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NOTE

EXISTENCE OF TWO TYPES OF Tl–O(Ac) BANDS IN THE FAR INFRARED SPECTRA OF SOME ALKYLTHALLIUM ACETATE DERIVATIVES

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INTRODUCTION

It has been reported[1,2] that there is an ionic or weakly bridging COO group with C_{2v} symmetry in some *di*alkylthallium carboxylates, while in *mono*methyl- and -ethylthallium diisobutyrates existence of an additional type of COO group with more reduced symmetry was found[2]. We report here evidence, obtained from far infrared spectra, for the existence of two types of Tl–O(Ac) interactions in the compounds, methyl- and phenylthallium diacetates.

EXPERIMENTAL

Dimethylthallium acetate[3] (Found: Tl, 69.55. $C_4H_9O_2Tl$ calcd.: Tl, 69.64%.) (m.p. above 270°), and phenylthallium diacetate[4] (Found: Tl, 50.92. $C_{10}H_{11}O_4Tl$ calcd.: Tl, 51.15%.) (m.p. 193–194°; lit.[4]: m.p. 193–195°) were prepared by the reported methods. Phenyl(cyano)thallium acetate was prepared in a manner similar to methyl(cyano)thallium acetate[5] (Found: C, 29.27; H, 2.29. $C_9H_8NO_2Tl$ calcd.: C, 29.49; H, 2.20%.) (m.p. 201–203° decompn.). The preparations of methyl(cyano)thallium acetate[5] and methylthallium diacetate[2] have been described previously. A commercial sample of phenylmercury acetate was recrystallized from chloroform/petroleum ether.

The IR spectra were recorded in Nujol and hexachlorobutadiene mulls using Hitachi EPI-2G (5000–400 cm^{-1}) and EPI-L (700–200 cm^{-1}) spectrophotometers, and in solid paraffin of a low melting point on a Hitachi FIS-1 vacuum spectrophotometer (500–80 cm^{-1}), all equipped with gratings. The results of some alkylthallium acetate derivatives are shown in Fig. 1, and the relevant frequencies and probable assignments are given in Table 1.

DISCUSSION

The spectra in the region above 400 cm^{-1} are readily interpreted, and the assignments given in Table 1 for this region are almost certainly correct. The spectra

TABLE 1

RELEVANT IR AND FAR IR ABSORPTION FREQUENCIES (CM^{-1}) OF SOME ALKYLTHALLIUM ACETATE DERIVATIVES

$(CH_3)_2TlY^a$ (I)	$CH_3(CN)TlY$ (II)	$C_6H_5(CN)TlY$ (III)	CH_3TlY_2 (IV)	$C_6H_5TlY_2$ (V)	Assignments
	2193 m	2183 m			$\nu(C{\equiv}N)$
			1613 vs	1595 vs	$\nu_{asym}(COO)$
1540 vs	1527 vs	1515 vs	1530 vs	1525 vs	
1419 vs	1433 vs	1428 vs	1428 vs	1405 vs	$\nu_{sym}(COO)$
			1375 vs	1374 vs	
548 s	538 m		527 w		$\nu(Tl–C)$
494 w					
			487 w	488 w	$\rho(CO)_2$
457 m	457 m	458 m	458 m	457 m	
		448 s		443 s	phenyl ring bend
	379^b s	386 s (br)			$\nu(Tl–CN)$
	367^b s				
	298 w	306 vw			$\delta(Tl–C–N)$
		298 vw			
			287 s	298 s	$\nu(Tl–O)$
166 s (vbr)	164 s (vbr)	165 s (vbr)	165 s (vbr)	153 s (br)	$\nu(Tl–O)$
105 s (br)	103 s (br)	145 s (sh)	114 m	120 m (br)	
135 s					$\delta(C–Tl–C)$
			ca. 200 (sh)?	206 m	other bands

[a] $Y = OCOCH_3$. [b] Crystal field splitting.

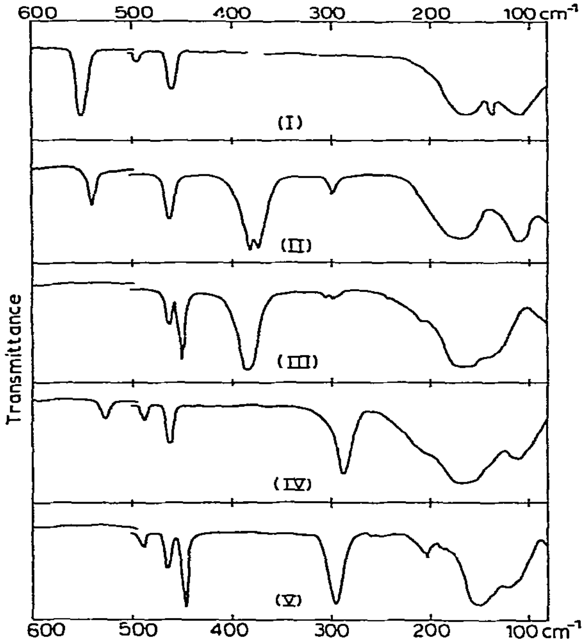
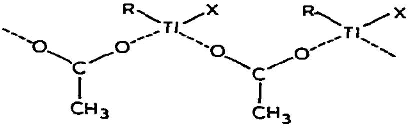


Fig. 1. Far IR spectra of $(CH_3)_2TlY$ (I), $CH_3(CN)TlY$ (II), $C_6H_5(CN)TlY$ (III), CH_3TlY_2 (IV) and $C_6H_5TlY_2$ (V) ($Y = OCOCH_3$).

