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Electron Spin Resonance Studies of the Reaction of Lithium Atoms with Lewis Bases in Argon Matrices: Formation of Reactive Intermediates. 1. Water and Ammonia†

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Abstract: The reactions of lithium atoms with water and with ammonia have been studied at liquid helium temperatures using ESR matrix isolation spectroscopy techniques. These experiments indicate the formation of molecular complexes in both reactions, with the stability of the complexes being due to the sharing of the Lewis base lone pair electrons with lithium. The complexes involve the interaction of a lithium atom with a single molecule in the case of NH_3 and H_2O; in addition, the lithium–water reaction yields a complex involving two H_2O molecules. Electronic g values and hyperfine interaction constants are reported for the complexes. The matrix isolated complexes were photolyzed by near-visible light. Possible reaction products of this photolysis are discussed for each complex.

Introduction

The alkali metal atoms, because of their electronic structures, constitute a group of very reactive elements. Reactions with molecules such as water and ammonia (classic Lewis bases) are spontaneous or easily initiated reactions at room temperature. Comparable chemical reactivity, however, is not expected on a monomolecular scale at cryogenic temperatures, as reaction rates are greatly impeded by reduced thermal activity.

Matrix isolation ESR has been used before to characterize small atomic and molecular radicals.[1,2] By this method, the molecular species to be observed are isolated at high dilution in an unreactive matrix which restricts thermal mobility and allows the preservation of unstable reactive intermediates and radical molecules. Free radicals may be generated in the gaseous state and then deposited in some matrix material; alternatively, radical species may be generated in situ in the matrix. The hyperfine structure observed in ESR spectra frequently allows complete identification of small systems. Recent work[3,4] has shown that matrix isolation is suitable for producing and studying reaction intermediates. The long-range goal of this approach is to study the chemical and physical properties of isolated chemical systems and apply these results to large-scale reactive systems.

In this work, lithium was reacted with water and ammonia on a molecular scale via codeposition with excess argon at approximately 15 K. Since Li(^{2}S) is paramagnetic in the atomic state, electron spin resonance (ESR) spectroscopy was used to investigate the extent of reaction of lithium with water and ammonia. Because ESR directly measures spin density, the experimental results provide a quantitative measure of the change in spin density at the lithium nucleus resulting from the formation of $Li_n(H_2O)_m$ and $Li_n(NH_3)_m$ complexes observed in these experiments. This change in spin density at the lithium nucleus can be caused by an electron transfer mechanism and concomitant atomic rehybridization. If these complexes may be induced to react further and form the same reaction products as those observed under standard conditions (STP), it is plausible that these species are a good representation of the intermediate species leading to the products observed under standard conditions.

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Theory

Fundamental to the analysis of the data for a paramagnetic system is the construction of a spin Hamiltonian for the system and the subsequent eigenvalue solution. In systems possessing spherical symmetry, such as lithium, the spin Hamiltonian is[5]

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + A\mathbf{S}\cdot\mathbf{I} - g_n\beta_n\mathbf{H}\cdot\mathbf{I} \quad (1)$$

g and g_n represent the electronic and nuclear g factors while β and β_n represent the Bohr and nuclear magneton, respectively. **S** and **I** are the spin and nuclear moments, and **H** represents the applied magnetic field. The first and third terms correspond to the Zeeman energies in a magnetic field and the second term is the hyperfine Fermi-contact interaction energy. A is the hyperfine coupling constant, and is related to the unpaired spin density ($|\psi(0)|^2$) at the nucleus.

$$A = (8\pi/3)g\beta g_n\beta_n|\psi(0)|^2 \quad (2)$$

For a spherical system, the electronic g tensor and the hyperfine coupling constant are isotropic and diagonal.

