The 1:1 Complex of KSCN with a Macrocyclic Polyether Ligand System Containing Two Phosphonate Groups at the Binding Site

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Abstract. (S)-2,3:4,5-Bis[1,2-(3-diethylphosphonyl-methylnaphtho)]-1,6,9,12,15,18-hexaoxacycloicosa-2,4-diene–KSCN–CHCl$_3$,† C$_{40}$H$_{54}$O$_{12}$P$_2$.KSCN.CHCl$_3$, $M_r = 1005 \cdot 4$, orthorhombic, $C222_1$, $a = 16 \cdot 292$ (4), $b = 19 \cdot 948$ (5), $c = 14 \cdot 782$ (5) Å, $V = 4804$ (2) Å^3, $Z = 4$ [$\frac{1}{2}$ SCN$^-$, $\frac{1}{2}$ CHCl$_3$, $\frac{1}{2}$ (K$^+$.host) in an asymmetric unit occurring eight times in the unit cell], D_m(295 K) $= 1 \cdot 34$, D_x(295 K) $= 1 \cdot 343$, D_x(115 K) $= 1 \cdot 390$ g cm^{-3}, λ(Mo $K\alpha$) $= 0 \cdot 7107$ Å, $\mu = 3 \cdot 92$ cm^{-1}, $F(000) = 2104$, $T = 115$ K, $R = 0 \cdot 086$ for 1523 observed reflections. The present host is the most powerful binder of K$^+$ yet studied that contains the 1,1′-binaphthyl group; the coordination of K$^+$ to eight nearby O atoms in this complex is approximately hexagonal-bipyramidal. The SCN$^-$ ion, the CHCl$_3$ molecule and one ethyl group are disordered.

Introduction. The introduction of additional binding sites in a host can strongly influence its binding power and affect its selectivity for the guest. This host, (I), containing§ a binaphthyl group with two attached —CH$_2$PO(OEt)$_2$ groups in addition to a 20-crown-6 macrocycle, can ligate the guest to give a chiral hexagonal-bipyramidal arrangement involving eight O atoms. Of all the 1,1′-binaphthyl hosts yet examined, (I) is the most powerful binder of K$^+$ (Cram & Trueblood, 1981).

(I)
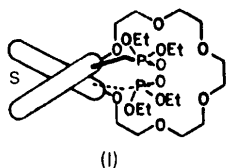
The substituted binaphthyl group (at the left) is shown as the S enantiomer.

Experimental. The 1:1 complex of KSCN with 2,3:-4,5-bis[1,2-(3-diethylphosphonylmethylnaphtho)]-1,6,-9,12,15,18-hexaoxacycloicosa-2,4-diene (II) was prepared as described (Helgeson, Weisman, Toner, Tarnowski, Chao, Mayer & Cram, 1979) and recrystallized from ethyl acetate/chloroform. Weissenberg photographs‡ show systematic absences $h + k = 2n +$ 1 and, for 00l reflections, $l = 2n + 1$. A colorless parallelepiped of (II), $0 \cdot 25 \times 0 \cdot 25 \times 0 \cdot 25$ mm, on a Syntex $P\bar{1}$ diffractometer, graphite monochromator, Mo $K\alpha$, at 115 K (Strouse, 1976): orientation matrix and unit-cell dimensions by least-squares refinement of 15 reflections ($20 \leq 2\theta \leq 29°$), intensities measured by θ–2θ scans, $2 \cdot 0°$ min^{-1} in 2θ, from 1° below $K\alpha_1$ to 1° above $K\alpha_2$; intensities measured for $2\theta < 55°$ for the range $h = 0$ to 21, $k = 0$ to 24, $l = 0$ to 19; intensities of three standard reflections monitored every 97 reflections with 3% maximum intensity variation from average and no significant change during data collection; total of 3062 independent reflections, 1523 with $I > 3\sigma(I)$ used in structure solution and refinement;§ absorption corrections were not made ($\mu = 3 \cdot 92$ cm^{-1}); no correction for extinction; K$^+$ and three O atoms found by direct methods, remaining atoms (including most H atoms) located on Fourier and difference Fourier maps. The host molecule consists of two

