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Simple charge transfer complexes of some new and of some known heterocyclic compounds of selenium and tellurium

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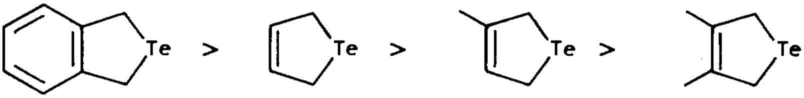
Abstract

Charge transfer (CT) complexes (1 : 1) of 2,5-dihydrotellurophene and the 3-methyl and 3,4-dimethyl compounds with TCNQ and tetrachlorobenzoquinone (TCB) are reported. The organotellurium compounds failed to give complexes with *p*-dinitrobenzene (DNB). The variation of solid state (disc) conductivity with temperature and as a function of methyl substituents is considered. The complexes show semi-conducting behaviour and a consideration of these data, together with IR and UV spectroscopic data, in comparison with those for 1,3-dihydro-2-tellurainddene given the following order of donor power with respect to TCNQ:



With respect to a given donor, the order of acceptor power is TCNQ > TCB > DNB.

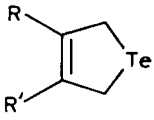
1,3-Dihydro-2-selenaindene forms a complex with TCNQ. The molecular ionisation potential of the selenaindene is 7.4 eV (by mass spectroscopy) and it has been shown that the compound may be electrochemically oxidized to materials such as $C_8H_8SePF_6$.

New quinoxalino-1-chalcogenacyclopentanes are reported; namely those derived from selenium, and for the 7,8-dimethyl series, those based on both selenium and tellurium. Their preparation and characterisation are described, and their chemistry shown to be strongly analogous to that of quinoxalino-1-telluracyclopentane. CT complexes of the new Se^{II} and Te^{II} compounds (1 : 1) are prepared with TCNQ which are believed to be strongly ionic.

Introduction

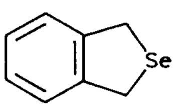
Interest in molecular charge transfer (CT) complexes, particularly those such as the strongly conducting black polymorph of the complex of tetramethyltetraselenafulvalene · tetracyanoquindimethane (TMTSF · TCNQ) [1] and in the series $(TMTSF)_2X$ ($X = PF_6$, ClO_4 etc.) [2] which show superconductivity at low temperature (ClO_4) or low temperature and high pressure (PF_6), continues to be strong. We have been interested in CT complexes formed by more simple organic derivatives, particularly of tellurium and have suggested the use of ^{125}Te Mossbauer spectroscopy to measure the degree of charge transfer in such systems [3]. In addition we have found quite strong interactions between bis-tellurides and some alkyl halides [4] as well as between some tellurium(IV) compounds and organic halides [5]. We believe that a CT interaction may be the first step in some reactions of simple tellurides [6] and note that the suggestion that several "diorganyl selenium diiodides" may be CT complexes of a selenide with diiodine is long stablished [7].

This paper is an extension of two previous pieces of work [3,5] in which we consider the effects of methyl substituents on the properties of the CT complexes formed by the compounds **1**–**3**; we also extend our studies to selenium. Some of the heterocyclic compounds are reported for the first time.

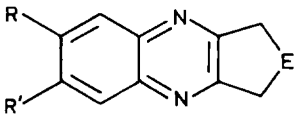


(**1**)

(R = R′ = H ;
R = Me, R′ = H ;
R = R′ = Me)



(**2**)



(**3**)

(R = R′ = H ; E = Se, Te ;
R = R′ = Me ; E = Se , Te)

Experimental and Results

Preparations

2,5-Dihydrotellurophene [8], 3-methyl-2,5-dihydrotellurophene [8], 3,4-dimethyl-2,5-dihydrotellurophene [8], 1,3-dihydro-2,2-telluraindene [9] and 1,3-dihydro-2-selenaindene [10] were prepared by the indicated literature methods, as was 3,4-quinoxalino-1-tellurapentane [5]. 3,4-Quinoxalino-1-selenacyclopentane and the 1 : 1 complex with 2,3-bis(iodomethyl)quinoxaline were prepared using the conditions previously described for the tellurium compounds, substituting elemental selenium for tellurium [5].

