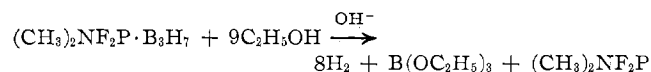


solid (mp 43° with slight decomposition), which is sensitive to air and water. It is soluble in carbon tetrachloride, trichlorofluoromethane, and benzene but insoluble in butane.

The infrared spectrum (4000–200 cm^{-1}) in carbon tetrachloride showed the following absorbances (cm^{-1}): 2935 (m), 2864 (w), 2189 (w), 2370 (s), 2335 (s), 2215 (w), 1740 (m), 1483 (m), 1452 (m), 1315 (s), 1182 (w), 1120 (w), 1072 (w), 1004 (s), 862 (vvs), 770 (s), 743 (vs), 590 (w), 527 (w), 449 (w).

The mass spectrum is given in Table I, and the results of nmr measurements are found in Table II.

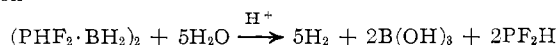
Dimethylaminodifluorophosphine-Triborane(7).—*Anal.* Calcd for $(\text{CH}_3)_2\text{NF}_2\text{P}\cdot\text{B}_3\text{H}_7$: B, 21.4; N, 9.19. Found: B, 21.3; N, 9.32. Hydrolysis of the compound in ethanolic potassium hydroxide gave 96% of the hydrogen calculated for the reaction



A molecular weight of 154 ± 4 (calcd 153) was found by a rapid gas density measurement at 92°; mp -35.5° .

The mass spectrum of the compound is given in Table I, and the results from the nmr spectra are to be found in Table II.

Bis(difluorophosphine)-Diborane(4).—*Anal.* Calcd for $(\text{F}_2\text{PH}\cdot\text{BH}_2)_2$: B, 13.05. Found: B, 13.9. Hydrolysis of the compound yielded 100% of the hydrogen calculated for the reaction

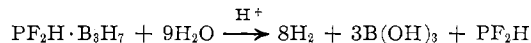


The vapor pressure is 19 mm at 0°; mp -53.2° .

The infrared spectrum (4000–600 cm^{-1}) showed the following absorbances (cm^{-1}): 2440 (s), 2400 (m), 2325 (w), 2310 (w), 2200 (vw), 1110 (w), 1035 (s), 975 (w), 875 (vs), 820 (s), 780 (m), 720 (w), 650 (vw).

The mass spectrum of the adduct is given in Table I and the results from the nmr spectra are to be found in Table II.

Difluorophosphine-Triborane(7).—*Anal.* Calcd for $\text{PF}_2\text{H}\cdot\text{B}_3\text{H}_7$: B, 29.8. Found: B, 31.8. Hydrolysis of the compound yielded 99% of the hydrogen calculated for the reaction



The adduct melted at -82.9° . The vapor pressure was 21 mm at 0°.

The infrared spectrum (4000–600 cm^{-1}) showed the following absorbances (cm^{-1}): 2550 (s), 2480 (m), 2320 (vw), 1995 (vw), 1575 (w), 1160 (m), 1050 (m), 1005 (w), 920 (s), 880 (s), 790 (vww), 730 (vw).

The mass spectrum of the adduct is given in Table I, and the results from the nmr measurements are to be found in Table II.

Acknowledgment.—We wish to thank Professor A. B. Burg of the University of Southern California, Los Angeles, Calif., for his assistance given by observing several nmr spectra on the Varian HA-100 spectrometer modified for boron, phosphorus, and fluorine.

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Elucidation of the Boron-11 Nuclear Magnetic Resonance Spectra of Some B_9H_{13} (ligand) Derivatives

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The ^{11}B nmr spectra at 32.1, 70.56, and 80.2 MHz of a series of specifically labeled B_9H_{13} (ligand) compounds with both neutral and negatively charged ligands have been examined. This has provided an assignment of the ^{11}B nmr of these compounds which is compatible with the known solid-state structure of this class of boron compounds.

