Beryllium Chelation by Dicarboxylic Acids in Aqueous Solution

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Maleic and phthalic acids are found to react with $Be(OH)_2$, generated in situ from $BeSO_4$(aq) and $Ba(OH)_2$(aq), in aqueous solution at pH 3.0 or 4.4, respectively (25 °C), to give solutions containing the complexes $(H_2O)_2Be[(OOCCH)_2]$ (**1**) and $(H_2O)_2Be[(OOC)_2C_6H_4]$ (**3**). The products can be isolated in high yield and identified by microanalytical data. With 2 equiv of the dicarboxylic acids and the pH adjusted to 5.5 and 5.9, respectively, by addition of ammonia, the bis-chelate complexes $[(NH_4)^+]_2\{[Be[(OOCCH)_2]_2\}^{2-}$ (**2**) and $[(NH_4)^+]_2\{Be[(OOC)_2C_6H_4]_2\}^{2-}$ (**4**) are obtained, which can also be isolated. The compounds show distinct ^{9}Be, ^{1}H, and ^{13}C resonances in their NMR spectra in aqueous solutions. Layering of an aqueous solution of compound **4** with acetone at ambient temperature leads to the precipitation of single crystals suitable for an X-ray structure determination. This salt (**5**) was found to contain the bis-chelated dianion $\{Be[(OOC)_2C_6H_4]_2\}^{2-}$ with the beryllium atom in the spiro center of two seven-membered rings and an overall geometry approaching closely C_2 symmetry. These anions are associated with two crystallographically independent but structurally similar counterions $[MeC(O)CH_2CMe_2NH_3]^+$, which are the product of a condensation reaction of the ammonium cation with the acetone solvent. In the crystal the ammonium hydrogen atoms of the cations form N−H···O hydrogen bonds with the oxo functions of the dianion.

Introduction

Owing to its extremely small ionic radius the beryllium(II) cation is unique in its performance as a coordination center.[1] Because of its large charge:radius ratio, the dication has a high affinity for fluorine and oxygen donors. It is generally classified as strongly oxophilic, as shown in particular by the characteristic coordination chemistry in aqueous solution.[2] The high oxophilicity can also be held responsible for the extreme toxicity of beryllium compounds,[3] since most biopolymers and their components offer a large variety of oxygen functions which may be the target of beryllium complexation. However, neither on a physiological nor on a molecular level is the mechanism of beryllium poisoning properly understood.[4]

Research in beryllium chemistry has largely come to a standstill during the last few decades because of growing concern about the dangers possibly associated with any long-term handling of beryllium compounds. Not surprisingly, the few more recent studies of the coordination chemistry of beryllium have concentrated largely on the equilibria of aqueous solutions containing beryllium and biologically relevant ligand systems [amino acids, carbohydrates,[5] glycerol, glycol, glycolic acid,[6] catechol,[7] salicylic acid,[8,9] malonic acid,[10] oxalic acid,[11] nitrilotris(propionic acid),[12] etc.], which may provide an answer to this key question in the physiological chemistry of beryllium. The emphasis has also been on the structural characterization, which may give a clue as to the coordination preferences.

Following the previous investigations of beryllium complexation by carboxylic and hydroxycarboxylic acids in our laboratory,[6−9] we have now studied the chelation of Be^{2+}(aq)[13] by maleic and phthalic acids in aqueous solution under different conditions of pH and concentration at ambient temperature.

Results and Discussion

The rigid molecular geometry of maleic and phthalic acids, with the two carboxylate groups held in a *cis* position, provides structural moieties for chelation with a strongly reduced loss of entropy. This preconditioning of ligands is important, because the overall energy characteristics of equilibria including Be^{2+}(aq) do not favor carboxylate over water complexation. Monocarboxylic acids are accepted in the coordination sphere of the metal only in neutral or alkaline solution with the formation of the well-known polynuclear oxide/carboxylate species $(RCOO)_6[Be_4O]$,[1,2] but much less is known about the species present in acidic solutions. This also applies for systems with dicarboxylic acids with nonrigid structures like malonic or succinic acid.

