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## Enthalpy of Chelation of a Series of Poly(1-pyrazolyl)borates with Some Divalent Transition Metal Ions in Water and Acetonitrile

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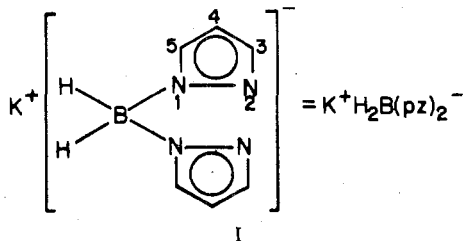
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The enthalpy of chelation of Co(II), Ni(II), Cu(II), and Zn(II) with four poly(1-pyrazolyl)borate ligands is reported in water and acetonitrile media. Whereas precipitation of the chelates occurs in every case in water, all product species are soluble in acetonitrile. Enthalpy results suggest that six-coordinate Cu(II) complexes may be tetragonal rather than octahedral. Evidence is presented which indicates the formation of six-coordinate, anionic chelates of Co(II) and Ni(II) with the bidentate, monoanionic dihydrobis(1-pyrazolyl)borate ligand in acetonitrile solution. Substitution of a methyl group in the pyrazole rings of this ligand molecule prevents chelate anion formation as a result of steric hindrance. Enthalpy values for the substituted ligand are lower than for the unsubstituted one in those cases where a steric effect is expected. Replacement of the remaining boron hydrogen of hydrotris(1-pyrazolyl)borate by a fourth pyrazole group results in substantially decreased enthalpies of reaction in both water and acetonitrile media, most likely because of coordination competition with the uncomplexed pyrazole ring. The much larger enthalpy values obtained in acetonitrile in all cases are attributed to the markedly weaker solvation of the metal and ligand ions by this solvent than by water.

### Introduction

A series of ligands has been reported by Trofimenko, Jesson, and Eaton<sup>2-5</sup> which offers unique opportunities for thermodynamic and stereochemical study of chelation reactions. The poly(1-pyrazolyl)borates are uninegative ligands of the general formula H<sub>n</sub>B(pz)<sub>4-n</sub><sup>-</sup>, where *n* is 0, 1, and 2 and the "pz" stands for the 1-pyrazolyl moiety. Potassium dihydrobis(1-pyrazolyl)borate is shown in I. This ligand molecule is bi-



dentate, coordination taking place through the pyrazole nitrogen atoms. Further replacement of the remaining borate hydrogens by pyrazole groups to form tri- and tetradentate compounds provides a series of chelating ligands, all of which react readily with the divalent first-row transition metal ions.<sup>3,5</sup> Both the ligand salts and the transition metal chelates are quite stable in the solid form (with the exception of some Mn(II) and Fe(II) chelates, which are air sensitive).<sup>5</sup> Aqueous solutions of the ligands exhibit lower and varying stabilities.<sup>5</sup>

Systematic studies of the stoichiometry and structure of the first-row transition metal complexes have shown that mixing

aqueous solutions of the divalent metal ion and the poly(1-pyrazolyl)borate ligand yields neutral, anhydrous precipitates.<sup>3</sup> In all cases the stoichiometry is one metal ion to two ligand molecules. With the H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup> ligand, either tetrahedral or planar complexes are formed with the transition metals, while the HB(pz)<sub>3</sub><sup>-</sup> and B(pz)<sub>4</sub><sup>-</sup> ligands are reported to form six-coordinate complexes.<sup>5</sup>

In order to compare the thermodynamic properties of a series of monoanionic bi-, tri-, and tetradentate ligands which have identical coordination sites and very similar reaction stoichiometry with a series of divalent metal ions, enthalpies of aqueous precipitation of cobalt(II), nickel(II), copper(II), and zinc(II) with four poly(1-pyrazolyl)borates were determined. An attempt was made to gain some information concerning the relative degrees of solvation of the metal and ligand ions by analysis of thermodynamic and conformational results of chelate formation in water and acetonitrile (MeCN). In contrast to water, soluble chelates were formed in this aprotic nonaqueous solvent, and therefore the heat of chelate formation is absent from the reaction enthalpy.

