

# Synthesis and Structural Characterization of the Beryllium Compounds [Be(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(OEt<sub>2</sub>)], [Be{O(2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(OEt<sub>2</sub>)}, and [Be{S(2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(THF)}·PhMe and Determination of the Structure of [BeCl<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub>]

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The preparations of some new classes of beryllium compounds that have a coordination number of 3 at beryllium are reported. They were synthesized by the reaction of BeCl<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub> with the appropriate lithium salt to give the products [BeMes<sub>2</sub>(OEt<sub>2</sub>)] (1; Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), [Be(OMes\*)<sub>2</sub>(OEt<sub>2</sub>)] (2; Mes\* = 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), and [Be(SMes\*)<sub>2</sub>(THF)]·PhMe (3). The compounds were characterized by <sup>1</sup>H NMR and IR spectroscopy, C and H analysis, and X-ray crystallography. The crystal structure of [BeCl<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub>] (4) was also determined. Crystal data (Mo Kα (λ = 0.710 69 Å) at 130 K) are as follows: [BeMes<sub>2</sub>(OEt<sub>2</sub>)] (1), *a* = 11.913(3) Å, *c* = 28.390(8) Å, *V* = 4029(2) Å<sup>3</sup>, tetragonal, space group *I*4<sub>2</sub>*m*, 975 (*I* > 3σ(*I*)) data, *R* = 0.042; [Be(OMes\*)<sub>2</sub>(OEt<sub>2</sub>)] (2), *a* = 25.022(9) Å, *b* = 9.834(3) Å, *c* = 16.290(4) Å, β = 96.48(3)°, *V* = 3982(2) Å<sup>3</sup>, monoclinic, space group *C*2/*c*, 3173 (*I* > 3σ(*I*)) data, *R* = 0.051; [Be(SMes\*)<sub>2</sub>(THF)]·PhMe (3), *a* = 8.695(4) Å, *b* = 17.399(10) Å, *c* = 17.437(8) Å, α = 60.80(4)°, β = 83.29(4)°, γ = 84.24(4)°, *V* = 2284(2) Å<sup>3</sup>, triclinic, space group *P*1̄, 3751 (*I* > 2σ(*I*)) data, *R* = 0.061; [BeCl<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub>] (4), *a* = 7.486(3) Å, *c* = 20.022(8) Å, *V* = 971.7(6) Å<sup>3</sup>, trigonal, space group *P*3<sub>1</sub>2, 646 (*I* > 2σ(*I*)) data, *R* = 0.028.

## Introduction

With the possible exception of the chemistry of radium, beryllium chemistry has received the least attention among main group 2 elements. The main reason for this is the high toxicity of beryllium and its compounds.<sup>1</sup> Not surprisingly, the lack of attention that beryllium chemistry has received is reflected in the very limited number of structurally characterized species currently available. A recent search in The Cambridge Structural Database<sup>2</sup> yielded a list of just 38 crystal structures containing beryllium. Most of these show beryllium to have a coordination number of 4, and only a handful of structures with lower coordination numbers have been published. Examples of structurally characterized three-coordinate compounds include the

amides [BeNMeSiMe<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>NMe]<sub>2</sub><sup>3</sup> and [Be(NMe<sub>2</sub>)<sub>2</sub>]<sub>3</sub>,<sup>4</sup> the alkoxide [Cl<sub>2</sub>Be<sub>3</sub>O(*t*-Bu)]<sub>4</sub>,<sup>5</sup> and the quasi-three-coordinate species LiBe(*t*-Bu)<sub>3</sub>.<sup>6</sup> Several other compounds that very probably involve three-coordinate beryllium are also known; examples are [Be{O(*t*-Bu)}<sub>2</sub>]<sub>3</sub>,<sup>7</sup> [Be(OCe<sub>t</sub>)<sub>2</sub>]<sub>2</sub>,<sup>8</sup> and M{BeO(*t*-Bu)}<sub>3</sub> (M = Li, Na, K, Rb, Cs).<sup>9</sup> It is also notable that very few molecular species that have Be bound to heavier main group elements have been well characterized. The only exceptions are the recently reported species Be{S<sub>2</sub>N(*i*-Pr)}<sub>2</sub><sup>10</sup> and Be(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)P(*t*-Bu)<sub>2</sub>.<sup>11</sup> Two-

