Ethylenediamine complexes of the beryllium halides and pseudo-halides†

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The suitability of ethylenediamine (en) as an alternative solvent to liquid ammonia in beryllium chemistry was evaluated. Therefore, BeF₂, BeCl₂, BeBr₂, BeI₂, [Be(NH₃)₄]₂(N₃)₂, [Be(NH₃)₄](CN)₂ and [Be(NH₃)₄](SCN)₂ were reacted with ethylenediamine and analysed via NMR and IR spectroscopy. Additionally single crystal structures of [BeF₂(en)₂]Cl₂, [Be(en)₂]Br₂ and [Be(en)₂]I₂ were obtained. The anions were found to have a distinct influence on the solubility as well as on the species present in solution and the solid state, while ethylenediamine can act as mono- and bidentate ligand or as a crystal solvent.

1. Introduction

Beryllium exhibits by far the highest electronegativity of all s-block metals and the ion potential of Be²⁺ is one of the highest out of all elements.¹ This results in a unique chemistry of beryllium, which is dominated by a high covalency of beryllium–element bonds and a predominance of four coordinated beryllium complexes.²,³ Even though the coordination chemistry and reactivity of beryllium has been expanded in recent years, this chemistry is still significantly less explored than of the other s-block elements.⁴,⁵ The main obstacle for this, are the health hazards associated with beryllium and its compounds.⁶ Though, a second problem is the low solubility of many beryllium compounds in common organic solvents. Therefore, most knowledge is available on the aqueous beryllium chemistry.⁷ O-Donor solvents, especially ethers are frequently employed,⁸ but this is only feasible if strongly coordinating ligands like N-heterocyclic⁹–¹¹ or carboxyclic amino carbenes,¹²,¹³ carbodiphosphoranes¹⁴ or chelating N-donor ligands like β-diketiminates¹⁶ or trispyrazolylborates are used.¹⁷–¹⁹ Furthermore, Lewis-acid induced activation of thf can occur in these systems.²⁰ While the high oxophilicity of beryllium leads to a relatively strong coordination of ethers, these ligands are still not good enough liga-

tors to displace charged ligands, especially halides, at the beryl-

lum atom. This results in the formation of pseudo-tetra-
hedral complexes of the type L₂BeX₂,²¹,²² which is also observed for other monodentate O-donor ligands and solvents.²³,²⁴ Crown ethers give significantly more stable beryllium compounds than monodentate ethers.²⁵–²⁷ Therefore, these chelating ligands are capable to displace charged ligands and lead to the formation of monocationic complex ions.²⁸–³⁰ If better donor ligands like dmf or chelating di- or trialcohols are used, also dicationic mononuclear beryllium complexes can be generated.³¹,³² But the high Lewis-acidity of the metal centre in these compounds frequently leads to activation and sometimes decomposition of these ligands.³²,³³ Additional problems accompanying strong O-donor ligands are the for-

mation of very insoluble complexes and the inability to replace these ligands. Thus O-donor ligands are of little use for further reactivity studies. An alternate approach is to use highly polar non-coordinating solvent like dichloromethane or chloroform.³⁴,³⁵ But this frequently results in activation of the solvent or halide exchange.³⁵,³⁶ Therefore, we decided to explore whether a middle ground could be found by using N-donor ligands. It was already known that in analogy to O-donor ligands also N-donors lead to the formation of pseudo-tetrahedral L₂BeX₂ complexes.³⁷ However, the solubility of the formed complexes is often low when small N-donors like MeCN are used.³⁸ In contrast to this NET₃ adducts to BeCl₂, BeBr₂ and BeI₂ are well soluble, but due to the huge steric demand of the amine only one ligand can coordinate.¹⁶ The smallest amine, ammonia, on the other hand readily dissolves even highly ionic salts like BeF₂ and shows beryllium solubilization properties comparable to water.²⁹–⁴² Hence NH₃ provides most characteristics needed to perform beryllium chemistry with strongly coordinating...
ligands. However, the physical properties of ammonia result in challenges concerning the experimental setup and make micro scale reactions slow-going and laborious. Accordingly, we were searching for a comparable solvent with a boiling point above ambient temperature. Ethylenediamine (en) fits this brief nicely and is extensively used as an alternative to ammonia in Zintl chemistry. Additionally ethylenediamine has the ability to form chelate compounds, which is widely used in transition metal complex chemistry. Due to this, we conducted experiments on the solubilization and coordination properties of ethylenediamine towards the beryllium halides and pseudo-halides.

