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# Crystal and Molecular Structure of a Complex Formed by Caesium Thiocyanate and 4-Nitrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecane (4-Nitrobenzo-18-crown-6)

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The crystal and molecular structure of the title compound, $C_{17}H_{23}O_8N_2SCs$, has been determined from 1858 observed three-dimensional data measured by a single-crystal automated X-ray diffractometer. The unit cell is monoclinic with $a = 8{\cdot}360$ (3), $b = 13{\cdot}388$ (5), $c = 21{\cdot}878$ (6) Å, $\beta = 113{\cdot}91$ (2)°, $V = 2239$ (1) Å$^3$ and contains four formula units. The space group is $P2_1/c$. The crystal structure was determined by the heavy-atom method and refined by the block-diagonal least-squares method. The final $R$ value is 0·049.

## Introduction

One of the important properties of macrocyclic polyethers is their ability to form complexes with various inorganic cations by means of ion–dipole and dipole–dipole interactions between the ion and negative O atoms situated in the macrocycle.

Some substituents on the macro-ring have been found to produce a pronounced effect on selectivity towards various cations. It is important for explaining the effect of substituents in the case of compounds containing the 1,4,7,10,13,16-hexaoxacyclooctadecane to make mutual comparisons of changes which arise on attaching various substituents.

Structures containing an unsubstituted hexaoxacyclooctadecane ring (further referred to as 18-crown-6) have been presented (Goldberg, 1975*a*; Dunitz, Dobler, Seiler & Phizackerley, 1974), as have structures containing various substituents on the ring (Bush & Truter, 1971; Bright & Truter, 1970; Goldberg, 1975*b*, 1976; Mallinson, 1975*a*,*b*). This paper belongs to the latter group.

## Experimental

The compound used in this investigation was prepared by Petránek & Ryba (1974). The molecular formula was confirmed by elemental chemical analysis. The crystals obtained were in the form of yellow irregular prisms. Crystal data are presented in Table 1.

Table 1. *Crystal data*

| | |
|---|---|
| Monoclinic, $P2_1/c$ | $C_{17}H_{23}O_8N_2SCs$ |
| $a = 8{\cdot}360$ (3) Å | $\mu$(Mo $K\alpha$) = 18·1 cm$^{-1}$ |
| $b = 13{\cdot}388$ (5) | $D_m = 1{\cdot}620$ g cm$^{-3}$ |
| $c = 21{\cdot}878$ (6) | $D_x = 1{\cdot}626$ |
| $\beta = 113{\cdot}91$ (2)° | $Z = 4$ |
| $V = 2239$ (1) Å$^3$ | $F(000) = 1096$ |
| FW 548·3 | m.p. 174–175°C |

Preliminary dimensions of the unit cell and systematic absences (for $h0l$: $l = 2n + 1$, for $0k0$: $k = 2n + 1$) were determined from oscillation and Weissenberg photographs. Definitive parameters were obtained by refining 15 reflexions measured with a Syntex $P2_1$ automatic diffractometer [$\lambda$(Mo $K\alpha$) = 0·71069 Å], graphite monochromator, room temperature, crystal ground to a sphere $d = 0{\cdot}16$ mm and placed on a goniometric head in a general position. Density was measured by flotation in a heptane–bromoform solution (Hašek & Huml, 1975).

### *Intensity measurement*

Intensities were measured with the same diffractometer by the $\omega$–$2\theta$ scan method. Intensities higher than $5 \times 10^3$ counts s$^{-1}$ were corrected to the coincidence of pulses. Reflexions with intensities higher than $50 \times 10^3$ counts s$^{-1}$ were measured with a lower anode current. The right and left background was measured for half the time of measurement of the maximum. The scanning interval was 1° below $K\alpha_1$ and 1° above $K\alpha_2$ of the Mo $K\alpha$ doublet.

