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Preliminary communication

THE INTERACTION OF TIN COMPOUNDS WITH STRONG π-ACIDS

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Summary

The complexes $Me_3SnTCNQ$, $MeCp_2Sn \cdot TCNQ$, $MeCp_2Sn \cdot n$TCNE (n = 1, 2), and $SnX_2 \cdot TCNE \cdot THF$ (X = Cl, Br) are described.

In recent years there has been considerable interest in the electrical properties of complexes formed between metallic and non-metallic cationic species and strong π-acids such as tetracyano-*p*-quinodimethane (TCNQ). As yet, however, no similar complexes involving tin species have been synthesised. In this communication we report some of our preliminary results concerning tin complexes of TCNQ and related reagents.

Although no reaction takes place between TCNQ and triorganotin chlorides in alcoholic or aqueous media, with $Li^+(TCNQ)^-$ and trimethyltin chloride in H_2O the complex $Me_3Sn(TCNQ)$ is readily isolated as an intense blue, air stable infusible (decomp. ca. 200°) solid. The infrared spectrum of the complex exhibits a single band at 555 cm^{-1} in the tin—carbon stretching region, which is assigned to the antisymmetric mode[*] of a planar Me_3Sn moiety, with bridging TCNQ residues resulting in a trigonal bipyramidal configuration at tin. Corroboration of this geometry comes from the large value of the tin-119*m* Mössbauer quadrupole splitting (3.88 mm/s), which is similar to that observed for model compounds of confirmed geometry[**]. The intense colouration of the compound is indicative of the retention of the $(TCNQ)^{\bar{\cdot}}$ radical anion on complexation. The complex is therefore best represented by the canonical form $(Me_3Sn^+)(TCNQ)^{\bar{\cdot}}$, and as such is the first example of an isolable paramagnetic organotin complex in which delocalisation of the free electron throughout the coordinated TCNQ molecule places unpaired spin density on the nitrogen atoms in the primary coordination sphere of the metal atom.

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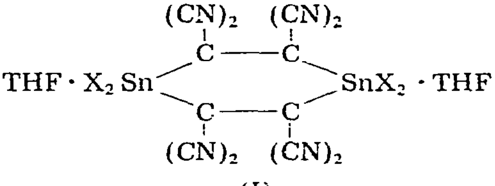
[*] Cf. the complex $Me_3SnX_2^-$ (X = Cl, Br) anions, which also possess the trigonal bipyramidal configuration, also have ν_{as}(Sn—C) at 555 cm^{-1} [1].

[**] E.g. the five-coordinate complex $Ph_3P{=}CH{-}CO{-}Me \cdot Me_3SnCl$ [2].

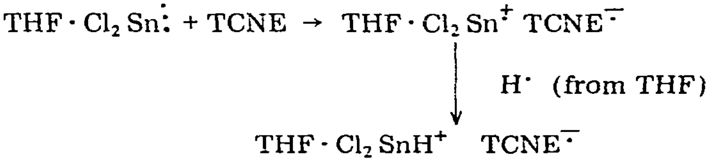
TCNQ also forms a pale green 1/1 complex with bis(methylcyclopentadienyl)tin(II), whilst with tetracyanoethylene (TCNE) both 1/1 (maroon-red) and 2/1 (yellow-brown) adducts are formed. All three complexes decompose at ca. 200° and are readily hydrolysed. The tin-119*m* Mössbauer isomer shifts for the complexes (3.38—3.83 mm/s) fall in the region normally accepted for derivatives of divalent tin, consistent with their formulation as simple charge transfer complexes in which the cyclopentadienyl groups function as electron donors to the π-acids.

The constitution of the products of the reaction of TCNE with tin(II) halides pose a problem. When the reactions are carried out in tetrahydrofuran, dark green, air-stable solids of composition $SnX_2 \cdot TCNE \cdot THF$ ($X = Cl, Br$) are obtained, which exhibit Mössbauer isomer shifts at ca. 0.15 mm/s, i.e. well within the region associated with tetravalent tin compounds. Experimental conditions rule out aerobic oxidation. Considerations of orbital symmetry exclude structures involving overlap between the tin lone pair (hybrid) orbital and antibonding orbitals on the TCNE molecule, although oxidative-addition resulting in distannacyclohexane species (I) is a possibility. Such a structure,



(I)

however, would not be consistent with the colour of the complexes (the similar adducts between tin(II) halides and acetylenes are white) [4]. Instead, we favour the formulation II involving (coordinated) $(TCNE)^{\overline{\cdot}}$ radical anions, via the scheme:



$$\begin{tikzcd}[column sep=small] THF \cdot Cl_2 Sn\colon + TCNE \arrow[r] & THF \cdot Cl_2 Sn^{\dot{+}}\ TCNE^{\overline{\cdot}} \arrow[d, "H^{\cdot}\ (\text{from THF})"] \\ & THF \cdot Cl_2 SnH^{+}\quad TCNE^{\overline{\cdot}} \end{tikzcd}$$

(II)

As such, these complexes are very similar in constitution to $Me_3SnTCNQ$

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