samples were contained in a 10-cm glass cell with sodium chloride windows. Mass spectra were recorded using a Hitachi Perkin-Elmer RMU-6A mass spectrometer. Vapor pressures were obtained using a static method.

Properties of Pentafluorosulfanylamine.—Experimental measurements gave a molecular weight of 141.5 ± 1.6 (average of seven determinations) compared to a molecular weight of 143.2 calculated for SF_5NH_2. Vapor pressures (given in Table I) in the range -23 to $+10°$ indicate a heat of sublimation of 9.59 ± 0.03 kcal/mole and an extrapolated normal sublimation point of 61°. The high heat of sublimation and also the high "boiling point" imply considerable hydrogen bonding in the condensed phases. The experimental data fit the expression $\log P_{\mathrm{mm}} = -2096/T + 9.145$. The melting point appears to be about 43°. The important infrared absorption peaks observed in the spectrum of gaseous SF_5NH_2 are as follows (cm^{-1}): 3550 (w) and 3440 (w) N–H stretch (*cf.* organic primary amines doublet in the 3500–3300 cm^{-1} region[8]), 1590 (m) N–H bend,[8] 1208 (w) S–N?, 930 (vs) and 885 (vvs) S–F stretch (doublet),[9] 776 (s) N–H bend,[8] and 694 (vw) S–F stretch.[9] Replicate spectra were taken at 2, 4.8, and 12.1 mm.

TABLE I

VAPOR PRESSURE OF SF_5NH_2

T, °C	*p*, mm	*T*, °C	*p*, mm
−22.9	5.7	−6.0	20.4
−18.0	9.6	−5.0	21.6
−16.9	9.2	−4.3	20.4
−16.0	9.6	0.0	29.3
−13.0	11.1	0.0	30.6
−12.3	13.4	0.0	30.7
−10.0	15.0	0.0	33.0
−9.8	15.5	3.5	35.6
−8.0	18.8	10.7	58.0

The mass spectrum of a sample of pure pentafluorosulfanylamine (as judged from the absence of NSF_3 peaks from the infrared spectrum) showed the major peaks above mass number 28 given in Table II. The intensities shown are relative to NSF_3^+.

TABLE II

MASS SPECTRUM OF SF_5NH_2 (70 v)

m/e	Assigned species	Intensity relative to NSF_3^+	*m/e*	Assigned species	Intensity relative to NSF_3^+
145	$S^{34}F_5NH_2^+$	0.002	89	SF_3^+	0.625
143	$SF_5NH_2^+$	0.069	86	$SF_2NH_2^+$	0.037
127	SF_5^+	0.102	85	SF_2NH^+	0.282
124	$SF_4NH_2^+$	0.065	84	SF_2N^+	0.417
105	$SF_3NH_2^+$	0.046	70	SF_2^+	0.361
104	SF_3NH^+	0.236	65	NSF^+	0.282
103	SF_3N^+	1.000	51	SF^+	0.153
91	$S^{34}F_3N^+$	0.028	46	SN^+	0.231

Pentafluorosulfanylamine hydrolyzes rapidly over aqueous base according to the equation

$$SF_5NH_2 + 6OH^- \longrightarrow SO_3NH_2^- + 5F^- + 3H_2O$$

The neutralization equivalent was determined by hydrolyzing the SF_5NH_2 and titrating the excess base with standardized hydrochloric acid to a phenolphthalein end point. Sulfamate ion was identified by its infrared absorption spectrum among the hydrolysis products after evaporation of the titrated solution. The titration equivalent for a 0.1476-g sample was 23.7 mg for the above reaction (calcd 23.85 mg). Fluoride was determined by standard methods on the same solutions. *Anal.* Calcd: F, 66.3. Found: F, 66. Pentafluorosulfanylamine is a white solid at room temperature. It can be stored indefinitely in glass at Dry Ice temperature and appears to be stable at room temperature in the complete absence of water. Traces of water, however, especially in the presence of glass, result in decomposition to NSF_3.