Treatment of an aqueous solution of equimolar quantities of beryllium sulfate tetrahydrate and maleic acid with the same molar amount of barium dihydroxide octahydrate at ambient temperature leads to an immediate precipitation of barium sulfate. After completion of the reaction under reflux conditions

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(1) Fenton, D. E. In *Comprehensive Coordination Chemistry*, 1st ed.; Wilkinson, G., Gillard, R. A., McCleverty, J. A.; Eds., Pergamon: Oxford, England, 1987; Vol. 3, p 1 ff.

(2) (a) Everest, D. A. *The Chemistry of Beryllium*; Elsevier: Amsterdam, 1964. (b) Wong, Ch. Y.; Woolins, J. D. *Coord. Chem. Rev.* **1994**, *130*, 143−173.

(3) (a) Petzow, G.; Zorn, H. *Chem.-Ztg.* **1974**, *98*, 236−241. Seidel, A. In *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer: Berlin, 1986; Be, Suppl. Vol. A1, p 300−315.

(4) (a) Skilleter, D. N. *Chem. Br.* **1990**, *26*, 26−30. (b) Kumberger, O.; Schmidbaur, H. *CHIUZ* **1993**, *27*, 310−316.

(5) Klüfers, P.; Mayer, P.; Schuhmacher, J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1373−1379.

(6) Kumberger, O.; Riede, J.; Schmidbaur, H. *Z. Naturforsch.* **1992**, *47b*, 1717−1720.

(7) Kumberger, O.; Riede, J.; Schmidbaur, H. *Chem. Ber.* **1992**, *125*, 2701−2703.

(8) Schmidbaur, H.; Kumberger, O.; Riede, J. *Inorg. Chem.* **1991**, *30*, 3101−3103.

(9) Schmidbaur, H.; Kumberger, O. *Chem. Ber.* **1993**, *126*, 3−9.

(10) Duc, G.; Faure, R.; Loiseleur, H. *Acta Crystallogr.* **1978**, *B34*, 2115−2118.

(11) Jaber, M.; Faure, R.; Loiseleur, H. *Acta Crystallogr.* **1978**, *B34*, 429−431.

(12) Chinea, E.; Dominguez, S.; Mederos, A.; Brito, F.; Arrieta, J. M.; Sanchez, A.; Germain, G. *Inorg. Chem.* **1995**, *34*, 1579−1587.

(13) Robl, C.; Hentschel, S. *Z. Naturforsch.* **1990**, *45b*, 1499−1502.

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and separation of the precipitate, the resulting clear solution has a pH of 3. It contains a single product as shown by the ^{9}Be NMR spectrum (in D_2O), which features only one resonance at δ 1.21 ppm [relative to Be^{2+}(aq)]. The ^{1}H and ^{13}C NMR spectra exhibit the expected sets of maleate signals. Upon concentration of the solution in a vacuum, this product can be isolated (69% yield) as a colorless solid, which loses water upon heating without melting. The elemental analysis is consistent with the composition of a dihydrate (**1**) (Scheme 1).

Scheme 1

$$BeSO_4 + Ba(OH)_2 + C_4H_4O_4 \rightarrow BaSO_4 + \underset{\mathbf{1}}{Be[C_4H_2O_4]\cdot 2H_2O} \quad (1)$$

$$BeSO_4 + Ba(OH)_2 + 2NH_4(C_4H_3O_4) \rightarrow BaSO_4 + \underset{\mathbf{2}}{(NH_4)_2[Be(C_4H_2O_4)_2]} + 2H_2O \quad (2)$$

