CRYSTAL STRUCTURE OF THE 1/1 MOLECULAR COMPLEX OF 5,5′,12,12′-BIS(TRISELENO)BIS(NAPHTHACENE-6,11-QUINONE) WITH BENZONITRILE, $(C_{18}H_8Se_3O_2)_2(C_6H_5CN)$

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Summary

The structure of the $(C_{18}H_8Se_3O_2)_2(C_6H_5CN)$ molecular complex isolated from the TSeT + HgI_2 reaction in benzonitrile has been determined. The –Se–Se–Se– fragment has been found to have Se–Se bond lengths equal to 2.348(3) and 2.350(4) Å.

Introduction

The cation-radical salts of tetrathiatetracene (TTT) and tetraselenotetracene (TSeT) are of much interest, since some of them are found to be quasi-one-dimensional metals in their conductive properties, and they retain the metallic state down to very low temperatures [1,2].

In order to obtain new organic metals, the reaction of TSeT with HgI_2 has been investigated in various solvents and at various temperatures and initial reagents ratios. In the case of the TSeT + HgI_2 reaction in benzonitrile, five complexes of TSeT with various iodinemercurate anions have been isolated, whose conductive properties vary in the range of 10^{-3}–10^3 Ω^{-1} cm^{-1} at room temperature [3]. The composition of the complexes depends on the initial ratio of of the reagents, their concentrations, and crystallization temperatures. When oxidizing TSeT with HgI_2 at temperatures below 100°C, a TSeT$\dot{}$ cation-radical is formed and the electronic absorption spectra show new bands characteristic of TSeT$\dot{}$ [1]. Prolonged heating for several days at 120°C leads to further oxidation of the TSeT, probably to a TSeT$\ddot{}$ di-cation (the colour of the solution changes from green to red), with a subsequent cleavage of half the Se–C bonds to produce quite, unexpectedly, a dimeric product A which can be isolated as crystals of its complex with the C_6H_5CN solvent.
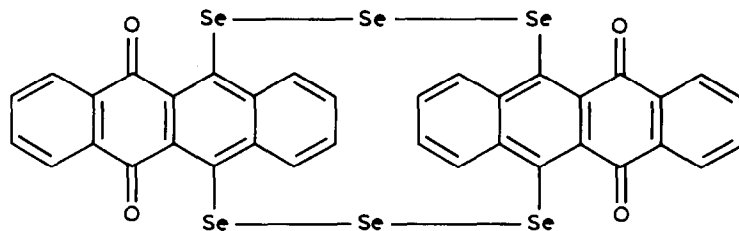
(A)

The composition and structure of A have been determined by X-ray analysis.

Experimental

The cell dimensions of the $(C_{18}H_8Se_3O_2)_2(C_6H_5CN)$ crystals and intensities of 1026 independent reflections with $I \geqslant 2\sigma$ were measured on a four-circle automatic

TABLE 1

ATOMIC COORDINATES ($\times 10^4$ FOR Se, $\times 10^3$ FOR C,N,O) AND THEIR ANISOTROPIC THERMAL PARAMETERS[a] ($\times 10^4$)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Se(1)	5455(2)	1012(1)	2727(2)	33	36	41	18	10	15
Se(2)	10056(2)	1094(1)	2710(2)	26	34	47	14	−3	4
Se(3)	9925(2)	47(1)	3709(2)	51	36	35	12	−24	−3
O(1)	606(1)	188(1)	126(1)	32	70	42	35	18	48
O(2)	984(1)	196(1)	129(1)	1	77	63	27	37	43
C(1)	680(2)	130(1)	287(2)	47	15	43	17	−12	23
C(2)	729(2)	123(2)	371(2)	26	35	51	14	11	17
C(3)	677(2)	116(2)	455(2)	126	58	0	31	28	19
C(4)	725(6)	109(1)	539(2)	26	10	46	−12	28	31
C(5)	828(2)	113(2)	538(2)	65	36	45	59	43	−7
C(6)	881(2)	120(1)	453(2)	80	30	50	70	28	−29
C(7)	832(2)	127(1)	370(2)	47	37	14	30	−15	16
C(8)	884(2)	134(1)	286(2)	54	10	44	−46	−24	−16
C(9)	839(2)	159(1)	204(2)	53	34	13	29	3	0
C(10)	895(2)	185(1)	122(2)	96	25	22	78	22	−10
C(11)	847(2)	194(2)	38(2)	18	47	98	19	10	27
C(12)	900(2)	200(2)	−45(2)	102	70	22	85	37	27
C(13)	852(2)	210(2)	−131(2)	70	44	59	8	−59	59
C(14)	749(2)	206(2)	−132(2)	135	57	35	44	−29	47
C(15)	696(2)	196(1)	−46(2)	86	42	50	48	1	54
C(16)	744(2)	190(1)	39(2)	92	62	67	65	−39	18
C(17)	691(2)	181(2)	123(2)	52	20	41	26	30	37
C(18)	735(2)	155(1)	205(2)	40	23	49	18	−1	7
N	750	0	−261(3)	144	94	117	82	0	0
C(19)	750	0	104(3)	267	6	52	−18	0	0
C(20)	836(3)	3(2)	59(4)	277	46	104	18	−197	−35
C(21)	837(3)	4(2)	−39(4)	242	14	199	130	−18	26
C(22)	750	0	−84(3)	149	9	76	102	0	0
C(23)	750	0	−182(3)	150	170	10	205	0	0