The minimum scanning rate was 0·5° min$^{-1}$. The intensities thus measured were corrected by using three reference reflexions recorded after every 30 reflexions. During the measurements the crystal did not exhibit any essential reduction in diffracted intensity. In the range up to $\sin\theta_{\max}/\lambda = 0{\cdot}4812$ Å$^{-1}$, 2165 independent reflexions were measured, of which 1858 were considered observed as they had $I_o > 0{\cdot}98\sigma(I)$, where $\sigma(I)$ was calculated from counting statistics.* The intensities were corrected for the Lp factor. No correction for absorption was made ($\mu r = 0{\cdot}14$).

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* Lists of measured intensities, with their e.s.d.'s, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32690 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

## Structure determination and refinement

The phase problem was solved by the heavy-atom method. The positions of Cs and S were determined from the Patterson function sharpened with the Lp factor. The subsequent Fourier map showed the whole 18-membered ring, the SCN group and the benzene ring. In the next step the position of the nitro group was determined.

The structure was refined in two ways. In both cases the least-squares method in the block-diagonal approximation was used; the function minimized was $\Sigma\, w(|F_o| - |F_c|)^2$. The atomic scattering factors were taken from Cromer (1974). The Cs atom was regarded as singly ionized. For the Cs and S atoms the correction for anomalous scattering was included. The atomic scattering factors of the H atoms were taken as a spherical approximation of the bonded atom (Stewart, Davidson & Simpson, 1965). Unobserved reflexions were eliminated from the refinement. The following coefficients were used in describing the agreement between the structure and the experiment: $R_1 = \Sigma\,(|F_o| - |F_c|)/\Sigma\,|F_o|$, $R_2 = [\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w(|F_o|)^2]^{1/2}$, $S = [\Sigma\, w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where $m$ is the number of reflexions used in the refinement, and $n$ is the number of refined parameters.

Table 2. *Final positional parameters and their e.s.d.'s of non-hydrogen atoms*

Fractional coordinates are ×10⁵.

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| C(1) | 22576 (107) | 39036 (83) | 752 (38) |
| O(2) | 20721 (83) | 29060 (37) | −128 (24) |
| C(3) | 22661 (121) | 25059 (66) | −5917 (38) |
| C(4) | 16463 (127) | 14784 (71) | −6697 (37) |
| O(5) | 27601 (77) | 8644 (44) | −1242 (26) |
| C(6) | 22526 (150) | −1621 (71) | −1834 (50) |
| C(7) | 32883 (162) | −7059 (74) | 4457 (54) |
| O(8) | 27840 (77) | −3499 (42) | 9622 (27) |
| C(9) | 35534 (133) | −9210 (64) | 15606 (47) |
| C(10) | 29715 (132) | −5010 (70) | 20690 (45) |
| O(11) | 37364 (84) | 4443 (43) | 22745 (27) |
| C(12) | 29952 (205) | 9427 (83) | 26796 (57) |
| C(13) | 37107 (204) | 19107 (81) | 28605 (50) |
| O(14) | 32973 (93) | 25745 (44) | 23070 (28) |
| C(15) | 16292 (134) | 30335 (76) | 20468 (44) |
| C(16) | 17091 (115) | 39464 (64) | 16567 (38) |
| O(17) | 18391 (75) | 35889 (38) | 10516 (26) |
| C(18) | 21011 (99) | 42868 (59) | 6553 (35) |
| C(19) | 22064 (112) | 52984 (65) | 7860 (43) |
| C(20) | 25163 (126) | 59689 (68) | 3664 (47) |
| C(21) | 27039 (112) | 56039 (63) | −1804 (39) |
| C(22) | 25948 (105) | 46039 (65) | −3448 (37) |
| N(23) | 30912 (105) | 63224 (60) | −6202 (35) |
| O(24) | 32423 (116) | 72007 (49) | −4736 (37) |
| O(25) | 32653 (109) | 59880 (53) | −11074 (34) |
| S(26) | 86151 (37) | 17499 (25) | 28559 (14) |
| C(27) | 83572 (111) | 8333 (73) | 23303 (50) |
| N(28) | 81848 (101) | 2156 (57) | 19674 (35) |
| $Cs^+$ | 46262 (7) | 17825 (4) | 12964 (2) |