moieties related by a twofold axis at $(0, y, \frac{1}{4})$, which passes between the two naphthyl groups, through the K^+, and between the crown ether $-CH_2-$ groups most distant from the binaphthyl group [C(18)]. The naphthyl group was refined as a rigid group with internal coordinates found in the complex of another binaphthyl crown that has two equivalent crown rings, which interact with the $[H_3N(CH_2)_4NH_3]^{2+}$ ion (Goldberg, 1977). One of the ethyl groups is disordered, with refined occupancies for C(24) of 0·53 and 0·47 and with a single C(23) (the $-CH_2-$ C atom); because of overlap an average C(23) position was refined. The SCN^- anion and the $CHCl_3$ molecule lie across twofold axes $(x,\frac{1}{2},0)$, each in a position of half-occupancy. The shortest distances between atoms of these disorder-related groups are 0·4 [C(1S)···C(1S) of $CHCl_3$] and 0·7 Å (S···S of anion). All other distances between such atoms are >1 Å. H atoms of $CHCl_3$ and of the disordered ethyl group [C(23), C(24)] were not included in the structure-factor calculations. All other H atoms were kept in geometrically reasonable positions with C—H = 1·08 Å and with fixed displacement* parameters. With the exception of the SCN^- and the C atoms of $CHCl_3$ and of the naphthyl group, all refined non-H atoms have anisotropic displacement parameters. Isotropic displacement parameters were refined for non-H atoms and a single overall displacement parameter was refined for H of methylene groups; for the remaining H atoms, displacement parameters were fixed: $\langle u^2 \rangle = 0·06$ for H on a naphthyl group, 0·09 (CH_2) and 0·14 $Å^2$ (CH_3) for H on a non-disordered ethyl group; refined by least squares on F (Sheldrick, 1976); refinement of 229 parameters converged to $R = 0·086$, $wR = 0·076$, $w = 1/\sigma^2(F_o)$, $S = 2·19$ (for all 3062 reflections $R = 0·165$, $wR = 0·085$, $S = 1·66$); maximum ratio in final least-squares cycle of shift to e.s.d. was 0·11 in a displacement parameter and 0·10 in a positional parameter; maximum and minimum heights of 0·7 and $-0·6$ e $Å^{-3}$ in the final difference Fourier synthesis; all peaks of 0·4 to 0·7 e $Å^{-3}$ were found in the region of the binaphthyl group (these C atoms have isotropic displacement parameters); atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations were performed on DEC VAX 11/750 and VAX 11/780 computers using the *UCLA Crystallographic Package* (1984) (locally edited versions of *CARESS, PROFILE, MULTAN, ORFLS, ORFFE, ABSORB, ORTEP* and *SHELX*, and a local molecular-geometry program, *MG*84) and *PLUTO*78 (Motherwell & Clegg, 1978).

Discussion. The K^+–host complex lies on a crystallographic twofold axis. The K^+ ion is coordinated in a

hexagonal-bipyramidal arrangement to the six O atoms of the hexaether macrocycle $[K^+···O$ 2·723 (7), 2·729 (8), and 2·818 (8) Å] and to one O atom of each of the two diethyl phosphonate groups $[K^+···O$ 2·702 (8) Å]. Coordination of the hexaether is similar to that found in KSCN–18-crown-6 (Seiler, Dobler & Dunitz, 1974); however, in that compound the six O atoms lie more nearly in a plane (deviation $\pm0·19$ Å) than in the present structure (deviations 0·604, $-0·079$, $-0·442$ Å). The dihedral angle of the binaphthyl unit in (II) is 67°. The present host is a powerful complexer of both Na^+ and K^+ (Helgeson et al., 1979), with a very slight preference for the former. The average $K^+···O$ distance in the complex reported here (2·74 Å) is somewhat shorter than that found in most crown complexes of K^+ (Dalley, 1978) for which the average is usually a little more than 2·8 Å. No crystalline complexes of Na^+ with diphosphonate crown hosts have been reported. The average $Na^+···O$ distance reported for crown complexes of Na^+ is in the neighborhood of 2·5 Å (Dalley, 1978). Although many crown ethers and related hosts are too large or too rigid to permit full coordination of Na^+, there is in the present host some flexibility in the phosphonate arms and in the hexaether moiety. This could permit shorter cation···O distances than those found in the present structure and consequent formation of a strong host–Na^+ complex.

Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 1; representative bond lengths and angles and torsion angles are given in Table 2.* The host exists as the S enantiomer [at a significance level of better than 0·005 (Hamilton, 1965)], as expected because it was synthesized from S-3,3'-dicarboxy-2,2'-dihydroxy-1,1'-binaphthyl. A *PLUTO*78 stereoview of the complex is shown in Fig. 1. There are no unusual intermolecular distances; the shortest intermolecular distance not involving H is 3·31 Å, from C(15) to O(25)$(\frac{1}{2} + x, -\frac{1}{2} - y, 1 - z)$. The shortest distance between K^+ and SCN^- is 6·59 Å (between K and N).

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* Commonly called 'vibration parameters' or 'temperature-factor parameters'.

* Lists of anisotropic displacement parameters, bond distances, bond angles and torsion angles, H-atom parameters and observed and calculated structure factors and the calculation of the significance level for the S enantiomer have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42554 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Position and displacement parameters for* $C_{40}H_{54}O_{12}P_2.KSCN.CHCl_3$

Units of each e.s.d., in parentheses, are those of the least-significant digit of the corresponding parameter.

	x	y	z	$\langle u^2 \rangle$ (Å^2)
K	0·0000	−0·2015 (2)	0·2500	0·023
O(11)	−0·0026 (6)	−0·0855 (3)	0·3471 (5)	0·029
C(12)	0·0534 (8)	−0·0752 (6)	0·4190 (9)	0·041
C(13)	0·1136 (9)	−0·1328 (7)	0·4152 (10)	0·046
O(14)	0·0724 (5)	−0·1952 (4)	0·4229 (6)	0·032
C(15)	0·1272 (9)	−0·2508 (6)	0·4257 (10)	0·045
C(16)	0·0813 (9)	−0·3141 (6)	0·4112 (9)	0·042
O(17)	0·0566 (5)	−0·3194 (4)	0·3199 (6)	0·032
C(18)	0·0086 (10)	−0·3761 (6)	0·2991 (8)	0·044
C(19)	−0·1570 (10)	−0·0951 (7)	0·4375 (10)	0·062
P(20)	−0·2004 (2)	−0·1665 (2)	0·3818 (3)	0·043
O(21)	−0·1587 (5)	−0·1837 (4)	0·2974 (6)	0·038
O(22)	−0·2971 (7)	−0·1504 (5)	0·3719 (8)	0·082
C(23)	−0·3357 (11)	−0·1421 (10)	0·2878 (11)	0·111
C(24A)	−0·3503 (21)	−0·0751 (13)	0·2578 (17)	0·060
C(24B)	−0·4265 (10)	−0·1390 (17)	0·2932 (16)	0·086
O(25)	−0·2033 (6)	−0·2238 (4)	0·4554 (6)	0·051
C(26)	−0·1276 (10)	−0·2576 (10)	0·4781 (12)	0·082
C(27)	−0·1206 (10)	−0·2603 (13)	0·5787 (15)	0·138
C(1)	−0·0429 (3)	0·0135 (3)	0·2696 (4)	0·032 (3)*
C(2)	−0·0581 (3)	−0·0332 (3)	0·3345 (4)	0·027 (3)*
C(3)	−0·1347 (3)	−0·0366 (3)	0·3776 (4)	0·040 (4)*
C(4)	−0·1967 (3)	0·0066 (3)	0·3544 (4)	0·058 (4)*
C(5)	−0·2363 (3)	0·1119 (3)	0·2829 (4)	0·062 (5)*
C(6)	−0·2211 (3)	0·1622 (3)	0·2243 (4)	0·062 (5)*
C(7)	−0·1471 (3)	0·1644 (3)	0·1780 (4)	0·059 (4)*
C(8)	−0·0885 (3)	0·1169 (3)	0·1925 (4)	0·041 (4)*
C(9)	−0·1762 (3)	0·0623 (3)	0·3005 (4)	0·039 (3)*
C(10)	−0·0989 (3)	0·0676 (3)	0·2595 (4)	0·028 (3)*
S	−0·1116 (4)	−0·5115 (4)	1·0185 (5)	0·045 (2)*
C	−0·0438 (16)	−0·4664 (14)	0·9678 (18)	0·041 (7)*
N	0·0021 (21)	−0·4325 (14)	0·9311 (20)	0·082 (9)*
C(1S)	−0·1676 (13)	−0·4942 (27)	0·5106 (33)	0·045 (8)*
Cl(1)	−0·2170 (6)	−0·4536 (5)	0·4205 (7)	0·073
Cl(2)	−0·1414 (8)	−0·5735 (5)	0·4810 (11)	0·134
Cl(3)	−0·2410 (7)	−0·4963 (7)	0·6014 (8)	0·106