The reaction of $BeSO_4(H_2O)_4$, maleic acid, and $Ba(OH)_2(H_2O)_8$ in the molar ratio 1:2:1 in water, with the pH adjusted to 5.5 by the addition of aqueous ammonia, at ambient temperature also leads to precipitation of $BaSO_4$. The solution contains again only one beryllium complex, as demonstrated by the ^{9}Be NMR spectrum, which has a single line at δ 2.02. It should be noted that the total chemical shift range for δ ^{9}Be of beryllium compounds is very narrow (ca. 40 ppm), and therefore the shift difference $\Delta\delta = 0.81$ ppm between the two compounds (**1** and **2**) is significant. There are also new sets of maleate signals in the ^{1}H and ^{13}C NMR spectra. The product can be isolated by crystallization (71% yield) and identified by its elemental analysis as the ammonium salt **2** (Scheme 1). It melts, with decomposition to liberate ammonia, at 184 °C.

Solutions containing Be^{2+}(aq) and maleic acid in a nonintegral ratio between 1:1 and 1:2 show ^{9}Be NMR spectra in which the signals of compounds **1** and **2** are present. This result is proof that there is no rapid ligand exchange (on the NMR time scale) between the two species. The individual signals are therefore diagnostic and can serve to trace the components of the equilibrium.

Similar preparative procedures using the corresponding aliquots of phthalic acid lead to analogous products **3** and **4** (Scheme 2).

Scheme 2

$$BeSO_4 + Ba(OH)_2 + C_8H_6O_4 \rightarrow BaSO_4 + \underset{\mathbf{3}}{Be[C_8H_4O_4]\cdot 2H_2O} \quad (3)$$

$$BeSO_4 + Ba(OH)_2 + 2NH_4(C_8H_5O_4) \rightarrow BaSO_4 + \underset{\mathbf{4}}{(NH_4)_2[Be(C_8H_4O_4)_2]} + 2H_2O \quad (4)$$

Compound **3** (yield 61%) crystallizes from an aqueous solution at pH 4.4, while compound **4** (yield 56%) results from solutions at pH 5.9. Both are colorless solids which lose water or ammonia, respectively, upon heating before melting. The ^{9}Be NMR spectra have signals similar to those of **1** and **2** (**3**; δ 1.20 ppm; **4**, ppm; δ 2.41 ppm), suggesting analogous complexation of the beryllium dication. In the ^{1}H and ^{13}C NMR spectra, the expected sets of phthalate resonances are observed.

None of the four compounds (**1**−**4**) could be obtained as single crystals suitable for X-ray crystallography. However, during one of the many attempts to grow better crystals, the ammonium cations of compound **4** were exchanged by a new, completely unexpected new set of cations originating serendipitously from the reaction of the acetone solvent with ammonia (Scheme 3).

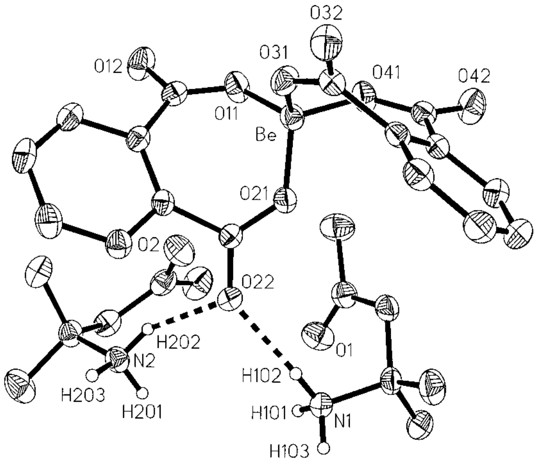
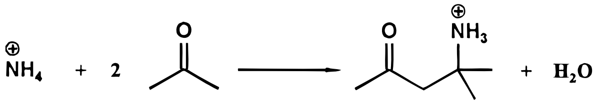


Figure 1. A section of the unit cell of compound **5** showing two crystallographically independent cations $[Me_2C(NH_3)CH_2C(O)Me]^+$ and one anion $\{Be[(OOC)_2C_6H_4]_2\}^{2-}$ engaged in hydrogen bonding.

