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## The Synthesis and Characterization of Some Transition Metal Complexes Prom Mixtures of Poly Pyrazolyl Borates

Robert Matthew Alway

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THE SYNTHESIS AND CHARACTERIZATION  
OF SOME TRANSITION METAL  
COMPLEXES FROM MIXTURES OF  
POLY PYRAZOLYL BORATES

by

Robert Matthew Alway

A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfilment of the  
requirements for the  
Degree of Master of Arts  
Department of Chemistry

Western Michigan University  
Kalamazoo, Michigan  
April 1984

THE SYNTHESIS AND CHARACTERIZATION  
OF SOME TRANSITION METAL  
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POLY PYRAZOLYL BORATES

Robert Matthew Alway, M.A.

Western Michigan Univesity, 1983

This is a report of the synthesis and separation of transition metal complexes of hydrotris(1-pyrazolyl)-borate and hydrotris(3,5-dimethyl-1-pyrazolyl)borate. These complexes contain a central metal ion and two tridentate ligands, one hydrotris(1-pyrazolyl)borate and one hydrotris(3,5-dimethyl-1-pyrazolyl)borate. Mass spectrometry proved to be an extremely useful technique for identifying products. Many mass spectra are included and discussed extensively.

Complexes containing hydrobis(pyrazole)(3,5-dimethyl-1-pyrazolyl)borate and hydrobis(3,5-dimethyl-1-pyrazole)(pyrazolyl)borate also were synthesised and mass spectra obtained.

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Robert Matthew Alway

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ALWAY, ROBERT MATTHEW

THE SYNTHESIS AND CHARACTERIZATION OF SOME TRANSITION  
METAL COMPLEXES FROM MIXTURES OF POLY PYRAZOLYL BORATES

WESTERN MICHIGAN UNIVERSITY

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## INTRODUCTION

### Ligands

Poly(1-pyrazolyl)borates were first reported in 1966 by Trofimenko.<sup>1</sup> These ligands have several unique properties including a -1 charge and some aromatic character. There has been some comparison with the cyclopentadienyl ion<sup>2</sup> due to the similar numbers of donated electrons and to the similar structures of cyclopentadiene and pyrazole (Pz) rings.

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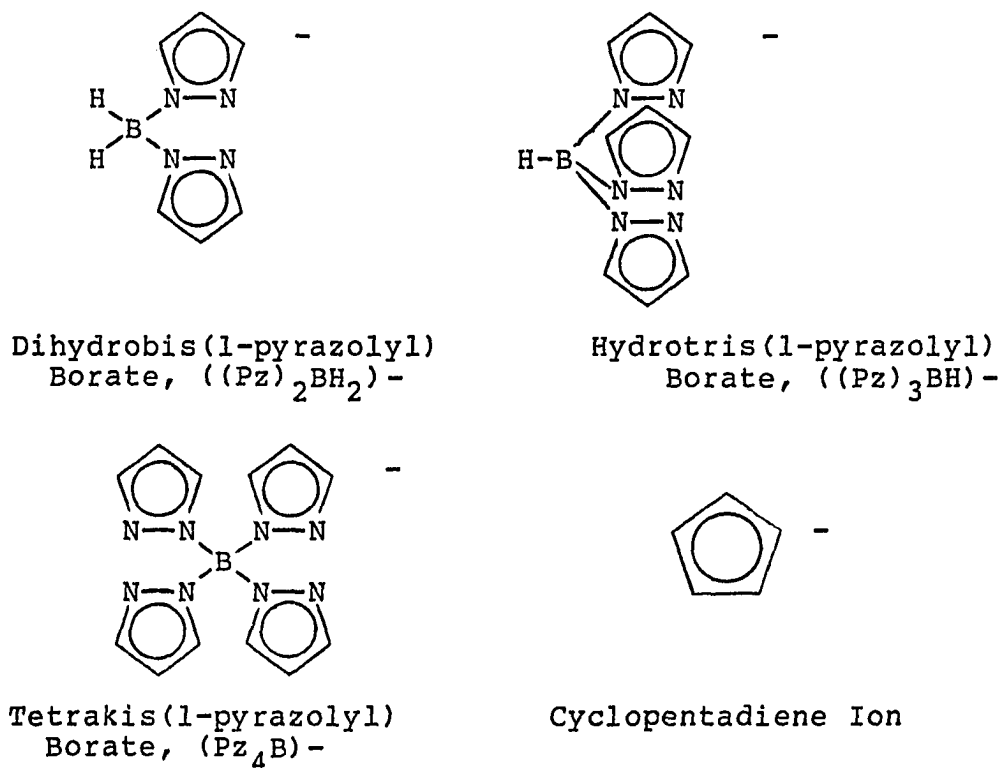
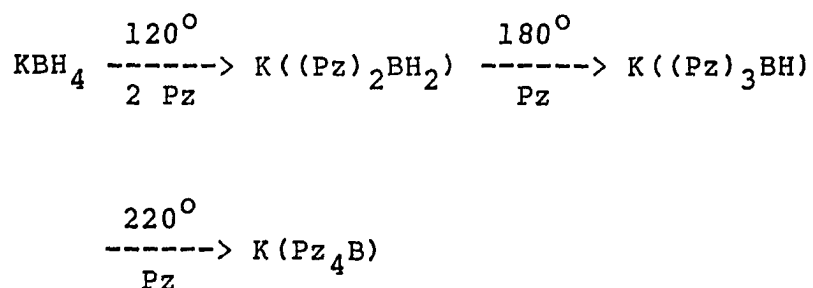


Figure 1. Pyrazolylborate Ligands and Analogs

In fact the similarities of the two ligands is minor as far as their chemistry is concerned. For example, while the pyrazolylborate ligands form stable compounds with most of the first row transition metals, only ferrocene of the cyclopentadiene compounds is air stable.

Polypyrazolylborates are synthesized by the direct reaction of borohydride ion with a pyrazole<sup>1,3</sup>. The reaction may be carried out so as to add two, three, or in some cases four pyrazole rings to the boron depending on reaction conditions. Below 120°C two rings are added. Between 180 and 210°C three rings are added. Above 220 degrees, if unsubstituted pyrazole is used, a fourth ring is added.

Table 1  
Synthesis of Pyrazolyl Borates



The reaction is exothermic and a solvent is used in the reaction to add two pyrazole rings for temperature control and as a catalyst. Three and four ringed

compounds are synthesized without solvents. For example, the synthesis of potassium dihydrobis(3,5-dimethyl-1-pyrazolyl)borate is most conveniently carried out in refluxing N,N-dimethylacetamide<sup>4,5</sup>. Four previously reported potassium (1-pyrazolyl)borates were synthesized in this study:

- 1) Potassium hydrotris(1-pyrazolyl)borate  
(K((Pz)<sub>3</sub>BH)),
- 2) Potassium dihydrobis(1-pyrazolyl)borate  
(K((Pz)<sub>2</sub>BH<sub>2</sub>)),
- 3) Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)  
borate (K((DMP)<sub>3</sub>BH)),
- 4) Potassium dihydrobis(3,5-dimethyl-1-pyrazolyl)  
borate (K((DMP)<sub>2</sub>BH<sub>2</sub>)).

Repeating the synthesis of these poly(1-pyrazolyl)-borates is one of the goals of this research.

### Pyrazoles

Two kinds of pyrazole were used in this research, unsubstituted pyrazole (Pz) and 3,5 dimethylpyrazole (DMP). Pyrazoles are characterized by a five membered ring with two adjacent nitrogen atoms and a pair of conjugated double bonds, one carbon-carbon bond, the other carbon-nitrogen.

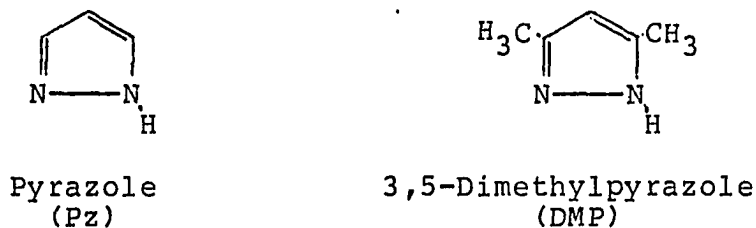


Figure 2. Structure of Pyrazoles

### Homogeneous Metal Complexes

The poly(1-pyrazolyl)borate ligands may be combined with +2 charged transition metals ( $M^{+2}$ ) to form stable compounds of the form  $ML_2$ .

Figure 3 illustrates the unsubstituted pyrazole transition metal complexes. The 3,5-dimethylpyrazole

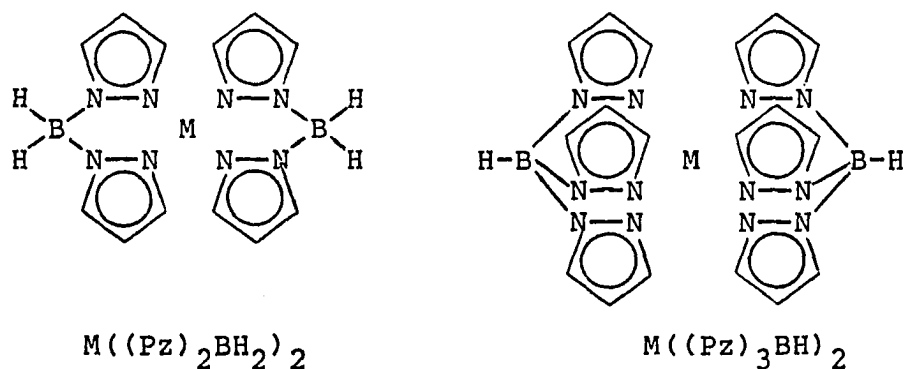


Figure 3. Simple Metal Complexes of Pyrazolyl Borate Ligands.

(DMP) complexes are similar but have methyl groups

attached to the 3 and 5 carbons adjacent to the nitrogens. Most metal complexes of the form  $M((Pz)_2BH_2)_2$  are tetrahedral. An exception is the square planar  $Ni((Pz)_2BH_2)_2$ <sup>7</sup>. The complexes of the form  $M((Pz)_3BH)_2$  are distorted octahedra (trigonal antiprism)<sup>8</sup>.

Previously reported homogenous  $ML_2$  complexes are formed by simply mixing stoichiometric water solutions of the appropriate transition metal ion and the ligand.<sup>4,6,7</sup> Examples are shown in Table 2. With some difficulty the resulting complex precipitate can be filtered. The precipitate is easily extracted with methylene chloride.

Table 2  
Complex Synthesis

- 
- 1)  $2 ((Pz)_3BH) - + M^{+2} \longrightarrow M((Pz)_3BH)_2$ , where M = Cobalt, Iron, Nickel, Copper, Zinc, or Manganese.
  - 2)  $2 ((DMP)_3BH) - + M^{+2} \longrightarrow M((DMP)_3BH)_2$ , where DMP = 3,5-dimethylpyrazole.
  - 3)  $2 ((Pz)_2BH_2) - + M^{+2} \longrightarrow M((Pz)_2BH_2)_2$
  - 4)  $2 ((DMP)_2BH_2) - + M^{+2} \longrightarrow M((DMP)_2BH_2)_2$
- 

In Table 2, the first reaction also forms precipitates with magnesium and calcium ions, the second forms precipitates with all the alkaline earth ions, and the third forms air sensitive iron and cobalt compounds. Trofimenko has studied the properties of the compounds in



Table 2, especially compounds of types 1 and 3<sup>4</sup>. The 3,5 dimethyl substituted compounds have similar properties but are less water soluble.

Repeating the synthesis of these complexes is one of the goals of this research.

### Mixed Complexes

There have been many reported pyrazolylborate complexes of the "Half Sandwich" type consisting of a central transition metal ion with one pyrazolylborate ligand and one or more different ligands. For example  $\text{Mo}((\text{Pz})_3\text{BH})(\text{CO})_2$ <sup>5</sup> and  $\text{Cu}((\text{Pz})_3\text{BH})\text{CO}$ <sup>10,11</sup>. There are no previous reports of complexes with two heterogeneous pyrazolyl borate ligands as illustrated in figure 4. In principle these complexes should be easy to

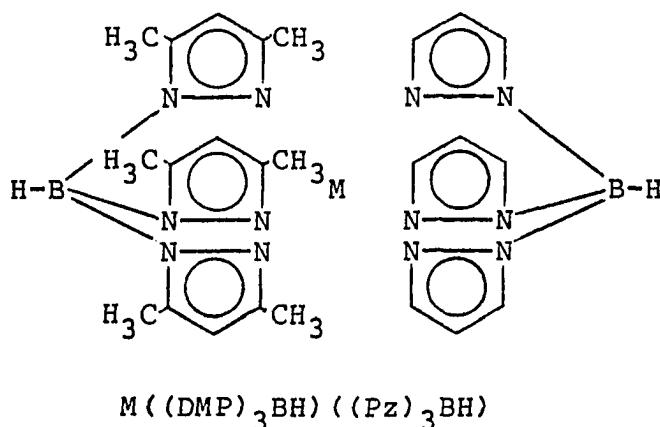


Figure 4. Metal Complex with Heterogeneous Poly(1-pyrazolyl)borate Ligands.

synthesize. One simply mixes a solution of two ligands and a solution of the appropriate transition metal ion and collects the precipitate.

In practice the product yields are low and the separation requires column chromatography.

Preparing these novel complexes is one of the goals of this research.

#### Novel Ligands

With one recent exception<sup>9</sup>, all previously reported poly(1-pyrazolyl)borate compounds contain only one form of pyrazole, i.e. all of the pyrazoles on one boron are 3,5-dimethylpyrazole or pyrazole or 4-methylpyrazole etc.. One object of this research was to synthesize compounds with more than one form of pyrazole on each boron. The main difficulty was the isolation of a single pure compound. The potassium compounds attempted were potassium hydrobis(3,5-dimethyl-1-pyrazolyl)(1-pyrazolyl)borate,  $(K((DMP)_2(Pz)BH))$ , and potassium hydrobis(1-pyrazolyl)(3,5-dimethyl-1-pyrazolyl)borate,  $(K((Pz)_2(DMP)BH))$ . (See Figure 5.)

Preparing these novel ligands is one of the goals of this research.