The relative occupancies of C(24A) and C(24B) are 0·43 (1) and 0·57 (1) respectively. The occupancies were refined in an earlier cycle. The isotropic displacement parameters for C(24A) and C(24B) were constrained to be equal for that refinement.
The occupancies of S, C, N, C(1S), Cl(1), Cl(2), and Cl(3) are 0·5.
Atoms C(1) through C(10) have been refined as a rigid naphthyl group.

* Atom refined isotropically. Other isotropic values are $1/8\pi^2 \times$ 'equivalent B value' defined by Hamilton (1959).
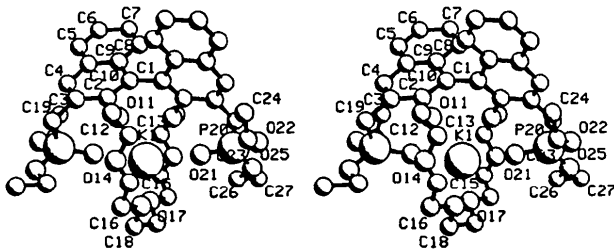

Fig. 1. Stereoview of the complex cation, showing the numbering scheme. For clarity, labels for O(17) and P(20) through C(27) are placed on the twofold-related side of the macrocycle (see text); H atoms have been omitted. For the disordered ethyl group, C(24B) has not been included.

Table 2. *Some features of the molecular geometry*

A complete list of bond distances, bond angles and torsion angles has been deposited.

	Average value	Range of values	Typical e.s.d. of an individual value
(a) Bond distances			
K···O$_{ether}$	2·757 Å	2·723–2·818 Å	0·008 Å
K···O$_{phos}$	2·702 (8)		
C$_{arom}$—O	1·39 (1)		
C$_{arom}$—C$_{CH_2}$	1·51 (2)		
C$_{CH_2}$—C$_{CH_2}$	1·49	1·48–1·51	0·02
C$_{CH_2}$—O	1·42	1·41–1·42	0·02
P=O	1·462 (9)		
P—O$_{Et}$	1·60	1·58–1·62	0·01
P—C	1·79 (2)		
(b) Bond angles			
C—O—C	114·1°	113·0–115·2°	0·9°
CH$_2$—CH$_2$—O	109·2	106·3–110·9	1·1
O$_{ether}$···K···O$_{ether}$			
O adjacent	61·9	59·4–63·6	0·2
opposite	166·4	157·9–174·9	0·2
other	119·9	115·7–122·6	0·2
O$_{ether}$···K···O$_{phos}$	89·9	74·7–109·8	0·2
O$_{phos}$···K···O$_{phos}$	164·9 (2)		
O=P—O$_{ethyl}$	115·3	114·9–115·6	0·5
O$_{ethyl}$—P—O$_{ethyl}$	100·2 (6)		
C$_{arom}$—C$_{CH_2}$—P	116·1 (9)		

(c) Torsion angles and dihedral angles

O(11)—C(12)—C(13)—O(14)	−58 (1)°		
O(14)—C(15)—C(16)—O(17)	72 (1)		
O(17)—C(18)—C(18′)—O(17′)	−64 (1)		
CH$_2$—CH$_2$—O—CH$_2$	174	166–177°	1°

Angles between normals to least-squares planes*

A–B	67·4°
A–C	91·1

* Plane A comprises C(1), C(2), C(3), C(4), C(9) and C(10). Plane B is in the other ring of the binaphthyl fragment and includes the same atoms related by a twofold axis. Plane C is the least-squares plane defined by the six O atoms of the hexaether.

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