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Complexes of Organothallium(III) with *Cis*-1,2-dicyanoethylenedithiolate Ion and a 'Tripod' Ligand. Synthesis, Infrared and Proton Magnetic Resonance Spectra and Reactivity

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The reaction of cis-*1,2-dicyanoethylenedithiolate ion (mnt^{2-}) with organothallium(III) derivatives has been examined. The complexes* $[(CH_3)_2Tl]_2mnt$ *and* $[(C_4H_9)_4N][(C_6H_5)_2Tl\ mnt]$ *have been synthesized. The results seem to indicate a trend in reactivity similar to that of arylmercury(II) derivatives towards chelating agents with nucleophilic character. In addition, the complex* $[(CH_3)_2Tl(tren)][BPh_4]$ *has been obtained as a test of the complexing ability of 2,2′,2″-triaminotriethylamine(tren) towards organometallic moieties. I.r. and* ^1H *n.m.r. are presented and discussed.*

Introduction

In a previous communication [1] we reported the synthesis and preliminary investigation of anionic complexes of the organometallic moieties methylmercury(II) and dimethylthallium(III) with the potentially bidentate ligand *cis*-1,2-dicyanoethylenedithiolate ion.

This work is part of a research aimed at elucidating the coordinating ability of sulphur-donor ligands towards organometallic moieties of biological interest.

Thiol-containing chelating agents have been shown to increase the uptake of thallium(I) by the brain, similarly to the activity of BAL (2,3-dimercapto-1-propanol) towards mercury [2]. In general, most research has focused on various aspects of the biological activity of organomercury derivatives [3]. Organothallium(III) compounds have received so far only scanty attention, in spite of the fact that there seem to be many analogies between RHg^+ and R_2Tl^+ derivatives [4].

The most relevant aspect which thallium has in common with mercury and lead is, apart from the known toxicity of thallous salts, the occurrence *in vivo* of a biomethylation process [5] which converts thallous salts into methylthallium(III) derivatives. It is worth noting that in the process the formal oxidation number of the metal ion is increased. The only other example of a similar change is reported [6] to occur in the case of the *in vivo* methylation of Pb^{2+}, while during biomethylation of mercury compounds [7] there is no change in the oxidation state. Previously [8] it had been found, examining model systems for the transfer of the methyl group from methyl vitamin B_{12} to thiolates (a process which leads to the biological synthesis of methionine) that methyl vitamin B_{12} will methylate Tl^{III} but not Tl^{I}, however the resulting methylthallium(III) species could not be isolated.

Huber *et al.* [5] could detect $(CH_3)_2Tl^+$ as the only methylated thallium species which is formed under anaerobic conditions.

This is understandable in view of the fact that the monomethylthallium(III) species tend to be rather unstable in water, in contrast with dimethylthallium(III).

In this work we explored the reaction of *cis*-1,2-dicyanoethylenedithiolate ion with arylthallium(III) derivatives (*i.e.* $PhTlCl_2$ and Ph_2TlCl), and the results seem to indicate a trend in reactivity similar to that of arylmercury(II) derivatives towards chelating agents with nucleophilic character and in addition we synthesized the neutral complex *cis*-1,2-dicyanoethylenedithiolatobis-(dimethylthallium(III)). Lastly, we examined the coordination ability of the multidentate ligand tren (2,2′,2″-triaminotriethylamine) belonging to the class of the socalled 'tripod' ligands, whose sequestering ability towards organometallic moieties such as $(CH_3)_2Tl^+$ and CH_3Hg^+ has not yet been tested.

Experimental

Disodium *cis*-1,2-dicyanoethylenedithiolate (Na_2-mnt, mnt^{2-} = maleonitriledithiolate dianion, a trivial name for the ligand) and organothallium(III) salts were prepared according to literature methods [10, 11]. 2,2′,2″-triaminotriethylamine was purchased from Strem Chemicals and used without purification.

TABLE I. Analytical Data (%) and Melting Points (uncorrected).

