Low-Temperature X-Ray Study of the Compound Tetraamminelithium(0)[1]

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Abstract: The compound $Li(NH_3)_4{}^0$ has been prepared by cooling solutions of lithium in liquid ammonia. X-Ray powder studies at 77°K indicate that $Li(NH_3)_4$ exists in two phases: a cubic form with $a_0 = 9.55$ Å, stable between 82 and 89°K, and a hexagonal form having $a = 7.0$ Å and $c = 11.1$ Å, stable below 82°K. At 77°K the measured density is 0.57 g/cc, corresponding to two molecules of $Li(NH_3)_4$ per hexagonal unit cell. Reflections of the type $00l$ (l odd) were not observed, suggesting that the space group is $P6_3$ or $P6_3mc$ with four ammonia molecules tetrahedrally disposed about each lithium atom. The c/a ratio together with reasonable assumptions for bond lengths suggests the $Li(NH_3)_4$ tetrahedra are in hexagonal close packing. Arguments are given for believing that the molecule $Li(NH_3)_4$ is unstable to dissociation in the gas phase but that the solid compound is stable because of a large electron delocalization energy. The energy change for the reaction $Li(s) + 4NH_3(s) \rightarrow Li(NH_3)_4(s)$ is estimated to be -20 kcal/mole.

The phase diagram of the lithium–ammonia system shows a deep eutectic at about 20 mole % lithium.[2] However, unlike the sodium and potassium systems, where the solid formed is a gray-white mixture of metal and solid ammonia, the lithium system gives a golden, conducting solid more like the compounds $M(NH_3)_6$ of the alkaline earth metals.[3] Although the characterization of the hexaammine alkaline earth metals is complicated by large deviations from stoichiometry arising from ammonia vacancies or interstitial ammonia, compound formation is rather clearly supported by maxima in the temperature–composition curves. No such maximum-melting composition exists in the lithium–ammonia case, so this primary criterion for compound formation is lacking. Still there is considerable indirect evidence that a compound (usually taken to be $Li(NH_3)_4$, although deviations from perfect stoichiometry analogous to alkaline earth hexaammines have also been observed[4]) actually exists in the lithium–ammonia system. Such evidence includes, for example, the large negative heat of solution for lithium in ammonia at intermediate concentrations,[5] the low vapor pressure of the saturated solution,[6] the persistence of the bronze color of the liquid into the solid state, and the high conductivity of the solid.[7] More direct evidence comes from breaks observed in the conductivity–temperature curve of the solid, suggesting solid–solid phase transitions,[8] and from the fact that the heat capacity of the solid is 20–50% higher than the sum of the heat capacities of the pure components.[4]

The present investigation was undertaken in an attempt to find X-ray evidence supporting the existence of the compound $Li(NH_3)_4$ in the solid state.

Experimental Section

Preparation of Material. The ammonia was obtained from Matheson and was their highest grade anhydrous 99.99%. The lithium, obtained from Lithium Corporation of America, was 99.9%. The lithium was cleaned mechanically under argon, weighed in a sealed tube, and transferred under argon into one arm of a modified Faraday tube. The tube was evacuated, and ammonia, dried over sodium, was condensed on the lithium in sufficient amount to give a 20 mole % lithium solution. The arm of the Faraday tube was then cooled in liquid nitrogen and evacuated to remove any traces of decomposition hydrogen. The solution was then allowed to warm up; the Faraday tube was turned and a drop of solution allowed to run over into the other arm which was drawn into a capillary. When an appropriate bead had collected, the capillary tip was quenched in liquid nitrogen and sealed off for transfer to the X-ray camera. The inner diameter of the capillary was about 1 mm.

X-Ray Data. A conventional Debye camera of 57-mm diameter was modified to allow for spray cooling of the target sample. The metal–ammonia capillary prepared as above was rotated and sprayed with liquid nitrogen during the 4–6-hr exposures. Radiation was Cu Kα. Film shrinkage was corrected for by tungsten calibration. The X-ray pictures showed no evidence of any decomposition products such as amide, imide, oxide, or hydroxide. However, many of the X-ray patterns obtained were of poor quality.

Density Determination. The density of $Li(NH_3)_4$ was measured at 77°K by gas displacement. A large sample of $Li(NH_3)_4$ was prepared in a 100-ml bulb of calibrated volume, cooled slowly through the 89°K solidification point, and then cooled very slowly (*vide infra*) through the 82°K solid–solid transition. After thorough annealing of the sample at 77°K, helium was allowed to expand from a known volume into a new volume including the sample. The pressure drop was measured and used to calculate the sample volume. The measured density, 0.57 g/cc, is believed to be accurate to within 0.03 g/cc.

