Derivatives of Bivalent Germanium, Tin, and Lead. Part XX.[1] Complex Formation Between Tin(II) Compounds and Tetracyanoethylene, 7,7,8,8-Tetracyanoquinodimethane, and 2,3,5,6-Tetrachlorobenzoquinone

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Complexes of tin(II) halides and bis(β-ketoenolates), bis(cyclopentadienyl)tin(II), and triethylammonium trichlorostannate(II) with tetracyanoethylene (tcne), 7,7,8,8-tetracyanoquinodimethane (tcnq), and 2,3,5,6-tetrachlorobenzoquinone (tcbq) have been synthesised and examined by i.r. and tin-119m Mössbauer spectroscopy. Complexes of $[Sn(C_5H_5)_2]$ with tcne and tcnq are formulated as charge-transfer complexes involving the π-electron system of the cyclopentadienyl rings, whereas the complexes $[SnX_2(tcne)\cdot thf]$ (X = Cl, Br, or I) and $[NEt_3H][SnCl_3(tcne)]$ are considered to contain a tin-substituted radical species. Linear chain structures in which the organic molecule bridges adjacent tin atoms are proposed for the complexes of tin(II) bis(β-ketoenolates) with tcne, tcbq, and tcnq.

COMPLEXES involving organic electron-acceptor molecules such as tetracyanoethylene (tcne) and 7,7,8,8-tetracyanoquinodimethane (tcnq) have been widely investigated because of their electrical properties.[2] In an attempt to construct tin-containing materials with anisotropic conducting properties, we have examined the reactions of a variety of tin(II) compounds with tcne, tcnq, and 2,3,5,6-tetrachlorobenzoquinone (tcbq).

RESULTS AND DISCUSSION

Tin(II) dihalides and triethylammonium trichlorostannate(II) reacted in tetrahydrofuran (thf) with tcne to form highly coloured complexes of composition $[SnX_2(tcne)\cdot thf]$ (X = Cl, Br, or I) and $[NEt_3H][SnCl_3(tcne)]$, respectively. The molecule of thf in the former complexes was not easily removed, and appears to be strongly bound to the metal. Similar 1 : 1 comcomplexes of tin(II) bis(β-ketoenolates) and tcne were also formed by stirring the reagents in benzene. Tin(II) halides did not react with tcnq or tcbq {except for tin(II) chloride with which the complex $[SnCl_2(tcbq)\cdot(thf)_{1.5}]$ was formed}, although $[NEt_3H][SnCl_3]$ formed a metallic grey complex with tcnq. Tin(II) bis(β-ketoenolates), in contrast, readily formed 1 : 1 complexes with both tcnq and tcbq. The perfluorinated tin(II) bis(β-ketoenolates), $[Sn\{OC(CF_3)\dot{:}CH\cdot C(\dot{:}O)Me\}_2]$ and $[Sn\{OC(CF_3)\dot{:}CH\cdot C(\dot{:}O)CF_3\}_2]$, did not react with tcne, tcnq, or tcbq, even on prolonged reflux in benzene, and could be recovered unchanged from the reaction mixture. Attempts to obtain complexes incorporating more than one molecule of the organic reagent were usually unsuccessful, only the complexes $[Sn(tcnq)_{1.5}(pd)_2]$ and $[Sn(pd)_2(tcbq)_2]$ being obtained with excess of reagent (pd = pentane-2,4-dionato). Bis(cyclopentadienyl)tin(II) formed both 1 : 1 and 1 : 2 complexes with tcne, but only a 1 : 1 complex with tcnq. No analogous complex with tcbq could be obtained. Tetracyanoethylene, but not tcnq or tcbq, reacted directly with tin metal in thf to afford the complex $[Sn(tcne)_2\cdot thf]$.

All the complexes are amorphous powders of various, sometimes very intense, colours, and are very hygroscopic. The bis(cyclopentadienyl)tin and bis(β-ketoenolato)tin derivatives undergo decomposition in air involving cleavage of groups from tin. The complexes are generally infusible, and decompose at elevated temperatures.

