

Supporting Information

For

Synthesis and Characterization of Calcium *N,N*-Dimethylaminodiboranates

as Possible Chemical Vapor Deposition Precursors

Andrew C. Dunbar and Gregory S. Girolami*

The School of Chemical Sciences, University of Illinois at Urbana-Champaign

600 South Mathews Avenue, Urbana, Illinois 61801

Ca(BH₃NMe₂BH₃)₂(Et₂O)₂, 2. The monoclinic lattice and the systematic absences *hkl* (*h* + *k* ≠ 2*n*) were consistent with the space groups *C2*, *Cm*, and *C2/m*; the non-centrosymmetric choice *C2* was suggested by the average value of the normalized structure factors and confirmed by successful refinement of the proposed model. A face-indexed absorption correction was applied, the minimum and maximum transmission factors being 0.915 and 0.951. All 4312 unique data were used in the least squares refinement. The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.043P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. Analysis of the diffraction intensities suggested slight inversion twinning; therefore, the intensities were calculated from the equation $I = xI_a + (1-x)I_b$, where *x* is a scale factor that relates the volumes of the inversion-related twin components. The twin scale factor refined to a value of 0.37(4). The largest peak in the final Fourier difference map (0.29 eÅ⁻³) was located 1.09 Å from Ca1.

Ca(BH₃NMe₂BH₃)₂(thf)₂, 3. The trigonal lattice and the systematic absences 00*l* (*l* ≠ 3*n*) were consistent with the space groups *P3*₁, *P3*₂, *P3*₂21, *P3*₂21, *P3*₁12, and *P3*₂12. The space group *P3*₂21 was chosen, and this choice was confirmed by successful refinement of the proposed model. A face-indexed absorption correction was applied, the minimum and maximum

transmission factors being 0.909 and 0.928. All 4850 unique data were used in the least squares refinement. Carbon atoms C10, C11, and C12 of the tetrahydrofuran ligand were each disordered over two positions. The C-C distances to C13 were restrained to be 1.52 ± 0.01 Å, the site occupation factors for the two components were constrained to sum to unity, and the major site occupancy factor refined to 0.51(1). The quantity minimized by the least-squares program was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0537P)^2 + 0.0359P\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. Analysis of the diffraction intensities suggested slight twinning ($F_o^2 > F_c^2$ for the many of the “most disagreeable” reflections) but no suitable twin law could be discovered. The Flack parameter refined to 0.00(2), which showed that the model chosen was the correct enantiomorph. The largest peak in the final Fourier difference map (0.49 eÅ^{-3}) was located 0.97 Å from C23.

Ca(BH₃NMe₂BH₃)₂(dme), 4. The triclinic lattice and the average values of the normalized structure factors suggested the space group $P\bar{1}$, which was confirmed by the success of the subsequent refinement. A face-indexed absorption correction was applied, the minimum and maximum transmission factors being 0.942 and 0.970. All 28755 unique data were used in the least squares refinement. The quantity minimized by the least-squares program was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.61971P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The Ca1-H31 and Ca1-H32 distances were restrained to be equal within an e.s.d. of 0.01 Å. An isotropic extinction parameter was refined to a final value of $x = 6.754 \times 10^{-3}$ where F_c is multiplied by the factor $k[1 + F_c^2 x \lambda^3 / \sin 2\theta]^{-1/4}$ with k being the overall scale factor. The largest peak in the final Fourier difference map (0.30 eÅ^{-3}) was located 1.11 Å from O2.

Ca(BH₃NMe₂BH₃)₂(diglyme), 5. The orthorhombic lattice and the systematic absences $0kl$ ($k + l \neq 2n$) and $hk0$ ($h \neq 2n$) were consistent with the space groups $Pnma$ and $Pna2_1$. The average values of the normalized structure factors suggested the centrosymmetric space group $Pnma$, and this choice was confirmed by successful refinement of the proposed model. A face-indexed absorption correction was applied, the minimum and maximum transmission factors being 0.948 and 0.985. All 2426 unique data were used in the least squares refinement. The quantity minimized by the least-squares program was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 +$

$(0.0136P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The largest peak in the final Fourier difference map ($0.20 \text{ e}\text{\AA}^{-3}$) was located 0.61 \AA from O2

Ca[BH₃NMe₂BH₃]₂(tmeda), 6. The monoclinic lattice and the systematic absences $h0l$ ($h + l \neq 2n$) and $0k0$ ($l \neq 2n$) were consistent with the space group $P2_1/n$, and this choice was confirmed by successful refinement of the proposed model. A face-indexed absorption correction was applied, the minimum and maximum transmission factors being 0.935 and 0.958. All 4583 unique data were used in the least squares refinement. There is some unresolved disorder in the backbone of the tmeda ligand, but was small enough that no splitting of C7 or C8 into partial atoms was warranted. The quantity minimized by the least-squares program was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0672P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The largest peak in the final Fourier difference map ($0.76 \text{ e}\text{\AA}^{-3}$) was located 0.96 \AA from C7.

[Ca(12-crown-4)₂][BH₃NMe₂BH₃]₂•2thf, 7. The monoclinic lattice and the systematic absences $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$) were uniquely consistent with the space group $P2_1/c$, and this choice was confirmed by successful refinement of the proposed model. A face-indexed absorption correction was applied, the minimum and maximum transmission factors being 0.929 and 0.954. All 8018 unique data were used in the least squares refinement. One of the BH₃NMe₂BH₃ groups is disordered over two positions; the site occupancy factors (s.o.f.'s) for the two components were constrained to sum to unity, and the s.o.f. for the major site refined to 0.750(6). The quantity minimized by the least-squares program was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0515P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The displacement parameters for the atoms of the two tetrahydrofuran (thf) molecules were restrained to be similar. The C-O and C-C bond distances of the two thf molecules were fixed to 1.47 ± 0.01 and $1.52 \pm 0.01 \text{ \AA}$, respectively. The chemically equivalent C-C-C, C-O-C, and C-C-O angles in the thf molecules were restrained to be the same within an e.s.d. of 0.02 \AA . The N-C and N-B distances within the major disordered component were fixed at 1.47 ± 0.001 and $1.58 \pm 0.001 \text{ \AA}$, respectively, and the minor component was restrained to have the same bond distances and angles within $\pm 0.01 \text{ \AA}$. The largest peak in the final Fourier difference map ($0.33 \text{ e}\text{\AA}^{-3}$) was located 1.07 \AA from Ca1.