

The Crystal Conformation of 1,4,7,10-Tetra-(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane in Complexes with NaSCN and KSCN at $-150\text{ }^{\circ}\text{C}$

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The crystals of the NaSCN-complex are orthorhombic with space group $Pna2_1$ and cell dimensions $a = 24.980(5)$, $b = 9.304(2)$, $c = 9.292(2)$ Å. Those of the KSCN-complex are monoclinic with space group $P2_1/n$ and cell dimensions $a = 11.015(4)$, $b = 31.863(10)$, $c = 12.988(3)$ Å, $\beta = 94.30(2)^{\circ}$. Data were collected on an automatic four circle diffractometer. The structures were solved by direct methods and refined by full-matrix least squares technique. The ring conformation is [3 3 3] in both complexes. The Na cation is heptacoordinated, making use of the three *gauche* side-chains and the four ring nitrogens. In the KSCN-complex, which has a disordered structure, all four side-chains are bent in and K^+ is octacoordinated. In both complexes all side-arms bend off towards the ring corner atoms.

The aim of the single crystal X-ray crystallographic investigations of the molecule 1,4,7,10-tetra-(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane as a hydrate, and in complexes with Li^+ , Na^+ and K^+ , is to study conformational dissimilarities of this molecule and to correlate the findings with ^{13}C NMR results.¹ Crystal structure determinations of the dihydrated (2:1) LiCl-complex and the hydrate have been reported earlier.^{2,3} The results obtained for the NaSCN- and KSCN-complexes are now reported.

Table 1. Final fractional coordinates with estimated standard deviations for the NaSCN-complex. Standard deviations for hydrogen atoms are about $\sigma_x = 0.001$, $\sigma_y = 0.003$ and $\sigma_z = 0.004$. Hm is bonded to Cm and HOM to Om.

ATOM	X	Y	Z
NA+	.91009(4)	-.09055(12)	-.17723(71)
S	.17353(4)	.61339(9)	.80099(70)
C	.1092(1)	.5826(3)	.8028(8)
N	.0632(1)	.5599(3)	.8040(8)
O1	.9576(1)	.0118(3)	.0246(8)
O2	.9710(1)	-.2810(3)	-.1232(8)
O3	.9838(1)	-.2975(3)	-.6143(8)
O4	.9652(1)	.1062(3)	-.2920(8)
N1	.8420(1)	-.0075(3)	.0123(8)
N2	.8553(1)	-.3123(3)	-.0945(8)
N3	.8611(1)	-.2079(3)	-.4000(8)
N4	.8476(1)	.0968(3)	-.2941(8)
C1	.8027(1)	-.1231(4)	.0349(8)
C2	.8277(1)	-.2722(4)	.0405(8)
C3	.8172(1)	-.3551(4)	-.2061(8)
C4	.8411(1)	-.3516(4)	-.5562(8)
C5	.8156(1)	-.1131(4)	-.4863(8)
C6	.8299(1)	.0455(4)	-.4361(8)
C7	.8011(1)	.1196(4)	-.1990(8)
C8	.8158(1)	.1249(4)	-.0391(8)
C9	.8720(1)	.0224(4)	.1460(8)
C10	.9246(1)	.0962(4)	.1181(8)
C11	.8948(1)	-.4277(4)	-.0655(8)
C12	.9473(1)	-.3676(4)	-.0141(8)
C13	.8970(1)	-.2258(4)	-.5249(8)
C14	.9524(1)	-.2790(4)	-.4857(8)
C15	.8787(1)	.2301(4)	-.3067(8)
C16	.9359(1)	.2072(4)	-.3717(8)
H11	.776	-.124	-.051
H12	.780	-.105	.124
H21	.800	-.344	.061
H22	.854	-.278	.127
H31	.784	-.292	-.205
H32	.803	-.462	-.193
H41	.813	-.388	-.428
H42	.871	-.418	-.358
H51	.785	-.130	-.372
H52	.800	-.134	-.536
H61	.800	.100	-.471

H62	.858	.059	-.502
H71	.774	.041	-.220
H72	.781	.214	-.223
H81	.781	.140	.014
H82	.840	.209	-.014
H91	.879	-.075	.190
H92	.849	.082	.215
H101	.943	.113	.214
H102	.918	.196	.066
H111	.902	-.483	-.158
H112	.882	-.496	.006
H121	.972	-.452	.010
H122	.942	-.302	.072
H131	.901	-.128	-.568
H132	.879	-.288	-.603
H141	.953	-.374	-.430
H142	.971	-.206	-.425
H151	.883	.274	-.206
H152	.858	.307	-.369
H161	.952	.307	-.375
H162	.933	.171	-.474
H01	.977	-.028	.078
H02	.996	-.321	-.151
H03	.972	-.391	-.656
H04	.980	.155	-.207

EXPERIMENTAL

Crystal and intensity data. The crystal data for $(C_{16}H_{36}O_4N_4) \cdot NaSCN$ are: $a=24.980(5)$, $b=9.304(2)$, $c=9.295(2)$ Å, $Z=4$, space group $Pna2_1$, $D_x=1.32$ gcm⁻³, $D_m=1.28$ gcm⁻³ (by flotation), $V=2160.29$ Å³, $\mu=2.06$ cm⁻¹ (MoK α), $\lambda(MoK\alpha)=0.71069$ Å. The crystal data for $(C_{16}H_{36}O_4N_4) \cdot KSCN$ are: $a=11.015(4)$, $b=31.863(10)$, $c=12.988(3)$ Å, $\beta=94.30(2)^\circ$, $Z=8$, space group $P2_1/n$, $D_x=1.30$ gcm⁻³, $D_m=1.25$ gcm⁻³ (by flotation), $V=4545.32$ Å³, $\mu=3.68$ cm⁻¹ (MoK α), $\lambda(MoK\alpha)=0.71069$ Å.

