Crystal Structures of Complexes between Alkali-metal Salts and Cyclic Polyethers. Part VIII.[1] Complexes formed by Caesium Thiocyanate with (7*R*,9*R*,18*S*,20*S*)-6,7,9,10,17,18,20,21-Octahydro-7,9,18,20-tetramethyldibenzo[*b*,*k*][1,4,7,10,13,16]Hexaoxacyclo-octadecin (Tetramethyldibenzo-18-crown-6, Isomer F) and its (18*R*,20*R*)-Isomer (Isomer G)

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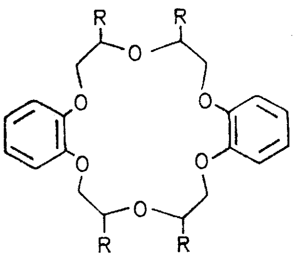
The crystal structures of the two title compounds have been determined by *X*-ray diffraction and refined by least squares. Crystals of the isomer F compound (II) are triclinic with $a = 11{\cdot}12(1)$, $b = 11{\cdot}87(1)$, $c = 13{\cdot}46(1)$ Å, $\alpha = 107{\cdot}75(2)$, $\beta = 95{\cdot}25(6)$, $\gamma = 121{\cdot}90(4)^\circ$, $Z = 2$, space group $P\bar{1}$, final R 0·062 on 2086 diffractometer data. Crystals of the isomer G complex (III) are tetragonal, with $a = 15{\cdot}22(1)$, $c = 11{\cdot}14(1)$ Å, $Z = 2$, space group $P4_2/n$, final R 0·11 on 1394 diffractometer data. Molecules of (II), a 1 : 1 complex, are dimeric and centrosymmetric with Cs–N–Cs bridges, the other co-ordinating atoms being the six oxygens of isomer F at 3·07—3·34 Å and the aryl carbons at 3·80 Å. The configuration of the methyl groups is *cis,anti,cis*. Compound (III) is a 1 : 2 complex consisting of [Cs(isomer G)$_2$]$^+$ cations having $\bar{4}$ symmetry with twelve Cs–O contacts (3·12—3·36 Å), and disordered thiocyanate ions. The methyl group configuration is *trans,anti,trans*. There are differences in conformation between (II) and (III).

COMPLEXES in the title series have been studied as models of the transport mechanism for alkali-metal cations across biological membranes. Complex formation tends to enclose the cation in a lipophilic shell, involving a change in conformation of the ligand. It is important to test the response of the model ligands to changes in their composition which may influence the ability to achieve the required conformation. One possible modification of (Ia) dibenzo-18-crown-6[2] is hydrogenation of the benzo-groups to cyclohexane, and the structures of complexes of two of the resulting five configurational isomers have been reported.[3,4] Alternatively, five isomers (Ib) are obtained by methyl substitution of four of the aliphatic carbons. The synthesis of these and the preparation of (II) and (III), the CsNCS complexes of isomers F and G were reported earlier.[5] Preliminary refinement of the structures showed isomer F in (II) to have the *cis,anti,cis*-configuration and isomer G in (III) the *trans,anti,trans*. We now compare the structures of (II) and (III) with those of unsubstituted dibenzo-18-crown-6 complexes.



(Ia) R=H
(Ib) R=Me

EXPERIMENTAL

Crystals of (II) and of (III) were prepared by the method of ref. 5. Features common to both in the experimental procedure are given for (II) with specific differences for (III) in square brackets.

Crystal Data.—(i) *Complex* (II). $C_{25}H_{32}CsNO_6S$. $M = 607$, Triclinic, $a = 11{\cdot}12(1)$, $b = 11{\cdot}87(1)$, $c = 13{\cdot}46(1)$ Å, $\alpha = 107{\cdot}75(2)$, $\beta = 95{\cdot}25(6)$, $\gamma = 121{\cdot}90(4)^\circ$, $U = 1364{\cdot}4$ Å^3, D_m (by flotation) $= 1{\cdot}45$, $Z = 2$, $D_c = 1{\cdot}48$ g cm^{-3}, $F(000) = 616$. Space group $P\bar{1}$. $\mu = 10{\cdot}11$ cm^{-1} for Mo-$K_{\alpha 1}$ radiation, $\lambda = 0{\cdot}70926$ Å (1 Å $\equiv 10^{-10}$ m).

(ii) *Complex* (III). $C_{49}H_{64}CsNO_{12}S$, $M = 1023$. Tetragonal, $a = 15{\cdot}22(1)$, $c = 11{\cdot}14(1)$ Å, $U = 2580{\cdot}6$ Å^3, $D_m = 1{\cdot}34$, $Z = 2$, $D_c = 1{\cdot}32$ g cm^{-3}, $F(000) = 1064$. Space group $P4_2/n$. μ(Mo-$K_{\alpha 1}$) $= 6{\cdot}26$ cm^{-1}.

