# Crystal Structures of Complexes Between Alkali-metal Salts and Cyclic Polyethers. Part VII.[1] Complex formed Between Dibenzo-24-crown-8 (6,7,9,10,12,13,20,21,23,24,26,27-Dodecahydrodibenzo[*b*,*n*]-1,4,7,10,13,-16,19,22-octaoxacyclotetracosin) and Two Molecules of Potassium Isothiocyanate

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Potassium thiocyanate reacts with dibenzo-24-crown-8 giving crystals of formula $C_{24}H_{32}O_8$,2KNCS. The molecular structure has been determined by three-dimensional *X*-ray analysis from diffractometer data. Crystals are monoclinic, space group $P2_1/c$, with $Z = 2$ in a unit cell of dimensions: $a$ = 9·902(8), $b$ = 18·55(4), $c$ = 8·572(8) Å, β = 106·9(2)°. All atoms, including hydrogen, were located. Full-matrix least-squares refinement led to a final $R$ factor of 0·079 for 1184 independent reflections.

The ligand oxygen atoms are almost coplanar, with potassium atoms 0·66 Å on each side of this plane. Each $K^+$ atom is within bonding distance of five oxygen atoms, three bonding independently (K–O 2·732—2·825 Å) and the fourth and fifth unequally shared between the two potassium atoms (K–O 2·898, 2·979 Å). One thiocyanate ion is above and one below the ligand ring plane, each bridging the two potassium ions through nitrogen (K–N 2·87, 2·88 Å). A benzene ring from another ligand is in a position for its π-electrons to form an electrostatic attraction to the potassium ion, so there are eight sources of electron density round the cation and the structure has three-dimensional electrostatic bonding throughout.

A satisfactory understanding of the functioning of any biological system requires knowledge of the detailed molecular structure and composition of that system. The problem of the transport of ions across cell membranes is still far from achieving this objective.[2-4] Our present series of studies[1] of the complexes formed between alkali-metal ions and macrocyclic polyethers,[5] have, as their immediate objective, the elucidation of the type of bonding site which will hold a specific metal ion in a hydrophobic environment.

This compound shows the novel feature of having two potassium ions attached to one cyclic polyether, at adjacent binding sites. This may be related to biological theory that postulates either ' carrier ' molecules, carrying more than one cation,[6] or could be extended to a theory which would postulate transport by an ion or a chain of ions, moving from one site to another, perhaps under the influence of either conformation change[7] or electric potential.[8]

The other novel features of this crystal structure are the close approach of an aromatic bond to potassium and double nitrogen bridging from thiocyanate ions across two potassium ions.

## EXPERIMENTAL

A mixture of potassium thiocyanate with dibenzo-24-crown-8 dissolves when warmed in ethanol, and crystals of composition $C_{29}H_{32}O_8$,2KCNS are obtained. A higher proportion of ligand did not cause the 1 : 1 complex to form.[9]

Preliminary *X*-ray photographs showed that the crystal system was monoclinic, and the systematic absences ($h0l$ $l = 2n$, $0k0$ $k = 2n$) uniquely determined the space group as $P2_1/c$.

The crystal used for the intensity determination had dimensions 0·30 × 0·16 × 0·10 mm. It was set up on a Picker four-circle diffractometer, using the accurately centred positions of 15 reflections, having an average 2θ value of 21°, which were used to refine the cell constants and orientation angles. Intensities were measured by the 2θ—θ scan procedure at a scan rate of 0·5° $min^{-1}$ from $2\theta_{calc}(K_{\alpha1}) - 0{\cdot}5°$ to $2\theta_{calc}(K_{\alpha2})$ 0·5°. Background counts for 25 s each were made at the ends of each scan. Zirconium-filtered molybdenum radiation was used throughout, with attenuators; intensities were monitored using a scintillation counter with pulse-height discrimination. Reflections were measured out to 2θ 45°, and the intensities of three standard reflections [1,3,4, 3,3,$\bar{4}$, and 5,2,1] were measured every 50 reflections and used to put the observations on a common scale. Intensities were corrected for Lorentz and polarisation effects. Reflections for which $I \leqslant 2\sigma(I)$ were removed from the data set. The photographs showed that the crystal quality was not ideal; each reflection was accompanied by a twinned diffuse trail. Because of this, a further 134 reflections were removed from the data set when one background count was more than twice the other, leaving a final total of 1184 reflections which were used in the analysis.

