October, 1988] © 1988 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 61, 3785—3787 (1988) 3785

New Applications of Crown Ethers. IX.[1] Crystal Structure of KSCN Complex of *N*-Heptylmonoaza-18-crown-6, and Conformational Features of the Pivot Nitrogen

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(Received May 20, 1988)

Synopsis. Vertical arrangement of the alkyl side arm in the crystal structure of KSCN complex of *N*-heptylmonoaza-18-crown-6 is well-consonant with the effective side-arm participation in N-pivot lariat ether complexes and supports the lack of 'biscrown effect' for bis(monoaza-18-crown-6)s.

The lariat ethers are a family of the macrocyclic polyethers which bear one or more donor atoms in the side arm through a nitrogen or carbon pivot atom.[2,3] Complexation behavior of the N-pivot lariat ethers has been extensively studied in solutions by comparison with that of the *N*-alkylmonoazacrown ether, an analogue without donor atom in the side arm.[4,5] Gokel et al. have shown the unequivocal evidence for the side-arm participation in the crystal structures of N-pivot lariat ether complexes.[6,7] A similar X-ray analysis was also done for $NaClO_4$ complex of *N*-phenylmonoaza-15-crown-5[8] and KI complex of *N*-allylmonoaza-18-crown-6.[9] However, these studies could not give the arrangement of a flexible non-coordinating side arm and the conformational feature around the pivot nitrogen was also not emphasized in these complexes, while such structural information is very important for considering the interaction with a donating group in the side arm, such as a lariat group in lariat ethers or a second crown ring in bis(crown ether)s. The present paper shows a clear picture about KSCN complex of *N*-alkylmonoaza-18-crown-6, in which the non-coordinating side arm is arranged vertically to the ring plane, and the K^+ ion is located in the center of the ring. The fact in turn may give an answer for the question why a large enhanced binding can be obtained in the complexation of N-pivot lariat ethers, and why the two crown rings of bis(monoaza-18-crown-6)s could not cooperate in the complexation with larger cations.

Experimental

$C_{19}H_{39}NO_5\cdot$KSCN. A white plate crystal was obtained from a methanol solution containing the ligand and excess KSCN by evaporating the solvent slowly at room temperature. Mp 78—80 °C; IR(Nujol): 2040, 1120, 960, 840 cm^{-1}; Calcd for $C_{20}H_{39}N_2O_5KS$: C, 52.37; H, 8.57; N, 6.11%. Found: C, 51.99; H, 8.49; N, 6.18%. The crystal used for X-ray analysis had approximate dimensions of 0.3×0.3×0.3 mm^3.

X-Ray Analysis. Crystal Data. monoclinic, $P2_1/c$, a=21.910(4), b=14.573(5), c=7.936(5) Å, β=94.36°, V=2527 Å^3, Z=4, D_m=1.21, D_c=1.21 g cm^{-3}. Intensity data were collected by ω-2θ scans of variable rate designed to yield measurements of equal relative precision for all significant reflections, using an Enraf-Nonius CAD4 diffractometer equipped with Mo$K\alpha$ radiation (λ=0.71073 Å) and a graphite monochromator. Data reduction included corrections for background, Lorentz, polarization, absorption. Independent 2702 reflections having $I>3\sigma(I)$ were used in the refinements. All structure were solved by MULTAN 82 and refined by full-matrix least square based on F with weights $w=\sigma^{-2}(F_o)$. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located in calculated positions. The final residual values were R=0.052, R_w=0.077. The final atomic parameters for non-hydrogen atoms are listed in Table 1, and the selected bond distances and bond angles are shown in Fig 2. The complete tables of atomic coordinates, thermal parameters, bond distances and angles are kept as Document

Table 1. Final Atomic Parameters and Thermal Parameters, with Their Estimated Standard Deviations in Parentheses