When $S = 1/2$, the equation $\mathcal{H}\psi_n = E\psi_n$ may be solved in closed form; the solution to the eigenvalue problem is well known and is called the Breit–Rabi formula.[6]

When lithium forms a complex with water or ammonia, the spherical symmetry of atomic lithium is destroyed. Proper analysis of the new system would require making a judgement on the new symmetry of this complex; then a new spin Hamiltonian can be formulated and the subsequent eigenvalue problem solved. Even if a symmetry could be assigned to the

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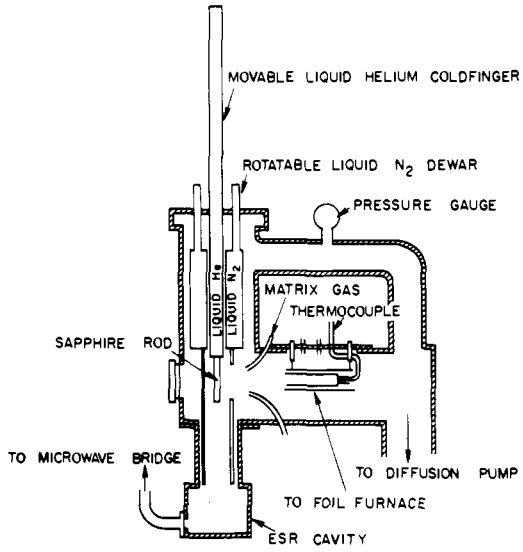


Figure 1. Schematic of the ESR apparatus used in these experiments.

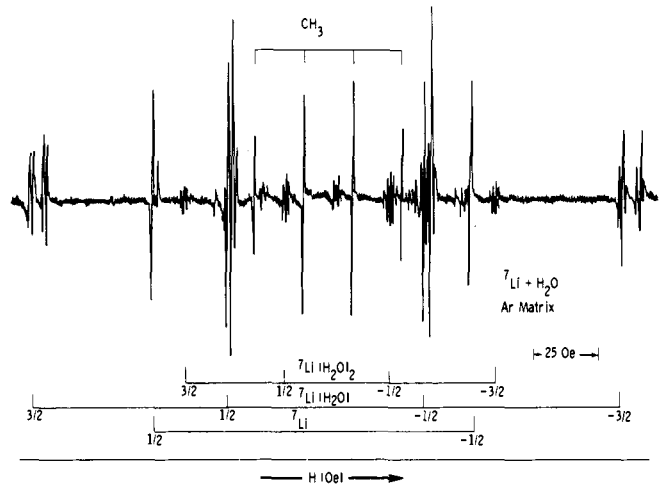


Figure 2. Spectrum observed in the codeposition reaction of Li and H_2O. In this experiment, as well as subsequent experiments, the resonant frequency, ν, is 9702 MHz.

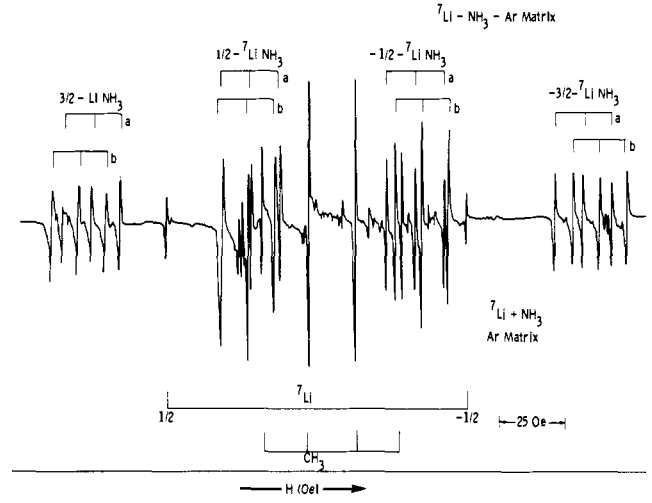


Figure 3. Spectrum observed in the codeposition reaction of Li and NH_3.

complex, the solution to this problem is difficult even for a system of relatively elemental symmetry.

The approach which will be used in this presentation is to consider the interaction of water or ammonia with lithium as a perturbation in the electronic configuration of the lithium. Using this approach, then, the electronic g tensor and the hyperfine interaction constant term for lithium in the complex is obtained. The validity of this approach will be examined later in this presentation.

After obtaining the hyperfine interaction constant A for lithium and the lithium complexes, eq 2 may be used to calculate the decrease in spin density on the lithium atom as a result of the formation of the complex. This value may be used to provide some insight for the strength of the interaction between lithium and the complexing molecule.

