Bis(pyridine)boronium Salts. Syntheses and Formation Kinetics

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Abstract: Salts of bis(pyridine)boronium ion have been synthesized in pyridine by four routes: from trimethylamine borane and iodine, from trimethylamine borane and bis(pyridine)mercury(II) chloride, from sodium borohydride and iodine, and from trimethylamine chloroborane. In addition, the B-deuterated ion has been prepared. The reaction between trimethylamine borane and iodine exhibits a deuterium isotope effect, which was established from competitive rates and from the reaction rates of the hydrogen and deuterium compounds (k_H/k_D = 2.0). A reaction mechanism is discussed.

Boronium salts, where two tertiary amines are coordinated to a BH_2^+ group, have been reported by Muetterties.[1] The basic structure was produced from an amine borane by reaction with an ammonium salt or, alternately, with diborane or $B_{12}H_{12}^{2-}$ salts. Either method requires relatively high temperatures and the use of high pressure. In our hands, the first method proved to be quite sensitive to reaction conditions, producing yield-reducing side reactions. The second method suffers from relatively low yields (~25%) and from the convenience of handling a reactive gas or preparing the intermediate borane anion.

We wish to report several new synthetic approaches to boronium salts, exemplified by the bis(pyridine)-boronium ion, which allow synthesis from readily obtained starting materials, under mild and convenient conditions, and in high yield.

Experimental Section

Materials. Trimethylamine borane was used as obtained from Callery Chemical Co. Some lots were purified by sublimation. Sodium borohydride and sodium borodeuteride were supplied in good purity by Metal Hydrides, Inc. All other compounds were reagent-grade materials and were used without further purification. Trimethylamine monochloroborane was prepared in 50% yield from trimethylamine borane and concentrated aqueous HCl mixed with benzene.[2,3] It was recrystallized from CCl_4 by slow addition of hexane: mp 82–84°, lit.[4] 85°. Alternately, the material could be prepared by passing anhydrous HCl into a trimethylamine borane solution in benzene.

Diborane-d_6 was prepared on the vacuum line from 1 g of sodium borodeuteride and boron trifluoride in diglyme solution.[5] The gas was allowed to react with excess trimethylamine to afford deuterated trimethylamine borane. After vacuum sublimation it melted sharply at 91°. The infrared spectrum agreed well with the published data.[6] The relative proportions of B–H and B–D bonds were established by comparison of the absorbancies at 2370 and 1790 cm^{-1} after calibration with a known mixture. The compound was 93% deuterated.

Preparation of Bis(pyridine)boronium Ion. From Trimethylamine Borane and Iodine. Trimethylamine borane, 3.64 g (50.0 mmoles), was dissolved in 30 ml of pyridine, and solid iodine, 12.7 g (50.2 mmoles), was added in small portions over a 15-min period. An exothermic reaction started immediately and was finished after 1 hr while warming the mixture gradually to a final temperature of 70°. After cooling, the precipitate of trimethylammonium iodide was filtered off, and the filtrate was evaporated at room temperature, affording 14.7 g of bis(pyridine)boronium iodide (99% yield). The ammonium salt after washing with benzene and a small amount of ether weighed 8.75 g (94% yield). The identity of the ammonium salt was established by its infrared spectrum and its iodide analysis. Reaction had thus proceeded according to the equation

$$N(CH_3)_3BH_3 + I_2 + 2C_5H_5N \longrightarrow (CH_3)_3NH^+I^- + (C_5H_5N)BH_2{}^+I^- \quad (1)$$

2. From Trimethylamine Borane and Bis(pyridine)mercury(II) Chloride. Trimethylamine borane, 3.76 g (56 mmoles), and mercury(II) chloride, 13.06 g (48.1 mmoles), were heated with 50 ml of pyridine to light reflux for 5 hr. During this period the solution turned cloudy and eventually deposited liquid mercury. After filtering off the metallic mercury (9.266 g, 96% recovery), 20 ml of benzene and 20 ml of carbon tetrachloride were added to the filtrate, yielding 14.42 g of light yellow solid as a precipitate. On adding excess potassium hexafluorophosphate to a water solution of this solid there was recovered, after washing with water and ether, 5.40 g (26.2 mmoles) of $(C_5H_5N)_2BH_2PF_6$ for a 55% yield of boronium salt. The compound was identical in spectrum and melting point with preparations from the iodide salt.

