

Structures of some lithium-containing salts of Na⁻

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Abstract

Structures of $(\text{Li}^+)_2(\text{TMTCY})_2(\text{CH}_3\text{NH}^-)\text{Na}^-$, **1**, $\text{Li}^+(\text{18C6})(\text{CH}_3\text{NH}_2)_2\text{Na}^-$, **2**, and $\text{Li}^+(\text{18C6})(\text{CH}_3\text{NH}_2)_2\text{Na}^-(\text{18C6})_3$, **3**, are reported. (TMTCY is trimethyl tricyclen and 18C6 is 18-crown-6). **1** and **2** show "normal" four-coordination to Li^+ but **3** apparently has Li^+ in the center of a nearly planar 18C6 ring with $\bar{3}$ symmetry and short (1.733 Å) Li^+-N distances to two axial methylamine molecules. An alternative model with static or dynamic disorder, but normal distances, is in poorer agreement with the X-ray diffraction data.

INTRODUCTION

In the 18 years since the first synthesis of an *alkalide* (a salt of an alkali metal anion) (ref. 1), the structures of more than 30 alkalides and 4 *electrides* have been determined (ref. 2). Of the alkalides with known structure, 18 are natrides (salts of Na^- , also called sodides). No lithides have yet been synthesized, but complexed Li^+ ions can provide the cations, with other alkali metals or trapped electrons serving as anions. In this paper we describe the structures of three previously unreported natrides in which complexed Li^+ serves as the cation.

The lithium cation has a pronounced tendency towards four-coordination with oxygen or nitrogen. The lithium amine compounds, $\text{Li}(\text{NH}_3)_4$ (ref. 3), $\text{Li}(\text{CH}_3\text{NH}_2)_4$ (ref. 4), and $\text{Li}^+(\text{ethylenediamine})_2\text{Na}^-$ (ref. 5), probably owe their stability to four rather strong Li^+-N bonds. Indeed, the species $\text{Li}^+(\text{CH}_3\text{NH}_2)_4$ is stable enough to permit its use as a solubilizing agent for sodium (as Na^-) in a number of amine and ether solvents (ref. 6). The structures of crown ether complexes of Li^+ also tend to have four-coordinate interactions. Of interest here are the 18-crown-6 (IUPAC name: 1,4,7,10,13,16-hexaoxacylooctadecane) complexes $\text{Li}^+(\text{18C6})\text{ClO}_4^- \cdot 2\text{H}_2\text{O}$ and $\text{Li}^+(\text{18C6})\text{SCN}^- \cdot 2\text{H}_2\text{O} \cdot \text{Li}^+\text{SCN}^-$ (ref. 7), each of which contain Li^+ ions coordinated to two crown ether oxygens and two H_2O molecules. Anionic coordination to Li^+ can also involve complexant molecules. The compound $(\text{Li}^+)_2(\text{18C6}) \cdot 2(\text{phenoxide}^-)$ has two Li^+ cations bound by one crown ether molecule (ref. 8), while $\text{Li}^+(1,7\text{-diazadecane})$ forms a dimer with bridging Li^+ ions between deprotonated aza-crown molecules (ref. 9). In this compound each Li^+ is coordinated to five hetero-atoms, two crown ether oxygens, one crown ether neutral NH nitrogen and two negatively charged amide nitrogens. The Li^+-N^- bond lengths are 2.111 Å while the Li^+-O and Li^+-NH bonds are somewhat longer [2.258, 2.327 Å (Li^+-O) and 2.186 Å (Li^+-N)]. The lithium cation in the aza-cage molecule TMPAND (4, 10, 15-trimethyl 1,4,7,10, 15-pentaazabicyclo [5.5.5] eptadecane) also has five-coordinate Li^+ with Li^+-N distances of 2.013, 2.080, 2.016 and 2.077 Å (ref. 10). This complexant has recently been used to synthesize the Na^- salt (ref. 11). The bridging of two aza-crown rings by Li^+ occurs in the compound $\text{Li}^+(\text{TMTCY})[\text{Li}^+(\text{DMTCY}) \cdot \text{CH}_3\text{NH}_2]\text{Na}^-$ (ref. 12), to be considered later in this paper. The abbreviations TMTCY and DMTCY

refer to trimethyl tricyclen (1,4,7-trimethyl-1,4,7-triazacyclononane) and dimethyl tricyclen (1,4-dimethyl-1,4,7-triazacyclononane), respectively.

