

Supporting Information for

**Preparation and Crystal Structures of the Beryllium  
Ammines  $[\text{Be}(\text{NH}_3)_4]\text{X}_2$  ( $\text{X} = \text{Br}, \text{I}, \text{CN}, \text{SCN}, \text{N}_3$ ) and  
 $\text{Be}(\text{NH}_3)_2\text{X}'_2$  ( $\text{X}' = \text{Cl}, \text{Br}, \text{I}$ ).**

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# 1 Experimental Procedures

**Caution!** Beryllium and its compounds are regarded as toxic and carcinogenic. As the biochemical mechanisms that cause beryllium associated diseases are still unknown, special (safety) precautions are strongly advised.<sup>1</sup>

## 1.1 General Experimental Techniques

All manipulations were performed either under solvent vapor pressure or dry argon using glovebox and *Schlenk* techniques. All glass devices have been flame dried *in vacuo* before use. Liquid ammonia at ambient temperature was handled in high pressure Schlenk tubes (NORMAG) with PTFE valves that allow the slow release of ammonia and hydrogen at ambient temperature. Ammonia was dried at least 24 h over Na at  $-78\text{ }^{\circ}\text{C}$  before it was distilled into the reaction tubes.  $\text{NH}_4\text{F}$  was used without prior purification.  $\text{NH}_4\text{X}$ ,  $\text{X} = \text{Cl, Br, I, SCN}$  were purified by sublimation *in vacuo* through  $3\text{ }\text{\AA}$  molecular sieve.  $\text{TMS-CN}$  and  $\text{TMS-N}_3$  were purified by distillation under argon.  $\text{BeBr}_2$  and  $\text{BeI}_2$  were prepared from the elements according to the literature.<sup>2</sup> Due to the expected extreme toxicity of the obtained compounds no elemental analysis or mass spectrometry could be performed. The purity was therefore determined by IR and Raman spectroscopy.

## 1.2 IR Spectroscopy

IR spectra were recorded on a *Bruker* alpha FTIR spectrometer equipped with a diamond ATR unit in an argon filled glovebox. Processing of the spectra was performed with the OPUS software package<sup>3</sup> and OriginPro 2017.<sup>4</sup> Single crystals or microcrystalline powder of the compounds were used for the IR spectroscopic measurements.

## 1.3 Raman Spectroscopy

Raman spectra were recorded on a *S&I* Confocal Raman Microscope MonoVista CRS+ at ambient temperatures. The Raman spectrometer was equipped with four laser diodes with excitation lines of 488, 532, 633 and 785 nm. Spectra of  $[\text{Be}(\text{NH}_3)_4](\text{N}_3)_2$  (**4**) and  $\text{Be}(\text{NH}_3)_2\text{X}_2$  ( $\text{X} = \text{Cl, Br, I}$ ) (**6a-c**) were recorded with the 532 nm laser. The spectrum of  $[\text{Be}(\text{NH}_3)_4](\text{SCN})_2$  (**3**) was recorded with the 633 nm laser due to fluorescence at 532 nm. Samples of  $[\text{Be}(\text{NH}_3)_4]\text{Br}_2$  (**1a**),  $[\text{Be}(\text{NH}_3)_4]\text{I}_2$  (**2**) and  $[\text{Be}(\text{NH}_3)_4](\text{CN})_2$  (**5**) showed intense fluorescence at all wavelengths. Therefore no spectra of these compounds were received. Either single crystals in high pressure Schlenk tubes or microcrystalline powder in sealed 0.3 mm borosilicate glass capillaries were used for the measurements. The spectra were plotted with OriginPro 2017.<sup>4</sup>

## 1.4 Single Crystal X-Ray Diffraction

Single crystals were selected under pre-dried argon in perfluorinated polyether (Fomblin YR 1800, *Solvay Solexis*) and mounted using the *MiTeGen* MicroLoop system. In case of compounds **1-5** a liquid nitrogen cooled nitrogen stream and perfluorinated polyether (Galden HT-270, *Solvay Solexis*) at  $-50\text{ }^{\circ}\text{C}$  was used for crystal preparation due to their temperature sensitivity. The mounted single crystals of **1-5** were transferred from the microscope to the diffractometer *via* liquid nitrogen cooled pliers. X-ray diffraction data were collected using the monochromated  $\text{Cu-K}\alpha$  radiation of a *Stoe* StadiVari diffractometer equipped with a Xenocs Microfocus Source and a *Dectris* Pilatus 300K Detector. The diffraction data were reduced with the X-Area software package.<sup>5</sup> The structures were solved using Direct Methods (SHELXT-2018/2) and refined against  $F^2$  (SHELXL-2018/3) using the ShelXle software package.<sup>6-8</sup> All atoms were located by Difference Fourier synthesis and non-hydrogen atoms refined anisotropically. Hydrogen atoms were refined isotropically.

## 1.5 X-Ray Powder Diffraction

The powder X-ray patterns were recorded with a *STOE & Cie* StadiMP diffractometer in Debye-Scherrer geometry using 0.3 mm sealed borosilicate glass capillaries. The diffractometer was operated with  $\text{Cu-K}\alpha_1$  radiation ( $1.5406\text{ }\text{\AA}$ , Ge monochromator) and equipped with a MYTHEN 1K detector. Non of the recorded powder X-ray patterns for samples of  $[\text{Be}(\text{NH}_3)_4]\text{Br}_2$  (**1a**),  $[\text{Be}(\text{NH}_3)_4]\text{I}_2$  (**2**),  $[\text{Be}(\text{NH}_3)_4](\text{CN})_2$  (**5**) and  $\text{Be}(\text{NH}_3)_2\text{X}_2$  ( $\text{X} = \text{Cl, Br, I}$ ) showed discrete reflexions.

## 1.6 Thermo Gravimetric Analysis (TGA)

Thermal measurements were done with a *Mettler Toledo* DCS-TGA 3 with heating rates of 1 and  $2\text{ }\frac{\text{K}}{\text{min}}$  in a nitrogen stream ( $20\text{ }\frac{\text{mL}}{\text{min}}$ ). The diagrams were plotted with OriginPro 2017.<sup>4</sup>

## 2 Synthesis and Characterization

### 2.1 Tetraammineberyllium(II) bromide ( $[\text{Be}(\text{NH}_3)_4]\text{Br}_2$ ) (1a)

Single crystals of  $[\text{Be}(\text{NH}_3)_4]\text{Br}_2$  were prepared using two methods:

**a:** 10 mg Be flakes (1.11 mmol; 1 eq.) and 220 mg  $\text{NH}_4\text{Br}$  (2.25 mmol; 2 eq.) were weighed into a high pressure Schlenk tube that was subsequently filled with approx. 2 mL liquid ammonia by vacuum distillation from a cooling trap, charged with Na. The Schlenk tube was then warmed to ambient temperature. A vivid gas evolution was observed and the Be flakes dissolved within two days to yield a colourless, clear solution containing some gray linty particles. A gas bubbler was attached to the Schlenktube and the PTFE valve was opened slowly to release the ammonia with a constant gas flow within ten hours. Colourless rod shaped crystals of  $[\text{Be}(\text{NH}_3)_4]\text{Br}_2$  were obtained.

**b:** 60 mg  $\text{BeBr}_2$  (0.36 mmol) were weighed into a high pressure Schlenk tube that was subsequently filled with approx. 2 mL liquid ammonia by vacuum distillation from a cooling trap, charged with Na. The Schlenk tube was then warmed to ambient temperature. A clear colourless solution was obtained. A gas bubbler was attached to the Schlenktube and the PTFE valve was opened slowly to release the ammonia with a constant gas flow within ten hours. Colourless rod shaped crystals of  $[\text{Be}(\text{NH}_3)_4]\text{Br}_2$  were obtained.

FT-IR ( $\text{cm}^{-1}$ ): 3276 (s), 3155 (s), 1604 (m), 1400 (vw), 1290 (s), 1143 (w), 892 (s), 739 (w), 624 (m).

### 2.2 Tetraammineberyllium(II) bromide ammonia(1/8) ( $[\text{Be}(\text{NH}_3)_4]\text{Br}_2 \cdot 8\text{NH}_3$ ) (1b)

10 mg Be flakes (1.11 mmol; 1 eq.) and 220 mg  $\text{NH}_4\text{Br}$  (2.25 mmol; 2 eq.) were weighed into a Schlenk tube that was subsequently filled with approx. 5 mL liquid ammonia by vacuum distillation from a cooling trap, charged with Na. The Schlenk tube was stored at  $-40^\circ\text{C}$  for two months. During this time we did not see any gas evolution but a constant shrinking of the Be flakes. After the complete consumption of Be, the ammonia was reduced *in vacuo* at  $-78^\circ\text{C}$  until the reaction mixture started to solidify. The Schlenk tube was then stored for another two weeks at  $-40^\circ\text{C}$ . During this time block shaped crystals of  $[\text{Be}(\text{NH}_3)_4]\text{Br}_2 \cdot 8\text{NH}_3$  grew and were isolated from the Schlenk tube at  $-78^\circ\text{C}$  for single crystal diffraction. After the removal of ammonia, the residue was analyzed *via* IR spectroscopy.

### 2.3 Tetraammineberyllium(II) iodide ( $[\text{Be}(\text{NH}_3)_4]\text{I}_2$ ) (2)

Single crystals of  $[\text{Be}(\text{NH}_3)_4]\text{I}_2$  were prepared using two methods:

**a:** 10 mg Be flakes (1.11 mmol; 1 eq.) and 330 mg  $\text{NH}_4\text{I}$  (2.25 mmol; 2 eq.) were weighed into a high pressure Schlenk tube that was subsequently filled with approx. 2 mL liquid ammonia by vacuum distillation from a cooling trap, charged with Na. The Schlenk tube was then warmed to ambient temperature. A vivid gas evolution was observed and the Be flakes dissolved within two days to yield a colourless, clear solution containing some gray linty particles. A gas bubbler was attached to the Schlenk tube and the PTFE valve was opened slowly to release the ammonia with a constant gas flow within several hours. Colourless needle shaped crystals of  $[\text{Be}(\text{NH}_3)_4]\text{I}_2$  were obtained.

**b:** 130 mg  $\text{BeI}_2$  (0.49 mmol) were weighed into a high pressure Schlenk tube that was subsequently filled with approx. 2 mL liquid ammonia by vacuum distillation from a cooling trap, charged with Na. The Schlenk tube was then warmed to ambient temperature. A clear colourless solution was obtained. A gas bubbler was attached to the Schlenktube and the PTFE valve was opened slowly to release the ammonia with a constant gas flow within five hours. Colourless needle shaped crystals of  $[\text{Be}(\text{NH}_3)_4]\text{I}_2$  were obtained.

FT-IR ( $\text{cm}^{-1}$ ): 3272 (s), 3155 (m), 1592 (m), 1398 (vw), 1307 (s), 1241 (s), 1150 (m), 985 (w), 887 (s), 738 (w), 613 (m), 524 (w).

## 2.4 Tetraammineberyllium(II) thiocyanate ( $[\text{Be}(\text{NH}_3)_4](\text{SCN})_2$ ) (3)

10 mg Be flakes (1.11 mmol; 1 eq.) and 170 mg  $\text{NH}_4\text{SCN}$  (2.22 mmol; 2.0 eq.) were weighed into a high pressure Schlenk tube that was subsequently filled with approx. 3 mL liquid ammonia by vacuum distillation from a cooling trap, charged with Na. The Schlenk tube was then warmed to ambient temperature. A vivid gas evolution was observed and the Be flakes dissolved within three days to yield a colourless, clear solution containing some gray linty particles. A gas bubbler was attached to the Schlenk tube and the PTFE valve was opened slowly to release the ammonia with a constant gas flow until the first crystals grew from the solution. The valve was closed and a Raman spectrum of  $[\text{Be}(\text{NH}_3)_4](\text{SCN})_2$  in ammonia atmosphere was recorded. Colourless block shaped crystals of  $[\text{Be}(\text{NH}_3)_4](\text{SCN})_2$  were obtained by the complete release of ammonia.

FT-IR ( $\text{cm}^{-1}$ ): 3288 (m), 3158 (m), 2807 (vw), 2120 (s), 2057 (s), 1601 (m), 1297 (s), 991 (w), 925 (m), 862 (s), 810 (s), 740 (m), 621 (w), 564 (w), 467 (w), 420 (w). Raman ( $\text{cm}^{-1}$ ): 3341 (m), 3279 (m), 3187 (w), 3053 (w), 2086 (vw), 2042 (s), 1270 (w), 1180 (w), 1075 (w), 934 (w), 898 (w), 810 (w), 738 (w), 644 (vw), 516 (w), 323 (w), 256 (w), 167 (vw).

## 2.5 Tetraammineberyllium(II) azide ( $[\text{Be}(\text{NH}_3)_4](\text{N}_3)_2$ ) (4)

10 mg Be flakes (1.11 mmol; 1 eq.) were weighed into a high pressure Schlenk tube and 330  $\mu\text{L}$  TMS- $\text{N}_3$  (3.33 mmol; 3 eq.) were added *via* an adjustable pipette inside a glovebox. The mixture was cooled with liquid nitrogen and the argon was pumped off. Then approx. 3 mL liquid ammonia were added by vacuum distillation from a cooling trap, charged with Na. The Schlenk tube was then warmed to ambient temperature. A vivid gas evolution was observed and the Be flakes dissolved within seven days to yield a colourless, clear solution containing some gray linty particles. A gas bubbler was attached to the Schlenk tube and the PTFE valve was opened slowly to release the ammonia with a constant gas flow within three hours. Remaining TMS- $\text{N}_3$  was removed *in vacuo*. Colourless column shaped crystals of  $[\text{Be}(\text{NH}_3)_4](\text{N}_3)_2$  were obtained.

FT-IR ( $\text{cm}^{-1}$ ): 3320 (m), 2080 (s), 1607 (m), 1369 (w), 1314 (m), 1282 (s), 989 (vw), 837 (s), 786 (s), 678 (m), 607 (m), 551 (m), 436 (m). Raman ( $\text{cm}^{-1}$ ): 3374 (w), 3293 (m), 3254 (m), 2119 (m), 3170 (s), 2955 (w), 2903 (w), 1638 (vw), 1387 (w), 1342 (s), 1260 (w), 642 (w), 574 (w), 490 (w), 317 (w), 171 (s), 79 (s).