*Crystal Data.*—$C_{24}H_{32}O_8$,2KSCN, $M$ = 642·88, Monoclinic, $a$ = 9·902(8), $b$ = 18·55(4), $c$ = 8·572(8) Å, β = 106·90(2)°, $U$ = 1506·8 Å$^3$, $D_m$ = 1·45, $Z$ = 2, $D_c$ = 1·42, $F(000)$ = 672. Space group $P2_1/c$ ($C^5_{2h}$, No. 14). Mo-$K_\alpha$ radiation, $\lambda(K_{\alpha1})$ 0·7093, $\lambda(K_{\alpha2})$ 0·7135 Å; $\mu$(Mo-$K_\alpha$) =

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5·0 cm$^{-1}$. No correction for absorption was made. One formula unit is centrosymmetric.

The Patterson vector map was readily solved for the $K^+$ ion, and the co-ordinates of all the remaining atoms, *i.e.* those of one thiocyanate ion and of half a macrocyclic ether, excluding hydrogen atoms, were found from two subsequent Fourier syntheses. The first electron-density map phased from potassium only ($R$ 0·53) enabled location of 17 of the 20 non-hydrogen atoms. The second Fourier synthesis revealed the remaining three carbon atoms; the molecular structure with the designations of the atoms is shown in Figure 1. The atomic co-ordinates, isotropic vibration parameters, and an overall scale factor were refined by use of block-diagonal least-squares, with unit weights and scattering factors from ref. 10. In three cycles $R$ was reduced to 0·20. Weighting schemes were of the form: $\sqrt{w} = 1/(P_1 + P_2|F_o| + P_3|F_o|^2 + P_4|F_o|^3 + P_5|F_o|^4)^{\frac{1}{2}}$, where the parameters $P_i$ were adjusted by computer programmes.[11b] The positions of the hydrogen atoms were first calculated, but later found on a difference-Fourier map at $R$ 0·09. Their positional parameters were refined, but a fixed value of $B_{iso}$ was assigned. Scattering factors for hydrogen were taken from ref. 12. Full-matrix least-squares refinement finalised $R$ at 0·079, and $R'$ at 0·10 with $P_1$ 2·122, $P_2$ 0·021, and $P_3$ 0·0038 $\{R' = [\Sigma w\Delta^2/\Sigma(wF_o)^2]^{\frac{1}{2}}\}$.

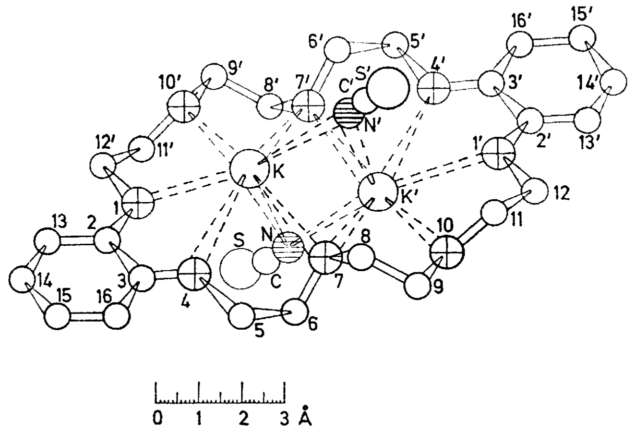

FIGURE 1 One molecule of the complex. Atoms with primes are centrosymmetrically related to those without. Oxygen atoms are marked with a cross, and nitrogen atoms are hatched

Final parameters are given in Table 1 with standard deviations in parentheses. Calculated and observed structure factors are listed in Supplementary Publication No. SUP 20830 (15 pp., 1 microfiche).*

The statistical validity of the least-squares refinement was checked by a weighting analysis to ensure that the average value of $w\Delta F^2$ was the same for various ranges of $|F_o|$ and of sin θ/λ. The analysis of the weighting scheme is shown in Table 2.