(I) In the first refinement procedure, the *NRC*-10 program was used (Ahmed, Hall, Pippy & Huber, 1966), with the weighting scheme $w = W_1 W_2$, and $W_1 = 1/|\sigma_F^2 + (0{\cdot}02F_o)^2|$ and $W_2 = |\sin\,\theta/(0{\cdot}4\lambda)|^{12}$. This weight was chosen so as to suppress the effect of the H atoms as done similarly by Dunitz *et al.* (1974) and Goldberg (1975*a*). The non-hydrogen atoms were refined anisotropically. The contributions of the H atoms were not included at all. The final $R_1 = 0{\cdot}048$.

(II) In the second refinement procedure we used the Syntex XTL system of programs. The non-hydrogen atoms were refined anisotropically up to $R_1 = 0{\cdot}054$, $R_2 = 0{\cdot}059$, $S = 1{\cdot}98$. The difference map contained 16 maxima in the positions assumed for the H atoms. Of these, however, only 13 remained in the expected positions after the subsequent refinement. All H atoms were therefore fixed in ideal tetrahedral and planar positions with respect to the skeleton of the molecule and only their isotropic temperature factors were refined. The weight calculated from the counting statistics was modified at the end of the refinement so that the dependence of $\langle w\Delta F^2\rangle$ on $\sin\theta$ and $F_o$ was approximately constant. The final weight was $w = W_1 W_2$, where $W_1 = 1/[\sigma_F^2 + (0{\cdot}02F_o)^2]$, $W_2 = [\sin\theta/(0{\cdot}35\lambda)]^{1{\cdot}2}$ for $\sin\theta/\lambda < 0{\cdot}35$, $W_2 = [\sin\theta/(0{\cdot}35\lambda)]^{-0{\cdot}2}$ for $\sin\theta/\lambda > 0{\cdot}35$. The refinement process was completed when shifts of all parameters had decreased below 0·2 e.s.d. The final agreement factors are: $R_1 = 0{\cdot}049$, $R_2 = 0{\cdot}057$, $S = 1{\cdot}29$. There were 6·5 observed reflexions per refined parameter.

Table 3. *Final parameters of hydrogen atoms*

Coordinates were fixed in ideal tetrahedral or planar positions so that C−H bond lengths were 1·00 Å. Only temperature factors were refined. Fractional coordinates are ×10⁴.

| | $x$ | $y$ | $z$ | $B$ (Å²) |
|---|---|---|---|---|
| H(31) | 3519 | 2527 | −521 | 5 (2) |
| H(32) | 1546 | 2905 | −959 | 4 (2) |
| H(41) | 1637 | 1205 | −1097 | 8 (2) |
| H(42) | 433 | 1462 | −687 | 5 (2) |
| H(61) | 2458 | −470 | −560 | 5 (2) |
| H(62) | 982 | −205 | −274 | 6 (2) |
| H(71) | 4563 | −584 | 576 | 12 (4) |
| H(72) | 3042 | −1439 | 376 | 10 (3) |
| H(91) | 4854 | −885 | 1731 | 7 (2) |
| H(92) | 3162 | −1631 | 1467 | 6 (2) |
| H(101) | 3347 | −956 | 2465 | 3 (1) |
| H(102) | 1671 | −432 | 1872 | 6 (2) |
| H(121) | 3272 | 539 | 3098 | 7 (2) |
| H(122) | 1706 | 984 | 2426 | 15 (5) |
| H(131) | 4996 | 1851 | 3090 | 23 (9) |
| H(132) | 3217 | 2197 | 3170 | 10 (3) |
| H(151) | 1297 | 3237 | 2421 | 7 (2) |
| H(152) | 729 | 2559 | 1745 | 6 (2) |
| H(191) | 2056 | 5553 | 1188 | 8 (2) |
| H(201) | 2601 | 6701 | 457 | 5 (2) |
| H(221) | 2752 | 4372 | −754 | 7 (2) |
| H(161) | 2757 | 4359 | 1925 | 3 (1) |
| H(162) | 625 | 4359 | 1540 | 5 (2) |

The resulting positional parameters of all non-hydrogen atoms are summarized in Table 2.* The atomic parameters for the H atoms are given in Table 3. The maximum value of the residual electron density on the final difference map did not exceed 0·4 e Å$^{-3}$.