## 2.6 Tetraammineberyllium(II) cyanide ( $[\text{Be}(\text{NH}_3)_4](\text{CN})_2$ ) (5)

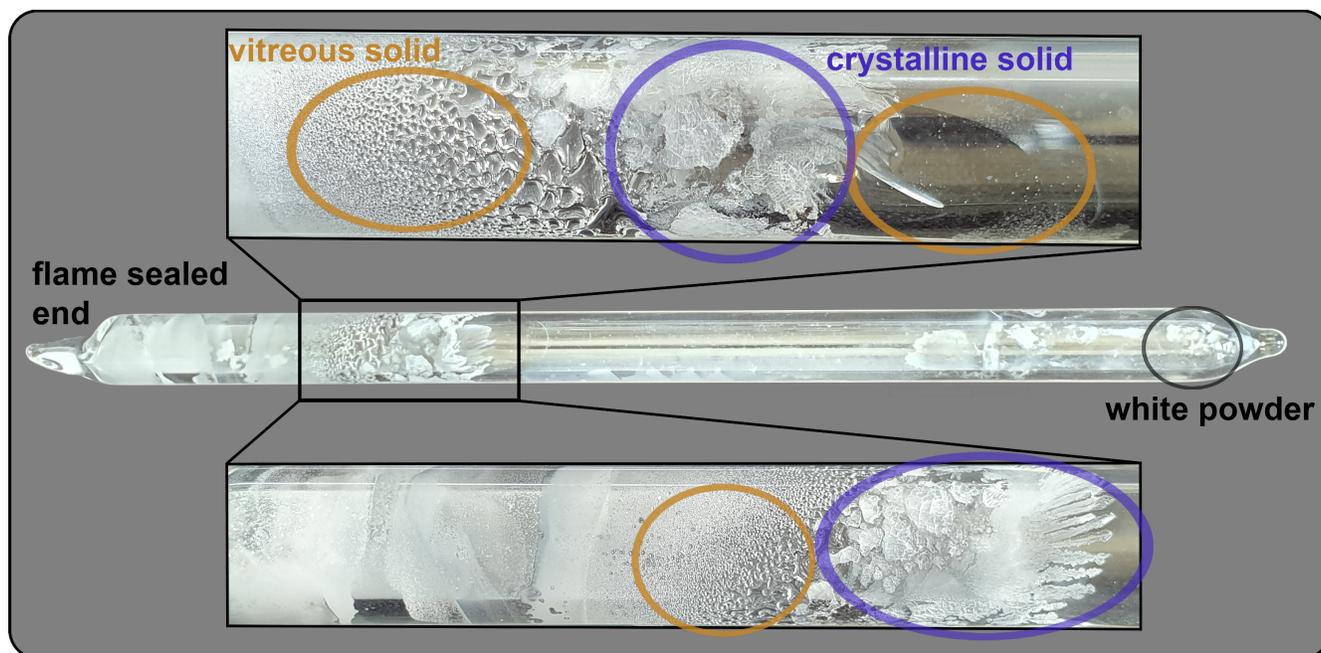
10 mg Be flakes (1.11 mmol; 1 eq.) were weighed into a high pressure Schlenk tube and 330  $\mu\text{L}$  TMS-CN (3.33 mmol; 3 eq.) were added *via* an adjustable pipette inside a glovebox. The mixture was cooled with liquid nitrogen and the argon was pumped off. Then approx. 3 mL liquid ammonia were added by vacuum distillation from a cooling trap, charged with Na. The Schlenk tube was then warmed to ambient temperature. A vivid gas evolution was observed and the Be flakes dissolved within one day to yield a colourless, clear solution containing some gray linty particles. A gas bubbler was attached to the Schlenk tube and the PTFE valve was opened slowly to release the ammonia with a constant gas flow within three hours. Remaining TMS-CN was removed *in vacuo*. Colourless column shaped crystals of  $[\text{Be}(\text{NH}_3)_4](\text{CN})_2$  were obtained.

FT-IR ( $\text{cm}^{-1}$ ): 3344 (m), 3233 (w), 2134 (w), 1628 (w), 1315 (w), 1278 (s), 854 (s), 794 (s), 644 (w), 598 (w), 431 (m).

## 2.7 Diammineberyllium dichloride ( $\text{BeCl}_2(\text{NH}_3)_2$ ) (6a)

3 mg Be flakes (0.33 mmol; 1 eq.) and 32 mg  $\text{NH}_4\text{Cl}$  (0.60 mmol; 1.8 eq.) were weighed into a fused silica ampule that was subsequently flame sealed under vacuum. The ampule was heated in a tube furnace with  $4 \frac{\text{K}}{\text{min}}$  to  $300^\circ\text{C}$  and was left at this temperature for one week. During this time the Be flakes shrank and were coated with a white powder and a clear colourless oily liquid deposited on the glass wall. After one week at  $300^\circ\text{C}$  the flame sealed side of the ampule was pulled a bit out of the furnace and the temperature was decreased with  $1 \frac{\text{K}}{\text{min}}$  to ambient temperature. Raman spectra of several point of the ampule were recorded. The ampule was opened inside a glovebox and a few single crystals were isolated for single crystal diffraction. The crystalline solid was scratched out and a capillary for X-ray powder diffraction was prepared. IR spectra were recorded from the obtained powder.

FT-IR ( $\text{cm}^{-1}$ ): 2216 (m), 3256 (m), 1616 (w), 1519 (vw), 1313 (s), 1007 (w), 746 (s), 552 (m), 502 (m). Raman ( $\text{cm}^{-1}$ ): 3320 (m), 3256 (s), 1312 (w), 782 (w), 344 (s), 225 (w).



**Figure 1** Photographs of the ampule after the reaction of Be with  $\text{NH}_4\text{Cl}$  at  $300^\circ\text{C}$ . Enlarged sections show vitreous and crystalline  $\text{BeCl}_2(\text{NH}_3)_2$ .

## 2.8 Diammineberyllium dibromide ( $\text{BeBr}_2(\text{NH}_3)_2$ ) (6b)

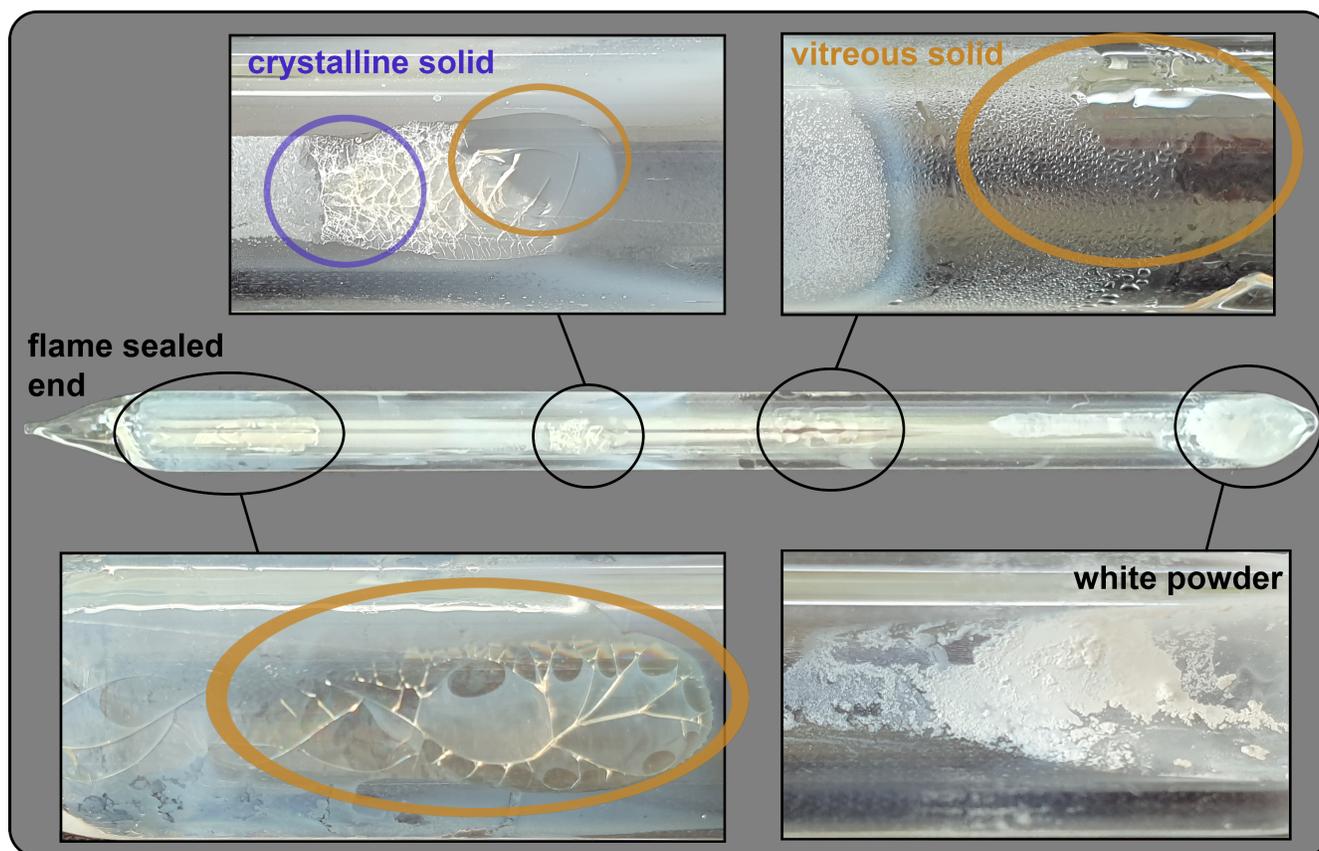
4 mg Be flakes (0.44 mmol; 1 eq.) and 78 mg  $\text{NH}_4\text{Br}$  (0.79 mmol; 1.8 eq.) were weighed into a fused silica ampule that was subsequently flame sealed under vacuum. The ampule was heated in a tube furnace with  $4 \frac{\text{K}}{\text{min}}$  to  $300^\circ\text{C}$  and was left at that temperature for one week. During this time the Be flakes shrank and were coated with a white powder and a clear colourless oily liquid deposited on the glass wall. After one week at  $300^\circ\text{C}$  the flame sealed side of the ampule was pulled a bit out of the furnace and the temperature was decreased with  $1 \frac{\text{K}}{\text{min}}$  to ambient temperature. Raman spectra of several point of the ampule were recorded. The ampule was opened inside a glovebox and a few single crystals were isolated for single crystal diffraction. The crystalline solid was scratched out and a capillary for X-ray powder diffraction was prepared. IR spectra were recorded from the obtained powder.

FT-IR ( $\text{cm}^{-1}$ ): 3286 (m), 3236 (m), 3174 (m), 1607 (m), 1515 (w), 1398 (vw), 1309 (s), 980 (m), 788 (s), 752 (s), 602 (w), 477 (vw), 416 (w). Raman ( $\text{cm}^{-1}$ ): 3304 (s), 3244 (s), 2435 (vw), 1611 (w), 1316 (w), 833 (w), 699 (w), 654 (w), 492 (w), 430 (w), 330 (s), 222 (s), 128 (m), 75 (m).

## 2.9 Diammineberyllium diiodide ( $\text{Be}(\text{NH}_3)_2\text{I}_2$ ) (6c)

4 mg Be flakes (0.44 mmol; 1 eq.) and 115 mg  $\text{NH}_4\text{I}$  (0.79 mmol; 1.8 eq.) were weighed into a fused silica ampule that was subsequently flame sealed under vacuum. The ampule was heated in a tube furnace with  $4 \frac{\text{K}}{\text{min}}$  to  $300^\circ\text{C}$  and was left at that temperature for one week. During this time the Be flakes shrank and were coated with a white powder and a clear colourless oily liquid deposited on the glass wall. After one week at  $300^\circ\text{C}$  the flame sealed side of the ampule was pulled a bit out of the furnace and the temperature was decreased with  $1 \frac{\text{K}}{\text{min}}$  to ambient temperature. Raman spectra of several point of the ampule were recorded. The ampule was opened inside a glovebox and a few single crystals were isolated for single crystal diffraction. The crystalline solid was scratched out and a capillary for X-ray powder diffraction was prepared. IR spectra were recorded from the obtained powder.

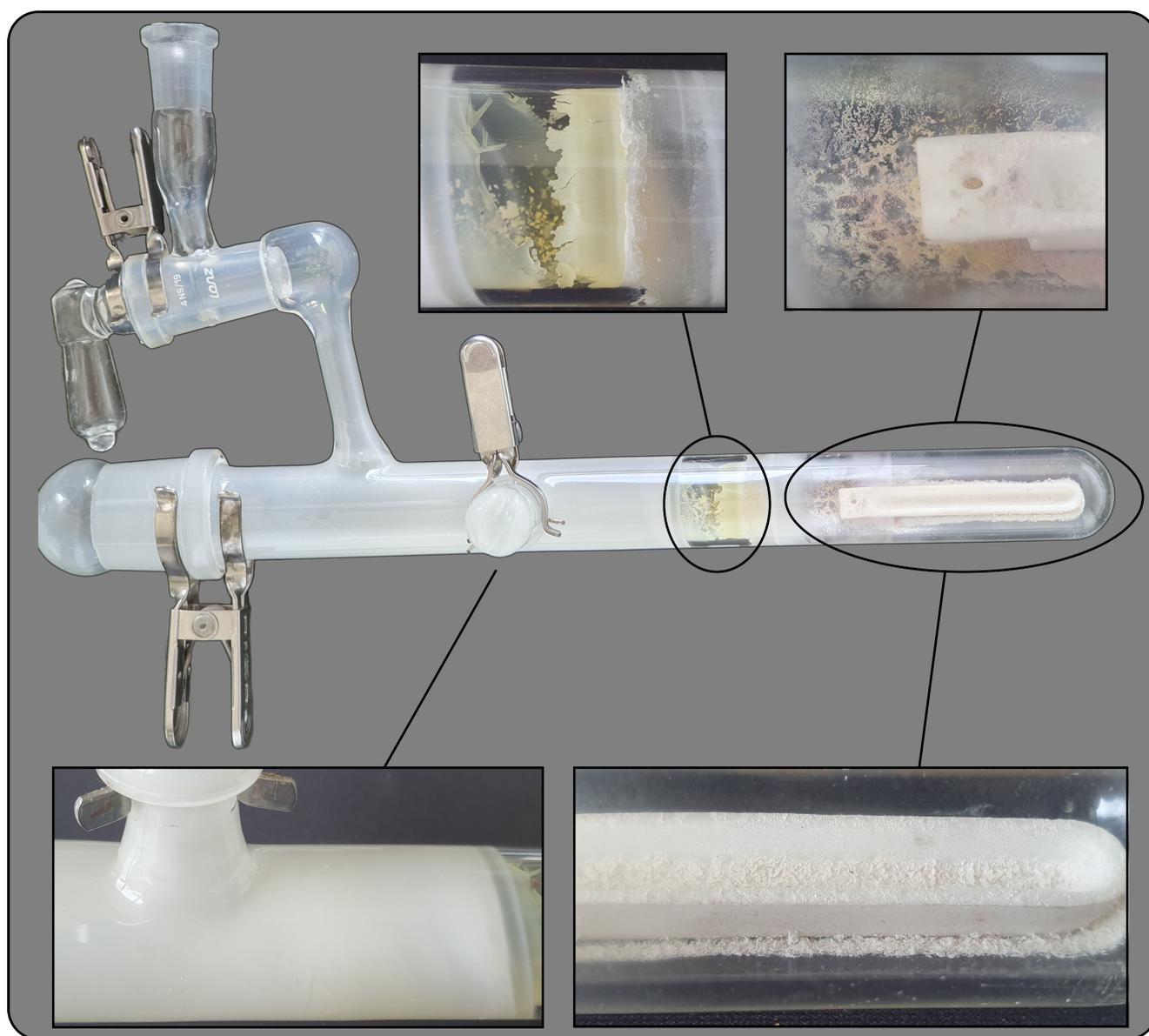
FT-IR ( $\text{cm}^{-1}$ ): 3269 (s), 3212 (s), 3160 (s), 1750 (w), 1591 (m), 1390 (m), 1305 (s), 782 (s), 594 (w), 430 (vw). Raman ( $\text{cm}^{-1}$ ): 3286 (s), 3222 (8s), 3168 (s), 1614 (w), 1318 (w), 820 (m), 652 (vw), 602 (w), 475 (br), 296 (m), 237 (w), 202 (m), 134 (vw), 89 (w), 54 (m).



**Figure 2** Photographs of the ampule after the reaction of Be with  $\text{NH}_4\text{I}$  at  $300^\circ\text{C}$ . Enlarged sections show the white residues as well as vitreous and crystalline  $\text{Be}(\text{NH}_3)_2\text{I}_2$ .

