Complexes of the Functionalized Crown Ether 17-Hydroxy-15⟨O_5(1,2)-benzeno.2_4-coronand-5⟩. X-ray Crystal and Molecular Structure of the KSCN Complex

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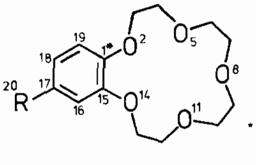
*The title ligand (*1c*) has been synthesized and studied in terms of its complexation properties towards alkali and alkaline earth metal ions. Crystalline complexes were obtained with LiI, NaSCN, KSCN, RbI, $Mg(ClO_4)_2$, $Ca(SCN)_2$, $Ba(SCN)_2$, and characterized by means of elemental analytical and spectroscopic methods. The complexes with Li-, Na- and Ca salts were found to be of 1:1, those with K-, Rb-, Ba salts of 2:1 (ligand:salt) stoichiometry, while the Mg^{2+} complex analysed as a 3:2 adduct. IR-spectra indicate the thiocyanate ions metal-coordinated in the corresponding 1:1 complexes but non-coordinated in those of the 2:1 cases. A crystal structure analysis of the 2:1 KSCN complex of* 1c *[triclinic P1 or $P\bar{1}$ with* a *= 9.615(2),* b *= 11.572(3),* c *= 14.893(4) Å, α = 91.63(2), β = 95.06(2), γ = 96.13(2), R = 0.10 for 2311 diffractometer data] revealed that the SCN^- anions are indeed separated from the K^+ ions and bound in a chain of hydrogen bonds with the pendant –OH functions. The metal ions are sandwiched between a pair of crown rings in a manner which deviates from the arrangement described for an analogous K^+ complex of the parent system* 1a, *in respect to the relative positioning of the ligand subunits.*

Introduction

Crown ethers (coronands) [1, 2] bearing pendant functional groups gain increasing interest because of their general value in systematically modifying complexation selectivities [3], as well as of ligand lipophilicities [4]. They also serve as useful intermediates in the synthesis of more complex ligand systems [5] and polymer bound crown catalysts [6]. The present investigation was undertaken in order to study whether the remote pendant phenolic OH group in 17-hydroxy-15⟨O_5-(1,2)benzeno.2_4-coronand-5⟩ (*1c*) may cooperate in complexation of cations, possibly providing a new coordination geometry with the phenolic oxygen being an additional donor site for a second crown molecule [7]. A further aspect refers to the *trans*-sandwich structure which is formed in the crystalline potassium complex of the basic 15⟨O_5-(1,2)benzeno.2_4-coronand-5⟩ system (*1a*) [8]. In contrast, hydrogen bonding between the OH-groups of two crown phenols *1c* was thought to enable a *cis*-sandwich with the benzene rings being layered in the same direction. By this way also a new control in K^+/Na^+ selectivity could be affected, comparable to the situation in alkylene- or oligo(oxyethylene)-chain linked bis(crown ether)s [9].



1a: R = H
1b: R = CHO
1c: R = OH

* atomic numbering scheme used in the crystal structure determination

Experimental

Melting points were determined on a Kofler apparatus, Reichert, Wien, and are uncorrected. Infrared spectra were recorded as potassium bromide discs on a Pye-Unicam SP-1100 spectrometer. ^{1}H-NMR spectra were run on a Varian EM-360 (60 MHz) in $CDCl_3$ as solvent and TMS as internal standard. Assignments are given in δ-values, ppm. Mass spectra

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TABLE I. Crystalline Complexes of Ligand *1c*.

Compound	Solvent	M.p. (°C)	Analyses (%)					
			Found			Calcd.		
			C	H	N	C	H	N
1c·LiI·½H_2O	ethyl acetate	138 (dec.)[a]	39.34	5.07	–	39.36	4.95	–
1c·NaSCN	ethyl acetate	154–156	49.13	5.45	3.98	49.30	5.52	3.83
(*1c*)$_2$·KSCN	methanol	223–225	52.24	6.02	2.19	52.31	6.06	2.10
(*1c*)$_2$·RbI	methanol	245–248	42.73	4.98	–	43.06	5.16	–
(*1c*)$_3$·[$Mg(ClO_4)_2$]$_2$	ethyl acetate	115 (dec.)[a]	38.96	4.82	–	38.82	4.65	–
1c·$Ca(SCN)_2$	ethyl acetate	210 (dec.)[a]	43.53	4.46	5.84	43.62	4.58	6.35
(*1c*)$_2$·$Ba(SCN)_2$	ethyl acetate	205 (dec.)[a]	43.92	4.51	3.44	43.83	4.90	3.41

[a] Refers to starting point of sintering or darkening of the crystals.

were recorded on a MS-50, A.E.I., Manchester, England. Elemental analyses were performed at the Microanalytical Laboratory of the Institut für Organische Chemie and Biochemie, Bonn.