Chemical reactions of pentafluorosulfanylamine are currently under investigation.

Acknowledgment.—This work was carried out under AEC Contract No. AT(11-1)-620 and NSF Grant No. GP-580. AEC Publication No. COO-620-1.

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CONTRIBUTION FROM THE CHEMICALS DIVISION,
OLIN MATHIESON CHEMICAL CORPORATION,
NEW HAVEN, CONNECTICUT

Elucidation of Boron (^{11}B) Nuclear Magnetic Resonance Spectra by Heteronuclear Spin Decoupling

BY G. D. VICKERS, H. AGAHIGIAN,
E. A. PIER, AND H. SCHROEDER

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^{11}Boron spectra are more difficult to evaluate than the spectra of the more popular nuclei. This difficulty arises because the spectra produced by commercially available spectrometers display the $^{11}B-^{1}H$ coupling constants in the same order of magnitude as the ^{11}B chemical shifts. Consequently, only the more simple boranes give completely interpretable spectra. For the higher boranes, one must be content to make symmetry comparisons between the spectrum and the molecule. To illustrate, the spectral assignments[1,2] for two of the dicarbaclovododecaborane(12) isomers have not yet been made.

Obviously, a spectrometer operating at higher field strength would improve the quality of ^{11}B spectra since the chemical shift is proportionate to field strength. Such a spectrometer was built by Nelson and Weaver.[3] Examples of the spectra it produced have been shown.[2] Unfortunately, it has been dismantled and such spectra are presently unobtainable.

We have sought to find if, and to what degree, heteronuclear spin decoupling[4,5] enhances the evaluation of ^{11}B spectra.

Experimental Section

The 19.3-Mc/sec spectra were obtained with a Varian[6] HR-60 spectrometer, modified with an NMR Specialties[7] HD-60 heteronuclear decoupler operating at 60 Mc/sec. Spectral integrals were measured with both the Varian V-3521 integrator and with

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(6) Varian Associates, Palo Alto, Calif.

(7) NMR Specialties, New Kensington, Pa.

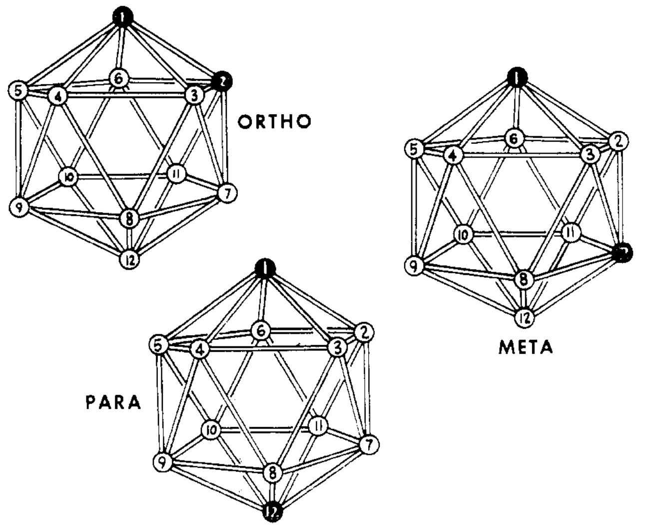

Figure 1.—Icosahedral borane configurations.

a planimeter. The samples were run in deuteriochloroform at about 30% concentration and referenced to external trimethyl borate.

The 64.2-Mc/sec spectra were determined with an experimental spectrometer at the Varian Associates Laboratories, which was assembled by Nelson and Weaver, using a cryogenic solenoid.[3] These samples were also run in deuteriochloroform, but were referenced to external boron trifluoride etherate. However, the chemical shifts are expressed in parts per million from trimethyl borate. (External boron trifluoride etherate resonates 18.2 ppm to higher field than trimethyl borate.)

All chemical shifts were measured by interpolation between the standard and its audio side band.

All spectra were field-swept from low to high field.

ortho and *meta* isomers of carborane were prepared by methods described in the literature.[8-10] The *p*-carborane[11] isomer was obtained from Dr. S. Papetti.

