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Concerning Dipyridinium Thallium(III) Pentachloride

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The problems associated with obtaining an anhydrous sample of thallium(III) chloride *via* a convenient synthetic method are well known [1]. In 1972, Multani and co-workers reported the isolation of dipyridinium thallium(III) pentachloride, $(C_5H_6N)_2TlCl_5$, as a white crystalline, thermally stable compound in high yield (85%) in a reaction starting from thallium(III) oxide [2]. In view of its reported high solubility in polar organic solvents, we regarded this compound as a potential source for synthetic purposes of anhydrous $TlCl_3$ which could, however, be both prepared in bulk and conveniently stored. Consequently, we investigated this reported preparation in some detail.

When hydrogen chloride in nitrogen carrier gas is passed through a cooled (0 °C) suspension of Tl_2O_3 (12 g) in water (200 ml), the dark gray oxide slowly passes into solution (over *ca.* 4 hr) yielding, when the system is saturated with HCl, a small amount of pale yellow solid suspended in a colorless solution. If the solid is filtered off, pyridine (5 ml) then added and the solution re-saturated with HCl, on concentrating the solution white crystals separate out as reported. Invariably, however, rather than finding this compound to be the pentachlorothallate(III), it analyzed to be the known binuclear enneachloride species $(C_5H_6N)_3Tl_2Cl_9$ [3] (see Table I).

If the required pyridine is not added, but the filtered solution evaporated slowly over KOH and concentrated H_2SO_4 in a vacuum desiccator, large white crystals of tetrachlorothallic acid, $HTlCl_4 \cdot 3H_2O$, m.p. 26–27 °C [5] separate out. Found: H, 1.71; O, 12.1; Cl, 35.2%. Calculated for $H_7Cl_4O_3Tl$: H, 1.74; O, 11.9; Cl, 35.4%.

One of Renz's original preparations of the enneachloride involved the treatment of an aqueous hydrochloric acid solution of $TlCl_3$ (which would contain $HTlCl_4$) with a solution of pyridinium chloride in HCl [3]. The synthesis described by Multani *et al.* would appear to be analogous to Renz's from the point at which the solution was filtered. Thus, the formation of the enneachloride is to be expected.

TABLE I. Analytical Data for the Compound $(C_5H_6N)_3Tl_2Cl_9$, Prepared *via* the Methods of Multani *et al.* and Renz.

Run	C(18.60)	H(1.87)	N(4.34)	Cl(32.96)	Tl(42.23)[a]
A. Multani's method					
1	18.52	2.11	4.25	33.1	41.87
2	18.12	1.92	4.06	31.6	41.59
3	18.42	2.09	4.09	32.5	42.05
4	18.65	1.97	4.19	33.3	41.47
B. Renz's method					
1	18.12	1.87	4.34	33.5	42.74
2	18.40	1.85	4.29	33.10	42.03

[a] Values in parentheses are calculated for $C_{15}H_{18}N_3Cl_9Tl_2$. C, H, N and Cl values were obtained via microanalysis (Australian Microanalytical Service, C.S.I.R.O. Division of Applied Organic Chemistry, Melbourne) while the metal was determined iodimetrically [4].

TABLE II. X-ray Powder Pattern and Refractive Index Measurements on the Two Forms of $(C_5H_6N)_3Tl_2Cl_9$.

Form A (m.p. 130 °C)		Form B (m.p. 120 °C)	
d(Å)	I[a]	d(Å)	I[a]
5.538	s	7.528	s
5.452	s	5.452	s
5.167	vw	5.184	vw
4.333	s	4.319	s
4.181	vw	3.933	vw
3.866	vw	3.866	vw
3.488	s	3.692	s
3.480	vw	3.493	vw
3.331	vw	3.337	vw
3.158	s	3.158	s
2.682	vw	2.636	w
2.600	m	2.566	s
2.561	vw	2.528	vw
2.478	vw	2.457	vw
2.329	m	2.329	s
2.222	vw	2.222	w
2.138	m	2.027	vw
2.113	vvw	1.931	w
1.940	m	1.886	m
1.877	m		
$\mu(\alpha) = 1.582 \pm 0.002$[a]		$\mu(\alpha) = 1.590 \pm 0.002$[a]	
$\mu(\beta) = 1.727 \pm 0.002$		$\mu(\beta) =$ *ca.* 1.750	
$\mu(\gamma) = 1.752 \pm 0.003$		$\mu(\gamma) =$ *ca.* 1.750	

[a] Using a Philips 57.3 mm radius camera, CuK_α radiation. [b] Obtained using the Becke line method [7].

The enneachloride salt exists in two distinct crystalline forms. The original precipitate, obtained by concentration of the solution, melts at 130 °C

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(form A). Often, crystallization from the remaining filtrate yields form B, m.p. 120 °C. Found: C, 18.72; H, 1.78; N, 4.35; Cl, 33.0%. X-ray powder pattern and refractive index investigations confirm that these two forms are indeed different (Table II).

From a dilute HCl solution or from ethanol, $(C_5H_6N)_3Tl_2Cl_9$ recrystallizes unchanged, but from water or tetrahydrofuran it recrystallizes as $C_5H_6NTlCl_4$, m.p. 151 °C. Found (two separate samples): C, 14.44, 14.16; H, 1.53, 1.52; N, 3.08, 3.38; Cl, 33.0, 33.7; Tl, 48.34, 47.27% and further checked against an authentic sample prepared *via* Meyer's method [5]: C, 14.36; H, 1.65; N, 3.47; Cl, 32.9; Tl, 47.64%. Calculated for $C_5H_6NCl_4Tl$: C, 14.08; H, 1.42; N, 3.29; Cl, 33.27; Tl, 47.95%. Such changes by chlorothallate species on recrystallization have been observed before [6]. It should be noted that the melting point of $C_5H_6NTlCl_4$ is exactly that which Multani *et al.* reported for the pentachlorothallate. They based their characterization solely on thallium (as $Tl_2O_3 \cdot H_2O$) and chloride analyses, with no microanalytical data being reported at all. In fact, it is the microanalytical results which are sensitive for distinguishing between the three chlorothallate species in question ($TlCl_4^-$ salt C = 14.08, H = 1.42, N = 3.29%; $TlCl_5^{2-}$ salt: C = 22.15, H = 2.23, N = 5.17%; $Tl_2Cl_9^{3-}$ salt: C = 18.60, H = 1.87, N = 4.34%), whereas the chloride analyses are not especially so ($TlCl_4^-$ salt, Cl = 33.27; $TlCl_5^{2-}$ salt, 32.72; $Tl_2Cl_9^{3-}$ salt, 32.96%). Further, it is the chromate precipitation which is generally regarded as the most reliable gravimetric method for the determination of thallium [8, 9] whereas the formulation of the oxide precipitate as $Tl_2O_3 \cdot H_2O$ seems to be difficult to sustain [10, 11].

We suggest that Multani *et al.* probably completed their analyses on the enneachloride salt, but then observed the melting point on a recrystallized sample which had in fact converted to the tetrachlorothallate. Since $C_5H_6NTlCl_4$ is more soluble in THF and similar solvents than is the enneachloride, we have found it a convenient compound to employ in place of $TlCl_3$ in some reactions.

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