3. From Sodium Borohydride and Iodine. (a) Sodium borohydride (94% hydride purity), 1.80 g (44.8 mmoles), was slurried with 25 ml of pyridine. While this solution was stirred in an ice bath, an 0.00984 *M* iodine solution was very slowly added. The iodine color was discharged immediately while a gas, presumably hydrogen, evolved. After 22.5 ml (22.2 mmoles) of iodine solution had been added, the reaction rate of iodine decreased abruptly and gas evolution ceased. The solution was now heated while more iodine was added; a persistent iodine color was obtained after an additional 44.5 ml (43.7 mmoles) of iodine solution had been added. The amounts of iodine used correspond closely to the quantities calculated from the equations representing two successive and separated reactions steps.

$$2BH_4^- + 2C_5H_5N + I_2 \longrightarrow 2C_5H_5NBH_3 + 2I^- + H_2 \quad (2)$$

$$C_5H_5NBH_3 + I_2 + 2C_5H_5N \longrightarrow (C_5H_5N)_2BH_2^+ + C_5H_5NH^+ + 2I^- \quad (3)$$

(b) Accordingly, in a similar experiment, the reaction was stopped after the first stage, the excess pyridine was evaporated, and the resulting residue of white solid and yellow liquid was extracted with carbon tetrachloride. After evaporation of the solvent there was obtained a 99% yield of pyridine borane, identical in infrared spectrum with an authentic sample. The solid, insoluble in carbon tetrachloride, was sodium iodide contaminated with water and pyridine.

Bis(pyridine)boronium iodide was isolated from reaction 3 by precipitating it with carbon tetrachloride. Preparations by this procedure always contained varying amounts of carbon tetrachloride which could not be removed by pumping.

4. From Trimethylamine–Monochloroborane. Trimethylamine monochloroborane, 0.551 g (5.19 mmoles), was refluxed with 15 ml of pyridine for 45 min. The mixture was evaporated to dryness and the water-soluble residue (0.954 g) was converted to the hexafluorophosphate salt by precipitation with excess NH_4PF_6 in 15 ml of water (crude yield, 0.936 g). A portion of this was recrystallized from water to give pure $(C_5H_5N)_2BH_2PF_6$, mp 114.5–115°, in 41%

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[1] (a) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964); (b) E. L. Muetterties, *Pure Appl. Chem.*, **10**, 53 (1965).

[2] K. Borer and J. Deuring, British Patent 881,376 (Nov 1, 1961).

[3] J. W. Wiggins, Ph.D. Dissertation, University of Florida, 1966.

[4] H. Noeth and H. Beyer, *Chem. Ber.*, **93**, 2251 (1960).

[5] Vapor pressure, 239 mm at −112°; lit. 238.5 mm [A. B. Burg, *J. Am. Chem. Soc.*, **74**, 1340 (1952)].

[6] B. Rice, R. J. Galiano, and W. J. Lehmann, *J. Phys. Chem.*, **61**, 1222 (1957).

Table I. Analyses (%)

		C	H	N	B	P or As	I or F	Mp, °C
$C_{10}H_{12}N_2BI$	Calcd	40.31	4.06	9.40	3.63		42.60	
	Found	40.08	4.28	9.13	3.49		41.76	120–125
$C_{10}H_{12}N_2BPF_6$	Calcd	38.01	3.82	8.87	3.42	9.80	36.05	
	Found	37.92	3.84	8.92	3.66	9.52	35.80	116
$C_{10}H_{12}N_2BAsF_6$	Calcd	33.37	3.36	7.78	3.01	20.87	31.67	
	Found	33.60	3.48	7.61	3.20	20.97	31.47	110.5–111

recovery. The maximum yield of chloride salt, according to the eq 4 was thus 88%; the minimum over-all yield of pure PF_6^- salt was 25%.

$$N(CH_3)_3BH_2Cl + 2C_5H_5N \longrightarrow N(CH_3)_3 + (C_5H_5N)_2BH_2^+Cl^- \tag{4}$$

Derivatives. The halide salts are very soluble in water as well as in many organic solvents (alcohols, acetone, acetonitrile, chloroform, methylene chloride) but insoluble in carbon tetrachloride, ether, or pentane. The complex fluorides show similar solubility relations but are much less soluble in cold water.