The final thermal parameters obtained from refinement procedures I and II differed very considerably, while differences between the respective interatomic distances did not exceed twice the e.s.d., with the exception of the atoms C(12), C(13) and C(22), where the bonds with the adjacent atoms changed by as much as 0·04 Å. The distances between the O atoms of the macro-ring and the distances between these O atoms and the Cs atom remained virtually unchanged. Unless otherwise indicated, the resulting atomic parameters from the second refinement procedure are used in the discussion of the molecular structure.

### Description and discussion of the structure

The numbering scheme, with the bond distances, O···O and O···Cs distances and with selected valency angles, is shown in Fig. 1(*a*), (*b*). The e.s.d.'s of the Cs···O distances are 0·005 Å, the e.s.d.'s of distances between the adjacent hexaether O atoms, O···O, are 0·008 Å and the e.s.d.'s of the other bond distances lie within the range 0·010–0·015 Å. E.s.d.'s of the angles lie between 0·5 and 1·0°.

Fig. 2 shows the thermal ellipsoids of 30% probability for non-hydrogen atoms derived from the first refinement procedure. The projection of the crystal structure along the [$\overline{20}$,4,3] direction is shown in Fig. 3.

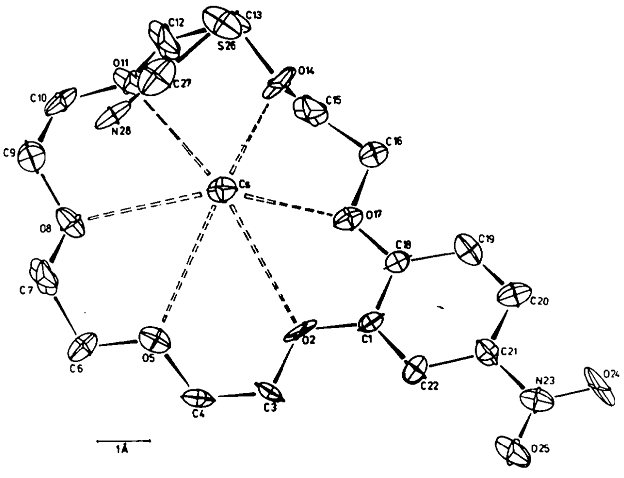
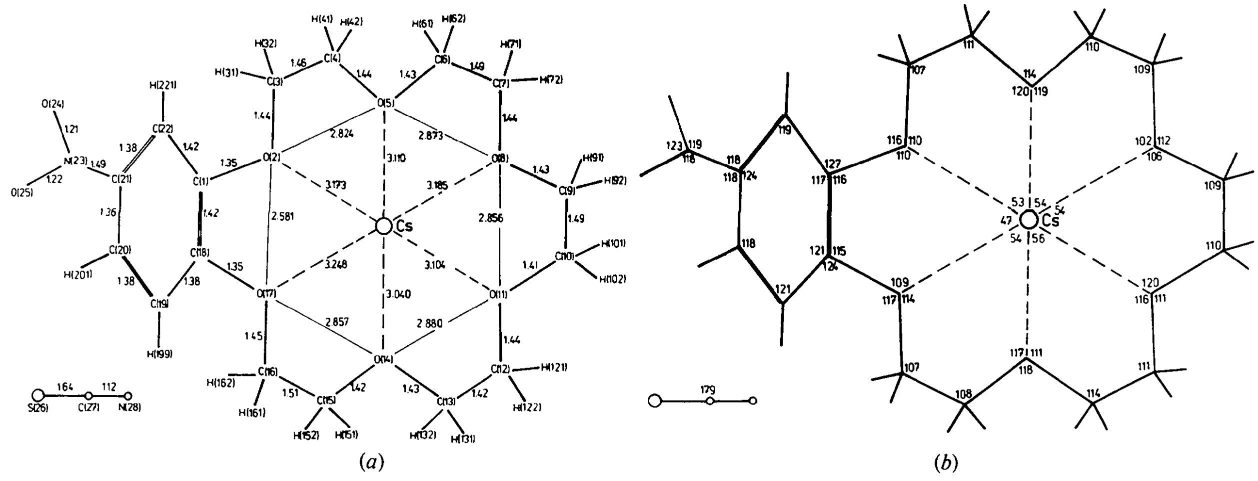