Scheme 3



The product (**5**) contains two (2-methyl-4-oxopentan-2-yl)ammonium cations $[MeC(O)CH_2CMe_2NH_3]^+$ formed in the condensation of two acetone molecules and an ammonium cation. It is not clear if the beryllium cation plays a role in the kinetics of this condensation. This question has not been investigated any further. (The formation of the above cation has been observed also in other media containing no beryllium.[14])

Crystals of compound **5** are monoclinic, space group $P2_1/n$, with four formula units in the unit cell. The lattice is composed of two crystallographically independent cations and one dianion which has no crystallographically imposed symmetry. The ions are linked through hydrogen bonds between the ammonium hydrogen atoms of the cations and the oxo functions of the dianions (Figure 1). The molecular geometry of the two cations is very similar and represents a largely strain-free conformation. The oxo carbon atoms of the cations have a planar configuration, while all other carbon atoms and the nitrogen atom are tetrahedrally coordinated.

The dianion features a tetrahedrally coordinated beryllium atom chelated by two phthalate anions. The metal is therefore in a spiro center of two seven-membered rings. The phthalate anions show no structural anomalies. The geometry of the complete dianion approaches C_2 symmetry with the 2-fold axis running through the Be atom and bisecting the angles O11−Be−O41 and O21−Be−O31 (Figure 2).

The Be−O distances are within the range established by previous structure determinations of related compounds[5−11] (caption to Figure 2). It is noteworthy that the dianion of compound **5** with two seven-membered rings extends the set of structural data for beryllium spiro compounds, which to date includes examples with two five-membered rings [in the bis(catecholate)][6] and two six-membered rings (in the salicylate and cresotate).[7,8] From the results it appears that beryllium is

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(14) Barry, J. E.; Finkelstein, M.; Ross, S. D.; Uebel, J. J. *Tetrahedron* **1978**, *34*, 3401−3404.

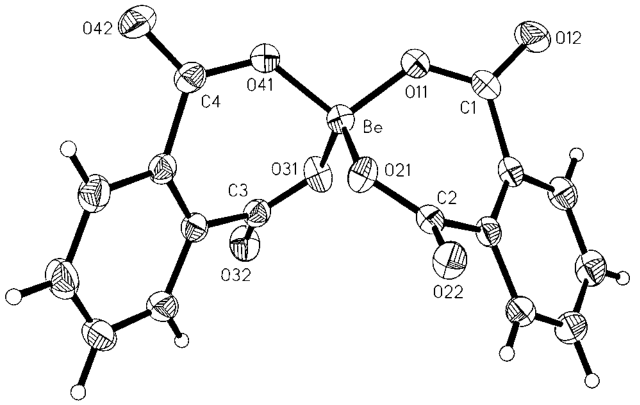

Figure 2. Structure of the dianion of compound **5** with atomic numbering (ORTEP, 50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Be−O11 1.590(2), Be−O21 1.611(2), Be−O31 1.605(2), Be−O41 1.604(2), O11−Be−O21 109.7(11), O11−Be−O31 109.6(1), O11−Be−O41 106.9(1), O21−Be−O31 112.2(1), O21−Be−O41 109.1(1), O31−Be−O41 109.1(1).

readily accommodated in any of these structural motifs even in aqueous solution, where solvation by water molecules is a competing process.

Experimental Section

General Procedures. Beryllium and its compounds are generally to be considered as highly toxic. Therefore all necessary precautions should be taken against any contamination of the environment. The reactions were carried out in pure, fully desalinated water. The reagents were commercial and p.a. grade. Standard equipment and instrumentation were used throughout. NMR: Jeol GX400. ^{1}H NMR: internal standard H_2O ($\delta = 4.6$ ppm), $^{13}C\{^1H\}$ NMR: external standard benzene ($\delta = 128$ ppm). ^{9}Be NMR: external standard $Be(H_2O)_4^{2+}$ ($\delta = 0.0$ ppm). Elemental analyses were performed in the microanalytical laboratory of this Institute by standard procedures.

