Alkali and Alkaline-earth Metal Complexes of 4′-Acetobenzo-crown Ethers. Crystal and Molecular Structure of (18-Acetyl-2,3,5,6,8,9,11,12,-14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclo-octadecin)diperchloratostrontium

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Alkali and alkaline-earth metal complexes of 4′-acetobenzo-15-crown-5 and 4′-acetobenzo-18-crown-6 have been prepared and characterised by i.r. and n.m.r. spectroscopy. The crystal and molecular structure of 4′-acetobenzo-18-crown-6·Sr[ClO$_4$]$_2$ (the title complex) has been determined. No intermolecular interaction between the metal ion and the aceto-group has been observed. The reaction of several metal salts with 4′-(bromoaceto)benzo-15-crown-5 gives rise to internal nucleophilic displacement of the bromine by the anion to yield novel crown ethers.

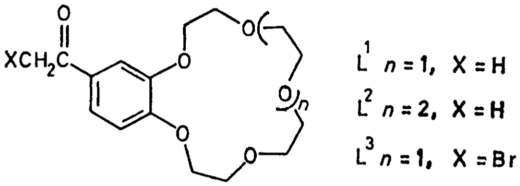
THE co-ordination chemistry of the alkali and alkaline-earth metal cations has been extensively studied [1] since the initial discovery [2] of the cyclic polyethers. The nature and stability of the complexes formed in the crystalline state and in solution has been shown to be dependent upon such factors as the size of the cation and polyether ring cavity, the nature of the anion of the solvent, and the type of substituent present on the polyether ring. Crown polyethers have been used to activate anions through complexation reactions with a metal salt. The co-ordination of the ligand to the metal cation generates the so called 'naked' anions [3] with accompanying enhancement of nucleophilic reactivity, and a wide range of anions, *e.g.* Br$^-$, F$^-$, CN$^-$, O$_2^-$, and CH$_3$COO$^-$, has been used in substitution reactions.[4]

In this paper we report the complexing properties of aceto-substituted benzo-crown ethers towards alkali and alkaline-earth metal perchlorates and thiocyanates, together with the crystal structure of 4′-acetobenzo-18-crown-6·Sr[ClO$_4$]$_2$. We also show that alkali and alkaline-earth metal complexes of 4′-(bromoaceto)benzo-15-crown-5 can act as 'self-reagents' by their ability to liberate reactive nucleophiles which will replace bromine and so generate bifunctional crown ethers of further synthetic value. The nomenclature used throughout this work for cyclic polyethers is based on that originally defined by Pedersen.[2]

EXPERIMENTAL

The polyethers, 4′-acetobenzo-15-crown-5 (L^1), 4′-acetobenzo-18-crown-6 (L^2), and 4′-(bromoaceto)benzo-15-crown-5 (L^3), were prepared according to literature procedures.[5,6] Calcium thiocyanate was used as a 78% solution in water (K and K Ltd.), and strontium thiocyanate was prepared by mixing aqueous solutions of strontium hydroxide and ammonium thiocyanate in stoicheiometric amounts and evaporating to dryness. The product was washed with ice-cold ethanol and dried over silica gel *in vacuo*.

Infrared spectra were recorded as KBr discs using a Perkin-Elmer 297 spectrometer. Hydrogen-1 n.m.r. spectra were obtained at 100 MHz (Varian HA100) or at 220 MHz (Perkin-Elmer R34). Carbon-13 n.m.r. spectra were recorded at 25.15 MHz (JEOL PFT-100 FT), with ^{1}H noise decoupled. Elemental analyses were carried out by the University of Sheffield Microanalytical Service.



Complexation Reactions of 4′-Acetobenzo-crown Ethers.—The following procedures were adopted to obtain crystalline complexes. The metal salt (0.001 mol) in hot ethanol (20 cm^3) was added to the crown ether (0.001 mol) in hot ethanol (20 cm^3) with stirring. In the reaction with Ba[ClO$_4$]$_2$ with L^2 a white precipitate formed immediately and was filtered off; in the other cases the mixture was filtered hot and left to cool whereupon the complex crystallised out. The crystals were collected, washed with diethyl ether to remove unreacted crown ether, and dried over silica gel *in vacuo*. If no complex crystallised out the solution was reduced in volume and ethyl acetate added to precipitate crystalline solids which were dried *in vacuo*. The analytical data are given in Table 1. **CAUTION:** It must be emphasised that, although we have experienced no problems of detonation, perchlorate complexes should be handled with care.

Reaction of 4′-(Bromoaceto)benzo-15-crown-5.—NaBr *and* KBr *Complexes.* Alkali-metal halide (0.001 mol) was added to a solution of 4′-(bromoaceto)benzo-15-crown-5 (0.001 mol) in ethanol (40 cm^3), and the mixture stirred for 18 h. After filtering, the ethanol was removed under reduced pressure and chloroform (20 cm^3) added to the residual oil. The solution was added dropwise to diethyl ether (100 cm^3) to give a precipitate which was collected. Yields: NaBr complex, 16%; KBr complex, 32% (Found: C, 35.9; H, 4.1; Br, 27.8. Calc. for $C_{16}H_{21}Br_2NaO_6 \cdot 2H_2O$: C, 36.4; H, 4.8; Br, 30.3%. Found: C, 41.5; H, 4.4; Br, 25.6. Calc. for $C_{32}H_{42}Br_3KO_{12}$: C, 42.2; H, 4.7; Br, 26.7%).

Reaction with Ca[NCS]$_2$. Calcium thiocyanate (0.32 g, 78% solution) was added to a solution of 4′-(bromoaceto)-benzo-15-crown-5 (0.62 g) in ethyl acetate (20 cm^3) to give a brown precipitate which was filtered off. Evaporation of