The i.r. spectra of the bis(β-ketoenolato)tin complexes indicate that the chelation of the β-ketoenolato-groups is preserved on complex formation. The complexes $[SnX_2(tcne)\cdot thf]$ (X = Cl, Br, or I), $[NEt_3H][SnCl_3(tcne)]$, $[Sn(tcne)(chtd)_2]$ (chtd = cyclohepta-2,4,6-triene-2,6-dionato), and $[Sn(tcne)_2\cdot thf]$ all exhibited a single broad C=N stretching band, but the other tcne and tcnq complexes showed more than one such band (Table 1). The tin-119m Mössbauer spectra of the complexes are most interesting, and demonstrate that, whereas the tcne and tcnq complexes of $[Sn(C_5H_5)_2]$ still contain Sn^{II}, tcne and tcbq completely oxidise the metal in the tin(II) halides and bis(β-ketoenolates) to the quadrivalent state. The tcnq complexes of tin(II) bis(β-ketoenolates) and $[Sn(tcne)_2\cdot thf]$ exhibited resonances due to both Sn^{II} and Sn^{IV}.

The bivalent nature of tin in $[Sn(C_5H_5)_2\cdot n(tcne)]$ ($n = 1$ or 2) and $[Sn(C_5H_5)_2(tcnq)]$ suggests that the organic molecule is forming charge-transfer complexes with the π-orbital system of the cyclopentadienyl rings, similar to that which has been characterised by *X*-ray diffraction for the analogous ferrocene complex $[Fe(C_5H_5)_2\cdot tcne]$.[3] In contrast, with the other tin(II) derivatives, electrophilic attack takes place at the tin lone pair resulting in total or partial oxidation. The complexing of the cyclopentadienyl ring π-orbital systems with tcne causes some electron drift away from tin as shown by the decrease in isomer shift from 3.84 mm s^{-1} in $[Sn(C_5H_5)_2]$ [4] to 3.03 and 3.12 mm s^{-1} in the complexes. Simultaneously, the quadrupole splitting increases from the barely resolvable value [4] of 0.84 mm s^{-1} to 2.37 and 2.26 mm s^{-1}. The interaction with tcnq is much weaker, and the isomer shift is unchanged on complex formation, but the quadrupole splitting increases to 1.30 mm s^{-1}.

The Mössbauer spectra of the halogenotin complexes

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[1] Part XIX, A. B. Cornwell and P. G. Harrison, preceding paper.

[2] R. C. Haddon, *Austral. J. Chem.*, 1975, **28**, 2333.

[3] E. Adman, M. Rosenblum, S. Sullivan, and T. N. Margulis, *J. Amer. Chem. Soc.*, 1967, **89**, 4540.

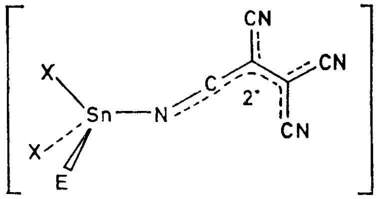
[4] P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1969, **91**, 6885; 1970, **92**, 2577.

