Inorganica Chimica Acta, *81* (1984) 109–115

On the Reported Pyridinium Pentachlorothallate(III) and some Related Compounds

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Received June 8, 1983

While $(C_5H_6N)_2TlCl_5$ cannot be prepared in water via the reported procedure it may be obtained in non-aqueous media. Although its low-energy infrared spectrum contains broad peaks and the Raman spectrum is deceptively simple, comparison of these spectra with those of other $TlCl_4^-$, $TlCl_5^{2-}$ and $TlCl_6^{3-}$ derivatives shows that $(C_5H_6N)_2TlCl_5$ contains a genuine pentacoordinate $TlCl_5^{2-}$ species which, however, appears to dissociate in dilute ethanol solution. While the related $(C_5H_6N)_3TlCl_6$ contains a genuine $TlCl_6^{3-}$ ion, $(C_5H_6N)_3Tl_2Cl_9$ probably contains both $TlCl_4^-$ and $TlCl_5^{2-}$ in the solid. Reactions of $(C_5H_6N)_2TlCl_5$ with dimethylsulfoxide, 2,2′-dipyridyl and 1,10-phenanthroline are described.

Introduction

A compound which was formulated as the pyridinium derivative of the pentachlorothallate(III) anion, $(C_5H_6N)_2TlCl_5$, was reported to be obtained by the reaction of pyridine with the product from saturation of a suspension of Tl_2O_3 in water with hydrogen chloride gas [1]. Because of our interest in this compound as a possible stable source of anhydrous $TlCl_3$, we reinvestigated the preparation and found that only the enneachloride, $(C_5H_6N)_3Tl_3Cl_9$, or the tetrachloride, $(C_5H_6N)TlCl_4$, could be obtained, the product depending on the solvent employed for recrystallization [2]. Later, we reported that an iron(III) compound obtained from aqueous solution by a similar HCl-saturation method, and formulated in analogous fashion as $(C_5H_6N)_2FeCl_5$, was similarly the compound $(C_5H_6N)_3Fe_2Cl_9$. In this latter case, however, the enneachloride is a derivative of tetrachloroferrate(III): $2(C_5H_6N)FeCl_4\cdot(C_5H_6N)Cl$ and a compound obtained from ethanol solution which did analyze as $(C_5H_6N)_2FeCl_5$ was also a double salt of $FeCl_4^-$: $(C_5H_6N)FeCl_4\cdot(C_5H_6N)Cl$ [3].

On the other hand, a genuine pentacoordinate $FeCl_5^{2-}$ species was isolated from a non-aqueous medium as the DMTEA salt [4] (DMTEA = N,N′-dimethyl quaternary ammonium dication of 1,4-diazabicyclo[2,2,2]octane) in a similar manner to the isolation of the DMTEA salt of the genuine $TlCl_5^{2-}$ ion [5]. Our studies addressed two questions: whether the elusive pyridinium pentachlorothallate(III) could be obtained from a non-aqueous medium and, if so, whether the compound was best formulated as containing a genuine pentacoordinate anion or whether it was some kind of double salt. This paper reports our investigations into this and some related chlorothallate systems.

Experimental

Chemicals employed were of laboratory reagent quality and commercial ‘absolute’ alcohol was used for syntheses without further purification. Other compounds were dried or recrystallized as necessary according to the procedures outlined by Perrin *et al.* [6]. Microanalyses were carried out by AMDEL Laboratories, Melbourne and thallium analyses were obtained via atomic absorption spectrophotometry. Hydrogen chloride was generated by dropping concentrated sulfuric acid onto concentrated hydrochloric acid, the evolved gas being carried into the reaction vessel via a scrubber of concentrated H_2SO_4 by means of a nitrogen gas stream.

Dipyridinium Pentachlorothallate(III)

(i) Using a system analogous to that employed for the preparation of $(C_5H_6N)_2FeCl_5$ [3], thallic oxide (12 g) was suspended in absolute alcohol (200 cm^3) and HCl gas was passed in for about 12 hours. Most of the Tl_2O_3 dissolved, leaving a small amount of pale solid which was filtered off. Pyridine (5 cm^3)

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TABLE I. X-Ray Powder Diffraction Data for Some Pentachlorothallates.

