Preparative, X-ray, and NMR Studies of the Interaction of Beryllium with Salicylic and *o*-Cresotic Acid: Crystal Structures of $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$ and $Na_3[Be(C_7H_6OCO_2)(OH)(CO_3)Be(C_7H_6OCO_2)] \cdot 8\ H_2O$

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The existence of well-defined crystalline beryllium salicylate(2−) and bis[salicylato(2−)]beryllate complexes as well as of their o-cresotate analogs is established. The structure of $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$ has been determined by an X-ray structure analysis. It contains a beryllate anion of the composition $[Be(C_6H_4OCO_2)_2]^{2-}$ with two salicylate(2−) ligands acting as chelate ligands. The considerable ^{9}Be NMR chemical shifts observed for aqueous solutions of the pure compounds indicate in all cases the persistence of the complexation of the metal ion by the catecholate ligands. ^{9}Be NMR studies of aqueous solutions containing $BeSO_4 \cdot 4\ H_2O$ and sodium salicylate(1−) or sodium o-cresotate(1−) in the molar ratios 1:1 and 1:2 show that a variety of beryllium/salicylate(2−) and beryllium/*o*-cresotate(2−) species are present in solution, the most prominent being $Be(C_6H_4OCO_2)(H_2O)_2$ and $[Be(C_6H_4OCO_2)_2]^{2-}$ (and their o-cresotate analogs). From such solutions in contact with air, a novel dinuclear beryllium hydroxido/*o*-cresotato(2−)/carbonato complex of the stoichiometry $Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$ is isolated. According to an X-ray analysis the compound contains a cyclic beryllate anion with two $Be(C_7H_6OCO_2)$ chelate units linked by bridging hydroxide and carbonate anions. In the light of the ubiquitous availability of phenolic and carboxylic groups in many biomolecules, the finding of strong bonding of Be^{2+} to these functions in aqueous solution is very important.

Beryllium has a number of unique properties as a metal and as a component of compounds that make it indispensable for specialized uses in nuclear, aerospace, and electronics technologies[1,2]. However, beryllium and its compounds are toxic to mammalian cells by interference with normal immune functions. After inhalation, pulmonary beryllium diseases ("berylliosis") or lung cancer[3–5] are likely to occur.

Our understanding of the molecular basis of beryllium toxicity is still rather speculative. Due to the near standstill of preparative beryllium chemistry[6], the interaction of beryllium with biomolecules has been left rather unexplored, and even the nature of very simple beryllium compounds, as e.g. complexes of beryllium with salicylic and *o*-cresotic acid (2-hydroxy-3-methylbenzoic acid), two of the very few established complexing agents for beryllium(2+), appears to be in doubt. Some beryllium salicylate compounds have been reported, but only the structure of beryllium salicylate dihydrate could be established[7,8]. $Be(C_6H_4OCO_2)(H_2O)_2$ features a chelate structure, with the beryllium cation complexed by two water molecules, a phenolate, and a carboxylate oxygen atom (Figure 1).

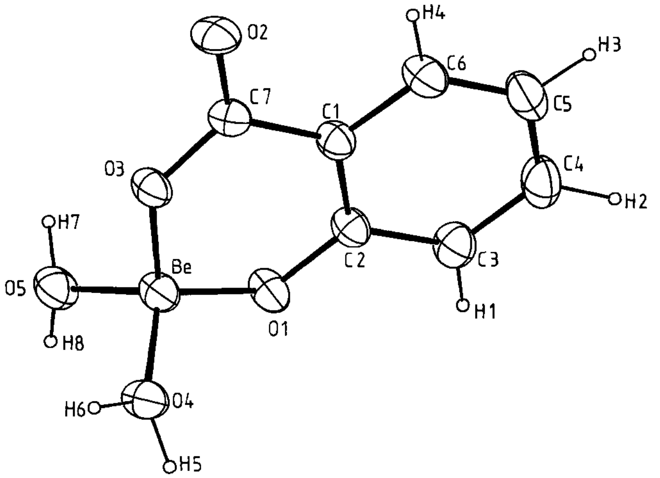

Figure 1. Molecular structure of $Be(C_6H_4OCO_2)(H_2O)_2$ (from ref.[7])

Salicylic acid has been regarded as one of the simplest model ligands for humic substances occurring in natural waters. A recent potentiometric study of the complex formation of beryllium(II) with salicylate and hydroxide anions gives insight into the complex equilibria present in aqueous solutions of beryllium salicylate[9]. *o*-Cresotic acid contains one additional methyl group at the aromatic ring, as compared to salicylic acid. This methyl group should not cause significant differences in the complex formation properties of salicylic and *o*-cresotic acid. Surprisingly, however, the results of a study in the very early literature suggest such differences between the two homologs[10].

As part of ongoing studies on the bioinorganic chemistry of alkali and alkaline earth metals[11] we have also reexamined the coordination chemistry of beryllium with salicylic and *o*-cresotic acid. We now report on the preparation and structural characterization of $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot$

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2.25 H_2O, $Be(C_7H_6OCO_2) \cdot 2\ H_2O$, $Na_2[Be(C_7H_6OCO_2)_2] \cdot H_2O$ and $Na_3[Be(C_7H_6OCO_2)(OH)(CO_3)Be(C_7H_6OCO_2)] \cdot 8\ H_2O$. In addition the results of ^{9}Be-NMR studies of aqueous solutions containing beryllium sulfate and sodium salicylate(1 –) or sodium *o*-cresotate(1 –) are described.