[a] $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

TABLE 2

COORDINATES ($\times 10^3$) AND ISOTROPIC THERMAL PARAMETERS (Å^2) OF HYDROGEN ATOMS [a]

Atom	x	y	z	B_j
H(3)	604	114	456	4.5
H(4)	687	102	599	3.4
H(5)	865	116	598	3.6
H(6)	954	122	452	4.3
H(12)	973	201	−45	5.3
H(13)	891	217	−193	4.3
H(14)	713	211	−193	6.3
H(15)	623	195	−46	4.9
H(19)	750	0	181	8.0
H(20)	898	7	94	7.8
H(21)	900	8	−74	7.4

[a] Numbering of the hydrogen atoms corresponds to those of the carbon atoms to which they are bonded.

diffractometer "Syntex P$\bar{1}$" (λ(Mo-K_α)) by the $\theta/2\theta$ scan technique, using a graphite monochromator, (sin θ/λ)$_{max}$ = 0.584. The single crystal dimensions were $0.2 \times 0.18 \times 0.25$ mm. No absorption correction was applied.

The structure was determined by Patterson synthesis analysis and a subsequent series of electronic density synthesis. The refinement of structures was performed by a least-squares procedure using a block-diagonal anisotropic approximation. Hydrogen atoms were localized by difference syntheses. Isotropic temperature parameters of the corresponding carbon atoms were assigned to hydrogen atoms and they were included in the refinement with fixed positional and thermal parameters. The final R-factor was equal to 0.079. All the calculations were performed using "Roentgen-75" [4].

Coordinates of atoms other than hydrogen and their anisotropic temperature factors are given in Table 1. Table 2 lists the hydrogen atom coordinates.

Results and Discussion

The crystals of the $(C_{18}H_8Se_3O_2)_2(C_6H_5CN)$ complex were found to be monoclinic, a 14.263(2), b 18.090(3), c 14.314(2) Å, γ 101.83(3)°, V 3614.7 Å^3, $M = 931.49$, $d_{calcd.}$ 1.72 g/cm^3, $Z = 4$, space group $I2/a$ (C_{2h}^6).

Figure 1 shows the projection of the crystal structure of the complex along the c direction. As is seen from this figure, the benzonitrile molecules are in the inner cavity of the A molecules and are situated on the two-fold axes. Figure 2 shows the molecules of A and of benzonitrile with atom numbering and some bond distances and angles. A complete list of bond lengths and angles is given in Tables 3 and 4. The e.s.d.'s of the bond lengths C–C, C–O, C–N and the bond angles CCC, OCC, NCC are equal to ±0.02–0.03 Å and ±1.5–2.5°, respectively. The C–H bond lengths are in the range of 1.0 to 1.1 Å.

