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Structure of Dimethylthallium Compounds Soluble in Non-polar Solvents

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Several dimethylthallium derivatives were studied by means of a study of their IR and NMR spectra and by measurements of their physical properties. These new compounds, $(CH_3)_2TlSC_6H_5$, $(CH_3)_2TlOC_6H_4Cl$-*o*, and $(CH_3)_2Tl[B(C_6H_5)_4]$, are described. By correlation with earlier reports, it is possible to classify dimethylthallium derivatives into two groups according to the nature of the hybridization of the Tl-bonding orbitals. The experimental results can be interpreted in a straightforward and consistent manner.

It is well known that most dialkylthallium derivatives, R_2TlY, are salt-like, with stable $[R\text{-}Tl\text{-}R]^+$ ions both in the solid state1) and in an aqueous solution.2) While we have been making our study,3) Shier and Drago have discussed the structure of some dimethylthallium compounds in several *polar* solvents on the basis of a study of their NMR and infrared spectra.4) Their results are quite similar to ours. The present paper will describe further results concerning the structure of dimethylthallium derivatives, including three new compounds, mainly in *non-polar* solvents.

Experimental

Dimethylthallium Chloride was prepared by the Grignard method5) and recrystallized from pyridine.

Dimethylthallium Nitrate and **Dimethylthallium Perchlorate** were prepared by double decomposition between $(CH_3)_2TlCl$ and the appropriate silver salts.

Dimethylthallium Tetraphenylborate was prepared from $(CH_3)_2TlOH$ and $Na[B(C_6H_5)_4]$ in an aqueous solution. These three products were purified by recrystallization from acetone.

Dimethylthallium Thiophenoxide. Phenoxide, *o*-Chlorophenoxide and **Salicylaldehydate** were all prepared by the same method; $[(CH_3)_2Tl]_2CO_3$ and a slight excess of the appropriate XH ($X=SC_6H_5$, OC_6H_5, OC_6H_4Cl-*o* and OC_6H_4CHO-*o*) were dissolved in an ethanol-benzene mixture and heated to boiling. The solutions were then concentrated; the desired compounds crystallized on cooling (yield, $(CH_3)_2TlSC_6H_5$, 70%; $(CH_3)_2TlOC_6H_5$, 50%; $(CH_3)_2TlOC_6H_4Cl$-*o*, 70%; $(CH_3)_2TlOC_6H_4CHO$-*o*, 50%). $(CH_3)_2TlSC_6H_5$ and $(CH_3)_2TlOC_6H_4CHO$-*o* were recrystallized from hot benzene. $(CH_3)_2TlOC_6H_5$ and $(CH_3)_2TlOC_6H_4Cl$-*o* were recrystallized from hot cyclohexane. The last two are sublimable under reduced pressure at about 100°C.

Dimethylthallium Thiomethoxide was prepared

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1) H. M. Powell and D. M. Crowfoot, *Z. Krist.*, **87**, 370 (1934).

2) P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 591 (1960).

3) H. Kurosawa, K. Yasuda and R. Okawara, *Inorg. Nucl. Chem. Letters*, **1**, 131 (1965).

4) G. D. Shier and R. S. Drago, *J. Organometal. Chem.*, **5**, 330 (1966).

5) R. J. Meyer and A. Bertheim, *Ber.*, **37**, 2051 (1904).

by the reported method,[6] and purified by sublimation under reduced pressure at 150°C. The properties and analytical data of these compounds are summarized in Table 1.

The molecular weights of $(CH_3)_2TlSC_6H_5$, measured in benzene using a vapor pressure osmometer at 25°C, were 730, 695, 705 and 715 at concentrations of 0.234, 0.290, 0.410, and 0.453 w(sample)/W(solvent) × 100 respectively. Calcd for $[(CH_3)_2TlSC_6H_5]_2$, mol wt, 687. The molecular weights of $(CH_3)_2TlOC_6H_5$, determined ebulliometrically in benzene, were 590, 586, 610, 577 and 596 at concentrations of 1.30, 1.83, 1.98, 2.36, and 2.75 w/W × 100 respectively. Calcd for $[(CH_3)_2TlOC_6H_5]_2$, mol wt, 654. The molecular weights of $(CH_3)_2TlOC_6H_4Cl$-*o*, measured cryoscopically in benzene, were 594, 650, 615 and 622 at concentrations of 2.20, 3.26, 3.30, and 4.25 w/W × 100 respectively. Calcd for $[(CH_3)_2TlOC_6H_4Cl$-*o*$]_2$, mol wt, 724.

