# On the Crystal Conformation of the (1:1) Complex between Potassium Thiocyanate Sesqui Hydrate and 10,10'-Ethylene Bis(1,4,7-trioxa-10-azacyclododecane) at −130 °C

P. GROTH

Department of Chemistry, University of Oslo, N-0315 Oslo 3, Norway

The syntheses of organic ligands of two monoaza-12-crown-4 rings linked together by a single alkylene bridge between nitrogen bridgeheads have been reported.[1]
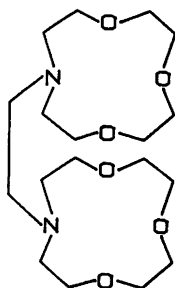
When the free *N,N'*-bridged bis(1,4,7-trioxa-10-azacyclododecane) is allowed to react with salt solutions containing Li^+, Na^+ or K^+ cations and SCN^- anions, stable complexes are obtained. Since no definite conclusions about ring conformations could be drawn from ^{13}C NMR studies of the free ligand and its complexes, X-ray crystallographic investigations have been undertaken. The crystal structure determinations of the (1:1) complex with LiSCN[2] and of the free ligand[3] have recently been reported. The results for the KSCN complex are now presented.

The crystals of $C_{18}H_{36}N_2O_6 \cdot KSCN \cdot 1\frac{1}{2}H_2O$ belong to the monoclinic system with space group $P2_1/c$ and cell dimensions $a=10.745(3)$, $b=12.501(3)$, $c=38.515(5)$ Å, $\beta=102.17(2)°$. There are two independent complexes in the asymmetric unit ($D_x=1.31$ g cm^{-3}, $D_m=1.33$ g cm^{-3}).

With $2\theta_{max}=50°$, ω-scan, scan width 0.8° and MoKα-radiation, 4927 reflections were recorded on an automatic four-circle diffractometer at *ca.* −130 °C [using an
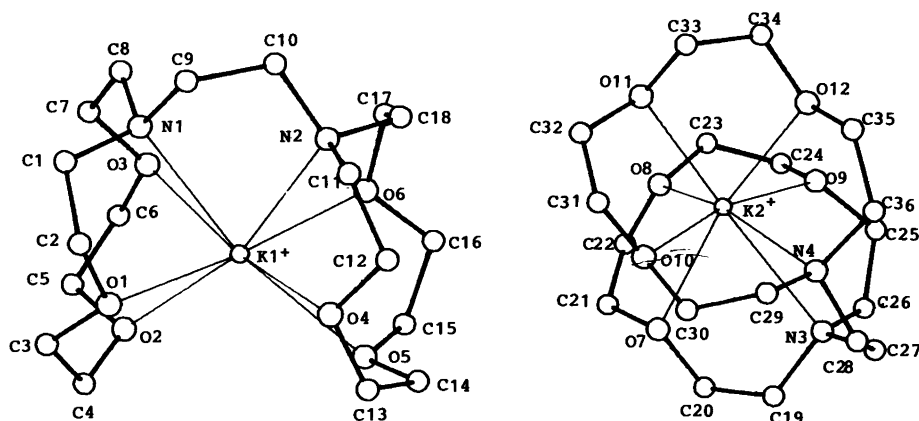

Fig. 1. Schematic drawing showing the numbering of atoms.

Table 1. Final fractional coordinates with estimated standard deviations for non-hydrogen atoms.