Ligand Synthesis

15⟨O_5-(1,2)Benzeno.2_4-coronand-5⟩ (1a)

This was obtained according to the procedure of Pedersen [10].

17-Formyl-15⟨O_5-(1,2)benzeno.2_4-coronand-5⟩ (1b)

This was synthesized from *1a* under Vilsmeier-conditions and purified *via* the bisulfite-adduct [11].

17-Hydroxy-15⟨O_5-(1,2)benzeno.2_4-coronand-5⟩ (1c)

A stirred solution of 29.6 g (100 mmol) of *1b* in 145 ml of 85%formic acid was cooled to –5 °C and combined with an ice-cold mixture of 48.5 ml of formic acid and 15 ml of 30% H_2O_2. After stirring for 16 h at –10 °C the dark-brown solution was poured into 1 l of ice-water and allowed to stand for 30 min. The mixture was extracted with chloroform, the organic layer separated and dried over $MgSO_4$. Evaporation of the solvent left a viscous red-colored oil which was purified by column chromatography (Al_2O_3, Brockmann, neutral; chloroform): 54% colorless needles (from heptane), m.p. 102–104 °C [12]. *Anal.* Calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09. Found: C, 58.95; H, 7.05%.M.W. Calcd for $C_{14}H_{20}O_6$: 284.3. Found: 284 (M^+). ^1H-NMR ($CDCl_3$): 6.73–6.10 (m, 3H, arom.), 4.18–3.50 (m, 16H, OCH_2). IR (KBr): 3220 (br, OH), 2980, 2940, 2900, 1620 (arom.), 1530 (arom.), 1470, 1370, 1310, 1235 (C–O, aryl), 1185, 1140 (C–O, alkyl), 1000, 950, 860 (arom.) cm^{-1}.

Preparation of the Complexes

142 mg (0.50 mmol) of ligand *1c* and 0.50 mmol of the corresponding salt were combined in 3 ml of the stirred solvent given in Table I. At this stage precipitation of the complex can occur. The mixture was gently refluxed for 2 h. After cooling, the complexes were collected by suction and dried (5 h, 15 Torr, 50 °C). Used solvents, yields, m.p. and analytical data are listed in Table I.

Crystal Data, Data Collection (KSCN complex of 1c)

A crystal of approximate dimensions 0.1 × 1 × 0.3 mm was selected for X-ray analysis. The unit cell, as determined from the least-squares fitting for 25 reflexions with high θ values, is triclinic P1 or P$\bar{1}$ (No. 1 and 2 [13]) with the dimensions a = 9.615(2), b = 11.572(3), c = 14.893(4)Å, α = 91.63(2), β = 95.06(2), γ = 96.13(2)°, Z = 2, D_c = 1.35 Mg m^{-3}, M_w = 665.8 (calculated for $C_{29}H_{40}$-$KNO_{12}S$), μ(MoK_α) = 0.0287 m^{-1}

5355 unique reflexions were collected (δ_{max} = 25 °C) in an ω–2θ scan on a CAD-4 diffractometer using monochromatized MoK_α radiation ($\bar{\lambda}$ = 0.71069 Å). 2101 of these with $I < 0$ were disregarded in further work. Intensity data were corrected for Lorentz and polarization effect but not for absorption.

Structure Solution and Refinement (KSCN complex of 1c)

Initially the structure was solved in the centrosymmetric space group P$\bar{1}$ by the application of a direct method [14]. An E-map computed from the most consistent phase set revealed the positions of the K^+ ion and of six other atoms from the coordinating distance to the metal ion (R = 0.52). The 37 remaining non-hydrogen atoms of the asymmetric

TABLE II. Atomic Coordinates ($\times 10^4$) with their e.s.d.s and B_{eq} Parameters for Non-hydrogen Atoms.