Results

Preparation and Characterization of $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$, $Be(C_7H_6OCO_2) \cdot 2\ H_2O$, $Na_2[Be(C_7H_6OCO_2)_2] \cdot H_2O$, and $Na_3[Be(C_7H_6OCO_2)(OH)(CO_3)Be(C_7H_6OCO_2)] \cdot 8\ H_2O$

Beryllium *o*-cresotate(2 –) dihydrate $[Be(C_7H_6OCO_2) \cdot 2\ H_2O]$ is obtained by using a procedure described for the preparation of beryllium salicylate(2 –) dihydrate according to equation (1)[7,8].

$$\begin{aligned} &BeSO_4 + Ba(OH)_2 + C_7H_6(OH)CO_2H \rightarrow \\ &BaSO_4 + Be(C_7H_6OCO_2) \cdot 2\,H_2O \end{aligned} \qquad (1)$$

After filtration of the $BaSO_4$ precipitate, the beryllium complex is obtained as an amorphous solid upon concentration of the filtrate (pH 4.9). Despite numerous efforts no single crystals of the compound could be grown. The identity of the complex was therefore established by microanalysis and by NMR spectroscopy. In aqueous solution the ^{9}Be-NMR spectrum of $Be(C_7H_6OCO_2) \cdot 2\ H_2O$ exhibits a singlet at $\delta = 2.8$. The chemical shift value $\delta(^9Be)$ is comparable to that observed for $Be(C_6H_4OCO_2) \cdot 2\ H_2O$ ($\delta = 2.6$)[7,8].

$(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$ and $Na_2[Be(C_7H_6OCO_2)_2] \cdot H_2O$ can be prepared by the reaction of beryllium sulfate with one equivalent of barium hydroxide and two equivalents of ammonium salicylate(1 –) or sodium *o*-cresotate(1 –), respectively, in aqueous solutions according to equations (2) and (3).

$$\begin{aligned} &BeSO_4 + Ba(OH)_2 + 2\,(NH_4)(C_6H_4OHCO_2) \rightarrow \\ &BaSO_4 + (NH_4)_2[Be(C_6H_4OCO_2)_2] + 2\ H_2O \end{aligned} \qquad (2)$$

$$\begin{aligned} &BeSO_4 + Ba(OH)_2 + 2\,Na(C_7H_6OHCO_2) \rightarrow \\ &BaSO_4 + Na_2[Be(C_7H_6OCO_2)_2] + 2\,H_2O \end{aligned} \qquad (3)$$

$(NH_4)(C_6H_4OHCO_2)$ and $Na(C_7H_6OHCO_2)$ are prepared in situ by treating salicylic or *o*-cresotic acid with ammonia or sodium hydroxide. After filtration of the $BaSO_4$ precipitate, the beryllate complexes are obtained by evaporation of the aqueous solutions. In the case of $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$, slow evaporation of an aqueous solution led after one month to the formation of single crystals, whereas despite numerous attempts no crystals of $Na_2[Be(C_7H_6OCO_2)_2] \cdot H_2O$ could be obtained. The identity of both complexes was established by microanalysis and NMR spectroscopy.

The structure of $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$ was determined by a single-crystal X-ray diffraction analysis. The compound contains a beryllate anion $[Be(C_6H_4OCO_2)_2]^{2-}$ with two salicylate(2 –) ligands acting as chelate ligands (Figure 2). This dianion has no crystallographic symmetry. The beryllium(II) cation lies in the center of a slightly distorted tetrahedron formed by the deprotonated carboxyl and phenolic oxygen atoms of the salicylate ligands. The Be – O bond lengths range from 1.59(1) to 1.630(9) Å, with no clear distinction between $Be-O_{phenolate}$ and $Be-O_{carboxylate}$ distances. Two water molecules could be located in the lattice of $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$. In addition, disordered water molecules are present, and a partial occupation model approaches the overall stoichiometry $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$.

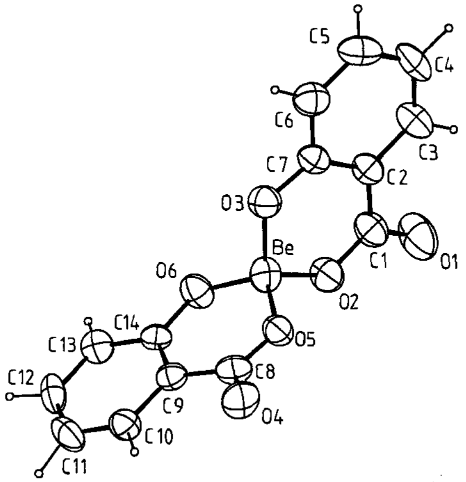

Figure 2. Structure of the $[Be(C_6H_4OCO_2)_2]^{2-}$ dianion in $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$ with atomic numbering (ORTEP, displacement parameters at the 50% probability level; H atoms with arbitrary radii). Selected interatomic distances [Å] and angles [°]: Be – O2 1.62(1), Be – O3 1.62(1), Be – O5 1.630(9), Be – O6 1.59(1), C1 – O1 1.244(8), C1 – O2 1.277(8), C7 – O3 1.326(7), C8 – O4 1.255(6), C8 – O5 1.284(9), C14 – O6 1.313(7); O2 – Be – O3 107.0(6), O2 – Be – O5 109.5(6), O2 – Be – O6 112.5(5), O3 – Be – O5 107.7(4), O3 – Be – O6 111.3(6), O5 – Be – O6 108.7(6)

The ^{9}Be-NMR spectra of the aqueous solutions of $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$ and of $Na_2[Be(C_7H_6OCO_2)_2] \cdot H_2O$ show singlets at $\delta = 4.0$ and 4.2, respectively.

From the experiments oriented towards the generation of beryllate complexes with the metal-to-ligand stoichiometries of 1 : 2 and 1 : 1, a crystalline beryllium *o*-cresotate(2 –) complex of the curious stoichiometry $Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$ was obtained serendipitously by the reaction of sodium *o*-cresotate(1 –) with beryllium hydroxide in boiling aqueous solutions. After filtration, crystallization was attempted in air with the filtrate (pH 11.5). Upon slow evaporation a precipitate consisting of amorphous, micro- and single-crystalline components was collected. The ^{9}Be-NMR spectrum of this crude product shows a singlet at $\delta = 4.2$, a value similar to that of the $[Be(C_7H_6OCO_2)_2]^{2-}$ dianion (above).