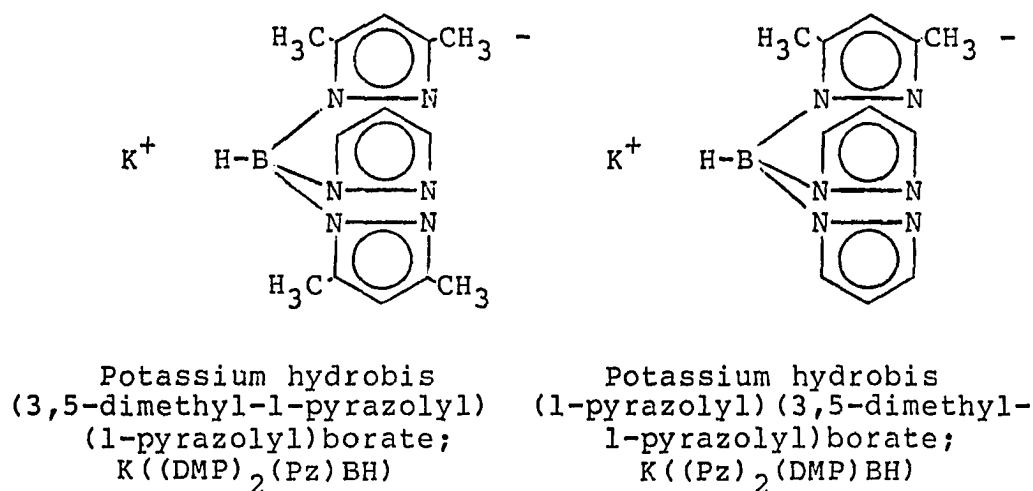
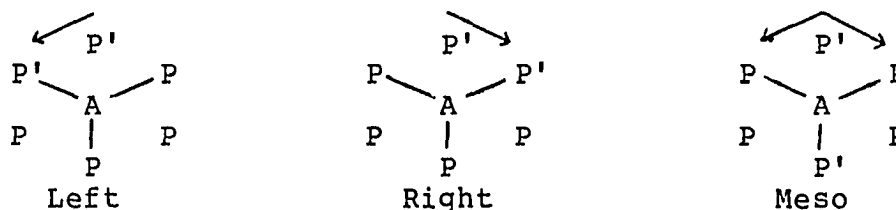


Figure 5. Novel Ligands

## Asymmetric Complexes

Complexes made with ligands containing more than one form of pyrazole may have optically active and meso forms. These complexes can be of three formula types,  $M((Pz)_2(DMP)BH)_2$ ,  $M((DMP)_2(Pz)BH)_2$ , and  $M((Pz)_2(DMP)BH)((DMP)_2(Pz)BH)$ . These compounds are illustrated in Figures 6, 7, and 8 as viewed along the boron-metal-boron axis.

Figure 6. Possible Structures of  $M((Pz)_2(DMP)BH)_2$ .

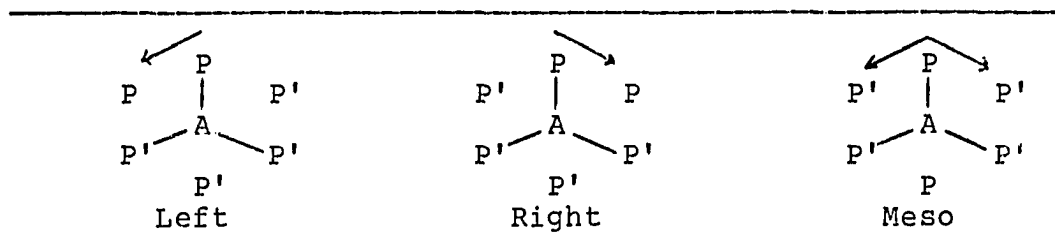


Figure 7. Possible Structures of  $M((DMP)_2(Pz)BH)_2$ .

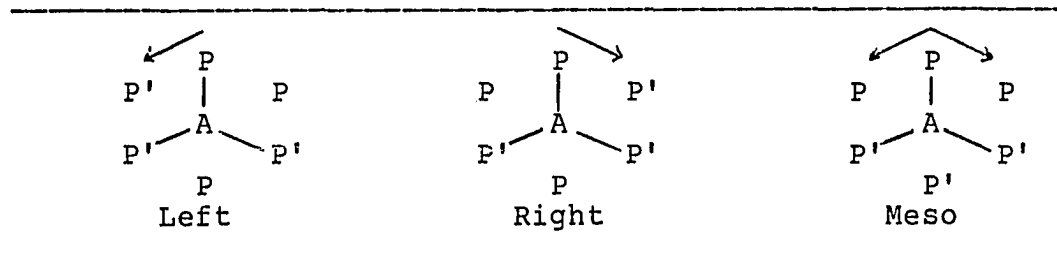


Figure 8. Possible Structures of  $M((Pz)_2(DMP)BH)((DMP)_2(Pz)BH)$ .

Where the P is pyrazole and the P' is 3,5-dimethylpyrazole. A is the boron-metal-boron axis.

Producing compounds that may be separated into these optical isomers is one of the goals of this research.

## EXPERIMENTAL SECTION

### Synthesis

#### Pyrazoles

##### The Synthesis of Pyrazole.<sup>19</sup>

Procedure. In a one neck, 1.5 liter round bottom flask, place 210 grams (2 moles) of hydrazine dihydrochloride, 400 mL of water and 300 mL of methanol. (See note 1.) Add 328 grams of malonaldehyde tetramethylacetal (1,1,3,3 tetramethoxypropane) to the mixture and fit the flask with a reflux condenser. Reflux the solution for 2 hours.

Evaporate the mixture to approximately one third its original volume. Slowly add, with stirring, 250 grams of sodium carbonate to the solution to neutralize the acid. Cool and filter the slurry. Extract the salt cake and then the pyrazole solution with three 200 mL portions of ether. Dry the ether extract with magnesium sulfate and evaporate it to yield 100 to 120 grams pyrazole (70-90%). The brown product melts at 67-70<sup>0</sup>, literature value 69.5-70<sup>0</sup> (See note 2).

Notes 1. The hydrazine dihydrochloride-methanol-water mixture may be generated in an alternate manner. Place 2 moles of hydrazine (64 grams anhydrous hydrazine or 100

grams hydrazine monohydrate) in 300 mL of methanol in the reaction flask. Place the flask in a liquid nitrogen bath until the liquid is frozen. In a hood, carefully add 330 mL of concentrated hydrochloric acid to the ice giving a strongly exothermic reaction. Add 70 mL of water to the warm mixture and use.

2. The brown product is satisfactory for the further procedures in this paper. However, if additional purification of pyrazole is desired, the product may be vacuum distilled using an air cooled condenser. Precautions should be taken to prevent the freezing of the product in the condenser. Be certain the starting material is water free to avoid bumping.

The synthesis of 3,5-dimethylpyrazole<sup>20</sup>

Procedure. In a hood, place 1 mole of hydrazine (32 grams anhydrous hydrazine or 50 grams of hydrazine monohydrate) in a 1 liter beaker containing 500 mL of water. Slowly add 1 mole (100 grams) of 2,4 pentanedione (acetylacetone) with stirring to give an exothermic reaction. Cover the beaker with a watch glass and stir magnetically. After the mixture has cooled to room temperature (about 2 hours) separate the crystals by filtration and dry. The yield is about 80 grams (83%) of 3,5-dimethylpyrazole with a melting point of 107°,

literature value 107-108°.

The yield may be increased by evaporating the filtered solution to a volume of about 100 mL and collecting a second less pure crop of crystals.

#### Pyrazolyl-Borate Ligands

$K((Pz)_3BH)$  and  $K((Pz)_2BH_2)$  were synthesized by methods reported by Trofimenko<sup>3</sup>. In addition  $K((Pz)_2BH_2)$  was synthesized in refluxing toluene to avoid the problem of overheating.  $K((DMP)_3BH)$  was synthesized in a manner similar to  $K((Pz)_3BH)$ <sup>4</sup>.  $K((DMP)_2BH_2)$  was synthesized in N,N-dimethylacetamide solvent. Syntheses of  $K((DMP)_3BH)$  and  $K((DMP)_2BH_2)$ , using the less reactive 3,5-dimethylpyrazole, are best carried out at somewhat higher temperatures than used for  $K((Pz)_3BH)$  and  $K((Pz)_2BH_2)$ .

#### The synthesis of potassium dihydrobis (1-pyrazolyl)borate, $K((Pz)_2BH_2)$ .

Procedure. In a 250 mL 3 neck round bottom flask fitted with a condenser, thermometer, and inert gas inlet place 13.5 grams (.25 mole) potassium borohydride, 68 grams (1 mole) pyrazole and 50 mL of toluene. Flush the flask with nitrogen or argon and then reflux for 24 hours. Recrystallize the product from 150 mL of toluene, filter, and wash with 100 mL of hexane. The yield is 33.5 grams (74%) of  $K((Pz)_2BH_2)$  with a melting point of

171-172°C, literature value 172°. The characteristic blue cobalt(II) derivative gave an infrared spectrum with multiple peaks from 4-4.5 microns indicating  $\text{BH}_2^6$ .

Note. For an alternate synthesis, react the potassium borohydride and pyrazole without a solvent using a controlled temperature bath to heat the flask to a temperature not greater than 120°C for 24 hours.<sup>3</sup>

~~The synthesis of potassium hydrotris~~  
~~(1-pyrazolyl)borate,  $\text{K}((\text{Pz})_3\text{BH})$ .~~<sup>5</sup>

Procedure. In a 250 mL 3 neck round bottom flask fitted with a condenser, thermometer, and inert gas inlet mix 13.5 grams (.25 mole) of potassium borohydride and 68 grams (1 mole) of pyrazole. Flush the flask with argon or nitrogen and heat the mixture with a heating mantle to a temperature of 180-210° for 4 hours. Pour the molten product into 150 mL of stirred toluene. After cooling to room temperature, filter the precipitated solid and wash with hexane. The yield of  $\text{K}((\text{Pz})_3\text{BH})$  is 47 grams (78%), with a melting point of 188-189°, literature value 189°. The characteristic yellow<sup>6</sup> cobalt(II) derivative gave an infrared spectrum with one peak at 4 microns indicating  $\text{BH}^6$ .



The synthesis of potassium dihydrobis-(3,5-dimethyl-1-pyrazolyl)borate,  $K((DMP)_2BH_2)$ .<sup>4,5</sup>

Procedure. In a 250 mL 3 neck round bottom flask fitted with a condenser, thermometer, and inert gas inlet place 13.5 grams (.25 mole) of potassium borohydride and 96 grams (1 mole) of 3,5-dimethylpyrazole. Flush the flask with nitrogen or argon and heat with a heating mantle until the 3,5-dimethylpyrazole begins to react vigorously. Remove the mantle until the reaction subsides. Then replace the mantle and heat the melt to 120°C for 24 hours. Pour the melt into 75 mL of stirred toluene. After the slurry has cooled to room temperature filter the precipitate and wash with hexane. The characteristic blue<sup>6</sup> cobalt(II) derivative gave an infrared spectrum with multiple peaks from 4-4.5 microns indicating  $BH_2$ <sup>6</sup>.

Notes. The (3,5-dimethyl-1-pyrazolyl)borates are more soluble than the unsubstituted pyrazole compounds in toluene.  $K((DMP)_2BH_2)$  may be synthesized in refluxing N,N-dimethylacetamide.

The synthesis of potassium hydrotris-(3,5-dimethyl-1-pyrazolyl)borate,  $K((DMP)_3BH)$ .

Procedure. In a 250 mL 3 neck round bottom flask fitted with a condenser, thermometer, and inert gas inlet place 13.5 grams (.25 mole) of potassium borohydride and 120 grams (1.25 mole) of 3,5-dimethylpyrazole. Flush the flask with nitrogen or argon and heat slowly to 210°C with a heating mantle. After 4 hours pour the melt (See note) into 100 mL of stirred toluene. After the slurry has cooled to room temperature filter the precipitate and wash with toluene and then hexane. The characteristic yellow<sup>6</sup> cobalt(II) derivative gave an infrared spectrum with a single peak at 4 microns indicating BH<sup>6</sup>.

Note The product frequently solidifies in the flask. The solid may be recovered by boiling the solid with toluene in the flask, cooling, filtering the precipitate, and repeating, reusing the filtrate as many times as needed.

The Synthesis of  $K((DMP)_2(Pz)BH)$  and  $K((Pz)_2(DMP)BH)$ .

Procedure. In a 250 mL 3 neck round bottom flask fitted with a condenser, thermometer, and inert gas inlet place 13.5 grams (.25 mole) of potassium borohydride, 34 grams (.5 mole) of pyrazole, and 48 grams (.5 mole) of 3,5-dimethylpyrazole. Flush the flask with argon or

nitrogen and heat to 120°C. Allow the reaction to subside, then heat to 210° with the heating mantle. After 4 hours pour the melt into a beaker and allow to cool to a tacky glass. The product is a mixture of several compounds including  $K((Pz)_2(DMP)BH)$  and  $K((DMP)_2(Pz)BH)$ . The characteristic yellow<sup>6</sup> cobalt(II) derivative gave an infrared spectrum with a narrow range of peaks at 4 microns indicating  $BH^6$ .

### Complex-Synthesis

#### The Synthesis and Purification of $Fe((Pz)_3BH)((DMP)_3BH)$ :

Procedure. Add 10 mL of water solution containing .01 mole of  $Fe^{+2}$  to a 20 mL N,N-dimethylformamide solution of .01 mole  $K((Pz)_3BH)$  and .01 mole  $K((DMP)_3BH)$ . (See Note 1) Recover the precipitate by vacuum filtration. Extract the N,N-dimethylformamide with 50 mL of carbon tetrachloride to collect as much of the soluble  $Fe((Pz)_3BH)((DMP)_3BH)$  as possible. Air dry both the filter cake and the carbon tetrachloride extract.

To purify the  $Fe((Pz)_3BH)((DMP)_3BH)$  dissolve about 1 gram of the filter cake or .5 gram of the extract material in a small (About 5 mL) amount of methylene chloride. Elute this sample on a 20mm diameter (Corning column #38450) silica gel column (EM silica gel 60 70-230

mesh) with methylene chloride. When both homogeneous complexes have been washed from the column (see note) elute the column with 95% ethanol. The  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$  will come off with the ethanol front. Air dry the ethanol to give a microcrystalline product with an indistinct melting point. The yield varies with the metal used. Cobalt gives about 30% and iron about 10% yield. For the iron compound the analytical sample was water washed and dried, anal. Calcd for  $\text{C}_{24}\text{H}_{32}\text{B}_2\text{FeN}_{12}$ : C, 50.92%, H, 5.70%, N, 29.70%, Cl, 0.0%; found: C, 50.60%, H, 5.42%, N, 29.89% Cl, 0.0%. The unwashed sample found: C, 46.55%, H, 5.60%, N, 25.23%, Cl, 6.72%. For the unwashed cobalt complex anal. calcd for  $\text{C}_{24}\text{H}_{32}\text{B}_2\text{CoN}_{12}$ : C, 50.65%, H, 5.67%, N, 29.53%; found: C, 43.85%, H, 5.20%, N, 23.78%. Unwashed products were used for all spectra, including the mass spectra. The characteristic red iron(II) and orange cobalt(II) complexes gave infrared spectra with a single band at 4 microns indicating  $\text{BH}^6$ .

Notes 1. The solutions of  $\text{K}((\text{Pz})_3\text{BH})$  and  $\text{K}((\text{DMP})_3\text{BH})$  are made by dissolving the salts separately in about half the N,N-dimethylformamide each. The solutions are then combined. The iron(II) is best made into a 1 molar stock solution from  $\text{Fe(II)Cl}_2$ . The iron solution is stabilized by adding KI and just enough  $\text{Na}_2\text{S}_2\text{O}_3$  to remove the

iodine.

2. This procedure will work with other +2 transition metals. Cobalt, iron, and copper have yellow, red, and blue colored complexes respectively that show clearly on the column allowing the determination of their positions. For colorless zinc and manganese the column should be washed with a large excess of methylene chloride.