	$(C_5H_6N)_2TlCl_5$	$(C_9H_8N)_2TlCl_5$	$[(C_2H_5)_4N]_2TlCl_5$
1	7.70w	7.76m	7.87s
2	7.35s	7.03w	7.14w
3	7.08s	6.51m	6.61m
4	6.56vw	6.07s	6.11vw
5	5.42vw	5.10vw	5.61vw
6	5.01s	4.80vw	4.73s
7	4.86s	4.39m	4.39vvw
8	4.25m	3.47vw	4.20s
9	4.02w	3.27m	4.00s
10	3.86vw	3.18vw	3.58w
11	3.72w	2.71w	3.30w
12	3.63vw	2.64vw	3.11s
13	3.27w	2.54vw	2.98s
14	3.08m	2.48w	2.81w
15	2.81w	2.41w	2.67s
16	2.58w	2.32w	2.41w
17	2.49w	2.25vw	2.33s
18	2.46w	2.19vvw	2.23s
19	2.36vw	2.08vvw	2.12s
20	2.24m	2.02vvw	2.04m
21	2.18vw	1.96vvw	2.01w
22	2.08vw		1.82w
23	2.03vw		1.75w
24	1.98vw		1.73w
25	1.94vw		1.653w
26			1.651w
27			1.644m
28			1.635vw

was added to the filtrate and HCl gas passed in again until saturation was reached (approximately 1 hour more). The solution was concentrated on a rotary evaporator and protected with a nitrogen blanket until crystals formed. These were collected by filtration in a nitrogen-filled glovebox and dried by pumping on a vacuum line. Yield *ca.* 80% of a white, moisture-sensitive solid, m.p. 139–140 °C (*Anal.* Calc. for $C_{10}H_{12}N_2Cl_5Tl$: C, 22.17; H, 2.23; N, 5.17; Cl, 32.72; Tl, 37.70%. Found: C, 21.83; H, 2.26; N, 5.48; Cl, 32.7; Tl, 36.78%).

(ii) By a method similar to that reported by Shriver and Wharf [5], Thallous chloride (4.8 g) was suspended in acetonitrile (70 cm^3) and oxidized with Cl_2 gas to yield a clear solution of $TlCl_3$. In a nitrogen-filled glovebox, this solution was mixed with another containing pyridinium chloride (4.62 g) in 70 cm^3 acetonitrile and the white crystalline product, m.p. 140 °C, separated on standing. (Found: C, 22.77; H, 2.35; Cl, 33.6%).

When a 40% excess of pyridinium chloride was employed and the solution evaporated, a white crystalline solid m.p. 125–6 °C is formed which analyzes as tripyridinium hexachlorothallate. (*Anal.* Calc. for $C_{15}H_{18}N_3Cl_6Tl$: C, 27.41; H, 2.76; N, 6.39; Tl, 31.09%. Found: C, 27.03; H, 2.61; N, 6.39; Tl, 29.43%).

Quinolinium Pentachlorothallate(III) (modification of method in ref. 7)

Thallous chloride (2 g) was suspended in water (36 cm^3) and oxidized with chlorine gas until a clear solution was obtained, then 7.2 cm^3 conc. hydrochloric acid was added. Separately, quinoline (2.70 cm^3) was dissolved in *ca.* 18 cm^3 water and 4 cm^3 of conc. hydrochloric acid was added. On mixing the thallic chloride and quinolinium chloride solutions, a turbidity developed after which fine off-white crystals appeared, m.p. 110–110.5 °C. (*Anal.* Calc. for $C_{18}H_{16}N_2Cl_5Tl$: C, 33.67; H, 2.53, Cl 27.61, Tl, 47.9%. Found: C, 33.88; H, 2.69; Cl, 28.1; Tl, 47.6%).

X-ray powder patterns of three pentachlorothallates are given in Table I as a further aid to characterization.

