Preparation and Crystal Structure of Lithium Nitride Chloride Li₄NCl

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Li₄NCl was prepared from Li₃N and dry OH-free LiCl at 450°C. It is found to be the more nitrogen-rich of two compounds in the quasi-binary system $Li_{3-2x}N_{1-x}Cl_x$. Following unit cell indexing using laboratory X-ray powder data, the previously unknown structure of the title compound was solved from neutron powder diffraction data recorded using the flat-cone and powder diffractometer E2 at the Berlin BERII reactor. Li₄NCl crystallizes in the hexagonal rhombohedral space group $R\bar{3}m$ (No. 166), $a = 366.225(4)$, $c = 1977.18(4)$ pm with three formula units per unit cell. Its structure comprises a 1:1-ordering variant of a cubic close anion packing, N^{3-} and Cl^- forming layers perpendicular to [001]. Li atoms occupy all the triangular voids of the N layers and all the NCl₃-tetrahedral holes. Nitrogen is in lithium nitride-like hexagonal bipyramidal coordination by Li, the equatorial six-membered ring being slightly puckered, while Cl is in distorted octahedral coordination. Calculation of the Madelung part of the lattice energy shows that the nitrogen hexagonal bipyramidal coordination polyhedron, peculiar for Li₄NCl and the Li₃N parent structure, is in agreement with a simple ionic picture and does not imply any covalent bonding. © 1997 Academic Press

INTRODUCTION

Lithium nitride halogenides, $Li_{3-2x}N_{1-x}Hal_x$ ($Hal = $ Cl, Br, I), originally investigated by Sattlegger and Hahn with the aim to prepare a per-lithiated analog to ammonium halide (1–3), are, like the parent compound Li₃N, of some interest as lithium ion conductors (4–7). Due to the lack of single crystals, the complexity of the powder patterns, and the presence of a heavy atom beside the light atom Li, little is known about their crystal structures. Recent neutron powder diffraction work on the Li–N–Br system however shows that the Li–N sublattices of these compounds, $Li_{3n+m}N_n^{m+}$, result from a reaction of the Lewis acid Li^+ rather with the 3D network of the Lewis base Li₃N than with a Li₃N molecule (8–10). For example, Li₁₀N₃Br contains a $Li_{10}N_3^+$ 3D net closely related to the Li₃N parent structure, Li₅NBr₂ comprises linear chains of vertex sharing Li₆N octahedra, and Li₆NBr₃ exhibits isolated Li_6N^{3+} octahedra. Out of seven lithium nitride halogenides, Li₄NCl

is the only compound with a composition analogous to NH₄Cl. However, as will be shown, even in this case discrete units of Li_4N^+ are not realized. Instead Li₄NCl lattice parameters indicate a Li₃N-like layer structure. In such a case for Li₄NCl the same question would arise as for Li₃N itself; namely, is the Li–N arrangement (Fig. 1) in agreement with a simple ionic picture or does it indicate the presence of covalent bonding (11, 12)?

In the present work an attempt is made to determine the accurate composition of the title compound and to solve its crystal structure. Calculations of the Madelung part of the lattice energy are presented in order to discuss the structural results in the light of an ionic bonding model.

EXPERIMENTAL

Sample Preparation

Ivory colored lithium nitride chloride was prepared from Li₃N and LiCl in a solid state reaction. Stoichiometric amounts of the reactants were finely ground and transfered into a cup of iron covered by a lid, heated under Ar to a temperature of 450°C for 1 day and slowly cooled to room temperature (50°/h). The inhomogeneous reaction product, still containing Li₃N and LiCl, was carefully reground and heated again. Depending on the grain size of the powders used this procedure had to be repeated several times in order to obtain a pure reaction product.[1]

LiCl (Merck, reinst) was further purified in a special apparatus to quartz glass. After predrying at 300°C the salt was molten under Ar (Linde, 5.0), rinsed with dry HCl gas to decompose any trace of LiOH, and returned to an Ar atmosphere again. The melt was then filtered *in vacuo*, cooled to room temperature, and stored under Ar until usage (13).

