Beryllium Dichloride Coordination by Nitrogen Donor Molecules

Martina P. Dressel, Stefan Nogai, Raphael J. F. Berger, and Hubert Schmidbaur

Anorganisch-chemisches Institut der Technischen Universität
München, Lichtenbergstraße 4, 85747 Garching, Germany

Reprint requests to Prof. Dr. H. Schmidbaur. E-mail: H.Schmidbaur@lrz.tum.de

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The reaction of anhydrous beryllium chloride with nitrogen donors L in diethylether as a solvent under mild conditions affords 1:2 complexes of the type L_2BeCl_2 [L = benzonitrile (**1**), pyridine (**2**), 3,5-dimethylpyridine, pyrrolidine, piperidine (**8**), and diethylamine (**10**)]. Structural studies of compounds **1**, **2**, **8** ($CHCl_3$), and **10** have shown that the complexes have the beryllium centers N_2Cl_2-tetracoordinated with a distorted tetrahedral geometry of the core unit. In crystals of **8** and **10** these molecules are associated to form helical strings via distinct N-H–Cl hydrogen bonding. The reaction of the weak donor pyrazole (pyz) with $(Et_2O)_2BeCl_2$ at low temperature gives the mixed complex $[(Et_2O)(pyz)BeCl_2]$ (**4**), in which one diethylether molecule is retained in the inner coordination sphere of the metal. In tetrahydrofuran (thf) solution, no reaction is observed with pyrazole, indicating that tetrahydrofuran is the stronger donor as compared to pyrazole, and the $(thf)_2BeCl_2$ solvate remains intact. By contrast, with the strong base pyrrolidine (pyrr) the same reaction leads to substitution of one chloride ligand to give the ionic product $[(pyrr)_3BeCl]^+Cl^-$, (**7**). Both products (**4**, **7**) have been structurally characterized. At room temperature the reactions with pyrazole or piperidine lead to ether cleavage as a side-reaction which may even become dominant at long reaction times and more forcing conditions. Dinuclear complexes of the type $[LBeCl(\mu_2\text{-}OR)]_2$ are formed, the structures of which have also been determined. The results suggest that hydrogen bonding may assist in the ether cleavage process, since this reaction is not observed for ligands devoid of N-H functions.

Key words: Beryllium Dichloride Coordination, Nitrogen Donor Molecules

Introduction

After a multi-decade slow-growth period there is renewed interest in the chemistry of beryllium owing to an increase in applications of the element and its compound in various technologies. Recent studies have focussed mainly on the solid state chemistry chemistry [1] and on the coordination chemistry in aqueous solutions [2 – 4]. From these studies it is obvious that the coordination chemistry of the small and hard Be^{2+} cation by *fluoride* and by *oxygen* donor components is by far the most important area. The chemistry of beryllium with oxygen-functional ligands is also of prime interest regarding the toxicity of the metal [5 – 10]. It appears that in complexes or solvation cages with multifunctional O/S/N-ligands, like amino acids or peptides, beryllium is coordinated solely to the oxygen donor centers [11 – 20].

The compounds with beryllium-*nitrogen* linkages described in the literature are very few in number and were all obtained from non-aqueous media [21 – 24]. With very few entries in crystallographical data bases [25], the knowledge of structural details has remained very limited [26 – 28]. In the present preparative and structural study, a series of representative nitrogen-functional molecules have been selected to probe the donor-acceptor interactions with anhydrous beryllium chloride in diethylether as a solvent (and a ligand). Nitriles [29], pyridines [30, 31] and pyrazoles, and secondary or tertiary amines [32, 33] are substrates with uni-, di- and tri-coordinated nitrogen donor atoms which become di-, tri- and tetracoordinated in the products, respectively.

Although diethylether was expected to be an "innocent" oxygen-donor solvent as compared to water, the investigations have shown that weakly basic nitrogen-donors may not be able to fully displace the ether ligands attached to the beryllium atoms. Moreover, donor-assisted ether cleavage may also occur even under mild conditions to give ethoxy-beryllium species.

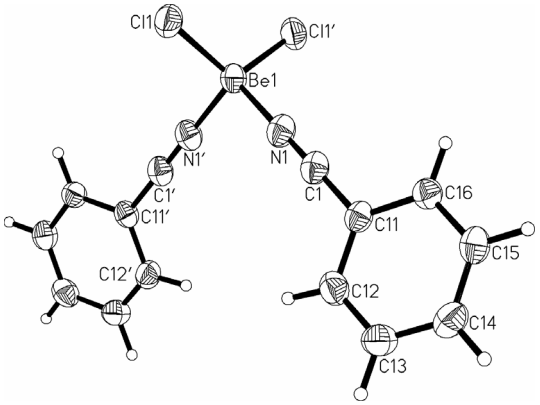


Fig. 1: Molecular structure of $(PhCN)_2BeCl_2$ (**1**). The two halves of the adduct are related by a twofold axis passing through the beryllium atom and bisecting the N-Be-N' angle. Selected bond lengths [Å] and angles [°]: Be-Cl 1.9685(19), Be-N 1.740(3), C1-N 1.145(2); Cl-Be-Cl' 117.68(17), N-Be-N' 102.1(2). Be-N-C1 178.78(17), N-C1-C11 179.8(2).