Comparison compounds: $(C_5H_6N)TlCl_4$ [2, 8], R_4NTlCl_4 [9], Cs_2TlCl_5 [10], $(C_5H_6N)_3Tl_2Cl_9$ [7] and $Cs_3Tl_2Cl_9$ [10] were all prepared by the methods described in the literature; as also was $[(C_2H_5)_4N]_2TlCl_5$ [5] except that a mixed solvent system was used ($TlCl_3$ in dry acetonitrile, Et_4NCl in dried CH_2Cl_2) and the tetraalkylammonium salt was freed from water by prior recrystallization from ethanol/ether. If the $(C_2H_5)_4NCl$ is not recrystallized first, then the product of the reaction is $[(C_2H_5)_4N]TlCl_4$, m.p. 256 °C (*Anal.* Calc. for $C_8H_{20}NCl_4Tl$: C, 29.92; H, 6.28; Cl, 27.77; Tl, 42.9%. Found: C, 30.18; H, 6.26; Cl, 27.6; Tl, 43.05%).

$C_9H_8NTlCl_4$ was prepared via the method described in Ref. 2, except that quinoline (*ca.* 7 cm^3) was substituted for pyridine. White crystals, m.p. 150 °C, separate immediately on the addition of the quinoline and a second crop may be obtained by evaporation. These recrystallize unchanged from 2 M HCl. (*Anal.* Calc. for $C_9H_8NCl_4Tl$: C, 22.69; H, 1.69; Cl, 29.8; Tl, 42.90%. Found: C, 22.83; H, 1.70; Cl, 29.5; Tl, 42.47%).

Reactions of Pyridinium Pentachlorothallate(III) with Some Ligands

(i) $(C_5H_6N)_2TlCl_5 \cdot (CH_3)_2SO$

Dimethylsulfoxide (8 cm^3) was added in a nitrogen-filled glovebox to a solution of $(C_5H_6N)_2TlCl_5$ (2.96 g) in ethanol. An oily yellow layer separated out which was collected and evaporated in an air stream until a white solid (m.p. 88 °C) crystallized out. (*Anal.* Calc. for $C_{12}H_{18}N_2Cl_5OSTl$: C, 23.24; H, 2.93; Cl, 28.59; O, 2.58; S, 5.17%. Found: C, 22.90; H, 2.92; Cl, 28.90; O, 3.9; S, 5.5%). The adduct gives an X-ray powder pattern containing many lines. Strong ones are observed at d spacings of 7.80, 7.47, 5.63, 4.98, 4.47, 3.10, 2.88 and 2.82 Å.

(ii) $(C_5H_6N)_2TlCl_5 \cdot$bipy

2,2′-bipyridyl (0.62 g) in 10 cm^3 acetonitrile was added to a solution of $(C_5H_6N)_2TlCl_5$ (2.37 g) in acetonitrile (30 cm^3). After about ½ min., a white precipitate (m.p. 224 °C) formed. (*Anal.* Calc. for $C_{20}H_{20}N_4Cl_5Tl$: C, 34.39; H, 2.87; N, 8.02; Cl, 25.38; Tl, 29.28%. Found: C, 35.44; H, 2.72; N, 8.10; Cl, 25.38; Tl, 30.83%). The compound shows strong lines in the X-ray powder pattern at d = 7.87, 7.26, 6.94, 5.63, 5.32, 3.86, 3.50 and 2.80 Å.

(iii) $(C_5H_6N)TlCl_4 \cdot$*o*-phen

A solution of 1,10-phenanthroline monohydrate (0.79 g) in ethanol was added to a solution of 2.13 g $(C_5H_6N)_2TlCl_5$ in ethanol. A white precipitate (m.p. 217–8 °C) formed immediately. This was collected quickly and dried *in vacuo*. (*Anal.* Calc. for $C_{17}H_{14}N_3TlCl_4$: C, 33.67; H, 2.33; N, 6.96; Cl, 23.38%. Found: C, 33.86; H, 2.33; N, 6.82; Cl, 23.25%).

Low energy infrared spectra were recorded between 525 and 50 cm^{-1} from nujol mulls sandwiched between polyethylene plates using the Perkin-Elmer 180 instrument at Monash University. Raman spectra were obtained on polycrystalline samples using the Spex Ramalog instrument at the University of Melbourne.

Conductivity measurements were made on a 10^{-3} *M* solutions in 'Super Dry' ethanol [11] using a Philips Resistance Bridge, Model PR 9500.

