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Crystal and Molecular Structure of a Lithium–C222B Cryptate Complex Isolated from *n*-Butylpyridinium Chloride–Aluminum(III) Chloride Molten Salt Medium

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The preparation of $Li^+(C_{22}H_{36}N_2O_6)AlCl_4^-$ is reported. This complex crystallizes in the monoclinic system, space group $P2_1/n$ (No. 14). Unit cell parameters are $a = 11.099$ (2) Å, $b = 11.796$ (2) Å, $c = 22.345$ (5) Å, $\beta = 96.15$ (2)°, and $Z = 4$. The complex is inclusive with six Li–O interactions (2.207 (5)–2.525 (6) Å) in a somewhat octahedral arrangement; the Li–N distances (2.777 (6) and 2.945 (6) Å) are long and indicate weak or no Li–N interactions. The $AlCl_4^-$ ion is a nearly ideal tetrahedron with an average Al–Cl distance of 2.127 Å and an average Cl–Al–Cl angle of 109.47°. The $AlCl_4^-$ ion is far removed from the lithium–C222B cryptate group (the Al and Cl distances from Li exceed 5.8 Å).

Introduction

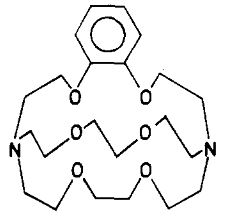
The use of molten salts as reaction media rapidly increased in popularity after Osteryoung et al.[1] pointed out that *n*-butylpyridinium chloride–aluminum(III) chloride mixtures, in the 45–67 mol % $AlCl_3$ range, are liquid at room temperature and behave as typical ionic liquids. It thus becomes possible to study a variety of chemical reactions in this new "nonaqueous solvent", whose solvent properties are vastly different from those of conventional molecular liquids.

It was of interest to us to explore the formation of macrocyclic complexes of alkali-metal cations in this medium. Preliminary studies of the lithium salts in "basic" melt ($AlCl_3 < 50$ mol %) by lithium-7 NMR showed that the complexation reactions occur with crown ethers[2] and with cryptands.[3] The stabilities of several crown ether complexes in this medium have been determined.[2]

Lithium-7 NMR and potentiometric measurements[2,3] clearly show that in basic melts lithium chloride interacts with the chloride ion to form the $LiCl_2^-$ ion. The structure of this newly postulated anion is unknown; it is also not not known whether the lithium ion in a macrocyclic cavity is still bonded to one or two chloride ions. It seems entirely possible that Li–Cl bonds persist in the two-dimensional crown ether complexes but would be less probable for three-dimensional lithium cryptates. In order to get some information on this problem, we isolated the lithium cryptate of the benzo-C222 cryptand and determined its structure.

Experimental Part

Reagents. Synthesis of *n*-butylpyridinium chloride, purification of aluminum(III) chloride, and the preparation of melts followed the procedures given by Osteryoung et al.[1] and are described elsewhere.[3] Lithium chloride (Fisher, analytical reagent grade) was dried for 3 days at 100 °C. The cryptand benzo-C222 (**1**, C222B, MCB) was used as received.



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Preparation of the Complex. A 1.0 mol % solution of LiCl was prepared in basic (45 mol % $AlCl_3$, 55 mol % (BP)Cl) melt. Weighted amounts of C222B were added to this solution until a 1:1 ligand:Li^+ mole ratio was reached. The precipitated complex was removed by filtration, and the precipitate was washed several times with benzene. All of the above manipulations were carried out in a drybox under a nitrogen atmosphere. The total concentration of $O_2 + H_2O$ in the drybox was <10 ppm.

The washed product was dried at room temperature at 10^{-5} torr. Anal. (Galbraith Laboratories) Found: C, 40.58; H, 6.33; N, 4.57; O, 18.47; Li, 0.95; Al, 3.69; Cl, 21.83. Calcd: C, 41.79; H, 5.74; N, 4.43; O, 20.24; Li, 1.10; Al, 4.27; Cl, 22.43. These results clearly indicate that instead of the expected C222B·LiCl complex, we actually obtained C222B·$LiAlCl_4$. The calculated composition of this complex is in good agreement with the experimental results.

