these complexes incorporate only the linear pentamine since identical results were obtained with pentamine purified *via* the hydrochloride[8] as with distilled pentamine fraction. Moreover, amine isolated by acidic decomposition of the complexes was shown by gas chromatography to comprise only one component and its retention time was identical with that of the major peak from hydrochloride-purified amine.

In their work on complexes of the type $[(\text{tetren})\text{CoCl}][\text{X}^-]_2$, House and Garner were able to distinguish between geometrical isomers, mainly on the basis of differences in NH_2 bending and NH stretching frequencies.[3] The major infrared bands for the iron complexes are listed in Table I, but these data cannot be correlated with those of House and Garner so the question of geometry remains open.

TABLE I
INFRARED SPECTRA OF TETRAETHYLENEPENTAMINE–IRON DERIVATIVES[a]

	Assignment and freq, cm⁻¹		
Compd	NH_2 str	CO	NH_2 bend
3	3310 m	1940 vs	1620 m
	3140 s		1600 w
4	3270 s	1960 vs	1600 m
5	3150 s	1950 vs	1600 m
6	3150 vs[b]		1580 s
7	3200 s[b,c]		1650 w
			1590 m

[a] Nujol mulls. [b] Doublet. [c] Also 3450 cm⁻¹ assigned to H_2O.

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The Action of Dimethyl Sulfide on Pentaborane(9)[1]

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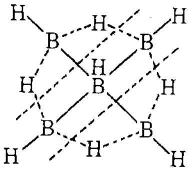
New insight into the action of bases on pentaborane(9) comes from its vapor-phase reaction with dimethyl sulfide at temperatures above 75°, to form diborane (or a BH_3 complex) and a resin containing $(CH_3)_2S$. Stronger aprotic bases such as trimethylamine were known to form 2:1 solid adducts with B_5H_9,[2–4] but heating these with excess base (in a closed chamber) produced 2 units of the base–BH_3 complex per B_5H_9. It seemed obvious that the base directly removed BH_3 from the structural pattern



leaving $(BH)_3$ to form the observed thermally stable resin containing the base.[2] The same process seemed evident in the B_5H_9-induced trimerization of $(CH_3)_2NBH_2$, wherein $(CH_3)_2NBH_2\cdot B_4H_6$ could be recognized as an intermediate.[5] However, no base as weak as $(CH_3)_2S$ could attack B_5H_9 by first removing BH_3, for the complex $(CH_3)_2S\cdot BH_3$ is extensively dissociated in the vapor phase,[6] as B_5H_9 itself is not. Instead, then, it appears that $(CH_3)_2S$ invades B_5H_9 to displace BH_3 and attach itself to the remaining B_4H_6 moiety, which then undergoes a condensation to resin. The driving force of the reaction would be the extreme Lewis-acid strength of the B_4H_6 moiety, beginning to take effect as the B–H–B bridges in B_5H_9 are loosened by thermal vibration. Thus it now seems reasonable that stronger bases, which require similar temperatures for dismemberment of B_5H_9, also first seize B_4H_6 and displace BH_3, although the order of events is less obvious because the displaced BH_3 is irreversibly captured by these strong bases.

Experimental Section

In the initial experiment, a mixture of B_5H_9 with excess $(CH_3)_2S$ was heated at 75–90°, forming hydrogen, nonvolatile solids, and diborane, which appeared as the dissociable complex $(CH_3)_2S\cdot BH_3$ on condensation at 25°.[6] However, the decomposition of some of the diborane prevented a quantitative interpretation.