Colourless, tabular crystals [truncated parallelepipeds] were obtained by recrystallisation from ethanol. A single crystal of dimensions $0{\cdot}5 \times 0{\cdot}2 \times 0{\cdot}1$ mm [$0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}2$ mm] was used for the measurment of 2954 [2290] independent *X*-ray intensities by 2θ scan from $2\theta_{\alpha 1}$ $-0{\cdot}5^\circ$ to $2\theta_{\alpha 2}$ $0{\cdot}5^\circ$ on a Picker four-circle automatic diffractometer, by use of zirconium-filtered Mo-K_α radiation. These comprised all possible reflections with $\sin\theta/\lambda \leqslant 0{\cdot}50$ Å^{-1} [$0{\cdot}59$ Å^{-1}]. 2086 [1394] reflections having $I > 2\sigma(I)$, were considered observed, where $\sigma^2(I) = C + (t_c/2t_b)^2(B_1 + B_2)$, where C is the total integrated count in time t_c, B_1 and B_2 are background counts, each obtained in time t_b, and $I = C - (t_c/2t_b)(B_1 + B_2)$. The intensities of three standard reflections monitored every 50 observations showed no reduction in intensity during data collection. Intensities were corrected[6] for Lorentz and polarisation effects but not for absorption. Unit-cell parameters were determined by least-squares refinement of diffractometer setting angles for 15 reflections.

Computations were carried out on an IBM 1130 computer in the Molecular Structures Department and an IBM 360/65 at University College Computer Centre. The principal computer programs used are listed in refs. 6 and 7.

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[7] NUCLS, Full-matrix Least Squares, R. J. Doedens and J. A. Ibers; ORFFE, Geometric Functions and Errors, W. R. Busing, K. O. Martin, and H. A. Levy.

Atomic scattering factors for hydrogen were taken from ref. 8, for carbon, oxygen, and caesium ion from ref. 9, and for nitrogen (1−) and sulphur from ref. 10; the anomalous dispersion terms for caesium were taken from ref. 11.

Determination of the Structure of (II).—The positions of the Cs and S atoms were deduced from the three-dimensional Patterson function, assuming space group $P\bar{1}$ in which all the atoms are in general positions. The $|F_o|$ scale factor was estimated from the height of the Patterson origin peak. A structure-factor calculation gave R 0·48, for observed reflections. The structure was solved by the heavy-atom method, the R factor being 0·40 with all atoms (except hydrogen) contributing. This was reduced to 0·12 after two cycles of least-squares refinement of all positional and isotropic thermal parameters. The temperature factor of C(21) after this refinement showed that its position was incorrect. The correct position was obtained from a difference map. The positions of the hydrogen atoms, other than those of the methyl groups, were estimated from the molecular geometry and included in subsequent calculations but not refined. Two cycles refining positional parameters, isotropic temperature factors for carbon, nitrogen, oxygen, and sulphur, and the anisotropic temperature factors for caesium brought R to 0·08. One hydrogen atom in each of three methyl groups was located in a difference map, enabling the remaining hydrogen positions, except those on C(21), to be estimated from the molecular geometry. No hydrogen atoms on C(21) were found.

In the full-matrix least-squares refinement the function minimised was $\Sigma w(|F_o| - |F_c|)^2 = \Sigma w\Delta^2$: the weighting scheme was $w = 1/\sigma^2$, where $\sigma = \sigma(F_o)\sqrt{22 \cdot 2 - 1 \cdot 1|F_o| + 0 \cdot 025|F_o|^2}$ if $|F_o| > 22$, and $\sigma = 3 \cdot 1\sigma(F_o)$ if $|F_o| \leqslant 22$. This gave similar average values of $w\Delta^2$ for various ranges of $|F_o|$ and of $\sin\theta/\lambda$. Nine cycles of full-matrix refinement of all co-ordinates and the anisotropic temperature factors of caesium, sulphur, and oxygen in alternate cycles with the anisotropic temperature factors of C and N reduced R to a final value of 0·062 for the 2086 observed reflections, with R' 0·068 [$R' = (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$]. In the final cycle $\Sigma w\Delta^2$ decreased by 0·3%, all co-ordinate shifts being $\leqslant 0 \cdot 46\sigma$ [except for C(21) with a shift of $0 \cdot 58\sigma$]. Final temperature factor shifts were $\leqslant 0 \cdot 56\sigma$, except for C(17) and C(18) with shifts of 0·89 and $1 \cdot 1\sigma$. A difference-Fourier synthesis computed from the final structure factors for the observed reflections, weighted according to the least-squares weights, showed no peaks or holes of magnitude $> 0 \cdot 3$ eÅ^{-3}.

Determination of the Structure of (III).—The Cs^+ ion is required by the space group to occupy two-fold positions of symmetry $\bar{4}$ at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ and $\frac{3}{4},\frac{3}{4},\frac{3}{4}$ (origin at $\bar{1}$). The ligand molecules must be in four-fold special positions either on centres of symmetry, or on two-fold axes either in 4_2 or in $\bar{4}$ (at $\frac{1}{4},\frac{1}{4},z$, *etc.*). The anions have to be disordered.

