mole of $(C_6H_5)_3PO \cdot NH_2SO_2NF_2$ to produce 1.8 moles of iodine, it was assumed that the same stoichiometry held for the uncomplexed sulfamide.

Triphenylphosphine Oxide Complex of N,N-Difluorosulfamide. —A solution containing 33.4 g. (0.12 mole) of triphenylphosphine oxide in 100 ml. of benzene was added to 15.9 g. (0.12 mole) of N,N-difluorosulfamide in 100 ml. of ether. The mixture was frozen and, after addition of dry magnesium sulfate, was allowed to warm to room temperature. After stirring for 1 hr. the drying agent was removed by filtration. Slow evaporation of the solvent under vacuum precipitated a white crystalline compound which was filtered off and recrystallized from a mixture of 10% benzene in ether. The compound melted at 96–97° and was soluble in alcohol and methylene chloride.

Anal. Calcd. for $(C_6H_5)_3PO \cdot H_2NSO_2NF_2$: C, 52.68; H, 4.17; N, 6.82; F, 9.64. Found: C, 53.10; H, 4.22; N, 6.71; F, 9.27.

Acid Hydrolysis.—A 10-ml. sample of the fluorination mixture containing 0.517 g. (3.91 mmoles) of $NH_2SO_2NF_2$ was placed in a flask and attached to the vacuum line. After evacuating the system, 20 ml. of 1 N phosphoric acid (1 N sulfuric acid can also be used) was slowly added to the cold (<5°) reaction mixture. The off gases passed through two −78° traps and into a −126° trap.[7] After stirring the reaction mixture for 1 hr. the contents of the −126° trap were refractionated through a −78° and a −126° trap and then analyzed by infrared and mass spectrometry. Difluoroamine, 0.155 g. (2.92 mmoles), was obtained essentially pure. Hydrolysis of the fluorination mixture occurred on standing 8 hr. at 25° without the addition of acid to produce difluoroamine in 62% yield.

Preparation of Chlorodifluoramine.—An aqueous solution of 13.2 g. (0.10 mole) of N,N-difluorosulfamide, prepared as described above, was evacuated on the vacuum line and frozen in a −78° bath. Then 5.8 g. (0.11 mole) of hypochlorous acid in 400 ml. of water was added slowly while the reactor was still immersed in the Dry Ice bath. On warming slowly, chlorodifluoramine was liberated and was collected in a −196° trap after passing through two −78° traps. After refractionation, a total of 6.2 g. (0.071 mole) of chlorodifluoramine was obtained; yield 71%. Identification of the product was accomplished by infrared spectroscopy[4] and vapor density molecular weight (calcd. 87.5; found 85, 86.).

(7) *Caution!* Do not trap difluoroamine in a liquid nitrogen bath since we have experienced numerous explosions when such traps were allowed to warm.

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Unsymmetrical Cleavage of Diborane by Dimethyl Sulfoxide[1]

BY G. E. McACHRAN AND S. G. SHORE

It is well recognized that the bridge system of diborane appears to be cleaved symmetrically by amines, phosphines, ethers, and sulfides to form BH_3 adducts.[2,2a]

At the present time, only two examples of apparent unsymmetrical cleavage exist in the literature. These are the reactions of diborane with ammonia to produce the diammoniate of diborane, $[BH_2(NH_3)_2]^+BH_4^-$,[3] and the reaction of amide ion with diborane to produce aminoborane, $(BH_2NH_2)_x$.[4] Perhaps the best documented example is the diammoniate of diborane. We wish to report the first documented example of apparent unsymmetrical cleavage of the bridge system of diborane by other than a nitrogen base.

