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Preliminary communication

X-RAY STRUCTURES OF THE DIMERIC DIMETHYLTHALLIUM(III) DERIVATIVES, $[(CH_3)_2TlX]_2$ ($X = OC_6H_5, OC_6H_4Cl-o, SC_6H_5$); RELEVANCE OF $^1J(^{205}Tl-^{13}C)$ AND $^2J(^{205}Tl-^1H)$ AS STRUCTURAL PROBES

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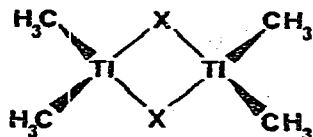
Summary

X-ray structures of dimethylthallium(III) derivatives, $[(CH_3)_2TlX]_2$ ($X = OC_6H_5, OC_6H_4Cl-o, SC_6H_5$) confirm their formulation as discrete dimers. There is no apparent correlation between the C—Tl—C angle ($< 17^\circ$ deviation from linearity) and the thallium-205—carbon and thallium-205—proton spin—spin coupling constants.

An important feature of the chemistry of diorganothallium(III) derivatives, R_2TlX , is their tendency to dimerise when the anion X is a good bridging group [1]. Molecular weight determinations in benzene indicate the presence of dimers for $X = N(CH_3)_2, SCH_3, SeCH_3$ [2], OC_6H_5, SC_6H_5 , and OC_6H_4Cl-o [3]. 1H and $^{205,203}Tl$ NMR studies [4] have unambiguously confirmed the existence of dimeric species for $X = OC_2H_5$ and $N(CH_3)_2$ in toluene. In the absence of detailed structural information, it has been generally assumed [1] that the environment around the thallium atom in these dimers approaches regular tetrahedral coordination (A). Since knowledge of the structures of such species are essential to the interpretation of the NMR spectra of dimethylthallium(III) derivatives [5], the single crystal X-ray structures of three of these compounds ($X = OC_6H_5, OC_6H_4Cl-o$, and SC_6H_5) have been determined.

Dimethylthallium(III) phenoxide (I), *ortho*-chlorophenoxide (II) and thiophenoxide (III) were prepared by methods similar to published procedures [3, 6] and recrystallised from benzene/hexane, cyclohexane, and benzene respectively. The crystallographic data for I, II, and III are summarised in Table 1, and their molecular structures are shown in Fig. 1, 2, and 3 respectively.

All three molecules have discrete dimeric structures with closest intermolecular contacts; I, Tl—Tl 4.26; II, Tl—C(phenyl) 3.64; III, Tl—S 3.40 Å. However, the



(A)

TABLE 1
CRYSTALLOGRAPHIC DATA

	I	II	III
a (Å)	10.056	8.107	10.536
b (Å)	11.434	16.899	11.510
c (Å)	15.833	15.163	7.674
β (°)	92.17	108.30	95.85
V (Å ³)	1819.2	1972.8	925.8
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$B2_1$	$P2_1/n$	$P2_1/c$
D_m (g cm ⁻³)	2.30		
D_c (g cm ⁻³)	2.39	2.44	2.46
Z for dimer	4	4	2
No. of reflections	999	976	783
$I/\sigma(I)$	2.0	3.0	3.0
R	0.11	0.049	0.049
Anisotropic	Tl	Tl and Cl	Tl and S

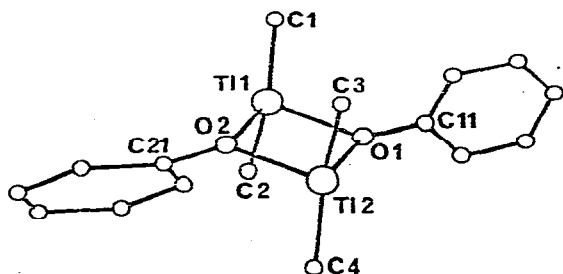


Fig. 1. The structure of I. The principal bond lengths average Tl(1)—O(1), Tl(2)—O(2) 2.37(9); Tl(1)—O(2), Tl(2)—O(1) 2.36(10); Tl—CH₃ 2.20(7) Å.

thiol ligand in III forms relatively weak bridging bonds, Tl—S' 2.99 Å, but this length is well within the sum of the Van der Waals radii for thallium and sulphur, estimated as approximately 3.6 Å from the reported values for mercury [7] and sulphur [8]. The non-standard space group $B2_1$ is used for I to emphasise its near orthorhombic symmetry in which there is a pseudo mirror plane perpendicular to the a axis. The deviation from m symmetry is due to slight tilting of the phenyl rings. The dominance of the thallium atoms in this situation has prevented satisfactory refinement of the light atom parameters but the main features of the structure are well established. Both I and II have almost planar coordination round the bridging oxygen atoms which is consistent with considerable π -character in the C—O bonds. In contrast each bridging sulphur atom in III