2. Results and discussion

To the best of our knowledge only water and ammonia are capable to dissolve beryllium fluoride at least to some extent. This is presumably caused by the very high lattice energy of BeF$_2$. Therefore, BeF$_2$ is a good benchmark to test the solubilizing properties of solvents. When ethylenediamine (en) was added to finely powdered BeF$_2$ only an increase in the volume of the solid could be observed and no signals were detected with $^9$Be NMR spectroscopy. Therefore, it could not be assessed if a reaction took place. However, when a solid piece of vitreous BeF$_2$ was placed in ethylenediamine its surface turned opaque and needle shaped microcrystals could be observed under the microscope. This was indicative for a reaction of BeF$_2$ with ethylenediamine. To drive this reaction to completion and to obtain crystals with a size suitable for single crystal X-ray diffraction, the reaction mixture was transferred into a quartz ampoule. After flame sealing, this ampoule was heated to 250 °C for three weeks. This led to the formation of rod shaped crystals of [BeF$_2$(en)]$_n$ according to eqn (1).

$$\text{BeF}_2 + \text{en} \rightarrow \frac{1}{n} [\text{BeF}_2(\text{en})]_n$$ (1)

In Fig. 1 a projection of the unit cell of [BeF$_2$(en)]$_n$ along the b axis is depicted as well as the coordination environment of the beryllium atoms including hydrogen bridged contacts. [BeF$_2$(en)]$_n$ crystallizes in the monoclinic space group $C2/c$ (15) with four formula units per unit cell. One ethylenediamine molecule coordinates to two BeF$_2$ units via its two nitrogen atoms, while each BeF$_2$ unit is coordinated by two ethylenediamine molecules. Therefore, one dimensional chains (n$_c$[[Be(en)$_2$]$_2$F$_{2n}$]) along the crystallographic c axis are formed (Fig. 1a). The beryllium atoms are pseudo-tetrahedrally coordinated by two fluorine and two nitrogen atoms (Fig. 1b). The N–Be–N (106.3(1)$^\circ$), F–Be–F (115.6(2)$^\circ$) and N–Be–F (108.33(4)$^\circ$–108.93(4)$^\circ$) angles are all very close to the ideal tetrahedral angle. The Be–F atomic distances are 1.516(1) Å and are significantly shorter than those in BeF$_2$ (1.541(1)–1.547(1) Å). These distances are also slightly shorter than in BeF$_2$(NH$_3$)$_2$ (1.520(1) Å and 1.531(1) Å). The short Be–F atomic distances in [BeF$_2$(en)]$_n$ suggest a stronger interaction between the beryllium and fluorine atoms compared to the other beryllium fluorides. This is indicative for weaker interactions with the coordinating ethylenediamine compared to the other ligands. This is confirmed by the Be–N distances, which are with 1.765(2) Å longer than those in BeF$_2$(NH$_3$)$_2$ (1.749(1) Å and 1.759(1) Å). The N–H bands of [BeF$_2$(en)]$_n$ are observed at 3261 and 3173 cm$^{-1}$ in the IR spectrum and are therefore batochromically shifted compared to non-coordinated ethylenediamine (3412 cm$^{-1}$). This indicates a weakening of the N–H bonds upon coordination to BeF$_2$ as would be expected. The position of the C–H-stretching bands of [BeF$_2$(en)]$_n$ (2977 and 2959 cm$^{-1}$) and free ethylenediamine (2950–2785 cm$^{-1}$) are very similar. This is also the case for the bands at lower wave numbers (ESI Fig. S7) and indicates little influence of the beryllium coordination on the backbone of the ethylenediamine. A distinctively strong band is observed at 724 cm$^{-1}$, which is close to one of the bands of neat BeF$_2$ (403 and 734 cm$^{-1}$). Therefore, this band is assigned to the Be–F band, which is also supported by the comparison with the IR spectra of the other ethylenediamine complexes described below, which all exhibit no beryllium halide or pseudo halide bonds and lack this band.

