The Quest for Beryllium Peroxides

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There is no experimental proof documented in the literature for the existence of any beryllium peroxide compound. All recent pertinent preparative attempts described in this work, using a range of beryllium salts with various peroxides as reagents under mild conditions, were equally unsuccessful. ^{1}H and ^{9}Be NMR investigations of aqueous solutions containing beryllium salts and hydrogen peroxide in a broad pH range also gave no definite evidence for the presence of peroxoberyllates as components of the manifold equilibria in such solutions. Quantum chemical calculations have therefore been carried out to delineate the energetics and structures of various beryllium peroxide model compounds. Standard Hartree−Fock and density functional methods were employed at various levels of sophistication. The series of prototypes considered consists of $[BeOH]^+$, $Be(OH)_2$, $Be(OH)(OOH)$, $Be(OOH)_2$, $[Be(O_2)_2]^{2-}$, $[BeO_2(OH_2)_2]$, and $[Be_2(O_2)_2(OH_2)_4]$ (all in the gas phase). Surprisingly, the triatomic cation $[BeOH]^+$ has been found to have a linear structure. All the Be−O(peroxide) bonds are found to be rather long, suggesting weaker bonding compared to the Be−O bonds in aquo, hydroxo, or oxo complexes. Hydrogen peroxide or anions derived therefrom are therefore not able to compete successfully with water (hydroxide anions) in aqueous solution. In the mononuclear beryllium peroxide molecules, the peroxide groups form chelating units at tetrahedrally 4-coordinate metal atoms. The binuclear compound $[Be_2(O_2)_2(OH_2)_4]$ has a puckered six-membered-ring structure, close to the standard chair conformation. A significant lengthening of the O−O bonds upon coordination to the Be^{2+} centers has been calculated, but it is unlikely that the polarization of the peroxide group by the high positive charge density at Be^{2+} is significant to cause an intrinsic instability of beryllium peroxides. All structures represent distinct local minima on the potential energy surface and are predicted to be (meta)stable species in nonaqueous media. The field of aluminum peroxides is a similar gray area on the map of metal and metalloid peroxides and is reminiscent of the well-established "diagonal-relation" of Be and Al in the periodic table of the elements.

Introduction

The peroxides of *lithium* and *boron* are classic examples in the inventory of compounds of these two elements,[1,2] and several of these peroxides are important industrial chemicals: Lithium peroxide in various forms (Li_2O_2 or Li_2O_{2-x}) is a potent disinfectant for water systems and an oxygen source in submarine and aerospace technology.[1−5] Several peroxoborates are used on a large scale as the oxidizing agents in detergents, the most prominent example being the sodium salt featuring the cyclic dianion $[(HO)_2B(OO)_2B(OH)_2]^{2-}$ (**1**) (as the tetrahydrate, Figure 1).[1,2,6,7]

By contrast, the literature is devoid of reports on the successful synthesis of any *beryllium* peroxide. Standard
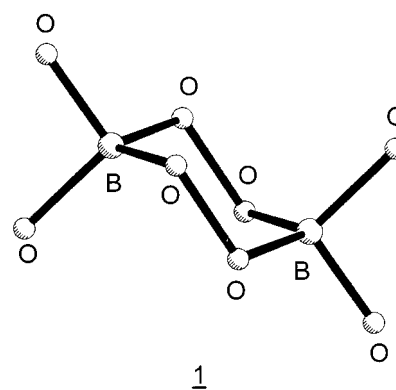
Figure 1. X-ray structure of **1** as it occurs in sodium perborate tetrahydrate.[6] Hydrogen atoms are not shown.

textbooks[1,2] have no entries on beryllium peroxides, and even the specialized comprehensive secondary and tertiary literature[8−10] includes only a few citations which all refer to early unsuccessful attempts to create such species.[11−13]

