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AN INFRARED STUDY OF ORGANOTHALLIUM THIOCYANATES

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Summary

Some structural aspects of the organothallium(III) thiocyanates R_2TlCNS (R = Me, Ph), $[Ph_4As][Me_2Tl(CNS)_2]$ and $PhTl(CNS)_2$ have been studied by IR spectroscopy. From the frequencies of the NCS group vibrations in the solids, and the integrated intensity of the C≡N stretching absorption in solution, it was ascertained that the diorganothallium derivatives are isothiocyanates with a certain amount of ionic character in the Tl—NCS bonds, whereas $PhTl(CNS)_2$ is essentially a Tl—SCN bonded compound. Apparently both solid Me_2TlCNS and $[Ph_4As][Me_2Tl(CNS)_2]$ do not show IR active $\nu_s(TlC_2)$bands. The compound Me_2TlCNS displays a double $\nu_{as}(TlC_2)$ band, from which the presence in the solid of non-equivalent Me_2Tl^{III} moieties could be inferred.

Possible configurations of the dimethylthallium derivatives are discussed.

While organothallium(III) thiocyanates have been known for a long time, no investigations of their structures have been reported The literature contains references to the preparation of R_2TlCNS (R = Me[1,2], Et[3], Ph[2]) and $PhTl(CNS)_2$ [4]. Compounds $[Ph_4As][R_2Tl(CNS)_2]$ (R = Me, Ph), formulated as salts containing $R_2Tl(CNS)_2^-$ anions in acetone solution, have also been reported [2] These anionic species, as well as $PhTl(CNS)_n^{2-n}$ (n = 3, 4) [5,6], have been detected also in aqueous solution (at suitable thiocyanate-ligand concentration). The monophenylthallium complexes, in contrast to the related $PhTlX_n^{2-n}$ (n = 3, X = Cl, Br, I, CN; n = 4, X = Cl) [2,4,7], have not been isolated in the solid state

This paper reports an infrared study on solid Me_2TlCNS, Ph_2TlCNS, $[Ph_4As][Me_2Tl(CNS)_2]$ and $PhTl(CNS)_2$, chosen as representative compounds The investigation has been extended to solution spectra, measuring the apparent integrated absorption intensity of the C≡N stretching frequency, in order better to elucidate the nature of thallium—thiocyanate bonds in these compounds

Experimental

The organothallium thiocyanates were prepared according to published methods[2,4]

TABLE 1

RELEVANT IR ABSORPTIONS (cm^{-1}) OF SOLID ORGANOTHALLIUM(III) THIOCYANATES

Me_2TlCNS	Ph_2TlCNS	$[Ph_4As][Me_2Tl(CNS)_2]$	$PhTl(CNS)_2$	Assignments
2050 (sb)	2050 vs (br)	2050 s	2130 m(br)	$\nu(C{\equiv}N)$
2035 vs (br)		2030 s		
950 w				$2 \times \delta(NCS)$
935 w				
800 vs (br)		800 m (br)		$\rho(CH_3)$
750 s	755 m			$\nu(C{-}S)$
550 m		545 mw		$\nu_{as}(Tl{-}C_2)$
540 m				
470 ms	480 w		455 m	$\delta(NCS)$
465 ms			420 w	
	455 s		435 ms	$\nu(Tl{-}Ph)$
			280 m	$\nu(Tl{-}S)$

All spectra were taken with a Perkin—Elmer Model 457 spectrometer. Solids were examined as Nujol mulls, and their absorption bands are listed below; in Table 1 are summarized the assignments made for internal vibrational modes of the thiocyanate group, as well as for other frequencies useful to the discussion. The compound $PhTl(CNS)_2$ showed appreciable decomposition in the radiation beam and its spectrum was recorded repeatedly renewing the sample during scanning.

Me_2TlCNS: 2050 (sh), 2035 vs(br), 1115 w(br), 950 w, 935 w, 800 vs(br), 750 s, 615 w(br), 550 m, 540 m, 470 ms, 465 m cm^{-1}

Ph_2TlCNS: 2030 vs(br), 1430 m, 1325 w, 1300 w, 1060w, 1015m, 995 m, 960 w(br), 900 mw(br), 755 m, 730 s, 720 s, 685 s, 665 (sh), 480 w, 455 s cm^{-1}

$[Ph_4As][Me_2Tl(CNS)_2]$: 2050 s, 2030 s, 1435 m, 1305 w(br), 1185 w, 1165 w, 1080 s, 1020 w, 995 m, 965 w, 920 w, 800 m(br), 740 (sh), 730 s, 685 s, 545 mw, 475 ms, 470 s, 350 m cm^{-1}

$PhTl(CNS)_2$: 2130 m(br), 1435 m, 1325 w, 1160 vw, 1060vw, 1010 ms, 990 ms, 910 w, 840 w(br), 735 s, 675 ms, 650 m, 455 m, 435 ms, 420 w, 280 m cm^{-1}.

