Natural Bond Orbital Analysis of the Bonding in Complexes of Li with Ammonia

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Abstract

The gas phase interactions of lithium with ammonia are studied by the DFT/B3LYP method. The calculated dissociation energies to Li and NH_3 of the optimized tetrahedral complexes $Li(NH_3)_4$ and $Li(NH_3)_4{}^+$ are 57.7 and 127.4 kcal.mol^{-1} with the 6-31G(d,p) basis set and show that they are stable compounds. Addition of diffuse functions on Li leads to 65.9 kcal.mol^{-1} for $Li(NH_3)_4$. Natural Bond Orbital analysis of the bonding of Li and Li$^+$ with the ligands has been done by computing the second order perturbation energy. One finds that the interactions that stabilize these complexes involve delocalization of charge from the lone pairs of the NH_3 molecules into Rydberg orbitals of the metal. Then for $Li(NH_3)_4$, a backwards donation of charge from the singly occupied orbital of Li to the Rydberg orbitals of N and H and to the $\sigma*_{N-H}$ is observed The results also show Wiberg bond indices of 0.135 and 0.177 for the Li-N bonds in $Li(NH_3)_4$ and $Li(NH_3)_4{}^+$ respectively which suggest that they are not covalent. These systems may be described as strong van der Waals complexes of Lewis acid-Lewis base type.

Keywords: DFT/B3LYP calculations, lithium-ammonia complexes, NBO analysis, metal-ligand interactions, strong Van der Waals complexes.

Introduction

The new crystalline compounds electrides (M$^+$Ln.e$^-$) and alkalides (M$^+$Ln.M$^-$) in which M is an alkali metal atom, L a ligand (cryptands, crown ethers or amines) and n a coordination number, display interesting physical and chemical properties[1,2,3]. Their study has opened a new area of research and given the opportunity to pursue investigations on metal-ammonia complexes. It has been shown that the species found in these solid ionic systems are similar to those found in mixtures that contain metal (alkali, alkaline earth, Eu or Yb) and polar non aqueous solvents such as ammonia, polyamines and polyethers[4]. Experimental and theoretical work has quite well revealed the nature of these species when metal concentration and temperature change[5-8]. The properties of lithium-ammonia complexes have been the most extensively studied[9-13]. Zurek and coworkers did a comprehensive theoretical study on the species that may exist in lithium-ammonia solutions by optimizing their geometries and studying their electron distributions[14]. Then a relation to observed properties has been done. It is also reported that $Li(NH_3)_4$ precipitates at 89 K from solutions that contain ammonia and 20 mol percent lithium and undergoes phase change as temperature is decreased[15,16]. Like the very concentrated solution from which it forms, this solid shows metallic character which decreased with the phase change as temperature is lowered. In a recent theoretical investigation on the electronic structure of this compound in the solid state at normal pressure by DFT/PBE and plane-wave basis sets, Zurek et al. have suggested that it is an electride[17]. The nature of the bonding between the solvent molecules and the metal atom in

this complex need therefore to be well elucidated in order to understand its properties. We have recently analyzed the nature of the Na-N bond in the gas phase systems $Na(NH_3)_4$ and $Na(NH_3)_5$ by the Natural Bond Orbital (NBO) method and aim here at extending this study to the Li-N bond in the monomer $Li(NH_3)_4$ considered in gas phase[18].

Methodology

Our study is done at the DFT/B3LYP level with 6-31G(d,p) (also noted 6-31G**) and another basis set noted B_2 that we constructed by using the 6-31+G basis for Li and the 6-31G** for NH_3[19]. The geometry optimizations are followed by vibration frequency calculations to confirm that the obtained geometries are minima on the potential surface. The total energies at these optimized geometries include zero point vibration corrections. In order to get insights into the nature of the bonds between Li and the NH_3 molecules, NBO analysis is performed with the NBO collection of codes provided by the Gaussian 03 program, the main program package that we used in the present work[20,21].

