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STUDIES ON SOME ALKYL(CYANO)THALLIUM DERIVATIVES

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SUMMARY

Seven new alkyl(cyano)thallium derivatives have been synthesized. The observed linear relation between ν(Tl–CN) and ν(C≡N) frequencies in these compounds could be interpreted in terms of the strength of Tl–ligand interaction.

INTRODUCTION

There has been much interest in the coordination chemistry of monoorganothallium compounds[1] since we succeeded in synthesizing monoalkylthallium derivatives[2]. Existence of a penta-coordinated thallium atom has been reported in some monoalkylthallium chelates, such as $RTlY_2$ ($R=CH_3$ or C_2H_5; Y=tropolonate[3], oxinate[2,3], $SSCNR'_2$[3] or carboxylates[2]). Organo(cyano)thallium acetates, R(CN)-TlOAc ($R=CH_3$[4–7], C_2H_5[6] and C_6H_5[7]) seem also of interest in that they contain comparatively strong Tl–R bonds and a covalently bonded C≡N group to form the apparently stable $C{-}Tl^+{-}C$ moiety characteristic of diorganothallium compounds. This paper describes a comparative study of infrared spectra of several new alkyl(cyano)thallium derivatives to make clear the nature of the Tl–CN bond in these compounds.

EXPERIMENTAL

Methyl- and ethyl(cyano)thallium oxinates

To an aqueous solution (20 ml) of methyl(cyano)thallium acetate[6] (0.92 g; 3 mmol) was added drop by drop 0.44 g of oxine (3 mmol) in 10 ml of methanol. The yellow precipitates immediately obtained were washed with chloroform and dried under vacuum to give 0.71 g (56%) of $CH_3(CN)Tl(C_9H_8NO)$. Ethyl(cyano)thallium oxinate was prepared similarly from the reaction of Et(CN)TlOAc[6] with oxine.

Methyl- and ethyl(cyano)thallium tropolonates

An aqueous solution (8 ml) of tropolone (0.24 g; 2 mmol) was added drop by drop to 0.61 g of methyl(cyano)thallium acetate in water (20 ml). The pale yellow powders immediately obtained were dried under vacuum to give 0.43 g (58%) of $CH_3(CN)Tl(C_7H_5O_2)$. Ethyl(cyano)thallium tropolonate was prepared in a manner similar to that for methyl(cyano)thallium tropolonate.

Methyl(cyano)thallium carboxylates

To a solution of methylthallium dipropionate, obtained *in situ* from MeTlO[4] (0.24 g) and C_2H_5COOH (0.2 g) in chloroform (20 ml), was added drop by drop a chloroform solution (5 ml) of Pr_3SnCN (0.28 g). The white precipitates obtained were washed with chloroform repeatedly and dried under vacuum to give 0.18 g (54%) of $CH_3(CN)Tl(OCOC_2H_5)$. The other methyl(cyano)thallium carboxylates were also prepared in a similar manner. Properties of these new compounds are tabulated in Table 1.

Spectra

The UV spectra were measured on a Hitachi 124 spectrophotometer using 1 cm cells. The IR spectra were recorded in Nujol mulls using Hitachi EPI-2G (4000–400 cm^{-1}) and Hitachi EPI-L (700–200 cm^{-1}) spectrophotometers, both equipped with gratings. The relevant frequencies of seven new alkyl(cyano)thallium

TABLE 1

PROPERTIES OF ALKYL(CYANO)THALLIUM DERIVATIVES, R(CN)TlY

R	Y	M.p. (°C)	Analysis, found (calcd.) (%)		
			C	H	N
CH_3	Tropolonate	168–170	29.57	2.16	3.61
		(dec.)	(29.49)	(2.20)	(3.82)
CH_3	Oxinate	152–153	34.11	2.44	7.01
		(dec.)	(33.91)	(2.33)	(7.19)
CH_3	$OCOC_2H_5$	152–153	18.52	2.51	4.11
		(dec.)	(18.86)	(2.53)	(4.40)
CH_3	$OCOC_3H_7$-i	154–155	21.22	2.75	4.33
		(dec.)	(21.67)	(3.03)	(4.21)
CH_3	$OCOCH_2Cl$	144–145	13.77	1.42	3.73
		(dec.)	(14.18)	(1.49)	(4.13)
C_2H_5	Tropolonate	157–158	31.66	2.89	3.63
		(dec.)	(31.56)	(2.65)	(3.68)
C_2H_5	Oxinate	153–155	35.81	2.84	6.95
		(dec.)	(35.71)	(2.75)	(6.94)