## 2.10 Thermal decomposition of $[\text{Be}(\text{NH}_3)_4]\text{I}_2$ (2)

600 mg  $[\text{Be}(\text{NH}_3)_4]\text{I}_2$  (1.8 mmol) were weighed into a flame dried corundum container. The corundum container was transferred into a flame dried Schlenk tube, that was greased with PTFE grease. The Schlenk tube was transferred into a tube furnace and was carefully evacuated for two hours at ambient temperature. The furnace was slowly heated stepwise to 100 °C according to the TGA measurements in a dynamic vacuum. After ten hours at 100 °C the  $[\text{Be}(\text{NH}_3)_4]\text{I}_2$  powder seemed unchanged. Then the temperature was increased stepwise to 250 °C within five hours. During this time, the  $[\text{Be}(\text{NH}_3)_4]\text{I}_2$  powder started to distribute inside the Schlenk tube. Afterwards the temperature was increased subsequently to 300 °C within two hours and this temperature was held for additional 24 hours. A white coat settled on the glass wall, a vitreous solid was formed several centimeters away from the corundum container and the major part of the initial  $[\text{Be}(\text{NH}_3)_4]\text{I}_2$  powder dispensed outside the corundum container. The temperature was finally raised to 400 °C for additional eight hours. The furnace was then cooled down and the Schlenk tube was transferred inside a glovebox. The corundum container was carefully removed and the remaining off white powder was filled into a 0.5 mm borosilicate glass capillary for powder diffraction and Raman spectroscopy. The one millimeter thick vitreous solid was scraped off the glass wall and also filled into a glass capillary. Both samples showed fluorescence in the Raman spectra and were amorphous. The samples were then opened to measure their IR spectra.



**Figure 3** Photographs of the Schlenk tube after  $[\text{Be}(\text{NH}_3)_4]\text{I}_2$  (2) was heated to 400 °C in a corundum container *in vacuo*.

### 3 X-Ray Crystallographic Data

**Table 1** Crystal data and details of the structure determination of [Be(NH<sub>3</sub>)<sub>4</sub>]Br<sub>2</sub> (**1a**), [Be(NH<sub>3</sub>)<sub>4</sub>]Br<sub>2</sub>·8NH<sub>3</sub> (**1b**) and [Be(NH<sub>3</sub>)<sub>4</sub>]I<sub>2</sub> (**2**).

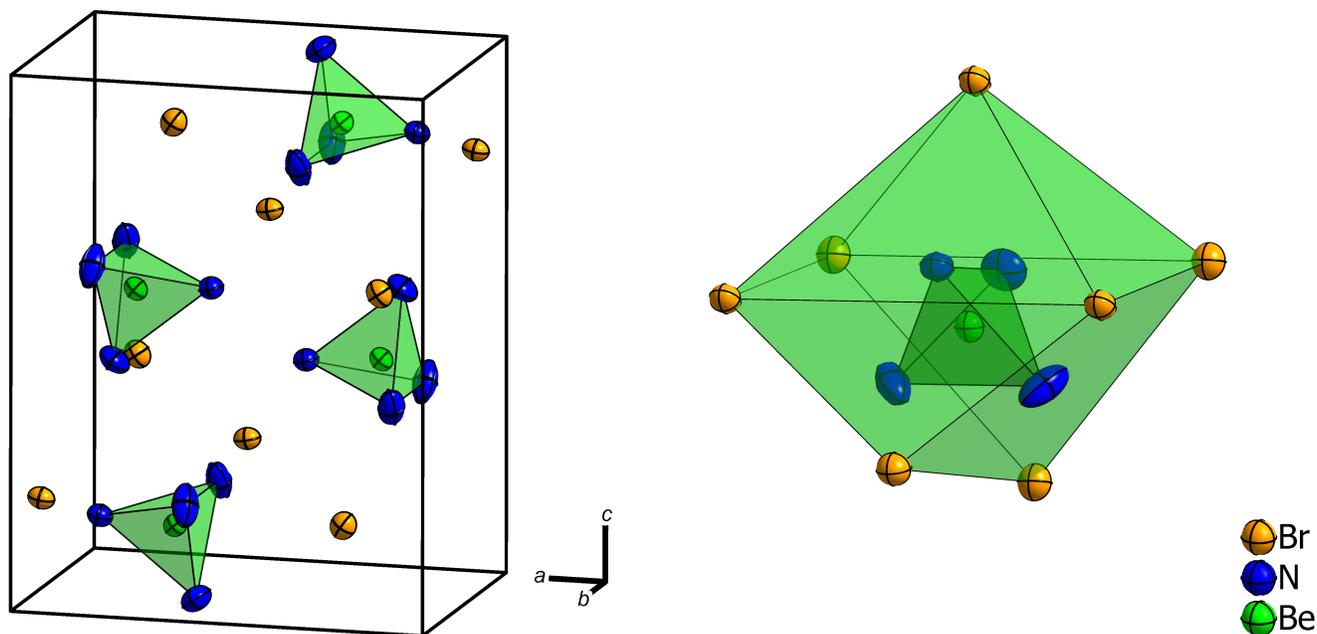
|  | <b>1a</b>   | <b>1b</b>   | <b>2</b>  |
|--|---|---|---|
| Empirical formula                                | [Be(NH <sub>3</sub> ) <sub>4</sub> ]Br <sub>2</sub>             | [Be(NH <sub>3</sub> ) <sub>4</sub> ]Br <sub>2</sub> ·8NH <sub>3</sub> | [Be(NH <sub>3</sub> ) <sub>4</sub> ]I <sub>2</sub>              |
| Relative molecular mass                          | 236.97  | 373.24  | 330.95  |
| Radiation / Å                                    | (Cu-Kα), 1.54178  | (Cu-Kα), 1.54178  | (Cu-Kα), 1.54178  |
| Crystal System                                   | orthorhombic  | monoclinic  | orthorhombic  |
| Space group (No.)                                | <i>Pnma</i> (62)  | <i>P2<sub>1</sub>/c</i> (14)  | <i>Pnma</i> (62)  |
| <i>a</i> / Å                                     | 9.5332(2)   | 10.4450(2)  | 9.9007(2)   |
| <i>b</i> / Å                                     | 6.93550(10)   | 11.5311(2)  | 7.3274(2)   |
| <i>c</i> / Å                                     | 12.2289(3)  | 16.3117(5)  | 12.7965(3)  |
| α / °  | 90  | 90  | 90  |
| β / °  | 90  | 101.353(2)  | 90  |
| γ / °  | 90  | 90  | 90  |
| <i>V</i> / Å <sup>3</sup>                        | 808.54(3)   | 1926.18(8)  | 928.34(4)   |
| <i>T</i> / K                                     | 100(2)  | 100(2)  | 100(2)  |
| <i>Z</i>   | 4   | 4   | 4   |
| <i>F</i> (000)                                   | 456   | 776   | 600   |
| <i>d</i> <sub>calc.</sub> / g·cm <sup>-3</sup>   | 1.947   | 1.287   | 2.368   |
| μ / mm <sup>-1</sup>                             | 12.030  | 5.340   | 52.617  |
| Θ / °  | 5.885–79.113  | 4.728–76.386  | 5.650–76.386  |
| Range of Miller indices                          | –12 ≤ <i>h</i> ≤ 11<br>–8 ≤ <i>k</i> ≤ 5<br>–14 ≤ <i>l</i> ≤ 15 | –13 ≤ <i>h</i> ≤ 10<br>–13 ≤ <i>k</i> ≤ 7<br>–18 ≤ <i>l</i> ≤ 20      | –10 ≤ <i>h</i> ≤ 12<br>–9 ≤ <i>k</i> ≤ 8<br>–15 ≤ <i>l</i> ≤ 15 |
| reflections collected / unique                   | 13697 / 948   | 9265 / 3782   | 8664 / 1056   |
| restraints / parameters                          | 0 / 44  | 18 / 291  | 0 / 43  |
| <i>R</i> <sub>int</sub>                          | 0.0174  | 0.0186  | 0.0354  |
| <i>R</i> <sub>1</sub> <i>I</i> ≥ 2σ( <i>I</i> )  | 0.0175  | 0.0234  | 0.0407  |
| <i>R</i> <sub>1</sub> (all data)                 | 0.0178  | 0.0265  | 0.0412  |
| <i>wR</i> <sub>2</sub> <i>I</i> ≥ 2σ( <i>I</i> ) | 0.0450  | 0.0586  | 0.1116  |
| <i>wR</i> <sub>2</sub> (all data)                | 0.0451  | 0.0600  | 0.1123  |
| <i>S</i>   | 1.190   | 1.048   | 1.186   |
| Δρ <sub>min, max</sub> / e·Å <sup>-3</sup>       | –0.558, 0.360   | –0.573, 0.684   | –1.981, 2.331   |

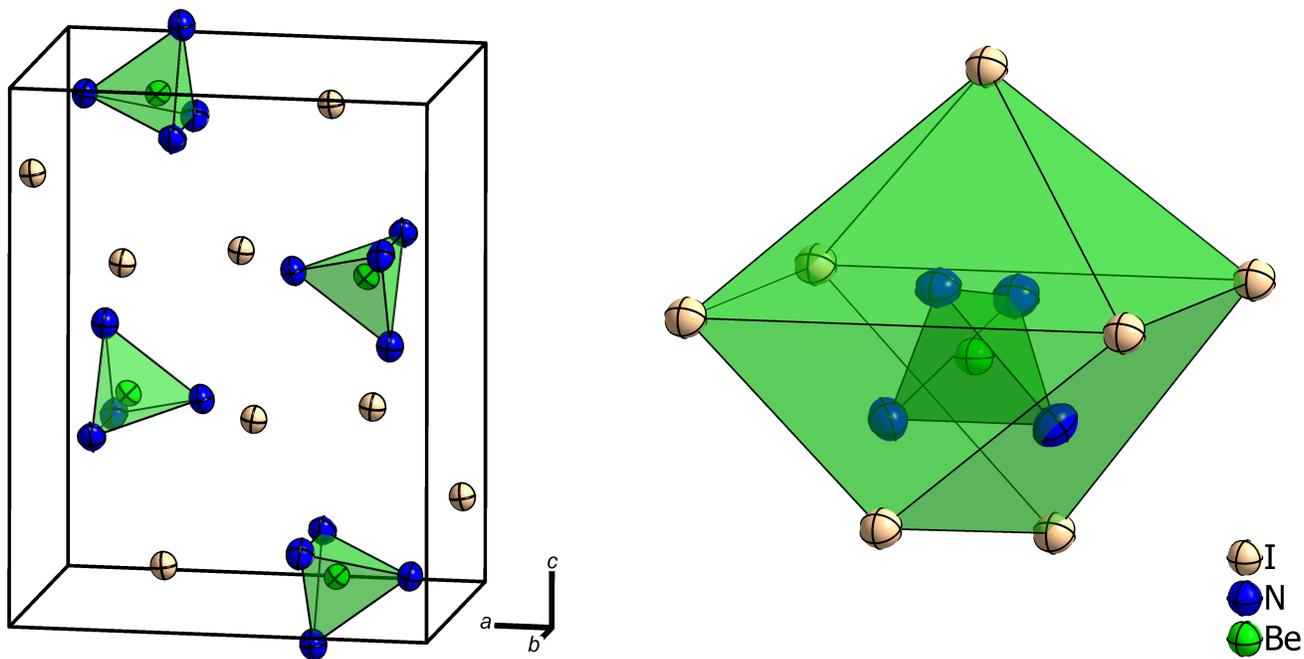
**Table 2** Crystal data and details of the structure determination of [Be(NH<sub>3</sub>)<sub>4</sub>](SCN)<sub>2</sub> (**3**), [Be(NH<sub>3</sub>)<sub>4</sub>](N<sub>3</sub>)<sub>2</sub> (**4**) and [Be(NH<sub>3</sub>)<sub>4</sub>](CN)<sub>2</sub> (**5**).

|  | <b>3</b>  | <b>4</b>   | <b>5</b>  |
|--|---|--|---|
| Empirical formula                                | [Be(NH <sub>3</sub> ) <sub>4</sub> ](SCN) <sub>2</sub>            | [Be(NH <sub>3</sub> ) <sub>4</sub> ](N <sub>3</sub> ) <sub>2</sub> | [Be(NH <sub>3</sub> ) <sub>4</sub> ](CN) <sub>2</sub>           |
| Relative molecular mass                          | 193.31  | 161.21   | 129.19  |
| Radiation / Å                                    | (Cu-Kα), 1.54178  | (Cu-Kα), 1.54178   | (Cu-Kα), 1.54178  |
| Crystal System                                   | orthorhombic  | tetragonal   | orthorhombic  |
| Space group (No.)                                | <i>Pbca</i> (61)  | <i>I</i> 42m (121)   | <i>Pna</i> 2 <sub>1</sub> (33)                                  |
| <i>a</i> / Å                                     | 11.9956(5)  | 8.0140(3)  | 9.1188(3)   |
| <i>b</i> / Å                                     | 11.7990(4)  | 8.0140(3)  | 12.6103(6)  |
| <i>c</i> / Å                                     | 13.2171(5)  | 6.4519(3)  | 6.9022(3)   |
| α / °  | 90  | 90   | 90  |
| β / °  | 90  | 90   | 90  |
| γ / °  | 90  | 90   | 90  |
| <i>V</i> / Å <sup>3</sup>                        | 1870.70(12)   | 414.37(4)  | 793.69(6)   |
| <i>T</i> / K                                     | 100(2)  | 100(2)   | 100(2)  |
| <i>Z</i>   | 8   | 2  | 4   |
| <i>F</i> (000)                                   | 816   | 172  | 280   |
| <i>d</i> <sub>calc.</sub> / g·cm <sup>-3</sup>   | 1.373   | 1.292  | 1.081   |
| μ / mm <sup>-1</sup>                             | 4.782   | 0.847  | 0.626   |
| Θ / °  | 6.236–76.296  | 8.824–78.225   | 5.988–78.681  |
| Range of Miller indices                          | –13 ≤ <i>h</i> ≤ 15<br>–11 ≤ <i>k</i> ≤ 14<br>–15 ≤ <i>l</i> ≤ 16 | –7 ≤ <i>h</i> ≤ 10<br>–7 ≤ <i>k</i> ≤ 7<br>–8 ≤ <i>l</i> ≤ 7       | –11 ≤ <i>h</i> ≤ 11<br>–15 ≤ <i>k</i> ≤ 15<br>–8 ≤ <i>l</i> ≤ 4 |
| reflections collected / unique                   | 12196 / 1955  | 725 / 234  | 8066 / 1390   |
| restraints / parameters                          | 0 / 149   | 0 / 26   | 1 / 133   |
| <i>R</i> <sub>int</sub>                          | 0.0194  | 0.0173   | 0.0367  |
| <i>R</i> <sub>1</sub> <i>I</i> ≥ 2σ( <i>I</i> )  | 0.0204  | 0.0334   | 0.0336  |
| <i>R</i> <sub>1</sub> (all data)                 | 0.0244  | 0.0339   | 0.0457  |
| <i>wR</i> <sub>2</sub> <i>I</i> ≥ 2σ( <i>I</i> ) | 0.0541  | 0.0945   | 0.0813  |
| <i>wR</i> <sub>2</sub> (all data)                | 0.0556  | 0.0946   | 0.0866  |
| <i>S</i>   | 0.992   | 1.188  | 0.998   |
| Δρ <sub>min, max</sub> / e·Å <sup>-3</sup>       | –0.151, 0.293   | –0.145, 0.185  | –0.155, 0.134   |