The Se–Se bond lengths in the A molecule are 2.348(3) and 2.350(4) Å and within the limits of error they coincide with the value of 2.352(1) Å in dimorpholinotriselane [5]. These distances are larger than the equivalent values in the neutral TSeT molecule and TSeT$\dot{}^+$ cation-radical. The Se–Se lengths in the neutral molecule is
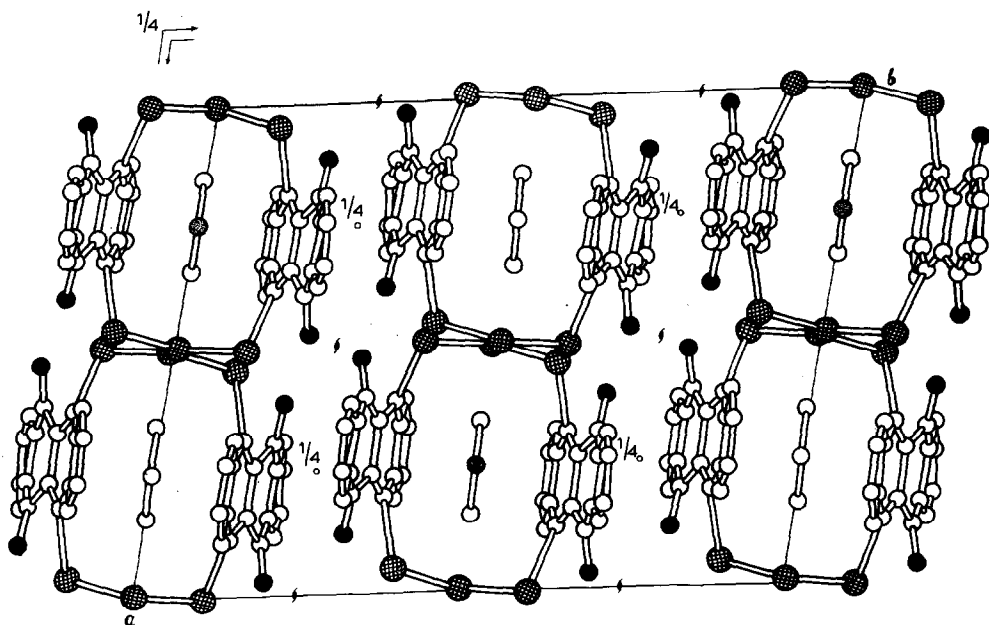
Fig. 1. Projection of the crystal structure of the $(C_{18}H_8Se_3O_2)_2(C_6H_5CN)$ molecular complex along the c direction.

(a)

(b)

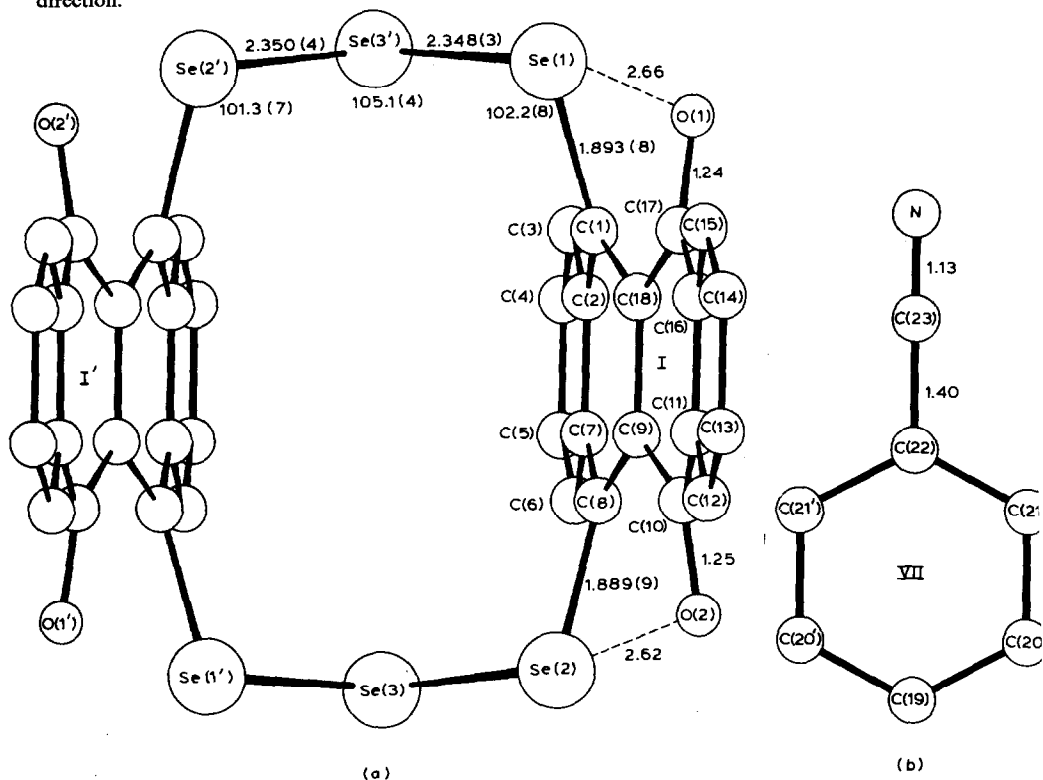Fig. 2. Labelling of atoms and some interatomic distances (Å) and angles (deg.) in (a) the A molecule and (b) benzonitrile.

