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# Crystal Structure of the Complex of 1,4,7,10,13,16-Hexaoxacyclooctadecane with Lithium Picrate Dihydrate

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A lithium dihydrate picrate complex with 18-crown-6 (18C6) has been synthesized. Solvent extraction in the $CH_2Cl_2/H_2O$ system was studied (log $K_{ex}$ =2.04). Crystals of $Li(H_2O)_2(18C6)$Picrate are triclinic, space group $P\bar{1}$, with a = 7.744(2), b = 11.848(3), c = 14.532(4), α= 76.33(2)°, β = 75.80(2)°, γ = 77.81(2)°, Z = 2; final R = 0.039, $wR^2$ = 0.094 (GOOF = 1.035) for 3218 independent reflections. The coordination polyhedron is a distorted trigonal bipyramid. The coordinated water molecules are involved in a hydrogen bond network with the oxygen atoms of 18C6 and the picrate ion. This network stabilizes the metal ion complex with the crown ether and changes the selectivity of the extraction process.

## INTRODUCTION

Many studies of the complexation of alkali metal ions $Na^+$, $K^+$, $Rb^+$ and $Cs^+$ by crown ethers and similar ligands have been performed, but relatively few investigations of the complexation of $Li^+$ by such ligands are available. As a result, despite the importance of $Li^+$ in biological systems, there are few macrocyclic ligands which are known to selectively bind $Li^+$ in aqueous solution at physiological concentration.[1,2] Moreover, because $Li^+$ is not bound strongly by most macrocyclic ligands, few data are available regarding the stabilities of $Li^+$ complexes. It has been assumed that because the ionic radius of $Li^+$ is small (0.60 Å[1]) and this cation is highly hydrated, it would not be bound by such ligands as 18-crown-6 and other relatively large macrocyclic compounds. However, it was found in liquid-liquid extraction experiments that enough $Li^+$ is extracted by such ligands to interfere with the selective extraction of other alkali metal cations. The crystal structures of 18-crown-6 complexes of $LiClO_4$ and LiSCN have been reported[3], but in both cases the anion is hydrophilic enough to prevent the extraction of $Li^+$ into the organic phase.

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TABLE I Crystal data and structure refinement for $Li(H_2O)_2$(18-crown-6)(Picrate)

| | |
|---|---|
| Empirical formula | $C_{18}H_{30}Li\ N_3\ O_{15}$ |
| Formula weight | 535.39 |
| Wavelength, Å | 0.71073 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions (Å): | |
| a | 7.744(2) |
| b | 11.848(3) |
| c | 14.532(4) |
| α | 76.33(2)° |
| β | 75.80(2)° |
| γ | 77.81(2)° |
| Volume ($A^3$) | 1239.3(6) |
| Z | 2 |
| Density (calculated) | 1.435g/$cm^3$ |
| Absorption coefficient ($mm^{-1}$) | 0.125 |
| F(000) | 564 |
| Reflections collected | 3500 ($4.5 < 2\theta < 45$) |
| Independent reflections | 3218 [R(int) = 0.0119] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| | $w^{-1} = [s^2(F_0^2) + (0.0467P)^2 + 0.4859P], = (F_0^2 + 2F_c^2)/3$ |
| Goodness-of-fit on $F^2$ | 1.035 |
| Final R indices [I > 2sigma(I)] | $R_1 = 0.039$, $wR^2 = 0.094$ |
| R indices (all data) | $R_1 = 0.047$, $wR^2 = 0.104$ |
| Largest diff. peak and hole | 0.252 and –0.133 $e.A^{-3}$ |

The goal of this structural study was to investigate the ability of rather large macrocyclic ligands to extract this small strongly hydrated cation into a hydrophobic organic phase. The picrate anion, which is more hydrophobic than most inorganic anions, was selected as the counter-ion.

## EXPERIMENTAL

A lithium picrate solution was prepared by carefully neutralizing a standardized solution of picric acid ("Aldrich") with LiOH ("Spectrum"). Solvent extraction experiments were performed using established procedures.[4] According to the manufacturer, the amounts of potassium and sodium in the lithium samples used in the extraction experiment were less than 0.002%.

