Supporting information for

Li$_2$B$_{12}$H$_{12}$·7NH$_3$: a new ammine complex for ammonia storage or indirect hydrogen storage

Zhenguof Huang, $^a$ Judith Gallucci, $^b$ Xuenian Chen, $^b$ Teshome Yisgedu, $^a$ Hima Kumar Lingam, $^a$ Sheldon Shore $^b$ and Ji-Cheng Zhao $^a$

$^a$ Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43210, USA
$^b$ Department of Chemistry, The Ohio State University, Columbus, OH, 43210, USA
E-mail: zhao.199@osu.edu
Experimental Section

General Procedures

All syntheses and ammonia charge and discharge were performed in a standard high-vacuum line and a glove box filled with high purity nitrogen unless otherwise stated. Tetrahydrofuran (THF) was dried over sodium/benzophenone and freshly distilled prior to use. Ammonia (Matheson) was distilled from sodium immediately prior to use. NMR spectra were recorded on a Bruker AM-250 spectrometer. $^{11}$B NMR spectra were obtained at 80.3 MHz and externally referenced to BF$_3$·OEt$_2$ in C$_6$D$_6$ at 0.00 ppm. Infrared (IR) spectra were recorded from Bruker Tensor 27 Fourier-transform spectrometer with 2 cm$^{-1}$ resolution. Sample powder was mixed with IR grade mineral oil.

X-ray single crystal diffraction data were collected on a Nonius Kappa CCD diffractometer, which employs graphite-monochromated Mo K$\alpha$ radiation ($\lambda=0.71073$ Å). Due to the sensitivity of the compound, single crystals were picked up from the mother liquid in a glove box and stored in Fomblin oil until just before data collection. A single crystal coated with Fomblin oil was mounted on the tip of a glass fiber. Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined by employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the DENZO-SMN package.$^1$ Absorption correction for the structure was accounted for by using SCALEPACK.$^1$ The structure was solved by direct method using the SHELXTL-97 (full-matrix least-squares refinements) structure solution package.$^2$ All nonhydrogen atoms were located and refined anisotropically. Hydrogen atoms on boron cage were located and refined isotropically, and other hydrogen atom positions were calculated assuming standard geometries.

The determination of the unit cell was not straightforward. Initially an orthorhombic unit cell was conjectured with a cell volume four times the size of the correct monoclinic unit cell. As structure solution proved to be difficult with this cell, a different method of unit
cell determination was tried. A primitive monoclinic cell was obtained by Dirax, which is the unit cell reported here. The data set was reintegrated with this cell and the structure was easily solved. However, refinement of the structure was problematic with a large R factor of around 13% and a large peak in the final difference map of about 1.3 e/Å³ for the complete model, i.e., all non-hydrogen atoms refined anisotropically and all of the hydrogen atoms included. These are signs of a twinned structure and Rotax was then used to obtain a twin law which resolved these problems. The twin law which corresponds to a 180° rotation about the [-1 0 1] direct lattice direction: (-1/2 0 -1/2 / 0 -1 0 / -3/2 0 1/2) was applied to the data set to create an HKLF5 file using WinGX. This is a non-merohedral twin law, as either a reflection and its twin component are exactly overlapped or there is no overlap at all. There are no partially overlapped reflections. The twin fraction refined to a value of 0.799(2).

X-ray powder diffraction data were collected on a Bruker D8 Advance X-ray powder diffractometer at room temperature, which employs a Ge 111 Vario monochromator at the X-ray tube with Cu Kα1 radiation (λ = 1.5406 Å). Due to the sensitivity to air and moisture, samples were ground and loaded into 1 mm Lindeman glass capillaries in an argon glove box. The scanning rate is 2 °/s with a step size of 0.017298°. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA 7 analyzer. Powder was loaded onto a quartz crucible and heated to 400 °C at a heating rate of 5 °C/min under an Ar flow of 40 cm³/min. Decomposition was also measured using Mettler Toledo high-pressure Differential Scanning Calorimeter (DSC27HP) in an argon glove box with a ramp rate of 1 °C/min, 5 °C/min and 10 °C/min.

Preparation of anhydrous Li₂B₁₂H₁₂
Heptahydrated lithium dodecahydro-closo-dodecaboratecloso-dodecaborates was prepared according to the published method. (H₅O)₂[B₁₂H₁₂] was produced by passing aqueous solution Cs₂B₁₂H₁₂ (BASF) over a strong acidic cation exchange resin (Dowex-50 WX 8). The diluted acidic solution was then neutralized with lithium hydroxide. After
evaporation of the solution to dryness, the powder was heated to 200 °C for 4 hours under dynamic vacuum to get anhydrous Li$_2$B$_{12}$H$_{12}$.\(^7\)

**Preparation of Li$_2$B$_{12}$H$_{12}$\(\cdot\)7NH$_3$**

This compound was obtained by charging anhydrous Li$_2$B$_{12}$H$_{12}$ with either dry gaseous ammonia at room temperature or dry liquid ammonia at -78 °C. For the room temperature reaction, Li$_2$B$_{12}$H$_{12}$ powder was soaked under 0.5 bar dry ammonia for 1 hour. For the reaction at -78 °C, Li$_2$B$_{12}$H$_{12}$ powder was soaked in liquid ammonia and magnetically stirred for 1 hour. A mixture of dry ice/isopropanol was used to maintain the temperature. In a glove box, the Li$_2$B$_{12}$H$_{12}$\(\cdot\)7NH$_3$ powder was dissolved in dry THF. Filtration of the solution through Celite on a frit afforded a colorless filtrate. Within 1-2 days at room temperature without disturbance, thin plate-shaped colorless crystals were produced.

**NMR analysis**

![NMR spectra](image)

Fig. 1. $^{11}$B NMR spectra in THF solution after 3$^{rd}$ cycle desorption. a. $^1$H coupled, b $^1$H decoupled.

The chemical shift (-15.6 ppm) of the compound in THF is in good agreement with literature,$^8$ which also indicates that the structure of the dodecahydro-closododecaborate is intact after three cycles of charging and discharging. This result corroborates the
unique high thermal stability of dodecahydro-closo-dodecaborate $[\text{B}_{12}\text{H}_{12}]^{2-}$ in boron hydride chemistry.\textsuperscript{9}

PXRD of Li$_2$B$_{12}$H$_{12}$·7NH$_3$ heated at 370 °C.

![X-ray powder diffraction pattern of Li$_2$B$_{12}$H$_{12}$·7NH$_3$ heated to 370 °C. Sample was loaded into a capillary and sealed in a glove box.](image)

After Li$_2$B$_{12}$H$_{12}$·7NH$_3$ was heated to 370 °C, a phase different from the parent Li$_2$B$_{12}$H$_{12}$ was found as indicated by the XRD pattern (Fig. 2). This is consistent with the DSC result, where an endothermic peak appears at 350 °C.

Notes and references