Results and Discussion

Geometries and energies: The optimized geometrical parameters for $Li(NH_3)_4$ and $Li(NH_3)_4{}^+$ are displayed on table-1. In accord with the results of neutron diffraction and other theoretical work, we have considered the complexes where the NH_3 groups surround the metal atom in a tetrahedral arrangement. The computed Li-N bond (2.06 Å with 6-

31G(d,p)) is slightly shorter than that of Li$^+$-N (2.12 Å with 6-31G(d,p)) and that reflects the relative strength of the steric repulsions of the NH$_3$ groups around Li and the smaller Li$^+$ ion. However as our data show, this does not change significantly the geometry of the ammonia molecules. The dissociation energy of the neutral complex to its fragments Li and NH$_3$ amounts to 57.7 and 65.9 kcal.mol^{-1} with 6-31G(d,p) and B$_2$ respectively. Our first result is in good agreement with the B3LYP/6-311+G(d,p) value of 54.06 kcal.mol^{-1} of Mierzwicki et al. and that of 51.2 kcal.mol^{-1} of Zurek et al. who used Slater type basis sets[14,22]. Moreover, it is higher than our previous calculated dissociation energy of 42.5 kcal.mol^{-1} for Na(NH$_3$)$_4$ obtained at the B3LYP/6-31G(d,p) level. This predicts that Li(NH$_3$)$_4$ is more stable than Na(NH$_3$)$_4$ [18]. The data on table-1 also indicate that the corresponding dissociation energies of Li(NH$_3$)$_4^+$ are 127.4 and 124.2 kcal.mol^{-1}. So, our results confirm that Li(NH$_3$)$_4^+$ and Li(NH$_3$)$_4$ may exist in gas phase as stable complexes. It would be interesting to know how the ligand binds to the metal in these systems. The present calculated adiabatic ionization energy of Li(NH$_3$)$_4$ is 2.60 eV with 6-31G(d,p) and 3.1 eV with B$_2$ and is, as expected, smaller than the first ionization energy of 5.6 eV of Li.

Natural Bond Orbital (NBO) analysis: The natural charge, spin density and isotropic Fermi contact density calculated at each atomic center are given in table-2. The spin densities and isotropic Fermi contact densities are given by a Mulliken population analysis. The interactions cause polarization of the N-H bonds and transfer some charges on the metal atoms. As expected, the total charge delocalized on Li$^+$ is significant (0.38 e with 6-31G(d,p), 0.40 e with B$_2$) compared to that on Li (0.0069 e with 6-31G(d,p), 0.14 e with B$_2$). The calculated spin densities indicate that about 80% of the unpaired electron

density remains on Li in Li(NH$_3$)$_4$. In the B$_2$ description of the wave function, the Fermi contact density is larger at N (0.108 au) but smaller and negative at H (-2.10^{-5} au). These data are in magnitude and sign in very good agreement with findings of other authors obtained by NMR Knight Shifts measurements and reflect the s character of the wave function of the odd electron of Li at these nuclei[23]. In our recent study, we have also computed these atomic properties for Na(NH$_3$)$_4$ and Na(NH$_3$)$_5$ and have made similar observations about the unpaired electron contact densities at N and H[18]. One may also notice that as expected, the metal-ligand interactions are stronger in the formation of Li(NH$_3$)$_4$ because our previous data show that only 0.0019 e is transferred onto Na in Na(NH$_3$)$_4$ according to the results of the 6-31+G(d,p) basis set compared to 0.140 e onto Li in Li(NH$_3$)$_4$ with B$_2$.

The get a picture of the delocalization of electrons between the amine groups and Li$^+$ or Li, we have included calculations of the second order perturbation energy E$^{(2)}$ of the occupied NBO(i) of an electron donor which interact with the unoccupied NBO(j) of an electron acceptor. According to the analysis, the stabilization energy E$^{(2)}$ is given by the expression:

$$E^{(2)} = \Delta E_{ij} = q_i \frac{(F_{ij})^2}{\varepsilon_j - \varepsilon_i}$$

q_i is the natural population of the donor NBO(i), F_{ij} is an off-diagonal element of the Fock matrix in NBO basis, ε_i and ε_j are the donor and acceptor NBOs energies. We intend in this analysis to get a clear understanding of the bonding in these complexes and find out what is the nature of the contributing orbitals of the metal and the ligand. Table-3 and table-4 list our results. The data on table-4 are from the wave functions described by B$_2$.

