

the first if the kinetics of the dimerization were not sufficiently rapid. If this were the case, electrolysis at 0.20 V should require 1.0 equiv/mol. After the electrolysis, only the second wave should appear, and it should be as large as the original first wave, assuming that the dimerization went to completion. This behavior was not observed.

The preparation of $B_{11}H_{11}^{2-}$ involves the synthesis of $CsB_{11}H_{14}$ and its conversion to $Cs_2B_{11}H_{13}$, followed by pyrolysis to $Cs_2B_{11}H_{11}$. Varying amounts of $Cs_2B_{10}H_{10}$ and $Cs_2B_{12}H_{12}$ are also formed in the pyrolysis. The data summarized in Table I indicate that the extraneous

TABLE I
VOLTAMMETRY AND ^{11}B CHEMICAL SHIFTS
OF IONS IN THE SYNTHESIS OF $B_{11}H_{11}^{2-}$

| Ion | $E_{p/2}^a$ | ^{11}B chem shift ^b |
|---------------------|-------------|----------------------------------|
| $B_{11}H_{14}^-$ | +1.6 | +35 |
| $B_{11}H_{13}^{2-}$ | -0.45 | +38.4 (10), +49.6 (1) |
| $B_{10}H_{10}^{2-}$ | +0.4 | +19 (1), +48 (4) |
| $B_{12}H_{12}^{2-}$ | +1.4 | +33.5 |
| $B_{11}H_{11}^{2-}$ | +0.05 | +35.0 ^c |

^a Anodic wave at stationary Pt electrode, in volts; aqueous saturated calomel electrode reference, in acetonitrile containing 0.10 M $(C_2H_5)_4NClO_4$; scan rate 4 V/min. ^b 32-MHz ^{11}B nmr chemical shift in acetonitrile, in ppm upfield from $B(OCH_3)_3$; relative areas in parentheses. ^c Literature³ report: 35.0 (10), 47.4 (1).

wave in the voltammetry and the high-field doublet in the nmr spectrum of the $Cs(CH_3)_4NB_{11}H_{11}$ obtained are probably due to the presence of some $B_{10}H_{10}^{2-}$.

Either stationary-electrode voltammetry or ^{11}B nmr can be used to detect easily more than 5% $B_{10}H_{10}^{2-}$ in $B_{11}H_{11}^{2-}$. Detection of contamination by $B_{12}H_{12}^{2-}$ remains difficult because of the extreme oxidative stability of $B_{12}H_{12}^{2-}$ and the similarity of its ^{11}B nmr and ir spectra to those of $B_{11}H_{11}^{2-}$. Amounts greater than 10% $B_{12}H_{12}^{2-}$ in $B_{11}H_{11}^{2-}$ can be detected by nmr.

The structure of $B_{11}H_{11}^{2-}$ is presumably very similar to that of $B_9C_2H_{11}$, with which it is isoelectronic.^{2b} The structure of the dimethyl derivative of $B_9C_2H_{11}$ indicates that five-, six-, and seven-coordinate borons would all be present in a capped decaborane-like structure.⁴ The observation of a single doublet in the nmr spectrum could be explained by an accidental equivalence of chemical shifts or by a polyhedral rearrangement that is fast on the nmr time scale. Experiments

(4) C. Tsai and W. E. Streib, *J. Amer. Chem. Soc.*, **88**, 4513 (1966).

on compounds with closed B_7 , B_9 , B_{10} , and B_{12} polyhedral structures all indicate a sufficiently high barrier to such a polyhedral rearrangement that such rearrangements should be slow on the nmr time scale.⁵ The only other case of a closed polyhedral borane anion having nonequivalent borons in its ground-stage geometry but showing a single nmr chemical shift is the $B_8H_8^{2-}$ ion.⁶ In the absence of a logical reason why rearrangements in $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ should have much lower barriers than those in $B_7H_7^{2-}$, $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{12}H_{12}^{2-}$, we prefer to say that $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ represent cases in which borons of different coordination numbers in the same molecule are spectroscopically equivalent at 32.0 MHz.

Experimental Section

Purification of $Cs_2B_{11}H_{11}$.—Both $Cs_2B_{11}H_{11}$ and $Cs(CH_3)_4NB_{11}H_{11}$ prepared by the published procedure² contained small amounts of $B_{10}H_{10}^{2-}$ which could not be removed by repeated recrystallizations from water. The procedure below could be applied to either of these compounds.

