Synthesis and Characterization of a New Ternary Imide—Li$_2$Ca(NH)$_2$

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Received May 6, 2006

The ternary imide Li$_2$Ca(NH)$_2$ was successfully synthesized by dehydrogenating a mixture of LiNH$_2$ and CaH$_2$ at a molar ratio of 2:1 in a stream of purified argon at 300 °C. A powder X-ray diffraction measurement revealed that Li$_2$Ca(NH)$_2$ was of the trigonal anti-La$_2$O$_3$ structure (space group P3m1) with lattice constants of $a = 3.5664(3)$ Å and $c = 5.9540(8)$ Å. Ca occupied the 1b site (0, 0, 1/2), Li occupied the 2d site (1/3, 2/3, 0.8841(22)), and N occupied the 2d site (1/3, 2/3, 0.2565(15)). Nuclear magnetic resonance and X-ray absorption fine structure analyses demonstrated that each Li ion was coordinated with four imide ions and each Ca ion was coordinated with six imide ions.

Introduction

Binary nitrides, amides, and imides of various metals and nonmetals have been well studied by Juza and co-workers since the 1920s.1 These compounds have many interesting properties that make them attractive for technological applications. Binary nitrides (e.g., GaN, InN, AlN, BN, and TiN) have a number of applications in the microelectronic, optoelectronic, abrasion, and corrosion protection industries.2,3 Nonmetals have been well studied by Juza and co-workers since the 1920s.1 These compounds have many interesting properties that make them attractive for technological applications. Binary amides, such as lithium and sodium amides, are widely used as deprotonating agents in organic synthesis.4 Recently, lithium nitride and lithium imide were found to exhibit strong affinity to H$_2$, which enable them to be potential candidates for hydrogen storage.5,6 Rapid growth in nitride chemistry occurred in the last decades owing to the improved classification of nitride crystal chemistry and the development of new synthetic techniques, leading to the discovery of a wide range of new ternary compounds with diverse crystal structures and interesting physical properties.1-4 Recent investigations on synthesis methods, structures, and properties of ternary and higher nitrides were summarized by Gregory and Niewa et al., respectively.2-4 However, research in ternary and higher inorganic imides is rare. It was only in recent years that ternary imides containing both an alkaline metal and an alkaline earth metal were synthesized and investigated.5,9 As an example, Li$_3$Mg(NH)$_2$ can be synthesized by reacting LiNH$_2$ with MgH$_2$ at elevated temperatures.5,9 Synchrotron X-ray diffraction (XRD) and neutron diffraction measurements reveal that Li$_3$Mg(NH)$_2$ possesses three different crystal structures depending on the synthesis temperature.10 A similar synthetic route was applied to the Li—Ca—N—H system, but little attention was paid to its structural identification and chemical properties.8 If the structure of Li$_2$Ca(NH)$_2$ is determined, the physical and chemical properties of this new ternary imide can be well predicted and understood by theoretical means.11,12

Systematic studies of amides and imides were performed by Juza et al., Jacobs and Schmidt, and Rouxel et al. previously.13-17 Normally, imides (e.g., Li$_2$NH, CaNH, and BaNH) are prepared by heating amides under vacuum.13-15

(10) Zhao, J. C. Phase formation and reaction pathway of Mg(NH)$_2$+2LiH mixture for reversible hydrogen storage. Presented at the International Partnership for the Hydrogen Economy, Jucca, Italy, June 19-22.
However, because of the lack of ternary amides, few ternary imides have been synthesized and reported in the literature. 13–17 The novel synthetic route involving reaction of a binary amide with a hydride under appropriate conditions has proven to be a viable method for making a variety of novel ternary imides. 8,9 In this paper, the synthetic approach mentioned above was applied to the preparation of the ternary imide of Li2Ca(NH)2. The synthesis was carried out at relatively low temperatures because of the poor thermal stability of Li2Ca(NH)2. As a consequence, only microcrystalline imides may be obtained. Determination of the structure merely by powder XRD alone may not be sufficiently accurate. Therefore, combined characterizations by means of XRD, vibrational spectra, X-ray absorption spectra, and nuclear magnetic resonance (NMR) were performed to acquire structural information on both the bulk and the atomic scales with the intention of obtaining a better understanding of the composition, structure, and properties of Li2Ca(NH)2.