Atom	X (σ)	Y (σ)	Z (σ)	B_{eq}[a]
C(1a)	−1896(21)	4769(15)	3705(12)	4.1
O(2a)	−1043(12)	3915(9)	4023(9)	4.1
C(3a)	−1384(20)	3287(17)	4784(12)	4.2
C(4a)	−324(25)	2509(21)	5138(16)	7.7
O(5a)	179(20)	1880(15)	4400(15)	10.1
C(6a)	1153(25)	1221(17)	4664(19)	7.5
C(7a)	2415(26)	1506(28)	4272(21)	10.8
O(8a)	2475(14)	2296(12)	3457(10)	5.9
C(9a)	3514(19)	3207(21)	3343(13)	5.3
C(10a)	3304(21)	3656(23)	2410(22)	6.8
O(11a)	2145(14)	4241(12)	2845(12)	6.0
C(12a)	2142(18)	5256(15)	2204(14)	4.5
C(13a)	727(21)	5725(18)	2383(18)	6.6
O(14a)	−505(13)	4938(10)	2511(10)	4.8
C(15a)	−1520(22)	5337(17)	2989(15)	7.1
C(16a)	−2262(20)	6225(17)	2534(15)	5.7
C(17a)	−3439(28)	6377(23)	2917(18)	10.5
C(18a)	−3753(20)	5942(19)	3637(18)	5.4
C(19a)	−3040(22)	5031(16)	4166(17)	5.8
O(20a)	−5032(17)	6146(15)	4098(11)	8.7
C(1b)	1357(17)	2627(22)	302(16)	7.0
O(2b)	252(12)	3056(11)	684(9)	5.7
C(3b)	−956(21)	2962(23)	127(13)	6.0
C(4b)	−2310(32)	3335(29)	364(18)	12.4
O(5b)	−2234(16)	3465(17)	1308(11)	8.0
C(6b)	−3699(34)	2736(29)	1645(23)	11.4
C(7b)	−3948(24)	1782(19)	1989(14)	6.9
O(8b)	−3012(16)	1598(13)	2838(11)	7.5
C(9b)	−3214(26)	511(19)	3266(20)	7.2
C(10b)	−2325(23)	−465(21)	2859(15)	6.3
O(11b)	−1088(14)	29(12)	2646(10)	6.1
C(12b)	−428(23)	−822(18)	2078(18)	6.0
C(13b)	750(22)	−234(15)	1688(15)	5.2
O(14b)	595(19)	867(16)	1213(15)	11.6
C(15b)	1658(24)	1435(22)	647(18)	7.7
C(16b)	2953(26)	971(21)	332(16)	11.1
C(17b)	3889(29)	1427(20)	−199(14)	7.6
C(18b)	3394(28)	2571(24)	−409(16)	7.8
C(19b)	2218(22)	3128(22)	−152(17)	7.6
O(20b)	4227(25)	3119(22)	−874(17)	13.2
C(1c)	1958(24)	5259(20)	6207(18)	5.9
O(2c)	1073(18)	6037(15)	5807(12)	7.3
C(3c)	1601(26)	6776(21)	5049(18)	6.8
C(4c)	129(26)	7304(21)	4837(15)	5.6
O(5c)	116(13)	8219(11)	5569(8)	3.4
C(6c)	−1197(35)	9003(28)	5628(23)	11.4
C(7c)	−2447(30)	8104(23)	5521(18)	8.3
O(8c)	−2331(19)	7927(17)	6453(14)	8.4
C(9c)	−3646(30)	7071(27)	6418(21)	8.8
C(10c)	−3315(24)	6448(20)	7300(20)	6.2
O(11c)	−1987(18)	5915(15)	7901(12)	7.6
C(12c)	−1834(27)	4764(23)	7620(19)	7.3
C(13c)	−651(25)	4286(23)	7575(19)	6.9
O(14c)	−2(18)	4908(15)	7097(14)	8.9
C(15c)	1443(23)	4718(19)	6950(16)	5.1
C(16c)	2200(29)	3919(17)	7324(19)	4.2
C(17c)	3500(21)	3537(16)	6965(14)	5.0
C(18c)	3905(19)	4185(16)	6243(13)	3.2
C(19c)	3172(20)	5054(17)	5838(15)	3.9
O(20c)	5034(12)	3939(11)	5772(9)	5.4
C(1d)	8474(23)	8661(20)	9246(15)	4.8
O(2d)	9332(16)	9123(13)	8764(10)	5.4
C(3d)	8834(28)	10074(25)	8235(20)	8.4
C(4d)	10422(29)	10602(20)	8056(17)	6.3
O(5d)	10861(16)	9902(12)	7400(10)	5.3
C(6d)	12570(29)	10264(22)	7390(20)	7.7
C(7d)	12792(29)	9611(27)	6709(26)	9.9
O(8d)	12982(17)	8367(16)	7263(14)	8.3
C(9d)	13942(34)	8515(39)	8014(34)	14.3
C(10d)	13715(20)	7128(25)	8338(16)	4.2
O(11d)	12472(16)	7508(14)	8791(12)	6.8
C(12d)	12166(21)	6705(16)	9497(14)	4.0
C(13d)	10827(26)	6774(20)	10046(20)	7.2
O(14d)	10106(25)	7381(21)	9389(16)	13.0
C(15d)	8721(24)	7579(20)	9600(16)	6.2
C(16d)	7859(29)	6972(26)	10138(18)	8.2
C(17d)	6641(26)	7420(20)	10411(17)	7.4
C(18d)	6480(24)	8606(22)	9984(18)	7.9
C(19d)	7329(23)	9161(20)	9451(16)	5.5
O(20d)	5198(17)	8928(15)	10424(13)	8.1
K(1)	−228(0)	2511(0)	2589(0)	5.8
S(1)	−6566(7)	8331(6)	3498(5)	8.0
N(1)	−6156(18)	8158(16)	1774(13)	7.1
C(1)	−6305(20)	8262(17)	2546(14)	4.9
K(2)	234(4)	7493(3)	7406(3)	2.7
S(2)	6569(9)	1619(7)	6487(6)	9.8
N(2)	6193(30)	1915(25)	8436(17)	9.1
C(2)	6374(19)	1855(18)	7684(16)	8.5