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[1] In the original work on lithium nitride halogenides (2, 3) the stoichiometry of the title compound was assigned as Li₁₁N₃Cl₂. My own experiments however show that this composition neither leads to a single-phase reaction product nor is it compatible with the unit cell volume determined for the title compound as will be seen later.
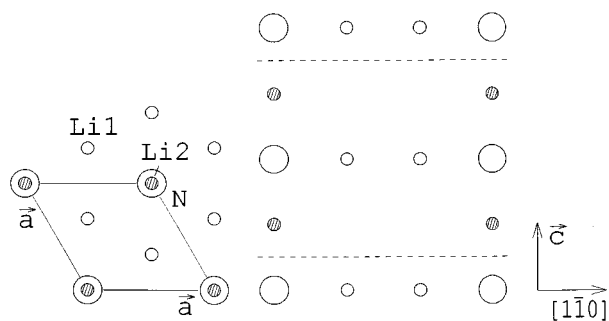
FIG. 1. Schematic view of the Li_3N structure. A formal separation in Li_4N^+ and Li_2N^- layers is indicated by broken lines.

TABLE 1
Experimental Details and Crystallographic Data
for the Neutron Powder Diffraction Experiment on Li_4NCl

Instrument	Flat-cone and powder diffractometer
Monochromator	Ge
Plane of reflection	(311)
Wavelength [pm]	121.66
Collimator in front of monochromator	10′
Collection time [h]	21
2Θ range [°]	9.5–89
Step size [°]	0.1
Space group	$R\bar{3}m$
z	3
a [pm]	366.25 (2)
c [pm]	1976.7 (1)
V [10^6 pm^3]	229.6 (1)
Number of reflections	66
Number of refined structural parameters	11
Number of refined profile parameters	15
R_I	3.0
R_{wp}	3.8
R_e	1.8

Li_3N was prepared by the reaction of Li (Aldrich 99.9%) with N_2 (Linde, 5.0) using Na as a solvent. The metals were mechanically cleaned from crusts and heated to 400°C for 1 day under nitrogen. Na was then removed *in vacuo* at 360°C (14).

Li_4NCl, as well as LiCl and Li_3N, is sensitive to both moisture and O_2 at higher temperatures. All manipulations were therefore carried out under Ar gas (O_2 and H_2O impurities below 1 ppm), and all glass and metal apparatus carefully heated *in vacuo* before usage. Reaction products obtained were characterized optically (stereolupe) and by X-rays using the Guinier–Simon technique (samples were ground, filled in glass capillaries and sealed).

STRUCTURE DETERMINATION

Data Collection

The neutron powder diffraction experiment was performed using the flat-cone and powder diffractometer E2 at the rebuilt research reactor BERII, Hahn–Meitner-Institut Berlin. Data were collected in the 2Θ range 10°–90° ($\lambda = 121.66$ pm).

Experimental details are summarized in Table 1 and are given in an earlier work (8). An X-ray powder diffraction measurement was performed using a Stoe powder diffractometer; data were collected in the 2θ range 8°–99° (CuKα_1 radiation).

Data Analysis

Using the X-ray powder data automatic indexing (15) followed by an intensity-only or Pawley refinement (16) leads to a hexagonal rhombohedral unit cell with $a = 366.225(4)$, $c = 1977.18(4)$ pm. An intensity refinement was then performed on the neutron powder data in the space group $R\bar{3}m$. The accurate neutron wavelength was determined by assuming a rough value and refining the already properly known cell parameters. Other profile para-

meters such as line width and background parameters were also refined at this stage. The fitted profile did not show any unfitted peaks and confirmed the rhombohedral translation symmetry as well as the purity of the sample. Intensities extracted did not show any further systematic absences and reduced the possible space groups to $R\bar{3}m$ and (rhombohedral) subgroups.

The starting model for the subsequent Rietveld refinement (17) was deduced from the Li_3N parent structure, which, for this purpose, was assumed to be composed of $(Li_4N^+)_n$ and $(Li_2N^-)_n$ units (compare Fig. 1). $(Li_4N^+)_n$ layers and close packed layers of Cl^- were stacked along the hexagonal c axis.[2] Of the two most likely stacking sequences $N_0^A Cl_{1/6}^B N_{1/3}^C Cl_{1/2}^A N_{2/3}^B Cl_{5/6}^C N_0^A$ was chosen allowing for uniform N–Cl distances.