Computation was carried out initially on an IBM 1130

TABLE 1

(*a*) Fractional atomic co-ordinates (×10$^4$) with estimated standard deviations in parentheses

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| K | 433(2) | 868(1) | −328(2) |
| S | −3486(3) | 934(2) | 2502(2) |
| N | −1064(9) | 386(5) | 1911(11) |
| C | −2069(10) | 628(5) | 2196(11) |
| O(1) | 207(6) | 2253(3) | 648(7) |
| O(4) | 2120(6) | 1473(3) | 2544(7) |
| O(7) | 2193(6) | −87(4) | 2099(6) |
| O(10) | 1962(6) | −1674(4) | 2031(7) |

(*b*) Anisotropic vibration parameters (×10$^4$) Å$^2$ of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}kha^*b^* + U_{22}k^2b^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + U_{33}l^2c^{*2})]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| K | 413(11) | 518(12) | 444(12) | 38(9) | 54(9) | −23(9) |
| S | 455(15) | 825(20) | 495(15) | 83(13) | 159(12) | 9(12) |
| C | 447(56) | 544(60) | 424(50) | −83(46) | 40(45) | −77(40) |
| N | 483(49) | 803(65) | 726(56) | 25(47) | 160(44) | −134(50) |
| O(1) | 415(33) | 555(39) | 580(36) | 59(28) | 8(28) | 11(30) |
| O(4) | 476(34) | 545(39) | 487(34) | −2(29) | −43(28) | 47(28) |
| O(7) | 522(35) | 693(42) | 351(30) | 90(31) | 58(27) | 3(27) |
| O(10) | 430(35) | 677(43) | 499(35) | −45(29) | 126(29) | 86(31) |

(*c*) Fractional atomic co-ordinates and isotropic vibration parameters (×10$^4$). Hydrogen atoms are numbered according to the carbon atoms to which they are bonded

| | $x/a$ | $y/b$ | $z/c$ | $U$/Å$^2$ |
|---|---|---|---|---|
| C(2) | 1336(9) | 2640(5) | 1623(10) | 424(20) |
| C(3) | 2370(9) | 2181(5) | 2655(11) | 463(22) |
| C(5) | 3099(11) | 999(5) | 3681(12) | 509(23) |
| C(6) | 2410(11) | 284(5) | 3620(11) | 503(23) |
| C(8) | 3342(10) | −572(6) | 2138(13) | 497(23) |
| C(9) | 3202(12) | −1267(6) | 2855(13) | 518(24) |
| C(11) | 2216(10) | −2175(6) | 918(12) | 513(23) |
| C(12) | 972(10) | −2680(6) | 331(13) | 496(23) |
| C(13) | 1508(11) | 3355(6) | 1670(12) | 542(24) |
| C(14) | 2712(17) | 3682(7) | 2745(20) | 742(32) |
| C(15) | 3672(12) | 3256(6) | 3748(12) | 580(25) |
| C(16) | 3560(11) | 2541(6) | 3718(13) | 631(27) |
| H(5A) | 4065(93) | 1037(46) | 3281(102) | 594(—) |
| H(5B) | 3252(97) | 1220(54) | 5101(111) | |
| H(6A) | 2936(96) | −100(52) | 4706(115) | |
| H(6B) | 1740(109) | 426(55) | 3861(114) | |
| H(8A) | 3443(100) | −620(53) | 1233(132) | |
| H(8B) | 4256(101) | −303(53) | 2782(110) | |
| H(9A) | 3847(119) | −1479(56) | 2876(115) | |
| H(9B) | 2861(104) | −1182(56) | 3669(126) | |
| H(11A) | 2377(102) | −1846(54) | 2(115) | |
| H(11B) | 2978(99) | −2597(52) | 1387(115) | |
| H(12A) | 1073(104) | −3010(58) | −618(120) | |
| H(12B) | 666(98) | −2877(53) | 1175(119) | |
| H(13) | 841(100) | 3726(55) | 986(116) | |
| H(14) | 2510(136) | 3979(69) | 2708(157) | |
| H(15) | 4613(110) | 3352(52) | 4406(111) | |
| H(16) | 4248(100) | 2135(54) | 4259(114) | |