Beryllium chloride does react exothermically with ethylenediamine, which is in contrast to beryllium fluoride. The solubility of BeCl$_2$ in ethylenediamine is considerably higher than

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Fig. 1 Solid state structure of [BeF$_2$(en)]$_n$: (a) projection of the unit cell along the b axis and (b) coordination environment of the beryllium atoms including hydrogen bonds. Ellipsoids are depicted at 70 % probability at 100 K. Hydrogen atoms in (a) are omitted for clarity.
that of BeF₂. Therefore, BeCl₂ can be converted to [Be(en)₃]Cl₂ within a few days at 80 °C according to eqn (2).

\[
\text{BeCl}_2 + 3\text{en} \rightarrow [\text{Be(en)}_3]\text{Cl}_2
\]  

(2)

Upon cooling to ambient temperature crystals of [Be(en)₃]Cl₂ Cl₂ are deposited at the glass wall of the reaction vessel. Beryllium bromide reacts more exothermically with ethylenediamine than BeCl₂. This is evident from the formation of ethylenediamine fume upon contact of the two reactants. The solubility of BeBr₂ in ethylenediamine is slightly higher than that of BeCl₂. The bromide can be converted to crystalline [Be(en)₃]Br₂ in the analogous way to BeCl₂ as illustrated by eqn (3).

\[
\text{BeBr}_2 + 3\text{en} \rightarrow [\text{Be(en)}_3]\text{Br}_2
\]  

(3)

[Be(en)₃]Cl₂ and [Be(en)₃]Br₂ crystallise isotypically in the triclinic space group P1 (2) with two formula units per unit cell, as exemplified in Fig. 2a. In contrast to BeF₂, ethylenediamine displaces all halides from BeCl₂ and BeBr₂. This results in the formation of pseudo-tetrahedrally coordinated beryllium atoms, which are coordinated κ³ by the two nitrogen atoms of one chelating ethylenediamine molecule and κ² by two additional ethylenediamine molecules via one amine group each (Fig. 2b). The N–Be–N angles in [Be(en)₃]Cl₂ (97.77(9)–112.15(10)°) and [Be(en)₃]Br₂ (97.55(14)–114.47(15)°) are very similar but deviate significantly from the ideal tetrahedron angle.

The Be–N atomic distances in [Be(en)₃]Cl₂ (1.705(2)–1.748(2) Å) and [Be(en)₃]Br₂ (1.712(3)–1.748(3) Å) are almost identical within the standard deviation and are significantly shorter than those in [BeF₂(en)]⁺. This is caused by the fact that in [Be(en)₃]Cl₂ and [Be(en)₃]Br₂ a [Be(en)₃]^2⁺ cation is present. This leads to a lower electron density at the metal centre, which is compensated through stronger donation from the amino groups. This results in a contraction of the Be–N atomic distances. In accordance to this the Be–N atomic distances in [Be(en)₃]Cl₂ and [Be(en)₃]Br₂ are comparable to the ones found in [Be(NH₃)₄]²⁺ cation (1.707(3)–1.744(4) Å).³⁹,⁴⁰ The hydrogen atoms of the coordinated and non-coordinated amino groups form hydrogen bonds to the nitrogen atoms of the non-coordinated amino groups as well as to the chloride or bromide ions, respectively (Fig. 2b). The presence of coordinated and non-coordinated amino groups is also observed in the IR spectra of [Be(en)₃]Cl₂ and [Be(en)₃]Br₂ (ESI Fig. S7†). Here four N–H bands are observed. Two for non-coordinated ([Be(en)₃]Cl₂: 3342 cm⁻¹, 3271 cm⁻¹; [Be(en)₃]Br₂: 3342 cm⁻¹, 3274 cm⁻¹) and two for coordinated ([Be(en)₃]Cl₂: 3151 cm⁻¹, 3086 cm⁻¹; [Be(en)₃]Br₂: 3155 cm⁻¹, 3092 cm⁻¹) amino groups. In accordance to the presence of two differently coordinating ethylenediamine molecules also more C–H stretching bands as well as more complex spectra at lower wave numbers are observed for [Be(en)₃]Cl₂ and [Be(en)₃]Br₂ in comparison to [BeF₂(en)]⁺. Also no bands close to the Be–Cl or Be–Br bands of BeCl₂ and BeBr₂ could be observed, which supports the complete dissociation of the halides.⁵⁰,⁵¹

The reaction of BeI₂ with ethylenediamine is significantly more exothermic than with BeCl₂ or BeBr₂. Upon contact of BeI₂ and ethylenediamine the latter starts boiling and a brown solution is obtained. The brown colour may be caused by partial thermal decomposition of the amine. Also BeI₂ is significantly more soluble than the other beryllium halides. Due to the significantly higher solubility of BeCl₂, BeBr₂ and BeI₂ in ethylenediamine compared to BeF₂, the reaction mixtures of the chloride, bromide and iodide could be investigated with ⁹Be NMR spectroscopy. Saturated ethylenediamine solutions of BeBr₂ and BeI₂ show one relatively sharp singlet at 5.4 ppm each with linewidths of 10.3 and 10.6 Hz, respectively (Fig. 3). In contrast to this the BeCl₂ solution yields two signals at 3.4 (ω₁/₂ = 31.6 Hz) and 5.4 ppm (ω₁/₂ = 7.8 Hz). These are all in the typical range of four coordinated beryllium nuclei.⁵²,⁵₃

