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STRUCTURAL STUDIES IN MAIN GROUP CHEMISTRY

XIX *. ORGANOTIN(IV) DERIVATIVES OF TETRACYANOETHYLENE, 7,7,8,8-TETRACYANOQUINODIMETHANE AND 2,3,5,6-TETRACHLOROBENZOQUINONE. THE ISOLATION OF STABLE ORGANOTIN-SUBSTITUTED RADICALS

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Summary

The reaction of organotin chlorides with the lithium salt of 7,7,8,8-tetracyanoquinodimethane (TCNQ) or hexaalkylditins with TCNQ yield stable organotin-substituted free radicals of the types $R_3SnTCNQ^{\cdot}$ (R = Me, n-Pr, n-Bu) and $Me_2Sn(TCNQ^{\cdot})_2$. The reaction of hexaphenylditin with TCNQ yields a ($\sigma \rightarrow \pi$) charge transfer complex of stoichiometry $(Ph_3SnSnPh_3)\cdot TCNQ$, whilst $[Me_2SnCl(terpyridyl)^+](TCNQ^{\cdot-})$ was isolated from the reaction of $[Me_2SnCl(terpyridyl)^+][Me_2SnCl_3^-]$ and LiTCNQ. The oxidation of hexaalkylditins by tetracyanoethylene (TCNE) yields stable free radicals of the type $R_3SnTCNE^{\cdot}$, but treatment with 2,3,5,6-tetrachlorobenzoquinone yields either $R_3SnOC_6Cl_4O^{\cdot}$-*p* (R = Me) or $R_3SnOC_6Cl_4OSnR_3$-*p* (R = n-Bu, Ph). Tin-119 Mössbauer spectroscopy shows that the derivatives $R_3SnTCNQ^{\cdot}$ and $R_3SnTCNE^{\cdot}$ have trigonally-bipyramidally coordinated tin with planar $[SnC_3]$ skeletons and bridging $[TCNQ^{\cdot}]$ and $[TCNE^{\cdot}]$ groups forming infinite one-dimensional chain structures. $Me_3SnOC_6Cl_4O^{\cdot}$-*p* was inferred to possess a similar structure but with oxy bridges forming chains with a Sn—O—Sn—O backbone. $Me_2Sn(TCNQ^{\cdot})_2$ has a structure intermediate between tetrahedral and octahedral with a nonlinear MeSnMe unit and anisobidentate chelation by two TCNQ groups. The TCNQ derivatives were of two types: (i) "green" or "brown", indicative of delocalisation of the lone electron over the cyanoquinone ligand, and (ii) a "blue" form in which spin-pairing of the lone electron between adjacent organic groups takes place. $Me_3SnTCNQ^{\cdot}$ may exist in both forms depending upon the mode of preparation.

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* For part XVIII see ref. 1

Introduction

The derivatives of 7,7,8,8-tetracyanoquinodimethane (TCNQ) have over the last decade been of considerable interest, mainly as a result of the magnetic properties and high electrical conductivity shown by some of them. TCNQ forms three types of complexes, which can be described as charge transfer complexes, simple salts and complex salts. The charge transfer complexes of TCNQ can be considered to involve transfer of a π-electron from a donor molecule or group to the delocalised π-system of the quinone acceptor, by overlap of the respective orbitals. Stable complexes are observed generally between the TCNQ π-acid and π-electron-rich Lewis bases, which can be totally organic or metal chelate systems. The strength of the π-acid in these complexes appears to be dependent on the relative size or extended nature of the π-system of the base [2], the interaction with more extended π-orbitals generally being stronger, and this approach has been utilised to explain the relative stability of TCNQ charge transfer complexes with *trans*-bis(trialkylphosphine)dialkynyl-nickel, -palladium and -platinum(II) complexes [3]. In solution partial dissociation takes place to give radical-ion species. The complexes are generally obtained by mixing of solutions containing stoichiometric quantities of the acid and base, and many such compounds are known [4,5].

Tetracyanoethylene (TCNE), which also forms similar charge transfer complexes to those with TCNQ, has in addition been reported to interact with the metal—metal bond in various polysilanes and hexamethyldi-silane and -germane in solution [6,7]. The electron paramagnetic resonance and charge transfer spectra of these complexes were interpreted in terms of σ-electron transfer to TCNE. Traven and West [6] also observed similar behaviour for hexamethyldisilane with 2,3,5,6-tetrachlorobenzoquinone (TCBQ), and for octamethyltrisilane and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. Hexamethyldistannane was reported to interact with TCNE, but no products were characterised.

TCNQ also forms two distinct types of salt-like derivatives involving the stable radical anion $TCNQ^{\cdot-}$; simple salts involving purely anionic and cationic species, $M^{n+}(TCNQ^{\cdot-})_n$, and complex salts which also encorporate neutral TCNQ molecules in addition to the ionic species, $M^{n+}(TCNQ^{\cdot-})_n(TCNQ^{0})$. The salts are intensely coloured, generally blue or violet, unlike the charge transfer complexes which may be a variety of colours. In the solid state and in saturated aqueous solution the salts are usually blue, attributed to dimerisation via electron pairing of the lone electrons [8,9], whilst in organic solvents and in dilute aqueous solution a green colouration due to the monomeric species is observed. The binding energy of the ion-pair in the solid state has been estimated to be ca. 14 kcal/mol-ion radical [10].

We have previously reported the synthesis and spectroscopic properties of TCNQ, TCNE and TCBQ derivatives of dicyclopentadienyltin(II), tin(II) halides and tin(II) bis(β-ketoenolates) [11]. In this paper, we present the results of our investigations into the synthesis and properties of organotin(IV) derivatives of these species.