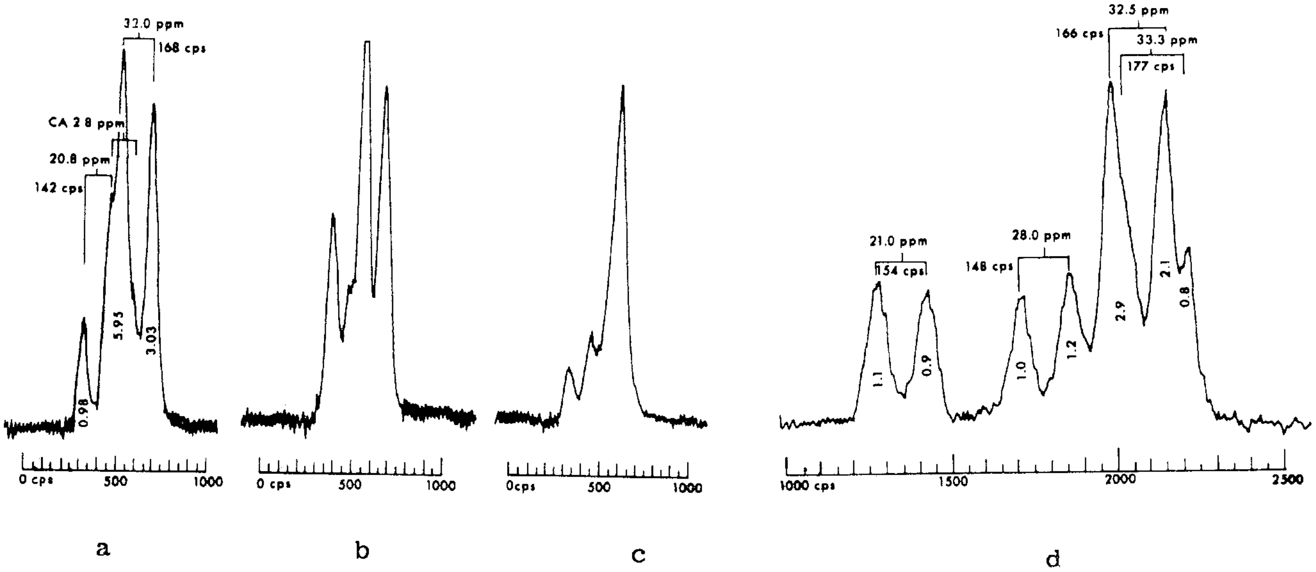

Figure 2.—^{11}B spectra of *o*-carborane: a, 19.3-Mc spectrum; b and c, 19.3-Mc spectra taken while irradiating hydrogen at 60 Mc; d, 64.16-Mc spectrum.

Discussion

The carborane [dicarbaclovododecaborane(12)] isomers were chosen for this study since they are typical of borane molecules that give nebulous spectra.

The *o*-carborane[8,9,12,13] isomer (Figure 1) gives a spectrum consisting of three definite lines (Figure 2a) at 326, 534, and 702 cps. Additionally there are two shoulders on the center line at 476 and about 598 cps. The decoupled spectrum detected in Figure 2b shows that the peak at 326 cps has merged with another, giving a decoupled peak at 402 cps. We, therefore, conclude that the line at 326 cps in the normal spectrum is part of a doublet of relative intensity 2 located at 20.8 ppm with a ^{11}B–^{1}H coupling constant of 142 cps. The high-field line of the doublet should then fall at 478 cps. This agrees with the shoulder at 476 cps.

The decoupled spectrum depicted in Figure 2c shows that the line at 702 cps merges with another to give a decoupled peak at 610 cps. Since the relative intensity of the line at 702 cps is 3, the relative intensity of the peak is, therefore, 6. So far, eight boron atoms are accounted for in two doublets. Intensity considerations indicate that there is a two-boron resonance that remains hidden under the major peak (Figure 2c), and since this could shift its apex, it would not be prudent to accept 610 cps as the chemical shift of the major doublet. Rather, the highest point of the line at 535 cps would most reasonably be assigned as the low-field line of the major doublet, since this line is less contaminated than the decoupled singlet. The major doublet is then evaluated as having a relative intensity of 6, a chemical shift of 32.0 ppm, and a coupling constant of 168 cps.