Introduction

In recent years, through an investigation of the proper derivatives, the nmr spectra of several boron hydrides have been assigned. The ^{11}B nmr spectra of $\text{B}_{10}\text{H}_{14}^2$ and $\text{B}_{10}\text{H}_{12}$ (ligand)₂³ have been elucidated along with the more complex ^1H nmr spectrum of $\text{B}_{10}\text{H}_{14}$.⁴

We wish to report a similar study of the ^{11}B nmr spectrum of B_9H_{13} (ligand) derivatives. A single-crystal X-ray study of the $\text{B}_9\text{H}_{13}\cdot\text{NCCCH}_3$ derivative by Wang, Simpson, and Lipscomb⁵ yielded the structure shown in Figure 1.⁶

(1) (a) Indiana University. (b) University of Pittsburgh.

(2) R. L. Pilling, F. N. Tebbe, M. F. Hawthorne, and E. A. Pier, *Proc. Chem. Soc., London*, 402 (1964); P. C. Keller, D. Maclean, and R. O. Schaeffer, *Chem. Commun.*, 204 (1965).

(3) D. E. Hyatt, F. R. Scholer, and L. J. Todd, *Inorg. Chem.*, **6**, 630 (1967).

(4) G. M. Bodner and L. G. Sneddon, *ibid.*, **9**, 1421 (1970); R. L. Williams, N. N. Greenwood, and J. H. Morris, *Spectrochim. Acta*, **21**, 1579 (1965).

(5) F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Chem. Phys.*, **85**, 1335 (1961).

(6) We have used the numbering system proposed by the Council of the American Chemical Society, *Inorg. Chem.*, **7**, 1945 (1968). This is not the same system which has been used in the past. Several workers in the field have numbered this compound as a derivative of $\text{B}_{10}\text{H}_{14}$, in which the B(6) position has been removed. To convert to this system renumber as follows: B(1) in Figure 1 = 4, B(2) = 1, B(3) = 3, B(4) = 9, B(5) = 10, B(6) = 5, B(7) = 2, B(8) = 7, B(9) = 8.

A previous investigation⁷ of the ^{11}B nmr of $\text{B}_9\text{H}_{13}\cdot\text{NH}_3$ at 19.3 MHz showed a poorly resolved but characteristic pattern of two overlapping doublets at -10.3 and -0.5 ppm (each of area 1), a broad multiplet of area 5 at $+18.4$ ppm and a high-field doublet of area 2 at $+39.3$ ppm. These authors noted that upon decoupling the two low-field doublets collapsed to singlets.

We have studied the ^{11}B nmr spectra at 32.1, 70.56, and 80.2 MHz of a series of specifically labeled B_9H_{13} (ligand) compounds with both neutral and negatively charged ligands. This has provided an assignment of the ^{11}B nmr of these compounds which is compatible with the known geometry shown in Figure 1.

Experimental Section

2-Bromodecaborane was prepared as described previously, mp $107-108^\circ$.⁸ The 1,2,3,4-decaborane-*d*₄ prepared by a literature method⁹ was kindly supplied by L. G. Sneddon, Indiana University. The B_9H_{13} (ligand) compounds and their substituted derivatives were prepared by the procedure of Graybill, Pito-

(7) E. L. Muettterties and F. Klanberg, *Inorg. Chem.*, **5**, 315 (1966).

(8) M. S. Cohen and C. E. Pearl, U. S. Patent 2,990,239 (1961).

(9) J. A. DuPont and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **84**, 1804 (1962).