TABLE 1

Analytical data

	Found (%)					Calc. (%)				
	C	H	N	S	Cl	C	H	N	S	Cl
(*a*) Complexes of 4′-acetobenzo-15-crown-5 (L^1)										
$L^1\cdot Li[NCS]$	53.7	6.1	4.2	9.9		54.4	5.9	3.7	8.8	
$L^1\cdot Na[NCS]$	52.5	5.5	3.4	8.5		52.2	5.6	3.5	8.2	
$2L^1\cdot K[NCS]$	55.3	6.1	1.9	4.6		55.2	6.2	1.5	4.5	
$L^1\cdot Mg[NCS]_2$	48.1	5.3	6.2	14.4		47.9	4.4	6.2	14.2	
$L^1\cdot Ca[NCS]_2$	46.5	4.6	5.7	13.6		46.3	4.7	6.0	13.7	
$L^1\cdot Sr[NCS]_2$	42.2	4.3	5.3	8.9 *		42.1	4.3	5.8	12.5	
$L^1\cdot Ba[NCS]_2$	38.0	4.2	4.8	9.9 *		38.3	3.9	4.9	11.4	
$L^1\cdot [NH_4][NCS]$	52.5	6.8	7.1	8.6		52.8	6.8	7.2	8.3	
$L^1\cdot Li[ClO_4]$	46.4	5.3			8.5	46.1	5.3			8.5
$L^1\cdot Na[ClO_4]$	44.6	5.2			8.0	44.4	5.1			8.1
$2L^1\cdot K[ClO_4]$	50.6	5.7			4.7	50.6	5.8			4.7
$L^1\cdot Mg[ClO_4]_2\cdot 2H_2O$	33.7	4.6			12.7	33.7	4.6			12.4
$L^1\cdot Ca[ClO_4]_2$	34.8	4.3			13.0	34.9	4.0			12.9
$2L^1\cdot Sr[ClO_4]_2$	41.6	5.1			7.8	41.9	4.8			7.7
$2L^1\cdot Ba[ClO_4]_2$	40.3	4.3			7.4	40.2	4.6			7.4
(*b*) Complexes of 4′-acetobenzo-18-crown-6 (L^2)										
$L^2\cdot Li[NCS]\cdot H_2O$	51.9	6.6	3.1	7.6		52.2	6.5	3.2	7.3	
$L^2\cdot Na[NCS]\cdot H_2O$	50.2	6.0	3.1	7.5		50.3	6.2	3.1	7.1	
$L^2\cdot K[NCS]$	50.8	5.7	3.1	7.6		50.5	5.8	3.1	7.1	
$L^2\cdot Mg[NCS]_2\cdot H_2O$	46.7	5.8	5.6	12.0		46.8	5.5	5.5	12.5	
$L^2\cdot Ca[NCS]_2$	47.3	5.0	5.2	12.3		47.0	5.1	5.4	12.6	
$L^2\cdot Ba[NCS]_2$	39.3	4.4	4.5	8.1 *		39.5	4.3	4.6	10.6	
$L^2\cdot Li[ClO_4]\cdot H_2O$	45.0	6.3			6.7	45.2	5.9			7.4
$L^2\cdot Na[ClO_4]$	45.1	5.4			6.3	45.3	5.5			7.4
$L^2\cdot K[ClO_4]$	43.7	5.2			7.5	43.9	5.3			7.2
$L^2\cdot Mg[ClO_4]_2\cdot 4H_2O$	33.2	5.2			10.5	33.3	5.3			10.9
$L^2\cdot Ca[ClO_4]_2$	36.5	4.4			11.7	36.4	4.4			11.9
$L^2\cdot Sr[ClO_4]_2$	33.9	4.2			11.1	33.7	4.1			11.1
$L^2\cdot Ba[ClO_4]_2$	31.2	3.5			10.5	31.3	3.8			10.3

* S values are low due to interference of insoluble sulphates.

the filtrate gave an off-white solid. The solid materials were combined, dissolved in distilled water (20 cm^3), and extracted with chloroform. After drying over $Mg[SO_4]$, the chloroform was removed under reduced pressure to give a pale yellow solid. Crystallisation from n-heptane gave 0.30 g (51%) of 4′-(thiocyanatoaceto)benzo-15-crown-5 as a pale yellow solid (m.p. 109—110 °C) (Found: C, 55.8; H, 5.6; N, 3.7; S, 8.9%; $M^{\cdot +}$ 367. Calc. for $C_{17}H_{21}NO_6S$: C, 55.6; H, 5.8; N, 3.8; S, 8.7%; *M* 367). I.r.: 2 170 cm^{-1} (SCN stretch), 1 680 cm^{-1} (CO stretch).

Reaction of potassium thiocyanate with 4′-(bromoaceto)benzo-15-crown-5 in aqueous ethyl acetate gave an 85% yield of 4′-(thiocyanatoaceto)benzo-15-crown-5.

Reaction with potassium phthalimide. Potassium phthalimide (0.15 g) was added to a solution of 4′-(bromoaceto)-benzo-15-crown-5 (0.3 g) in ethyl methyl ketone (20 cm^3). After 24 h stirring, the mixture was filtered and the filtrate evaporated to give a yellow oil. Extraction with ethyl acetate followed by solvent evaporation gave yellow crystals of 4′-(phthalimidoaceto)benzo-15-crown-5 (0.21 g, 58%), m.p. 144—146 °C (Found: C, 63.4; H, 5.7; N, 3.0%; $M^{\cdot +}$ 455. Calc. for $C_{24}H_{25}NO_8$: C, 63.3; H, 5.5; N, 3.1%; *M* 455. I.r.: 1 760, 1 710, and 1 670 cm^{-1} (C=O stretches).

Reaction with potassium kojate (5-*hydroxy*-2-*hydroxymethyl*-4H-*pyran*-4-*onate*). Potassium hydroxide (0.15 g) in distilled water (2 cm^3) was added to a solution of kojic acid (0.37 g) in warm ethanol (20 cm^3) followed by 4′-(bromoaceto)benzo-15-crown-5 (1.0 g) in warm ethanol (10 cm^3). After refluxing for 4 h the mixture was cooled to give a yellow precipitate. Recrystallisation from ethanol gave off-white microcrystals of 2(phenacyl-15-crown-5 koiate)·KBr·2H$_2$O (1.0 g, 87%), m.p. 156—158 °C (Found: C, 47.9; H, 5.2; Br, 7.1%; $M^{\cdot +}$ 450. Calc. for $C_{44}H_{52}BrKO_{20}\cdot 2H_2O$: C, 48.4; H, 5.4; Br, 7.3%; $M(P - KBr\cdot 2H_2O)$ 450). I.r.: 1 680, 1 640, 1 615, and 1 600 cm^{-1} (C=C, C=O stretches).

Crystal Data.—$C_{18}H_{26}Cl_2O_{15}Sr$, $M_r = 640.91$, Triclinic, space group $P\bar{1}$, $a = 17.174(15)$, $b = 9.036(9)$, $c = 19.959(16)$ Å, $\alpha = 87.42(5)$, $\beta = 124.82(7)$, $\gamma = 96.07(5)$°, $U = 2\,528.19$ Å^3, Mo-K_α, $\lambda = 0.710\,69$ Å, $D_m = 1.77$, $Z = 4$, $D_c = 1.75$ Mg m^{-3}, μ(Mo-K_α) = 2.34 mm^{-1}, $F(000) = 1\,304$.