$Be(C_4H_2O_4)\cdot 2H_2O$ (1). $BeSO_4\cdot 4H_2O$ (1.77 g, 10.0 mmol) is dissolved in 25 mL of water. Maleic acid (1.16 g, 10.0 mmol) is added to the solution followed by 3.18 g (18.1 mmol) of $Ba(OH)_2\cdot 8H_2O$ in small portions. Precipitation of $BaSO_4$ occurs. The reaction mixture is stirred at room temperature for 17 h and then heated under reflux for 3 h. The hot suspension is filtered and left to cool to room temperature. The resulting clear solution (pH 3.0) is concentrated under reduced pressure until precipitation of a white solid occurs. The solid is filtered and dried in vacuo. A 1.12 g yield (6.9 mmol; 69.1%) of $Be(C_4H_2O_4)\cdot 2H_2O$ (mp >300 °C) is isolated.

Anal. Calcd for $BeC_4H_6O_6$ (159.10): C, 30.20; H, 3.80. Found: C, 29.94; H, 3.84. ^{1}H NMR (D_2O, 20 °C): $\delta = 6.05$ ppm, s, 2H, C*H*; $^{13}C\{^1H\}$ NMR (D_2O, 20 °C): $\delta = 171.0$ ppm, 2C, *C*OO; $\delta = 133.3$ ppm, 2C, *C*H. ^{9}Be NMR (D_2O, 20 °C): $\delta = 1.21$ ppm, s, 1Be.

Hydrolysis Products. ^{1}H NMR (D_2O, 20 °C): $\delta = 6.02$ ppm, s, 2H, C*H*. $^{13}C\{^1H\}$ NMR (D_2O, 20 °C): $\delta = 171.6$ ppm, 2C, *C*OO; $\delta = 134.6$ ppm, 2C, *C*H.

$(NH_4)_2[Be(C_4H_2O_4)_2]$ (2). Maleic acid (2.32 g, 20.0 mmol) and 1.3 mL of a 25% aqueous solution of ammonia (20.0 mmol of NH_3) are dissolved in 30 mL of water. After the addition of 1.77 g (10.0 mmol) of $BeSO_4\cdot 4H_2O$ and 3.15 g (10.0 mmol) of $Ba(OH)_2\cdot 8H_2O$ the mixture is stirred at room temperature for 16 h and then heated under reflux for 5 h. The hot suspension is filtered and left to cool to room temperature. The resulting clear solution (pH 5.5) is evaporated under reduced pressure until precipitation of a white solid occurs. The solid is filtered off, dried in a vacuum, and identified as $(NH_4)_2[Be(C_4H_2O_4)_2]$ (yield: 1.94 g, 7.1 mmol, 71.0%). The compound decomposes at 184 °C.

Anal. Calcd for $BeC_8H_{12}N_2O_8$ (273.20): C, 35.17; H, 4.43. Found: C, 34.24; H, 4.45. ^{1}H NMR (D_2O, 20 °C): $\delta = 6.02$ ppm, s, 2H, C*H*. $^{13}C\{^1H\}$ NMR (D_2O, 20 °C): $\delta = 171.2$ ppm, 2C, *C*OO; $\delta = 134.6$ ppm, 2C, *C*H. ^{9}Be NMR (D_2O, 20 °C): $\delta = 2.02$ ppm, s, 1Be.

Hydrolysis Products. ^{1}H NMR (D_2O, 20 °C): $\delta = 6.01$ ppm, s, 2H; $\delta = 5.99$ ppm, s, 2H, C*H*. $^{13}C\{^1H\}$ NMR (D_2O, 20 °C): $\delta = 171.5$ ppm, 2C, *C*OO; $\delta = 133.2$ ppm, 2C, *C*H; $\delta = 171.1$ ppm, 2C, *C*OO; $\delta = 133.3$ ppm, 2C, *C*H. ^{9}Be NMR (D_2O, 20 °C): $\delta = 1.21$ ppm, s, 1Be.

