components of the ^2E, $^2T_1$ states. These are most easily measured through excitation spectroscopy, which, however, generally requires low temperatures.

The question still remains whether the doublets can be fit within a ligand field theoretical framework to the accuracy required and whether the parameters so obtained have any meaning. The *fac*-Cr(gly)$_3$ molecule is a good test case. Unlike the situation for tetragonal symmetry,[10] the doublet (and quartet) energies are not strongly dependent on the ligand field asymmetry, so that it is not as easy to cover defects in the model by adjusting the parameters.

What can be said is that the doublet energies and splittings depend quite strongly on the angular geometry, operating synergistically with the ligand field asymmetry. The 10 K doublet energies could not be reproduced with use of the room-temperature geometry, whereas certain more or less arbitrary distortions led to a much better fit. The "best-fit" values for the AOM parameters themselves were not much affected by the distortions, although the statistical errors were large and $e_{\pi \mathrm{O}}$ was at or near the boundary we imposed (2000 cm^{-1}).

The AOM parameters derived appear reasonable. $e_{\sigma \mathrm{N}}$ for the amino group is somewhat lower than for NH_3 or ethylenediamine,[66] while $e_{\sigma \mathrm{O}}$ for the carboxylate group is in the top range of values reported for π-donor ligands such as OH^- and F^-.[29,33] Inductive electron donation from amine to carboxylate may well account for this.

Similarly, e_π values have been reported from OH^- and F^- from 1400 to above 2000 cm^{-1},[29,33,67] so again 2000 cm^{-1} is a reasonable value for the glycine carboxylate, even though it was a boundary value in the calculation.

Some specific conclusions apply to future work in which spin-forbidden peaks form most of the data base for ligand field calculations.

1. s–d mixing, as predicted,[58] should be ignored for six-coordinate complexes.
2. Inclusion of differential orbital expansion has proven very useful. Arguments against this approach[56,57] have been based largely on data from octahedral complexes. For lower symmetry complexes it does not appear possible to fit at least the spin-forbidden bands without invoking differential orbital expansion in some form.
3. The strong angular dependence of the doublet energies suggests incorporation of one or more geometric parameters in the fitting process. Lever and Hollebone[68] have attempted this using one azimuthal angle (formally equivalent to a bite angle), representing trigonal distortion. Although they could not check the angles so calculated (the Cr(III) was present as impurity ions), they suggest in any case that the azimuthal angle may properly be regarded as a phenomenological parameter in the fitting process, without necessarily requiring agreement with crystallographic data. The idea behind this is presumably to consider the angle as a generator of the low-symmetry ligand field.

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Registry No. *fac*-Cr(gly)$_3$, 14325-26-9.

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Lithiated Ammonia, Amide Anions, and Ammonium Ions. An ab Initio Study of Structures, Bonding, and Energetic Relationships

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Monomeric lithiated nitrogen species, in anionic ($NLi_{2-n}H_n^-$), neutral ($NLi_{3-n}H_n$), and cationic ($NLi_{4-n}H_n^+$) forms, were studied by ab initio molecular orbital theory. Geometries were calculated at the 3-21G//3-21G and 4-31+G//4-31+G basis set levels (the latter being particularly appropriate for the description of the anions). The lithiated ammonias, $LiNH_2$, Li_2NH, and Li_3N, are planar, $LiNH^-$ is linear, and Li_2N^- is bent. Angles involving Li tend to be wider than those with H. Lithiation increases the proton and lithium cation affinities markedly. Nevertheless, the presence of a larger number of lithiums is unfavorable, and disproportionation reactions (in which the lithium substituents are distributed to different molecules) are exothermic. The corresponding carbon compounds, Li_3CH and Li_4C, behave differently in this respect. While lithium substitution in $Li_2NH_2^+$ and Li_4N^+ reduces the preference for tetrahedral over planar geometries markedly, the effect is smaller than in the analogous carbon compounds. Heats of formation are estimated, e.g., $\Delta H_f°_0(LiNH_2) = 13.8 \pm 1.2$ kcal/mol. The Li–N bond energy $D_0(Li{-}NH_2) = 65 \pm 4$ kcal/mol, is about 20 kcal/mol larger than the Li–C bond energy in $Li{-}CH_3$. The estimated heat of formation, $\Delta H_f°_0(Li_3N) = 84 \pm 8$ kcal/mol, is indicated to be over 130 kcal/mol more positive for the gas phase than the experimental value for the solid state. This underscores the importance of aggregation of lithium compounds. The nature of nitrogen–lithium bonding is complex. The ionic component (σ donation from lithium to nitrogen) may predominate, but considerable π back-bonding from nitrogen to lithium can take place, and these species have some covalent character. Polylithiated species, e.g., NLi_3, are not indicated to be more ionic than those with fewer lithiums. Although it is customary to write a formal positive charge on nitrogen in ammonium ions, Mulliken populations indicate these nitrogens to be negatively charged; the positive charge resides on the more electropositive substituents.

Introduction

Owing to its superionic conductivity in the solid state, lithium nitride, Li_3N, has been the subject of extensive experimental studies.[2] The other lithiated ammonias, $LiNH_2$ and Li_2NH, also are well-known.[3,4] Lithium reacts with

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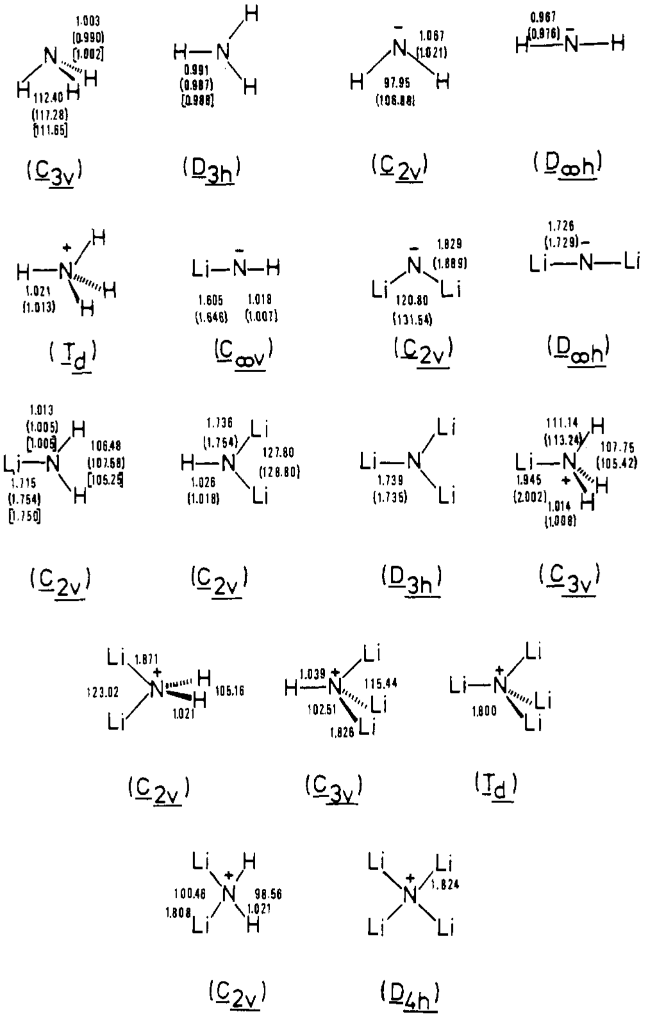