X-ray Data Collection. A colorless, irregular fragment crystal of the C222B complex of lithium tetrachloroaluminate, $Li^+(C_{22}H_{36}N_2O_6)AlCl_4^-$, having approximate dimensions of 0.70 × 0.70 × 0.90 mm, was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation ($\lambda = 0.71073$ Å) on a Nicolet P3F computer-controlled four-circle diffractometer equipped with a graphite crystal incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, with use of the setting angles of 20 reflections in the range $35 < 2\theta < 40°$. The monoclinic cell parameters and calculated volume are $a = 11.099$ (2) Å, $b = 11.796$ (2) Å, $c = 22.345$ (5) Å, $\beta = 96.15$ (2)°, and $V = 2908.7$ (10) Å^3. For $Z = 4$ and fw = 600.28 the calculated density is 1.37 g/cm^3. From the systematic absences

$$h0l\colon\ h + l = 2n + 1$$

$$0k0\colon\ k = 2n + 1$$

and from subsequent least-squares refinement, the space group was determined to be $P2_1/n$ (No. 14).

The data were collected at a temperature of 26 (1) °C using the θ–2θ scan technique. The scan rate was 1°/min (in 2θ). Data were collected to a maximum 2θ of 55°. The scan range (in degrees) was determined as a function of 2θ to correct for the separation of the Kα doublet;[4] the scan width was calculated as

$$2\theta \text{ scan width} = 1.60 + (2\theta(K\alpha_2) - 2\theta(K\alpha_1))$$

The ratio of peak counting time to background counting time was 1:1.

X-ray Data Reduction. A total of 7496 reflections were collected, of which 6714 were unique and not systematically absent. As a check on crystal and electronic stability 2 representative reflections were measured every 45 reflections. A steady decrease in intensity was observed such that the intensity after about 500 h of data collection was about 85% of the original intensity. In order to include data later recollected at reduced milliamp settings, an anisotropy decay correction was applied. The correction factors on I ranged from 1.001 to 7.614 with an average value of 1.221.

Lorentz and polarization corrections were applied to the data. An empirical absorption correction based on a series of ψ scans was applied to the data. Relative transmission coefficients ranged from 0.939 to 0.999 with an average value of 0.974. A secondary extinction correction was applied.[5] The final coefficient, refined in least squares, was 1.7×10^{-8} (in absolute units). Intensities of equivalent reflections were averaged. The agreement factors for the averaging of the 68 observed and accepted reflections were 1.5% based on intensity and 0.7% based on F_o.

X-ray Structure Solution and Refinement. The structure was solved by Patterson methods, yielding the positions of the Al and four Cl atoms; remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride

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Table I. Non-Hydrogen Atom Positional Parameters and Their Estimated Standard Deviations for the C222B Complex of Lithium Tetrachloroaluminate[a]

atom	x	y	z	B, Å^2
Cl1	0.22641 (6)	0.02104 (7)	0.29166 (3)	5.02 (1)
Cl2	0.41340 (7)	−0.02555 (8)	0.42434 (4)	6.65 (2)
Cl3	0.25951 (8)	−0.25060 (7)	0.35178 (5)	7.03 (2)
Cl4	0.09881 (7)	−0.04829 (8)	0.42179 (4)	6.24 (2)
Al1	0.25041 (7)	−0.07530 (7)	0.37270 (4)	3.83 (2)
O4	0.6506 (1)	0.5623 (2)	0.34791 (7)	4.22 (4)
O7	0.8723 (2)	0.5300 (2)	0.3803 (1)	5.93 (5)
O13	0.7263 (2)	0.4224 (2)	0.24300 (8)	4.37 (4)
O16	0.5874 (2)	0.2620 (2)	0.28402 (8)	4.56 (4)
O21	0.7273 (2)	0.3277 (2)	0.43754 (9)	5.87 (5)
O24	0.8272 (2)	0.2075 (2)	0.35468 (8)	5.08 (4)
N1	0.4908 (2)	0.3835 (2)	0.3794 (1)	4.21 (5)
N10	0.9660 (2)	0.3790 (2)	0.3028 (1)	4.47 (5)
C2	0.4565 (2)	0.5025 (2)	0.3771 (1)	4.16 (5)
C3	0.5217 (2)	0.5649 (2)	0.3316 (1)	3.89 (5)
C1B	0.8823 (3)	0.6863 (3)	0.4527 (1)	5.57 (7)
C2B	0.8216 (3)	0.7756 (3)	0.4764 (1)	6.14 (8)
C3B	0.7015 (3)	0.7942 (3)	0.4588 (1)	5.32 (7)
C4B	0.6404 (2)	0.7237 (2)	0.4163 (1)	4.20 (5)
C5	0.6994 (2)	0.6353 (2)	0.3918 (1)	3.51 (5)
C6	0.8225 (2)	0.6169 (2)	0.4101 (1)	4.10 (5)
C8	0.9989 (2)	0.5062 (3)	0.3900 (2)	6.01 (7)
C9	1.0375 (3)	0.4719 (3)	0.3311 (2)	6.23 (8)
C11	0.9412 (2)	0.3952 (3)	0.2375 (1)	5.17 (7)
C12	0.8330 (2)	0.4712 (3)	0.2231 (1)	5.36 (7)
C14	0.6713 (2)	0.3405 (2)	0.2020 (1)	4.65 (6)
C15	0.5569 (2)	0.3046 (2)	0.2251 (1)	4.46 (6)
C17	0.4877 (3)	0.2196 (2)	0.3117 (1)	5.52 (7)
C18	0.4147 (2)	0.3127 (2)	0.3368 (1)	5.19 (7)
C19	0.5091 (3)	0.3384 (3)	0.4403 (1)	5.62 (6)
C20	0.6330 (3)	0.3696 (3)	0.4702 (1)	6.29 (8)
C22	0.7528 (3)	0.2214 (3)	0.4484 (1)	7.43 (8)
C23	0.8557 (3)	0.1795 (3)	0.4152 (1)	7.11 (8)
C25	0.9184 (3)	0.1791 (2)	0.3171 (1)	5.02 (6)
C26	1.0162 (2)	0.2674 (2)	0.3189 (1)	5.13 (6)
Li1	0.7341 (5)	0.3724 (5)	0.3385 (2)	5.5 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