Where geometries of the reaction product are the same for a particular ligand, differences between the aqueous and MeCN data for the same metal are interpreted mainly as differences in the degree of solvation of metal and ligand ions in the two solvents. In comparing the enthalpy data of one ligand with those of another, differences in chelate geometries must be considered in accounting for the results. Further, the results in aqueous solution have to be discussed with caution, since it is likely that the heats of crystallization for complexes of different geometry are different. Since the magnitude of these crystallization heats are not known at this time, com-

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Table I. Enthalpy of Precipitation of Co(II), Ni(II), Cu(II), and Zn(II) by Some Poly(1-pyrazolyl)borates in Aqueous Media<sup>a</sup>

| (a) H <sub>2</sub> B(pz) <sub>2</sub> <sup>-</sup> |               |                             | (b) H <sub>2</sub> B(Me(pz)) <sub>2</sub> <sup>-</sup> |               |                             | (c) HB(pz) <sub>3</sub> <sup>-</sup> |               |                             | (d) B(pz) <sub>4</sub> <sup>-</sup> |              |                             |
|--|---------------|-----------------------------|--|---------------|-----------------------------|--------------------------------------|---------------|-----------------------------|-------------------------------------|--------------|-----------------------------|
| Metal  | ΔH, kcal/mol  | Av ΔH/<br>bond <sup>b</sup> | Metal  | ΔH, kcal/mol  | Av ΔH/<br>bond <sup>b</sup> | Metal                                | ΔH, kcal/mol  | Av ΔH/<br>bond <sup>c</sup> | Metal                               | ΔH, kcal/mol | Av ΔH/<br>bond <sup>c</sup> |
| Co(II)   | -10.25 ± 0.08 | -2.56                       | Co(II)   | -5.62 ± 0.28  | -1.40                       | Co(II)                               | -24.32 ± 0.40 | -4.06                       | Co(II)                              | -4.57 ± 0.20 | -0.76                       |
| Ni(II)   | -11.69 ± 0.28 | -2.92                       | Ni(II)   | -6.70 ± 0.32  | -1.67                       | Ni(II)                               | -27.11 ± 0.47 | -4.52                       | Ni(II)                              | -8.09 ± 0.28 | -1.35                       |
| Cu(II)   | -23.18 ± 0.29 | -5.79                       | Cu(II)   | -21.16 ± 0.22 | -5.28                       | Cu(II)                               | -26.07 ± 0.13 | -4.35                       | Cu(II)                              | -8.83 ± 0.17 | -1.47                       |
| Zn(II)   | -14.16 ± 0.13 | -3.54                       | Zn(II)   | -10.19 ± 0.12 | -2.55                       | Zn(II)                               | -18.30 ± 0.30 | -3.05                       | Zn(II)                              | +0.94 ± 0.3  | +0.15                       |

<sup>a</sup> Stoichiometry of all complexes 1:2 metal:ligand; error limits are average deviations. <sup>b</sup> Based on four-coordination. <sup>c</sup> Based on six-coordination.

parison of aqueous results for the same ligand is somewhat hazardous unless geometries are known to be the same.

### Experimental Section

**Instrumentation.** Enthalpy data were obtained by differential thermometric titration of the ligand salts by metal ion solutions. The titration apparatus was essentially the same as that of Tyson, McCurdy, and Bricker.<sup>6</sup> By the use of the differential mode undesirable heat effects from stirring, solvent mixing, dilution of solute (titrant), and the like are canceled.

The temperature sensitivity of the apparatus was about 90 mV/deg. Two electrical heat calibrations were performed before each titration and two after. The average of four or more enthalpy determinations was taken for each metal ion–ligand reaction. Titrations were performed at ambient temperature, 22–27°, as variations of the enthalpy with temperature were found to be small and within the precision limits of the method, ±(0.2–0.5) kcal/mol. The thermometric titration system was checked by performing reactions of known enthalpy change (aqueous silver halide precipitations) and an accuracy better than 1% was obtained. Spectral studies in the visible region were carried out on a Perkin-Elmer Model 350 uv–visible spectrophotometer.

**Chemicals and Solutions.** Fisher Certified MeCN, originally containing 0.1% water, was refluxed over calcium hydride for at least 24 hr and distilled from calcium hydride.<sup>7</sup> The middle 80% fraction, boiling at 81.6°, was retained. The dried solvent was stored in a brown bottle over calcium hydride and dispensed using air pressure from a squeeze bulb passing through a drying train containing calcium chloride, silica gel, and sulfuric acid. The water content was determined by Karl Fischer titration<sup>8</sup> to be about 0.03%.

