

## Evidence for Associative Ligand Exchange Processes on Solvated Lithium Cations

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The ligand exchange mechanism of solvated lithium cations has been studied using DFT calculations (RB3LYP/6-311+G\*\*). The water exchange mechanism on  $[\text{Li}(\text{H}_2\text{O})_4]^+$  was found to be limiting associative (A) involving a five-coordinate intermediate, whereas ammonia exchange on  $[\text{Li}(\text{NH}_3)_4]^+$  was found to follow an associative interchange ( $I_a$ ) mechanism. The suggested mechanisms are discussed in reference to available experimental and theoretical data.

Lithium salts are widely used in industrial applications, synthesis, and medicine, e.g., psychiatry.<sup>1</sup> Therefore, detailed knowledge of fundamental reactions of solvated lithium cations, for example ligand exchange reactions in different solvents, is essential. Ligand exchange in water has been studied both experimentally and theoretically for a wide range of metal ions.<sup>2</sup> Mechanistically, associative (A), interchange (I), and dissociative (D) pathways are conceivable. Solvent exchange at  $\text{Li}^+$  in water, however, is extremely fast, making it difficult to study directly. An exchange rate constant of approximately  $10^9 \text{ s}^{-1}$  at 25 °C was predicted on the basis of complex-formation data.<sup>2b,c</sup> Previous theoretical studies focused on the structures of various aqua complexes of  $\text{Li}^+$ .<sup>3</sup> Recently, Hermansson et al. reported evidence for associative water exchange processes for 512 water molecules and one lithium cation in a cubic simulation box by employing the reactive flux method in combination with very long molecular dynamics simulations based on effective three-body

ion–water potentials.<sup>4</sup> According to their results, both the simulation and reactive flux exchange events show that in about 80% of the cases the exchange mechanisms have an associative (A) or an associative interchange ( $I_a$ ) character to almost the same degree. However, only schematic pictures of the exchange mechanisms could be presented, and detailed structures of the transition states involved are not available.

We have now studied the ligand exchange process in more detail and report computational evidence for a limiting associative exchange mechanism on the aquated lithium cation and for an associative interchange mechanism in the case of the tetraammine complex. Structures were fully optimized at B3LYP/6-311+G\*\*<sup>5</sup> and characterized by computation of vibrational frequencies (performance of density functional and basis set is discussed in ref 5d). Single point energy calculations were performed at MP4(full)/6-311+G\*\*//B3LYP/6-311+G\*\*,<sup>6</sup> the influence of bulk solvent was probed using the IPCM formalism<sup>7</sup> and water as solvent, i.e., B3LYP(IPCM)/6-311+G\*\*//B3LYP/6-311+G\*\*. The Gaussian 98 suite of programs was used throughout.<sup>8</sup>

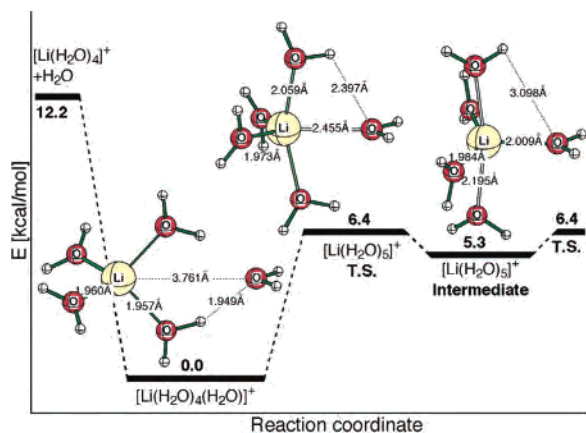
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**Figure 1.** Energy profile for water exchange around the lithium cation (relative energies: B3LYP/6-311+G\*\*).