Figure 1. 3-21G (4-31+G) [6-31G*] optimized structures.

ammonia to give lithium amide, $LiNH_2$.[3,4] Lithium imide, Li_2NH, is prepared by heating $LiNH_2$ under vacuum.[4] All these species are aggregated in the solid state.[2,3] Very limited gas-phase data on the monomeric lithiated ammonias—the neutral, cationic, and anionic species—are available.[5,6] Although $LiNH_2$,[7,8] NH_3Li^+,[6,8,9] and $NHLi^-$[7c] have been examined theoretically, only one prior study dealt with a set of lithiated amines at a uniform computational level. Hinchliffe and Dobson[8] called attention to the increasing p–π Li–N interactions along the series $LiNH_2$, Li_2NH, and Li_3N, and the "far removal" of Li_3N and Li_2NH "from the ionic ideal". However, only partial geometry optimizations were carried out; the analysis of gross populations, charge distributions, and bonding was emphasized.

Table I. Absolute Energies of Lithiated Amines, with Relative Energies (in kcal/mol) for Isomeric Forms

species	3-21G//3-21G	4-31+G//4-31+G	6-31G*//6-31G*
NH_3 (D_{3h})	−55.86964 (1.61)	−56.11479 (0.18)	−56.17399 (6.51)
(C_{3v})	−55.87220 (0.0)	−56.11508 (0.0)	−56.18436 (0.0)
NH_2Li (C_{2v})	−62.69512	−62.98062	−63.04195
$NHLi_2$ (C_{2v})	−69.49747	−69.81812	
NLi_3 (D_{3h})	−76.31006	−76.66543	
NH_2^- ($D_{\infty h}$)	−55.04502 (57.1)	−55.39662 (29.6)	
(C_{2v})	−55.13599 (0.0)	−55.44372 (0.0)	
$NHLi^-$ ($C_{\infty v}$)	−61.98471	−62.27984	
NLi_2^- ($D_{\infty h}$)	−68.79495 (3.7)	−69.10980 (12.2)	
(C_{2v})	−68.80079 (0.0)	−69.12921 (0.0)	
NH_4^+ (T_d)	−56.23386		−56.53077
NH_3Li^+ (C_{3v})	−63.14877		−63.49065
$NH_2Li_2^+$ (C_{2v})	−70.00901 (0.0)		
planar (C_{2v})	−69.96313 (28.8)		
$NHLi_3^+$ (C_{3v})	−76.83885		
NLi_4^+ (T_d)	−83.66225 (0.0)		
planar (D_{4h})	−83.62103 (25.9)		

Table II. Higher Level Calculational and Experimental Reference Energies[a]

species	MP4SDQ/6-31G**//6-31G*[b]	MP4SDQ/6-311G**//6-31G*[b]	zero-point, kcal/mol 3-21G	6-31G*	exptl[a]	$\Delta H_f{}^\circ{}_0$[a]
H^+						365.24
H	−0.49823	−0.49981				51.63
H_2	−1.16453	−1.16772	6.7	6.6	6.3	0.00
Li^+						162.38
Li	−7.43137	−7.43203				38.03
LiH	−8.00755	−8.01551	2.0	2.0	2.0	33.65
Li_2	−14.89429	−14.89761	0.5	0.5	0.5	50.30
CH_3	−39.71271	−39.72807	19.5	19.4	18.2	35.62
CH_4	−40.38548	−40.40110	30.1	30.0	27.1	−15.97
CH_3Li				22.3		28.0[c]
NH_2	−55.72757	−55.74964	12.3	12.9	11.3	40.8 ± 3
NH_2^-			(11)[d]			24, 25.4
NH_3	−56.39778	−56.42265	22.6	23.2	20.6	−9.34
NH_4^+	−56.74989	−56.77090	33.0	33.4		149.1[e]
$LiNH_2$	−63.25542	−63.28428	15.7	15.6		12.6[b]
$LiNH_3^+$	−63.70496	−63.72815	25.8	25.9		111.9 ± 2[g]
Li_2NH			(10)[d]			51 ± 5[b]
Li_3N			(4)[d]			84 ± 8[b]

[a] Unless otherwise indicated, experimental gas-phase data (in kcal/mol) are from ref 5 and 31. [b] Energies in hartrees. [c] See ref 30. [d] Estimated by analogy. [e] Theoretical estimate.[22] [f] Theoretical estimates, this work. [g] See ref 6 and 9b.

We have found that compounds of lithium often exhibit unusual geometries, electronic structures, bonding, and energetic relationships.[7a,9b,10] As part of a broad examination of such species, we report here the results of ab initio calculations on all members of the series $NLi_{3-n}H_n$, $NLi_{2-n}H_n^-$, and $NLi_{4-n}H_n^+$.

Computational Methods

Calculations were carried out at the restricted Hartree–Fock level by using the GAUSSIAN series of programs.[11] The structures of all

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molecules were fully optimized with use of analytic force evaluation routines[12] and the split-valence basis set 3-21G.[13] The adequate description of anions requires basis sets augmented with diffuse functions.[14] Hence, additional geometry optimizations were carried out for the anions and, for reference, for the corresponding neutral molecules with use of the 4-31+G basis set[14] (the split-valence 4-31G basis[15]—5-21G for lithium[16] is implied—augmented with a set of diffuse s and p orbitals for the non-hydrogen atoms with exponents 0.053 for nitrogen and 0.012 for lithium).[14] In several cases, less stable isomeric structures which could be defined by symmetry, e.g., linear NH_2^- and NLi_2^-, as well as planar $NH_2Li_2^+$ and NLi_4^+, also were examined. Absolute energies are given in Table I; geometries are indicated in Figure 1. Reference 17 is a convenient source of data for reference molecules needed to evaluate energetic relationships.