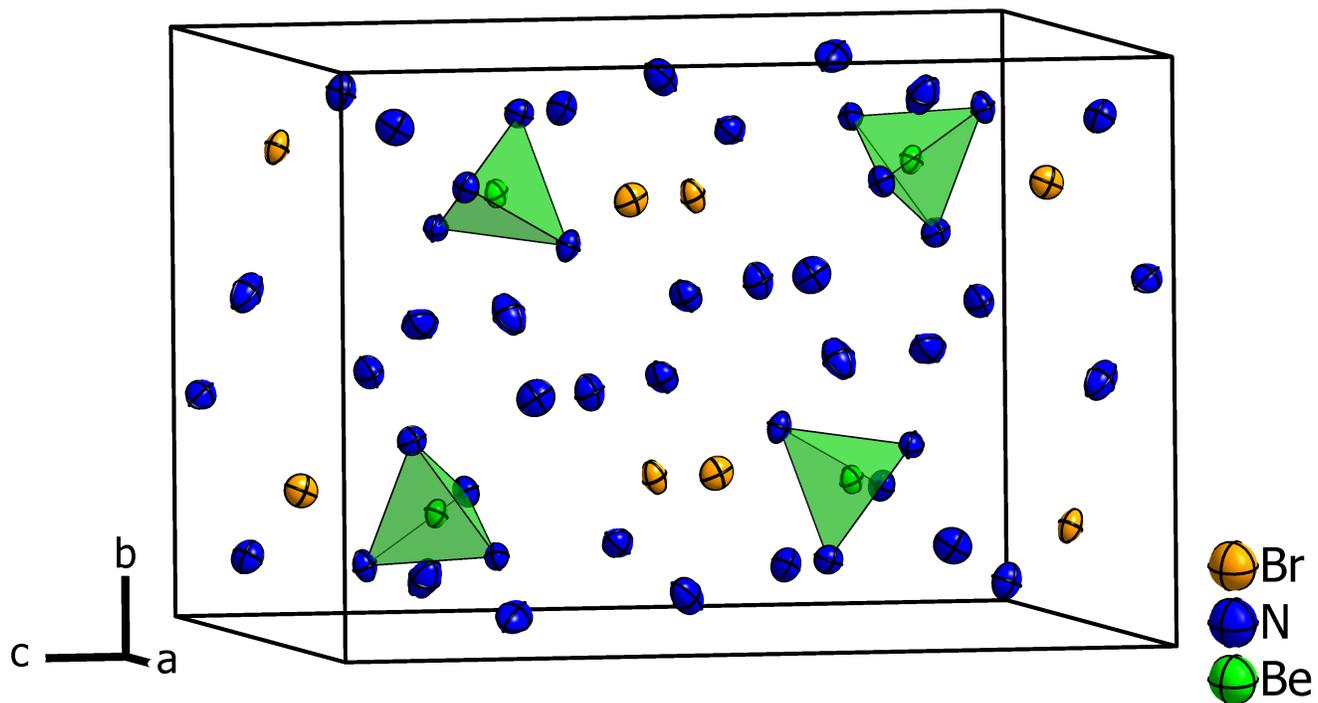
**Table 3** Crystal data and details of the structure determination of  $\text{BeCl}_2(\text{NH}_3)_2$  (**6a**),  $\text{BeBr}_2(\text{NH}_3)_2$  (**6b**) and  $\text{Be}(\text{NH}_3)_2\text{I}_2$  (**6c**).

|   | <b>6a</b>  | <b>6b</b>  | <b>6c</b>  |
|---|--|--|--|
| Empirical formula   | $\text{BeCl}_2(\text{NH}_3)_2$                                   | $\text{BeBr}_2(\text{NH}_3)_2$                                   | $\text{Be}(\text{NH}_3)_2\text{I}_2$                             |
| Relative molecular mass                                       | 113.98   | 202.90   | 296.88   |
| Radiation / Å   | (Cu-K $\alpha$ ), 1.54178  | (Cu-K $\alpha$ ), 1.54178  | (Cu-K $\alpha$ ), 1.54178  |
| Crystal System  | monoclinic   | monoclinic   | monoclinic   |
| Space group (No.)   | $P2_1/n$ (14)  | $P2_1/n$ (14)  | $P2_1/n$ (14)  |
| $a$ / Å   | 6.5519(2)  | 6.8278(2)  | 7.2739(4)  |
| $b$ / Å   | 11.8065(3)   | 12.2863(2)   | 13.1326(6)   |
| $c$ / Å   | 6.6589(2)  | 6.9291(2)  | 7.3586(4)  |
| $\alpha$ / °  | 90   | 90   | 90   |
| $\beta$ / °   | 100.321(3)   | 101.446(2)   | 102.674(5)   |
| $\gamma$ / °  | 90   | 90   | 90   |
| $V$ / Å <sup>3</sup>  | 506.76(3)  | 569.71(3)  | 685.80(6)  |
| $T$ / K   | 100(2)   | 100(2)   | 100(2)   |
| Z   | 4  | 4  | 4  |
| F(000)  | 232  | 376  | 520  |
| $d_{\text{calc.}}$ / $\text{g}\cdot\text{cm}^{-3}$            | 1.494  | 2.366  | 2.875  |
| $\mu$ / $\text{mm}^{-1}$                                      | 10.140   | 16.827   | 71.021   |
| $\Theta$ / °  | 7.504–78.689   | 7.209–78.914   | 7.029–79.205   |
| Range of Miller indices                                       | $-8 \leq h \leq 7$<br>$-14 \leq k \leq 14$<br>$-5 \leq l \leq 8$ | $-8 \leq h \leq 7$<br>$-12 \leq k \leq 15$<br>$-8 \leq l \leq 8$ | $-7 \leq h \leq 9$<br>$-16 \leq k \leq 13$<br>$-9 \leq l \leq 9$ |
| reflections collected / unique                                | 8180 / 1092  | 14114 / 1225   | 11337 / 1482   |
| restraints / parameters                                       | 0 / 71   | 0 / 49   | 0 / 49   |
| $R_{\text{int}}$  | 0.0323   | 0.0214   | 0.0613   |
| $R_1$ $I \geq 2\sigma(I)$                                     | 0.0338   | 0.0195   | 0.0485   |
| $R_1$ (all data)  | 0.0368   | 0.0215   | 0.0640   |
| $wR_2$ $I \geq 2\sigma(I)$                                    | 0.0918   | 0.0498   | 0.1170   |
| $wR_2$ (all data)   | 0.0957   | 0.0507   | 0.1285   |
| S   | 1.097  | 1.056  | 1.053  |
| $\Delta\rho_{\text{min, max}}$ / $\text{e}\cdot\text{Å}^{-3}$ | -0.376, 0.316  | -0.450, 0.394  | -2.272, 1.522  |

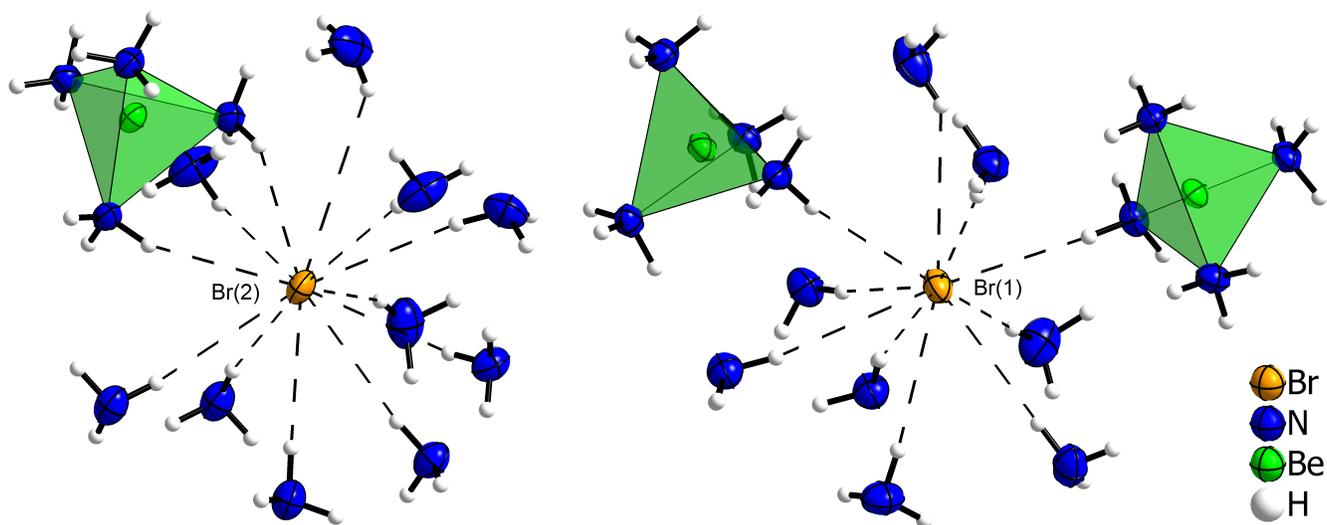
**Figure 4** Projection of the unit cell of  $[\text{Be}(\text{NH}_3)_4]\text{Br}_2$  (left) and the coordination polyhedron around  $[\text{Be}(\text{NH}_3)_4]^{2+}$  (right). Ellipsoids are depicted at 70% probability at 100 K.  $[\text{Be}(\text{NH}_3)_4]^{2+}$  cations shown as tetrahedra. Hydrogen atoms are omitted for clarity.



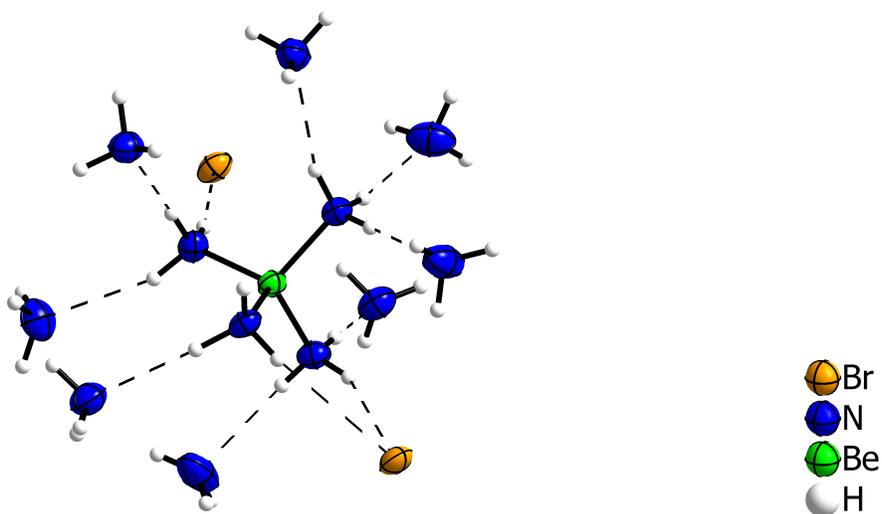
**Figure 5** Projection of the unit cell of  $[\text{Be}(\text{NH}_3)_4]\text{I}_2$  (left) and the coordination polyhedron around  $[\text{Be}(\text{NH}_3)_4]^{2+}$  (right). Ellipsoids are depicted at 70% probability at 100 K.  $[\text{Be}(\text{NH}_3)_4]^{2+}$  cations shown as tetrahedra. Hydrogen atoms are omitted for clarity.



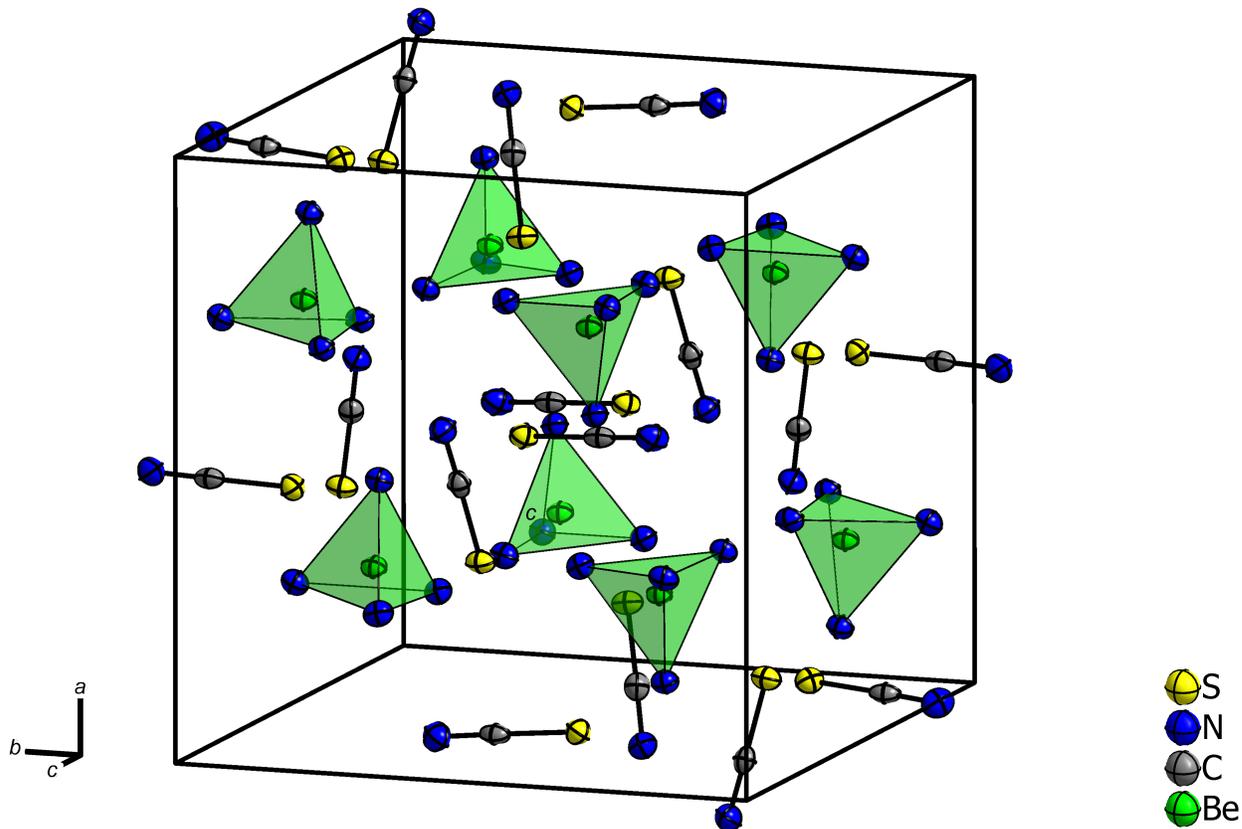
**Figure 6** Projection of the unit cell of  $[\text{Be}(\text{NH}_3)_4]\text{Br}_2 \cdot 8\text{NH}_3$ . Ellipsoids are depicted at 70% probability at 100 K.  $[\text{Be}(\text{NH}_3)_4]^{2+}$  cations shown as tetrahedra. Hydrogen atoms are omitted for clarity.