The water used was distilled or deionized.

All metal ion titrant solutions were prepared from metal nitrate salts. Aqueous solutions were made 0.1 M; those in MeCN, 0.02 M. The hexaaquocobalt(II) nitrate, hexaaquonickel(II) nitrate (Baker and Adamson reagent grade), and the triaquocopper(II) nitrate (Fisher Certified reagent) solutions were standardized volumetrically with EDTA using murexide indicator.<sup>9</sup> Hydrated zinc(II) nitrate was titrated with EDTA using Eriochrome Black T indicator. Aqueous EDTA solutions were used to standardize both the MeCN and water solutions of the metal ions.

The water introduced into the MeCN solutions by using hydrated metal ion salts was removed by allowing the solutions to stand over Linde Type 4A molecular sieves. Before drying over the sieves nearly the theoretical amount of water (from solvent plus hydrated salt) was found by the Karl Fischer method. Titration of dried copper(II) nitrate solution showed the water content to be about 0.03%, about the same as that of the pure, dried MeCN solvent. Standardizations were performed *after* drying as the sieves absorbed some of the metal ions.

The ligands used were potassium dihydrobis(1-pyrazolyl)borate [KH<sub>2</sub>B(pz)<sub>2</sub>], potassium hydrotris(1-pyrazolyl)borate [KHB(pz)<sub>3</sub>], potassium tetrakis(1-pyrazolyl)borate [KB(pz)<sub>4</sub>], and potassium dihydrobis(3-methyl-1-pyrazolyl)borate [KH<sub>2</sub>B(Me(pz))<sub>2</sub>]. These were prepared according to the method of Trofimenko.<sup>5</sup> Elemental analyses were within 0.3% of theoretical values in all cases. The solid ligand salts were stored over silica gel desiccant. Aqueous solutions<sup>10</sup> were made about 2 mM, and those in MeCN about 0.5 mM. Solutions of KH<sub>2</sub>B(Me(pz))<sub>2</sub> in MeCN were somewhat cloudy, but the solution after titration was always completely clear.

### Results and Discussion

In both aqueous and nonaqueous media chelation was accomplished by titrating the ligand solution with a solution of the transition metal nitrate. Thermometric end points were

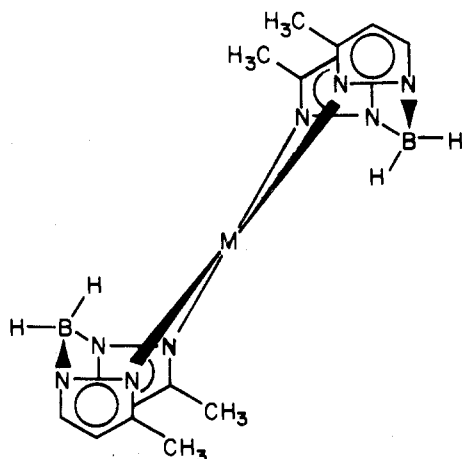
generally sharp and the stoichiometry of the reaction was easily calculated. In aqueous media, two ligand molecules precipitate one metal ion, in agreement with the stoichiometry reported by Trofimenko.<sup>5</sup> The colors of the metal chelates were likewise in accord with those observed earlier.<sup>5</sup> A difficulty associated with the aqueous enthalpies is that, as indicated earlier, the heats of crystallization are not known. It is possible that complexes of different geometries may have crystallization enthalpies which differ by several kilocalories per mole. Therefore, except for broad generalizations, comparisons between complexes of the same ligand, but having different geometries, cannot be made based on the aqueous data. In comparing the aqueous reaction enthalpy of one ligand with that of another one must take into consideration the fact that the different numbers of nitrogen atoms involved may lead to varying degrees of hydrogen bonding in water. A “ΔH per bond” is calculated to facilitate comparison between ligands, where each “bond” contains the same number of nitrogen atoms. In the aprotic MeCN medium weaker solvation of the anion ligands is expected, so that comparisons between complexes containing different ligands can be more safely made.