Compound (colour)	C calcd. (found)	H calcd. (found)	N calcd. (found)	S calcd. (found)
$[(C_4H_9)_4N][(C_6H_5)_2Tl(S_2C_2(CN)_2]$ (orange)	51.85 (51.80)	6.21 (6.22)	5.67 (5.75)	8.67 (8.81)
$[(CH_3)_2Tl]_2[S_2C_2(CN)_2]$ (yellow)	15.76 (15.90)	1.97 (2.00)	4.60 (4.40)	
$[(CH_3)_2TlN(C_2H_4(NH_2))_3][B(C_6H_5)_4]$ (white)	54.92 (54.83)	6.29 (6.25)	8.01 (7.79)	

TABLE II. Selected Infrared Data for $Ph_2Tl(mnt)^-$ and $(CH_3)_2Tl(tren)^+$ Ions.[a]

Compound		Qualitative Assignments
$[Bu_4N][Ph_2Tl(mnt)]$	2205 s 2198 vs	ν(C≡N)
	445 s 435 w	$TlPh_2$ y and y′ mode[b]
	282 m	ν(Tl–S)
$[(CH_3)_2Tl(tren)][BPh_4]$	890 m	$\rho(CH_2)$tren
	750 m	$\rho(NH_2)$tren
	532 m, bd	$\nu(TlC_2)$ + tren

[a] Abbreviations: w = weak, m = medium, s = strong, vs = very strong. [b] Whiffen's notation.

Synthesis of $[Bu_4N][Ph_2Tl(mnt)]$ *and* $[(CH_3)_2Tl]_2$*-mnt*

The complex $[Bu_4N][Ph_2Tl(mnt)]$ was prepared according to the procedure previously outlined [1]. Attempts to synthesize the Ph_4As^+ analog invariably yielded the inorganic thallium(III) complex, *i.e.* $Tl(mnt)_2^-$.

The neutral species $[(CH_3)_2Tl]_2$mnt was obtained by mixing ethanolic solutions of $(CH_3)_2TlNO_3$ (0.538 g, 1.815 mmol) and the ligand (0.169 g, 0.9 mmol), under stirring and gentle heating. A yellow precipitate appeared, which was collected on a sintered glass filter, washed thoroughly with absolute ethanol and dried in vacuo over P_4O_{10}. Heated under reflux, some decomposition of the complex was observed. The yield was 24%.

Reaction of $PhTlCl_2$ *with* Na_2mnt

A solution of $PhTlCl_2$ (0.478 g, 1.35 mmol) in 20 ml of absolute ethanol was added to an ethanolic solution of Na_2mnt (0.253 g, 136 mmol) and stirred under gentle heating for 1 hr. The solution turned from yellow to deep red and a white precipitate separated, which was filtered. The analytical data and the infrared spectra helped to identify it as Ph_2TlCl. The filtrate was evaporated to dryness with a rotary evaporator giving a brown paste. The infrared spectra do not agree with known pure compounds ($Ph_2Tl(mnt)^-$ or $Tl(mnt)_2^-$).

Synthesis of $[(CH_3)_2Tl(tren)][BPh_4]$ *(tren = 2,2′,2″-triaminotriethylamine)*

To a solution of $(CH_3)_2TlNO_3$ (0.450 g, 1.51 mmol) dissolved in 20 ml of ethanol dried over molecular sieves 3A - type, an equimolar amount of 2,2′,2″-triaminotriethylamine was added under stirring. Upon addition of $NaBPh_4$, dissolved in the minimum amount of ethanol, a white precipitate was instantly formed in nearly quantitative yield, which was filtered, washed with dry ethanol and dried in vacuo over P_4O_{10}. The compound is soluble only in donor solvents as pyridine and dimethylsulphoxide. Microanalyses were performed by Laboratorio di Microanalisi, Istituto di Chimica Organica dell'Università, Milano. Analytical data are reported in Table I. Infrared spectra were obtained as split mulls and in pyridine solution using Perkin Elmer Model 457 and 580 spectrometers and CsI disks in the 4000–250 cm^{-1} region and KBr cells, 0.1 mm path length, for the solution. Selected i.r. data are reported in Table II for $Ph_2Tl(mnt)^-$ and $[(CH_3)_2Tl(tren)][BPh_4]$, while the observed frequencies and qualitative assignments for

TABLE III. Infrared Data and Qualitative Assignments for $[(CH_3)_2Tl]_2$mnt in the Region below 1000 cm^{-1}.[a]

890w 850s	(860 m)	ν(C–S)mnt
790 s, bd 722 m, bd		ϵ(Tl–CH$_3$)
565 m 520 s	(545 m) (520 s)	$\nu_{as}(TlC_2)$
	(462 w)	$\nu_s(TlC_2)$
280 m		ν(TlS)

[a] Values in parenthesis refer to the spectrum in pyridine solution. Abbreviations: w = weak, m = medium, s = strong, bd = broad.