The coordination environment of the beryllium nuclei is identical in the solid state structures of [Be(en)₃]Cl₂ and [Be(en)₃]Br₂ ([Be(en)₃]^2⁺) but different in the ethylenediamine complex of beryllium iodide ([Be(en)₃]^2⁺, vide infra). However, the ethylenediamine solutions of these three beryllium halides all exhibit a ⁹Be NMR signal at 5.4 ppm with comparable linewidths. This suggests that in solution the same species are present. We therefore assume that fast exchange between coordinated and free ethylenediamine takes place in solution according to eqn (4).

\[
[\text{Be(en)}_3]^{2+} \overset{\text{en}}{=} [\text{Be(en)}_3]^{2+} + [\text{Be(en)}_4]^{2+}
\]  

(4)

This ligand exchange is also supported by the ¹H and ¹³C NMR spectra of these solutions. Here only one signal set for
ethylenediamine is observed with chemical shifts, which are virtually identical to neat ethylenediamine. However, the NMR signals are broadened. This is expected for fast ligand exchange on the NMR timescale. Due to the huge excess of non-coordinated ethylenediamine the averaged signal of free and coordinated ligand is very close to neat ethylenediamine.

The additional $^9$Be NMR signal at 3.4 ppm in the chloride solution is presumably caused by displacement of one amino by a chlorido ligand at the beryllium centre according to eqn (5).

$$\text{BeI}_2 + 3\text{en} \rightarrow \text{[Be(en)$_2$I$_2$]} \cdot \text{en} \quad (6)$$

Single crystals of the ethylenediamine complex of BeI$_2$ could be obtained by adding BeI$_2$ to an ethylenediamine solution saturated with BeI$_2$ and recrystallising the obtained precipitate at 80 °C over a time period of seven days. This led to the formation of [Be(en)$_2$I$_2$-en according to eqn (7).

$$\text{BeI}_2 + 3\text{en} \rightarrow \text{[Be(en)$_2$I$_2$]} \cdot \text{en} \quad (6)$$

[Be(en)$_2$I$_2$]-en crystallises in the monoclinic space group C2/c (15) with four formula units per unit cell. The beryllium atom in [Be(en)$_2$I$_2$]-en is, in contrast to [Be(en)$_3$]Cl$_2$ and [Be(en)$_3$]Br$_2$, only coordinated by two ethylenediamine ligands, which are $\kappa^2$ coordinating with both their nitrogen atoms resulting in a [Be(en)$_2$]$_2^{2+}$ cation (Fig. 4a). The metal atom is also coordinated pseudo-tetrahedrally with N–Be–N angles of 98.20(17)–116.22(18)°. These are comparable to the angles found in the chloro and bromo compounds. Also the Be–N atomic distances are with 1.727(5) and 1.732(5) Å within the standard deviation identical to [Be(en)$_3$]Cl$_2$ and [Be(en)$_3$]Br$_2$. The amino hydrogen atoms of the [Be(en)$_2$]$_2^{2+}$ moiety form hydrogen bonds to the neighbouring iodine anions as well as to the non-coordinated ethylenediamine molecules as shown in Fig. 4a. This crystal ethylenediamine fills the voids in between the [Be(en)$_2$]$_2^{2+}$ cations as shown in the projection of the unit cell (Fig. 4b).

Despite the different coordination modes of the ethylenediamine molecules in the solid state structures of [Be(en)$_3$]Cl$_2$, [Be(en)$_3$]Br$_2$ and [Be(en)$_2$]$_2$-en, the N–H and C–H bands in the IR spectra are observed at similar wave numbers. Only the region below 2000 cm$^{-1}$ in the spectrum of [Be(en)$_2$]$_2$-en shows less bands than the chloro and bromo complexes (ESI Fig. S7†). This is in accordance with the higher symmetry of [Be(en)$_2$]$_2$-en. Like for [Be(en)$_3$]Cl$_2$ and [Be(en)$_3$]Br$_2$ no beryllium halide band was observed.$^{30}$

The anions seemed to have a significant effect on the solid state structure of the ethylenediamine complexes of BeCl$_2$, BeBr$_2$ and BeI$_2$, but not on the major species present in solu-
tion. To evaluate this further we wanted to conduct reactions with sterically more demanding pseudo-halides like azide, cyanide and thiocyanate. However, the synthesis of binary Be(N₃)₂ and Be(CN)₂ involves the reaction of either HN₃ or HCN with beryllium organyles or prolonged heating of BeCl₂ in the corresponding trimethylsilyl pseudo-halide, while binary Be(SCN)₂ is not known. Therefore, we decided to use tetramineberyllium pseudo-halides as starting materials instead.