Discussion

With water as a solvent, the similar procedures described by Multani *et al.* [1] for thallium(III) and by Sharma and Kumar [12] for iron(III) produced only the known enneachloride derivatives. In accordance with the results obtained for iron(III), we expected that a pentachloro derivative for thallium(III) would be favoured in a non-aqueous medium. Indeed, thallic oxide slowly dissolved in ethanol as anhydrous HCl was passed through the suspension in the manner described by Multani *et al.* for the aqueous system. Addition of pyridine, followed by re-saturation with HCl in this case yielded a compound which analyzed as the desired $(C_5H_6N)_2TlCl_5$. Analyses were performed for all the elements present to establish the formula unambiguously. We pointed out previously [2] that the molecular formula could not be established with confidence from metal and chloride percentages alone. The melting point of the complex is quite well-defined at 139–140 °C, while the previously reported melting point of 151 °C corresponds to that of the tetrachlorothallate(III). The infrared spectrum in the usual range, 4000–400 cm^{-1}, displays only bands which are characteristic of the pyridinium ion and not those of the inorganic entity since Tl–Cl (and Fe–Cl) vibrational frequencies fall below this range.

TABLE II. Molar Conductivity.

	Λ_m*
$(Et_4N)_2TlCl_5$	71.9
$(C_5H_6N)_2TlCl_5$	139.6
$(C_5H_6N)_2FeCl_5$	141.0
$(C_5H_6N)_3Tl_2Cl_9$	207.9
$(C_5H_6N)_3Fe_2Cl_9$	215.6
$(C_5H_6N)_3TlCl_6$	196.0

*Typical Λ_m values in ethanol solution are quoted by Geary [14]:

1:1 electrolytes, 30–45 ohm^{-1} cm^2 mol^{-1}

2:1 electrolytes, 70–90 ohm^{-1} cm^2 mol^{-1}

3:1 electrolytes, approx. 120 ohm^{-1} cm^2 mol^{-1}.

Shriver and Wharf also had employed non-aqueous solvents to obtain tetra-alkylammonium derivatives of $TlCl_5^{2-}$ and noted the influence of the solvent on the product obtained [5]. However, when we attempted a synthesis of the pyridinium derivative from $(C_5H_6N)Cl$ and $TlCl_3$, using a 40% excess of the former, in a manner analogous to Shriver's preparation of $(Et_4N)_2TlCl_5$, the product was the hexachloro compound, $(C_5H_6N)_3TlCl$. Only using the exact stoichiometric quantities of $(C_5H_6N)Cl$ and $TlCl_3$ were we able to isolate $(C_5H_6N)_2TlCl_5$ from these reagents. In marked contrast, the quinolinium derivative, $(C_9H_8N)_2TlCl_5$, separated from aqueous solution [7]. This was surprising in view of the studies which have shown that the equilibrium constant for $TlCl_5^{2-}$ formation in water is quite small [13].

A very pronounced similarity in solution behaviour between the Tl(III) and Fe(III) compounds is evident from the molar conductivity data (ethanol solution) presented in Table II. While $(Et_4N)_2TlCl_5$ behaves as expected for a characteristic 2:1 electrolyte (See also ref. 5), the Λ_m values for the pyridinium chlorothallate salts are approximately double those expected and are virtually identical with those of the corresponding Fe(III) compounds, which are known to be double salts. These results suggest that either the Tl(III) compounds are also double salts or that they dissociate in solution.

Generally, as the coordination number of the central metal atom increases, the infrared-active metal–ligand stretching frequency decreases [15]; this rule provides a straightforward test for coordination number in simple complexes. Thus, it was quite easy to show that $(C_9H_8N)_2FeCl_5$ [ν(Fe–Cl) = 375 cm^{-1}] was a derivative of $FeCl_4^-$ [ν(Fe–Cl) ≅ 375

TABLE III. Vibrational Frequencies for Derivatives of $TlCl_4^-$.

	ν_1	ν_2	ν_3		ν_4		Ref.
	(R)	(R)	(IR)	(R)	(IR)	(R)	
$Ph_4AsTlCl_4$	312	60		296		78	23
	(300sh)		296, 278sh		~88		19
			304sh, 293, 281s				33
			306, 292		107, 93		34
			307, 294, 284				17
$(C_5H_6N)TlCl_4$	306	80		297			23*
	305		286	281	113, 105, 92	80	This work
$(Me_4N)TlCl_4$			302		115, 98		34
	312			294			23
	310		310, 288, 255	290	102, 88		This work
	303	88	293	290	104		35
$(Et_4N)TlCl_4$	312		293	290	110, 93		34**
			305, 292, 283				17
			295, 285		108, 50		16
	304	90	289, 255	(274)292	104, 96	90	This work
$C_9H_8NTlCl_4$	307	92		289	98		This work