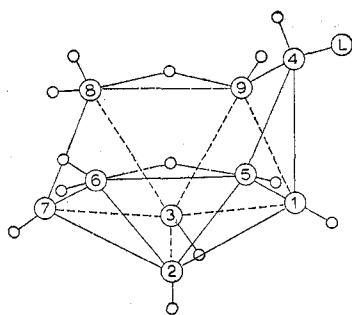


Figure 1.—The structure and numbering system of B₉H₁₃(ligand) derivatives.

chelli, and Hawthorne.¹⁰ The B₉H₁₂Br[S(CH₃)₂] derivative was prepared from 2-bromodecaborane by this method, mp 123–125°. *Anal.* Calcd for B₉H₁₂Br[S(CH₃)₂]: C, 9.55; H, 7.17; Br, 31.78. Found: C, 9.79; H, 7.16; Br, 31.18. B₉H₁₃(P(C₆H₅)₃) was found to be only marginally stable both as a solid and in solution. The 7-CH₃OB₉H₁₂[S(CH₃)₂] was prepared by the method of Plesek and coworkers.¹¹

The 32.1-MHz ¹¹B nmr spectra were obtained *via* a field sweep operation in the HR mode on a Varian HA-100 spectrometer. The 80.2-MHz ¹¹B nmr spectra were obtained on an instrument described previously.¹² Instrument stability was better than ±2Hz in 24 hr when operated without the lock system. The chemical shifts were measured relative to a capillary of trimethyl borate and are reported relative to boron trifluoride etherate.¹³

TABLE III
80.2-MHz ¹¹B NMR DATA ON B₉H₁₃(LIGAND) DERIVATIVES IN CH₂Cl₂

Compd	Chem shifts of boron positions ^a					
	7	1	5,9	6,8	4	2,3
B ₉ H ₁₃ [NH(C ₂ H ₅) ₂]	-16.4 (150)	-3.5 (132)		(19.2) ^a		40.0 (142)
1,2,3,7-D ₄ B ₉ H ₉ [NH(C ₂ H ₅) ₂]	-16.5	-3.8		(19.3) ^a		40.0
B ₉ H ₁₃ [S(C ₆ H ₅) ₂]	-17.5 (138)	-4.0 (129)	14.4 (138)	21.8	25.9 (131)	38.8 (147)
7-CH ₃ OB ₉ H ₁₂ [S(CH ₃) ₂]	-37.7	-5.3		(23.8) ^a		42.3 (150)
B ₉ H ₁₃ [NH ₃]	-15.3 (151)	-4.7 (139)	17.5 (158)		22.8 (144)	40.0 (149)

^a Peak maxima.

The spectra were calibrated with an audio side band of known frequency. Integrations were done manually with a planimeter.

Wide-band, white-noise heteronuclear spin decoupling was accomplished by monitoring 32.1 MHz while irradiating at 100 MHz with a decoupler built by A. O. Clouse of Indiana University. A single-frequency spin-tickling experiment was also carried out using this apparatus.

The 70.6-HMz ¹¹B nmr spectra were obtained on a Varian HR-220 spectrometer with an experimental boron probe built by A. O. Clouse based on the design of the standard Varian proton probe. The spectra were obtained by a digitized linear sweep of the main radiofrequency carrier developed by a Hewlett-Packard 5100B frequency synthesizer. The receiver local oscillator was replaced with a coherent phase-locked difference frequency which was maintained at precisely 5 MHz removed from the detection frequency. This gives a capability of greater than 20-kHz linear sweep.

Results and Discussion

The ¹¹B nmr spectra of a series B₉H₁₃X (X = S(CH₃)₂, S(CH₂CH₃)₂, pyridine, P(C₆H₅)₃, NCS⁻,

(10) B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 626 (1962).

(11) J. Plesek, S. Hermanek, and B. Stibr, *Collect. Czech. Chem. Commun.*, **35**, 344 (1970).

(12) J. Dadok, Abstracts, 10th Experimental NMR Conference, Pittsburgh, Pa., Feb 1969; J. Dadok, R. F. Sprecher, A. A. Bothner-By, and T. Link, Abstracts, 11th Experimental NMR Conference, Pittsburgh, Pa., April 1970.