Table-1
Energies and geometries

System		E(au)	ΔE (kcal.mol^{-1})	R$_{Li-N}$ (Å)	R$_{N-H}$ (Å)	Θ$_{NLiN}$ (°)	Θ$_{LiNH}$ (°)	Θ$_{HNH}$ (°)
NH$_3$, C$_{3V}$	6-31G(d,p)	-56.523324	-	-	1.018	-	(111.869)	105.747
NH$_3$, experim.		-	-	-	1.012	-	-	106.7
Li(NH$_3$)$_4^+$ T$_d$	6-31G(d,p)	-233.580948	127.43	2.116	1.019	109.471	113.230	105.465
	B$_2$	-233.575765	124.16	2.114	1.019	109.471	113.165	105.538
Li(NH$_3$)$_4$ T$_d$,	6-31G(d,p)	-233.676211	57.67	2.062	1.024	109.471	111.852	106.989
	B$_2$	-233.689490	65.93	2.091	1.022	109.471	112.607	106.162

E(Li)= -7.490985 H and E(Li$^+$) = -7.284544 H with 6-31G(d,p); E(Li)= -7.491113 H and E(Li$^+$)= -7.284567 H with B$_2$

Table-2
Atomic and molecular properties with B_2

System		Natural charge (e)			Spin densities (au)			Isotropic Fermi contact couplings (au)			Wiberg bond index		
		Li	**N**	**H**	**Li**	**N**	**H**	**Li**	**N**	**H**	**Li-N**	**Li-H**	**N-H**
Li	6-31G**	0.0	-	-	1.0	-	-	0.209	-	-	-	-	-
	B_2	0.0	-	-	1.0	-	-	0.215	-	-	-	-	-
NH_3 C_{3V}	6-31G**	-	-1.125	0.375	-	-	-	-	-	-	-	-	0.861
Li $(NH_3)_4^+$ T_d	6-31G**	0.603	-1.145	0.415	-	-	-	-	-	-	0.184	0.0015	0.826
	B_2	0.620	-1.148	0.414	-	-	-	-	-	-	0.177	0.0013	0.827
Li $(NH_3)_4$ T_d	6-31G**	-0.0069	-1.161	0.387	0.762	-0.0222	0.0272	0.0779	0.234	$2.5.10^{-4}$	0.146	0.0176	0.814
	B_2	-0.140	-1.170	0.402	0.832	-0.0089	0.0170	0.0207	0.108	-2.10^{-5}	0.135	0.0112	0.820

Table-3
Contribution of donor and acceptor NBOs to the stabilization of $Li(NH_3)_4$ and $Li(NH_3)_4^+$ with B_2.

System	alpha spin orbitals		6-31G(d,p)		B_2	
	Donor NBO(i)	**Acceptor NBO(j)**	**Occupancies NBO(i)/NBO(j)**	**$E^{(2)}$ (kcal.mol^{-1})**	**Occupancies NBO(i)/NBO(j)**	**$E^{(2)}$ (kcal.mol^{-1})**
[a]$Li(NH_3)_4$	LP(1)Li	BD*(1)N-H	0.6957/0.0235	6.70	0.846/0.0119	2.76
	LP(1)Li	RY*(1)Li	0.6957/0.0099	2.21	0.846/0.0235	1.30
	LP(1)Li	RY*(1)N	0.6957/0.0035	2.20	0.846/0.0020	0.63
	LP(1)Li	RY*(1)H	0.6957/0.0022	0.66	0.846/0.0013	0.58
	LP(1)N	LP*(2)Li	0.9682/0.0386	4.23	0.9684/0.0377	4.15
	LP(1)N	LP*(3)Li	0.9682/0.0386	4.23	0.9684/0.0377	4.15
	LP(1)N	LP*(4)Li	0.9682/0.0386	4.23	0.9684/0.0377	4.15
	LP(1)N	RY*(1)Li	0.9682/0.0099	1.05	0.9684/0.0377	1.99
	BD(1)N-H	LP*(2)Li	0.9978/0.0386	0.90	0.9982/0.0377	0.83
	BD(1)N-H	LP*(3)Li	0.9978/0.0386	0.90	0.9982/0.0377	0.83
$Li(NH_3)_4^+$	LP(1)N	LP*(1)Li	1.9046/0.1644	19.86	1.908/0.1542	18.72
	LP(1)N	LP*(2)Li	1.9046/0.0756	8.29	1.908/0.0749	8.28
	LP(1)N	LP*(3)Li	1.9046/0.0756	8.29	1.908/0.0749	8.28
	LP(1)N	LP*(4)Li	1.9046/0.0756	8.29	1.908/0.0749	8.28
	BD(1)N-H	LP*(1)Li	1.9961/0.1644	1.05	1.9962/0.1542	1.37
	BD(1)N-H	LP*(2)Li	1.9961/0.0756	1.67	1.9962/0.0749	1.66
	BD(1)N-H	LP*(3)Li	1.9961/0.0756	1.67	1.9962/0.0749	1.66
	BD(1)N-H	LP*(4)Li	1.9961/0.0756	0.79	1.9962/0.0749	0.77