Experimental Section

In the experimental arrangement, the reactants were sprayed in gaseous form and co-condensed onto a rectangular sapphire rod cooled by liquid helium. ^7Li was vaporized in a tantalum foil furnace and codeposited with water or ammonia gas on the surface of the sapphire rod. The matrix trapping gas used in all of these experiments was argon, and the ratio of argon to lithium and the complexing gas was in excess of 100:1. Liquid helium was transferred from a Dewar to the sapphire rod using a movable transfer line. The transfer line was in thermal contact with the sapphire rod, and the temperature of the rod could be controlled by adjusting the flow rate of the liquid helium. In all the experiments, the trapping procedure was carried out for a period of 1 h. A schematic diagram of the experimental apparatus is shown in Figure 1. As shown in the figure, after the trapping period, the sapphire rod must be lowered into the ESR cavity in order to record the spectrum. The ESR spectrometer, a Varian Fieldial Mark II model, and the experimental apparatus are described in ref 4a. Ammonia and argon gases were obtained using standard Matheson gas cylinders; water was purified by freezing in liquid nitrogen and then evacuating the system to provide water vapor. The lithium metal was obtained from Alfa Inorganic Ventron Co.

After the spectrum of the matrix trapped species was recorded, two additional experimental techniques were applied to yield other information about the complexes. Annealing the matrix was done by warming and then quickly recooling the matrix. The purposes of this technique are twofold: (1) When molecular systems are isolated in a matrix of rare gas atoms, the system may occupy different sites in the rare gas lattice. If some of the occupied sites are more stable than others, an annealing of the matrix may effect a reorientation of the less stable sites to the more stable matrix sites. (2) The annealing might allow further interactions between the isolated molecular systems as the quick warmup permits the isolated molecular systems to diffuse in the matrix, and the chances of encountering another molecule are enhanced. This may lead to additional chemical reactions.

A second technique used was an application of radiant energy to the matrix surface and the species deposited on it. The ESR cavity used in these experiments was made with a small window so that radiant energy could easily be transmitted to the matrix surface. In this way, photolysis of the complexes might be induced. The radiant energy source used in these experiments was an unfiltered high-pressure xenon short-arc lamp.

Results

Figures 2 and 3 show the ESR spectra obtained for matrices containing (1) lithium and water and (2) lithium and ammonia, respectively. Each of these scans shows lines which may be identified as free ^7Li atoms and CH_3 radicals. ^7Li, which has a nuclear moment with a spin of $3/2$, will generate a quartet of nearly equally spaced lines; the spectra in Figures 2 and 3 show the inside two lines of this lithium quartet. The g value for ^7Li trapped in an argon matrix is 2.001 03 and the isotropic hyperfine interaction constant A is 413.74 MHz.[1a] The ESR spectrum for a methyl radical is well known; in an argon matrix, the g value for a CH_3 radical is 2.002 03 and the isotropic hyperfine constant is 64.64 MHz.[1b] The ^7Li lines come from unreacted lithium and the methyl radicals are generated from pyrolysis of the diffusion pump oil. Both lithium and the methyl radicals were used as internal calibrants to calculate the line positions of the other spectral lines.

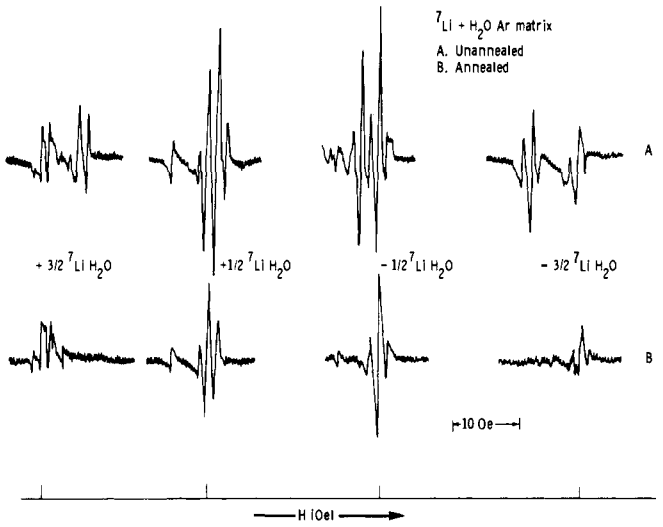


Figure 4. Expanded scan depicting the observed Li-H_2O complexes. B shows the effect of a quick annealing, indicating the disappearance of one of the observed complex species.