on the atom to which they are bonded. The structure was refined in full-matrix least squares, where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined at 1.0 for all observed reflections.

Scattering factors were taken from Cromer and Waber.[6] Anomalous dispersion effects were included in F_c;[7] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[8] Only the 4538 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 326 variable parameters and converged (largest parameter shift was 0.47 times its esd) with the unweighted and weighted agreement factors

$$R1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.041$$

$$R2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.037$$

The standard deviation of an observation of unit weight was 0.98. The highest peak in the final difference Fourier had a height of 0.44 e/Å^3 with an estimated error based on $\sigma(F)$[9] of 0.07. Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends.

All calculations were performed on a VAX-11/750 computer using SDP-PLUS.[10]

Table II. Bond Distances (Å) for the C222B Complex of Lithium Tetrachloroaluminate

atom 1	atom 2	dist	atom 1	atom 2	dist
Cl1	Al1	2.130 (1)	N1	C2	1.454 (3)
Cl2	Al1	2.122 (1)	N1	C18	1.464 (3)
Cl3	Al1	2.125 (1)	N1	C19	1.455 (3)
Cl4	Al1	2.129 (1)	N1	Li1	2.945 (6)
O4	C3	1.438 (3)	N10	C9	1.457 (4)
O4	C5	1.372 (3)	N10	C11	1.468 (4)
O4	Li1	2.442 (6)	N10	C26	1.460 (4)
O7	C6	1.370 (3)	N10	Li1	2.777 (6)
O7	C8	1.427 (3)	C2	C3	1.502 (4)
O7	Li1	2.525 (6)	C1B	C2B	1.385 (5)
O13	C12	1.430 (3)	C1B	C6	1.373 (4)
O13	C14	1.423 (3)	C2B	C3B	1.366 (4)
O13	Li1	2.207 (5)	C3B	C4B	1.384 (4)
O16	C15	1.416 (3)	C4B	C5	1.375 (4)
O16	C17	1.416 (4)	C5	C6	1.401 (3)
O16	Li1	2.324 (5)	C8	C9	1.483 (5)
O21	C20	1.426 (4)	C11	C12	1.505 (4)
O21	C22	1.417 (4)	C14	C15	1.482 (4)
O21	Li1	2.284 (5)	C17	C18	1.508 (4)
O24	C23	1.395 (4)	C19	C20	1.508 (4)
O24	C25	1.423 (4)	C22	C23	1.476 (5)
O24	Li1	2.214 (6)	C25	C26	1.502 (4)

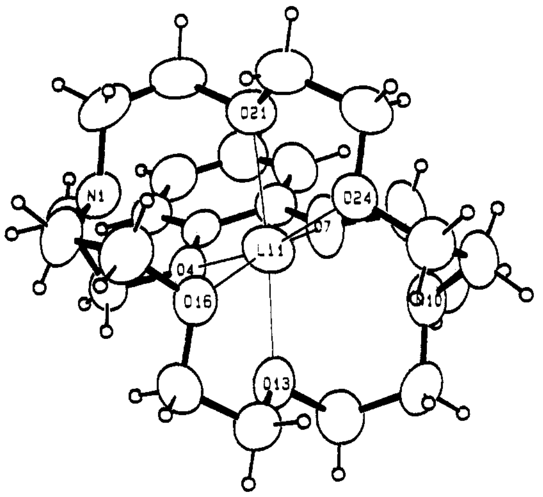

Figure 1. ORTEP drawing of the lithium–C222B cryptate complex showing the Li–O interactions and the numbering of the Li, N, and O atoms.