For a better experiment, we employed a vertical double-walled reaction vessel, with a 5 × 18 cm outer tube electrically heated to temperatures as high as 250°, while the inner 2.5 × 12 cm coldfinger was cooled to −33° by refluxing liquid ammonia. A lower tubulature at −23° collected BH_3 as the $(CH_3)_2S$ complex while the B_5H_9–$(CH_3)_2S$ mixture refluxed from the −33° coldfinger. Under these conditions it was possible to prove a quantitative process by the millimole stoichiometry accompanying the equation

$$\begin{array}{lllll}
3(CH_3)_2S & + \; B_5H_9 \longrightarrow & & & \\
8.91 & 3.060 & H_2 \; + & (CH_3)_2S\cdot BH_3 \; + & (1/n)[(CH_3)_2SB_2H_2]_{2n} \\
\underline{-5.10} & \underline{-1.793} & 1.297 & 1.267 & 1.267/n \\
3.81 & 1.267 & & &
\end{array}$$

This process was conducted in a series of stages at higher and higher outer wall temperatures. During 48 hr at 100° the progress was only 2%; in 9 hr at 135°, 6%; in 9 hr at 185°, 17%; and in 3 hr at 250–260°, 25%. The effective reaction temperatures must have been much lower, on account of rapid convection between the inner and outer walls.

The nonvolatile solid product included an amorphous resin but also a more definitely crystalline component, the X-ray powder pattern of which appeared as a series of peaks above a broad continuum. The relative displacements were 3.18 (s), 3.99 (m), 4.31 (w), 4.58 (w), 5.16 (w), and 5.75 (vw).[7] Also

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[1] It is a pleasure to acknowledge the generous support of this research by the Office of Naval Research.

[2] A. B. Burg, *J. Amer. Chem. Soc.*, **79**, 2129 (1957).

[3] A. B. Burg, XVIIth International Congress of Pure and Applied Chemistry, Butterworths, London, 1960, p 57.

[4] M. L. Denniston and S. G. Shore, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR 104.

[5] A. B. Burg and J. S. Sandhu, *J. Amer. Chem. Soc.*, **89**, 1626 (1967).

[6] A. B. Burg and R. I. Wagner, *ibid.*, **76**, 3307 (1954).

[7] Kindly recorded for us by Dr. D. F. Palmer of our Department of Geological Sciences.

suggestive was the ^{11}B nmr spectrum of the carbon disulfide extract, which showed peaks no broader than normal for polyboranes. With δ measured in ppm upfield from trimethyl borate, the record showed a doublet at 4.8 (J = 139 cps), a doublet at 18.6 (J = 128 cps), a singlet at 41.3 (strongest peak, broad enough to suggest an unresolved multiplet), and a doublet at 61.7 (J = 167 cps). Efforts toward elucidation of the molecular identity of this component seem justified.

A similar action upon B_5H_9 by H_2S was attempted, but no reaction occurred. With CH_3SH or CH_3SSCH_3 in simple reaction tubes at 80–100°, B_5H_9 produced only resinous material and the known trimer $(CH_3SBH_2)_3$, recognized by its ^{11}B nmr spectrum.[8] This spectrum showed no trace of $B(SCH_3)_3$, which would have appeared as a relatively broad singlet at 42.6 ppm downfield of $B(OCH_3)_3$.[9]

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(8) E. L. Muetterties, N. E. Miller, K. J. Packer, and H. C. Miller, *Inorg. Chem.*, **3**, 870 (1964).

(9) As recorded for a sample kindly furnished to us by Dr. R. J. Brotherton of the U. S. Borax Research Laboratories.

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Polarized Raman Scattering by Tetraethylammonium Pentachloroindate(III) Single Crystals. Vibrational Assignments for the Square-Pyramidal $InCl_5^{2-}$ Ion

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There are two principal reasons for an interest in the molecular vibrations of $InCl_5^{2-}$. First, vibrational frequencies of MX_5 species are important because of the bearing they have on the problem of stereochemical nonrigidity, which is a common phenomenon for five-coordinate compounds.[2,3] Second, $InCl_5^{2-}$ is unusual in that it displays a square-pyramidal geometry in its tetraethylammonium salt.[4] With the exception of an analogous $TlCl_5^{2-}$ salt,[5] this geometry is unknown for other simple complexes of d^{10} ions. However, square-pyramidal intermediates or transition states generally are thought to be involved in the process by which apical and equatorial ligand interchange occurs for trigonal-bipyramidal molecules.[2,3]

Unlike the situation for tetrahedral MX_4 and octahedral MX_6 molecules, where assignment of the optically active modes is generally straightforward, the assignments for MX_5 species present significant difficulties. For example there are ambiguities in the description of the vibrations for such a simple molecule as PF_5.[3] Fortunately, single-crystal laser Raman spectroscopy affords a method of making otherwise difficult assignments, providing the compound crystallizes with high site symmetry and favorable orientation. This method is applied to $[(C_2H_5)_4N]_2[InCl_5]$ in the present paper.