Results and Discussion

Nitrile coordination

It has been reported as early as 1925 that anhydrous $BeCl_2$ can be dissolved in *nitriles* [29]. For *acetonitrile* the existence of a 2:1 adduct has been confirmed by analytical data and the structure of the complex has later been determined [28]. In the present study therefore no diethylether solvent was employed for the reaction of $BeCl_2$ with excess *benzonitrile*. The reaction was investigated in order to determine the extent of the chloride substitution with an excess of nitrile under forcing conditions (boiling point of PhCN: 190 °C). Pale-yellow needles separated from the clear solutions upon slow cooling to room temperature, which were identified as $(PhCN)_2BeCl_2$, (**1**), m. p. 214 °C (86% yield). The compound is hygroscopic, but stable in a dry atmosphere at room temperature and soluble in polar solvents. The NMR spectra (in $CDCl_3$ at 20 °C) show the benzonitrile resonances (^1H, ^{13}C) and a broad ^9Be signal at 2.01 ppm (at 50 °C, rel. aqueous 1 M $BeSO_4$ solution).

$$(Et_2O)_2BeCl_2 + 2L \rightarrow L_2BeCl_2 \qquad (1)$$

L = PhCN, **1**
L = pyridine, **2**
L = $3,5-Me_2C_5H_3N$, **3**
L = pyrrolidine, **6**
L = piperidine, **8**
L = Et_2NH, **10**

Crystals of $(PhCN)_2BeCl_2$ are monoclinic, space group $P2/n$ with $Z = 2$ molecules in the unit cell. The asymmetric unit contains one half of the molecule with the other half generated by a twofold axis passing through the beryllium atom and bisecting the Cl-Be-Cl' angle (Fig. 1). The Be-N distance is 1.740(3), the Be-Cl distance 1.9685(19) Å, and the angles N-Be-N' and Cl-Be-Cl' are 102.1(2) and 117.68(17)°, respectively. The (N_2Cl_2)Be tetrahedron is therefore significantly distorted with a smaller angle between the nitrogen atoms and a much larger angle between the chlorine atoms. The nitrile triple bond has a length of 1.145(2) Å as compared to 1.138 Å in the free PhCN molecule [34]. These details corroborate the data documented for $(MeCN)_2BeCl_2$ and show that there is little influence of the nitrile substituent (Me *vs.* Ph) on the coordinative bonding in the (N_2Cl_2)Be core unit. The packing of the molecules in the crystal shows no anomalies.

Pyridine coordination

From early work (1925, [29]) it is also known that beryllium chloride can be dissolved in *pyridine* (pyr) as an adduct the nature of which has not been fully established. In later studies the structure of $(pyr)_2Be(SCN)_2$ has been determined which was obtained from $(MeCN)_2Be(SCN)_2$ and pyridine [27].

$(pyr)_2BeCl_2$, (**2**), has now been prepared from the components in a pyridine/benzene or pyridine/diethylether mixed solvent [2:3 or 1:1], from which it was obtained as colourless, hygroscopic crystals.

The same reaction was carried out with 3,5-dimethylpyridine in diethylether and shown to give the corresponding 2:1 adduct [$(3,5\text{-}Me_2C_5H_3N)_2BeCl_2$ (**3**), m. p. 197 °C, 79% yield]. The product was identified by analytical and spectroscopic data, but no single crystals could be grown. With regard to the observations made with piperidine (below) it should be noted that there was no evidence for cleavage of the diethylether solvent molecules with excess pyridine or 3,5-dimethylpyridine.

Crystals of $(pyr)_2BeCl_2$ (**2**) are monoclinic, space group $P2_1$ with $Z = 8$ formula units in the unit cell. The asymmetric unit contains four independent molecules which all have a very similar geometry. One example is shown in Fig. 2. The Be-N and Be-Cl distances are in the range 1.742(5)–1.773(5) and 1.992(4)–2.014(5) Å, respectively. The N-Be-N

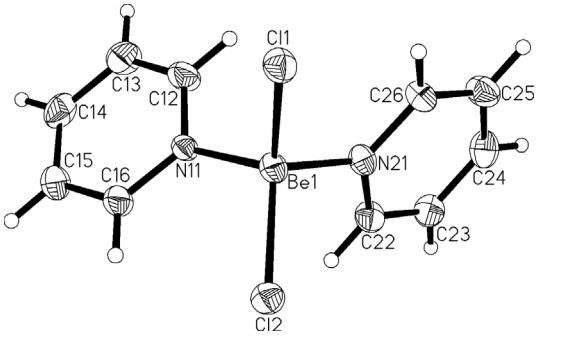


Fig. 2. Molecular structure of $(pyr)_2BeCl_2$ (**2**). Only one of the four independent units present in the asymmetric unit is shown. The adducts have no crystallographically imposed symmetry. Selected structural parameters: Be1-Cl1 1.997(4), Be1-Cl2 2.011(5), Be1-N11 1.741(5), Be1-N21 1.758(5) Å. Cl1-Be1-Cl2 114.7(2), N11-Be1-N12 105.2(3)°.

angles [101.9(3)–106.8(3)°] are consistently smaller than the Cl-Be-Cl angles [113.5(2)–115.1(2)°] and this deviation represents the major distortion of the tetrahedral arrangement of the complex.

The packing of the molecules in the crystal leads to a stacking of one of the two pyridine rings, but the distances of neighbouring rings are too large (*ca.* 3.90 Å) to suggest significant π-π interactions.

Pyrazole coordination

Treatment of a solution of $BeCl_2$ in diethylether with pyrazole (pyz) at −78 °C gives a colourless precipitate which has been identified as the 1:1 adduct still containing one solvent molecule attached to the beryllium atom: $[(pyz)(Et_2O)BeCl_2]$ (**4**) (72% yield). The product is sensitive to moisture and looses solvent upon heating. The residue finally melts at 264 °C. Solutions in $CDCl_3$ show the $^1H/^{13}C$ resonances expected for the two ligands and a broad ^9Be signal at 1.04 ppm. The parent ion (m/z 179.3) is observed in the FAB mass spectrum, but the cation $[(Et_2O)BeCl_2]^+$ is the most abundant species indicating that the pyrazole ligand is less tightly bound than the diethylether molecule.

$$(Et_2O)_2BeCl_2 + \underset{\text{(pyrazole)}}{C_3H_4N_2} \rightarrow \underset{\mathbf{4}}{(C_3H_4N_2)(Et_2O)BeCl_2} \quad (2)$$

Crystals of $[(pyz)(Et_2O)BeCl_2]$ (**4**), are orthorhombic, space group $P2_12_12_1$, with $Z = 4$ molecules in the unit cell. The structure of the individual monomer is shown in Fig. 3. The environment of the beryllium atom is distorted tetrahedral with Be-Cl distances of 1.979(3) and 1.997(4) Å, a Be-N distance of 1.717(4) Å and a Be-O distance of 1.677(4) Å. The angle Cl1-Be1-Cl2 of 115.30(18)° is the largest of the six angles at the Be center, while all others are close to the tetrahedral standard [107.9(2)–108.7(2)°]. The pyrazole molecule is attached to the beryllium atom through its non-protonated nitrogen atom N11 which reaches a trigonal planar configuration in the product. Through hydrogen bonding of the protonated nitrogen atom N12 with a chlorine atom Cl2' of a neighbouring molecule the monomers are aggregated into helical strings [N12-H12 0.89(4), H12–Cl2' 2.43(3) Å, N12-H12–Cl2' 147(3)°]. There may also be a very weak hydrogen bonding between H12 and Cl1, but the geometrical data suggest that this contribution is small (Fig. 4).