A difference synthesis phased by the caesium atoms showed the catechol residue, with its reflection in the pseudo-mirror plane at $z = \frac{1}{4}$, resulting from the special position of the caesium atom. A second Fourier synthesis, phased by the caesium atoms and catechol group, revealed all the remaining atoms except for the SCN^- anion. Two cycles of full-matrix refinement of the carbon and oxygen co-ordinates with the isotropic thermal parameters of all the located atoms reduced R for the 2290 reflections from 0·33 to 0·18. Difference maps phased by the partially refined structure failed to show the anion, except for an extended region of electron density around the 4_2 axis

TABLE 1(a)

(*a*) Fractional atomic co-ordinates (×10⁴) for (II), with standard deviations in the least significant digits in parentheses, unless the co-ordinate was not refined. Hydrogen atoms are numbered according to the carbon atoms to which they are attached

	x/a	*y/b*	*z/c*
Cs	0272(1)	−1439(1)	−1309(1)
C(1)	−0339(14)	−1963(14)	1888(9)
C(2)	−1261(15)	−1632(14)	2354(10)
C(3)	−2549(16)	−2032(15)	1739(12)
C(4)	−2993(13)	−2832(13)	0604(10)
C(5)	−2140(12)	−3186(12)	0124(9)
C(6)	−0802(12)	−2755(12)	0758(9)
C(7)	1400(14)	−2665(13)	0834(10)
C(8)	2089(12)	−3171(12)	0062(10)
C(9)	3204(14)	−2578(15)	−1309(10)
C(10)	3629(16)	−1548(18)	−1846(12)
C(11)	2292(15)	−1498(13)	−3339(10)
C(12)	3547(16)	−0520(13)	−3499(11)
C(13)	3393(18)	−0047(16)	−4314(14)
C(14)	2063(23)	−0566(21)	−4928(14)
C(15)	0785(18)	−1576(18)	−4788(12)
C(16)	0889(15)	−2067(15)	−3983(10)
C(17)	−1729(16)	−3900(21)	−4471(11)
C(18)	−2723(14)	−5127(18)	−4162(11)
C(19)	−4078(14)	−5368(14)	−2863(10)
C(20)	−3919(13)	−4476(13)	−1701(10)
C(21)	−2116(23)	−6014(19)	−4046(19)
C(22)	3365(15)	−2997(14)	0721(11)
C(23)	−5546(14)	−5906(15)	−3605(11)
C(24)	2463(19)	−4121(17)	−2105(13)
C(25)	−2857(14)	−1139(13)	−2043(11)
N	−2263(13)	−0851(11)	−1172(9)
O(1)	−0012(8)	−3122(8)	0202(6)
O(2)	2480(9)	−2345(8)	−0575(6)
O(3)	2256(9)	−2042(10)	−2558(7)
O(4)	−0267(9)	−3060(11)	−3754(7)
O(5)	−2853(8)	−4406(9)	−3145(6)
O(6)	−2510(8)	−3961(8)	−0986(6)
S	−3599(4)	−1546(5)	−3300(3)
H(1)	0636	−1736	2460
H(2)	−0840	−0839	3206
H(3)	−3340	−1787	2049
H(4)	−4023	−3164	0075
H(7)	1163	−3163	1398
H(7)	2055	−1533	1232
H(8)	1236	−4337	−0459
H(9)	4497	−2108	−0804
H(10)	4079	−0561	−1269
H(10)	4252	−1673	−2353
H(12)	4692	−0028	−2856
H(13)	4458	0776	−4371
H(14)	2129	−0063	−5448
H(15)	−0327	−2103	−5312
H(17)	−1890	−4367	−5299
H(17)	−2270	−3361	−4306
H(18)	−3705	−6188	−4767
H(19)	−4081	−6246	−2854
H(20)	−3915	−3576	−1641
H(20)	−4773	−5165	−1418
H(22)	3596	−3651	0350
H(22)	3212	−3125	1465
H(22)	4379	−1904	0950
H(23)	−6524	−6481	−3353
H(23)	−5325	−4888	−3513
H(23)	−5807	−6556	−4455
H(24)	2517	−4888	−1730
H(24)	2882	−4227	−2800
H(24)	1296	−4588	−2420

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TABLE 1(b)

(*b*) Fractional co-ordinates ($\times 10^4$) for (III)

