positive. Furthermore, the perpendicularly polarized band must be assigned as the E_1 fundamental. Thus our experiment rigorously establishes an interpretation of the $M_2(CO)_{10}$ spectra proposed by Flitcroft, Huggins, and Kaesz[7] on the basis of intensities and force constant calculations.

The infrared data provide strong support for the generalization[2] from nmr experiments[8] and polarized electronic spectroscopy[2] that *solute molecules with a long axis tend to align with that axis parallel to the long axis of the liquid crystal molecules.* For $Mn_2(CO)_{10}$, where we have determined that S_{zz} is positive, the distance across the molecule along the z axis is 1.5 times longer than the distance across the x axis.[4]

Because of experimental difficulties inherent in single crystal methods, relatively few infrared band polarizations have been determined. The technique described in this communication should facilitate such polarization studies and allow more band assignments to be placed on a firm basis.

[7] N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 3, 1123 (1964).

[8] G. Englert and A. Saupe, *Mol. Cryst.*, **1**, 503 (1966).

[9] Air Force Office of Scientific Research Postdoctoral Fellow, 1968.

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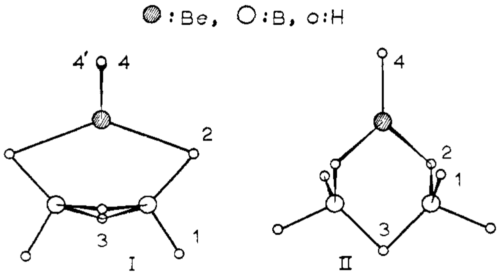
The Structure of Beryllium Borohydride

Sir:

A recent electron diffraction study[1] has disproved the classical structure for beryllium borohydride and proposed structure I as being consistent with the data. Subsequent calculations for this structure[2,3] indicate rather weak bonding interactions between the BeH_2 and "diborane" moieties. For this reason, as well as the disturbingly long beryllium-hydrogen bonds, 1.60 and 1.85 Å respectively for terminal and bridge hydrogens, we question the validity of I. We propose that the true structure is II based largely on infrared and mass spectral data.



I II

A special gas cell, with modified, inert windows, had to be constructed for the infrared study owing to the rapid reaction of this compound with KBr plates. The earlier study[4] did not take this into account, and some of the reported bands are definitely due to this reaction. The gas-phase infrared spectra of both BeB_2H_8 and BeB_2D_8 consist of 22 bands in the 4000–400-cm^{-1} region. At this time we wish to demonstrate only the presence of BH_2 and the absence of BH terminal groupings. Studies of several boron hydride compounds indicate very sharp differentiation between these modes.[5]

Bands at 2630, 2531, 1017, and 974 cm^{-1} (shifting to 1910, 1816, 860, and 698 cm^{-1} respectively, in BeB_2D_8) clearly correspond to BH_2 terminal group frequencies. In diborane the analogous absorptions appear at 2612, 2525, 1035, and 974 cm^{-1} (shifting to 1985, 1840, 860, and 720 cm^{-1}, respectively, in B_2D_6). In borane compounds containing only BH terminal bonds, the last two bands are absent and there is only one BH stretching frequency. All known compounds containing BH terminal bonds have an absorption in the 890–910-cm^{-1} region. The absence of absorption in this region in BeB_2H_8 therefore indicates the absence of BH terminal bonds.[4] These arguments are consistent for II but not for I.

The mass spectra of both BeB_2H_8 and BeB_2D_8 were recorded at 80° using ionizing voltages of 70 and 15 eV. Typical ions present at 70 eV include Be^+, $^{10}B^+$, BeH^+, $^{11}B^+$, BH_2^+, $BeBH_2^+$, $B_2H_2^+$, $B_2H_5^+$, $BeB_2H_2^+$, $BeB_2H_4^+$ (the most abundant species), $BeB_2H_6^+$, $BeB_2H_8^+$. At 15 eV the relative abundances of larger fragments (*e.g.*, $BeB_2H_8^+$) increase relative to smaller fragments and the Be^+, $^{10}B^+$, BeH^+, $^{11}B^+$, and BH_2^+ ions no longer are present. No peaks were observed beyond the mass corresponding to the monomeric parent ions. Several metastable peaks were observed in BeB_2H_8 and BeB_2D_8, which correspond to the following reactions

$$Be^{10}B^{11}BD_7^+ \longrightarrow Be^{10}B^{11}BD_5^+ + D_2 \quad (m^* = 36.38)$$

$$BeB_2D_6^+ \longrightarrow BeB_2D_4^+ + D_2 \quad (m^* = 35.39)$$

$$Be^{10}B^{11}BD_6^+ \longrightarrow Be^{10}B^{11}BD_4^+ + D_2 \quad (m^* = 34.45)$$

$$BeB_2D_5^+ \longrightarrow BeB_2D_3^+ + D_2 \quad (m^* = 33.48)$$

These data show that the beryllium atom is strongly bonded within the compound. The predominance of the $BeB_2H_4^+$ ion at 70 eV indicates an especial stability for this grouping which is the "core" of II. Structure I, on the other hand, contains very long, and therefore weak, Be–H–B bonds which would result in a quite different mass spectrum.

