Complexation Behaviour of Caesium and Tetramethylammonium Trichlorostannates(II) with 7,7,8,8-Tetracyanoquinodimethane and of Tin(IV) Chloride with $\Delta^{2,2'}$-Bis(5-methyl-1,3-benzodithiolidene) and $\Delta^{2,2'}$-Bis(1,3-diphenylimidazolidene)

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The reaction of caesium trichlorostannate(II) with 7,7,8,8-tetracyanoquinodimethane affords two products, the 1:1 adduct, $CsSnCl_3 \cdot TCNQ$, and the complex $SnCl_2 \cdot (TCNQ)_2 \cdot \frac{1}{2}thf$, whilst with tetramethylammonium trichlorostannate, three complexes, $Me_4NSnCl_3 \cdot TCNQ$, $Me_4NSn(TCNQ)_3$, and $(Me_4NSnCl_3) \cdot TCNQ$, have been isolated. Tin(IV) chloride reacts with $\Delta^{2,2'}$-bis(5-methyl-1,3-benzodithiolidene) and $\Delta^{2,2'}$-bis(1,3-diphenylinidazolidene) to afford complexes of composition, $(SnCl_4)_3 \cdot (TTF)_2 \cdot (C_6H_6)_{3/2}$ and $SnCl_4 \cdot (TNF^{Ph})_{1/2}$, respectively. The structures of the complexes are discussed on the basis of infrared and tin-119 Mössbauer data.

Introduction

The chemistry and magnetic properties of strong π-acids such as 7,7,8,8-tetracyanoquinodimethane, (TCNQ), tetracyanomethylene, (TCNE), and 2,3,5,6-tetrachlorobenzene, (TCBQ), and π-bases such as tetraamino, tetrathia- and tetraselena-fulvalenes, have been extensively studied [1–4]. Tetracyanoquinodimethane, tetracyanoethylene and tetrachlorobenzene form metal salts with alkali metals, as well as lead and tin. However, whereas TCBQ and TCNQ only form the mono-radical anion [5], TCNE can form both the mono- and diradical anions [6]. The interaction of TCNQ with hexamethyldilead affords Pb(TCNQ) [7] We have previously reported the syntheses of several tin(II) and tin(IV) derivatives of TCNE, TCBQ and TCNQ [8, 9] including $(MeC_5H_4)_4Sn(TCNQ)_2$, $SnX_2(TCNE)thf$ (X = Cl, Br) [8], $R_3Sn(TCNE)$ (R = Me, Bu), $R_3Sn(TCNQ)$ (R = Me, Bu), and $R_6Sn(TCNQ)$ (R = Ph) [9]. The $R_3SnTCNE$ and $R_3SnTCNQ$ complexes are organotin substituted TCNE or TCNQ radical species, whilst Ph_6Sn_2-TCNQ appears to be a (σ–π) charge transfer complex analogous to the polysilane and digermane complexes of TCNE qnd TCNQ [10].

The π-bases, tetraamino-, tetrathia- and tetraselenafulvalenes are powerful nucleophiles and reducing agents. Cleavage of the central double bond usually occurs in the reaction of tetrakis- (aryl or alkyl amino)ethylenes to afford reaction products which are derived from half the molecule [12, 13].

In this paper we report further studies of the complexation behaviour of TCNQ with bivalent tin compounds, and of the reactions of tin(IV) chloride with $\Delta^{2,2'}$-bis(5-methyl-1,3-benzodithiolidene)(TTF) and $\Delta^{2,2'}$-bis(1,3-diphenylimidazolidene)(TNF^{Ph}).

Experimental

$\Delta^{2,2'}$-Bis(5-methyl-1,3-benzodithiolidene), TTF and $\Delta^{2,2'}$-bis(1,3-diphenylimidazolidene), TNF^{Ph} were prepared by standard methods [14, 15]. Physical and analytical data for the complexes are presented in Tables I and II.

The Reaction of $CsSnCl_3$ with TCNQ

To a suspension of white $CsSnCl_3$ (1.43 g, 4 mmol) in dry thf (20 ml) was added a bottle green solution of TCNQ (0.82 g, 4 mmol) also in dry thf (10 ml) with stirring at room temperature. After two days, the white solid had dissolved and an intense blue precipitate was produced, which was filtered off, washed with ether and dried *in vacuo* giving the deep blue $CsSnCl_3 \cdot TCNQ$ adduct (yield = 0.78 g). On further concentration of the dark green filtrate, a deep yellow product which analysed as $SnCl_2$-$(TCNQ)_2$ was obtained (yield 0.86 g).