Results and Discussion

The $[(C_2H_5)_4N]_2[InCl_5]$ salt crystallizes in a tetragonal space group P4/n (C_{4h}^3) with two formula units per unit cell related by a center of symmetry.[4] The site symmetry of $InCl_5^{2-}$ is C_4. For the hypothetical isolated $InCl_5^{2-}$ of C_{4v} symmetry the total vibrational representation is $\Gamma_v = 3\ A_1 + 2\ B_1 + 1\ B_2 + 3\ E$; of these 2 A_1, 1 B_1, and 1 E represent stretching modes and the remainder are deformations.

As a consequence of the center of symmetry, mutual exclusion of infrared and Raman modes is expected for the crystal, with only the motions which are in phase between the two $InCl_5^-$ ions having Raman activity. The pertinent correlations between isolated square-pyramidal $InCl_5^{2-}$ (C_{4v}) and the unit cell (C_{4h}^3) are $A_1 \rightarrow A_u, A_g$; $B_1 \rightarrow B_u, B_g$; $B_2 \rightarrow B_u, B_g$; $E \rightarrow E_u, E_g$. Thus, B_1 and B_2 modes of the isolated molecule take on identical selection rules in the solid, while the A_1 and E modes of the isolated complex maintain their totally symmetric and doubly degenerate character, respectively, in the crystal. The irreducible representations of the polarizability tensor elements are: for A_g: $\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$; for B_g: $\alpha_{xx} - \alpha_{yy}, \alpha_{xy}$; for E_g: α_{yz}, α_{zx}. From this it is evident that scattering by A_g modes will preserve the orientation of the incident electric vector, while B_g modes will uniquely scatter incident x-polarized radiation in the y direction and E_g will uniquely scatter incident x or y polarized radiation in the z direction. Therefore, three alignments of the crystal and incident electric vector are necessary and sufficient to characterize the internal modes of $InCl_5^{2-}$. The spectra resulting from three such orientations are displayed in Figures 1–3. Complete extinction of peaks is not observed in all cases where it is expected, because the crystals possess some internal and surface imperfections as well as prismatic edges. (Errors introduced by the latter characteristic are probably the

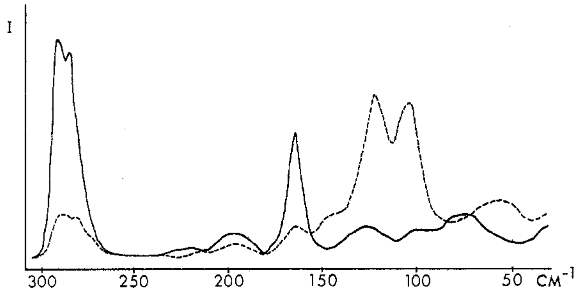

Figure 1.—Raman spectra of single-crystal $[(C_2H_5)_4N]_2$-$[InCl_5]$. Orientations: $z(x,x)y$ (——) and $z(x,z)y$ (-----). Intensities of the 289- and 294-cm^{-1} bands are reduced by one-third. Following the notation of T. C. Damen, S. P. S. Porto, and B. Tell, *Phys. Rev.*, 142, 570 (1966), the first coordinate specifies the direction of the incident laser beam, the second specifies the electric vector of the incident light, the third specifies the electric vector for the scattered light, and the fourth specifies the direction of the scattered light. All axes refer to the coordinates of the crystal.

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(1) (a) NSF Undergraduate Research Participant, 1969. (b) NDEA Fellow, 1968–1970. (c) Alfred P. Sloan Fellow, 1967–1969; addressee for correspondence.

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(5) D. F. Shriver and I. Wharf, *ibid.*, **8**, 2167 (1969).