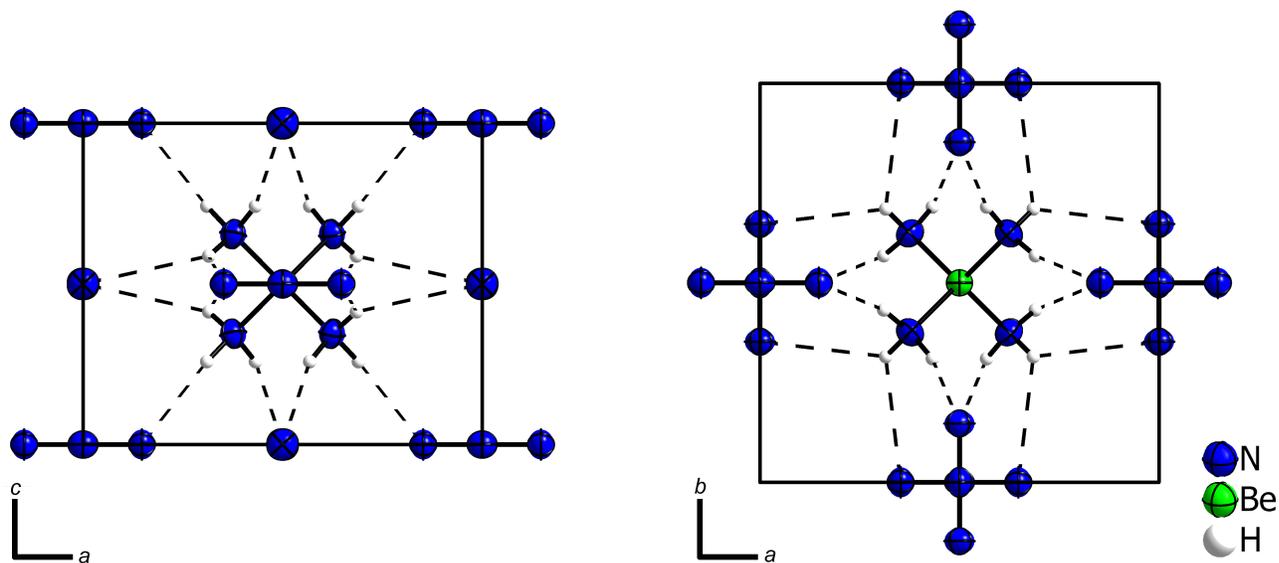
**Figure 7** Illustration of the coordination of Br(1) and Br(2) in  $[\text{Be}(\text{NH}_3)_4]\text{Br}_2 \cdot 8\text{NH}_3$  by ammonia and  $[\text{Be}(\text{NH}_3)_4]^{2+}$  cations. Ellipsoids are depicted at 70% probability at 100 K.  $[\text{Be}(\text{NH}_3)_4]^{2+}$  cations shown as tetrahedra. Hydrogen atoms are depicted with arbitrary radii. Hydrogen bonds are shown as dashed lines



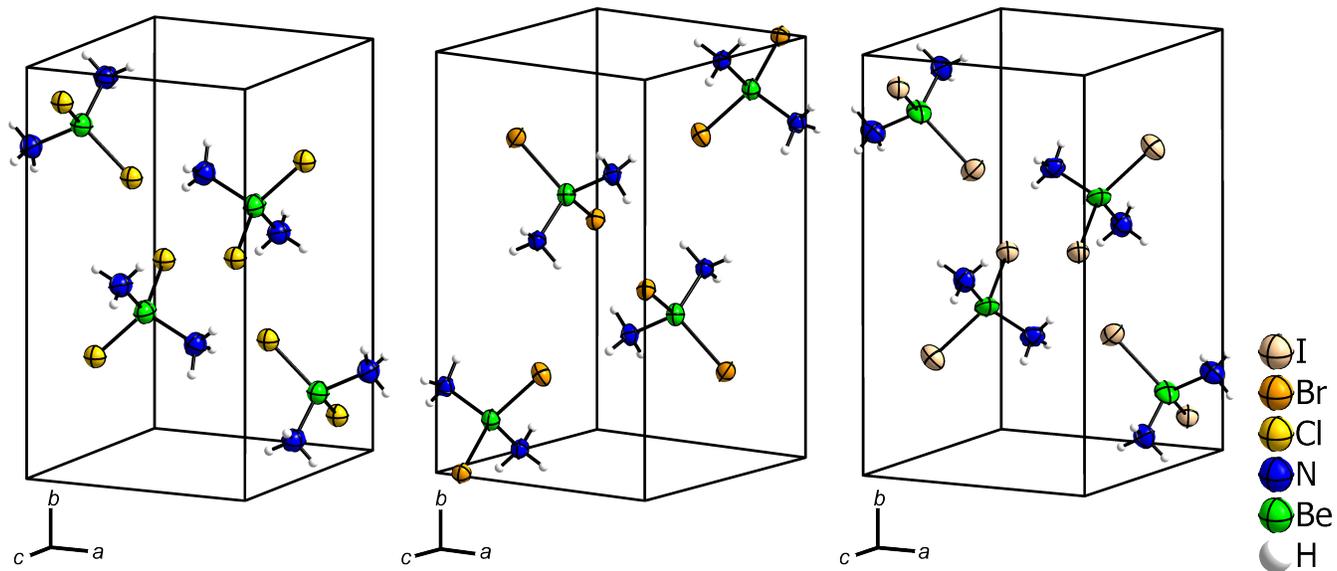
**Figure 8** Illustration of the coordination of  $[\text{Be}(\text{NH}_3)_4]^{2+}$  in  $[\text{Be}(\text{NH}_3)_4]\text{Br}_2 \cdot 8\text{NH}_3$  by ammonia and  $\text{Br}^-$  anions. Ellipsoids are depicted at 70% probability at 100 K. Hydrogen atoms are depicted with arbitrary radii. Hydrogen bonds are shown as dashed lines.



**Figure 9** Projection of the unit cell of  $[\text{Be}(\text{NH}_3)_4](\text{SCN})_2$ . Ellipsoids are depicted at 70% probability at 100 K.  $[\text{Be}(\text{NH}_3)_4]^{2+}$  cations shown as tetrahedra. Hydrogen atoms are omitted for clarity.



**Figure 10** Projection of the unit cell of  $[\text{Be}(\text{NH}_3)_4](\text{N}_3)_2$  along the  $a$  and  $c$  axis. Ellipsoids are depicted at 70% probability at 100 K. Hydrogen atoms are depicted with arbitrary radii. Hydrogen bonds are shown as dashed lines



**Figure 11** Projection of the unit cell of  $\text{Be}(\text{NH}_3)_2(\text{X})_2$ ,  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ . Ellipsoids are depicted at 70% probability at 100 K. Hydrogen atoms are depicted with arbitrary radii.

#### 4 IR and Raman Spectra

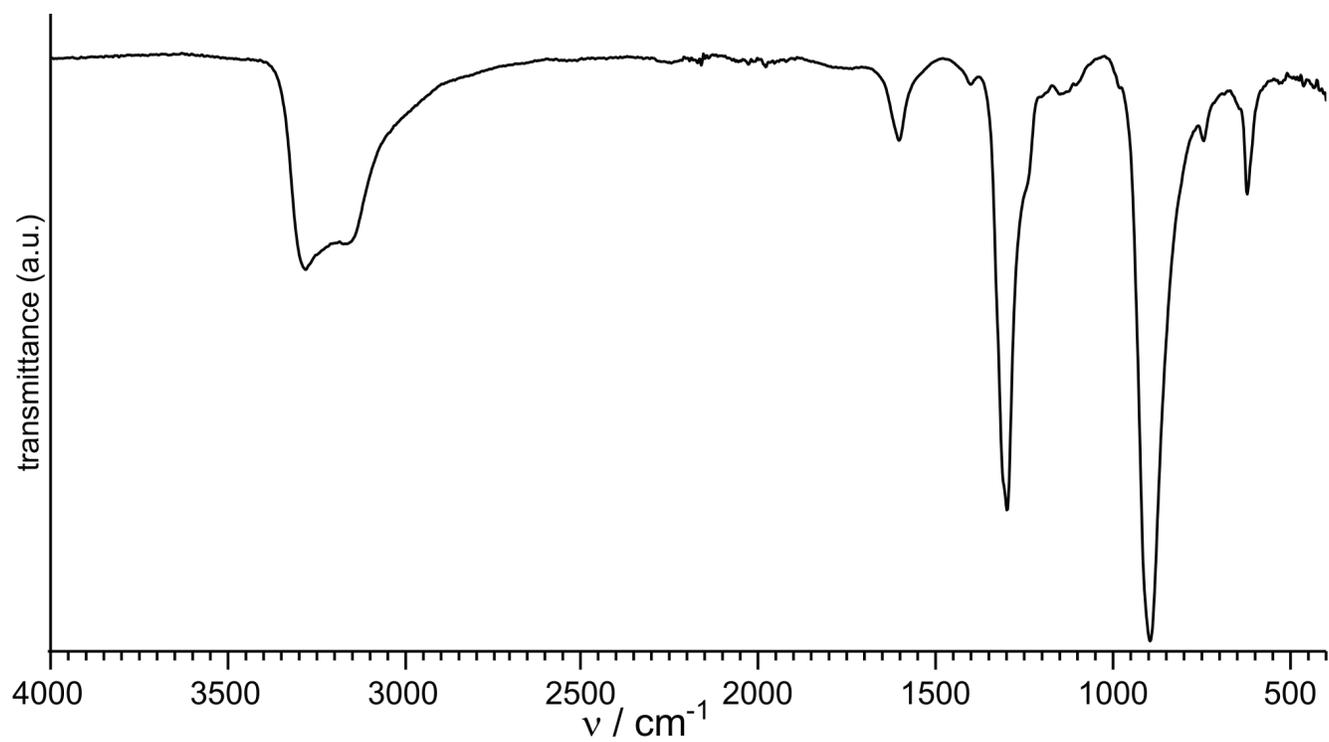


Figure 12 IR spectrum of  $[\text{Be}(\text{NH}_3)_4](\text{Br})_2$ .

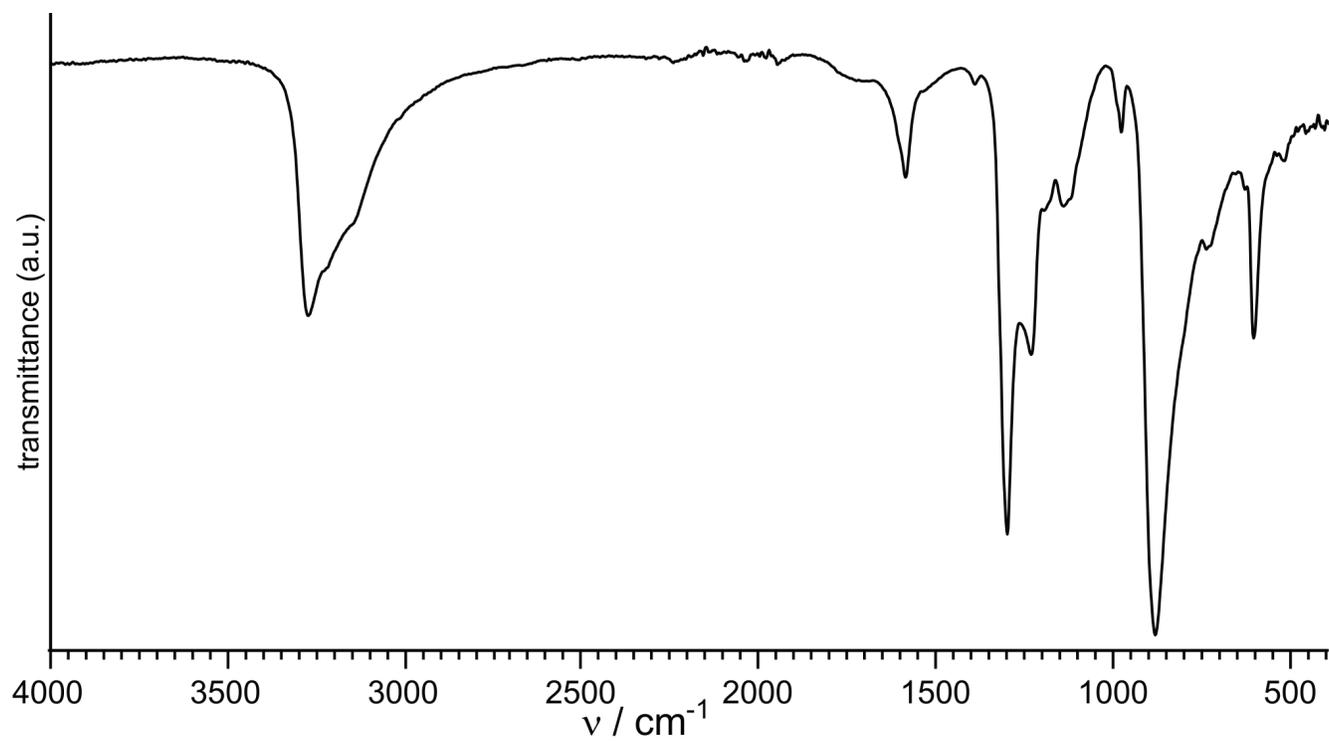
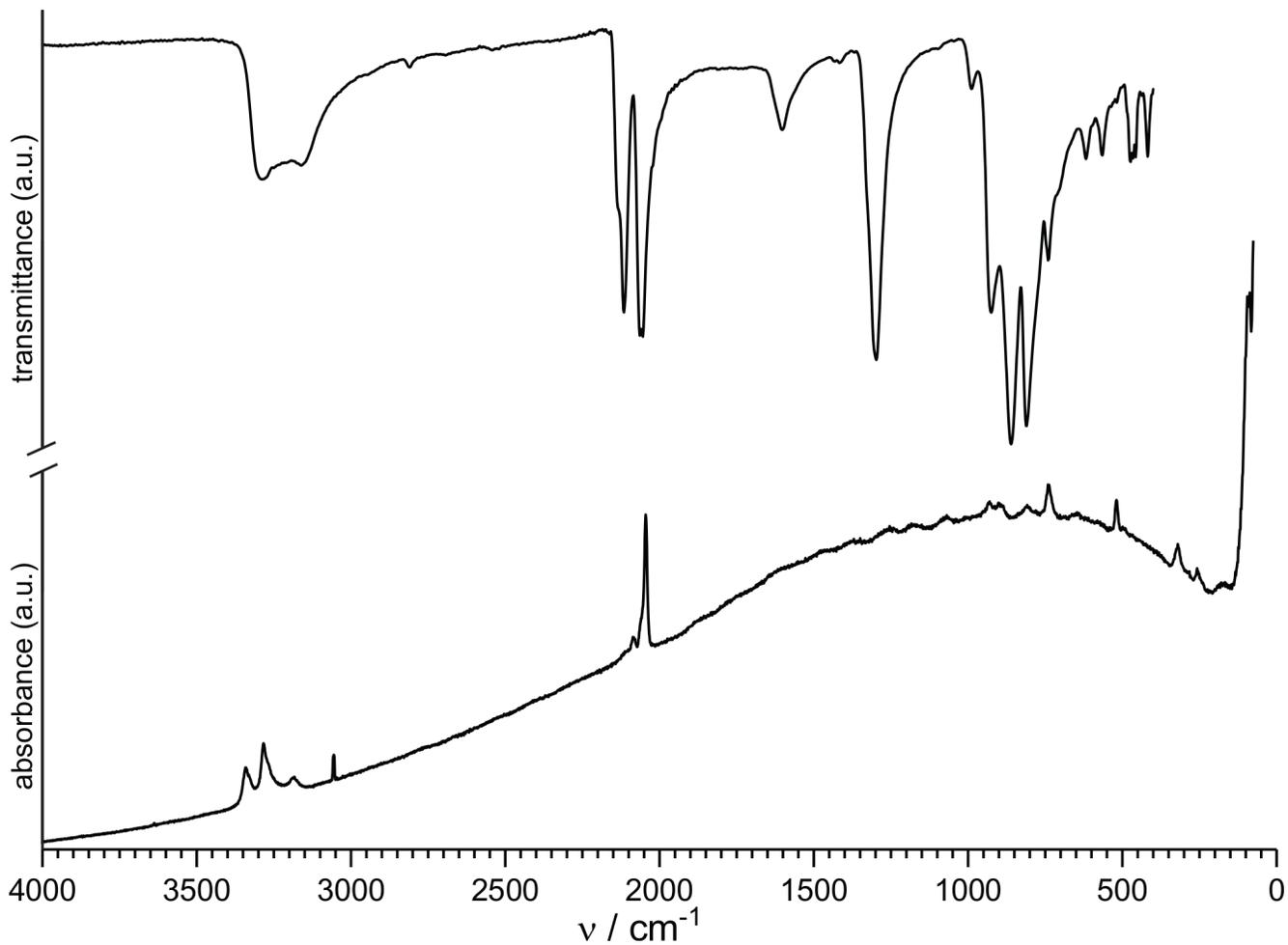
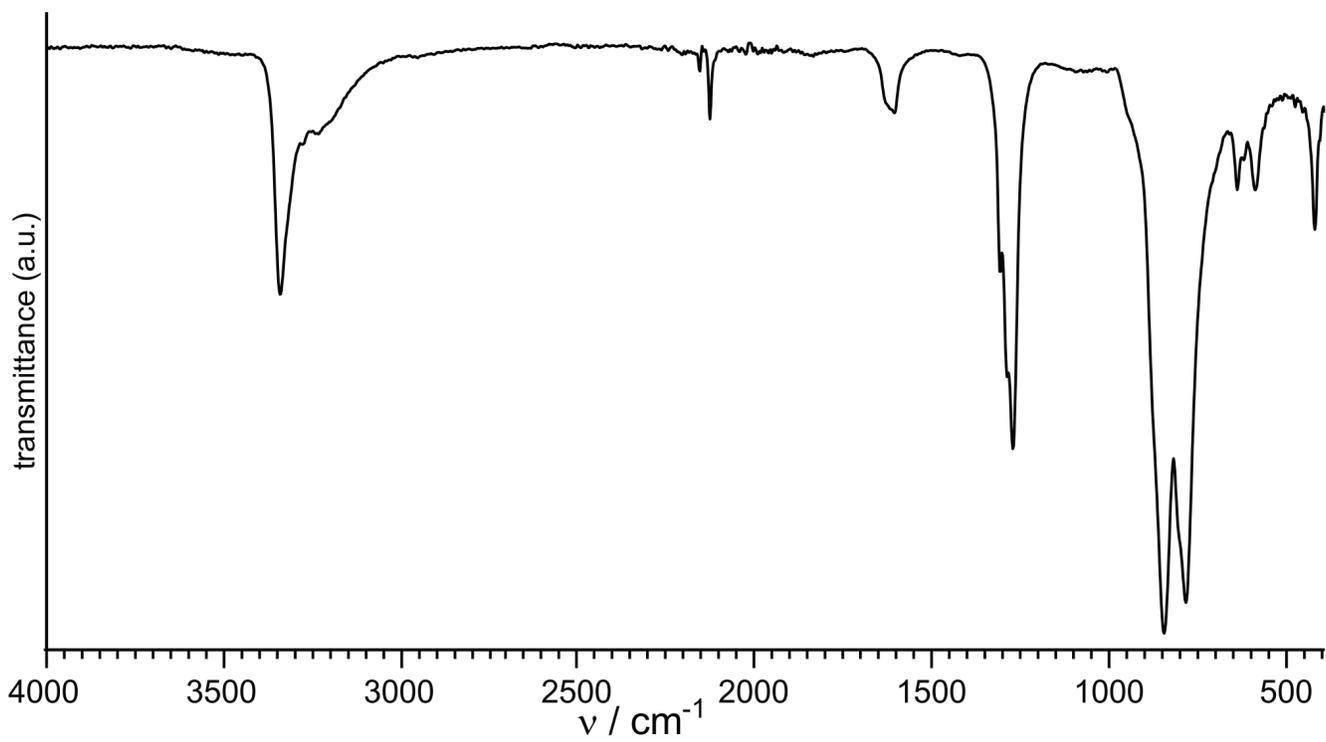