Table 1

Spectroscopic data for the complexes

Compound	$\nu(C\equiv N)/cm^{-1}$	Tin–119m Mössbauer/mm s^{-1}						^1H N m.r.	
		I.s.	Q.s.	Γ_1	Γ_2	I_1	I_2	$\tau(CH)$	$\tau(CH_3)$
$[Sn(tcne)_2\cdot thf]$	2 220m, br	0.42	1.09	1.06	1.33	0.49	0.35		
		3.33	2.10	1.65	1.06	0.87	1.00		
$[SnCl_2(tcne)\cdot thf]$	2 220m, br	0.60	0	0.61					
$[SnBr_2(tcne)\cdot thf]$	2 210m, br	0.45	0	0.68					
$[SnI_2(tcne)\cdot thf]$	2 220m, br	0.38	0	0.68					
$[NEt_3H][SnCl_3(tcne)]$	2 210m	0.41	0	0.72					
$[Sn(C_5H_5)_2(tcne)]$	2 210mw, 2 180m, 2 100m	3.03	2.37	0.78	0.80	0.99	1.00		
$[Sn(C_5H_5)_2(tcne)_2]$	2 200m, 2 100m	3.12	2.26	0.85	0.77	0.91	1.00		
$[Sn(tcne)(pd)_2]$	2 220m, 2 180m	0.29	0	1.51				4.02	7.82
$[Sn(tcne)(pbd)_2]$	2 210mw (sh), 2 180m, br	0.16	0	1.47				3.25	7.78
$[Sn(tcne)(bppd)_2]$	2 210w (sh), 2 180m, br	0.26	0	1.45				3.08	
$[Sn(tcne)(chtd)_2]$	2 185m, br	0.32	0	1.55					
$PPh_3\cdot tcne$	2 205m								
$[Sn(C_5H_5)_2(tcnq)]$	2 190mw, 2 130m, 2 080m	3.84	1.30	0.88	0.95	0.96	1.00		
$[Sn(tcnq)(pd)_2]$	2 210w, 2 160m, 2 100ms, br	0.10	0	1.30		1.78			
		3.17	1.86	0.89	0.85	0.85	1.00		
$[Sn(tcnq)_{1.5}(pd)_2]$	2 220w (sh), 2 170m, 2 100ms, br	0.09	0	1.31		3.01			
		3.20	1.79	1.23	0.94	0.69	1.00		
$[Sn(tcnq)(pbd)_2]$	2 220vw, 2 160m, 2 100m, 2 060m	0.10	0	1.50		4.56			
		3.17	1.84	0.79	0.93	0.96	1.00		
$[Sn(tcnq)(bppd)_2]$	2 220m (sh), 2 170m, br, 2 100w (sh)	0.05	0	1.04		6.59			
		3.15	1.78	0.73	0.92	0.92	1.00		
$[Sn(tcnq)(chtd)_2]$	2 220w, 2 165s, 2 090m	0.19	0	1.50		2.62			
		3.39	1.92	0.86	1.8	0.96	1.00		
$[NEt_3H][SnCl_3(tcnq)]$	2 200mw, 2 160m, vbr	0.29	0	0.75					
$[Sn(tcbq)(pd)_2]$		0.09	0	1.37					
$[Sn(tcbq)_2(pd)_2]$		0.10	0.65	0.82	0.85	0.99	1.00		
$[Sn(tcnq)(pbd)_2]$		0.10	0	1.15					
$[Sn(tcnq)(bppd)_2]$		0.07	0	1.08					
$[Sn(tcnq)(chtd)_2]$		0.08	0	1.10					
$[SnCl_2(tcbq)\cdot(thf)_{1.5}]$		0.35	0	1.46					

$[SnX_2(tcne)\cdot thf]$ ($X = Cl$, Br, or I) and $[NEt_3H][SnCl_3(tcne)]$ consisted of sharp ($\Gamma < 0.7$ mm s^{-1}) single resonances in the range 0.38—0.60 mm s^{-1}, indicative of an almost perfect cubic disposition of ligands about tin. This, together with the intense colour of the complexes, suggests that the complexes are the tetrahedral tin-substituted radical species (I), similar to the radical species produced by homolytic cleavage of metal–metal bonds by tcne.[5] Single, although rather broad (Γ 1.45—1.55 mm s^{-1}), lines were also observed in the Mössbauer spectra of the tin bis(β-ketoenolate)–tcne complexes, again indicative of a cubic, though distorted, arrangement of ligands about tin. The lower values of the isomer shift (0.16—0.32 mm s^{-1}) and the chelating nature of the β-ketoenolato-ligands suggest an octahedral geometry in which tcne radical-anionic ligands bridge adjacent metal cations, (II). The analogous tin bis(β-ketoenolate)–tcbq complexes had very similar Mössbauer spectra, although the resonance lines were significantly sharper (Γ 1.08—1.37 mm s^{-1}), presumably due to the presence of oxygen rather than nitrogen ligands, and a similar chain structure, (III), is proposed. The 1 : 2 complex of $[Sn(pd)_2]$ with tcbq had an identical isomer shift to the 1 : 1 complex, but exhibited a resolvable quadrupole splitting of 0.65 mm s^{-1}, indicative of a similar geometry at tin.



(I) X = Cl, E = Cl⁻
X = Cl, Br, or I; E = thf

The spectra of the tcnq complexes of the tin bis(β-ketoenolates) exhibited single broad resonances in the range 0.05—0.19 mm s^{-1}, together with doublet resonance with isomer shifts and quadrupole splittings in the ranges 3.15—3.39 and 1.78—1.92 mm s^{-1}, respectively, indicating the presence of both tin(IV) and tin(II) sites. These Mössbauer data suggest an octahedral environment for the tin(IV) atoms, but the exact geometry of the tin(II) atoms cannot be determined from the Mössbauer data alone, although the co-ordination must be irregular with perhaps a stereochemically active lone pair. However, the parameters for the tin(II) sites are sufficiently different from the parent tin(II) bis(β-ketoenolates) to demonstrate that isolated molecules are not present in the material. Whereas tcne can accommodate one or two electrons to form mono- or di-radical anions, tcnq is able to accept only one electron forming a $[tcnq]^{-\cdot}$ radical anion, and the $[tcnq]^{2-\cdot}$ radical anion is unknown, and so we propose a structure for the complexes in