Crystal Structure

All atoms lie in "general" positions (Tables I and II). No crystallographic symmetry is imposed on the molecular structure (Figure 1). The $AlCl_4^-$ ion is a nearly ideal tetrahedron with Al–Cl bond distances from 2.122 (1) to 2.130 (1) Å (average 2.127 Å) and Cl–Al–Cl bond angles from 108.53 (5) to 110.70 (5)° (average 109.47°) (Table III).

The Li^+ ion is complexed within the cryptand 222B with four short Li–O contacts (average 2.257 Å), two longer Li–O contacts (average 2.484 Å), and two long Li–N contacts (average 2.861 Å). The six oxygen atoms form a somewhat octahedral arrangement around the Li^+ ion; the approximately orthogonal angles range from 60.9 (1) to 111.2 (2)° (average 90.1°), and the approximately straight angles range from 165.2 (3) to 175.3 (3)° (average 168.8°). The two nitrogen atoms lie above opposite three-oxygen planes (along what would be a three-fold axis of the octahedron) with N–Li–O angles from 62.6 (1) to 69.9 (2)° (average 66.0°). The four-oxygen planes form dihedral angles of 112.9, 108.0, and 71.6° (octahedral angles 90°) with each other, and the two-nitrogen and two-oxygen planes form dihedral angles of 116.7, 64.3, and 52.4° with each other (octahedral angles 60, 120°).

There appears to be no close interactions between the Li^+ ion and the $AlCl_4^-$ ion (Figure 2, supplementary material) as the shortest Li–Cl separation is 5.89 Å and the shortest Li–Al separation is 6.81 Å.

Discussion

The structure of the C211·LiI complex has been reported by Moras and Weiss.[11] Although C221·Li^+ and C222·Li^+ complexes

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Table III. Bond Angles (deg) for the C222B Complex of Lithium Tetrachloroaluminate

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cl1	Al1	Cl2	109.66 (5)	O7	C6	C1B	126.4 (2)
Cl1	Al1	Cl3	109.68 (5)	O7	C6	C5	114.0 (2)
Cl1	Al1	Cl4	108.93 (4)	C1B	C6	C5	119.6 (3)
Cl2	Al1	Cl3	109.33 (5)	O7	C8	C9	107.0 (2)
Cl2	Al1	Cl4	110.70 (5)	N10	C9	C8	113.2 (3)
Cl3	Al1	Cl4	108.53 (5)	N10	C11	C12	110.6 (2)
C3	O4	C5	118.3 (2)	O13	C12	C11	111.2 (2)
C3	O4	Li1	112.0 (2)	O13	C14	C15	107.1 (2)
C5	O4	Li1	120.9 (2)	O16	C15	C14	107.3 (2)
C6	O7	C8	121.0 (2)	O16	C17	C18	112.4 (2)
C6	O7	Li1	118.0 (2)	N1	C18	C17	111.2 (2)
C8	O7	Li1	117.4 (2)	N1	C19	C20	110.7 (2)
C12	O13	C14	112.7 (2)	O21	C20	C19	111.9 (2)
C12	O13	Li1	117.4 (2)	O21	C22	C23	108.2 (3)
C14	O13	Li1	114.2 (2)	O24	C23	C22	108.7 (3)
C15	O16	C17	114.3 (2)	O24	C25	C26	112.2 (2)
C15	O16	Li1	111.9 (2)	N10	C26	C25	111.3 (2)
C17	O16	Li1	120.4 (2)	O4	Li1	O7	60.9 (1)
C20	O21	C22	113.1 (2)	O4	Li1	O13	82.1 (2)
C20	O21	Li1	121.2 (2)	O4	Li1	O16	107.9 (2)
C22	O21	Li1	111.3 (2)	O4	Li1	O21	94.3 (2)
C23	O24	C25	114.5 (2)	O4	Li1	O24	165.2 (3)
C23	O24	Li1	114.8 (2)	O4	Li1	N1	64.1 (1)
C25	O24	Li1	117.3 (2)	O4	Li1	N10	111.8 (2)
C2	N1	C18	113.4 (2)	O7	Li1	O13	96.9 (2)
C2	N1	C19	113.4 (2)	O7	Li1	O16	165.9 (3)
C2	N1	Li1	106.1 (2)	O7	Li1	O21	83.9 (2)
C18	N1	C19	114.3 (2)	O7	Li1	O24	109.4 (2)
C18	N1	Li1	104.9 (2)	O7	Li1	N1	113.2 (2)
C19	N1	Li1	103.5 (2)	O7	Li1	N10	62.6 (1)
C9	N10	C11	111.7 (2)	O13	Li1	O16	72.0 (2)
C9	N10	C26	113.3 (2)	O13	Li1	O21	175.3 (3)
C9	N10	Li1	112.0 (2)	O13	Li1	O24	111.2 (2)
C11	N10	C26	112.9 (2)	O13	Li1	N1	110.2 (2)
C11	N10	Li1	102.0 (2)	O13	Li1	N10	69.9 (2)
C26	N10	Li1	104.1 (2)	O16	Li1	O21	106.5 (2)
N1	C2	C3	110.7 (2)	O16	Li1	O24	83.2 (2)
O4	C3	C2	110.9 (2)	O16	Li1	N1	64.8 (2)
C2B	C1B	C6	120.0 (3)	O16	Li1	N10	119.0 (2)
C1B	C2B	C3B	120.7 (3)	O21	Li1	O24	72.7 (2)
C2B	C3B	C4B	119.5 (3)	O21	Li1	N1	65.3 (2)
C3B	C4B	C5	120.7 (2)	O21	Li1	N10	114.4 (2)
O4	C5	C4B	126.3 (2)	O24	Li1	N1	114.6 (2)
O4	C5	C6	114.1 (2)	O24	Li1	N10	69.0 (2)
C4B	C5	C6	119.5 (2)	N1	Li1	N10	175.6 (2)