The halides readily absorb water from the atmosphere. The anhydrous iodide (0.5143 g, 1.72 mmoles) was exposed in a closed container to saturated water vapor at room temperature. After 30 hr the sample had come to constant weight, 0.5438 g. The calculated weight for a monohydrate is 0.5453 g. Simultaneously there appeared in the infrared spectrum a doublet at 3500 and 3430 cm^{-1} and a sharp band at 1580 cm^{-1}, and two bands at 760 and 740 cm^{-1}. The first three bands apparently correspond to the stretching and bending modes of water, respectively, whereas the latter two absorptions may be caused by librational modes of lattice water.[7] The absorbed water could be removed quantitatively by evacuation over P_2O_5.

The iodide or chloride was readily converted to the less soluble perchlorate (mp 97–99°), hexafluorophosphate, or hexafluoroarsenate by precipitating these salts from aqueous solution with $NaClO_4$, NH_4PF_6, or $KAsF_6$, respectively. The latter two salts are easily recrystallized from hot water. The chloride salt was obtained from the iodide by reaction with a slight excess of mercury(II) chloride in aqueous solution, which resulted in precipitation of HgI_2. Excess Hg^{2+} was removed immediately by shaking with metallic mercury in order to avoid oxidation of the boronium ion. On evaporation of the filtered solution, the chloride was obtained in 30% yield as the hydrated salt, mp 59–62°.

On shaking aqueous solutions of the iodide with CCl_4, there resulted a white precipitate which proved to be very similar to the product obtained when the boronium salt was precipitated with CCl_4 from pyridine solution. The materials showed all the infrared absorption bands of the pure boronium salt but contained from 0.25 to 0.9 mole of CCl_4 per mole of $(C_5H_5N)_2BH_2I$. Carbon tetrachloride could be removed either by heating under vacuum above the melting point (110–125°) or by distilling a solution; depending on the water content of the system, either the hydrate or the anhydrous salt was thus obtained.

Preparation of Deuterated Bis(pyridine)boronium Hexafluorophosphate. Trimethylamine borane-d_3 (1.00 mmole) in 5 ml of pyridine was allowed to react with iodine (0.98 mmole) for 40 hr at 25°. After evaporating the solvent below room temperature, the resulting iodide salt was converted to the hexafluorophosphate derivative in the usual manner. The amount of deuteration on boron in the recrystallized product (mp 114.5–115°) was the same as in the starting material, as evidenced by the infrared spectrum.

In an abortive attempt to deuterate the boronium salt by exchange, 1.15 mmoles of the iodide salt was dissolved in 1 ml of D_2O; the relative intensity of the B–H absorption at 2480 cm^{-1} remained unchanged over 24 hr. at room temperature. Neither did there appear an absorption at 1900 cm^{-1}, characteristic of B–D, even when a solution acidified (pH $\sim$1) with thionyl chloride was left at room temperature for 3 days.

Characterization. All the boronium salts had similar infrared spectra, except for the expected differences caused by the known absorptions of the complex anions. The main features are the two bands, 2480 and 2380 cm^{-1}, showing relatively high wavenumbers for B–H bonds, which are shifted to 1900 and 1760 cm^{-1}, respectively, in the deuterated compound. The B–H deformations appear at 1160 (B–D, 915) and 1065 cm^{-1} (B–D, probably masked by anion and solvent absorptions). In addition, a sharp absorption at 1640 cm^{-1} indicates the presence of the pyridine ring.

In the ultraviolet spectrum there are three bands in all the salts with similar molar absorptivities, a: 2538 A, $a = 6.90 \times 10^3$; 2591 A, $a = 7.58 \times 10^3$; 2657 A, $a = 5.01 \times 10^3$. Elemental analyses are given in Table I.

The cation, like the bis(trimethylamine) compound previously reported,[1] is stable toward acid or base; no change in the ultraviolet spectrum was noticed in 0.1 M HCl or 0.1 M NaOH, even after a week at room temperature.

The B^{11} nuclear resonance spectra were kindly obtained by Dr. Brey of this department at 19.3 Mc in CH_2Cl_2. The undeuterated and deuterated salts showed identical shifts of +16.2 ppm relative to trimethyl borate. Because of the broadness of the resonance, the B–H and B–D coupling constants could not be determined.