Results and discussion

Organotin(IV)-TCNQ derivatives

The oxidation of Ph_3SnI in ethyl acetate by the one-electron reduction of a TCNQ molecule, a method which has frequently given salt derivatives with other metal iodides, failed to show any sign of reaction after an extended period at reflux, and TCNQ was recovered unchanged. Similarly, the reaction of β-tin metal and TCNQ in acetonitrile at reflux did not proceed, although the reaction of β-tin with TCNE afforded $Sn(TCNE)_2$ [11]. This situation is reflected by the relative strengths of the π-acids with respect to one-electron reduction; TCNE is considered the stronger [4].

The reaction of Li^+ $TCNQ^{\overline{\cdot}}$ with trimethyltin chloride in water gave a distinctive colour change, violet to blue, and the product was obtained as an intense blue solid. This product contained a non-stoicheiometric quantity of water which could be removed by washing with anhydrous ether and drying in vacuo to give $Me_3SnTCNQ^{\cdot}$ (Ia) as a blue solid. No reaction occurred when Li^+ $TCNQ^{\overline{\cdot}}$ and Me_2SnCl_2 were mixed in dry tetrahydrofuran, but in water reaction was immediate affording $Me_2Sn(TCNQ^{\cdot})_2$ (II). Similarly, the reaction of tin(IV) chloride with Li^+ $TCNQ^{\overline{\cdot}}$ did not proceed in anhydrous benzene, even after reflux. Apparently the lithium salt must be soluble to some extent in the reaction medium for metathesis to take place. The insolubility and ready hydrolysis of the majority of organotin compounds in aqueous media is clearly a complicating factor in the preparation of TCNQ derivatives by this method. In addition, the salts and complexes of TCNQ are very insoluble, and recrystallisation is frequently accompanied by degradation. Aqueous methanol proved to be a satisfactory solvent for the preparation of n-$Pr_3SnTCNQ^{\cdot}$ (Ib) by metathesis from n-Pr_3SnCl, but the reaction with Ph_3SnCl under similar conditions gave products which could not readily be identified.

The formation of TCNQ radical anion salt of the complex cation, monochloro-2,2′,2″-terpyridyltin(IV), $[Me_2Sn(Cl)(terpy)^+][(TCNQ^{\overline{\cdot}})]$ (III), takes

TABLE 1

TIN-119 MOSSBAUER DATA FOR ORGANOTIN-TCNQ DERIVATIVES

Compound	Ref.	*IS* ^{a}	*QS* ^{a}	Γ_1 ^{a}	Γ_2 ^{a}
$Me_3Sn(TCNQ^{\cdot}) \cdot nH_2O$		1.43	4.02_5	1.02_5	1.22
$Me_3Sn(TCNQ^{\cdot})$ (blue form)		1.41	4.11	2.53	2.13
$Me_3Sn(TCNQ^{\cdot})$ (brown form)		1.46	4.08	0.84	1.00
n-$Pr_3Sn(TCNQ^{\cdot})$		1.54	3.92_5	0.82	0.91
n-$Bu_3Sn(TCNQ^{\cdot})$		1.58	4.05	0.79_5	0.79
$Me_2Sn(TCNQ^{\cdot})_2$		1.18	3.04	1.15	1.18
$[Me_2SnCl(ter)^+](TCNQ^{\overline{\cdot}})$		1.36	3.80	0.88	0.84
$(Ph_3SnSnPh_3)(TCNQ)$		1.46	0	0.84	
Me_3SnCl	29	1.41	3.31		
n-Pr_3SnCl	30	1.62	3.61		
$Me_3SnSnMe_3$	31	1.46	0		
$Ph_3SnSnPh_3$	32	1.38	0		
$[Me_2SnCl(ter)^+]I^-$	22	1.38	3.56		

^{a} mm s^{-1} (*IS* $BaSnO_3 = 0$).

place readily when solutions of $Li^+ TCNQ^-$ and $[Me_2Sn(Cl)(terpy)^+]$-$[Me_2SnCl_3^-]$ in methanol are mixed. However, non-ionic species such as $Me_2SnCl_2 \cdot bipy$ on mixing with $Li^+ TCNQ^-$ in methanol gave products which could not be identified, although the insoluble tin complex was observed to dissolve on progressive addition of the radical anionic species. Reactions of a similar nature with bipyridyliron(II) complexes have afforded complex salt derivatives which contain neutral TCNQ in addition to the radical anion through interaction of the TCNQ species with the π-rich bipyridyl chelates [5].

The ready oxidation of the hexaorganodistannanes by halogens is well known [12], and suggests that the corresponding one-electron reduction of TCNQ in the presence of these compounds might provide an alternative route to triorganotin(IV)-TCNQ derivatives. The heterogeneous reaction of hexamethyl- or hexabutyl-distannanes in THF with TCNQ resulted in the slow formation of the corresponding trialkyltin(IV)-TCNQ derivatives (IVa and IVb) as brown-green and pale green precipitates, respectively:

$$R_3SnSnR_3 + 2\,TCNQ \xrightarrow{THF} 2\,R_3SnTCNQ^{\bullet}$$

(IVa, R = Me;
IVb, R = Bu)

Under identical conditions, hexaphenyldistannane was reluctant to react, but over a period of days the reaction mixture became progressively blue. After several weeks, unreacted TCNQ was filtered off, and the royal blue 1/1 complex V of hexaphenyldistannane and TCNQ was obtained on concentration:

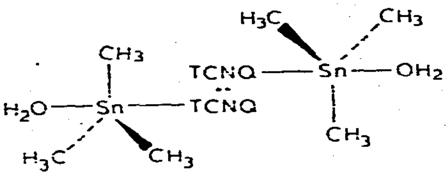
$$Ph_3SnSnPh_3 + TCNQ \xrightarrow{THF} Ph_3SnSnPh_3 \cdot TCNQ$$

(V)

The reaction of tin(IV) chloride and TCNQ in anhydrous benzene gave a bright yellow solid which contained no tin from the absence of a Mössbauer spectrum and had an infrared spectrum very similar to that of TCNQ itself, but this product was not investigated further.