(13) The conversion was made by setting $\delta_{\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2} = \delta_{\text{B}(\text{OCH}_2)_3} - 19.0$. This is a refined conversion factor as measured *via* a linear digitized sweep at 70.6 MHz.

TABLE I
32.1-MHz ¹¹B NMR DATA OF B₉H₁₃(LIGAND) DERIVATIVES

Compd	Chem shifts of boron positions ^a			
	7	1	5,9; 6,8; 4	2,3
B ₉ H ₁₃ [S(CH ₃) ₂]	-17.9 (154) ^b	-4.9 (132)	(14.0, 19.1, 24.2) ^c	38.6 (154)
B ₉ H ₉ D ₄ [S(CH ₃) ₂]	-17.3	-4.7	(14.7, 19.8, 24.5)	39.1
B ₉ H ₁₂ Br[S(CH ₃) ₂]	-18.1 (148)	-9.7 (148)	(13.1, 18.2, 23.1)	36.5 (149)
B ₉ H ₁₃ (CH ₃ CN)	-16.5 (160)	-4.2 (141)	(13.4, 17.8, 25, 30.0)	39.2 (148)
B ₉ H ₁₃ (NCS ⁻)	-16.8 (145)	-5.9 (136)	(12.6, 17.5)	34.1 (147)
B ₉ H ₁₃ (py)	-18.3 (140)	-5.5 (135)	(10.8, 14.3, 18.6)	34.2 (147)
B ₉ H ₁₃ (NH ₂ CSCH ₃)	-17.0 (138)	-3.6 (134)	(14.2, 18.4, 24, 28.3)	38.6 (149)

^a ±0.67 ppm, chemical shifts relative to BF₃·O(C₂H₅)₂ = 0 ppm. ^b J_{11B-H} ± 10 Hz. ^c Peak maxima.

TABLE II
70.56-MHz ¹¹B NMR DATA OF B₉H₁₃(LIGAND)₃ DERIVATIVES

Compd	Chem shifts of boron positions					
	7	1	5,9	6,8	4	2,3
B ₉ H ₁₃ [S(CH ₃) ₂]	-17.8 ^a (150) ^b	-5.0 (135)	15.7 (140)	21.4 (130)		39.4 (150)
B ₉ H ₁₃ [P(C ₆ H ₅) ₃] ^c	-18.5	-4.9 (135)	13.8 (140)	20.2 (130)	34.2 (145)	37.4 (145)

^a ±0.15 ppm. ^b J_{11B-H} ± 5 Hz. ^c As obtained *via* 20 scans on a Varian C-1024 time-averaging computer.

NH₂CSCH₃, CH₃CN, NH₃, and NH(C₂H₅)₂) were found to be quite similar to the characteristic pattern seen at 19.3 MHz.⁷ They consist of two low-field doublets, a broad multiplet, and a high-field doublet of relative intensities 1:1:5:2. The chemical shift and coupling constant data are presented in Tables I–III.

As shown in Figure 1, B₉H₁₃X consists of six non-equivalent boron environments. These are B(1), B(2,3), B(4), B(5,9), B(7), and B(6,8). This should give rise, barring hydrogen atom exchange, to a boron nmr spectrum containing five doublets of areas 1:1:1:2:2 and a triplet of area 2. The spectrum of 1,2,3,7-D₄B₉H₉[NH(C₂H₅)₂] shown in Figure 2B contains a singlet at highest field of area 2 which must be associated with B(2,3) and two singlets at low field assigned to B(1) and B(7) in an indeterminate manner. The same results were also obtained with 1,2,3,7-D₄B₉H₉[S(CH₃)₂].