X-*Ray Intensity Measurements.*—Crystal quality was poor and great difficulty was found in selecting a crystal suitable for data collection. Eventually a crystal of approximate dimensions 0.16 × 0.22 × 0.31 mm was mounted with the *a* axis coincident with the ω axis of a Stöe Stadi 2 two-circle diffractometer. Data were collected using monochromated Mo-K_α radiation and the background-ω scan-background technique. Corrections for Lorentz and polarisation effects were applied but no corrections for absorption were made. 2 054 Observed reflections having $I \geqslant 3\sigma(I)$ were used in the subsequent structure analysis.

Structure Determination and Refinement.—Interpretation of a three-dimensional Patterson map on the basis of two independent molecules in the asymmetric unit (*i.e.* space group $P\bar{1}$) readily afforded the positions of the two independent strontium atoms. The perchlorate groups and the non-hydrogen atoms of the macrocyclic ligands were located from successive electron-density maps. High correlation was observed between the refined parameters of the two independent molecules which appeared to be related by a translation of $a/2$. However, the failure to find a higher-symmetry space group and the observation of small yet significant differences in the conformations of the molecules led to continuation of the refinement in $P\bar{1}$. Within each of the macrocyclic ligands, two sets of positions were found for the acetyl group [being attached to C(20) or C(21)] and refinement of a disordered model with 50% occupancy for each acetyl group gave satisfactory thermal parameters. However, geometry calculations showed unrealistically short intermolecular contacts between acetyl oxygen atoms (< 1.5 Å) and refinement was attempted in $P1$. The extent of correlations between all four of the independent molecules was such as to prevent a more satisfactory refinement. In view of the extreme length of computations in $P1$ and the apparent correctness of the centrosymmetric space group for all but the acetyl groups, the final stages of refinement were conducted in $P\bar{1}$ with the acetyl groups being statistically disordered. Scattering factors were calculated using an analytical approxim-

TABLE 2

Final fractional co-ordinates (× 10^4) with estimated standard deviations in parentheses

	Molecule I			Molecule II		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Sr	7 156(2)	7 992(4)	7 115(2)	2 016(2)	7 889(4)	6 838(2)
C(1)	9 501(20)	9 249(32)	8 801(16)	4 167(17)	9 262(29)	8 634(13)
O(2)	9 025(13)	8 032(26)	8 427(12)	3 801(12)	7 978(22)	8 275(10)
C(3)	9 579(19)	6 815(32)	8 402(16)	4 405(18)	7 008(30)	8 333(16)
C(4)	8 916(19)	5 525(33)	7 938(17)	3 796(21)	5 562(33)	7 833(19)
O(5)	8 204(16)	6 005(29)	7 131(14)	3 158(14)	5 934(26)	7 018(13)
C(6)	7 811(19)	4 972(32)	6 519(16)	2 875(17)	4 853(29)	6 384(15)
C(7)	7 141(18)	5 671(31)	5 762(16)	2 301(23)	5 756(35)	5 612(20)
O(8)	6 473(13)	6 320(24)	5 813(11)	1 553(14)	6 314(26)	5 562(12)
C(9)	5 689(20)	7 181(32)	5 007(17)	888(20)	7 188(32)	4 787(17)
C(10)	4 965(19)	7 529(32)	5 125(16)	32(20)	7 182(32)	4 728(16)
O(11)	5 458(13)	8 675(25)	5 819(11)	322(14)	7 924(26)	5 480(12)
C(12)	4 830(18)	9 131(32)	5 987(16)	−464(18)	8 328(32)	5 457(17)
C(13)	5 401(18)	10 020(31)	6 737(15)	−232(20)	8 667(33)	6 240(19)
O(14)	6 099(12)	9 316(24)	7 421(11)	728(13)	9 417(26)	6 784(12)
C(15)	6 517(19)	10 019(32)	8 190(16)	1 000(19)	9 611(32)	7 601(17)
C(16)	7 391(19)	10 869(32)	8 446(16)	1 980(21)	10 773(33)	7 997(18)
O(17)	8 038(13)	9 812(25)	8 500(11)	2 652(12)	9 827(23)	8 091(11)
C(18)	8 984(19)	10 501(32)	8 817(16)	3 613(18)	10 322(30)	8 555(15)
C(19)	9 359(20)	11 729(33)	9 141(17)	3 929(19)	11 708(32)	8 865(16)
C(20)	10 322(20)	12 166(33)	9 440(17)	4 959(20)	12 195(32)	9 334(17)
C(21)	10 843(19)	11 139(32)	9 401(16)	5 490(18)	10 912(31)	9 411(16)
C(22)	10 444(19)	9 645(32)	9 101(16)	5 219(21)	9 550(33)	9 120(17)
C(23A)	11 898(29)	11 556(39)	9 807(25)	6 730(29)	11 275(38)	9 984(25)
C(23B)	10 803(29)	13 666(39)	9 882(26)	5 445(29)	13 516(39)	9 768(25)
O(24A)	12 258(23)	10 570(36)	9 896(20)	7 137(24)	10 311(36)	10 061(21)
O(24B)	10 283(23)	14 434(36)	9 994(21)	4 890(25)	14 413(36)	9 766(21)
C(25A)	12 302(30)	13 318(39)	10 077(27)	6 927(29)	12 893(38)	10 183(26)
C(25B)	11 770(29)	14 244(39)	9 985(26)	6 541(30)	13 900(39)	10 167(27)
Cl(1)	7 928(5)	10 861(12)	6 476(5)	2 986(5)	10 793(13)	6 375(5)
Cl(2)	6 115(7)	5 023(15)	7 587(6)	1 134(6)	5 071(13)	7 527(6)
O(31)	7 928(15)	9 371(27)	6 374(12)	3 200(15)	9 325(27)	6 473(13)
O(32)	7 344(15)	11 542(27)	5 673(12)	2 739(16)	11 285(28)	5 628(13)
O(33)	7 478(13)	11 058(26)	6 895(12)	2 202(14)	10 812(26)	6 435(12)
O(34)	8 838(15)	11 638(28)	6 953(13)	3 818(15)	11 587(27)	7 019(13)
O(41)	7 014(15)	5 988(27)	7 987(13)	1 662(20)	6 618(32)	7 861(17)
O(42)	5 810(15)	5 186(28)	8 088(13)	136(18)	5 094(31)	7 173(17)
O(43)	6 111(17)	3 799(30)	7 237(15)	1 576(22)	3 949(33)	8 064(19)
O(44)	5 448(18)	5 643(30)	6 829(15)	1 123(21)	5 147(33)	6 847(18)