For the intensity measurements of the $\nu(C{\equiv}N)$ band of compounds in acetone solution (c = 1 to $2 \times 10^{-2} M$), a CsI cell of 0.03 cm path length (l) was used in order to record solvent and solution spectra in the region 2200 to 2000 cm^{-1}, employing a 10 × abscissa expansion of the instrument. The apparent intensity of the band (A) was evaluated by direct graphic integration of the expression [8]:

$$A = \frac{2 \cdot 3}{ncl} \int \lg \frac{T_0}{T}\, d\nu$$

where n is the number of thiocyanate groups in the compound, in order to normalize results for different stoichiometries. T_0 and T are respectively the transmittances of solvent and sample solution.

All experiments were run in duplicate; for comparison purposes, analogous measurements were performed on KCNS and Me_4NCNS solutions. The results are reported in Table 2.

TABLE 2

FREQUENCY (cm^{-1}), AND INTEGRATED ABSORPTION INTENSITY A(M^{-1} cm^{-2}) OF THE ν(C≡N) BAND, OF THIOCYANATES IN ACETONE SOLUTION

Compound	ν(C≡N)	$A \times 10^{-4}$
Me_2TlCNS	2040	6 0
Ph_2TlCNS	2050	5 5
$[Ph_4As][Me_2Tl(CNS)_2]$	2050	5 4
$PhTl(CNS)_2$	2120, 2055	1 1
Me_4NCNS	2055	3 6
KCNS	2060	3 9

Discussion

Vibrations of thiocyanate groups

Using the latest IR spectroscopic criteria [9—15] for distinguishing the types of bonding of thiocyanates, it may be inferred that values of ν(C≡N), ν(C—S) and δ (NCS) for R_2TlCNS (R = Me, Ph) indicate a coordination through the N atom. However, the energies of thiocyanate vibrational modes in these compounds are not substantially different from those displayed by ionic thiocyanates and, in consideration of the solution data discussed below, it seems reasonable to assume that this spectral behaviour is indicative also of a consistent ionic character of the Tl—NCS bonds. The ν(C≡N) and ν(C—S) modes of R_2TlCNS are very close to those of Tl^I CNS [12,16], which has been described as an ionic compound; besides no Tl—NCS stretch could be identified in these compounds above 250 cm^{-1}; this is analogous to findings concerning Tl^ICNS In the spectrum of $[Ph_4As][Me_2Tl(CNS)_2]$, the regions where ν(C—S)(760—880 cm^{-1}) and δ(NCS)(460—485 cm^{-1}) are expected to occur for *N*-bonded thiocyanate [11,14,15] are obscured by absorptions due to methyl and phenyl groups. However, no bands are observed between 400 and 450 cm^{-1}, where the bending mode of *S*-bonded derivatives would appear [11,14,15]; this fact, together with the value of ν(C≡N), strongly suggest [10—12] that the compound has the isothiocyanato structure.

A substantially different pattern is shown by $PhTl(CNS)_2$. All absorptions attributable to phenyl ring modes are essentially coincident with those observed in the spectrum of $PhTlCl_2$ [17]. This leads us to assign the sole band at 435 cm^{-1}, of the three bands in the range 400—500 cm^{-1}, to a Tl—Ph vibration (a y mode in Whiffen's nomenclature [18]), which corresponds to the unique absorption in this region detected in the spectra of $PhTlCl_2$ (440 cm^{-1} [17]) and other $PhTlX_2$ compounds (X = F, Br, OH) [17] The remaining two bands, at 420 cm^{-1} and 455 cm^{-1}, are thus assigned to δ (NCS) and strongly suggest an *S*-coordination [11,14,15] The value of ν(C≡N) is not at variance with this conclusion, though it does not exclude the occurrence of bridging thiocyanate groups [9—12] The 280 cm^{-1} absorption seems, however, better attributable to a Tl—SCN than to a Tl—NCS stretch [18,19] It is worth noting that, among thiocyanates of Group IIIB elements, those of B^{III} [20], Al^{III} [21] and Ga^{III} [22] are *N*-bonded, whereas $In(CNS)_3$ [23,24] contains bridging NCS (pure inorganic Tl^{III} thiocyanates are not known). The proposed Tl^{III}—SCN coordination can be understood, at least qualitatively [25], in terms of increasing softness character along the Group.

Solution data on the intensity of the C≡N stretching frequency are essentially in agreement with solid state results. The criterion, according to which values of A below ~$2.5 \times 10^4\ M^{-1}\text{cm}^{-2}$ are indicative of S-bonding, those above ~$8 \times 10^4\ M^{-1}\ \text{cm}^{-2}$ suggest N-bonding, while "ionic" thiocyanates give intermediate values (~ 4–$6 \times 10^4 M^{-1}\ \text{cm}^{-2}$), has been widely exploited [12,26–30]. The measured values of A for the R_2Tl^{III} derivatives here studied, though excluding a coordination via the S atom of NCS groups, are intermediate between those of KCNS and Me_4NCNS and those expected for isothiocyanates. This is again interpreted as indicating the consistent ionic character of Tl–NCS bonds. In acetone solution Me_2TlCNS does not behave as a strong electrolyte, however, the measured conductivity ($\Lambda_m = 8.1\ \text{ohm}^{-1}\ \text{cm}^{-2}\ \text{mole}^{-1}$, at $5 \times 10^{-3}\ M$) compares with that reported for Me_2TlNO_3 and may also be due to ion pairs formation in this solvent [31]. The second band at 2055 cm^{-1} in the solution spectrum of $PhTl(CNS)_2$ may arise from free NCS^-, but the value $A = 1.1 \times 10^4 M^{-1}\ \text{cm}^{-2}$ leaves no doubts about the thiocyanato nature of this compound.