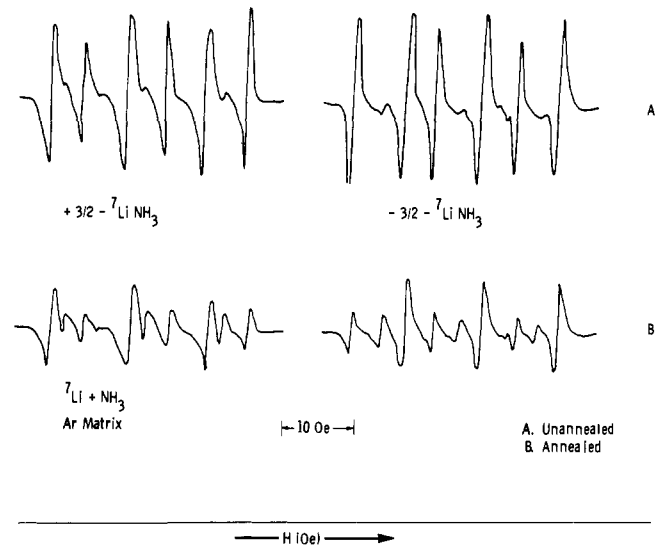


Figure 5. Expanded scan depicting two of the four groupings of Li-NH_3 complexes. As in Figure 4, B shows the effect of a quick annealing.

As the labels in Figure 2 and 3 illustrate, the other spectral lines have been attributed to the molecular complexes formed from the reaction of lithium and water or lithium and ammonia. In Figure 2, there is a widely spaced set of four groups of lines which has been labeled ^7Li-H_2O and a less widely spaced set of four groups of lines which has been labeled ^7Li-$(H_2O)_2$. An expansion of the ^7Li-H_2O lines is shown in Figure 4. As shown in this figure, annealing the matrix removes one group of these lines and leaves a triplet with an apparent intensity ratio of 1:2:1. Since the nuclear spin for ^7Li is $3/2$, the interpretation of these results seems clear. The differentation of the spectral lines into four major groups is due to the interaction of the unpaired electron with the nuclear moment of lithium. Since lithium has formed a complex with the water molecule, the nuclear hyperfine interaction has decreased relative to the interaction for the free ^7Li atom. The additional triplet splitting is caused by the nuclear moments of the two hydrogen nuclei in the water molecule. This would suggest that lithium has formed a molecular complex with a single water molecule; the formation of this complex has caused a decrease in the spin density in the 2s atomic orbital of the lithium atom as revealed by the decrease in the hyperfine constant of the complex relative to free lithium atoms. The annealing data (Figure 4) suggest that there are two distinct forms of ^7Li-H_2O complexes, one of which is interacting more strongly with the lithium atom than the other. (A possible explanation for these two types of ^7Li-H_2O complexes will be discussed later.)

Table I. g Values, Hyperfine Constants, and Spin Densities for Lithium and the Molecular Complexes[a]

	System	g value	A, MHz	$(\lvert\psi(0)\rvert^2)$, a_0^{-3}
	^7Li	2.00103	413.74	2.99
A	^7Li-H_2O	2.00032	255.32	1.85
B	^7Li-H_2O	2.00095	241.70	1.75
	^7Li-$(H_2O)_2$	1.99944	156.32	1.13
A	^7Li-NH_3	1.99981	247.18	1.79
B	^7Li-NH_3	2.00059	220.12	1.59

[a] A and B correspond to the stable and annealed complexes, respectively, for both water and ammonia.

