Preparation and Crystal Structure of $Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$

Otto Kumberger, Jürgen Riede, and Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München,
Lichtenbergstraße 4, W-8046 Garching, F.R.G.

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Crystalline $Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$ was prepared from beryllium hydroxide and a strongly alkaline aqueous solution of catechol. In an X-ray structure determination the complex was shown to feature dianions $[Be(o\text{-}C_6H_4O_2)_2]^{2-}$ with two chelating catechol ligands. The ^9Be-NMR spectrum of an aqueous solution of the compound shows a singlet at $\delta = 7.5$. This signal is shifted considerably from the Be^{2+}_{aq} reference and indicates persistence of the complexation of the metal ion by the catecholate ligands in alkaline aqueous solution. This result is important in the light of the ubiquitous availability of phenolic groups in many biomolecules, such as e.g. catecholamines.

A steady decline of experimental work on beryllium chemistry has been observed in the second half of this century, when the dangers associated with the handling of beryllium and its compounds became evident. Presently, beryllium is considered particularly dangerous owing to its latent toxicity[1-3], and therefore experimental beryllium chemistry has nearly come to a standstill. As early as 1975, theoretical papers on organoberyllium chemistry outnumbered the experimental reports[4]. Beryllium metal, its alloys, and beryllium compounds such as e.g. beryllium oxide are materials indispensable for a number of applications, however, and of paramount importance for a variety of "high-tech" areas such as high-energy radiation technology (beryllium metal), microelectronics[5,6] (beryllium oxide), or aircraft engineering[2,6] (beryllium alloys). In order to rationalize the risk of work with beryllium-based materials, a better knowledge of the interaction of the beryllium ion with ligands present in biological systems or in the environment is highly desirable. As part of ongoing pertinent studies on the bioinorganic chemistry of alkali and alkaline earth metals[7] we have recently become also interested in the coordination chemistry of beryllium. A literature survey shows that there is surprisingly little information available on the structural chemistry of beryllium complexes with biomolecules. Following up earlier results on beryllium salicylate complexes[8,9], we have now directed our efforts towards beryllium catechol complexes. Two phenolic oxygen atoms in the *ortho* position of an aromatic ring are present in a variety of important biomolecules such as e.p. the catecholamines, a well-established class of biological regulators[10,11]. Several beryllium compounds with catechol have been reported in the very early literature, but the structure of these compounds could not be established[12].

We now report on the preparation, crystallization and X-ray structure determination of $Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$.

Results

For the preparation of sodium bis(catecholato)beryllate solutions, beryllium hydroxide is added to a boiling, strongly alkaline aqueous solution of catechol, with the pH of the solution adjusted to pH > 12 by NaOH. After filtration, the beryllium complex $Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$ can be crystallized from the filtrate at 4°C after the addition of a small amount of ethanol. The identity of the complex could be established by micronanalysis, NMR spectroscopy, and a single-crystal X-ray diffraction study.

In the X-ray structure determination the expected ionic lattice was confirmed, which features a beryllate anion of the composition $[Be(o\text{-}C_6H_4O_2)_2]^{2-}$ with two catechol dianions acting as chelate ligands (Figure 1). The dianions have no crystallographic symmetry element. The beryllium(II) cation occupies the center of a slightly distorted tetrahedron formed by the deprotonated phenolic oxygen atoms of the two catechol ligands. The Be–O bond lenghts range from 1.632(6) to 1.649(6) Å. These distances are at the lower end of the range given for beryllium(II) ions coordinated by four oxygen atoms (1.60–1.69 Å)[13], but are