The chemical reactivity of BeB_2H_8 is also more compatible with II. Several isolatable 1:1 adducts with bases such as trimethylphosphine have been reported.[6] Such adducts could be easily formed by bonding through the vacant p orbital on the sp^2-hybridized beryllium in II, but would necessitate bond breaking in I. The trimethylphosphine adduct absorbs a second mole of base to ultimately form trimethylphosphine borane and a viscous liquid characterized to be polymeric beryllium hydride.[6] Examination of structure II reveals a more convenient path for attack of the borons than is present in I.

We have constructed a model of II and calculated a radial distribution curve which is in satisfactory agree-

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[1] A. Almenningen, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, 22, 859, (1968).

[2] D. R. Armstrong and P. G. Perkins, *Chem. Commun.*, 353 (1968).

[3] G. Gundersen and A. Haaland, *Acta Chem. Scand.*, **22**, 867 (1968).

[4] W. C. Price, *J. Chem. Phys.*, **17**, 227, (1949).

[5] L. J. Bellamy, W. Gerrard, M. F. Lappert, and R. L. Williams, *J. Chem. Soc.*, 2412 (1958).

[6] L. Banford and G. E. Coates, *ibid.*, *A*, 274 (1966).

ment with the experimental plot.[1] These data have not been refined and are therefore estimated to only 0.1 Å. Parameters of the model are: Be–H(4) = 1.3, Be–H(2) = 1.4, B–H(3) = 1.3, Be–B = 1.8, B–B = 1.8 B–H(2) = 1.3, B–H(1) = 1.2 Å; ∠H(2)–Be–H(2) = 125°, ∠H(3)–B–H(2) = 120°, ∠H(1)–B–H(1) = 92°, ∠B–H(3)–B = 83°, ∠Be–H(2)–B = 83°. Only two Be–H bond distances are known. In the short-lived species BeH, Be–H is 1.343 Å[7] and in $[NaOEt_2]\cdot[Et_4Be_2H_2]$ the bridging Be–H distance is 1.48 Å.[8] These values are consistent for II but not for I.[9]

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(7) L. S. Sutton, "Interatomic Distances," The Chemical Society, London, 1968.

(8) G. W. Adamson and H. M. M. Shearer, *Chem. Commun.*, 240 (1965).

(9) Professor Linus Pauling informs us that his estimation of bond lengths from a consideration of bond numbers agrees to within 0.05 Å of our bond lengths.

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Samarium(II) Dicyclopentadienide 1-Tetrahydrofuranate

Sir:

Although numerous cyclopentadienyl compounds of lanthanides have been reported,[1–7] the only known species of the type $(C_5H_5)_2Ln$ have been possible of synthesis only because of the solubility of Eu and Yb in liquid ammonia.[5,7] We report here the first synthesis of a cyclopentadienyl compound of an ammonia-insoluble lanthanide, *i.e.*, samarium(II) dicyclopentadienide which was isolated as the 1-tetrahydrofuranate. The synthesis procedure employed was a modification of that described previously;[8] the reaction involved is

$$Sm(C_5H_5)_3 + KC_{10}H_8 + C_4H_8O \longrightarrow Sm(C_5H_5)_2\cdot C_4H_8O + KC_5H_5 + C_{10}H_8$$

In a typical experiment, 0.499 g of $Sm(C_5H_5)_3$, 0.0527 g of K, 0.128 g of $C_{10}H_8$ (a 25% molar deficiency of naphthalene), and 25 ml of tetrahydrofuran (THF) (freshly distilled under reduced pressure after drying over sodium benzophenone) were mixed in one arm of a U-tube reaction vessel in an anhydrous oxygen-free helium atmosphere and stirred for 48 hr. The purple insoluble product was separated by decantation and washed by a succession of back-distillations of THF. Residual solvent was removed at *ca.* 10^{-3} mm for 18 hr at 24°. (This product is very pyrophoric and must be handled only in an anhydrous oxygen-free atmosphere.) *Anal.* Calcd for $Sm(C_5H_5)_2\cdot C_4H_8O$: C, 47.7; H, 5.12; Sm, 42.7. Found: C, 46.0; H, 5.15; Sm, 42.6.

This tetrahydrofuranate is similar to $Eu(C_5H_5)_3\cdot C_4H_8O$ in that desolvation at elevated temperatures under reduced pressure is accompanied by decomposition.