### Synthesis

The title complex was prepared by mixing the aqueous solution of lithium picrate (ca. 20 mM) with a solution of 18-crown-6, the crown ether being in excess. The resulting solution was allowed to evaporate. Dark yellow crystals of the complex appeared. They were recrystallized from an aqueous solution and the resulting crystals were suitable for an X-ray study.

Anal.: Calcd for $Li(H_2O)_2(C_{12}H_{24}O_6)(C_6H_2N_3O_7)$: Li, 1.30. Found: Li, 1.2 (ICP spectrometry) $^1H$ NMR ($CDCl_3$): 3.8(24 H), 8.9(2H).

### X-ray Structure Analysis

A single crystal study was performed using a Siemens R3m/V automated diffractometer which

TABLE II Atomic coordinates ( × $10^4$) and equivalent isotropic displacement parameters ($Å^2$ × $10^3$)

| Atoms | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Li | 5993(7) | 8585(4) | 8301(4) | 89(1) |
| O(1) | 7314(2) | 8520(2) | 9547(1) | 65(1) |
| O(2) | 7056(2) | 10038(1) | 7867(1) | 62(1) |
| O(3) | 5168(2) | 9512(1) | 6690(1) | 65(1) |
| O(4) | 2627(2) | 7847(1) | 7529(1) | 55(1) |
| O(5) | 2858(2) | 6341(1) | 9344(1) | 55(1) |
| O(6) | 4311(2) | 7262(1) | 10550(1) | 63(1) |
| O(8) | 3458(3) | 8921(2) | 8873(2) | 64(1) |
| O(9) | 6543(3) | 6899(2) | 8338(1) | 65(1) |
| C(1) | 8184(5) | 9533(3) | 9281(3) | 81(1) |
| C(2) | 8660(4) | 9859(3) | 8226(3) | 79(1) |
| C(3) | 7252(5) | 10593(3) | 6867(2) | 75(1) |
| C(4) | 5522(5) | 10675(2) | 6583(2) | 75(1) |
| C(5) | 3568(4) | 9507(3) | 6385(2) | 70(1) |
| C(6) | 3246(4) | 8280(3) | 6526(2) | 65(1) |
| C(7) | 2360(4) | 6651(2) | 7748(2) | 58(1) |
| C(8) | 1560(3) | 6341(2) | 8798(2) | 60(1) |
| C(9) | 2126(4) | 6245(3) | 10356(2) | 66(1) |
| C(10) | 3595(4) | 6189(2) | 10860(2) | 66(1) |
| C(11) | 5957(5) | 7150(3) | 10866(3) | 89(1) |
| C(12) | 6695(5) | 8270(3) | 10572(2) | 82(1) |
| C(21) | 12323(3) | 14069(2) | 4113(1) | 41(1) |
| C(22) | 11571(3) | 13049(2) | 4726(1) | 39(1) |
| C(23) | 11199(3) | 12854(2) | 5715(2) | 43(1) |
| C(24) | 11472(3) | 13657(2) | 6189(1) | 43(1) |
| C(25) | 12141(3) | 14666(2) | 5677(2) | 44(1) |
| C(26) | 12567(3) | 14858(2) | 4687(1) | 40(1) |
| O(11) | 12710(2) | 14257(1) | 3218(1) | 67(1) |
| N(1) | 11115(2) | 12183(2) | 4303(1) | 50(1) |
| O(12) | 11014(2) | 12417(2) | 3456(1) | 72(1) |
| O(13) | 10807(3) | 11241(2) | 4819(1) | 87(1) |
| N(2) | 11036(3) | 13446(2) | 7233(1) | 56(1) |
| O(14) | 10510(3) | 12521(2) | 7673(1) | 85(1) |
| O(15) | 11224(3) | 14186(2) | 7644(1) | 75(1) |
| N(3) | 13296(3) | 15932(2) | 4204(1) | 56(1) |
| O(16) | 13221(3) | 16669(2) | 4663(2) | 94(1) |
| O(17)[a] | 14347(16) | 15937(9) | 3408(3) | 79(3) |
| O(17A)[a] | 13130(42) | 16344(10) | 3344(5) | 84(7) |

$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor [a]Disordered, population 0.5