For a few of the smaller species, high-level single-point calculations were carried out on geometries optimized with the d-orbital augmented 6-31G* basis set.[18] These employed the 6-31G** (plus p orbitals on hydrogen)[18] and the triply split valence 6-311G**[19] basis sets and Møller-Plesset corrections for electron correlation to fourth order including all single, double, and quadruple excitations (MP4SDQ).[20] These data are collected in Table II.

The Mulliken populations,[21] an assignment of electrons to the contributing atomic orbitals, provide a basis for a detailed analysis of the bonding in these molecules. Although the basis set dependence of the values obtained and other deficiencies of this method are well-known,[7b] comparisons among a set of closely related molecules at a uniform theoretical level are useful interpretively. Table III summarizes the overlap populations (a measure of bonding–antibonding between atoms) and the atomic charges with the 3-21G basis set. Since many of the species considered are linear or planar, strict separation of total charges and populations into σ and π contributions are possible. This dissection reveals (Table III) the π-acceptor–σ-donor character of lithium clearly. For H_3NLi^+, formal separation of total charges indicates the π contribution (due to hyperconjugation) to be negligibly small.

The performance of the theory at the levels employed can be evaluated by comparison with available experimental energies, i.e., proton and lithium cation affinities. Data are collected in Table IV. The theoretical values refer to the hypothetical motion-free state. So that the experimental data could be put on the same basis, corrections for zero-point and translational energy differences[22] were applied. The magnitudes of the corrections are summarized in Table II, along with reference thermochemical data.

Discussion

We are concerned with the structural and energetic changes that occur when hydrogens in NH_2^-, NH_3, and NH_4^+ are replaced sequentially by lithium. A few general comments are in order. As lithium is more electropositive than hydrogen, lithium bonds generally are much more ionic than corresponding bonds involving hydrogen. For all neutral and

Table III. Mulliken Population Analysis (3-21G//3-21G)

	overlap populations									charges						
				N–Li			Li–Li			N			Li			
species	N–H	H–H	Li–H	total	σ	π	total	σ	π	total	σ	π	total	σ	π	H
NH_3 (C_{3v})	0.673	−0.065								0.876−						0.292+
NH_2Li (C_{2v})	0.612	−0.077	−0.060	0.686	0.475	0.211				0.946−	1.178−	0.232+	0.458+	0.690+	0.232−	0.244+
$NHLi_2$ (C_{2v})	0.538		−0.056	0.666	0.482	0.184	−0.444	−0.538	0.094	0.895−	1.474−	0.579+	0.333+	0.622+	0.289−	0.228+
NLi_3 (D_{3h})				0.606	0.447	0.159	−0.098	−0.178	0.080	0.781−	1.622−	0.841+	0.260+	0.540+	0.280−	
NH_2^- ($D_{\infty h}$)	0.742	−0.095								1.345−	1.354−	0.000[a]				0.177+
(C_{2v})	0.450	−0.167								0.992−	0.992−	0.000				0.004−
$NHLi^-$ ($C_{\infty v}$)	0.528		−0.098	1.043	0.409	0.317[a]				0.759−	1.336−	0.577+[a]	0.409−	0.168+	0.577−[a]	0.168+
NLi_2^- ($D_{\infty h}$)				0.752	0.354	0.199[a]	0.214	0.015	0.199	0.592−	1.516−	0.924+[a]	0.204−	0.258+	0.462−[a]	
(C_{2v})				0.466	0.331	0.135	0.029	−0.002	0.031	0.544−	0.811−	0.267+	0.228−	0.094−	0.134−	
NH_4^+ (T_d)	0.592	−0.021								0.880−						0.470+
NH_3Li^+ (C_{3v})	0.615	−0.042	−0.013	0.336	0.318	0.018				0.949−			0.783+	0.799+	0.016−[a]	0.389+
$NH_2Li_2^+$ (C_{2v})	0.589	−0.062	−0.028	0.430			−0.167			0.999−			0.690+			0.310+
planar (C_{2v})	0.584	−0.036	−0.058	0.375	0.263	0.112	0.066	0.045	0.021	1.068−	1.276−	0.208+	0.714+	0.818+	0.104−	0.320+
$NHLi_3^+$ (C_{3v})	0.506		−0.306	0.487			−0.226			0.986−			0.578+			0.250+
NLi_4^+ (T_d)				0.489			−0.132			0.915−			0.479+			
planar (D_{4h})				0.480	0.363	0.117	−0.036	−0.076	0.040	0.903−	1.606−	0.703+	0.476+	0.652+	0.176−	

[a] Degenerate π orbitals are present.

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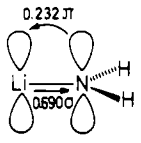
Table IV. Proton and Lithium Cation Affinities (kcal/mol)

	3-21G//3-21G		4-31+G//4-31+G		MP4SDQ/6-311G**//6-31G*[a]		exptl (cor)[b]	
species	H^+	Li^+	H^+	Li^+	H^+	Li^+	H^+	Li^+
NH_3	−226.9	−56.2	−221.0[c]	−48.4[c]	−218.5	−43.3	−213.2[d]	−44.3 ± 2[e]
NH_2Li	−284.6	−79.5	−280.2[c]		−278.5			
$NHLi_2$	−321.0	−96.8						
NLi_3	−331.8	−103.6						
NH_2^-	−462.0	−233.5	−421.3	−190.5			−410.8[f]	
$NHLi^-$	−445.8	−204.4	−439.7	−191.4				
NLi_2^-	−437.2	−202.2	−432.2	−190.0				

[a] Data from Table II. [b] Corrected to the hypothetical vibration-free state at 0 K to correspond to the theoretical data. The indicated corrections are added to the experimental values. See the text, ref 22, and Table II. [c] 4-31G//4-31G. [d] Corrected by −8.6 kcal/mol.[22] [e] Corrected by −4.2 kcal/mol.[6,9b] [f] Corrected by −7.2 kcal/mol. The calculated value at MP2/4-31+G//4-31+G is −408.7 kcal/mol.[14]

cationic species, the lithium atoms have much larger positive charges than the corresponding hydrogen atoms (Table II). This is especially true when the most appropriate comparison, H vs. the σ-Li charges, is made. Coulombic repulsions involving lithiums are more important than those involving hydrogens. The structural consequences, e.g., the greater widening of bond angles involving lithium, are apparent in Figure 1 and will be discussed below.