[Be(NH₃)₄]⁺(N₃)₂ readily dissolves in ethylenediamine under vigorous gas evolution under the formation of [Be(en)_2]⁺(N₃)_2·en according to eqn (7).

\[ [\text{Be(NH}_3)_4]_2^+ | (\text{N}_3)_2 + 3\text{en} \rightarrow [\text{Be(en)}]_2^+ | (\text{N}_3)_2 | \text{en} \quad (7) \]

This azido complex is significantly more soluble than the corresponding halides. Removal of the solvent in vacuo gave a colourless oil in which colourless crystals of [Be(en)_2](N₃)_2·en formed. [Be(en)_2](N₃)_2·en crystallises in the monoclinic space group C2/c (15) with four formula units per unit cell. Like in [Be(en)_2]I_2·en two ethylenediamine ligands, are κ² coordinated via both their nitrogen atoms to the beryllium atom (Fig. 5). The N–Be–N angles are with 98.53(4)–117.75(4)° almost identical to those in [Be(en)_2]I_2·en. Also the Be–N atomic distances are with 1.721(1) and 1.738(1) Å within the standard deviation almost identical to those in [Be(en)_2]I_2·en. The amino hydrogen atoms form extensive hydrogen bond networks between the azide ions and ethylenediamine molecules. These strong interactions might be the reason why the N–H bands could not be observed in the IR spectrum and the asymmetric N₃ stretching band shows a strong bathochromic shift to 1607 cm⁻¹ (ESI Fig. S7†).

In the ⁹Be NMR spectrum of the ethylenediamine solution of [Be(NH₃)₄](N₃)₂ one singlet at 4.9 ppm (ω₁/₂ = 8.0 Hz) is present. Almost at the same chemical shift (5.1 ppm, ω₁/₂ = 14.7 Hz) the signal of [Be(NH₃)₄](SCN)₂ in ethylenediamine is observed, while [Be(NH₃)₄](CN)₂ gives rise to two very broad signals at 4.9 (ω₁/₂ = 82.0 Hz) and 6.0 ppm (ω₁/₂ = 92.9 Hz) (Fig. 3). Considering that the beryllium species in the solid state of [Be(en)_2]I_2·en, [Be(en)_2]I_2·en and [Be(en)_2]SCN·Cl (see below) is identical and due to the fact that for BeCl₂, BeBr₂ and BeI₂ the same species are observed via ³⁵Cl NMR spectroscopy, we assume that also for the pseudo-halides the equilibria from eqn (4) are present in solution. The small difference in shift between the halides and pseudo-halides is presumably caused by different pH-values of the solutions due to the presence of ammonia in the latter solutions according to generalised eqn (8).

\[ [\text{Be(NH}_3)_4]_2^+ | X_2 + 2\text{en} \rightarrow [\text{Be(en)}]_2^+ | X_2 + 4\text{NH}_3 \quad (8) \]

The second ³⁵Cl NMR signal in the ethylenediamine solution of [Be(NH₃)₄](CN)₂ is presumably caused by a monocatioinic species where one cyanido ligand is coordinated to the beryllium atom, similar to the chloride system shown in eqn (5). Like the ethylenediamine complex of beryllium azide, also the cyanide and thiocyanate are very soluble in ethylenediamine and even complete removal of excess ethylenediamine did not yield solids. The IR spectrum of the cyanide shows weak and the thiocyanate strong N-H and C-H bands, which are comparable to [Be(en)_2]Cl₂, [Be(en)_2]Br₂ and [Be(en)_2]I₂·en. While the C–N stretching bands of the thiocyanate ions are clearly observable at 2098 and 2048 cm⁻¹ the C–N band of the cyanide is barely noticeable at 2109 cm⁻¹ (ESI Fig. S7†). The poor quality of the spectrum of the ethylenediamine adduct to beryllium cyanide complex might be caused by strong interaction of the cations and anions, which were also observed NMR spectroscopically.