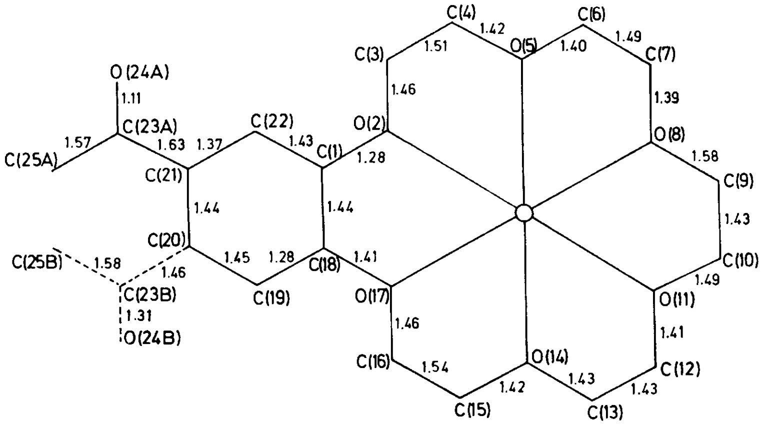


FIGURE 1 Average bond distances (Å) for the two independent macrocyclic ligands in $L^2\cdot Sr[ClO_4]_2$. Estimated standard deviations *ca.* 0.04 Å

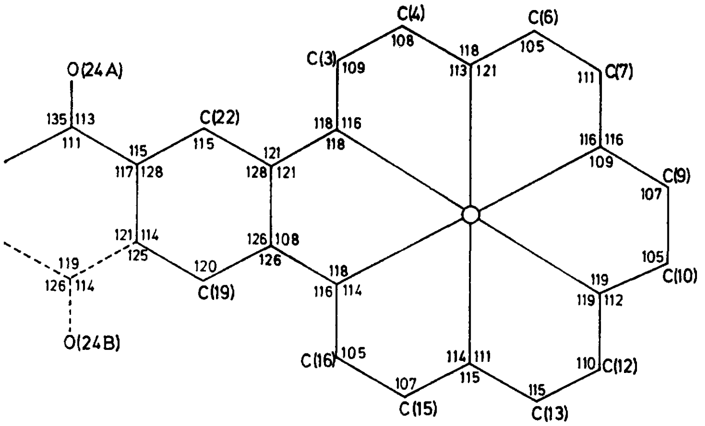


FIGURE 2 Average bond angles (°) for the two independent macrocyclic ligands in $L^2\cdot Sr[ClO_4]_2$. Numbering of atoms is as in Figure 1. Estimated standard deviations *ca.* 2°

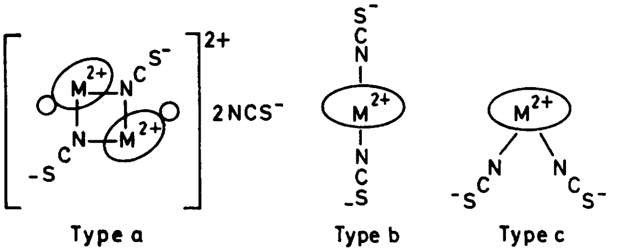
ation [7] and the weighting scheme adopted was $w = 4.1767/[\sigma^2(F_o) + 0.0034(F_o)^2]$. Full-matrix refinement with anisotropic thermal parameters applied to all atoms gave the final $R = 0.103$ and $R' = 0.103$. Final atomic parameters are listed in Table 2; average bond distances and angles for the two independent macrocyclic ligands are given in Figures 1 and 2. Observed and calculated structure factors and thermal parameters have been deposited as Supplementary Publication No. SUP 23174 (13 pp.).*

Structure Calculations.—All calculations, apart from preliminary data processing, were carried out on an IBM 370/165 computer using the SHELX computing package.[8]

RESULTS AND DISCUSSION

In general the stoicheiometries for the alkali and alkaline-earth metal complexes of L^1 and L^2 follow the trends reviewed in the literature.[1] 1 : 1 Complexes are formed between L^2 and all of the cations used, and it is probable that the ligand circumscribes the metal for the smaller cations, and is disposed to one side of the metal as the cation size increases as has been observed for the corresponding complexes of 18-crown-6 and dibenzo-18-crown-6.[9] The complexes of the smaller cations, Li^+ ($r = 0.60$ Å), Na^+ (0.95 Å), and Mg^{2+} (0.65 Å), show retention of water molecules whereas the remaining complexes are dehydrated.

Compound L^1 gives two classes of compounds; 1 : 1 species with Li^+, Na^+, Mg^{2+}, and Ca^{2+} as the cation, and with the thiocyanates of Sr^{2+} and Ba^{2+}, and 2 : 1 complexes with K^+ as the cation, and with the perchlorates of Sr^{2+} and Ba^{2+}. Ionic size and ring-cavity compatibility are of importance in determining the nature of complexes formed with polyethers. With benzo-15-crown-5 it was shown that Mg^{2+} forms only a 1 : 1 complex, whereas only 2 : 1 complexes are isolated for K^+ (1.33 Å), Sr^{2+} (1.13 Å), and Ba^{2+} (1.35 Å). The cations Na^+ and Ca^{2+} were shown to be able to form either 1 : 1 or 2 : 1 complexes.[2,10,11] Calcium forms 1 : 1 complexes when a co-ordinating anion such as thiocyanate is used but a 2 : 1 complex with tetraphenylborate present. Perchlorate complexes of Ca^{2+} have been prepared but not well characterised. These appear to be 2 : 1 with some degree of hydration.[10] The Na^+ ion generally forms 1 : 1 complexes, but from concentrated solution a 2 : 1 perchlorate complex has been recovered.[11] The 1 : 1 complexes formed between L^1 and the thiocyanates of Sr^{2+} and Ba^{2+} would appear to have anomalous stoicheiometry. However, by analogy with the caesium (1.69 Å) complexes of 18-crown-6 [12] and tetramethyldibenzo-18-crown-6 [13] it is possible to postulate that a dimeric species is formed in which the cation sits to one side of the heteroatom ring and two such units are bridged by thiocyanate anions (type a). The i.r. spectrum (see later) does not differentiate between a tetrabridged species, or a dibridged species with two free anions. No crystals suitable for *X*-ray analysis could be grown for these compounds.



Type a Type b Type c

Infrared Spectra.—Relevant i.r. stretching and bending modes for the aceto-group and the thiocyanate and perchlorate anions are listed in Table 3. The CN and CS stretching frequencies have been used to diagnose the mode of thiocyanate bonding [14] in metal complexes, as have the asymmetric Cl–O stretching and bonding frequencies.[15] In the complexes of L^1 and L^2, ligand absorptions obscure the CS stretch and Cl–O stretch; it is however possible to detect the CN stretch and Cl–O bonding frequency.

