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Anion Coordination by Protonated Tris(pyrazolyl)hydroborato Derivatives: Crystal Structure of the Host–Guest Complex $[\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}\text{Cl}][AlCl_4]$

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Introduction

The formation of complexes between cations and multidentate ligands (e.g. podands, cryptands, and crown ethers and other coronands) is well-established and forms an important subdivision of host–guest complex chemistry.[1] In contrast, the coordination chemistry of anions is noticeably undeveloped. Pioneering studies by several research groups have recently shown that certain acyclic, macrocyclic, and macropolycyclic ammonium derivatives are capable of binding selectively to a large number of anions in solution, including halide, azide, carboxylate, and ATP. These investigations have laid the foundations for the field of anion coordination chemistry.[2] In view of the significant roles that anionic species play in both chemical and biological processes, the development of anion coordination chemistry is particularly important. Here we report that, in the triprotonated form, tris(pyrazolyl)hydroborato derivatives[3] are also capable of acting as receptors for anions, as illustrated by the crystal structure determination of the host–guest complex of the chloride anion $[\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}\text{Cl}][AlCl_4]$ (3-Bu^{t}pz = 3-$C_3N_2Bu^tH_2$).

Results and Discussion

The host–guest complex $[\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}\text{Cl}]^+$, consisting of a chloride anion substrate bound to a protonated tris(pyrazolyl)hydroborato receptor, is readily obtained from the reaction of $Tl\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$[4] with HCl(aq). Addition of $AlCl_3$ to the product allows the chloride anion complex to be isolated as the $[AlCl_4]^-$ derivative, $[\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}\text{Cl}][AlCl_4]$ (Scheme I). Evidence for the composition of the complexes is provided by ^{1}H NMR spectroscopy, which clearly demonstrates that the ligand is triprotonated (Figure 1). Furthermore, the molecular structure of the host–guest complex $[\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}\text{Cl}][AlCl_4]$ has been determined by single-crystal X-ray diffraction, which illustrates that the chloride anion substrate is bound to the N–H groups of the $\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}^{2+}$ receptor by three almost linear (173–175°) hydrogen bonds, for which the hydrogen atoms were both located and refined (Figure 2). The distances between Cl and N for each of the three Cl···H–N interactions are 3.085 (4), 3.084 (4), and 3.069 (4) Å, significantly less than the sum of the N and Cl van der Waals radii (3.30 Å), so that each N–H···Cl interaction represents a strong hydrogen bond.[5] The bond angles subtended at Cl are rather acute (70–75°), so that one face of the chloride substrate is exposed. The closest nonbonding interactions to the chloride substrate are *intra*complex contacts with the hydrogen atoms of the *tert*-butyl substituents (ca. 3 Å), and these are located only marginally at the exposed surface of the chloride substrate. Furthermore, the closest *inter*molecular contacts (>3 Å) of the chloride substrate are with hydrogen atoms of the *tert*-butyl substituents of neighboring molecules.

Other crystallographic studies on anion coordination complexes are rare. Anion complexes that have been structurally characterized are illustrated in Figure 3.[6] The most unique feature of the triprotonated tris(3-*tert*-butylpyrazolyl)hydroborato receptor is that it is only capable of binding to one face of the chloride substrate, thus leaving the opposite face exposed. In contrast, other anion receptor molecules effectively cover the surface of the bound anions. For example, within the series of anion complexes $[(C_{24}H_{54}N_8O_3)H_6X]^{5+}$ (X = F, Cl, Br), the coordination environment about X varies from tetrahedral for fluoride to octahedral for the chloride and bromide derivatives (Figure 3). Thus, tri-