Atom	X	Y	Z	B_{eq}/Å^2
K1	0.82150(4)	0.00067(5)	0.0242(1)	4.29(2)
N1	0.6965(1)	0.0516(2)	−0.0858(4)	4.10(6)
O1	0.7957(1)	0.1814(2)	−0.0686(3)	4.53(6)
O2	0.9041(1)	0.1444(2)	0.1263(3)	4.26(5)
O3	0.9358(1)	−0.0453(2)	0.1777(3)	4.61(6)
O4	0.8425(1)	−0.1778(2)	0.1398(3)	4.41(5)
O5	0.7339(1)	−0.1399(2)	−0.0593(3)	4.59(6)
S1	0.22658(8)	0.00009(9)	0.5711(2)	7.69(4)
C20	0.1697(2)	0.0041(3)	0.4198(6)	6.9(1)
N2	0.1299(1)	0.0049(2)	0.3235(4)	4.70(7)
C1	0.6987(2)	0.1338(3)	−0.1911(5)	4.65(9)
C2	0.7352(2)	0.2116(3)	−0.1101(5)	4.38(8)
C3	0.8355(2)	0.2526(2)	−0.0084(5)	4.72(9)
C4	0.8990(2)	0.2166(3)	0.0047(5)	5.27(9)
C5	0.9644(2)	0.1108(3)	0.1557(6)	5.9(1)
C6	0.9650(2)	0.0285(3)	0.2708(6)	5.7(1)
C7	0.9363(2)	−0.1271(3)	0.2745(5)	5.4(1)
C8	0.9045(2)	−0.2007(3)	0.1696(5)	5.23(9)
C9	0.8063(2)	−0.2483(2)	0.0576(5)	5.11(9)
C10	0.7414(2)	−0.2194(3)	0.0442(5)	5.11(9)
C11	0.6731(2)	−0.1157(3)	−0.0936(6)	5.30(9)
C12	0.6681(2)	−0.0240(3)	−0.1835(5)	5.04(9)
C13	0.6722(2)	0.0662(3)	0.0798(5)	5.2(1)
C14	0.6067(2)	0.0935(4)	0.0855(6)	7.4(1)
C15	0.5931(2)	0.1124(4)	0.2755(6)	7.3(1)
C16	0.5256(3)	0.1195(4)	0.2995(7)	9.1(2)
C17	0.5138(2)	0.1374(4)	0.4879(7)	8.3(1)
C18	0.4455(3)	0.1374(4)	0.5130(7)	10.2(2)
C19	0.4342(3)	0.1513(4)	0.6963(8)	10.4(2)

Anisotropically refined atoms given in the form of the isotropic equivalent thermal parameter defined as: (4/3)·[a2·B(1,1)+b2·B(2,2)+c2·B(3,3)+ab(cos gamma)·B(1,2)+ac(cos beta)·B(1,3)+bc(cos alpha)·B(2,3)].

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No. 8837 at the Editor of the Bulletin of the Chemical Society of Japan. All the measurements and calculations were performed at the Center of Advanced Instrument Analysis, Kyushu University.

Results and Discussion

The structure of the KSCN complex of *N*-heptylmonoaza-18-crown-6 is shown in Fig 1. Figure 2 gives its skeletal drawing along with the selected bond distances and bond angles. The skeletal drawing shows the arrangement of donor atoms around the cation. The macroring donor atoms are located in a chair-like arrangement to give the D_{3d} conformation of the ring, which is very close to those in the K^+ complexes of *N*-(2-methoxyethyl)monoaza-18-crown-6[6] and *N*-allylmonoaza-18-crown-6.[9] Interestingly, C13-N1-K1 bond angle of the complex is 99.5°, i.e. the non-coordinating alkyl side arm is directed almost upright to the ring plane. Although some effects might come from the crystal lattice packing the direction of C13-N1 bond is considered to be determined by the preferred conformation of the ring and coordination state of the pivot nitrogen. A further examination of CPK model shows that through simple rotations around the C13-N1 and C13-C14 bonds by 180° (two anti conformations to two eclipsed conformations) C15 can be put at such the position just above the K^+ ion without any deformation of the D_{3d} conformation, and this is just the position for the lariat oxygen atom in the N-pivot lariat ether complexes. Combined with the present result and the crystal structures of lariat ether complexes, we can conclude that the pyramidal structure of the pivot nitrogen and the conformation around the pivot nitrogen atom may account for the large enhanced binding observed in N-pivot lariat ether complexes. Very recently it was reported that the binding ability of C-pivot lariat ethers can be improved by introduction of an additional substituent (ex. methyl) on the pivot carbon, suggesting that the first side arm is arranged in an equatorial position in the C-pivot lariat ether complexes in the absence of the second substituent.[10,11]