The Rietveld refinement (programs CN13LS (20) and Fullprof (21)) of this model lead to an R_I value of 3.0% in the space group $R\bar{3}m$. No attempt was made to refine in a lower symmetry space group. The final structural model comprises anisotropic thermal displacement parameters for all atoms (Tables 1 and 2, Fig. 2). The scattering length of Li was determined to $1.89(2) \times 10^{-15}$ m by means of an overall site occupation factor for the Li atoms. It was found identical to the tabulated value (1.9×10^{-15} m). An absorption correction was carried out.

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[2] Replacement of Li_2N^- by Cl^- is possible as the intralayer N–N distances in Li_3N (364.8 pm) (18) and the Cl–Cl distances in rock salt type LiCl (363.4 pm) (19) are almost equal.

TABLE 2
Atomic Coordinates and Anisotropic Temperature Factors for Li$_4$NCl

Atoms	in	x/a	y/b	z/c	U_{11} [pm^2]	U_{33} [pm^2]
N	$3a$	0	0	0	47(20)	130(10)
Cl	$3b$	0	0	1/2	120(20)	110(10)
Li1	$6c$	0	0	0.6547(4)	62(30)	290(20)
Li2	$6c$	0	0	0.0970(3)	160(40)	80(20)

Madelung Part of the Lattice Energy Calculations

The Madelung part of the lattice energy (program GULP (22)) was calculated for a Li$_2$O-like structure $A_2^+ X^{2-}$ as well as a Li$_4$NCl-like ordering variety $A_4^+ X^{3-} Y^-$. For means of comparision a hexagonal rhombohedral setting was chosen suitable for both structures (space group $R\bar{3}m$). Ideal a and c lattice parameters were calculated for an A–X distance of 210 pm ($a_{\text{hex}} = 1/2\sqrt{2}a_{\text{cub}}$, $c_{\text{hex}} = 2\sqrt{3}a_{\text{cub}}$; A atoms occupy the tetrahedral holes of the anion close packing). Anions were placed on the special positions $3a$ and $3b$, 0 0 0 and 1/3 2/3 1/6, cations $A1$ and $A2$ were placed each on the position $6c$, 1/3 2/3 z with $z = 0$, 1/2 as starting values. The Madelung energy was then calculated as a function of the cation z parameter. The cell parameters were kept constant.

RESULTS AND DISCUSSION

The structure of Li$_4$NCl comprises close packed layers of nitrogen and chlorine in an $ABCABCA$ stacking. One half of the Li atoms (Li1) occupies the triangular voids within the nitrogen layers shifted only slightly toward a neighboring chlorine atom along the c axis. The other half of the metal atoms (Li2) is situated in the tetrahedral holes formed by one nitrogen and three chlorine atoms. As a result, nitrogen is in hexagonal bipyramidal coordination by Li, the N(Li$_{\text{eq}}$)$_6$ unit being slightly puckered. The coordination polyhedron for chlorine is a distorted (compressed) octahedron with $D3d$ point symmetry (Fig. 3). The Li$_{\text{ax}}$–N (192 pm), Li$_{\text{eq}}$–N (213 pm), and Li–Cl (252 pm) distances as well as the N–N and Cl–Cl nonbonding distances (366 pm) obtained for Li$_4$NCl (Table 3) are in close agreement with those of the binary compounds (194, 211, and 257 pm, 365 and 363 pm, respectively).