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TABLE I. Physical and Analytical Data for the Complexes.

Complex	Colour	D.P.[a] (°C)	Microanalytical data (calc. values in parentheses)				
			C	H	N	Hal.	S
$CsSnCl_3 \cdot TCNQ$	Blue	*Ca.* 286	18.71	0.86	6.65	22.69	
			(17.99)	(0.52)	(6.99)	(23.13)	
$SnCl_2(TCNQ)_2 \cdot thf_{1/2}$	Yellow	*Ca.* 190	51.65	2.57	18.66	4.96	
			(52.34)	(1.69)	(18.78)	(5.94)	
$Me_4NSnCl_3 \cdot TCNQ$	Slate	*Ca.* 68	35.37	4.00	12.27	24.02	
			(35.32)	(3.31)	(12.71)	(23.00)	
$Me_4NSn(TCNQ)_3$	Green	*Ca.* 280	60.48	3.24	22.77		
			(59.65)	(3.00)	(22.60)		
$(Me_4NSnCl_3)_4TCNQ$	Brown	*Ca.* 298	24.73	3.47	7.43	14.07	
			(24.71)	(3.58)	(6.63)	(14.59)	
$(SnCl_4)_3(TTF)_2(C_6H_6)_{3/2}$	Blue	>310	31.21	2.31		26.90	23.18
			(31.47)	(2.20)		(27.24)	(24.63)
$(SnCl_4)_2TNF^{Ph} \cdot (C_6H_6)$	Yellow	*Ca.* 230	38.00	2.68	5.87	29.10	
			(37.34)	(2.92)	(5.81)	(29.46)	

[a] Decomposition point.

TABLE II. Spectroscopic Data for Tin(II) and Tin(IV) Complexes of π-Acids and π-Bases.

Complex	ν(C≡N) (cm^{-1})	Tin 119*m* Mössbauer Data (mm s^{-1})						Ref.
		I.S.	Q.S.	Γ_1	Γ_2	Γ_3	Γ_4	
$CsSnCl_3 \cdot TCNQ$	2185vs	0.536	0.0	1.026				
	2200m-s							
$SnCl_2(TCNQ)_2thf_{1/2}$	2210mw	0.207	0.0	1.286				
	2250wbr							
$Me_4NSnCl_3 \cdot TCNQ$	2150vvs	0.501	0.0	1.067				
	2170vvs							
	2210m							
$Me_4NSn(TCNQ)_3$	2140mw	0.357	0.0	1.105				
	2150mw							
	2170mw							
	2180mw							
	2255mw							
	2260mw							
$(Me_4NSnCl_3)_4 \cdot TCNQ$	2150ms	0.212	0.0	1.697				
	2170ms							
	2180ms							
	2210w							
	2250w							
$SnCl_2(TCNE) \cdot thf$	2220mbr	0.60	0.0	0.61				8
$SnBr_2(TCNE) \cdot thf$	2210mbr	0.45						8
$Sn(TCNE)_2 \cdot thf$	2220mbr	0.42	1.09	1.06	1.33	0.49	0.35	8
$(CH_3)_3Sn(TCNQ) \cdot xH_2O$	2200vvs	1.429	4.025	1.205	1.217			9
	2184vvs							
$(CH_3)_3Sn(TCNQ)$	2200vvs	1.407	4.113	2.531	2.113			9
(blue form)	2184vvs							
$(CH_3)_3Sn(TCNQ)$	2226ms	1.457	4.077	0.835	1.004			9
	2210vvs							
(brown form)	2184s							

(continued on facing page)

TABLE II. *(continued)*

Complex	$\nu(C{\equiv}N)$ (cm^{-1})	Tin 119*m* Mössbauer Data ($mm\ s^{-1}$)						Ref.
		I.S.	Q.S.	Γ_1	Γ_2	Γ_3	Γ_4	
$(n\text{-}C_3H_7)_3Sn(TCNQ)$	2200vvs	1.541	3.925	0.816	0.906			9
$(n\text{-}C_4H_9)_3Sn(TCNQ)$	2263vw 2193vvs	1.581	4.047	0.795	0.791			9
$(CH_3)_2Sn(TCNQ)_2$	2127mw	1.181	3.044	1.151	1.184			9
$CsSnCl_3$		3.642	1.226	1.214	1.169			
Me_4NSnCl_3		3.765	1.256	0.905	0.845			
$(SnCl_4)_3\cdot(TTF)_2\cdot(C_6H_6)_{3/2}$		0.505	0.0	1.268				
		4.042	0.0	1.803				
$(SnCl_4)_2\cdot(TNF^{Ph})\cdot(C_6H_6)$		0.398	0.0	1.088				