*In this ref., a dry crystalline compound could not be obtained and the Raman spectrum was run on 'an aqueous slush'. By contrast, we had no difficulty in obtaining a dry product. **Adams and Morris reported that 'white chlorothallates did not yield good Raman spectra' and reported only on the Et_4NTlCl_4 salt. By contrast, we found little difficulty in obtaining Raman spectra on any sample.

cm^{-1}] rather than a derivative of $FeCl_5^{2-}$, which has two stretching frequencies at 336 cm^{-1} and 270 cm^{-1} [3]. It appeared that in the case of chlorothallate complexes, however, the application of this test was rather less obvious for a number of reasons, as follows. The reported Tl–Cl stretching frequencies in the $(TlCl_{3+n})^{n-}$ ions are somewhat closer together than the corresponding modes in the Fe(III) analogs. Also, the low energy infrared bands are in any event very broad and difficult to locate with confidence. Indeed, the bands in the pyridinium compounds are broader than those for analogs with quaternary ammonium cations – and this may well indicate hydrogen bonding in the solids as in the case with diethylammonium tetrachlorothallate [16]. Further, the geometry of the $TlCl_5^{2-}$ ion appears to be quite flexible and cation-dependent [5] – thereby leading to uncertainty not only in the identified positions of the peaks but also in the number of them to be expected. As a result, we decided that the best application of the rule was via comparison with a range of similar known compounds. While the vibrational spectra of some of these compounds had already been published, we decided that it was prudent to compare all the spectra on the instruments which were available to us. By this procedure it is possible to avoid instrumental variations between different research groups; also transposition errors, incorrect assignments or disagreements in published data were minimized. Thus, the absolute reliance on published work was eliminated whilst still retaining it as a guide.

Since $(C_5H_6N)_2TlCl_5$ and $(C_5H_6N)_3TlCl_6$ could prove to be derivatives of $TlCl_4^-$, it was imperative that the vibrational characteristics of this ion be identified unambiguously. Our results, together with those of other workers, show that in this tetrahedral species a strong Raman mode appears just above 300 cm^{-1} (ν_1) with a shoulder around 290 cm^{-1} (ν_3). The ν_3 mode is also infrared-active and appears as a broad, reasonably strong absorption in all the compounds. The other infrared-active mode (ν_4) occurs as a moderately strong peak around 100 cm^{-1} but is often overlapped with bands from the counter ion. The Raman-active ν_2 mode occurs to even lower wavenumber and suffers not only from overlaps with counter ion vibrations but also from the rising background present from polycrystalline samples as the exciting line is approached. Nevertheless, in retrospect, the vibrational modes of $TlCl_4^-$ are quite well-defined despite their broadness in the infrared (See Table III). The Raman spectra generally provided clearer information than the infrared because all the vibrations were active, the intensities generally strong and the lines were not usually as broad.

