Solid State Structure of the Hydrated Potassium Thiocyanate Complex of Benzodinaphthopyridino-21-crown-7, $C_{37}H_{31}NO_6 \cdot KSCN \cdot H_2O$ (1 : 1 : 1)

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Abstract. Single crystal X-ray analysis of the hydrated KSCN complex of benzodinaphthopyridino-21-crown-7 (**1**) (1 : 1 : 1) is reported. Crystals of the complex are orthorhombic, *Pnma*, with $a = 16.946(4)$, $b = 22.298(4)$, $c = 10.390(8)$ Å and $D_c = 1.184$ g cm^{-1}, $Z = 4$. The host macroring (**1**) has a mirror symmetry and exists in a so-called 'dentists chair' conformation. The cation (K$^+$) is coordinated to all the six ether oxygen atoms and also weakly to the pyridine N atom. The SCN$^-$ anion group has a statistical type of disorder with opposite orientations of S and N such that nitrogen and sulphur are coordinated to K$^+$. Packing of the host molecules is in columns to form quasi channels with K$^+$, SCN$^-$, and H$_2$O being located inside the stacks.

1. Introduction

During the last few years, crown compounds incorporating a pyridine nucleus and two or three extra aromatic units, such as benzene or naphthalene moieties, have been shown to be capable of readily forming crystalline inclusion complexes with uncharged organic guests [1–6]. In this class of compounds, the host behaviour strongly depends on each single constituent of the macroring and also on the positional isomers of a given building block. By comparison, little is known about the cation complexation of this type of macroring [1, 7]. On the other hand, non-pyridino large ring crowns with benzo/naphtho condensations show exceptional cation complexing ability [8]. The crystal structure of the title compound, **1** · KSCN · H$_2$O (1 : 1 : 1), was undertaken to extend our knowledge of the metal ion complexes of oligoaryl-condensed pyridino crowns and to establish the particular conformation of **1** affected by the coordination of a K$^+$ ion.

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2. Experimental

2.1. SYNTHESIS AND SAMPLE PREPARATION

The methods for preparation of the host compound, **1**, has been described earlier
[3]. The title complex, **1** · KSCN · H_2O (1 : 1 : 1), was synthesized by combining hot
solutions of **1** in methanol–ethyl acetate (1 : 1) and of KSCN in MeOH to
precipitate the solid complex on cooling: 60% yield; m.p. 148–150°C; IR (KBr)
3600 (OH), 2100 (SCN), 1645, 1520 (Ar), 1270 cm^{-1} (C—O).
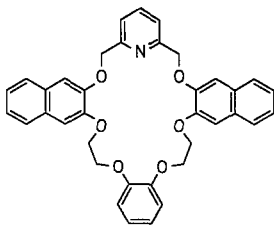
1

Anal. Calcd. for $C_{38}H_{33}KN_2O_7S$: C, 65.12; H, 4.75; N, 4.00%. *Found*: C, 64.86;
H, 4.69; N, 4.12.

Recrystallization from methanol yielded suitable crystals for X-ray crystallography.

2.2. X-RAY DATA COLLECTION AND PROCESSING

A colourless crystal of the complex of dimensions 0.5 × 0.4 × 0.3 mm was used.
Preliminary studies for the unit cell dimensions and space group were carried out by
photographic methods. More accurate cell dimensions were obtained using an
Enraf-Nonius CAD4 diffractometer equipped with CuK_α radiation and a graphite
monochromator by least-squares fit of the 2Θ values of 20 general reflections
(20° < 2Θ < 40°).

The crystal data are as follows: $C_{37}H_{31}NO_6$ · KSCN · H_2O (1 : 1 : 1), $F_W = 700.8$,
orthorhombic, *Pnma*, $a = 16.946(4)$, $b = 22.298(4)$, $c = 10.390(8)$ Å, $V = 3925.99$
Å^3, $Z = 4$, $D_c = 1.184$ g cm^{-3}, $CuK_\alpha = 1.5418$ Å, $\mu = 19.4$ cm^{-1}, $F(000) = 1420$,
$T = 296$ K. Three-dimensional data were collected from 3158 reflections, 1864 being
considered as observed with $I > 3\sigma(I)$, CuK_α radiation, max. $2\Theta = 120°$, ω-2Θ scan,
data collection range $h = 0$ to 16, $k = 0$ to 24 and $l = 0$ to 11. Lp^{-1} corrections
were applied. An empirical absorption correction factor based on a series of
psi-scans was applied to the data [9]. Relative transmission coefficients ranged from
0.9987 to 0.9145 with an average value of 0.9566.