Results and Discussion

Table I shows the results of a typical X-ray exposure. Diffraction lines of observable intensity were exceedingly difficult to obtain, particularly for the relatively weak lines of the supercooled cubic phase. All pictures could be accounted for by assuming that two phases were present: a low-temperature hexagonal phase and a high-temperature cubic phase. The persistence of the cubic phase to lower temperature is not surprising, since the 82°K transition is a very sluggish

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[2] See, for example, the review article by M. J. Sienko in "Metal Ammonia Solutions," G. Lepoutre and M. J. Sienko, Ed., W. A. Benjamin, Inc., New York, N. Y., 1964, p 25.

[3] H. J. Holland and F. W. Cagle, Jr., presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963.

[4] N. Mammano and L. V. Coulter, *J. Chem. Phys.*, 47, 1564 (1967).

[5] L. V. Coulter and L. Monchick, *J. Am. Chem. Soc.*, 73, 5687 (1951).

[6] P. R. Marshall and H. Hunt, *J. Phys. Chem.*, **60**, 732 (1956).

[7] H. Jaffe, *Z. Physik*, **93**, 741 (1935).

[8] J. A. Morgan, R. L. Schroeder, and J. C. Thompson, *J. Chem. Phys.*, 43, 4494 (1965).

Table I. X-Ray Data for $Li(NH_3)_4(s)$

2θ	Intensity	d_{obsd}, Å	d_{calcd}, Å^a	(hkl)
13.35	vvw	6.63	6.75 c	(110)
14.55	s	6.09	6.09 h	(100)
16.70	vw	5.26	5.31 h	(101)
18.75	w	4.73	4.78 c	(200)
21.88	m	4.06	4.10 h	(102)
26.52	w	3.36	3.37 h	(111)
27.93	m	3.20	3.18 c	(300)
30.55	ms	2.93	2.93 h	(201)
32.44	vw	2.76	2.77 h, c	(004), (222)
35.14	vw	2.55	2.55 h, c	(113), (321)
38.95	mw	2.31	2.30 h	(210)

[a] (c) cubic, $a_0 = 9.55$ Å; (h) hexagonal, $a = 7.0$ Å, $c = 11.1$ Å.

one. The heat capacity studies of Mammano and Coulter[4] indicated that their 82.18 °K transition required several hours for thermal equilibration under adiabatic conditions. Resistivity studies, carried out at Cornell in collaboration with the Cryogenic Physics group, suggest that at least a day may be required to pass through the transition on cooling. There is some evidence that the transition, which may involve a homogeneous shear as in a martensitic transformation, can be facilitated by tapping.

The principal phase present at 77 °K., believed to be stable at this temperature, has hexagonal symmetry with $a = 7.0$ Å and $c = 11.1$ Å. Two molecules of $Li(NH_3)_4$ per unit cell lead to a calculated density of 0.53 g/cc, in acceptable agreement with the experimentally determined density at 77 °K of 0.57 g/cc. The cubic phase, which appears to be stable between 82 and 89 °K., has a unit cell with $a_0 = 9.55$ Å. Assignment of four molecules of $Li(NH_3)_4$ per unit cell leads to a calculated density of 0.57 g/cc.

Although a unique space group cannot be assigned to the hexagonal phase, the absence of reflections of the type $(00l)$ with l odd together with a probable tetrahedral configuration of the NH_3 molecules around the lithium suggests $P6_3$ or $P6_3mc$. A tentative assignment of the eight ammonia molecules and two lithium atoms per unit cell is as follows: six NH_3 in the c positions, two NH_3 in b positions at z, and two lithium in b positions at z'. These positions correspond to two tetrahedra related to each other by a twofold screw axis through the center of the primitive cell.

A tetrahedral arrangement of NH_3 molecules about lithium has previously been suggested by Sienko[2] on the basis of a simple valence-bond model for $Li(NH_3)_4$. Promotion of the 2s electron of lithium to the 3s orbital opens up the 2s orbital for sp^3 hydridization. The lone pair of an NH_3 molecule can occupy an sp^3 hybrid of the lithium to form a σ bond between the NH_3 and the Li. The dimensions of the $Li(NH_3)_4$ molecule can be crudely estimated by taking the Li–N distance to be about the same as the 1.94 Å in Li_3N, the N–H distance to be 1.01 Å as in NH_3, and the Li–N–H bond angle to be 111° (calculated to fit with the observed H–N–H bond angle of 107° in NH_3). The Li-to-H distance so computed comes to about 2.5 Å. Using 1.2 Å for the van der Waals radius of hydrogen, the effective radius of the $Li(NH_3)_4$ molecule would be about 3.7 Å. Assuming hard-sphere contact in the solid, the closest Li-to-Li distance would be 7.4 Å, which in close packing of spheres would lead to an interplanar spacing of 6.0 Å. As seen from Table I, the most intense X-ray line observed is at 6.09 Å. It is probably more than just a coincidence that Schmidt,[9] in his study of the X-ray scattering of concentrated *liquid* solutions of lithium in ammonia, found an intense scattering peak at 0.117 radian, which, for the Mo Kα radiation used, corresponds to 6.04 Å. Schmidt's experiments were done at −75° with 20.6 atom % Li in NH_3. Thus, there is the strong possibility that some of the structure observed in the solid at 77 °K persists in the liquid state at higher temperature. Morgan, Schroeder, and Thompson,[8] in fact, suggest that the positive temperature coefficient of conductivity observed in liquid metal–ammonia solutions is associated with structure in the solutions. It might be noted also that Schmidt's concentration data, when combined with a not unreasonable estimate 0.5 g/cc for the solution density, lead to a calculated layer spacing of 5.7 Å if it is assumed the liquid consists of close-packed lithium atoms coordinated by four NH_3 molecules.