Much of the evidence for assignment of the bonding modes for thiocyanates has been obtained from transi-

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

tion-metal complexes,[14] *e.g.* CN stretch: *N*-bonded, 2 040—2 080 cm^{-1}; *S*-bonded, 2 080—2 120 cm^{-1}; and ionic NCS$^-$, *ca.* 2 100 cm^{-1}. It has been shown that a simple translation of these assignments to alkaline-earth metal and main-group species can present problems of unambiguous assignment as there is no longer a clear correlation between wavenumber and bonding mode.[16] Nevertheless, certain features emerge from the i.r. spectra. The alkali-metal complexes of L^1 and L^2 show a single CN band at wavenumber varying between 2 055 and 2 100 cm^{-1}; $\mathrm{L^{1}\cdot Mg[NCS]_{2}}$ has a single band at 2 080 cm^{-1}. As these compounds are expected to be ' ionic ' or *N*-bonded by analogy with known structures,[9] *e.g.* benzo-15-crown-5·$\mathrm{Mg[NCS]_{2}}$ has structure type b,[17] the problem of assignment within the literature range is immediately apparent. The remaining alkaline-earth metal complexes show two bands in their complexes with L^1. The crystal structure of benzo-15-crown-5·$\mathrm{Ca[NCS]_{2}\cdot ROH}$ is of structure type c;[17] the i.r. spectrum shows two bands at 2 080 and 2 100 cm^{-1} attributable to an asymmetry in the co-ordination geometry. Structure type c is therefore proposed, by analogy, for $\mathrm{L^{1}\cdot Ca[NCS]_{2}}$. As has been noted earlier, the i.r. evidence is not incompatible with the proposal of structure type a for $\mathrm{L^{1}\cdot Sr[NCS]_{2}}$ and $\mathrm{L^{1}\cdot Ba[NCS]_{2}}$ as two bands are discerned for the CN stretch. The alkaline-earth metal thiocyanate complexes with the larger macrocycle, L^2, show single bands for the CN stretch, with the exception of Ba^{2+}, and so are designated as structure type b. The complex $\mathrm{L^{1}\cdot Ba[NCS]_{2}}$ has two bands and so is proposed as having structure type c.

TABLE 3

Infrared spectra (cm^{-1})

Metal salt	C=O stretch	CN stretch	Cl–O asym. bend
(*a*) Complexes of 4′-acetobenzo-15-crown-5			
Uncomplexed	1 660		
Li[NCS]	1 670	2 080	
Na[NCS]	1 670	2 060	
K[NCS]	1 675	2 055	
$\mathrm{Mg[NCS]_{2}}$	1 680	2 080	
$\mathrm{Ca[NCS]_{2}}$	1 675	2 100, 2 070	
$\mathrm{Sr[NCS]_{2}}$	1 670	2 090, 2 060	
$\mathrm{Ba[NCS]_{2}}$	1 660	2 090, 2 050	
$\mathrm{Li[ClO_{4}]}$	1 675		625
$\mathrm{Na[ClO_{4}]}$	1 675		625
$\mathrm{K[ClO_{4}]}$	1 680		625
$\mathrm{Mg[ClO_{4}]_{2}\cdot 2H_{2}O}$	1 670		625
$\mathrm{Ca[ClO_{4}]_{2}}$	1 670		630
$\mathrm{Sr[ClO_{4}]_{2}}$	1 670		625
$\mathrm{Ba[ClO_{4}]_{2}}$	1 675		625
(*b*) Complexes of 4′-acetobenzo-18-crown-6			
Uncomplexed	1 660		
$\mathrm{Li[NCS]\cdot H_{2}O}$	1 665	2 075	
$\mathrm{Na[NCS]\cdot H_{2}O}$	1 675	2 100	
K[NCS]	1 680	2 060	
$\mathrm{Mg[NCS]_{2}\cdot H_{2}O}$	1 670	2 095, 2 090	
$\mathrm{Ca[NCS]_{2}}$	1 665	2 050	
$\mathrm{Sr[NCS]_{2}}$	1 665	2 050	
$\mathrm{Ba[NCS]_{2}}$	1 670	2 080, 2 065	
$\mathrm{Li[ClO_{4}]\cdot H_{2}O}$	1 665		625
$\mathrm{Na[ClO_{4}]}$	1 665		620
$\mathrm{K[ClO_{4}]}$	1 670		620
$\mathrm{Mg[ClO_{4}]_{2}\cdot 4H_{2}O}$	1 665		630
$\mathrm{Ca[ClO_{4}]_{2}}$	1 665		625
$\mathrm{Sr[ClO_{4}]_{2}}$	1 665		625
$\mathrm{Ba[ClO_{4}]_{2}}$	1 665		630

The perchlorate complexes show a strong sharp band at *ca.* 625 cm^{-1} in all of the complexes and this is indicative of ' ionic ' perchlorate. Certainly in the 2 : 1 complexes this assignment is substantiated as the anion would be separated from the metal. It is conceivable that some unidentation could occur, but that any splitting of the band would be masked by the proximal ligand bands. In order to solve this problem, and to determine the potential involvement of the aceto-side chain in complex formation, the *X*-ray crystal structure of $\mathrm{L^{2}\cdot Sr[ClO_{4}]_{2}}$ was determined.

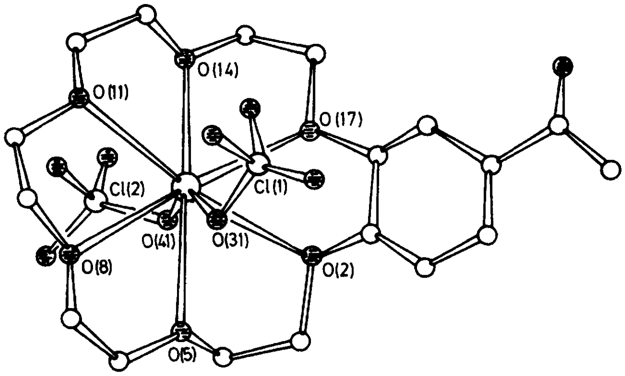


FIGURE 3 Molecule I of $\mathrm{L^{2}\cdot Sr[ClO_{4}]_{2}}$

The Structure of $\mathrm{L^{2}\cdot Sr[ClO_{4}]_{2}}$.—While the combination of poor crystal quality and crystallographic difficulties preclude a detailed discussion of the structure, the following features may nevertheless be noted. The overall arrangement about the strontium ion is the same in each independent molecule, with the metal ion interacting with both perchlorate groups and with all six macrocyclic oxygen atoms (Figures 3 and 4). The resulting eight-co-ordination may be contrasted with the nine-co-ordination found in the complex benzo-18-crown-6·$\mathrm{Sr[ClO_{4}]_{2}\cdot 3H_{2}O}$.[18] In this species the perchlorates are not co-ordinated to the metal which is surrounded by the six ether oxygen atoms and three oxygens from the water molecules. There is no evidence that the acetyl group is involved in bonding to a neighbouring