1,1-Diiodo-7,8-dimethyl-3,4-quinoxalino-selenacyclopentane. 1,4-Dibromo-2,3-butanedione (1.20 g, 0.5 mmol) in warm benzene (20 cm^3) was added to a solution of 4,5-dimethyl-*o*-phenylenediamine (0.68 g, 0.5 mmol) in benzene (20 cm^3). The mixture was refluxed for 40 min and cooled to afford white crystals. Recrystallisation from ethanol gave pure 7,8-dimethyl-2,3-bis(bromomethyl)quinoxaline (m.p. 149–151 °C), which (0.5 mmol) was then treated with sodium iodide (1.5 g, 20 mmol) and selenium powder (0.2 g, 5 mmol) in 2-methoxyethanol (50 cm^3) under gentle reflux for 2 h. After cooling, the mixture was treated with distilled water (100 cm^3) which caused additional precipitation. The crude material was separated, dried, and recrystallised from 2-methoxyethanol to give a deep violet solid, m.p. 168–169 °C.

Replacement of sodium iodide by potassium iodide and reduction of the reflux period to 1 h gave a yellow product, which recrystallised slowly from acetone to give

Table 1

Analytical data for new compounds

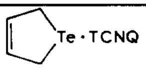
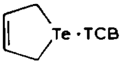
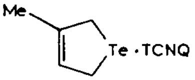
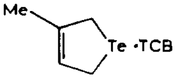
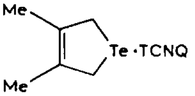
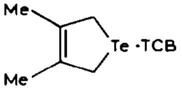
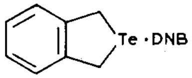
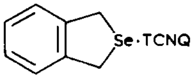
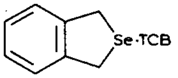
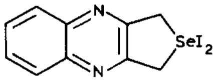
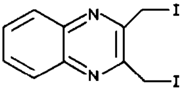
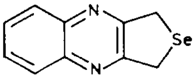
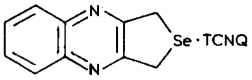
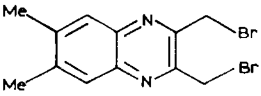
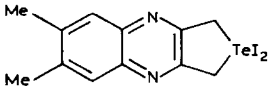
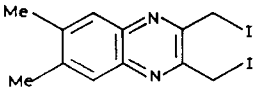
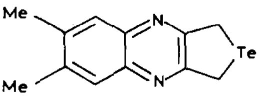
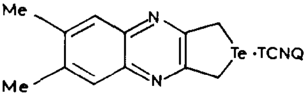
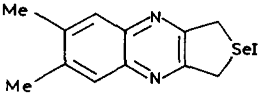
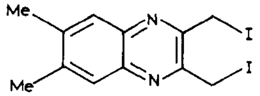
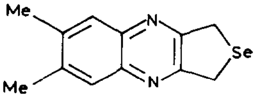
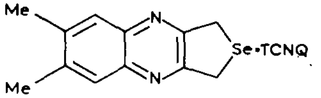
Compound		Colour (M.p. (°C))	Yield (%)	Analyses (Found (calc) (%))		
				C	H	N
	(1)	deep violet (102–104)	84	50.1 (49.8)	2.6 (2.6)	14.1 (14.5)
	(2)	dark brown (198–200)	78	28.5 (28.0)	1.45 (1.40)	33.6 [a] (33.1)
	(3)	red-black (92–95)	82	51.4 (51.0)	3.1 (3.0)	13.5 (14.0)
	(4)	deep brown (171–173)	80	28.2 (29.9)	2.3 (1.8)	31.6 [a] (32.1)
	(5)	black (83–85)	86	52.5 (52.2)	3.7 (3.4)	14.1 (13.5)
	(6)	brown-black (159–161)	76	32.0 (31.6)	2.7 (2.1)	31.9 [a] (31.2)
	(7)	black (108–110)	82	42.9 (42.0)	2.8 (3.0)	6.0 (7.0)
	(8)	blue-black (135–137)	85	62.2 (62.0)	3.3 (3.1)	14.0 (14.4)
	(9)	violet (197–199)	75	39.6 (39.0)	2.1 (1.8)	33.3 [a] (33.1)
	(10)	deep violet (138–140)	61	24.8 (24.5)	1.7 (1.6)	5.4 (5.7)
10 • 	(11)	yellow (145–147)	80	29.8 (29.8)	1.85 (1.90)	7.0 (6.9)
	(12)	pale-yellow (148–150)	62	50.4 (51.0)	3.3 (3.4)	11.4 (11.9)
	(13)	black (135–136)	80	59.7 (60.2)	2.5 (2.7)	18.2 (19.1)
	(14)	white (149–151)	75	41.8 (41.8)	3.50 (3.48)	8.5 (8.1)
 [b]	(15)	deep-violet (169–171)	53	25.7 (25.4)	1.6 (2.1)	4.1 (4.9)
15 •  [b]	(16)	yellow (164–165)	65	28.7 (28.7)	2.3 (2.3)	5.1 (5.5)