The Synthesis of  $\text{Co}((\text{Pz})_2\text{BH}_2)_2$  and  $\text{Co}((\text{DMP})_2\text{BH}_2)_2$

Procedure. Add a water solution of .01 mole of  $\text{Co(II)Cl}_2$  to .02 mole of ligand in 20 mL of N,N-dimethylformamide. Pour the mixture into 400 mL of water and collect the precipitate by filtration. The characteristic green iron(II) and blue cobalt(II) compounds give infrared spectra with multiple peaks from 4-4.5 microns indicating  $\text{BH}_2^6$ .

Note. The air sensitive  $\text{Fe}^{+2}$  may be stabilized by adding KI and  $\text{Na}_2\text{S}_2\text{O}_3$  to its solutions, including the water the precipitate is formed in. The precipitate should be stored in an inert gas or vacuum desiccator.

The Synthesis of  $\text{Fe}((\text{Pz})_3\text{BH})_2$  and  $\text{Fe}((\text{DMP})_3\text{BH})_2$ <sup>7</sup>

Procedure. Add a water solution of .01 mole of  $\text{Fe(II)Cl}_2$  to .02 mole of ligand in 25 mL of N,N-dimethyl-

formamide. Collect the precipitate by filtration and air dry. The characteristic yellow cobalt(II) and red iron(II) compounds give infrared spectra with a single peak at 4 microns indicating  $\text{BH}^6$ . The anal. calcd for  $\text{Fe}((\text{Pz})_3\text{BH})_2$ ,  $\text{C}_{18}\text{H}_{20}\text{B}_2\text{FeN}_{12}$  is: C, 44.86%; H, 4.18%; N, 34.88%. Found: C, 44.59%; H, 4.14%; N, 35.09%. Anal. calcd for  $\text{Fe}((\text{DMP})_3\text{BH})_2$ ,  $\text{C}_{30}\text{H}_{44}\text{B}_2\text{FeN}_{12}$  is: C, 55.42%; H, 6.82%; N, 25.85%. Found: C, 55.09%; H, 6.76%; N, 25.71%.

Note. The air sensitive  $\text{Fe}^{+2}$  ion may be stabilized by adding KI and  $\text{Na}_2\text{S}_2\text{O}_3$  to its solutions.

#### The Synthesis of $\text{Co}((\text{Pz})_x(\text{DMP})_{3-x}\text{BH})_2$

Procedure. Add a solution of .01 mole of  $\text{Co(II)Cl}_2$  per 10ml of water to a clear, filtered, solution of .02 mole of  $\text{K}(\text{Pz}_x\text{DMP}_{3-x})$ , calculated as  $\text{K}((\text{Pz})_3\text{BH})$ , in 20 mL of N,N-dimethylformamide. As each milliliter of metal solution is added stir the mixture and filter the precipitate. There will be some separation of products in the various precipitates. Further separation may be attempted with column chromatography.

### Chromatography

#### Thin Layer Chromatography

Thin layer chromatography is used to determine appropriate solvents for the separation of products on a

larger scale in column chromatography. Silica gel coated plates are used to determine the best solvent for separations on the silica gel columns. Glass backed Analtech Uniplate Silica Gel GF 250 micron scored 20 x 10 cm and plastic backed Kodak fluorescence silica gel plates were used. Several solvents and solvent mixtures were tested including 1-chlorobutane, cyclohexane, methylene chloride, chloroform, carbon tetrachloride, ethanol, methanol and various of their mixtures. The spots were detected by exposing the developed plates to iodine vapor.

A two dimensional plate using methylene chloride as the first eluent and ethanol as the second showed the solvents to be an effective pair for separating the homogeneous from the heterogeneous complexes. The less available 1-chlorobutane is a satisfactory substitute for methylene chloride as is methanol for ethanol.

Preliminary experiments with asymmetric complexes indicate mixtures of cyclohexane or carbon tetrachloride with polar solvents such as ethanol or methylene chloride may give adequate band separation.

#### Column Chromatography

The columns used for this research were 20mm diameter Corning #38450 columns packed with 20cm of EM silica gel

60 70-230 mesh. The coarse mesh allowed gravity feed of solvent at a reasonable rate of elution.

The translation of the thin layer chromatography for homogeneous heterogeneous complexe separation is relatively straightforward. Instead of using two dimensions the first solvent (methylene chloride) is washed down the column until the homogeneous complexes are removed. Then the alcohol solvent is used to wash the heterogeneous complexe through the column. The locations of the bands were detected visually.

Translation of the asymmetric separation from thin layer to column chromatography is more difficult. There is not a direct one to one correspondence between bands on a column and spots on a plate due to differences in silica gel mesh and composition and surface effects of the plate. Often bands contain dilute solutions of weakly colored material making visual detection difficult.

### Extractions

Initial runs of heterogeneous complexes gave very low yields. Several extraction solvents; methylene chloride, hexane, 1-chlorobutane, 1-nitropropane, chloroform, and carbon tetrachloride were then tested for relative yield of heterogeneous complexes. A mixture of heterogeneous



and homogeneous iron(II) complexes was synthesised from aqueous solutions of  $\text{Fe(II)Cl}_2$  (.05 mole) and the ligands  $\text{K((Pz)}_3\text{BH)}$  and  $\text{K((DMP)}_3\text{BH)}$  (.05 mole each). The filtered precipitate was cut into equal sections and each section extracted with 50 mL of a different solvent.

The order of yield of  $\text{Fe((Pz)}_3\text{BH)((DMP)}_3\text{BH)}$  relative to the homogeneous complexes from best to worst solvent is carbon tetrachloride >> chloroform > 1-nitropropane > 1-chlorobutane > hexane > methylene chloride.

#### Instrumentation

Several instruments were used to collect the data for this research. The NMR data was collected with a Perkin-Elmer R-12B with deuterio-chloroform solvent and TMS standard. The infrared spectra were collected on a Beckman IR-8 using a mineral oil mull in a sodium chloride cell. The UV-visible spectra were taken on a Cary 14 using a one centimeter glass cell with methylene chloride as solvent. Elemental analyses were performed commercially by Midwest Microlabs.

Several mass spectrometers were used for this research: a Hewlett-Packard HP 5995 A GC/MS<sup>13</sup>, a Dupont MS<sup>14</sup>, and a Varian MAT CH-7<sup>15</sup>. The Varian and the Hewlett-Packard machines yielded digital data. All of the machines can easily resolve whole mass units.

Identical samples run on different instruments gave similar results. All of the samples were low vapor pressure solids and were placed directly into the mass spectrometer's ionization chamber to obtain spectra.

Infrared spectrometry was helpful in confirming the synthesis of previously reported compounds and determining whether the boron was bonded to one or to two hydrogen atoms<sup>7</sup>. The instrument used was a Beckman IR-8. The samples for analysis were prepared as mineral oil mulls.

## RESULTS

### Characterization

Several methods, NMR, IR, mass spectrometry, UV-visible, and elemental analysis were used to characterize the products synthesized in this research. Ligands were characterized from their metal complex derivatives. NMR proved most useful for showing the relative shielding of the N-hydrogen in pyrazole and in 3,5-dimethylpyrazole. NMR confirms a less shielded N-hydrogen on the unsubstituted pyrazole accounting for its greater reactivity (Figure 13). In the study of the metal complexes, however, the technique was limited by the frequently strong paramagnetism generated by unpaired electrons on the metal ion.

### UV-visible Spectrometry

The heterogeneous complexes of cobalt and iron have visible absorptions far more intense than the homogeneous complexes. For example, the  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$  complex has an absorption intensity approximately two orders of magnitude greater than the homogeneous complexes of iron. At 481 nanometers the molar absorbance of  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$  is 3500. The UV-visible spectrum of  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$  is shown in

UV-visible spectrum of  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$  is shown in Figure 9. The concentration is about  $10^{-4}$  M in methylene chloride. Two small peaks with absorbances on the order of 1 - 10 are at 781 and 844 nanometers. The intensity of the charge transfer bands ruled out an interpretation of D-D transitions.

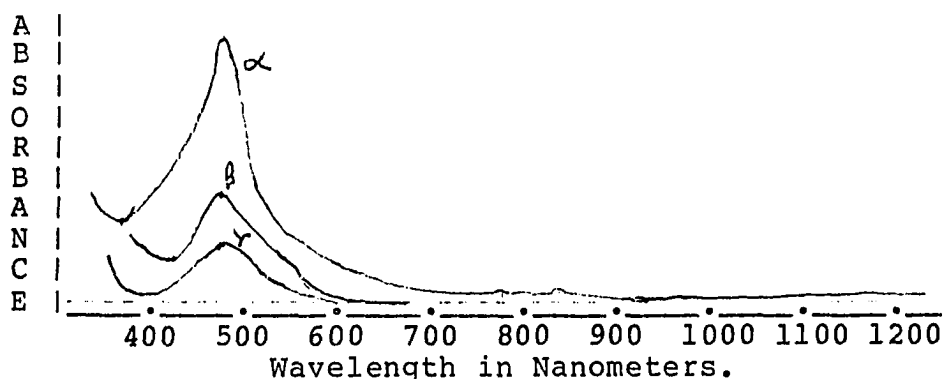


Figure 9. The UV-Visible Spectrum of  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})^\alpha$ ,  $\text{Fe}((\text{Pz})_3\text{BH})_2^\beta$ , and  $\text{Fe}((\text{DMP})_3\text{BH})_2^\gamma$ . (Not to scale)

#### Elemental Analysis

Elemental analysis is used as a confirmatory technique. The results of elemental analysis are not entirely satisfactory. There is strong evidence in the form of high chlorine content to indicate the presence of substantial quantities of solvent in the unwashed products. Analytical laboratory personnel suggested the presence of chlorides of iron. Unwashed material was used for all spectra.

## Infrared and NMR Spectra

### Infrared Spectra

For a single hydrogen there is one small peak at about 4 microns, for two hydrogens there will be a series of peaks between 4 and 4.5<sup>6</sup> microns. The cobalt(II) complex examples of this are illustrated in Figure 10. The infrared spectra in Figures 11 and 12 are of the homogeneous and heterogeneous complexes of iron(II). The B-H band at 4 microns confirms  $((Pz)_3BH)^-$  and  $((DMP)_3BH)^-$  around the metal.

### NMR Spectra

NMR spectra were not interpreted for the metal complexes due to paramagnetic interference. The spectra of the pyrazoles (Figure 13) are of interest due to the illustration of the greater shielding on the N-hydrogen on 3,5-dimethylpyrazole compared to the N-hydrogen on the pyrazole. This would indicate less electron charge on the pyrazole hydrogen for a greater net positive charge on the hydrogen with increased acid properties. The greater reactivity of pyrazole is in agreement with this conclusion.

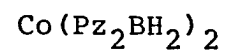
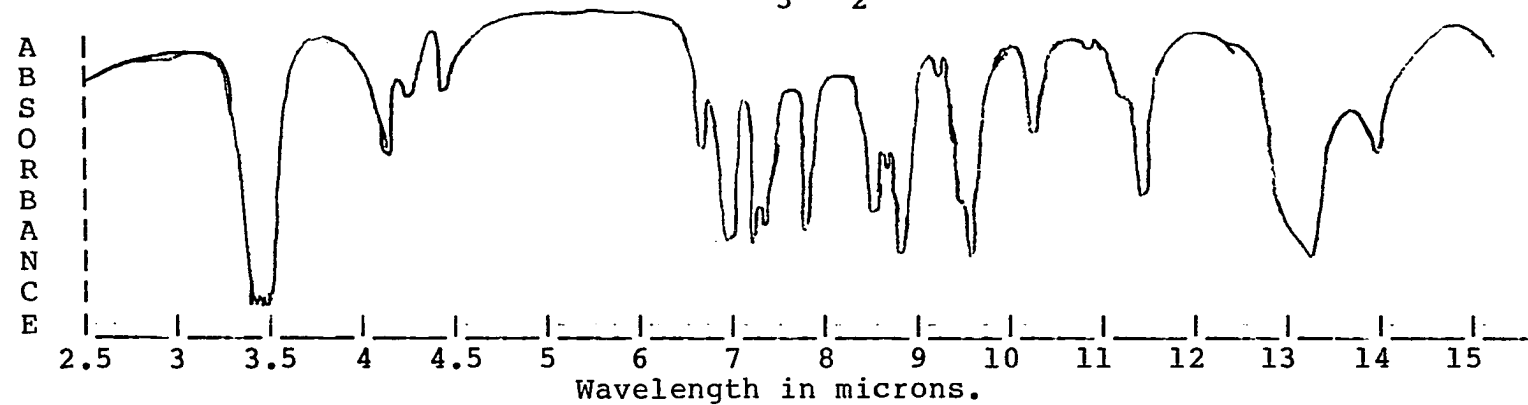
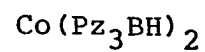
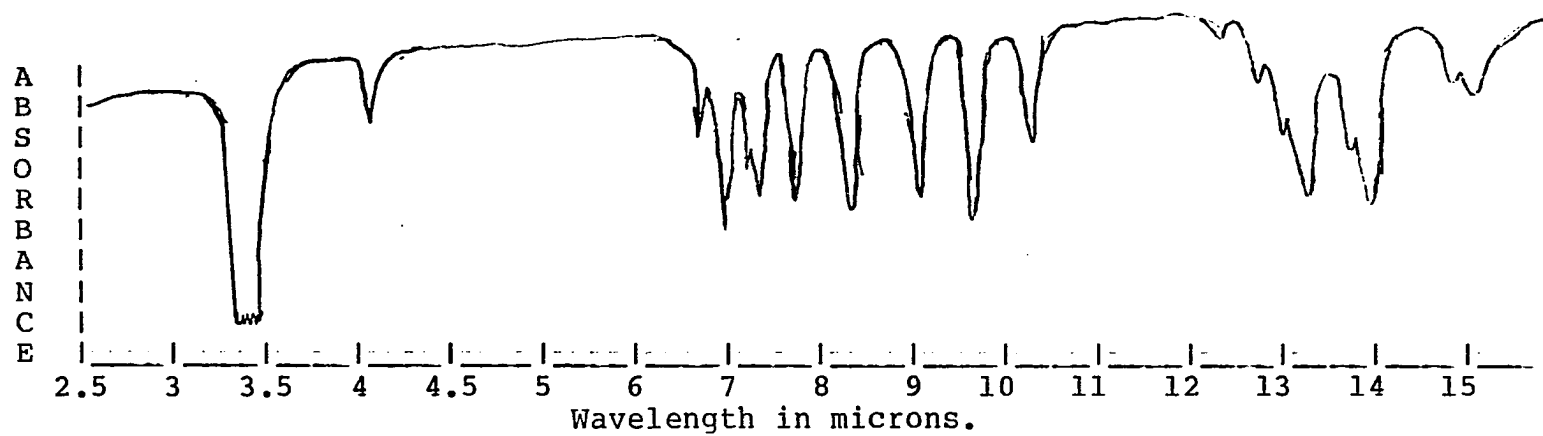


Figure 10. Infrared Spectra of Complexes with One or Two B-H Bonds.  
Mineral oil mull.