The degradation of 2-BrB₁₀H₁₂[S(CH₃)₂]₂ in methanol recently reported by Plesek and coworkers is believed to produce 7-CH₃OB₉H₁₂[S(CH₃)₂] as indicated by an X-ray structure study.¹¹ Under slightly different conditions we were able to isolate 1-BrB₉H₁₂[S(CH₃)₂] from degradation of 2-BrB₁₀H₁₂[S(CH₃)₂]₂ in ethanol. The 32.1-MHz spectrum of BrB₉H₁₂[S(CH₃)₂] shown in Figure 3B and the 80.2-MHz spectrum of 7-CH₃-

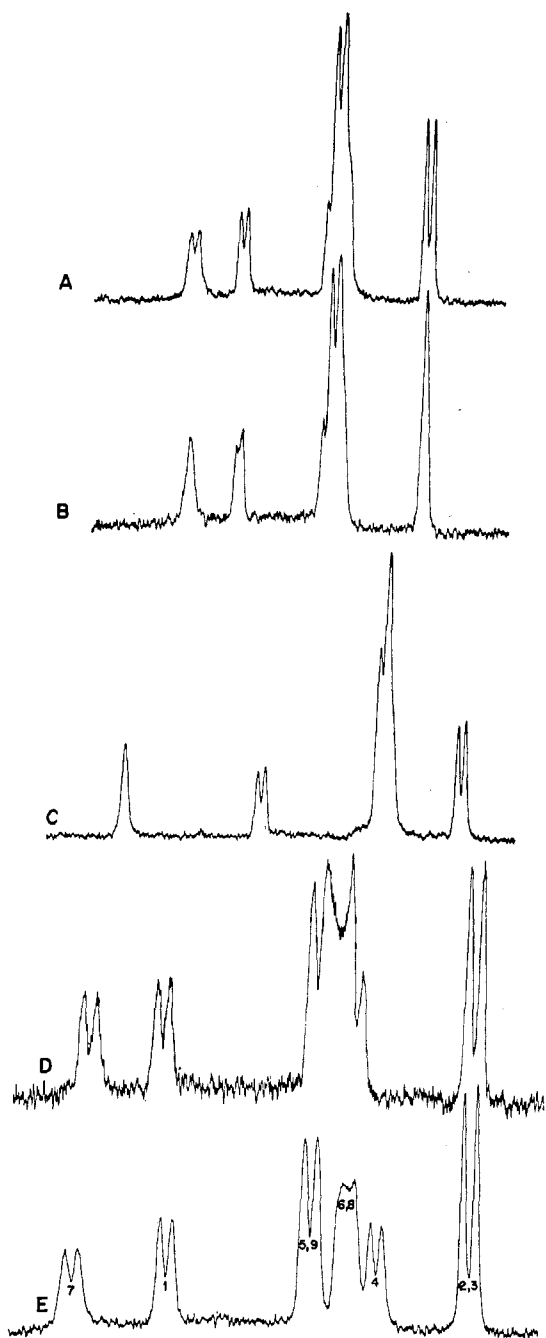


Figure 2.—The 80.2-MHz ^{11}B nmr spectra in CH_2Cl_2 of (A) $\text{B}_9\text{H}_{13}[\text{NH}(\text{C}_2\text{H}_5)_2]$, (B) $1,2,3,7\text{-D}_4\text{B}_9\text{H}_9[\text{NH}(\text{C}_2\text{H}_5)_2]$, (C) $7\text{-CH}_3\text{OB}_9\text{H}_{12}[\text{S}(\text{CH}_3)_2]$, (D) $\text{B}_9\text{H}_{13}[\text{NH}_3]$, and (E) $\text{B}_9\text{H}_{13}[\text{S}(\text{C}_2\text{H}_5)_2]$.

$\text{OB}_9\text{H}_{12}[\text{S}(\text{CH}_3)_2]$ shown in Figure 2C clearly suggest that the signal of unit area at lowest field is associated with B(7) and that the signal of unit area next to B(7) at higher field is associated with B(1).