However, the single-crystal X-ray structure analysis of one of the crystals revealed that in the crystals a dinuclear beryllium complex of the stoichiometry $Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$ is present. In the anion (Figure 3) two $Be(C_7H_6OCO_2)$ units are linked by bridging hydroxide and carbonate anions. This diberyllate anion has C_s symmetry with a crystallographic mirror plane (through O4, C9, O6). The [$Be_2(OH)(CO_3)$] ring is almost planar (with a maximum deviation from planarity for C9 of 0.05 Å). Accordingly, the sum of the internal angles at the ring atoms is 717.6°, very close to the 720° required for a planar system. However, the internal angles at O4 and O5 are significantly larger than 120°, and those at the beryllium centers significantly smaller. Somewhat unexpected in the bridging carbonate ligand of $[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2]^{3-}$ is the fact that the terminal C–O bond is significantly longer than the ring bond lengths [C9–O5/O5′ 1.293(2); C9–O6 1.257(4) Å].

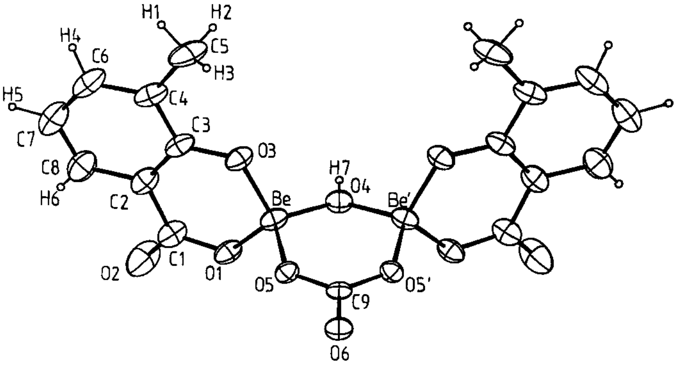

Figure 3. Structure of the $[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2]^{3-}$ trianion in $Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$ with atomic numbering (ORTEP, displacement parameters at the 50% probability level; H atoms with arbitrary radii). Selected interatomic distances [Å] and angles [°]: Be–O1 1.624(3), Be–O3 1.610(3), Be–O4 1.597(3), Be–O5 1.631(3), C1–O1 1.292(3), C1–O2 1.232(3), C3–O3 1.334(3), C9–O5 1.293(2), C9–O6 1.257(4); O1–Be–O3 108.2(2), O1–Be–O4 110.8(2), O1–Be–O5 105.9(2), O3–Be–O4 113.5(2), O3–Be–O5 111.1(2), O4–Be–O5 107.1(2), Be–O4–Be′ 123.6(2), Be–O5–C9 129.5(2), O5–C9–O5′ 120.8(2), O5–C9–O6 119.6(1)

The beryllium atoms lie in the centers of slightly distorted tetrahedra formed by the deprotonated carboxyl and phenolic oxygen atoms of the *o*-cresotate ligand, by the bridging hydroxide anion, and by an oxygen atom of the CO_3^{2-} bridge. The Be–O bond lengths range from 1.597(3) ($Be-O_{hydroxide}$) to 1.631(3) Å ($Be-O_{carbonate}$). These distances are at the lower end of the range given for beryllium(II) coordinated by four oxygen atoms (1.60–1.69 Å)[12]. The Be–OH bond length in $[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2]^{3-}$ [1.597(3) Å] is significantly longer than the Be–OH distances reported for the $[Be_3(OH)_3]^{3+}$ ring of $Be_3(OH)_3(C_5H_4NCO_2)_3 \cdot H_2O$ (1.571–1.580 Å)[13].

In the crystal lattice the oxygen atoms of the $[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2]^{3-}$ unit have contacts to the sodium atoms. The asymmetric unit contains one full and one half occupied sodium position, the latter being positioned on the mirror plane, which is also the origin of the C_s symmetry of the $[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2]^{3-}$ unit. Five water molecules are coordinated to the dinuclear beryllate anion. One additional water molecule could be located in a position with full occupation, but additional disordered water molecules are also present in the lattice. Na–O contacts and hydrogen bonds appear to contribute significantly to the overall stability of the crystal lattice.

As already mentioned, together with the larger crystals of $Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$, amorphous and microcrystalline components were also obtained. An elemental analysis of the *micro*crystalline product showed a carbon content of only ca. 8% ($Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$: 33.56%), suggesting the presence of sodium carbonate ($Na_2CO_3 \cdot H_2O$). The carbonate in the reaction mixture is probably formed by absorption of CO_2 from the air into the alkaline aqueous solution. All attempts to crystallize pure $Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$ from aqueous solutions containing one equivalent of $BeCl_2$ (or $BeSO_4$), one equivalent of sodium *o*-cresotate(1–) and half an equivalent of Na_2CO_3 have failed. Upon crystallization only mixtures were obtained, which contained — among other products — sodium carbonate[8].

The ^{9}Be-NMR spectra of aqueous solutions, which contain $BeSO_4$, sodium *o*-cresotate(1–) and Na_2CO_3 (molar ratio 1:1:0.5), and with the pH adjusted to 11 or 6, show no significant differences as compared to spectra of aqueous solutions free of carbonate at the same pH values[8]. It appears that in aqueous solutions the species $Be(C_7H_6OCO_2)(H_2O)_2$ and $[Be(C_7H_6OCO_2)_2]^{2-}$ are prevailing. Crystallization of $Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$ is probably due to a local minimum of the lattice energy of this phase.