ATOM	X	Y	Z	Uiso
K1+	.7882(1)	.1565(1)	.5519(1)	1.97
K2+	.3912(1)	.3291(1)	.3215(1)	1.83
O1	.9481(3)	-.0032(3)	.5378(1)	2.49
O2	.6778(4)	-.0119(3)	.5142(1)	2.42
O3	.6518(4)	.0192(3)	.5854(1)	2.65
O4	.9820(4)	.2905(3)	.5028(1)	2.50
O5	.7192(4)	.3181(3)	.5730(1)	2.47
O6	.6657(4)	.3188(3)	.2572(1)	2.65
O7	.2886(3)	.2334(3)	.3151(1)	2.03
O8	.1653(3)	.2229(3)	.3190(1)	1.96
O9	.1761(3)	.4500(3)	.3141(1)	2.07
O10	.6122(3)	.2340(3)	.3803(1)	2.28
O11	.5391(4)	.2213(3)	.3774(1)	2.58
O12	.5157(4)	.6510(3)	.6127(1)	2.50
N1	.9273(5)	.0379(4)	.2602(1)	2.13
N2	.9433(5)	.4685(4)	.6005(1)	2.50
N3	.3131(4)	.4699(4)	.5184(1)	1.90
N4	.5868(4)	.5551(5)	.4950(1)	2.02
C1	1.0436(6)	-.0314(5)	.6005(1)	2.74
C2	.8872(6)	-.0938(5)	.5589(1)	3.22
C3	.7661(7)	-.0571(5)	.6116(1)	3.01
C4	.6136(6)	-.0898(5)	.6330(1)	2.84
C5	.5569(6)	-.0307(5)	.6399(1)	2.85
C6	.7197(6)	.0528(5)	.6399(1)	2.74
C7	.8332(6)	.0036(5)	.5965(1)	2.59
C8	1.0215(6)	.1084(5)	.5595(1)	2.65
C9	.9737(6)	.2200(5)	.5000(1)	2.93
C10	1.0595(6)	.3217(5)	.5114(1)	3.15
C11	1.0089(6)	.3685(5)	.4969(1)	3.10
C12	.9366(6)	.3353(5)	.5144(2)	3.19
C13	.8146(7)	.3944(5)	.5490(1)	3.18
C14	.6109(7)	.3661(5)	.6084(1)	2.93
C15	.6325(7)	.4082(5)	.6124(1)	3.39
C16	.7248(7)	.3492(5)	.2286(1)	3.25
C17	.8636(7)	.3777(5)	.2278(2)	3.07
C18	.2973(9)	.4008(6)	.2612(2)	4.87
C19	.2479(10)	.2985(6)	.2833(2)	6.04
C20	.2017(8)	.1704(6)	.3189(2)	6.65
C21	.1155(7)	.2856(7)	.2961(2)	5.96
C22	.0769(7)	.3944(7)	.2624(1)	4.41
C24	.0628(8)	.5358(7)	.2601(2)	5.05
C25	.1624(8)	.5223(7)	.2742(2)	5.32
C27	.1923(8)	.5462(6)	.3063(2)	4.82
C28	.4124(7)	.5256(7)	.2967(2)	5.31
C29	.5427(7)	.4090(6)	.3429(1)	5.82
C30	.6998(7)	.2990(6)	.3589(2)	5.41
C31	.6855(8)	.1760(6)	.4076(1)	5.23
C32	.6212(8)	.1456(8)	.4092(2)	6.27
C33	.6030(9)	.2862(7)	.3355(2)	5.61
C34	.5436(8)	.3855(7)	.3725(2)	5.65
C35	.6151(9)	.5170(9)	.9336(1)	6.17
C36	.6132(8)	.5481(6)	.9150(2)	4.72
S1	.1821(2)	.1576(7)	.9049(1)	5.28
CS1	-.0228(13)	.1500(7)	1.2216(1)	6.35
NS1	-.0667(4)	.1447(5)	1.1986(2)	1.02
S2	.8489(2)	.3485(10)	1.1879(2)	6.19
CS2	.6815(14)	.3345(10)	1.0701(2)	6.47
NS2	.6118(6)	.3336(10)	1.1229(3)	3.34
OW1	.4182(6)	.2674(5)	1.1356(3)	8.82
OW2	-.4448(16)	.3954(13)	1.0160(2)	9.18
OW3	.3570(13)	.3471(12)		7.95
OW4	.3034(7)	.1272(6)		12.56

Table 2. Torsion angles with estimated standard deviations.