$[(CH_3)_2Tl]_2$mnt are reported in Table III. ^1H n.m.r. spectra were obtained with a Jeol C60 spectrometer operating at 60 M Hz, the temperature of the probe being *ca.* 26 °C, using $[^2H_5]$ pyridine as solvent and TMS as internal standard and are presented in the text under Discussion.

Results and Discussion

The reaction of Na_2mnt with the diorganothallium(III) derivatives not unexpectedly shows some similarity as far as chemical reactivity and stability of their complexes are concerned with the corresponding organomercury(II) derivatives, since the two moieties are isoelectronic.

The stability of the complexes is apparently affected by the nature of the organic group attached to the metal atom. Both $PhHg^+$ and Ph_2Tl^+ undergo a carbon–metal σ bond cleavage reaction which afford $Hg(mnt)_2^{2-}$ [1] and $Tl(mnt)_2^-$ respectively. Moreover, at least in the case of diorganothallium-(III)–mnt complexes, the choice of the counterion seems to be critical. Packing forces in the crystal are believed to be the determining factor [12]. Preferential stabilization of certain complexes by using specific counterions has been observed in other mnt^{2-} complexes. Reaction with diaryltin(IV) dihalides yields pentacoordinate tin complexes $[Ph_4As]$-$[Ph_2Sn(mnt)Cl]$ or hexacoordinate $[Bu_4N]_2[Ph_2Sn(mnt)_2]$ analogs, while in the case of dialkyllead(IV) derivatives with any of the aforementioned cations $Pb(mnt)_2^{2-}$ was obtained [12]. The influence of the ligand itself is more evident in the reaction between $PhTlCl_2$ and Na_2mnt which was expected to yield the neutral complex by means of a metathetical reaction. The formation of Ph_2TlCl indicates that a symmetrization reaction did occur. A thermally induced symmetrization reaction is known to occur with $PhTlCl_2$ in boiling water, yielding Ph_2TlCl and $TlCl_3$ [13]. In the case of $PhHg^+$ derivatives such reaction is reported to occur under milder conditions [14] (*i.e.* room temperature): $(PhHg)_2BALH(BALH_3$ = 2,3-dimercapto-1-propanol) and $(PhHg)_2DMPH(DMPH_3$ = 1,3-dimercapto-1-propanol) undergo a symmetrization reaction yielding Ph_2Hg and Hg(BALH) and Hg(DMPH) respectively. A detailed multi-step mechanism for the case of arylmercury(II) salts in the presence of a chelating agent has been proposed [15]. The nucleophilicity of the formed chelate complex seems to be a critical factor in determining the symmetrization. If the ligand is a poor nucleophile, the presence of an auxiliary ligand (ammonia, amine, *etc.*) is needed. Mnt^{2-}, an unsaturated bidentate sulphur chelating ligand appears to promote similar reactions both in the case of arylmercury(II) [1] and arylthallium(III) derivatives.

I.r. and ^1H Nmr Spectra

The infrared spectra of $Ph_2Tl(mnt)^-$ have been compared with those of the $(CH_3)_2Tl(mnt)^-$ analog. Vibrational assignments for the organometallic moiety are based on those of Srivastava *et al.* [16]. Only minor variations are observed in the vibrations associated with the ligand in $Ph_2Tl(mnt)^-$, $(CH_3)_2Tl(mnt)^-$ and $Tl(mnt)_2^-$. This might indicate that the bonding is largely ionic in character. The Ph_2Tl^+ complex has vibrational bands attributable to 'X-sensitive' modes of the Ph_2Tl^+ group at 445 and 435 cm^{-1}. The vibration is an out-of-plane bending mode of the aromatic ring ("y" in Whiffen's notation) [17] and is known to undergo splitting (y') due to interaction between phenyl ring vibrations. This frequency is reported to be metal dependent in phenyl derivatives of Si, Ge, Sn and Pb [18]. Identification of the remaining modes in the spectra of this compound is somewhat difficult due to their low intensity or since they are obscured by the Bu_4N^+ cation vibrations. The medium intensity band at 282 cm^{-1} is tentatively assigned to the ν(Tl–S) vibration, since the vibrations of the Ph_2Tl^+ group expected in the low frequency region are reported [16] to be weaker in intensity.