The proton spectrum, obtained with a Varian A-60A spectrometer at ambient temperature, showed the expected pattern for the pyridine-ring hydrogens: a doublet, a triplet, and a triplet with relative integrated intensities of 2.0:1.0:2.0. The resonances had considerable fine structure and were, in water solution, centered about −8.78, −8.35, and −7.35 ppm, respectively, relative to external tetramethylsilane. In $CDCl_3$ with internal tetramethylsilane, the resonances appeared at −9.08, −8.38, and −8.00 ppm, respectively. No resonances arising from boron-attached protons could be detected in either solvent.[8]

Deuterium Isotope Effect in Trimethylamine Borane–Iodine Reaction. 1. Competitive Reactions. Normal and deuterated (1.00 mmole of each) trimethylamine boranes in 5 ml of pyridine were mixed with 0.99 mmole of iodine; after 8 hr at room temperature (24°) the iodine color had disappeared. Following removal of the solvent below room temperature, the hexafluorophosphate salt was prepared as above but not recrystallized, and the deuterium content was determined by an infrared analysis of CH_2Cl_2 solutions from the ratio of absorbancies at 2460 and 1890 cm^{-1}.[9] In a second experiment, a similar mixture was heated for 3.5 hr at 90° prior to adding iodine to the cooled solution. The reaction in this instance was completed in less than 3.5 hr. The results are given in Table II and are compared with the results calculated from the rate constants.

Table II.

Initial concn, mmoles		I_2,	Final ratio
BH_3	BD_3[a]	mmoles	BH:BD
1.05	1.04	0.99	1.84
1.01	0.96	0.99	1.72[c]
1.00	1.00	1.00	1.77[b]

[a] 93%. [b] Calculated from k_H/k_D. [c] Heated prior to reaction.

2. Specific Rates in Pyridine Solution. Weighed amounts of normal or deuterated trimethylamine borane were dissolved in 3.00 ml of pyridine in the absorption cell, 100 μl of approximately 0.2 M I_2 in pyridine was immediately injected, and the change of absorbance at 400 mμ was recorded using a Beckman DB-G spectrophotometer with scale expansion attachment and a logarithmic recorder. The data gave an excellent fit for a reaction first order in iodine concentration, over a 15-fold change, provided that the mixture was first allowed to react completely, and data were taken

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[7] J. van der Elsken and D. W. Robinson, *Spectrochim. Acta*, 17, 1249 (1961).

[8] In bis(trimethylamine)boronium iodide the quartet arising from the BH_2 group is also very broad and barely detectable.

[9] The accuracy of the measurement was checked by calibration with mixtures of known deuterium content.

Table III

Compound	Concn, *M*	1st-order rate constant $\times 10^4$, $sec^{-1\,a}$	2nd-order rate constant $\times 10^2$, l. $mole^{-1}$ sec^{-1}
$(CH_3)_3NBH_3$	0.054	10.0	1.85
		10.3	1.91
$(CH_3)_3NBH_3$	0.038	7.21	1.90
		7.55	1.99
$(CH_3)_3NBH_3$	0.028	5.17	1.85
		5.46	1.95
		Average	1.90
$(CH_3)NBD_3$	0.054	4.89	0.906
		5.24	0.970
		Average	0.938
		k_H/k_D =	2.03

[a] 24 ± 1°.

after a second portion of iodine was injected.[10] The rate dependence on trimethylamine borane concentration agreed well with a first-order dependence on this component. The results are listed in Table III.

Discussion

The formation of bis(pyridine)boronium ion from sodium borohydride occurs *via* a clear-cut reaction sequence involving hydride transfer from borohydride to iodine,[11] trapping of the BH_3 group by the solvent base, and a second similar sequence involving the intermediate pyridine borane. Hydride transfer to the iodine species in pyridine results in iodide ion and pyridinium ion, which also produces pyridine borane in a side reaction with borohydride.[12] The processes can be represented by

$$BH_4^- + I_2 + 2py \longrightarrow pyBH_3 + pyH^+ + 2I^-$$

$$BH_4^- + pyH^+ \longrightarrow pyBH_3 + H_2$$

$$pyBH_3 + I_2 + py \longrightarrow (py)_2BH_2^+ + pyH^+ + 2I^-$$

The great difference in reactivity between BH_4^- and $pyBH_3$ toward electrophilic attack by either iodine or pyH^+ makes it possible to observe a clean separation of the reaction steps. The data also imply that the borohydride–pyridinium reaction proceeds more rapidly than the pyridine borane–iodine reaction; otherwise, more than the observed stoichiometric ratio of iodine should have been used at the point where hydrogen evolution had stopped.

The foregoing suggests a somewhat similar sequence in the reaction of trimethylamine borane with iodine. But since in this reaction the bispyridine ion is obtained in high yield, the question arises as to which stage of the reaction the necessary displacement of trimethylamine occurs: before or after attack on the B–H bond by iodine.