Table 1 (continued)

Compound		Colour (M.p. (°C))	Yield (%)	Analyses (Found (calc) (%))		
				C	H	N
 b	(17)	pale-yellow (167–169)	60	45.7 (46.2)	3.7 (3.8)	8.5 (8.9)
	(18)	black (164–166)	80	56.2 (55.8)	2.8 (3.1)	15.5 (16.2)
	(19)	deep violet (168–169)	54	28.2 (27.8)	2.0 (2.3)	4.9 (5.4)
19 • 	(20)	yellow (163–164)	70	33.5 (33.5)	2.7 (2.7)	6.1 (6.4)
	(21)	pale-yellow (169–171)	61	54.2 (54.8)	4.5 (4.6)	10.1 (10.6)
	(22)	black (144–146)	85	62.2 (61.7)	3.5 (3.4)	18.8 (18.0)

[a] % Cl. [b] Satisfactory tellurium analysis were obtained for these compounds.

yellow crystals (m.p. 163–164 °C) of *1,1-diiodo-7,8-dimethyl-3,4-quinoxalino-selenacyclopentane : 7,8-dimethyl-2,3-bis(iodomethyl)quinoxaline (1 : 1) complex.*

The corresponding tellurium compounds were prepared by identical procedures but with elemental tellurium in place of selenium.

7,8-Dimethyl-3,4-quinoxalino-1-selenacyclopentane. Violet 1,1-diiodo-7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane (1.2 g, 2.3 mmol) in suspension in ethanol (75 cm^3) and water (15 cm^3) was treated dropwise with hydrazine hydrate (0.45 g, 9 mmol) in ethanol (15 cm^3). The reaction mixture was then warmed gently until all the violet crystals had reacted; it was then poured into distilled water (200 cm^3) and an ether extraction was carried out. The separated ethereal solution was dried over anhydrous Na_2SO_4 and the solvent then removed on a rotatory evaporator. The yellow powder obtained was treated with charcoal and ether to give yellow needles, m.p. 169–171 °C. The tellurium compound was obtained similarly by reduction of $C_{12}H_{12}N_2I_2Te$.

Charge transfer complexes. A common procedure was adopted, and only one example of which is given as an illustration. In this, 7,8-dimethyl-3,4-quinoxalino-1-selenacyclopentane (0.26 g, 1 mmol) in acetonitrile (20 cm^3) was added to a solution of TCNQ (0.2 g, 1 mmol) in acetonitrile (30 cm^3). The mixture was stirred under reflux for 1 h, and its volume than reduced to 10 cm^3 to give black crystals (m.p. 144–146 °C).