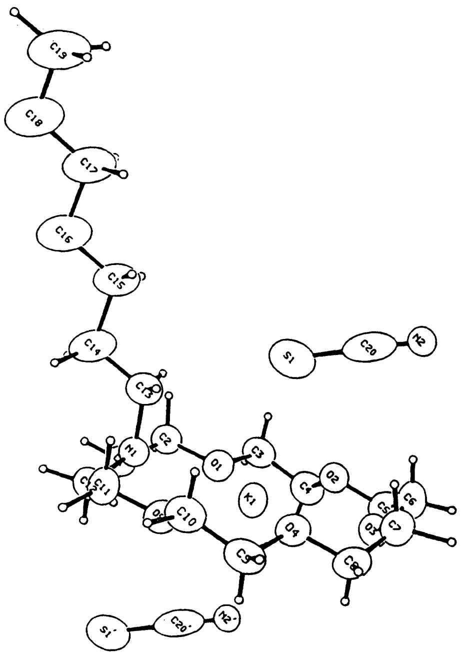
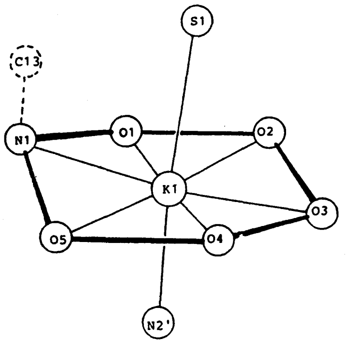


Fig. 1. Perspective drawing of the structure of KSCN complex of *N*-heptylmonoaza-18-crown-6.



K1-N1	2.908(3)	K1-O3	2.783(2)
K1-O1	2.781(3)	K1-O4	2.785(2)
K1-O2	2.845(3)	K1-O5	2.851(2)
K1-S1	3.455	K1-N2′	3.043

C13-N1-K1	99.5(2)	N1-K1-O3	171.54(8)
C1-N1-K1	108.0(2)	O1-K1-O4	175.51(8)
C12-N1-K1	108.7(2)	O2-K1-O5	176.06(8)
S1-K1-N2′	176.7		

Fig. 2. Skeletal drawing of KSCN complex of *N*-heptylmonoaza-18-crown-6, along with the selected bond distances (Å) and bond angles (°).

For monoaza-18-crown-6 the presence of the pivot nitrogen differentiates each side of the macroring in D_{3d} conformation, which is so stable as to be maintained in the complexation with larger cations,[12] i.e., one side (the side below in Fig. 1) with three axial nonbonding lone pairs (n_{ax}) of oxygen, and the other side(up side in Fig. 1) with only two n_{ax}.[1,13] The vertical arrangement of the *N*-alkyl side arm makes the environment of the two sides more different, and a larger cation would be favorably located the side having three n_{ax} (below the ring in Fig. 1). So that the formation of an intramolecular sandwich complex with a larger cation is very difficult for the bis(monoaza-18-crown-6)s linked by a short bridging chain because two unfavorable sides with two n_{ax} have to be used, although there is no hindrance to form an intermolecular sandwich complex with two monoaza-18-crown-6 rings. This reasoning is consistent with the results that the bis(monoaza-18-crown-6)s behave very similarly with the corresponding monocyclic analogues in the solvent extraction, homogeneous binding constants and cation transport experiment.[1,14,15]

The position of K^+ ion in the present complex, in the center of the macroring, is also noticeable, since the cation is known to be located above the ring plane in the complexes containing a monoaza-18-crown-6 ring reported before.[6,9] It seems that the relative position of the cation to the macroring is determined not only by the ring size but also by the coordination balance of the axial ligands. In the present complex a good balance between the two axial anionic ligands makes the cation reside within the macroring.

This work was partly supported by a Grant-in-Aid for Scientific Research(No. 61470088) from the Ministry of Education, Science and Culture.

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