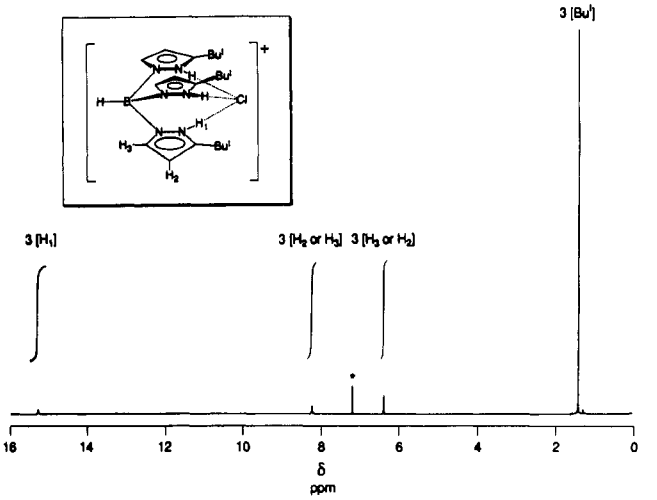

Figure 1. ^{1}H NMR spectrum of $[\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}\text{Cl}][AlCl_4]$ in $CDCl_3$ (✱ = solvent).

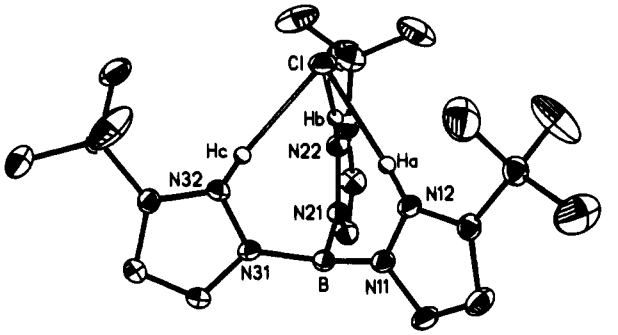

Figure 2. ORTEP drawing of $[\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}\text{Cl}][AlCl_4]$. For clarity, $[AlCl_4]^-$ and C_6H_6 of crystallization are not included. Selected bond distances (Å) and angles (deg): Cl···H$_a$–N12 = 3.085 (4), Cl···H$_b$–N22 = 3.084 (4), Cl···H$_c$–N32 = 3.069 (4), Cl···H$_a$ = 2.23 (4), Cl···H$_b$ = 2.12 (6), Cl···H$_c$ = 2.27 (4); H$_a$···Cl···H$_b$ = 73 (5), H$_a$···Cl···H$_c$ = 75 (5), H$_b$···Cl···H$_c$ = 70 (5), Cl···H$_a$–N$_{12}$ = 175 (3), Cl···H$_b$–N22 = 173 (3), Cl···H$_c$–N32 = 173 (3).

Scheme I

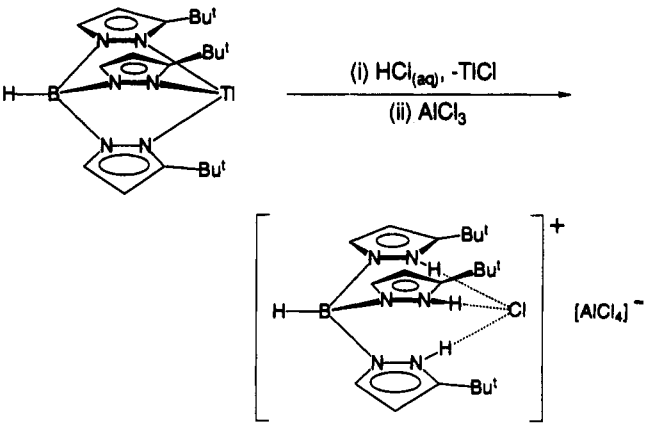

Table I. Crystal and Intensity Collection Data

formula	$C_{27}H_{43}N_6BAlCl_5$	Z	8
fw	666.74	space group	$C2/c$ (No. 15)
lattice	monoclinic	radiation (λ, Å)	Mo Kα (0.710 73)
cell consts	a = 25.144 (5) Å	ρ(calcd)	1.19 g cm^{-3}
	b = 10.246 (2) Å	μ(Mo Kα)	4.4 cm^{-1}
	c = 29.420 (5) Å	goodness of fit	1.818
	β = 101.40 (1)°	R	0.0529
	V = 7429 (2) Å^3	R_w[a]	0.0705

[a] Weighting scheme: $w = [\sigma^2(F) + 0.0067F^2]^{-1}$.