Vibrations of the Me_2Tl^{III} moiety

The $\nu_{as}(TlC_2)$ and $\nu_s(TlC_2)$ vibrations for dimethylthallium derivatives are expected to occur in the ranges 560–510 cm^{-1} and 500–450 cm^{-1}, respectively [32]. These portions of spectra of Me_2TlCNS and $[Ph_4As][Me_2Tl(CNS)_2]$ are reported in Fig. 1. Whereas a single $\nu_{as}(TlC_2)$ absorption at 545 cm^{-1} is observed for the latter, a double band with peaks at 550 cm^{-1} and 540 cm^{-1} is displayed

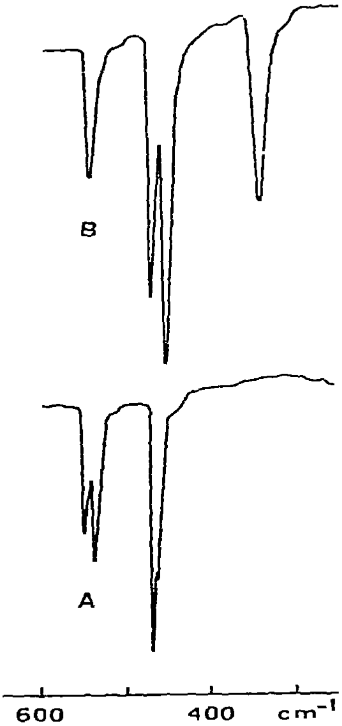

Fig. 1. Low frequency IR spectra of Me_2TlCNS (A) and $[Ph_4As][Me_2Tl(CNS)_2]$ (B)

by Me$_2$TlCNS, which would indicate the existence in the solid of non-equivalent Me$_2$Tl^{III} moieties

Whether an IR-active ν_s(TlC$_2$) is present or not in both spectra is questionable, as in the region of interest there are absorptions due to δ(NCS) and to phenyl groups (for the tetraphenylarsonium salt) Nevertheless, some cosiderations seem to indicate the IR-inactivity of this band In fact, published data[32] show that the difference between ν_{as}(TlC$_2$) and ν_s(TlC$_2$) frequencies in dimethylthallium derivatives is of the order of 45—65 cm^{-1}, and that there exists a linear correlation between the methyl rocking frequency, ρ(CH$_3$), and ν_s, ν_{as}(TlC$_2$) [33] These criteria should locate the value of ν_s(TlC$_2$), for Me$_2$TlCNS and [Ph$_4$As] [Me$_2$Tl(CNS)$_2$], in the regions 505—475 cm^{-1} and 500—480 cm^{-1}. These frequency ranges in the recorded spectra are actually free from bands, suggesting the possible linearity of Me$_2$Tl^{III} moieties in both compounds.

A linear C—Tl—C skeleton has been reported in many solid compounds Me$_2$TlX (X = Cl, Br, I, ClO$_4$, NO$_3$and others) Vibrational studies on Me$_2$TlClO$_4$ and Me$_2$TlNO$_3$ [1,31] indicate that these are ionic compounds containing Me$_2$Tl$^+$ cations and the corresponding free anions. The X-ray structure of dimethylthallium halides[34] consists of layers in which a Me$_2$Tl^{III} group is surrounded by four halogens and each halogen by four Me$_2$Tl^{III} groups; this structure has been often referred to as an ionic lattice, but, at least in the case of the chloride, it has been also described [35] as an extended polymer with bridging halogens, where Tl^{III} would assume an octahedral stereochemistry

For dimethylthallium thiocyanate an ionic Me$_2$Tl$^+$NCS$^-$structure seems unlikely (as there will be a certain amount of covalency in the Tl—NCS bonds), and an explanation of both linearity and non-equivalence of the Me$_2$Tl moieties should perhaps consider the solid formulated as[Me$_2$Tl][Me$_2$Tl(NCS)$_2$], containing (as limit case) Me$_2$Tl$^+$ cations and polymeric Me$_2$Tl(NCS)$_2^-$ species in which Tl atoms are hexacoordinated. The structure of Me$_2$TlCNS and of[Ph$_4$As] [Me$_2$Tl(CNS)$_2$] would then probably be closely related. Further structural investigations on these compounds are clearly needed, and will be soon carried out in this laboratory.

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