In separate experiments it was verified that pyridine borane reacts with the halogen much more rapidly than trimethylamine borane.[13] Thus, the displacement would have to be rate determining if it occurred prior to reaction with iodine (eq 5)

$$N(CH_3)_2BH_3 \xrightarrow[\text{slow}]{\text{py}} pyBH_3 \xrightarrow[\text{fast}]{I_2,\ \text{py}} (py)_2BH_2^+ \qquad (5)$$

The alternate path would produce $N(CH_3)_3BH_2I$, $N(CH_3)_3pyBH_2^+$, or $pyBH_2I$ as intermediates, and, finally, $(py)_2BH_2^+$ (eq 6). In view of the results obtained with trimethylamine chloroborane, the proposed iodoborane intermediates could hardly be expected to survive long without iodide solvolysis in the reaction medium, but one might expect the mixed boronium ion to be capable of isolation.[14] Nevertheless, it was not possible to isolate this material even from mixtures which were not heated. If this compound indeed appears as an intermediate, it is also solvolyzed rather rapidly.[15]

$$N(CH_3)_3BH_3 \xrightarrow{I_2,\ \text{py}} \begin{array}{l} N(CH_3)_3BH_2I \\ \text{or } pyBH_2I \\ \text{or } N(CH_3)_3pyBH_2^+\ I^- \end{array} \xrightarrow{\text{py}} (py)_2BH_2^+I^- \qquad (6)$$

The experiments with the deuterated borane, however, do allow a distinction between paths 5 and 6. The rate-determining transamination should not be sensitive to deuterium substitution on boron, whereas a hydride transfer should exhibit a pronounced isotope effect.[16] Moreover, in eq 5 the rate of disappearance of iodine should be independent of iodine concentration, but path 6 would predict a simple rate dependence on iodine. The experimental results clearly show that the rate depends on the iodine concentration (first order) and that there is a large deuterium isotope effect (k_H/k_D = 2.0). The directly determined rate constants lead to a calculated isotope distribution in the product from the competitive reactions in most satisfactory agreement with the observed distribution. It is therefore concluded that the initial reaction step is a hydride abstraction from trimethylamine borane and that this step is the rate-determining one.

The maximum value for the ratio k_H/k_D can be estimated from the B–H and B–D stretching vibrations under the assumption that the rate constants differ primarily because of different zero-point energies in the ground state which are lost on stretching the bonds in the transition state. The ratio calculated from the experimental frequencies for trimethylamine borane is 4.4 at 25°. One can interpret the substantially lower experimental value, k_H/k_D = 2.0, as being the consequence of incomplete loss of zero-point energy in the transition state, corresponding to the retention of some bonding between boron and hydrogen. Nevertheless, the present value constitutes the largest isotope effect for reactions on B–H bonds which have come to our attention.[17,18]

It now seems plausible to view the reaction with the mercury(II) complex as analogous to the above examples: hydride transfer from the borane to the mer-

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(10) In the initial reaction log *A vs. t* plots had a slight curvature; the slope of log (rate) *vs.* log *A* plots indicated an apparent initial order of 0.8.

(11) G. F. Fueguard and L. H. Long, *Chem. Ind.* (London), 471 (1965), report a high yield of diborane from $NaBH_4$ and I_2 in diglyme.

(12) P. A. Chopard and R. F. Hudson, *J. Inorg. Nucl. Chem.*, **25**, 801 (1963); D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 395 (1963); H. Noeth and H. Beyer, *Chem. Ber.*, **93**, 928 (1960); G. W. Schaeffer and E. R. Anderson, *J. Am. Chem. Soc.*, **71**, 2143 (1949).

(13) Pyridine borane in fivefold excess over iodine reacted completely in 15 min; trimethylamine borane under the same conditions required more than 2.5 hr.

(14) Muetterties[1] reports displacement at 180° for 10 hr.

(15) We have prepared several salts of $NMe_3pyBH_2^+$; it is converted to $(py)_2BH_2^+$ in boiling pyridine within 5 min.

(16) K. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(17) k_H/k_D = 1.45 for H_2 elimination in $(CH_3)_2HNBH_3$: ref 3, to be published.