The third peak is believed to be around 28 ppm, since that is about the center of the range where it could remain undetected.

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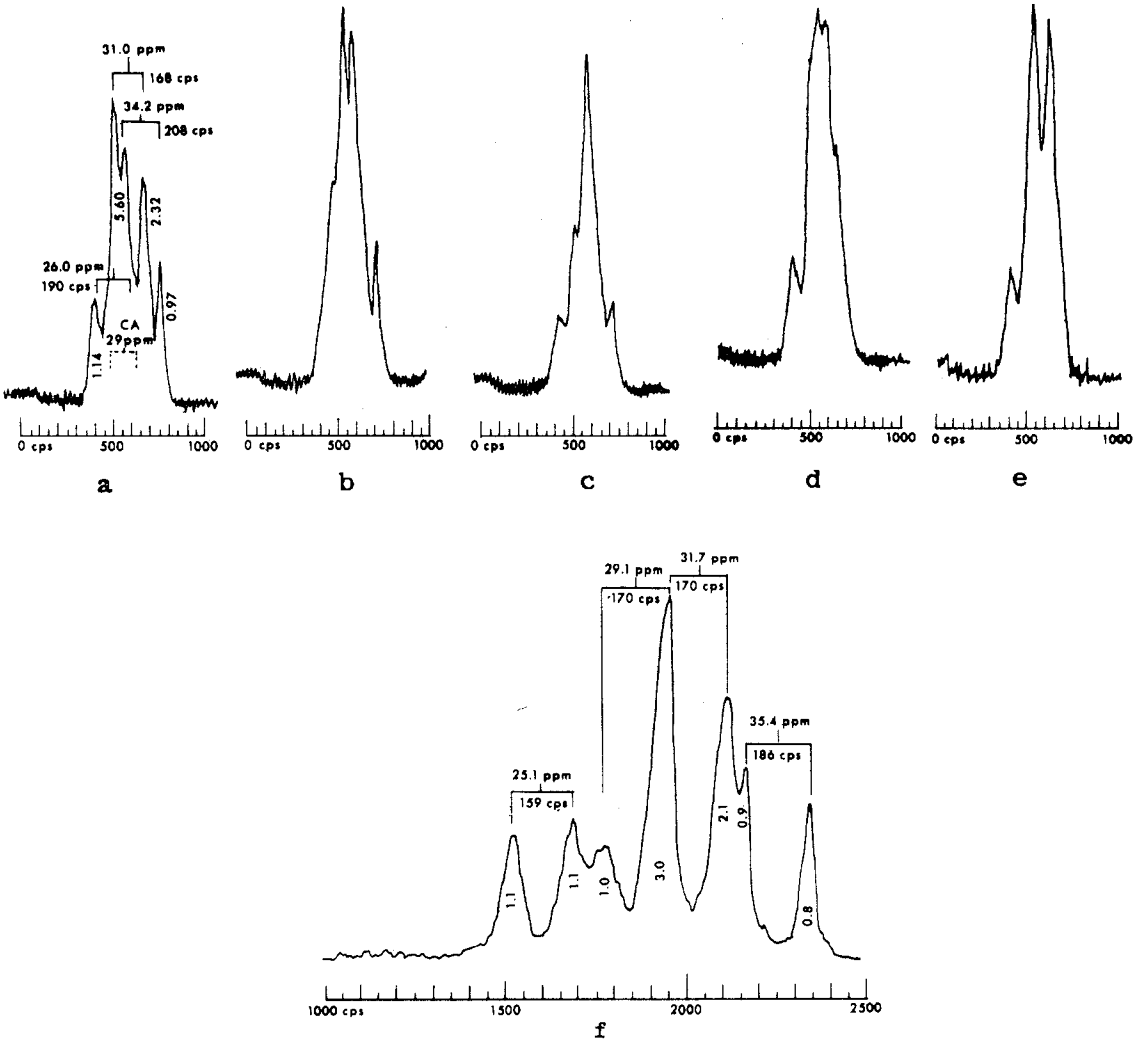

Figure 3.—^{11}B spectra of *m*-carborane: a, 19.3-Mc spectrum; b–e, 19.3-Mc spectra taken while irradiating hydrogen at 60 Mc; f, 64.16-Mc spectrum.