Unlike the azide, no crystals could be obtained for the cyanide and thiocyanate from the reactions of the tetramineberyllium salts and ethylenediamine. However, attempts to prepare beryllium thiocyanate from beryllium chloride and trimethylsilyl isothiocyanate according to eqn (9) and subsequent reaction with ethylenediamine yielded crystals suitable for X-ray crystallography.

\[ \text{BeCl}_2 + 2\text{Me}_3\text{Si} - \text{NCS} \rightarrow \text{Be}(\text{SCN})_2 \quad (9) \]

Though the reaction with TMS–NCS seems to not completely convert BeCl₂ into Be(SCN)₂, therefore, instead of the
anticipated homoleptic pseudo-halide complex a mixed salt, which contained chloride and thiocyanate anions was obtained as illustrated in eqn (10).

\[
7\text{Be(}\text{SCN})_2 + \text{BeCl}_2 \rightarrow 2[\text{Be(en)}]_2(\text{SCN})_7\text{Cl}
\]  

(10)

\[\text{[Be(en)]_2(SCN)Cl}\] crystallises in the monoclinic space group \(P2_1/c\) (14) with eight formula units per unit cell. Like in \[\text{[Be(en)]_2N}_3\text{en and [Be(en)]_2[N}_3\text{en the beryllium atoms are pseudo-tetrahedrally coordinated by two ethylenediamine molecules, which both coordinate } \kappa^2 \text{ with both their nitrogen atoms. The N–Be–N angles (97.6(2)–121.4(3)°) and Be–N atomic distances (1.525(12)–1.879(16) Å)} \text{ show significantly larger deviations than the other ethylenediamine adduct, but their range is still comparable. The chloride ions aid the crystallisation of } \text{[Be(en)}_2(\text{SCN})_7\text{Cl through the formation of hydrogen bonds to three } \text{[Be(en)}_2]^2+ \text{ units as shown in Fig. 6a. In the centre of three of these } \text{[Be(en)}_2]^2+(\text{SCN})_7^+ \text{ moieties lies one additional } \text{[Be(en)}_2]^2+ \text{ unit (Fig. 6b). The voids between the } \text{[Be(en)}_2]^2+ \text{ and } \text{[Be(en)}_2]^2+(\text{SCN})_7^+ \text{ cations are then filled with the thiocyanate anions (Fig. 6c). The IR spectra of the product of the reaction of } \text{[Be(NH}_3)_4(\text{SCN})_2 \text{ with ethylenediamine and of the single crystals of } \text{[Be(en)}_2(\text{SCN})_7\text{Cl are virtually identical (ESI Fig. S8†). From this, we conclude that } \text{[Be(en)}_2]^2+ \text{ cations are present in both compounds and therefore supports the assumption made in eqn (8).}

Due to the high oxophilicity of beryllium, even complexes with strong N-donor ligands like ammonia or amides are highly sensitive towards traces of moisture.39,41 This is also the case for the ethylenediamine compounds described here. This was found by accident, when attempts were undertaken to crystallize the reaction product of \[\text{[Be(NH}_3)_4(\text{SCN})_2 \text{ with ethylenediamine}. \text{This oil was cooled to 0 °C for several weeks in a flask equipped with a J. Young valve. Due to the different coefficient of thermal expansion of glass and PTFE the content of the flask was exposed to moisture. This led to the formation of single crystals of } \text{[Be}_3(\text{OH})_3(\text{en)}_3][\text{C}_2\text{H}_6\text{N}_2](\text{SCN})_4 \text{ in the oil according to eqn (11).}

\[
3^+[\text{Be(en)}_2]_2(\text{SCN})_2 \overset{\text{H}_2\text{O}}{\text{+}} \text{[Be}_3(\text{OH})_3(\text{en)}_3][\text{C}_2\text{H}_6\text{N}_2]^2+(\text{SCN})_4
\]  