The infrared spectra of $[(CH_3)_2Tl(tren)][BPh_4]$ are dominated by the absorption due both to the ligand and the anion. Vibrations due to the ligand are recognized on the basis of the work of Watt *et al.* [19] on complexes of polyamines with transition metal ions. They show a complex structure in the region where $\nu(NH_2)$ is expected (3300–3000 cm^{-1}) due to hydrogen bonded amino groups. A slightly broadened band, present at 532 cm^{-1}, in a region where $\nu_{as}(TlC_2)$ is expected, is interpreted as a superimposition of the vibration due to the organometallic moiety and coordinated ligand. The region 500–450 cm^{-1} where $\nu_s(TlC_2)$ the symmetric stretching vibration is expected, is obscured by vibrations due to BPh_4^-. The complex is insoluble in most non-donor solvents and decomposes above 250 °C which seems to indicate the presence of strong inter- and/or intramolecular interactions in the solid state.

In the ^{1}H n.m.r. spectra of the complex, the usual pattern due to coupling with ^{205}Tl and ^{203}Tl isotopes, both having spin I = 1/2 and high natural abundances (70.5 and 29.5% respectively) is observed. The concentration was *ca.* 20% by weight in [$^2H_5$] pyridine and τ and $^2J(^1H-^{205}Tl)$ values are 9.00 p.p.m. and 411 Hz respectively. $^2J(^1H-^{203}Tl)$ is *ca.* 3 Hz less than $^2J(^1H-^{205}Tl)$. ^2J has been shown [20] to be dependent on solvent and concentration. Under comparable conditions $^2J(^1H-^{205}Tl)$ is found to be 414 Hz in dimethylthallium(III) tetraphenylborate, although by comparison with the ^{1}H n.m.r. spectrum of the ligand it may be inferred that the cation with the chelating 2,2′,2″-triaminotriethylamine does not undergo dissociation at the temperature of the experiment. Tren is reported [21] to bind selectively Cu^{2+} in presence of Ca^{2+} and Mn^{2+} ions. Selective uptake of mono- and divalent cations in biological systems is based upon the competitive binding of the metal(s) for the functional sites and depends on the charge, size and preference for liganding donors. While the use of 2,2′,2″-triaminotriethylamine as masking agent has found applications in analytical chemistry (*e.g.* titrations with EDTA) the possibility of using it as antidote for metal poisoning has yet to be tested, but it looks promising, even in the case of CH_3Hg^+, in view of the high binding constant of the ligand, effective at physiological pH, with class B metal [21].

The infrared spectrum of the neutral complex shows only a single intense band at 2198 cm^{-1}, due to ν(C≡N) stretching vibration, while both in $Me_2Tl(mnt)^-$ and $Ph_2Tl(mnt)^-$ this appears to be split into a doublet. Assignments for the vibrations associated with the ligand are based on those of Nakamoto *et al.* [22].

In the region above 1000 cm^{-1} the spectrum of the complex resembles that of the free ligand ion even in the case of the band associated with ν(C=C) (1440 cm^{-1}) which reportedly [22] shows a marked increase in dithiolato complexes of transition metal ions, in addition to being sensitive to changes in the electronic structure of the complex. Since the same vibration in the complex $Tl(mnt)_2^-$ and $(CH_3)_2Tl(mnt)^-$ recurred at 1435 cm^{-1} and 1440 cm^{-1} respectively, this might be an indication of the poorer acceptor properties of thallium(III) ions. Vibrations associated with the dimethylthallium(III) moiety are tentatively assigned to a weak band at 1172 cm^{-1} (methyl deformation) while strong absorptions due to the ligand are present at 1154 and 1112 cm^{-1}.

In the region below 1000 cm^{-1} bands due both to the ligand and $(CH_3)_2Tl^+$ appear to be split into doublets. Two ligand vibrations which reportedly contain some ν(C–S) character, are present at 890 and 850 cm^{-1}. Rocking vibrations associated with $(CH_3)_2Tl^+$ are assigned to a band at 790 cm^{-1} which is followed by a less intense, broad one, at 722 cm^{-1}, which we cannot confidently assign to a similar vibration in view of the lack of the expected linear relationship between this frequency and any of the $\nu_{as}(TlC_2)$ [23].