Tin-119*m* Mössbauer data for the complexes I—V are listed in Table 1. The trialkyltin-TCNQ derivatives prepared by the two different routes show large quadrupole splitting values in the range 3.90—4.12 mm s^{-1}, which are incompatible with tin in a tetrahedral, four-coordinate environment, and suggest a *trans*-R_3SnX_2 five-coordinate geometry.

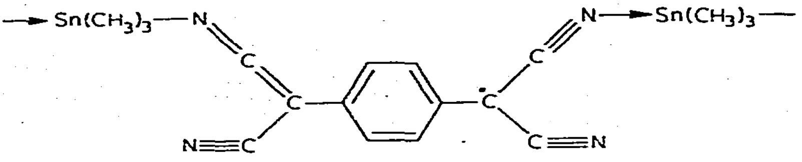
The hydrated trimethyltin-TCNQ compound, which from the analytical data contains between three and four molecules of water, has a single band in the tin—carbon stretching region of the infrared at 555 cm^{-1}, which may be assigned as the antisymmetric Sn—C stretching mode of a planar Me_3Sn moiety, the corresponding symmetric mode being active only in the Raman. Absorptions resulting from lattice water molecules are also clearly apparent, although the appearance of a broad medium band at 333 cm^{-1} and a strong band at 720 cm^{-1} suggest the coordination of one water molecule to the tin, in which case these bands can be assigned to the $Sn—OH_2$ stretching and rocking modes, respectively. The high value of the quadrupole splitting and the infrared data therefore suggest a trigonal bipyramidal geometry for the first coordination sphere of the tin in which the equatorial positions are occupied by methyl groups and the axial sites by water molecules and a TCNQ radical anion, adjacent radical anions being electron-paired forming dimeric species (VI).



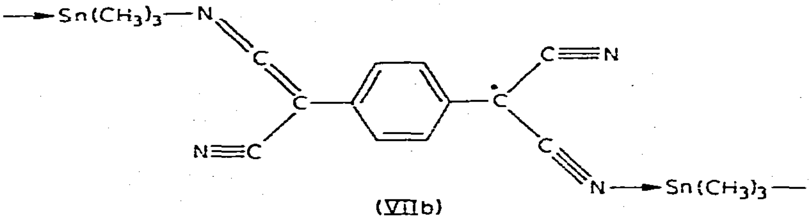
(VI)

Dehydration of the hydrated material gives "blue" anhydrous $Me_3SnTCNQ^{\cdot}$. The Mössbauer parameters of which show small differences from those of the hydrated material and the brown form of $Me_3SnTCNQ^{\cdot}$ (vide infra), although the half-height line widths of the blue form were exceptionally large. These differences are also reflected in the infrared spectra of the three trimethyltin derivatives. The spectrum of the blue form in the 500—600 cm^{-1} region contains a medium intensity band at 558 cm^{-1} with shoulders at 565 and 574 cm^{-1}. The band at 558 cm^{-1} may be confidently assigned to the antisymmetric Sn—C stretching mode, whilst the two shoulders are attributable to —C—C≡N bending modes which appear as weak bands in this region [13]. It is clear that as a result of the similarity of the absorptions arising from the TCNQ residue and those observed in the spectrum of Li^{+} $TCNQ^{\bar{\cdot}}$, that in both the hydrated and anhydrous materials it can be considered to be essentially the radical anion, the infrared spectrum of which is characteristic [4], and has been studied previously for various simple and complex TCNQ salts [13]. Corroboration of the trigonal bipyramidal geometry is available from a comparison of the Mössbauer and IR data with those of compounds known to possess this geometry from diffraction studies. Thus $Me_3SnO_2CCF_3$ (*IS* 1.38 mm s^{-1}, *QS* 4.22 mm s^{-1}) and Me_3SnO_2CMe (*IS* 1.35 mm s^{-1}, *QS* 3.65 mm s^{-1}), each also exhibiting a single Sn—C stretching band at 555 cm^{-1}, are known to have structures in which the carboxylate residues bridge planar Me_3Sn units [14,15]. The structure of the blue form of $Me_3SnTCNQ^{\cdot}$ in the solid may therefore be interpreted as consisting of chains of planar Me_3Sn groups with bridging TCNQ radical anionic species, interaction of adjacent chains occurring via electron pairing of the odd electrons on the [$TCNQ^{\cdot}$] species thus giving rise to the blue colour. In solution the compound is green indicating the presence or uncoupled radical anions. [TCNQ] bridging can occur in any one of three possible ways. With the $SnMe_3$ groups *cis* (VIIa) or *trans* (VIIb), or through the cyano groups attached to the same carbon. This latter mode must be considered very unlikely on steric grounds. Although the *cis* form was found to predominate in the TCNE complex, $(Ph_3P)_2(OC)Ir$-$(TCNE)Ir(CO)(PPh_3)_2$, on the basis of dipole moment and infrared data [16], the actual orientation of the radical anionic species in this instance will be largely determined by crystal packing and anion pairing energy considerations.

The blue tri-n-propyltin derivative has a similar *QS* value to that of the trimethyltin derivative, and the infrared spectrum is again dominated by the bands



(VIIa)



(VIIb)

attributable to essentially unperturbed TCNQ$^{\overline{\cdot}}$ radical anion vibrations. However, the tin—carbon stretching region contains four bands at 583vw, 550w, 537m and 518m cm^{-1}, indicating the possibility of *cis* and *gauche* isomerism of the n-propyl groups [17]. Okawara and Ohara [18] have observed only one tin—carbon stretching mode at 515 cm^{-1} for $(n\text{-}C_3H_7)_3SnO_2CH$ which was assigned a planar $[SnC_3]$ skeleton with bridging formate groups. Thus, if we assign this compound a similar structure to that of the trimethyltin compounds as indicated by the Mössbauer spectra, the band at 518 cm^{-1} may be assigned to the tin—carbon stretching model The three remaining bands in this region may then be assigned to the tin—carbon stretching mode. The three remaining bands in this region may then be assigned as radical anion vibrations since there are three similar bands in the spectrum of Li^{+} TCNQ$^{\overline{\cdot}}$.

