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Organomercury(II) and Organothallium(III) Complexes with *Cis*-1,2-dicyanoethylenedithiolate Ion

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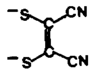
There is a considerable interest in the interaction of organomercurials with nucleosides and nucleotides [1]. These studies are essentially devoted to defining metal binding sites, stabilities of the complexes and changes in the conformation and properties of the base moiety following the metallation. On the other hand, it has been established for a long time that the strongest affinity of both Hg^{II} and organo Hg^{II} is toward the –SH group, hence the name "mercaptans" for thiols [2]. Uchida *et al.* isolated from shellfish an organomercurial compound which they characterized as methyl(methylthio)mercury(II) [3]. BAL (2,3-dimercapto-1-propanol), penicillamine and their derivatives are the sulphur chelating agents most widely tested for their therapeutic activity and ability in sequestering the (organo)metallic moiety and acting as antidotes for metal poisoning. Analogies in the biological activity of organomercurials and organothallium(III) derivatives have been found [4].

X-ray structure determinations of 1:1 and 2:1 derivatives of DL-penicillamine with CH_3Hg^{II} have been reported [5].

In this communication we report the synthesis and a preliminary infrared and ^1H n.m.r. study of anionic complexes of the CH_3Hg^{II} and $(CH_3)_2Tl^{III}$ moieties with the potentially bidentate ligand *cis*-1,2-dicyanoethylenedithiolate. The ligand itself is



interesting not only from the point of view of general considerations on metal–sulphur bonding and electron delocalization in transition metal complexes but also because of the potential biological activity of these complexes.

Experimental

The complexes were obtained in moderate yield (30%) according to the following procedure: A suspension of CH_3HgCl or $(CH_3)_2TlCl$ (2 mmol) in dry acetone was added to a solution containing an equimolar amount of $(C_6H_5)_4AsCl$ and $2Na^+$ $S_2C_2(CN)_2^{2-}$ after removal of solid NaCl. The mixture was refluxed until all solids dissolved. After cooling, a precipitate of the tetraphenylarsonium salts of $CH_3Hg(mnt)$ and $(CH_3)_2Tl(mnt)$ respectively (mnt^{2-} = maleonitriledithiolate dianion, a trivial name for the ligand) was obtained, and the solids were recrystallized from absolute ethanol.

Analytical data are consistent with 1:1 complexes of the ligand and organometallic moiety and are reported in Table I. Both complexes are electrolytes in solution, hence they are formulated as $[Ph_4As][CH_3Hg(mnt)]$ and $[Ph_4As][(CH_3)_2Tl(mnt)]$. Selected i.r. data are reported in Table II. ^1H n.m.r. data for solutions of the complexes are shown in Table III.

Results and Discussion

Qualitative vibrational assignments reported in Table II are based on those of Nakamoto *et al.* [6]. In the region above 600 cm^{-1} the ligand vibrations are quite often obscured by those due to the $(C_6H_5)_4As^+$ ion and only slight changes in the ligand vibrational modes can be observed. The same was reported for Group IV B complexes [7]. Only the ligand vibration at 1160 cm^{-1} which reportedly arises from a contribution of a C–S stretching mode appears to be shifted towards lower frequencies (1147 cm^{-1} in both complexes). Metal–sulphur vibrations are probably associated with bands occurring at 300 cm^{-1} (see Table II). While some mixing of metal–sulphur modes with ring deformation [6] modes is to be expected, the comparison with complexes of both organometallic moieties with thiols, thiocyanate and potentially bidentate sulphur ligands enables a tentative assignment. In CH_3HgSCH_3, ν(Hg–S) is present at 333 cm^{-1} [8]; for CH_3HgSCN in methanol, where the compound is deemed to be present as a monomer.

TABLE I. Analytical Data (%) and Melting Points (uncorrected) of mnt^{2-} Complexes.

Compound (Colour)	C calcd. (found)	H calcd. (found)	N calcd. (found)	M.P. (°C)
$[(C_6H_5)_4As][(CH_3)_2Tl(S_2C_2(CN)_2)]$ (Yellow)	47.53 (47.24)	3.43 (3.61)	3.70 (3.70)	187
$[(C_6H_5)_4As][CH_3Hg(S_2C_2(CN)_2)]$ (Orange)	47.07 (47.30)	3.11 (2.90)	3.78 (3.89)	216
$[(C_6H_5)_4As]_2[Hg(S_2C_2(CN)_2)_2]$ (Yellow Green)	53.86 (53.96)	3.20 (3.27)	4.48 (4.32)	213

TABLE II. Infrared Spectra.[a]