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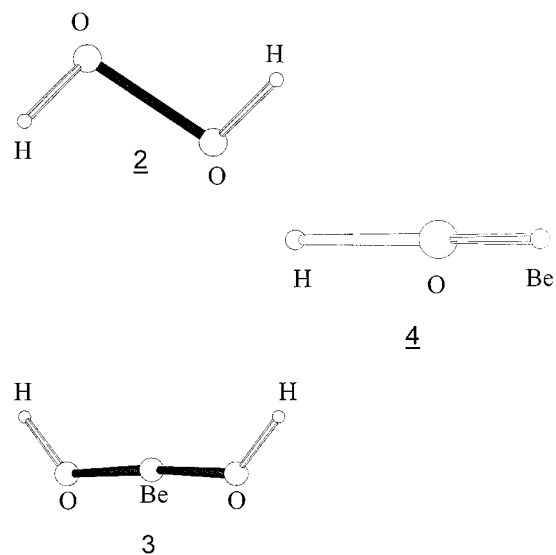
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It is certainly not by accident that the situation is similar for the element *aluminum*: Although the chemistry of aluminum is generally much more advanced than the chemistry of beryllium, there is again a complete lack of information on inorganic aluminum peroxides.[1,2] The well-established "diagonal relation" between Be and Al in the periodic table of the elements[1,14] is often attributed to a similar (and extremely high) ratio of charge to ionic radius (6.5 Å^{-1} for Be, 6.0 Å^{-1} for Al).[1,2,8,15] It therefore might appear that the high charge density concentrated at the cations Be^{2+} and Al^{3+} exerts such a strongly polarizing influence on hydrogen peroxide H$_2$O$_2$ or its anions HOO$^-$ and O$_2^{2-}$ that the rather labile O$-$O bond undergoes facile cleavage. However, the stability of peroxo ligands at other very highly charged metal cations,[1,2,15] such as chromium(VI) and titanium(IV), suggests that this argument alone may not be a satisfactory explanation.

We have therefore undertaken a series of experiments to prepare a beryllium peroxide compound. It is very likely that most of our experiments have already been attempted more than once in the past in other laboratories, but without detailed coverage in the literature. However, all of our many preparative approaches proved unsuccessful (Experimental Section). Although our experimental efforts continue, at this stage it was necessary to turn to quantum chemical calculations to establish whether the synthetic goals were realistic targets. The results have shown, for example, that the projected analogues of the peroxoborates (above) and related species are indeed species which represent local minima on the potential energy hypersurface and that there should be a pathway to reach these metastable individuals. These studies are presented in this paper. The present investigation is an extension of our recent general work on the chemistry of oxo, hydroxo,[16,17] alkoxo,[18,19] siloxo,[20] fluoro,[21] and carboxylato[22-24] complexes of beryllium, which has demonstrated that the pertinent aqueous and nonaqueous systems are rich in unexpected polynuclear species.

Results

Experimental Studies. In the more recent experiments in our laboratory directed at the synthesis of beryllium peroxide compounds, several different approaches were explored using metallic beryllium, beryllium fluoride, chloride, and sulfate, sodium beryllate, and basic beryllium carbonate as the starting materials. Aqueous hydrogen peroxide, sodium peroxide, and bis(trimethylsilyl) peroxide were used as the reagents. The reactions were carried out in aqueous or nonaqueous solvents (mainly diethyl ether) at or below room temperature. None of the products showed any significant peroxide content as tested

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Figure 2. Calculated structures of **2**−**4**.

Table 1. Experimentally Observed (Neutron Diffraction[25] and Electron Diffraction[26]) and Calculated Bond Lengths (Å) and Angles (deg) of H$_2$O$_2$ (**2**)

H$_2$O$_2$	neutron diff[25]	microwave[26]	calcd
H$-$O	0.988(3)	0.965(5)	0.986
O$-$O	1.458(4)	1.452(4)	1.461
H$-$O$-$O	101.9(1)	100(1)	99.8
H$-$O$-$O$-$H	90.2(4)	119.1(18)	121.3

Table 2. Calculated Bond Lengths (Å) and Angles (deg) in **3**, Compared with Sums of Covalent Radii[41] of Matching Atoms

Be(OH)$_2$	calcd	sum of r_{kov}[41]
H$-$O	0.950	1.02
Be$-$O	1.418	1.62
O$-$Be$-$O	177.1	

by conventional methods. In most cases oxygen gas was evolved either during the reactions or upon workup.