[a] $B_{eq} = 4(B_{11}B_{22}B_{33}/(a^*)^2(b^*)^2(c^*)^2)^{1/3}$.

unit in $P\bar{1}$ where then found in subsequent electron-density syntheses. In the course of the refinement in $P\bar{1}$, high thermal parameters of some atoms and extreme geometries around them indicated that the structure is suffering from extensive disorder. The R value could not be lowered below 15%, even when introducing anisotropic thermal factors for most of the atoms. Even the –OH functions seemed to exhibit quite unusual bonding and high thermal parameters. Similarly, the disorder in the crown rings could not be improved, in contrast to a recently described 'regular' crown-ring disorder [15], by applying alternating sites and partial occupancies.

Hence, the space group was converted to P1 and the second (the symmetry-independent complex molecule) was located and also refined.

The adjustment of atomic parameters terminated at a final R of 0.10 for 2311 contributing reflexions with $I > 3*\sigma(I)$. However there are still some distorted bonding dimensions coupled with very high thermal parameters of certain atoms in the model, which indicates that the disorder could not be eliminated by lowering the symmetry alone. Since introduction of further new parameters would lead to further worsening of the observations/parameters ratio, we did not carry out further refinement. For the same reason, no contribution of hydrogen atoms was included in the model. Final atomic coordinates of the low-symmetry (P1) model are as appear in Table II.

Results and Discussion

Ligand Synthesis and Complexation

Various substituted benzocrown ethers have been prepared by either electrophilic substitution of benzocrown ethers [16], or crown ring cyclization of substituted catechols [17]. We have used a substitution approach to synthesize the crown ether phenol *1c* in two steps, starting from parent crown ether *1a* (benzo[15]crown-5). Substitution of *1a* was effected by formylation under Vilsmeier conditions to give the formyl derivative *1b* [11] which was converted *via* Baeyer-Villiger oxidation with performic acid into *1c* in an overall yield of 31%. A closely related reaction sequence has recently been reported by Wada *et al.* [12].