(18) k_H/k_D = 1.52 for hydrolysis of $pyB(C_6H_5)_2$: H. M. F. Hawthorne and E. S. Lewis, *J. Am. Chem. Soc.*, **80**, 4296 (1958).

cury atom, followed by decomposition of the complex into atomic mercury, the ligands, and a proton. The question whether the mercury-attached ligand can transfer simultaneously to the boron atom, or whether it leaves the reaction sphere, at present remains unresolved, but we hope to contribute in the future to the solution of this problem.

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Spectra and Structure of Some Transition Metal Poly(1-pyrazolyl)borates

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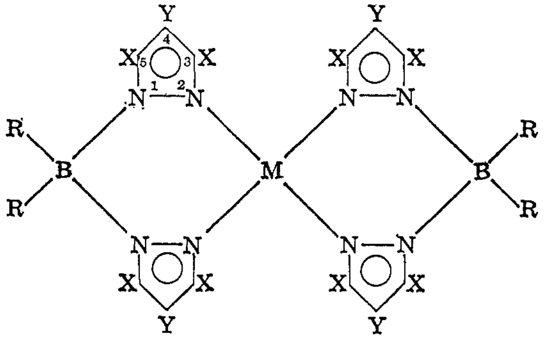
Abstract: Spectral and magnetic data are presented for a new family of transition metal chelates involving poly-(1-pyrazolyl)borate ligands. These molecules behave as univalent ligands which can be either bidentate or tridentate depending on the number of pyrazolyl groups. Neutral complexes with the ions Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} have been studied. The bidentate Ni^{2+} and Cu^{2+} complexes are essentially planar. Other complexes with bidentate ligands are tetrahedral. The tridentate ligands give rise to octahedral complexes. Thus the poly(1-pyrazolyl)borate ligands provide an opportunity for physical studies of a range of complexes with different geometries and different metal ions but with essentially constant ligand characteristics. The results of such a study are reported.

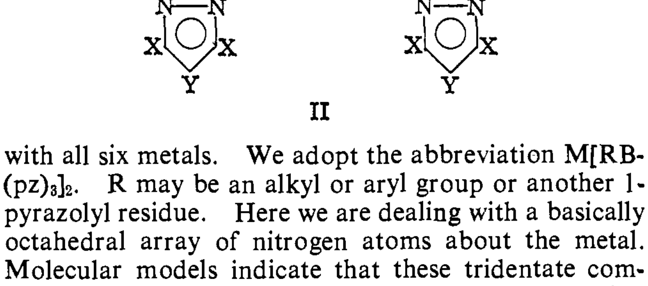
In another publication[1] the synthesis and properties of a number of poly(1-pyrazolyl)borate transition metal complexes have been reported briefly. The series of complexes with divalent transition metal ions is of particular interest in that these ligands offer the opportunity of forming chelates of the same metal ion with different geometries. In the present paper, nuclear magnetic resonance, magnetic susceptibility, and electronic spectral data are described for complexes with the ions Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. Both bidentate and tridentate ligands are involved, and the physical evidence presented suffices to characterize the geometries of the complexes. In the following paper the spin equilibria found with the Fe^{2+} complexes will be discussed in more detail.[2]

The complexes fall into two general classes. It is shown that in the first of these the bis(1-pyrazolyl)borate unit behaves as a bidentate chelating ligand and that the resulting compounds have structures of type I, where R is H, alkyl, or aryl, and the pyrazolyl residues may contain substituents. We adopt the convenient abbreviation $M[R_2B(pz)_2]_2$ and will indicate specifically when substituted pyrazolyl groups are involved. These complexes may have either an essentially planar configuration about the metal (Ni^{2+}, Cu^{2+}) or an essentially tetrahedral array (Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}).



I

In the second class, tridentate ligands are involved as exemplified by structure II, and this structure occurs with all six metals. We adopt the abbreviation $M[RB(pz)_3]_2$. R may be an alkyl or aryl group or another 1-pyrazolyl residue. Here we are dealing with a basically octahedral array of nitrogen atoms about the metal. Molecular models indicate that these tridentate complexes can be formed without strain, and the resulting molecule is highly symmetrical and compact. When R, X, and Y are hydrogen, molecules of type II have a structure belonging to the D_{3d} point group, and a predominantly octahedral ligand field is expected with a pronounced trigonal component. The evidence on



II

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[1] S. Trofimenko, *J. Am. Chem. Soc.*, 88, 1842 (1966).

[2] J. P. Jesson, S. Trofimenko, and D. R. Eaton, *ibid.*, 89, 3158 (1967).