^{9}Be NMR studies were carried out on aqueous solutions of beryllium salts with various relative molar concentrations of peroxide and in a wide pH range (Experimental Section). No significant variations in chemical shift were observed which could be taken as convincing evidence for the existence of a beryllium peroxide species in solution. In the intermediate pH range (between acidic and basic) the measurements were unreliable due to the precipitation of beryllium hydroxide.

Calculations

Since no experimental data on beryllium peroxides are known, our first approach was to study the bonding motifs in the gas phase for simple model compounds **2**−**6** (Figures 2 and 3) including Be(OH)(OOH) (**5**) and Be(OOH)$_2$ (**6**). To provide benchmarks for peroxo and beryllium compounds, H$_2$O$_2$ (**2**, Figure 2) and Be(OH)$_2$ (**3**, Figure 2) were chosen as model systems. The molecular geometry of **2** is in very good agreement with the neutron diffraction[25] and microwave[26] data (see Table 1).

The calculations on **3** (Figure 2, Table 2) yielded a geometry with an O$-$Be$-$O angle of 177.1°. Surprisingly, this value is significantly smaller than 180°, while the Be$-$O distances (1.418

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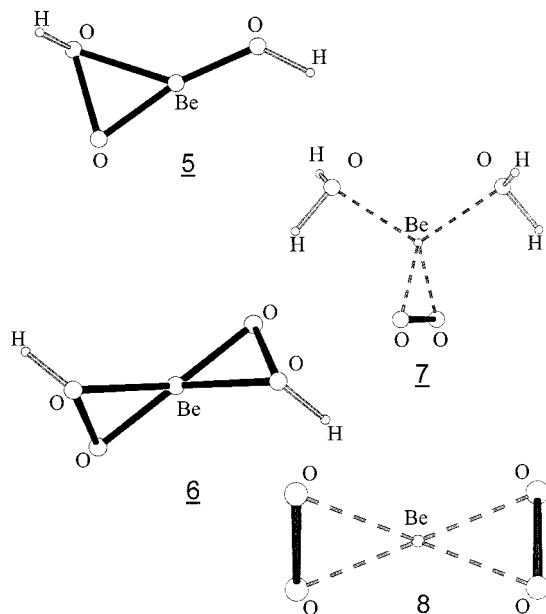
Figure 3. Calculated structures of the mononuclear beryllium peroxide species **5**–**8**.

Table 3. Calculated Bond Lengths (Å) and Angles (deg) in **5**

(H^{1}O^1)Be(O^{2}O$^{2'}$H)	calcd	(H^{1}O^1)Be(O^{2}O$^{2'}$H)	calcd
H^1–O^1	0.955	Be–O–O–H	116.3
Be–O^1	1.433	Be–O–O	69.2
Be–O^2	1.507	O–Be–O	166.1
O–O	1.521		
Be–O$^{2'}$	1.719		
H^2–O^2	0.969		

Table 4. Calculated Bond Lengths (Å) and Angles (deg) in **6**

Be(OOH)$_2$	calcd	Be(OOH)$_2$	calcd
H–O	0.984	O–Be–O	153.5
O–O	1.519	Be–O–O–H	116.0
Be–O	1.514	Be–O–O	69.0

Å) and the O–H distances (0.950 Å) are in the expected range for covalent bonds.