coordination at Be has yet to be demonstrated in the solid state although BeR<sub>2</sub><sup>12,13</sup> (R = Me, *t*-Bu) and Be{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub><sup>14</sup> were shown to be monomeric and to have two-coordinate linear structures in the vapor. A monomeric, presumably two-coordinate, formulation has also been established for Be{O(2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>}<sub>2</sub> in solution.<sup>8</sup> In this paper we report the synthesis and characterization of the new mononuclear beryllium derivatives [BeMes<sub>2</sub>(OEt<sub>2</sub>)] (1), [Be(OMes\*)<sub>2</sub>(OEt<sub>2</sub>)] (2), and [Be(SMes\*)<sub>2</sub>(THF)] (3) (Mes\* = 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), which display the rare coordination number of 3 at beryllium. The last species 3 is also the first well-characterized beryllium thiolate. In addition, a structural determination of the important starting material [BeCl<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub>] is reported.

## Experimental Section

**General Procedures.** All work was performed by using Schlenk techniques under N<sub>2</sub> or in a Vacuum Atmospheres HE 43-2 drybox under N<sub>2</sub>. Solvents were freshly distilled under N<sub>2</sub> from Na/K alloy and degassed twice immediately before use. BeCl<sub>2</sub> and *n*-BuLi were purchased from commercial suppliers and used as received. HOMes\* (Aldrich) was purified by distillation and recrystallized several times from ether and hexane. LiMes,<sup>15</sup> BeCl<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub>,<sup>16</sup> and HSMes\*<sup>17</sup> were synthesized via literature procedures. <sup>1</sup>H NMR spectra were obtained with a General Electric QE-300 spectrometer. IR spectra were recorded as a Nujol mull between CsI plates using a Perkin-Elmer PE 1430 spectrometer. All compounds gave satisfactory C and H elemental analyses.

**Synthesis of Compounds 1-3. [BeMes<sub>2</sub>(Et<sub>2</sub>O)] (1).** LiMes (1.1 g, 8 mmol) was suspended in 30 mL of diethyl ether and 20 mL of *n*-hexane, and the suspension was added dropwise to a solution of 0.32 g of BeCl<sub>2</sub> (4 mmol) in 20 mL of diethyl ether at 0 °C. The white suspension was stirred at room temperature for 18 h, after which the solvent was removed under reduced pressure. Extraction with *n*-hexane (40 mL), followed by filtration through a Celite-padded filter frit, resulted in a colorless solution.

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Table I. Summary of Data Collection<sup>a</sup> and Structure Solution and Refinement Parameters for 1–4

	1	2	3	4
formula	BeC <sub>22</sub> H <sub>23</sub> O	BeC <sub>40</sub> H <sub>78</sub> O <sub>3</sub>	BeC <sub>47</sub> H <sub>74</sub> OS <sub>2</sub>	BeC <sub>8</sub> Cl <sub>2</sub> H <sub>20</sub> O <sub>2</sub>
fw	321.51	616.07	728.2	228.17
crystal color and shape	colorless tetrahedron	colorless parallelepipeds	colorless needles	colorless plates
crystal size	0.83 × 1.0 × 0.63	0.25 × 0.70 × 1.8	0.09 × 0.09 × 0.80	0.10 × 0.10 × 0.25
a, Å	11.913(3)	25.022(9)	8.695(4)	7.486(3)
b, Å	11.913(3)	9.834(3)	17.399(10)	7.486(3)
c, Å	28.390(8)	16.290(4)	17.437(8)	20.022(8)
α, deg	90	90	60.80(4)	90
β, deg	90	96.48(3)	83.29(4)	90
γ, deg	90	90	84.24(4)	120
V, Å <sup>3</sup>	4029(2)	3982(2)	2284(2)	971.7(6)
Z	8	4	2	3
space group	I $\bar{4}2m$	C2/c	P $\bar{1}$	P3 <sub>1</sub> 2 <sub>1</sub>
d(calc), g/cm <sup>3</sup>	1.06	1.03	1.059	1.17
linear abs coeff, cm <sup>-1</sup>	0.57	0.57	1.48	4.72
2θ range, deg	0–55	0–55	0–44	0–50
no. of obs reflns	975 (I > 3σ(I))	3173 (I > 3σ(I))	3751 (I > 2σ(I))	646 (I > 2σ(I))
no. of variables	130	230	460	66
R, R <sub>w</sub>	0.042, 0.048	0.051, 0.058	0.061, 0.065	0.028, 0.026

