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NOTE

STUDIES ON SOME MONOALKYLTHALLIUM BIS(DITHIOCARBAMATES) AND DITROPOLONATES

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Little work has been reported on the monoorganothallium coordination compounds except $C_6H_5TlX_2 \cdot Py$[1] (X=Cl and Br), $[C_6H_5TlX_n]^{(n-2)-}$ (X=CN[1] and halogen[2]; n=3 or 4) and $C_6H_5Tl(Ox)_2$[3]. Recently, some monomethyl- and monoethylthallium dicarboxylates and dioxinates were prepared in our laboratory containing a penta-coordinated thallium atom[4]. In this paper we will describe the preparation of several monoalkylthallium bis(dithiocarbamates) and ditropolonates and some results of their infrared and PMR spectroscopic investigations.

All the alkylthallium bis(*N,N*-dialkyldithiocarbamates) and ditropolonates prepared in this study were found to be monomeric in chloroform (Table 1), thus excluding the possibility of the intermolecular bridging through the donor atoms. The infrared spectra of $RTl(SSCNR'_2)_2$ in chloroform solutions show the bands associated with ν(C=N) at about 1500 cm^{-1} (Table 1) and only one intense band

TABLE 1

PROPERTIES OF SOME $RTlX_2$

R	X	M.p.(°C)	C(%) found (calcd.)	H(%) found (calcd.)	Mol.wt. found (calcd.)	Concn. (wt.%)	ν(C=N) or ν(C=O) (cm^{-1})[a]
CH_3	$SSCN(CH_3)_2$	117–118	18.17 (18.28)	3.54 (3.29)	453 (460)	0.63	1506
CH_3	$SSCN(C_2H_5)_2$	116–117	25.27 (25.61)	4.40 (4.49)	508 (516)	0.86	1493
C_2H_5	$SSCN(CH_3)_2$	107–108	20.28 (20.28)	3.61 (3.62)	477 (474)	0.95	1504
C_2H_5	$SSCN(C_2H_5)_2$	96–97	27.38 (27.20)	4.92 (4.75)	521 (530)	0.81	1492
CH_3	Tropolonate	151–152 (dec.)	38.86 (39.03)	2.88 (2.84)	480 (462)	0.74	1592
C_2H_5	Tropolonate	138–139 (dec.)	40.16 (40.40)	3.32 (3.18)	471 (476)	0.92	1592

[a] In chloroform solutions (5 wt.%).

in the region 1000±70 cm^{-1} (977 cm^{-1} in $R=R'=CH_3$; 989 cm^{-1} in $R=CH_3$, $R'=C_2H_5$; 975 cm^{-1} in $R=C_2H_5$, $R'=CH_3$; 989 cm^{-1} in $R=R'=C_2H_5$). These facts together with other appearance in the region of 1500 to 300 cm^{-1} are all suggestive of the existence of bidentate dithiocarbamate ligands as has been reported in the corresponding $R_2TlSSCNR'_2$ and $Tl(SSCNEt_2)_3$[5] and other metal dithiocarbamates[6]. The position of $\nu(C{=}O)$ in alkylthallium ditropolonates (Table 1) is about 20 cm^{-1} lower than that of tropolone, indicating the intramolecular coordination of the C=O groups. Consequently, a penta-coordinated thallium atom could also be assumed for these monoalkylthallium chelate compounds.

TABLE 2

$J(Tl{-}CH_3)$, $\rho(CH_3)$ AND $\nu(Tl{-}CH_3)$ FOR SOME CH_3TlX_2

X	$J(^{205}Tl{-}CH_3)$[a] (cps)	$\rho(CH_3)$[b] (cm^{-1})	$\nu(Tl{-}CH_3)$[b] (cm^{-1})	Additional bands around $\nu(Tl{-}CH_3)$
OCOPr-iso	902[c]	813 (s)	[d]	534 (vs, broad)
$OCOCH_3$	892[c]	810 (s)	527 (m)	
Tropolonate	835	806 (s)	510 (m)	527 (w), 499 (m)
Oxinate	790[c]	[d]	514 (m)	496 (vs), 489 (s)
$SSCNMe_2$	678	781 (s)	487 (m)	
$SSCNEt_2$	675	778 (s)	485 (m)	508 (w), 466 (w)

[a] In $CDCl_3$ solutions (5 wt.%); $J(^{203}Tl{-}CH_3)$ is smaller than $J(^{205}Tl{-}CH_3)$ by 8–9 cps for X = OCOPr-iso, $OCOCH_3$, tropolonate and oxinate and 5–6 cps for $X=SSCNMe_2$ and $SSCNEt_2$. [b] In Nujol mulls. [c] Ref. 4. [d] Obscured by the strong absorptions due to the ligand.