Data were collected on an automatic four-circle diffractometer at ca. -150°C by the ω -scan technique ($2\theta_{\text{max}}=50^\circ$) with MoK α radiation. The scan rate varied from 2° to 23° min⁻¹, depending on the intensity of the reflection. The intensities of two test reflections remeasured after every 50 reflections showed no significant changes during data collection. The intensities were corrected for

Table 2. Bond distances and angles and dihedral angles with estimated standard deviations for the NaSCN-complex.

DISTANCE		(Å)	DISTANCE		(Å)	DIHEDRAL ANGLE		(°)
NA+ - O1	2.417(3)		NA+ - O2	2.388(3)	N1 - C9 - C10 - O1	-57.8(4)		
NA+ - O4	2.526(3)		NA+ - N1	2.569(3)	N2 - C11 - C12 - O2	-63.4(4)		
NA+ - N2	2.591(3)		NA+ - N3	2.643(3)	N3 - C13 - C14 - O3	177.4(3)		
NA+ - N4	2.579(3)		N - O2'	2.820(4)	N4 - C15 - C16 - O4	-57.5(4)		
N - O3'	2.812(4)		O1 - O4'	2.779(4)	C8 - N4 - C1 - C2	161.4(3)		
S - C	1.632(3)		C - N	1.168(4)	C1 - N4 - C8 - C7	-77.4(4)		
O1 - C10	1.432(4)		O2 - C12	1.424(4)	C9 - N1 - C1 - C2	-76.1(4)		
O3 - C14	1.441(4)		O4 - C16	1.429(4)	C1 - N1 - C9 - C10	158.7(3)		
N1 - C1	1.471(4)		N1 - C8	1.474(4)	C9 - N4 - C8 - C7	159.5(3)		
N1 - C9	1.479(4)		N2 - C2	1.481(4)	C8 - N4 - C9 - C10	-78.1(4)		
N2 - C3	1.464(5)		N2 - C11	1.482(4)	C3 - N2 - C2 - C1	-77.3(4)		
N3 - C4	1.483(4)		N3 - C5	1.477(4)	C2 - N2 - C3 - C4	161.9(3)		
N3 - C13	1.475(4)		N4 - C6	1.473(5)	C11 - N2 - C2 - C1	158.7(3)		
N4 - C7	1.475(4)		N4 - C15	1.467(4)	C2 - N2 - C11 - C12	-84.6(4)		
C1 - C2	1.521(5)		C3 - C4	1.519(6)	N1 - C1 - C2 - N2	-61.5(4)		
C5 - C6	1.517(5)		C7 - C8	1.533(6)	C11 - N2 - C3 - C4	-75.0(4)		
C9 - C10	1.505(5)		C11 - C12	1.504(5)	C3 - N2 - C11 - C12	151.3(3)		
C13 - C14	1.520(5)		C15 - C16	1.521(5)	C5 - N3 - C4 - C3	-75.4(4)		
ANGLE		(°)	ANGLE		(°)	C4 - N3 - C5 - C6	161.6(3)	
S - C - N	179.7(3)		O1 - C10 - C9	111.0(3)	C13 - N3 - C4 - C3	163.4(3)		
O2 - C12 - C11	110.2(3)		O3 - C14 - C13	109.7(3)	C4 - N3 - C13 - C14	-77.0(3)		
O4 - C16 - C15	112.4(3)		N1 - C1 - C2	115.4(3)	N2 - C3 - C4 - N3	-59.5(4)		
O1 - N1 - C8	113.8(3)		C1 - N4 - C9	110.8(3)	C13 - N3 - C5 - C6	-77.7(4)		
O1 - N1 - C9	113.2(3)		C8 - N4 - C9	109.9(3)	C5 - N3 - C13 - C14	162.0(3)		
N1 - C9 - C10	112.5(3)		N2 - C2 - C1	113.1(3)	C7 - N4 - C6 - C5	-78.0(4)		
C2 - N2 - C3	111.6(3)		C2 - N2 - C11	109.7(3)	C6 - N4 - C7 - C8	161.3(3)		
N2 - C3 - C4	113.0(3)		C3 - N2 - C11	111.4(3)	C15 - N4 - C6 - C5	159.5(3)		
N2 - C11 - C12	111.7(3)		N3 - C4 - C3	113.8(3)	C6 - N4 - C15 - C16	-71.5(4)		
C4 - N3 - C5	109.9(3)		C4 - N3 - C13	109.3(3)	N3 - C5 - C6 - N4	-62.0(4)		
N3 - C5 - C6	113.5(3)		C5 - N3 - C13	110.3(3)	C15 - N4 - C7 - C8	-75.7(4)		
N3 - C13 - C14	113.5(3)		N4 - C6 - C5	112.7(3)	C7 - N4 - C15 - C16	165.9(3)		
C6 - N4 - C7	110.4(3)		C6 - N4 - C15	111.1(3)	N4 - C7 - C8 - N4	-59.2(4)		
N4 - C7 - C8	113.5(3)		C7 - N4 - C15	110.1(3)				
N4 - C15 - C16	113.2(3)							

Lorentz and polarization effects, but no corrections for absorption or secondary extinction were made (crystal sizes $0.4 \times 0.6 \times 0.2$ mm and $0.2 \times 0.3 \times 0.2$ mm for the NaSCN-complex and the KSCN-complex, respectively). With an observed-unobserved cutoff at $2.5\sigma(I)$, 1709 and 5306 reflections were regarded as observed.