The trimethyltin (TCNQ) complex, prepared by the oxidation of hexamethyldistannane under anhydrous conditions, is a dark green/brown colour, and clearly different from the "blue" form discussed above, although the electronic spectra of the two forms in acetonitrile solution are superimpossable (Fig. 1), and exhibit the general characteristics of the TCNQ$^{\overline{\cdot}}$ radical anion suggesting dissociation of both forms in this solvent to solvated trimethyltin cations and TCNQ$^{\overline{\cdot}}$ radical anions. The solid state infrared spectrum of the "brown" form is compatible with that of a TCNQ$^{\overline{\cdot}}$ radical anion derivative, and contains no absorptions from free TCNQ or hexamethyldistannane. It is however, sufficiently different from that of the "blue" form to suggest that they possess different structures. The Mössbauer parameters of the two forms are very similar, indicating that the "brown" form also involves trigonal bipyramidal geometry about the tin atom. On exposure to the atmosphere, The "brown" form slowly becomes blue, and on mixing with water the dried extract, which is blue, gives an infrared spectrum identical to the previously discussed "blue" form.

The similarly prepared tri-n-butyltin(TCNQ$^{\cdot}$) derivative (IVb) also has a Mössbauer spectrum consistent with a trigonal bipyramidal geometry at tin, and similarly undergoes a change in colour from pale green to blue on exposure to the atmosphere or water. It would appear, therefore, that the trialkyltin-TCNQ

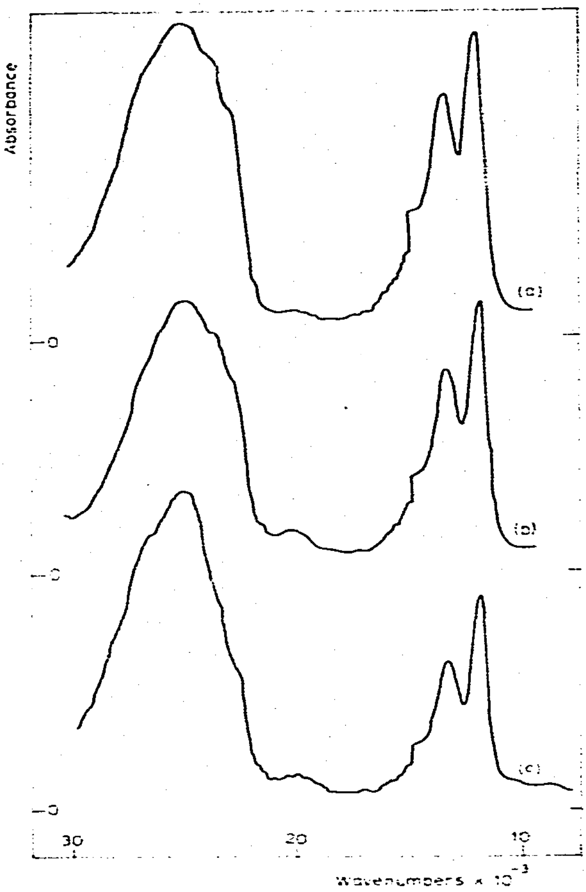
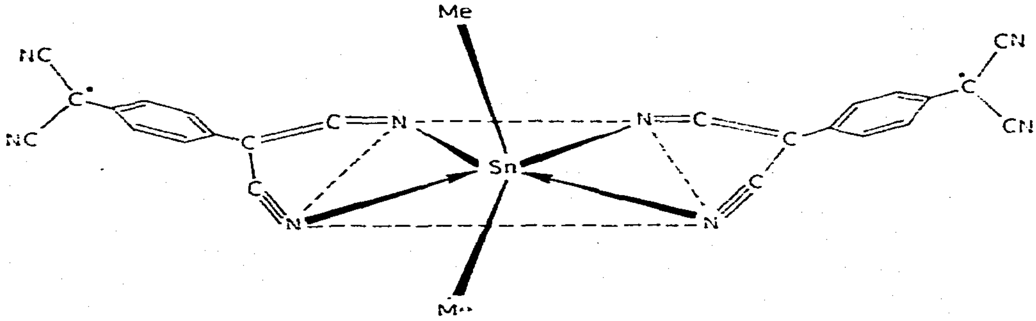


Fig. 1. The electronic spectra of the brown (a) and blue (b) forms of $(CH_3)_3Sn(TCNQ)$, and of $(CH_3)_2Sn(TCNQ)_2$ (c) in CH_3CN.

derivatives are capable of existing in two forms, both of which consist of chain structures in which [TCNQ] groups bridge planar [R_3Sn] moieties: a "green" or "brown" form in which the lone electron is delocalised over the cyanoquinone ligand, and a "blue" form in which electron-pairing of the lone electrons between adjacent cyanoquinone ligands takes place. That the "green" and "brown" forms are readily converted into the "blue" form is consistent with the available thermodynamic data: the binding energy of the $(TCNQ^{\overline{\cdot}})_2$ radical-ion-pair in the solid state having been estimated to be ca. 14 kcal/mole-ion radical [10].