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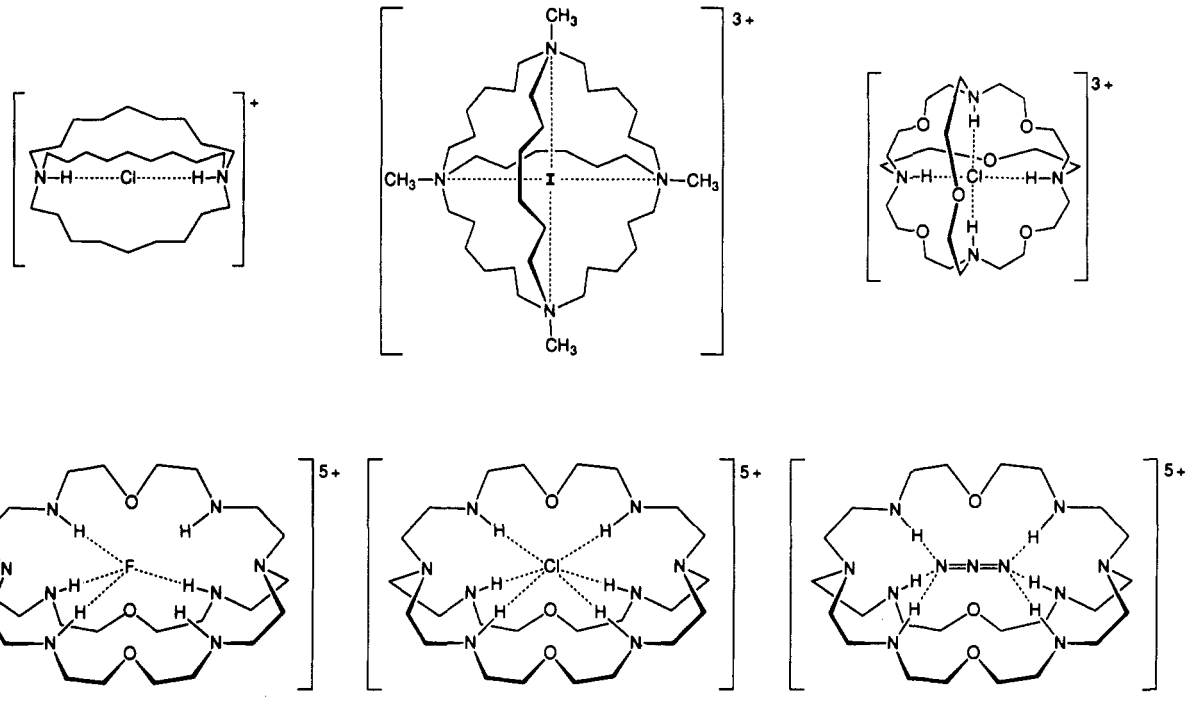

Figure 3. Other structurally characterized anion Host–Guest complexes.

protonated tris(pyrazolyl)hydroborato derivatives offer the potential that, following anion binding, subsequent attack at a particular substrate may be enhanced compared with that for complexes of more restrictive receptors. Furthermore, replacement of the *tert*-butyl substituents by other groups may allow modification of the shape and size of the binding pocket and may therefore influence binding selectivity.

The binding of a protonated tris(pyrazolyl)hydroborato derivative to an anion provides another example of the versatility of tris(pyrazolyl)hydroborato ligands, which, since the initial discovery in the late 1960s, have found widespread use in providing stable coordination environments for the investigation s-, p-, d-, and f-block metal complexes.[3] Indeed, the binding of the protonated receptor species $\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}^{2+}$ to the chloride anion substrate bears a close analogy to the binding of cations by the complementary anionic $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}^-$ derivative.