$Be(C_8H_4O_4)\cdot 2H_2O$ (3). $BeSO_4\cdot 4H_2O$ (3.2 g, 18.1 mmol) is dissolved in 25 mL of water. Phthalic acid (3.0 g, 18.1 mmol) is added to the solution followed by 5.7 g (18.1 mmol) of $Ba(OH)_2\cdot 8H_2O$ in small portions. Precipitation of $BaSO_4$ occurs. The reaction mixture is stirred at room temperature for 17 h and then heated under reflux for 3 h. The hot suspension is filtered and allowed to cool to room temperature. The resulting clear solution (pH 4.4) is concentrated under reduced pressure until precipitation of a white solid occurs. The solid is filtered off and dried in vacuo. Yield: 2.3 g (11.0 mmol, 60.8%) of $Be(C_8H_4O_4)\cdot 2H_2O$ (decomposition >300 °C).

Anal. Calcd for $BeC_8H_8O_6$ (209.16): C, 45.95; H, 3.85. Found: C, 46.56; H, 3.66. ^{1}H NMR (D_2O, 20 °C): $\delta = 7.21-7.40$ ppm, m, 4H, aryl *H*. $^{13}C\{^1H\}$ NMR (D_2O, 20 °C): $\delta = 174.9$ ppm, 2C, *C*OO; $\delta = 133.6$ ppm, 2C, *C-1/2*; $\delta = 131.2$ ppm, 2C, *C-3/6*; $\delta = 130.2$ ppm, 2C, *C-4/5*. ^{9}Be NMR (D_2O, 20 °C): $\delta = 1.20$ ppm, s, 1Be.

Hydrolysis Products. $^{13}C\{^1H\}$ NMR (D_2O, 20 °C): $\delta = 175.2$ ppm, 2C, *C*OO; $\delta = 134.0$ ppm, 2C, *C-1/2*; $\delta = 131.4$ ppm, 2C, *C-3/6*; $\delta = 129.8$ ppm, 2C, *C-4/5*.

$(C_6H_{14}NO)_2[Be(C_8H_4O_4)_2]$ (5). Phthalic acid (3.32 g, 20.0 mmol) and 2.5 mL of a 25% aqueous solution of ammonia (36.8 mmol of NH_3) are dissolved in 30 mL of water. After the addition of 1.77 g (10.0 mmol) of $BeSO_4\cdot 4H_2O$ and 3.15 g (10.0 mmol) of $Ba(OH)_2\cdot 8H_2O$ the mixture is stirred at room temperature for 16 h and then heated under reflux for 5 h. The hot suspension is filtered and left to cool to room temperature. The resulting clear solution (pH 5.9) is evaporated under reduced pressure until precipitation of a white solid occurs. The solid was filtered off, dried in a vacuum, and identified as $(NH_4)_2[Be(C_8H_4O_4)_2]$ (**4**) (yield: 2.10 g, 5.6 mmol, 56.3%). After layering of a concentrated aqueous solution of $(NH_4)_2[Be(C_8H_4O_4)_2]$ with acetone, single crystals of $(C_6H_{14}NO)_2[Be(C_8H_4O_4)_2]$ formed within 1 week, which decompose at 178 °C.