In contrast to the case for hydrogen, lithium has low-lying vacant p orbitals, which can take part in bonding. Multicenter MO's involving such p orbitals have important consequences, e.g., in planar CH_2Li_2,[10a] in perpendicular $CH_2{=}CLi_2$,[10b] and in triplet CLi^+.[10d] Lithium, acting as a π-electron acceptor, can even become *negatively* charged as is illustrated by the anionic examples in Table II. The π-acceptor ability of lithium is also important in the neutral molecules. While the HOMO of ammonia is the familiar "lone-pair" orbital ($3a_1$, in C_{3v} symmetry),[23] the corresponding orbital in $LiNH_2$ benefits from participation of the Li p orbital perpendicular to the molecular plane (I). The Li p coefficients, although smaller than the N p coefficients, are significant. The Mulliken population analysis (Table III) provides details. In planar $LiNH_2$, 0.232e is transferred from the nitrogen lone-pair p orbital to the lithium p orbital. The resulting π overlap population, 0.21, is over 30% of the total N–Li overlap population. This confirms earlier interpretations[7a,c,10] but contrasts with the conclusion, based on projection function analysis, of another group[7b] that lithium p orbitals play essentially no role.



I

However, we agree that the partial ionic character of lithium bonds contributes significantly to the preferred geometries. Thus, σ donation from Li to the NH_2 group in $LiNH_2$ (0.690e) increases the occupancy of the nitrogen s orbitals and favors the planar geometry. The bonding in lithium compounds thus reflects an interplay among several effects which sometimes reinforce and sometimes oppose one another. Thus, in $LiNH_2$, lithium donates 0.690 σ electron, but this is partially compensated by the receipt ("back-donation") of 0.232 π electron from nitrogen (I). A total charge on Li of 0.458+ results.

While the ammonium ion is written with the formal positive charge on nitrogen, H_4N^+, the Mulliken populations (Table III) indicate nitrogen to have nearly a full *negative* charge. Each hydrogen therefore has about half of a positive charge. That the positive charge in NH_4^+ should reside completely on the hydrogens is perfectly reasonable in view of the electronegativities. Interestingly, the charge distribution in NH_4^+ and in NLi_4^+ are indicated to be similar, despite the greater electropositive character of lithium vs. that of hydrogen. In general, the total charges on nitrogen (Table III) do not vary as much as the component charges, σ and π. This illustrates the compensating effect of back-bonding involving lithium.

Geometries. While ammonia is pyramidal with an experimental inversion barrier of 5.8 kcal/mol,[24] $LiNH_2$, Li_2NH, and Li_3N are indicated to be planar at all theoretical levels employed. While both 3-21G and 4-31+G bases underestimate the inversion barrier of ammonia, the 6-31G* basis reproduces the experimental value reasonably well (Table I); $LiNH_2$ is also planar at this level.[17] Earlier studies have come to the same conclusion.[7,8] As for $LiNH_2$ the planarity of Li_2NH and Li_3N can also be attributed to both σ and π effects, as in I. In ammonia, planarity is favored by better overlap in the 1e orbitals, but the energy of the lone-pair ($3a_1$) orbital is reduced greatly by the gain in s character upon pyramidalization and this effect dominates. In the lithiated ammonias, valence orbitals of the same general symmetry are occupied, but the s contributions are greater. It is well-known that electropositive substituents will reduce or eliminate the ammonia inversion barrier.[25] Compare the PH_3 and PLi_3 barriers, 34.4 vs. 2.2 kcal/mol, respectively.[26]

The most remarkable geometrical changes due to lithium substitution are found in the anions. The amide ion, NH_2^-, isoelectronic with water, is calculated to be strongly bent (Figure 1). The linearization energy, most reliably given with the 4-31+G basis set, is 29.6 kcal/mol, about the same value calculated for water. In contrast, the monolithiated amide ion, $LiNH^-$, like the isoelectronic LiOH,[7,17] is found to prefer a linear arrangement. However, Li_2N^- favors a *bent* over a linear geometry by 12.1 kcal/mol (4-31+G); the isoelectronic Li_2O is indicated to be linear in accord with Walsh's rules for eight-valence-electron AB_2 systems.[27] What are the reasons for these preferences?

The structures of AH_2 molecules provide textbook examples of the use of Walsh diagram arguments.[27,28] Linear and bent NH_2^- forms conform to expectations. Due to better overlap in the $1\sigma_u$ orbital (II), the N–H bonds are shorter (Figure 1) and have larger overlap populations (Table III) in the linear

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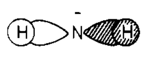
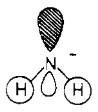


II



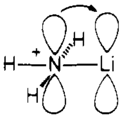
III

geometry. However, the energy of one of the nonbonding degenerate π orbitals in the linear form is reduced greatly by bending; the resulting 3a MO has more s and some bonding character (III). Bending in AH_2 molecules is favored by more electropositive central atoms.[28] In HAB or AB_2 systems, electropositive substituents, B, tend to give widened angles. In linear $Li-N-H^-$, the degenerate π orbitals are bonding due to the availability of p orbitals on lithium. The resulting multiple-bond character is reflected in the exceptionally short N-Li distance and the large total N-Li overlap population (Table III). Walsh predicted that HAB and AB_2 systems with eight valence electrons would be linear.[27] Why then is Li_2N^- bent? In contrast to the case for NH_2^-, bending results in *lowering* of the energy of the $1b_1$ (π) orbital.

The positive charge distribution, Li > H, results in the widening of the LiNH bond angle in $LiNH_2$ and the LiNLi bond angle in Li_2NH from the idealized 120° values. The LiNLi angle widening in Li_2NH occurs despite the three-center (Li_2N) π bonding, which would, in itself, favor a smaller angle. The overlap populations (Table III) confirm this analysis. Similar repulsive interactions and widened bond angles are found in $LiNH_3^+$ ($\angle LiNH = 111°$, 3-21G) as well as in $Li_2NH_2^+$ and Li_3NH^+ ($\angle LiNLi = 123$ and $115°$, respectively). The energetic consequences of these repulsive interactions are discussed below.

While the N-Li bond lengths are nearly constant (1.735 ± 0.02 Å) in the neutral species, there is a regular decrease in r_{N-Li} with increasing Li substitution in the ammonium cations (i.e., from 1.945 Å in NH_3Li^+ to 1.800 Å in NLi_4^+, Figure 1). With the exception of the decrease in the NH bond length in going from NH_4^+ to NH_3Li^+, there is a regular lengthening of the N-H distances with increasing Li substitutions in the neutral and cationic species. The Mulliken overlap populations (Table III) reflect these trends consistently.