DIHEDRAL ANGLE				(°)
C2	O1	C5	C4	65.( )
C5	O1	C2	C1	-84.( )
C4	O2	C5	C6	65.( )
C5	O2	C4	C3	-76.( )
C6	O3	C4	C8	68.( )
C7	O3	C6	C5	-77.( )
C12	O4	C15	C14	-77.( )
C15	O4	C12	C11	68.( )
C14	O5	C15	C16	-75.( )
C15	O5	C14	C13	62.( )
C16	O6	C17	C18	-78.( )
C17	O6	C16	C15	62.( )
C20	O7	C21	C22	-95.( )
C21	O7	C20	C19	55.( )
C22	O8	C25	C24	-91.( )
C25	O8	C22	C21	50.( )
C24	O9	C25	C26	-99.( )
C25	O9	C24	C25	54.( )
C50	O10	C51	C52	156.( )
C51	O10	C50	C29	-97.( )
C52	O11	C55	C54	154.( )
C55	O11	C52	C51	-87.( )
C54	O12	C55	C56	156.( )
C55	O12	C54	C53	-87.( )
C1	N1	C8	C7	-68.( )
C8	N1	C1	C2	156.( )
C1	N1	C9	C10	163.( )
C9	N1	C1	C2	-82.( )
C8	N1	C9	C10	-75.( )
C9	N1	C8	C7	170.( )
C10	N2	C11	C12	168.( )
C11	N2	C10	C9	-74.( )
C10	N2	C18	C17	-84.( )
C18	N2	C10	C9	165.( )
C11	N2	C18	C17	157.( )
C18	N2	C11	C12	-74.( )
C19	N3	C26	C25	142.( )
C26	N3	C19	C20	-85.( )
C19	N3	C27	C28	-87.( )
C27	N3	C19	C20	155.( )
C26	N3	C27	C28	150.( )
C27	N3	C26	C25	-96.( )
C28	N4	C29	C30	-95.( )
C29	N4	C28	C27	148.( )
C28	N4	C55		158.( )

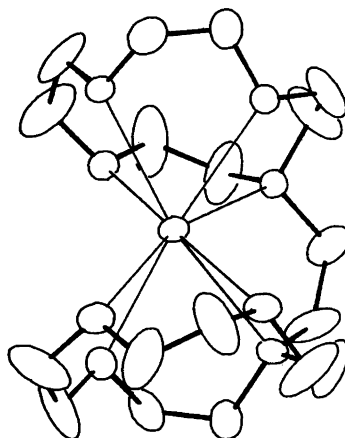| DIHEDRAL ANGLE				(°)
C36	N4	C28	C27	-91.( )
C29	N4	C36	C55	-84.( )
C56	N4	C29	C50	145.( )
N1	C1	C2	O1	-64.( )
O1	C5	C4	O2	-61.( )
O2	C5	C6	O3	-61.( )
O3	C7	C8	N1	-65.( )
N1	C9	C10	O4	-66.( )
N2	C11	C12	O4	-60.( )
O4	C15	C14	O5	-62.( )
O5	C15	C16	O6	-62.( )
O6	C17	C18	N2	-66.( )
N5	C19	C20	O7	-45.( )
O7	C21	C22	O8	-40.( )
O8	C25	C24	O9	-45.( )
O9	C25	C26	N5	-43.( )
N5	C27	C28	N4	-48.( )
N4	C29	C50	O10	-45.( )
O10	C51	C52	O11	-53.( )
O11	C55	C54	O12	-45.( )
O12	C35	C56	N4	

Fig. 2. Schematic drawing illustrating the probable disorder of the K2$^+$ complex carbon atoms.

observed−unobserved cutoff at 2.5 $\sigma(I)$]. No corrections for absorption ($\mu=0.35$ mm^{-1}) or secondary extinction were applied (crystal size 0.3×0.5×0.2 mm). The structure was solved by direct methods[4] and refined by the full-matrix least squares technique.[5] All programs used (except those for phase determination) are included in Ref. 5. Hydrogen atom positions were calculated. Anisotropic temperature factors were used for non-hydrogen atoms, and weights in least squares were calculated 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. H-atoms were refined with isotropic temperature factors. The final R-value was 7.9 % ($R_w=6.8$ %) for 4927 observed reflections.