Complex formation was carried out by combining *1c* with an equimolar amount of the corresponding salt in methanol or ethyl acetate as solvent. The isolated complexes of *1c* (Table I) are colorless to pale pink crystalline compounds. Melting points were found to be higher than in the free ligand. The complexes with alkaline earth metal ions seem thermally less stable, showing decomposition rather than sharp melting points. Elemental analyses (Table I) confirm the complexes to be of different stoichiometries, 1:1 (ligand:salt), 2:1 and 3:2, depending on the cation type [18]. A clear controlling effect of crown ether interior and cation diameter on complex stoichiometry is demonstrated [2]. Na^+ and also Ca^{2+} match the ring hole of *1c* ideally, thus forming a 1:1 complex. K^+ and even more pronounced Rb^+ and Ba^{2+} are too large in size to fit into the 15-membered ring. Consequently, 2:1-complexes are found. In case of Li^+ which is too small to enable a close contact with the five ring oxygens, a molecule of water is needed to stabilize the complex arrangement [19]. A $Mg(SCN)_2$ complex of unsubstituted 15⟨O_5-(1,2)benzeno.2_4-coronand-5⟩ *1a* has been described as a 1:1-complex with the two thiocyanate ions being coordinated at axial positions of a pentagonal bipyramid [20]. The $Mg(ClO_4)_2$ complex of *1c*, however, analyses to 3:2 (ligand:salt) stoichiometry. Since the perchlorate ions were both found to be uncoordinated (see below) a more complex structure can be assumed, possibly of club-sandwich type [21]. It is also worthwhile to mention that the known complexes of $Ca(SCN)_2$ with unsubstituted *1a* exclusively crystallize in a solvated form (H_2O, MeOH) [20], whereas the analogous $Ca(SCN)_2$ complex of *1c* does not show solvation. The extra OH-group of *1c* might be interpretated as taking the place of a solvating molecule.

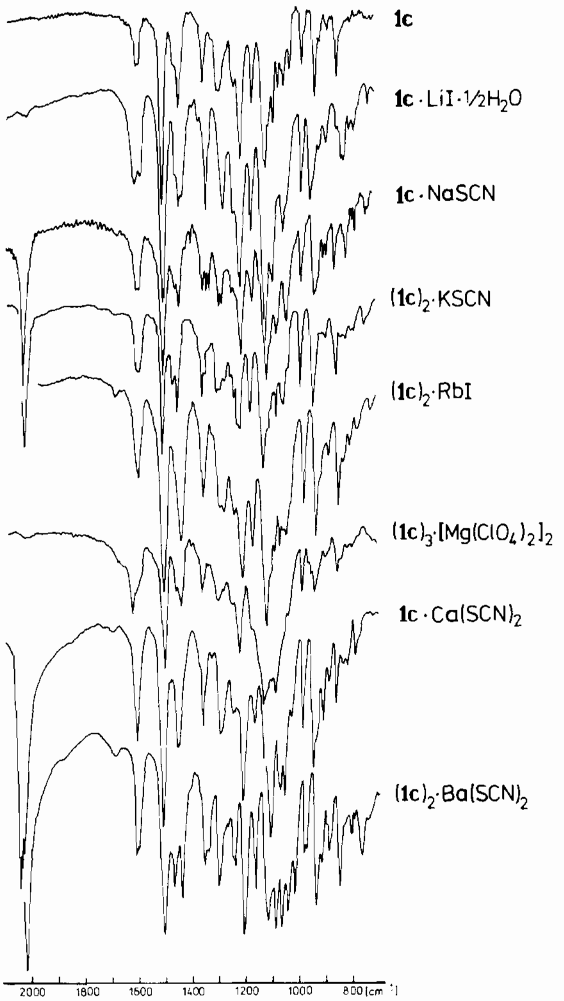

Fig. 1. Part or the IR spectra (KBr) of the free ligand *1c* and of its cation complexes.

IR Spectroscopy Determinations

Bond formation between *1c* and alkali/alkaline earth metal ions is also evidenced in the IR spectra of the crystalline complexes (Fig. 1). The vibration modes of the free ligand undergo substantial shifts and splittings upon complexation, most distinct for the ν(C–O–C) absorption of the aliphatic ether bond at 1100 cm^{-1}. In the case of the alkali metal ion

TABLE III. Coordination Distances with their e.s.d.s to the K^+ Ions.