TABLE III Selected bond lengths(Å) and angles (°)

| | | | |
|---|---|---|---|
| O(2)-Li | 1.967(5) | O(8)-Li | 1.931(5) |
| O(9)-Li | 1.943(5) | | |
| O(1)-Li | 2.268(6) | O(3)-Li | 2.514(6) |
| O(1)-C(1) | 1.428(3) | O(1)-C(12) | 1.427(3) |
| O(2)-C(2) | 1.419(3) | O(2)-C(3) | 1.432(3) |
| O(3)-C(4) | 1.428(3) | O(3)-C(5) | 1.415(3) |
| O(4)-C(6) | 1.424(3) | O(4)-C(7) | 1.424(3) |
| O(5)-C(8) | 1.425(3) | O(5)-C(9) | 1.428(3) |
| O(6)-C(10) | 1.426(3) | O(6)-C(11) | 1.428(4) |
| C(2)-C(1) | 1.463(5) | C(7)-C(8) | 1.488(4) |
| C(4)-C(3) | 1.474(4) | C(10)-C(9) | 1.479(4) |
| C(6)-C(5) | 1.485(4) | C(11)-C(12) | 1.483(5) |
| O(8)-Li-O(9) | 106.2(2) | O(9)-Li-O(3) | 106.2(2) |
| O(8)-Li-O(2) | 110.8(3) | O(2)-Li-O(3) | 74.7(2) |
| O(9)-Li-O(2) | 142.9(3) | O(1)-Li-O(3) | 153.3(2) |
| O(8)-Li-O(1) | 102.2(3) | O(8)-Li-O(3) | 87.3(2) |
| O(9)-Li-O(1) | 95.2(2) | O(2)-Li-O(1) | 78.6(2) |
| C(1)-O(1)-C(12) | 109.4(2) | C(7)-O(4)-C(6) | 113.8(2) |
| C(2)-O(2)-C(3) | 113.6(2) | C(8)-O(5)-C(9) | 113.3(2) |
| C(5)-O(3)-C(4) | 112.3(2) | C(10)-O(6)-C(11) | 111.0(2) |

utilized graphite monochromated $MoK_\alpha$ radiation ($\lambda$ = 0.71073 Å). The yellow prismatic crystal had approximate dimensions of 0.5 × 0.5 × 0.6 mm. Unit cell parameters were obtained using a least-square procedure involving 24 centered reflections and are listed in Table I. These parameters differ considerably from those reported for the anhydrous Li(18-crown-6)(Picrate) complex[5]: a = 7.84(7), b = 13.22(5), c = 15.78(4), $\alpha$ = 96.9(8), $\beta$= 87.3(6), $\gamma$ = 95.8(6), which suggests that the crystal structure of the title compound contained solvent molecules. The structure was solved by direct methods[6] with succeeding Fourier synthesis. Full-matrix least squares refinement[7] with anisotropic thermal parameters for all non-hydrogen atoms converged to the agreement factors shown in Table I. All hydrogens were located in difference maps and refined isotropically. Experimental conditions are summarized in Table I. Positional and thermal parameters for non-hydrogen atoms are listed in Table II and bond distances and angles are contained in Table III. Some disorder was observed in -$NO_2$ group oxygen atoms.