Final fractional coordinates and U_{iso} for non-hydrogen atoms are listed in Table 1. Fig. 1 is a schematic drawing of the ligands and the K$^+$ cations with their numbering. The range of the maximum r.m.s. amplitudes for the carbon atoms of the K2$^+$ complex is 0.33−0.42 Å while that of the other atoms shown in Fig. 1 is 0.17−0.27 Å. This disorder-indication for the K2$^+$ complex carbon-atoms, visualized in Fig. 2, is reflected in the average C−C bond distance of 1.41 Å (corresponding value for the K1$^+$ complex is 1.51 Å), and also in some of the N−C−C and O−C−C bond angles (being unusually large). However, attempts to introduce partial carbon atoms by calculating their probable positions from the thermal parameters,[6] and then carefully refine their position, isotropic temperature factors and occupancies, were (for unknown reasons) not successful for this complex. Apart from those mentioned, all bond distances and angles of the ligands are normal within error limits. The torsion angles of Table 2 show that all four 12-membered rings adopt the familiar [3 3 3 3] conformation.[7]

[3 3 3 3]
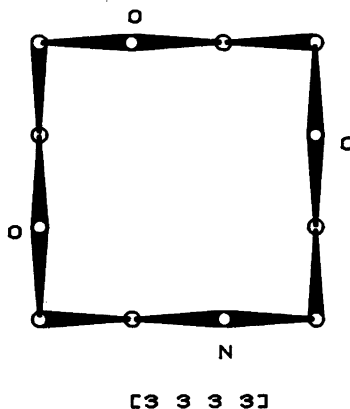
It may be noted that the nine angles at the bottom of this table are about 20° smaller than the nine angles above, again reflecting the probable disordering of these carbon atoms. Both potassium cations are eight coordinated, with average K^+-O and K^+-N bonds of 2.752 and 2.875 Å, respectively.

The thiocyanate anions, having no contacts at all with the potassium cations, are linked by three water molecules, at least one of which is disordered. The thermal parameters and bond distances arrived at for the anions demand disorder. The carbon atoms are smeared out in the $S-N$ direction (maximum r.m.s. amplitudes 0.46 and 0.47 Å) and one of the nitrogens has extremely small thermal vibration amplitudes. These findings are most likely explained in terms of a mixture of SCN^- anions occupying approximately the same crystal site, and orientated in opposite directions. Although the attempts to refine a disordered model of this type were made with great care in order to avoid singularities, the results were not satisfactory.

These unsolved disorder problems must take some responsibility for the relatively high final R-value. Bad background recordings due to the long c-axis and the use of Mo-radiation may be another reason.

Lists of thermal parameters, hydrogen atom parameters, bond distances and angles and observed and calculated structure factors are available from the author.

1. Calverley, M.J. and Dale, J. *J. Chem. Soc. Chem. Commun.* (1981) 684.
2. Groth, P. *Acta Chem. Scand. A 38* (1984) 337.
3. Groth, P. *Acta Chem. Scand. A 38* (1984) 342.
4. Germain, G., Main, P. and Woolfson, M.M. *Acta Crystallogr. A 27* (1971) 368.
5. Groth, P. *Acta Chem. Scand. 27* (1973) 1837.
6. Kartha, G. and Ahmed, F.R. *Acta Crystallogr. 13* (1960) 532.
7. Dale, J. *Acta Chem. Scand. 27* (1973) 1115.