Planar Tetracoordinate Nitrogen. Lithium substitution has a remarkable effect in reducing the tetrahedral-planar energy difference of tetracoordinate carbon compounds.[10a] Table V presents a summary of updated results for the series CLi_nH_{4-n} at two geometry-optimized split valence basis set levels (3-21G and 4-31G/5-21G). CH_2Li_2, $CHLi_3$, and CLi_4 are indicated to have low barriers toward planar inversion. The effects responsible are related to those resulting in the planar preferences of NH_2Li, $NHLi_2$, and NLi_3. The HOMO of planar tetracoordinate methane is a p orbital perpendicular to the molecular plane. π-Acceptor-σ-donor substituents like lithium stabilize this form preferentially (see IV for planar NH_3Li^+; compare I).[10a] The tetrahedral-planar energy difference for NH_4^+ (126 kcal/mol, MP2/6-31G*//6-31G*) is reduced by 34 kcal/mol relative to the value for CH_4 (160 kcal/mol).[29] If lithium substitution were as effective in stabilizing planar tetracoordinate nitrogen as with carbon, some of the lithiated ammonium ions might actually prefer planar structures! Although the effects of Li are dramatic, this is not indicated to be the case.



IV

We examined planar forms of $NH_2Li_2^+$ (cis, C_{2v}) and NLi_4^+ (D_{4h}). The energies of both are unfavorable relative to those of the "tetrahedral" alternatives. At 3-21G//3-21G, the differences are 28.8 and 25.9 kcal/mol, respectively (Table I). These are larger than the corresponding values for CH_2Li_2 (7.5) and CLi_4 (14.4 kcal/mol) (Table V). Due to the greater electronegativity of positive nitrogen relative to that of carbon, π delocalization in planar lithiated ammonium ions is not as effective as in the lithiated methanes. This is shown by the relatively small π populations of lithium in planar $NH_2Li_2^+$ and NLi_4^+ (Table III).

Disproportionation Energies. Disproportionation reactions are among the several ways the energies of these species can be analyzed. Is polylithiation thermodynamically favorable? As is illustrated by the isodesmic reactions eq 1-3 (3-21G//3-21G energies), the lithium atoms prefer to be in different nitrogen molecules rather than together in the same species, charged or neutral. This corresponds generally with chemical experience: $LiNH_2$ gives Li_2NH and Li_3N only on pyrolysis whereby NH_3 is lost.[4] In the cations, where the disproportionation energies are particularly large, the magnitudes are greater when more lithiums are present. Compare eq 1 with eq 4-6.

$$NH_2Li_2^+ + NH_4^+ \rightarrow 2NH_3Li^+ \quad -34.3\ \text{kcal/mol} \quad (1)$$

$$NHLi_2 + NH_3 \rightarrow 2NH_2Li \quad -13.0\ \text{kcal/mol} \quad (2)$$

$$NLi_2^- + NH_2^- \rightarrow 2NHLi^- \quad -8.3\ \text{kcal/mol} \quad (3)$$

$$NHLi_3^+ + NH_4^+ \rightarrow NH_2Li_2^+ + NH_3Li^+ \quad -53.4\ \text{kcal/mol} \quad (4)$$

$$NLi_4^+ + NH_4^+ \rightarrow NHLi_3^+ + NH_3Li^+ \quad -57.3\ \text{kcal/mol} \quad (5)$$

$$NLi_4^+ + NH_4^+ \rightarrow 2NH_2Li_2^+ \quad -76.5\ \text{kcal/mol} \quad (6)$$

In the lithiated amines, this is not found. Compare eq 2 and 7.

$$NLi_3 + NH_3 \rightarrow NHLi_2 + NH_2Li \quad -6.2\ \text{kcal/mol} \quad (7)$$

The corresponding carbon compounds, the lithiated methanes, behave quite differently. With the exception of CH_2Li_2 (eq 8) polylithiation is *favored* thermodynamically (eq 9-11; 3-21G//3-21G energies from Table V).

$$CH_2Li_2 + CH_4 \rightarrow 2CH_3Li \quad -2.1\ \text{kcal/mol} \quad (8)$$

$$CHLi_3 + CH_4 \rightarrow CH_2Li_2 + CH_3Li \quad +11.0\ \text{kcal/mol} \quad (9)$$

$$CLi_4 + CH_4 \rightarrow CHLi_3 + CH_3Li \quad +23.9\ \text{kcal/mol} \quad (10)$$

$$CLi_4 + CH_4 \rightarrow 2CH_2Li_2 \quad +36.9\ \text{kcal/mol} \quad (11)$$

This variation in behavior is chiefly due to the electronegativity of the central atom and the overall charge. In the ammonium ions and the amines, the positive charge resides on lithium to a greater extent than on hydrogen (Table III). The magnitudes of the charges on these atoms are greater in the ammonium ions than in the neutral amines, and the repulsive effects leading to destabilization of polylithiated species also are greater (compare eq 1 and 4-6 with eq 2 and 7).

Because the electronegativity of carbon is less than that of nitrogen, the charges on lithium in the polylithiated methanes are lower than in the lithiated amines; less repulsion results.

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Table V. Lithiated Singlet Methanes: Absolute and Relative Energies[a]

	3-21G//3-21G[b]		4-31G(5-21G)//4-31G(5-21G)[c]	
species	"tetrahedral"	planar	"tetrahedral"	planar
CH_4, T_d vs. D_{4h}	−39.97688 (0.0)	−39.70558 (170.2)	−40.13977 (0.0)	−39.87147 (168.4)[c]
CH_3Li, C_{3v} vs. C_{2v}	−46.75248 (0.0)	−46.69307 (37.3)	−46.96000 (0.0)	−46.89858 (38.5)
CH_2Li_2, C_{2v} vs. C_{2v}	−53.52480 (0.0)	−53.51281 (7.5)[d]	−53.77541 (0.0)	−53.76246 (8.1)[d]
$CHLi_3$, C_{3v} vs. C_{2v}	−60.31791 (0.0)[e]	−60.30976 (5.1)[e]	−60.61063 (0.0)	−60.59682 (8.7)[c]
CLi_4, T_d vs. D_{4h}	−67.13154 (0.0)[e]	−67.10864 (14.4)	−67.46685 (0.0)	−67.44124 (16.1)

[a] Absolute energies in hartrees; relative energies (in parentheses) in kcal/mol. [b] Unless otherwise noted, from ref 17. [c] Further optimization from 4-31G//STO-3G data in ref 10a. We thank J. Chandrasekhar and B. Tidor for some of these calculations. [d] Cis form. [e] This work.