^{9}Be-NMR Studies of Aqueous Solutions Containing Salicylic or *o*-Cresotic Acid and Beryllium Sulfate

The ^{9}Be-NMR studies of aqueous solutions of $Be(C_6H_4OCO_2) \cdot 2\ H_2O$[7,8], $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$, $Be(C_7H_6OCO_2) \cdot 2\ H_2O$, and $Na_2[Be(C_7H_6OCO_2)_2] \cdot H_2O$ have shown that the complexation of the beryllium(II) cation by salicylate and *o*-cresotate ligands gives rise to a considerable chemical shift $\delta(^9Be)$ as compared with the Be^{2+}_{aq} reference ($\delta = 0$). Since ^{9}Be-NMR spectroscopy[14–16] therefore appears to be an excellent analytical tool for the investigation of the equilibria present in aqueous solutions containing the beryllium(II) cation and salicylate or *o*-cresotate ligands, aqueous solutions containing $BeSO_4 \cdot 4\ H_2O$ and sodium salicylate(1–) or sodium *o*-cresotate(1–) in the molar ratios 1:1 and 1:2 have been investigated in greater detail. The pH value of the aqueous solutions was adjusted by NaOH. Figures 4 and 5 show the ^{9}Be-NMR spectra recorded for beryllium salicylate solutions at molar ratios 1:1 and 1:2 and at different pH values. Interestingly, in both figures some of the spectra show *several* ^{9}Be resonances. This result is remarkable, because well-defined beryllium salicylate and *o*-cresotate compounds exhibit only one ^{9}Be-NMR singlet[7,8]. It could be argued that the observation of only one ^{9}Be singlet does not exclude the presence of several beryllium-containing species in solution, because fast ligand exchange on the NMR time scale could cause averaged spectra. However, the observation of several distinct ^{9}Be-NMR singlets in some of the spectra recorded here makes it highly improbable that such a fast ligand exchange process occurs in the systems investigated.

The ^{9}Be-NMR spectra summarized in Figure 4 were recorded from aqueous solutions containing $Be(SO_4) \cdot 4\ H_2O$

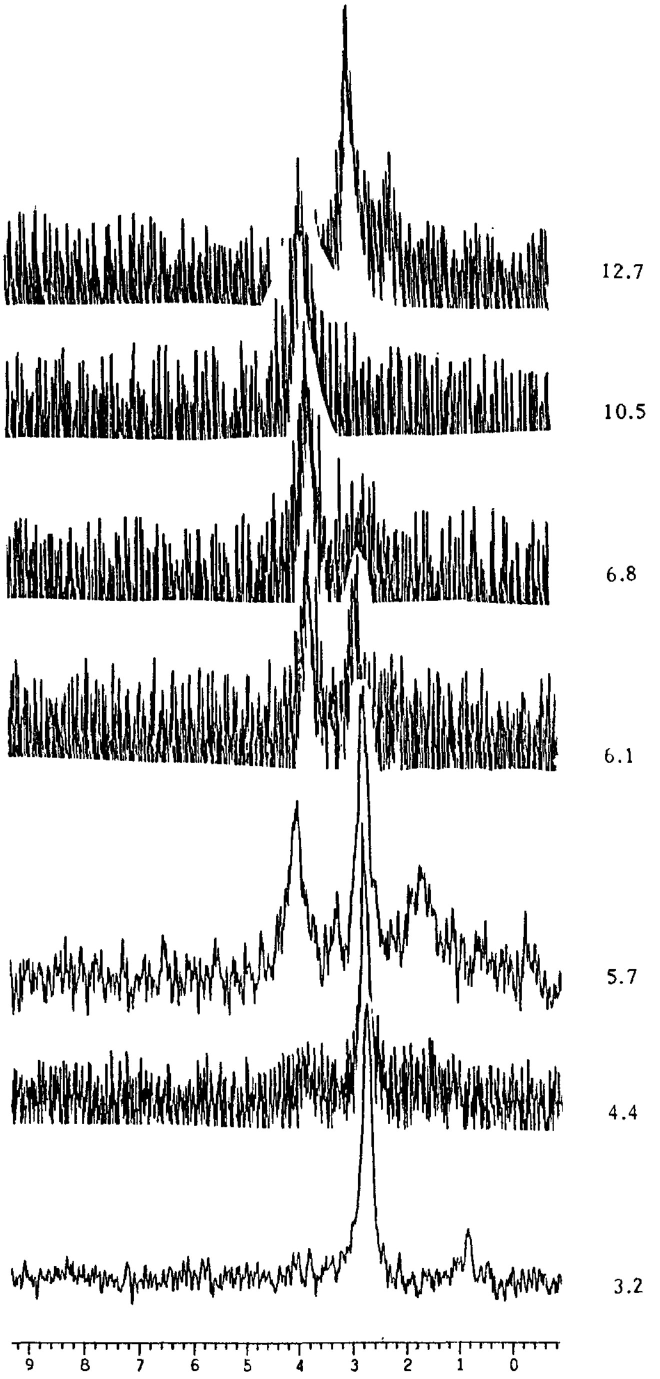

Figure 4. ^{9}Be-NMR spectra (δ scale) of aqueous solutions containing $BeSO_4 \cdot 4\ H_2O$ and sodium salicylate(1−) in the molar ratio 1:1 ($[BeSO_4 \cdot 4\ H_2O] = [Na(C_6H_4OHCO_2)] = 0.25$ mol/l) as a function of pH