Experimental Section

Preparation of Li2Ca(NH)2. LiNH2 and CaH2 were synthesized by reacting metallic Li (99.9%, Aldrich Chemicals) with ammonia (99.98%, BOC Gases) and by reacting metallic Ca (99.9%, Aldrich Chemicals) with hydrogen (99.99%, National Oxygen), respectively. LiNH2 and CaH2 at a molar ratio of 2:1 were thoroughly mixed by a SPEX 8000M mixer/mill. Li2Ca(NH)2 was synthesized by heating the post-milled mixture in a flow of purified argon from room temperature to 300 °C at a ramping rate of 1 °C/min. Gaseous products were analyzed by an on-line HPR20 mass spectrometer (MS) in tandem with a gas chromatograph (GC). For the quantitative analysis of ammonia, gaseous products were slowly introduced to distilled water. A Metrohm 781 pH/ion meter equipped with an NH3-selective electrode was used to detect the concentration of ammonia in distilled water. A quantitative measurement of hydrogen desorption was conducted in a commercial pressure composition isotherm (PCI) unit from Advanced Materials Corporation.

Structure Determination. XRD data were collected using a BRUKER D8 Advance X-ray diffractometer with Cu Kα radiation at a power of 40 kV × 40 mA. Stepwise scans were performed in the 20 range of 10°–90° at steps of 0.05°. The obtained data were indexed using the TREOR or DICVOL program. Lattice parameters were refined by a least-squares refinement method using the Rietica program.18

N–H vibration was recorded using a Perkin-Elmer Fourier transform infrared (FTIR) spectroscopy 2000 spectrometer equipped with a diffuse reflectance infrared Fourier transform (DRIFT) cell. The scan range was 400–4000 cm−1, and the resolution was 4 cm−1.

Transmission X-ray absorption fine structure (XAFS) spectra were collected in the vicinity of the Ca K edge (4.038 keV) at room temperature at the XDD beamline of the Singapore Synchrotron Light Source (SSLS, Singapore).19 Each sample was ground and mixed with LiF powder (99%, Fluka) at a weight ratio of 1:10. The mixture was pressed into a pellet under a pressure of 2.5 tons and then coated with solid wax in the glovebox to avoid air contamination during XAFS measurements. The sample thickness was adjusted to achieve the X-ray absorption edge jump of approximately one for each sample.

Analysis of the XAFS data followed the standard procedures using the WINXAS code.20 After normalization, transformation from energy space to momentum (k) space, and extraction of the background absorption were carried out, the γ(k) function was extracted in the range of 2.2–9.2 Å−1 and weighted by k4. Fourier transform of k4γ(k) into R space was performed using the Bessel function. The data fit of the first coordination shell was performed using CaNH as the reference.

6Li magic-angle spinning (MAS) NMR measurements were carried out at room temperature in a Bruker Advance 400 spectrometer with a 4 mm broadband cross-polarization (CP)/MAS probe operating at a 6Li frequency of 58.8 MHz. Each sample was packed in a zirconia rotor with a Kel-F cap and rotated at a rotor-spinning rate of 10 kHz. Chemical shifts were reported with respect to a 1 M LiCl aqueous solution. The peaks in the NMR spectra were fitted to obtain the values of the full width at half-maximum and chemical shift.

As the starting materials and products were sensitive to air, all sample loadings were performed in an MBRAUN glovebox. The glovebox was filled with purified argon gas. Water and oxygen concentrations were below 10 ppm.