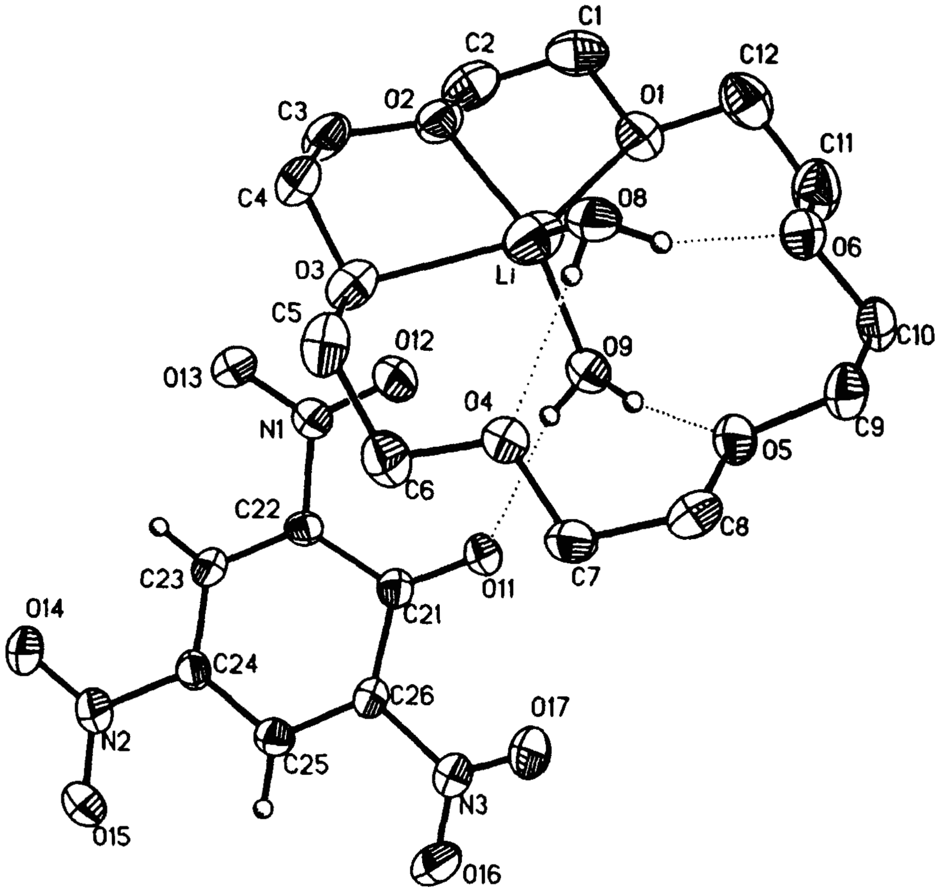

FIGURE 1 Molecular structure of $Li(H_2O)_2(18C6)$Picrate. Hydrogens of 18C6 molecule are omitted.

## RESULTS AND DISCUSSION

### Crystal Structure

The complex exists as a solvent-shared ion pair (Figure 1). The lithium ion is coordinated by three oxygen atoms of the crown ether ligand and by two water oxygen atoms. The three remaining oxygen atoms of the 18-crown-6 molecule serve as hydrogen bond receptors for two hydrogen atoms of one water molecule and one hydrogen atom of a second water molecule. The second hydrogen atom of the second water molecule is involved in a hydrogen bond with the phenol oxygen atom of the picrate anion (see Figure 1). The hydrogen bond data are listed in Table IV.

The coordination polyhedron (Figure 2) is a distorted trigonal bipyramid (coordination number 5). The three short equatorial Li...O bonds (1.93–1.96 A) are significantly shorter than the axial bonds Li...O1(2.27 A) and Li...O3(2.51A). Trigonal bipyramidal coordination has been found in a number of other lithium complexes.[1]

TABLE IV Hydrogen bond parameters

| D H A | r(D..A), Å | r(H...A), Å | ∠(D-H...A),° |
|---|---|---|---|
| O9-H9a...O11 | 2.795 | 2.04 | 163 |
| O9-H9b...O5 | 3.001 | 2.07 | 167 |
| O8-H8a...O4 | 2.826 | 2.06 | 165 |
| O8-H8b...O6 | 2.867 | 1.92 | 160 |

The geometrical parameters of this rather unusual complex are similar to those found in other crown complexes. The C-O and C-C interatomic distances (Table III) are typical for macrocyclic polyether complexes (average values for crown ethers are 1.43(3) and 1.49(2)Å, respectively).[8] The C-O-C and C-C-O bond angles are also normal. The 18-crown-6 ligand has a pseudo-$D_{3d}$ conformation which has been found in most complexes of this ligand. The torsion angles of the macrocyclic framework are also typical with O-C-C-O torsion angles being gauche (56–74°) and C-O-C-C torsion angles being trans (168–179°). The maximum deviation of oxygen donor atoms from the least-squares plane involving these atoms (0.39 Å) is slightly larger than normal. The $Li^+$ cation and one water molecule are above this plane while the other water molecule is below with the distances from the plane being 0.33($Li^+$), 1.84(O9) and -1.24(O8) Å.