The Reaction of Me_4NSnCl_3 with TCNQ

To a suspension of Me_4NSnCl_3 (0.90 g, 3 mmol) in thf (20 ml) was added a solution of TCNQ (0.61 g, 3 mmol) also in thf (10 ml), with stirring, at room temperature. After 4 days, the solution was filtered off to obtain a slate coloured precipitate of $Me_4NSnCl_3(TCNQ)$ (yield 0.29 g) which was washed with ether and dried *in vacuo*. On concentration of the mother liquor, a green precipitate, $Me_4NSn(TCNQ)_3$, was obtained (yield 0.42 g). This precipitate was washed with ether and dried *in vacuo*. On further concentration of the mother liquor a third crop of product, $[Me_4NSnCl_3]_4\cdot[TCNQ]$, which is brown in colour, was obtained. This precipitate was also washed with ether and dried *in vacuo* for several hours (yield 0.21 g).

The Reaction of $SnCl_4$ with TNF^{Ph}

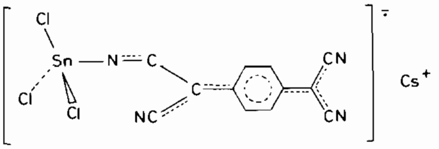
To a solution of $\Delta^{2,2'}$-bis(1,3-diphenylimidazolidene) (0.22 g, 0.5 mmol) in benzene (60 ml), under argon, was added anhydrous tin(IV) chloride (0.14 g, 0.5 mmol). The solution was stirred for six hours after which the product, $SnCl_4\cdot(TNF^{Ph})\cdot(C_6H_6)_{1/2}$, precipitated out and was isolated as before (yield 0.21 g).

The Reaction of $SnCl_4$ with TTF

To a solution of $\Delta^{2,2'}$-bis(5-methyl-1,3-benzodithiolidene) (0.16 g, 0.5 mmol) in benzene (40 ml) was added anhydrous tin(IV) chloride (0.13 g, 0.5 mmol) with stirring, under argon, at room temperature. The solution was stirred for one hour after which the deep blue precipitate of $(SnCl_4)_3(TTF)_2Bz_{3/2}$ was separated as before.

Results and Discussion

The reaction of a suspension of $CsSnCl_3$ with TCNQ in thf gives rise to more than one complex containing both tin and TCNQ. The initial product obtained is the deep blue 1:1 adduct. The infrared spectrum of this complex exhibits two bands at 2185 and 2200 cm^{-1} due to $\nu(C{\equiv}N)$ vibrations (*cf.* LiTCNQ(TCNQ) which exhibits two bands at 2190 and 2210 cm^{-1}). The tin-119 Mössbauer spectrum is unlike that of $CsSnCl_3$, which comprises a doublet in the tin(II) region (I.S. = 3.64 $mm\ s^{-1}$, Q.S. = 1.22 $mm\ s^{-1}$), and consists of a single resonance in the tin(IV) region at 0.54 $mm\ s^{-1}$. The absence of a resolvable quadrupole splitting (Γ = 1.03 $mm\ s^{-1}$) indicates cubic electronic symmetry, and it is likely that this material consists of Cs^+ cations and $[Cl_3SnNCC(CN)C_6H_4C(CN)_2^{\cdot-}]$ radical anions in which tin has tetrahedral coordination as in I,



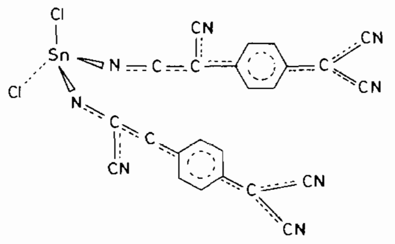
I

and similar to the structure proposed for the tin(II) halide-tetracyanoethylene complexes, $SnX_2\cdot TCNE\cdot THF$ (X = Cl, Br) [8]. The blue colour of the complex is indicative of electron pairing between TCNQ residues of adjacent molecules as in $Me_3SnTCNQ\cdot H_2O$ [9]. The electronic spectrum of $CsSnCl_3\cdot TCNQ$ in acetonitrile, like the $Me_3SnTCNQ$ analogue [9], exhibits the general characteristics of the TCNQ radical anion.