I. To K(1)$^+$					
a)			b)		
	–O(2a)	= 2.86(1) Å		–O(2b)	= 2.99(1) Å
	–O(5a)	= 2.82(3)		–O(5b)	= 2.92(2)
K(1)	–O(8a)	= 2.84(2)	K(1)	–O(8b)	= 2.83(2)
	–O(11a)	= 2.86(1)		–O(11b)	= 2.91(1)
	–O(14a)	= 2.85(2)		–O(14b)	= 2.97(3)
II. To K(2)$^+$					
c)			d)		
	–O(2c)	= 3.09(2) Å		–O(2d)	= 2.97(2) Å
	–O(5c)	= 2.88(2)		–O(5d)	= 2.79(2)
K(2)	–O(8c)	= 2.84(2)	K(2)	–O(8d)	= 2.76(2)
	–O(11c)	= 2.82(2)		–O(11d)	= 2.85(2)
	–O(14c)	= 3.00(2)		–O(14d)	= 2.97(3)

10-fold coordinated $K^+\cdots O$ mean distances with r.m.s.d. s
I: 2.89(6) Å; II: 2.90(9) Å

complexes, frequency shifts for this absorption were found to be in the order of –5 to –15 cm^{-1}. Due to stronger coulombic interactions, complexation by the doubly charged alkaline earth metal ions Mg^{2+}, Ca^{2+}, Ba^{2+} causes shifts up to –30 cm^{-1}. The marked splitting in the 1100 cm^{-1} region for the 2:1 (ligand:salt) $Ba(SCN)_2$ complex points to the fact that the two macrocycles are probably not equivalent in the solid state. The ν(C–O–C) of the aromatic ether bond at 1220 cm^{-1} is displaced in the complexes by about 5–10 cm^{-1} towards lower wave numbers, which is attributable to the lower donor capacity of the catechol oxygen atoms. Obvious changes in the ν-arom. region at 1600 cm^{-1} are observed for the LiI- and for the $Mg(ClO_4)_2$ complexes, possibly indicating coordinative interaction of the phenolic OH-group with these metal ions. The strong OH-absorption, which has moved from 3270 cm^{-1} in the free ligand to 3420 cm^{-1} in the $Mg(ClO_4)_2$ complex, might also be interpreted in this regard. OH-stretching of the other complexes are located at 3250–3270 cm^{-1}.

Information about the bonding mode of the anions can also be drawn from the IR spectra. They may be summarized in the following simplified way: Anion–metal coordinations are derived for the 1:1-stoichiometric NaSCN- and $Ca(SCN)_2$ complexes. The thiocyanate ion being N-bonded, as deduced from the absence of absorptions at 700 cm^{-1} but the presence of frequencies near 800–850 cm^{-1} [22]. The split (C–N) stretching frequency at 2100–2065 cm^{-1} displayed in the IR of the $Ca(SCN)_2$ complex reflects the presence of at least three non-equivalent thiocyanate ions in the crystal lattice [23]. The metal ions in the KSCN- and $Ba(SCN)_2$ complexes, both of 2:1 (ligand:salt) stoichiometry, are each supposed to be coordinatively saturated by two crown ether rings (ten ether oxygens). Hence, absorptions at 2060 cm^{-1} show evidence for the uncoordinated nature of the thiocyanate anions [22]. The assumption that ionic perchlorate is the only species in the crystalline $Mg(ClO_4)$ complex is favoured by the absence of an intensive IR frequency (sym. bend) in the 920 cm^{-1} region and by the presence of a characteristic broad absorption (as. stretch) at 1100 cm^{-1} as well as of a strong band (as. bend) at 625 cm^{-1} [24].

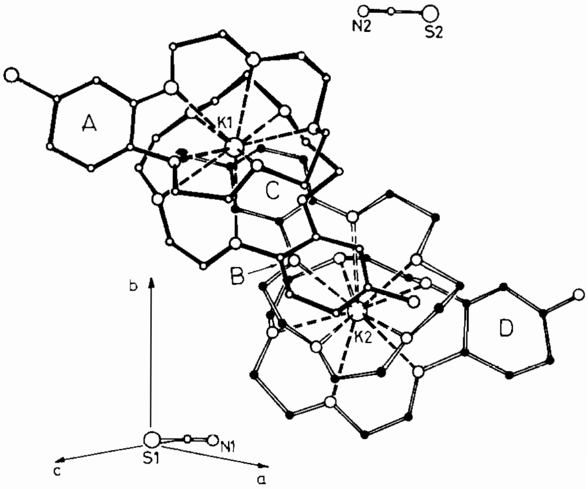

Fig. 2. View of the structure of the *1c* KSCN complex.