TABLE 1. PROPERTIES OF DIMETHYLTHALLIUM DERIVATIVES: $(CH_3)_2TlY$

Compound	Mp, °C [reported]	%C Found (Calcd)	%H Found (Calcd)	%Tl Found (Calcd)
Y = Cl	280 (dec.)	9.04	2.21	75.63
		(8.90)	(2.24)	(75.72)
NO_3	>300	8.51	2.05	68.82
		(8.10)	(2.04)	(68.94)
ClO_4	105 (explod.)			61.51
				(61.22)
$B(C_6H_5)_4$	215 (dec.)	56.27	4.61	
		(56.40)	(4.73)	
SC_6H_5	182	28.03	3.28	59.17
		(27.96)	(3.23)	(59.48)
SCH_3	207			72.77
	[207—208][6]			(72.64)
OC_6H_5	201	29.58	3.32	62.36
	[202][4]	(29.34)	(3.39)	(62.39)
OC_6H_4Cl-*o*	179	26.26	2.52	56.24
		(26.54)	(2.78)	(56.46)
OC_6H_4CHO-*o*	200 (dec.)			57.96
	[200][7]			(57.48)

Distribution of $(CH_3)_2TlOC_6H_5$ and $(CH_3)_2TlOC_6H_4Cl$-*o* between Benzene and Water. The experiments were carried out as follows: A benzene solution of $(CH_3)_2TlOC_6H_5$ (or $(CH_3)_2TlOC_6H_4Cl$-*o*) (1 g solute/2.25 mol solvent) was vigorously shaken with 40 g of water (2.25 mol) for about 10 min. After the mixture had then been allowed to stand, the water layer was separated and evaporated. The residue was identified as $(CH_3)_2TlOC_6H_5$ (or $(CH_3)_2TlOC_6H_4Cl$-*o*) by its melting point and its IR spectra. In the case of $(CH_3)_2TlOC_6H_5$, the water layer contained 0.796 g of solute; the balance of about 0.2 g was recovered from the benzene solution. For $(CH_3)_2TlOC_6H_4Cl$-*o*, the recovery of solute was 0.57 g from water and about 0.4 g from benzene.

The Infrared Spectra were obtained using a Hitachi EPI-2G spectrometer equipped with gratings.

The Proton NMR Spectra were measured using a JNR-3H-60 spectrometer at 60 Mc/s and 20°, 55° and 100°C.

Results and Discussion

The results of the study of the infrared and NMR spectra of dimethylthallium compounds are listed in Tables 2 and 3 respectively.

Because of the appearance of several additional bands in the region where TlC_2 stretching vibrations were expected, it is difficult to assign these vibrations without ambiguity. Shier and Drago[4] have assigned the bands at 552 cm⁻¹ and 507

TABLE 2. RELEVANT INFRARED ABSORPTION FREQUENCIES (in cm⁻¹) OF DIMETHYLTHALLIUM DERIVATIVES, $(CH_3)_2TlY$ (Nujol mulls)

Group	Compound	Methyl rocking $\rho(CH_3)$[a]	TlC_2 stretching ν_{asym}	ν_{sym}	Additional band around $\nu(TlC_2)$
A	Y = SCH_3	*ca.* 770 (s)	523 (s)	469 (m)	
	SC_6H_5	*ca.* 788 (s)	534 (s)	473 (m)	478 (w)
	OC_6H_5	793 (s)	541 (s)	478 (w)	552 (s), 505 (s)
	OC_6H_4Cl-*o*	799 (s)	542 (s)	480 (w)	570 (s), 512 (m)
	OC_6H_4CHO-*o*	793 (s)	538 (s)	obscured	553 (s)
	(acac)[c]	790 (s)	538 (overlapped)	482 (w)	566 (m)
	(ox)	*ca.* 787 (s)[b]	538 (s)	481 (w)	565 (m), 495 (s), 498 (s)
B	Y = NO_3	*ca.* 810 (s)[b]	560 (s)		
	ClO_4	*ca.* 825 (s)	557 (s)		
	Cl	802 (s)	550 (s)		
	$B(C_6H_5)_4$	825 (s)[b]	549 (m)		

a) Very broad.
b) Partly obscured by the absorptions due to the ligand.
c) Solution spectra in $CHCl_3$ and $CHBr_3$ (Ref. 3).

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6) G. E. Coates and R. A. Whitcombe, *J. Chem. Soc.*, **1956**, 3351.

7) R. C. Menzies, N. V. Sidgwick, E. F. Cutcliffe and J. M. C. Fox, *ibid.*, **1928**, 1288.