2.3. STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by the 'heavy atom' method using SHELX-86 [10]. It gave
most of the non-hydrogen atoms and the remaining non-hydrogen atoms were

located from a difference Fourier map. Refinement was carried out by full-matrix least-squares [11]. However, the thiocyanate moiety did not fully appear in successive difference Fourier computations. The difference Fourier is expected to give three peaks corresponding to the S, C and N atoms of the anion (SCN$^-$). Instead, it gave only a dumb-bell shaped peak leading to two locations which are approximately 1.35 Å apart. A careful study of these two peaks gave evidence for the fact that the anion SCN$^-$ is statistically disordered by orientation along its length in opposite ways (i.e. SCN$^-$ and NCS$^-$). Each of the two locations of the dumb-bell shaped peak corresponds to unresolved S, N, and C atoms. This situation in a statistical type of disorder leading to two locations instead of three, is mainly due to the large difference in lengths of the S—C and C≡N covalent bonds (i.e., 1.75 and 1.15 Å, respectively). The composite 'NCS' atoms [consisting of $f(N) + f(C) + f(S)$ in scattering amplitude] were refined with 1/3 occupancy. It was interesting to note in the final stage of structure completion, that two isolated weak peaks appeared in the difference Fourier map, which were assumed to be that of a disordered water oxygen (OW', OW''). However, these positions cannot be identified as the missing peak of the anion S—C≡N$^-$ from stereochemical considerations. Isotropic temperature factors were assumed for these two locations of the disordered water oxygens and the positional parameters and occupancy factor were refined. There was a significant reduction of the R factor after introducing the disordered location of the assumed water oxygen atom. Most of the hydrogen atoms were obtained from a difference Fourier map computed at an R of 0.12 and the remaining hydrogen atoms (except water molecule hydrogens) were fixed by stereochemical considerations. The hydrogen atoms were included in the final cycle of refinement. The refinement converged at $R = 0.092$, $R_w = 0.108$ [$w = 1.0/(\sigma(F_0)^2 + 0.000241 F_0^2)$] and $(\Delta/\sigma)_{max.} = 0.02$. Maximum and minimum peak heights in the final difference Fourier map are 0.39 and -0.40 e Å^{-3}, respectively. Scattering factors were taken from [12].

3. Results and Discussion

The final atomic coordinates of the non-hydrogen atoms are listed in Table I; atom labelling is in accordance with Figure 1. Table II shows bond distances and angles, and Table III gives a selection of torsion angles. Table IV gives intramolecular bond distances and angles. Lists of anisotropic thermal parameters (Table V) and structure factors have been deposited. The molecular structure of the complex is shown in Figure 1 and the packing diagram is illustrated in Figure 2.