In Table 2 are given the values of $J(Tl{-}CH_3)$, $\rho(CH_3)$* and $\nu(Tl{-}CH_3)$* and in Table 3 those of $J(Tl{-}CH_2)$, $J(Tl{-}C{-}CH_3)$ and $\nu(Tl{-}C_2H_5)$* for several mono-

TABLE 3

$J(Tl{-}CH_2)$, $J(Tl{-}C{-}CH_3)$ AND $\nu(Tl{-}C_2H_5)$ FOR SOME $C_2H_5TlX_2$

X	$J(Tl{-}CH_2)$[a] (cps)	$J(Tl{-}C{-}CH_3)$[a] (cps)	$\nu(Tl{-}C_2H_5)$[b] (cm^{-1})	Additional bands around $\nu(Tl{-}C_2H_5)$
OCOPr-iso	822[c]	1626[c]	492 (w)	535 (vs, broad)
Tropolonate	793	1485	481 (w)	522 (w), 506 (m)
Oxinate	769	1398	465 (w)	492 (s), 482 (s)
$SSCNMe_2$	631	1370	463 (m)	
$SSCNEt_2$	631	1355	459 (m)	503 (w), 465 (w)

[a] In $CDCl_3$ solutions (5 wt.%); the separation of $J(^{205}Tl{-}H)$ and $J(^{203}Tl{-}H)$ was not obtained. [b] In Nujol mulls. [c] Ref. 4.

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* These vibrational frequencies were tentatively assigned by comparing the infrared spectra of the corresponding CH_3TlX_2 and $C_2H_5TlX_2$ compounds.

methyl- and monoethylthallium derivatives, respectively, all of which are thought to have a penta-coordinated thallium atom. These values decrease, with a few exceptions, in the approximate order, X = carboxylate > tropolonate > oxinate > dithiocarbamate. This order may be interpreted in terms of the increasing order of the strength of Tl–ligand interaction. A somewhat stronger Tl–ligand covalent bond would bring about weaker Tl–C bond and smaller *s* character in this bond. The correlation between the values of $\rho(CH_3)$ and $\nu(Tl-CH_3)$ has already been proposed[7] and is well established[8] in a variety of dimethylthallium derivatives, where these frequencies for the compounds having Tl–S bonds are also lower than those for others. Thus, generally in dialkyl- and monoalkylthallium compounds, the thallium atom seems to interact with sulfur more strongly than oxygen and/or nitrogen.

EXPERIMENTAL

Materials

All of the alkylthallium bis(*N*,*N*-dialkyldithiocarbamates) were prepared from alkylthallium diisobutyrates[4] and potassium *N*,*N*-dialkyldithiocarbamates. In a typical preparation, a methanol solution (10 ml) of $C_2H_5Tl(OCOC_3H_7\text{-iso})_2$ (0.4 g) was added drop by drop to 0.35 g of $KSSCN(CH_3)_2$ in the same solvent (10 ml). The pale yellow precipitates obtained immediately were recrystallized from chloroform/petroleum ether to give a pale yellow crystalline solid of $C_2H_5Tl[SSCN(CH_3)_2]_2$ (0.36 g; 75%).

Ethylthallium ditropolonate was prepared by mixing a methanol solution (10 ml) of $C_2H_5Tl(OCOC_3H_7\text{-iso})_2$ (0.4 g) and an aqueous solution (40 ml) of tropolone (0.25 g) which was then allowed to stand in solution for a day. The pale yellow powders were dried under vacuum (0.24 g; 50%). Methylthallium ditropolonate was prepared in the same manner.

Properties and analytical data of these compounds are given in Table 1.

Molecular weight

Molecular weights of alkylthallium chelates were determined using a Mechrolab vapor pressure osmometer Model 302 in chloroform at 25°.

Infrared spectra

The infrared spectra were obtained using a Hitachi EPI-2G spectrophotometer equipped with gratings. Spectra were measured in either Nujol or hexachlorobutadiene mulls and in chloroform solutions (5 wt.%).

PMR spectra

The PMR spectra were measured on a Japan Electron Optics JNM-3H-60 spectrometer at 60 MHz and a Varian 3H-100 spectrometer at 100 MHz.

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