In this manner, compounds **1** were treated with TCNQ and also with chloranil (tetrachlorobenzoquinone, TCB) and with 1,4-dinitrobenzene (DNB). True complexes were obtained with TCNQ and TCB, but with DNB incorrect analytical data were obtained and careful examination of the products revealed mixtures of crystals of the individual components. Compounds **2** and **3** were treated with TCNQ only.

Analytical and other data for the new compounds are summarised in Table 1.

Physical measurements

Infra-red spectra were recorded for KBr discs (solids) or liquid film with a Perkin–Elmer 599B instrument. UV/VIS spectra were recorded for solutions in 1 cm pathway quartz cells with a Pye Unicam SP8-100 spectrophotometer. Nuclear magnetic resonance data were obtained at 60 MHz (proton) with a Perkin–Elmer RB12 instrument (TMS standard). ESR data were obtained with a JEOL-IX spectrometer using a manganese(II)/MgO standard. Mass spectra were obtained with an AE1 MS9 instrument; appearance potential measurements were obtained by varying the exciting voltage within the range 70–6 eV, argon being incorporated with the sample as a substance of known ionisation potential.

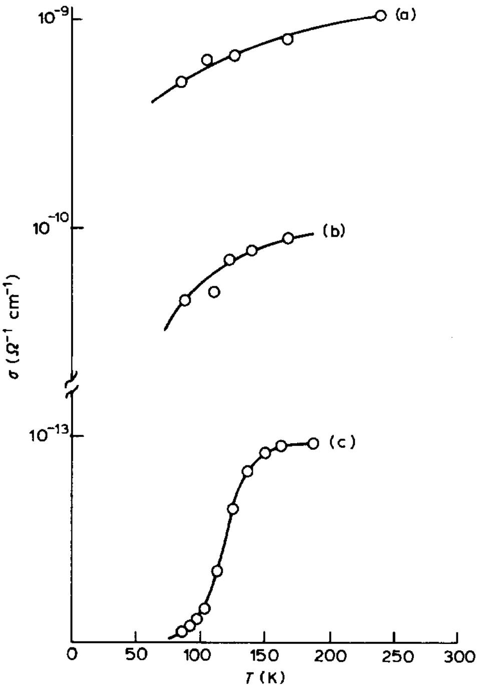
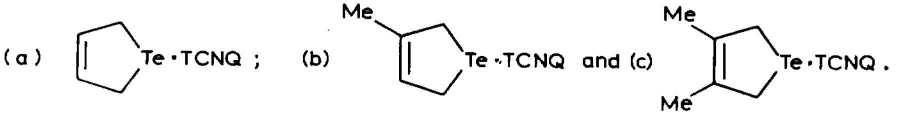


Fig. 1. Temperature dependence of the electrical conductivity of



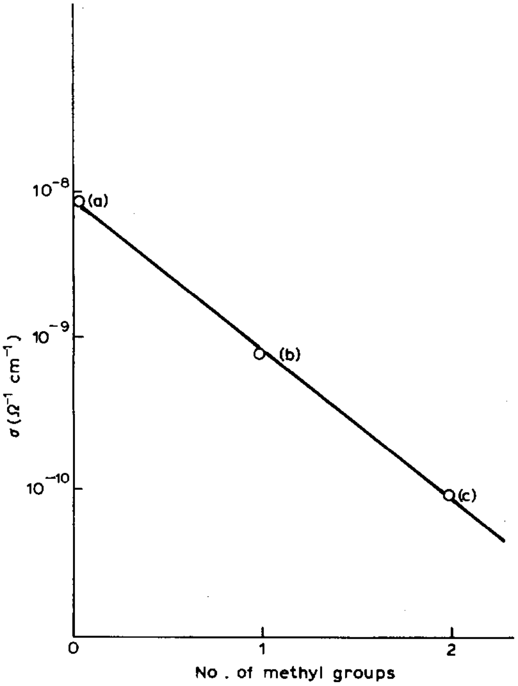


Fig. 2. The relationship between the conductivity and the number of methyl groups at 330 K,