Determination and refinement of the structures. The phase problem was solved by direct methods.⁴ For the KSCN-complex the *E*-map corresponding to the best figure of merit contained several split peaks indicating a disordered structure. The procedure from this map to the final structure was somewhat lengthy: repeated use of weighted Fourier calculations, parameter-

shift refinements (to avoid singular-matrix problems in least-squares), intermediate introduction of anisotropic temperature factors (in order to calculate probable positions for partial atoms),⁵ careful refinements of multiplicity factors, and calculation of partial hydrogen atom positions (to be used in structure factor calculations).^{6,*} For the NaSCN-complex, anisotropic temperature factors were introduced for all non-hydrogen atoms. Maximum r.m.s. amplitudes lay between 0.13 and 0.22 Å. For the KSCN-complex, anisotropic temperature factors were used for the 21

* All programs used (except those for phase determination) are included in this reference.

Table 3. Final fractional coordinates with estimated standard deviations for the non-hydrogen atoms of the KSCN-complex. The two statistically disordered forms are labelled "A" and "B", respectively.

ATOM	X	Y	Z				
K1	.92502(9)	.17886(3)	.51104(8)	C2A	1.1425(9)	.2650(3)	.4933(14)
K2	.25746(9)	.42236(3)	.78485(7)	C2B	1.1487(19)	.2628(6)	.4566(32)
S2	.1657(1)	.1109(0)	1.002(1)	C3A	.9331(6)	.2905(2)	.4616(6)
C34	.1418(4)	.1300(1)	1.1154(4)	C3B	.9714(16)	.2944(5)	.5174(15)
N10	.1253(3)	.1432(1)	1.1970(3)	C4A	.8999(14)	.2902(2)	.5759(8)
N1	1.1767(3)	.1949(1)	.5722(3)	C4B	.8547(26)	.2896(5)	.5551(16)
N2	1.0192(3)	.2578(1)	.4442(3)	C5A	.8198(10)	.2475(2)	.7088(5)
N3	.8222(3)	.2520(1)	.5994(3)	C5B	.8807(32)	.2489(7)	.7227(18)
N4	.9815(4)	.1889(1)	.7504(3)	C6A	.9404(8)	.2335(3)	.7648(6)
N5	.1714(3)	.5024(1)	.8401(3)	C6B	.9056(22)	.2099(8)	.7692(17)
N6	.3756(3)	.4931(1)	.6931(3)	C7A	1.1077(11)	.1833(6)	.7572(9)
N7	.2175(3)	.4300(1)	.5617(2)	C7B	1.1212(18)	.1966(10)	.7447(15)
N8	.0115(3)	.4393(1)	.7077(3)	C8A	1.1876(7)	.2096(3)	.6842(6)
C10	1.1936(4)	.1277(1)	.4755(4)	C8B	1.2076(18)	.1851(7)	.6717(15)
C12	.9337(5)	.2273(1)	.2785(3)	C9A	1.2432(6)	.1547(2)	.5663(5)
C14	.6369(4)	.2182(1)	.5157(4)	C9B	1.2594(18)	.1723(6)	.4944(16)
C16	.8998(6)	.1163(1)	.7225(5)	C11A	1.0277(6)	.2521(2)	.3300(5)
C26	.2263(4)	.4734(1)	1.0154(3)	C11B	.9635(22)	.2717(7)	.3424(17)
C28	.5561(4)	.4628(1)	.7954(3)	C13A	.6953(6)	.2581(2)	.5522(5)
C30	.3102(4)	.3586(1)	.5803(4)	C13B	.6922(21)	.2380(7)	.6079(19)
C32	-.0188(4)	.3696(1)	.7912(4)	C15A	.9114(6)	.1586(2)	.7875(5)
S1A	1.0650(2)	.3788(0)	.2574(1)	C15B	.9810(23)	.1383(8)	.7612(18)
S1B	.9968(8)	.3759(2)	.2835(5)	C17A	.2199(8)	.5362(2)	.7694(10)
C35A	1.0258(10)	.3873(3)	.1342(17)	C17B	.2351(16)	.5362(5)	.8147(22)
C35B	1.0382(21)	.3828(7)	.1686(31)	C18A	.3567(7)	.5301(2)	.7513(5)
N9A	.9983(7)	.3942(2)	.0481(5)	C18B	.2940(21)	.5345(6)	.7172(16)
N9B	1.0576(25)	.3863(6)	.0826(21)	C19A	.3326(12)	.4971(2)	.5816(6)
O1A	1.0770(3)	.1103(1)	.5055(3)	C19B	.3818(33)	.4909(7)	.5909(17)
O1B	1.0930(14)	.1330(4)	.3952(11)	C20A	.3121(8)	.4554(3)	.5232(6)
O2A	.9436(3)	.1817(1)	.3036(3)	C20B	.2779(22)	.4721(9)	.5317(15)
O2B	.8498(14)	.2089(4)	.3075(11)	C21A	.0931(7)	.4486(3)	.5349(5)
O3A	.6928(4)	.2022(1)	.4295(3)	C21B	.1000(17)	.4261(8)	.5296(14)
O3B	.6835(12)	.1793(4)	.4816(11)	C22A	-.0080(8)	.4316(4)	.5988(6)
O4A	.8184(4)	.1193(1)	.6395(3)	C22B	.0144(23)	.4462(10)	.5890(16)
O4B	.9345(14)	.1034(5)	.6011(12)	C23A	-.0145(6)	.4860(2)	.7278(6)
O5A	.3210(4)	.4452(1)	.9892(3)	C23B	-.0419(18)	.4675(7)	.7619(16)
O5B	.2412(15)	.4318(4)	.9925(11)	C24A	.0440(6)	.5017(2)	.8326(8)
O6A	.5085(3)	.4208(1)	.8080(3)	C24B	.0292(18)	.5053(6)	.7808(22)
O6B	.4900(15)	.4460(5)	.8720(13)	C25A	.2209(6)	.5109(2)	.9487(5)
OT A	.2506(3)	.3472(1)	.6720(3)	C25B	.1289(22)	.4985(7)	.9499(17)
OT B	.3728(14)	.3621(4)	.6794(11)	C27A	.5100(6)	.4822(2)	.6974(5)
OB A	.0795(3)	.3717(1)	.8656(3)	C27B	.4922(23)	.5044(8)	.7596(20)
OB B	.1075(14)	.3522(5)	.7866(12)	C29A	.2224(6)	.3870(2)	.5167(4)
C1A	1.2212(7)	.2259(2)	.5059(7)	C29B	.3106(20)	.3980(6)	.5208(15)
C1B	1.2080(18)	.2418(7)	.5462(18)	C31A	-.0721(5)	.4438(2)	.7657(5)
				C31B	-.0510(22)	.3927(8)	.7137(19)