In many of the derivatives, resonances of the remaining five boron atoms overlap to such a degree that measurement of chemical shifts and coupling constants was not possible. The spectrum in Figure 2D of $\text{B}_9\text{H}_{13}[\text{NH}_3]$ is an example of this problem. With heteronuclear spin decoupling it was possible sufficiently to simplify the 32-MHz ^{11}B nmr spectrum of $\text{B}_9\text{H}_{13}[\text{S}(\text{C}_2\text{H}_5)_2]$ so as to confirm the existence of six distinct boron environments and to demonstrate that B(4) was the farthest upfield component of the multiplet of area 5. In the 80.2-MHz spectrum of the

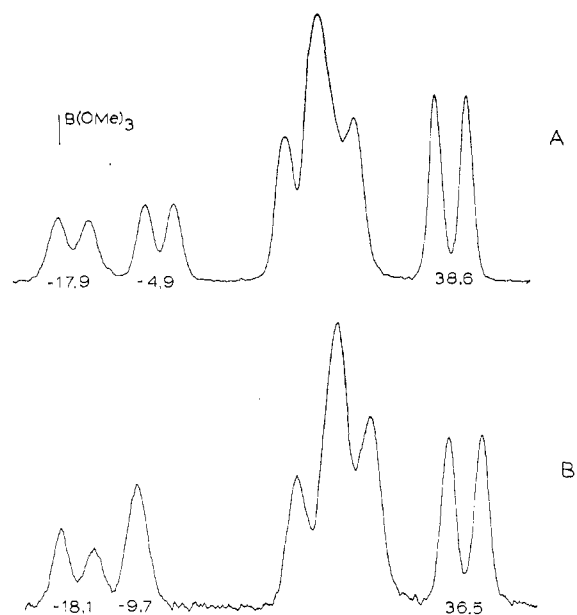


Figure 3.—The 32.1-MHz ^{11}B nmr spectra in acetone of (A) $\text{B}_9\text{H}_{13}[\text{S}(\text{CH}_3)_2]$ and (B) $\text{B}_9\text{H}_{12}\text{Br}[\text{S}(\text{CH}_3)_2]$.

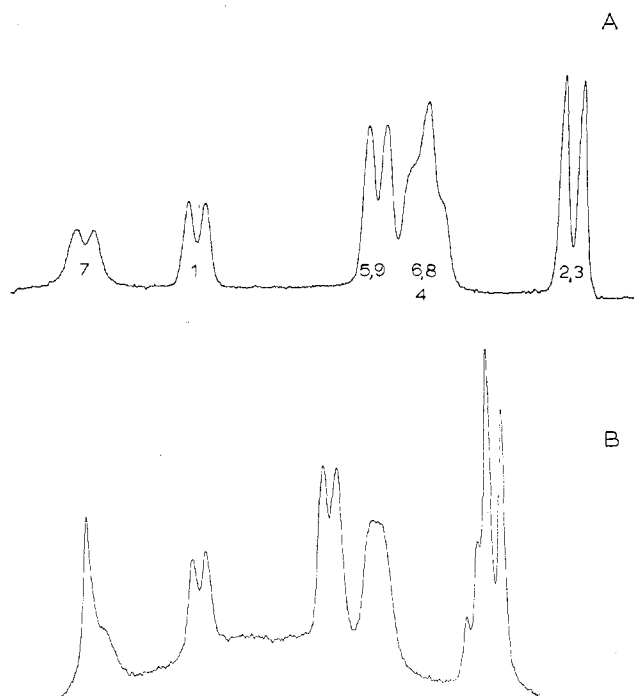


Figure 4.—The 70.56-MHz ^{11}B nmr spectra in acetone of (A) $\text{B}_9\text{H}_{13}[\text{S}(\text{CH}_3)_2]$ and (B) $\text{B}_9\text{H}_{13}[\text{P}(\text{C}_6\text{H}_5)_3]$ (the singlet signal at lowest field is a borate impurity).

diethyl sulfide derivative (Figure 2E), the doublet of area 1 at 25.9 ppm is associated with B(4). We have observed a substantial upfield shift in the resonance of the B(4) position as the strength of the ligand attached to this position was varied. In the ^{11}B nmr spectrum of $\text{B}_9\text{H}_{13}[\text{P}(\text{C}_6\text{H}_5)_3]$ (Figure 4B) the doublet attributed to B(4) now appears to be overlapped with the doublet attributed to B(2,3) at highest field.

