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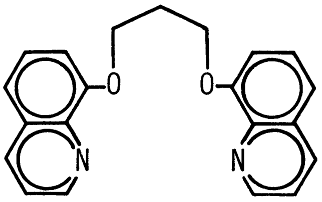
Crystal Structure of a 1 : 1 Complex of 1,3-Bis(8-quinolyloxy)propane and Lithium Perchlorate(1)

Katsuhiko UENO, Kazuhisa HIRATANI,*† Kazuhiro TAGUCHI,†
Tatsuhiro OKADA,† and Hideki SUGIHARA†
Research Institute for Polymers and Textiles,
Yatabe-machi Higashi, Tsukuba-gun, Ibaraki 305
† Industrial Products Research Institute,
Yatabe-machi Higashi, Tsukuba-gun, Ibaraki 305

1,3-Bis(8-quinolyloxy)prppane, which exhibits highly lithium ion-selective transport through liquid membrane, forms a 1 : 1 complex with lithium perchlorate. The X-ray analysis of this complex revealed that lithium ion is pentacoordinated in a nearly square pyramidal geometry.

Complexation tendencies toward lithium ion have been reported for several cyclic polyethers(crown ethers),2 - 11) [2.1.1.]cryptand,12) and noncyclic polyethers.13 - 16) Crystal structure analyses have been presented for the lithium complexes with only several of these cyclic ionophores.17 - 22) Recently, we have reported that some noncyclic quadridentate compounds, which have essentially the structures derived from 1,3-bis(8-quinolyloxy)propane,23) can exhibit excellently lithium ion-selective transport among alkali and alkaline earth metal ions through chloroform liquid membrane when they were used as carriers.24) In this paper, we wish to report the crystal structure of the complex of 1,3-bis(8-quinolyloxy)-propane(1) with lithium perchlorate.

Single crystals were grown by slow evaporation from chloroform solution of the complex of noncyclic polyether, 1, with lithium perchlorate.



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Crystal data of $LiC_{21}H_{18}O_2N_2ClO_4$, M = 436.8 are as follows: space group

$P2_1/n$, λ(CuKα) = 1.5418, a = 9.668(2), b = 13.717(3), c = 15.048(3) Å, β = 97.97(2)°, U = 1976.3(7) Å^3, D_x = 1.468 g cm^{-3}, Z = 4, μ(Cu-Kα) = 19.7 cm^{-1}.

A single crystal of approximate dimensions of 0.32 x 0.24 x 0.12 mm^3 was used for data collection. The integrated intensities were measured on a Nicolet P3/F automated four circle diffractometer with graphite monochromated Cu Kα radiation Scanning mode of $\theta/2\theta$ was applied. Corrections were made for background, Lorentz and polarization effects. Because of the small size of the crystal no absorption correction was made. A total of 3437 independent reflections ($3<2\theta<150°$) were obtained, of which 2403($|Fo|>3\sigma(|Fo|)$) were considered as observed. The structure was solved by direct method and refined by full matrix least squares procedure.[25)] Hydrogen atoms were geometrically located and included in Fc calculations. The refinement using anisotropic thermal factors for non-hydrogen atoms gave the final R value of 0.060 for 2403 observed reflections. The weighting system used at the final stage was $w = ((\sigma Fo)^2 + 0.001(Fo)^2)^{-1}$.

The molecular structure of the complex and a stereoview of the final structure of the complex are depicted in Figs. 1 and 2, respectively. The lithium ion in the inclusion complex with 1 is present in a 5-coordinate, nearly square pyramidal geometry. It is coordinated by the 2 ethereal oxygen and 2 aromatic nitrogen atoms of 1, and one axial perchlorate oxygen atom. The two ethereal oxygens and two aromatic nitrogens are coplanar with the maximum deviation of 0.054 Å, and the lithium ion is out of this plane by 0.62 Å. The dihedral angle between the two quinoline planes is 125.3°. The observed mean Li-O and Li-N distances to the

