

Supplementary material

Synthesis

All steps of the synthesis are executed under exclusion of air and humidity in an atmosphere of protective gas. For the preparation of $[\text{Li}(\text{NH}_3)_4]_2\text{B}_6\text{H}_6 \cdot 2 \text{NH}_3$, 0.092 g of dried $[\text{N}(\text{C}_4\text{H}_9)_4]\text{B}_6\text{H}_7$ (1.6 mmol) and 0.012 g of distilled lithium (1.6 mmol) were put in a Schlenk vessel, and approximately 20 mL dried ammonia were condensed at -78°C . This resulted in a deep-blue solution. After 10 days at -38°C , colourless, air- and temperature sensitive cubic crystals were obtained.

Computational Details

For all calculations the Gaussian03 [ref#1] program system has been used. For calculations of energies and gradients the Møller-Plesset perturbation theory 2nd order (MP2) [ref#2] has been employed and the standard basis set 6-311+G(2d,2p) [ref#3] has been used for all atoms. For calculations of the anion $[\text{B}_6\text{H}_6]^{2-}$ and the contact ion pair $[(\text{Li}(\text{NH}_3)_4)]^+_2[\text{B}_6\text{H}_6]^{2-}$ the initial coordinates have been taken from X-ray structure analysis data without symmetry constraints and were fully optimized. Calculations of bond critical points and topological analysis have been performed using the AIM2000 program. [ref#4]

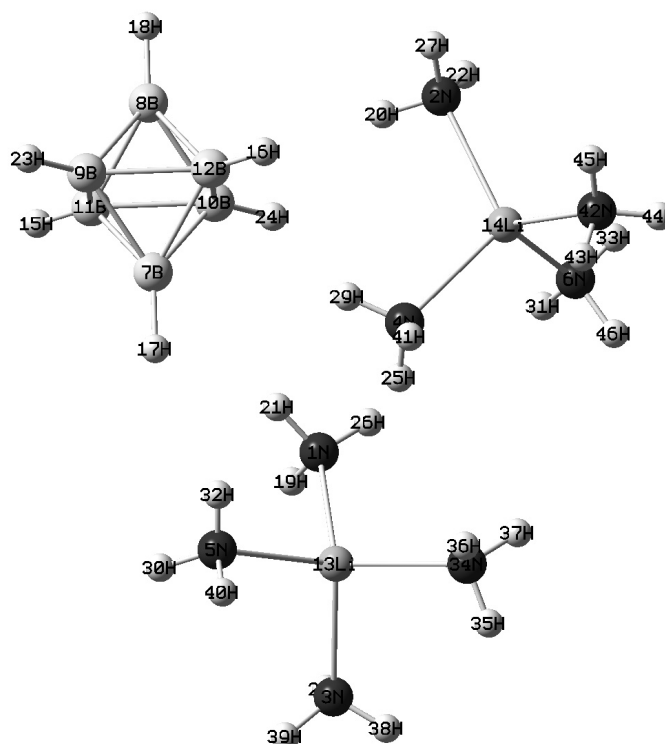


Figure1: Graphical representation of the optimized structure of the contact ion pair $[(\text{Li}(\text{NH}_3)_4)]^+_2[\text{B}_6\text{H}_6]^{2-}$.

[ref#1] Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.

[ref#2] C. Møller and M. S. Plesset, *Phys. Rev.* **46**, 618 (1934).

[ref#3] R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.* **54**, 724 (1971).

[ref#4] F. Biegler-König, J. Schönbohm, AIM2000 - A program to Analyze and Visualize Atoms in Molecules, Vers. 2, Bielefeld (Germany) 2002.