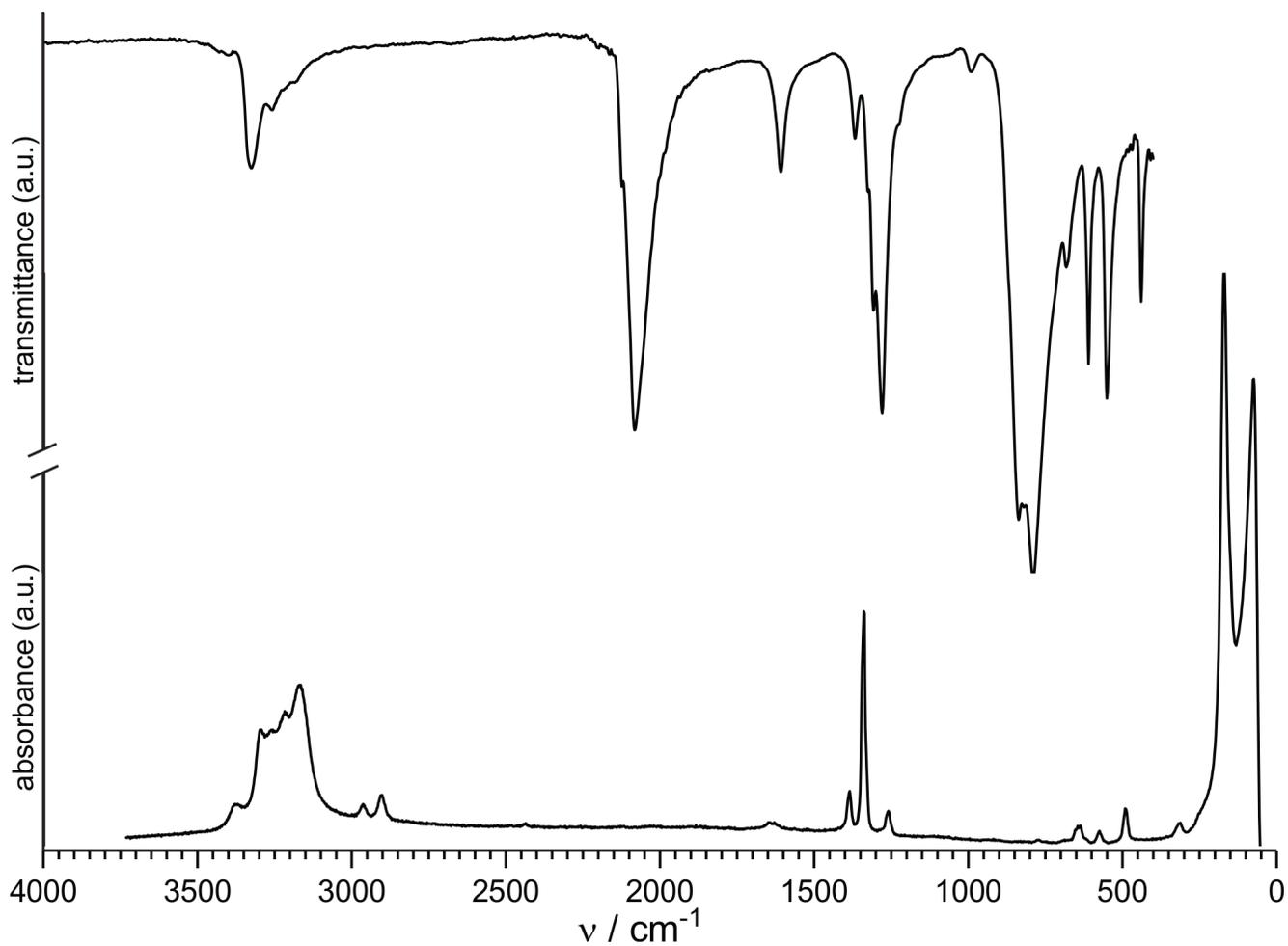
Figure 13 IR spectrum of  $[\text{Be}(\text{NH}_3)_4](\text{I})_2$ .



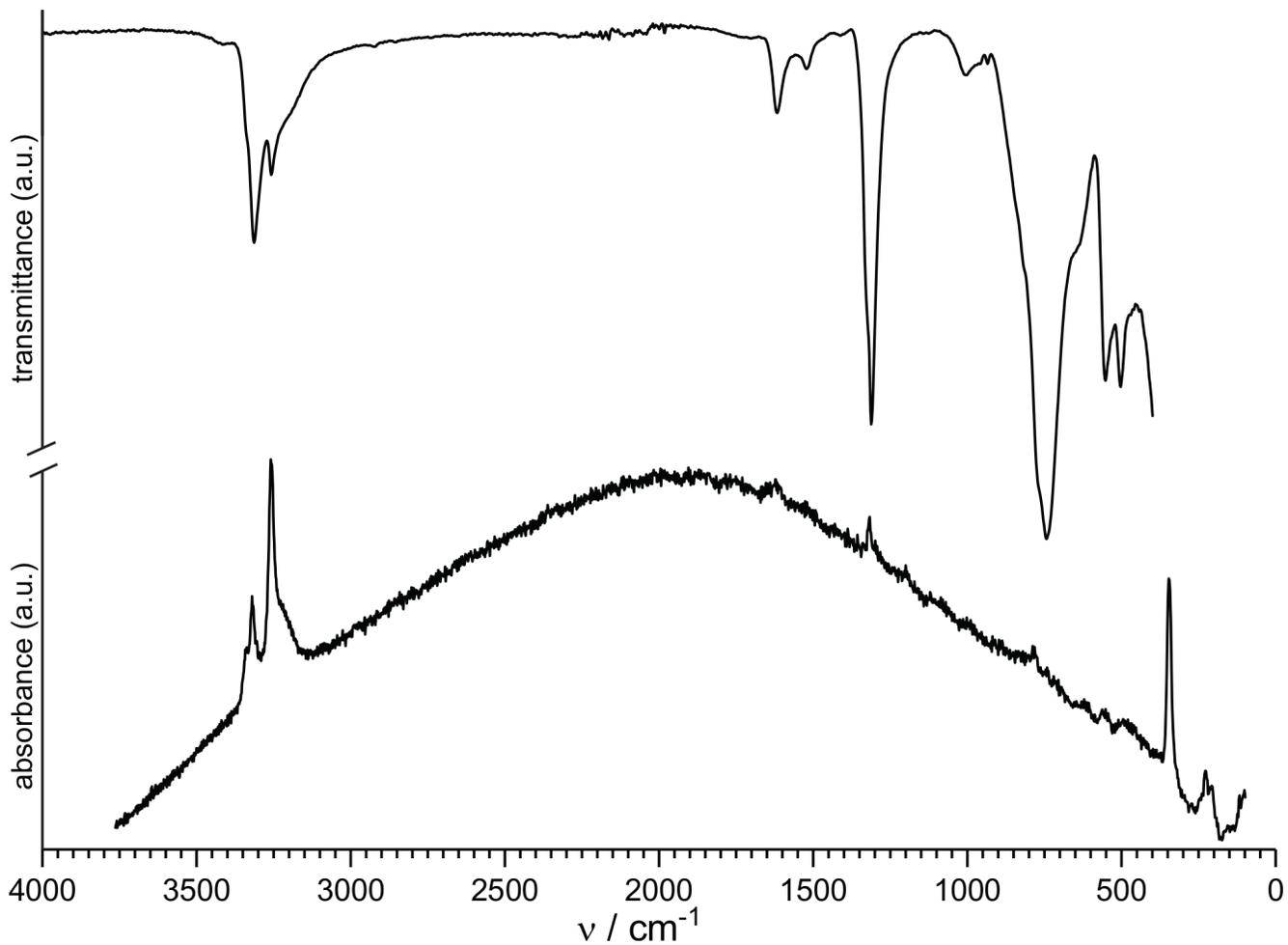
**Figure 14** IR (top) and Raman (bottom) spectra of  $[\text{Be}(\text{NH}_3)_4](\text{SCN})_2$ .



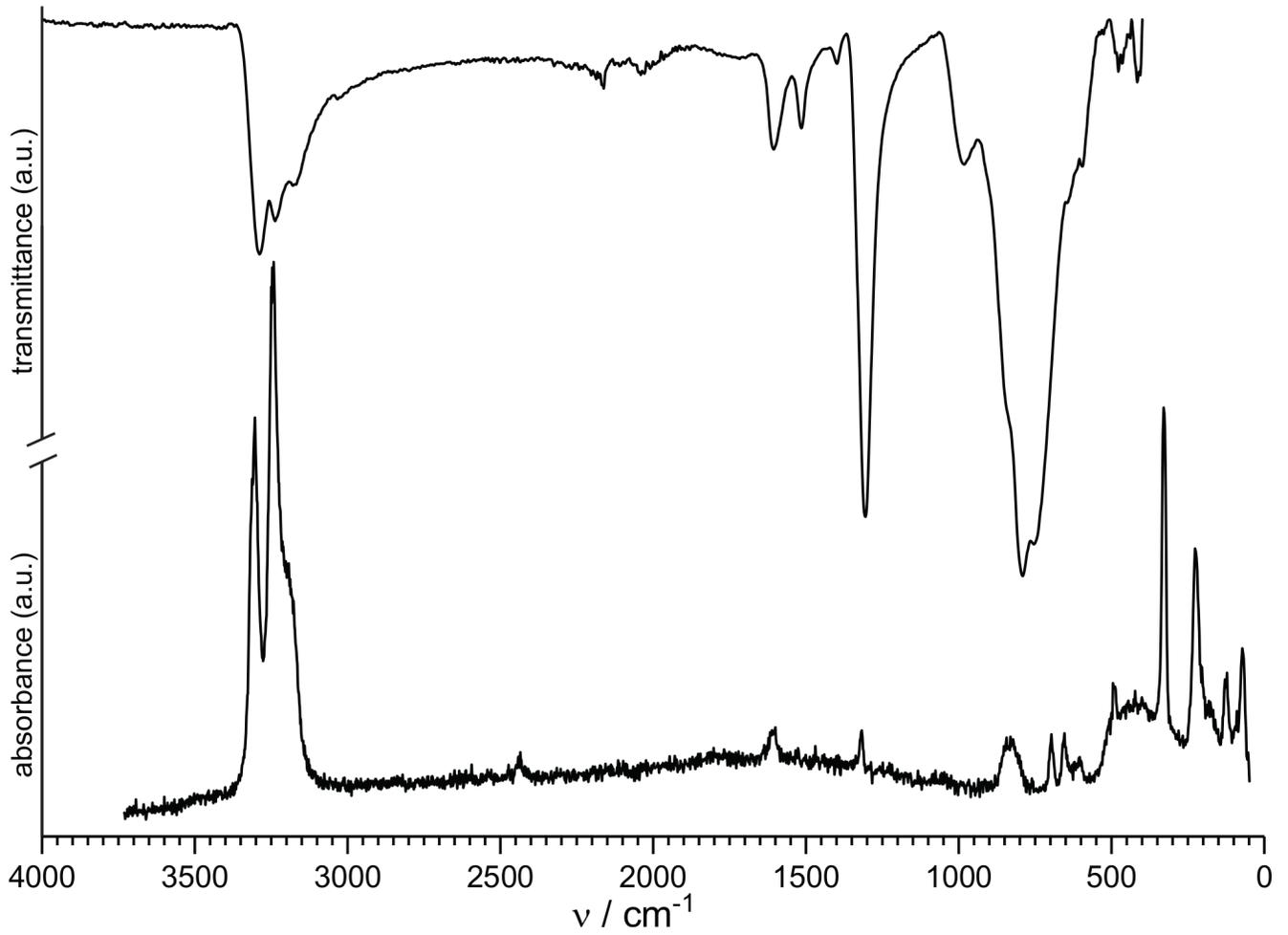
**Figure 15** IR spectrum of  $[\text{Be}(\text{NH}_3)_4](\text{CN})_2$ .