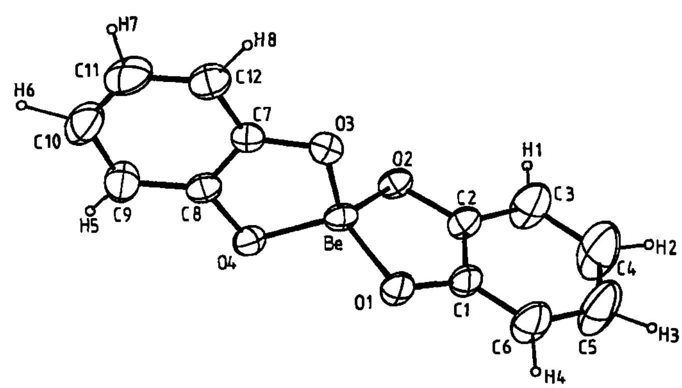

Figure 1. Crystal structure of $Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$ with atomic numbering (ORTEP, displacement parameters at the 50% probability level; hydrogen atoms with arbitrary radii); selected interatomic distances [Å] and angles [°]: Be–O1 1.641(5), Be–O2 1.638(6), Be–O3 1.632(6), Be–O4 1.649(6), C1–O1 1.351(4), C2–O2 1.353(4), C7–O3 1.352(4), C8–O4 1.369(4); O1–Be–O2 99.8(3), O1–Be–O3 113.5(3), O2–Be–O3 111.4(3), O1–Be–O4 116.8(3), O2–Be–O4 116.6(3), O3–Be–O4 99.4(3)

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slightly longer than the Be – $O_{phenolic}$ bond lenghts observed in beryllium salicylate complexes[8,9].

The two crystallographically independent sodium ions of the phase $Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$ adopt an octahedral coordination sphere, which consists of three phenolic oxygen atoms and three water molecules. Sodium – oxygen contacts appear to contribute singificantly to the overall stability of the crystal lattice. In addition to the three water molecules, which could be located in the environment of the sodium ions, the crystal lattice features several disordered water molecules. The overall stoichiometry indicated by a partial occupation model (see Experimental) approaches the formula $Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$.

$Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$ is an air-sensitive white solid, which decomposes when exposed to air, turning first red and then black. Aqueous solutions of the compound proved to be even more air-sensitive and turned black in air immediately.

$Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$ is readily soluble in water to give a solution with pH ≈ 11. ^1H- and ^{13}C-NMR spectra indicate the presence of catecholate groups in equivalent positions, with chemical shifts in the expected range for ligands as chelating groups. The ^9Be-NMR[14–16] spectrum of the solution shows a singlet at $\delta = 7.5$. $Be(H_2O)_4^{2+}$ and cationic polynuclear aquo/hydroxo/beryllium species formed in the hydrolysis of beryllium(II) compounds [such as e.g. $Be_3(OH)_3^{3+}$ and $Be_2(OH)^{3+}$][17,18], are known to exhibit narrow resonance lines very close to $\delta = 0$[19] for all cases investigated to date. For $Be[o\text{-}C_6H_4(O)CO_2] \cdot 2\ H_2O$[8,9] and $[Be\{o\text{-}C_6H_4(O)CO_2\}_2]^{2-}$ $\delta(^9Be)$ values of 2.6 and 4.0, respectively, have been observed[8]. The total range of $\delta(^9Be)$ values reaches from ca. +20 to −20, with typical extremes represented by the cyclopentadienyl derivatives $(C_5H_5)BeX$ (e.g. $X = BH_4$, $\delta = -22.1$; $X = CH_3$, $\delta = -20.4$; $X = Cl$, $\delta = -19.5$) and the three-coordinate derivatives $(CH_3)_2BeN(CH_3)_2$ ($\delta = 19.9$) and $(CH_3)_2Be(OEt_2)$ ($\delta = 20.8$)[14–16]. Given this overall very narrow range, the ^9Be resonance line of $[Be(o\text{-}C_6H_4O_2)_2]^{2-}$ is therefore significantly shifted to lower field as compared to the values reported for other well-defined four-coordinate beryllium(II) ions {normal range: $\delta = -2$ to $+6$[20]; e.g. $[BeF_4]^{2-}$, $\delta \approx -2$; $Be(NH_3)_4^{2+}$, $\delta = 1.7$; $BeCl_2(OEt_2)_2$, $\delta = 3.1$; $BeCl_2[S(CH_3)_2]_2$, $\delta = 5.5$}[14–16].