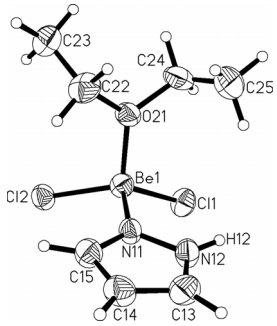


Fig. 3. Molecular structure of $(pyz)(Et_2O)BeCl_2$ (**4**). Selected structural parameters: Be1-Cl1 1.979(3), Be1-Cl2 1.997(4), Be1-O21 1.677(4), Be1-N11 1.717(4) Å. Cl1-Be1-Cl2 115.30(18), O21-Be1-N11 108.2(2)°.

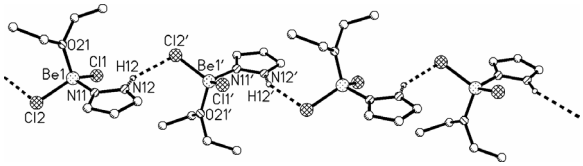


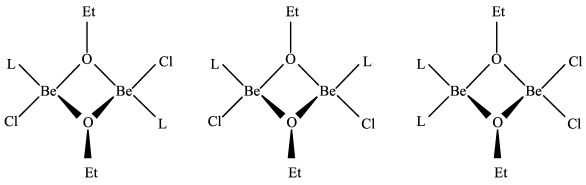
Fig. 4. Association of the $(pyz)(Et_2O)BeCl_2$ molecules (**4**) into strings via hydrogen bonds: N12-H12 0.89(4), H12–Cl2' 2.43(3), N12–Cl2' 3.219(2) Å, N12-H12–Cl2' 147°.

The reaction of a solution of $BeCl_2$ in diethylether with two equivalents of pyrazole at room temperature leads to the formation of a colourless, crystalline precipitate which was identified as an ether cleavage product $[(pyz)BeCl(OEt)]_2$ (**5**) (81% yield). The solid gradually looses volatile components upon heating and the residue finally melts at 317 °C. In air it is hydrolyzed only very slowly. The NMR spectra (in $CDCl_3$) show the resonances expected for a pyrazole ligand and an

ethoxy group in the ratio 1:1 suggesting equivalent ligands in the dimer. However, there are two ^{9}Be resonances (5.57 and 5.97 ppm, at −50 °C) of equal intensity which indicate two beryllium atoms in a different environment. In the FAB mass spectrum the parent ion $[(pyz)_2(EtO)_2Be_2Cl]^+$ (7%) confirms the dimeric nature of the compound. No single crystals could be grown of compound **5** and therefore structure assignments must remain tentative. The most plausible alternatives are formulae **5a** and **5b**.

$$(2Et_2O)_2BeCl_2 + 2L \rightarrow [L(EtO)BeCl]_2 \qquad (3)$$

L = pyrazole **5**
L = pyrimidine **9**



9, 5a **5b** **5c**

Solutions of $BeCl_2$ in tetrahydrofuran (thf) show no reaction with pyrazole at room temperature. Upon cooling of the reaction mixture to −20 °C crystals of the adduct $(C_4H_8O)_2BeCl_2$ separate, but no pyrazole adduct can be isolated. It therefore appears that pyrazole is not able to displace thf in the coordination sphere of the beryllium atom. As observed for many other hard Lewis acid centers, thf is a stronger base than Et_2O.

Pyrrolidine coordination

Treatment of a diethylether solution of $BeCl_2$ with two equivalents of pyrrolidine (pyrr) at room temperature leads to the precipitation of a 1:2 adduct (**6**) which can be isolated in 78% yield. The colourless solid, which is hygroscopic and rapidly decomposes in air (m.p. 181 °C), was identified by elemental analysis. Solutions in $CDCl_3$ show a very broad ^{9}Be resonance at 1.70 ppm, and the molecular ion can be observed in the FAB mass spectrum (m/z 221.4, 27%). However, both in the NMR and mass spectra small amounts of an ether cleavage product could be detected for the precipitate of the room temperature reaction. These byproducts were only absent if the reaction was carried out at temperatures below −30 °C.

$$BeCl_2 + 3C_4H_8NH \rightarrow [(C_4H_8NH)_3BeCl]Cl \qquad (4)$$
(pyrrolidine) **7**

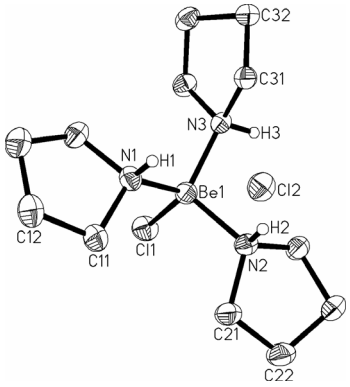


Fig. 5. The ionic structure of $[(pyrr)_3BeCl]^+Cl^-$ (**7**). Selected bond lengths: Be1-Cl1 1.9981(18), Be1-N1 1.755(2), Be1-N2 1.746(2), Be1-N3 1.761(2) Å.