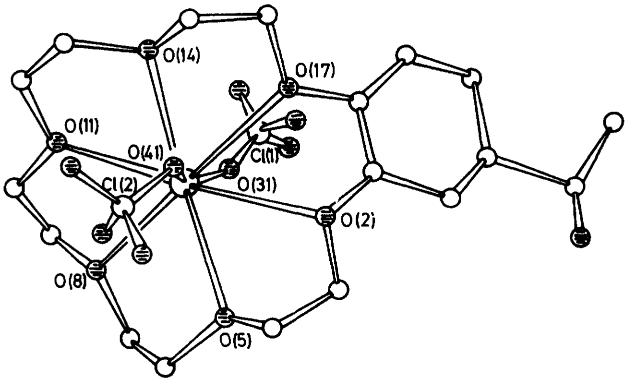


FIGURE 4 Molecule II of $\mathrm{L^{2}\cdot Sr[ClO_{4}]_{2}}$

TABLE 4

Complex	Range of M–O (macrocycle) distances/Å	Mean M–O (macrocycle) distance/Å	Distance of M from weighted mean plane through six macrocyclic oxygen atoms/Å	Sum of van der Waals radius of oxygen and ionic radius of M/Å [a]	Ref.
4′-Acetobenzo-18-crown-6·$\mathrm{Sr[ClO_4]_2}$	2.624—2.782 Molecule I 2.611—2.749 Molecule II	2.688 2.671	0.01 0.01	Sr^{2+}, O 2.65	This work
4′-Nitrobenzo-18-crown-6·Rb[NCS]	2.964—3.082	3.008	1.17	Rb^{+}, O 3.00	19
18-Crown-6·Rb[NCS]	2.929—3.146	3.024	1.19	Rb^{+}, O 3.00	*b, c*
4′-Nitrobenzo-18-crown-6·Cs[NCS]	3.040—3.248	3.146	1.46	Cs^{+}, O 3.18	20
18-Crown-6·Cs[NCS]	3.035—3.274	3.146	1.44	Cs^{+}, O 3.18	12, *c*

[a] Van der Waals radius of oxygen taken as 1.40 Å (L. Pauling, ' The Nature of the Chemical Bond,' 2nd edn., Cornell University Press, Ithaca, 1960). Ionic radii taken from ref. 22. [b] M. Dobler and R. P. Phizackerley, *Acta Crystallogr., Sect. B*, 1974, **30**, 2746. [c] J. D. Dunitz, M. Dobler, P. Seiler, and R. P. Phizackerley, *Acta Crystallogr., Sect. B*, 1974, **30**, 2733.

metal ion. This is in contrast to the rubidium and caesium thiocyanate complexes of 4′-nitrobenzo-18-crown-6, where intermolecular alkali-metal–nitro-oxygen interactions are observed.[19,20] The estimated radius of the macrocyclic cavity for 18-crown-6 (1.3—1.6 Å)[21] is such that the strontium ion (ionic radius 1.25 Å)[22] would be expected to fit readily into the cavity of L^2. This would appear to be the case, for in both independent molecules the metal ion is found to be essentially coplanar with the weighted mean plane through the six macrocyclic oxygen atoms. This may be contrasted with related rubidium and caesium complexes where the metal ions lie out of the macrocyclic cavity, the extent of displacement reflecting the size of the metal ion (Table 4). The Sr–O (macrocycle) distances vary from 2.611(16) to 2.782(21) Å (Table 5), with the Sr–O(2),O(17) values being substantially greater than the remaining values. The mean Sr–O (macrocycle) distance of 2.679 Å lies close to the sum of the van der Waals radius of oxygen and the ionic radius of strontium (2.65 Å), and fits into the pattern of mean values given in Table 4. While the conformations of the major portion of the macrocycle are similar in the two independent molecules, there are differences in the O(14) portion of the ring and the torsion angles about C(12)–C(13), O(14)–C(15) are strikingly different (Table 6).

TABLE 5

Selected bond distances and angles for $L^2\cdot\mathrm{Sr[ClO_4]_2}$

	Molecule I	Molecule II
(*a*) Strontium ion environment		
(*i*) Distances (Å)		
Sr–O(2)	2.75(2)	2.75(1)
Sr–O(5)	2.66(3)	2.64(3)
Sr–O(8)	2.63(2)	2.63(2)
Sr–O(11)	2.68(2)	2.61(2)
Sr–O(14)	2.62(3)	2.68(3)
Sr–O(17)	2.78(2)	2.72(2)
Sr–O(31)	2.69(3)	2.72(3)
Sr–O(41)	2.55(3)	2.63(4)
(*ii*) Angles		
O(2)–Sr–O(5)	61.9(7)	62.1(6)
O(5)–Sr–O(8)	60.1(6)	60.9(6)
O(8)–Sr–O(11)	66.0(7)	59.9(8)
O(11)–Sr–O(14)	63.4(7)	60.6(7)
O(14)–Sr–O(17)	60.8(6)	62.6(6)
O(31)–Sr–O(2)	83.2(7)	75.1(6)
O(31)–Sr–O(5)	76.0(9)	79.2(8)
O(31)–Sr–O(8)	76.0(7)	73.6(8)
O(31)–Sr–O(11)	87.3(7)	104.1(7)
O(31)–Sr–O(14)	122.5(7)	118.4(8)
O(31)–Sr–O(17)	99.5(7)	91.7(7)
O(41)–Sr–O(2)	79.4(7)	77.6(7)
O(41)–Sr–O(5)	79.4(9)	117.8(8)
O(41)–Sr–O(8)	97.5(7)	95.3(10)
O(41)–Sr–O(11)	112.9(7)	103.1(8)
O(41)–Sr–O(14)	81.8(8)	73.2(9)
O(41)–Sr–O(17)	85.3(7)	71.2(8)
O(41)–Sr–O(31)	154.5(8)	152.6(6)
(*b*) Perchlorate groups		
(*i*) Distances (Å)		
Cl(1)–O(31)	1.37(3)	1.39(3)
Cl(1)–O(32)	1.47(2)	1.36(3)
Cl(1)–O(33)	1.45(3)	1.42(3)
Cl(1)–O(34)	1.40(2)	1.41(2)
Cl(2)–O(41)	1.47(2)	1.53(3)
Cl(2)–O(42)	1.39(4)	1.44(3)
Cl(2)–O(43)	1.33(3)	1.37(3)
Cl(2)–O(44)	1.41(3)	1.34(4)
(*ii*) Angles (°)		
O(31)–Cl(1)–O(32)	110(1)	110(2)
O(31)–Cl(1)–O(33)	109(2)	107(2)
O(31)–Cl(1)–O(34)	115(2)	105(1)
O(32)–Cl(1)–O(33)	106(2)	110(2)
O(32)–Cl(1)–O(34)	111(2)	112(2)
O(33)–Cl(1)–O(34)	106(2)	113(2)
O(41)–Cl(2)–O(42)	103(2)	111(2)
O(41)–Cl(2)–O(43)	114(2)	113(2)
O(41)–Cl(2)–O(44)	109(2)	96(2)
O(42)–Cl(2)–O(43)	130(2)	116(2)
O(42)–Cl(2)–O(44)	107(2)	100(2)
O(43)–Cl(2)–O(44)	93(2)	119(3)