The Li$_4$N$^+$ layer is the characteristic building unit of the Li$_4$NCl structure. It can be thought of as resulting from the reaction of Li$^+$ with the (Li$_{\text{ax}}$–N)$_\infty$ chain of the Li$_3$N 3D net
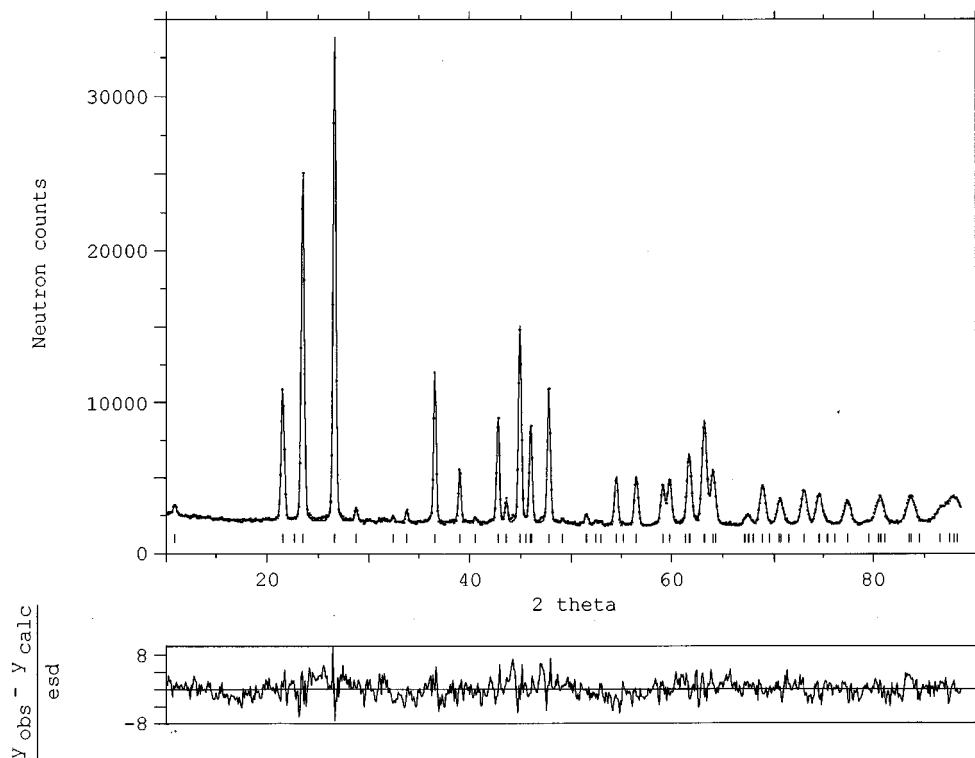

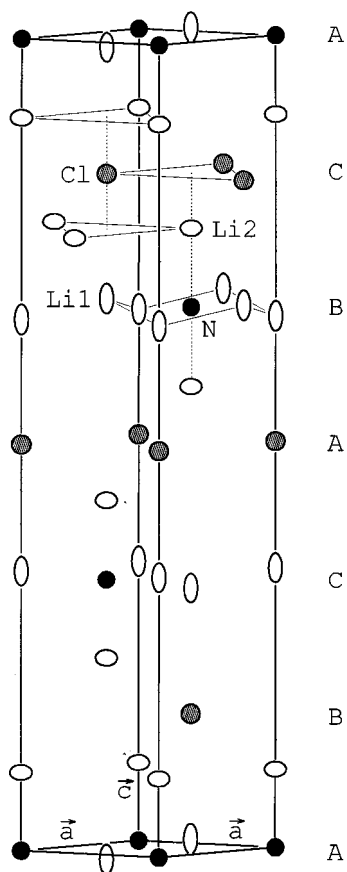**FIG. 2.** The observed, calculated, and difference profiles of Li$_4$NCl.

FIG. 3. The Li$_4$NCl structure (ellipsoids of 80% probability; capitals A, B, C indicate the N–Cl stacking along c; atoms belonging to the coordination spheres of the N, Cl, and Li2 central atoms are grouped together by thin lines).

TABLE 3
Interatomic Distances (pm) and Angles in Li$_4$NCl

N–Li1	×6	212.8 (2)	Li2–N–Li2	×1	180°
N–Li2	×2	191.8 (13)			
Cl–Li1	×2	305.9 (15)	Li2–Cl–Li2	×6	86.9 (3)°
Cl–Li2	×6	252.3 (7)	Li2–Cl–Li2	×6	93.1 (3)°
Li1–N–Li1	×6	61.2 (1)°	N–Li1–N	×3	118.8 (2)
Li1–N–Li1	×6	118.8 (1)°	N–Li1–Cl	×3	96.4 (4)
Li1–N–Li2	×6	83.6 (4)°	N–Li2–Cl	×3	123.1 (3)
Li1–N–Li2	×6	96.4 (4)°	Cl–Li2–Cl	×3	93.1 (4)

