Tetrahedron Letters,Vol.30,No.19,pp 2489-2492,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

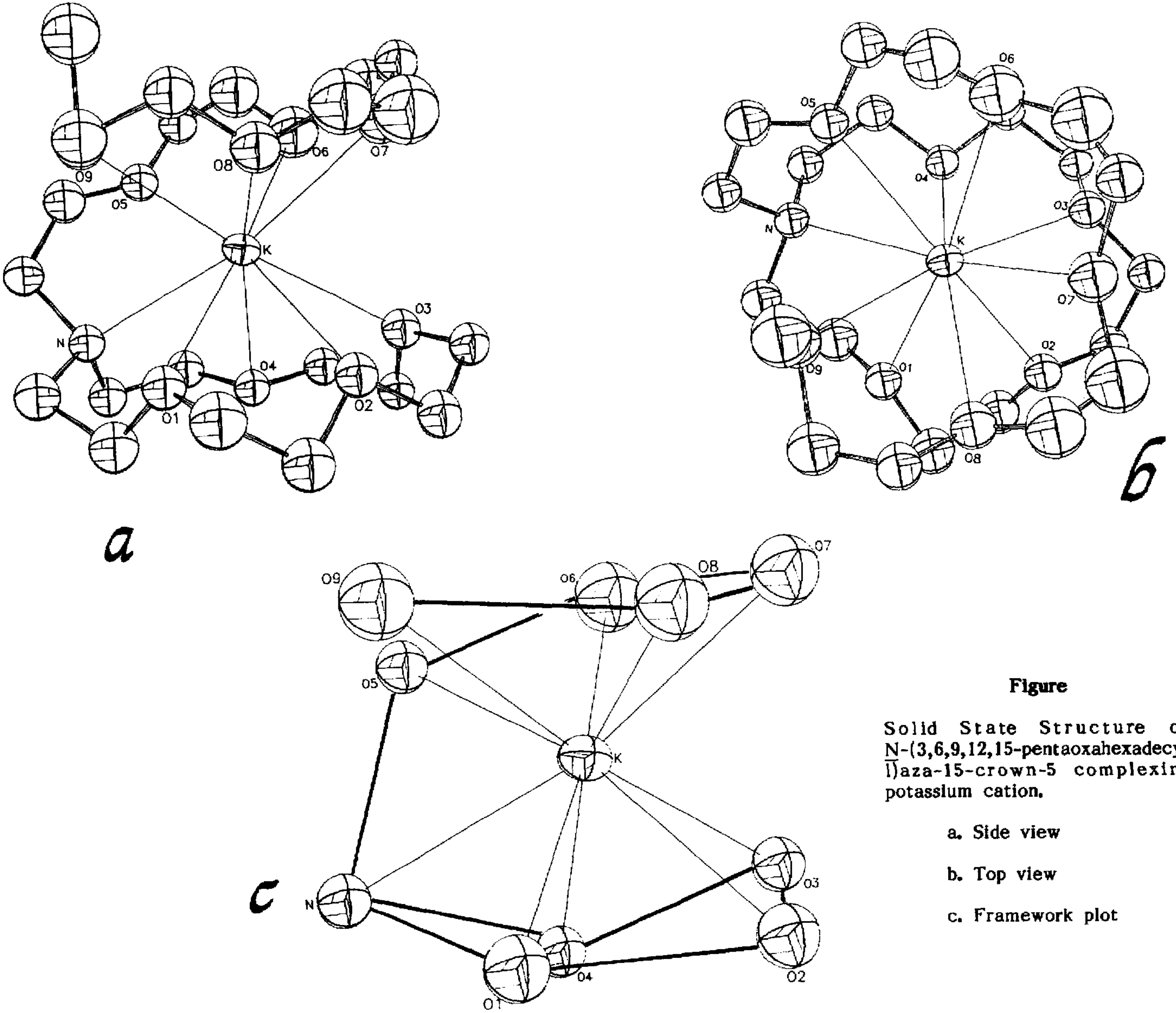
THE FIRST EXAMPLE OF A LARIAT ETHER THAT FORMS A PSEUDO-SANDWICH COMPLEX

Hyunsook K. Yoo, Hongming Zhang,[#] Jerry L. Atwood,[#] and George W. Gokel*
Departments of Chemistry, [#]University of Alabama, University, AL 35486
and University of Miami, Coral Gables, FL 33124 U.S.A.