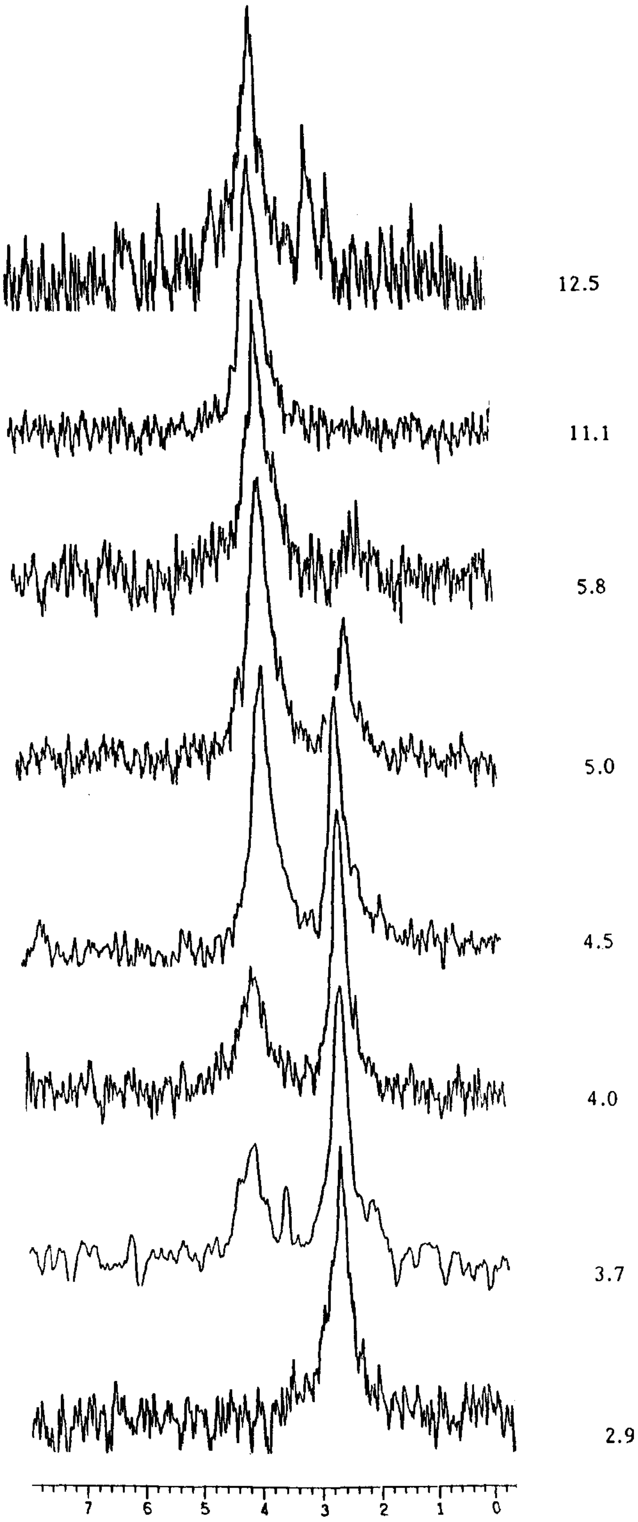

Figure 5. ^{9}Be-NMR spectra (δ scale) of aqueous solutions containing $BeSO_4 \cdot 4\ H_2O$ and sodium salicylate(1−) in the molar ratio 1:2 ($[BeSO_4 \cdot 4\ H_2O] = 0.25$ mol/l; $[Na(C_6H_4OHCO_2)] = 0.50$ mol/l) as a function of pH

and sodium salicylate(1−) in the molar ratio 1:1 ($[Be(SO_4) \cdot 4\ H_2O] = [Na(C_6H_4OHCO_2)] = 0.25$ mol/l). At pH 3.2 a white suspension is present, and the ^{9}Be-NMR spectrum shows a singlet at $\delta = 2.7$ for the species in solution. This chemical shift value is comparable to that observed for an aqueous solution of $Be(C_6H_4OCO_2) \cdot 2\ H_2O$[7,8] and is to be assigned to this 1:1 beryllium salicylate. At pH 4.4 the spectrum is largely unchanged, but upon further addition of NaOH a clear solution is obtained and three ^{9}Be-NMR resonances are observed at pH 5.7. The singlets at $\delta = 2.7$ and 4.0 can be assigned to the species $Be(C_6H_4OCO_2)(H_2O)_2$ and $[Be(C_6H_4OCO_2)_2]^{2-}$, respectively (above). The ^{9}Be-NMR resonance at $\delta = 1.6$ cannot be assigned unambiguously to a beryllium-salicylate complex. It disappears as the pH value is raised to 6.1. Already at pH 5.8 the solution becomes turbid again, and precipitation of beryllium hydroxide is observed[1,8].

$$2\ Be(C_6H_4OCO_2)_{aq} + 2\ OH^- \rightleftharpoons Be(OH)_2\downarrow + [Be(C_6H_4OCO_2)_2]^{2-}$$

The ^9Be-NMR spectrum at pH 6.1 shows two singlets at $\delta = 2.7$ and 4.0, which indicate that $Be(C_6H_4OCO_2)(H_2O)_2$ and $[Be(C_6H_4OCO_2)_2]^{2-}$ are still present. At pH 6.8 only the singlet for $[Be(C_6H_4OCO_2)_2]^{2-}$ at $\delta = 4.0$ is retained, and the excess beryllium is trapped in the $Be(OH)_2$ precipitate. Surprisingly, upon further addition of NaOH a clear solution results at pH > 12.5. The ^9Be-NMR spectrum exhibits one singlet at $\delta = 3.1$, clearly distinct from the values for $Be(C_6H_4OCO_2) \cdot 2\ (H_2O)$ ($\delta = 2.6$) and $[Be(C_6H_4OCO_2)_2]^{2-}$ ($\delta = 4.0$)[7,8]. The signal is tentatively assigned to an anion of the stoichiometry $[Be(C_6H_4OCO_2)(OH)_2]^{2-}$. To date, attempts to isolate this species have failed.

In Figure 5 representative ^9Be-NMR spectra for aqueous solutions containing $Be(SO_4) \cdot 4\ H_2O$ and sodium salicylate(1−) in the molar ratio 1:2 ($[Be(SO_4) \cdot 4\ H_2O] = 0.25$ mol/l; $[Na(C_6H_4OHCO_2)] = 0.50$ mol/l) are presented. Spectra of suspensions at pH 2.9 indicate that only $Be(C_6H_4OCO_2)_2(H_2O)$ ($\delta = 2.7$) is present in solution. As the pH value is raised, a clear solution is obtained, and the ^9Be-NMR spectrum shows that already at pH 3.7 the beryllate anion $[Be(C_6H_4OCO_2)_2]^{2-}$ ($\delta = 4.0$) appears in solution. Upon further addition of NaOH the concentration of $Be(C_6H_4OCO_2)(H_2O)_2$ in solution is gradually diminished, whereas the concentration of $[Be(C_6H_4OCO_2)_2]^{2-}$ is increased. At pH 5.8 only the beryllate anion $[Be(C_6H_4OCO_2)_2]^{2-}$ is present. In strongly alkaline aqueous solution (pH > 12.5) an additional ^9Be-NMR resonance is observed at $\delta = 3.1$, which is probably due to the species $[Be(C_6H_4OCO_2)(OH)_2]^{2-}$.