In the region 600–400 cm^{-1} where $\nu_{as}(TlC_2)$ and $\nu_s(TlC_2)$ are expected to occur, the infrared spectrum of the solid shows absorptions at 565 (w) and 520 (s) cm^{-1}, while in the spectrum of pyridine solution the first appears to be shifted to 545 cm^{-1}, the second remains unchanged and additionally a 462 cm^{-1} absorption is detected. The last one is assigned to the skeletal $\nu_s(TlC_2)$ symmetric stretching vibration. In the previously investigated $(CH_3)_2Tl(mnt)^-$, the $\nu_{as}(TlC_2)$ was present at 520 cm^{-1}, while the region where $\nu_s(TlC_2)$ is expected, was obscured by absorptions due to the $(C_6H_5)_4As^+$ ion. By comparison, the spectrum of dimeric $[(CH_3)_2TlSCH_3]_2$ [20] exhibits $\nu_s(TlC_2)$ at 469 cm^{-1}.

In the lower region of the spectrum, a ν(Tl–S) vibration is found at 280 cm^{-1} in good agreement with the value of the analogous vibration in $(CH_3)_2Tl(mnt)^-$ [1].

It is tempting to suggest, comparing the spectra of the neutral complex with those of the $(CH_3)_2Tl(mnt)^-$ ion, that two non-equivalent $(CH_3)_2Tl^+$ moieties are present, one being $(CH_3)_2Tl(mnt)^-$. Owing to the poor solubility in non-donor solvents no molecular weight or conductivity data could discriminate between the formulation of the complex as a neutral binuclear species $[(CH_3)_2Tl]_2$mnt, analogous to the simple thiolato derivatives $[(CH_3)_2Tl(SR)]_2$ (R = CH_3, C_6H_5) [20], and an ionic formulation $[(CH_3)_2Tl][(CH_3)_2Tl(mnt)]$, where the cation might be bound by sulphur bridging atoms from the anion. Nor can we extract from a simple skeletal vibrational analysis a definite proof of the structure, given the low symmetry of the molecule in both instances.

The i.r. spectra in pyridine solution also support the ionic formulation. In addition to the absorption at 520 cm^{-1}, the band at 545 cm^{-1} compares closely with the value of the $\nu_{as}(TlC_2)$ for $(CH_3)_2TlClO_4$ in pyridine solution (548 cm^{-1}), where the $(CH_3)_2Tl^+$ ion is believed to be coordinated by pyridine while the anion appears to be not bound [20]. Moreover, going from the spectrum in the solid state or solutions of this salt in oxygen donor solvents to a pyridine solution, a strong shift of the asymmetric stretch is observed towards lower frequency [20], and that may offer an explanation for the shift of the band at 565 cm^{-1} (solid) to 545 cm^{-1} (solution). Since the separation between $\nu_{as}(TlC_2)$ and $\nu_s(TlC_2)$ is reported [20] to be in the range of 45–65 cm^{-1}, we are inclined to assign the $\nu_s(TlC_2)$ vibration at 462 cm^{-1} to the $(CH_3)_2Tl(mnt)^-$ moiety. An intense absorption due to pyridine near 500 cm^{-1} prevents any possibility of locating $\nu_s(TlC_2)$ due to the cation

$(CH_3)_2Tl^+$. The absence of an observable symmetric stretching frequency in the i.r. spectrum in the solid state seems to indicate a linear structure for the dimethylthallium(III) moiety, in a centrosymmetric molecular geometry; since the i.r. spectrum of a pyridine solution contains both the symmetric and asymmetric stretch, it seems plausible that in solvents such as pyridine the nearly linear $(CH_3)_2Tl^+$ is somewhat distorted.

In the ^1H NMR spectrum of the complex a single set of ^2J is observed, $^2J(^1H-^{205}Tl)$ being 396 Hz, $^2J(^1H-^{203}Tl)$ *ca.* 3 Hz less, and τ 8.57 p.p.m. Clearly we are at loss explaining it on the basis of the rather extreme ionic formulation given above, although this might be the result of a ligand exchange process caused by the interaction with the donor solvent, which is fast on the ^1H n.m.r. time scale. It seems more reasonable to suggest, in accordance with the reported structures [24] of dimethylthallium(III) thiocyanate and the chelate complex with acetylacetonate, that extensive polymerization takes place in the solid state, where each monomeric unit is held together by further Tl–S bonds, while in pyridine solution we must take into account the donor ability of the solvent.

Caution must be exercised in comparing ^1H n.m.r. spectra obtained in different conditions, in view of the dependence of τ and ^2J from solvent and concentration. We may only remark that, as previously observed [20], the smaller ^1H n.m.r. parameters in the case of the complex having Tl–S bonds, relative to those of $(CH_3)_2Tl(tren)^+$, suggest that organothallium(III) interacts more strongly with sulphur than with nitrogen donors.

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