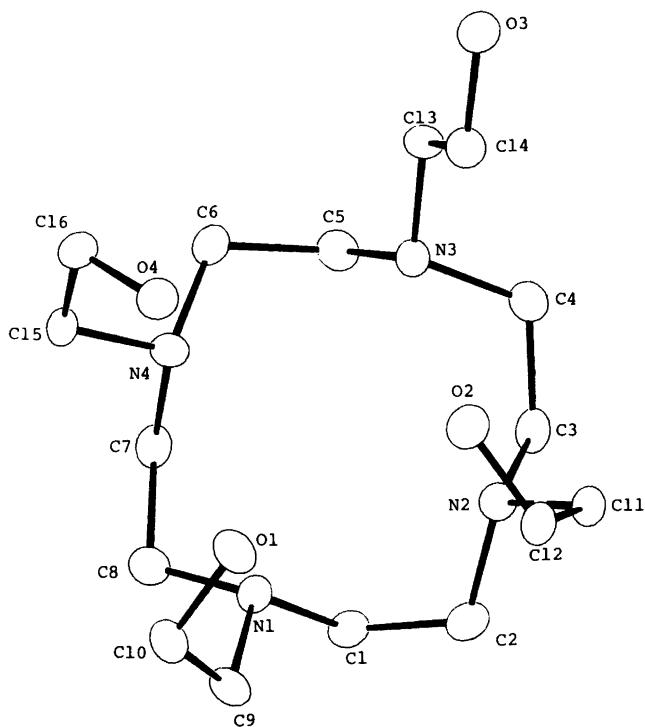


Fig. 1. Schematic drawing of the ligand of the NaSCN-complex showing the numbering of atoms.

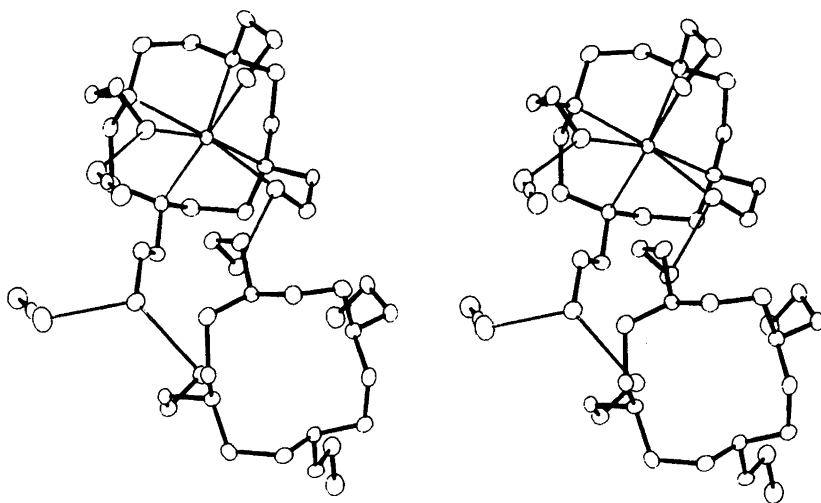


Fig. 2. Stereoscopic view of the NaSCN-complex, illustrating the coordination and hydrogen bonding system.

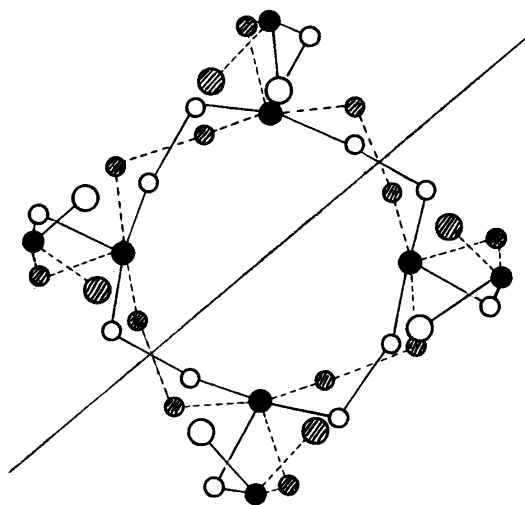


Fig. 3. Schematic drawing indicating the type of disorder (due to the presence of statistical pseudo mirror planes) for the ligands of the KSCN-complex.