Compound	ν(Ligand) (cm^{-1})	ν(M–S) (cm^{-1})
$[(C_6H_5)_4As]_2[Hg(mnt)_2]$	531 m 522 s	315 w
$[(C_6H_5)_4As][CH_3Hg(mnt)]$	535 m 515 s	315 m 305 w, sh
$[(C_6H_5)_4As][(CH_3)_2Tl(mnt)]$	535 w 520 s (+ν(TlC$_2$)) 505 m asym	272 m 268 w, sh

[a] Infrared spectral data and qualitative assignments for *cis*-1,2-dicyanoethylenedithiolato complexes in the solid state. The spectra were obtained as split mulls using a Perkin Elmer Model 577 spectrometer and CsI disks in the 4000–200 cm^{-1} region. Abbreviations: w = weak, m = medium, s = strong, sh = shoulder.

the same vibration occurs at 283 cm^{-1} [9]; while Adams and Cornell [10] generally assigned ν(M–S) vibrations for metal–dithiolates to the range 465–267 cm^{-1}. Among Tl^{III} derivatives, phenylthallium(III) thiocyanate [11] exhibits a thallium–sulphur vibration at 280 cm^{-1} and ν(Tl–S) modes lie in the range 300–250 cm^{-1} in the complexes of dialkylthallium (III) dithiophosphates [12]. Hence the assignments of the 272 and 268 cm^{-1} vibrations to metal–sulphur modes seems reasonable. Unfortunately vibrations associated with CH$_3$–Hg^{II} and (CH$_3$)$_2$Tl^{III} organometallic moieties are partially obscured by the ligand vibrations. We attempted to gain further information on metal–carbon vibrations by comparison with complexes of the mnt ligand with inorganic thallium and mercury. The synthesis of $[(C_6H_5)_4As][Tl(mnt)_2]$ was according to literature methods [13] while a novel Hg^{II}–mnt (see Table I) complex was obtained when mercury–carbon bond cleavage occurred in the course of an attempted synthesis of C$_6$H$_5$Hg–mnt derivatives. This was helpful only as far as the (CH$_3$)$_2$-Tl^{III} derivative is concerned.

The two bands of $[(CH_3)_2Tl(mnt)]^-$ at 520(s) and 505 cm^{-1} (m) cannot be unambiguously assigned. Ligand modes [13] are present at 534 (m) and 508 cm^{-1} (m) in $[Tl(mnt)_2]^-$. Essentially on the basis of intensity, the strong band at 520 cm^{-1} is assigned tentatively to the thallium–carbon asymmetric stretching (such a vibration occurs at 524 cm^{-1} in (CH$_3$)$_2$TlSCH$_3$ [14]) probably mixed with a ligand mode. The region below 500 cm^{-1} where ν_{sym}(TlC$_2$) might be expected in the case of a non-linear C–Tl–C unit, is obscured by absorptions due to the (C$_6$H$_5$)$_4$-As$^+$ ion.

^{1}H n.m.r. solution data are reported in Table III. No evidence of a ligand exchange process was detectable. $[(CH_3Hg(mnt)]^-$ shows values of the chemical shift and $^2J(^1H-^{199}Hg)$ which fall in the range expected for non chelated (monodentate) thiols [15]. It has been shown [15, 16] that $^2J(^1H-^{199}Hg)$ for CH$_3$HgX derivatives correlate to some extent with stability constants for the formation of CH$_3$HgX, pK$_H$ of the ligand and electronegativity of X. These observations are based on the assumption that the relative magnitude of $^2J(^1H-^{199}Hg)$ is dominated by the Fermi contact mechanism. As typical examples, for (CH$_3$)$_2$Hg and CH$_3$HgCl (in pyridine) $^2J(^1H-^{199}Hg)$ values are 104.3 and 215.2 Hz respectively. It is worth noting that a correlation between ^2J and pK$_H$ has been tested as a mean for ascertaining whether the ligand is acting as a chelate [16]. Unfortunately the dithiols corresponding to mnt^{2-} are unstable. In general, an increase in $^2J(^1H-^{199}Hg)$ is to be expected with increasing electronegativity of X. If we adopt a bonding scheme which involves hybridization of mercury 6s and 6p orbitals (a 5d$_{z^2}$–6s contribution appears to be insignificant [18]) a linear C–Hg–X is to be expected and standard theory will predict that an increase in the *s* character of the hybrid orbital of mercury involving in bonding to carbon such as might be expected [17] with increasing electronegativity of X, along with an increase of the effective nuclear charge which causes a contraction of the mercury valence 6s orbital, will lead to higher $^2J(^1H-^{199}Hg)$ values.