Anhydrous $BeCl_2$ is only sparingly soluble in pyrrolidine in the absence of an ether solvent even under reflux conditions. After separation from the undissolved solid, colourless crystal separate on cooling from the mother liquor, which have been shown to be a 3:1 adduct of the ionic formula $[(pyrr)_3BeCl]^+Cl^-$ (**7**) (m.p. 183 °C; for 500 mg of $BeCl_2$ in 10 ml of pyrrolidine the yield was 28%). Solutions in $CDCl_3$ show a ^{9}Be resonance at 1.64 ppm, and the FAB mass spectrum features predominantly the cations $[(pyrr)_2BeCl]^+$ and $[(pyrr)_4Be]^{2+}$, suggesting ligand redistribution.

Crystals of compound **7** are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell. The structure is built of $[(pyrr)_3BeCl]^+$ cations and Cl^- anions (Fig. 5). The cation has no crystallographically imposed symmetry and the conformation and relative orientation of the pyrrolidine ligands does not approach the maximum attainable symmetry of point group C_{3v} or C_3. The orientation is probably determined or at least influenced by weak hydrogen bonding of the N-H groups and the chloride anion (below). The three Be-N bonds are of similar length [1.755(2), 1.746(2) and 1.761(2) Å for N1, N2 and N3, respectively], the Be-Cl distance is 1.9981(18) Å. All six angles at the beryllium atom are very close to the ideal angle of a regular tetrahedron [in the range 107.60(11)–110.61(10)°].

The three pyrrolidine rings have flat envelop conformations. Owing to their narrow C-N-C angles the ligands can easily be accommodated at the small beryllium atom without steric congestion. Even substitution of the remaining chloride ligand would appear to be sterically possible, but no such product was detected

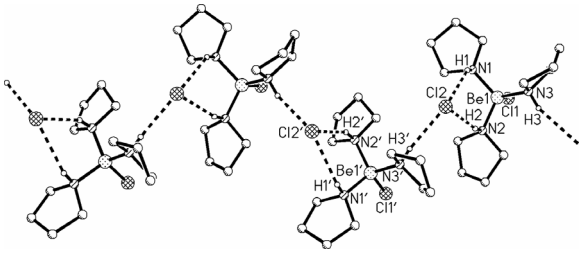


Fig. 6. Hydrogen bonding between cation and anion in $[(pyrr)_3BeCl]Cl$, (**7**). N1-H1 0.88(2), H1–Cl2 2.63(2), N1–Cl2 3.3691(12) Å; N1-H1–Cl2 141.3(17)°. N2-H2 0.89(2), H1–Cl2 2.36(2), N2–Cl2 3.2025(12) Å; N2-H2–Cl2 156.4(18)°. N3'-H3' 0.89(2), H3'–Cl2 2.48(2), N3'–Cl2 3.3097(12) Å; N3'-H3'–Cl2 155.5(17)°.

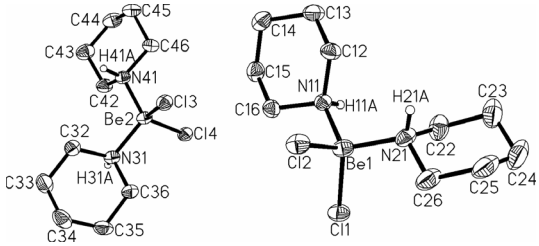


Fig. 7. Molecular structures of the two independent molecules $(pip)_2BeCl_2 \cdot (CHCl_3)$ in the crystals of the chloroform solvate **8a**. Selected structural parameters: Be1-Cl1 2.017(3), Be1-Cl2 2.014(3), Be1-N11 1.756(3), Be1-N21 1.747(4) Å; Cl1-Be1-Cl2 114.36(15), N11-Be1-N21 110.60(19). Be2-Cl3 2.019(3), Be2-Cl4 2.014(3), Be2-N31 1.756(4), Be2-N41 1.745(3) Å; Cl3-Be2-Cl4 114.25(15), N31-Be2-N41 112.28(19)°.

even though a large excess of pyrrolidine was applied under rather forcing conditions. This observation suggests that no +2 charge can be built up at the beryllium center without the proximity of at least one counterion.

The independent chloride anion (Cl2) has close contacts to three N-H groups suggesting weak hydrogen bonding. Two of these contacts are to the same cation (N1-H1, N2-H2) while the third one involves N3'-H3' of a neighbouring unit (Fig. 6).

Piperidine coordination

The reaction of $BeCl_2$ with two equivalents (or an excess) of piperidine (pip) in diethylether at room temperature gives a mixture of two products. Fractional crystallization gave pure samples of the mononuclear 1:2 adduct $(pip)_2BeCl_2$ (**8**) and the dinuclear $[(pip)BeCl(\mu_2\text{-}OEt)]_2$ (**9**), the latter resulting from cleavage of the diethylether solvent. The relative amount of the ethoxy compound **9** could be reduced by carrying out the reaction at −50 °C, but the cleavage was not fully suppressed even under these much milder conditions. The results suggest that piperidine strongly promotes the ether cleavage by $BeCl_2$ and is more efficient in this respect than the more weakly basic pyrrolidine, pyrazole, pyridine, or nitrile ligands. The high basicity together with the ability to form hydrogen bonds with the ether oxygen atom may lead to a concerted process with lower activation energy.

Both products of the piperidine/diethylether/$BeCl_2$ reaction are hygroscopic and decompose in air. Gradual decomposition is observed on heating and the solid residues finally melt at 259 °C (**8**) and 376 °C (**9**), respectively. Solutions of **8** in $CDCl_3$ show the expected NMR spectra including a broad ^{9}Be resonance at −0.95 ppm. Only small amounts of a very pure sample of compound **9** (single crystals of a chloroform solvate **9a** $[(pip)BeCl(\mu_2\text{-}OEt)]_2 \cdot (CHCl_3)$) could be isolated which were identified by the mass spectrum and an X-ray diffraction study. Compound **8** also crystallized as a chloroform solvate $[(pip)_2BeCl_2] \cdot (CHCl_3)$, **8a**.