The crude product of the pyrolysis of $Cs_2B_{11}H_{13}$ (ca. 5.5 g) was dissolved in 150 ml of warm water and filtered through Celite to remove colloidal material. While still hot, the filtrate was passed through a sodium ion exchange column. The warm solutions both before and after passing through the column were protected by nitrogen atmosphere. The effluent (about 250 ml) was evaporated under reduced pressure to about 75 ml and treated with an aqueous solution of tetraethylammonium bromide. The resulting precipitate was collected by filtration and dried at room temperature under vacuum. The $[(C_2H_5)_4N]_2B_{11}H_{11}$ was then recrystallized repeatedly from an acetonitrile-water mixture until no waves other than the oxidation wave at +0.05 V were observed by stationary-electrode voltammetry at platinum in acetonitrile, and no peaks due to $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ could be observed in the ^{11}B nmr spectrum. About half of the $CsB_{11}H_{13}$ pyrolyzed was realized as pure $[(C_2H_5)_4N]_2B_{11}H_{11}$.

Electrochemistry.—Voltammetry was carried out using a stationary platinum-inlay electrode in acetonitrile containing 0.10 M $(C_2H_5)_4NClO_4$ at a scan rate of 4 V/min. The potentiostat was built according to a design of M. D. Hawley.⁷

Exhaustive electrolysis was carried out at a Pt gauze electrode, using a Kepco OPS 40-0.5 power supply. Current was monitored as a voltage across a precision resistor in series with the working electrode, using a strip chart recorder.

Nmr.—Spectra were run on a Varian HA-100 spectrometer operated at 32 MHz. An external capillary of $B(OCH_3)_3$ was used as a reference. Spectra were calibrated by use of an audio side band.

(5) Reference 2c, Chapter 3.

(6) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967).

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Correspondence

The Structure of Bis(tri-*n*-butyltin) Sulfate. Solid-State Monomer or Polymer?

Sir:

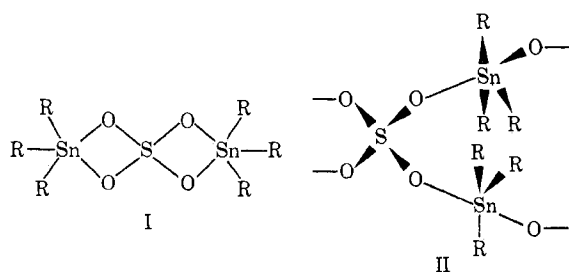
Stapfer, Leung, and Herber¹ have reported recently

Mössbauer and infrared data for $[(n-C_4H_9)_3Sn]_2SO_4$

(1) C. H. Stapfer, K. L. Leung, and R. H. Herber, *Inorg. Chem.*, **9**, 970 (1970).

and have concluded the compound has a monomeric structure I and not a polymeric structure II in the solid state. We feel these data do not warrant such a conclusion.

First, we briefly discuss data for the closely related compounds $[(CH_3)_3Sn]_2SO_4$, $[(CH_3)_3Sn]_2SeO_4$, and $[(CH_3)_3Sn]_2CrO_4$.²⁻⁴ The ir spectra indicate T_d sym-



metry for the XO_4 groups, and the tin-carbon stretching frequency regions show only $\nu(\text{Sn}-\text{C}_3)_{\text{asym}}$. For $[(\text{CH}_3)_3\text{Sn}]_2\text{SO}_4$, the Raman spectrum⁵ shows only $\nu(\text{Sn}-\text{C}_3)_{\text{sym}}$. These results clearly suggest a planar $(\text{CH}_3)_3\text{Sn}$ moiety and are thus consistent with structure II and inconsistent with I.²⁻⁴