Cs	2500	2500	2500
O(1)	4118(6)	3265(5)	4130(8)
O(2)	2783(6)	4253(5)	3905(9)
O(3)	3842(5)	1509(5)	4481(7)
C(1)	4304(9)	4131(8)	3788(12)
C(2)	5124(9)	4437(9)	3483(12)
C(3)	5207(10)	5352(10)	3193(14)
C(4)	4512(10)	5902(10)	3182(13)
C(5)	3632(10)	5550(10)	3424(12)
C(6)	3555(9)	4641(8)	3715(12)
C(7)	2061(8)	4756(8)	4405(13)
C(8)	1583(8)	4153(8)	5235(11)
C(9)	4556(9)	1937(8)	5065(13)
C(10)	4858(10)	2659(8)	4277(13)
C(11)	2136(10)	3713(11)	6197(13)
C(12)	5384(10)	1362(11)	5265(16)
H(2)	5723	4009	3473
H(3)	5826	5632	2993
H(4)	4590	6596	2990
H(5)	3044	5980	3337
H(7)	1606	4969	3707
H(7)	2285	5328	4872
H(8)	1092	4523	5760
H(9)	4360	2201	5935
H(10)	5055	2403	3402
H(10)	5424	3005	4638

near $z = \frac{1}{4}$. Attempts to refine the positions of peaks within this region on the basis of their being the missing disordered atoms were unsuccessful. For the anisotropic refinement, hydrogen-atom positions were estimated from the molecular geometry assuming C–H 1·084 Å for the benzo- and 1·073 Å for the alkyl-group hydrogen atoms. These were included in the calculations but not refined. The methyl hydrogen atoms were not located; neither these nor the anionic atoms were included in the calculations. The weighting scheme was $w = 1/\sigma^2$ where $\sigma = \sigma(F_o)\sqrt{58 - 3{\cdot}9|F_o| + 0{\cdot}1|F_o|^2}$ except that if $|F_c| < 0{\cdot}5|F_o|$ or if $|\Delta| > 20$, $w = 0$. This gave similar average values of $w\Delta^2$ for various ranges of $|F_o|$ and of $\sin\theta/\lambda$. 25 Medium or strong reflections had $|\Delta| > 20$, presumably owing to the lack of contribution from the 60 electrons of the missing thiocyanate ions. Anomalous scattering corrections were applied for Cs^+. The constraints on the caesium thermal parameters imposed by the special positions are $\beta_{11} = \beta_{22}$, and $\beta_{12} = \beta_{13} = \beta_{23} = 0$. Four cycles of full-matrix refinement of all co-ordinates (except those of Cs) with anisotropic thermal parameters for all the atoms brought R to a final value of 0·11 for the 1394 observed reflections, with R' 0·12. In the final cycle, all shifts were $\leqslant 0{\cdot}36\sigma$, except for Cs with temperature-factor shift of 2·3σ. A difference synthesis computed from the final structure factors for the observed reflections, weighted according to the least-squares weights, showed no peaks or holes of magnitude $> 0{\cdot}4$e Å^{-3}.

RESULTS

Atomic co-ordinates and temperature factors with their estimated standard deviations are in Tables 1 and 2 for both structures. Observed and calculated structure factors are in Supplementary Publication No. SUP 21205 (8 pp.).† Figures 1(a) and (b) show the bond lengths and angles in (II); Figure 1(c) shows the values for (III). The standard deviations in Figures 1(a) and (b) were calculated from the least-squares variance–covariance matrix with allowance for the errors of the unit-cell dimensions; those in Figure 1(c) were obtained from the estimated standard deviations in Table 1. Torsion angles of the ring bonds in the two isomers are compared in Figures 2(a) and (b). The crystal structure of (III) viewed in projection along [001] is shown in Figure 3. Figures 4 and 5 show (II) and the complex cation of (III).

TABLE 2

Vibration parameters ($\times 10^3$) in the expression: $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + U_{22}k^2b^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + U_{33}l^2c^{*2})]$. Hydrogen atoms are assigned isotropic temperature factors $U = 0{\cdot}07$ Å^2