Fig. 2. Thermal motion ellipsoids of 30% probability of the complex 4-nitrobenzo-18-crown-6.CsSCN. Projection along **a**.

### Coordination of the Cs$^+$ cation and position of the anion

The Cs$^+$ cation is bonded in the molecule by interaction with the SCN group and also by ion–dipole interaction with six O atoms of the 18-membered chain (Fig. 4). Short distances between Cs$^+$ and both O atoms, O(24$^{\rm i}$) and O(25$^{\rm i}$), of the nitro group suggest that the dipole moment induced on the nitro group of one molecule interacts with the cation of the molecule related by a centre of symmetry (Fig. 5). This seems to be confirmed by the angular deviation of the benzene ring, the nitro group and the plane C(3), O(2), C(1), C(18), O(17), C(16) towards the cation (Table 4). Other intermolecular contacts shorter than the sum of the van der Waals radii were not observed.



(*a*) (*b*)

Fig. 1. Diagram of the complex 4-nitrobenzo-18-crown-6.CsSCN showing the bond lengths (Å) and some valence angles (°) of non-hydrogen atoms. E.s.d.'s are in the range from 0·005 to 0·015 Å for bond lengths and from 0·2 to 1·2° for valence angles.

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* See previous footnote.

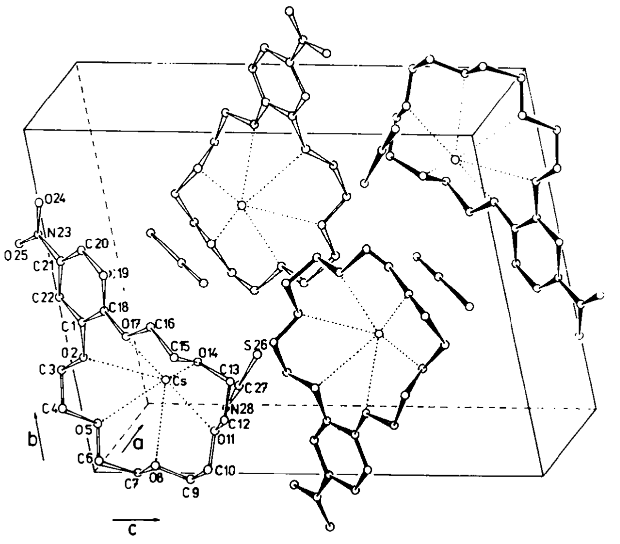

Fig. 3. Projection of 4-nitrobenzo-18-crown-6.CsSCN along the [$\overline{20}$,4,3] direction.

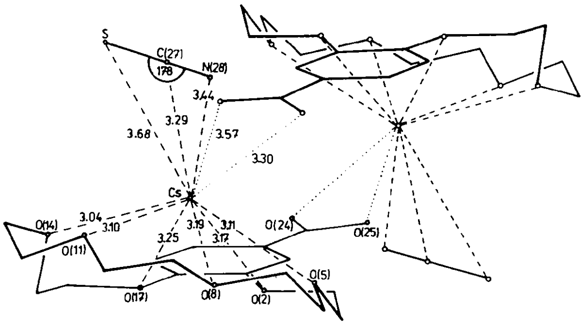

Fig. 4. Position of the Cs atom in the complex 4-nitrobenzo-18-crown-6.CsSCN. Projection along the [4,$\overline{20}$,3] direction.