atoms for which no disorder could be observed. For these atoms the maximum r.m.s. amplitudes range from 0.15 to 0.30 Å. The form factors used were those of Hanson *et al.*,⁷ except for hydrogen.⁸ Weights in least squares were obtained from the standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I) = C_T + [(0.02C_N)^2]^{1/2}$, where C_T is the total number of counts, and C_N

the net count. Methylene hydrogen positions were calculated. The hydroxyl hydrogen atoms of the NaSCN-complex were localized in a difference Fourier map. No attempt to find the corresponding partial hydrogens in the KSCN-complex was made. The final R -values were $R=3.5\%$ ($R_w=3.0\%$) for the 1709 observed reflections of the NaSCN-complex, and $R=6.6\%$ ($R_w=6.5\%$) for the 5306 observed reflections of the KSCN-complex. Standard deviations in bond distances and angles and torsional angles were calculated from the correlation matrixes of the final least-squares refinement cycles. Final fractional atomic coordinates are given in Tables 1 and 3, the latter containing only non-hydrogen atoms. Lists of observed and calculated structure factors, as well as the temperature factors, are obtainable from the author.

DISCUSSION

The NaSCN-complex. Fig. 1 is a schematic drawing of the ligand showing the numbering of atoms. The bond distances and angles of Table 2 have normal values within estimated limits of error. From the list of dihedral angles it may be seen that the 12-membered ring adopts the [3 3 3 3] conformation² and that three of the side-chains are *gauche* and the fourth *anti*. As to be expected from the ¹³C NMR studies,¹ the ring conformation corresponds to that of the (2:1)

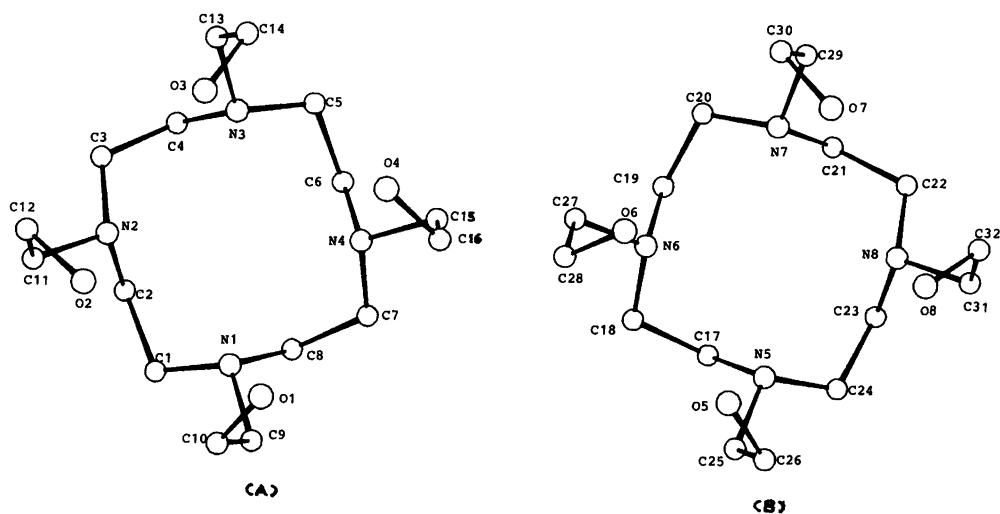


Fig. 4. Schematic drawings of the A-forms of the two crystallographically independent ligands, (A) and (B), of the KSCN-complex. The numbering of atoms (with the A's omitted) is indicated.

Table 4. Bond distances and angles and torsional angles with estimated standard deviations for the A-form of the KSCN-complex.

DISTANCE	(Å)	DISTANCE	(Å)	DIHEDRAL ANGLE	(°)
N1 - C1A	1.42(1)	N1 - C8A	1.52(1)	C8A - N1 - C1A - C2A	-70.(1)
N1 - C9A	1.48(1)	N2 - C2A	1.47(1)	N1 - C1A - C2A - N2	-63.(2)
N2 - C3A	1.44(1)	N2 - C11A	1.55(1)	C3A - N2 - C2A - C1A	161.(1)
N3 - C4A	1.53(1)	N3 - C5A	1.43(1)	C2A - N2 - C3A - C4A	-71.(1)
N3 - C13A	1.50(1)	N4 - C6A	1.57(1)	N2 - C3A - C4A - N3	-71.(1)
N4 - C7A	1.42(1)	N4 - C15A	1.47(1)	C5A - N3 - C4A - C3A	166.(1)
N5 - C17A	1.54(1)	N5 - C24A	1.40(1)	C4A - N3 - C5A - C6A	-70.(1)
N5 - C25A	1.50(1)	N6 - C18A	1.42(1)	N3 - C5A - C6A - N4	-63.(1)
N6 - C19A	1.45(1)	N6 - C27A	1.52(1)	C7A - N4 - C6A - C5A	161.(1)
N7 - C20A	1.44(1)	N7 - C21A	1.51(1)	C6A - N4 - C7A - C8A	-73.(1)
N7 - C29A	1.45(1)	N8 - C22A	1.44(1)	N4 - C7A - C8A - N1	-66.(1)
N8 - C23A	1.54(1)	N8 - C31A	1.48(1)	C1A - N1 - C8A - C7A	164.(1)
C10 - O1A	1.42(1)	C10 - C9A	1.53(1)	C24A - N5 - C17A - C18A	-164.(1)
C12 - O2A	1.49(1)	C12 - C11A	1.43(1)	N5 - C17A - C18A - N6	67.(1)
C14 - O3A	1.41(1)	C14 - C13A	1.45(1)	C19A - N6 - C18A - C17A	73.(1)
C16 - O4A	1.35(1)	C16 - C15A	1.59(1)	C18A - N6 - C19A - C20A	-161.(1)
C26 - O5A	1.44(1)	C26 - C25A	1.47(1)	N6 - C19A - C20A - N7	64.(1)
C28 - O6A	1.45(1)	C28 - C27A	1.47(1)	C21A - N7 - C20A - C19A	71.(1)
C30 - O7A	1.45(1)	C30 - C29A	1.52(1)	C20A - N7 - C21A - C22A	-163.(1)
C32 - O8A	1.40(1)	C32 - C31A	1.55(1)	N7 - C21A - C22A - N8	61.(1)
C1A - C2A	1.52(1)	C3A - C4A	1.56(1)	C23A - N8 - C22A - C21A	75.(1)
C5A - C6A	1.53(1)	C7A - C8A	1.58(2)	C22A - N8 - C23A - C24A	-160.(1)
C17A - C18A	1.55(1)	C19A - C20A	1.54(1)	N8 - C23A - C24A - N5	67.(1)
C21A - C22A	1.54(2)	C23A - C24A	1.55(1)	C17A - N5 - C24A - C23A	69.(1)