The reaction of hexaphenyldistannane with TCNQ gave a blue solid of stoichiometry $(Ph_3Sn)_2(TCNQ)$. The Mössbauer spectrum of this derivative exhibited a single narrow resonance as does hexaphenyldistannane itself although with a marginally increased *IS* value. The infrared spectrum of the complex is almost identical to that of hexaphenyldistannane, although in addition it contains absorptions at 2192 and 2148 cm^{-1} [ν(C=N)], and at 1593, 1573, 860 and 488 cm^{-1} as well as other less intense bands due to the presence of a TCNQ species. The absence of an observable *QS* is incompatible with the formation of a $Ph_3Sn(TCNQ^{\cdot})$ species similar to the trialkyltin derivatives discussed above, and, together with the *IS* value [19], the presence of tin—nitrogen bonding. The blue colouration suggests some degree of charge transfer, and the complex is probably best rationalised in terms of a ($\sigma \rightarrow \pi$) charge transfer from the tin—tin bond to the π-orbitals of the quinone, analogous to those reported by West [6] and Sakurai [7] between polysilanes and TCNE. Hexamethyldilead, in contrast is reduced by TCNQ in benzene to afford $Pb(TCNQ)_2$ [20].

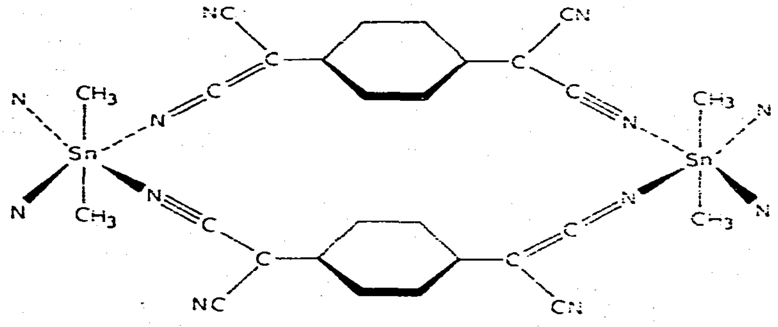
The olive-green colour of the dimethyltin bis($TCNQ^{\cdot}$) derivative is indicative of the absence of spin-pairing in the solid, and in contrast to the trialkyltin derivatives exposure to air or water does not promote spin-pairing. The value of the *QS*, 3.04 nm s^{-1}, is intermediate between the values expected for *cis* and *trans* octahedral dimethyltin complexes and is larger than the values found for four-coordinate tetrahedral tin derivatives. Thus it would seem that in this derivative the TCNQ groups are functioning as anisobidentate chelating ligands towards the tin giving rise to distorted octahedral coordination (VIII). From a plot of *QS* against MeSnMe bond angle for compound of known structure [21], it is



(VIII)

possible to estimate the value of the MeSnMe angle as ca. 135°. Alternative structures such as IX, which involve bridging TCNQ groups, would necessarily impose linearity on the MeSnMe skeleton giving tise to a *QS* value of ca. 4 mm s^{-1}. A non-linear MeSnMe skeleton is corroborated by the infrared spectrum in the region 500—600 cm^{-1}. Three bands are observed at 530w and a barely resolved doublet at 565 and 578 cm^{-1}. The two former bands are assigned to the symmetric and antisymmetric tin—carbon stretching vibrations, respectively. The band at 578 cm^{-1} is assigned to a (C—C=N) bending mode of the radical anion. In acetonitrile solution the complex gives an intense green colouration, and the electronic spectrum shows the absorptions for free monomeric $TCNQ^{\cdot-}$ radical ions.

The Mössbauer parameters of the $[Me_2SnCl(ter)^+](TCNQ^{\cdot-})$ "simple" salt are almost identical to those of other salts of this cation [22] indicating the retention of unperturbed complex tin cations in the TCNQ derivative. The solid, which is blue, is therefore composed of isolated $[Me_2SnCl(ter)^+]$ cations [23] and electron-paired dimeric anions. It is conceivable however that the radical



(IX)

anion interacts with the π-orbital system of the terpyridyl group, which may rationalise the higher *QS* observed in the TCNQ derivative.

Organotin(IV)-TCNE derivatives

Krusic and his coworkers [25] have observed ESR signals from a mixture of hexa-n-butyldistannane and TCNE which they attributed to the $Bu_3N{=}C{=}C$-$(CN)\dot{C}(CN)_2$ radical in solution. Stable radicals of this type may actually be isolated from the reaction of hexaalkyldistannanes with TCNE in THF as intensely coloured amorphous solids X:

$$R_3SnSnR_3 + 2\,TCNE \rightarrow R_3Sn{-}N{=}C{=}C(CN)\dot{C}(CN)_2$$

(Xa, R = Me;
Xb, R = n-Bu)

The Mössbauer data (Table 2) for the tributyltin derivative Xb is almost identical to that of the corresponding TCNQ derivative, indicating a similar polymeric chain structure in which TCNE groups now bridge essentially planar [Bu_3Sn] moieties. The *QS* for the trimethyltin derivative IXa is, however, significantly smaller than either of the two forms of $Me_3SnTCNQ^{\cdot}$ indicating distortion from ideal trigonal bipyramidal geometry suggesting a much weaker $-C{\equiv}N \rightarrow Sn$ coordinate interaction in this case. A non-planar Me_3Sn unit is also indicated from the infrared spectrum, where now both antisymmetric (555m cm^{-1}) and symmetric (525mw cm^{-1}) tin—carbon stretching modes are observed. Both compounds exhibit bands due to $C{\equiv}N$ stretching modes at 2200ms (IXa) and 2180—2260ms (vbr) (IXb). The mass spectra of both derivatives do not exhibit any fragments of mass higher than the parent ion (Table 3). In both cases

TABLE 2

TIN-119 MOSSBAUER DATA FOR $R_3SnN{=}CC(CN)\dot{C}(CN)_2$ SPECIES

R	*IS* [a]	*QS* [a]	Γ_1 [a]	Γ_2 [a]
Me	1.33	3.38	1.00	1.18
n-Bu	1.58	4.10	0.83	1.03

[a] mm s^{-} (*IS* $BaSnO_3$ = 0).