_Crystals of this solvate **8a** are triclinic, space group $P1$, with $Z = 2$ formula units in the unit cell. There are two independent complex molecules and two chloroform molecules in the asymmetric unit, one of the latter being highly disordered. The two adducts **8** have a very similar geometry as shown in Fig. 7. The four Be-N distances are in the narrow range 1.745(3)–1.756(3) Å, the Be-Cl distances between 2.014(3) and 2.019(3) Å. The angles N-Be-N [110.60(19) and 112.28(19)°] differ much less from the Cl-Be-Cl angles [114.36(15) and 114.25(15)°] than in the related pyrrolidine or pyridine compounds (above). We ascribe this difference to the increased steric bulk of piperidine with its larger C-N-C angle. These differences may also be responsible for the reluctance of complex **8** to accept another piperidine ligand the way it was observed for the pyrrolidine ligand (above).

The piperidine ligands adopt the usual chair conformation (Fig. 7). Their imino groups are engaged in hydrogen bonding with chlorine atoms of neighbouring complexes to form chains with an alternating sequence of non-equivalent molecules (Fig. 8). In these chains the beryllium atoms are spiro centers between puckered eight-membered rings. There are no sub-van-der Waals contacts between the chains of complexes and the chloroform molecules.

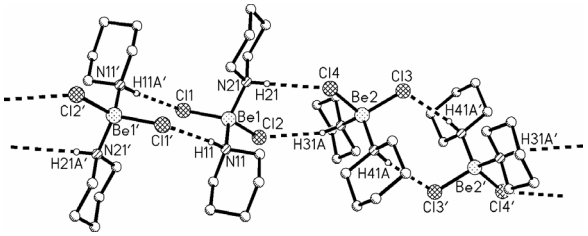


Fig. 8. Association of the molecular units shown in Fig. 7 *via* hydrogen bonds to give helical strings. N11-H11A 0.90(3), H11A–Cl1' 2.56(3), N11–Cl1' 3.461(2) Å; N11-H11A–Cl1' 175(3)°. N21-H21A 0.85(4), H21A–Cl4' 2.54(4), N21–Cl4' 3.371(2) Å; N21-H21A–Cl4' 167(3)°. N31-H31A 0.85(3), H31A-Cl2' 2.65(3), N31–Cl2' 3.468(2) Å; N31-H31A–Cl2' 160(2)°. N41-H41A 0.89(3), H41A–Cl3' 2.58(3), N41–Cl3' 3.459(2) Å; N41-H41A–Cl3' 170(2)°.

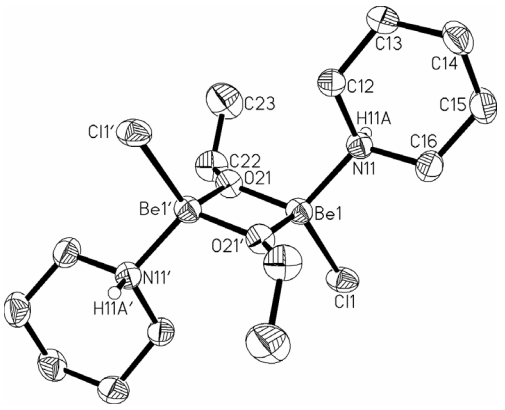


Fig. 9. Molecular structure of the dimer [(pip)BeCl(μ_2-OEt)]$_2$ (**9**) in the trichlormethane solvate **9a**. The two monomers are related by a center of inversion. The ethyl groups are disordered. Selected structural parameters: Be1-Cl1 2.032(2), Be1-N11 1.755(2), Be1-O21 1.609(2), Be1-O21' 1.604(2) Å; O21-Be1-O21' 89.91(11), Be1-O21-Be1' 90.09(11)°, N1-Be1-Cl1 106.72(11)°.

Crystals of [(pip)BeCl(μ_2-OEt)]$_2 \cdot (CHCl_3)_2$, (**9a**), are monoclinic, space group $P2_1/c$, with $Z = 2$ formula units in the unit cell. The two monomers associated in the dimer are related by a center of inversion (Fig. 9). The methyl groups of the μ-ethoxy bridges are disordered over two positions which are about equally populated (57:43; only one orientation is shown in the figure). The Be-N and Be-Cl distances [1.755(2) and 2.032(2) Å] are only slightly longer than in the piperidine reference compound **8**. The Be-O distances are equal within the standard deviations of the data [1.604(2) and 1.609(2) Å] and together with angles O-Be-O' and Be-O-Be' at 89.91(11) and 90.09(11)° indicate an almost perfect square for the core unit of the dimer.

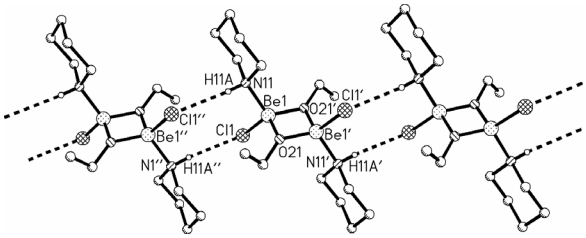


Fig. 10. Association of the molecular units shown in Fig. 9 *via* hydrogen bonds to give chains of alterating eight- and four-membered rings. N11-H11A 0.87(2), H11–Cl1' 2.53(2), N11–Cl1' 3.3825(14); N11-H11A–Cl1' 165.4(19).

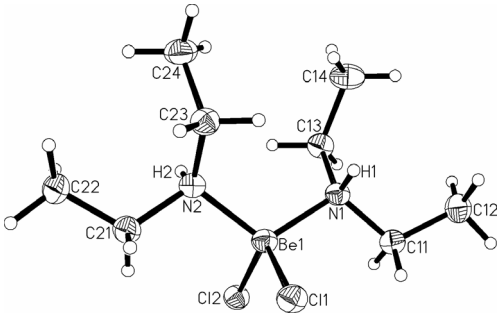


Fig. 11. Molecular structure of $(Et_2NH)_2BeCl_2$ (**10**). The adduct has no crystallographically imposed symmetry. Selected structural parameters: Be1-Cl1 2.011(2), Be1-Cl2 2.017(2), Be1-N1 1.763(3), Be1-N2 1.754(3) Å; Cl1-Be1-Cl2 114.94(11), N1-Be1-N2 112.33(13)°.