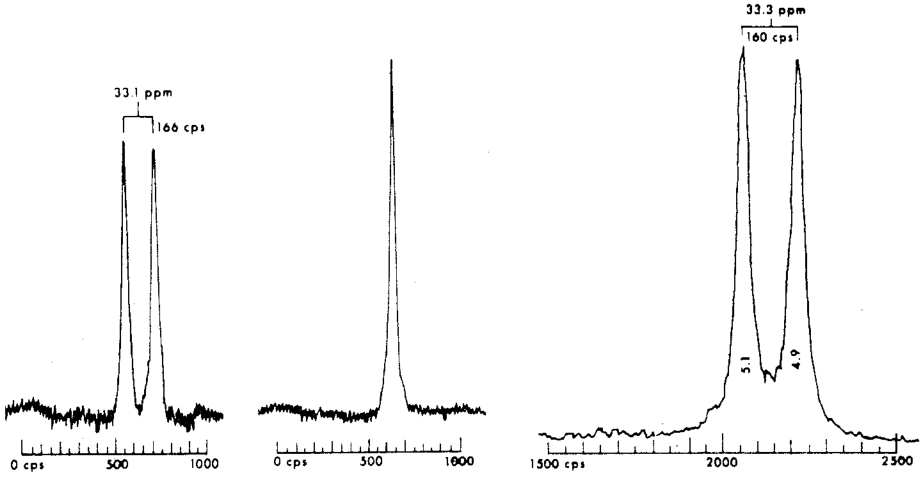

Figure 4.—^{11}B spectra of *p*-carborane: a, 19.3-Mc spectrum; b, 19.3-Mc spectrum taken while irradiating hydrogen at 60 Mc; c, 64.12-Mc spectrum.

The 64.2-Mc/sec spectrum (Figure 2d) as well as the 60-Mc/sec spectrum[2] confirms the evaluation of the 19.3-Mc/sec spectrum with the exception that the 32.0 ppm doublet of the 19.3-Mc/sec spectrum is shown to be actually two doublets which partially resolve at higher field strengths.

The *m*-carborane[1] isomer gave a spectrum (Figure 3) that could be completely evaluated with the aid of heteronuclear decoupling in a manner similar to that described for *o*-carborane. The evaluation is in good agreement with the corresponding 64.2-Mc/sec spectrum (Figure 3f).

The critical lines in the decoupled spectra are singlets at 502 cps in Figure 3b, 598 cps in Figure 3c, and 660 cps in Figure 3d.

A potential pitfall of this technique is shown in the singlet at 634 cps in Figure 3e. This spectrum was obtained at a relative decoupling frequency of −12,448 cps. Since the spectra shown in Figures 3b, 3c, and 3d were obtained at relative decoupling frequencies of −13,139, −12,880, and −12,632 cps, respectively, and since Figures 3b and 3d show the extreme low-field and the extreme high-field peaks, respectively, decoupled, this merging of peaks at 634 cps is most reasonably interpreted as a superimposition of two lines, each of a different peak.

The *p*-carborane isomer was used to test the compatibility of techniques. Since the 19.3-Mc/sec spectrum consisted of two lines of equal intensity which fall at 556 and 722 cps (Figure 4a), the decoupled spectrum should have only one peak at 639 cps. The decoupled singlet was found at 640 cps. The coupling constants and chemical shifts measured from the 19.3-Mc/sec spectrum and the 64.2-Mc/sec spectrum are in good agreement.