<sup>a</sup> All data were collected at 130 K on a Syntex P2<sub>1</sub> (1, 2, 4) or Siemens R3m/V diffractometer (3) by using Mo Kα radiation (λ = 0.710 69 Å).

A reduction of the volume to 10 mL afforded 0.63 g of colorless crystals in 49% yield. Mp: dec > 170 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 7.37 (s, 2H, *m*-H), 3.73 (m, br, 4H, CH<sub>3</sub>CH<sub>2</sub>O), 2.73 (s, 6H, *o*-*t*-Bu), 2.37 (s, 3H, *p*-*t*-Bu), 1.10 ppm (m, br, 4 H, CH<sub>3</sub>CH<sub>2</sub>O). IR: ν(Be–C) 1020, ν(Be–O(ether)) 682 cm<sup>-1</sup>.

[Be(OMes\*)<sub>2</sub>(Et<sub>2</sub>O)] (2). HOMes\* (1.05 g, 4 mmol) was dissolved in diethyl ether (20 mL), and the solution was cooled in an ice bath. Treatment with *n*-BuLi (2.5 mL, 4 mmol of 1.6 *m* in hexane) under exclusion of light gave a cloudy mixture, which was stirred for 3 h at room temperature. A suspension of BeCl<sub>2</sub> (0.16 g, 2 mmol) in diethyl ether (20 mL) was cooled in an ice bath and treated under exclusion of light with the LiOMes\* suspension. The cloudy solution was stirred for 18 h at room temperature, after which the solvent was evaporated under reduced pressure. The white solid was extracted with warm *n*-hexane, and the extract was filtered. After reduction of the volume to ca. 15 mL, colorless crystals of the product 2 were obtained. When dried under 0.01-mm vacuum, the crystals of 2 decomposed due to the loss of coordinated diethyl ether. Yield: 0.75 g, 62%. Mp: dec > 120 °C with formation of \*OMes\* radicals. Mp of the ether-free compound: dec > 152 °C. <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>): 7.49 (s, 2H, *m*-H), 3.40 (m, br, 4H, CH<sub>3</sub>-CH<sub>2</sub>O), 1.66 (s, 18H, *o*-*t*-Bu), 1.42 (s, 9H, *p*-*t*-Bu), 0.38 ppm (m, br, 4H, CH<sub>3</sub>CH<sub>2</sub>). IR: ν(Be–O) 1280, ν(O–C) 1022, ν(Be–O(ether)) 676 cm<sup>-1</sup>.

[Be(SMes\*)<sub>2</sub>(THF)]-PhMe (3). HSMes\* (1.114 g, 4 mmol) was dissolved in toluene (20 mL) and THF (ca. 0.2 mL). *n*-BuLi (2.5 mL of 1.6 *m* in hexane) was added slowly using a syringe. The solution was stirred for 5 h at room temperature. BeCl<sub>2</sub> (0.16 g, 2 mmol) was dissolved in toluene (20 mL) and THF (0.2 mL), and the solution of LiSMes\* was added slowly. The reaction started immediately, resulting in a pale yellow cloudy mixture. The suspension was stirred for 18 h at room temperature, and filtered over a Celite-padded filter frit. After reduction of the volume to 15 mL, colorless crystals of the product 3 were obtained. When 3 was dried under reduced pressure, the crystals decomposed to a white solid due to the loss of toluene and traces of THF. Yield: 0.79 g, 54%. Mp: dec > 150 °C. Mp of the ether-free compound: dec > 245 °C. <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>): 7.40 (s, 2H, *m*-H), 3.19 (m, br, 4H, THF), 1.79 (s, 18H, *o*-*t*-Bu), 1.60 (s, 9H, *p*-*t*-Bu), 0.92 (m, br, 4H, THF). IR: ν(Be–S) 800, ν(S–C) 722, ν(Be–O(ether)) 690 cm<sup>-1</sup>.