3.1. MOLECULAR STRUCTURE

3.1.a. *Host Conformation*

The host molecule has a mirror symmetry, passing through the N(1) and C(23) atoms and bisecting the opposite C—C bonds of the phenylene ring. This implies a highly symmetrical molecular geometry (Figure 1a and Figure 1c), with five hetero atoms N(1), O(4), O(7), O(7)*, and O(4)* being coplanar to within ±0.004(6) Å
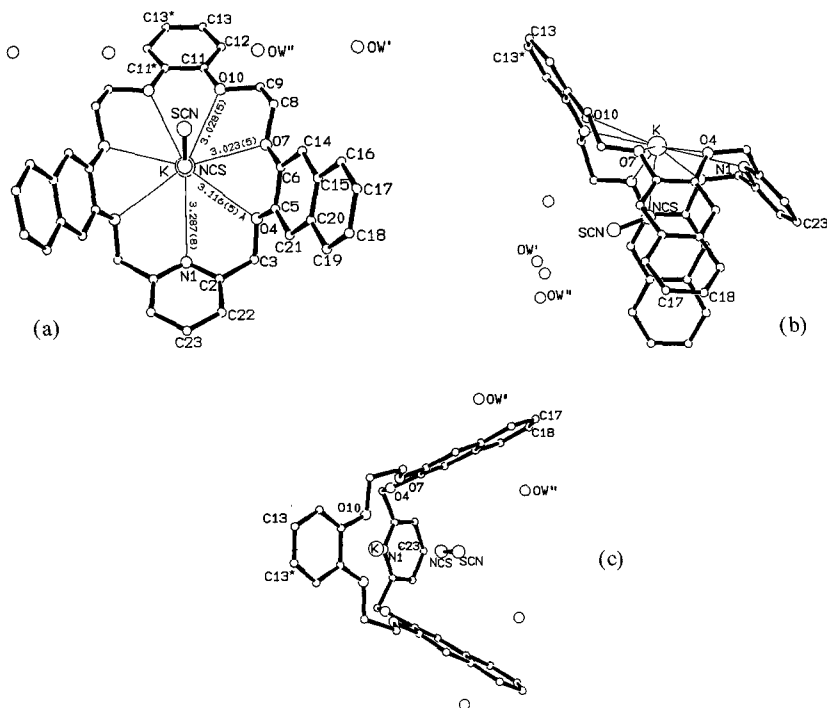
Fig. 1. Molecular structure of the **1** · KSCN · H$_2$O (1 : 1 : 1) complex: (a) top view giving indication of the numbering scheme for the atoms; (b) side view showing the 'dentist's chair' form; (c) front view (along the mirror plane).
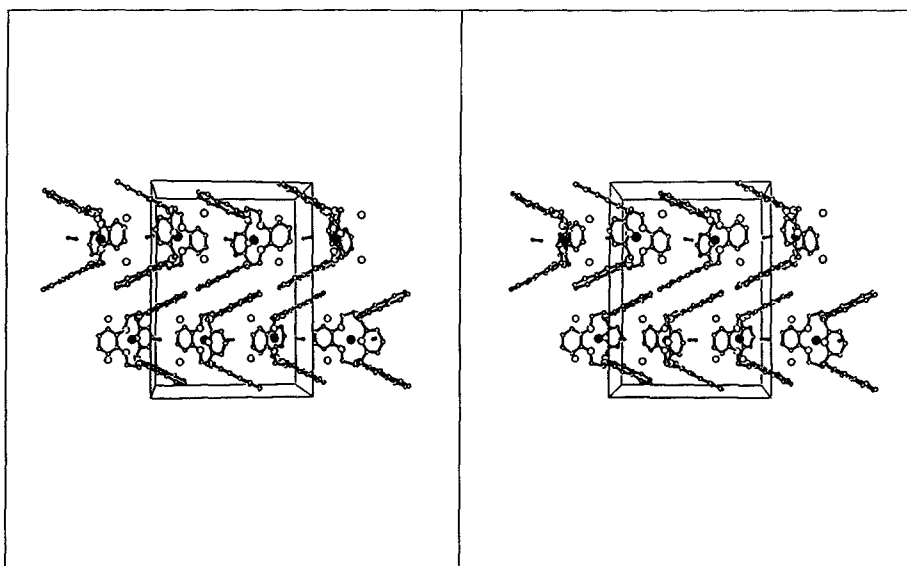

Fig. 2. Crystal packing of the **1** · KSCN · H$_2$O (1 : 1 : 1) complex (stereo view). The K$^+$ ions are indicated as bold dots, SCN$^-$ as small sticks; the molecules of water (OW$''$) are specified as open circles; OW$'$ is omitted.