The doublet of area 2 at 14.4 ppm in the spectrum of $\text{B}_9\text{H}_{13}[\text{S}(\text{C}_2\text{H}_5)_2]$ (Figure 2E) appears to be best assigned to B(5,9). The broadened signal of area 2 centered at 21.8 ppm does not show the expected triplet structure and indicates that the BH_2 groups at

B(6,8) may behave in an unusual fashion, probably involving hydrogen-exchange and/or spin-coupling processes. It should be noted that the assignments suggested here are quite similar to the results found earlier for $B_{10}H_{12}(\text{ligand})_2$ derivatives.³

The X-ray crystal structure of $B_9H_{14}^-$ has been shown to fit a 2613 topological representation and to be different than that of $B_9H_{13}(\text{CH}_3\text{CN})$.¹⁴ At room temperature in solution both the ^{11}B and proton nmr spectra suggest that $B_9H_{14}^-$ is undergoing a relatively fast hydrogen atom exchange process. There are three boron atom environments of area 3 each with one nonexchanging hydrogen attached to each of the nine boron atoms and five rapidly exchanging hydrogen

(14) N. N. Greenwood, H. J. Gysling, J. A. McGinnety, and J. D. Owen; *Chem. Commun.*, 505 (1970).

atoms. In the case of the anionic derivative $B_9H_{13}(\text{NCS})^-$ a ^{11}B nmr spectrum quite similar to that of the neutral $B_9H_{13}(\text{ligand})$ derivatives was observed. Thus in this case the rapid exchange process described above is not operative.

Acknowledgment.—It is a great pleasure to acknowledge the assistance of A. O. Clouse of the Indiana University nmr laboratories, both in the design of equipment and in the facilitation of this work. This work was generously supported by the Office of Naval Research. The research conducted at the University of Pittsburgh was partially supported by National Science Foundation Grant GP 8321, and the 80.2-MHz spectrometer was constructed under Grant FR-00292 from the National Institutes of Health.

CONTRIBUTION FROM THE INSTITUTE OF INORGANIC CHEMISTRY,
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Ternary Complexes in Solution. IX. The Stability-Increasing Effect of the Pyridyl and Imidazole Groups on the Formation of Mixed-Ligand-Copper(II)-Pyrocatecholate Complexes^{1,2}

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The stability constants of the ternary Cu^{2+} complexes containing pyrocatecholate and, as a second ligand, 2,2'-bipyridyl, 4-(2'-pyridyl)imidazole, 2-picolyamine, 4-aminomethylimidazole, and ethylenediamine were determined by potentiometric titration. For the equilibrium $\text{Cu}(\text{pyrocatecholate})_2^{2-} + \text{Cu}(\text{amine})_2^{2+} \rightleftharpoons 2\text{Cu}(\text{pyrocatecholate})(\text{amine})$ the corresponding constants are $\log X = 6.15, 5.47, 4.64, 3.46,$ and 2.65 ($I = 0.1$; temperature 25°). All five mixed-ligand complexes are more stable than one would expect on purely statistical grounds ($\log X = 0.6$). The importance of the π system of the N ligand for the stability of the ternary complexes is obvious from the given series. The imidazole group, often suggested as a binding site for metal ions in enzymes, clearly has qualities similar to those of the pyridyl group; *i.e.*, the stability of ternary Cu^{2+} complexes containing these groups is increased.