Table IV. Lithium Ion–Heteronuclear Atom Bond Distances (Å)

C211·LiI	$C222B·LiAlCl_4$
Li–O 2.081–2.173	2.207–2.525
Li–N 2.288	2.777–2.945
Li–I >6.5	
Li–Al	≥6.81
Li–Cl	≥5.89

have been studied in water[12] and in nonaqueous solvents,[13] their crystal structures have not been reported in the literature. It should be noted that the cavity size of the C211 cryptand is commensurate with the dimensions of the Li^+ ion and, therefore, this ligand forms a stable Li^+ complex.[14] On the other hand, the C222 (or C222B) cavity is much too large for Li^+, and the resulting complex is quite unstable,[14] which may account for the difficulties of isolating crystalline $C222·Li^+$ complexes from conventional solvents.

It is interesting, therefore, to compare the structures of C211·LiI[11] and $C222B·LiAlCl_4$. In both cases the Li^+ ion is inside the cavity ("inclusive complex") and is in a distorted-octahedral environment. As seen in Table IV, the Li^+–heteroatom bond distances are shorter in the case of the C211 cryptate, where the coordination octahedron is formed by four oxygen and two nitrogen atoms. In the C222B case the octahedron is formed by the six oxygen atoms and the Li–N distances are too long for bond formation. In both cases the anions are far removed from the cation. Lithium–heteroatom bond distances are consonant with the observed stabilities of the respective Li^+ cryptates in solutions. For example, in methanol solutions the respective log K_f values are as follows: $C222B·Li^+$, 2.19;[15] $C222·Li^+$, 2.6;[12] $C221·Li^+$, 5.36;[12] $C211·Li^+$, 8.04.[12] It should be noted, parenthetically, that while it seems impossible to isolate crystals of the unstable $C221·Li^+$ and $C222·Li^+$ complexes from conventional organic solvents, crystalline $C222B·Li^+AlCl_4^-$ cryptate is readily obtained from the basic $AlCl_3$–(BP)Cl melt although its formation constant in this medium is only 1.60 ± 0.025[3] (log K_f).

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Registry No. $Li^+(1)AlCl_4^-$, 102648-74-8.

Supplementary Material Available: Stereographic packing diagram (Figure 2) and listings of hydrogen atom positions and isotropic thermal parameters (Table S1), anisotropic thermal parameters for non-hydrogen atoms (Table S2), and least-squares planes (Table S3) (6 pages). Ordering information is given on any current masthead page.

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