Table I. Final fractional coordinates and equivalent thermal vibrational parameters for non-hydrogens of the $1 \cdot KSCN \cdot H_2O$ $(1:1:1)$ complex (e.s.ds are in parentheses). $U_{eq} = (U_{11} + U_{22} + U_{33})/3$

Atom	x/a	y/b	z/c	U_{eq}
N(1)	0.8581(5)	0.2500(0)	−0.2245(7)	0.050(5)
C(2)	0.8840(5)	0.3015(3)	−0.2780(6)	0.052(4)
C(3)	0.8500(5)	0.3570(3)	−0.2170(7)	0.059(4)
O(4)	0.8693(3)	0.3614(2)	−0.0841(4)	0.054(3)
C(5)	0.9417(5)	0.3877(3)	−0.0511(6)	0.044(4)
C(6)	0.9518(4)	0.3966(3)	0.0817(6)	0.042(4)
O(7)	0.8899(3)	0.3764(2)	0.1575(4)	0.049(3)
C(8)	0.8957(5)	0.3892(3)	0.2913(6)	0.051(4)
C(9)	0.8200(5)	0.3714(3)	0.3556(6)	0.052(4)
O(10)	0.8140(3)	0.3076(2)	0.3510(4)	0.054(3)
C(11)	0.7586(4)	0.2818(3)	0.4316(7)	0.047(4)
C(12)	0.7079(5)	0.3114(3)	0.5098(7)	0.058(5)
C(13)	0.6566(5)	0.2806(3)	0.5904(7)	0.066(5)
C(14)	1.0177(5)	0.4256(3)	0.1277(6)	0.046(4)
C(15)	1.0790(4)	0.4450(3)	0.0413(7)	0.048(4)
C(16)	1.1473(4)	0.4747(3)	0.0861(7)	0.052(4)
C(17)	1.2052(5)	0.4916(3)	0.0045(9)	0.069(5)
C(18)	1.1969(5)	0.4803(4)	−0.1276(8)	0.064(5)
C(19)	1.1316(6)	0.4521(3)	−0.1747(7)	0.065(5)
C(20)	1.0700(5)	0.4343(3)	−0.0900(7)	0.049(4)
C(21)	0.9995(5)	0.4059(3)	−0.1354(6)	0.052(4)
C(22)	0.9347(5)	0.3043(4)	−0.3800(7)	0.065(5)
C(23)	0.9598(5)	0.2500(0)	−0.4358(11)	0.078(9)
K	0.8401(2)	0.2500(0)	0.0905(3)	0.089(2)
N,C,S(1)	0.9952(8)	0.2500(0)	0.0851(14)	0.103(10)
S,C,N(2)	1.0335(11)	0.2500(0)	0.2021(15)	0.153(15)
OW′a	0.0583(4)	−0.0081(3)	0.4484(7)	0.084(2)c
OW″b	0.1730(20)	0.1422(17)	0.4241(32)	0.111(11)c

aOccupancy factor 0.8.
bOccupancy factor 0.2.
cIsotropic thermal parameter.

[O(10) and O(10)* deviation from the mean plane is 1.545(5) Å]. Individual torsion angles are as usually observed for benzo crown compounds [13]: *anti* (for C—X—C—C, X = O, N), $\pm$*gauche* (for O—C—C—O) and *syn* (at *ortho*-substituted aryl groups). Starting from the N(1)—C(2) bond, the macrocycle has the conformation $agg*asaaga*asaa*g^-aasag^-*g^-a$ (where $g* = \pm 60° \pm 25°$ and $a* = \pm 180° \pm 20°$; these correspond to distorted *gauche* and *anti* conformations of the macroring), which gives rise to a so-called 'dentist's chair' conformation with regard to the shape of the molecule (Figure 1b). A similar ring conformation was found earlier for the analogous dibenzo pyridino crown ether in its ethanol inclusion complex [14].

3.1.b. *Bond Distances and Angles*

There is one aliphatic —CH$_2$—CH$_2$— bond in this structure [C(8)—C(9)], the bond length is slightly small [1.500(11) Å] in comparison to the normal value of

Table II. Bond distances (Å) and bond angles (°) for the $1 \cdot KSCN \cdot H_2O$ (1 : 1 : 1) complex (e.s.ds are in parentheses).