TABLE 3. Tl-H SPIN-SPIN COUPLING CONSTANTS a): $J_{\underline{\mathrm{Tl}}-\mathrm{C}\underline{\mathrm{H}}_3}$ (in cps) FOR $(CH_3)_2TlY$
(concentrations: *ca.* 0.5—5 wt%)

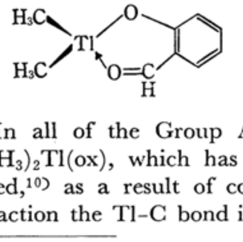
Group	Compound	Solvent					
		Toluene	Benzene	CCl_4	$CDCl_3$	CH_2Cl_2	D_2O
A	Y = SC_6H_5	355 b)					
	OC_6H_5	368 c)	370 c)	360 c)			405*
	OC_6H_4Cl-*o*	373 c)	368 c)	365 c)			407
	OC_6H_4CHO-*o*		382				407
	SCH_3 d)					371 (saturated)	
	(acac) e)		381*		372*		411*
	(ox) e)				391		
B	NO_3 f)						407*
	ClO_4 f)						406*

a) The separation of $J_{^{203}\underline{\mathrm{Tl}}-\mathrm{C}\underline{\mathrm{H}}_3}$ and $J_{^{205}\underline{\mathrm{Tl}}-\mathrm{C}\underline{\mathrm{H}}_3}$ was not observed except as noted.
b) Measured at 100°C.
c) At 20°C methyl signals are broad (*ca.* 15 cps) possibly because of monomer-dimer exchange. At above 50°C they are of the ordinary order of width. At lower temperature the low solubility in the solvents used precluded the separation of signals due to monomer and dimer. There was no appreciable change in *J* on varying the concentrations and temperature.
d) Ref. 4. e) Ref. 3. f) Ref. 8.
* The value of $J_{^{205}\underline{\mathrm{Tl}}-\mathrm{C}\underline{\mathrm{H}}_3}$; $J_{^{203}\underline{\mathrm{Tl}}-\mathrm{C}\underline{\mathrm{H}}_3}$ is 2—4 cps less than $J_{^{205}\underline{\mathrm{Tl}}-\mathrm{C}\underline{\mathrm{H}}_3}$.

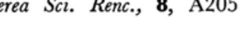
cm⁻¹ in the spectrum of $(CH_3)_2TlOC_6H_5$ to ν_{asym} (TlC_2) and ν_{sym} (TlC_2) respectively. However, we prefer to assign the bands at 541 cm^{-1} and 478 cm^{-1} to these vibrations respectively, because this is consistent with the spectrum of $(CH_3)_2TlOC_6H_4Cl$-*o*, which would have a similar configuration as to the TlC_2 group. In a previous report[3] a band at 566 cm^{-1} in the solution spectrum of $(CH_3)_2Tl(acac)$ was assigned to ν_{asym} (TlC_2). However, this band seems to be too weak and to occur at too high a frequency relative to ν_{sym} (TlC_2); therefore, we have re-assigned the ν_{asym} (TlC_2) as is shown in Table 2.

Those compounds which are soluble in non-polar organic solvents (Group A) may be distinguished from typical ionic dimethylthallium derivatives (Group B) by the values of their methyl rocking[*1] and TlC_2 stretching frequencies. The Group A compounds are characterized by $\rho(CH_3) < 800$ cm^{-1}, ν_{asym} $(TlC_2) \simeq 540$ cm^{-1} and a weak band of ν_{sym} (TlC_2); Group B, by $\rho(CH_3) > 800$ cm^{-1}, ν_{asym} $(TlC_2) \simeq 550$—560 cm^{-1}, and no bands attributable to $\nu_{\mathrm{sym}}(TlC_2)$. The spectra of the Group B derivatives also show the characteristic infrared absorption bands due to free anion groups such as NO_3^-, ClO_4^- or $[B(C_6H_5)_4]^-$.

The results of the molecular-weight determination show that $(CH_3)_2TlSC_6H_5$, $(CH_3)_2TlOC_6H_5$ and $(CH_3)_2TlOC_6H_4Cl$-*o* are dimeric in benzene, though the last two are partially dissociated into monomers. Tetra-co-ordinated thallium similar to $[(CH_3)_2TlSCH_3]_2$[6] would be established in these compounds through sulfur bridging or relatively weak oxygen bridging bonds, as is shown below. Judging from the ν(C=O) value of $(CH_3)_2TlOC_6H_4CHO$-*o*, which is about 30 cm^{-1} lower than that of $C_6H_4(OH)CHO$-*o*, dimethylthallium salicylaldehydate might have a chelate structure similar to those of $(CH_3)_2Tl(acac)$ and $(CH_3)_2Tl[CH(COC_6H_5)_2]$.[4]



(X=S or O
R=CH_3 or C_6H_5)



(Dimethylthallium salicylaldehydate)

In all of the Group A compounds, including $(CH_3)_2Tl(ox)$, which has been shown to be chelated,[10] as a result of considerable Tl-ligand interaction the Tl-C bond is weaker, the Tl-C bond

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8) J. V. Hatton, *J. Chem. Phys.*, **40**, 933 (1964).