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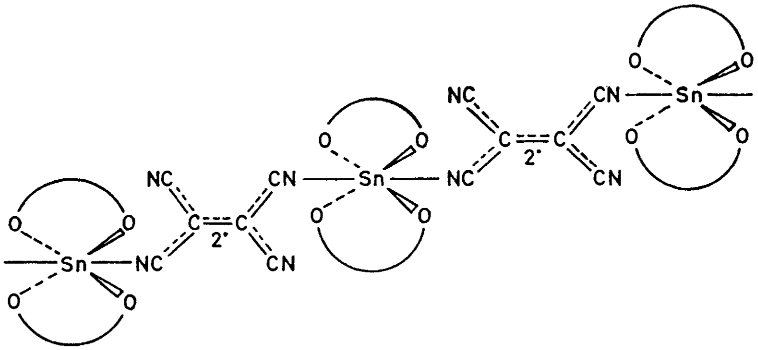
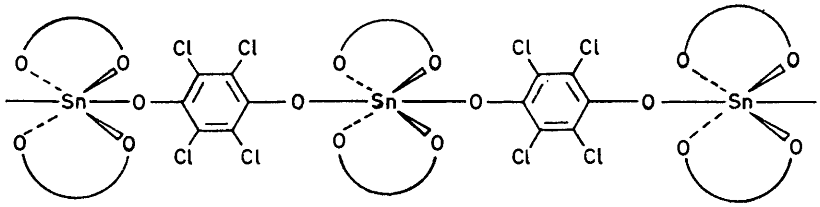
[5] P. J. Krusic, H. Stoklosa, L. E. Manzer, and P. Meakin, *J. Amer. Chem. Soc.*, 1975, **97**, 667.

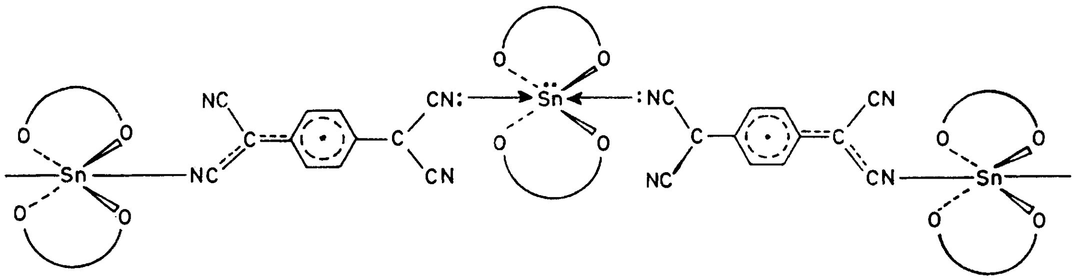
which [tcnq]$^{-\bullet}$ radical-anionic moieties alternately bridge octahedral tin(IV) and pseudo-pentagonal-bipyramidal tin(II) ions,[6,7] (IV). The intensity of the tin(II) resonances decreased markedly as the bulkiness of the β-ketoenolato-residues increased. The area under the resonance is related to the recoil-free fraction, and is a measure of the strength of binding of the Mössbauer nuclide in the lattice. Thus it is inferred that the tin(II) atom becomes progressively less tightly held as the bulk of the ligand increases, *i.e.* in the order pd > chtd > 4-phenylbutane-2,4-dionate(pbd) > 1,3-diphenylpropane-1,3-dionate (bppd). On the proposed model, it is easy to rationalise the observed decrease in the recoil-free fraction as the steric bulk of the β-ketoenolato-group increases, since each tin(II) atom will be surrounded by four oxygen atoms (from two chelating β-ketoenolato-groups), two nitrogen atoms (from two tcnq molecules), and a (stereochemically active) lone pair, and will thus be very susceptible to perturbations arising from bulky groups.



(II)



(III)



(IV)

The product obtained from the oxidation of tin metal by tcne in thf, [Sn(tcne)$_2$·thf], also contains tin in both valence states, as illustrated by the presence of quadrupole-split resonances at 0.42 and 3.33 mm s^{-1} in the Mössbauer spectrum, and a similar structure in which tcne molecules or radical anions bridge adjacent tin ions may be postulated. Since the ratio of the resonance intensities does not yield information concerning the relative abundances of the two valence states, and tcne may accommodate one or two electrons, the constitution of the material is best represented as [(Sn^{2+},Sn^{4+})(tcne^0, tcne$^{-\bullet}$, tcne$^{2-\bullet}$)·thf].