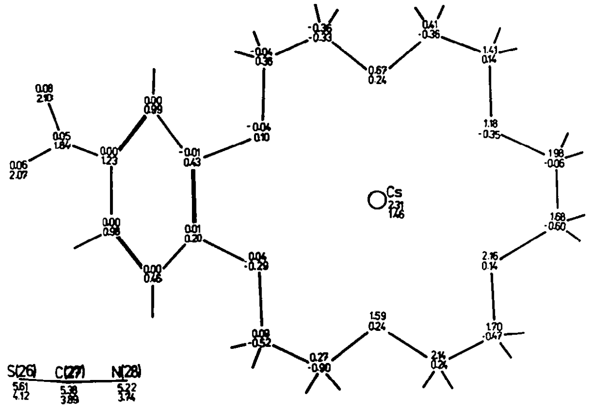

Fig. 5. Diagram of the complex 4-nitrobenzo-18-crown-6.CsSCN showing deviations of atoms (Å) from the weighted mean plane through the benzene ring (first line) and the weighted mean plane through oxygen atoms of the 18-membered ring, O(2), O(5), O(8), O(11), O(14), O(17) (second line).

Table 4. *Angles between some weighted mean planes through* 4-*nitrobenzo*-18-*crown*-6 . CsSCN

| Plane | Atoms defining plane | $\chi^2$ | Maximum deviation (Å) |
|---|---|---|---|
| *a* | Benzene ring | 4·0 | 0·013 |
| *b* | $NO_2$ group | – | – |
| *c* | C(3) O(2) C(1) C(18) O(17) C(16) | 16·8 | 0·027 |
| *d* | O(2) O(5) O(8) O(11) O(14) O(17) | 7570·0 | 0·35 |
| *e* | $Cs^+$ S(26) C(27) N(28) | 0·6 | 0·007 |
| *f* | O(17) O(2) O(5) O(8) | 172·1 | 0·055 |
| *g* | O(2) O(5) O(11) O(14) | 286·1 | 0·071 |
| *h* | O(24) O(25) O(2) O(17) | 13·7 | 0·022 |
| *i* | O(17) O(14) O(11) O(8) | 35·1 | 0·030 |
| *j* | O(5) O(8) O(11) | – | – |
| *k* | O(2) O(17) O(14) | – | – |

Selected angles between planes (°)
*a–b* 2·7, *a–c* 1·6, *a–d* 22·5, *a–e* 71·3
*d–e* 48·9, *f–i* 23·4, *g–j* 23·9, *g–k* 19·9
*h–k* 39·9, *h–g* 23·5

Because of the small angle between the plane through the nitrobenzene group and that through O(2), C(3), O(17), C(16) (see below), the O atoms O(25), O(24), O(2), O(17) also lie almost in the plane (Table 4, plane *i*).

Characteristic of the ordering of the O atoms in the macro-ring is an almost planar tetragon O(2), O(5), O(11), O(14), from which the atoms O(8) and O(17) depart on opposite sides away from the $Cs^+$ cation. Further characteristics of the above formation are given in Table 4.

The atoms S(26), C(27), N(28) lie approximately in a straight line (Fig. 1). The angle $Cs^+\cdots C(27)–S(26)$ is 91·0 (8)°. Owing to the free mobility of the charge in the SCN group, we believe that the orientation of this group is mainly determined by steric effects of the surrounding molecules in the crystal. This is also corroborated by the quite different position of the above group in the complexes 18-crown-6.NaSCN, 18-crown-6.KSCN, 18-crown-6.RbSCN, 18-crown-6.CsSCN (Dunitz *et al.*, 1974), in the complex dibenzo-18-crown-6.NaRbNCS (Bright & Truter, 1970) and in the complexes of two isomers of tetramethyldibenzo-18-crown-6.CsSCN (Mallinson, 1975*a*).