In molecule **5** (Figure 3, Table 3) the beryllium oxygen bond length is larger for the hydroperoxide oxygen atom than for the hydroxide oxygen atom. The O–O bond length (1.521 Å) is larger than in the hydrogen peroxide molecule [1.458(4), 1.452(4) (exptl)[25,26]] and is, in fact, larger than in most experimentally observed peroxide compounds.[27] The most remarkable structural feature of molecule **5** is the short distance between the beryllium atom and the β-oxygen atom of the hydroperoxide group (1.719 Å) which is associated with small angles for O–Be–O (166.1°) and Be–O–O (69.2°). The geometry thus approaches that in "side on" peroxide coordination compounds like [CrO$_5$·py].

Compound **6** (Figure 3, Table 4) shows the same "side on" bonding trend as in **5**. Its formal deprotonation gives the Be(O$_2$)$^{2-}$ anion (**8**, Figure 3, Table 5), which is a molecule of S_4 symmetry. Both the O–O and the Be–O distances are significantly increased compared to those in **6** (1.519 Å in **6**, 1.564 Å in **8** for O–O, 1.514 Å in **6**, 1.600 Å in **8** for Be–O) which may indicate very weak bonding in this dianion.

In the C_2-symmetric complex (H$_2$O)$_2$BeO$_2$ (**7**, Figure 3, Table 6) containing a "side on" bound peroxide ligand, the O–O

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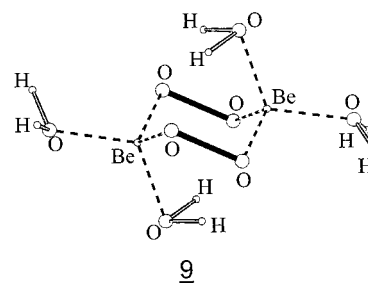
Figure 4. Calculated structure of the dinuclear beryllium peroxide species **9**.

Table 5. Calculated Bond Lengths (Å) and Angles (deg) in **8**

[Be(O$_2$)$_2$]$^{2-}$	calcd
O–O	1.564
Be–O	1.600
O–Be–O	63.6

Table 6. Calculated Bond Lengths (Å) and Angles (deg) in **7**

(H$_2$O)$_2$BeO$'_2$	calcd	(H$_2$O)$_2$BeO$'_2$	calcd
H–O	0.966, 0.974	H–O–H	107.9
Be–O′	1.495	O′–Be–O′	63.6
Be–O	1.706	O–Be–O	114.5
O′–O′	1.576		

Table 7. Calculated Bond Lengths (Å) and Angles (deg) in **9**. Average Values for Equivalent Parameters

(H$_2$O)$_2$Be(O$'_2$)$_2$Be(H$_2$O)$_2$	calcd	(H$_2$O)$_2$Be(O$'_2$)$_2$Be(H$_2$O)$_2$	calcd
O′–O′	1.509	O′–Be–O′	112.6
Be–O	1.718	O–Be–O	118.3
Be–O′	1.588	Be–O′–O′	100.0
		Be–O′–O′–Be	59.1

distance of 1.576 Å is again larger than in **6** and even larger than in **8**. This long O–O distance seems to be a compromise between tetrahedral coordination at the beryllium atom (OO–Be–OO = 63.6°) and the standard O–O bonding. As in the case for **6** the beryllium peroxide bonding in **8** also turns out to be very weak.

The dinuclear beryllium peroxide hydrate molecule (H$_2$O)$_2$-Be(OO)$_2$Be(OH$_2$)$_2$ (**9**, Figure 4, Table 7), designed by analogy with the corresponding peroxoborate dianion [(H$_2$O)$_2$B(O–O)$_2$B(OH)$_2$]$^{2-}$ (**1**), appears to fulfill many intuitively established criteria for a stable compound: It contains coordinatively saturated beryllium atoms, is neutral, and is expected to have a largely strain-free heterocyclic core unit. The calculated O–O distances (1.509 Å) in this compound are relatively short compared to those in **7** and **8** while the Be–O distance of 1.588 Å is in the "longer range". The O–Be–O angles in this compound of 112.6° (peroxide) and 118.3°(to H$_2$O) are much more "tetrahedral" than in **7** [63.6° (peroxide) and 114.5° (to H$_2$O)] or **8** [63.6° (peroxide)].