ANGLE	(°)	ANGLE	(°)
C1A - N1 - C8A	111.(1)	C1A - N1 - C9A	112.(1)
C8A - N1 - C9A	108.(1)	C2A - N2 - C3A	115.(1)
C2A - N2 - C11A	109.(1)	C3A - N2 - C11A	109.(1)
C4A - N3 - C5A	109.(1)	C4A - N3 - C13A	110.(1)
C5A - N3 - C13A	109.(1)	C6A - N4 - C7A	110.(1)
C6A - N4 - C15A	106.(1)	C7A - N4 - C15A	110.(1)
C17A - N5 - C24A	111.(1)	C17A - N5 - C25A	109.(1)
C24A - N5 - C25A	111.(1)	C18A - N6 - C19A	113.(1)
C18A - N6 - C27A	111.(1)	C19A - N6 - C27A	107.(1)
C20A - N7 - C21A	112.(1)	C20A - N7 - C29A	109.(1)
C21A - N7 - C29A	109.(1)	C22A - N8 - C23A	108.(1)
C22A - N8 - C31A	111.(1)	C23A - N8 - C31A	108.(0)
O1A - C10 - C9A	106.(0)	O2A - C12 - C11A	113.(1)
O3A - C14 - C13A	111.(0)	O4A - C16 - C15A	113.(1)
O5A - C26 - C25A	111.(0)	O6A - C28 - C27A	112.(0)
O7A - C30 - C29A	107.(0)	O8A - C32 - C31A	111.(0)
N1 - C1A - C2A	115.(1)	N2 - C2A - C1A	115.(1)
N2 - C3A - C4A	111.(1)	N3 - C4A - C3A	112.(1)
N3 - C5A - C6A	115.(1)	N4 - C6A - C5A	113.(1)
N4 - C7A - C8A	111.(1)	N1 - C8A - C7A	114.(1)
N1 - C9A - C10	112.(1)	N2 - C11A - C12	116.(1)
N3 - C13A - C14	113.(1)	N4 - C15A - C16	108.(1)
N5 - C17A - C18A	113.(1)	N6 - C18A - C17A	111.(1)
N6 - C19A - C20A	115.(1)	N7 - C20A - C19A	113.(1)
N7 - C21A - C22A	115.(1)	N8 - C22A - C21A	114.(1)
N8 - C23A - C24A	113.(1)	N5 - C24A - C23A	115.(1)
N5 - C25A - C26	114.(1)	N6 - C27A - C28	114.(1)
N7 - C29A - C30	112.(0)	N8 - C31A - C32	112.(0)

dihydrated LiCl-complex,² which also was found to be preferred in the hydrate.³ The dissimilarity in conformation stems from the various number of *anti* and *gauche* side-chains. In the Li⁺-complex there is one *gauche* chain while the hydrate has two. From Fig. 1 it may be seen that all side-arms bend off towards the "corner" atoms of the ring. The same pattern was observed in the earlier reported structures.^{2,3}

Fig. 2 is a stereoscopic view of the complex. It shows that Na⁺ is coordinated to four nitrogen atoms and to the three oxygens of the *gauche*

side-chains. The nitrogen atom of the thiocyanate anion accepts hydrogen bonds from the hydroxyl group of the *anti* side-arm and from one of the *gauche* chains in a symmetry related ligand. The two remaining *gauche* side-chains are also hydrogen bonded to symmetry related ligands. (One of these hydrogen bonds, O3-O4'''=2.742(4) Å, is missing in Table 2.) The C-H and O-H bond distance ranges are 0.94-1.06 and 0.78-1.00 Å, respectively.

The KSCN-complex. There are two complexes in the asymmetric unit, both of which are

Table 5. Bond distances and angles with estimated standard deviations for the B-form of the KSCN-complex.