The ^7Li-$(H_2O)_2$ lines show four groups of lines which have been further split into quintets. The division into four groups of lines is again due to the nuclear moment of lithium. In this ^7Li-$(H_2O)_2$ complex, the paramagnetic interaction with the lithium nucleus is now greatly reduced relative to the free ^7Li atom. Within each group of lines, the quintets result from the coupled interaction of four protons. As in the ^7Li-H_2O complex, the symmetric splittings indicate that the interactions due to the protons are equivalent.

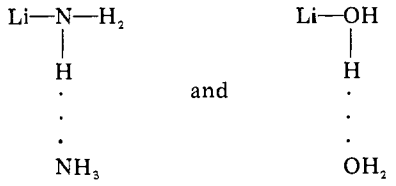
The results for the reaction involving lithium and ammonia (Figure 3) are analogous to the previous analysis for the lithium-water reaction. The differentiation of the spectral lines into four major groupings may again be ascribed to the isotropic hyperfine interaction with the nuclear moment of ^7Li. Figure 5 shows an expansion of two of these four line groups. Within each grouping, there are apparently two sets of triplets, each triplet possessing equal line intensities. The triplet splitting results from the nuclear moment of 1 for ^{14}N. In analogy to the lithium-water reaction, these results suggest that lithium has formed a molecular complex with a single ammonia molecule and, the spin density localized in the lithium 2s atomic orbital has decreased relative to free atomic lithium. As Figure 5 depicts, there seem to be two distinct major types (and even a third less important type) of ^7Li-NH_3 complexes one of which interacts most strongly with lithium. Unlike the lithium-water reaction, however, there are no spectral lines which suggest the formation of a complex involving two ammonia molecules.

By using the line position of the molecular complexes, the g values and isotropic hyperfine constants (A) may be calculated. These values, along with those for a free ^7Li atom in an argon matrix, have been listed in Table I. Also listed in this table are the spin densities ($|\psi(0)|^2$) which have been obtained from eq 2. Within experimental error, none of the g values differs significantly from the free electronic g value, indicating that spin-orbit coupling is not a major consideration in these reaction complexes.

The spin density values listed in Table I show a decrease in spin density in the Li 2s orbital as a result of the formation of these complexes. Since the triplet splitting in the Li-NH_3 complexes is due to the nuclear moment of nitrogen (^{14}N), one can also calculate the spin density which interacts with the nitrogen atomic nuclear moment. This calculation involving the nuclear moment of ^{14}N was done using a first-order perturbation approximation in which the resonant frequency is given by $h\nu = g\beta H + AM_I$. These values are listed in Table II.

As Figures 4 and 5 indicate, there are two major distinct forms of molecular complexes formed in each reaction, one of which may be removed by annealing the matrix. Because of

the size of a water or ammonia molecule, it is unlikely that either observed molecular complex results from any sort of interstitial matrix site where one atom or molecule resides in unoccupied space in the rare-gas lattice; more likely, each of these distinct sites occupies some form of a substitutional site.



The division into two sites, then, may be caused by a slightly different arrangement of rare gas atoms (in this case, argon) around the complex. If one arrangement is more stable than the other, an annealing of the matrix may cause one of the sites to disappear. Another possibility is that one of the observed spectral sites is due to complexes of the form $LiOH_2 \cdot OH_2$. The major cause of differentiation in this case would be caused by the formation of a hydrogen-bonded dimer in one of the complexes. While unpublished matrix work on the lithium-water system has indicated that this hydrogen-bonded dimer complex is a possibility, it certainly does not agree with the observed symmetrical splitting of the protons, as shown in Figure 4. Interestingly, the data in Table I show that the ^7Li-H_2O or ^7Li-NH_3 complex having the greatest interaction between the lithium atom and the complexing molecule(s), i.e., the smallest lithium hyperfine interaction, which indicates more complete electron-transfer, is also the system which is most easily annealed.

Regardless of the exact assignment of the major interaction resulting in the formation of these complexes, the spin density values listed in Table I provide a rather crude scale of relative interactive strengths. As the table illustrates, the ammonia molecule interacts more strongly with lithium than with water. Comparison of the spin densities of either of the ^7Li-H_2O systems with the ^7Li-$(H_2O)_2$ system show that the average interaction of the two water molecules in ^7Li-$(H_2O)_2$ is weaker than the interaction of a single water molecule with lithium. Thus, if the internuclear separations between lithium and oxygen are equivalent or at least comparable for either the mono- or diwater complexes, it is clear that the interactions between the lithium atom and the water molecules are not strictly additive as the number of water molecules in the complex increases.