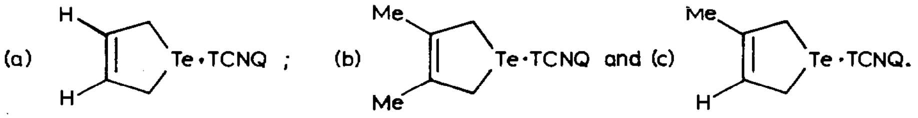


Table 2

Physical data for CT complexes of dihydrotellurophenes

Compound	Solid conductivity (350 K, Ω^{-1} cm^{-1})	ν(CN) (TCNQ), ν(CO) (TCB)	ESR (g-value)	UV-VIS λ_{max} (nm)
1	10^{-8}	2198, 2166	2.0026	656
2	10^{-8} (r.t.)	1682, 1694	2.0038	508
3	10^{-9}	2238, 2198, 2160	2.0040	654
4	10^{-11} (r.t.)	1682, 1693	–	506
5	10^{-10}	2236, 2197, 2158	2.0048	648
6	10^{-12} (r.t.)	1683, 1693	–	504
8	10^{-11} (r.t.)	2228, 2198	2.0041	623
9	10^{-13} (r.t.)	1684, 1696	–	–
13	10^{-13} (r.t.)	2132, 2158, 2196	2.0036	
18	10^{-13} (r.t.)	2132, 2182	2.0025	
22	10^{-14} (r.t.)	2146, 2188	2.0038	

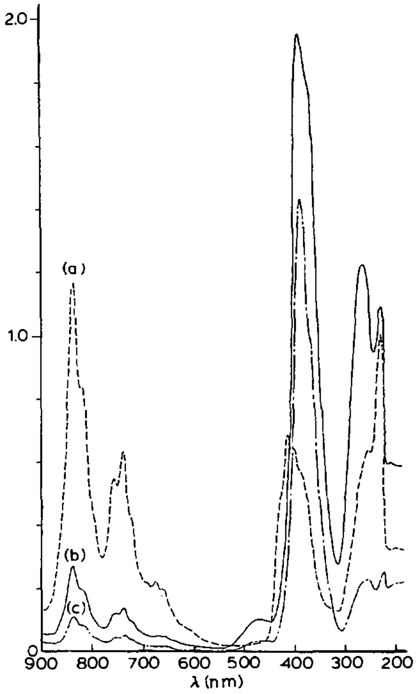
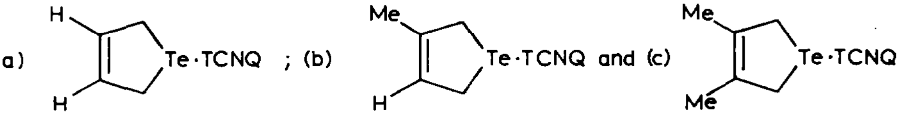


Fig. 3. Electronic spectra of the tellurophene complexes with TCNQ;



Solid state conductivity measurements were made on samples which had been pressed into discs of diameter 13 mm and thickness 0.6–1.0 mm. Silver paste was carefully applied to each side of the disc and thin gold wires were attached with a dab of silver paste. A two-pulse method was used. A solid state electrometer (Keithley A610C) and stabilised power supply (Kingshill model 305) were used. Facilities for variable temperature measurements were available. (We are most grateful to Mr. Basi of the Department of Electronic Engineering and Applied Physics for help with these measurements).

The variation of the solid state conductivity for compounds **1** with TCNQ is shown graphically in Fig. 1, and the variation of conductivity at a fixed temperature with the number of methyl substituents is shown in Fig. 2. Figure 3 shows the UV spectra for **1** · TCNQ in acetonitrile solution. Table 2 gathers together pertinant IR, ESR and UV data for **1** · TCNQ. Table 3 includes similar relevant physical data for the quinoxaline derivatives.