Structure Description of the 2:1 KSCN Complex of 1c

The high standard deviations and the presence of disorder do not support a detailed analysis of individual bonding dimensions, which in general correspond to the expected values. The somewhat long distances in the coordination polyhedra (Table III) fall in the range of $K^+\cdots O$ distances found in other crown K^+ complexes [8, 15, 25].

There are, however, some other unique features of this complex with respect to the 2:1 KI complex of *1a* [8] and other substituted benzo-crown compounds [*cf.* 7] which should be mentioned. An inspection of the arrangement of the molecules in the unit cell (Fig. 2) shows that the relative positioning of the benzene rings of ligands A, B and C, D, respectively, with respect to each other and to the central metal ions, is no longer perfect *anti* as in *1a* [8] but exhibits a ~50° rotation towards the *syn* range. This is also illustrated by the angles of the lines passing through a particular K^+ ion and the corresponding centres of the aromatic C(1)–C(15) bonds of ligands A, B (129°) and C, D (133°), respectively.

TABLE IV. Possible H-Bonding Donor-Acceptor Distances.

O(20a)···S(1)	= 3.17(2) Å
O(20d)···N(1)$_{[1,0,1]}$	= 2.62(3)
O(20c)···S(2)	= 3.36(2)
O(20b)···N(2)$_{[0,0,-1]}$	= 2.72(4)

Further, the pendant HO-C$_\phi$- bonds in ligands A, B are quasi *anti* situated, *i.e.* reflecting a centrosymmetric arrangement in regard of the K$^+$ ion, while those in the molecules C and D are rotated in the same sense as the benzene rings. This latter may also be interpreted as if one of the ligands in the C, D complex would bind to the metal ion with the 'other face' (*i.e.* mirror imaged) of the molecule.

Another remarkable feature of the title complex is the behaviour of the pendant –OH groups and the SCN$^-$ anions in establishing the crystal lattice. In contrast to other functionalized benzo-crown complexes [25], neither the pendant groups nor the anions participate in the coordination of the metal ions. Instead, they are all involved in short intermolecular contacts which may be inferred as hydrogen bonds from the bridge-head distances of possible donor–acceptor atoms (Table IV). The result is a complete shielding of the anions from their counter ions. This fact suggests, as also supported by the IR investigations, that one may hope to achieve not only cation but a certain anion binding by systematically modifying functionalized crown ethers of *1c* type.

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References

1 Notation system, see E. Weber and F. Vögtle, *Inorg. Chim. Acta, 45,* L65 (1980).

2 F. Vögtle and E. Weber, in 'The Chemistry of the Ether Linkage', S. Patai (Ed.), p. 59, Wiley, London, 1980.

3 M. Takagi, M. Tazaki and K. Ueno, *Chem. Lett.,* 1179 (1978);
E. Amble and J. Dale, *Acta Chem. Scand., B33,* 698 (1979);
J. S. Leigh and I. O. Sutherland, *J. Chem. Soc. Perkin I,* 1089 (1979);
J. P. Behr, J. M. Girodeau, R. C. Hayward, J. M. Lehn and J. P. Sauvage, *Helv. Chim. Acta, 63,* 2096 (1980);
G. W. Gokel, D. M. Dishong and C. J. Diamond, *J. Chem. Soc. Chem. Commun.,* 1053 (1980);
I. Cho and S.-K. Chang, *Chem. Lett.,* 515 (1981).

4 F. Montanari and P. Tundo, *Tetrahedron Lett.,* 5055 (1979);
I. Ikeda, S. Yamamura, Y. Nakatsuji and M. Okahara, *J. Org. Chem., 45,* 5355 (1980).

5 E. Weber, *Angew. Chem., 91,* 230 (1979); *Angew. Chem. Int. Ed. Engl., 18,* 219 (1979);
C. G. Krespan, *J. Org. Chem., 45,* 1177 (1980);
R. Kruse and E. Breitmaier, *Chem. Ber., 114,* 832 (1981).