Discussion

The present experimental studies have shown that beryllium salts do not form significant quantities of beryllium peroxide species in aqueous solution. All preparative attempts have failed as have ^{9}Be NMR tests at various concentrations of the reactants and in a wide pH range. These observations indicate that hydrogen peroxide and its corresponding anions cannot compete favorably with water and its anionic counterparts for coordination at dicationic beryllium centers. In nonaqueous media rapid decomposition with evolution of oxygen takes place.

The results of theoretical calculations on mono- and dinuclear beryllium peroxo complexes indicate that coordination of

hydrogen peroxide, hydroperoxide anion, or peroxide dianion to beryllium dications leads to a significant lengthening of the O−O bond and, more importantly, to rather long Be−O equilibrium distances compared to data for aquo and hydroxo complexes. These long Be−O(peroxide) distances are in agreement with the experimental findings which also suggested that hydrogen peroxide (peroxide anions) will not displace water (hydroxide anions) from the coordination sphere of beryllium.

The lengthening of the O−O bond upon complexation at beryllium (in the gas-phase models) can also be taken as an indication that the beryllium peroxide complexes are of low stability in nonpolar media. Notwithstanding, several of the model compounds represent pronounced minima on the energy hypersurface, which suggests that compounds of this type should be available as metastable species at least in matrixes and at low temperature.

Computational Details

After evaluating a suitable level of theory that is sufficiently accurate in predicting structural parameters and relative energies of beryllium complexes in general (while being economic in terms of computer resources), we decided to use Becke's three-parameter hybrid functional in conjunction with the correlation functional according to Lee, Yang, and Parr.[28,29] The basis set chosen for the geometry optimizations of the complexes presented in this work is either the standard 6-311+G-(d,p) basis set[30] or an augmented TZVP(DIFF) based on Schäfer, Horn, and Ahlrichs[31,32] as implemented in the Gaussian 98[33] and the Turbomole V5.2[34−36] program packages, respectively. All geometries were further verified to represent local minima on their respective energy surface by calculation of their harmonic frequencies. For the frequency analysis performed with Turbomole, each optimized structure was recalculated using the Hartree−Fock SCF method,[37,38] as the current version of this program only supports the evaluation of second derivatives at this level of theory. Further details of these calculations as well as Cartesian coordinates of the structures presented in this study are summarized in the Supporting Information.

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Table 8. ^{9}Be NMR Data (δ in ppm) of Beryllium Sulfate Solutions (1 mol L^{-1}): Volume V in mL, Concentration c in mol L^{-1} for the Reagents, pH (prec: precipitate)