DISTANCE	(Å)	DISTANCE	(Å)	DIEDRAL ANGLE	(°)
N1 - C1B	1.58(2)	N1 - C8B	1.35(2)	C8B - N1 - C1B - C2B	-160.(2)
N1 - C9B	1.58(2)	N2 - C2B	1.43(2)	N1 - C1B - C2B - N2	47.(4)
N2 - C3B	1.62(2)	N2 - C11B	1.48(2)	C3B - N2 - C2B - C1B	85.(2)
N3 - C4B	1.39(2)	N3 - C5B	1.68(3)	C2B - N2 - C3B - C4B	-157.(2)
N3 - C13B	1.51(2)	N4 - C6B	1.21(2)	N2 - C3B - C4B - N3	48.(3)
N4 - C7B	1.56(2)	N4 - C15B	1.66(3)	C5B - N3 - C4B - C3B	80.(2)
N5 - C17B	1.34(2)	N5 - C24B	1.70(2)	C4B - N3 - C5B - C6B	-153.(2)
N5 - C25B	1.54(2)	N6 - C18B	1.64(2)	N3 - C5B - C6B - N4	63.(4)
N6 - C19B	1.34(2)	N6 - C27B	1.54(3)	C7B - N4 - C6B - C5B	76.(3)
N7 - C20B	1.56(2)	N7 - C21B	1.34(2)	C6B - N4 - C7B - C8B	-153.(3)
N7 - C29B	1.57(2)	N8 - C22B	1.56(2)	N4 - C7B - C8B - N1	46.(4)
N8 - C23B	1.31(2)	N8 - C31B	1.64(2)	C1B - N1 - C8B - C7B	83.(2)
C10 - O1B	1.47(2)	C10 - C9B	1.61(2)	C24B - N5 - C17B - C18B	-84.(2)
C12 - O2B	1.18(2)	C12 - C11B	1.66(2)	N5 - C17B - C18B - N6	-49.(3)
C14 - O3B	1.42(1)	C14 - C13B	1.45(2)	C19B - N6 - C18B - C17B	158.(2)
C16 - O4B	1.70(2)	C16 - C15B	1.22(2)	C18B - N6 - C19B - C20B	-82.(3)
C26 - O5B	1.37(2)	C26 - C25B	1.54(2)	N6 - C19B - C20B - N7	-47.(4)
C28 - O6B	1.38(2)	C28 - C27B	1.55(3)	C21B - N7 - C20B - C19B	153.(3)
C30 - O7B	1.42(2)	C30 - C29B	1.48(2)	C20B - N7 - C21B - C22B	-81.(3)
C32 - O8B	1.50(2)	C32 - C31B	1.28(2)	N7 - C21B - C22B - N8	-53.(4)
C1B - C2B	1.46(4)	C3B - C4B	1.42(3)	C23B - N8 - C22B - C21B	159.(3)
C5B - C6B	1.40(4)	C7B - C8B	1.44(3)	C22B - N8 - C23B - C24B	-76.(4)
C17B - C18B	1.47(3)	C19B - C20B	1.46(4)	N8 - C23B - C24B - N5	-57.(3)
C21B - C22B	1.41(3)	C23B - C24B	1.45(3)	C17B - N5 - C24B - C23B	156.(2)

ANGLE	(°)	ANGLE	(°)
C1B - N1 - C8B	112.(1)	C1B - N1 - C9B	99.(1)
C9B - N1 - C9B	113.(1)	C2B - N2 - C3B	103.(2)
C2B - N2 - C11B	114.(2)	C3B - N2 - C11B	100.(1)
C4B - N3 - C5B	111.(1)	C4B - N3 - C13B	124.(2)
C5B - N3 - C13B	102.(1)	C6B - N4 - C7B	125.(2)
C6B - N4 - C15B	115.(2)	C7B - N4 - C15B	98.(2)
C17B - N5 - C24B	109.(1)	C17B - N5 - C25B	120.(2)
C24B - N5 - C25B	95.(1)	C18B - N6 - C19B	118.(2)
C18B - N6 - C27B	99.(1)	C19B - N6 - C27B	118.(2)
C20B - N7 - C21B	115.(1)	C20B - N7 - C29B	100.(1)
C21B - N7 - C29B	119.(1)	C22B - N8 - C23B	119.(1)
C22B - N8 - C31B	102.(2)	C23B - N8 - C31B	113.(1)
O1B - C10 - C9B	108.(1)	O2B - C12 - C11B	113.(1)
O3B - C14 - C13B	120.(1)	O4B - C16 - C15B	108.(1)
O5B - C26 - C25B	118.(1)	O6B - C28 - C27B	107.(1)
O7B - C30 - C29B	113.(1)	O8B - C32 - C31B	113.(1)
N1 - C1B - C2B	121.(2)	N2 - C2B - C1B	115.(2)
N2 - C3B - C4B	118.(1)	N3 - C4B - C3B	120.(2)
N3 - C5B - C6B	121.(2)	N4 - C6B - C5B	115.(2)
N4 - C7B - C8B	125.(1)	N1 - C8B - C7B	116.(2)
N1 - C9B - C10	103.(1)	N2 - C11B - C12	104.(1)
N3 - C13B - C14	114.(2)	N4 - C15B - C16	118.(2)
N5 - C17B - C18B	117.(2)	N6 - C18B - C17B	119.(2)
N6 - C19B - C20B	117.(2)	N7 - C20B - C19B	124.(2)
N7 - C21B - C22B	117.(2)	N8 - C22B - C21B	123.(2)
N8 - C23B - C24B	114.(2)	N5 - C24B - C23B	120.(2)
N5 - C25B - C26	108.(1)	N6 - C27B - C28	108.(2)
N7 - C29B - C30	110.(1)	N8 - C31B - C32	118.(2)

disordered. The disorder arises from the presence of statistical pseudo mirror planes as indicated in Fig. 3. Least-squares refinement of multiplicity factors showed that there are about 75 % and 25 % of the two forms (labelled "A" and "B"), respectively. Fig. 4 (A) and (B) are schematic drawings of the A-ligands showing the numbering of atoms, (the A's being omitted). One of the thiocyanate anions is also disordered. The disorder was not observable for all the ligand atoms (black circles in Fig. 3), and these were refined anisotropically with multiplicity factors

equal to 1.0. The same scheme was used for the potassium cations and the other thiocyanate anion.