TABLE 2

Analysis of computed weighting scheme

| Av. $\lvert F_o\rvert$ | $R$ | Av. $w$ $(\Delta F)^2$ | sin θ/λ | Av. $\lvert F_o\rvert$ | $R$ | Av. $w$ $(\Delta F)^2$ |
|---|---|---|---|---|---|---|
| 6·19 | 0·18 | 0·82 | 0·258 | 40·73 | 0·08 | 1·20 |
| 7·61 | 0·15 | 1·13 | 0·325 | 26·21 | 0·07 | 0·86 |
| 9·32 | 0·10 | 0·47 | 0·373 | 19·49 | 0·07 | 0·68 |
| 11·05 | 0·11 | 1·06 | 0·410 | 16·04 | 0·09 | 1·02 |
| 13·25 | 0·09 | 0·77 | 0·442 | 17·10 | 0·08 | 0·76 |
| 15·74 | 0·08 | 0·75 | 0·470 | 14·13 | 0·09 | 0·91 |
| 18·94 | 0·07 | 0·64 | 0·494 | 11·56 | 0·10 | 0·68 |
| 24·32 | 0·07 | 0·92 | 0·517 | 11·54 | 0·11 | 0·76 |
| 32·71 | 0·07 | 1·11 | 0·538 | 10·40 | 0·13 | 1·09 |
| 58·62 | 0·07 | 1·24 | 0·558 | 7·67 | 0·19 | 1·60 |

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[10] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[11] (*a*) P. R. Mallinson and M. R. Truter, *J.C.S. Perkin II*, 1972, 1818; (*b*) see ref. 15 of ref. 11; (*c*) see ref. 16 of ref. 11.

[12] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

computer with programmes of the *X*-Ray ARC system.[11b] Final refinement was carried out on the University College IBM 360/65I system.[11c] Bond lengths and angles and some significant non-bonding distances are shown in Table 3, and torsion angles for this ligand in Table 4. Table 5 gives the environment of the $K^+$ ion, and Table 6 shows planes through various groups of atoms.

TABLE 3

Bond lengths (Å) and bond angles (°) in the complexed ligand, with estimated standard deviations in parentheses

(*a*) Bonding distances

(i) Benzene ring

| | | | |
|---|---|---|---|
| C(2)–C(3) | 1·43(1) | C(15)–C(14) | 1·34(2) |
| C(3)–C(16) | 1·43(1) | C(14)–C(13) | 1·41(2) |
| C(16)–C(15) | 1·33(2) | C(13)–C(2) | 1·34(2) |

(ii) Ligand

| | | | |
|---|---|---|---|
| C(12′)–O(1) | 1·46(1) | C(6)–H(6B) | 0·8(1) |
| O(1)–C(2) | 1·39(1) | C(8)–H(8A) | 0·8(1) |
| C(3)–O(4) | 1·33(1) | C(8)–H(8B) | 1·0(1) |
| O(4)–C(5) | 1·45(1) | C(9)–H(9A) | 0·8(1) |
| C(5)–C(6) | 1·49(1) | C(9)–H(9B) | 0·9(1) |
| C(6)–O(7) | 1·43(1) | C(11)–H(11A) | 1·0(1) |
| O(7)–C(8) | 1·44(1) | C(11)–H(11B) | 1·1(1) |
| C(8)–C(9) | 1·45(2) | C(12)–H(12A) | 0·9(1) |
| C(9)–O(10) | 1·44(1) | C(12)–H(12B) | 0·9(1) |
| O(10)–C(11) | 1·41(1) | C(13)–H(13) | 1·0(1) |
| C(11)–C(12) | 1·51(1) | C(14)–H(14) | 0·4(1) |
| C(5)–H(5A) | 1·1(1) | C(15)–H(15) | 1·0(1) |
| C(5)–H(5B) | 1·2(1) | C(16)–H(16) | 1·0(1) |
| C(6)–H(6A) | 1·2(1) | | |