Reaction of tcne with triphenylphosphine yielded a very dark red adduct of composition [PPh$_3$·tcne], but from the analogous reaction with triphenyl-arsine and -stibine only the starting materials were recovered,

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[6] P. F. R. Ewings, P. G. Harrison, T. J. King, and A. Morris, *J.C.S. Chem. Comm.*, 1974, 53; *J.C.S. Dalton*, 1976, 1602.

[7] F. P. van Remoortere, J. J. Flynn, F. P. Boer, and P. P. North, *Inorg. Chem.*, 1971, **10**, 1511.

although some interaction was apparent from the orange-red colour of the reaction mixtures.

EXPERIMENTAL

All manipulations were under an atmosphere of dry oxygen-free nitrogen or argon. Solvents were dried and freed from dissolved oxygen by standard methods, and re-distilled immediately before use. Bis(β-ketoenolato)tin derivatives were freshly prepared as described previously.[8,9] Bis(cyclopentadienyl)tin was obtained by the reaction of tin(II) chloride and lithium cyclopentadienide in thf and sublimed *in vacuo*. Commercial anhydrous tin(II) chloride and bromide were not further purified, but tin(II) iodide was recrystallised from tetrahydrofuran (thf).

TABLE 2

Physical and analytical data for the complexes

Compound	Colour	Decomposition temperature (θ_c/°C)	Microanalysis (%) Found C	H	N	Halogen	Calc. C	H	N	Halogen
[Sn(tcne)$_2$·thf]	Very dark green	*ca.* 240	42.55	2.05	24.7		42.9	1.80	25.05	
[SnCl$_2$(tcne)·thf]	Green	*ca.* 200	30.6	1.80	13.95	17.9	30.8	2.05	14.35	18.2
[SnBr$_2$(tcne)·thf]	Green	*ca.* 200	24.85	1.80	11.75	33.15	25.05	1.65	1.17	33.5
[SnI$_2$(tcne)·thf]	Green	*ca.* 200	20.65	2.05	8.80		20.95	1.40	9.80	
[NEt$_3$H][SnCl$_3$(tcne)]	Very dark red	>250	32.25	3.30	15.15		31.65	3.55	15.4	
[Sn(C$_5$H$_5$)$_2$(tcne)]	Pale brown	*ca.* 160	51.15	2.80	13.95		50.95	2.65	14.85	
[Sn(C$_5$H$_5$)$_2$(tcne)$_2$]	Brown	*ca.* 170	51.95	2.20	21.55		52.3	2.00	22.2	
[Sn(tcne)(pd)$_2$]	Brown	*ca.* 180	43.45	3.35	12.2		43.2	3.15	12.6	
[Sn(tcne)(pbd)$_2$]	Brown	*ca.* 220	54.85	3.55	9.50		54.7	3.15	9.85	
[Sn(tcne)(bppd)$_2$]	Fawn	*ca.* 230	62.0	3.15	6.85		62.35	3.20	8.10	
[Sn(tcne)(chtd)$_2$]	Dark green	*ca.* 200	48.7	2.50	10.8		49.1	2.05	11.45	
PPh$_3$·tcne	Dark red	108—110 (m.p.)	72.45	4.85	13.15		73.85	3.85	14.35	
[Sn(C$_5$H$_5$)$_2$(tcnq)]	Pale lime-green	*ca.* 190	58.45	2.70	12.0		58.3	3.10	12.35	
[Sn(tcnq)(pd)$_2$]	Dark green	*ca.* 160	51.05	3.35	9.50		50.7	3.50	10.75	
[Sn(tcnq)$_{1\cdot5}$(pd)$_2$]	Green	*ca.* 170	53.75	2.95	13.15		54.0	3.20	13.45	
[Sn(tcnq)(pbd)$_2$]	Brown	*ca.* 175	59.25	3.30	8.30		59.4	3.45	8.65	
[Sn(tcnq)(bppd)$_2$]	Dark blue-green	*ca.* 190	65.2	3.40	7.00		65.55	3.40	7.30	
[Sn(tcnq)(chtd)$_2$]	Dark green	185—186 (m.p.)	55.65	2.45	9.80		55.25	2.50	9.90	
[NEt$_3$H][SnCl$_3$(tcnq)]	Grey	*ca.* 160	39.95	3.85	12.1		41.0	3.05	13.3	
[Sn(tcbq)(pd)$_2$]	White	*ca.* 240	32.35	1.95		34.8	32.65	1.75		35.05
[Sn(tcbq)$_2$(pd)$_2$]	Cream	*ca.* 250	33.85	2.15			34.15	2.50		
[Sn(tcbq)(pbd)$_2$]	Pale yellow	255—257 (with melting)	45.1	2.85			45.35	2.65		
[Sn(tcbq)(bppd)$_2$]	Yellow	*ca.* 280	53.45	3.10			53.3	2.75		
[Sn(tcbq)(chtd)$_2$]	Pale yellow	*ca.* 250	40.0	2.10			39.6	1.65		
[SnCl$_2$(tcbq)·(thf)$_{1\cdot5}$]	Pale yellow	*ca.* 250	26.75	2.45			26.5	2.25		