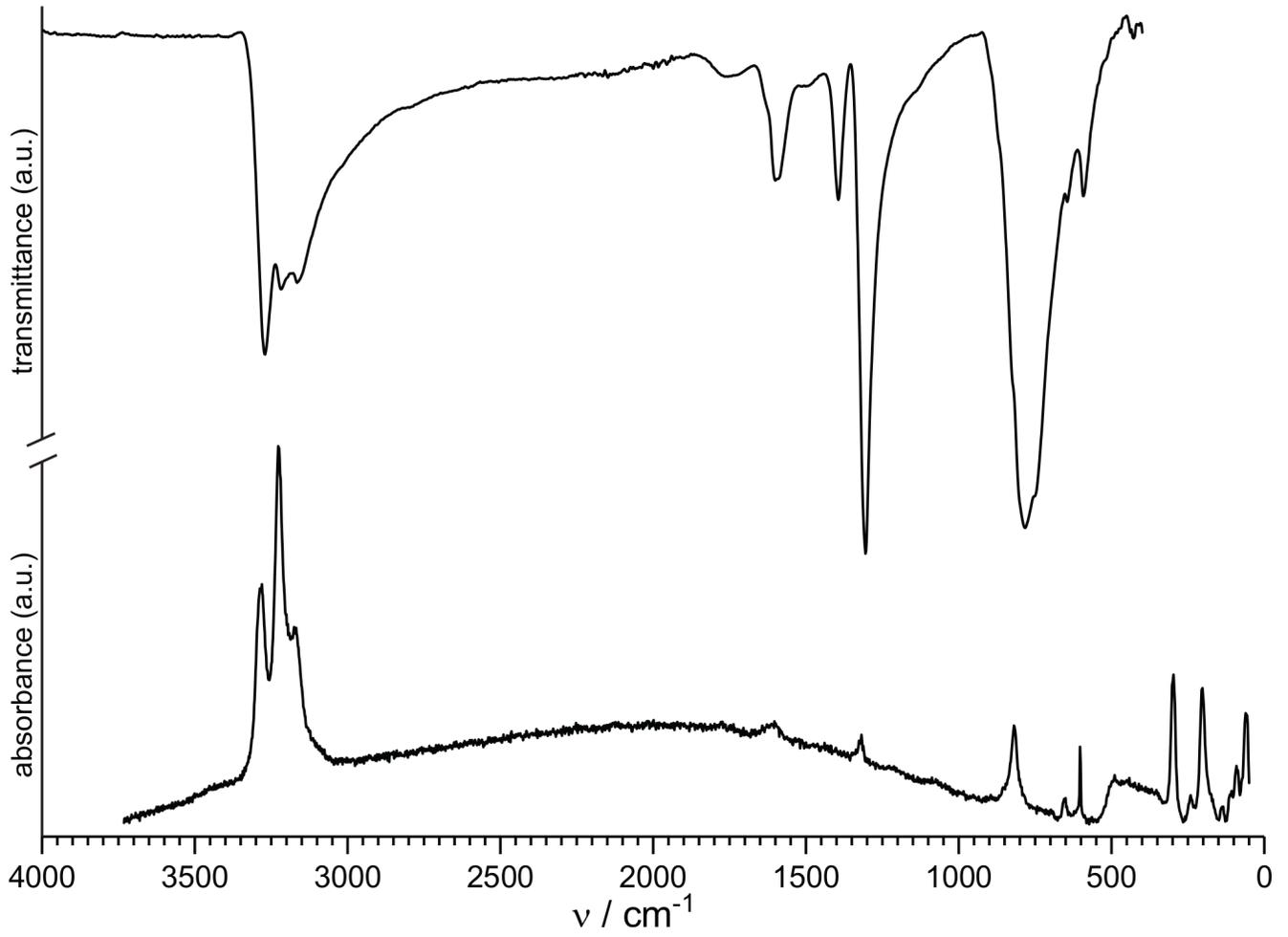
**Figure 16** IR (top) and Raman (bottom) spectra of  $[\text{Be}(\text{NH}_3)_4](\text{N}_3)_2$ .



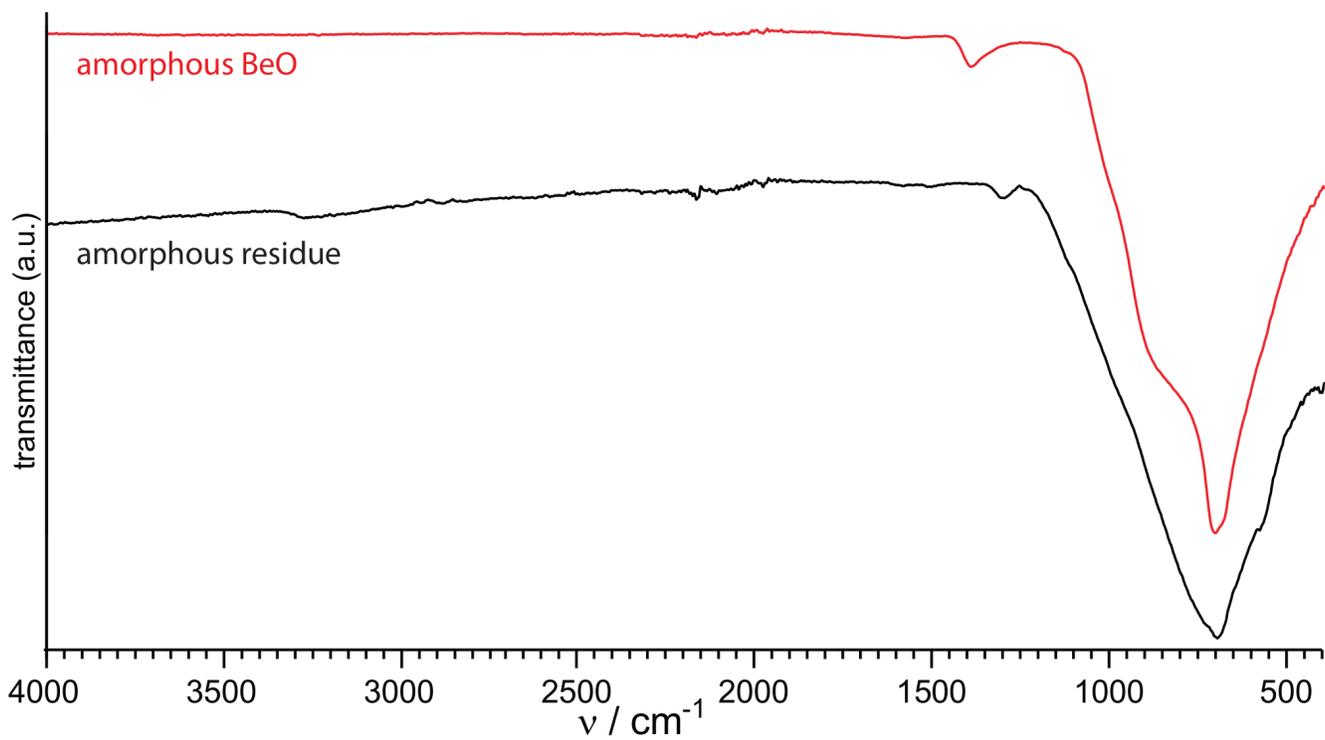
**Figure 17** IR (top) and Raman (bottom) spectra of  $\text{BeCl}_2(\text{NH}_3)_2$ .



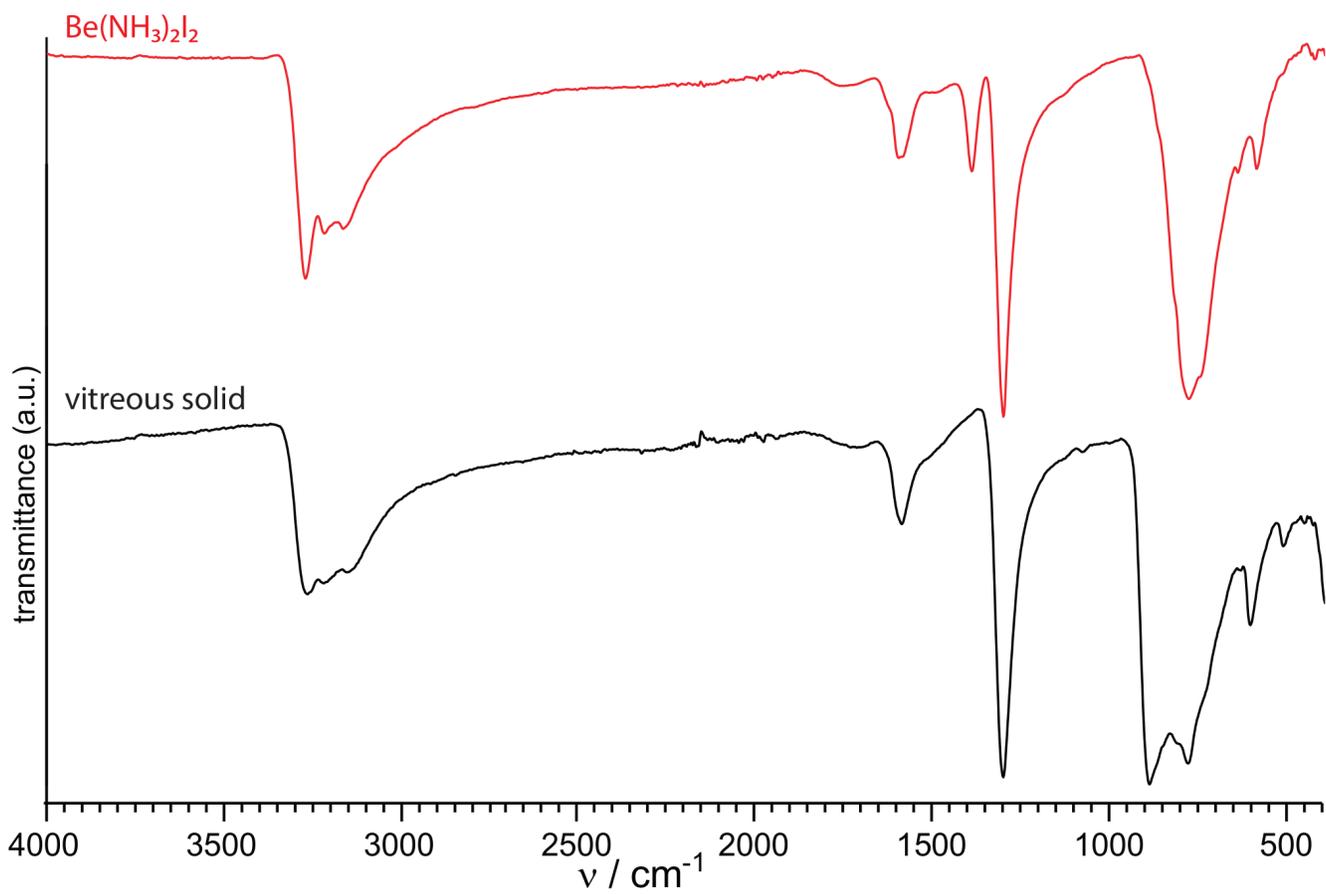
**Figure 18** IR (top) and Raman (bottom) spectra of  $\text{BeBr}_2(\text{NH}_3)_2$ .



**Figure 19** IR (top) and Raman (bottom) spectra of  $\text{Be}(\text{NH}_3)_2\text{I}_2$ .

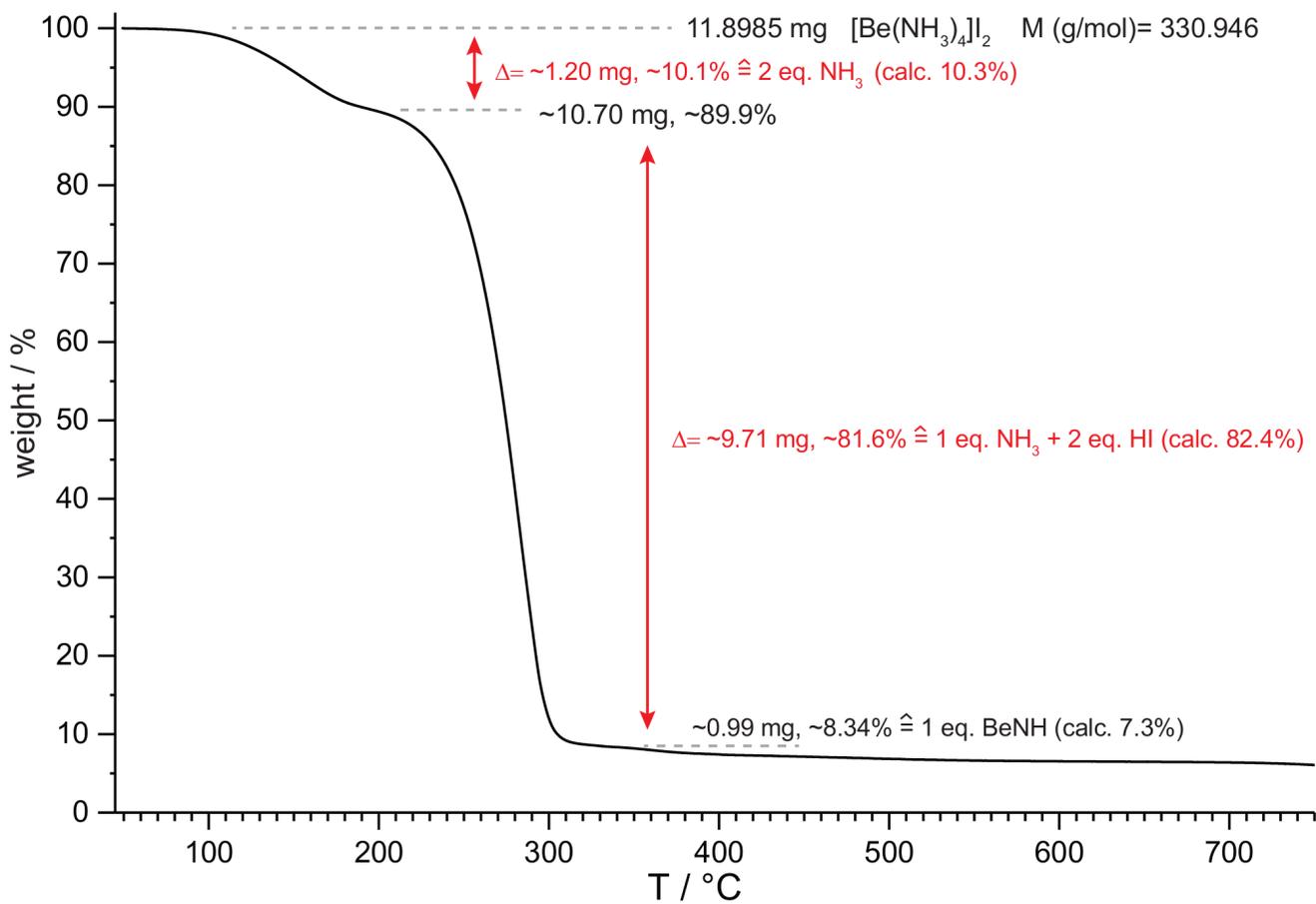


**Figure 20** IR spectra of annealed, amorphous beryllium oxide (red) and the white residue obtained for the thermal decomposition of  $[\text{Be}(\text{NH}_3)_4]_2$  at 400 °C in a corundum container *in vacuo* (black).