(*b*) Non-bonding ligand distances

| | | | |
|---|---|---|---|
| O(1) · · · C(3) | 2·33(1) | C(5) · · · O(7) | 2·44(1) |
| O(1) · · · O(4) | 2·55(1) | C(5) · · · C(16) | 2·89(1) |
| O(1) · · · C(13) | 2·44(1) | | |
| | | C(8) · · · O(10) | 2·44(1) |
| O(4) · · · C(6) | 2·38(1) | | |
| O(4) · · · O(7) | 2·92(1) | C(3) · · · C(5) | 2·39(1) |
| O(4) · · · C(16) | 2·48(1) | C(3) · · · C(13) | 2·40(1) |
| | | C(3) · · · C(14) | 2·80(1) |
| O(7) · · · C(9) | 2·42(1) | C(3) · · · C(15) | 2·41(1) |
| O(7) · · · O(10) | 2·96(1) | | |
| | | C(6) · · · C(8) | 2·38(1) |
| C(2) · · · O(4) | 2·35(1) | C(6) · · · C(9) | 3·10(1) |
| C(2) · · · C(14) | 2·40(1) | | |
| C(2) · · · C(15) | 2·74(1) | C(9) · · · C(11) | 2·37(1) |
| C(2) · · · C(16) | 2·41(1) | O(10) · · · O(1′) | 2·86(1) |

(*c*) Bond angles in the ligand

(i) Benzene ring

| | | | |
|---|---|---|---|
| C(2)–C(3)–C(16) | 115·2(9) | C(14)–C(15)–C(16) | 122·4(12) |
| C(3)–C(2)–C(13) | 120·9(8) | C(13)–C(14)–C(15) | 118·2(13) |
| C(3)–C(16)–C(15) | 121·9(10) | | |

(ii) Carbon angles

| | | | |
|---|---|---|---|
| O(4)–C(5)–C(6) | 107·9(9) | C(8)–C(9)–O(10) | 115·6(9) |
| C(5)–C(6)–O(7) | 114·0(8) | O(10)–C(11)–C(12) | 110·2(8) |
| O(7)–C(8)–C(9) | 113·0(9) | C(11)–C(12)–O(1′) | 107·3(8) |

(iii) Oxygen angles

| | | | |
|---|---|---|---|
| C(3)–O(4)–C(5) | 118·3(7) | O(4)–C(3)–C(16) | 127·3(8) |
| C(6)–O(7)–C(8) | 111·6(7) | O(1)–C(2)–C(13) | 127·3(8) |
| C(9)–O(10)–C(11) | 113·6(7) | C(2)–C(3)–O(4) | 117·4(8) |
| C(12)–O(1′)–C(2′) | 116·0(7) | C(3)–C(2)–O(1) | 111·9(7) |

TABLE 4

Torsion angles (°) for the complexed ligand system

| | | | |
|---|---|---|---|
| C(11)–C(12)–O(1′)–C(2′) | −165 | C(3)–O(4)–C(5)–C(6) | −165 |
| C(12)–O(1′)–C(2′)–C(3) | 174 | C(2)–C(3)–O(4)–C(5) | 175 |
| O(10)–C(11)–C(12)–O(1′) | −68 | O(1)–C(2)–C(3)–O(4) | 0 |
| C(9)–O(10)–C(11)–C(12) | −169 | C(13)–C(2)–C(3)–C(16) | −1 |
| C(8)–C(9)–O(10)–C(11) | −95 | C(14)–C(13)–C(2)–C(3) | 0 |
| O(7)–C(8)–C(9)–O(10) | −61 | C(15)–C(14)–C(13)–C(2) | 1 |
| C(6)–O(7)–C(8)–C(9) | −84 | C(16)–C(15)–C(14)–C(13) | −3 |
| C(5)–C(6)–O(7)–C(8) | −94 | C(3)–C(16)–C(15)–C(14) | 3 |
| O(4)–C(5)–C(6)–O(7) | −67 | C(2)–C(3)–C(16)–C(15) | −1 |

TABLE 5

Environment of the potassium and isothiocyanate ions

(*a*) Bond distances (Å)

| | | | |
|---|---|---|---|
| K–O(1) | 2·732(6) | K–N′ | 2·87(1) |
| K–O(4) | 2·778(6) | N–C | 1·18(1) |
| K–O(7) | 2·898(6) | S–C | 1·60(1) |
| K–O(7′) | 2·979(6) | N–S | 2·78(1) |
| K–O(10′) | 2·825(6) | | |
| | | K–C(13*) | 3·38(2) |
| K · · · K′ | 3·41(1) | K–C(14*) | 3·27(1) |
| K–N | 2·88(1) | | |