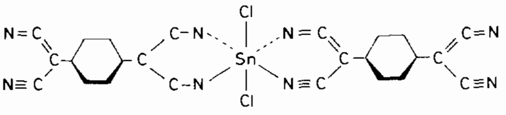
The second product obtained from the reaction of $CsSnCl_3$ and TCNQ in thf is a deep yellow solid of composition $SnCl_2(TCNQ)_2\cdot\frac{1}{2}thf$. This is probably derived from the dissociation product of $CsSnCl_3$ in thf (equation 1).

$$CsSnCl_3 \rightleftharpoons CsCl + SnCl_2 \xrightarrow{2TCNQ} SnCl_2(TCNQ)_2 \qquad (1)$$

The infrared spectrum again exhibits two $\nu(C\equiv N)$ vibrations, one sharp band at 2210 cm^{-1} and a broad band which is centred at 2250 cm^{-1}. The Mössbauer spectrum is similar to that of the $CsSnCl_3{\cdot}TCNQ$ complex in that it consists of only one sharp signal with no splitting. However, the isomer shift is, as expected, now lower than that of the $CsSnCl_3{\cdot}TCNQ$ complex (Table II) due to a greater electron drift away from tin to the cyano groups of the TNCQ molecules. The electronic spectrum of $SnCl_2(TCNQ)_2$ is qualitatively similar to that of $CsSnCl_3{\cdot}TCNQ$ in the 10,000–15,000 cm^{-1} region, but differs markedly at higher wave-numbers (Table II) due to the presence of an extra shoulder at *ca.* 24,500 cm^{-1} to give an almost symmetrical spectrum in this region. All the above spectroscopic data are indicative of an almost perfect cubic geometry around the tin atom. The tin atom may be tetrahedrally coordinated by two chlorine atoms and two unidentate TCNQ ligands as in II, or octahedrally by bidentate chelating (or bridging) TCNQ ligands as in III.



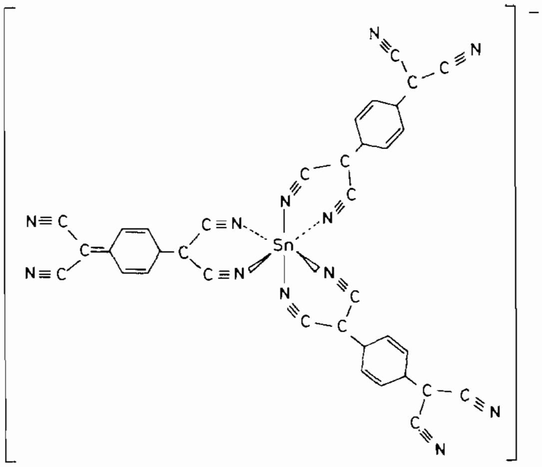
II



III

The 1:1 adduct of $Me_4NSnCl_3{\cdot}TCNQ$, is a slate-coloured complex and is the first product to crystallise out on mixing the two solutions of Me_4NSnCl_3 and TCNQ in thf. The $\nu(C\equiv N)$ band in the infrared now comprises two sharp, strong bands of doublet at 2150 and 2170 cm^{-1} and a singlet at 2210 cm^{-1}, similar to the $CsSnCl_3{\cdot}TCNQ$ complex. The electronic spectrum and the Mössbauer parameters (I.S. = 0.50 mm s^{-1}, Q.S. = 0 mm s^{-1}) also show a marked similarity to those of $CsSnCl_3{\cdot}TCNQ$, indicating the presence of the $SnCl_3{\cdot}TCNQ^{\bar{\cdot}}$ radical anion. The structure of the $Me_4NSnCl_3{\cdot}TCNQ$ adduct, therefore, is completely analogous to the $CsSnCl_3{\cdot}TCNQ$ adduct, comprising $[Me_4N^+]$ cations and $[Cl_3Sn{\cdot}TCNQ^{\bar{\cdot}}]$ radical anions.

Concentration of the mother liquor obtained from the reaction of Me_4NSnCl_3 with TCNQ, gave a second green product, of composition $Me_4NSn(TCNQ)_3$. The $\nu(C\equiv N)$ region comprises three doublets at 2140 and 2150 cm^{-1}, 2170 and 2180 cm^{-1}, and 2250 and 2260 cm^{-1}, respectively. Again the Mössbauer data (I.S. = 0.36 mm s^{-1}, Q.S. = 0 mm s^{-1}) are indicative of tetravalent tin in a cubic electronic environment, and the electronic spectrum is analogous to that of the $SnCl_2{\cdot}(TCNQ)_2{\cdot}$thf complex in which the tin enjoys octahedral coordination by bidentate chelating TCNQ radical anions, suggesting the symmetrical structure IV for the $[Sn(TCNQ)_3^-]$ complex anion.

