Preparation and Crystal Structure of a Binuclear Complex of Potassium with one Molecule of Cyclic Polyether: Bis(potassium thiocyanate)dibenzo-24-crown-8

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Summary Reaction between potassium thiocyanate and 2,3,14,15-dibenzo-1,4,7,10,13,16,19,22-octaoxocyclotetracosa-2,14-diene gives a 2:1 complex shown by crystal structure analysis to be centrosymmetrical with two potassium ions each positioned among eight sources of electron density, namely, two nitrogen atoms of bridging thiocyanate groups, five oxygen atoms of the cyclic ether (two of the eight oxygen atoms are shared) and two carbon atoms of a benzene ring.

IN continuation of our investigations[1] of macrocyclic ethers,[2] model "carrier" molecules for alkali metals, we now report a novel complex in which two potassium ions are attached to one cyclic ether ligand. Other new features are N-bridging by the thiocyanate ion, like that of NCO in silver cyanate,[3] and close approach of an aromatic bond to potassium. 2:1 complexes of Ni have recently been reported with octadentate cyclic ligands containing nitrogen[4] and sulphur[5] as donor atoms. No structure determinations are available, and postulated structures do not include the possibility of donor atom sharing, as has been found here.

The macrocyclic ether (**I**) dibenzo-24-crown-8 (named systematically in the summary) contains 8 oxygen atoms in a 24-atom ring. A mixture of a potassium salt, KX, with (**I**) will dissolve when warmed in ethanol, if X=Br, I or NCS. Crystals of composition $(KNCS)_2$(**I**) can be obtained but no potassium bromide or iodide complex crystallises out. A higher proportion of (**I**) in the starting mixture yields crystals of the 2:1 complex and of (**I**).

In the i.r. spectrum changes in the 900—1000 cm^{-1} region for the cyclic ether are found on formation of the complexes. For the thiocyanate there is a sharp band at 2058 cm^{-1} in the complex and the identifiable lines are consistent with either ionic or N-bonded thiocyanate. An *X*-ray crystal structure analysis has established the stereochemistry of the complex.

Crystal data $C_{24}H_{32}O_8,2KNCS$. $M = 642{\cdot}9$, m.p. (decomp.) 131—132°, monoclinic, $a = 9{\cdot}902$, $b = 18{\cdot}55$, $c = 8{\cdot}57$ Å, $\beta = 106{\cdot}0°$, $Z = 2$; Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å. Space group $P2_1/c$, formula unit requires a centre of symmetry. 1277 diffractometer observations, current R value 0·09.

The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares with anisotropic vibration parameters for the potassium, sulphur, and oxygen atoms and isotropic parameters for the other non-hydrogen atoms.

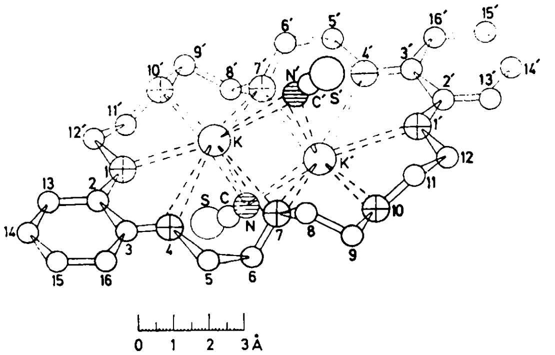

FIGURE 1. *One molecule of the complex. Atoms with primes are centrosymmetrically related to those without.* ○ = *carbon,* ⊜ = *oxygen.*

Figure 1 shows one centrosymmetrical molecule of the complex. The ether oxygen atoms are approximately coplanar and each potassium ion is co-ordinated by five of them, at distances ranging from 2·74 to 3·01 Å (± 0·01 Å); O(7) and O(7′) are shared by both potassium ions. The potassium ions are also bridged by nitrogen atoms of the thiocyanate ions with K–N distances 2·84 and 2·89 (±0·015) Å; the K–N–C angles are 130° and 137° and the K–N–K′ angle is 73°.

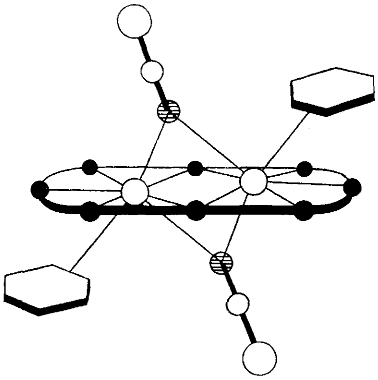

FIGURE 2. *Diagrammatic representation of the co-ordination about the* K⁺ *ions. The plane of the ligand ring shows only oxygen atoms. The benzene rings belong to two other ligand molecules in the crystal.*

In Figure 2 the co-ordination about the potassium ions, which are 3·8 Å apart, is depicted; in addition to the two nitrogen and five oxygen atoms there are two carbon atoms at 3·27 and 3·37 (±0·02) Å so the aromatic bond forms an eighth contact for the cation. This contact is longer than the Ag–C (aromatic) in the silver salt of the antibiotic X-537A,[6] but shorter than the Hg–C (aromatic) in the benzene solvate of hexathiocyanatocobalt(II)-dimercury(II);[7] all three compounds have the metal in similar geometrical relation to the benzene ring.

Naturally-occurring antibiotics which affect ion transport through membranes appear to form 1 : 1 complexes with the ions. The stoicheiometry of one natural transport system is that three sodium ions and two potassium ions move in opposite directions for every molecule of adenosine triphosphate hydrolysed. Our work suggests the possibility of carrier molecules for more than one cation.

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