(*b*) Bond angles (°)

| | | | |
|---|---|---|---|
| O(1)–K–O(4) | 55·27(19) | O(1)–K–C(13*) | 84·48(22) |
| O(4)–K–O(7) | 61·95(18) | O(1)–K–C(14*) | 92·55(22) |
| O(7′)–K–O(7) | 108·80(18) | O(10′)–K–C(13*) | 77·53(24) |
| O(7′)–K–O(10′) | 60·93(17) | O(10′)–K–C(14*) | 101·71(22) |
| O(10′)–K–O(1) | 61·74(18) | | |
| | | K–O(7)–K′ | 71·20(24) |
| N′–K–C(13*) | 73·93(23) | K–N–K′ | 73·04(30) |
| N′–K–C(14*) | 62·06(32) | K–N–C | 136·29(30) |
| | | K′–N–C | 130·27(30) |
| O(4)–K–C(13*) | 105·12(22) | N–C–S | 177·00(81) |
| O(4)–K–C(14*) | 91·08(31) | | |

Unprimed atoms are at $x, y, z$ as in Table 1, primed atoms at $-x, -y, -z$, and asterisked atoms at $x, \frac{1}{2} - y, -\frac{1}{2} + z$.

TABLE 6

Planes through various groups of atoms. Equations are in the form $lX + mY + nZ = P$ where $X$ is along the $a$ axis, $Y$ in the $ab$ plane, and $Z$ along the $c^*$ axis. Deviations of the atoms are $\times 10^3$ Å and are given in square brackets

(i) Benzene rings *

Plane (1): $0{\cdot}715X - 0{\cdot}058Y - 0{\cdot}697Z = -0{\cdot}552$
Plane (2): $0{\cdot}715X - 0{\cdot}058Y - 0{\cdot}697Z = +0{\cdot}552$
Plane (3): $0{\cdot}715X + 0{\cdot}058Y - 0{\cdot}697Z = -3{\cdot}760$
[C(2) −5(9), C(3) 2(9), C(13) 4(10), C(14) 14(17), C(15) −13(11), C(16) 8(11)]

(ii) Ligand oxygen atoms: O(1,4,7,10,1′,4′,7′,10′)

Plane (4): $0{\cdot}770X - 0{\cdot}059Y - 0{\cdot}635Z = 4{\cdot}112$
[O(1) −55(6), O(4) 31(6), O(7) 170(6), O(10) −131(6), O(1′) 55(6), O(4′) −31(6), O(7′) −170(6), O(10′) 131(6), C(2) 153(9), C(3) 155(9), C(5) −149(10), C(6) −709(11), C(8) 963(11), C(9) 270(12), C(11) 799(10), C(12) 214(11), K 661(2)]

(iii) Potassium bridge: K, N, K′

Plane (5): $-0{\cdot}689X + 0{\cdot}098Y - 0{\cdot}718Z = 0$

(iv) Potassium bridge: K, O(7), K′

Plane (6): $0{\cdot}668X - 0{\cdot}324Y - 0{\cdot}670Z = 0$

(v) Angles (°) between normals to planes

(1)–(4) 4·7 (5)–(6) 90·6 (1)–(3) 6·5

* Planes (1) and (2) are benzene rings in the molecule centred at 000, plane (3) is π-bonded to potassium.

## DISCUSSION

Dibenzo-24-crown-8 is a ligand intermediate in size between dibenzo-18-crown-6 and dibenzo-30-crown-10. The eighteen-membered ring has been shown by stability-constant measurements [13,14] to be the optimum size for the uptake of $K^+$, whereas the largest ligand, whose complex structure with potassium iodide has been determined by *X*-ray crystallographic methods,[15] has been shown to wrap around the $K^+$ ion ' like the seam of a tennis ball.' [16] With a ligand too large for formation of a 1 : 1 complex and insufficiently flexible to wrap around, the 2 : 1 complex forms, even in the presence of excess of ligand.