of the methylthallium acetates, $(CH_3)_2TlOAc$ (I), $CH_3(CN)TlOAc$ (II) and $CH_3Tl(OAc)_2$ (IV) in the region below 400 cm^{-1} are also rather simple. In this region, the bands due to the bending vibrations of the C–Tl–C group of $(CH_3)_2Tl$* and CH_3TlCN** moieties would be expected to appear in the spectra of (I) and (II) but not (IV). Therefore, we prefer to assign the strong and broad bands in the region 166–103 cm^{-1} to Tl–O stretching vibrations associated with very weakly coordinated (probably bridging) acetoxy groups of anionic character, because the spectra of these three compounds also show similar ν(COO) frequencies characteristic of C_{2v} symmetry[9] (Table 1). Similar bands [both ν(Tl–O) and ν(COO)] are observed in the spectra of the analogous phenylthallium acetates, $C_6H_5(CN)TlOAc$ (III) and $C_6H_5Tl(OAc)_2$ (V). A possibility that the strong bands at 166–103 cm^{-1} are due to lattice vibrations cannot completely be ruled out; however in the case of such a heavy molecular unit these modes may appear only at lower frequencies. This possibility also seems less probable in view of the fact that the far IR spectra of (I) at liquid nitrogen temperature and at room temperature showed no significant differences in either the wavelength or shapes of these bands. In any case, the location of these ν(Tl–O) bands at frequencies no higher than 166 cm^{-1} indicates that the interaction between these acetate groups and thallium is very weak.

More notable is the fact that the spectra of the monoalkylthallium diacetates, (IV) and (V), show an additional strong band at 287 and 298 cm^{-1}, respectively. The occurrence of this band is most likely to be associated with the existence of another type of acetoxy group (probably unidentate). This is consistent with the additional ν_{asym}(COO) and ν_{sym}(COO) bands at higher and lower frequencies, respectively, observed only in these compounds (Table 1). Accordingly, the band at about 300 cm^{-1} is most probably due to the stretching of a Tl–O bond of more covalent character [X = unidentate OAc in formula (A) shown below].



(A)

In the spectra of (II) and (III), the strong bands at 367–386 cm^{-1} may be attributed to Tl–CN stretching modes and the weak ones at about 300 cm^{-1} to Tl–C–N bending vibrations.

TABLE 2

COMPARISON OF ν(M–O) AND ν(COO) IN SOME ORGANOMETALLIC ACETATES (CM^{-1})

CH_3TlY_2[a] (IV)	$C_6H_5TlY_2$ (V)	C_6H_5HgY	$(CH_3)_2SnY_2$[b]	$(CH_3)_3SbY_2$[c]	Assignments
1613	1595	1592	1607	1650	ν(COO)
1375	1374	1379[d] 1366[d]	1380	1286	
287	298	304	305	ca. 280	ν(M–O)

[a] Y = $OCOCH_3$. [b] Ref. 10. [c] Ref. 11. [d] Crystal field splitting.

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* δ(C–Tl–C) appeared at 101–114 cm^{-1} in $(CH_3)_2Tl^+$ [6,7].

** δ(C–Hg–C) appeared at 75 cm^{-1} in CH_3HgCN[8].

For comparison, in Table 2 are given ν(M–O) and ν(COO) frequencies found in some organometallic acetate derivatives and those of the more covalently bonded acetoxy group of the thallium diacetates, (IV) and (V). It can be seen that the ν(Tl–O) frequencies are as high as that of ν(Sn–O) in non-symmetrically chelated dialkyltin diacetates[10] and that of ν(Sb–O) in more ester-like trialkylantimony diacetates[11]. In particular, the ν(Tl–O) and ν(COO) frequencies of the more covalent acetoxy group of (IV) and (V) are comparable to those of the corresponding bands in phenylmercury acetate. Moreover, the frequencies of ν(Tl–CN) and ν(C≡N) in (II) and (III) shown in Table 1 are very close to those of the corresponding bands at 386 and 2180 cm^{-1} in methylmercury cyanide[8], which has been reported[12] to contain a linear C–Hg–CN moiety. Hence, in all of these thallium compounds in the solid state*, the thallium atom seems to interact with one alkyl and one ligand group as strongly as in alkylmercury derivatives[13,14] but very weakly with the remaining acetate anion [(A) $R=CH_3$ or C_6H_5; X=CN or OAc]. This situation can be related to the well-known fact that the dimethylthallium cation, which is isoelectronic with dimethylmercury, generally behaves as a very weak Lewis acid[13–15]. However, unlike a linear C–Hg–X group, the configuration of the C–Tl–X skeleton is presumed to be non-linear as is the case for the C–Tl–C moiety in dimethylthallium acetate**.

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* The higher of the two ν_{asym}(COO) frequencies of $CH_3Tl(OAc)_2$ or its diisobutyrate analogue[2] is reduced by *ca.* 35 cm^{-1} in chloroform solution. This might have come from a structural change between the two states. Attempts to obtain the solution spectra in the region below 300 cm^{-1} were unsuccessful, however no bands attributable to ν(Tl–O) above 300 cm^{-1} were observed.

** In the spectrum of dimethylthallium acetate, the appearance of a weak band at 494 cm^{-1} associated with the TlC_2 symmetric stretching vibration is indicative of a non-linear C–Tl–C configuration.