Discussion

The present investigation establishes the existence of a well-defined crystalline beryllium catecholate complex of the composition $Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$.

The considerable chemical shift in the ^9Be-NMR spectrum observed for aqueous solutions of the compound indicates the persistence of the complexation of the metal ion by the catecholate ligands even in alkaline medium.

The formation and stability of the beryllate anion $[Be(o\text{-}C_6H_4O_2)_2]^{2-}$ in alkaline solution are remarkable, because only few chelate anions of the composition $[M(o\text{-}C_6H_4O_2)_2]^{2-}$ are known for dications M^{2+}[21], whereas well-defined catecholate metal complexes of the stoichiometry $M[C_6H_4(OH)O]_2(solv)$[22] and $M(o\text{-}C_6H_4O_2)(solv)$[23] are legion. In the light of the ubiquitous availability of phenolic groups in many biomolecules, such as e.g. catecholamines, the finding of such strong bonding of Be^{2+} to phenolate oxygen atoms is importat. This is particularly true since the Be – $O_{phenolate}$ bonds appear to be fully retained in aqueous solution.

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Experimental

General: All experiments were carried out in pure, fully desalinated and nitrogen-saturated water under nitrogen. 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]. – NMR: Bruker WP100SY (^1H, ^{13}C) and Jeol CX400 (^9Be); ^1H NMR: internal standard *t*BuOH ($\delta = 1.20$); ^{13}C NMR: internal standard dioxane ($\delta = 66.7$); ^9Be NMR: external standard $Be(H_2O)_4^{2+}$ ($\delta = 0.0$). – Elemental analysis: Microanalytical laboratory of this institute according to standard procedures.

Preparation of $Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$: 3.99 g (36.2 mmol) of catechol and 5.07 g (127 mmol) of NaOH are dissolved in 25 ml of water. The solution is heated under reflux for 20 min. Freshly precipitated beryllium hydroxide[24] is added to the hot solution in small portions, until the added beryllium hydroxide does not dissolve any more. The reaction mixture is heated under reflux for 4 hours. The hot solution is filtered and left to cool to room temperature. The resulting clear solution is reduced to 10 ml under reduced pressure. Then 2 ml of ethanol is added to the solution. After 2 months at 4°C, crystals of $Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$ are formed [2.17 g (17%)]. The compound decomposes in air. – ^1H NMR (D_2O, 20°C): $\delta = 6.4$ (br. s). – $^{13}C\{^1H\}$ NMR (D_2O, 20°C): $\delta = 155.4$ (C – O), 116.7 (*C*HC – O), 111.6 (H*C*CHC – O). – ^9Be NMR (D_2O, 20°C): $\delta = 7.5$ (s).