[*1] Goggin and Woodward (Ref. 2) have assigned the weak line at 569 cm^{-1} to $\rho(CH_3)$ in the Raman spectra of $(CH_3)_2TlNO_3$ and $(CH_3)_2TlClO_4$ in a H_2O solution. However, our Raman spectra of $(CH_3)_2TlNO_3$, both in the solid state and in H_2O, show no lines in this region. The $\rho(CH_3)$ vibration would not be expected to occur at such low frequencies. In the case of the $(CH_3)_2Pb^{2+}$ ion, a similar error has already been pointed out (Ref. 9).

9) C. E. Feidline and R. S. Tobias, *Inorg. Chem.*, **5**, 354 (1966).

10) G. Faraglia, L. Roncucci and R. Barbieri, *Ricerea Sci. Renc.*, **8**, A205(1965).

length is greater, and the C–Tl–C bond angle is smaller than in the Group B compounds. Thus, the ν_{asym} (TlC_2) value of the Group A compounds*2 are observed at lower frequencies than those of group B. Furthermore, the longer Tl–C bond produces greater Tl···H distances and, hence, a smaller value of the $F_{\mathrm{Tl\cdots H}}$ term in a simple Urey-Bradley force field. As a consequence, lower $\rho(CH_3)$ frequencies in the Group A compounds may be expected; indeed, they have been observed.

In terms of electronic structure, the dimethylthallic cation characteristic of the Group B compounds can be described as being bonded by essentially *sp* hybrids. The solvent dependence of $J_{\underline{\mathrm{Tl}}-\mathrm{C}\underline{\mathrm{H}}_3}$ for the linear $[(CH_3)_2Tl]^+$ (408—475 cps) has been discussed in terms of a dz^2-s mixing scheme.4) On the other hand, in the Group A derivatives with a non-linear C–Tl–C configuration, the Tl–C bond would have smaller *s*-character than *sp* hybrids and, thus, a weaker Fermi contact interaction, resulting in smaller values of the thallium-proton spin-spin coupling constants.8,11,12) This may be seen in Table 3 for the Group A compounds dissolved in non-polar solvents.

$(CH_3)_2TlOC_6H_5$, $(CH_3)_2TlOC_6H_4Cl$-*o* and $(CH_3)_2TlOC_6H_4CHO$-*o* are soluble in water, giving a strongly alkaline solution (pH 10—11). These compounds recrystallize unchanged from aqueous solutions. These facts suggest that they are dissociated in water to give the $[(CH_3)_2Tl]^+$ aquo ion and the corresponding anions. The dissociation in water was also confirmed by the NMR results; the *J* values of $(CH_3)_2TlOC_6H_5$, $(CH_3)_2TlOC_6H_4$-Cl-*o*, and $(CH_3)_2TlOC_6H_4CHO$-*o* measured in a D_2O solution are identical with those8) of ionic dimethylthallium compounds in a D_2O solution. The distribution experiments between equimolar benzene and water showed that about 80% of $(CH_3)_2TlOC_6H_5$ and 60% of $(CH_3)_2TlOC_6H_4Cl$-*o* were found in the water layer. It is likely that, in the case of these compounds, an essentially linear $[C\text{–}Tl\text{–}C]^+$ configuration is favored. This is consistent with the general features of dimethylthallium chemistry.

We wish to thank Dr. Y. Kawasaki of our laboratory for his assistance in this work and Dr. C. R. Dillard*3 for his helpful discussions.

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*2 The infrared spectra of $(CH_3)_2TlOC_6H_5$ and $(CH_3)_2TlOC_6H_4Cl$-*o* measured in a benzene solution were practically identical with those in the solid state. We may, therefore, presume that there are no appreciable structural differences between the solid state and solution for any of the Group A compounds except $(CH_3)_2Tl$(acac) (Ref. 3).

11) J. P. Maher and D. F. Evans, *J. Chem. Soc.*, **1965**, 637; **1963**, 5534.

12) G. Klose, *Ann. Physik.*, **9**, 262 (1962).

*3 Fulbright Research Fellow at Osaka University, 1965—1966.