An alternate view of the $Li(NH_3)_4$ molecule can be obtained from a hydrogenic 3s wave function with equivalent screening. Using Slater rules to calculate an effective nuclear charge of 1.30, we find that Ψ_{300} has maxima at 1.4 and 4.7 Å and nodes at 0.8 and 2.9 Å. Given that the bond distances suggest an Li-to-H distance of 2.5 Å, it appears that the great bulk of the 3s electron density is outside the shell of the 12 hydrogen atoms of $Li(NH_3)_4$. As a result, the molecule $Li(NH_3)_4$ can perhaps be better visualized as an $Li(NH_3)_4{}^+$ ion enclosed in a spherical sheath of one-electron charge density. The observed metallic properties would then be a consequence of the considerable overlap of expanded 3s orbitals.

Free-energy considerations indicate that the molecule $Li(NH_3)_4$ is probably unstable to dissociation in the gas phase, at least at 238 °K. The reaction $Li(g) + 4NH_3(g) \rightarrow Li(NH_3)_4(g)$ can be considered the sum of three steps: (a) ionization; (b) ammoniation; (c) electron affinity.

(a) The ionization energy $Li(g) \rightarrow Li^+(g) + e^-$ is 124 kcal/mole.

(b) The ammoniation energy $Li^+(g) + 4NH_3(g) \rightarrow Li(NH_3)_4{}^+(g)$ is estimated to be about −72 kcal/mole. (This value is obtained as follows: Marshall's value[10] of −9.2 kcal for $\Delta G°$ of $Li(s) \rightarrow Li^+(am) + e^-(am)$ is combined with other standard data and Jolly's value[11] of −39 kcal for $\Delta H°$ of $e^-(g) \rightarrow e^-(am)$ to get an experimental value of −123 kcal for the process $Li^+(g) \rightarrow Li^+(am)$. An estimated value of −51 kcal is obtained for $Li(NH_3)_4{}^+(g) \rightarrow Li(NH_3)_4{}^+(am)$ by applying the Born equation to a 2.5-Å ion in liquid ammonia, for which the Latimer cation-radius correction appears to be 0.6 Å. The difference between the solvation energies of $Li^+(g)$ and of $Li(NH_3)_4{}^+(g)$ is taken as a measure of the interaction energy between Li^+ and NH_3 in the gas phase.)

(c) The electron affinity $Li(NH_3)_4{}^+(g) + e^- \rightarrow Li(NH_3)_4(g)$ is estimated to be −44 kcal, *i.e.*, the difference between the 2s → 3s promotion energy[12] and the 2s → ∞ ionization energy for lithium.

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(9) P. W. Schmidt, *J. Chem. Phys.*, 27, 23 (1957).

(10) P. R. Marshall in ref 2, p 107.

(11) W. L. Jolly, *Progr. Inorg. Chem.*, 1, 264 (1959).

(12) C. E. Moore, "Atomic Energy Levels as Derived from the Analyses of Optical Spectra," Circular 467, National Bureau of Standards, Washington, D. C., 1958.

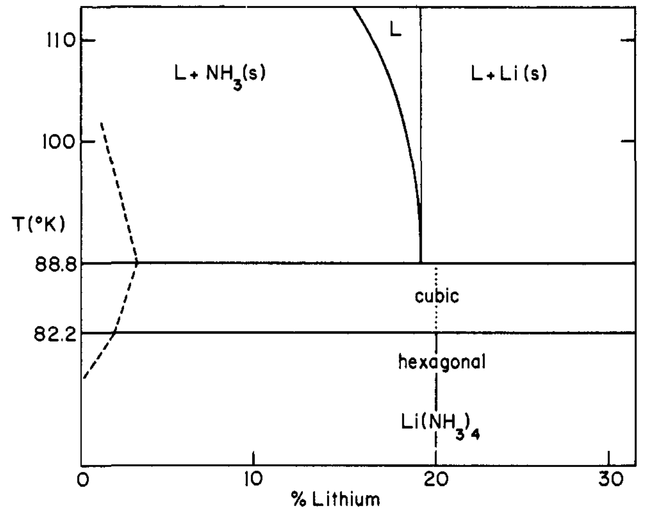

Figure 1. Phase diagram for lithium–ammonia system in the low-temperature region. The dashed lines on the left suggest possible solid–solution formation. The dotted line at 20 mole % in the cubic region may actually be a solid line if $Li(NH_3)_4$ compound formation occurs at 88.8°K. The eutectic has been placed at 19.4 mole % lithium to conform with the findings of Mammano and Coulter[4] that the heat effects peak at $Li(NH_3)_{4.15}$.