Anal. Calcd for $BeC_{28}H_{36}N_2O_{10}$ (569.61): C, 59.04; H, 6.37; N, 4.92. Found: C, 58.51; H, 6.30; N, 5.09. ^{1}H NMR (D_2O, 20 °C): $\delta = 7.41-7.67$ ppm, m, 8H, aryl-*H*; $\delta = 2.89$ ppm, s, 4H, C*H*$_2$; $\delta = 2.15$ s, 6H, C(O)C*H*$_3$; $\delta = 1.30$ s, 12H, NCC*H*$_3$. $^{13}C\{^1H\}$ NMR (D_2O, 20 °C): $\delta = 212.7$ ppm, 2C, *C*=O; $\delta = 175.3$ ppm, 4C, *C*OO; $\delta = 134.2$ ppm, 4C, *C-1/2*; $\delta = 131.3$ ppm, 4C, *C-3/6*; $\delta = 129.9$ ppm, 4C, *C-4/5*; $\delta = 52.8$ ppm, 2C, *C*N; $\delta = 49.8$ ppm, 2C, *C*H$_2$; $\delta = 30.9$ ppm, 2C, C(O)*C*H$_3$; $\delta = 25.3$ ppm, 4C, NC*C*H$_3$). ^{9}Be NMR (D_2O, 20 °C): $\delta = 2.41$ ppm, s, 1Be.

Hydrolysis products. $^{13}C\{^1H\}$ NMR (D_2O, 20 °C): $\delta = 176.6$ ppm, 2C, *C*OO; $\delta = 136.8$ ppm, 2C, *C-1/2*; $\delta = 129.7$ ppm, 2C, *C-3/6*; $\delta = 128.1$ ppm, 2C, *C-4/5*. ^{9}Be NMR (D_2O, 20 °C): $\delta = 1.36$ ppm, s, 1Be. $^{13}C\{^1H\}$ NMR (D_2O, 20 °C): $\delta = 175.1$ ppm, 2C, *C*OO; $\delta = 133.9$ ppm, 2C, *C-1/2*; $\delta = 131.6$ ppm, 2C, *C-3/6*; $\delta = 130.4$ ppm, 2C, *C-4/5*. ^{9}Be NMR (D_2O, 20 °C): $\delta = 1.83$ ppm, s, 1Be.

Crystal Structure Determination. A suitable single crystal of compound **5** was sealed inside a glass capillary and used for measurement of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Diffraction intensities were corrected for Lorentz polarization and absorption effects. The structure was solved by direct methods and refined by full-matrix least-squares calculations against F^2 [SHELXL-93].[15] The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were located and isotropically refined. Important interatomic distances and angles are given in the caption below Figure 2.

Crystal data of compound **5** at 205 K: $C_{28}H_{36}BeN_2O_{10}$, $M_r = 569.60$, monoclinic, space group $P2_1/n$, $a = 9.768(1)$ Å, $b = 22.283(2)$ Å, $c = 12.852(1)$ Å, $\beta = 90.39(1)°$, $V = 2797.3(4)$ Å^3, crystal dimensions $0.30 \times 0.35 \times 0.35$ mm, $Z = 4$, $d_{calcd} = 1.353$ g/cm^{-3}, $F(000) = 1208$ e, Enraf-Nonius CAD4 diffractometer, Mo K$_\alpha$ radiation ($\lambda = 0.710\,73$ Å, $\mu = 1.0$ cm^{-1}). From 7787 measured and 5428 unique reflections

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(15) Sheldrick, G. M. *SHELXL-93*; University of Göttingen: Göttingen, 1993.

[4289 observed reflections with $F_o \geq 4\sigma(F_o)$], 5425 were used for refinement. The structure converged for 514 parameters to wR2 = 0.0870, R1 [$F_o \geq 4\sigma(F_o)$] = 0.0328, $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $w = 1/2\sigma^2(F_o^2) + (ap)^2 + bp$, $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0426$, $b = 0.7496$, $\rho_{\text{final}} = +0.22/-0.16$ e Å^{-3}.

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Supporting Information Available: Tables of crystal data, structure determination details, atomic coordinates, thermal parameters and bond distances and angles (8 pages). Ordering information is given on any current masthead page. Atomic coordinates, bond lengths, bond angles, and thermal parameters have also been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD No. 406700.

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