Atoms	Distance	Atoms	Distance
N(1)—C(2)	1.349(8)	C(11)—C(11)*	1.418(10)
C(2)—C(3)	1.502(10)	C(11)—C(12)	1.354(10)
C(2)—C(22)	1.366(11)	C(12)—C(13)	1.389(11)
C(3)—O(4)	1.429(9)	C(13)—C(13)*	1.365(10)
O(4)—C(5)	1.402(10)	C(14)—C(15)	1.440(10)
C(5)—C(6)	1.405(9)	C(15)—C(16)	1.412(10)
C(5)—C(21)	1.375(11)	C(15)—C(20)	1.393(10)
C(6)—O(7)	1.387(8)	C(16)—C(17)	1.350(11)
C(6)—C(14)	1.376(10)	C(17)—C(18)	1.403(13)
O(7)—C(8)	1.423(8)	C(18)—C(19)	1.364(13)
C(8)—C(9)	1.500(11)	C(19)—C(20)	1.422(12)
C(9)—O(10)	1.427(8)	C(20)—C(21)	1.432(11)
O(10)—C(11)	1.383(8)	C(22)—C(23)	1.408(11)
N,C,S(1)—S,C,N(2)	1.370(22)		

Atoms	Angle	Atoms	Angle
C(2)*—N(1)—C(2)	116.7(5)	C(11)*—C(11)—C(12)	119.2(5)
N(1)—C(2)—C(3)	113.8(5)	C(11)—C(12)—C(13)	121.2(5)
N(1)—C(2)—C(22)	124.3(5)	C(12)—C(13)—C(13)*	119.6(6)
C(3)—C(2)—C(22)	121.9(6)	C(6)—C(14)—C(15)	120.7(5)
C(2)—C(3)—O(4)	112.0(5)	C(14)—C(15)—C(16)	121.8(5)
C(3)—O(4)—C(5)	117.8(4)	C(14)—C(15)—C(20)	118.7(5)
O(4)—O(5)—C(6)	114.0(5)	C(16)—C(15)—C(20)	119.5(5)
O(4)—C(5)—C(21)	126.2(5)	C(15)—C(16)—C(17)	121.3(5)
C(6)—C(5)—C(21)	119.8(5)	C(16)—C(17)—C(18)	119.4(6)
C(5)—C(6)—O(7)	114.8(5)	C(17)—C(18)—C(19)	121.0(6)
C(5)—C(6)—C(14)	120.4(5)	C(18)—C(19)—C(20)	120.2(6)
O(7)—C(6)—C(14)	124.7(5)	C(15)—C(20)—C(19)	118.6(6)
C(6)—O(7)—C(8)	116.0(4)	C(15)—C(20)—C(21)	119.3(5)
O(7)—C(8)—C(9)	108.9(5)	C(19)—C(20)—C(21)	122.1(6)
C(8)—C(9)—O(10)	108.1(5)	C(5)—C(21)—C(20)	121.0(5)
C(9)—O(10)—C(11)	116.3(4)	C(2)—C(22)—C(23)	118.1(6)
O(10)—C(11)—C(11)*	114.6(5)	C(22)—C(23)—C(22)*	118.6(7)
O(10)—C(11)—C(12)	126.2(5)		

Table III. Selected torsion angles for the $1 \cdot KSCN \cdot H_2O$ (1 : 1 : 1) complex (e.s.ds are in parentheses).

Atoms	Angle
C(2)*—N(1)—C(2)—C(3)	177.4(6)
N(1)—C(2)—C(3)—O(4)	60.4(8)
C(2)—C(3)—O(4)—C(5)	85.6(7)
C(3)—O(4)—C(5)—C(6)	172.9(6)
O(4)—C(5)—C(6)—O(7)	1.8(8)
C(5)—C(6)—O(7)—C(8)	−175.1(6)
C(6)—O(7)—C(8)—C(9)	172.9(5)
O(7)—C(8)—C(9)—O(10)	68.0(7)
C(8)—C(9)—O(10)—C(11)	164.9(5)
C(9)—O(10)—C(11)—C(11)*	−175.4(6)
O(10)—C(11)—C(11)*—O(10)*	0.0(8)

Table IV. Intramolecular bond distances (Å) and bond angles (°) for the **1** · KSCN · H₂O (1 : 1 : 1) complex (e.s.ds are in parentheses).