[a]Alpha spin orbitals are considered

Table-4
Contribution of NAOs to selected NBOs for Li(NH₃)₄ and Li(NH₃)₄⁺ (in brackets) with B₂

NBO	NAO						
	$\%s_{Li}$	$\%p_{Li}$	$\%s_N$	$\%p_N$	$\%d_N$	$\%s_H$	$\%p_H$
LP(1)Li	100(2s)	-	-	-	-	-	-
BD*(1)N-H 29.35%N;70.65%H		-	24.96(2s)	74.97($2p_{xyz}$)	0.07	99.89(1s)	0.11($2p_{xyz}$)
RY*(1) Li	100(3s)	-	-	-	-	-	-
RY*(1)N	-	-	48.0(3s)	51.97($3p_{xyz}$)	0.02	-	-
RY*(1)H	-	-	-	-	-	94.54(2s)	5.46($2p_{xyz}$)
LP(1)N	-	-	24.99(2s) [22.05(2s)]	74.97($2p_{xyz}$) [77.92($2p_{xyz}$)]	0.04 [0.04]	-	-
LP*(1)Li (or RY*(1) Li)	[100(3s)]	-	-	-	-	-	-
LP*(2)Li	-	100($3p_x$) [100($3p_x$)]	-	-	-	-	-
LP*(3)Li	-	100($3p_y$) [100($3p_y$)]	-	-	-	-	-
LP*(4)Li	-	100($3p_z$) [100($3p_z$)]	-	-	-	-	-
BD(1)N-H 70.65%N;29.35%H [70.78%N;29.22%H]	-	-	24.96(2s) [25.95(2s)]	74.97($2p_{xyz}$) [73.98($2p_{xyz}$)]	0.07 [0.07]	99.89(1s) [99.89(1s)]	0.11($2p_{xyz}$) [0.11($2p_{xyz}$)]

As one can see from our data on table-3, the most stabilizing interactions in Li(NH₃)₄⁺ involve the LP(1)N (the lone pair of the ligand) with unoccupied antibonding NBOs (noted LP*(1,2,3,4)Li) of Li⁺. Values of $E^{(2)}$ as high as 19.9 kcal.mol⁻¹ are observed. Other interactions occur between the occupied BD(1)N-H (σ_{N-H}) with those same antibonding orbitals on Li⁺ and the values of $E^{(2)}$ range from 0.8 to 1.7 kcal.mol⁻¹. Not listed on table-3 are weaker interactions in which NBOs described by the core orbital of N and these same empty NBOs of Li⁺ are involved. The results on table-4 indicate the nature of the Natural Atomic Orbitals (NAOs) of Li⁺, N and H which contribute to the formation of the interacting NBOs. The lone pair of the ligand (LP(1)N) is a $2s2p_{xyz}$ hybrid on the N atom while σ_{N-H} is a $2s2p_{xyz}$ hybrid on N mixed with the 1s of H and polarization functions of both atoms. The LP*(1)Li is solely its 3s orbital while LP*(2,3,4)Li are its $3p_{xyz}$ orbitals. It is interesting to note that the 2s and $2p_{xyz}$ of Li⁺ are not used in the description of these NBOs. One may also observe from table-3 and table-4 that in the case of Li(NH₃)₄, these same NBOs are mainly involved in the interactions of Li and NH₃ with $E^{(2)}$ values of 0.83 to 4.15 kcal.mol⁻¹ in the description of the wave function by B₂. Besides, other important stabilizing interactions occur between the singly occupied orbital of Li (LP(1)Li) and the unoccupied σ^*_{N-H} (BD*(1)N-H) in addition to Rydberg orbitals on N and H. The stabilization energies are 0.6 to 6.7 kcal.mol⁻¹. LP(1)Li is mainly the 2s orbital of Li mixed with its 3s (RY*(1)Li) as shown by their interaction energy of 1.30 kcal.mol⁻¹. For σ^*_{N-H}(BD*(1)N-H), a $2s2p_{xyz}$ hybrid on N mixed