^9Be-NMR studies of aqueous solutions containing $BeSO_4 \cdot 4\ H_2O$ and sodium *o*-cresotate(1−) in the molar ratio 1:1 and 1:2 did not produce results sufficiently different from those obtained for the analogous $Be(SO_4) \cdot 4\ H_2O$/sodium salicylate(1−) systems[8] to justify a separate discussion. Contrary to earlier data[10], the two systems should rather be taken as analogous.

Discussion

The present investigation establishes the existence of well-defined crystalline beryllium salicylate(2−) and bis[salicylato(2−)]beryllate complexes as well as of their *o*-cresotate(2−) analogs. The straightforward formation of complexes of the stoichiometries $Be(C_6H_4OCO_2)(H_2O)_2$ and $[Be(C_6H_4OCO_2)_2]^{2-}$ and their methyl derivatives is noteworthy with respect to the behavior of other divalent metal ions toward the salicylate(2−) ligand. Although many salicylate(1−) salts of the stoichiometry $M(C_6H_4OHCO_2)_2$-(solv) (M = divalent metal ion) are known[17–20], only few salicylate(2−) salts containing units of the stoichiometry $M(C_6H_4OCO_2)$ or $[M(C_6H_4OCO_2)_2]^{2-}$[21] have been isolated. It appears that the small beryllium cation with its very high charge-to-radius ratio is able to polarize a coordinated phenolic function so effectively that the acidified phenolic function is deprotonated immediately in aqueous solution of low pH. Further support for this assumption is provided by the structure of $Na_2[Be(C_6H_4O_2)_2] \cdot 5\ H_2O$, where the beryllium(II) cation is coordinated to no less than four deprotonated phenolic oxygen atoms[22] of the catecholate(2−) ligands.

By isolation and characterization of $Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$ the existence of beryllium/hydroxo/carbonato complexes could be proven for the first time. Such complexes had been postulated, but their structures could not be established[23].

In the light of the ubiquitous availability of phenolic and carboxylic groups in many biomolecules, the finding of strong bonding of Be^{2+} to these functions in aqueous solution is very important. This is particularly true since ^9Be-NMR studies show that the complexation of the metal ion persists in aqueous solution over a wide pH range and may thus be relevant for metal transport and for fixation of beryllium at specific coordination sites in biopolymers.

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Experimental

All experiments were carried out in pure, fully desalinated water. Reagents were commercial and of p.a. grade. Beryllium hydroxide was precipitated from an aqueous solution of $Be(SO_4) \cdot 4\ H_2O$ by the addition of stoichiometric amounts of NaOH[24]. – pH values: Knick apparatus, reference electrodes (AgCl/KCl) Ingold. – NMR: Bruker WP100SY (^1H, ^{13}C) and Jeol CX400 (^9Be) instruments. ^1H: internal standard *tert*-butyl alcohol ($\delta = 1.20$); ^{13}C: internal standard dioxane ($\delta = 66.7$); ^9Be: external standard $Be(H_2O)_4^{2+}$ ($\delta = 0.0$). – Elemental analyses: Microanalytical laboratory of this institute according to standard procedures.

$(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$: To 3.37 g (19.02 mmol) of $BeSO_4 \cdot 4\ H_2O$ dissolved in 20 ml of water 5.25 g (38.01 mmol) of salicylic acid and 4 ml of a 25% aqueous solution of ammonia (53.4 mmol NH_3) are added. After the addition of 5.99 g (18.99 mmol) of $Ba(OH)_2 \cdot 8\ H_2O$ in small portions the resulting suspension is stirred at room temp. for 2 h and then heated under reflux for 4 h. The hot solution is filtered and left to cool to room temp. By the addition of ammonia (25% aqueous solution) a pH of 9 is adjusted. Slow evaporation of the solution yields after one month crystals of $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$ (2.62 g, 39%), m.p. >350°C. – ^1H NMR (D_2O, 20°C): $\delta = 6.63$ (m, 2H), 7.24 (m, 1H), 7.65 (m, 1H). – $^{13}C\{^1H\}$NMR (D_2O, 20°C): $\delta = 173.4$ (CO_2), 164.8 (C–O), 134.4 (HCCHC–O), 131.0 ($HCCCO_2$), 120.1 (HCCO), 118.1 (CCO_2), 115.8 ($HCCHCO_2$). – ^9Be NMR (D_2O, 20°C): $\delta = 4.0$, s.

$C_{14}H_{16}BeN_2O_6 \cdot 2.25\ H_2O$ (357.8)				
Calcd.	C 46.99	H 5.63	N 7.83	
Found	C 47.09	H 5.62	N 7.52	

$Be(C_7H_6OCO_2) \cdot 2\ H_2O$: 1.06 g (5.98 mmol) of $BeSO_4 \cdot 4\ H_2O$ is dissolved in 20 ml of water. 0.91 g (5.98 mol) of *o*-cresotic acid is added to the solution followed by 1.89 g (5.98 mmol) of $Ba(OH)_2 \cdot 8\ H_2O$ in small portions. Precipitation of $BaSO_4$ occurs. The re-

action mixture is stirred at room temp. for 2 h and then heated under reflux for 4 h. The hot solution (pH 4.9) is filtered and left to cool to room temp. The resulting clear solution is concentrated under reduced pressure until precipitation of a white solid occurs. The solid is filtered and dried in vacuo. Yield: 0.86 g of $Be(C_7H_6OCO_2) \cdot 2\ H_2O$ (74%). At 290°C decomposition of the compound occurs. – ^1H NMR (D_2O, 20°C): $\delta = 1.98$ (s, CH_3), 6.52 [m, $(CH_3)CCHCH$], 7.16 [d, $(CH_3)CH$, $^3J_{H,H} = 7.5$ Hz], 7.48 (d, $CO_2C{-}CH$, $^3J_{H,H} = 7.3$ Hz). – ^9Be NMR (D_2O, 20°C): $\delta = 2.8$, s.