Abstract. A lariat ether having a five-oxygen sidearm, forms a mono-potassium complex that appears to be more closely related to a *bis*(crown), sandwich complex than to a lariat ether.

The interesting recent report of Matsuda and coworkers[1] in which the question is raised of whether a *bis*(azacrown ether) behaves as a *bis*(crown ether) or as a lariat ether prompts us to report the most appropriate complement or counter-example yet known. This example is especially important because the precise role of very long lariat ether sidearms in cation complexation has been in question for some time.[2] Matsuda found that 1,5-*bis*(*N*-aza-15-crown-5)-3-oxapentane (1) formed a complex with KSCN of the type 1 $(KSCN)_2$. Although any such interpretation is necessarily subjective, Matsuda concluded that the complex had distinct lariat ether properties. Of course, the second ring theoretically permits a second cation to be complexed and this has never, to our knowledge, been observed in any lariat ether system.[3] Previous reports from our group[4] and from other groups[5] have shown that the sidearm may play a major role in complexation. Indeed, even though aza-12-crown-4[6] and other 12-crown-4 compounds[7] usually form sandwich complexes, when a $CH_3(OCH_2CH_2)_3$ sidearm is attached to the macroring nitrogen atom of aza-12-crown-4, a 1:1 complex forms between the ligand and large potassium cation. We now report that an analog of 1, *N*-(3,6,9,12,15-pentaoxahexadecyl)-aza-15-crown-5, 2, forms a potassium iodide complex of the form 2·KI which more closely resembles a sandwich complex than a lariat ether[9] and that the sidearm is fully involved in complexation of a single cation.

Compound 2 was prepared by reaction of $CH_3O(CH_2CH_2O)_5Ts$ with the anion of aza-15-crown-5 (Na_2CO_3, DMF).[10] The product was purified by chromatography over alumina, distilled (Kugelrohr, bp 180 °C/0.05 Torr), and obtained in 26% yield as slightly yellow but nearly colorless oil.[11] Crystals of the complex were deposited from an anhydrous tetrahydrofuran solution containing an equimolar mixture of KI and 2. The complex was obtained in 40% yield as a white solid having mp 77-80 °C.



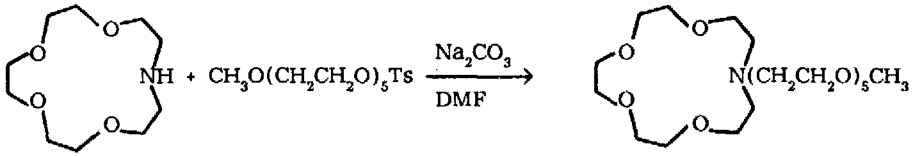
Figure

Solid State Structure of $\underline{N}$-(3,6,9,12,15-pentaoxahexadecy-l)aza-15-crown-5 complexing potassium cation.

a. Side view

b. Top view

c. Framework plot



An ORTEP plot of the observed structure is shown on the opposite page along with the computer-drawn, framework molecular diagram indicating the donor groups and connectivities. In the Matsuda structure, K-O bond distances for what might be called the macroring portion of the "lariat ether," range from 2.731 to 2.967A. The second macroring, which appears to act as a sidearm, shows similar bond distances. Indeed, these distances are typical of lariat ethers and are similar to those observed for the complex of 2. The latter bond distances are shown in the Table.

Table. Selected bond lengths for 2·KI

K	N	3.02(2)	K	O1	2.76(2)
K	O2	2.93(2)	K	O3	2.95(2)
K	O4	3.14(2)	K	O5	2.81(2)
K	O6	3.08(3)	K	O6	2.83(3)
K	O7	2.87(2)	K	O8	2.97(2)
K	O9	3.05(2)			

The ligands differ in two important respects. The most obvious is that there is a single macroring in the present case. Since there is no second pivot point required, there is also one less nitrogen atom. The second difference is an obvious consequence of the first, namely that a single potassium cation is present in the lariat ether structure reported here. The key difference between the *bis*(crown) ethers and the lariat ethers is thus that the higher level of organization (higher rigidity, lower flexibility) in 1 permits the complexation of two cations. In lariat ether 2, the sidearm is flexible enough to further envelop the ring-bound cation but lacks sufficient pre-organization to occlude a second cation. Some uncertainty remains in this interpretation because the macrorings in 1 are separated by a CH$_2$CH$_2$OCH$_2$CH$_2$ unit. Had the spacing been a single ethylene, sandwich complexation might have occurred.