**X-ray Crystallographic Studies.** The crystals were removed from the Schlenk tube under a stream of N<sub>2</sub> and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream as described in ref 18.

X-ray data for 1–4 were collected at 130 K using Mo Kα radiation. Intensity data sets for 1, 2, and 4 were collected on a Syntex P2<sub>1</sub> diffractometer equipped with a locally modified LT-2 device. Data for 3 were collected using a Siemens R3m/V diffractometer equipped with an Enraf-Nonius universal low-temperature device. Calculations were

Table II. Selected Coordinates and Isotropic Thermal Parameters for Compounds 1–4

	x	y	z	U, Å <sup>2</sup>
[BeMes <sub>2</sub> (OEt <sub>2</sub> )] (1)				
Be(1)	6403(4)	2500	1250	21(1)
C(1)	7047(2)	1233(2)	1111(1)	22(1)
O(1)	5029(2)	2500	1250	33(1)
[Be(OMes*) <sub>2</sub> (OEt <sub>2</sub> )] (2)				
Be(1)	0	1605(3)	7500	20(1)
O(1)	529(1)	2297(1)	7596(1)	22(1)
O(2)	0	-78(2)	7500	24(1)
C(1)	1054(1)	2252(2)	7469(1)	20(1)
[Be(SMes*) <sub>2</sub> (THF)]-PhMe (3)				
Be(1)	2516(8)	-2563(4)	7572(4)	22(3)
S(1)	1073(2)	-1544(1)	7422(1)	25(1)
S(2)	1355(2)	-3594(1)	7810(1)	25(1)
C(1)	1270(5)	-817(3)	7584(3)	20(2)
C(19)	2725(5)	-4616(3)	7566(3)	21(2)
O(1s)	4353(3)	-2557(2)	7515(2)	25(2)
[BeCl <sub>2</sub> (OEt <sub>2</sub> ) <sub>2</sub> ] (4)				
Be(1)	0	4528(7)	1667	22(2)
Cl(1)	-1479(1)	2401(1)	976(1)	34(1)
O(1)	1677(3)	6779(3)	1300(1)	24(1)

carried out using a SHELXTL-PLUS program<sup>19</sup> installed on a Data General Eclipse computer or a Vax station 3200. Scattering factors were from common sources;<sup>20</sup> an absorption correction was applied by using the method described in ref 21.

Some details of data collection and refinement are given in Table I. Further details are provided in the supplementary material. The crystal structures were solved by direct methods and refined by full-matrix least-squares refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, except the meta-hydrogen atoms in 1, were included in the refinement at calculated positions, using a riding model with C–H = 0.96 Å, U<sub>H</sub> = 1.2U<sub>C</sub> for 1, 2, and 4, and fixed U<sub>H</sub> = 0.05 Å for 3. The meta-hydrogen atoms from 1 were found in a difference map; the riding model as described above was used for their refinement. Selected atom coordinates and isotropic thermal parameters are listed in Table II. Selected bond distances and angles are provided in Table III. The largest features on the final difference maps were 0.50, 0.37, 0.69, and 0.19, respectively.

## Results and Discussion

**Synthesis.** The novel species 1–3 were prepared by the straightforward reaction of 2 equiv of the appropriate lithium

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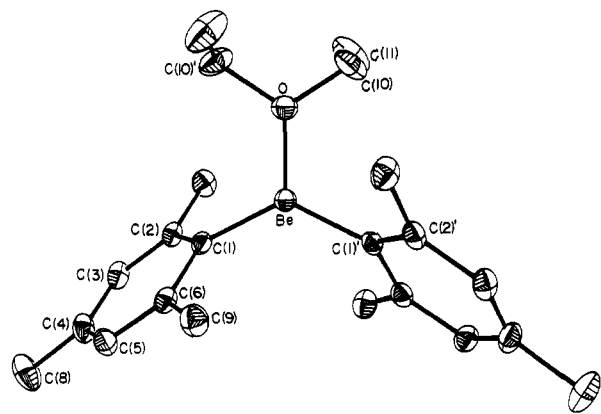


Figure 1. Computer-generated plot of 1. H atoms have been omitted for clarity.