Mössbauer data⁴ are quoted in Table I along with

TABLE I
MÖSSBAUER PARAMETERS FOR TRIALKYL TIN
DERIVATIVES OF DIBASIC ACIDS

| Absorber | Temp, °K | IS, ^a mm/sec | QS, mm/sec | Ref |
|------------------------------------------------------|-------------|----------------------------|-----------------|-----|
| $[(n\text{-C}_4\text{H}_9)_3\text{Sn}]_2\text{SO}_4$ | 80 | 1.56 ± 0.02 | 4.01 ± 0.02 | 1 |
| | 294 | No effect | | |
| $[(\text{CH}_3)_3\text{Sn}]_2\text{SO}_4$ | 80 | 1.37 ± 0.05 | 4.06 ± 0.05 | 4 |
| | 295 | No effect | | |
| $[(\text{CH}_3)_3\text{Sn}]_2\text{SeO}_4$ | 80 | 1.39 ± 0.05 | 4.09 ± 0.05 | 4 |
| | 295 | 1.33 ± 0.05 | 4.14 ± 0.05 | |
| $[(\text{CH}_3)_3\text{Sn}]_2\text{CrO}_4$ | 80 | 1.36 ± 0.05 | 3.77 ± 0.05 | 4 |
| | 295 | 1.35 ± 0.05 | 3.73 ± 0.05 | |

^a Relative to SnO_2 .

Herber's values¹ for $[(n\text{-C}_4\text{H}_9)_3\text{Sn}]_2\text{SO}_4$. The isomer shift (IS) of the butyl compound is somewhat higher than those of the methyl derivatives, a trend also found in trialkyltin carboxylates.⁶ The quadrupole splittings (QS) are closely similar for all four compounds, making it appear unlikely that the butyl derivative has a structure basically different from that of the methyl compounds (*vide infra*). The presence of well-resolved room-temperature effects for the selenate and chromate suggests that these compounds are polymeric. We conclude that all three methyl compounds have structure II. Is there good reason to rule out this structure for $[(n\text{-C}_4\text{H}_9)_3\text{Sn}]_2\text{SO}_4$?

According to Stapfer, *et al.*,¹ the sulfate group in $[(n\text{-C}_4\text{H}_9)_3\text{Sn}]_2\text{SO}_4$ shows only two ir-active modes (1100 and 614 cm^{-1}), and bands at 667 and 523 cm^{-1} are "obviously related to the tin-hydrocarbon bond vibrations."¹ It is inferred that the SO_4 group is tetrahedral with all oxygens coordinated. No assignments in the tin-carbon region are made by these authors,¹ but we feel it is reasonable to assign the band at 523 cm^{-1} to $\nu(\text{Sn}-\text{C}_3)_{\text{asym}}$ and that at 667 cm^{-1} to a $\text{Sn}-\text{C}_4\text{H}_9$ rocking mode.^{2,7} If this is so, these data are

(2) H. C. Clark and R. G. Goel, *Inorg. Chem.*, **4**, 1428 (1965).

(3) H. C. Clark, "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, Cambridge, U. K., 1968.

(4) B. F. E. Ford, J. R. Sams, R. G. Goel, and D. R. Ridley, *J. Inorg. Nucl. Chem.*, in press.

(5) J. R. Sams, unpublished observations.

(6) B. F. E. Ford, B. V. Liengme, and J. R. Sams, *J. Organometal. Chem.*, **19**, 53 (1969).

(7) D. M. Adams, "Metal-Ligand and Related Vibrations," Edward Arnold, London, 1967.

more compatible with structure II than with I. Even if we assume these bands to be $\nu(\text{Sn}-\text{C}_3)_{\text{sym}}$ and $\nu(\text{Sn}-\text{C}_3)_{\text{asym}}$, respectively, this would not allow one to rule out (a slightly distorted) structure II.

The argument¹ against structure II for $[(n\text{-C}_4\text{H}_9)_3\text{Sn}]_2\text{SO}_4$ rests mainly upon (1) the failure to observe Mössbauer absorption with the absorber at room temperature and (2) the essential identity of the Mössbauer spectra of the neat solid and of a frozen solution (concentration not stated) in methylhydrofuran (MHF).

Point (1) in no way allows a choice between I and II. While it is very reasonable to argue that the presence of a room-temperature effect in such compounds implies a polymeric structure, the negative of this is by no means true. $[(\text{CH}_3)_3\text{Sn}]_2\text{SO}_4$ does not show a room-temperature effect but is undoubtedly polymeric,²⁻⁴ and there are other examples of polymeric tin(IV) compounds which do not appear to give room-temperature resonance.