The piperidine ligands are in a chair conformation and their N-H groups are engaged in hydrogen bonding with chlorine atoms of neighbouring dinuclear complexes to form, together with the Be-O rings, chains with an alternating sequence of eight- and four-membered rings in which the beryllium atoms are spiro centers between the two different types of rings (Fig. 10).

Diethylamine coordination

Beryllium dichloride forms a 1:2 addition compound **10** with diethylamine which is readily isolated in large colourless crystals and identified by its analytical and spectroscopic data. The crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell. The mononuclear complex has no crystallographically imposed symmetry, but its geometry approaches quite closely a structure with point group C_2 symmetry (Fig. 11). The bond lengths and angles of the core unit are very similar to those of the bis(piperidine)

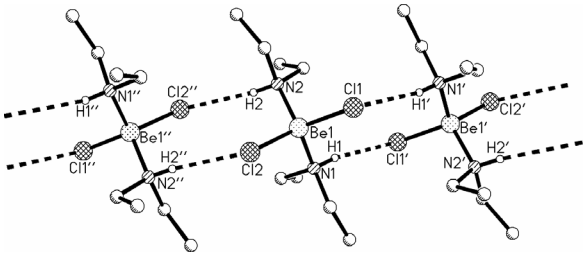


Fig. 12: Association of molecule **10** into helical chains via hydrogen bonds. N1-H1 0.87(2), H1–Cl1' 2.64(2), N1–Cl1' 3.5020(15) Å; N1-H1–Cl1' 169.3(16)°. N2-H2 0.86(2), H2–Cl2" 2.61(2), N2–Cl2" 3.4688(15) Å; N2-H2–Cl2" 173.8(19)°.

analogue **9** above: Be-N1/N2 1.760(3)/1.753(3) Å; Be-Cl1/Cl2 2.010(2)/2.015(2) Å; N1-Be-N2 112.33(13)°, Cl1-Be-Cl2 114.96(10)°. This similarity is not unexpected considering the close analogy between piperidine and diethylamine: The difference only arises because in the former the two ethyl groups are tied together by a bridging methylene unit.

The molecular units are arranged in chains through N-H–Cl hydrogen bonds to give an array closely analogous to the structure of the piperidine complex **8** (Fig. 12).

Conclusions

The reaction of anhydrous beryllium dichloride $BeCl_2$ with nitrogen donors L in diethylether was shown to give – in the standard case – the expected 1:2 complexes L_2BeCl_2 with a tetrahedrally coordinated beryllium atom. The geometry of the N_2BeCl_2 polyhedron is distorted depending on the steric requirements of the donor molecules L. If on the one hand the donor is a small and strongly basic amine, like pyrrolidine, a third ligand may replace one of the two chloride ligands to give a rare cationic complex of the type $[L_3BeCl]^+$ Cl^-. On the other hand, with weak donors like pyrazole, a stepwise substitution of the ether molecules in the solvated precursor $(Et_2O)_2BeCl_2$ gives $L(R_2O)BeCl_2$. With the stronger donor solvent tetrahydrofuran no reaction occurs between $(thf)_2BeCl_2$ and pyrazole.

Secondary amines like pyrrolidine and piperidine were found to promote the cleavage of diethylether by $BeCl_2$ to give dinuclear beryllium(alkoxide)chloride compounds of the type $[(L)BeCl(\mu_2\text{-}OR)]_2$. This side-reaction can be suppressed by carrying out the reaction at low temperature. It is assumed that hydrogen bonding assists the formation of an energetically lower-lying transition state of the ether cleavage.

Hydrogen bonding also plays a role in the crystal structures of all complexes with secondary amines (pyrrolidine, piperidine and diethylamine). The monomeric units are tied together via N-H–Cl bridges to form helical one-dimensional chains with the beryllium atoms in the bridge-head positions.

Experimental Section

All beryllium compounds should be considered extremely toxic. The experiments should therefore be carried out with greatest care to avoid any contamination. Most manipulations were conducted in a dedicated glove-box in argon. All wastes were disposed of following pertinent regulations. Otherwise standard equipment was used throughout. Solvents were dried and kept under nitrogen. Glassware was oven-dried and filled with nitrogen. All chemicals were commercially available.

*Bis(benzonitrile)dichloroberyllium (**1**)*

$BeCl_2$ (500 mg, 6.30 mmol) was added to benzonitrile (7.5 ml) and the mixture heated to reflux temperature until all $BeCl_2$ had dissolved. On slow cooling to 20 °C pale yellow, hygroscopic, needle-shaped crystals separated which were filtered off and dried in a vacuum (1.55 g, 86% yield, m.p. 214 °C). NMR ($CDCl_3$, 20 °C), ^{1}H: 7.36 – 7.71 ppm, m, Ph. $^{13}C\{^1H\}$: 129.10, 132.16, 132.73 for C_2,C_3,C_4, resp.; C_1 and **C**N were not observed. ^{9}Be: 2.01, broad. $C_{14}H_{10}BeCl_2N_2$ (286.17): calcd. Cl 24.80; found Cl 24.03.

*Bis(pyridine)dichloroberyllium (**2**)*

$BeCl_2$ (1.5 g, 18.7 mmol) was dissolved in a mixture of benzene (30 ml) and pyridine (20 ml) with gentle heating. Colourless crystals separated on cooling (3.3 g, 74% yield). For analytical data see ref. [29].