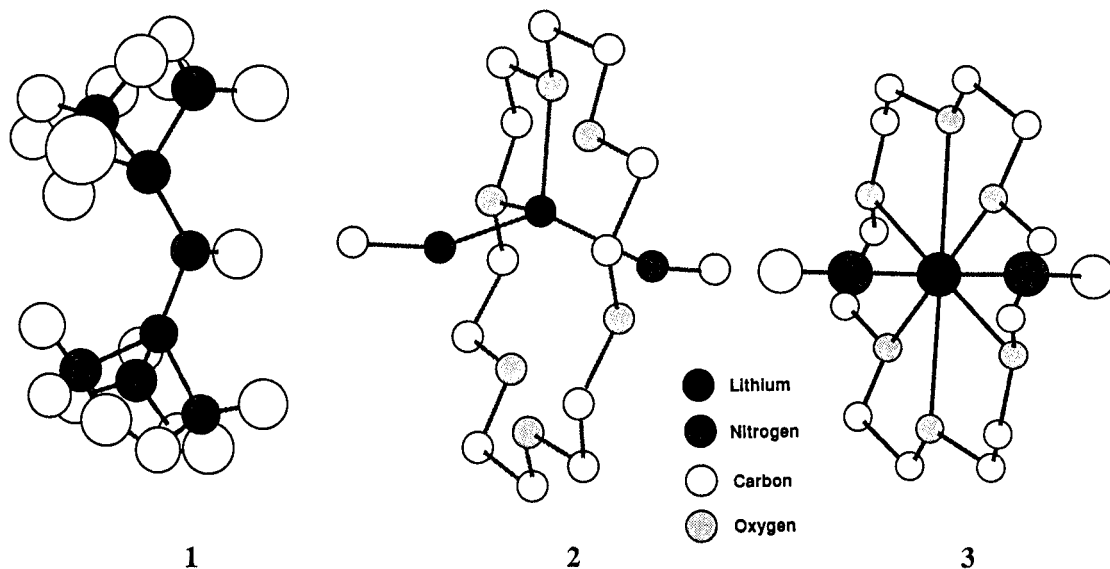


Fig. 1. Structures of the three lithium complexes. Not shown are the hydrogens, Na^- , or the three "free" 18C6 molecules in 3.

AZA-CROWN LITHIUM NATRIDES

Because of the greater resistance of the aza group to irreversible reduction by M^- or e^- compared with the corresponding oxo group (ref. 13), we have been exploring the use of aza-crown ethers and aza-cage complexants in the synthesis of alkaliides and electrides. Tertiary amine nitrogens are required because of the tendency for M^- or e^- to deprotonate N-H groups. Hexamethyl hexacyclen forms Na^- salts by complexing K^+ , Rb^+ or Cs^+ (ref. 13). The corresponding pentacyclen and tetracyclen appear to have promise as Li^+ complexants. Space-filling models of trimethyl tricyclen (TMTCY) suggested the possible formation of sandwich complexes with Li^+ , but lithium was insoluble in solvents such as dimethyl ether (Me_2O) even in the presence of TMTCY, suggesting that TMTCY is not a powerful complexant for Li^+ . Crystals were obtained by dissolving Li, Na and TMTCY in methylamine (MeNH_2), evaporating most of the MeNH_2 , adding Me_2O , and crystallizing from a mixture of Me_2O and diethyl ether. Instead of the expected sandwich compound, a compound that included deprotonated DMTCY was formed. (ref. 12). In this structure, one Li^+ ion forms a bridge between a TMTCY molecule and the amide nitrogen of DMTCY^- . A second lithium cation is coordinated to the three nitrogens of DMTCY^- and to the nitrogen of a methylamine molecule. An isolated Na^- ion balances the net +1 charge on the dimeric unit.