(*a*) For complex (II)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs	60(1)	59(1)	46(1)	34(0)	17(0)	19(0)
C(1)	75(10)	72(10)	36(8)	40(8)	9(7)	20(7)
C(2)	72(11)	66(10)	54(10)	27(9)	25(8)	11(8)
C(3)	78(11)	69(10)	76(11)	42(9)	46(9)	33(9)
C(4)	56(9)	45(8)	57(9)	22(7)	18(7)	13(7)
C(5)	50(8)	34(7)	44(8)	23(7)	16(7)	14(6)
C(6)	35(7)	49(8)	50(8)	22(7)	12(6)	18(7)
C(7)	58(9)	57(8)	62(9)	37(7)	12(7)	21(7)
C(8)	41(7)	50(8)	59(8)	30(7)	6(6)	19(7)
C(9)	63(9)	90(11)	64(9)	52(9)	25(8)	43(9)
C(10)	73(11)	119(13)	77(11)	58(10)	27(9)	47(10)
C(11)	78(10)	49(9)	51(9)	36(8)	21(8)	16(7)
C(12)	96(12)	35(8)	72(10)	29(8)	30(9)	24(8)
C(13)	88(12)	70(11)	107(14)	28(10)	60(11)	42(11)
C(14)	142(17)	134(17)	95(14)	94(15)	70(13)	69(13)
C(15)	104(13)	126(15)	64(10)	79(12)	26(10)	42(10)
C(16)	62(10)	76(10)	54(9)	36(9)	12(8)	20(8)
C(17)	55(10)	188(18)	42(9)	61(12)	7(8)	36(10)
C(18)	31(8)	120(14)	46(9)	2(9)	7(7)	−10(9)
C(19)	62(9)	60(9)	52(9)	37(8)	0(7)	17(7)
C(20)	49(8)	54(9)	64(9)	23(7)	18(7)	27(7)
C(21)	153(19)	89(14)	235(24)	85(14)	110(18)	48(15)
C(22)	75(10)	65(10)	67(10)	40(9)	3(8)	23(8)
C(23)	51(9)	78(10)	69(10)	26(8)	6(8)	26(8)
C(24)	127(14)	95(13)	95(13)	75(12)	47(11)	30(11)
C(25)	60(9)	49(8)	60(9)	38(8)	11(7)	14(7)
N	99(10)	48(7)	63(8)	40(7)	1(7)	16(7)
O(1)	44(5)	71(6)	53(5)	34(5)	8(4)	21(5)
O(2)	65(6)	61(5)	54(5)	43(5)	22(5)	25(5)
O(3)	53(6)	103(7)	66(6)	44(6)	20(5)	42(6)
O(4)	60(6)	116(8)	54(6)	51(6)	14(5)	35(6)
O(5)	46(5)	58(6)	52(5)	21(5)	6(4)	12(4)
O(6)	42(5)	52(5)	55(5)	25(4)	2(4)	14(4)
S	78(3)	86(3)	54(3)	37(3)	8(2)	20(2)
(*b*) For complex (III)						
Cs	35(1)	35	46(1)	0	0	0
O(1)	44(5)	30(5)	83(7)	0(4)	3(5)	6(5)
O(2)	44(5)	31(4)	85(7)	3(4)	16(5)	−8(5)
O(3)	42(5)	45(5)	42(5)	1(4)	1(4)	2(4)
C(1)	51(8)	36(7)	45(8)	0(6)	2(6)	−11(6)
C(2)	47(8)	55(8)	51(8)	−14(7)	−12(7)	7(7)
C(3)	61(9)	61(9)	60(10)	−21(8)	−1(8)	10(8)
C(4)	66(10)	64(10)	45(9)	−16(8)	−4(8)	15(8)
C(5)	55(8)	61(9)	50(9)	−18(7)	1(7)	−5(7)
C(6)	50(8)	35(7)	44(8)	−4(6)	7(7)	−2(6)
C(7)	33(7)	40(8)	64(10)	8(6)	−1(7)	−6(7)
C(8)	35(7)	53(8)	40(8)	3(6)	−11(6)	−2(6)
C(9)	56(8)	35(7)	61(9)	−9(6)	−2(7)	0(7)
C(10)	46(8)	38(7)	61(9)	14(6)	5(7)	8(7)
C(11)	51(9)	86(11)	45(9)	3(8)	−11(7)	−9(8)
C(12)	54(9)	80(11)	88(12)	24(9)	−5(9)	35(10

DISCUSSION

Isomer F.—The structure of (II) consists of crystallographically centrosymmetric complex dimers (Figure 4). The molecules contain double bridges with Cs–N distances 3·19(1) and 3·25(1) Å, with co-ordination by the six oxygens at 3·07—3·34(1) Å and an aryl carbon atom, C(3), at 3·80(1) Å in the symmetry-related

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† See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index Issue.

ligand. The co-ordination polyhedron formed by the eight nearest neighbours may be represented by one of Britton and Dunitz's octagons.[12] Numbers 10, 12, 13, 47, 49, and 124 in their scheme are possible representations, depending on the degree of coplanarity of the oxygens, and whether the faces formed by the pair of nitrogens and a pair of catechol oxygens are regarded as being planar. All the possible polyhedra are related to the cube.