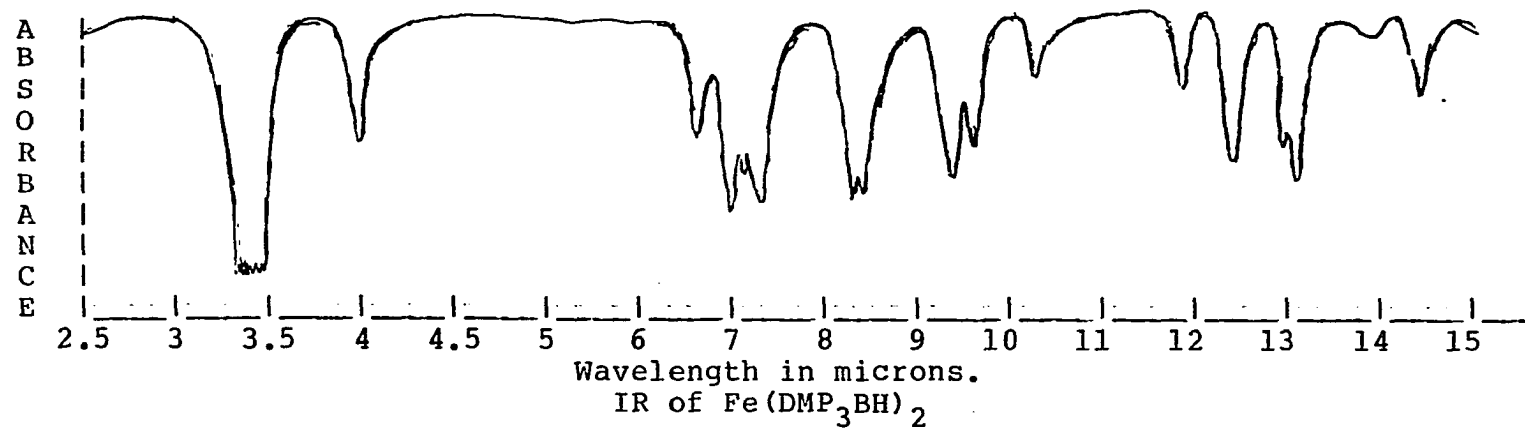
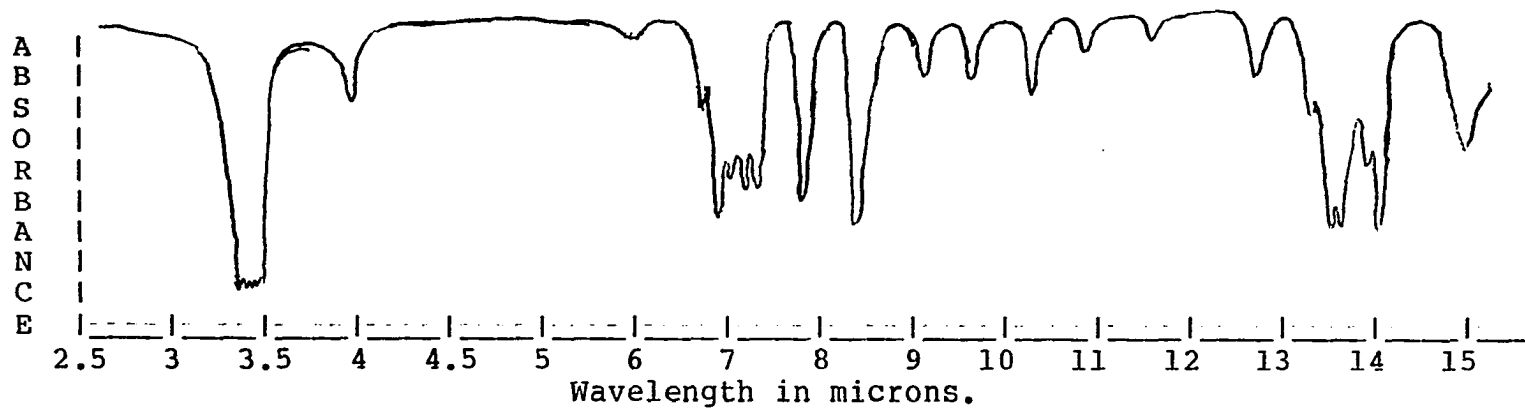


Figure 11. Infrared Spectra of the Homogeneous Iron Compounds.  
Mineral oil mull.

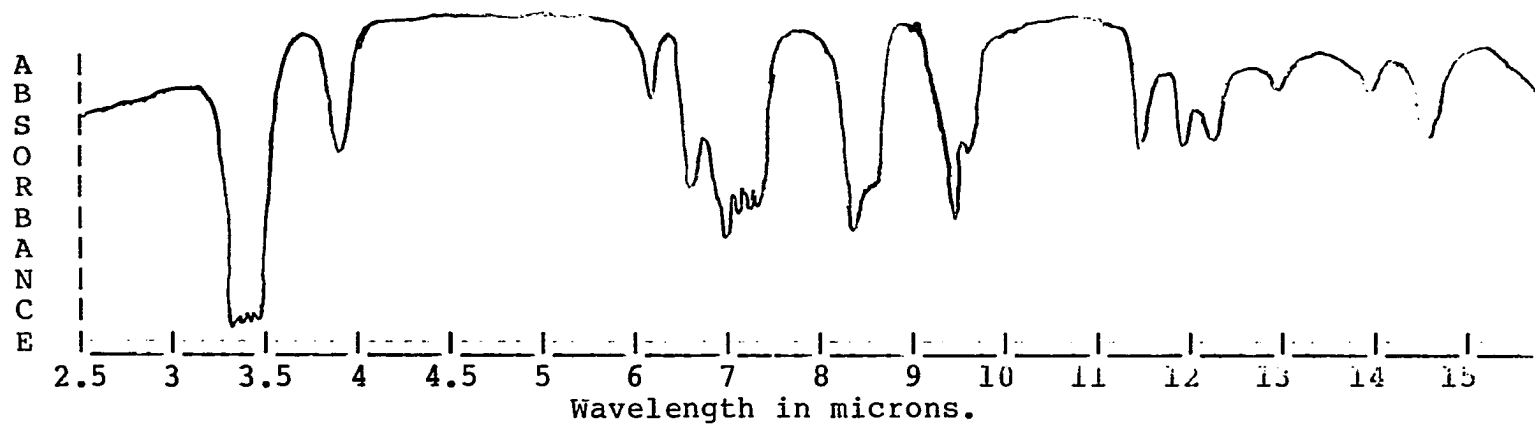


Figure 12. IR of  $\text{Fe}(\text{Pz}_3\text{BH})(\text{DMP}_3\text{BH})$   
the Heterogeneous Iron Compound.  
Mineral oil mull.



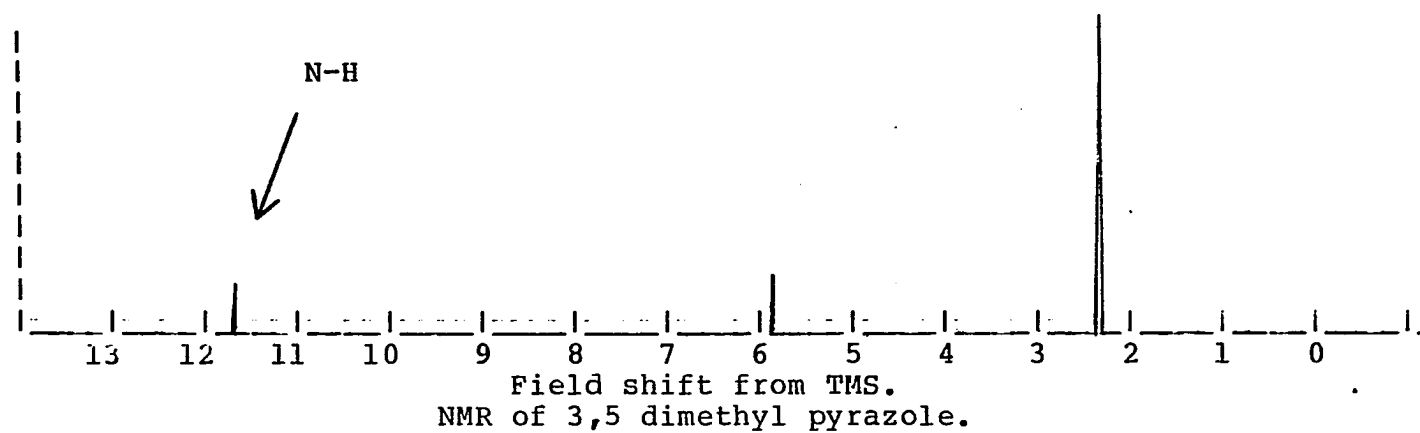
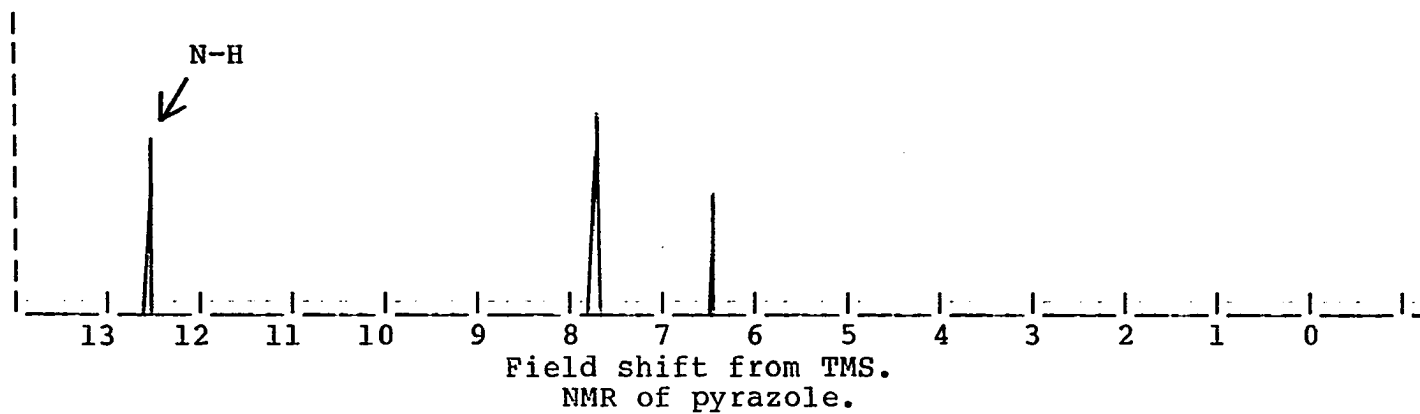


Figure 13. NMR of Pyrazoles.  
R.C. Beaumont, Perkin-Elmer R12B NMR, Alma College

## Mass Spectrometry

### Introduction

Mass spectrometry proved the most useful technique for determining the composition of newly synthesized compounds. Mass spectrometry was suggested as a screening technique before using more time-consuming analytical methods<sup>16</sup>. The technique had not been reported previously for this class of compounds. Using the difference in mass between pyrazole and 3,5-dimethylpyrazole of two methyl groups (28 AMU) it was easy to determine the total numbers of each pyrazole in any compound. It also gave an idea of how many different compounds there were in an unpurified sample. Caution had to be used in that there often were several possible isomers with the same molecular weight. For example  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$  and  $\text{Fe}((\text{Pz})_2(\text{DMP})\text{BH})((\text{DMP})_2(\text{Pz})\text{BH})$  both have a formula weight of 566.

In addition to the principal peak, there are several additional decomposition product peaks that aid in the interpretation of the spectra. Examples include:  $\text{Fe}((\text{DMP})_3\text{BH})(\text{DMP}_2\text{BH})^+$ ,  $\text{Fe}((\text{DMP})_3\text{BH})^+$ ,  $\text{Fe}((\text{Pz})_3\text{BH})^+$ , and  $\text{Fe}(\text{N}_{12}\text{H}_6)^+$ . Knowledge of the relative abundance of isotopes gives an indication of numbers of types of atoms in a fragment. Boron, for example, has two natural

isotopes, atomic weights 10 and 11, with abundances of 19.6 and 80.4% respectively. A fragment with one boron atom will have two peaks, one with a height of 19.6 relative to a peak height of 80.4 one mass unit heavier. A fragment with two boron atoms will have three peaks which heights have the ratios  $19.6^2$ ,  $2 \times 19.6 \times 80.4$ , and  $80.4^2$  (3.84 : 31.52 : 64.64) each one mass unit heavier.

Many of the transition metals have more than one isotope. Iron has  $\text{Fe}^{56}$  at 91.66% abundance and  $\text{Fe}^{54}$  at 5.82% abundance, nickel has two main isotopes  $\text{Ni}^{58}$  and  $\text{Ni}^{60}$  at 67.88% and 26.23% abundance respectively. Copper has  $\text{Cu}^{63}$  and  $\text{Cu}^{65}$  at 69.09% and 30.91%. Zinc has three main isotopes along with several less abundant isotopes  $\text{Zn}^{64}$  at 48.89%,  $\text{Zn}^{66}$  at 27.81%, and  $\text{Zn}^{68}$  at 18.57%. The zinc mass spectra tend to be very complicated due to the large number of isotopes among other reasons.

#### Examples of Mass Spectra

As a specific example of how ms data may be interpreted, the following is the data from a sample of  $\text{Fe}((\text{DMP})_3\text{BH})_2$  collected with the Hewlett-Packard instrument:

Table 3.  
 $\text{Fe}((\text{DMP})_3\text{BH})_2$  MS data.<sup>13</sup>

MASS:	213	215	216	230	242	243
ABUNDANCE:	7.5	4.6	12.1	99.9	7.5	13.4

MASS:	256	257	258	259	269	277
ABUNDANCE:	3.9	7.8	4.0	3.9	3.4	4.9

MASS:	278	284	309	337	351	352
ABUNDANCE:	4.2	3.5	3.2	5.6	4.4	15.6

MASS:	353	354	555	648	649	650
ABUNDANCE:	47.9	10.6	2.7	3.6	15.2	34.0

MASS:	651
ABUNDANCE:	12.3

This data includes the important peaks with masses above 200 AMU.

The expected mass of  $\text{Fe}((\text{DMP})_3\text{BH})_2$ , or  $(\text{Fe}_1\text{B}_2\text{C}_{30}\text{N}_{12}\text{H}_{44})$  is 650 AMU. Not surprisingly one of the stronger peaks is 650. The explanation of the associated peaks 648, 649, and 651 AMU comes from the concentrations of natural isotopes for the various elements. Boron as listed above is 80.22%  $\text{B}^{11}$  and 19.78%  $\text{B}^{10}$ , Iron is 91.66%  $\text{Fe}^{56}$  and 5.82%  $\text{Fe}^{54}$ , Carbon is 98.89%  $\text{C}^{12}$  and 1.11%  $\text{C}^{13}$ , Nitrogen is 99.63%  $\text{N}^{14}$  and .37%  $\text{N}^{15}$ , and Hydrogen is 99.985%  $\text{H}^1$  and .015%  $\text{H}^2$ . With boron, as calculated above, a .6435 fraction is at the expected mass, a .3174 fraction is one mass unit lighter and a .0391 fraction is two units lighter. Iron has a .9403 fraction at the normal mass and a .0597 fraction 2 mass units lighter. Together the boron and iron isotopes largely account for the 648 and 649 peaks. The 651 peak is accounted for principally by  $\text{C}^{13}$ , There is a  $.9889^{30}$  or .7154 probability that a molecule will not have a  $\text{C}^{13}$  in it

with a .2059 chance ( $1 - .7154 = .2846$  chance of one or more  $C^{13}$ ,  $.2846 \times .9889^{29} = .2059$ ) of having one  $C^{13}$  and a .0787 chance of having two or more  $C^{13}$  along with a .0435 chance of  $N^{15}$  and a .0066 chance of  $H^2$  account for the 651 peak. The 652 peak is below detection limits. Using boron isotope values for peaks below 650 and carbon isotope values for peaks above 650 amu an abundance of 34.0 at 650 gives calculated abundances of 9.8 at 651, 16.5 at 649 and 2.0 at 948 amu. These values are in good agreement with the experimental values in Table 3.