$C_8H_{10}BeO_5$ (195.2) Calcd. C 49.24 H 5.12
Found C 48.63 H 5.28

$Na_2[Be(C_7H_6OCO_2)_2] \cdot H_2O$: To 2.41 g (13.57 mmol) of $BeSO_4 \cdot 4\ H_2O$ dissolved in 60 ml of water 4.13 g (27.13 mmol) of *o*-cresotic acid and 1.09 g (27.13 mmol) of NaOH are added. After the addition of 4.28 g (13.57 mmol) of $Ba(OH)_2 \cdot 8\ H_2O$ in small portions the resulting suspension is stirred at room temp. for 8 h. The solution is filtered and the filtrate concentrated under reduced pressure until precipitation of a white solid occurs. The crude product is recrystallized from methanol. Yield: 3.65 g of $Na_2[Be(C_7H_6OCO_2)_2] \cdot H_2O$ (72%). At 290°C decomposition of the compound occurs. – ^1H NMR (D_2O, 20°C): $\delta = 2.02$ (s, CH_3), 6.52 [m, $(CH_3)CCHCH$], 7.18 [m, $(CH_3)CH$], 7.57 (dd, $CO_2C{-}CH$, $^3J_{H,H} = 7.9$, $^4J_{H,H} = 1.8$ Hz). – $^{13}C\{^1H\}$NMR (D_2O, 20°C): $\delta = 174.1$ (CO_2), 163.9 (C–O), 135.0 [$HCC(CH_3)$], 128.9 ($C{-}CH_3$), 128.7 ($HCCCO_2$), 117.3 (CCO_2), 115.1 ($CHCHCO_2$), 16.4 (CH_3). – ^9Be NMR (D_2O, 20°C): $\delta = 4.2$, s.

$C_{16}H_{14}BeNa_2O_7$ (373.3) Calcd. C 51.43 H 3.75
Found C 50.56 H 3.73

$Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$: 1.50 g (9.86 mmol) of *o*-cresotic acid and 0.40 g (10.0 mmol) of NaOH are dissolved in 15 ml of water. The resulting clear solution is heated under reflux, and to the hot solution beryllium hydroxide is added in small portions, until the added beryllium hydroxide does not dissolve any more. The reaction mixture is heated under reflux for 4 h. The hot solution is filtered and left to cool to room temp. Upon slow evaporation of the resulting clear solution (pH 11.5) a solid precipitate containing amorphous, micro- and single-crystalline components is obtained after one month. The ^9Be-NMR spectrum of this crude product shows a singlet at $\delta = 4.2$, which indicates the presence of the $[Be(C_7H_6OCO_2)_2]^{2-}$ dianion in solution. The crystalline components can be isolated by mechanical separation. The larger crystals were suitable for single-crystal X-ray structure analysis.

Crystal Structure Determinations[25]: Enraf-Nonius CAD4 diffractometer for $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$ (a) and Syntex $P2_1$ for $Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$ (b), Mo-K_α radiation, $\lambda = 0.71069$ Å, graphite monochromator, $T = 23$°C (a) and -50°C (b). During data collection three standard reflections were periodically measured as a general check of crystal and instrument stability. No significant change was observed for both compounds. Reduced cell calculations did not indicate any higher symmetry (DELOS, LEPAGE). Lp correction was applied, but intensity data were not corrected for absorption effects. The structures were solved by direct methods (SHELXS-86) and completed by difference Fourier syntheses (SHELX-76). The final atomic positional parameters and isotropic equivalent displacement factors are listed in Tables 1 (a) and 2 (b).

$(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$: $C_{14}H_{16}BeN_2O_6 \cdot 2.25\ H_2O$, $M_r = 357.84$, orthorhombic, $a = 24.859(2)$, $b = 16.933(2)$, $c = 8.198(1)$ Å, $V = 3450.85$ Å^3, space group *Pccn* (No. 56), $Z = 8$, $D_{calc} = 1.377$ g cm^{-3}, $F(000) = 1508$, μ(Mo-K_α) = 1.1 cm^{-1}, $\Theta{-}2\Theta$ scan. 2488 intensity data were measured up to $(\sin\Theta/\lambda)_{max} = 0.593$ Å^{-1}. 1328 independent structure factors were considered "observed" [$F_o > 4\sigma(F_o)$] and used for refinement. The hydrogen atoms (6 found, 13 calculated at idealized geometrical positions, other hydrogen atoms neglected) were included in the refinement with fixed isotropic displacement parameters ($U_{iso} = 0.05$ Å^2). The non-H atoms were refined with anisotropic displacement parameters with the exception of the oxygen atoms of the disordered water molecules, which were refined with isotropic displacement parameters. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$. Final R and R_w values were 0.078 and 0.054, respectively (number of refined parameters: 230). Residual electron density: $+0.28/-0.39$ e Å^{-3}.