Electrochemical oxidation of 1,3-dihydro-2-selenaindene

It was recently reported [11] that 1,3-dihydro-2-telluraindene can be electrochemically oxidised to compounds such as $[C_8H_8Te]PF_6$, we decided to ascertain whether

Table 3

Spectroscopic data for new quinoxalino-1-chalcogenacyclopentane derivatives

Compound	UV-VIS λ (nm)	^{1}H NMR (δ (ppm) vs. TMS)
10	247, 270, 330	4.82 (CH_2, s, 4H) 7.7–8.4 (aromatic, m, 4H)
12	241, 318	4.74 (CH_2, s, 4H) 7.2–8.1 (aromatic, m, 4H)
14	255, 349	4.92 (CH_2, s, 4H) 2.52 (CH_3, s, 6H) 7.3–7.8 (aromatic, m, 2H)
15	243, 269, 331, 343	4.88 (CH_2, s, 4H) 2.52 (CH_3, s, 6H) 7.3–7.9 (aromatic, m, 2H)
17	246, 257, 333	4.58 (CH_2, s, 4H) 2.50 (CH_3, s, 6H) 7.3–7.6 (aromatic, m, 2H)
19	251, 267, 348	4.8 (CH_2, s, 4H) 2.57 (CH_3, s, 6H) 7.3–7.8 (aromatic, m, 2H)
21	248, 326, 338	4.68 (CH_2, s, 4H) 2.46 (CH_3, s, 6H) 7.3–7.7 (aromatic, m, 2H)

the selenium analogue behaved similarly. Thus recrystallised 1,3-dihydro-2-selenaindene (10 mmol) in pure dichloromethane (200 cm^3) containing tetra-n-butylammonium hexafluorophosphate (20 mmol) was electrolysed between two platinum electrodes with a spacing of ~ 1 cm at a constant current of 2 mA. A shiny deposit formed on the anode after a few minutes but the yield in all experiments was very low. The material analysed as $C_8H_8SePF_6$: Found: C, 29.2; H, 2.50%. $C_8H_8F_6PSe$ calc: C, 29.2; H, 2.43%. The melting point was 125 °C and the infra-red spectrum confirmed the presence of ionic hexafluorophosphate (848 vs, 570s cm^{-1}). The molar conductivity in acetonitrile was 117 Ω^{-1} cm^2 mol^{-1}. No ESR signal was observed.

Discussion

2,5-Dihydrotellurophene derivatives

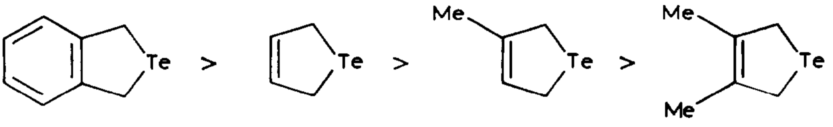
No complexes with DNB were isolable. With both TCNQ and DTB, complexes of 1 : 1 stoichiometry were obtained. The infra-red spectra of the DTB complexes were virtually the superposition of the spectra of the individual components and, (Table 2), there is no shift of ν(CO) with change of donor. This implies an extremely weak CT interaction, and this observation is in line with results previously obtained for the 1,3-dihydro-2-telluraindene · DTB complex [3]. The spectra of the TCNQ complexes are also virtually the sum of the component parts, but the ν(CN) region shows a little variation for the compounds **1**, **3** and **5** (Table 1). Thus **3** and **5** show a band at ~ 2235 cm^{-1} which is absent in **1**. Bands close to 2230 cm^{-1} can be attributed to neutral TCNQ and those near 2180 cm^{-1} to TCNQ$^{\cdot(-)}$ [12]. The infra-red data thus suggests that there is less radical ion character in the complexes of the methyl-substituted 2,5-dihydrotellurophenes. All these complexes give ESR signals in the solid state. Within experimental error the g values are the same, and close to 2.0023 (Table 2), thus the unpaired electron density detected is on TCNQ.