At the same time, attractive interactions among lithium tend to increase the overall stabilization of the polylithiated species. While the Li–Li overlap populations in CH_2Li_2 (as in the polylithiated amines and ammonium ions) are repulsive, attractive interactions are indicated to be increasingly important in $CHLi_3$ and CLi_4.[30] The same trend with increasing substitution (toward less Li–Li repulsion) is found in going from $NHLi_2$ to NLi_3 and along the series $NH_2Li_2^+$, $NHLi_3^+$, NLi_4^+ (Table III). The total effect, of course, is also influenced by the number of Li–Li interactions, which increase with polylithiation.

We can conclude that the charge effect favors disproportionation to a decreasing extent in going from the ammonium ions to the amines to the methane derivatives. Negative charge also is unfavorable for anionic polysubstitution; NLi_2^- and NH_2^- disproportionate into $NHLi^-$ (eq 3). The isoelectronic oxygen analogues are indicated to behave similarly (eq 12).[17]

$$\begin{gathered} Li_2O + H_2O \rightarrow 2LiOH \\ -21.0\ \text{kcal/mol (3-21G//3-21G);} \\ -19.5 \pm 6.5\ \text{kcal/mol (exptl}^{31}\text{)} \end{gathered} \tag{12}$$

The trend in reaction energies, eq 12 > eq 3, continues, and the disproportionation energy of FLi_2^+ is even more exothermic (eq 13).[17,32] Like Li_2O, but in contrast to Li_2N^-, Li_2F^+ is linear at 3-21G//3-21G.[17,32]

$$\begin{gathered} Li_2F^+ + FH_2^+ \rightarrow 2LiFH^+ \\ -51.3\ \text{kcal/mol (3-21G//3-21G)} \end{gathered} \tag{13}$$

Proton and Lithium Cation Affinities. The proton affinities (PA) of $NLi_{2-n}H_n^-$ and $NLi_{3-n}H_n^-$ species calculated in the present work are listed in Table IV along with the available experimental estimates for NH_2^- and NH_3. The 3-21G value for NH_3 is in reasonable agreement with experiment; larger basis sets only improve the results marginally.[22] Therefore, it was not considered necessary to carry out larger basis set PA calculations for the other neutral species. Anions are different. With NH_2^-, comparison with the experimental PA shows that the 4-31+G basis set leads to a significant improvement over the 3-21G value. For this reason, results from 4-31+G calculations for the anionic species will be discussed.[14]

The PA values are found to increase proportionally with increasing lithium substitution along the series NH_3, $LiNH_2$, Li_2NH, Li_3N. This is due to the superior ability of Li to stabilize positive charge. The PA for the neutral base, NLi_3, is very large, comparable to that of the *anion*, Cl^-.[5] The 4-31+G/4-31+G PA values increase from NH_2^- to $NHLi^-$ but decrease in going from NHLi to NLi_2^-.

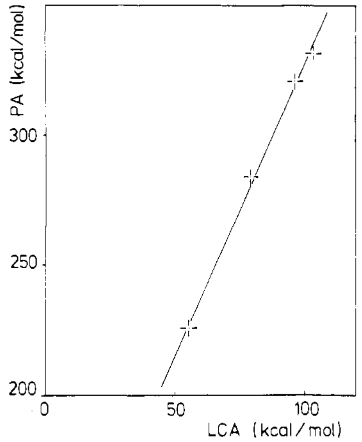

Figure 2. Relationship between proton (PA) and lithium cation (LCA) affinities (3-21G//3-21G).

The lithium cation affinities for the $NLi_{2-n}H_n^-$ and $NLi_{3-n}H_n$ species also are presented in Table IV along with the experimental results available for NH_3. The theoretical result calculated by using the 3-21G basis set is found to be somewhat higher than the experimental value for NH_3, but this is improved with larger basis sets.[9b] The trends in the 3-21G calculated lithium cation affinities along the series NH_3, $LiNH_2$, Li_2NH, Li_3N parallel the PA results (Figure 2). The 4-31+G lithium cation affinities of the anions NH_2^-, $NHLi^-$, and NLi_2^- do not differ significantly and do not fall on the correlation line of Figure 2.

Heats of Formation and Bond Energies. Heats of formation are not provided directly by ab initio calculations but can be evaluated from the calculated energies of appropriate reactions and experimental thermochemical data (listed in Table II).[5,31] Lithium amide illustrates the procedure. The hydrogenation energy (eq 14) is evaluated at the highest theoretical level

$$\begin{gathered} LiNH_2 + H_2 \rightarrow LiH + NH_3 \\ +8.7\ \text{kcal/mol (MP4SDQ/6-311G**);} \\ +3.0\ \text{kcal/mol } (\Delta ZPE) \end{gathered} \tag{14}$$

$$\Delta H_f{}^\circ{}_0(LiNH_2) = 12.6\ \text{kcal/mol}$$

available. The calculated value is then corrected by adding the zero-point energy change (ΔZPE).[33] The experimental $\Delta H_f{}^\circ{}_0$ values for H_2, LiH, and NH_3 (Table II) yield the indicated heat of formation of $LiNH_2$.

Proton affinities (eq 15) and the lithiation reactions (eq 16 and 17) can also be used similary to estimate heats of for-

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[31] Stull, D. R.; Prophet, H., et al. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1971**, *NSRDS-NBS 37*.

[32] The 3-21G//3-21G energy of FLi_2^+ is −113.68188 au: Würthwein, E.-U., unpublished results. For an earlier study of FLi_2^+, see: Rechsteiner, C. E.; Buck, R. P.; Pedersen, L. *J. Chem. Phys.* **1976**, *65*, 1659.