no.	V (H$_2$O$_2$)	c (H$_2$SO$_4$)	c (NaOH)	pH	δ (^{9}Be)
1	0.0	2.0×10^{-1}	0.0	1.03	0.6
2	0.0	2.0×10^{-2}	0.0	1.43	0.6
3	0.0	2.0×10^{-3}	0.0	1.52	0.6
4	0.0	2.0×10^{-4}	0.0	1.56	0.6
5	0.0	2.0×10^{-5}	0.0	1.53	0.6
6	0.0	2.0×10^{-6}	0.0	1.54	0.7
7	0.0	0.0	4.0×10^{-1}	3.54	0.7, 1.25, 0.8
8	0.0	0.0	4.0×10^{-2}	1.04	0.4
9	0.0	0.0	0.0		prec
10	0.0	0.0	4.0	5.33	1.25, 0.7
11	0.0	0.0	2.0	3.57	0.7, 1.25
12	0.0	0.0	10.0	13.00	2.1
13	1.0	2.0×10^{-1}		0.91	0.4
14	1.0	2.0×10^{-2}	0.0	1.24	0.4
15	1.0	2.0×10^{-3}	0.0	1.31	0.4
16	1.0	2.0×10^{-4}	0.0	1.43	0.4
17	1.0	2.0×10^{-5}	0.0	1.38	0.4
18	1.0	2.0×10^{-6}	0.0	1.36	0.4
19	1.0	0.0	4.0×10^{-1}	3.42	0.4, 1.0, 0.6
20	1.0	0.0	4.0×10^{-2}	0.86	0.4
21	1.0	0.0	0.0		prec
22	1.0	0.0	4.0	5.35	1.0
23	1.0	0.0	2.0	3.41	0.4, 1.0, 0.6
24	1.0	0.0	1.0×10^1	12.50	2.1, prec
25	2.0	2.0×10^{-1}	0.0	0.80	0.3
26	2.0	2.0×10^{-2}	0.0	1.05	0.3
27	2.0	2.0×10^{-3}	0.0	1.13	0.3
28	2.0	2.0×10^{-4}	0.0	1.34	0.3
29	2.0	2.0×10^{-5}	0.0	1.20	0.3
30	2.0	2.0×10^{-6}	0.0	1.21	0.3
31	2.0	0.0	4.0×10^{-1}	3.06	0.3, 1.0
32	2.0	0.0	4.0×10^{-2}	0.67	0.3
33	2.0	0.0	0.0		prec
34	2.0	0.0	4.0	5.15	1.0
35	0.0	0.0	2.0	3.35	0.3, 1.0
36	0.0	0.0	1.0×10^1	12.59	2.1, prec

Experimental Section

CAUTION! Beryllium and its compounds are extremely toxic and have been linked to cancer.[39] All samples should be handled with great care. Inhalation and any skin contact must be strictly avoided. All apparatus must be decontaminated and all residues disposed of following the relevant regulations.

All reactions in aqueous media were carried out in deionized, CO$_2$-free, N$_2$-saturated water. The reactions in nonaqueous media were performed using dry solvents and Schlenk techniques.

Infrared spectra were registered on a Perkin-Elmer FT-IR 1600 spectrometer using KBr disks.

The ^{9}Be NMR measurements were performed at room temperature on a JEOL-LA 400 spectrometer at a frequency of 56.2 MHz.

Measurements of pH were carried out with the Schott CG 818 pH-meter, calibrated with commercial phosphate buffer solutions (Merck).

BeCO$_3$·2Be(OH)$_2$·2.5H$_2$O was prepared using the literature method.[40] Me$_3$SiO$_2$SiMe$_3$ is commercially available.

Reaction of Be Metal with H$_2$O$_2$. Metallic beryllium (10 mmol) in the form of a fine powder was placed in a Schlenk flask and an excess of aqueous H$_2$O$_2$ (30%, 10 mL, 100 mmol) added at −10 °C. A container for measuring the volume of the gas evolved was connected with the Schlenk flask. During warming to 0 °C approximately 850 mL of a colorless gas was collected from the suspension and identified as oxygen gas. The reaction mixture was filtered at room temparature and the volume of the filtrate reduced to 0.5 mL in a high vacuum. The remaining colorless liquid showed no signal in the ^{9}Be NMR spectrum. The precipitate consisted of Be(OH)$_{2(aq)}$ as indicated by IR spectroscopy.

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IR: 3134 (broad), 1400, 1112 (broad), 616 (sharp) cm^{-1}.

Reaction of Sodium Beryllate with H$_2$O$_2$. An aqueous NaOH solution (10% w/w) was added to a solution of BeSO$_4$·4H$_2$O (10 mmol) in 30 mL of water with rapid stirring until the mixture had become clear (about 9 mL). An aqueous H$_2$O$_2$ solution (30% w/w) was added dropwise, leading to the precipitation of a white gel-like solid and evolution of oxygen. The precipitate was filtered, washed twice with water, and dried in a vacuum. Yield: 13 mg, white solid.

Calcd for Be(OH)$_2$·2H$_2$O ($M = 79.057$): H, 7.65; O, 80.95. Found: H, 7.89; O, 81.23.