When the complexes were irradiated by visible light, a radical change occurred in the observed spectra. One-minute photolysis of the lithium-water system resulted in a decrease of the spectral lines assigned to the complexes to less than half the original intensity; exposure for 10 min caused a complete disappearance of the molecular complex lines. Two new lines, with a splitting of slightly over 500 Oe, were formed as a result of the photolysis. These lines may be attributed to free hydrogen atoms. Thus the application of the external energy source has induced a photolytic reaction with one of the products being hydrogen atoms. Diffusion of these atoms to form H_2 is inhibited since the hydrogen atoms are produced from the lithium-water complexes; these complexes are isolated from one another by the argon atoms. The other product of this photolytic reaction, which is not paramagnetic, is likely to be lithium hydroxide. Thus application of visible light probably induces the following reaction of the lithium-water adduct:

$$Li\text{-}H_2O \xrightarrow{h\nu} LiOH + H$$

Application of this same photolytic technique to the lithium-ammonia system also caused a disappearance of the molecular complex lines. However, no new paramagnetic signal was generated indicating that all of the reaction products were either dimagnetic systems or a radical species with a sufficiently large orbital angular momentum component to prevent any signal from being seen. Considering all of the possible products resulting from an Li-NH_3 complex, a likely mechanism would seem to be the following:

$$Li\text{-}NH_3 \xrightarrow{h\nu} LiNH_2 + H \rightarrow LiNH + H_2$$

The NH radical is a π radical which would not be observed because of its large orbital angular momentum component. A simple consideration of bond energies indicates that this mechanism is indeed thermodynamically possible.

Table II. Hyperfine Constants and Spin Densities at the Nitrogen Nucleus in the Lithium-Ammonia Molecular Complexes

	System	A, MHz	$(\lvert\psi(0)\rvert^2)$, a_0^{-3}
A	^7Li-NH_3	36.96	1.08
B	^7Li-NH_3	39.48	1.15

Discussion

Since the configuration of these stable complexes may be directly related to the reaction pathways for these systems at standard temperature and pressure, it would be useful to know the structures involved in these molecular systems. Matrix IR studies which are in progress should provide vibrational frequencies and some additional ideas about the symmetries of the complexes. Knowledge of the configuration of these systems would yield an accurate estimate of the size of the complex, making it easier to speculate as to which of the possible occupational sites the complex assumes in the matrix. Consequently electronic calculations on these systems would be useful in determining the structure of these systems.

Ab initio calculations have been used before for theoretically determining hyperfine interaction constants.[7-9] For example, Hardcastle, Gammel, and Keown[9] report a calculation of the splitting constant for ^7Li within the Hartree-Fock approximation; the reported zero-field value of $2.097a_0^{-3}$ (A = 289.9 MHz) may be compared with the experimental value of $2.906a_0^{-3}$ (A = 401.75 MHz).[10] An ab initio calculation should provide a value of the hyperfine interaction constant for lithium which may be directly correlated to the experimental values listed in Tables I and II.

A nonempirical SCF-LCAO study has been completed by Nicely and Dye[11] for the Li-NH_3 system. Assuming a C_{3v} configuration with lithium on the C_3 axis of ammonia, Nicely and Dye report an Li-N distance of 3.858 79 Bohr (2.042 Å) and a hyperfine interaction constant of $1.55a_0^{-3}$ (214.25 MHz) for a lithium atom; for the Li-NH_3 complex a hyperfine interaction constant of $0.93a_0^{-3}$ (128.55 MHz) for lithium and $0.53a_0^{-3}$ (73.25 MHz) for nitrogen are reported. While the theoretical value of $1.55a_0^{-3}$ is not in very good agreement with the experimental value of $2.906a_0^{-3}$, it is possible that the decrease in the hyperfine interaction constant for lithium due to the complex formed with ammonia would follow a qualitative trend within the limits of the basis set used in these calculations. Consequently, a comparison between the experimental values in this paper (Tables I and II) with the theoretical values of Nicely and Dye should indicate whether the configuration of their Li-NH_3 complex is the same as the complex found in these experiments. If the experimental value of lithium reported in this paper is multiplied by a factor making it equal to the value of $1.55a_0^{-3}$ reported by Nicely and Dye, this same factor may be used to make a comparison between the experimental values for the most stable Li-NH_3 complex reported in this paper with the values reported by