TABLE 3

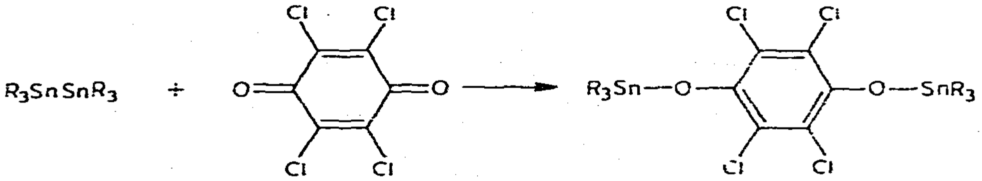
MASS SPECTRAL DATA (70 eV) FOR $R_3SnN{=}CC(CN)\bar{C}(CN)_2$ SPECIES

m/e	Assignment	Relative intensity
R = Me		
292	$Me_3SnN{=}CC(CN)C(CN)_2^+$	2.6
266	$Me_3SnN{=}CC(CN)C(CN)^+$	2.6
228	$Me_3SnN{=}CC(CN)^+$	1.3
190	Me_3SnCN^+	30.8
164	Me_3Sn^+	100
149	Me_2Sn^+	34.7
134	$MeSn^+$	70.7
119	Sn^+	48.7
R = n-Bu		
412	$n\text{-}Bu_3Sn \cdot N{=}C(CN) \cdot C(CN)_2^+$	0.26
356	$n\text{-}Bu_3SnN{=}CCN^+$	0.52
316	$n\text{-}Bu_3SnNC^+$	2.6
290	$n\text{-}Bu_3Sn^+$	60.6
233	$n\text{-}Bu_2Sn^+$	60.6
176	$n\text{-}BuSn^+$	100
119	Sn^+	57.9

the majority of the ion current is carried by R_nSn^+ (n = 0—3) ions, but in both ions resulting from cleavage of the TCNE may be discerned. In particular for $Me_3SnN{=}C{=}C(CN)\bar{C}(CN)_2$, one fragmentation pathway involves the successive loss of CN, C_2N, C_2N and CN.

Organotin(IV)-TCBQ derivatives

Hexa-n-butyl- and hexaphenyl-distannanes reacted slowly in benzene to afford 1,4-bis(triorganostannoxy)-2,3,5,6-tetrachlorobenzene derivatives XI as a purple oil and white solid respectively:



(XIa, R = n-Bu;
XIb, R = Ph)

The Mössbauer quadrupole splittings of these two compounds (Table 4) were much lower (2.83 mm s^{-1} (XIa) and 2.55 mm s^{-1} (XIb)) than values for typical five-coordinate triorganotin—oxygen bonded compounds [25], indicating the absence of intermolecular coordination and consistent with the four-coordinate *trans* configuration determined for the ethyl analogue by two-dimensional X-ray methods [26]. The reaction of TCBQ with hexamethyldistannane in benzene yielded a pale cream solid which analysed as $Me_3Sn(TCBQ^\cdot)$, however ESR

TABLE 4

TIN-119 MOSSBAUER DATA FOR ORGANOTIN-TCBQ DERIVATIVES

Compound	*IS* [a]	*QS* [a]	Γ_1 [a]	Γ_2 [a]
$Me_3Sn(TCBQ^\cdot)$	1.34	2.93	0.88	0.88
$n\text{-}Bu_3Sn(TCBQ)Sn\text{-}n\text{-}Bu_3$	1.44	2.83	1.18	1.19
$Ph_3Sn(TCBQ)SnPh_3$	1.29	2.55	0.77	0.75

[a] mm s^{-1} (*IS* $BaSnO_3$ = 0).

data are needed to corroborate the proposed free-radical nature. In the solid, the Mössbauer parameters suggest a phenoxy-bridged chain structure as has been determined for Me_3SnOMe [27] and $Me_3SnONC_6H_{10}$ [28].

Experimental

All manipulations were performed under an atmosphere of dry argon or nitrogen. TCNQ was obtained commercially (Eastman Kodak Co.) and recrystallised from boiling acetonitrile prior to use. TCNE and TCBQ were used without further purification. Lithium-TCNQ was prepared by the method of Acker and Blomstrom [5]: an acetone solution of anhydrous lithium iodide and an acetonitrile solution of TCNQ were refluxed together and the resultant intense blue filtrate filtered off, washed several times and dried. The yield was 100%, and the lithium salt subsequently used as prepared. Infrared, mass spectra and tin-119 Mössbauer spectra were recorded as described previously [25].

Reactions between organotin halides and lithium-TCNQ.

(a) Reaction with trimethyltin chloride. An aqueous solution (20 cm^3) of lithium-TCNQ (0.760 g; 3.62 mmol) was added dropwise to a stirred aqueous solution (15 cm^3) of trimethyltin chloride (0.720 g; 3.61 mmol), with the immediate formation of a dark blue precipitate. The reaction mixture was filtered to give the intense blue solid and a leaf-green filtrate. The solid was washed twice with water, and left for 16 h in the atmosphere, and subsequently weighed (yield 1.32 g). (Found: C, 41.09; H, 5.15; N, 12.19%). Mössbauer and IR data were recorded; the latter showed the presence of water. The solid was washed with anhydrous ether and dried to give trimethyltin-7,7,8,8-tetracyanoquinodimethanate as an intense blue solid m.p. (ca. 150°C decomp.). Found: C, 48.77; H, 3.77; N, 14.93. $C_{15}H_{13}N_4Sn$ calcd.: C, 48.96; H, 3.56; N, 15.22%.