Results and Discussion

Temperature programmed desorption (TPD) of the post-milled 2LiNH2 + CaH2 sample was performed by using purified argon as a carrier gas. The temperature was raised from room temperature to 300 °C at a ramping rate of 1 °C/min. The sample (100.2 mg) was loaded, and plots of temperature versus the mass spectrometer signals of the outlet gas were obtained (Figure 1a). Ammonia was undetectable by MS during the whole testing period, indicating that the amount of coproduced ammonia was negligible. Notably, the

Figure 1. TPD (a) and volumetric release (b) measurements on the post-milled 2LiNH2—CaH2 samples.
NH₃ concentration in the desorbed hydrogen was below 100 ppm according to the amount of ammonia detected by the Metrohm 781 pH/ion meter. Hydrogen appeared at temperatures above 50 °C and peaked at 140 °C and 206 °C. After the dehydrogenation, 95.7 mg of the solid residue was obtained, indicating a release of 4.5 mg of hydrogen which was equivalent to ~4.0 H atoms per 2LiNH₂ + CaH₂. Volumetric measurement of the amount of hydrogen desorbed during the thermal treatment also gave a similar result. As shown in Figure 1b, about 4.3 wt % of hydrogen was absorbed during the thermal treatment also gave a similar result. Volumetric measurement of the amount of hydrogen desorbed during the thermal treatment also gave a similar result. As shown in Figure 1b, about 4.3 wt % of hydrogen was absorbed during the thermal treatment also gave a similar result.

Because the scattering factor of hydrogen is very small compared to those of the other elements, hydrogen has little effect on XRD and can therefore be neglected. In order to locate hydrogen, neutron diffraction of a deuterium-substituted sample should be performed. Li⁺, Ca²⁺, and N³⁻ positions in the initial model for Rietveld refinement were derived from published structures of ternary nitrides. Ternary lithium nitrides can be divided mainly into two groups, that is, those with anti-fluorite type crystal structures represented by a general formula Li₂⁻N₃⁻M⁺⁻N₆⁻⁻⁻(n ≥ 2) and those with the anti-La₂O₃ type structure represented by a general formula Li₂MN₂. As evidenced by the indexing result of the TREOR program, Li₂Ca(NH)₂ should possess the anti-La₂O₃ type structure, which belongs to the hexagonal structural. CaMg₂N₂ (JCPDS-ICDD card no. 83-0042)²¹ has the anti-La₂O₃ type structure with lattice constants of a = 3.5405 Å and c = 6.0908 Å. Since the ionic radii of Li⁺ and Mg²⁺ are almost identical (0.68 and 0.67 Å),²² the structure of CaMg₂N₂ was adopted as the starting model to study Li₂Ca(NH)₂, wherein Mg²⁺ was substituted by Li⁺. The experimental powder XRD pattern of Li₂Ca(NH)₂ was in excellent agreement with the calculated pattern derived from the starting model (Figure 2), which implied that the structural model adopted in the present simulation was reasonable and acceptable. A series of parameters, including background, zero shift, scale, lattice parameter, graphic parameter (U, V, W), and Li and N coordinates, were refined by the Rietica program (Table 1). Li₂Ca(NH)₂ belongs to the space group P3m1 with lattice constants of a = 3.566(4) Å and c = 5.9540(8) Å. Ca occupies the 1b site (0, 0, 1/2), Li occupies the 2d site (1/3, 2/3, 0.3841(22)), and N occupies the 2d site (1/3, 2/3, 0.2565(15)). The regular octahedral and tetrahedral holes of the approximately cubic closed-packed matrix of nitrogen in the Li₂Ca(NH)₂ lattice (Figure 3) are the occupation sites for Ca and Li, respectively.

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**Table 1. Li₂Ca(NH)₂ Crystallographic Data**