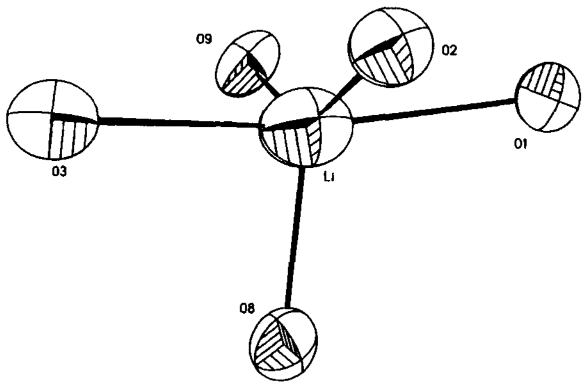

FIGURE 2 Coordination polyhedron of $Li^+$ ion.

The dihedral angle between the benzene ring of picrate anion and the least-squares plane of the oxygens of the macrocycle is 32°. The anion forms an additional hydrophobic covering for the hydrated cation causing it to be more soluble in the organic solvent.

### Solvent Extraction Data

Data for several solvent extraction systems involving alkali metal picrates are available in the literature.[4,9,10] Those extraction constants (including the constant for Li(18-crown-6)(Picrate) extraction into $CH_2Cl_2$ obtained in this work) are summarized in Table V. In benzene as well as in dichloromethane, the extraction constant of $Li^+$ by 18-crown-6 is large enough to interfere with the selective extraction of potassium and sodium complexes from aqueous solution. A possible explanation of this phenomenon is that the lithium species which is extracted is a hydrated cation associated with two molecules of water. In such a case the formation of the complex could be stabilized by the network of hydrogen bonds. The extraction of 2.5 $H_2O$ molecules with $Li18C6^+$ cation in nitrobenzene has been observed in[9], while only one water molecule was extracted with the sodium complex and only 0.3–0.1 water molecules were extracted with other alkali metal cations.

TABLE V Solvent extraction data for Li, Na and K in different systems

| Cation | $N(H_2O)^a$ | Log $K_{ex}$[b] | | Log K(M/Li)[c] | |
|---|---|---|---|---|---|
| | | $CH_2Cl_2$ | $C_6H_6$ | $CH_2Cl_2$ | $C_6H_6$ |
| $Li^+$ | 2.5 | 2.04[d] | 1.92[f] | - | - |
| $Na^+$ | 1.2 | 3.34[e] | 3.39[f] | 1.30 | 1.47 |
| $K^+$ | 0.3 | 6.21[e] | 5.97[f] | 4.17 | 4.05 |

[a] Number of water molecules co-extracted with $M\text{-}18C6^+$ cation in nitrobenzene [9].

[b] $K_{ex} = [M(18C6)Picrate]_{org}/[M^+]_{aq}\backslash[18C6]_{org}[Picrate^-]_{aq}$

[c] Selectivity coefficient $K(M/Li) = K_{ex}(M)/K_{ex}(Li)$

[d] This work

[e] Ref. 4

[f] Ref. 10

The crystal structure of the lithium dihydrate complex with 18C6, which is reported in this paper, is further evidence of this possibility. Unlike anhydrous $Li^+$, the $Li(H_2O)_2{}^+$ cation appears to fit well in the 18-crown-6 cavity using all six oxygen crown ether donor atoms by direct coordination or by means of hydrogen binding. The picrate counter-ion is strongly attracted to the solvated cation by hydrogen bonding. The resulting compound is hydrophobic. Both water molecules are completely involved in a hydrogen bond network within the solvent-shared ion pair. There is no possibility for additional hydration of this compound. This leads to its easy transfer from the aqueous solution into the organic phase. The formation of the complex cation does not require a complete dehydratation of lithium ion. Such dehydratation is thermodynamically unfavorable.

## CONCLUSIONS

The formation of the comparatively hydrophobic lithium picrate dihydrate complex with 18-crown-6 allows $Li^+$ to be extracted into the organic phase, thus decreasing the selectivity of $K^+$ and $Na^+$ solvent extraction separations. The formation of intermolecular hydrogen bonds stabilizes the metal ion complexes with the crown ether significantly and effects the selectivity of the separation process.

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