c) is unlikely on steric grounds[4] since, with the bizarre exception of $Pd(phen)_2^{2+}$, no *trans* bis (1,10-phenanthroline) complexes have been characterised.[4] Displacement of the thallium atom above the $N_4$ plane would relieve the steric interactions of the ligands but a very large displacement would be necessary to eliminate such interaction. Thus a more probable distortion is that in which the phenanthroline ligands are twisted in opposite directions about their individual $C_2$ axes out of the plane illustrated in 3(c) towards either structure 3(a) or 3(b). Intuitively preference is for 3(b) or some more distorted structure (*e.g.* that in which one ligand lies in the trigonal plane of the pseudo trigonal bipyramid) since this is more in accord with expectation from Nyholm-Gillespie theory. However the surprising fact that the hexahalotellurates(IV) are not significantly distorted[15] indicates that it may be dangerous to assume that electron pairs need be stereochemically active. For 3(b) the two halves of the phenanthroline rings are magnetically non-equivalent and the reasoning of Miller and Prince becomes applicable. The data of Table II show that in dimethyl sulphoxide (DMSO) solution the two halves of the phenanthroline rings are equivalent, in particular the observed coupling constants are in good agreement with published data.[4,14] This result favours structure 3(a), however two other possibilities exist: (a) that the phenanthroline is no longer co-ordinated in DMSO solution, or (b) that there is some form of pseudo-rotation rendering the two ligands equivalent on the n.m.r. time scale. We are unable to eliminate (b) with available data but we feel such a mechanism to be unlikely for the bulky phenanthroline ligands. The observed chemcial shifts for the phenanthroline protons in DMSO solutions of $[Tl(phen)_2]^+$ differ from those reported for the free base thus suggesting that the ligand remains co-ordinated to thallium; $^{203}Tl$ and $^{205}Tl$ n.m.r. data would provide the most satisfactory confirmation of this.

The infra-red spectra of $[Tl(phen)_2]Y$ ($Y = NO_3^-$, $ClO_4^-$) were recently recorded[13] to 200 cm$^{-1}$, but we are unable to accept the assignment of a band close to 250 cm$^{-1}$ as $\nu(TlN)$. Our data show the spectra to be very simple to 80 cm$^{-1}$ and the most probable assignment for $\nu(TlN)$ is close to 120 cm$^{-1}$ (Table III). $[Tl(bipy)_2](ClO_4]$ gave a less satisfactory spectrum but here too a band at 125 cm$^{-1}$ is possibly $\nu(TlN)$. The simplicity of the spectra appear to supplement the tentative conclusions from the n.m.r. work that the stereochemical environment of thallium(I) in these compounds is not greatly distorted. We have observed that the X-ray powder photographs of $[Tl(phen)_2](NO_3)$ and $[Ag(phen)_2](NO_3)$ are sufficiently similar for isomorphism to be possible, but we are unable to be absolutely conclusive on this point.

*Acknowledgment.* We thank Dr. E. R. Clark (University of Aston) for measuring the Raman spectra of $[Tl(phen)Cl_3]$ and $[Tl(phen)Br_3 . DMF]$.

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(14) J. D. Miller and R. H. Prince, *J. Chem. Soc.* (*A*), 519, (1969).

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