*Bis(3,5-dimethylpyridine)dichloroberyllium (**3**)*

$BeCl_2$ (500 mg, 6.30 mmol) was reacted with 3,5-$Me_2C_5H_3N$ (1.35 g, 12.6 mmol, 1.43 ml) in 50 ml of diethylether at 20 °C. A small amount of undissolved material was filtered off and the filtrate was cooled to 8 °C. Colourless crystals formed which were separated and dried in a vacuum (1.47 g, 79% yield, m. p. 197 °C). NMR ($CDCl_3$, 20 °C), ^{1}H: 2.53 (s, 6H) Me; 7.99 (s, 1H) and 8.39 (s, 2H), C_6H_3. ^{13}C: 29.37, s, Me; 137.60, 146.35, 155.00 (s, C_5H_3N). ^{9}Be: 1.73, s. MS (FAB) m/z 396.3 and 294.3 $[L_2BeCl_2]^+$; 260.3 and 258.3 $[L_2BeCl]^+$. $C_{14}H_{18}BeCl_2N_2$ (294.23): calcd. Cl 24.10, found Cl 24.14.

Table 1. Crystal data, data collection, and structure refinement of **1**, **2**, **4**, **7**.

	1	**2**	**5**	**7**
Empirical formula	$C_{14}H_{10}BeCl_2N_2$	$C_{10}H_{10}BeCl_2N_2$	$C_7H_{14}BeCl_2N_2O$	$C_{12}H_{27}BeCl_2N_3$
M	286.15	238.11	222.11	293.28
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2/n$	$P2_1$	$P2_12_12_1$	$P2_1/c$
a/[Å]	7.4494(6)	12.1648(1)	7.2396(2)	11.7155(2)
b/[Å]	6.4675(3)	12.7283(2)	12.4141(4)	11.2452(2)
c/[Å]	14.9115(12)	15.2121(2)	12.8139(4)	11.9975(2)
α/[°]	90	90	90	90
β/[°]	91.484(4)	89.9967(5)	90	94.6932(13)
γ/[°]	90	90	90	90
V/[Å^3]	718.15(9)	2355.40(5)	1151.63(6)	1575.29(5)
ρ_{calc}/[g cm^{-3}]	1.323	1.343	1.281	1.237
Z	2	8	4	4
$F(000)$	292	976	464	632
μ (Mo-K$_\alpha$) [cm^{-1}]	4.36	5.16	5.28	4.0
T/[K]	143	143	143	143
Refls. measured	9511	66578	32224	47072
Refls. unique	1551	5411	1361	3559
	[$R_{int} = 0.038$]	[$R_{int} = 0.053$]	[$R_{int} = 0.033$]	[$R_{int} = 0.049$]
Refined parameters/restraints	107 / 0	542 / 1	124 / 0	271 / 0
$R1[I \geq 2\sigma(I)]$	0.0406	0.0264	0.0323	0.0368
$wR2$[a]	0.1086	0.0625	0.0860	0.0991
Weighting scheme	$a = 0.0487$	$a = 0.0290$	$a = 0.0428$	$a = 0.0553$
	$b = 0.2910$	$b = 0.2163$	$b = 0.4770$	$b = 0.6143$
σ_{fin}(max/min)/eÅ^{-3}	0.308 / –0.369	0.155 / –0.170	0.283 / –0.230	0.302 / –0.298

[a] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

*Dichloro(diethylether)(pyrazole)beryllium (**4**)*

$BeCl_2$ (509 mg, 6.37 mmol) was dissolved in 50 ml of Et_2O, the solution cooled to −78 °C and treated with pyrazol (430 mg, 6.37 mmol) dissolved in 10 ml of Et_2O. The reaction mixture was filtered to remove undissolved material, and the filtrate warmed to 20 °C. Colourless crystals were isolated and dried in a slow stream of nitrogen (1.02 g, 72% yield, m.p. 264 °C). NMR ($CDCl_3$, 20 °C), ^{1}H: 1.19 (t, 6 H, J = 8 Hz) Me, 3.45 (q, 2 H) CH_2, 6.66 (m, 1 H) and 7.96 (m, 2 H) $C_3N_2H_3$; NH not observed. ^{13}C: 15.27, Me; 65.79, CH_2; 106.94 and 132.35, C_3N_2. ^{9}Be: 1.04, broad. MS (FAB) m/z 179.3 $[M]^+$; 155.2 $[(Et_2O)BeCl_2]^+$. $C_7H_{14}BeCl_2N_2O$ (222.11): calcd. C 37.85, H 6.35, N 12.61, Cl 31.92; found C 37.05, H 6.67, N 12.15, Cl 30.91.

*Bis[chloro(ethoxy)(pyrazol)beryllium] (**5**)*

$BeCl_2$ (495.5 mg, 6.20 mmol) was reacted with pyrazol (420 mg, 6.20 mmol) in a total of 55 ml of Et_2O at 20 °C. A precipitate formed which was filtered, washed three times with 5 ml of Et_2O and dried in a vacuum (0.79 g, 81% yield, m.p. 317 °C). NMR ($CDCl_3$, 20 °C), ^{1}H: 1.19 (t, 3 H) Me; 3.45 (q, 2 H) CH_2; 6.65 and 7.96 (m, 2H/1H) $C_3H_3N_2$; NH not observed. ^{13}C: 15.21 and 65.77, Et; 107.04 (1 C) and 132.20 (2 C), $C_3N_2H_4$. ^{9}Be: 5.57 (s, 1 Be) and 5.97 (s, 1 Be), broad. MS (FAB) m/z 279.4 $[L_2(EtO)_2Be_2Cl]^+$. $C_{10}H_{18}Be_2Cl_2N_4O_2$ (315.21): calcd. C 38.10, H 5.76, N 17.77, Cl 22.49; found C 37.25, H 5.67, N 16.98, Cl 22.10.

*Bis(pyrrolidine)dichloroberyllium (**6**)*

$BeCl_2$ (504.8 mg, 6.32 mmol) was reacted with pyrrolidine (900 mg, 13 mmol, 1.04 ml) in 50 ml of diethylether at 20 °C. A colourless precipitate was collected, washed with three 15 ml portions of hexane and dried in a vacuum (1.10 g, 78% yield, m.p. 181 °C). NMR ($CDCl_3$, 20 °C), ^{1}H: 2.01 (m, 4 H) and 3.31 (m, 4 H) CH_2; 9.71 (s, 1 H) NH. ^{9}Be: 1.70, very broad. MS (FAB) m/z 221.4 $[M]^+$. $C_8H_{18}BeCl_2N_2$ (222.16): calcd. C 43.25, H 8.17, N 12.61, Cl 31.92; found C 42.63, H 8.64, N 10.99, Cl 31.42.