Table III. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1–4

[BeMes <sub>2</sub> (OEt <sub>2</sub> )] (1)			
Be–C(1)	1.739(3)	Be–O	1.638(5)
C(1)–Be–O	116.2(1)	C(1)–Be–C(1a)	127.6(3)
[Be(OMes*) <sub>2</sub> (Et <sub>2</sub> O)] (2)			
Be–O(1)	1.481(2)	O(1)–C(1)	1.355(3)
Be–O(2)	1.655(3)		
O(1)–Be–O(2)	117.4(1)	Be–O(1)–C(1)	147.1(1)
O(1)–Be–O(1a)	125.3(2)		
[Be(SMes*) <sub>2</sub> (THF)]·PhMe (3)			
Be(1)–S(1)	1.991(7)	S(1)–C(1)	1.799(6)
Be(1)–S(2)	1.987(8)	S(2)–C(19)	1.810(5)
Be(1)–O(1s)	1.590(7)		
S(1)–Be(1)–S(2)	111.0(3)	Be(1)–S(1)–C(1)	106.1(3)
S(1)–Be(1)–O(1s)	124.6(4)	Be(1)–S(2)–C(19)	106.3(3)
S(2)–Be(1)–O(1s)	124.3(4)		
[BeCl <sub>2</sub> (OEt <sub>2</sub> ) <sub>2</sub> ] (4)			
Cl–Be	1.978(3)	O–Be	1.683(3)
Cl–Be–Cl(a)	116.6(2)	O–Be–Cl(a)	109.0(1)
Cl–Be–O	109.7(1)	Cl(a)–Be–O(a)	109.8(1)
Cl–Be–O(a)	108.9(1)	O–Be–O(a)	101.8(3)

reagent with [BeCl<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub>]. The syntheses of both [BeMes<sub>2</sub>(Et<sub>2</sub>O)] and [Be(OMes\*)<sub>2</sub>(Et<sub>2</sub>O)] were carried out in ether solution. Both 1 and 2 crystallized well as mono(etherate) adducts. The synthesis of 3 was carried out in THF, and the compound crystallized as a mono(THF) adduct. The subsection of 2 and 3 to reduced pressure resulted in desolvation and disintegration of the crystals. The reduction in the relative intensity of the ether peaks may be monitored by <sup>1</sup>H NMR. No crystals of desolvated 1–3 suitable for X-ray crystallography have been obtained to date. The desolvation of 2 is consistent with the behavior previously noted for Be[O(2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]<sub>2</sub>,<sup>8</sup> which was formed when all the ether solvent was removed. In contrast to this behavior, the diethyl ether donor in 1 is more strongly bound and is much more difficult to remove. Attempts to prepare compounds 1–3 in the absence of donor solvents did not afford crystalline products.

**Structural Descriptions.** [BeMes<sub>2</sub>(OEt<sub>2</sub>)] (1). This compound crystallizes in the tetragonal space group *I*4<sub>2</sub>*m* with the molecule located on a 2-fold symmetry axis that lies along the Be–O bond. A view of the molecule is given in Figure 1, and important bond lengths and angles are summarized in Table III. The beryllium atom is three-coordinate, coordinated by Et<sub>2</sub>O and two mesityl groups. The coordination of the Be center is planar, as crystallographically required, and has the widest angle, 127.6(3)°, between the Be–C bonds. The Be–C distance is 1.739(2) Å, the Be–O bond length being 1.638(5) Å.

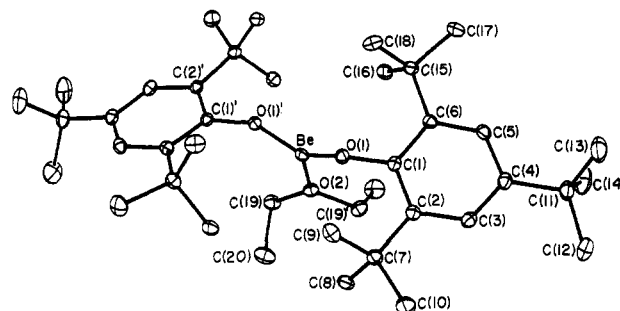


Figure 2. Computer-generated plot of 2. H atoms have been omitted for clarity.