TABLE 3

BOND LENGTHS (Å)

Se(1)–Se(3′)	2.348	C(12)–C(13)	1.44
Se(2)–Se(3)	2.350	C(13)–C(14)	1.46
Se(1)–C(1)	1.893	C(14)–C(15)	1.44
Se(2)–C(8)	1.889	C(15)–C(16)	1.41
O(1)–C(17)	1.24	C(16)–C(17)	1.41
O(2)–C(10)	1.25	C(17)–C(18)	1.45
C(1)–C(2)	1.41	C(18)–C(1)	1.43
C(2)–C(3)	1.41	C(2)–C(7)	1.46
C(3)–C(4)	1.40	C(9)–C(18)	1.47
C(4)–C(5)	1.46	C(11)–C(16)	1.46
C(5)–C(6)	1.42	C(13)–C(14)	1.46
C(6)–C(7)	1.40	C(19)–C(20)	1.38
C(7)–C(8)	1.41	C(20)–C(21)	1.40
C(8)–C(9)	1.45	C(21)–C(22)	1.39
C(9)–C(10)	1.44	C(22)–C(23)	1.40
C(10)–C(11)	1.41	C(23)–N	1.13
C(11)–C(12)	1.40		

2.339 Å in TSeT itself [6] and 2.335(3) Å in the $(TSeT)_3(Hg_2Br_6)$ complex [7]. For the TSeT^{+} cation-radical, the Se–Se bonds are 2.317(3), 2.322(3), 2.323(1), 2.320(7) and 2.325(2) Å in the complexes $(TSeT)(CuBr_2)$ [8], $(TSeT)_3(Hg_2Br_6)$ [7], $(TSeT)_2Cl$ [9], $(TSeT)_2SCN$ [10] and $(TSeT)_2(Hg_2I_6)$, respectively.

In the molecule A, there is probably a strong interaction between some non-bonded

TABLE 4

BOND ANGLES (°)

Se(1′)–Se(3)–Se(2)	105.1	O(2)–C(10)–C(11)	124
C(1)–Se(1)–Se(3′)	102.2	C(10)–C(11)–C(16)	120
C(8)–Se(2)–Se(3)	101.3	C(10)–C(11)–C(12)	118
Se(1)–C(1)–C(2)	124	C(12)–C(11)–C(16)	122
Se(1)–C(1)–C(18)	117	C(11)–C(12)–C(13)	118
Se(2)–C(8)–C(7)	125	C(12)–C(13)–C(14)	120
Se(2)–C(8)–C(9)	118	C(13)–C(14)–C(15)	120
C(1)–C(2)–C(3)	118	C(14)–C(15)–C(16)	120
C(1)–C(2)–C(7)	120	C(15)–C(16)–C(17)	119
C(2)–C(3)–C(4)	119	C(15)–C(16)–C(11)	119
C(3)–C(4)–C(5)	120	C(17)–C(16)–C(11)	122
C(4)–C(5)–C(6)	122	C(16)–C(17)–C(18)	118
C(5)–C(6)–C(7)	118	O(1)–C(17)–C(16)	122
C(6)–C(7)–C(2)	120	O(1)–C(17)–C(18)	120
C(6)–C(7)–C(8)	118	C(7)–C(18)–C(9)	118
C(2)–C(7)–C(8)	121	C(1)–C(18)–C(9)	120
C(7)–C(8)–C(9)	117	C(1)–C(18)–C(17)	121
C(8)–C(9)–C(18)	119	C(20)–C(19)–C(20′)	124
C(8)–C(9)–C(10)	121	C(19)–C(20)–C(21)	118
C(10)–C(9)–C(18)	121	C(20)–C(21)–C(22)	117
C(9)–C(10)–C(11)	119	C(21)–C(22)–C(23)	118
O(2)–C(10)–C(9)	118	C(22)–C(23)–N	180
		C(21)–C(22)–C(21′)	124