To avoid the deprotonation problem, TMTCY without any of the incompletely methylated DMTCY was used in a second attempt to form the sandwich compound. Instead, deprotonation of MeNH_2 resulted, and the MeNH^- ion formed a bridge between two Li^+ ions, each of which completed its coordination sheath by complexation to the three nitrogen atoms of TMTCY. Thus, compound 1, $(\text{Li}^+)_2(\text{TMTCY})_2 \cdot \text{CH}_3\text{NH}^- \text{Na}^-$, formed, again yielding four-coordinate Li^+ with an anion (MeNH^-) participating in coordination to *two* Li^+ ions. Some pertinent crystal data are given in Table 1 and Li-N distances are given in Table 2. Details of the structure of this compound and the others described in this paper will be published elsewhere.

LITHIUM 18-CROWN-6 NATRIDES

Initial synthesis

The first isolation of a compound in which Li⁺ is complexed by 18C6 and the counter-ion is Na⁻ was accidental. During an attempt to synthesize K⁺(18C6)·Na⁻, MeNH₂ was used as the primary solvent and some lithium metal was added to help stabilize the solution (ref. 14). Standard synthesis procedures were used (ref. 15) followed by slow cooling to promote the growth of large crystals (ref. 16). Upon removal of the solvent the material was found to be mostly amorphous or polycrystalline, except for a few shiny, golden, blocky crystals. The X-ray diffraction pattern and structure determination showed that *no potassium was present*, the Na⁻ ion was well-defined, and one 18C6 molecule was present with methylamine (or methylamide) molecules above and below the plane of the 18C6 ring. We presumed that Li⁺ was present between two methylamine molecules but the lithium occupancy was too high (2.3) and one Li⁺-N bond was unreasonably short (1.60Å). A number of attempts to repeat the synthesis have been unsuccessful, so the nature (indeed, even the composition) of this crystalline natride remains a mystery.

A "normal" compound, Li⁺(18C6)Na⁻·(MeNH₂)₂

Since we presumed that the first crystals synthesized had the composition Li⁺(18C6)Na⁻ and contained no potassium, subsequent syntheses were made with Li:Na:18C6 ratios of 1:1:1. These yielded a compound, **2**, with the indicated stoichiometry, but the crystal structure was very different from that initially obtained. The structure of the complexed cation is similar to that of Li⁺(18C6)ClO₄⁻·2H₂O (ref.7). A stereoscopic view is shown in Fig 2 and some crystal data are given in Tables 1 and 2. The lithium cation is coordinated to two oxygens of 18C6 and to the nitrogens of two MeNH₂ molecules, situated above and below the 18C6 ring. The Li⁺-O distances are 2.046 and 2.181Å and the Li⁺-N distances are 1.955 and 2.021Å. All of these distances are normal for coordination of Li⁺ to neutral ligands. The Na⁻ ion is well-isolated and surrounded by a "sea" of protons from the 18C6 and MeNH₂ molecules. Thus, compound **2** was not unusual in its coordination of Li⁺.

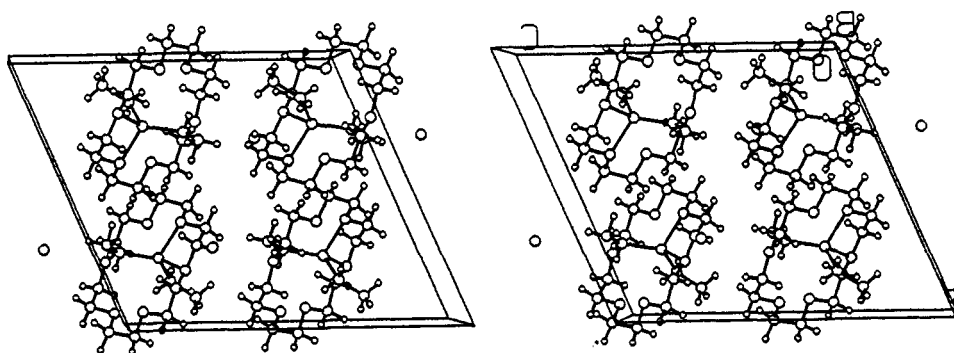


Fig. 2. Stereoscopic view of a unit cell of **2**.