(11)

\[\text{[Be}_3(\text{OH})_3(\text{en)}_3][\text{C}_2\text{H}_6\text{N}_2](\text{SCN})_4\] crystallises in the triclinic space group \(P1\) (2) with two formula units per unit cell. Here \text{H}_2\text{O} molecules have been deprotonated by ethylenediamine and the formed hydroxido ligands act as } \mu_2\text{-bridges between two beryllium atoms. This generates a six-membered } \text{[Be}_3(\text{OH})_3]^{1+} \text{ cation as depicted in Fig. 7. This structural motive is frequently observed in beryllium chemistry as a hydrolysis product and the observed } \text{Be–O distances of 1.566 (2)–1.594(2) Å are virtually identical to the known } \mu_2\text{-hydroxido bridged, six-membered beryllium heterocycles.48,26,39,58–62 The beryllium atoms are coordinated by two hydroxido ligands and one ethylenediamine molecule, which coordinates } \kappa^2 \text{ via both of its nitrogen atoms. The Be–N atomic distances are with 1.7969(2)–1.792(2) Å slightly longer than in the } \text{[Be(en)}_2]^2+ \text{ and } \text{[Be(en)}_2]^2+ \text{ cations or in } \text{[BeF}_2(\text{en})]_n^+. \text{This reflects a weaker interaction between the amino nitrogen atoms and the beryllium atoms in } \text{[Be}_3(\text{OH})_3(\text{en)}_3]^{1+} \text{ due to higher electron density at the metal centres.}

The beryllium atoms in the } \text{[Be}_3(\text{OH})_3(\text{en)}_3]^{1+} \text{ ring are pseudo-tetrahedrally coordinated with N–Be–N, N–Be–O and
O–Be–O angles of 94.0(1)–94.6(1)°, 109.9(1)–116.5(1)° and 110.0(1)–111.0(1)°, respectively. The Hydrogen atoms at the hydroxido ligands form hydrogen bonds to the sulphur atoms of the thiocyanate ions as well as to the non-protonated amino group of the 1-ammonium-2-aminoethane cations, which co-crystallise with the [Be₃(OH)₃(en)₃]³⁺ cations.

3. Conclusions

Ethylenediamine is a good solvent for the beryllium halides and pseudo-halides. However, the formed ethylenediamine adducts to BeCl₂ and BeBr₂ are only little soluble, while the BeF₂ complex is virtually insoluble in the amine. The beryllium atoms in all ethylenediamine compounds are co-ordinated pseudo-tetrahedrally. The amine is capable to displace all halides and pseudo-halides with the exception of fluoride. This reflects the extraordinarily strong Be–F bond, which also leads to a slightly increased Be–N distance in the fluoride complex compared to the median Be–N bond lengths in the other ethylenediamine adducts as evident from the boxplot depicted in Fig. 8. The anions have strong influence on the solubility of the ethylenediamine adducts and also on their solid state structures.

The ethylenediamine solutions of BeCl₂, BeBr₂, BeI₂ and of the pseudo-halides show one distinct signal between 5.4 and 4.9 ppm, which was attributed to a fast equilibrium in solution between [Be(en)₂]²⁺, [Be(en)₃]²⁺ and [Be(en)₄]²⁺, on the NMR time scale. Additional species were observed for the chloride and cyanide, which are presumably caused by stronger interaction between the beryllium cation and these anions. This is also in agreement with a stronger Be–Cl bond strength compared to the other halides, while there is no published data an cyanido complexes of beryllium. However, the high group-electronegativity of cyanide hints at strong Be–CN bonds. Eventually, the advantages of the physical properties of ethylenediamine over ammonia are countered by lower solubility and more complex coordination modes. Therefore, both solvents have to be tested on the specific beryllium precursor together with the ligand system to evaluate the suitability of the solvents.

4. 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,¹,⁶³ special (safety) precautions are strongly advised.⁶

4.1. General experimental techniques

All manipulations were performed either under solvent vapour pressure or dry argon using glovebox and Schlenk techniques. Ethylenediamine was dried over 4 Å molecular sieve and sub-
was heated to 80 °C for 7 days, upon which all BeCl₂ dissolved which led to a slightly exothermic reaction. The sealed tube mine was added with a piston-driven air displacement pipette, the vitreous BeF₂ was converted into a colourless microcrystal-mine was added with a piston-driven air displacement pipette. After the volume of the obtained colourless solution was reduced, all solids had dissolved the solvent was removed and 9Be NMR (42 MHz, en) δ = 5.4 (ω₁/₂ = 10.3 Hz); FT-IR (cm⁻¹): 3342(m), 3274(w), 3155(m), 3092(s), 2951(m), 2892(m), 2863(m), 1613(m), 1588(s), 1474(vw), 1462(vw), 1446(vw), 1360(w), 1342(m), 1315(m), 1274(m), 1221(m), 1158(m), 1136 (w), 1119(vw), 1024(s), 1005(m), 968(w), 928(s), 881(s), 817(s), 760(s), 617(w), 532(m), 479(w), 434(w).