atoms, as shown by some interatomic distances being shorter than the sum of Van der Waals' radii (i.e. Se(1)...O(1) 2.66 Å and Se(2)...O(2) 2.62 Å) (Fig. 2a).

The conformation of the molecule A may be derived from the data in Table 5 which lists the equations of the averaged planes of a few of its components and the deviations of the atoms from these planes. Two terminal rings in the tetracyclic carbon frame of the molecule A are approximately planar (planes II and III), whereas the central rings (planes IV and V) have the conformation of a flat boat, such that the central section containing the C(2), C(7), C(9), C(11), C(16), and C(18) atoms is also planar (plane VI), and the selenium and oxygen atoms are displaced from plane VI in different directions, at distances of 0.59 and 0.75 Å (Se) and −0.36 and −0.27 Å (O). The five-membered groupings SeOCCC have an approximate envelope conformation, the Se(1) and Se(2) atoms deviating from the CCCO planes by 0.69 and 0.72 Å, respectively. A dihedral angle between the mean planes of

TABLE 5

COEFFICIENTS FOR THE EQUATIONS [a] FOR SOME PLANAR GROUPINGS (I–VII) IN THE STRUCTURE, AND DEVIATIONS (Å) OF ATOMS FROM THESE PLANES

Atom	I	II	III	IV	V	VI	VII	Angles between planes (°)
Se(1)	0.70 [b]			0.59 [b]		0.59 [b]		II : III 0
Se(2)	0.75 [b]			0.75 [b]		0.75 [b]		
O(1)	−0.37 [b]				−0.37 [b]	−0.36 [b]		II : VI 8
O(2)	−0.37 [b]				−0.28 [b]	−0.27 [b]		III : VI 8
C(1)	0.21			0.13 [b]		0.13 [b]		
C(2)	0.12	0.01		0		−0.01		I : I′ 157
C(3)	−0.02	−0.01						
C(4)	−0.11	0.01						
C(5)	−0.14	−0.01						
C(6)	0.00	0.01						
C(7)	0.10	−0.01		0		−0.01		
C(8)	0.23			0.19 [b]		0.20 [b]		
C(9)	0.01			0	0	0.02		
C(10)	−0.19				−0.12 [b]	−0.11 [b]		
C(11)	−0.13		−0.02		0	0.01		
C(12)	0.02		0.03					
C(13)	0.07		−0.02					
C(14)	0.10		0.01					
C(15)	0.01		0.01					
C(16)	−0.11		−0.01		0	−0.01		
C(17)	−0.21				−0.18 [b]	−0.18 [b]		
C(18)	0.03			0	0	0.02		
C(19)							−0.001	
C(20)							∓0.009	
C(21)							±0.008	
C(22)							−0.001	
C(23)							0	
N							0	
A	−0.405	−0.448	−0.466	−0.639	−0.639	−0.639	0.724	
B	17.456	17.720	17.698	17.369	17.279	17.326	−17.872	
C	2.821	1.466	1.655	3.323	3.611	3.468	0	
D	3.019	2.408	3.079	2.904	2.953	2.944	0.543	

[a] $Ax + By + Cz = D$. [b] Atoms not included in the plane calculation.

tetracyclic carbon sections of the A molecule, which are related with each other by a two-fold axis, is equal to 157° (the I : I′ angle in Table 5).

The structure of $(C_{18}H_8Se_3O_2)_2(C_6H_5CN)$ contains a number of shortened (as compared with the sum of Van der Waals' radii) contacts between the A molecules and benzonitrile: C(9)...C(19) 3.23, C(18)...C(19) 3.21 and C(10)...C(20) 3.35 Å.

Acknowledgement

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