TABLE 2

RELEVANT INFRARED FREQUENCIES FOR R(CN)TlY IN NUJOL MULLS

R	Y	$\nu(C{\equiv}N)$ (cm^{-1})	$\nu(Tl{-}CN)$ (cm^{-1})	$\delta(Tl{-}C{\equiv}N)$ (cm^{-1})
CH_3	Tropolonate	2167	352	281
CH_3	Oxinate	2170	351	290
CH_3	$OCOC_2H_5$	2175	365	304
CH_3	$OCOC_3H_7$-i	2177	366	305
CH_3	$OCOCH_2Cl$	2180	375	298
C_2H_5	Tropolonate	2164	353	275
C_2H_5	Oxinate	2160	334	288
C_2H_5	$OCOCH_3$	2174	358	303

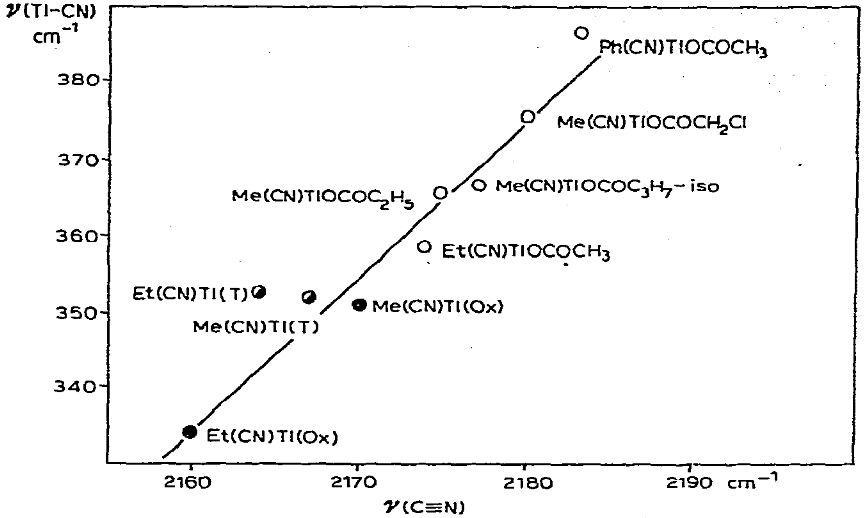

Fig. 1. IR frequencies of ν(C≡N) and ν(Tl–CN) in R(CN)TlY (in nujol mulls). T = tropolonate, Ox = oxinate.

compounds and $C_2H_5(CN)TlOAc$[6] are given in Table 2. Data for the compounds shown in Table 2 and an available compound*, $C_6H_5(CN)TlOAc$[7] are cited in Fig. 1.

RESULTS AND DISCUSSION

In the UV spectra of methyl- and ethyl(cyano)thallium oxinates in pyridine, the absorption maxima are found at 412 mμ and 408 mμ, respectively, indicating the existence of a chelating oxinate ligand[8]. The infrared spectra of alkyl(cyano)thallium compounds (Table 2) show the characteristic bands due to the covalently bonded C≡N group[9] as well as Tl–CN stretching and Tl–C≡N bending vibrations[7], and the appearance in other regions is very similar to the spectra of the corresponding dialkylthallium compounds, R_2TlY (Y = OCOR′ [2,7], oxinate[8,10], tropolonate[10]). Hence, in all of these alkyl(cyano)thallium compounds in the solid state, the ligand Y may interact with thallium atom in a chelating and/or bridging fashion to give a tetra- or penta-coordinated thallium atom analogous to that in dialkylthallium compounds, R_2TlY[10].

It has been reported that in the monoalkylthallium compounds, $RTlY_2$[3] as well as dialkylthallium derivatives, R_2TlY[10], the decrease in both the *J*(Tl–H) values and the ν(Tl–C) frequencies is interpreted in terms of the increasing thallium–ligand (Y) interaction. In the infrared spectra of the alkyl(cyano)thallium compounds, R(CN)TlY, not all of the Tl–R stretching bands could be assigned because these bands are rather weak in intensity and some strong bands due to ligands are overlapped with them. However, the ν(Tl–CN) bands, which are unambiguously assignable because of their strong intensity, hold a linear relation with ν(C≡N) frequencies as shown in Fig. 1. From Fig. 1 it is seen that the compounds containing the ligands which interact with thallium more strongly show the smaller ν(Tl–CN) and ν(C≡N) frequencies

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* The data for $CH_3(CN)TlOAc$ in ref. 7 are excluded because of the splitting of the ν(Tl–CN).

($OCOCH_2Cl > OCOC_nH_{2n+1} >$ tropolonate $>$ oxinate). For some metal cyanides in which a π-interaction, such as is often found in transition metal complexes, does not contribute significantly to the metal–cyanide bond, higher values of $\nu(C{\equiv}N)$ are observed in compounds having more covalent metal–cyanide bonds[9]. Therefore, the observed decreasing order of both $\nu(C{\equiv}N)$ and ν(Tl–CN) in some organo(cyano)thallium compounds could simply be interpreted in terms of the decreasing order of Tl–CN σ-bond strength which is brought about by the increase in Tl–ligand interaction.

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