**Table 1.** Relative Energies (kcal/mol) of the Stationary Points within the Water and Ammonia Exchange Reactions<sup>a</sup>

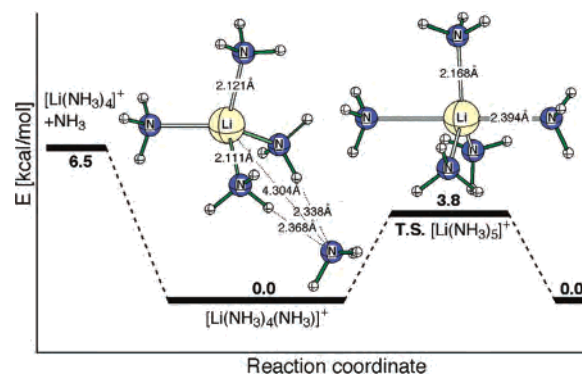
	P.G.	B3LYP	MP4	IPCM	volume
[Li(H <sub>2</sub> O) <sub>4</sub> ] + H <sub>2</sub> O	C <sub>1</sub> /C <sub>2v</sub>	12.2	12.9	4.6	141.4
[Li(H <sub>2</sub> O) <sub>4</sub> (H <sub>2</sub> O)] <sup>+</sup>	C <sub>2</sub>	0.0	0.0	0.0	143.0
T.S. [Li(H <sub>2</sub> O) <sub>5</sub> ] <sup>+</sup>	C <sub>1</sub>	6.4	4.5	6.8	136.3
[Li(H <sub>2</sub> O) <sub>5</sub> ] <sup>+</sup>	C <sub>2</sub>	5.3	2.4	5.1	135.9
[Li(NH <sub>3</sub> ) <sub>4</sub> ] + NH <sub>3</sub>	T <sub>d</sub> /C <sub>3v</sub>	6.5	7.8	-1.0	177.2
[Li(NH <sub>3</sub> ) <sub>4</sub> (NH <sub>3</sub> )] <sup>+</sup>	C <sub>s</sub>	0.0	0.0	0.0	173.4
T.S. [Li(NH <sub>3</sub> ) <sub>5</sub> ] <sup>+</sup>	C <sub>3h</sub>	3.8	3.3	3.9	176.3

<sup>a</sup> Additional details follow: B3LYP, B3LYP/6-311+G\*\*/B3LYP/6-311+G\*\*; MP4, MP4sdtq(full)/6-311+G\*\*/B3LYP/6-311+G\*\*; IPCM, B3LYP(IPCM)/6-311+G\*\*/B3LYP/6-311+G\*\*; energies corrected for ΔZPE//B3LYP/6-311+G\*\*; volume, IPCM solute cavity, Å<sup>3</sup>.

Experimental<sup>9</sup> and theoretical<sup>3</sup> studies agree that the first coordination shell around Li<sup>+</sup> consists of four tightly bound water molecules. The computed Li–O distance is 1.964 Å. Additional solvent molecules do not coordinate to the lithium cation, but instead form a second coordination sphere, with hydrogen bonds to the coordinating water molecules. The gas-phase hydrogen bonding energy for the fifth water molecule in [Li(H<sub>2</sub>O)<sub>4</sub>(H<sub>2</sub>O)]<sup>+</sup> is 12.2 kcal/mol; inclusion of the IPCM solvent model reduces this value to 4.6 kcal/mol. The Li–O distance is 3.76 Å (see Figure 1).

Water exchange proceeds through a trigonal bipyramidal reactive intermediate [Li(H<sub>2</sub>O)<sub>5</sub>]<sup>+</sup> that is reached via a late transition state. The entering water molecule approaches the lithium cation directly, and pushes two coordinated water molecules away toward the axial positions. In line with the experimental observation of a very fast exchange process,<sup>9</sup> the computed activation barrier is only 6.4 kcal/mol, while the five-coordinate intermediate is 5.3 kcal/mol less stable than the precursor complex. The very low barrier toward dissociation of only 1.1 kcal/mol means that the five-coordinate intermediate will be very short-lived. Inclusion of solvent effects at the IPCM/B3LYP/6-311+G\*\* level only results in minor changes in the computed energies (see Table 1).