We conclude from the information here that the lariat ethers, unlike other macroring systems, optimize the ring-sidearm cooperativity so that maximum cation solvation is achieved. If the sidearm is too long for a linear arrangement to be utilized, a coil is formed that optimizes cation solvation.

Acknowledgment. We warmly thank the National Institutes of Health for grants (GM 31846 and GM 36262) which supported this work.

Notes and References

1. He, G.-X.; Kikukawa, K.; Ohe, H.; Machida, M.; Matsuda, T.; *J. Am. Chem. Soc.* **1988**, *110*, 603.
2. Arnold, K.A.; Mallen, J.; Trafton, J.E.; White, B.D.; Fronczek, F.R.; Gehrig, L. M.; Gandour, R.D.; Gokel, G.W.; *J. Org. Chem.* **1988**, **53**, 5652.
3. Gandour, R.D.; Fronczek, F.R.; Gatto, V.J.; Minganti, C.; Schultz, R.A.; White, B.D.; Arnold, K.A.; Mazzocchi, D.D.; Miller, S.R.; Gokel, G.W.; *J. Am. Chem. Soc.*, **1986**, *108*, 4078.
4. a. Fronczek, F.R.; Gatto, V.J.; Schultz, R.A.; Jungk, S.J.; Colucci, W.J.; Gandour, R.D.; Gokel, G.W.; *J. Am. Chem. Soc.*, **1983**, *105*, 6717. b. Fronczek, F.R.; Gatto, V.J.; Minganti, C.; Schultz, R.A.; Gandour, R.D.; Gokel, G.W.; *J. Am. Chem. Soc.*, **1984**, *106*, 7244. c. Arnold, K.A.; Echegoyen, L.; Fronczek, F.R.; Gandour, R.D.; Gatto, V.J.; White, B.D.; Gokel, G.W.; *J. Am. Chem. Soc.*, **1987**, *109*, 3716. d. White, B.D.; Fronczek, F.R.; Gandour, R.D.; Gokel, G.W.; *Tetrahedron Lett.* **1987**, *27*, 1753.
5. Gandour, R.D.; Fronczek, F.R.; "Structural Chemistry of Lariat Ethers," Chapter 7 in Inoue, Y. and Gokel, G.W.; *Cation Binding by Macrocycles*, Marcel Dekker, New York, 1989, in press.
6. White, B. D.; Arnold, K. A.; Garrell, R.L.; Fronczek, F. R.; Gandour, R. D.; Gokel, G. W. *J. Org. Chem.* **1987**, *52*, 1128.
7. a. Van Remoortere, F. P.; Boer, F. P. *Inorg. Chem.* **1974**, *13*, 2071. b. Boer, F. P.; Neuman, M. A.; Van Remoortere, F. P.; Steiner, E. C. *Inorg. Chem.* **1974**, *13*, 2827. c. Mason, E.; Eick, H. A. *Acta Crystallogr. Section B* **1982**, *38*, 1821.
8. White, B.D.; Arnold, K.A.; Fronczek, F.R.; Gandour, R.D.; Gokel, G.W.; *Tetrahedron Lett.*, **1985**, *26*, 4035.
9. a. Gokel, G. W.; Dishong, D. M.; Diamond, C. J. *J. Chem. Soc. Chem. Commun.*, **1980**, 1053. b. Dishong, D. M.; Diamond, C. J.; Cinoman, M. I.; Gokel, G. W. *J. Am. Chem. Soc.* **1983**, *105*, 586.
10. a. Schultz, R.A.; Dishong, D. M., Gokel, G.W.; *J. Am. Chem. Soc.*, **1982**, *104*, 625. b. White, B. D.; Dishong, D. M.; Minganti, C. M.; Arnold, K. A.; Goli, D. M.; Gokel, G. W. *Tetrahedron Lett.* **1985**, *26*, 151. c. Schultz, R. A.; White, B. D.; Dishong, D. M.; Arnold, K. A.; Gokel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6659.
11. Crystal data: $C_{21}H_{45}NO_9{\cdot}KI$, FW = 607.6, space group PnZ_1a, a = 18.036(4), b = 11.712(3), c = 13.514(3) A, z = 4, d_c = 1.44 g-cm^{-1}, Mo*Kalpha* (*mu* = 13.25 cm^{-1}) R = 0.076 for 1484 unique reflections with I > 2*sigma*(I) (of 2590 unique data) measured by an Enraf-Nonius CAD4 X-ray spectrometer by *omega*-2Θ scans, 2° < Θ < 4°.

(Received in USA 14 February 1989)