The DMP fragment has a mass of 95 thus the 555 peak is the compound without one 3,5-dimethylpyrazole ring. The 353 AMU peak is  $Fe((DMP)_3BH)^+$ . Much of the associated peaks 351, 352, and 354 AMU can be rationalized in a manner similar to the 650 peaks with the 351 peak also requiring the loss of a hydrogen atom.

The most interesting peak is at a mass of 230. There is very little or nothing in the way of associated isotope peaks eliminating both boron and carbon as components of the ion. The formula for the ion has to be  $Fe_1N_{12}H_6^+$ , representing the core of the complex with the outer layer of boron and carbon stripped away. This fragment is unique to homogeneous complexes of  $((DMP)_3BH)^-$ .

The following data for  $Fe((Pz)_3BH)_2$  was collected on

the Varian instrument:

Table 4  
Fe((Pz)<sub>3</sub>BH)<sub>2</sub> MS data<sup>15</sup>

MASS:	200	201	202	206	207	239
ABUNDANCE:	11.2	40.9	6.3	3.2	10.9	1.1
MASS:	240	241	266	267	268	269
ABUNDANCE:	3.9	4.3	1.2	4.7	12.0	42.2
MASS:	270	334	335	336	337	344
ABUNDANCE:	5.8	3.9	14.9	54.4	9.7	2.0
MASS:	345	346	347	413	414	415
ABUNDANCE:	6.4	10.7	4.0	1.6	3.6	7.1
MASS:	416	479	480	481	482	483
ABUNDANCE:	1.5	3.7	15.2	53.5	99.9	24.3
MASS:	484					
ABUNDANCE:	3.2					

The isotope spreading of peaks is similar to that for Fe((DMP)<sub>3</sub>BH)<sub>2</sub>. The 482 peaks are the parent peaks. The Pz fragment has a mass of 67 thus the 415 and 346 peaks represent the loss of one and two pyrazole rings respectively. 336 is (Pz)Fe((Pz)<sub>3</sub>BH)<sup>+</sup>. 269 represents the loss of a complete ligand (with mass 213), leaving Fe((Pz)<sub>3</sub>BH)<sup>+</sup>. The 201 peak represents Fe(B(Pz)<sub>2</sub>)<sup>+</sup>. 207 is probably a trimer of pyrazole.

#### Mass Spectra of Mixed Complexes

The following sections contain mass spectral data on transition metal complexes with equimolar mixtures of ((Pz)<sub>3</sub>BH)- and ((DMP)<sub>3</sub>BH)-, mixed iron complexes

extracted with various solvents, asymmetric complexes, and a pure compound.

Pure Mixed Complex

The following table and figure contains the mass spectral data for  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$  purified by column chromatography. The parent peak is at 566 amu.

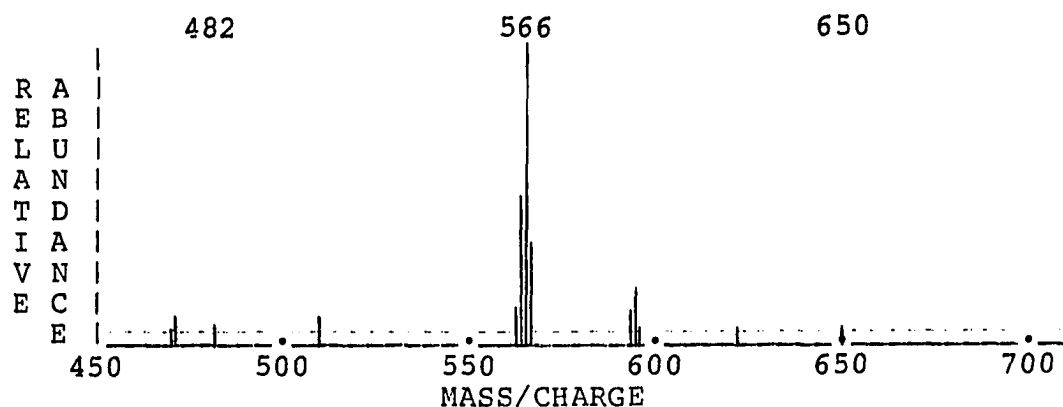


Figure 14. Mass Spectrum of  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$ .<sup>13</sup>

Table 5.  
 $\text{Fe}((\text{DMP})_3\text{BH})((\text{Pz})_3\text{BH})$  MS data.<sup>13</sup>

MASS:	257	258	268	269	270	283
ABUNDANCE:	9.8	6.1	7.8	22.8	5.1	7.1
MASS:	295	296	297	298	309	323
ABUNDANCE:	10.2	20.6	31.5	5.9	7.7	8.6
MASS:	324	325	326	336	337	352
ABUNDANCE:	28.2	88.3	16.7	11.9	9.5	13.5
MASS:	353	354	364	419	420	470
ABUNDANCE:	30.2	6.8	11.7	5.2	12.3	5.0
MASS:	471	482	510	564	565	566
ABUNDANCE:	8.4	6.5	7.1	12.7	49.7	99.9
MASS:	567	593	594	595	622	650
ABUNDANCE:	32.1	9.7	16.3	6.4	5.4	6.4

#### Crude Mixed Complexes

The mass spectra in this section are of the products of water solutions of divalent transition metal ions (Mn, Fe, Co, Ni, Cu, and Zn) mixed with equimolar water solutions of  $\text{K}((\text{Pz})_3\text{BH})$  and  $\text{K}((\text{DMP})_3\text{BH})$ . The product



mixtures were extracted from the solutions with methylene chloride and dried.

The iron compounds tend to have relatively clean spectra. This is probably due to the ease of forming the  $\text{Fe}^{+3}$  ion allowing greater stability for the principal peaks 650, 566, and 482. The 555 ( $\text{Fe}((\text{DMP})_3\text{BH})(\text{DMP}_2\text{BH})^+$ ) and 415 ( $\text{Fe}((\text{Pz})_3\text{BH})(\text{Pz}_2\text{BH})^+$ ) peaks are relatively small. 336 is  $\text{Fe}((\text{Pz})_3\text{BH})(\text{Pz})^+$ . 269 is  $\text{Fe}((\text{Pz})_3\text{BH})^+$ . A clue for the formula of mass peak 201 comes from the manganese data. Although the mass is equivalent to a  $\text{Pz}_3^+$  species the 200 peak for the one AMU lighter manganese compound indicates  $\text{Fe}(\text{Pz}_2\text{B})^+$  to be the likely ion.

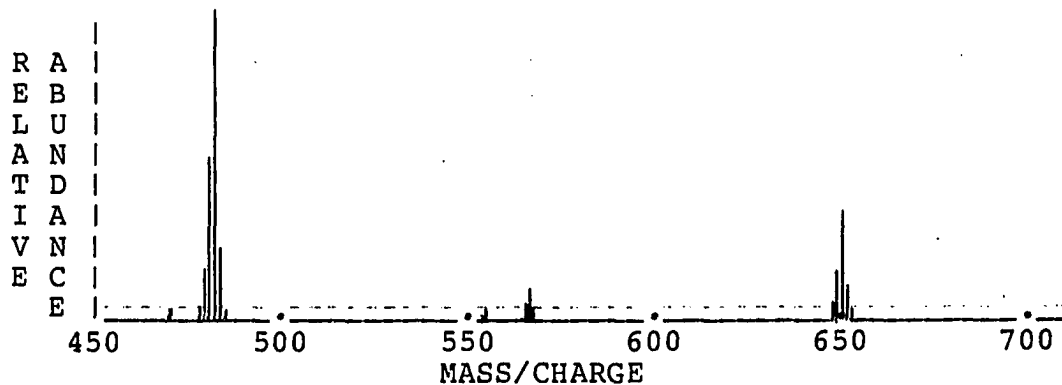


Figure 15. Fe(II) Complex

Table 6.  
MS data for Fe(II) mixed complexes.<sup>15</sup>

MASS:	200	201	202	206	207	213
ABUNDANCE:	10.4	37.4	7.4	1.9	8.3	1.0
MASS:	216	228	229	230	239	240
ABUNDANCE:	1.7	1.2	4.1	13.4	1.0	3.6

MASS:	241	242	243	267	268	269
ABUNDANCE:	4.1	1.7	2.4	3.6	8.8	31.2
MASS:	270	325	334	335	336	337
ABUNDANCE:	3.9	3.4	3.3	12.8	46.2	9.2
MASS:	338	344	345	346	347	351
ABUNDANCE:	1.0	1.7	5.5	9.3	3.5	1.3
MASS:	352	353	354	413	414	415
ABUNDANCE:	4.7	15.8	3.3	1.5	3.2	6.5
MASS:	416	448	471	479	480	481
ABUNDANCE:	1.3	1.3	1.3	3.8	15.0	54.1
MASS:	482	483	484	554	555	564
ABUNDANCE:	99.9	24.2	3.3	1.1	2.4	1.3
MASS:	565	566	567	648	649	650
ABUNDANCE:	5.1	10.7	3.7	4.1	16.1	36.8
MASS:	651	652				
ABUNDANCE:	13.9	3.1				

The manganese mixture gave a spectrum similar to the iron mixture. Whole molecule peaks are at 481, 565, and weakly at 649. The 470 peak is the heteroligand complex without a 3,5-dimethylpyrazole ring. 414 is the mass of  $\text{Mn}((\text{Pz})_3\text{BH})(\text{Pz}_2\text{BH})^+$ . 324, 296, and 268 are  $\text{Mn}((\text{DMP})_2(\text{Pz})\text{BH})^+$ ,  $\text{Mn}((\text{Pz})_2(\text{DMP})\text{BH})^+$ , and  $\text{Mn}((\text{Pz})_3\text{BH})^+$  respectively. Clearly there is B-N breaking and forming during the analysis. The 200 mass number is from  $\text{Mn}(\text{Pz}_2\text{B})^+$ .

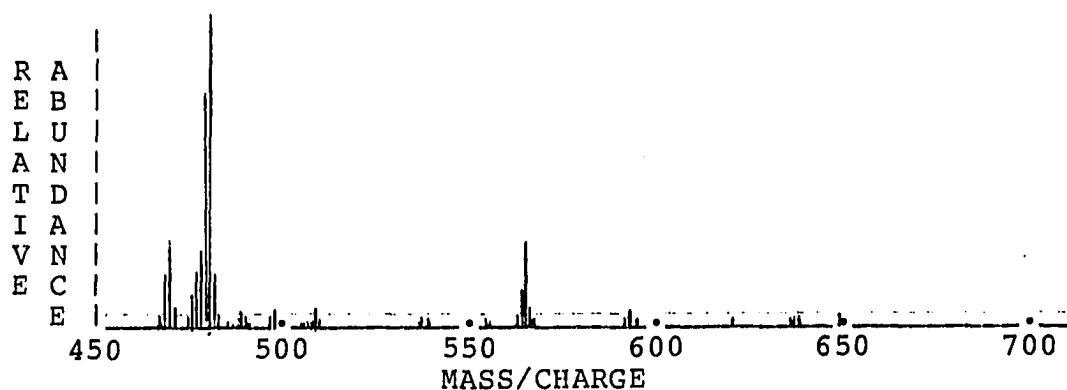


Figure 16. Mn(II) Complex

Table 7.  
Mn(II) Complex MS data.<sup>15</sup>

MASS:	199	200	201	206	207	209
ABUNDANCE:	8.0	33.6	7.8	12.6	3.2	5.0
MASS:	210	212	212	214	215	225
ABUNDANCE:	2.4	2.6	1.1	1.3	3.5	2.2
MASS:	227	228	219	236	237	238
ABUNDANCE:	2.2	5.2	2.5	4.2	2.4	2.2
MASS:	239	248	264	265	266	267
ABUNDANCE:	1.9	1.9	3.4	7.3	4.3	11.2
MASS:	268	269	275	276	277	291
ABUNDANCE:	47.5	45.0	2.5	1.9	1.4	1.4
MASS:	292	294	295	296	302	303
ABUNDANCE:	2.1	1.0	1.9	7.8	2.3	1.5
MASS:	304	305	323	324	325	331
ABUNDANCE:	1.0	1.2	4.0	13.1	2.2	1.9
MASS:	332	334	335	336	342	343
ABUNDANCE:	1.4	4.3	5.9	2.7	1.5	1.2

MASS:	344	345	346	351	352	353
ABUNDANCE:	1.0	1.9	1.7	2.4	5.1	1.3
MASS:	354	356	383	384	387	405
ABUNDANCE:	1.6	1.1	1.3	1.0	1.2	2.0
MASS:	406	407	408	410	411	412
ABUNDANCE:	3.3	1.5	2.0	2.6	4.9	4.8
MASS:	413	414	415	416	420	421
ABUNDANCE:	29.9	53.0	10.3	2.2	3.9	7.0
MASS:	422	423	424	427	433	434
ABUNDANCE:	6.2	4.8	2.4	1.4	1.2	1.1
MASS:	435	441	442	467	468	469
ABUNDANCE:	1.1	2.1	3.3	2.9	2.0	13.8
MASS:	470	471	472	476	477	478
ABUNDANCE:	26.2	5.0	1.7	2.0	9.3	16.4
MASS:	479	480	481	482	482	484
ABUNDANCE:	22.4	73.8	99.9	19.1	2.8	1.3
MASS:	487	488	489	490	491	492
ABUNDANCE:	1.6	2.8	2.2	3.5	1.1	1.6
MASS:	497	498	505	506	507	508
ABUNDANCE:	2.2	4.9	1.0	1.2	1.7	2.9
MASS:	509	510	536	537	538	552
ABUNDANCE:	6.9	2.9	1.7	3.8	1.2	1.1
MASS:	554	561	562	563	564	565
ABUNDANCE:	1.2	1.5	2.0	3.6	12.4	26.9
MASS:	566	567	592	592	594	621
ABUNDANCE:	6.2	1.1	2.1	5.1	1.7	1.9
MASS:	636	637	638	649		
ABUNDANCE:	1.3	1.7	1.5	1.9		

Cobalt yields a spectrum very similar to that of iron. Equivalent peaks will be 3 AMU heavier and there is a slightly greater tendency to fragment the principal peaks. For example peaks 474 and 418 are more intense

than the similar peaks in the iron spectra.