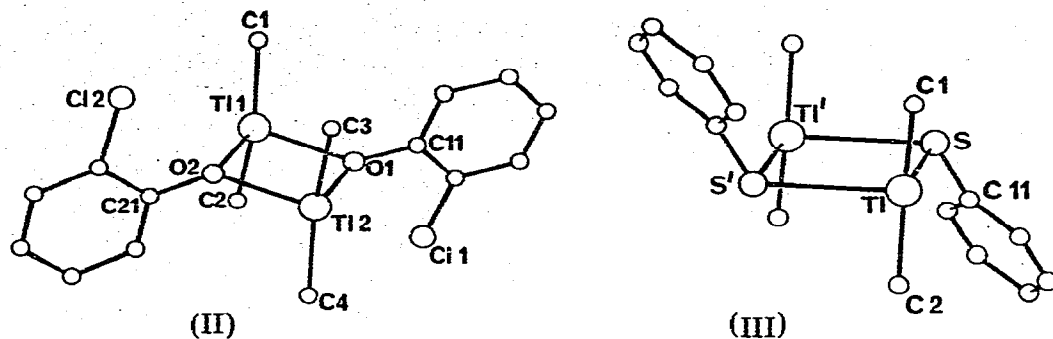


Fig. 2. The structure of II. The principal bond lengths average $\text{Tl}(1)\text{—O}(1)$, $\text{Tl}(2)\text{—O}(2)$ 2.43(1); $\text{Tl}(1)\text{—O}(2)$, $\text{Tl}(2)\text{—O}(1)$, 2.40(1); $\text{Tl}(1)\text{—C}(1)$, $\text{Tl}(1)\text{—C}(2)$, $\text{Tl}(2)\text{—C}(3)$, $\text{Tl}(2)\text{—C}(4)$ 2.14(2); $\text{O}(1)\text{—C}(11)$, $\text{O}(2)\text{—C}(21)$ 1.35(2)(in Å)

Fig. 3. The centrosymmetric structure of III. The principal bond lengths are $\text{Tl}\text{—S}$ 2.748(8), $\text{Tl}\text{—S}'$ 2.991(8), $\text{Tl}\text{—C}(1)$ 2.10(3), $\text{Tl}\text{—C}(2)$ 2.11(3), $\text{S}\text{—C}(11)$ 1.78(1) Å.

has the pyramidal coordination expected for a Group VIB atom with a non-bonding electron pair (Fig. 3). In all three structures the four bridging atoms are coplanar within experimental error. The structures of II and III are centrosymmetric (III has exact crystallographic C_i symmetry), with the respective phenyl rings parallel, whereas the symmetry of I is approximately C_{2v} with the two phenyl rings almost perpendicular to each other.

An important feature of all three structures is the near linearity of the dimethylthallium units (Table 2). Clearly the coordination around each thallium atom does not approximate to regular tetrahedral geometry and is better envisaged as distorted trigonal bipyramidal with axial methyl groups and a vacant equatorial coordination site. There are no close contacts with other molecules so that the large $\text{C}\text{—Tl}\text{—C}$ angles cannot be explained by intermolecular interactions. It is therefore reasonable to assume that these large angles are due to internal bonding factors and will have similar values in non-polar solvents where molecular weight data [3] indicate that the dimeric structures are maintained.

We have extended the ^1H NMR measurements [3] for I and II in non-polar solvents. The line widths of the thallium-coupled methyl resonances for both I and II show similar temperature dependent behaviour in toluene; as the temperature is lowered from 90° to -70° , the line widths increase from ca. 5 Hz to a maximum of ca. 30 Hz around 0° , followed by a decrease as the lower temperature is approached. This pattern is similar to that found for $(\text{CH}_3)_2\text{TlOC}_2\text{H}_5$ [9]

TABLE 2

$\text{C}\text{—Tl}\text{—C}$ ANGLES AND COUPLING CONSTANTS IN $(\text{CH}_3)_2\text{Tl}$ UNITS

	I	II	III	$(\text{CH}_3)_2\text{TlNO}_3$ in H_2O
$\text{C}\text{—Tl}\text{—C}$ angle ^a (°)	173(3)	166.2(10)	163.5(9)	180 ^b
$^2J(^{205}\text{Tl}\text{—}^1\text{H})^c$ (Hz)	372 ± 2^d	385 ± 2^d	$355^{d,e}$	410 ± 2^f
$^1J(^{205}\text{Tl}\text{—}^{13}\text{C})^c$ (Hz)	$2556 \pm 10^{d,f}$	2516 ± 4^d		2478 ± 3^f

^ae.s.d. given in parentheses. ^bIR and Raman data are consistent with a linear $\text{C}\text{—Tl}\text{—C}$ unit [10]. ^cIn toluene solution except as noted. ^dSignals broadened such that separate coupling to ^{205}Tl and ^{203}Tl was unresolved. ^eData from ref. 3. ^fData from ref. 5.

and explained [4] in terms of an equilibrium between exchanging monomeric and dimeric molecules. Low solubility precluded similar studies on III.

The values of ${}^2J({}^{205}\text{Tl}-{}^1\text{H})$ for I, II and III shown in Table 2 are lower than the values (> 400 Hz) found for $(\text{CH}_3)_2\text{TlY}$ ($\text{Y} = \text{anionic species}$) in polar solvents [5]. In contrast the values of ${}^1J({}^{205}\text{Tl}-{}^{13}\text{C})$ are larger than that for $(\text{CH}_3)_2\text{TlNO}_3$ in H_2O . Previously the lower values for ${}^2J({}^{205}\text{Tl}-{}^1\text{H})$ have been attributed [3] to a reduction in the s -character of the Tl-C bonds as the C-Tl-C angle deviates from 180° , an argument based on the assumption of the dominance of the Fermi contact term. Recent work [11] has shown that although there is a good correlation between the s -character in the Tl-C bond and both ${}^1J({}^{205}\text{Tl}-{}^{13}\text{C})$ and ${}^2J({}^{205}\text{Tl}-{}^1\text{H})$ for gross geometrical changes in the series RTl^{2+} , R_2Tl^+ , and R_3Tl , there is a lack of detailed correlation when smaller changes are considered. The present results indicate no obvious relationship between measured bond angles and coupling constants and emphasise a severe limitation on the use of these coupling constants as structural probes for diorganothallium(III) derivatives.

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