In the ligand the mean aliphatic C–C distance is 1·48, the benzene ring C–C is 1·38, and the C–O distance is 1·42 Å. These values are the same as those found in other polyether complexes of this type.[1,17-19] The C–O and aromatic C–C bond lengths are normal but the aliphatic C–C bonds are apparently shortened; this effect has been ascribed [20] to overweighting of planes at low $\sin\theta/\lambda$ but our weighting analysis (Table 2) does not support this explanation.

The torsion angles (Table 4) correspond to the observations made with other cyclic polyethers,[15,17-19] that the torsion angles about the aliphatic C–C bonds are *ca.* 60° confirming the *gauche* configuration. The difference in conformation, compared with that of other planar cyclic polyethers, is found in the deviation from the usual [17,18] C–C–O–C torsion angles often being close to 180°. In this complex, the angles about C(9)–O(10), C(8)–O(7), and C(6)–O(7) are *ca.* 90°.

The environment of the $K^+$ ion is shown in Table 5 and Figure 2. The K–O bond distances range from 2·732 to 2·979(6), compared with 2·850—2·931(6) in the dibenzo-30-crown-10 complex [15] and 2·777—2·955(8) Å in the (benzo-15-crown-5)$_2$K$^+$ complex.[11]

In the other complexes the metal is completely enclosed by ten oxygen atoms. In this present complex it is available for interaction with anion and solvent, or, as in the crystal, another source of electron density. The angles subtended at potassium are in the range 55—65°, as is usual,[1,15] for the adjacent pairs O(7)–O(4)–O(1)–O(10′)–O(7′) and that for the catechol groups is smaller than the others. For O(7)–K–O(7′) however, the angle is 108·8°, while the angle subtended at oxygen K–O(7)–K′ is less than that to be expected on the basis of a lone pair of electrons directed towards each potassium.

The bonding of oxygen atoms to metal ions, in cyclic polyethers, has been discussed in some detail.[1] Table 7 shows the deviations of the O $\rightarrow$ K directions from those expected for either one of two lone-pairs of electrons completing a tetrahedron about the oxygen or a lone-pair of electrons along the bisector of the C–O–C bond, designated trigonal. The intermediate situation is found in all cases except for O(10)–K, which is almost tetrahedral.

The O(7)–K′ bond, although intermediate between tetrahedral and trigonal, forms a bond type commonly found in other cyclic polyethers. The other half of the bridge [K–O(7)] forms angles which have not been found previously. The estimated lone-pair plane misses the $K^+$ atom by 1·6 Å, compared with an out-of-plane deviation of <0·5 Å found in all other cases. It may be possible to conclude from this that O(7) is bonding more strongly to one $K^+$ than the other, *i.e.* that the bridge is not even, although K–O(7) is the shorter of the two bonds, and may thus compensate by greater electrostatic interaction.

TABLE 7

Deviations (deg.) from calculated direction of lone pairs

| | Tetrahedral (1) | Tetrahedral (2) | Trigonal | Bond class * |
|---|---|---|---|---|
| O(1) | 72·7 | 36·4 | 18·5 | Int. (1) |
| O(4) | 72·8 | 36·2 | 18·4 | Int. (1) |
| O(7)–K | 82·0 | 31·2 | 31·0 | |
| O(7)–K′ | 94·0 | 18·1 | 40·7 | Int. (3) |
| O(10) | 102·8 | 8·0 | 48·6 | Tet. |

* For definition of intermediate class types see ref. 1; int = intermediate, tet = tetrahedral.

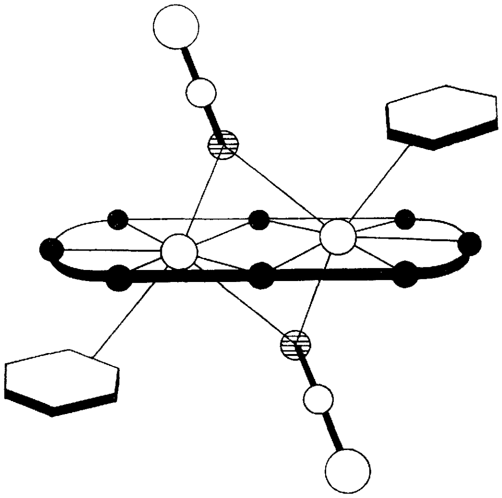

FIGURE 2 Diagrammatic representation of the co-ordination about the K+ ions. The plane of the ligand ring shows only oxygen atoms. The benzene rings belong to two other ligand molecules in the crystal

Figure 2 also shows the positions of aromatic carbon atoms, at 3·27 and 3·37 Å, forming another electrostatic contact for the $K^+$ ion. This type of contact is very

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[13] R. M. Izatt, J. H. Rytting, D. P. Nelson, B. L. Haymore, and J. J. Christensen, *Science*, 1969, **164**, 443; *J. Amer. Chem. Soc.*, 1971, **93**, 1619.