to form (Li$_{ax}$)$_2$N units (leaving the (Li$_{eq}$)$_6$N units unchanged). This view implies the same type of chemical bonding between Li and N for both compounds regardless of whether these bonds are covalent or ionic in nature. On the other hand, focusing on the N–Cl arrangement of the Li$_4$NCl structure it is found to be closely related to (ionic) Li$_2$O crystallizing in the antifluorite structure. It may be derived from the latter simply by replacing successive O^{2-} layers $\perp$ to a cubic [111] direction alternately by layers of N^{3-} and Cl$^-$ and by shifting the cations occupying the N$_3$Cl tetrahedra into the N$_3$ triangular faces. This relationship implies an ionic type of bonding between Li and N or Cl. Moreover it suggests different cation arrangements being energetically favorable for an $A_2^+X^{2-}$ and an $A_4^+X^{3-}Y^-$ compound.

In order to work out these arrangements, calculations of the Madelung part of the lattice energy (MAPLE) were performed for both compounds as a function of the cation
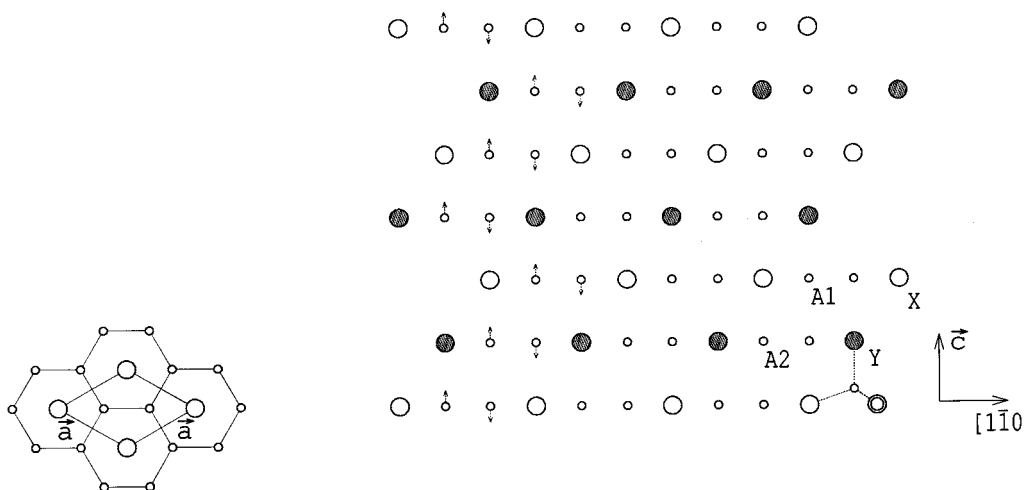

FIG. 4. Fictive A_4XY model structure for the Madelung part of lattice energy (MAPLE) calculations. X and Y form an ideal close packing with $ABCABC$ stacking ($c = 2\sqrt{6}a$). As indicated by arrows cations $A1$ and $A2$ occupying the trianglular voids within the X and Y layers may be shifted into the corresponding tetrahedral holes to obtain a Li$_2$O type structure.

positional parameters. A fictive layer structure given in Fig. 4 was used as a starting point. The results of the calculations are summarized in Figs. 5a and 5b.

In the case of $A_2^+ X^{2-}$ the minimum in Madelung energy is obtained for $z(A1) = 1/24$ and $z(A2) = 13/24$ which corresponds to the structure of Li$_2$O. For $A_4^+ X^{3-} Y^-$ the minimum is obtained for $z(A1) = 0.003$ and $z(A2) = 13/24$.[3] These numbers are in good qualitative agreement with the Li z parameters obtained for Li$_4$NCl during the Rietveld refinement.

Madelung energy calculations thus show that the hexagonal bipyramidal Li$_8$N unit in the Li$_4$NCl structure is in agreement with a simple ionic model and that there is no need to assume any directed bonding between N and Li. Naturally such bonds cannot be ruled out purely on the basis of such calculations.

Further experiments are planned on the second compound in the Li–N–CL system, Li$_5$NCl$_2$, which shows an order/disorder transition from a Li$_2$O-type structure to a Li$_4$NCL-type structure.