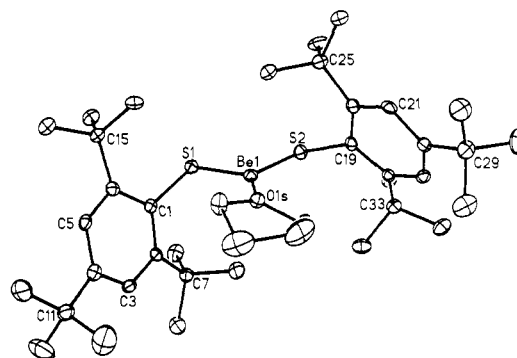


Figure 3. Computer-generated plot of 3. H atoms have been omitted for clarity.

[Be(OMes\*)<sub>2</sub>(Et<sub>2</sub>O)] (2). The molecular structure of 2 is illustrated in Figure 2, and important bond distances and angles are given in Table III. As in the case of 1, there is a crystallographically imposed 2-fold axis of symmetry along the Be–O(ether) bond. The coordination at Be is thus rigorously planar with an angle of 125.3(2)° between the Be–OMes\* bonds. The Be–OMes\* distance is 1.481(2) Å, whereas the Be–OEt<sub>2</sub> bond length is 1.655(3) Å. The angle between the O–Mes\* bond and the plane at Be is 36.9(1)°.

[Be(SMes\*)<sub>2</sub>(THF)]·PhMe (3). The molecular structure of [Be(SMes\*)<sub>2</sub>(THF)] consists of neutral discrete molecules with no crystallographically imposed symmetry. Each asymmetric unit also contains one toluene molecule. A view of the molecule is shown in Figure 3, and important bond lengths and angles are given in Table III. The compound displays an essentially planar three-coordinate beryllium center which is surrounded by two thiolato ligands and one tetrahydrofuran donor molecule. The angles between the S–C vectors and the beryllium planes are 18, and 18.1°, respectively. The three-coordinate beryllium atom is located very slightly above the plane of the two sulfur atoms and the oxygen atom (0.003 Å). The angles at beryllium range from 111.0(3)° (S(1)–Be(1)–S(2)) to 124.6(4)°, the sum of angles being 359.9°. The Be–S distances average 1.989(8) Å, and the Be–O bond length is 1.590(7) Å.

[BeCl<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub>] (4). The compound crystallizes in the trigonal space group *P*3<sub>2</sub>*1* with monomeric, well-separated molecules of [BeCl<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub>] that have C<sub>2</sub> symmetry. The molecular structure of 4 is illustrated in Figure 4, and important bond lengths and angles are given in Table III. The Be atom is located on a 2-fold axis of symmetry and surrounded, in a distorted tetrahedral fashion, by two Cl atoms and two ether molecules. The Be–Cl distance is 1.978(3) Å, and the Be–O bond length is 1.683(3) Å. The angles at Be vary from 101.8(3)° between the two ether molecules to 116.6(2)° between the two chlorine atoms.

## Discussion

As already mentioned in the Introduction, only a small number of structurally characterized beryllium  $\sigma$ -bonded compounds with

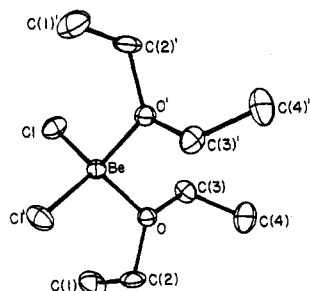


Figure 4. Computer-generated plot of **4**. H atoms have been omitted for clarity.