Table III. Comparison of the Theoretical Values of Nicely and Dye with the Experimental Results of This Presentation

	Nicely and Dye[11]	This presentation
$\|\psi(0)\|^2$ – Li	0.93	0.93
$\|\psi(0)\|^2$ – N	0.53	0.56

Nicely and Dye. This comparison may be seen in Table III. As Table III illustrates, the comparison is quite good indicating that the configuration reported by Nicely and Dye in their paper is likely an accurate representation of the Li-NH_3 complex observed in these experiments. Since no calculation of the spin density for the Li-H_2O system could be found, an ab initio calculation is presently being done in this laboratory. A cursory investigation of the configuration for the Li-H_2O system has been done using the MOLE Quantum Chemistry system.[12] Using a six Gaussian replacement for a Slater-type orbital, these results indicate that the complex has a C_{2v} configuration, with the Li-O equilibrium bond distance being 3.4158 au (1.81 Å). A recent publication[13] reports a similar configuration, with the Li-O equilibrium bond distance being 1.93 Å.

Although the results of this experiment can be interpreted in terms of partial electron-transfer complexes, the direction of the electron transfer is not implicit. Chemical intuition would seem to suggest that lithium would transfer an electron to water (or ammonia) since lithium has a relatively small ionization potential. However, electron transfer from water (or ammonia) to lithium could result in the same observed decrease in the hyperfine constants. A bonding between the lone pair electrons of the Lewis base with the p orbital of lithium would cause a rehybridization of the lithium 2s electron; this atomic rehybridization could cause the observed change in the hyperfine splittings. This form of electron transfer would indicate a slight increase in the overall electronic population on lithium. In fact, the work by Nicely and Dye as well as the cursory investigation done in this laboratory indicates an increase in the electronic population on lithium for both Li-NH_3 and Li-H_2O. In other words, the Lewis base transfers charge to the alkali metal atom in the process of forming these complexes.

Nicely and Dye have also made a theoretical study comparing the difference in charge distributions for Li-NH_3 and Li-$(NH_3)_2$ complexes. Their results show that the reaction

$$Li + NH_3 \rightarrow Li\text{-}NH_3$$

has a ΔE (products − reactants) of −18.3 kcal/mol and that the reaction showing the addition of another NH_3 molecule

$$Li\text{-}NH_3 + NH_3 \rightarrow Li\text{-}(NH_3)_2$$

has a ΔE of 13.3 kcal/mol.[11] This change in the reactivity of Li toward a Lewis base is attributed to an accumulation of electronic charge on Li through an electron-transfer mechanism from ammonia when the Li complexes with a single ammonia molecule. This resulting $Li^{\delta-}\cdots(NH_3)^{\delta+}$ charge arrangement is a deterrent to the addition of another ammonia and would explain why no Li-$(NH_3)_2$ complex was observed. While this same type of covalent bonding mechanism probably leads to the lithium-water complex formation, the charge accumulation in lithium would not be as large since this interaction is weaker than in the lithium-ammonia complex (see Table I). If this accumulation is not as significant, it would be a less restrictive problem in forming a diwater complex.

A simplified treatment was used to obtain the isotropic hyperfine constants and g values for the molecular complex systems to reduce the complexity of the calculations. This approach treats the observed atomic hyperfine splittings as due entirely to isotropic effects. Spin-orbit anisotropic effects due to partial occupation of a lithium atomic 2p orbital are apparently quite small. The electronic densities listed in Table I should be accurate to within a few percent and confirm the comments made about the interactions in the mono- and diwater complexes.

Further reactions are being carried out in this laboratory on similar systems involving lithium atoms and various Lewis-base type molecules.

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