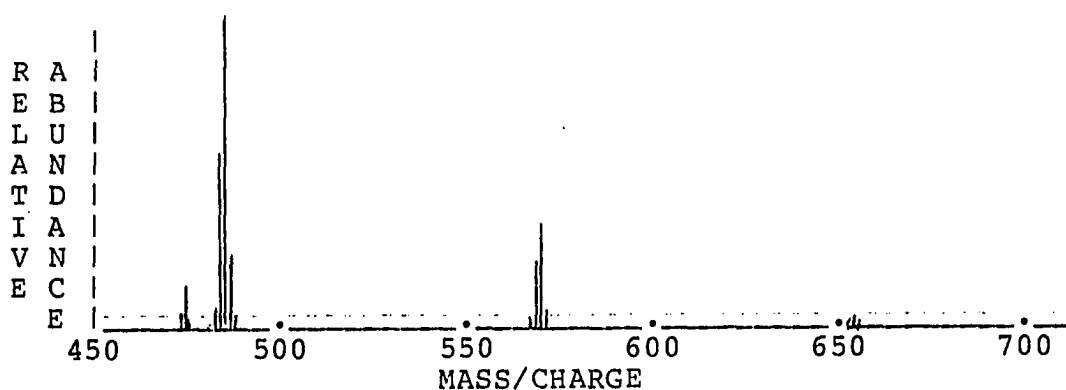


Figure 17. Co(II) Complex

Table 8.  
MS data for Co(II) Mixed complexes.<sup>15</sup>

MASS:	201	203	204	205	206	208
ABUNDANCE:	1.4	11.1	33.8	6.2	1.0	2.6
MASS:	218	222	225	231	232	243
ABUNDANCE:	1.3	1.0	1.0	2.0	2.4	1.4
MASS:	269	270	271	272	273	280
ABUNDANCE:	1.3	2.5	11.9	48.0	5.6	1.2
MASS:	281	300	321	322	323	327
ABUNDANCE:	1.0	3.0	1.1	1.2	1.2	2.3
MASS:	328	329	338	348	349	350
ABUNDANCE:	8.7	2.7	2.0	5.6	15.9	4.1
MASS:	356	405	406	416	417	418
ABUNDANCE:	2.5	1.1	1.2	2.8	11.9	22.0
MASS:	419	473	474	475	482	483
ABUNDANCE:	6.6	5.6	14.4	3.9	3.0	6.5
MASS:	484	485	486	487	567	568
ABUNDANCE:	56.7	99.9	22.1	2.7	3.0	19.0
MASS:	569	570	571	652	653	654
ABUNDANCE:	32.9	6.0	1.5	1.3	1.5	1.3

Nickel complexes display a greater tendency to fragment while undergoing mass spectrometry than manganese, iron or cobalt. The peaks occur at one mass unit less than that for cobalt. Peaks 473 and 417 ( $\text{Ni}((\text{Pz})_3\text{BH})(\text{DMP}_2\text{BH})^+$  and  $\text{Ni}((\text{Pz})_3\text{BH})(\text{Pz}_2\text{BH})^+$  respectively) are especially intense. Nickel's two isotopes  $\text{Ni}^{58}$  and  $\text{Ni}^{60}$  tend to form more side peaks.

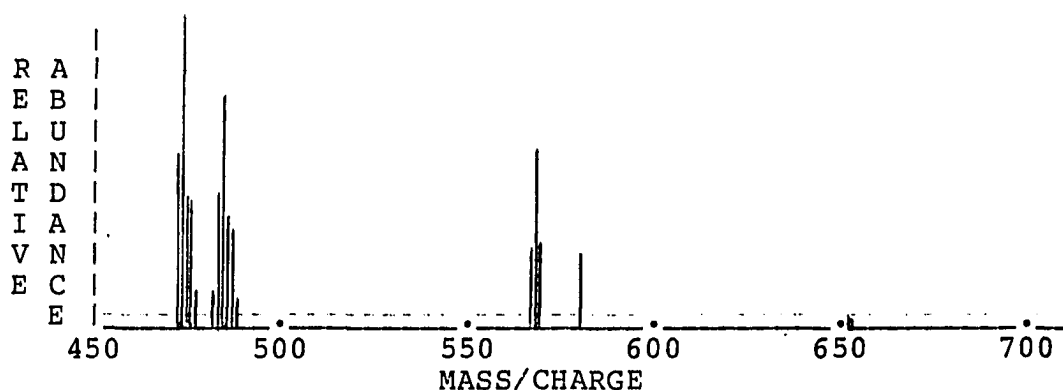


Figure 18. Ni(II) Complex

Table 9.  
MS data for Ni(II) Mixed Complexes.<sup>15</sup>

MASS:	203	204	270	271	273	327
ABUNDANCE:	19.9	16.7	10.3	41.4	15.6	26.1
MASS:	329	415	416	417	418	419
ABUNDANCE:	11.0	12.8	44.3	66.5	26.4	26.7
MASS:	472	473	474	475	476	482
ABUNDANCE:	54.5	99.9	40.9	40.2	12.9	13.5
MASS:	483	484	485	486	487	567
ABUNDANCE:	44.0	72.9	37.4	33.0	10.9	25.5
MASS:	568	569	578	652	653	
ABUNDANCE:	55.3	26.9	25.7	1.3	1.4	

Copper complexes tend to fragment to a much greater extent than the previous mixed complexes when undergoing mass spectrometry. It is interesting to note that copper has a very unstable or nonexistent +3 state in its chemistry. The 489 peak for  $\text{Cu}((\text{Pz})_3\text{BH})_2$  is reasonably intense but the  $\text{Cu}((\text{Pz})_3\text{BH})(\text{Pz}_2\text{BH})^+$  peak at 420 is far stronger. The 477  $\text{Cu}((\text{Pz})_3\text{BH})(\text{DMP}_2\text{BH})^+$  and 553  $\text{Cu}((\text{DMP})_3\text{BH})(\text{DMP}_2)^+$  ion peaks are far stronger than their parent peaks. More side peaks are caused by the presence of two copper isotopes,  $\text{Cu}^{63}$  and  $\text{Cu}^{65}$ .

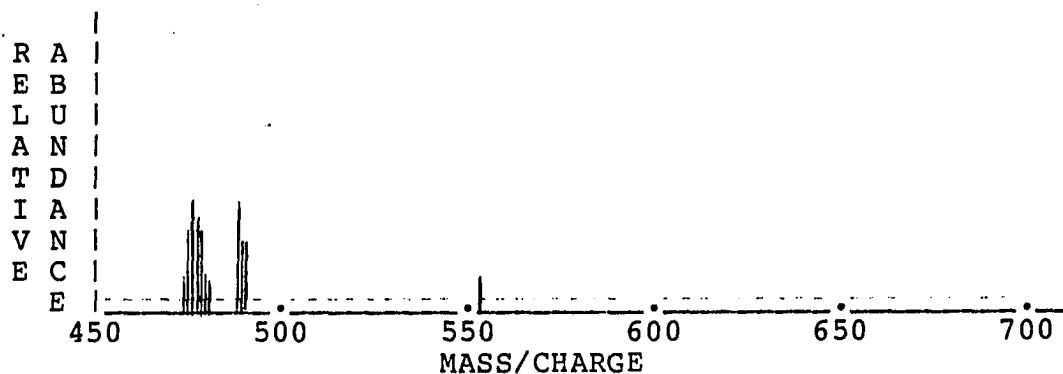


Figure 19.  
Cu(II) Complex, additional peak at 420.

Table 10.  
MS data for Cu(II) Mixed Complexes.<sup>15</sup>

MASS:	208	209	210	211	248	265
ABUNDANCE:	21.8	76.8	14.3	28.6	13.7	19.1
MASS:	275	276	277	354	355	404
ABUNDANCE:	20.0	10.9	10.9	14.3	26.2	18.2

MASS:	405	406	407	410	419	420
ABUNDANCE:	28.9	18.4	21.5	14.3	29.0	84.0
MASS:	421	422	423	433	434	435
ABUNDANCE:	65.0	41.4	24.6	12.7	10.4	10.7
MASS:	466	476	477	478	479	480
ABUNDANCE:	11.4	22.5	36.6	27.4	25.9	11.6
MASS:	481	488	489	490	491	553
ABUNDANCE:	11.4	12.8	35.0	23.7	23.4	11.1

Zinc complexes break down completely while undergoing mass spectrometry. The wide bands in the mass regions of 310 and 244 contain zinc in its three main isotopes  $\text{Zn}^{64}$ ,  $\text{Zn}^{66}$ , and  $\text{Zn}^{68}$ . 310 may be  $\text{Zn}((\text{Pz})_2(\text{DMP})\text{BH})^+$ , the 244 band  $\text{Zn}(\text{PzDMPBH})^+$ .



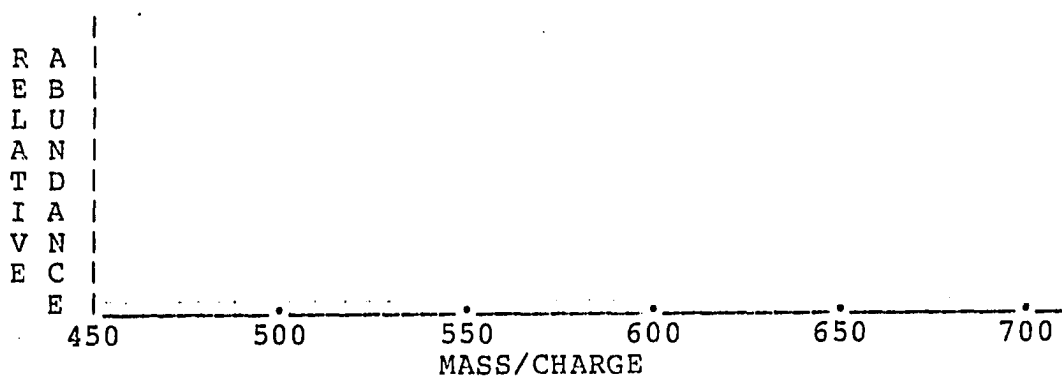


Figure 20.  
Zn(II) Complex, peaks at 310 and 244.

Table 11.  
MS data for Zn(II) Mixed Complexes.

MASS:	208	243	244	245	246	247
ABUNDANCE:	13.3	25.1	99.9	31.8	94.5	29.6
MASS:	248	249	250	276	278	309
ABUNDANCE:	58.54	11.4	12.2	20.6	11.3	11.2
MASS:	310	311	312	313	314	315
ABUNDANCE:	53.6	33.5	51.1	31.7	33.5	14.2

### Iron Mixed Complexes

An attempt was made to determine the effectiveness of various organic solvents in extracting  $\text{Fe}((\text{Pz})_3\text{BH})-(\text{DMP})_3\text{BH}$  from a precipitated mixture of complexes. The mixture was made by mixing an equimolar solution of  $\text{K}((\text{Pz})_3\text{BH})$  and  $\text{K}((\text{DMP})_3\text{BH})$  with a water solution of  $\text{Fe}^{+2}$ . Each extraction was done on a sample from the same filter cake. The mass spectral data shown on the figures and tables in this section illustrate the effectiveness of the various solvents in extracting the  $\text{Fe}((\text{Pz})_3\text{BH})-(\text{DMP})_3\text{BH}$ . Of the solvents tried carbon tetrachloride was superior. The principal peak for  $\text{Fe}((\text{Pz})_3\text{BH})-(\text{DMP})_3\text{BH}$  is 566. The two homogeneous complexes have peaks at 482 and 650. The solvents used were: Methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), hexane, 1-chloropropane (1-Cl), 1-nitropropane (1-N), chloroform ( $\text{CHCl}_3$ ), and carbon tetrachloride ( $\text{CCl}_4$ ).

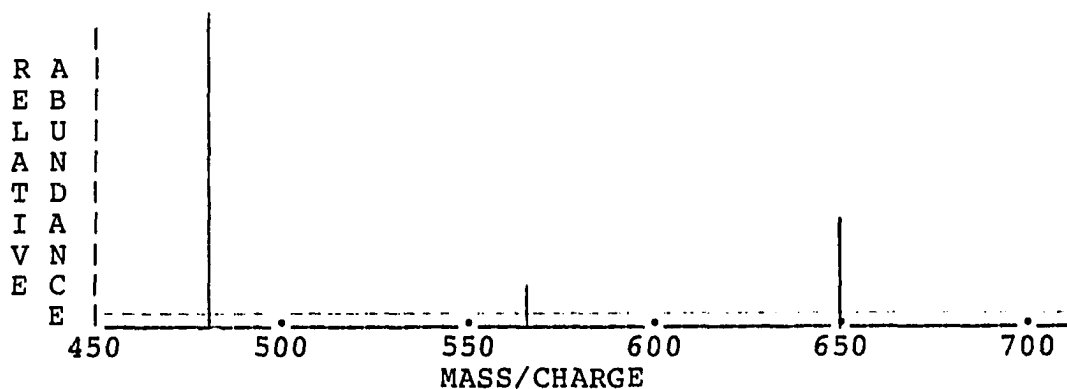


Figure 21.  $\text{Fe}((\text{Pz})_3\text{BH})-(\text{DMP})_3\text{BH}$   
Extracted with Methylene Chloride.

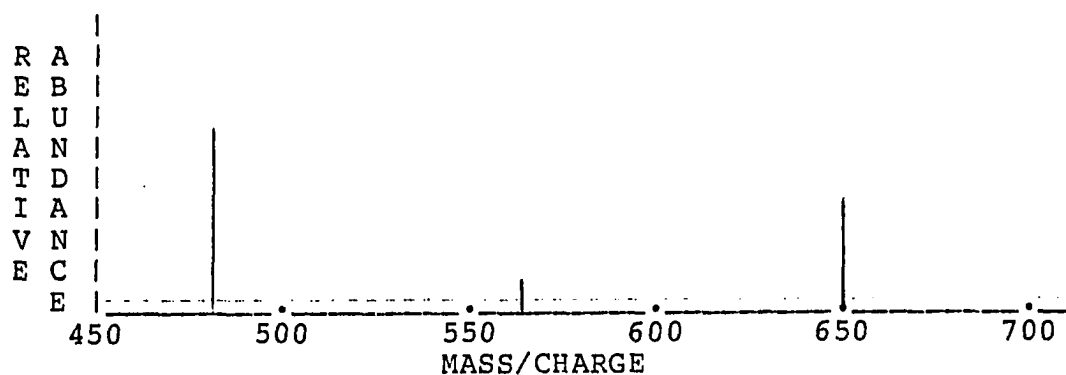


Figure 22.  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$   
Extracted with Hexane.

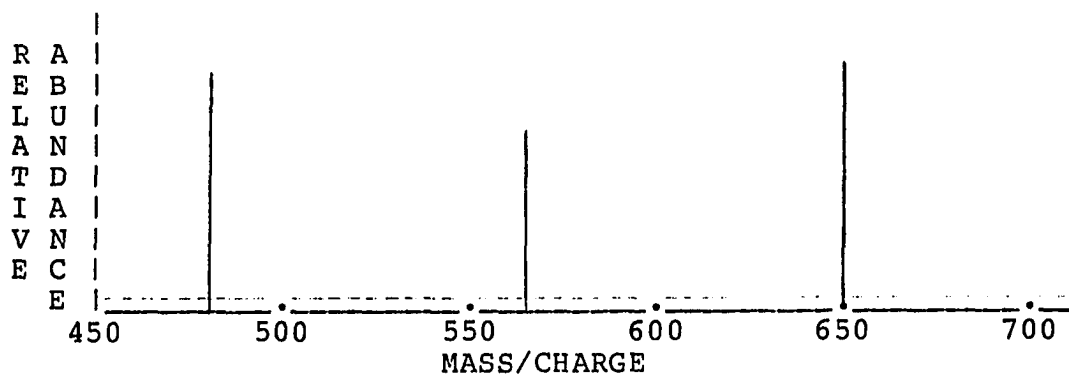


Figure 23.  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$   
Extracted with 1-Chloropropane.