Stapfer, *et al.*,¹ argued that (2) demonstrates the absence of a monomer-polymer transition in going from solution to solid state. We feel there are at least two other possibilities. First, it is conceivable that cooling the solution could lead to precipitation of microcrystals of the compound, having Mössbauer parameters identical with those of the bulk solid. Second, stable adducts of bis(trimethyltin) sulfate and selenate can be isolated from such solvents as water, methanol, pyridine, and *N,N*-dimethylformamide,^{2,4} and with the exception of the pyridine adduct (which has a somewhat lower QS) the Mössbauer parameters are virtually identical with those of the unsolvated compound. Such adduct formation might also conceivably occur with the butyl homolog in MHF. We feel that unless these two possibilities can be eliminated, the frozen-solution results must be regarded with reservation.

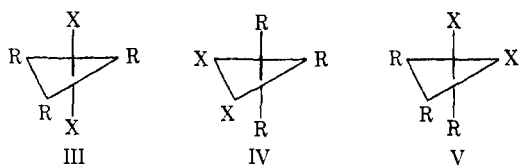
Finally, we consider the explanation offered for the magnitude of the QS in $[(n\text{-C}_4\text{H}_9)_3\text{Sn}]_2\text{SO}_4$: "Since the quadrupole splitting which is observed in $(n\text{-C}_4\text{H}_9)_3\text{SnF}$ (presumed to be five-coordinate with $\sim C_{3v}$ symmetry along the $\text{F}-\text{SnF}$ axis) and $(n\text{-C}_4\text{H}_9)_2\text{SnF}_2$ (presumed to be six-coordinate with trans alkyl groups) is 3.75 and 4.00 mm/sec , respectively, it is reasonable to associate the large quadrupole splitting observed in $[(n\text{-C}_4\text{H}_9)_3\text{Sn}]_2\text{SO}_4$ with the steric requirements imposed by the postulated four-membered cyclic arrangement $\text{Sn} < \overset{\text{O}}{\text{O}} > \text{S}$."¹ The implication is clearly that a structure involving a planar $(n\text{-C}_4\text{H}_9)_3\text{Sn}$ group and a (nearly) linear $\text{O}-\text{Sn}-\text{O}$ arrangement would be expected to show a QS smaller than that observed. There are excellent reasons to suppose the contrary.

Trimethyltin acetate and the corresponding haloacetates are known to be polymeric in the solid state, with planar trimethyltin groups bridged by carboxylate oxygens.^{6,8} The QS values range from 3.68 mm sec^{-1} for $(\text{CH}_3)_3\text{SnO}_2\text{CCH}_3$ (tri-*n*-butyltin acetate

(8) M. J. Janssen, J. G. A. Luijten, and G. J. M. vander Kerk, *Recl. Trav. Chim. Pays-Bas*, **82**, 90 (1963); R. Okawara and M. Ohara, *J. Organometal. Chem.*, **1**, 360 (1963); C. Poder and J. R. Sams, *ibid.*, **19**, 67 (1969).

shows the same splitting⁶) to 4.22 mm sec⁻¹ for (CH₃)₃-SnO₂CCF₃. We can therefore take this range of values as being fairly typical for cases of planar trialkyltin moieties with axial O-Sn-O bridging. Thus, there is nothing unusual about a QS of ~4 mm/sec for a structure such as II.

The dependence of the QS upon geometry is worth considering in some detail, and we present here the results of a simple point-charge calculation.⁹ Letting [X] denote the contribution of ligand X to the electric field gradient, the QS Δ is $\Delta \propto V_{zz}(1 + \eta^2/3)^{1/2}$, where $V_{zz} = \Sigma_X(3 \cos^2 \theta_X - 1)[X]$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$. We consider the three possible disubstituted trigonal-bipyramidal isomers



In each case the axes were chosen to diagonalize the *efg* tensor and such that $|V_{zz}| \geq |V_{xx}| \geq |V_{yy}|$. We obtain the relative values for Δ