A tensiometric investigation in dichloromethane at −78° revealed that diborane and dimethyl sulfoxide react in the mole ratio $0.5B_2H_6:(CH_3)_2SO$. On the basis of evidence provided below, the following reaction is proposed.

$$B_2H_6 + 2(CH_3)_2SO \longrightarrow BH_2[OS(CH_3)_2]_2{}^+BH_4^-$$
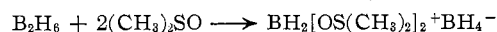
Low-temperature (−40 to −50°) Raman spectra of the solid product and of a solution of the product in dichloromethane were essentially identical in the B–H stretching region. A microphotometer trace of this region is compared with traces from the corresponding region in the Raman spectra of BH_3NH_3[5] and $[BH_2(NH_3)_2]^+BH_4^-$[6] in Figure 1. The number, shapes, and positions of the envelopes in the spectrum of the dimethyl sulfoxide–diborane reaction product most clearly match those of $[BH_2(NH_3)_2]^+BH_4^-$, indicating that diborane is cleaved unsymmetrically to give $BH_2{}^+$ and BH_4^-. Borane (BH_3) adducts in general present very simple spectra in the region under discussion, usually showing only two characteristic frequencies attributed to BH_3 in the B–H stretching region.[7,8]

Treatment of the dimethyl sulfoxide–diborane reaction product with HCl produced the reaction

$$BH_2[OS(CH_3)_2]_2{}^+BH_4^- + HCl \longrightarrow$$
$$BH_2[OS(CH_3)_2]_2{}^+Cl^- + H_2 + {}^1/_2 B_2H_6$$
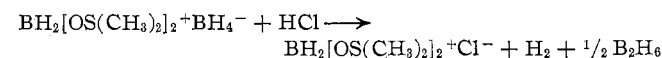
A Raman spectrum of the resulting solution after H_2 and B_2H_6 had been distilled away revealed that only the absorptions assigned to $(DMSO)_2BH_2{}^+$ were present.

Low-temperature (−40 to −50°) n.m.r. studies in dichloromethane lend credence to the ionic formulation. The spectrum shows a quintet which is attributed to BH_4^-. The spin–spin coupling constant, 86 c.p.s., and chemical shift, 38 p.p.m., relative to $(C_2H_5)_2O \cdot BF_3$ are in good agreement with values observed for BH_4^-.[9] A well-defined spectrum of $BH_2{}^+$ could not be observed, but appeared to just overlap the low-field side of the BH_4^- quintet. No evidence was observed for a quartet which could be attributed to BH_3.

(1) Presented before the Inorganic Division at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

(2) H. I. Schlesinger and A. B. Burg, *Chem. Rev.*, **31**, 1 (1942); F. G. A. Stone, *Advan. Inorg. Chem. Radiochem.*, **2**, 279 (1960).

(2a) NOTE ADDED IN PROOF.—We have found, very recently, that diborane can be cleaved unsymmetrically by methylamine and dimethylamine.

(3) R. W. Parry, D. R. Schultz, S. G. Shore, and P. R. Giradot, *J. Am. Chem. Soc.*, **80**, 1 (1958); R. W. Parry, G. Kodama, and D. R. Schultz, *ibid.*, **80**, 24 (1958).

(4) G. W. Schaeffer and L. J. Basile, *ibid.*, **77**, 331 (1955).

(5) R. C. Taylor, "The Chemistry of Boron Hydrides and Related Hydrides," WADD Technical Report 59-207 (1959).

(6) R. C. Taylor, D. R. Schultz, and A. R. Emery, *J. Am. Chem. Soc.*, **80**, 27 (1958).

(7) R. C. Taylor, "The Chemistry of Boron Hydrides and Related Hydrides," WADD Technical Report 60-262 (1960).

(8) R. C. Taylor, private communication.