Reaction of BeCO$_3$·2Be(OH)$_2$·2.5H$_2$O with H$_2$O$_2$. Aqueous H$_2$O$_2$ (30% w/w) was added dropwise to a stirred suspension of freshly precipitated BeCO$_3$·2Be(OH)$_2$·2.5H$_2$O (10 mmol) in water (5 mL) at 0–5 °C. A colorless gas was evolved which was shown to contain mainly CO$_2$ [precipitation of BaCO$_3$ from Ba(OH)$_2$ solution; negative flame test, IR, MS]. Filtration of the reaction mixture and washing of the precipitate twice with water followed by drying over P$_2$O$_5$ gave 510 mg of a white solid which showed negative standard peroxide tests.

Reaction of BeF$_2$ with Me$_3$SiO$_2$SiMe$_3$. A solution of Me$_3$SiO$_2$SiMe$_3$ (10 mmol) in 10 mL of diethyl ether was added dropwise to a suspension of finely powdered BeF$_2$ (10 mmol) in 30 mL of diethyl ether at −78 °C. A slow evolution of oxygen and no Me$_3$SiF was observed (positive flame test, GC/MS). A small sample of the reaction mixture was filtered and the filtrate shown to have no signal in the ^{9}Be NMR spectrum. The reaction mixture was slowly warmed to room temperature, stirred for 24 h, and filtered. The volume of the filtrate was reduced to 0.5 mL by vacuum. The concentrated sample showed no ^{9}Be NMR signal and left no residue after complete evaporation.

Reaction of BeCl$_2$ with Me$_3$SiO$_2$SiMe$_3$. A solution of Me$_3$SiO$_2$-SiMe$_3$ (10 mmol) in 10 mL of diethyl ether was added dropwise to a solution of BeCl$_2$ (10 mmol) in 30 mL of diethyl ether at −78 °C. Slow evolution of oxygen was observed (positive flame test). A small amount of the reaction mixture was filtered. The filtrate showed one singlet resonance in the ^{9}Be NMR spectrum (BeCl$_2$·2Et$_2$O, 4.1 ppm, d_8-THF). The reaction mixture was slowly warmed to room temperature, stirred for 24 h, and filtered. After concentration in a vacuum to a volume of 0.5 mL the ^{9}Be NMR spectrum of the filtrate showed, once again, only the signal for BeCl$_2$·2Et$_2$O.

Reaction of BeCl$_2$ with Na$_2$O$_2$. A solution of BeCl$_2$ (2 mmol) in 5 mL of diethyl ether was added dropwise to a suspension of Na$_2$O$_2$ (2 mmol) in 5 mL of diethyl ether at −78 °C. Slow evolution of oxygen was observed (positive flame test). A small amount of the reaction mixture was filtered. In the ^{9}Be NMR spectrum the filtrate showed a singlet resonance of BeCl$_2$·2Et$_2$O (4.1 ppm, d_8-THF). The reaction mixture was slowly warmed to room temperature, stirred for 24 h, and filtered. The volume of the filtrate was reduced to 0.5 mL. The ^{9}Be NMR spectrum of this sample showed only a signal for BeCl$_2$·2Et$_2$O.

pH-Dependent ^{9}Be NMR Measurements of Aqueous BeSO$_4$ Solutions with Different H$_2$O$_2$ Concentrations. All samples contained 1 mL of an aqueous BeSO$_4$ solution (1 M), 1 mL of D$_2$O, and 1 mL of H$_2$SO$_4$ or NaOH solution with concentrations as shown in Table 8.

The different H$_2$O$_2$ concentrations were adjusted by addition of nothing or 1 or 2 mL of the H$_2$O$_2$ solution (30%), respectively. All sample tubes were filled with water to a volume of 5 mL where necessary.

Supporting Information Available: Table S1, listing geometrical parameters of **4** calculated at three levels of theory, and Cartesian coordinates of all calculated molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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