An increase in coordination number of mercury from two to three by chelation, if an sp^2 hybridization scheme is adopted, would lower the value of the coupling constant as it lowers the *s* electron density in the mercury–carbon bond. Compared with reported oxygen and nitrogen complexes [15, 16],

TABLE III. ^{1}H n.m.r. Data.[a]

Compound	τ(CH$_3$–M)	$^2J(^1H-^{199}Hg)$ (Hz)	$^2J(^1H-^{205}Tl)$ (Hz)	$^2J(^1H-^{203}Tl)$ (Hz)
CH$_3$Hg mnt$^{-(a)}$	9.28	183		
(CH$_3$)$_2$Tl mn$^{-(b)}$	9.15		373	370

*^{1}H n.m.r. data (Chemical shifts τ(ppm) and coupling constants (Hz) for mnt complexes). Solvent: ^{a}[^{2}H] Chloroform, ^{b}[^{2}H$_6$]-acetone, τ values are relative to TMS as internal standard. Other signals due to (C$_6$H$_5$)$_4$As$^+$ ion are present at τ 2–3 ppm. The sign of the coupling constant $^2J(H-^{199}Hg)$ is assumed to be negative [17]. ^{199}Hg, ^{205}Tl, ^{203}Tl have all spins I = 1/2 and high natural abundances (16.8, 70.5 and 29.5% respectively). The spectra were obtained with a Jeol C60 spectrometer operating at 60 M Hz. Temperature of the probe was *ca.* 26 °C.

for CH_3Hg–mnt a smaller $^2J(^1H–^{199}Hg)$ is observed; this is consistent with theory predictions and in agreement with the well established "softness" of both organometallic and ligand [2] moieties. This was also observed in complexes with monodentate sulphur ligands [15], therefore we are inclined to believe, in view of the well known tendency of methylmercury (II) ion to form two-coordinate mercury derivatives even with potentially multidentate ligands as amino-acids [19], that only one sulphur is strongly bonded in solution.

For the linear dimethylthallium(III) ion a similar bonding scheme has been advanced [14] but a substantial mixing of the filled $5d_{z^2}$ and empty 6s valence orbitals of the thallium(III) atom has been proposed. However, the coordinating ability of CH_3HgX and $(CH_3)_2Tl^+$ moieties is different and many complexes of the latter, essentially ionic in character, are known. The average value of $^2J(^1H–Tl)$ found in the case of the dithiolato complex reported in this work is essentially the same as $[(CH_3)_2TlSCH_3]_2$ which is dimeric in benzene solution [14] with bridging sulphur atoms. This might indicate that the dithiolate ligand is acting as a chelate in solution.

^1H n.m.r. spectra show only minor differences in chemical shifts compared with those of O or N bonded methylmercury(II) and dimethylthallium(III); on the contrary, it has been reported [19] that, at least in the case of methylmercury(II) derivatives, methyl ^{13}C signals are strongly dependent on the mercury bonded atom (sulphur gives the largest shifts as in the case of cysteine, thioglycolic acid and penicillamine). No evident correlation has been found [20] between the relative shielding effects of the different anions on the ^1H, ^{13}C and ^{205}Tl nuclei.

In conclusion, solid state i.r. spectra indicate coordination of the ligand to the organometallic moiety and that for $[(CH_3)_2Tl(mnt)]^-$ possibly chelation also did occur; two metal–sulphur vibrations are in fact present. Only minor changes in the ligand vibrations occur; this is not unexpected as the bonding, at least in $(CH_3)_2TlX$ derivatives, is deemed to be essentially ionic.

In view of the fact that coordination of mercury is almost entirely restricted to linear two-coordinate geometry, the possibility of chelation is open to question. The possibility of the mnt^{2-} unit acting as a unidentate ligand exists, in spite of the known chelating ability of the ligand. A reasonable model for this mnt complex is given by the known structures of methyl(2,2′-bipyridine)mercury(II) nitrate [21] and methyl(N,N′-diethyldithiocarbamato)mercury(II) [22]. In both cases the ligand is acting as anisobidentate, *i.e.* with unequal metal–sulphur lengths. In the latter, the angle C–Hg–S is 171.2° and the other sulphur of the dithiocarbamate group is weakly bonded to two mercuric ions with intramolecular and intermolecular Hg- - -S distances of 2,964 and 3.147 Å respectively. Similar weak interactions in the solid state may be responsible for the occurrence of more than one ν(Hg–S) vibration in $[CH_3Hg(mnt)]^-$. For $[(CH_3)_2Tl(mnt)]^-$ we suggest a comparison with the known structures [23] of such dimethylthallium(III) chelates as the acetylacetonate and dicyanamide. In both compounds the thallium atom is octahedrally coordinated with an almost linear C–Tl–C unit and four equatorial oxygen or nitrogen atoms, forming infinite polymers where monomeric units are held together by further Tl–O(N) bonds.

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