Using a modified Curie–Cheneveau balance calibrated with $HgCo(SCN)_4$, $Sm(C_5H_5)_2\cdot C_4H_8O$ was found to have a molar paramagnetic susceptibility of 5600 × 10^{-6} cgsu at 298°K ($\mu_{cor} = 3.6 \pm 0.2$). This value compares very favorably with those reported for Sm(II)[9] and Eu(III)[1,9] compounds.

X-Ray diffraction patterns were obtained using CuKα radiation (Ni filter), 35 kV, 15 mA, and exposure times of 6–12 hr; relative intensities were estimated visually. The *d* spacings (Å) corresponding to the most intense lines (I/I_0 in parentheses) were 8.42 (0.5), 4.05 (0.6), 7.34 (1.0), 2.68 (0.5), 5.60 (0.7), 4.78 (0.5), 4.34 (0.5), and 2.99 (0.4).

Tris(cyclopentadienyl)samarium(III) was prepared by the method of Wilkinson and Birmingham.[3,4] *Anal.* Calcd for $Sm(C_5H_5)_3$: C, 52.5; H, 4.3; Sm, 43.5. Found: C, 51.0; H, 4.7; Sm, 43.5. This yellow-orange solid sublimed at 145° (~10^{-3} mm), melted at ~330° under helium, $\mu_{corr} = 1.9 \pm 0.3$, and was unstable in air, although much more stable than $Sm(C_5H_5)_2\cdot C_4H_8O$. X-Ray diffraction data for $Sm(C_5H_5)_3$ were 7.46 (0.3), 7.02 (0.4), 5.88 (1.0), 4.86 (0.5), 2.97 (0.3), 2.84 (0.2), and 2.45 (0.3).

Infrared spectra were recorded on mulls in Nujol and hexachlorobutadiene. The infrared spectrum of $Sm(C_5H_5)_3$ is quite similar to those of $(C_5H_5)_2Fe$,[10] $(C_5H_5)_2Eu$, and $(C_5H_5)_2Yb$,[11] having a C–H stretching frequency at 3100 cm^{-1} and intense bands at 1014 (C–H bend parallel) and 764 cm^{-1} (C–H bend perpendicular), with a high-energy shoulder on the latter at 796 cm^{-1}. The antisymmetric metal–ring vibration appears at 390 cm^{-1}. Other weaker bands are found at 1445, 1344, 1309, 1263, 1171, and 1076 cm^{-1}. The ir spectrum of $Sm(C_5H_5)_2\cdot C_4H_8O$ has bands and intensities very similar to those of $Sm(C_5H_5)_3$ (*i.e.*, 3080 (C–H stretch), 1475, 1347, 1308, 1263, 1163, 1070, 1008 (C–H bend parallel), 775, 740 (C–H bend perpendicular), and 350 cm^{-1} (antisymmetric metal–ring vibration). Other bands at 2980, 2880, 1375, 725, and 565 cm^{-1} due to the coordinated tetrahydrofuran are located approximately as expected[12–14] and of intensities similar to the weaker metallocene bands. Interpretation of the spectra as suggested by Fritz[15] indicates that the cyclo-

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(1) S. Manastyrskyj and M. Dubeck, *Inorg. Chem.*, 3, 1647 (1964).

(2) R. E. Maginn, S. Manastyrskyj, and M. Dubeck, *J. Am. Chem. Soc.*, 85, 672 (1963).

(3) J. M. Birmingham and G. Wilkinson, *ibid.*, 78, 42 (1956).

(4) G. Wilkinson and J. M. Birmingham, *ibid.*, 76, 6210 (1954).

(5) E. O. Fischer and H. Fischer, *Angew. Chem.*, 76, 52 (1964).

(6) S. Manastyrskyj, R. E. Maginn, and M. Dubeck, *Inorg. Chem.*, **2**, 904 (1963).

(7) E. O. Fischer, and H. Fischer, *J. Organometal. Chem.*, **6**, 141 (1966).

(8) G. W. Watt and F. O. Drummond, Jr., *J. Am. Chem. Soc.*, **88**, 5926 (1966).

(9) P. W. Selwood, *ibid.*, **56**, 2392 (1934).

(10) L. Kaplan, W. L. Kester, and J. J. Katz, *ibid.*, **74**, 5531 (1952).

(11) E. O. Fischer and H. Fischer, *J. Organometal. Chem.*, 3, 181 (1965).

(12) G. M. Barrow and S. Searles, *J. Am. Chem. Soc.*, 75, 1175 (1953).

(13) V. W. Zeil, R. Dautel, and W. Honsberg, *Z. Elektrochem.*, 60, 1131 (1956).

(14) F. F. Bentley, L. D. Smithson, and A. L. Rozek, "Infrared Spectra and Characteristic Frequencies 700–300 cm^{-1}," Interscience Publishers, New York, N. Y., 1968, Spectrum No. 1283.

(15) H. P. Fritz in "Advances in Organometallic Chemistry," Vol. I, F. G. A. Stone and R. West, Ed., Academic Press, New York, N. Y., 1964, pp 289–290.