For the octahedral $TlCl_6^{3-}$, the situation should be similarly straightforward in that there are only two infrared-active modes (ν_3 and ν_4) while ν_1, ν_2 and ν_5 are Raman-active. For the compound $K_3TlCl_6 \cdot 2H_2O$, Spiro made the original assignments: ν_1 = 280 cm^{-1}, ν_2 = 262 cm^{-1} and ν_3 = 230 cm^{-1} [19]. It appears, however, that this compound is better formulated as $K_3TlCl_6 \cdot (13/7)H_2O$ and to contain $TlCl_5(H_2O)^{2-}$ octahedra in addition to the $TlCl_6^{3-}$ species [13]. Certainly, the infrared spectrum of this compound contains an unusually broad peak between 200 and 240 cm^{-1} (approximate center 220 cm^{-1}) and another between 142 and 164 cm^{-1}, these being consistent with the presence of more than one anionic species. The later 'tentative assignments' for $TlCl_6^{3-}$ made on the $Co(NH_3)_6^{3+}$ derivative [18] and given as ν_1 = 264 cm^{-1}, ν_2 = 192, ν_3 = 230, ν_4 = 146 cm^{-1} certainly leave Spiro's assignments in doubt. Spiro's 280 cm^{-1} band was the strongest in his spectrum [19] while there was not any evidence at all for a peak at 190 cm^{-1}. We have confirmed the frequencies given by Barrowcliffe *et al.* [18] and have found that a fresh sample of $(C_5H_6N)_3TlCl_6$ yields a very broad infrared peak in the 230 cm^{-1} region expected for the ν_3 mode of the octahedral species, and certainly not in the characteristic region for $TlCl_4^-$. The broadness of the peak (which seems to stretch between 250 and 140 cm^{-1} is probably due to overlapping Tl–Cl and pyridinium vibrations. Another weak future *ca.* 120 cm^{-1} may be assigned to ν_4. Also, the Raman spectrum displays an intense peak at 259 cm^{-1} (ν_1). On the other hand, an older sample of $(C_5H_6N)_3TlCl_6$ displays a Raman spectrum which has a pronounced shoulder (at 280 cm^{-1}) on the 259 cm^{-1} peak. Since the compound is moisture-sensitive, it seems likely that the 280 cm^{-1} feature is best assigned to ν(Tl–Cl) in a species such as $TlCl_5(H_2O)^{2-}$. It is clear that the pyridinium salt of $TlCl_6^{3-}$ is not a double salt of the $TlCl_4^-$ anion, unlike the iron compound of similar stoichiometry [3].

For $TlCl_5^{2-}$, the situation is equally complicated, but for the different reason that in the tetraethylammonium salt, the ion appears to be close to square pyramidal (C_{4v}) whilst it is trigonal bipyramidal (D_{3h}) in the DMTEA salt [5]. In each case, the relatively large numbers of Raman active modes were indeed observed (see Table IV). Our spectra match very well those reported by Shriver and Wharf, although the 275 cm^{-1} band is so intense that the other peaks appear rather weak by comparison – and it is obvious that much careful checking would have been necessary before their weaker bands were verified. The infrared spectrum of $(Me_4N)_2TlCl_5$ is dominated by a broad, intense absorption centered on 260 cm^{-1} and a less intense, but equally broad absorption around 240 cm^{-1}, in accordance with Shriver's results. The moderately strong peaks reported around 120 cm^{-1} and 140 cm^{-1} certainly were evident in our results, but not well resolved. Again,

TABLE IV. Vibrational Frequencies for Derivatives of $TlCl_5^{2-}$.

	ν_1		ν_7		ν_2		ν_4		ν_6	ν_8		ν_3		ν_5		ν_9		Ref.
	IR	R	IR	R	IR	R	IR	R	R	IR	R	IR	R	IR	R	IR	R	
$(Et_4N)_2TlCl_5$	285	275	253	260	245	–	–	171	153	138	–	123	120	116	113	95	99	5*
	286	275	250	258	234		170	170	151	137		124		118	110	95		This work
$(Me_4N)_2TlCl_5$	282		262		244					140		123		117				5
	274	286	261	260	233	230			153				129		107		96	This work
Cs_2TlCl_5		277	260		246				146		142	120			108		78	This work
$(C_5H_6N)_2TlCl_5$	282	280	269	270	245							126						This work
$(C_9H_8N)_2TlCl_5$	274	283	254sh		242sh													This work

*In the DMTEA salt, the Raman spectrum was recorded as: 196m, 189m, 169vs, 102mbr, 87mw, 76mbr, 61vw, 48s and 33m, but assignments of these frequencies were not made.

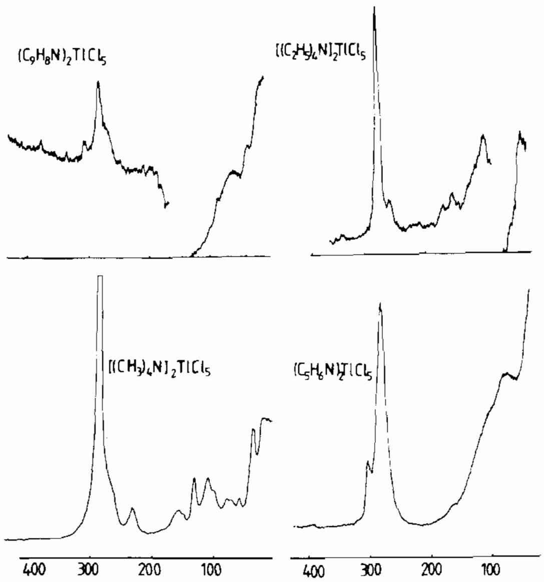

Fig. 1. Raman spectra of some pentachlorothallates(III). Note the extreme intensity of the ν_1 band in most cases. (The quinolinium derivative fluoresced somewhat.)