$C_{12}H_{18}BeNa_2O_9$ (361.26)	Calcd.	C 39.90	H 5.02
	Found	C 40.11	H 4.89

Crystal-Structure Determination[25]: $Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$; $C_{12}H_{18}BeNa_2O_9$ (361.26); monoclinic; $a = 6.771(1)$, $b = 20.882(3)$, $c = 13.474(2)$ Å; $\beta = 92.96(1)°$; $V = 1902.57$ Å^3; space group $P2_1/a$ (No. 14); $Z = 4$; $D_{calcd.} = 1.261$ g cm^{-3}; $F(000) = 752$; μ(Mo K_α) = 1.3 cm^{-1}. Data collection was performed by use of an Enraf-Nonius CAD4 diffractometer (Mo-K_α radiation, $\lambda = 0.71069$ Å, graphite monochromator, θ-θ scan, $T = 23$°C). Data were corrected for Lorentz polarization effects, but no absorption correction was applied. 4192 intensity data were measured up to $(\sin\Theta/\lambda)_{max} = 0.616$ Å^{-1}. After merging of equivalent data ($R_{int} = 0.016$), 2718 of the remaining 3709 independent structure factors were considered "observed" [$F_o \geqslant 4\sigma(F_o)$] and used for refinement. The structure was solved by direct methods (SHELXS-86)[26] and refined by full-matrix least-squares techniques (SHELX-76)[27]. 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 nonhydrogen atoms were refined with anisotropic displacement parameters with the exception of the oxygen atoms of the disordered water molecules. These were included in the refinement with fixed isotropic displacement parameters ($U_{iso} = 0.05$ Å^2) and fixed geometrical positions. Only the site-occupation factors were refined. The sum of the refined occu-

Table 1. Fractional atomic coordinates and thermal displacement parameters [Å^2] for $Na_2[Be(o\text{-}C_6H_4O_2)_2] \cdot 5\ H_2O$

ATOM	X/A	Y/B	Z/C	U(eq.)
Be	0.0906(8)	0.1202(2)	0.5606(4)	0.027
O1	0.1144(4)	0.1859(1)	0.4956(2)	0.035
O2	0.0874(4)	0.0672(1)	0.4710(2)	0.029
O3	-0.1124(4)	0.1179(1)	0.6207(2)	0.030
O4	0.2534(4)	0.1087(1)	0.6542(2)	0.029
C1	0.0927(6)	0.1674(2)	0.3996(3)	0.033
C2	0.0787(6)	0.1012(2)	0.3855(3)	0.031
C3	0.0526(9)	0.0754(2)	0.2918(3)	0.055
C4	0.042(1)	0.1174(3)	0.2105(3)	0.079
C5	0.057(1)	0.1823(2)	0.2228(4)	0.076
C6	0.0814(8)	0.2081(2)	0.3191(3)	0.055
C7	-0.0598(6)	0.1030(2)	0.7161(3)	0.028
C8	0.1444(6)	0.0971(2)	0.7350(3)	0.030
C9	0.2205(7)	0.0794(2)	0.8285(3)	0.043
C10	0.0888(8)	0.0675(2)	0.9030(3)	0.053
C11	-0.1095(8)	0.0742(2)	0.8832(3)	0.055
C12	-0.1889(7)	0.0919(2)	0.7903(3)	0.043
Na1	0.2489(2)	0.28398(7)	0.5627(1)	0.036
Na2	0.2577(2)	-0.03404(7)	0.4797(1)	0.033
O5	0.5276(4)	-0.0051(1)	0.3859(2)	0.035
O6	0.0680(5)	0.3591(1)	0.4601(2)	0.053
O7	-0.0282(4)	0.2810(1)	0.6680(2)	0.042
O8	0.11282	0.39207	0.26542	0.050
O9	0.04356	0.36746	0.17287	0.050
O10	0.01617	0.41975	0.11197	0.050
O11	0.00050	0.39419	0.25832	0.050
O12	0.52697	0.26330	0.86074	0.050
O13	0.65124	0.26041	0.85087	0.050
O14	0.43524	0.26419	0.89513	0.050
O15	0.62485	0.24505	0.94311	0.050
O16	0.03259	0.35465	0.08691	0.050
O17	0.81614	0.24191	0.84757	0.050
O18	0.47332	0.23139	0.96393	0.050
O19	0.79531	0.25025	0.94391	0.050

pation factors equals approximately 2. The function minimized was $\Sigma w\,(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. Final R and R_w values were 0.072 and 0.056, respectively (number of refined parameters: 211). Residual electron density: $+0.54/-0.63$ eÅ^{-3}. The final atomic positional parameters and isotropic equivalent displacement factors are listed in Table 1.

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[199/92]

CAS Registry Number

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