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<th>atom</th>
<th>position</th>
<th>x</th>
<th>y</th>
<th>z</th>
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<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Li</td>
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<td>1/3</td>
<td>2/3</td>
<td>0.8841(22)</td>
</tr>
<tr>
<td>N</td>
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<td>1/3</td>
<td>2/3</td>
<td>0.2565(15)</td>
</tr>
<tr>
<td>H</td>
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</tbody>
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Because the scattering factor of hydrogen is very small compared to those of the other elements, hydrogen has little effect on XRD and can therefore be neglected. In order to locate hydrogen, neutron diffraction of a deuterium-substituted sample should be performed. Li⁺, Ca²⁺, and N³⁻ positions in the initial model for Rietveld refinement were derived from published structures of ternary nitrides. Ternary lithium nitrides can be divided mainly into two groups, that is, those with anti-fluorite type crystal structures represented by a general formula Li₂⁻N₃⁻M⁺⁻N₆⁻⁻⁻(n ≥ 2) and those with the anti-La₂O₃ type structure represented by a general formula Li₂MN₂. As evidenced by the indexing result of the TREOR program, Li₂Ca(NH)₂ should possess the anti-La₂O₃ type structure, which belongs to the hexagonal structural. CaMg₂N₂ (JCPDS-ICDD card no. 83-0042)²¹ has the anti-La₂O₃ type structure with lattice constants of a = 3.5405 Å and c = 6.0908 Å. Since the ionic radii of Li⁺ and Mg²⁺ are almost identical (0.68 and 0.67 Å),²² the structure of CaMg₂N₂ was adopted as the starting model to study Li₂Ca(NH)₂, wherein Mg²⁺ was substituted by Li⁺. The experimental powder XRD pattern of Li₂Ca(NH)₂ was in excellent agreement with the calculated pattern derived from the starting model (Figure 2), which implied that the structural model adopted in the present simulation was reasonable and acceptable. A series of parameters, including background, zero shift, scale, lattice parameter, graphic parameter (U, V, W), and Li and N coordinates, were refined by the Rietica program (Table 1). Li₂Ca(NH)₂ belongs to the space group P3m1 with lattice constants of a = 3.566(4) Å and c = 5.9540(8) Å. Ca occupies the 1b site (0, 0, 1/2), Li occupies the 2d site (1/3, 2/3, 0.3841(22)), and N occupies the 2d site (1/3, 2/3, 0.2565(15)). The regular octahedral and tetrahedral holes of the approximately cubic closed-packed matrix of nitrogen in the Li₂Ca(NH)₂ lattice (Figure 3) are the occupation sites for Ca and Li, respectively.

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ment.\textsuperscript{23} For example, there is a proportional correlation between the $^6$Li chemical shifts and the oxygen coordination number in lithium silicate.\textsuperscript{23} As shown in Figure 4, Li in Li$_2$Ca(NH)$_2$, Li$_2$NH, Li$_3$N, and LiNH$_2$ has the chemical shifts of 3.433, 3.455, 7.493, and 2.748 ppm, respectively. Similar chemical shifts of Li in Li$_2$Ca(NH)$_2$ and Li$_2$NH indicate the identical chemical environment of Li in these two compounds. Li$_2$NH has a simple face-centered cubic (fcc) structure with $Fm\overline{3}m$ symmetry.\textsuperscript{13} Each lithium cation in Li$_2$NH is coordinated with four imide anions. It is likely that the coordination number of the lithium cation in Li$_2$Ca(NH)$_2$ is the same as that in Li$_2$NH, in agreement with the XRD results.

X-ray absorption near-edge structure (XANES) spectroscopy is a powerful technique in determining metal atom/ion coordination number, especially when an appropriate model compound with well-defined coordination structure is available for comparison. In the present study, Ca$_3$N$_2$ was used as the reference for Ca in tetrahedral coordination,\textsuperscript{24} and CaNH was used as the reference for Ca in octahedral coordination.\textsuperscript{14,25} Figure 5 shows the XANES spectra of Ca$_3$N$_2$, CaNH, and Li$_2$Ca(NH)$_2$ samples at the Ca K edge. The peak at 4.050 keV is ascribed to the Ca 1s to 4p dipole transition. The peak at 4.038 keV is the pre-edge transition, which is related to the direct 1s to 3d quadrupole transition or the dipole transitions due to the d$\to$ p mixing between the 3d orbitals and the 4p orbitals of the central atom or neighboring atoms.\textsuperscript{26,27} Therefore, the intensities of the pre-edge features are sensitive to the local coordination geometry of the metal atom.\textsuperscript{26,27} It can be seen in Figure 5 that the intensity of the peak at 4.038 keV is much higher for Ca in the tetrahedral site than that in the octahedral site. Similar to that of CaNH, the intensity of the peak at 4.038 keV for Li$_2$Ca(NH)$_2$ is very weak, indicating an octahedral coordination.