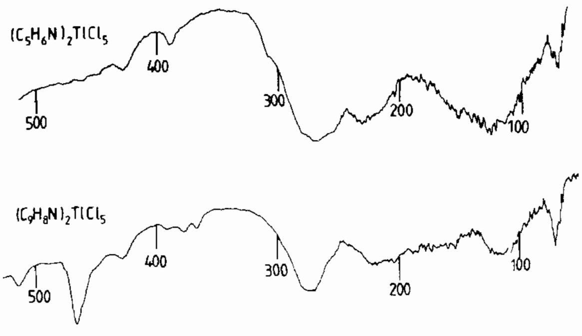

Fig. 2. Low-energy infrared spectra of the pyridinium and quinolinium derivatives of $TlCl_5^{2-}$. The broadness of the infrared peaks may be contrasted with the relatively sharp ones in the Raman spectra.

the Raman spectra provide clearer information on structure. To summarize our results, it appears that a five-coordinate $TlCl_5^{2-}$ ion would be characterized by a very strong Raman mode above 270 cm^{-1} (ν_1), with the shoulder around 260 cm^{-1} (ν_7), while ν_7 and ν_2 (near 240 cm^{-1}) appear as strong, broad bands in the infrared. Further weak Raman bands are expected near 170 cm^{-1} (ν_4), 150 cm^{-1} (ν_6) and 110 cm^{-1} (ν_5) with infrared-active bands around 120 cm^{-1} (ν_3) and 140 cm^{-1} (ν_8) (See also Fig. 1). The spectra for the cesium salt correspond well with this pattern and the compound appears to contain a pentacoordinate anion, as expected.

Turning to $(C_5H_6N)_2TlCl_5$, we find that the low energy infrared spectrum is quite simple, displaying only broad absorptions: one centered on 270 cm^{-1}, another around 130 cm^{-1} while broad bands of relatively weak pyridinium vibrations are superimposed between 250 and 140 cm^{-1} (See also Fig. 2). A strong Raman peak is observed at 280 cm^{-1}, but from about 170 cm^{-1} downwards only a broad absorption is seen, peaking around 75 cm^{-1} and with asymmetries near 110 cm^{-1} and 160 cm^{-1}. While, on first impression, these spectra could reflect the presence of an ion of high symmetry ($TlCl_4^-$), a comparison of patterns observed with those from other $TlCl_4^-$ and $TlCl_5^{2-}$ species reasonably indicates that there is a close correspondence between $(C_5H_6N)_2TlCl_5$ and the genuine $TlCl_5^{2-}$ species. The spectra are thus deceptively simple in this regard. Those additional weak bands expected for an ion of relatively low symmetry are obscured by the broad band envelopes and the vibrations due to the counter ion. On the other hand, the bands would appear to be too narrow, especially in the Raman, to sustain a formulation of $(C_5H_6N)_2TlCl_5$ as a double salt of the type $(C_5H_6N)TlCl_4$. $(C_5H_6N)_3TiCl_6$ for which multiple Tl–Cl vibrations would be expected. The equally simple spectra obtained for the quinolinium derivative also fit the pattern expected of a genuine $TlCl_5^{2-}$ ion. In these simple salts, the pyridinium ion is able to sustain a chlorothallate ion of coordination number greater than four, whereas it was unable to do so in the case of Fe(III).