According to the computed molecular volumes, the intermediate is more compact than the precursor complex



**Figure 2.** Energy profile for ammonia exchange around the lithium cation (relative energies: B3LYP/6-311+G\*\*).

[Li(H<sub>2</sub>O)<sub>4</sub>(H<sub>2</sub>O)]<sup>+</sup>, which clearly indicates a limiting associative substitution mechanism. In general, this finding is in agreement with the conclusion drawn by Hermansson et al.,<sup>4</sup> but the mechanistic details do differ. Their MD simulations predict the entering water molecule to approach the tetrahedral [Li(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup> moiety through a face of the tetrahedron and the reaction to proceed with an S<sub>N</sub>2-like *trans* exchange stereochemistry, i.e., through a trigonal bipyramidal intermediate or transition structure with both the entering and leaving water molecules in axial positions. In contrast, we find that the entering water molecule assumes an equatorial position; i.e., the reaction must proceed with *cis* stereochemistry.

The axial Li–O distances, 2.195 Å, are 0.2 Å longer than the equatorial ones, which might be taken as an indication that one of the axial ligands will be expelled. However, the structure of [Li(H<sub>2</sub>O)<sub>5</sub>]<sup>+</sup> is highly fluxional: the barrier toward pseudorotation (simultaneous movement of two axial ligands to equatorial positions and two equatorial ligands to axial positions) is less than 1 kcal/mol.

Whereas ligand exchange in aqua complexes of Li<sup>+</sup> has been studied extensively, the corresponding ammine complexes have so far received very little attention. Nevertheless, the different complexation properties of NH<sub>3</sub> compared to H<sub>2</sub>O, and the importance of solvated Li<sup>+</sup> in liquid ammonia in organic synthesis, e.g., in the Birch reduction,<sup>10</sup> prompted us to compare the exchange reaction for these solvents.

The interaction of an ammonia molecule (belonging to the second coordination sphere) with [Li(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> is weaker than in the case of water: the interaction energy is 6.5 kcal/mol at B3LYP and virtually zero at B3LYP(IPCM). The structure of [Li(NH<sub>3</sub>)<sub>4</sub>(NH<sub>3</sub>)]<sup>+</sup> shows an interesting feature: instead of one H-bond, as one might expect since nitrogen has only one lone pair, the fifth ammonia molecule forms two long, weak bonds to two different NH<sub>3</sub> ligands in the first coordination sphere (see Figure 2).

Ammonia exchange proceeds with *trans* stereochemistry, very similar to the well-known S<sub>N</sub>2 mechanism. In the five-coordinate, trigonal-bipyramidal transition structure, the entering and leaving ammonia molecules are axial, with

(9) <sup>17</sup>O NMR experiments on water exchange reactions on solvated Li<sup>+</sup> as a function of temperature (5–85 °C) showed no characteristic line-broadening effects, from which it is concluded that water exchange is too fast to be detected by line-broadening techniques.

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rather long Li–N bonds. The three in-plane NH<sub>3</sub> ligands show modestly lengthened bonds of 2.168 Å, whereas the entering or leaving ammonia ligands have bonds elongated to 2.394 Å, typical for an associative interchange mechanism.

The activation barrier is only 3.8 kcal/mol. As in the case of water, the influence of the bulk solvent is negligible (see Table 1). Ammonia exchange at Li<sup>+</sup> thus might be even faster than in the case of water. The molecular volume changes very little; i.e., the transition structure is only slightly larger than the precursor complex. Thus, the exchange is best described as proceeding via an associative interchange mechanism.

We attribute the mechanistic difference between water exchange (associative) and ammonia exchange (associative interchange) on Li<sup>+</sup> to the nature of the Li–O versus Li–N bonds. In the case of water, the fifth ligand is relatively strongly (6.9 kcal/mol) bound, whereas for ammonia the fifth ligand is much more weakly (2.7 kcal/mol) bound to Li<sup>+</sup>. The same energetic order is seen when going from 3 to 4 bound ligands: 15.4 kcal/mol in the case of H<sub>2</sub>O versus 13.7 kcal/mol for NH<sub>3</sub>.<sup>11</sup> This is in line with qualitative expectations based on size and electronegativity: H<sub>2</sub>O is smaller

(IPCM: 29.3 Å<sup>3</sup>) than NH<sub>3</sub> (36.5 Å<sup>3</sup>); O is more electronegative than N.<sup>12</sup>

In conclusion, the mechanism of water exchange around the lithium cation can be considered a borderline case between associative and associative interchange, in accord with the conclusions of Hermansson et al.<sup>4</sup> In the ammine case, we find strong indications of an associative interchange mechanism.

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