In conclusion, these results demonstrate that protonated tris(pyrazolyl)hydroborato derivatives belong to a new class of receptors for anions. Furthermore, the ready availability of a series of poly(pyrazolyl)hydroborato derivatives, $[B(Rpz)_4]^-$, $[HB(Rpz)_3]^-$ and $[H_2B(Rpz)_2]^-$, that may also be functionalized by substitution at both the boron atom and pyrazolyl rings by a range of substituents bodes extremely well for the use of such protonated ligands in anion coordination chemistry.

Experimental Details

General Considerations. All manipulations were performed by using a combination of glovebox, high-vacuum, or Schlenk techniques.[7] ^{1}H NMR and ^{13}C NMR spectra were measured on Varian VXR 200, 300, and 400 spectrometers. IR spectra were recorded as Nujol mulls on a Perkin-Elmer 1420 spectrophotometer. Elemental analyses were measured by using a Perkin-Elmer 2400 CHN elemental analyzer. Tl{HB(3-Bu^{t}pz)$_3$} was prepared by the literature method.[4]

Synthesis of $[\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}\text{Cl}][\text{AlCl}_4]$. Hydrochloric acid (0.71 mL of 12 M, 8.5 mmol) was added to a stirred solution of $\text{Tl}\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}$ (1.0 g, 1.7 mmol) in $CHCl_3$ (10 mL) at room temperature, resulting in the formation of a white precipitate (TlCl). The mixture was filtered after 10 min, and the solvent was removed from the filtrate under reduced pressure at room temperature, giving a white solid. The white solid was dissolved in $CHCl_3$ (10 mL), and $AlCl_3$ (0.325 g, 2.44 mmol) was added to the stirred solution. The mixture was filtered after 5 min, giving a colorless solution. The solvent was removed from the filtrate under reduced pressure at room temperature, giving $[\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}\text{Cl}][\text{AlCl}_4]$ as a white solid (0.84 g, 84%). $[\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}\text{Cl}][\text{AlCl}_4]$ may be recrystallized from a concentrated $CHCl_3$ solution by addition of pentane. IR (Nujol mull, cm^{-1}): ν_{NH} = 3145 (w). Anal. Calcd: C, 42.9; H, 6.3; N, 14.3. Found: C, 44.3; H, 6.7; N, 14.2. ^{1}H NMR ($CDCl_3$): δ 1.45 [27 H, s, $HB\{HC_3N_2H_2C(CH_3)_3\}_3$], 6.53 [3 H, s, 3 H of $HB\{HC_3N_2H_2C(CH_3)_3\}_3$], 8.27 [3 H, s, 3 H of $HB\{HC_3N_2H_2C(CH_3)_3\}_3$], 15.30 [3 H, s, 3 H of $HB\{HC_3N_2H_2C(CH_3)_3\}_3$]. ^{13}C NMR ($CDCl_3$): δ 29.8 [9 C, q, $^1J_{C-H}$ = 127, $HB\{HC_3N_2H_2C(CH_3)_3\}_3$], 32.3 [3 C, s, $HB\{HC_3N_2H_2C(CH_3)_3\}_3$], 106.4 [3 C, d, $^1J_{C-H}$ = 186, d, $^2J_{C-H}$ = 5, 3 C of $HB\{HC_3N_2H_2C(CH_3)_3\}_3$], 142.2 [3 C, d, $^1J_{C-H}$ = 195, $^2J_{C-H}$ = 5, 3 C of $HB\{HC_3N_2H_2C(CH_3)_3\}_3$], 162.2 [3 C, s, 3 C of $HB\{HC_3N_2H_2C(CH_3)_3\}_3$].