## Conformation of the macro-ring

The conformation of the macro-ring is mainly determined by the ion–dipole interaction between the $Cs^+$ cation and the six O atoms of the 18-membered ring. The average distance between Cs and the O atoms of the macro-ring is 3·147 Å, in very good agreement with 3·146 Å determined for the caesium thiocyanate complex of 18-crown-6 (Dobler & Phizackerley, 1974); on the other hand, however, much longer Cs···O distances were found in complexes of two isomers of tetramethyldibenzo-18-crown-6 with CsSCN. The Cs atom lies at a distance of 1·46 Å from the weighted mean plane through the six O atoms of the macro-ring (compare with 1·44 Å for the unsubstituted 18-membered ring). The very short distance between the atoms O(2) and O(17), due to the substitution of the benzene ring, and the reduced angles C(18)–C(1)–O(2) 116° and O(17)–C(18)–C(1) 115° (Fig. 1) can be compared with the deformation of the respective groups in the vicinity of substituted benzenes in the uncomplexed 2,3,11,12-dibenzo-18-crown-6 and in its complex with RbSCN (Bright & Truter, 1970).

The lengths of the C–C bonds in the macro-ring vary from 1·42 to 1·51 Å. The shortest bond, 1·42 Å, is that between C(12) and C(13) and lies just in that part of the macro-ring in which a large torsion angle was observed (see below). The average C–C bond length in the macro-ring, 1·474 Å, is in good agreement with the respective value, 1·475 Å, of the caesium thiocyanate complex of unsubstituted 18-crown-6 (Dobler & Phizackerley, 1974).

The atoms in the groups of C–C–O–C–C type in the macro-ring lie approximately in the plane, and the main torsion of the macro-ring takes place around the C–C bonds. The only exception is the group with the central atom O(14), where large deviations from the mean plane occur, namely, –0·46 Å for C(13) and 0·31 Å for C(12). Atoms C(12) and C(13) have comparatively high $B_{11}$ values and hence their thermal ellipsoids are greatly extended in one direction. The hydrogen atoms, H(122) and H(131), bonded to these C atoms have large isotropic temperature factors (Table 3); it seems, therefore, that they are not situated in the calculated tetrahedral positions.

## Nitrobenzene substituent

The angles between the benzene ring and the planes through the nitro group, the C(3), O(2), C(1), C(16), O(17), C(18) group and the six O atoms of the macro-ring are given in Table 4.

It seems that the angular deviation of the benzene ring from the plane C(3), O(2), C(1), C(16), O(17), C(18) by 1·6° and the angular deviation of the plane of the nitro group from the benzene plane by 2·7° are due to a tendency for the O atoms of the nitro group to approach the cation $Cs^{i}$.

The maximum deviations of the atoms of the nitrobenzene group and of the atoms C(3), O(2), C(1), C(16), O(17), C(18) from the plane of the benzene ring is 0·1 Å; also the angles between planes *a*, *b*, *c* are small (Table 4). Within such limits of accuracy it can be said, therefore, that the whole nitrobenzene ring and the atoms C(3), O(2), C(1), C(16), O(17), C(18) lie approximately in one plane, so as to make possible a maximum overlapping of the *p* orbitals 'perpendicular' to the plane of the benzene ring. The deviations from the mean plane through the benzene ring are given in Fig. 5.

In agreement with Bright & Truter (1970), the bond C(1)–C(18) is markedly extended compared with the mean C–C bond length, 1·395 Å, in the aromatic ring (*International Tables for X-ray Crystallography*, 1962); the valency angles O(2)–C(1)–C(22) and O(17)–C(18)–C(19) are increased to 127° and 124° respectively. The increased angle C(20)–C(21)–C(22), 124°, in the benzene ring agrees with the angle 125° given for nitrobenzene (Trotter, 1959).

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