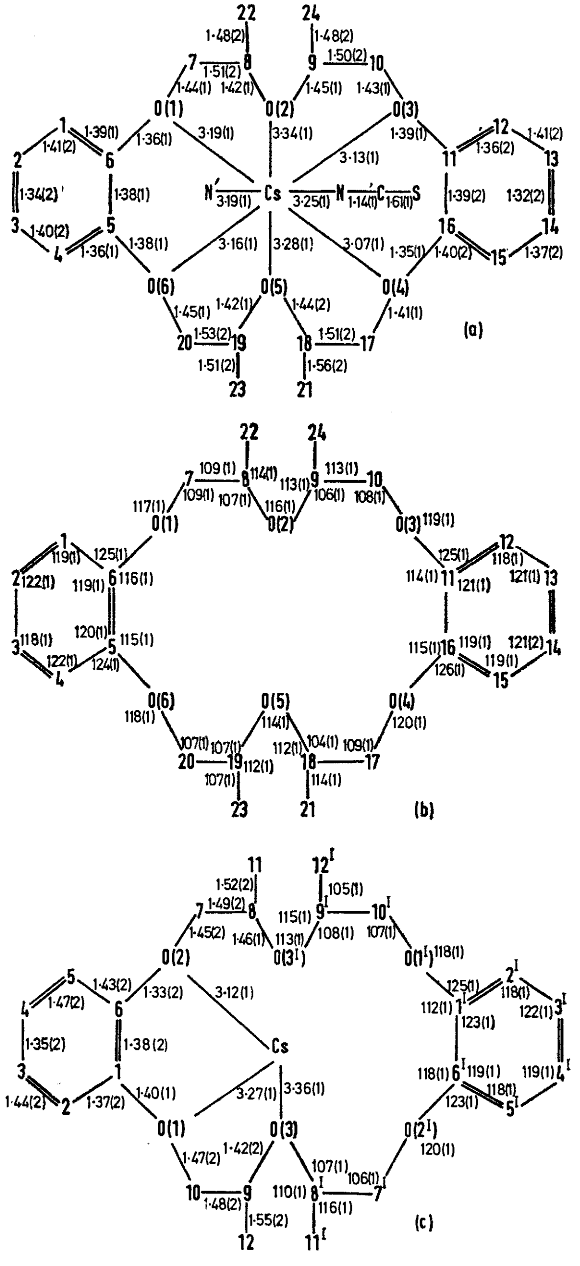

FIGURE 1 (a) Bond lengths (Å) and (b) bond angles (°) in (II). (c) Bond lengths (Å) and angles (°) in (III); the halves of the molecule are related by a two-fold axis, *e.g.* C(1), C(1^{I}), *etc.*

Figure 4 shows the ligand configuration to be *cis,anti,cis*, *cis* referring to the positions of the methyl groups relative to the benzene ring. The molecule has a near-symmetry plane perpendicular to the mean plane of the oxygen atoms, which relates the methyl groups in axial and equatorial pairs, so that the complex molecule is optically mesomeric. The mirror symmetry is shown by the similarity of the torsion angles in the two halves of the molecule in Figure 2(a).

The overall shape of the complexed ligand is similar to that of complexed (Ia), the angles between the normals to the benzene rings and the plane through the oxygen atoms being 38 and 27° (Table 3), compared with 35 and 36°.[13] The torsion angles of the ring bonds are nearly equal to the corresponding ones in complexed (Ia) [Figure 2(a)], the C–O bonds being *trans* and the C–C *gauche*, as found in other complexed polyethers.[13]

The bond lengths and angles [Figures 1(a) and (b)] in the ligand molecule are similar to those in other macrocyclic ethers.[13] The Cs–O distances show the usual spread of significantly different values. The two Cs–N distances are also significantly different. The centrosymmetrically-related N and Cs atoms lie nearly on the corners of a square, with the angles N–Cs–N′ 93°

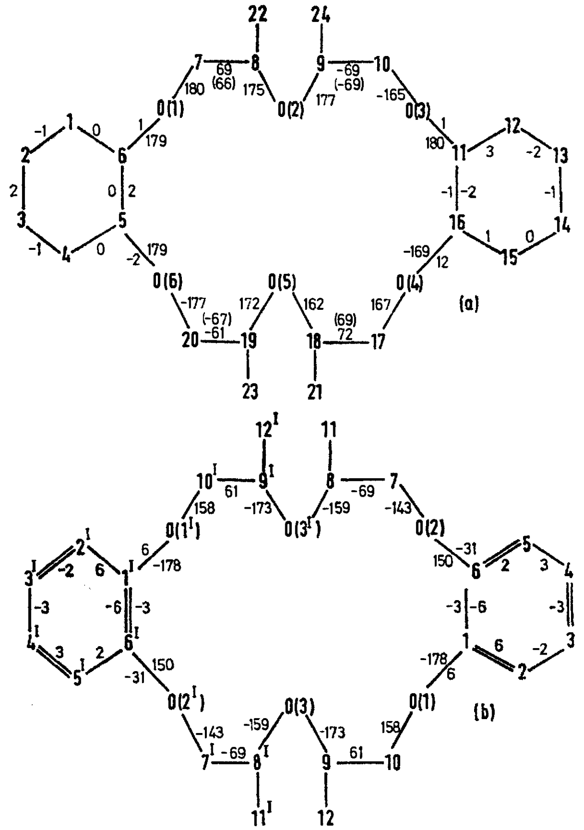

FIGURE 2 (a) Torsion angles (°) in (II), with in parentheses the corresponding values for a complexed molecule of (Ia) (from ref. 13). The atom labels are those adopted for isomer F. (b) Torsion angles (°) in (III). Two-fold symmetry-related angles have the same values

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[12] D. Britton and J. D. Dunitz, *Acta Cryst.*, 1973, **A29**, 362.