low (2 or 3) coordination numbers are known at present. If this classification is restricted solely to unassociated mononuclear species, the number is reduced even further. Thus, apart from the gas-phase structures of  $\text{BeMe}_2$ ,<sup>13</sup>  $\text{Be}(t\text{-Bu})_2$ ,<sup>13</sup> and  $\text{Be}[\text{N}(\text{SiMe}_3)_2]_2$ ,<sup>14</sup> the compounds  $(\eta^5\text{-C}_5\text{H}_5)\text{Be}(\eta^1\text{-C}_5\text{H}_5)$ <sup>22</sup> and  $(\eta^5\text{-C}_5\text{Mes})\text{Be}\text{-Me}\cdots\text{Yb}(\eta^5\text{-C}_5\text{H}_5)_2$ ,<sup>23</sup> the phosphido derivative  $(\eta^5\text{-C}_5\text{Me}_5)\text{BeP}(t\text{-Bu})_2$ ,<sup>11</sup> and  $\text{LiBe}(t\text{-Bu})_3$ <sup>6</sup> constitute the only such unassociated  $\sigma$ -bonded species whose structures are known in the solid state. It may be noted that three of these four species involve the  $\eta^5\text{-C}_5\text{R}_5$  (R = H or Me) ligand in their coordination spheres. The reasons for the paucity of well-characterized species and structural information are not difficult to fathom: beryllium and its compounds are considered extremely dangerous owing to their latent toxicity and should be handled cautiously or not at all. As Schmidbaur pointed out in a recent paper,<sup>24</sup> most chemists seem to opt for the second solution and as early as 1975 theoretical papers on organoberyllium species had outnumbered experimental reports.

The work presented in this paper is confined to the synthesis and structural investigation of beryllium compounds with  $\sigma$ -bonding sterically demanding ligands. The first of these is  $[\text{BeMe}_2(\text{OEt}_2)]$  (**1**), which has a planar three-coordinate environment at Be. The low coordination is presumably due to the large size of the mesityl substituents, with further association blocked by  $\text{Et}_2\text{O}$  coordination. The Be–C distance, 1.739(2) Å, may be compared with those observed in  $\text{BeMe}_2$  (1.698(5) Å),<sup>12</sup>  $\text{Be}(t\text{-Bu})_2$  (1.699(3) Å),<sup>13</sup> and  $\text{LiBe}(t\text{-Bu})_3$ <sup>6</sup> (one Be–C of 1.812(4) Å and two Be–C bonds, which involve bridging to Li, of 1.854(4) and 1.864(4) Å). Clearly, the distances in **1** are rather longer (by about 0.14 Å) than those in the two-coordinate species. This is almost certainly a consequence of the increase in coordination number. In contrast, the Be–C bonds in **1** are over 0.07 Å shorter than the shortest Be–C distance in  $\text{LiBe}(t\text{-Bu})_3$ .<sup>6</sup> This large difference is probably due to overall negative charge on the latter molecule, which significantly reduces the ionic contribution to the Be–C bond strength. Also, it could be argued that Be–C distances in  $\text{LiBe}(t\text{-Bu})_3$ <sup>6</sup> are lengthened since the Be has, in effect, four-coordinate character. This is because the Be–Li distance is only 2.227(6) Å, which is within the sum of the covalent radii of these elements. The Be–C bond lengths in **1** therefore suggest that they are of a  $\sigma$  type with a strong ionic component. This view is consistent with bond length estimates generated from the sum of the atomic radii for Be (1.12 Å)<sup>25</sup> and  $\text{sp}^2$ -hybridized C (0.74 Å)<sup>26</sup> modified for ionic contributions.<sup>27</sup> The sum of these values is 1.86 Å, which, less an ionic correction of 0.093 Å,<sup>26</sup> gives a predicted value of 1.767 Å for the Be–C

bond. This value falls between those of **1** and  $\text{LiBe}(t\text{-Bu})_3$  but is significantly longer than the ca. 1.7 Å observed for the two-coordinate species. It is probable that, since the radius of Be has been derived from the hcp solid-state structure of elemental Be in which Be is 12-coordinate, a slightly lower value than 1.12 Å for the Be radius is more appropriate for the more common coordination numbers (i.e. 4 or less) seen in Be species.<sup>27</sup> Various attempts were made to synthesize the ether-free compound, but the insolubility of  $\text{BeCl}_2$  in solvents such as hexane or toluene makes these experiments difficult. Removal of the ether molecule by keeping **1** in high vacuum for 24 h shows no loss of ether when monitored by  $^1\text{H}$  NMR. Finally, the three-coordinate structure of **1** may be compared with those observed for  $[\text{MgMe}_2(\text{THF})_2]$  and  $[\text{Mg}(\text{Trip})_2(\text{THF})]$ ,<sup>28</sup> where the larger size of the Mg atom (1.4 Å for Mg vs 1.12 Å for Be) permits a higher coordination number.