(9) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).
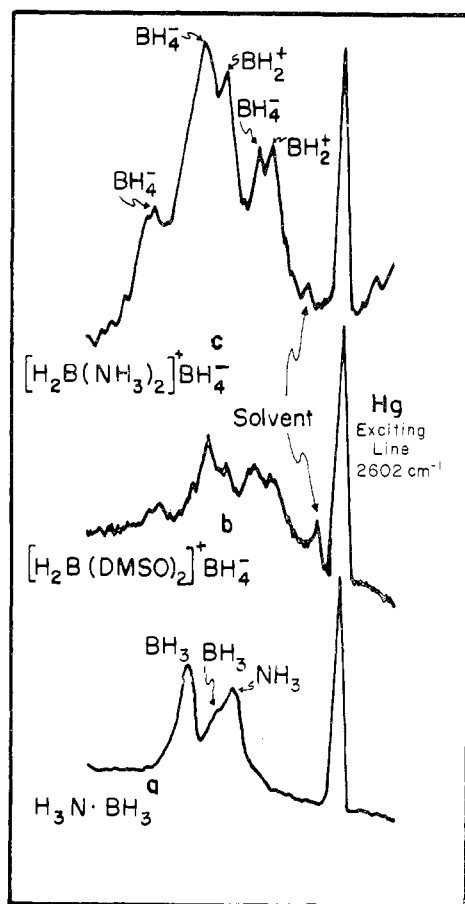
Figure 1.—Raman spectra of the B–H region: a, BH₃ (2263 ± 5, 2316 ± 5 cm.⁻¹); b, BH₂⁺ (2315 ± 5, 2422 ± 5 cm.⁻¹), BH₄⁻ (2145 ± 5, 2265 ± 5, 2390 ± 5 cm.⁻¹); c, BH₂⁺ (2321 ± 3, 2437 ± 3 cm.⁻¹), BH₄⁻ (2140, 2265 ± 2, 2403 ± 3 cm.⁻¹).[6]

Although its seems clear that unsymmetrical cleavage occurs in the reaction of diborane with dimethyl sulfoxide, the nature of the coordinate bond involving boron in the cation is not yet established. From the direction of the shift in the S–O stretching frequency it is possible to determine, in principle, whether sulfur or oxygen is involved in the coordinate bond.[10] Unfortunately, the stretching frequency of this bond could not be located with certainty in the dimethyl sulfoxide-diborane reaction product because of appreciable structure in this region of the spectrum, plus the fact that the S–O stretching frequency is not a particularly strong band in the Raman spectrum, as it is in the infrared. However, recent work on salts containing BH_2^+ indicates that a Lewis base containing oxygen as the electron-pair donor is stronger than one containing sulfur as the electron-pair donor.[11] From this information and steric considerations we believe that the structure of the cation is

$$(CH_3)_2SO\overset{H_+}{\underset{H}{-B-}}OS(CH_3)_2$$
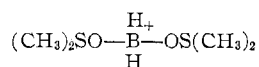
Both $BH_2[OS(CH_3)_2]_2{}^+BH_4{}^-$ and $BH_2[OS(CH_3)_2]_2{}^+$-Cl^- give off hydrogen slowly at temperatures above

(10) F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960).
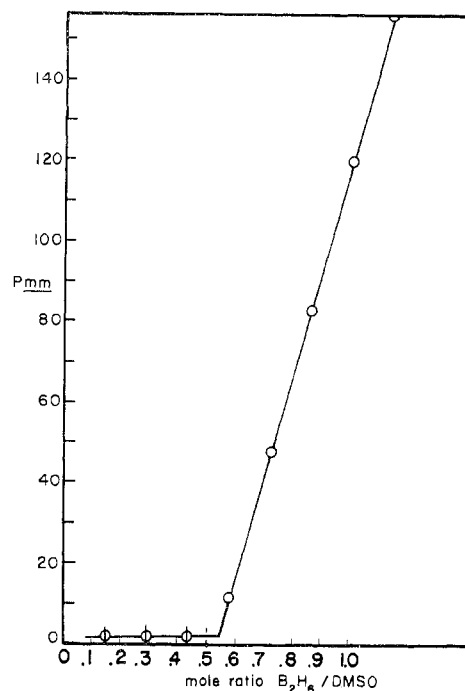(11) N. E. Miller and E. L. Muetterties, *ibid.*, **86**, 1033 (1964).

Figure 2.—Vapor tension plot in dichloromethane solvent.

$-33°$. Rapid and violent decomposition begins at about $-6°$. On occasion, decomposition amounted to a detonation, destroying the apparatus. Approximately 1 mole of H_2 per mole of $BH_2[OS(CH_3)_2]_2{}^+BH_4{}^-$ is evolved rapidly. A second mole of H_2 is given off slowly over an extended period of time. The over-all decomposition reaction is

$$BH_2[OS(CH_3)_2]_2{}^+BH_4{}^- \longrightarrow$$
$$2H_2 + {}^1\!/_3\ B_2H_6 + 2(CH_3)_2S + {}^2\!/_3\ B_2O_3$$
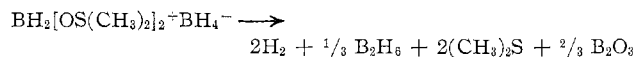
Experimental