Structure of Li⁺(18C6)Na⁻(MeNH₂)₂·(18C6)₃

Had compound **2** been obtained first, it is unlikely that attempts at further synthesis would have been made. However, the unusual nature of the first crystals prompted us to try various conditions of synthesis. When an excess of 18C6 was used, the unusual compound Li⁺(18C6)Na⁻(MeNH₂)₂·(18C6)₃, **3**, was formed, in which three "free" crown ether molecules are symmetrically located around a central Li⁺(18C6) unit in the rather rare space group R $\bar{3}$. The three "free" 18C6 molecules are in their regular configuration with oxygens and carbons

Table 1. Crystallographic and refinement data for the three structures

| Structure | 1* | 2 | 3 |
|---|-------------|--------------------|---------------|
| Space group | Pbca | P2 ₁ /c | R $\bar{3}$ |
| Cell params. | | | |
| a, Å | 14.9975(53) | 13.8772(53) | 11.9817 (66) |
| b, Å | 17.7177(42) | 12.4072(40) | 11.9699 (49) |
| c, Å | 22.7060(72) | 15.7071(67) | 11.9685 (49) |
| α , ° | 90 | 90 | 99.413 (33) |
| β , ° | 90 | 113.243(27) | 99.359 (40) |
| γ , ° | 90 | 90 | 99.591 (40) |
| Z | 8 | 4 | 1 |
| Cryst. dimens., mm | .4x.2x1.0 | .5x.4x.4 | 1.1 x .8 x .7 |
| No. of reflctns. meas. | 4412 | 14296 | 7848 |
| No. used in refinement with $F_o^2 > 3\sigma(F_o^2)$ | 1505 | 2564 | 2018 |
| R | 0.047 | 0.040 | 0.048 |
| R _w | 0.047 | 0.045 | 0.048 |
| High peak in final diff. map, e/Å ³ | 0.15 | 0.41 | 0.41 |

* Also crystallizes in space group P2₁2₁2₁ but with the same molecular structure.

Table 2. Selected bond distances and angles

| Structure | Bond | Bond Distance | Bond Angle |
|-----------|---------------------------|---------------------------------|---------------|
| 1 | Li-N (amide) | 1.90, 1.93 | |
| | Li-N (TMTCY) | 2.06-2.14 | |
| 2 | Li-N (MeNH ₂) | 2.021, 1.955 | N-Li-N, 123.8 |
| | Li-O (18C6) | 2.181, 2.046 and 2.713-3.623 | |
| | | | |
| 3 | Li-N (MeNH ₂) | 1.733 | N-Li-N, 180 |
| | Li-O (18C6) | 2.763 | |

alternating along the oxygen plane. They are related to one another by the 3-fold and central symmetry. The Na⁻ ions lie on the 3-fold axis and are well-separated from other atoms as usual.

Because of the unusual *apparent* structure obtained by direct methods and Fourier difference analysis, we can only be certain of the *average* structure. In what follows, we first describe the results obtained directly from the X-ray diffraction data and later discuss the possible effects of dynamic or static disorder. The structure was determined for two crystals from different syntheses with essentially the same results.

The central 18C6 molecule has $\bar{3}$ symmetry and Li⁺ sits exactly at the center of the oxygen plane. The Li⁺-O distance is 2.764 Å, certainly much longer than the contact distance of 2.0 Å. The N and C atoms of MeNH₂ are on the 3-fold axis with normal C-N distances of 1.327 Å but with very short Li⁺-N distances of 1.733 Å.

The hydrogens of all four 18C6 molecules were refined isotropically, but the H atoms of MeNH₂ were located by the difference map and fixed in the final refinement. The multiplicity of Li⁺ was refined to a value of 1.58. Some crystal data are given in Tables 1 and 2, and a partial stereoscopic view is shown in Fig 3.