The Fourier transform of the extended XAFS (EXAFS) spectrum for Li$_2$Ca(NH)$_2$ is presented in Figure 6. The peak at the radial distance of about 2.0 Å corresponds to the above-mentioned Ca–N coordination of the first shell. For the data evaluation, the peak between 1 Å and 2.5 Å was isolated by

\begin{thebibliography}{9}
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means of a filter function, and fitted with the amplitude reduction factor of $S_0^2 = 0.73$. The value of 0.73 is derived from the fitting results of the EXAFS data of CaNH using the coordination number and distance of the first shell from crystallographic data.\(^{(14,25)}\) The coordination number of Ca obtained from the EXAFS data of Li$_2$Ca(NH)$_2$ is 6.3, which indicates that each Ca is coordinated with six N, in good agreement with the XRD results.

To investigate the position of H in the lattice and the nature of the N–H bond, Li$_2$Ca(NH)$_2$ was further analyzed by FTIR spectroscopy. A broad absorbance in the range of 3050 cm$^{-1}$ to 3200 cm$^{-1}$ was detected (Figure 7), which correlates with the stretch of the N–H bond in imide ions.\(^{(7,28)}\) For example, N–H stretches in Li$_2$NH and CaNH are 3160 cm$^{-1}$ and 3183 cm$^{-1}$, respectively.\(^{(7,28)}\) The broad peak is characteristic of imide ions, which may be the result of dynamic or static disorder of hydrogen over the equivalent sites that broadens the localized vibrational states into bands.\(^{(11,25)}\) The overall absorbance of the ternary imide resembles that of Li$_2$NH except the asymmetric nature caused by the presence of Ca. Thus, the hydrogen site in Li$_2$Ca(NH)$_2$ can refer to that in the Li$_2$NH lattice. In the crystal structure model of Li$_2$NH, the hydrogen site is $16e$ ($F43m$) or $48h$ ($Fm3m$).\(^{(29)}\) The recent neutron diffraction and XRD results and the DFT calculations revealed that Li$_2$ND can have a disordered cubic ($Fd3m$) structure with partially occupied Li sites below 360 K and have the disordered cubic ($Fm3m$) structure with D atoms randomized over the 192I sites above that temperature.\(^{(30)}\) According to the $^1$H NMR measurement result of the solid lithium imide, the N–H vector is oriented to the middle point of two adjacent lithium sites.\(^{(31)}\) The first-principles calculations based on the density functional theory (DFT) were used to identify H positions in Li$_2$Ca(NH)$_2$ (details in Supporting Information). Our detailed DFT calculations on Li$_2$Ca(NH)$_2$ reveal that H atoms may distribute over the 6i equivalent sites (0.1838, 0.8162, 0.1723) around nitrogen atoms, and the N–H vector orient toward the middle point of two adjacent lithium sites (Li–Li distance 3.566 Å). Further investigations by neutron powder diffraction, NMR, and neutron inelastic scattering are needed to provide more information on the position and dynamics of hydrogen in Li$_2$Ca(NH)$_2$.

**Conclusions**

Thermal dehydrogenation of a mixture of LiNH$_2$ and CaH$_2$ at a molar ratio of 2:1 led to the formation of a new ternary imide Li$_2$Ca(NH)$_2$. The crystal structure of Li$_2$Ca(NH)$_2$ was determined by powder XRD. It adopts the trigonal anti-La$_2$O$_3$ structure (space group $P\overline{3}$_1). The cell parameters and atomic fractional coordinates were refined by the Rietveld method. Furthermore, local coordination states around Li and Ca in the Li$_2$Ca(NH)$_2$ crystal were investigated by $^6$Li MAS NMR and by XAFS at the Ca K edge, respectively, and the results were in good agreement with the results of the XRD measurement.

**Acknowledgment.** The present work is financially supported by the Agency of Science, Technology, and Research, Singapore (A*STARS). Work of XAFS was performed at Singapore Synchrotron Light Source (SSLS) under NUS Core Support C-380-003-003-001, A*STAR/MOE RP 3979908M, and Grant A*STAR 12 105 0038. We thank Dr. Ping Yang for the technical support at the XDD beamline.

**Supporting Information Available:** H positions in Li$_2$Ca(NH)$_2$ were investigated by the first-principles calculations based on the density functional theory (DFT). This material is available free of charge via the Internet at http://pubs.acs.org.

**IC060769Y**