Tensiometric Titration of DMSO with B_2H_6.—In the nitrogen atmosphere of a drybox, a 7-mmole quantity of anhydrous DMSO was pipetted into a 50-ml. reaction tube which contained a magnetic stirring bar. The tube was capped with a standard taper joint which was attached to a vacuum stopcock. This reaction system was then transferred to a vacuum line where it was cooled to $-78°$ and evacuated. A 15-ml. quantity of dry CH_2Cl_2 was distilled into the tube. After warming the reaction tube to room temperature and stirring its contents, it was cooled to $-196°$ and 1 mmole of B_2H_6 was added. The tube was then warmed to $-78°$ and its contents were stirred to ensure thorough mixing. After the system had achieved equilibrium at $-78°$, the B_2H_6 pressure above the solution was recorded. Additional 1-mmole increments of B_2H_6 were added to the system until a total of 8 mmoles had been introduced. Figure 2 is a plot of equilibrium B_2H_6 pressure *vs.* the mole ratio of reactants. For the particular quantities used in this system it is seen that B_2H_6 is taken up in the ratio $0.52B_2H_6:DMSO \approx 1B_2H_6:2DMSO$.

Reaction of $BH_2[OS(CH_3)_2]_2{}^+BH_4{}^-$ with HCl.—In a typical experiment, a 7-mmole quantity of HCl was distilled into a reaction flask which contained 7 mmoles of $BH_2[OS(CH_3)_2]_2{}^+BH_4{}^-$ in 15 ml. of CH_2Cl_2 at $-196°$. The system was warmed to $-78°$, whereupon gas evolution was observed. The reaction was followed to completion by determining the amount of H_2 evolved (7 mmoles). Diborane, the other volatile product from this reaction, was trapped and identified by mass spectrometry.

Decomposition of $BH_2[OS(CH_3)_2]_2{}^+BH_4{}^-$.—From -33 to $-6°$ $BH_2[OS(CH_3)_2]_2{}^+BH_4{}^-$ gives off hydrogen slowly. Above $-6°$, sudden and violent decomposition occurs. A 7-mmole sample of solid $BH_2[OS(CH_3)_2]_2{}^+BH_4{}^-$, from which solvent (CH_2Cl_2) had

been pumped away, was maintained at 0° during a study of the decomposition process. Shortly after bringing the sample to 0°, decomposition was detected by a sudden increase in pressure which scattered material throughout the system. At this point the system was quenched to −196° and the hydrogen gas produced (7 mmoles) was measured volumetrically and identified mass spectrometrically. Upon warming the system to 0°, $(CH_3)_2S$ and B_2H_6 which were produced in the initial decomposition reaction were distilled away and identified mass spectrometrically. An additional 7 mmoles of H_2 plus B_2H_6 and $(CH_3)_2S$ were formed very slowly at 0° over a period of about 1 week. The solid residue from the decomposition was shown to be B_2O_3 from analysis and by converting it to H_3BO_3, which was identified by X-ray powder diffraction.

Spectroscopic Equipment.—Raman spectra at −40 to −50° of the solid product and of a solution of the product (*ca.* 5 *M*) in dichloromethane were obtained through the courtesy of Dr. A. J. Dahl and Dr. R. C. Taylor of the University of Michigan using a spectrograph and light source which have been described previously.[12]

B^{11} n.m.r. at −40 to −50° of a solution (*ca.* 5 *M*) of the product in dichloromethane were obtained at 19.25 Mc. through the courtesy of Dr. D. Gaines of Indiana University and Dr. William Richey of the Sohio Oil Company.

(12) G. L. Vidale and R. C. Taylor, *J. Am. Chem. Soc.*, **78**, 294 (1956).