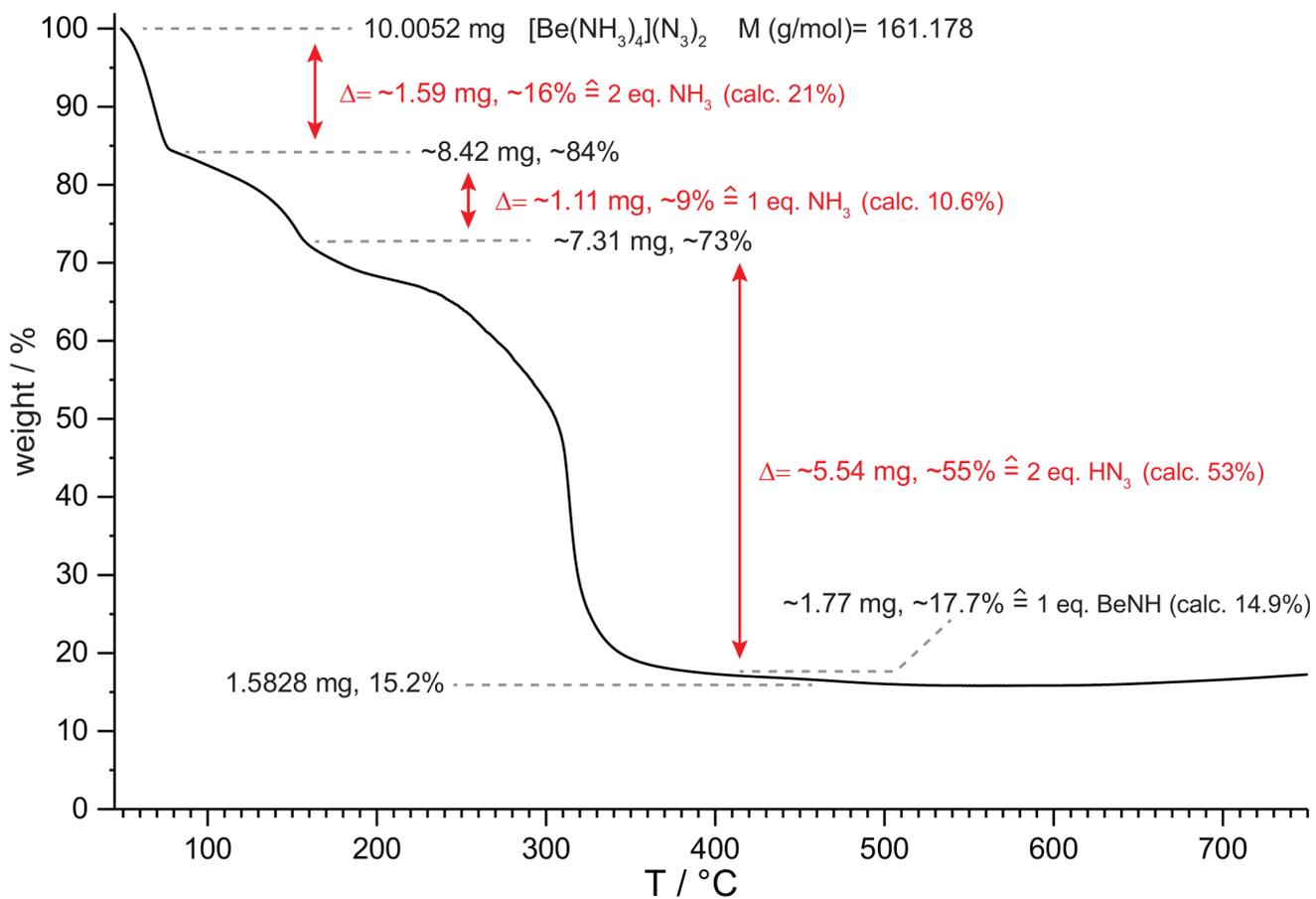


**Figure 21** IR spectra of  $\text{Be}(\text{NH}_3)_2\text{I}_2$  (red) and the off white, vitreous solid obtained for the thermal decomposition of  $[\text{Be}(\text{NH}_3)_4]\text{I}_2$  at 400 °C *in vacuo* (black).

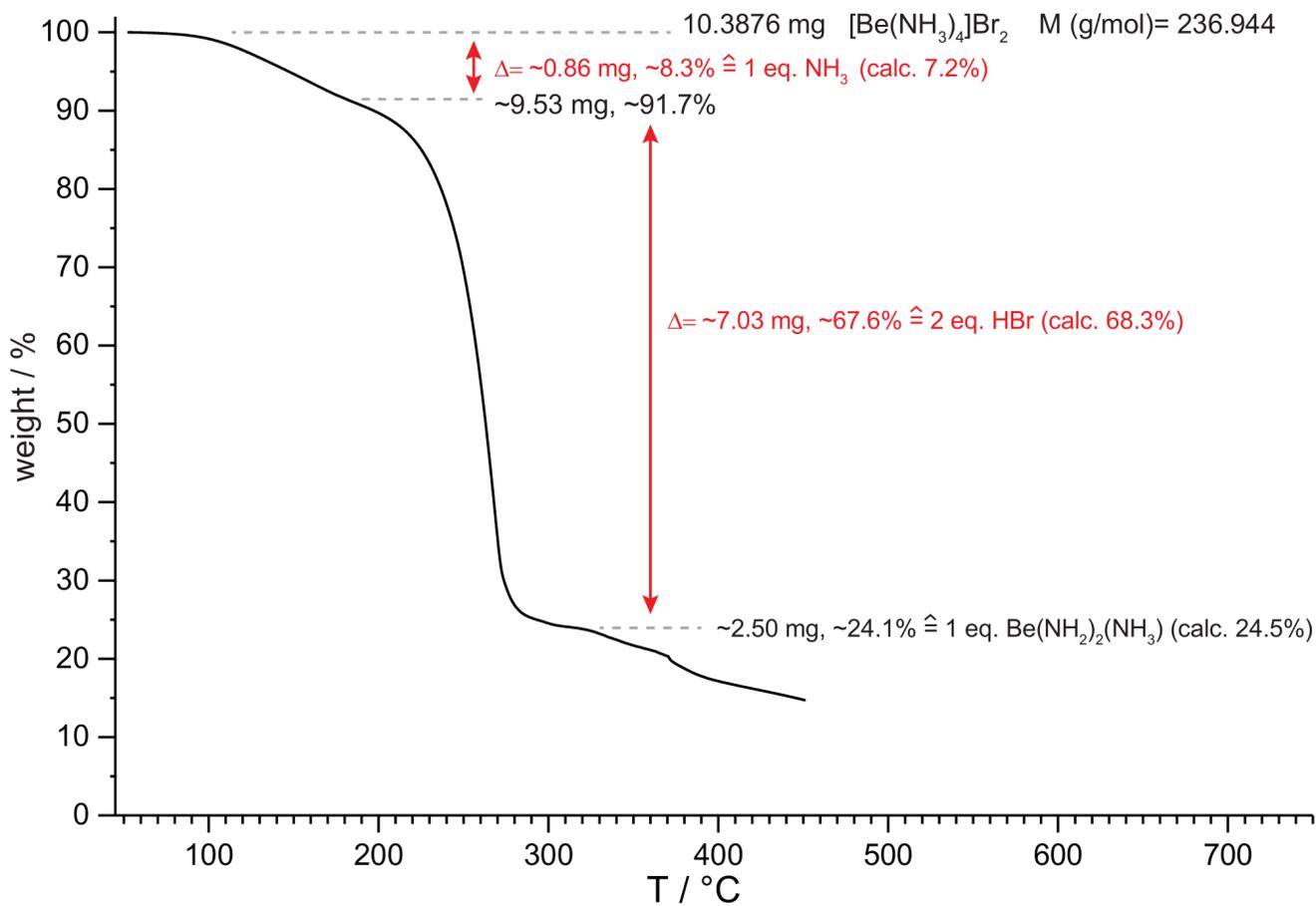
## 5 Thermo Gravimetric Analysis



**Figure 22** TGA plot of thermal decomposition of  $[\text{Be}(\text{NH}_3)_4]\text{I}_2$  from 50 to 750 °C with a heating rate of  $2 \frac{\text{K}}{\text{min}}$ .



**Figure 23** TGA plot of thermal decomposition of  $[\text{Be}(\text{NH}_3)_4](\text{N}_3)_2$  from 50 to 450 °C with a heating rate of  $2 \frac{\text{K}}{\text{min}}$ .



**Figure 24** TGA plot of thermal decomposition of  $[\text{Be}(\text{NH}_3)_4]\text{Br}_2$  from 50 to 450 °C with a heating rate of  $1 \frac{\text{K}}{\text{min}}$ .

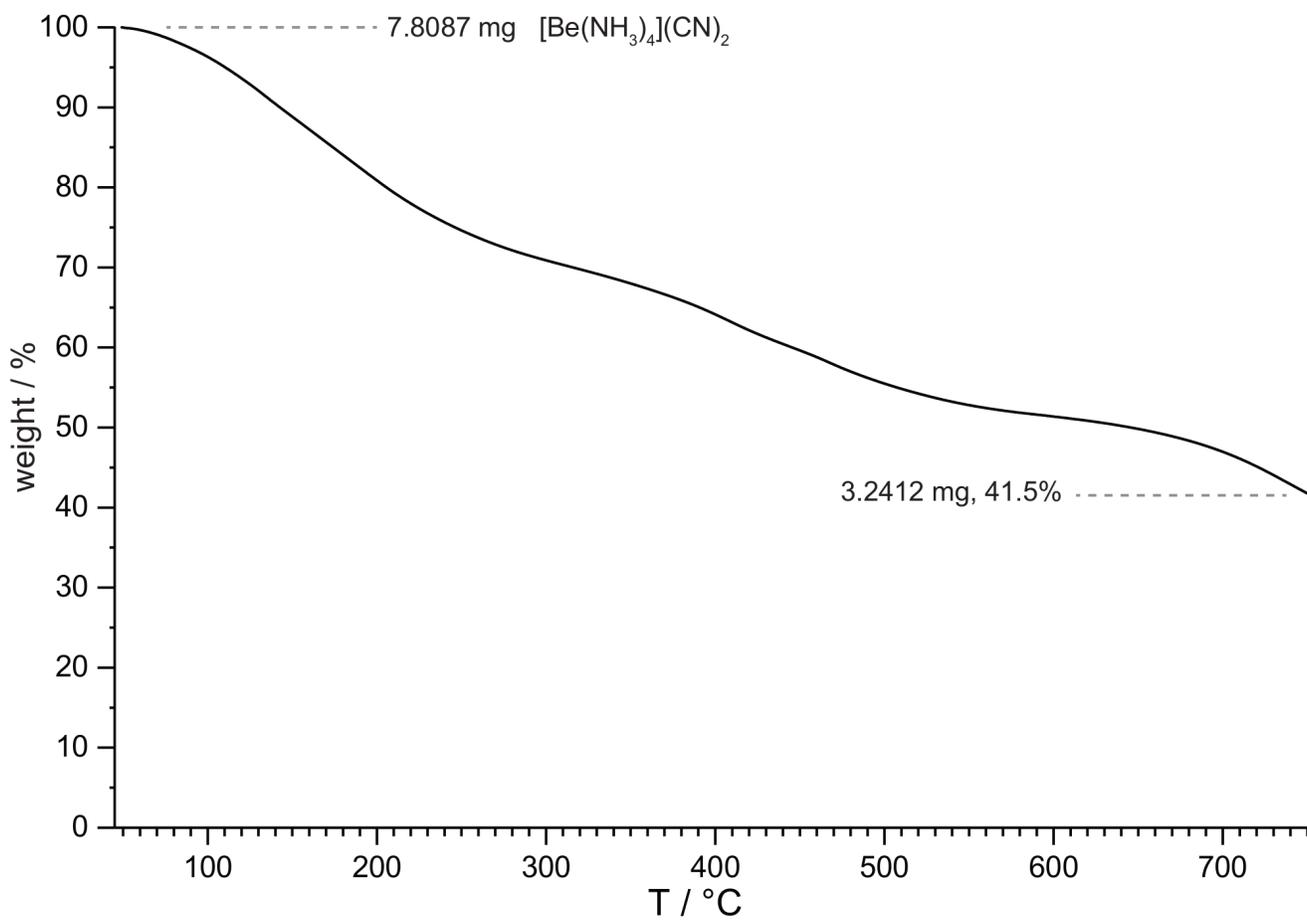
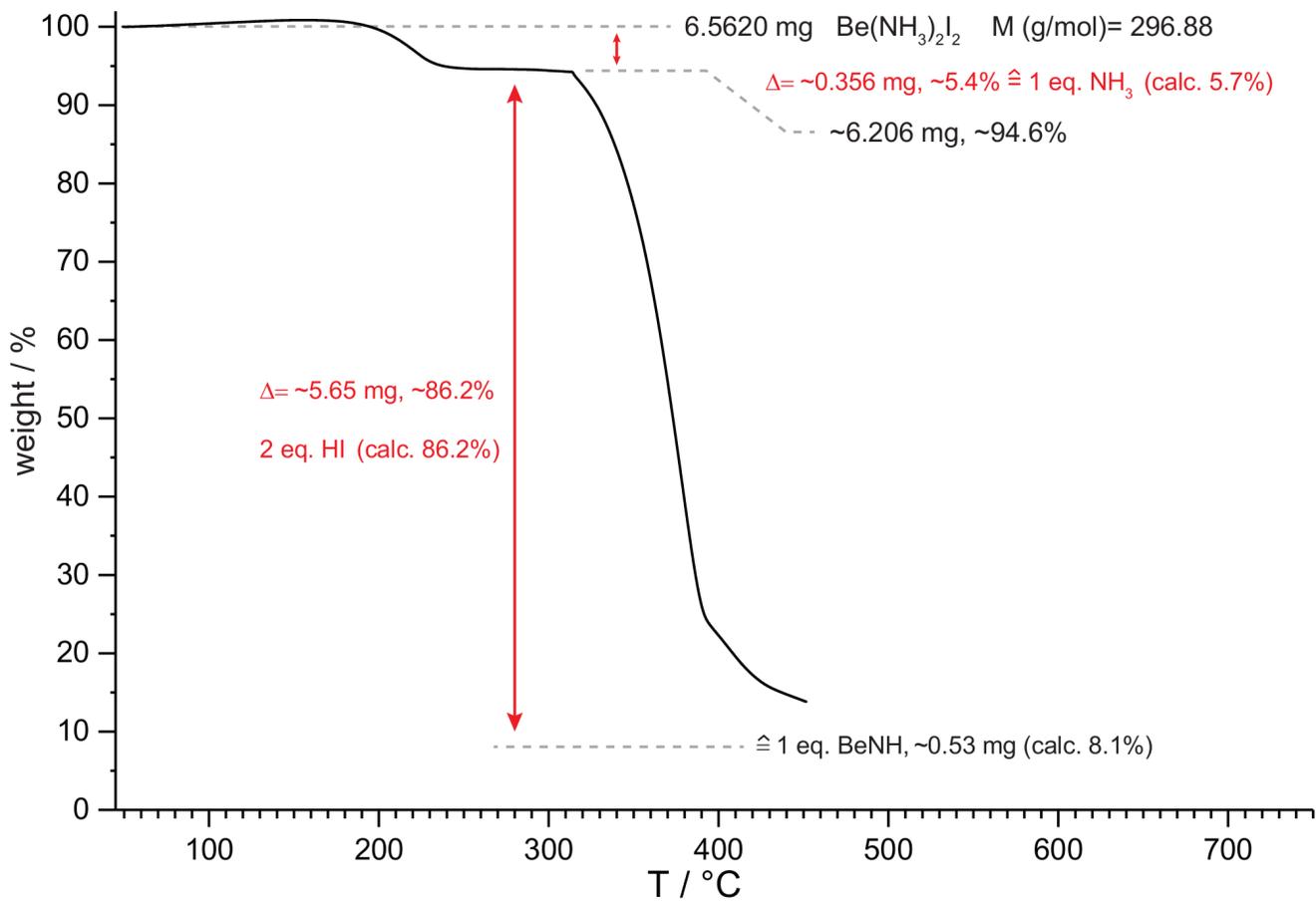


Figure 25 TGA plot of thermal decomposition of  $[\text{Be}(\text{NH}_3)_4](\text{CN})_2$  from 50 to 450 °C with a heating rate of  $2 \frac{\text{K}}{\text{min}}$ .



**Figure 26** TGA plot of thermal decomposition of  $\text{Be}(\text{NH}_3)_2\text{I}_2$  from 50 to 450 °C with a heating rate of  $2 \frac{\text{K}}{\text{min}}$ .

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