Table 1. Fractional atomic coordinates and thermal displacement parameters for $(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$

ATOM	X/A	Y/B	Z/C	U(eq.)
O1	0.3067(2)	0.1079(4)	-0.0990(5)	0.079
O2	0.3818(2)	0.1138(3)	0.0410(4)	0.049
O3	0.4045(2)	0.0022(3)	0.2479(4)	0.047
C1	0.3373(3)	0.0800(5)	0.0066(7)	0.049
C2	0.3224(3)	0.0060(4)	0.0920(6)	0.040
C3	0.2748(3)	-0.0325(5)	0.0543(6)	0.054
C4	0.2595(3)	-0.1013(5)	0.1247(7)	0.057
C5	0.2945(3)	-0.1368(4)	0.2356(7)	0.057
C6	0.3419(3)	-0.1010(4)	0.2757(6)	0.049
C7	0.3575(3)	-0.0288(4)	0.2063(6)	0.037
O4	0.4582(2)	0.2104(3)	0.5441(4)	0.059
O5	0.4207(2)	0.1495(3)	0.3331(4)	0.043
O6	0.4840(2)	0.0843(3)	0.1171(4)	0.046
C8	0.4619(3)	0.1778(4)	0.4071(6)	0.044
C9	0.5160(3)	0.1675(4)	0.3322(6)	0.037
C10	0.5608(3)	0.2044(4)	0.4010(6)	0.044
C11	0.6106(3)	0.1979(4)	0.3360(7)	0.053
C12	0.6187(3)	0.1515(5)	0.1991(7)	0.049
C13	0.5752(3)	0.1133(4)	0.1285(6)	0.045
C14	0.5239(3)	0.1203(4)	0.1914(6)	0.035
Be	0.4239(4)	0.0874(6)	0.1814(8)	0.043
O7	0.5036(2)	-0.0908(3)	0.2237(4)	0.079
O8	0.4049(3)	0.4746(4)	0.1003(5)	0.105
O9	0.1489(9)	0.248(2)	-0.049(2)	0.079
N1	0.3564(3)	0.2850(4)	0.1743(5)	0.074
N2	0.2968(3)	0.3400(5)	-0.1206(6)	0.111

Table 2. Fractional atomic coordinates and thermal displacement parameters for $Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$

ATOM	X/A	Y/B	Z/C	U(eq.)
Na1	-0.00101(8)	0.33068(3)	0.36992	0.034
Na2	0.1912(1)	0.25000	0.0843(3)	0.053
O1	-0.1919(1)	0.33494(6)	0.3774(3)	0.029
O2	-0.2116(2)	0.39957(8)	0.5337(3)	0.056
O3	-0.2924(1)	0.32691(6)	0.0799(3)	0.030
O4	-0.2582(2)	0.25000	0.2794(3)	0.027
O5	-0.10450(9)	0.28990(5)	0.1190(3)	0.025
O6	0.0203(1)	0.25000	-0.0104(3)	0.027
O7	-0.0031(2)	0.38856(6)	0.1170(4)	0.059
O8	-0.1708(1)	0.31842(8)	0.7657(3)	0.046
O9	-0.5887(2)	0.25000	0.4530(4)	0.047
O10	-0.3842(2)	0.25000	0.5863(4)	0.057
C1	-0.2278(2)	0.37737(9)	0.3966(4)	0.033
C2	-0.2888(2)	0.39851(9)	0.2504(4)	0.031
C3	-0.3201(2)	0.37206(8)	0.1031(4)	0.030
C4	-0.3837(2)	0.3941(1)	-0.0249(4)	0.037
C5	-0.4261(2)	0.3660(1)	-0.1747(4)	0.051
C6	-0.4091(2)	0.4412(1)	-0.0049(4)	0.044
C7	-0.3749(2)	0.46808(9)	0.1374(5)	0.047
C8	-0.3174(2)	0.44632(9)	0.2651(4)	0.041
C9	-0.0623(2)	0.25000	0.0759(4)	0.021
Be	-0.2154(2)	0.2999(1)	0.2123(4)	0.026
O11	0.11394	0.03258	0.49985	0.079
O12	0.15296	0.04891	0.38938	0.080
O13	0.08834	0.01134	0.61245	0.092
O14	0.12191	0.03009	0.17260	0.085

$Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$: $C_{17}H_{29}Be_2Na_3O_{18}$, $M_r = 608.40$, orthorhombic, $a = 13.000(1)$, $b = 28.181(3)$, $c = 7.592(1)$ Å, $V = 2781.35$ Å^3, space group *Abm*2 (No. 39), $Z = 4$, $D_{calc} = 1.453$ g cm^{-3}, $F(000) = 1264$, μ(Mo-K_α) = 1.6 cm^{-1}, ω

scan. 2714 intensity data were measured up to $(\sin\Theta/\lambda)_{max} = 0.595$ Å^{-1}. After merging of equivalent data ($R_{int} = 0.03$) 2410 of the remaining 2418 independent structure factors were considered "observed" $[F_o > 1\sigma(F_o)]$ and used for refinement. 14 hydrogen atoms could be located and were included in the refinement with fixed isotropic displacement parameters ($U_{iso} = 0.05$ Å^2). The other hydrogen atoms were neglected. The non-H atoms were refined with anisotropic displacement parameters with the exception of the oxygen atoms of the disordered water molecules. These were refined with isotropic displacement parameters at fixed geometrical positions. A satisfactory model of the crystal structure was obtained with a partial occupation model, in which the sum of the site occupation factors of the oxygen atoms of the disordered water molecules equals 2. Refinement of the inverse coordinate set yielded no differences in R values and geometrical parameters. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$. Final R and R_w values were 0.038 and 0.039, respectively (number of refined parameters: 184). Residual electron density: $+0.50/-0.35$ e Å^{-3}.

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CAS Registry Numbers

$(NH_4)_2[Be(C_6H_4OCO_2)_2] \cdot 2.25\ H_2O$: 143007-21-0 / $Be(C_7H_6OCO_2) \cdot 2\ H_2O$: 110872-91-8 / $Na_2[Be(C_7H_6OCO_2)_2]$: 143007-22-1 / $Na_3[Be_2(OH)(CO_3)(C_7H_6OCO_2)_2] \cdot 8\ H_2O$: 143007-23-2 / Be: 7440-41-7