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A Case of Anomalous Isomorphism

BY A. CHAKRAVORTY[1]

It has been convincingly proven[2-4] that bis(N-alkylsalicylaldimine)nickel(II) (A) exhibits a planar–tetrahedral equilibrium in a solution of noncoordinating solvents when R is a secondary or tertiary alkyl group. However in the solid phase the compounds are either diamagnetic and hence planar or fully paramagnetic (μ_{eff} = 3.30 B.M.) and pseudotetrahedral depending on the nature of R and X. Thus the intramolecular steric factors[2a] that are responsible for planar–tetrahedral equilibria in solutions are favored or disfavored to one extreme by the static crystal forces. In the

A
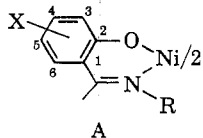
R = i-C_3H_7 series,[2b] X = H is paramagnetic and tetrahedral,[5] X = 5-CH_3 is diamagnetic, X = 5-

(1) Correspondence should be addressed to the Department of Chemistry, Indian Institute of Technology, Kanpur, India.
(2) (a) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963); (b) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964).
(3) L. Sacconi, P. Paoletti, and M. Ciampolini, *ibid.*, **85**, 411 (1963).
(4) A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1010 (1964).
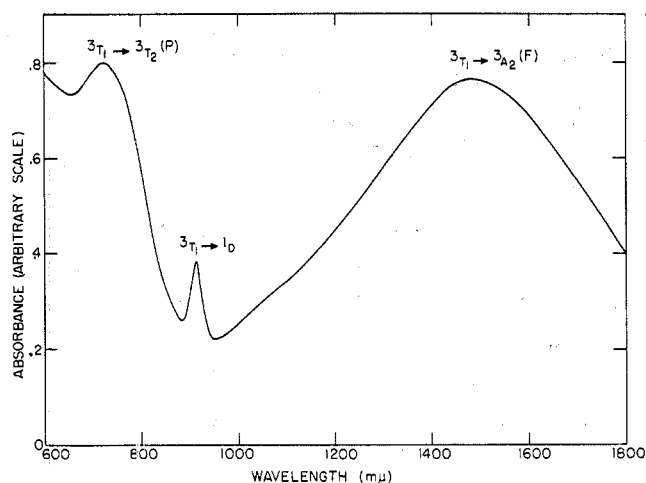

Figure 1.—Ligand field spectrum of R = i-C_3H_7, X = 5-CH_3 (25% Ni and 75% Zn) taken in Nujol mull.

C_2H_5 is paramagnetic, and X = 5-n-C_3H_7 is again diamagnetic. Only the tetrahedral Ni(II) complexes are isostructural with the corresponding Zn(II), which in all probability are tetrahedral irrespective of R and X.[2a,6] The interesting sequence mentioned above clearly indicates that the favored form in the crystalline phase is determined by a delicate balance of crystal forces and steric effects. This suggested that the planar diamagnetic compounds though not isostructural with Zn(II) complexes in their pure solid phases might still be introduced into the Zn(II) lattice to assume a tetrahedral structure. In other words, there is a possibility that two compounds having completely different individual crystal structures might still form mixed crystals due to the forced change in the molecular geometry of one of the components.

In fact the above-mentioned R = i-C_3H_7, X = 5-CH_3, diamagnetic in its pure solid phase, could be grown in the corresponding Zn(II) lattice. The Ni(II) content can be made 25% and probably more. The mixed crystals are strongly paramagnetic. Since the Zn(II) complex is tetrahedral,[2a] this paramagnetism arises from isomorphous replacement of Zn(II) by Ni(II). Convincing evidence for the presence of tetrahedral Ni(II) in these crystals is obtained from their crystal field spectrum taken in Nujol mull on a Cary Model 14 recording spectrophotometer. The band at 1460 mμ is characteristic of all tetrahedral Ni(II)–salicylaldimines; this band is absent in all planar complexes in this series[2a,4] including pure R = i-C_3H_7, X = 5-CH_3. The spectrum and assignment are shown in Figure 1. Similar paramagnetic mixed crystals were grown in other cases, *e.g.*, R = i-C_3H_7, X = 5-C_6H_5; here again the pure Ni(II) complex is diamagnetic in the solid phase. Undoubtedly the situation could be achieved in many more cases. Similar examples of forced configuration have also been observed in pyrrole-2-aldimine complexes.[7] Unsuccessful at-

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(6) E. Frasson and C. Panattoni, *Z. Krist.*, **116**, 154 (1961).
(7) A. Chakravorty, L. J. Theriot, and R. H. Holm, to be published.