X-ray Structure Determination of $[\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}\text{Cl}][\text{AlCl}_4]$. Crystal data and data collection and refinement parameters are summarized in Table I. A single crystal of $[\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}\text{Cl}][\text{AlCl}_4]\cdot C_6H_6$, grown from a solution in benzene at room temperature, was mounted in a glass capillary and placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photo-

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Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$)

atom	x	y	z	U^a
Cl	2339 (1)	7438 (1)	2059 (1)	55 (1)*
H_a	2060 (15)	6473 (38)	1373 (13)	43 (11)
H_b	2628 (23)	8575 (57)	1555 (21)	95 (20)
H_c	1669 (15)	8747 (38)	1674 (13)	44 (12)
Al	-1156 (1)	10168 (2)	683 (1)	52 (1)*
Cl(1)	-1810 (1)	11504 (2)	647 (1)	83 (1)*
Cl(2)	-539 (1)	11030 (2)	377 (1)	84 (1)*
Cl(3)	-1459 (1)	8481 (2)	295 (1)	91 (1)*
Cl(4)	-824 (1)	9683 (2)	1381 (1)	87 (1)*
N(11)	1778 (2)	7026 (4)	750 (1)	46 (1)*
N(12)	1946 (2)	6166 (4)	1101 (1)	44 (1)*
N(21)	2366 (2)	9110 (4)	885 (1)	44 (1)*
N(22)	2712 (2)	9093 (4)	1304 (1)	46 (1)*
N(31)	1394 (2)	9137 (4)	1042 (1)	42 (1)*
N(32)	1435 (1)	9155 (4)	1509 (1)	45 (1)*
C(1)	4838 (3)	9514 (8)	635 (3)	185 (5)
C(2)	4767 (3)	10786 (8)	465 (3)	214 (5)
C(3)	5021 (3)	11823 (8)	730 (3)	175 (4)
C(4)	5345 (3)	11587 (8)	1164 (3)	152 (4)
C(5)	5417 (3)	10315 (8)	1334 (3)	201 (5)
C(6)	5163 (3)	9278 (8)	1069 (3)	188 (5)
C(11)	1608 (2)	6294 (5)	374 (2)	62 (2)*
C(12)	1669 (2)	5003 (6)	484 (2)	67 (2)*
C(13)	1889 (2)	4932 (4)	955 (2)	45 (2)*
C(14)	2068 (2)	3805 (5)	1272 (2)	54 (2)*
C(15)	2678 (3)	3767 (8)	1381 (3)	149 (5)*
C(16)	1871 (4)	3949 (7)	1724 (2)	121 (4)*
C(17)	1854 (4)	2563 (6)	1042 (3)	148 (5)*
C(21)	2609 (2)	9825 (5)	604 (2)	55 (2)*
C(22)	3107 (2)	10236 (6)	841 (2)	64 (2)*
C(23)	3169 (2)	9759 (5)	1291 (2)	53 (2)*
C(24)	3621 (2)	9868 (6)	1700 (2)	71 (2)*
C(25)	4006 (3)	10963 (7)	1625 (3)	108 (3)*
C(26)	3926 (3)	8570 (7)	1762 (3)	139 (4)*
C(27)	3400 (3)	10196 (9)	2139 (2)	121 (4)*
C(31)	948 (2)	9815 (5)	871 (2)	51 (2)*
C(32)	709 (2)	10257 (5)	1223 (2)	57 (2)*
C(33)	1026 (2)	9818 (5)	1628 (2)	46 (2)*
C(34)	970 (2)	9973 (6)	2127 (2)	57 (2)*
C(35)	1513 (2)	10302 (8)	2433 (2)	95 (3)*
C(36)	582 (3)	11091 (7)	2164 (2)	101 (3)*
C(37)	746 (3)	8701 (7)	2278 (2)	119 (4)*
B	1792 (2)	8540 (6)	755 (2)	45 (2)*

[a] Asterisks indicate equivalent isotropic U defined as one-third of the trace of the orthongalized U_{ij} tensor.

graphs. Intensity data were collected with the use of graphite-monochromated Mo Kα X-radiation ($\lambda = 0.71073$ Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz and polarization effects. The structure was solved by using direct methods and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[8] Systematic absences were consistent with the space groups *Cc* (No. 9) and *C2/c* (No. 15), but consideration of the *E* value statistics suggested the choice *C2/c* (No. 15). Most of the hydrogen atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically, but hydrogens on carbon were allowed to refine in calculated positions ($d_{C-H} = 0.96$ Å; $U_{iso}(H) = 1.2U_{iso}(C)$). Block-diagonal least-squares refinement converged to $R = 0.0529$ ($R_w = 0.0705$). Atomic coordinates and thermal parameters are listed in Table II.