(b) Reaction with tri-n-propyltin chloride. Tri-n-propyltin chloride (0.752 g; 2.65 mmol) in a 50/50 methanol/water mixture (10 cm^3) was added dropwise with stirring to a suspension of lithium-TCNQ (0.560 g; 2.65 mmol) in water (10 cm^3), with the immediate formation of a pale blue precipitate. This was filtered off and redissolved in acetone (3 cm^3). Addition of ether to the acetone solution reprecipitated a grew powder which was filtered off and dried to give tri-n-propyltin-7,7,8,8,-tetracyanoquinodimethanate (yield 0.21 g) which became dark blue over a period of days. Found: C, 54.56; H, 5.67; N, 12.53. $C_{21}H_{25}N_4Sn$ calcd.: C, 55.79; H, 5.57; N, 12.39%. Extraction of the washings

gave a tacky blue solid (0.20 g), which could not be identified. (Found: C, 50.43; H, 6.59; N, 8.28%.)

(c) Reaction with triphenyltin chloride. Triphenyltin chloride 0.835 g; 2.17 mmol) in methanol (10 cm^3) was added dropwise with stirring to lithium TCNQ (0.457 g; 2.17 mmol) in water (20 cm^3). A blue solid was immediately formed which clung to the sides of the flask. This solid changed slowly to green/yellow, the change being complete after 18 h. The solid was filtered off and dried. (Found: C, 54.74; H, 3.17; N, 9.11%.) The blue filtrate was reduced in volume, when a blue solid was formed which was filtered off, washed with water and dried. Yield of the two solids was (i) 0.22 g, (ii) 0.65 g, respectively. Found: C, 62.74; H, 3.83; N, 7.17. $C_{30}H_{19}N_4Sn$ calcd.: C, 65.02; H, 3.46; N, 10.11%.

(d) Reaction with dimethyltin dichloride. (i) a solution of dimethyltin dichloride (0.394 g; 1.80 mmol) in THF (20 cm^3) was added to lithium TCNQ (0.758 g; 3.50 mmol) under THF (20 cm^3) with no reaction. The mixture was refluxed for 2 h and left stirring overnight, with no apparent change. The blue solid was filtered off and identified as lithium TCNQ.

(ii) An aqueous solution (10 cm^3) of dimethyltin dichloride (0.335 g; 1.52 mmol) was added with stirring to lithium TCNQ (0.643 g; 3.05 mmol) in water (20 cm^3), with immediate formation of a grey/green flocculent precipitate. The solid was filtered off, washed with water, acetone and finally ether, and dried to give dimethyltinbis-7,7,8,8-tetracyanoquinodimethanate, as an olive-green powder (yield 0.77 g). Found: C, 53.50; H, 2.02; N, 18.42. $C_{26}H_{14}H_8Sn$ calcd.: C, 54.80; H, 2.45; N, 19.42%.

(e) Reaction with tin(IV) chloride. Tin(IV) chloride (anhydrous) 0.570 g; 2.19 mmol) in dry benzene (10 cm^3) was added to a stirred mixture of lithium TCNQ (0.924 g; 4.30 mmol) in benzene with no apparent change. After 20 h the blue solid was filtered off and identified as lithium-TCNQ. Found: C, 68.46; H, 1.76; N, 25.13. $C_{12}H_4N_4Li$ calcd.: C, 68.27; H, 1.91; N, 26.54%.

(f) Reaction with $[(CH_3)_2SnCl, \text{terpyridyl}]^+ [(CH_3)_2SnCl]^-$. Dimethyltin dichloride (0.848 g; 3.86 mmol) and 2,2′,2″-terpyridyl (0.450 g; 1.93 mmol) were treated as previously described to give the required ionic complex. The solid residue from the above reaction, after evaporation of the solvent, was redissolved in the minimum quantity of methanol, which was added dropwise to a methanolic solution (20 cm^3) of lithium-TCNQ. A blue-green precipitate formed immediately; this was filtered off, washed with methanol, benzene and finally ether and dried in vacuo, to give monochlorobismethyl-2,2′,2″-terpyridyltin-7,7,8,8-tetracyanoquinodimethanate (yield 0.95 g; 79.2%) as a green-blue crystalline solid. Found: C, 56.05; H, 3.39; N, 16.38. $C_{29}H_{21}N_7ClSn$ calcd.: C, 56.03; H, 3.40; N, 15.77%.

(g) Reaction with dimethyltin dichloride bipyridyl. 2,2-Bipyridyl (0.175 g; 1.12 mmol) in benzene (10 cm^3) was added dropwise with stirring to a benzene solution (10 cm^3) of dimethyltin dichloride (0.246 g; 1.12 mmol) with immediate formation of a white precipitate. The reaction mixture was brought to reflux, when a methanolic solution (20 cm^3) of lithium-TCNQ (0.474 g; 2.24 mmol) was added. The white complex dissolved immediately to give an intense green solution. The solution was evaporated to dryness and the resulting solid was extracted twice with THF (2 × 10 cm^3) and dried (yield 0.59 g). Found: C, 53.19; H, 2.99; N, 16.62. $C_{36}H_{22}N_{10}Sn$ calcd.: C, 60.62; H, 3.11; N, 19.64%. No further attempt was made to identify the product.

Reactions of hexaorganoditins with TCNQ

(a) Reaction with hexamethylditin. Hexamethylditin (1.010 g; 3.08 mmol) in anhydrous THF (6 cm^3) was added dropwise to a stirred mixture of TCNQ (1.259 g; 6.17 mmol) in anhydrous THF (20 cm^3) in an argon atmosphere. A gelatinous brown precipitate formed over a period of 50 h, which was filtered off under argon and subsequently handled in the dry box. The compound was identified as $(CH_3)_3Sn \cdot TCNQ$. Found: C, 50.16; H, 3.43; N, 15.09. $C_{15}H_{13}N_4Sn$: calcd.: C, 48.96, H, 3.56; N, 15.23%. Dissolution in acetonitrile gave an identical electronic spectrum to that obtained for $(CH_3)_3Sn^+ TCNQ^-$ obtained from the aqueous reaction of trimethyltin chloride with lithium-TCNQ. Also on exposure to the atmosphere the compound gradually became an intense blue.