[14] H. K. Frensdorff, *J. Amer. Chem. Soc.*, 1971, **93**, 600.

[15] M. A. Bush and M. R. Truter, *J.C.S. Perkin II*, 1972, 345.

[16] M. Dobler, J. D. Dunitz, and B. T. Kilbourn, *Helv. Chim. Acta*, 1969, **52**, 2573.

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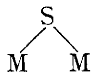
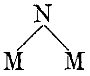
[20] J. D. Dunitz and P. Seiler, *Acta Cryst.*, 1973, **B29**, 589.

common for Group Ib metals. A series of aromatic interactions to Ag$^+$ has been reported[21] at shorter distances than aromatic interactions to K$^+$ (*e.g.* 2·44—2·51 Å), including the silver salt of the antibiotic X-537A.[22] The mercury(II)-aromatic bond (3·6 Å) in the benzene solvate of hexathiocyanatomercuriocobalt-(II)[23] is longer than the value for K in the present complex. In all these examples there is the same geometrical relation of the metal to the aromatic ring.

The mode of bonding of the thiocyanate ion is a novel feature of this compound. The i.r. spectrum showed a band at 2058 cm$^{-1}$, which was consistent with either 'free' ionic or nitrogen-bonded NCS. Nitrogen would be expected to bond to class (*a*) metals, sulphur to class (*b*) metals;[24] in intermediate cases bonding of the type M–S–C–N–M′ is known.[25] Sulphur-bridging of the type  has been confirmed,[23,26] but authentication of the postulated[25]  is very recent.[6] There seems to be no other interaction between K$^+$ and the isothiocyanate group. The closest approach of K$^+$ to S is 4·0 Å, and π-electron interaction with the metal as postulated in ref. 27 is unlikely.

The two potassium ions are quadruply bridged, the K–N–K′ bridges being perpendicular (within 0·6°) to the K–O–K′ bridges and the thiocyanate ion 52° to the normal to the K–N–K′ plane. A pair of potassium ions bridged by one oxygen and one thiocyanate nitrogen has been reported for the 1 : 1 adduct of potassium thiocyanate and bis(pyridine-2-carboxylato)copper(II).[28] In the adduct the K$^+$ and NCS$^-$ ions lie in a crystallographic plane of symmetry, the angles around nitrogen are C–N–K 167, C–N–K′ 100, and K–N–K′ 93°, and the distances N–K 2·839 and N–K′ 2·997 Å. A thiocyanate nitrogen has been found as the only bridging atom in a bis(ethylenediamine)thiocyanatocopper(II) perchlorate;[29] the thiocyanate ion is 57° to the normal to the Cu–N–Cu′ plane and C–N–Cu is 97°. The variety of C–N–M angles (*cf.* 130° in Table 5) in all three compounds is consistent with the constant value of ν(CN) in the i.r. spectrum, suggesting electrostatic, not covalent, interaction.

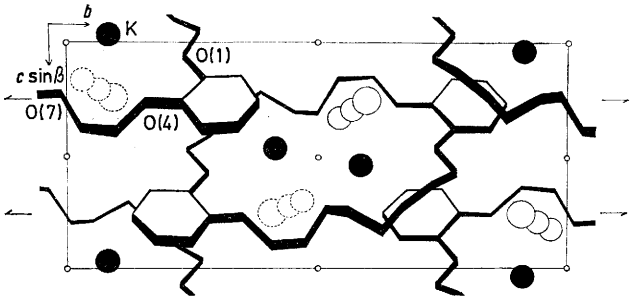


FIGURE 3 Packing of structure in the crystal, with the *a* axis, towards the reader in a left-handed system of axes

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