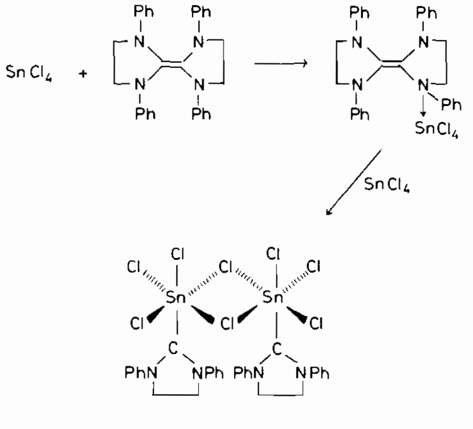


IV

When the mother liquor obtained from the reaction of Me_4NSnCl_3 with TCNQ was further concentrated, a brown product, $[Me_4NSnCl_3]_4{\cdot}TCNQ$ was obtained. The infrared bands associated with $\nu(C\equiv N)$ are now at 2150, 2170, 2180, 2210 and 2250 cm^{-1}, indicative of stronger $Sn{-}C\equiv N$ interaction.

The I.S. (0.21 mm s^{-1}) and Q.S. (0.00 mm s^{-1}) values of this complex are identical to those of $SnCl_2(TCNQ)_2{\cdot}$thf (I.S. = 0.21 mm s^{-1}, Q.S. = 0.00 mm s^{-1}), although the half-height line width is much broader (Γ = 1.7 mm s^{-1}) probably due to the presence of an unresolved doublet. The spectrum exhibited no resonance due to tin(II). The tin atom is probably, therefore, essentially octahedrally coordinated with the electrons arising from the tin lone pair delocalised into a band structure.

The addition of an equimolar amount of $SnCl_4$ under argon to a solution of TNF^{Ph} in benzene, resulted in the formation of greenish-yellow precipitate of composition $(SnCl_4)_2TNF^{Ph}(C_6H_6)$. The region of interest in the infrared is between 1620 and 1500 cm^{-1} which contains $\nu(CN)_2$ vibrations. In the $(SnCl_4)_2(TNF^{Ph})Bz$ complex, $\nu(CN)_2$ bands occur at 1665, 1595, 1585 and 1570 cm^{-1}, indicating that this is a carbene-metal type of complex analogous to the [RuCl(L$^{C_6H_4Me-4}$)(PEt$_3$)$_2$], *cis*-[Cr(CO)$_4$(L^{Et})$_2$], (L = TNF^{Et}), and [Rh{CH(NMe$_2$)}Cl$_2$H(PMe$_2$Ph)$_2$] complexes in which ν(CN)$_2$ is 1519, 1482 and 1602 cm^{-1} respectively [12, 13]. These bands are absent in olefin-NN″–metal complexes such as [Mo(CO)$_4$(L$_2$^{Me}-NN″)] [13] due to lower $\ddot{N}$–cp$^{\pi}$–p$^{\pi}$ interaction. The .reaction mechanism for the formation of (SnCl$_4$)$_2$TNF^{Ph} is probably analogous to that proposed for *cis*-[Cr(CO)$_4$(L^{Et})$_2$] (Scheme 1), with initial coordination of TNF^{Ph} to tin *via* nitrogen, followed by cleavage of the carbon–carbon double bond:



V

Scheme 1.

The Mössbauer spectrum of the product comprises a single resonance (I.S. = 0.40 mm s^{-1}) indicative of a cubic electronic environment for tin, most probably arising from chlorine–bridging as in (V).

Interaction of tin(IV) chloride with TTF in dry benzene affords a navy blue, high-melting adduct of composition (SnCl$_4$)$_3$(TTF)$_2$·(C$_6$H$_6$)$_{3/2}$. In the infrared, the band at 1565 cm^{-1} may be ascribed to the ν(CS$_2$) vibration. The Mössbauer spectrum comprises two resonances at 0.50 mm s^{-1} and 4.04 mm s^{-1} with relative intensities of 3:1 indicating the presence of both tin(IV) and tin(II) sites in the solid. Although both single lines, the large half-height widths (ΓSn(IV) = 1.23 mm s^{-1}, ΓSn(II) = 1.80 mm s^{-1}) indicate some distortion from ideal cubic symmetry at both tin sites. The exact structural nature of this material is therefore very complex; it must, however, contain similar features to that of the SnCl$_4$–TNF^{Ph} complex, *i.e.* C-bonded 2,3-dithiacyclopentane ligands, chlorine-bridging, and six-coordinated tin.

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