6 S. L. Regen, *Angew. Chem. 91,* 464 (1979); *Angew. Chem., Int. Ed. Engl., 18,* 421 (1979);
K. Fukunishi, B. Czech and S. L. Regen, *J. Org. Chem., 46,* 1218 (1981).

7 *Cf.* J. Hašek, D. Hlavatá and K. Huml, *Acta Crystallogr., B33,* 3772 (1977);
idem, B34, 416 (1978).

8 P. R. Mallinson and M. R. Truter, *J. Chem. Soc. Perkin II,* 1818 (1972).

9 K. Kimura, H. Tamura, T. Tsuchida and T. Shono, *Chem. Lett.,* 611 (1979);
K. H. Wong and H. L. Ng, *Tetrahedron Lett.,* 4295 (1979);
F. Wada, Y. Wada, T. Goto, K. Kikukawa and T. Matsuda, *Chem. Lett.,* 1189 (1980).

10 C. J. Pedersen, *J. Am. Chem. Soc., 89,* 7017 (1967).

11 E. M. Hyde, B. L. Shaw and I. Shepherd, *J. Chem. Soc. Dalton,* 1696 (1978).

12 F. Wada, R. Arata, T. Goto, K. Kikukawa and T. Matsuda, *Bull. Chem. Soc. Jpn., 53,* 2061 (1980); *cf.* behaviour in m.p. of a trihydrated product species which was obtained under different reaction conditions.

13 'International Tables for X-ray Crystallography', Vol. I, Kynoch Press, Birmingham, 1962.

14 All programs used throughout this work, including a PDP 11/34 implemented MULTAN-76 version, were those of the ENRAF-NONIUS SDP program package, release V18.0, July 1980, and ancillary programs written by Dr. L. Párkányi of the CRIC.

15 M. Czugler and A. Kálmán, *Acta Crystallogr., B38,* 799 (1982).

16 *E.g.* W. M. Feigenbaum and R. H. Michel, *J. Polym. Sci. Part A9,* 817 (1971);
M. Bourgoin, K. H. Wong, J. Y. Hui and J. Smid, *J. Am. Chem. Soc., 97,* 3462 (1975);
R. Ungaro, B. El Haj and J. Smid, *J. Am. Chem. Soc., 98,* 5198 (1976);
B. Shaw and I. Shepherd, *J. Chem. Soc. Dalton,* 1635 (1979);
K. J. Odell, E. M. Hyde, B. L. Shaw and I. Shepherd, *J. Organomet. Chem., 168,* 103 (1979);
F. Wada, H. Hirayama, H. Namiki, K. Kikukawa and T. Matsuda, *Bull. Chem. Soc. Jpn., 53,* 1474 (1980);
P. E. Stott, J. S. Bradshaw and W. W. Parish, *Heterocycles, 15,* 179 (1981).

17 *E.g.,* J. Smid, B. El Haj, T. Majewicz, A. Nonni and R. Sinta, *Org. Prep. Proced., 8,* 193 (1976);
G. R. Brown and A. J. Foubister, *J. Med. Chem., 22,* 997 (1979).

18 N. S. Poonia, in 'Progress in Macrocyclic Chemistry', R. M. Izatt and J. J. Christensen (Eds.), Vol. 1, p. 115, Wiley, New York, 1979.

19 *Cf.* M. Czugler and E. Weber, *J. Chem. Soc. Chem. Commun.,* 472 (1981).

20 J. D. Owen, *J. Chem. Soc. Dalton,* 1418 (1978).

21 *Cf.* C. J. Pedersen, *J. Am. Chem. Soc., 92,* 386 (1970).

22 R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mills, *Coord. Chem. Rev., 6,* 407 (1971).

23 *Cf.* J.-C. G. Bünzli, D. Wessner and H. T. T. Oauh, *Inorg. Chim. Acta, 32,* L33 (1979).

24 R. P. Scholer and A. E. Merbach, *Inorg. Chim. Acta, 15,* 15 (1975).

25 N. S. Poonia and A. V. Bajaj, *Chem. Rev., 79,* 389 (1979);
R. Hilgenfeld and W. Saenger, in 'Topics in Current Chemistry', F. L Boschke and F. Vögtle (Eds.), Vol. 101, p. 1, Springer, Berlin–Heidelberg, 1982.