with the 1s of H and polarization functions on these atoms are also used. RY*(1)N is a $3s3p_{xyz}$ hybrid of N and RY*(H), a $2s2p_{xyz}$ hybrid of H.

So, in Li(NH₃)₄, the singly occupied NBO may result from mixing the 2s and 3s orbitals of Li with the σ^*_{N-H} and Rydberg orbitals of N and H and is expected to be quite diffuse. With such description of the wave function of the singly occupied NBOl of Li(NH₃)₄, one may understand our results such as the relative magnitude of the electron contact densities at the nuclei and the decrease in ionization energy from Li to Li(NH₃)₄. The non negligible contributions of the 2s and 3s orbitals of the N atoms in this wave function reinforce the presence of the electron at these nuclei. Their mixing with the 2s and 3s orbitals of Li would also give to this NBO a spherical character and render Li(NH₃)₄ a pseudo-alkali metal. The H nuclei may be near a node of the pseudo-spherical NBO which also uses the 2p orbitals of these atoms.

Therefore, as NH₃ approaches Li, there is charge delocalization from either side: from the lone pair of the ligands onto the 3s and $3p_{xyz}$ orbitals of Li and then from the singly occupied orbital of Li described here as a combination of its 2s and 3s orbitals onto the unoccupied σ^*_{N-H} and Rydberg orbitals of N and H.

The computed Wiberg bond indices given on table-2 indicate a value of 0.135 for the Li-N bonds in Li(NH₃)₄ and 0.177 for those bonds in Li(NH₃)₄⁺. They are relatively small and suggest

that the Li-N bonds in these clusters are not covalent. These systems might just be described as strong van der Waals complexes of the Lewis acid-Lewis base kind.

The interaction energy of $Li(NH_3)_4^+$ may have electrostatic contributions due to the large dipole moment of NH_3 (1.85 D in our work). However this electrostatic part should be small in the formation of $Li(NH_3)_4$ given that a small amount of charge is shared by the ligands and Li according to our results.

Conclusion

We have done a theoretical investigation of the gas phase interactions of lithium with ammonia by DFT/B3LYP. The dissociation energies of $Li(NH_3)_4$ and $Li(NH_3)_4^+$ to Li and NH_3 at the optimized geometries are 57.7 and 127.4 kcal.mol^{-1} with the 6-31G(d,p) basis set. When diffuse functions are added on Li, the dissociation energy amounts to 65.9 kcal.mol^{-1} for $Li(NH_3)_4$. The calculated Fermi contact densities at the nuclei agree in magnitude and sign with experimental results. NBO analysis of the bonding between Li and Li$^+$ with the ligands has been done by computing the second order perturbation energy. The results show that the interactions that stabilize these complexes involve delocalization of charge from the lone pairs of the NH_3 molecules into Rydberg orbitals of the metal. Then for $Li(NH_3)_4$, a backwards donation of charge from the singly occupied NBO to the Rydberg orbitals of N and H and to the σ^*_{N-H} is observed The Wiberg bond indices are 0.135 and 0.177 for the Li-N bonds in $Li(NH_3)_4$ and $Li(NH_3)_4^+$ respectively and suggest the non covalent character of these bonds. These systems may be strong van der Waals complexes that result from interactions of electron donors and acceptors.

Acknowledgments

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