The sum of a, b, and c suggests +8 kcal for the free-energy change of the reaction $Li(g) + 4NH_3(g) \rightarrow Li(NH_3)_4(g)$ at 238°K.

In the solid state, possibly also in the liquid state, $Li(NH_3)_4{}^0$ would have an additional large stabilization energy arising from electron delocalization. This would be analogous to the metal lattice cohesive energy associated with, for example, the condensation of infinitely attenuated sodium gas to sodium metal crystal. It can be viewed as the quantum-mechanical lowering of kinetic energy that accompanies expansion of a particle-in-a-box, *viz.*, from an electron confined to a single $Li(NH_3)_4$ molecule to an electron spread over all $Li(NH_3)_4$ molecules of the entire sample. The magnitude of the delocalization energy can be estimated from a modified Hartree model[13] as equal to $[(-1.80/r_s) + (2.21/r_s{}^2)]$ rydbergs, where r_s is the radius of the Wigner–Seitz sphere in units of Bohr radii. Given that there are two molecules of $Li(NH_3)_4$ and hence two metallic electrons per unit cell, the Wigner–Seitz radius comes out to be $7.25a_0$, and the corresponding energy is −65 kcal. This energy does not include any correction for correlation energy, which, following the interpolation method of Nozières and Pine,[14] can be estimated to add an additional −28 kcal. The total stablization energy, −93 kcal, more than compensates for the vaporization energy of lithium (+37 kcal/mole) and that of ammonia (+7 kcal/mole), so, even assuming that the binding energy is unfavorable by 8 kcal in the gas phase, we find for $Li(s) + 4NH_3(s) \rightarrow Li(NH_3)_4(s)$ a favorable energy change that amounts to −20 kcal.

Because the above X-ray work was confined to 77°K, it is not possible at this time to make a definitive case for compound formation in the range 82–89°K. The results for this temperature region are, however, consistent with the high heat capacity, high electrical conductivity, and golden color of the solid, in that they uphold the view that the solid freezing at 89°K is not a simple binary eutectic of lithium and ammonia crystals. On the other hand, the formation of a solid solution in this temperature range is not precluded. Figure 1 shows the most probable phase relations, given that the dotted lines represent conjecture. Two principal possibilities present themselves.

(a) Case I. The vertical dotted line at 20 mole % lithium may in fact not exist in the cubic region. In such case the 88.8°K line would represent a eutectic where liquid solution separates into solid lithium and a solid solution of lithium and excess ammonia. (A solid solution of ammonia in excess lithium is possible but unlikely in view of structural considerations.) The 82.2°K line would then be where the solid solution and solid lithium react to form the compound $Li(NH_3)_4$ in its hexagonal form.

(b) Case II. The vertical dotted line at 20 mole % lithium may actually be a solid line in the cubic region. In such case the 88.8°K line represents an equilibrium between the liquid solution, solid lithium, solid ammonia, and the compound $Li(NH_3)_4$ in its cubic form. The 88.8°K line might actually be two closely spaced lines: the upper of which corresponds to a eutectic temperature for the equilibrium, liquid $\rightleftarrows Li(s) + NH_3(s)$ and the lower, to a peritectoid temperature for the equilibrium $Li(s) + 4NH_3(s) \rightleftarrows Li(NH_3)_4(s)$. If the eutectic temperature and the peritectoid temperature coincide, there is a quadruple point with zero degrees of freedom. For case II, the 82.2°K line represents the temperature at which the cubic and hexagonal forms of $Li(NH_3)_4$ convert into each other.

The present evidence, summarized by Mammano and Coulter,[4] favors case II. X-Ray studies in the range 82–89°K would be informative, but these are difficult because of the greater problem encountered in keeping sample temperature constant at other than liquid nitrogen temperature. Further studies on this surprising material will be continued, but the case for compound formation seems to be substantially supported.

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[13] See, for example, C. Kittel, "Quantum Theory of Solids," John Wiley and Sons, Inc., New York, N. Y., 1963, p 88.

[14] P. Nozières and D. Pines, *Phys. Rev.*, **111**, 442 (1958).