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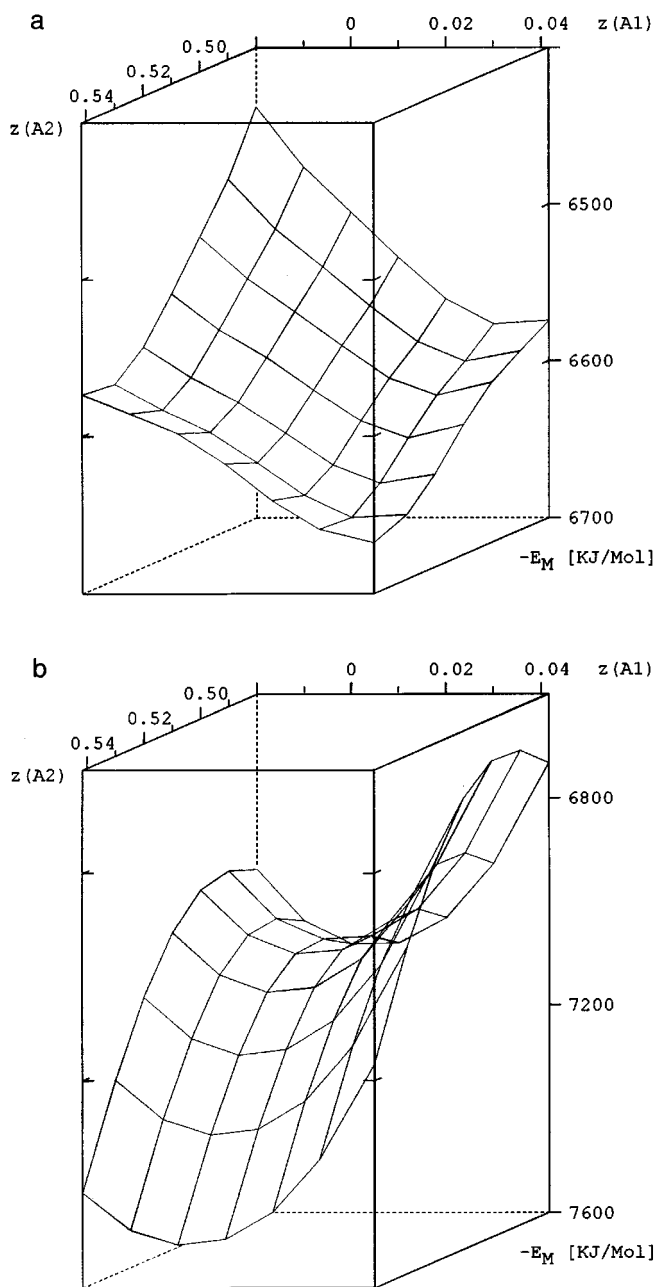12. A. Rabenau, *Solid State Ionics* **6,** 227 (1982).

FIG. 5. MAPLE calculations for the $A_4 XY$ model structure of Fig. 4 as a function of the cation $A1$ and $A2$ z parameter. (a) MAPLE for $A_4^+ X_2^{2-}$ (lattice parameters kept constant). (b) MAPLE for $A_4^+ X^{3-} Y^-$ (lattice parameters kept constant).

[3] It should be noted that the calculations presented were carried out on ideal model compounds with infinitely small cations and anions. In real structures, however, ions are of finite size and changes in the cation positions will lead to variations of the lattice parameters so as to accommodate and roughly maintain the A–X distances. Additional calculations have been carried out in order to assess how far the results of Fig. 5 would be affected. In the case of $A_2 X$, variation of the lattice parameters is not critical as the changes in energy obtained while keeping a and c constant are increased and the position of the minimum is retained. In the case of $A_4 XY$, variation of the a lattice parameter is critical as it leads to a less pronounced minimum at $z(A1) = 0.023$ and $z(A2) = 0.542$. However even in this worst case the minimum in energy is situated well away from $z(a1) = 0.042$ which corresponds to ideal tetrahedral coordination. Changes of the a lattice parameter can be assumed to be of minor importance if Y is appreciably larger than X (as is the case for Li$_4$NCl).

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