Infrared spectra were recorded on Perkin-Elmer 521 and 457 spectrophotometers calibrated with polystyrene film. Proton n.m.r. spectra were obtained on a Varian HA-100 spectrometer with SiMe$_4$ as internal lock signal. Tin-119m Mössbauer spectra were recorded at 77 K on a Harwell spectrometer with a Ba^{119m}SnO$_3$ source as described previously.[10] Data reduction to Lorentzian lineshapes was effected by the usual least-squares methods. Isomer-shift and quadrupole-splitting values (Table 1) are accurate to at least ±0.05 and ±0.10 mm s^{-1}, respectively. Isomer shifts are quoted with respect to SnO$_2$.

Preparation of the Complexes.—The majority of the syntheses were essentially similar, and complete descriptions are only given for a few cases. Physical and analytical data are presented in Table 2.

(a) [Sn(tcne)$_2$·thf]. To tin powder (0.59 g, 0.005 mol) suspended in thf (10 cm^3) was added tetracyanoethylene (tcne) (1.28 g, 0.010 mol) also in thf (5 cm^3), and the mixture stirred at room temperature. After 4 d, the tin metal had dissolved and a dark solid was produced, which was filtered off, washed, and dried *in vacuo* giving the *complex* as a very dark green amorphous powder.

(b) [SnX$_2$(tcne)·thf] (X = Cl, Br, *or* I). Tetracyanoethylene (0.64 g, 0.005 mol) in thf (10 cm^3) was added to a solution of the respective tin(II) halide (0.005 mol) also dissolved in thf. After stirring for 48 h, a deep green solution was produced. Partial removal of the solvent, followed by dropwise addition of pentane, induced crystallisation of the *complex* which was isolated as before.

(c) [SnCl$_2$(tcbq)(thf)$_{1\cdot5}$]. Tin(II) chloride (1.51 g, 0.008 mol) in thf (20 cm^3) was added to 2,3,5,6-tetrachlorobenzoquinone (tcbq) (1.16 g, 0.008 mol). After stirring for 1.5 h a suspension began to form. The creamy yellow *complex* precipitated overnight.

(d) tcne, tcnq, *and* tcbq *Complexes of bis(cyclopentadienyl)tin and bis(β-ketoenolato)tin derivatives*. The tin(II) derivative (0.0015 mol) dissolved in benzene (10—20 cm^3) was added to tcne, 7,7,8,8-tetracyanoquinodimethane (tcnq), or tcbq (0.0015 mol) {or 0.030 mol of tcne in the case of [Sn(C$_5$H$_5$)$_2$(tcne)$_2$]} also in benzene (20 cm^3), and stirred for either 24 (tcne and tcbq) or 48 h (tcnq). After this time, the *product* precipitated and was separated as before.

(e) [Sn(tcnq)$_{1\cdot5}$(pd)$_2$]. To 7,7,8,8-tetracyanoquinodimethane (0.41 g, 0.002 mol) suspended in benzene (20 cm^3) was added [Sn(pd)$_2$] (0.32 g, 0.001 mol) dissolved in benzene (10 cm^3). After stirring for 72 h, the *complex* precipitated from solution. The same product was obtained after refluxing the mixture, and no 1 : 2 complex could be obtained.

One of us (A. B. C.) thanks the S.R.C. for a research studentship.

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[8] P. F. R. Ewings, P. G. Harrison, and D. E. Fenton, *J.C.S. Dalton*, 1975, 821.

[9] A. B. Cornwell and P. G. Harrison, *J.C.S. Dalton*, 1975, 1722.

[10] C. C. Addison, P. G. Harrison, N. Logan, L. Blackwell, and D. H. Jones, *J.C.S. Dalton*, 1975, 830.