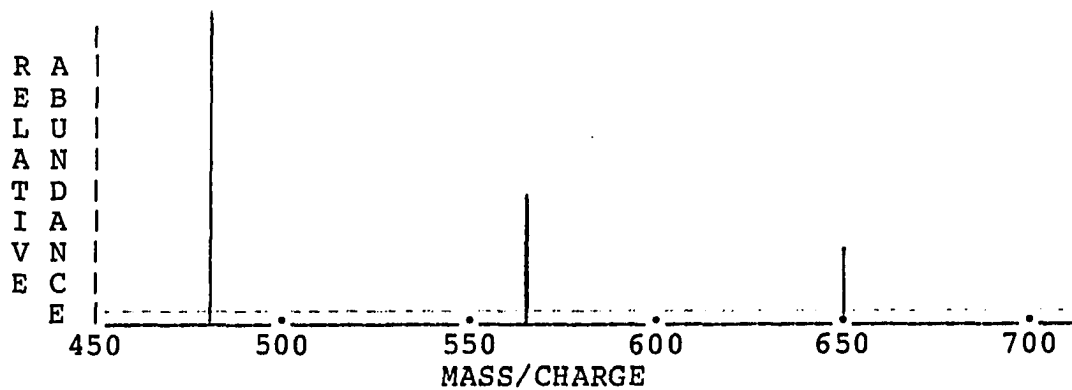


Figure 24.  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$   
Extracted with 1-Nitropropane.

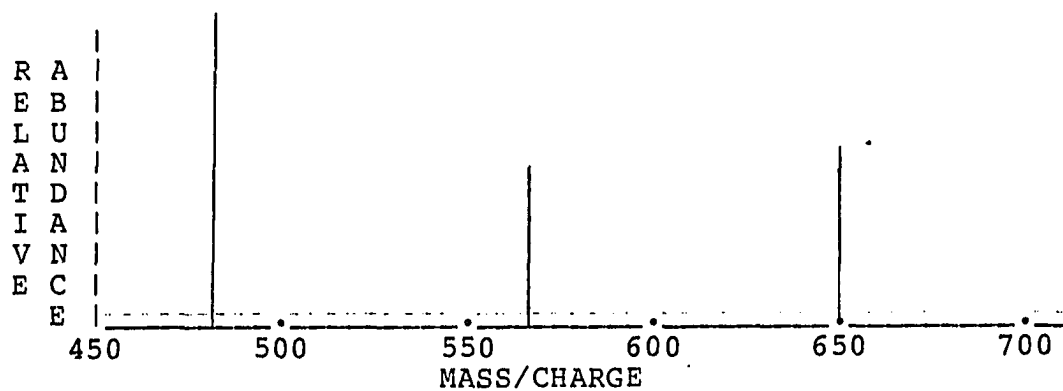


Figure 25.  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$   
Extracted with Chloroform.

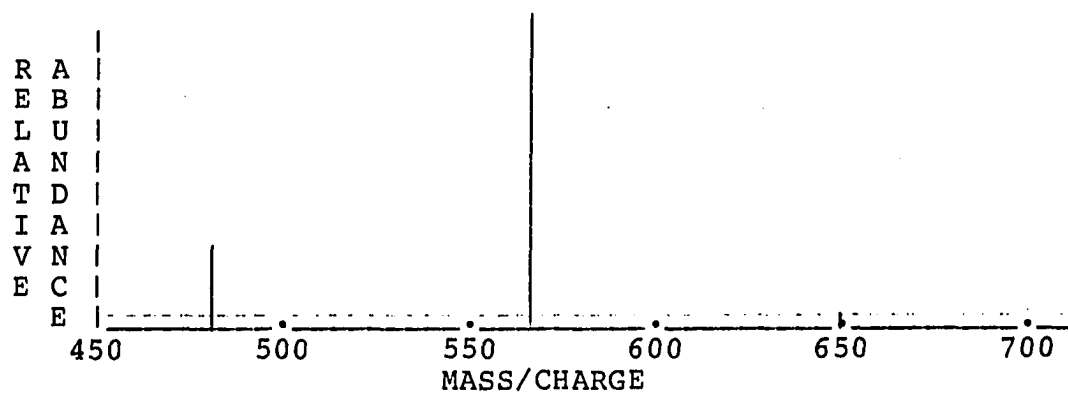


Figure 26.  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$   
Extracted with Carbon Tetrachloride.

Table 12.  
MS data for  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$  extracted  
with various solvents.

MASS	$\text{CH}_2\text{Cl}_2$	Hexane	1-Cl	1-N	$\text{CHCl}_3$	$\text{CCl}_4$
362	.2	.1	.9	.3	0.0	1.2
363	.3	.3	1.7	.7	1.1	2.8
364	.6	.9	4.3	3.5	3.8	7.9
365	.1	.2	.9	.6	.8	1.6
401	.1	0.0	.8	.7	.4	1.7
402	.2	.1	1.3	.8	.7	2.6
403	.1	.1	.9	.6	.3	1.7
413	1.5	1.0	2.2	2.3	1.7	.6
414	3.2	2.7	3.7	5.8	2.5	1.3
415	6.5	5.7	6.6	10.8	7.0	2.1
416	1.3	.7	1.6	2.5	1.3	.5
418	.1	.3	.7	.4	.2	1.3
419	.3	.4	2.6	1.6	2.5	4.8
420	.9	1.0	7.5	5.4	6.3	15.1
421	.1	.4	1.9	1.2	2.8	3.7
469	.1	.3	1.4	1.1	1.4	2.6
470	.6	.6	3.7	3.9	5.2	7.3
471	1.3	1.7	7.1	6.8	9.1	13.8
472	.3	.5	1.7	2.1	2.5	3.7
479	3.8	1.0	3.0	4.9	3.6	1.1
480	15.0	8.0	12.0	19.1	14.7	4.1
481	54.1	30.9	42.2	71.1	49.0	14.0
482	99.9	59.1	76.7	99.9	99.9	25.7
483	24.2	15.2	19.2	32.3	22.0	6.8
484	3.3	1.6	3.0	4.7	1.9	.9
554	1.1	1.2	2.5	.5		2.1
555	2.4	1.3	5.3	1.0		4.3
556	.8	1.1	1.6	.3		1.3
563	.3	.2	2.0	1.2	1.4	3.4
564	1.3	1.2	7.4	5.7	6.2	13.3
565	5.1	4.3	27.3	20.1	22.7	48.9
566	10.7	9.7	56.6	42.0	51.2	99.9
567	3.7	2.0	16.9	12.7	18.1	30.7
568	.7	.3	2.9	1.9	2.3	5.0
647	.9	.8	2.6	.9	.2	1.9
648	4.1	3.5	10.5	3.2	.5	7.3
649	16.1	10.3	38.4	13.5	1.7	27.6
650	36.8	25.6	80.6	22.8	3.1	57.3
651	13.9	9.0	29.5	7.0	1.5	21.0
652	3.1	1.1	5.8	1.4		4.1

### Asymmetric Complexes

Figures 27 and 28 contain mass spectra of mixtures of asymmetric complexes. Individual peaks may represent more than one compound. For example while the iron compound 510 peak only represents  $\text{Fe}((\text{Pz})_3\text{BH})((\text{Pz})_2(\text{DMP})\text{BH})$  the 538 peak could be  $\text{Fe}((\text{Pz})_2(\text{DMP})\text{BH})_2$ ,  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_2(\text{Pz})\text{BH})$  or a combination of both. The 510 to 594 peaks represent complexes with various ratios of pyrazole to 3,5-dimethylpyrazole. The peaks 269 to 364 represent their decomposition products. The cobalt spectrum is similar to the iron spectrum. Isotope peak widening confirms the empiracle formula of the compounds.

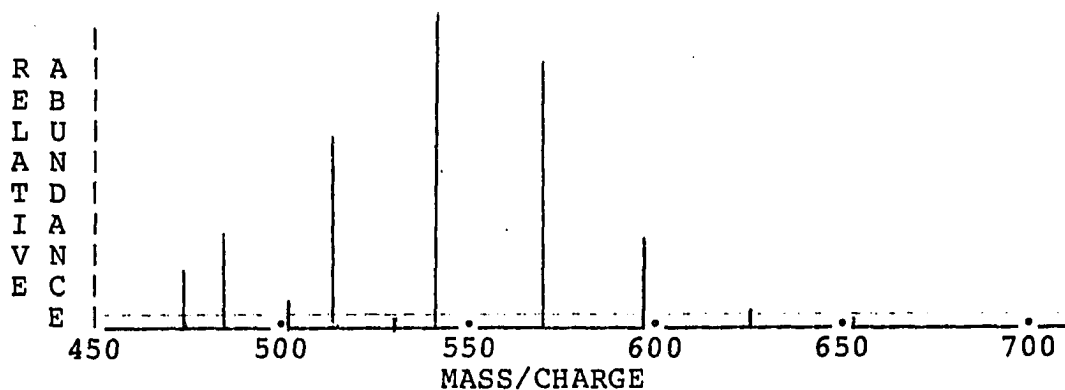


Figure 27. Cobalt Product of  $\text{Co}((\text{DMP})_2\text{BH}_2)_2$  plus Pyrazole.

Table 13.  
MS data of  $\text{Co}((\text{DMP})_2\text{BH}_2)_2$  plus pyrazole.<sup>14</sup>

MASS:	418	446	474	485	502	513
ABUNDANCE:	15.0	22.0	17.0	30.5	8.5	62.5
MASS:	530	541	569	597	625	653
ABUNDANCE:	1.5	99.9	85.0	30.5	5.0	.5

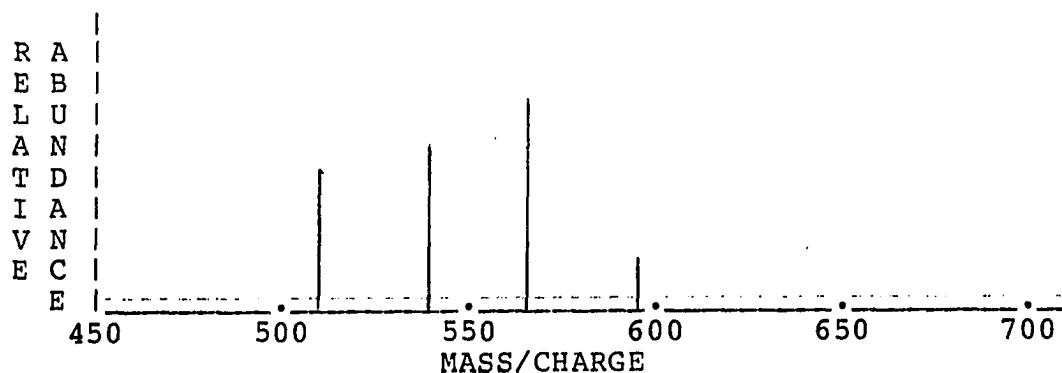


Figure 28. Iron Complexed with  
 $\text{K}((\text{DMP})_2(\text{Pz})\text{BH})$ ,  $\text{K}((\text{Pz})_2(\text{DMP})\text{BH})$  Mixture.<sup>13</sup>

Table 14.  
MS data for asymmetric iron complex.

MASS:	269	297	309	325	336	353
ABUNDANCE:	24.0	63.0	7.9	45.0	7.9	5.3
MASS:	364	392	510	538	566	594
ABUNDANCE:	18.0	16.0	45.0	53.0	68.0	16.0

## DISCUSSION

### Synthesis Descriptions

The synthesis of the simple ligands and their homogeneous complexes are covered in the introduction and referenced literature. In this section the synthesis, purification, and evidence for existence of the heterogeneous complexes and the complexes of the novel ligands are discussed.

Mixed complexes of the form  $((Pz)_3BH)M((DMP)_3BH)$  are synthesized by the reaction  $M^{+2} + ((Pz)_3BH)^- + ((DMP)_3BH)^- \rightarrow M((Pz)_3BH)_2 + M((DMP)_3BH)_2 + M((Pz)_3BH)((DMP)_3BH)$ . This is similar to the first and second reactions shown in Table 2. The problem arises in the separation and purification of the three complexes thus formed. By simple statistics it would be assumed that fifty percent of the product should be the desired material, i.e. for Ligand 1 equal in concentration to ligand 2, that is a .5 fraction each, the product yield should be  $.5^2$  (.25) each for the homogeneous complexes and  $2 \times .5^2$  (.50) for the mixed complex. This is illustrated in Table 15.



Table 15.  
The Possible Combinations of a Metal with Two Ligands.

	((Pz) <sub>3</sub> BH)	((DMP) <sub>3</sub> BH)
((Pz) <sub>3</sub> BH)	$M((Pz)_3BH)_2$	$M((Pz)_3BH)((DMP)_3BH)$
((DMP) <sub>3</sub> BH)	$M((Pz)_3BH)((DMP)_3BH)$	$M((DMP)_3BH)_2$

In practice the yields of mixed complexes are much lower than this expected value. For example, the cobalt complex gives a 30% yield of the products collected and the iron complex about 10%. The reason for this low yield is unclear although it may be due to differences in the chelating power of different ligands. Several methods of separating the heterogeneous complex from the other two compounds were attempted. Among them were; fractional crystalization, sublimation, solvent extraction and column chromatography. Column chromatography using a short column and two solvents of differing polarity was the most effective. First using moderately polar methylene chloride to remove the homogeneous complex then very polar ethanol to collect the desired heterogeneous complex. The heterogeneous complexes synthesized tend to form fine powders rather than large crystals when their solutions are evaporated.

Growing large crystals proved to be quite difficult.

The adsorbent used for column chromatography was silica gel. Silica gel thin layer plates were used for solvent testing. Solvents were tested by spotting the test plates with the appropriate sample material. First the plates were developed in pure solvents of differing polarity. With pure solvents there is a tendency for materials to have  $R_f$ s of one or zero, for example, a mixture of  $M((Pz)_3BH)_2$  and  $M((DMP)_3BH)_2$  had an  $R_f$  of one with methylene chloride and nearly zero with hexane as eluents. A solution of 5% methylene chloride in hexane gave a good separation. All of the complexes with a mixture of pyrazoles proved to be far more polar than the homogeneous complexes. Once this was discovered the purification of  $M((Pz)_3BH)((DMP)_3BH)$  was found to be very straightforward. A short silica gel column containing the mixture of complexes was washed with a moderately polar solvent (methylene chloride) to remove the homogeneous complexes and then with a very polar solvent (methanol or ethanol) to extract the pure heterogeneous complex. The main impurity in the iron compound after removal from the column appears to be organic and water soluble chlorides of iron.