(b) Reaction with hexabutylditin. Hexabutylditin (0.630 g; 1.09 mmol) and TCNQ (0.44 g; 2.17 mmol) were treated under identical conditions to a, to give a pastel green solid which was filtered off and dried in vacuo to give $(n\text{-}C_4H_9)_3Sn - TCNQ$. Found: C, 57.54; H, 6.28; N, 10.74. $C_{24}H_{31}N_4Sn$ calcd.: C, 58.33; H, 6.32; N, 11.34%. Again on exposure to the atmosphere the compound gradually adopted an intense blue colouration.

(c) Reaction with hexaphenylditin. Hexaphenylditin (0.700 g; 1.00 mmol) in dry THF (10 cm^3) was added to a mixture of TCNQ (0.408 g; 2.00 mmol) and dry THF (20 cm^3) with no apparent reaction. A green colouration gradually formed over a period of 24 h, but the mixture still retained free TCNQ. The mixture was refluxed for 24 h and on cooling, crystals of TCNQ again formed. The mixture was left stirring for several weeks under argon, during which time a blue solution formed. The mixture was filtered to give a brown solid, unreacted TCNQ and a blue filtrate, which on concentration gave a blue solid which was filtered off, washed with pentane and dried in vacuo to give $(Ph_3Sn)_2TCNQ$ (yield 0.83 g) as a blue solid. Found: C, 63.24; H, 3.63; H, 6.21. $C_{48}H_{34}N_4Sn_2$ calcd.: C, 63.76; H, 3.79; N, 6.20%.

(d) Reaction with triphenyltin iodide. A benzene solution of iodine (0.458 g; 1.80 mmol) was added to a benzene solution of hexaphenylditin (1.263 g; 1.80 mmol), such that the solution just remained pink, and was then evacuated to dryness in vacuo. The resulting solid was redissolved in a mixture of benzene (3 cm^3) and ethylacetate (10 cm^3) and mixed with a solution of TCNQ (0.737 g; 3.61 mmol) in ethylacetate (220 cm^3). The solution was refluxed for 36 h without reaction; TCNQ was obtained on concentration of solution.

(e) Reaction with tin(IV) chloride. A dry benzene solution (10 cm^3) of tin(IV) chloride (anhydrous) (0.850 g; 3.26 mmol) was added dropwise with stirring to a mixture of TCNQ (0.666 g; 3.26 mmol) and dry benzene (20 cm^3), with no apparent reaction within the first hour. On stirring for 16 h a bright-yellow flocculent precipitate formed which was filtered off and dried in vacuo. A Mössbaur sample of this solid showed no tin signal. (Found: C, 69.46; H, 3.37; N, 19.60%.) The IR spectrum showed great similarity to that of TCNQ but showed additional absorptions.

(f) Reaction with tin metal. Powdered tin metal (0.293 g; 2.47 mmol) and TCNQ (1.007 g; 4.93 mmol) were refluxed together in acetonitrile (dry) under argon, for several days without reaction.

Reactions of hexaorganoditins with TCNE

(a) Reaction with hexamethylditin. To hexamethylditin (0.99 g, 0.003 mol) was added TCNE (0.78 g, 0.006 mol) in THF (50 cm^3). After the addition, the orange colour slowly changed through green-brown and dark brown, finally giving a black solution. The slow addition of pentane (30 ml) produced a black graphite-like powder which decomposed at 180°C. Found: C, 37.3; H, 3.55; N, 18.7. $C_9H_9N_5$ calcd.: C, 37.1; H, 3.11; N, 19.1%.

(b) Reaction with hexabutylditin. To hexabutylditin (1.61 g, 0.028 mol) was added TCNE (0.71 g, 0.0056 mol) in THF (50 ml). After stirring for 4 h, the solution had become a deep red colour. The volume of the reaction mixture was reduced to ca. 10 ml, and pentane (20 ml) was added slowly yielding a very dark purple, hygroscopic amorphous powder (decomp. 190—200°C). Found: C, 51.5; H, 6.55; N, 13.1. $C_{18}H_{22}N_5$ calcd.: C, 51.75; H, 6.51; N, 13.4%.

Reaction of hexaorganoditins with TCBQ

(a) Reaction with hexamethylditin. To TCBQ (3.71 g, 0.150 mol) in benzene (40 ml) was added hexamethylditin (2.47 g, 0.075 mol) also in benzene (10 ml). The mixture was stirred for 24 h under argon until no further colour change occurred. The pale cream powder which had been deposited was filtered off, washed with pentane and dried in vacuo. Found: C, 26.0; H, 2.23; Cl, 38.9 $C_9H_9Cl_4O_2Sn$ calcd.: C, 26.4; H, 2.21; Cl, 39.8%.

(b) Reaction with hexabutylditin. TCBQ (1.87 g, 0.076 mole) in benzene (40 ml) was mixed with hexabutylditin (2.20 g; 0.038 mole) also in benzene (10 ml), and the mixture stirred. On mixing the mixture became a very dark brown colour which changed to a very dark black-green colour after 1 h. After stirring for 24 h, the mixture was filtered and a yellow-green powder was collected which was identified as unreacted TCBQ. Removal of the solvent from the filtrate yielded a heavy viscous purple oil. Found: C, 44.0; H, 6.43%. $C_{30}H_{54}Cl_4O_2Sn_2$ calcd.: C, 43.6; H, 6.60%.

(c) Reaction with hexaphenylditin. To TCBQ (0.98 g, 0.0041 mol) in benzene (50 ml) was added hexaphenylditin (1.40 g, 0.00205 mol) also in benzene (30 ml). After stirring for 3 days the mixture was filtered when some unreacted TCBQ was removed. Concentration of the filtrate, followed by the slow addition of pentane (20 ml) yielded a white powder. Found: C, 54.4; H, 3.60. $C_{42}H_{30}Cl_4O_2Sn_2$ calcd.: C, 53.3; H, 3.19%.

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