[33] Zero-point energies (listed in Table V) were calculated from available experimental or theoretically derived frequencies or were estimated by analogy. See ref 9b and 22.

$$\begin{gathered} H^+ + NH_2Li \rightarrow NH_3Li^+ \\ -278.5\ \text{kcal/mol};\ +10.3\ \text{kcal/mol}\ (\Delta ZPE) \end{gathered} \tag{15}$$

$$\Delta H_f{}^\circ{}_0(LiNH_2) = 14.9\ \text{kcal/mol}$$

$$\begin{gathered} Li + NH_3 \rightarrow H + LiNH_2 \\ +44.3\ \text{kcal/mol};\ -7.6\ \text{kcal/mol}\ (\Delta ZPE) \end{gathered} \tag{16}$$

$$\Delta H_f{}^\circ{}_0(LiNH_2) = 13.8\ \text{kcal/mol}$$

$$\begin{gathered} Li_2 + NH_3 \rightarrow LiH + LiNH_2 \\ +12.8\ \text{kcal/mol};\ -6.1\ \text{kcal/mol}\ (\Delta ZPE) \end{gathered} \tag{17}$$

$$\Delta H_f{}^\circ{}_0(LiNH_2) = 14.1\ \text{kcal/mol}$$

mation (MP4SDQ/6-3116**//6-316* data). All these evaluations agree quite well: $\Delta H_f{}^\circ{}_0(LiNH_2) = 13.8 \pm 1.2$ kcal/mol. On this basis, the N–Li bond dissociation energy, $D_0(H_2N–Li)$, is 65 ± 4 kcal/mol with use of the experimental data for Li and NH_2 (Table II). However, the latter value has a rather lage uncertainty. Ab initio calculations of bond dissociation energies are expected to underestimate bond energies, because of residual errors in the estimation of electron correlation. Indeed, the MP4SDQ/6-311G**//6-31G* value, $D_e(H_2N–Li) = 64.4$ kcal/mol, after zero-point correction, gives $D_0(H_2N–Li) = 61.7$ kcal/mol. While somewhat lower, this value is within the range of uncertainty given above.

The N–Li bond in NH_2Li is thus indicated to be about 20 kcal/mol stronger than the C–Li bond in CH_3Li, $D_0(H_3C–Li) = 45$ kcal/mol.[30] This also is reflected by the exchange reaction (eq 18; the average C–H bond energy in CH_4 is about

$$\begin{gathered} CH_3Li + NH_3 \rightarrow CH_4 + NH_2Li \\ -29.8\ \text{kcal/mol (3-21G//3-21G)}; \\ -23.4\ \text{kcal/mol (6-31G*//6-31G*)}; \\ \Delta ZPE = 0.1\ \text{kcal/mol} \end{gathered} \tag{18}$$

6 kcal/mol larger than the average N–H bond energy in NH_3). Reactions similar to eq 14–17, the disproportonation reactions (eq 1–7), and the proton and lithium cation affinities (Table IV) can be used to evaluate the heats of formation of the other lithiated species, e.g., $\Delta H_f{}^\circ{}_0(Li_2NH) = 51 \pm 5$ kcal/mol and $\Delta H_f{}^\circ{}_0(Li_3N) = 84 \pm 8$ kcal/mol.

Consistent with the known ability of lithium metal to react with nitrogen, the experimental heat of formation of NLi_3 in the crystal,[31] $\Delta H_f{}^\circ{}_{298}(Li_3N) = -47.2 \pm 1.0$ kcal/mol, is strongly negative. In contrast, the value we estimate for the isolated (gas-phase) species, $\Delta H_f{}^\circ{}_0(Li_3N) = 84 \pm 8$ kcal/mol, is strongly positive. This emphasizes the enormous aggregation energies typically found for lithium compounds (e.g., $\Delta H_f{}^\circ{}_{298}(Li_2O)$ values are −143.1 ± 0.5 (crystal), −132.13 (liquid), and −39.9 ± 2.5 (gas) kcal/mol).[31]

Relationship to NLi_3 in the Solid State. In the solid state, NLi_3 has a remarkable structure: graphite-like sheets of Li hexagons, each with a N in the center, are held together by interstitial Li atoms, one above and one below each nitrogen.[2,34] Nitrogen is thus eight-coordinate. The N–Li distances are 2.13 Å in the hexagons and 1.94 Å to the interstitial lithiums. On the basis of the interpretation of Compton profiles and other evidence, the bonding is considered to be ionic, involving N^{3-} and lithium cations.[2,35]

Our calculations on the NLi_3 monomer indicate a much shorter N–Li distance, 1.74 Å, and relatively little ionic character. The total Mulliken charge on N, 0.781− at 3-21G//3-21G, is even smaller than the charge on N in ammonia, 0.876−, calculated with the same basis set (Table III). Although the larger N–Li distances in solid-state NLi_3 and lattice effects leading to electrostatic stabilization (the aggregation energy is over 130 kcal/mol, see above) may result in enhanced ionic character, it can be questioned whether triply negatively charged nitrogen, N^{3-}, is a reasonable interpretation. The Watson-sphere model[36] used to analyze the X-ray scattering factors[37] as well as the Compton profile[35] of solid-state NLi_3 is oversimplified on two grounds: (a) a spherical rather than a more realistic potential is used to stimulate the lattice, and (b) the virial theorem is not satisfied due to the extra potential assumed in the model.

Conclusions

We stress that these calculations refer to isolated species. The effects of association and solvation, known to be important for lithium compounds, are not considered here but will be discussed in future publications.

The principal conclusions to be gathered from the present study are as follows.

1. Lithium amide, $LiNH_2$, lithium imide, Li_2NH, and lithium nitride, Li_3N, are planar molecules; the σ-donor–π-acceptor character of lithium is responsible. N–Li pπ interactions also are important in the anions, $LiNH^-$ and Li_2N^-. The former is linear as expected by analogy with LiOH. However, Li_2N^- is bent although isoelectronic Li_2O and Li_2F^+ are linear.

2. Although the planar–tetrahedral energy difference is sharply reduced in going from NH_4^+ to $Li_2NH_2^+$ and Li_4N^+, the effect is less than that calculated for the corresponding carbon compounds Li_2CH_2 and Li_4C. Due to the greater electronegativity of nitrogen, π delocalization is less effective in stabilizing the planar tetracoordinate nitrogen forms.[38]

3. Due to the inherent electronegativities, positive charges on lithium tend to be greater than on hydrogen. The resulting Coulombic repulsive effects widen bond angles involving lithium more than those with hydrogen. The proton and lithium cation affinities of the lithiated amines increase with the number of lithiums present, due to the greater ability of lithium to stabilize positive charge.

4. The Li–Li Coulombic repulsive effects are responsible for the instability of the polylithiated nitrogen species toward disproportionation (eq 1–6). Both Li_2O and Li_2F^+ behave similarly (eq 12 and 13), but opposite results are calculated with $CHLi_3$ and CLi_4, which favor the presence of several lithiums in the same molecule (eq 9–11).