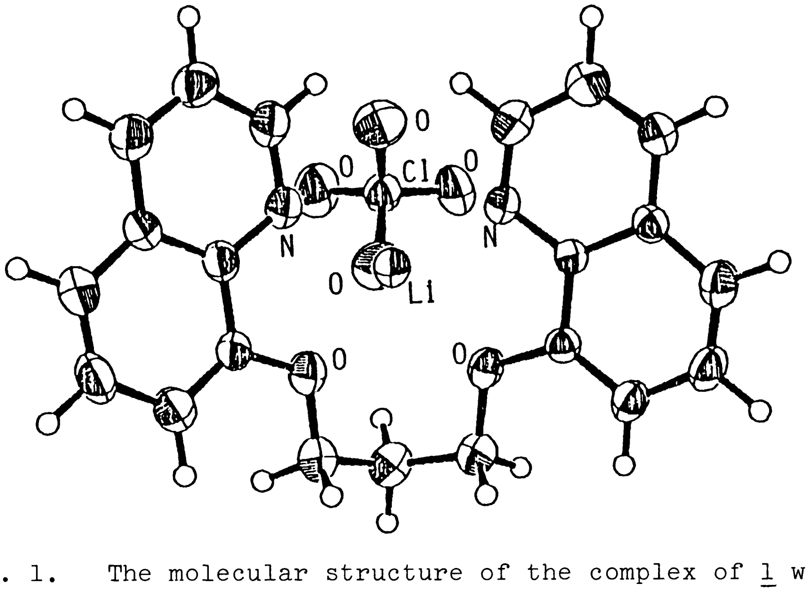

Fig. 1. The molecular structure of the complex of 1 with $LiClO_4$.

polyether hetero atoms are 2.17 and 2.12 Å, respectively. These values are somewhat larger than those in pentacoordinated cyclic crown.[20,21] The mean value of diagonal O-N distances is 4.065 Å. The rather short Li-O distance of the fifth apical perchlorate ligand(2.00 Å) is observed. It should be noted that the single crystal of this complex contains no water molecules, i.e., the complexed lithium ions are completely free from water. As far as we know this is the first direct demonstration, using crystallographic methods, of a water-free lithium complex with a noncyclic ligand. The water free lithium ion in this complex is pentacoordinated; such a pentacoordinate geometry has been reported in the lithium complexes of cyclic crown ethers, benzo-13-crown-4, dibenzo-14-crown-4, and others by W. N. Lipscomb et al.[20 - 22]

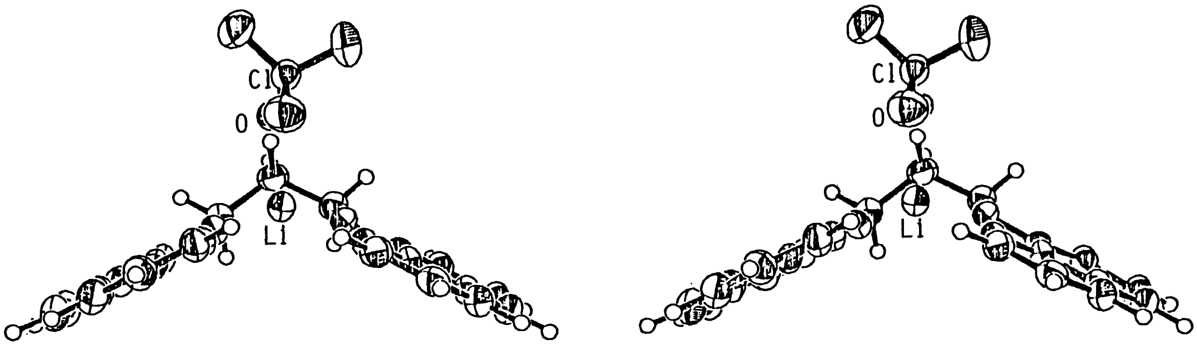

Fig. 2. Stereo drawing of the complex of 1 with $LiClO_4$(side view).

These results help us in appreciating the results of highly lithium ion-selective transport by 1 and its derivatives as previously reported.[24] The formation of the complex with sodium and potassium ions seems unfavorable because such cations with larger ionic size can not be located in position which permit the coordination of two oxygens and two nitrogens of 1, alternatively because the complexation of 1 with such large cationsmay bring about the torsion of ligand conformation. Furthermore, the extremely low ability of transport of 1 for alkaline earth metal ions could be also presumed on the basis of this crystal structure. Because of the large dihedral angle(125.3°) between the two quinoline planes, the second anionic ligand can not coordinate the divalent cation from the opposite side of the first anionic one so that 1 may not take a stable complex comformation. It might be one of the reasons why **1** and its derivatives can hardly transport such divalent ions. Thus, the crystal structure obtained in this study seems appropriately to reflect the ability of cation transport of **1** through liquid membrane, although the complex structure in the liquid membrane may not be the same as that in the crystal.

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