Three-coordinate planar geometry at Be is also observed in the structure of **2**. Greatly differing lengths of 1.481(2) and 1.655(3) Å distinguish the two types of Be–O bonds. The use of radii of 1.12 Å for Be and 0.66 Å for two-coordinate O affords a value of 1.78 Å for the Be–O bond, which, when modified for the strong ionic character, becomes 1.597 Å. As in the case of **1**, this value lies between the two observed Be–O distances. Clearly, the Be–OEt<sub>2</sub> distance is the longer owing to higher coordination and lower negative charge on O. The Be–OMes\* distance is ca. 0.07 Å shorter than the predicted value. It is unlikely that this is due to significant p–p Be–O  $\pi$  overlap since there is an angle of ca. 37° between the planes at oxygen and beryllium. The discrepancy may, as previously explained, be due to the bias of the radius of Be toward higher coordination numbers.

Compound **3** is the first beryllium thiolate to be characterized by X-ray crystallography. The only other crystal structure of a molecular Be–S compound is that of bis(dialkyldithiocarbamato)beryllium,<sup>10</sup> which contains a four-coordinate Be center. The structure of **3** is very similar to that observed for **2**. As in the case of **2**, there is a discrepancy between the predicted and measured bond distances at Be. In the case of the Be–S bonds, the predicted value is 2.053 Å (cf. average Be–S = 1.989(8) Å), which is, in fact, closer to that observed in the dithiocarbamate derivative  $\text{Be}(\text{S}_2\text{CNPr}_2)_2$ , average Be–S = 2.098(9) Å. Clearly, the Be–S distances, like their Be–O and Be–C counterparts, are extremely sensitive to changes in coordination number and ligand type at Be. It is interesting to note that the Be–OEt<sub>2</sub> bond in **2** is 0.06 Å longer than the Be–O(THF) bond in **3**. Most of the explanation of this difference could be steric ( $\text{Et}_2\text{O}$  and  $-\text{OMes}^*$  are more crowding than THF and  $-\text{SMes}^*$ ). The strength of the Be–O(THF) bond is underlined by the fact that it is much more difficult to remove the THF from **3** than to remove the ether from **2**. Several (10) hours' pumping on **2** at 0.01 mmHg pressure results in a very small percentage of reduction in the amount of THF present.

The crystallographic studies of Be compounds were completed by the determination of the structure of  $[\text{BeCl}_2(\text{OEt}_2)]_2$  (**4**). The crystal structure of **4** has been determined previously.<sup>29</sup> There were, however, significant problems in the solution and refinement of the data. The structure described here was obtained with data (646 for  $I > 2\sigma(I)$ ; cf. 238 data in ref 29) collected at 130 K, using Mo K $\alpha$  radiation. No difficulties were encountered and a structure of much higher precision, with esd's of an order of magnitude lower than those previously described, was obtained.

The Be–Cl distance of 1.978(3) Å is in accordance with those of previously reported  $\text{BeCl}_2$  etherates such as  $[\text{BeCl}_2(\text{THF})_2]$ <sup>30</sup>

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or  $[\text{BeCl}_2(15\text{-crown-2})]^{31}$  but considerably shorter than the Be-Cl distance in polymeric  $\text{BeCl}_2$  (2.02(3) Å), in which the chlorine atoms are bridging.<sup>32</sup> The Be-O(ether) bond length of 1.683(3) Å is very similar to those observed in **1** and **2** but significantly longer (0.09 Å) than the Be-O bond in **3**. This is partly explained by the greater basic characteristics of the THF molecule. The same effect is apparent in a comparison of the Be-O distances in  $[\text{BeCl}_2(\text{OEt}_2)_2]$  and  $[\text{BeCl}_2(\text{THF})_2]$ .

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**Supplementary Material Available:** Full tables of crystallographic data, atom coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (27 pages). Ordering information is given on any current masthead page.

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