5. Although formal positive charges are customarily written on nitrogen in ammonium ions, these atoms are negatively charged due to their greater electronegativity. As shown by the Mulliken populations in Table III, the total negative charge on nitrogen varies little in going from ammonia to the ammonium ion and is similar in most of the other species. As discussed by Greenberg, Liebman, et al.,[39] the positive charges in CH_5^+, NH_4^+, OH_3^+, FH_2^+, etc. all reside on hydrogen; the central atoms are negative.

6. The N–Li bond in $LiNH_2$ is indicated to be about 15 kcal/mol stronger than the C–Li bond in $LiCH_3$.[40] The greater ionic character and a contribution of π N–Li bonding contributes to this difference. Although the magnitude is difficult to assess, N–Li bonds are partially covalent. We

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regard wholly ionic formulations, like $3Li^+\cdot N^{3-}$ for Li_3N, to be exaggerated.

Acknowledgment. This work was supported at Erlangen by the Fonds der Chemischen Industrie and at Pittsburgh by the National Science Foundation (Grant CHE-79-01061) and was facilitated by a NATO Grant as well as an Alexander von Humboldt Fellowship (to K.D.S.) and a special von Humboldt Award (to J.A.P.). Earlier calculations related to this work were carried out by E. D. Jemmis. We also thank J. Liebman for comments.

Registry No. NH_3, 7664-41-7; NH_2Li, 7782-89-0; $NHLi_2$, 12135-01-2; NLi_3, 26134-62-3; NH_2^-, 17655-31-1; $NHLi^-$, 75491-75-7; NLi_2^-, 83560-66-1; NH_4^+, 14798-03-9; NH_3Li^+, 52472-72-7; $NH_2Li_2^+$, 83560-67-2; $NHLi_3^+$, 83560-68-3; NLi_4^+, 83560-69-4; Li^+, 17341-24-1.

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Cyclopentadienyl Bonding in Bis(cyclopentadienyl)neptunium(IV) Compounds from ^{237}Np Mössbauer Spectra[1]

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^{237}Np Mössbauer spectra were measured for a series of Np(IV) compounds of the general compositions NpX_4, NpX_2Y_2, and NpX_2YY' [X = acac, bis(1-pyrazolyl)borate, tris(1-pyrazolyl)borate; Y, Y′ = Cl, Cp, MeCp]. Comparison of the isomer shifts of the Mössbauer spectra showed no evidence for covalent bonding between the Cp ligand and Np(IV) in the Cp_2Np^{IV} and $CpNp^{IV}$ moieties. It is proposed that ligand repulsion in NpX_2Cp_2 and $NpX_2(MeCp)_2$ compounds lengthens the Np(IV)–Cp and Np(IV)–(MeCp) bonds and thus prevents any appreciable Np(IV)–ligand orbital overlap. Mössbauer magnetic splitting and quadrupole splitting parameters are greater for [tris(1-pyrazolyl)borato]neptunium(IV) compounds than for [bis(1-pyrazolyl)borato]neptunium(IV) compounds, a result attributed to the stronger field from the tridentate coordination of the tris(1-pyrazolyl)borate ligand.

Introduction

Previous work has used the isomer shift of the ^{237}Np Mössbauer effect to investigate covalent effects in the bonding of Np(IV) organometallic compounds.[2,3] The isomer shift (δ) of Np(IV) in $NpCl_4$ is −0.35 cm/s; δ for $NpCl_3$ is 3.54 cm/s. Covalency in Np(IV)–ligand bonding changes the isomer shift of a Np(IV) compound toward the 3+ valence shift. For example, the isomer shift of bis(cyclooctatetraenyl)neptunium(IV),[4] the Np(IV) analogue of uranocene,[5] is 1.94 cm/s, which is interpreted to indicate that the cyclooctatetraenyl ligands have contributed electron density to the Np(IV) ion equivalent to one-half that of a 5f valence electron.

The covalent contribution π-cyclopentadienyl (Cp) ligands have been of particular interest in previous work[2,3] because of recent interest in the chemistry of uranium(IV) cyclopentadienyl and uranium(IV) pentamethylcyclopentadienyl (Me_5Cp) compounds.[6-11] Compounds of Np(IV) and U (IV) are normally isostructural and have essentially identical chemical properties except for the tendency of Np(IV) compounds to reduce to Np(III) compounds. Previous work[2,3] has shown that the Cp or MeCp ligands in the Cp_3Np^{IV} moiety contribute covalently to the bonding of Cp_3NpZ (Z = Cl, BH_4, R, OR, Ar). δ for Cp_3NpCl is 1.4 cm/s; δ for $(MeCp)_3NpBH_4$ is 1.45 cm/s. R, OR, and Ar are σ-bonding ligands; their effect on the Np(IV) isomer shift is the opposite of that of the Cp ligand. δ for Cp_3NpBu is 0.27 cm/s, and δ for Cp_3NpO-*i*-Pr is 0.86 cm/s, to be compared with the 1.4 cm/s for Cp_3NpCl.[2a]

Rather than the increased positive δ expected, compared to that of $NpCp_3Cl$, δ for $NpCp_4$ is 0.72 cm/s.[12] This is explained by the crystal structures of the U(IV) analogues—UCp_4 and UCp_3Cl—which show that the U–C(ring) bond lengths in UCp_4 are 0.07 Å longer than the U–C(ring) bond lengths in UCp_3Cl.[13-15] The longer bond length decreases the overlap of Cp and Np(IV) orbitals and is reflected in a smaller isomer shift in $NpCp_4$ than in Cp_3NpCl.[2a]

The object of this work was to use the ^{237}Np Mössbauer effect to investigate the bonding properties of a Cp_2Np^{IV} moiety. The success of a variety of syntheses with the bis(pentamethylcyclopentadienyl)uranium(IV) [$(Me_5Cp)_2U^{IV}$] moiety[9,10] leads to the assumption that the ligand contributes substantial electron density to the U(IV) ion in $(Me_5Cp)_2U^{IV}$ compounds and also the expectation that $(Me_5Cp)_2Np^{IV}$, Cp_2Np^{IV}, and $(MeCp)_2Np^{IV}$ moieties might show a covalent contribution to their bonding.

A report of the preparation of UCp_2Cl_2[16] was later found to have mistaken a mixture of UCp_3Cl and $UCpCl_3L_2$ (L = solvent) for the desired compound.[17,18] Attempts to synthesize $NpCp_2Cl_2$ also yielded a mixture of $NpCp_3Cl$ and $NpCpCl_3\cdot 2THF$.[19] However, the Cp_2U^{IV} moiety can be

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