The electronic spectra (acetonitrile solutions) of compounds **1**, **3**, and **5** are shown in Fig. 3. The absorptions around 700–900 nm are attributable to TCNQ$^{\cdot(-)}$ and those at 380–420 nm to a combination of TCNQ$^{\cdot(-)}$ and TCNQ · **13**. The greater relative intensity in the 700–900 nm region for compound **1** is notable, and again implies greater radical ion character. Indeed, the acetonitrile solution of complex **1** is quite conducting (108 Ω^{-1} cm^2 mol^{-1}), in contrast to solutions of **2** and **3**, again implying a greater ionic character. Bands at 656 (**1**), 654 (**2**), and 648 nm (**3**) that are not attributable to the dihydrotelluraphene or to TCNQ are seen, and can be assigned to the CT (HOMO → LUMO) transition. If this assignment is correct, the band for the 2,5-dihydrotelluraphene complex is at marginally lower energy than those for compounds **3** and **5**.

The disc conductivities of the three TCNQ complexes were measured over a range of temperature. The values increase with temperature, initially quite steeply (80–150 K), then more gradually to the plateau values of 350 K given in Table 2. This behaviour is illustrated in Fig. 1, and Fig. 2 shows the variation of the plateau conductivity with the number of methyl substituents. The apparent linear relationship is regarded as fortuitous.

The low ionisation potentials of both 1,3-dihydro-2-telluraindene (**3**) and 1,3-dihydro-2-selenaindene (see below) are quite unlike those of acyclic tellurides [14]. Furthermore, the detailed behaviour with TCNQ is dependent upon the 3 and 4 substituent on the 2,5-dihydrotellurophene ring. (We regard the telluraindene as a special case of a substituted 2,5-dihydrotelluraphene.) If donation is from the double bond (π-system), this result is contrary to expectation and would favour our previous contention [3], supported by ^{125}Te Mossbauer measurements, that donation is from the tellurium p_z lone pair.

A complex (No. 7 in Table 1) of 1,3-dihydro-2-telluraindene with DNB was isolated. Thus a combination of data in this and earlier three papers suggests that the order of donor strength is:



and that of acceptor strength:

TCNQ > TCB > DNB.

1,3-Dihydro-2-selenaindene

This compound was synthesised for comparison of its behaviour with that of the tellurium analogue. Complexes with both TCNQ and TCB are formed (Nos. 8 and 9, Table 1).

The complexes with both TCNQ and TCB have low room temperature conductivities and the infra-red spectra imply that the selenium compound may be less ionic than the tellurium analogue. A value of 6.55 eV was found for the ionisation potential of 1,3-dihydro-2-telluraindene (**3**). The same mass spectroscopic method (Warren's extrapolated voltage difference method [15]) was used to determine a value of 7.4 eV for the selenium compound. The telluraindene may be electrochemically oxidised in acetonitrile in the presence of appropriate supporting electrolytes [11], and we have now shown that the selenium compound also behaves in this way: indeed, the parallel is so close that the discussion need not be repeated.

Quinoxaline derivatives

The preparation of the compounds **3** has been extended to compounds of selenium and the studies extended to consider the effect of 7,8-dimethyl substituents (compounds **12**, **17**, **21**, Table 1). The synthesis developed earlier [5] worked well, and it was noted that the interesting molecular complex of 1,1-diiodo-7,8-dimethyl-3,4-quinoxalino-1-telluracyclopentane and 2,3-bis(iodomethyl)quinoxaline is not unique, and has parallels in compounds **11**, **16** and **20** (Table 1). The new diiodides (**10**, **15**, **19**), 1 : 1 complexes (**11**, **16**, **20**), and quinoxalino-1-chalcogenacyclopentanes (**12**, **17**, **21**) were characterised by analysis, infra-red, UV and ^{1}H NMR spectroscopy, and mass spectroscopy. The data are consistent with those presented in our earlier paper [5], and some are presented in Tables 1, 2 and 3.

Compounds **12**, **17**, and **21** form complexes with TCNQ (**13**, **18**, **22**) which all have disappointing room temperature solid state conductivities (Table 2). However, the ν(CN) region of the infra-red spectrum shows no band above 2200 cm^{-1} and imply that the ground state is strongly ionic.

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