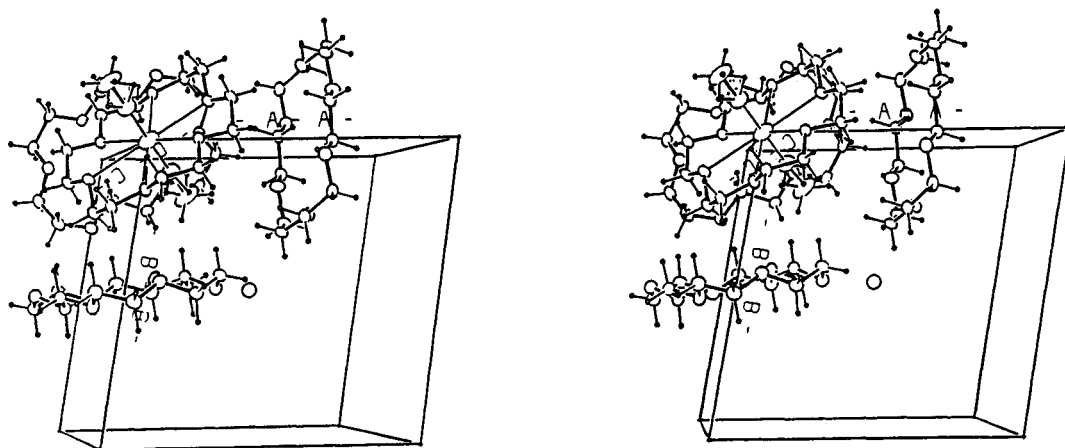


Fig. 3. Stereoscopic view of one molecule of 3.

DISCUSSION

Two of the three structures reported here (1 and 2) are "normal" in the sense that Li⁺ is four-coordinated to N and O with normal distances of ~2.0 Å. The distance between Li⁺ and an amide nitrogen in such structures is about 0.1 Å shorter than that to an amine nitrogen. The structure of a crystal that appeared to be an isomer of 2 was very different, but our inability to repeat the synthesis leaves it as an unknown substance. It is the third structure, 3, that is unusual. We focus the remainder of the discussion on this structure.

The overall framework of the structure is not in doubt. It consists of the three "free" 18C6 molecules and a central one, with two MeNH₂ molecules on the 3-fold axis. The thermal parameters of the N and C atoms of MeNH₂ are about twice as large as anticipated for fixed molecules, but not large enough to allow significant deviations from linearity of the C-N...N-C chain. The major question is the location of the Li⁺ ion and the H atoms of the NH₂ group. If the structure is accepted at face value, it implies the existence of most unusual Li⁺-N bonding. According to this picture, the lithium cation forms a linear symmetric bridge between the two nitrogens with Li⁺-N distances of only 1.733 Å to two *neutral* methylamine molecules. Such a structure is unprecedented, both from crystal structures and theory (refs. 17-20). Such a short distance is seen in Li⁺ bonds to a single *amide* ion (ref. 17) but not to neutral molecules.

One can visualize an alternative model that preserves the *average* structure but has more normal bond lengths. In this model, three-fold static or dynamic disorder would be present in the CH₃H₂N-Li⁺-NH₂CH₃ chain by rotation about the C-N bond. This would permit hydrogen bonding of each of the NH₂ hydrogens to an ether oxygen and close interaction of Li⁺ with two ether oxygens. The instantaneous Li⁺-N distance would then be about 2.0 Å, with a distance of N from the center of the ring of ~1.75 Å. In any one configuration, all six crown ether oxygens would participate in either a hydrogen bond or in a bond to Li⁺, which would have a coordination number of four.

Two tests were made of this plausible model. In one, the -NH₂ hydrogens were allowed to ride on the nitrogens with normal distances and angles and the Li⁺ ion

was left out. The hydrogen occupancies were adjusted to account for the presumed disorder. The resulting electron density difference map showed a sharp peak ($1.5 \text{ e}/\text{\AA}^3$) in the center of the crown ether ring. The electron density at 1.0 \AA from the center (where the Li^+ would ride according to the disorder model) was only 4% of that at the center. Thus, the residual density is not in accord with this model.

In a second test, both the Li^+ and the hydrogens were allowed to ride on the nitrogens, with partial occupancies included. This resulted in a marked increase in the R_w factor, from 0.048 for the initial refinement to 0.079 by this model, and with an even higher peak ($3\text{e}/\text{\AA}^3$) at the center of the 18C6 ring.

We must conclude that the disordered model used is not in accord with the X-ray diffraction data. Yet the structure with 3-fold symmetry and short Li^+ -N distances is so unusual (refs. 17-20) that we are reluctant to endorse it without confirmatory information. Alkalides are difficult to work with because of their reactivity and thermal instability, so that caution must be used in interpreting the data from only a few measurements. Perhaps some other disordered structure would be in better agreement with the diffraction data. Meanwhile, we are exploring other ways to characterize this compound, such as NMR, IR, neutron diffraction, etc.

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