[13] D. Bright and M. R. Truter, *J. Chem. Soc.* (*B*), 1970, 1544; M. A. Bush and M. R. Truter, *ibid.*, 1971, 1440; *J.C.S. Perkin II*, 1972, 341, 345; P. R. Mallinson and M. R. Truter, *ibid.*, 1972, 1818.

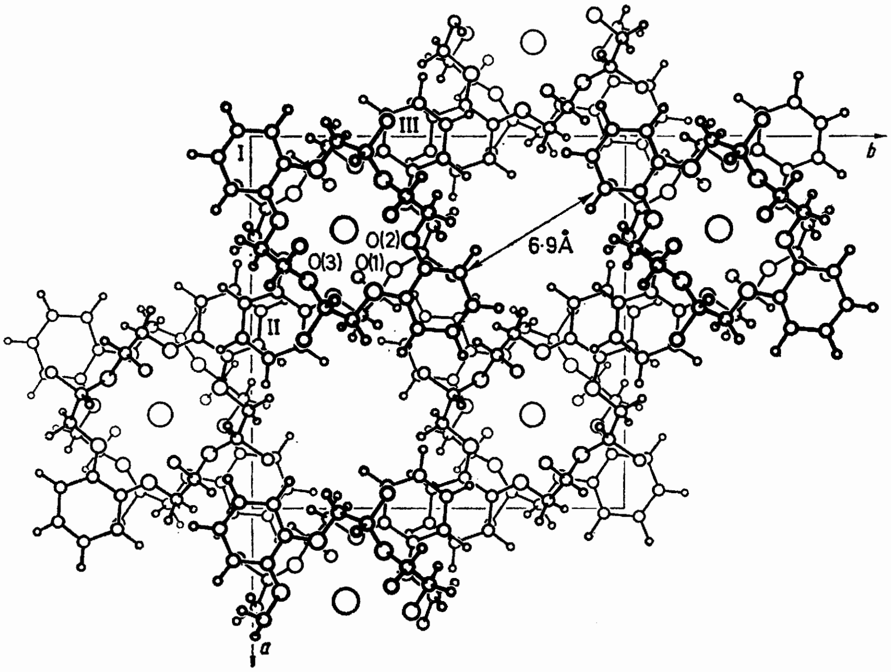

FIGURE 3 Projection of the structure along [001]. The disordered anions are presumed to occupy tunnels of diameter 6·9 Å surrounding the 4_2 axes. Large circles represent Cs atoms on $\bar{4}$ axes. Roman numerals refer to the following equivalent positions with respect to the asymmetric unit at x, y, z:

I $\frac{1}{2} - x, \frac{1}{2} - y, z$ II $y, \frac{1}{2} - x, \frac{1}{2} - z$ III $\frac{1}{2} - y, x, \frac{1}{2} - z$

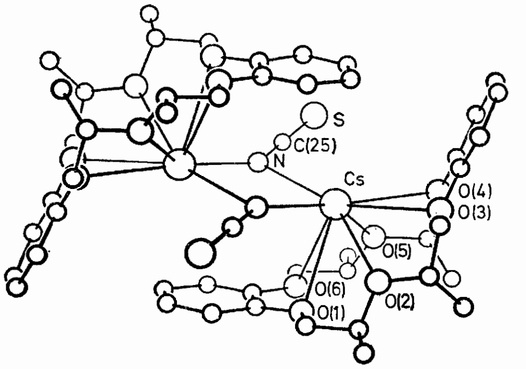

FIGURE 4 The centrosymmetric complex molecule of (II)

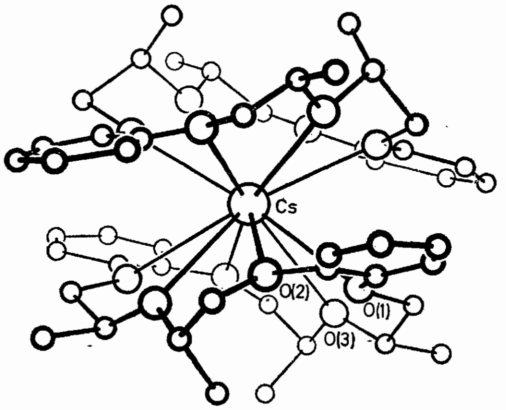

FIGURE 5 The complex cation of (III), with symmetry $\bar{4}$. The two ligands are enantiomerically related

and Cs–N–Cs′ 87°. The configuration of the nitrogen is irregular, angles Cs–N–C(25) 108°, Cs′–N–C(25) 151°. The anion is just significantly non-linear, with the angle N–C(25)–S 176(1)°; bond lengths are N–C(25) 1·14(1), C(25)–S 1·61(1) Å.