The most important method for characterizing mixed complexes is mass spectrometry. Figure 14 illustrates

the mass spectrum of  $\text{Fe}((\text{Pz})_3\text{BH})((\text{DMP})_3\text{BH})$  prepared by column chromatography. Note the intense peak at the formula weight of the compound, 566. A mixture of homogeneous complexes would have intense peaks at 482 and 650 amu without the 566 peak.

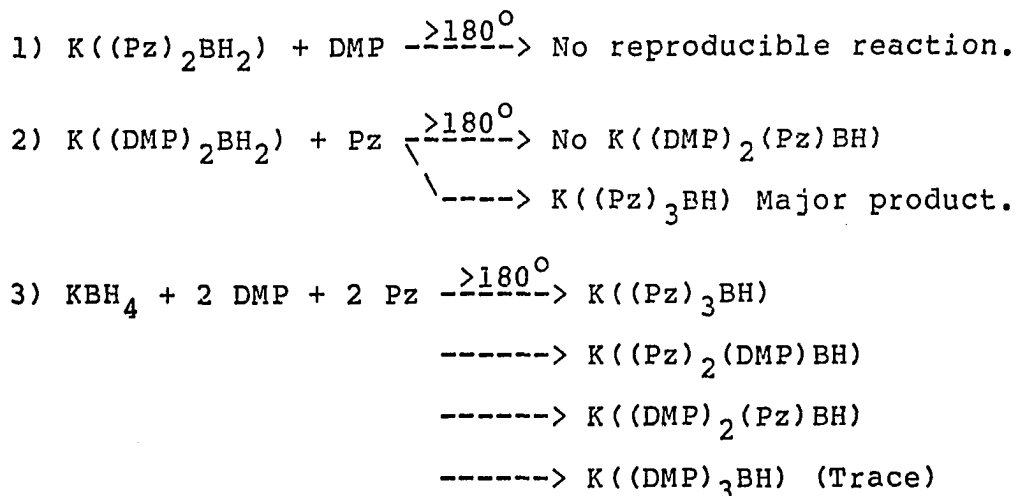
A less successful but noteworthy method for separation of the heterogeneous complex was solvent extraction. The ms data for the products of six solvents used to extract the complex from a water precipitate are shown in Table 12 and Figures 21-26. Carbon tetrachloride is the solvent that yields the largest fraction of the iron heterogeneous complex. The suitability of the solvents follows the order: carbon tetrachloride >> chloroform > 1-nitropropane > 1-chlorobutane > hexane > methylene chloride.

### Asymmetric Complexes

Originally ligands for asymmetric complexes were to be synthesised by reacting the dihydrobispyrazolyl compound with a different pyrazole. For example  $K((Pz)_2BH_2)$  was reacted with 3,5 Dimethylpyrazole in excess at over  $180^{\circ}C$  to synthesize  $K((Pz)_2(DMP)BH)$ .  $K((DMP)_2BH_2)$  was reacted with excess pyrazole at over  $180^{\circ}C$  to synthesize  $K((DMP)_2(Pz)BH)$ . The purpose of synthesizing these ligands was to create transition metal complexes of the form  $ML_2$  which have the potential for forming optical isomers. Isolating these compounds proved to be surprisingly difficult. The reaction of 3,5-dimethylpyrazole with  $K((Pz)_2BH_2)$  did not usually give  $K((Pz)_2(DMP)BH)$ . Surprisingly, during the formation of  $K((Pz)_2(DMP)BH)$  large amounts of potassium hydrotris(1-pyrazolyl)borate are formed even with an excess of 3,5-dimethylpyrazole. The source of the additional pyrazole is unknown, but is presumably residual material in the  $K((Pz)_2BH_2)$  or a product of its decomposition. In the reaction of  $K((DMP)_2BH_2)$  with pyrazole, it was found that the reaction went beyond the formation of  $K((DMP)_2(Pz)BH)$  to the creation of potassium hydrotris(1-pyrazolyl)borate,  $K((Pz)_3BH)$ , as almost the only product. The reactivity of pyrazole is sufficiently greater than 3,5-dimethyl-

pyrazole that the latter is completely displaced from the boron. These reactions are illustrated in Table 16.

Table 16  
Novel Ligands



A mixture of ligands is obtained by reacting  $KBH_4$  and limited quantities of pyrazole along with an excess of 3,5-dimethylpyrazole. The reaction (Shown in Table 16) yields primarily  $K((Pz)_3BH)$  and  $K((Pz)_2(DMP)BH)$  with a smaller fraction of  $K((DMP)_2(Pz)BH)$  and trace amounts of  $K((DMP)_3BH)$ . The mass spectrum of the iron derivative is illustrated in Figure 28 and Table 14.

#### Complex Modification

As an alternative to synthesizing ligands with mixed pyrazoles in order to form potentially optically active

complexes, the investigator attempted modifying complexes of the form  $M((Pz)_2BH_2)_2$  by reaction with a distinct pyrazole ( $Pz'$ ). The speculation was that the product would be  $M(Pz_2Pz'BH)_2$  with a minimal exchange of the original pyrazole due to its stabilization by the metal. One advantage of this technique is the relative ease of purifying the starting materials.

Some of the reactions carried out using this method included:

Table 17  
Complex Modification

---

$Co((DMP)_2BH_2)_2 + Pz \xrightarrow{210^\circ}$	
----> $Co((Pz)_3BH)_2$	FW = 485
----> $Co((Pz)_3BH)((Pz)_2(DMP)BH)$	FW = 513
----> $Co((Pz)_2(DMP)BH)_2$	FW = 541
----> $Co((DMP)_2(Pz)BH)((Pz)_3BH)$	FW = 541
----> $Co((DMP)_2(Pz)BH)((Pz)_2(DMP)BH)$	FW = 569
----> $Co((DMP)_2(Pz)BH)_2$	FW = 597
Produced in small quantities:	
----> $Co((DMP)_3BH)((Pz)_3BH)$	FW = 569
----> $Co((DMP)_3BH)((Pz)_2(DMP)BH)$	FW = 597
----> $Co((DMP)_3BH)((DMP)_2(Pz)BH)$	FW = 625
----> $Co((DMP)_3BH)_2$	FW = 653

---

Using a slight excess of pyrazole these products were produced in approximately equal amounts. Note that more

than one compound may have the same molecular weight. The peak heights in the mass spectra (Figure 27) were consistent with similar amounts of  $((\text{Pz})_3\text{BH})^-$ ,  $((\text{Pz})_2(\text{DMP})\text{BH})^-$ , and  $((\text{DMP})_2(\text{Pz})\text{BH})^-$ , with trace amounts of  $((\text{DMP})_3\text{BH})^-$ .

Clearly, according to the second reaction in Table 16, if the reaction of the  $((\text{DMP})_2\text{BH}_2)$  coordinated to cobalt(II) proceeded analogously to that of the bare  $((\text{DMP})_2\text{BH}_2)$ - ligand the product would have been nearly 100%  $\text{Co}((\text{Pz})_3\text{BH})_2$ . It is clear that the metal ion gave some protection to the 3,5-dimethylpyrazole from displacement. The completion of this reaction was easily followed by the color change from blue  $\text{Co}((\text{DMP})_2\text{BH}_2)_2$  to yellow  $\text{Co}((\text{Pz})_3\text{BH})_2$ <sup>6</sup>. The reaction of  $\text{Co}((\text{Pz})_2\text{BH}_2)_2 + \text{DMP}$  was less successful, presumably due to the lower reactivity of DMP. In addition, due to the air sensitivity of  $\text{Co}((\text{Pz})_2\text{BH}_2)_2$  it was not possible to remove all unreacted pyrazole, giving largely the pyrazole products. Still, a mixture of complexes was obtained.

Several methods were attempted to separate and purify the mixtures of complexes formed in the synthesis reactions. Recrystallization, vacuum sublimation, and column chromatography were all tried. Only column chromatography using moderately polar solvents, as

methylene chloride, met with any success.

Separating mixtures of complexes with mixed pyrazole ligands is more difficult than separating homogeneous from heterogeneous complexes, requiring a tall chromatography column for separations. The bare ligands cannot be separated on silica gel columns at all, because the materials to be separated decompose.

The products of the columns were only weight biased mixtures of the original material with the compounds containing the most 3,5-dimethylpyrazole having the lower Rfs.

One product of the investigator's attempts at synthesizing asymmetric complexes was particularly insoluble in organic solvents and water. The cobalt form has a molecular weight of 597 according to mass spectra (Figure 29). This is consistent with a formula of  $\text{Co}((\text{DMP})_2(\text{Pz})\text{BH})_2$  or  $\text{Co}((\text{DMP})_3\text{BH})((\text{Pz})_2(\text{DMP})\text{BH})$ . This was the only product separated by a solubility difference. Unfortunately, elemental analysis indicated the sample contained a large proportion of inert material.



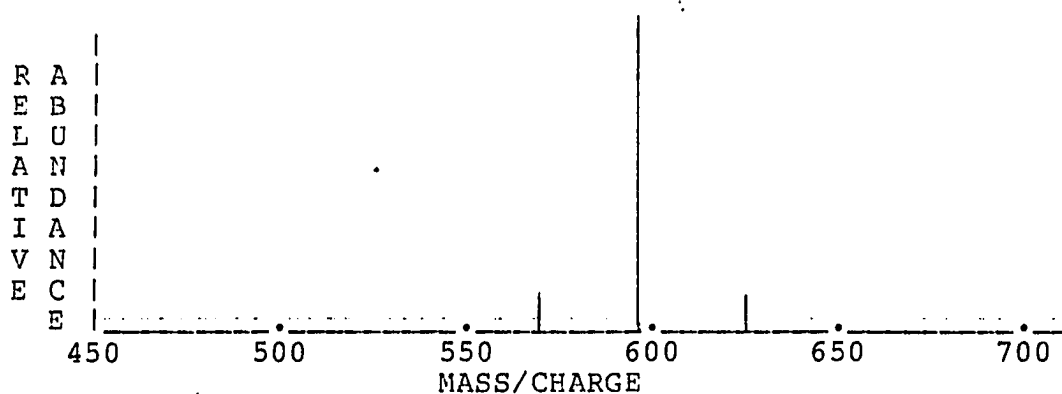


Figure 29. Mass Spectrum,  
Insoluble Cobalt Complex.<sup>14</sup>

### Interpretation of Mass Spectra

The mass spectrometer was critical to this research. The strongest evidence for the existence of compounds with mixed or novel ligands comes from the spectra.

The first attempts at using mass spectra to look at heterogeneous complexes were the crude mixed complexes Figures 15-20 and Tables 6-11. This "quick and dirty" approach showed that iron and cobalt had the easiest spectra to interpret. It is for this reason that most of this study centers on those two elements. Both iron and cobalt have stable +3 oxidation states, manganese and nickel have less stable +3 oxidation states, with copper and zinc having no oxidation states above +2. The stabilities of the parent ions of their complexes follow the order in descending stability Fe,Co > Ni,Mn > Cu > Zn. This supports the conclusion that if the metal ion can

hold an additional charge, the parent ion is stabilized.

The mass spectra illustrated in Figures 27 and 28 give strong evidence to the existence of a mixture of distinct compounds rather than the decomposition of a single compound.

The single peak that generates the most concern is the 230 amu peak listed in Table 3 for  $\text{Fe}((\text{DMP})_3\text{BH})_2$ . The derth of neighboring peaks indicates a formula of  $\text{FeN}_{12}\text{H}_6^+$  as the most rational. The 3,5-dimethylpyrazole rings are bound directly to the iron by the nitrogens in the parent compound. The rings are formed by a condensation with hydrazine. This may be at least a partial rational for the stability of the 230 ion.

## RECOMMENDATIONS

Attempts at purifying the novel ligands containing two kinds of pyrazole or their derivative complexes were not successful. Conventional column chromatography had very limited success in separating different complexes, usually eluting several compounds in one band. Only in the simple case of separating the homogeneous from the mixed complexes was the technique useful. Modern HPLC methods were not used. In future investigations such techniques would prove very useful. With careful choice of solvent, such as N,N-dimethylformamide, even the decomposition prone ligands might be separated. Pure ligands would allow the synthesis of racemic mixtures of metal complexes.

It is not clear why the yields of mixed complexes are so low. There is little enthalpy data on the formation of the homogeneous complexes covering only a few ligands and metals.<sup>12</sup> There is no data on the mixed complexes. Thin layer chromatography using precipitate samples recovered at several points of a metal ion ligand titration was inconclusive. Careful measurements of the products of a metal ion titrated into a mixed solution of ligands plus good thermodynamic data would help clarify the relative chelating strengths of the ligands for various metals.

# APPENDIX

		Mixed Metal Complex AMU of Significant Peaks				
ION	AMU	Mn	Co	Ni	Cu	Zn
Fe (DMP) <sub>3</sub> BH) <sub>2</sub> <sup>+</sup>						
M ((DMP) <sub>3</sub> BH) <sub>2</sub> <sup>+</sup>	650	649	653	652		
M ((DMP) <sub>3</sub> BH) (DMP) <sub>2</sub> BH) <sup>+</sup>	555					
M ((DMP) <sub>3</sub> BH) <sup>+</sup>	353					
M ((DMP) <sub>3</sub> BH) (DMP) <sub>2</sub> <sup>+</sup>					553	
Fe ((Pz) <sub>3</sub> BH) <sub>2</sub>						
M ((Pz) <sub>3</sub> BH) <sub>2</sub> <sup>+</sup>	482	481	485	484	489	
M ((Pz) <sub>3</sub> BH) (Pz) <sub>2</sub> BH) <sup>+</sup>	415	414	418	417	420	
M ((Pz) <sub>2</sub> BH) <sub>2</sub> <sup>+</sup>	346		349		355	
M (Pz) ((Pz) <sub>3</sub> BH) <sup>+</sup>	336					
M ((Pz) <sub>3</sub> BH) <sup>+</sup>	269	268	272	271	275	
(Pz) <sub>3</sub>	207					
Fe ((Pz) <sub>3</sub> BH) (DMP) <sub>3</sub> BH)						
M ((Pz) <sub>3</sub> BH) (DMP) <sub>3</sub> BH) <sup>+</sup>	566	565	569	568		
M ((Pz) <sub>3</sub> BH) (DMP) <sub>2</sub> BH) <sup>+</sup>		470		473	477	
M ((DMP) <sub>2</sub> (Pz)BH) <sup>+</sup>		325	324	328	327	
M ((Pz) <sub>2</sub> (DMP)BH) <sup>+</sup>		297	296	300		310
M ((Pz)(DMP)BH) <sup>+</sup>						244

Asymmetric Complex	AMU of Parent Peaks	
	Fe	Co
$M(DMP)_3BH)_2$	650	653
$M((DMP)_3BH)((DMP)_2(Pz)BH)$	622	625
$M((DMP)_3)_3BH)((Pz)_2(DMP)BH)$	591	594
$M(DMP)_2(Pz)BH)_2$	591	594
$M((DMP)_2(Pz)BH)((Pz)_2(DMP)BH)$	566	569
$M((DMP)_3BH)(Pz)_3BH)$	566	569
$M((Pz)_2(DMP)BH)_2$	538	541
$M((Pz)_3BH)((DMP)_2(Pz)BH)$	538	541
$M((Pz)_3BH)((Pz)_2DMPBH)$	510	513
$M((Pz)_3BH)_2$	482	485

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