While the Fe(III) and Tl(III) chloro systems differ in this respect, it is interesting to note that there are some similarities. Both metals yield cesium salts of composition $Cs_3M_2Cl_9$ in which a bridged binuclear species is present [20–22]. Whereas $Cs_3Tl_2Cl_9$ exhibits only the one strong Raman band at 287 cm^{-1} expected of the D_{3h} binuclear ion [23], the vibrational spectra of $(C_5H_6N)_3Tl_2Cl_9$ in contrast are characterized by two strong Raman peaks at 302 and 277 cm^{-1} and an infrared spectrum which is abnormally broad in the region 320–210 cm^{-1}, these patterns suggesting the presence of both $TlCl_4^-$ and $TlCl_5^{2-}$ ions. Thus the pyridinium thallium(III) enneachloride appears to be a double salt of the type $(C_5H_6N)_2TlCl_5 \cdot (C_5H_6N)TlCl_4$. Recall that $(C_5H_6N)_3Fe_2Cl_9$ was also a mixed salt [24]. Since the pentachlorothallate(III) species is generally unstable in water, it is not surprising in retrospect that $(C_5H_6N)TlCl_4$ could be obtained by recrystallizing $(C_5H_6N)_3Tl_2Cl_9$ from this medium [2]. Although $(C_5H_6N)_3Tl_2Cl_9$ can exhibit two distinct crystalline forms [2], the vibrational spectra of these forms are virtually identical, ruling out the possibility that one form contains the bridged binuclear ion. Although the ^{205}Tl NMR results of Figgis originally indicated that added chloride produced $Tl_2Cl_9^{3-}$ as the principal species in solution [25], Spiro suggested that an equilibrium analysis of his Raman results favoured the high coordination number species being $TlCl_6^{3-}$ [26]. This is in accord with more recent solution X-ray diffraction measurements which found no evidence that polynuclear species are present in solution [27]. Thus, while the $Tl_2Cl_9^{3-}$ ion has been characterized in a solid, its existence in solution is by no means proved – and its existence in solids may be markedly cation-dependent. Certainly, we were unable to prepare a quinolinium derivative of $Tl_2Cl_9^{3-}$.

The reaction of $(C_5H_6N)_2TlCl_5$ with dimethylsulfoxide yields a 1:1 adduct. The S–O stretching frequency in the adduct appears at 942 cm^{-1}, the downward shift with respect to that in free DMSO being indicative of coordination through the oxygen atom [28]. A more reliable test involving the γ(CSO) vibration has been suggested recently [29]. This moves from 380 cm^{-1} in free DMSO to the 300–350 cm^{-1} range in O-coordinated DMSO or to 375–385 cm^{-1} in an S–coordinated ligand. In $(C_5H_6N)_2TlCl_5 \cdot DMSO$, this peak occurs at 332 cm^{-1} and compares well with that at 334 cm^{-1} in the adduct $TlCl_3 \cdot 2DMSO$ reported by Walton [16]. A peak at 415 cm^{-1} may be assigned to the 'ν(Tl–O)' vibration analogous to that in $TlCl_3 \cdot 2DMSO$ [16], and the Tl–Cl stretching frequency (263 cm^{-1}) observed in the Raman spectrum decreases only slightly from that observed in $(C_5H_6N)_2TlCl_5$ itself. Similarly, 2,2'-bipyridyl also forms a 1:1 adduct. Such infrared spectroscopic tests for coordination of the ligand as the 402 cm^{-1} ring vibration moving to higher frequency (420 cm^{-1} in the adduct), the 760 cm^{-1} band splitting (into 770 and 734 cm^{-1}) and the moderately strong 1418 and 1583 cm^{-1} bands shifting to higher frequency (to 1458 and 1601 cm^{-1}, respectively) [30–32] – generally indicate ligand coordination, but there is no significant shift observed in the Raman active Tl–Cl stretching vibration. It would appear that the Tl–Cl bond is not significantly weakened in this adduct with respect to that in the pentachloride. On the other hand, the interaction of 1,10-phenanthroline with the pentachlorothallate(III) eliminates a chloride ligand to produce $(C_5H_6N)TlCl_4 \cdot$*o*-phen, which appears to be analogous to the tetraethylammonium derivative prepared by Walton [16].

Thus, it appears that while $(C_5H_6N)_2TlCl_5$ contains a genuine $TlCl_5^{2-}$ species in the solid state, it dissociates in ethanol solution to yield conductivity behaviour analogous to that of $(C_5H_6N)_2FeCl_5$. Accordingly, reactions with Lewis bases increase the coordination number, but have the possibility of displacing a chloride ligand. Further investigations into the solid state and solution properties of these compounds are currently in progress.

Acknowledgements

We are especially grateful to Mr. M. E. Beyer, Chemistry Department, University of Melbourne for assistance with Raman spectra and to Mr. M. Hughes, Chemistry Department, Monash University for assistance with the low energy infrared.

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