With ligands containing O as donor atoms, Cu^{2+} -2,2'-bipyridyl forms ternary complexes that are more stable than the corresponding binary Cu^{2+} -O ligand 1:1 complexes.^{2,4-6} In addition, the Cu^{2+} -2,2'-bipy 1:1 complex has discriminating qualities: O rather than N ligands are more stably bound.^{2,5} For the Cu^{2+} -histamine 1:1 complex a similar but less pronounced behavior was found.⁷

It was suggested^{2,5} that the "aromaticity" of the ligand containing N as donor atoms is important for the stability of the resulting mixed-ligand complexes. To test this hypothesis, the following series of bidentate N ligands was chosen and the stability of their ternary complexes with Cu^{2+} and pyrocatecholate was deter-

mined by potentiometric titrations: 2,2'-bipyridyl,⁸ 4-(2'-pyridyl)imidazole, 2-picolyamine, 4-aminomethylimidazole, and ethylenediamine.⁸

One way to characterize the stability of ternary complexes is according to eq 1, *i.e.*, by comparing the difference in stability between eq 2 and 3.⁹ The connection

$$\Delta \log K = \log K^{\text{Cu}(\text{NL})_{\text{Cu}(\text{NL})\text{pyr}}} - \log K^{\text{Cu}_{\text{Cu}(\text{pyr})}} \quad (1)$$

$$K^{\text{Cu}(\text{NL})_{\text{Cu}(\text{NL})\text{pyr}}} = \frac{[\text{Cu}(\text{NL})\text{pyr}]}{[\text{Cu}(\text{NL})][\text{pyr}]}$$

$$K^{\text{Cu}_{\text{Cu}(\text{pyr})}} = \frac{[\text{Cu}(\text{pyr})]}{[\text{Cu}][\text{pyr}]} \quad (3)$$

between eq 2 and 4 is given by eq 5. Another way to

$$\beta^{\text{Cu}_{\text{Cu}(\text{NL})\text{pyr}}} = \frac{[\text{Cu}(\text{NL})\text{pyr}]}{[\text{Cu}][\text{NL}][\text{pyr}]} \quad (4)$$

$$\log K^{\text{Cu}(\text{NL})_{\text{Cu}(\text{NL})\text{pyr}}} = \log \beta^{\text{Cu}_{\text{Cu}(\text{NL})\text{pyr}}} - \log K^{\text{Cu}_{\text{Cu}(\text{NL})}} \quad (5)$$

characterize the stability of ternary complexes is by eq 6 and 7.

$$X = \frac{[\text{Cu}(\text{NL})_2 + \text{Cu}(\text{pyr})_2]}{[\text{Cu}(\text{NL})\text{pyr}]^2 / ([\text{Cu}(\text{NL})_2][\text{Cu}(\text{pyr})_2])} \quad (6)$$

$$\log X = 2 \log \beta^{\text{Cu}_{\text{Cu}(\text{NL})\text{pyr}}} - (\log \beta^{\text{Cu}_{\text{Cu}(\text{NL})_2}} + \log \beta^{\text{Cu}_{\text{Cu}(\text{pyr})_2}}) \quad (7)$$

(1) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969; see Abstract No. BIOL 53. This work was supported by a research grant from the Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung.

(2) Part VIII: R. Griesser and H. Sigel, *Inorg. Chem.*, **9**, 1238 (1970).

(3) Correspondence should be addressed to this author.

(4) G. A. L'Heureux and A. E. Martell, *J. Inorg. Nucl. Chem.*, **28**, 481 (1966).

(5) H. Sigel, *Chimia*, **21**, 489 (1967).

(6) The terms "O ligand" and "N ligand" are used for ligands containing O or N as donor atoms.

(7) P. R. Huber, R. Griesser, B. Prijs, and H. Sigel, *Eur. J. Biochem.*, **10**, 238 (1969).

(8) The 2,2'-bipyridyl- Cu^{2+} -pyrocatecholate² and the ethylenediamine- Cu^{2+} -pyrocatecholate⁷ systems were already investigated in different connections; these results^{2,7} are also used now.

(9) Abbreviations: pyrocatecholate, pyr; ligand with N as donor atom, NL; general ligand, L. Charges are omitted in all equations.