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Supplementary Material Available: Tables SI-SVI, listing crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters, and an ORTEP drawing for [{η^3-HB(3-Bu^{t}pzH)$_3$}Cl][AlCl$_4$]·C$_6$H$_6$ (11 pages); a listing of calculated and observed structure factors (18 pages). Ordering information is given on any current masthead page.

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Beryllium Salicylate Dihydrate

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Introduction

Beryllium and its compounds are considered extremely dangerous owing to their latent toxicity[1-3] and *should be handled cautiously or not at all.*[4] Most chemists seem to opt for the second solution: Already as early as 1975, theoretical papers on organoberyllium chemistry outnumbered the experimental reports.[5] Nevertheless, the lack of experimental work on beryllium chemistry leads to the embarrassing situation that knowledge of the interaction of one of the perhaps most toxic metal cations with ligands present in biological systems or in the environment is very limited indeed. Even the nature of a very simple beryllium compound, beryllium salicylate, which is of interest in this respect and has been known since the beginning of the century,[6] appears to be in doubt: The salt has been formulated as a dihydrate Be(C$_6$H$_4$OCO$_2$)·2H$_2$O with the beryllium cation complexed by a phenolate and a carboxylate oxygen atom. In other reports, however, beryllium salicylate is proposed to be a trihydrate, Be(C$_6$H$_4$OCO$_2$)·3H$_2$O,[8] or to have the curious stoichiometry BeOH(C$_6$H$_4$OHCO$_2$)·2H$_2$O.[9]

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 ions gives insight into the complex equilibria present in aqueous solutions of beryllium salicylate.[10] No crystal structure determination of beryllium salicylate has been reported, however. For the species BeOH(C$_6$H$_4$OHCO$_2$)·2H$_2$O, only the crystal parameters ($a = 7.068$ Å, $b = 7.950$ Å, $c = 9.443$ Å, $\alpha = 100°10'$, $\beta = 102°36'$, $\gamma = 112°34'$) were determined by powder photographs.[9] We therefore decided to synthesize beryllium salicylate and try to obtain single crystals of this compound suitable for X-ray structure determination.

Experimental Section

General Data. All experiments were carried out in pure, fully desalinated water. Reagents were of p.a. quality. Elemental analyses were performed by the microanalytical laboratory of the Anorganisch-chemisches Institute, by standard procedures. NMR spectra were obtained on Bruker WP100SY (^{1}H) and Jeol CX400 (^{9}Be) instruments.

Preparation. A 3.01-g (17.00-mmol) sample of BeSO$_4$·4H$_2$O is dissolved in 30 mL of water. A 2.35-g (17.01-mmol) sample of salicylic acid is added to the solution followed by 5.36 g (17.00 mmol) of Ba(OH)$_2$·8H$_2$O in small portions. Upon addition of the barium hydroxide, precipitation of BaSO$_4$ occurs. The reaction mixture is stirred for 12 h at room temperature and then heated under reflux for 2 h. The hot solution (pH 4.8) is filtered and left to cool to room temperature. The resulting clear solution is evaporated under reduced pressure until precipitation of a white solid occurs. The solid is filtered and dried in a vacuum. A 1.98-g yield of Be(C$_6$H$_4$OCO$_2$)·2H$_2$O (mp >350 °C) is isolated (yield 64%). Anal. Calcd for BeC$_7$H$_8$O$_5$: C, 46.41; H, 4.45. Found: C, 44.94; H, 4.56. ^{1}H NMR [D$_2$O, 20 °C, internal standard *tert*-butyl alcohol (δ

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