*Tris(pyrrolidine)chloroberyllium chloride (**7**)*

A suspension of $BeCl_2$ (500 mg, 6.26 mmol) in 10 ml of pyrrolidine was heated to reflux temperature for 2 h. Subsequently the reaction mixture was filtered and the filtrate cooled to 8 °C. Colourless crystals precipitated which were dried in a vacuum (514 mg, 28% yield, m.p. 183 °C). NMR ($CDCl_3$, 20 °C), ^{1}H: 2.00 (m, 4 H) and 3.29 (m, 4 H) CH_2; 9.68 (s, 1 H) NH. ^{13}C: 24.35 and 45.92 (s) C_4H_4NH. ^{9}Be: 1.64, broad s. MS (FAB) m/z 181.3 and 179.3 $[L_2BeCl]^+$. $C_{14}H_{18}BeCl_2N_2$ (293.28): calcd. Cl 24.18, found Cl 23.14.

Table 2. Crystal data, data collection, and structure refinement of **8**, **9a** and **10**.

	8a	**9a**	**10**
Empirical formula	$C_{21}H_{45}Be_2Cl_7N_4$[b]	$C_{16}H_{34}Be_2Cl_8N_2O_2$	$C_8H_{22}BeCl_2N_4$
M	619.78[b]	588.07	452.37
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/[Å]	11.2993(2)	7.1927(1)	10.3616(3)
b/[Å]	12.4853(3)	23.4250(4)	8.9624(3)
c/[Å]	14.3964(3)	8.5790(2)	13.6822(5)
α/[°]	76.5020(8)	90	90
β/[°]	82.8108(8)	98.6625(8)	98.2645(15)
γ/[°]	65.2506(8)	90	90
V/[Å^3]	1792.61(7)	1428.98(5)	1257.40(7)
ρ_{calc}/[g cm^{-3}]	1.148[b]	1.367	1.195
Z	2	2	4
$F(000)$	652[b]	608	488
μ (Mo-K$_\alpha$) [cm^{-1}]	5.69[b]	8.04	4.79
T/[K]	143	143	143
Refls. Measured	52047	32999	35784
Refls. Unique	6135 [$R_{int} = 0.035$]	3284 [$R_{int} = 0.035$]	2254 [$R_{int} = 0.051$]
Refined parameters /restraints	487 / 0[b]	203 / 1	206 / 0
$R1[I \geq 2\sigma(I)]$	0.0456	0.0382	0.0318
$wR2$[a]	0.1267	0.1044	0.0759
Weighting scheme	$a = 0.0653$	$a = 0.0515$	$b = 0.7556$
	$b = 1.4109$	$a = 0.0318$	$b = 0.4874$
σ_{fin}(max/min)/eÅ^{-3}	0.763 / - 0.436	0.428 / –0.540	0.222 / –0.217

[a] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$;

[b] without contributions of disordered solvent.

*Bis(piperidine)dichloroberyllium (**8**), and Bis[chloro(μ_2-ethoxy)(piperidine)beryllium] (**9**)*

The reaction of $BeCl_2$ (510 mg, 6.39 mmol) with piperidine (1.09 g, 13 mmol, 1.26 ml) was carried out at 20 °C and at −78 °C. In both cases mixtures of the two products **8** and **9** were obtained. Only small amounts of the pure compounds could be obtained by fractional crystallization from chloroform/diethylether. Yields of the two compounds have therefore not been determined (**8**: m.p. 259 °C, **9**: m.p. 376 °C).

The products decompose rapidly in air. NMR data were only collected for compound **8**: NMR ($CDCl_3$, 20 °C), ^{1}H: 1.65 (q, 1 H, J = 5 Hz) H-C4, 187 and 3.12 (m, 2+2 H) H-C3,5/H-C2,6; 2.17 (s, 1 H) NH. ^{13}C: 22.43, 29.83 and 44.56 for C4, C3/5 and C2/6 resp. ^{9}Be (−50 °C): −1.10.

*Bis(diethylamine)dichloroberyllium (**10**)*

Diethylamine (6.5 ml, 62 mmol, excess) was mixed with 100 ml of diethylether and treated with a solution of $BeCl_2$ (1.0 g, 12.5 mmol) in 100 ml of diethylether. A two-phase reaction mixture contained the product in both the upper and lower layer. Colourless crystals (1.85 g, 66% yield). For analytical data see ref. [32].

Crystal structure determinations

Specimens of suitable quality and size of **1**, **2**, **4**, **7**, **8a**, **9a** and **10** were mounted on the ends of quartz fibers in inert perfluoropolyalkylether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K$_\alpha$ radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97) [35]. The thermal motion was treated anisotropically for all non-hydrogen atoms. The hydrogen atoms in all structures were located and refined isotropically except those of the methyl groups in **4**, **9a** and all hydrogen atoms in the structure of **2**, which were calculated in ideal positions and allowed to ride on their parent atoms with fixed isotropic contributions. The scattering contributions of a highly disordered chloroform molecule in **8a** were taken into account using the SQUEEZE method (total potential solvent accessible volume is 308.2 Å^3 containing 16 electrons/cell) [36]. The structure of **2** was refined as a pseudo-merohedral twin in space group $P2_1$ with a β-angle near 90° emulating orthorhombic symmetry. The refined BASF parameter for the pseudo-merohedral twinning is 0.4991(17). Further informations on crystal data, data collection and structure refinement are summarized in Tables 1 and 2.

Displacement parameters and complete tables of interatomic distances and angles for the structures **1**, **2**, **4**, **7**, **8a**, **9a** and **10** have been deposited with the Cambridge Crystallographic Data Centre, CCDS 200898-200904. Copies of the data can be obtained free of charge on application

to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk.

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