TABLE 6

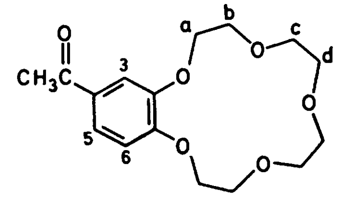
Torsion angles (°) in the macrocyclic rings. Estimated standard deviations are ≈2.5°

	Molecule I	Molecule II
C(18)–C(1)–O(2)–C(3)	178	175
C(1)–O(2)–C(3)–C(4)	−179	−178
O(2)–C(3)–C(4)–O(5)	58	61
C(3)–C(4)–C(5)–C(6)	151	149
C(4)–O(5)–C(6)–C(7)	−178	−173
O(5)–C(6)–C(7)–O(8)	−55	−58
C(6)–C(7)–O(8)–C(9)	179	−177
C(7)–O(8)–C(9)–C(10)	170	160
O(8)–C(9)–C(10)–O(11)	67	60
C(9)–C(10)–O(11)–C(12)	179	167
C(10)–O(11)–C(12)–C(13)	171	164
O(11)–C(12)–C(13)–O(14)	−59	36
C(12)–C(13)–O(14)–C(15)	−166	−174
C(13)–O(14)–C(15)–C(16)	−97	−168
O(14)–C(15)–C(16)–O(17)	−60	−74
C(15)–C(16)–O(17)–C(18)	−175	−167
C(16)–O(17)–C(18)–C(1)	−179	176
O(17)–C(18)–C(1)–O(2)	11	−3

N.M.R. Spectra.—The ^1H n.m.r. spectra of the complexes were recorded in $[^2H_6]$acetone thus allowing comparison with studies on non-substituted crown ethers.[23] The unsymmetrical nature of the acetobenzo-crown ethers has made exact assignments of the ring protons complicated, but tentative assignments are given in Table 7. It has been noted that the shifts are similar for both acetobenzo- and benzo-crown ethers indicating that the conformations in solution are similar. *X*-Ray studies have shown that in the solid state benzo-crown ethers and their complexes can have similar conformations, and that small changes can occur on complexation.[24-26] In general all the resonances in the n.m.r. spectra are shifted to lower field on complexation; the exceptions are the potassium complexes of L^1 where several upfield shifts are detected. These can be attributed to 2 : 1 complex formation by analogy with the work of Lockhart *et al.*[27] in which the direction of the shift has been empirically related to the stoicheiometry of the complex formed. A 1 : 1 complex gives a downfield shift and a 2 : 1 complex gives an upfield shift, relative to the free ligand.

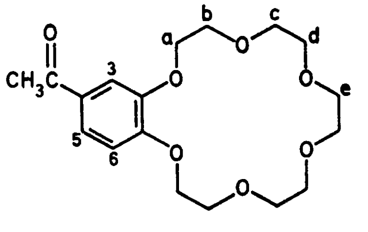
TABLE 7

Proton n.m.r. spectra (in $[^2H_6]$acetone)



(*a*) Complexes of 4′-acetobenzo-15-crown-5

	Chemical Shift (τ)					
Metal salt	H^5	H^3	H^6	aa′	bb′	cc′, dd′
Uncomplexed	2.40	2.51	3.02	5.85	6.15	6.33
Li[NCS]	2.31	2.43	2.88	5.71	6.04	6.25
Li[ClO$_4$]	2.26	2.38	2.79	5.61	5.98	6.18
Na[NCS]	2.26	2.34	2.77	5.60	5.96	6.18
Na[ClO$_4$]	2.26	2.35	2.78	5.61	5.99	6.18
K[NCS]	2.38	2.80	3.12	5.98	6.27	6.18
K[ClO$_4$]	2.36	2.76	3.12	5.95	6.26	6.16
Mg[NCS]$_2$	2.18	2.29	2.68	5.40	5.74	5.99
Mg[ClO$_4$]$_2$	2.15	2.25	2.60	5.30	5.68	5.86
Ca[ClO$_4$]$_2$	2.19	2.20	2.63	5.40	5.80	5.92
Ba[ClO$_4$]$_2$	2.25	2.42	2.78	5.50	5.91	5.91



(*b*) Complexes of 4′-acetobenzo-18-crown-6

	H^5	H^3	H^6	aa′	bb′	c—e
Uncomplexed	2.38	2.49	2.99	5.80	6.12	6.30—6.42
Li[NCS]	2.35	2.46	2.93	5.74	6.07	6.28—6.36
Li[ClO$_4$]	2.35	2.49	2.91	5.72	6.07	6.30—6.34
Na[NCS]	2.32	2.48	2.88	5.69	6.01	6.25—6.34
Na[ClO$_4$]	2.32	2.48	2.88	5.70	6.05	6.30—6.32
K[NCS]	2.31	2.42	2.83	5.61	6.00	6.22—6.29
K[ClO$_4$]	2.31	2.42	2.83	5.62	6.02	6.24—6.31
Mg[ClO$_4$]$_2$	2.36	2.48	2.94	5.71	6.05	6.26—6.30
Ca[ClO$_4$]$_2$	2.24	2.37	2.76	5.48	5.88	6.09—6.13
Sr[ClO$_4$]$_2$	2.24	2.34	2.74	5.48	5.85	6.02—6.10
Ba[ClO$_4$]$_2$	2.24	2.34	2.72	5.46	5.85	6.04—6.08