Atoms	Distance	Atoms	Distance
N(1)...O(4)	2.887(6)	K...N(1)	3.287(8)
O(4)...O(7)	2.556(6)	K...O(4)	3.116(5)
O(7)...O(10)	2.837(6)	K...O(7)	3.023(5)
O(10)...O(10)*	2.569(6)	K...O(10)	3.028(5)
		K...S (or) N	2.629(14)

Atoms	Angle
N(1)...K...O(4)	53.5(2)
O(4)...K...O(7)	49.2(2)
O(7)...K...O(10)	55.9(2)
O(10)...K...O(10)*	50.2(2)
Mean value	52.5
σ	±2.7

1.537 Å; this behaviour is frequently seen in crown complexes [13, 15]. The mean C—C bond length of the naphthaleno moieties is 1.397(11) Å, while the mean $C(sp^2)$—O and $C(sp^3)$—O bond lengths are 1.391(9) and 1.426(8) Å, respectively. The mean $C(sp^2)$—N bond distance of the pyridine ring is 1.349(8) Å. There is good agreement of bond lengths and angles with that of the dinaphthopyridino-18-crown-6 host in its complex with acetonitrile (1 : 2) [6] and with related crown compounds [4, 16].

The intramolecular distances between hetero atoms are N(1)—O(4) = 2.887(6), O(4)—O(7) = 2.556(6), O(7)—O(10) = 2.837(6), and O(10)—O(10)* = 2.569(6) Å. The mean values of the bond angles at the hetero atoms are 116.7(4)° for C—O—C of the macrocycle and 116.7(5)° for C—N—C of the pyridine ring. Considerable ring strain can be seen at C(2), C(5), C(6), and C(11); maximum distortion (from 120°) is noted at C(5), C(6), and C(11).

3.2. HOST-GUEST INTERACTION AND CRYSTAL PACKING

The projection of the macroring exhibits a quasi-regular $K^+ \cdots X (X = N, O)$ heptagon (Figure 1a) characterized by an average $X \cdots K^+ \cdots X (X = N, O)$ angle of 52.5° ± 2.7° (Table IV). The K^+ is located at a special position. The cation is coordinated to all the six oxygen atoms of the macrocycle with a mean value of $K^+ \cdots O$ of 3.056(5) Å and to N(1) with $K^+ \cdots N(1)$ of 3.287 Å. The eighth coordination bond to K^+ is N (or S) of SCN⁻ at a distance of 2.63(1) Å, which suggests a strong interaction compared to another reported structure [17]. The angle of $K^+ \cdots N \equiv C$ is 118.2°. It is interesting to observe in this structure that the anion $N \equiv C$—S is in a statistical type of disorder [18] with the N co-ordinating with K^+ by the anion SCN⁻ existing in two opposite ways. The SCN⁻ group is located on the mirror plane of the space group at $y = 0.25$ (cf. Figure 2). Figure 1b indicates that the thiocyanate group is in between the two host naphthalene rings, unlike reported structures [1, 7] where the thiocyanate group is pointing away from the host atoms of the macroring.

In cases where the cation is too small to enable a close contact with the crown donor atoms, a molecule of water may be used to stabilize the complex arrangement [13, 19], unlike here where the water molecules in the two disordered sites (OW', OW") apparently maintain no close contacts to their environments. The OW'- and OW"-positions are at a distance of 3.883(5) Å.

The lattice structure (Figure 2) is such that the quasi cone-shaped molecules defined by the pyridine and the two naphthalene planes are embedded in one another with the protruding phenylene ring of one molecule partly filling the cone interior of another molecule making a column in the a direction. In this respect, the packing principle relates to cyclotriveratrylenes [20]. Intramolecular stacking between the naphthalene units of neighbouring host columns is another characteristic feature of the lattice structure.

Acknowledgements

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