$$\Delta_{III} = 4[X] - 3[R]$$

$$\Delta_{IV} = (7[X]^2 + 12[R]^2 - 18[X][R])^{1/2}$$

$$\Delta_V = (4[X]^2 + 3[R]^2 - 6[X][R])^{1/2}$$

The possible values of [R] and [X] are such that $-1 \leq [R]/[X] \leq 1$. Data for (CH₃)₂SnF₂ and (CH₃)₃SnF⁹ and the point-charge result for a trans-octahedral structure⁹ lead to [CH₃] \simeq 0.26 mm sec⁻¹ ([n-C₄H₉] \simeq 0.25 mm sec⁻¹ from data¹ for the butyltin fluorides). This value with our data⁴ for [(CH₃)₃Sn]₂SO₄ yields [SO₄] \cong -0.81 mm sec⁻¹. While very tentative, these results indicate that in such compounds [R]/[X] will be fairly small and negative. For all values $-0.6 \leq [R]/[X] \leq 0$, $\Delta_{IV} \leq 0.811\Delta_{III}$, and $\Delta_V \leq 0.51\Delta_{III}$. (Even for [R] = -[X], Δ_{IV} is only 0.87 Δ_{III} .) Taking 4.0 mm sec⁻¹ as a typical value of Δ_{III} as discussed above, then $\Delta_{IV} \lesssim 3.2$ mm sec⁻¹ and $\Delta_V \lesssim 2.0$ mm sec⁻¹. Even severe distortions from regular geometry change Δ_{IV} and Δ_V by $\lesssim 10\%$. Thus, a compound having structure I (clearly related either to IV, V, or an intermediate between them) should show $\Delta \lesssim 3.5$ mm sec⁻¹.

We have shown that the structure discarded by Stapfer, *et al.*,¹ for [(n-C₄H₉)₃Sn]₂SO₄ is in fact possessed by a number of closely related compounds, that there are plausible alternatives to their interpretations of their data, and that point-charge calculations indicate the observed QS is considerably larger than that expected for structure I. While these arguments are not conclusive, we feel the weight of evidence casts reasonable doubt upon the structural assignments of Stapfer, *et al.*¹

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Coupling with Cobalt-59 to Account for the Anomalous Proton Magnetic Resonance Spectrum of Tris(ethylenediamine)cobalt(III) Ion

Sir:

The methylene proton resonance spectrum of N-deuterated tris(ethylenediamine)cobalt(III) ion in D₂O is anomalous when compared with the spectra of the tris-ethylenediamine complexes of Pt(IV),¹ Rh(III),¹ Ir(III),¹ and Ru(II),² all of which have a spin-paired d⁶ electron configuration. Although the appearance of these spectra varies widely, from a single sharp line for Pt (with satellites due to ¹⁹⁵Pt) to a well-resolved AA'-BB' spectrum for Ru(II), in each case the line widths are relatively narrow. The cobalt(III) spectrum, however, consists of a single broad unresolved band. The spectrum is also peculiar in having the same line width (approximately 18 Hz) reported at both 60 and 100 MHz. Froebe and Douglas³ recently observed the line width to be strongly temperature dependent; we have observed in contrast that the well-resolved Ru(II) spectrum has little temperature dependence.²

From our observations of the spectrum of the related tris(propylenediamine)cobalt(III) ion and the 220-MHz spectrum of Co(en)₃³⁺ we conclude that the unusual features of the spectra of amine complexes of Co(III) are due to scalar coupling with the ⁵⁹Co quadrupolar nucleus ($I = 7/2$). This hypothesis, which was first suggested by Powell and Sheppard,⁴ can account for all of the following features of these spectra.

1. The spectrum of Co(pn)₃³⁺ has been analyzed⁵ and the protons are assigned as shown in Figure 1. The important feature for the present discussion is that the equatorial methylene proton, H², appears as a single broad band rather than the predicted four-line multiplet. The other spectral lines are not appreciably broadened. Coupling with the ⁵⁹Co nucleus might plausibly be larger for proton H² than for either of the axial protons, due to the dihedral angles made with the Co-N bond as shown in Figure 1. The methyl protons are an additional bond removed from the cobalt and are apparently not affected. The equatorial proton H² is the only one which is strongly coupled to the cobalt nucleus and is thereby broadened. Similar differences in

(1) T. G. Appleton, J. R. Hall, and C. J. Hawkins, *Inorg. Chem.*, **9**, 1299 (1970).

(2) H. Elsbernd and J. K. Beattie, *J. Amer. Chem. Soc.*, **92**, 1948 (1970).

(3) L. R. Froebe and B. E. Douglas, *Inorg. Chem.*, **9**, 1513 (1970).

(4) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 791 (1959).

(5) J. K. Beattie and L. H. Novak, *J. Amer. Chem. Soc.*, in press.

(9) R. V. Parish and R. H. Platt, *J. Chem. Soc. A*, 2145 (1969); *Inorg. Chim. Acta*, **4**, 65 (1970). The result for V has not been reported previously.