Conclusions

These studies indicate that heteronuclear spin decoupling does aid the evaluation of ^{11}B spectra in that the information obtained is compatible with the information obtained from the 64.2-Mc/sec spectra.

Further, we note that these spectral evaluations might suggest an unexpected consideration pertaining to spectral assignments. Both the *ortho* and *meta* isomers have one pair of equivalent boron nuclei more intimately neighbored to carbon than the four equivalent boron nuclei and two pairs of equivalent boron nuclei further removed from carbon than the four equivalent boron nuclei. This suggests that the spectra should have one doublet on one side of the resonance of the four equivalent boron nuclei and two doublets on the other side. In both cases, the doublet is at higher field than the resonance of the four equivalent boron nuclei, and the pair of doublets is at lower field. This seems to suggest that carbon could be imparting a diamagnetic shift to its neighboring boron nuclei. A paramagnetic shift would be expected if only relative electronegativities were considered.

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Contribution from the Department of Chemistry,
State University of New York at Buffalo,
Buffalo, New York 14214

Basicity of Coordinated Oxalate in Ammine Oxalatocobalt(III) Complexes

By Shih-Fan Ting,[1] H. Kelm, and G. M. Harris

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It is well-known that coordination of a compound to a metallic ion considerably alters its acid–base properties. Water, for example, becomes appreciably acidic in ligand form, as exemplified by the pK_1 values for the species[2] $Co(NH_3)_5(H_2O)^{+3}$ and $Co(NH_3)_4(H_2O)_2{}^{3+}$ (6.55 and 5.95, respectively, at 25°, compared to the nominal pK of water of about 16). In the present work, a study has been made of the proton affinity of the typical mono- and bidentate oxalato complexes, $Co(NH_3)_5C_2O_4{}^+$ and $Co(NH_3)_4C_2O_4{}^+$.

Experimental Section

$[Co(NH_3)_5CO_3]NO_3$ was obtained by standard procedure[3] and converted to the aquoperchlorate by treatment with excess of concentrated $HClO_4$. The crystals of $[Co(NH_3)_5H_2O](ClO_4)_3$ were filtered off, washed with ice water, and redissolved to form a saturated aqueous solution at 50°. This solution was treated with the stoichiometric amount of boiling saturated solution of $NaHC_2O_4$. The red crystalline salt obtained on cooling was purified by recrystallization and subjected to chemical analysis. *Anal.* Calcd for $[Co(NH_3)_5HC_2O_4](ClO_4)_2$: Co, 13.65; C_2O_4, 20.40; ClO_4, 46.05. Found: Co, 14.04; C_2O_4 20.45; ClO_4, 46.42. The deprotonated form of this complex was obtained by neutralization of a saturated solution to pH ~8 with dilute alkali and recrystallization of the $[Co(NH_3)_5C_2O_4]ClO_4$ product from the cooled solution. The tetraammine analog was obtained by a very similar procedure, using $[Co(NH_3)_4CO_3]NO_3$, prepared by standard methods,[4] as the starting material. The deep red crystals of $[Co(NH_3)_4C_2O_4]ClO_4 \cdot H_2O$ on chemical analysis yielded data in good agreement with that calculated from the formula given.

pH measurements were made on a Beckman Research Model pH meter, and conductance data were obtained by use of a General Radio Type 1650-A impedance bridge with a suitable conductance cell. A Varian A60 instrument was used to provide the nmr spectra. All chemicals used were of AR or CP grade.

Results and Discussion

Titrimetric experiments in which 0.01 *M* $[Co(NH_3)_4C_2O_4]ClO_4$ solution was titrated with 0.1 *M* HCl solution showed that no acid–base equilibrium was detectable in this system. The pH *vs.* titer of HCl curve was identical within experimental error with that obtained in a blank experiment with complex salt absent. It was further found that the pH of 0.01 *M* HCl solution remains essentially unchanged for as long as 30 min on addition of sufficient solid complex tetraammine salt to

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(1) NSF Summer Research Participant, 1963 and 1965.

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