4.2.4. [Be(en)₂]₂-Br₂. The synthesis was performed analogous to [Be(en)₁]Cl₂, ⁹Be NMR (42 MHz, en) δ = 4.9 (ω₁/₂ = 8.0 Hz); FT-IR (cm⁻¹): 2902(s), 2847(m), 2673(vw), 1698(vw), 1607(s), 1548(w), 1515(w), 1456(s), 1344(w), 1313(m), 1262(w), 1187(w), 1121(w), 1095(m), 979(w), 930(m), 838(s), 821(m), 787(s), 764(m), 744(m), 689(s), 518(vw), 501(vw).

4.2.5. [Be(NH₃)₄]²⁺. Approximately 20 mg [Be(NH₃)₄]₃(N₃) were placed into a J. Young NMR tube in a glovebox and 550 μl ethylenediamine was added with a piston-driven air displacement pipette, which led to vigorous gas evolution. The volume of the obtained colourless solution was reduced in vacuo upon which single crystals of [Be(en)₂]₃(N₃)₂-en formed. ⁹Be NMR (42 MHz, en) δ = 4.9 (ω₁/₂ = 8.0 Hz); FT-IR (cm⁻¹): 2902(s), 2847(m), 2673(vw), 1698(vw), 1607(s), 1548(w), 1515(w), 1456(s), 1344(w), 1313(m), 1262(w), 1187(w), 1121(w), 1095(m), 979(w), 930(m), 838(s), 821(m), 787(s), 764(m), 744(m), 689(s), 518(vw), 501(vw).

4.2.6. [Be(NH₃)₄]₄(SCN) in ethylenediamine. The synthesis was performed analogous to [Be(en)₂]₃(N₃)₂-en, however removal of the solvent in vacuo gave a colourless oil. ⁹Be NMR (42 MHz, en) δ = 4.9 (ω₁/₂ = 8.0 Hz); FT-IR (cm⁻¹): 2902(s), 2847(m), 2673(vw), 1698(vw), 1607(s), 1548(w), 1515(w), 1456(s), 1344(w), 1313(m), 1262(w), 1187(w), 1121(w), 1095(m), 979(w), 930(m), 838(s), 821(m), 787(s), 764(m), 744(m), 689(s), 518(vw), 501(vw).

4.2.7. [Be(NH₃)₄]₄(SCN) in ethylenediamine. The synthesis was performed analogous to [Be(en)₂]₃(N₃)₂-en, however removal of the solvent in vacuo gave a colourless oil. ⁹Be NMR (42 MHz, en) δ = 4.9 (ω₁/₂ = 14.7 Hz); FT-IR (cm⁻¹): 3227(s), 3134(s), 2955(s), 2891(m), 2098(s), 2048(s), 1581(m), 1532(w), 1462(m), 1361(w), 1326(w), 1287(m), 1122(m), 1093(m), 1035(m), 936(s), 914(s), 862(m), 782(m), 724(m), 675(m), 607(m), 570(m), 515(w), 494(w), 461(w).

4.2.8. [Be(en)₂]₄(SCN)·Cl. 15 mg (0.19 mmol) BeCl₂ and 52 μl (55 mg, 0.43 mmol) trimethylsilyloxyethane were placed in a J. Young NMR tube in a glovebox and 550 μl SMes₂ was added with a piston-driven air displacement pipette. After all solids had dissolved the solvent was removed in vacuo and the remaining colourless solid was redissolved in 550 μl ethylenediamine. Single crystals of [Be(en)₂]₄(SCN)·Cl were obtained after the volume of the obtained colourless solution was
reduced in vacuo. FT-IR (cm⁻¹): 3208(s), 3119(s), 2957(m), 2894(w), 2800(wh), 2097(s), 2043(s), 1677(wh), 1644(wh), 1579(s), 1519(w), 1458(m), 1360(wh), 1326(w), 1289(m), 1189(w), 1130(s), 1036(s), 1008(wh), 926(m), 881(m), 812(m), 759(m), 702(m), 630(wh), 569(wh), 526(w), 504(w), 469(w).

4.2.9. [Be₃(OH)₃(en)₃][C₂H₉N₂](SCN)₄. The oil received from the reaction of [Be(NH₃)₄(SCN)₂ with ethylenediamine was stored in a flask with a PTFE valve at 0 °C for several weeks. This lead to partial hydrolysis of [Be(en)₂]²⁺[SCN]⁻ and the formation of a few colourless single crystals of [Be₃(OH)₃(en)₃][C₂H₉N₂][SCN]₄.

Conflicts of interest
There are no conflicts to declare.

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