TABLE 3

Deviations (Å) of the atoms from planes. The equations are referred to Cartesian axes a, b', and c', where b' is in the plane of a and b

(a) Complex (II)

Plane (1) O(1)—(6)

$$0{\cdot}389x - 0{\cdot}840y - 0{\cdot}378z - 3{\cdot}444 = 0$$

O(1) −0·05, O(2) +0·21, O(3) −0·14, O(4) −0·08, O(5) 0·24, O(6) −0·17, Cs −1·71

Plane (2): C(1)—(6)

$$0{\cdot}014x + 0{\cdot}993y - 0{\cdot}116z + 3{\cdot}277 = 0$$

Plane (3): C(11)—(16)

$$0{\cdot}546x - 0{\cdot}508y - 0{\cdot}666z - 4{\cdot}665 = 0$$

(b) Cation of (III)

Plane (4): O(1)—(3), O(1^{I})—(3^{I})

$$z = 4{\cdot}647$$

O(1) 0·05, O(2) 0·30, O(3) −0·34, Cs 1·86

Plane (5): C(1)—(6)

$$-0{\cdot}132x - 0{\cdot}222y - 0{\cdot}966z + 6{\cdot}299 = 0$$

Intermolecular and Intramolecular Contacts.—The dimeric complex molecule consists of a ‘ sandwich ’ of the cations and anions between the ligand molecules, and the crystal may be regarded as being formed by the packing of oblate spheroids, with no holes in the lattice. The shortest distances between atoms in different monomers are C(H) ··· C(H) 3·93, C(H) ··· C 3·92, C(H) ··· C(H_2) 3·90, C(H) ··· Me 3·77, C ··· C(HMe) 3·97, C ··· Me 3·70, C(H_2) ··· Me 3·66, C(HMe) ··· O 3·60, and Me ··· O 3·36 Å. These are typical van der Waals distances. There are some short intramolecular distances involving a pair of adjacent methyl groups: C(22) ··· C(24) 3·47; and the axial methyl groups: C(21) ··· O (4) 2·84 and C(24) ··· O(3) 2·83 Å. The shortest contacts made by the anion are: N ··· C(H) 3·57, N ··· C (aryl) 3·61, N ··· C(H_2) 3·45, N ··· O 3·66, C ··· C(H) 3·44, C ··· C(aryl) 3·86, C ··· C(H_2) 3·60, C ··· O 3·71, S ··· C(H) 3·81, S ··· C(H_2) 3·80, S ··· Me 3·99, and S ··· O 3·95 Å. All other contacts (not including hydrogen) are >4 Å.

Isomer G.—The ligand molecules lie on crystallographic two-fold axes in $\bar{4}$ at $\frac{1}{4},\frac{1}{4},z$, *etc.*, giving a cation with $\bar{4}$ symmetry. Figure 5 shows the *trans,anti,trans*-configuration of the ligands. One optically active isomer G molecule of each hand is present in the complex cation. The 12 oxygen atoms form a hexagonal antiprism configuration around the caesium, with Cs–O contacts ranging from 3·12 to 3·36 Å [Figure 1(c)]. The range is similar to that in (II), contrary to the result published [5] at an earlier stage of refinement.

Experiments with models do not suggest any steric reason for the different stoicheiometries of the complexes. The geometrical ' flatness ' of (III) is shown by the relatively small inclination (15°) of the benzo-group normals to the oxygen mean-plane normal (Table 3), compared with 38 and 27° in (II). While the C–C torsion angles are comparable with those in (II) (Figure 2), the C–O bond conformations differ by up to 34°, being less *trans* in character. The bond lengths and angles in the ligand are not significantly different from the corresponding ones in (II) (Figure 1).

Intermolecular and Intramolecular Contacts.—Figure 3 shows the crystal packing of the complex cations, with holes around the 4_2 axes. The disordered and unlocated thiocyanate anions must occupy these non-polar tunnels, without interaction with the cations. The shortest distances between atoms in different ligand molecules are: O ··· O 3·74, O ··· C 3·76, O ··· C(H) 3·79, O ··· C(H_2) 3·72, C ··· C(H) 3·53, C ··· C(H_2) 3·83, C(H) ··· C(H) 3·75, C(H) ··· C(H_2) 3·70, C(H) ··· C(HMe) 3·91, C(H) ··· Me 3·87, C(H_2) ··· Me 3·55, C(HMe) ··· Me 3·87, and Me ··· Me 3·98 Å. These are greater than or equal to typical van der Waals distances. The intramolecular methyl-group separations are 3·98 Å for the pair attached to adjacent carbon atoms, C(11) ··· C(12^{I}), and 3·86 Å for the pair of symmetry-related axial groups, C(11) ··· C(11^{I}). Hence the absence of short contacts involving the methyl groups in (III) might explain its difference in conformation from that of (II), but does not explain why it is different from complexed (Ia),[13] which has no substituents and also forms a 1 : 2 complex with caesium thiocyanate.[14] All other contacts (not including hydrogen atoms) are >4 Å.

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[4/1302 *Received*, 1*st July*, 1974]

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[14] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1970, **92**, 386.