Bond distances and angles and dihedral angles may be found in Tables 4, 5 and 6. Within the relatively large estimated limits of error all values are normal for the A-form. Problems connected with the design of a proper least-squares refinement scheme, due to close contacts between partial atoms, are probably responsible for some rather awkward values arrived at for the B-ligands. The torsional angles correspond to the

Table 6. Coordination bonds, hydrogen bonds and bond distances and angles of the anions with estimated standard deviations for the KSCN-complex.

DISTANCE	(Å)	DISTANCE	(Å)
S2 - C34	1.631(6)	S1A - C33A	1.649(24)
S1E - C33E	1.615(38)	C34 - N10	1.167(6)
C33A - N9A	1.157(25)	C33B - N9B	1.158(49)
K1 - N1	2.872(4)	K1 - N2	2.878(4)
K1 - N3	2.866(4)	K1 - N4	2.829(4)
K1 - O1A	2.757(4)	K1 - O1B	2.871(15)
K1 - O2A	2.719(4)	K1 - O2B	2.874(15)
K1 - O3A	2.795(5)	K1 - O3B	2.659(14)
K1 - O4A	2.837(4)	K1 - O4B	2.673(16)
K2 - N5	2.833(4)	K2 - N6	2.904(4)
K2 - N7	2.911(4)	K2 - N8	2.869(4)
K2 - O5A	2.791(5)	K2 - O5B	2.734(15)
K2 - O6A	2.755(4)	K2 - O6B	2.824(17)
K2 - O7A	2.817(4)	K2 - O7B	2.726(16)
K2 - O8A	2.803(4)	K2 - O8B	2.781(16)
N10 - O1B	2.644(16)	N10 - O2A	2.801(6)
N10 - O6A	2.852(6)	N10 - O7B	2.775(16)
N9A - O8A	2.692(8)	N9B - O3B	2.878(31)
N9B - O5E	2.812(31)	O1A - O6A	2.800(6)
O2A - O7A	2.782(6)	O3A - O8A	2.763(6)
O4A - O5A	2.837(6)	O1B - O6B	2.767(23)
O2B - O7B	2.831(22)	O3B - O8B	2.794(22)
O4B - O5B	2.717(22)		

ANGLE	(°)	ANGLE	(°)
S1A - C33A - N9A	178.5(9)	S1B - C33B - N9B	173.6(25)
S2 - C34 - N10	175.2(5)		

familiar [3 3 3 3] conformation for all four 12-membered rings, and the N-N-C planes of the side-chains are again tilted towards the ring corner atoms. The profound conformational alteration suggested by the NMR investigation¹ is caused by the fact that all four side-arms are *gauche* in the KSCN-complex.

Fig. 5 is a stereoscopic view of the two A-complexes illustrating the eight-coordination of the potassium cations and the hydrogen

bonding system. The potassium cation coordinates to four ring nitrogens and the four oxygens of the side-chains in both complexes. The thiocyanate anions are involved in four hydrogen bonds donated by two ligands. N10 accepts two bonds, while N9A and S1A accept one each. The same two ligands are finally linked by four hydrogen bonds to form the dimers shown in Fig. 5.

Concluding remarks. The modest upfield dis-

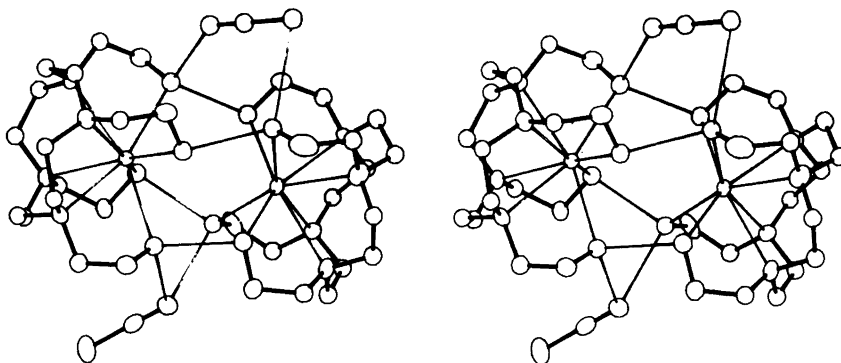


Fig. 5. Stereoscopic view of the A-form of the KSCN-complex illustrating the coordination and hydrogen bonding system.

placement of the ring ^{13}C signals¹ is in accordance with the recurrence of the same [3 3 3 3] ring conformation in the structures of the dihydrated (2:1) complex with LiCl ,² the hydrate,³ and the complexes with NaSCN and KSCN . The slight variations of torsional angles are a natural consequence of the adjustment of the donor-acceptor distances. The side-chains invariably bend off towards the corner atoms of the ring. When a side-arm is rejected, the C-C bond is anti, and when it coordinates to the cation (or water molecule), it is *gauche* of the same helicity as the corner bonds of the ring. Accommodation to the varying size of the cation occurs mainly by adjustment of this *gauche* torsional angle. In none of these structures is there any direct anion-cation contact. The ligand can thus be considered a sensitive probe for optimal coordination numbers of Li^+ , Na^+ and K^+ .

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