Comparison of the spectra for 1 : 1 thiocyanate and perchlorate complexes of L^1 and L^2 show that δ is relatively independent of the anion; this suggests that ion pairing is not important in $[^2H_6]$acetone. For sodium complexes of dibenzo-18-crown-6 a significant difference in shift was detected for similar complexes and attributed to ion pairing.[23] A less pronounced effect was noted for sodium complexes of benzo-18-crown-6 and it was suggested that extra flexibility in the benzo-18-crown-6 was responsible for the effect.[23]

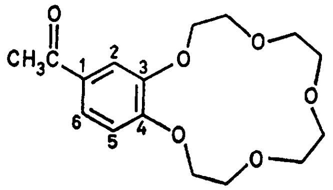
The low solubility of the complexes made it difficult to obtain ^{13}C n.m.r. spectra. The results for complexes of L^1 are shown in Table 8, and indicate small changes in chemical shift which may be related to changes in conformation on complexation. The asymmetry of the crown has led to an assignment problem for the carbons in the heteroatom ring, and so only the values of the shifts are given. Carbon-13 n.m.r. spectroscopy has also been used to observe the thiocyanate anion and to determine its mode of bonding.[28] *S*-Bonded species lie in the range 112—118 p.p.m., *N*-bonded in the range 134—141 p.p.m., and ionic thiocyanates in the range 133—134 p.p.m. The resonance for L^1·Na[NCS] is at 132.7 p.p.m., and for $2L^1$·K[NCS] is *ca.* 131.5 p.p.m. where it is somewhat masked by the aromatic resonances. These values lie closest to the range for ionic species further indicating the absence of ion pairing.

Reactions of 4′-(*Bromoaceto*)*benzo*-15-*crown*-5, L^3.—Monobromination of L^1 by bromine in chloroform yields L^3.[5] Compound L^3 readily forms a 1 : 1 monohydrated complex with NaBr, and a 2 : 1 sandwich complex with KBr. However, when the complexation reaction was attempted with Ca[SCN]$_2$ in ethyl acetate the product recovered analysed as L^3·Ca[SCN]$_2$ but showed i.r. peaks at 2 170, 2 100, and 2 070 cm^{-1} indicating that as well as metal co-ordination an internal nucleophilic displacement has occurred to give 4′-(thiocyanatoaceto)benzo-15-crown-5 (L^4), as its complex, L^4·Ca[SCN]Br. Treatment of the complex with water, followed by chloroform extraction, yielded pure L^4, with a single peak at 2 170 cm^{-1} attributable to *S*-bonded thiocyanate. Compound L^4 is also prepared by reaction of aqueous K[NCS] with L^3 in ethyl acetate.

The reaction, which proceeds in good yield, is believed to proceed *via* initial complexation of the metal thiocyanate to release the activated nucleophile, followed by the substitution reaction at the side chain. Compound L^4 has been characterised by i.r. and mass spectroscopy, in which a parent peak is seen at $M^{\cdot+}$ 367, followed by a characteristic polyether breakdown pattern.[29] The ^{13}C-$\{^1H\}$ n.m.r. spectrum shows a peak at 112.1 p.p.m. assignable to the S*C*N carbon atom (C_2H_5SCN, 112.1 p.p.m.).[28] Compound L^4 can act as an intermediate in the preparation of bifunctional polyethers.[30] For

TABLE 8

^{13}C-{^1H} n.m.r. spectra of 4′-acetobenzo-15-crown-5 complexes in [$^2H_6$]acetone

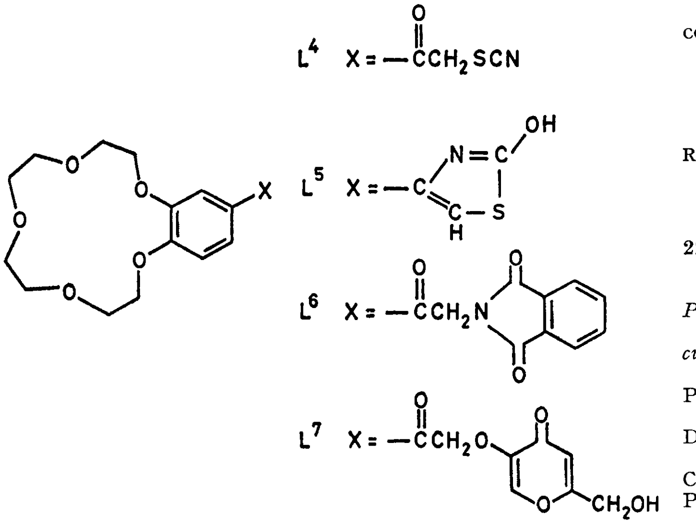


	Chemical shift/p.p.m.													
									Ether carbons *					
Metal salt	CH_3	C=O (NCS)	C^1	C^2	C^3	C^4	C^5	C^6						
Uncomplexed	26.3	196.2	131.4	113.4	149.6	154.2	112.7	123.9	72.0	71.2	71.0	70.1	69.9	69.5
Li[ClO$_4$]	26.4	196.4	132.1	112.5	147.7	151.8	112.1	124.5	69.6	69.4	68.5	69.4	67.9	67.7
Na[NCS]	26.5	196.5 (132.7)	132.3	113.3	148.2	152.5	113.2	124.7	69.9	69.3	68.7	68.6	68.3	
K[NCS]	26.5	196.3 (131.5)	131.5	112.5	148.0	152.5	112.5	124.3	69.5	68.6	68.5	67.9	67.7	

* Specific assignments for the ring ether carbon atoms have not been made.

example, the thiazole derivative L^5 is prepared by reaction of L^4 with aqueous HCl.

The role of alkali-metal complexes as ' self-reagents ' has been extended to include other anions. Potassium phthalimide reacted readily to give L^6, and sodium iodide gave 4′-(iodoaceto)benzo-15-crown-5. However, no reaction was found for KF or KCl and this is a reflection of the poor complexation of these salts by the more rigid polyethers. Compound L^4 was also used to prepare an analogue of phenacyl kojate, itself a good complexor of alkali-metal cations.[31] The addition of L^4 to an aqueous ethanol solution of K[OH] and kojic acid gave a yellow precipitate which on recrystallisation from ethanol gave white crystals of 2L^7·KBr. Similar reactions using Li[OH] and Na[OH] gave hydrated complexes of formula L^7·1.2 MBr. The stoicheiometries observed suggest that the metal ions are preferentially complexed by the crown ether ring. A higher alkali-metal load per molecule of L^7 would be expected if the kojate chains were also participating in complexation.



Attempts to obtain free L^7 from the complexes using aqueous extraction techniques were unsuccessful in contrast to the easy removal of alkali-metal halide from phenacyl kojate.[32]

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