**Chelation in Aqueous Media.** The enthalpy values for reaction of the transition metal ions with the bidentate ligands H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup> and H<sub>2</sub>B(Me(pz))<sub>2</sub><sup>-</sup> are given in Table I(a) and (b). The chelates of H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup>, as reported by Jesson et al., possess different geometries; Co(II) and Zn(II) are tetrahedral, and Cu(II) and Ni(II) are square planar. That Cu(II) has an enthalpy of reaction so much larger than the others can be attributed in part to Jahn–Teller stabilization energy for this planar complex, tetragonal distortion taken to its limit.<sup>11</sup> This effect is not present for the Ni(II) species.

The effect of replacing a hydrogen in the pyrazole rings with a methyl group yields a marked effect on the enthalpy of reaction. Because of tautomerism in the free pyrazole molecule<sup>12</sup> it is not known a priori whether the methyl group resides in the 3 or the 5 position when the two heterocyclic rings are fixed in the ligand molecule. A PMR investigation of KH<sub>2</sub>B(pz)<sub>2</sub>, KH<sub>2</sub>B(Me(pz))<sub>2</sub>, and KH<sub>2</sub>B(Me<sub>2</sub>(pz))<sub>2</sub> and the corresponding nickel(II) chelates has shown that only the 3-methyl isomer of H<sub>2</sub>B(Me(pz))<sub>2</sub><sup>-</sup> is formed in the synthesis.<sup>13</sup> Additional evidence supporting the assignment of the methyl group in H<sub>2</sub>B(Me(pz))<sub>2</sub><sup>-</sup> to the 3 position is that the pale yellow iron(II) chelate of this ligand appears to be indefinitely stable in air and aqueous suspension. This is in contrast to the iron(II) chelate of H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup> which turns brown in a few minutes. Protection of the metal ion from oxygen has also been observed with (3,5-dimethyl-1-pyrazolyl)- and (3,4,5-trimethyl-1-pyrazolyl)borate and ascribed to steric screening of the metal by the 3-methyl groups.<sup>14</sup> It would be of interest to study the 5-methyl derivative in this regard, but, unfortunately, no method of preparing this isomer has yet been discovered.

Trofimenko has noted that planar chelates of H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup> can adopt either the boat or the chair form, with both boron atoms up in the former and one up and one down in the latter.<sup>3</sup> With methyl substitution in the 3 position of the pyrazole rings, however, only the chair form is possible because of methyl–methyl crowding. Note that the pyrazole rings are not parallel.

Rather, the 4 carbons project away from the opposite ring.



It is observed that  $\Delta H$  for the 3-methyl derivative is lower than for the corresponding reaction with  $\text{H}_2\text{B}(\text{pz})_2^-$ , so that a steric effect is indeed present. It may be too that steric hindrance of the methyl group is a factor in crystal as well as molecule formation, but the relative importance of these cannot be determined from the aqueous results.

The colors of the chelates of  $\text{H}_2\text{B}(\text{Me}(\text{pz}))_2^-$  are identical with those of the unmethylated chelates, the same situation observed by Trofimenko for the 3,5-dimethylated ligand.<sup>14</sup> This fact indicates that the spatial configuration of ligand donor atoms around the central metal ion has not been changed materially by methyl substitution. The reason for the smaller enthalpy decrease for Cu(II) compared to that for the other three metals is not apparent at this time.

With addition of a third pyrazole group to the boron central atom a 1:2 metal:ligand stoichiometry permits six-coordination. Jesson et al. constructed molecular models of the chelate compounds and showed that octahedral configuration can be attained without undue bond stretching.<sup>3</sup> From the enthalpy values in Table I(c) it is seen that chelation of Cu(II) results in a  $\Delta H$  smaller than that of Ni(II). This is a reversal of the usual situation for six-coordination (the Irving-Williams order).<sup>15</sup> In addition,  $\Delta H$  for the supposedly six-coordinate chelate of copper with  $\text{HB}(\text{pz})_3^-$  is only slightly ( $\sim 3$  kcal/mol) larger than that for the four-coordinate complex with  $\text{H}_2\text{B}(\text{pz})_2^-$ . If the  $\Delta H$  per bond calculated for the four-coordinate species is assumed to be proportional to the copper-nitrogen bond energy, then approximately 35 kcal/mol should be obtained for the six-coordinate species. That  $\Delta H$  is considerably smaller than expected may stem from two causes. If the Cu(II) complex is forced into octahedral symmetry by ligand geometry, then the Jahn-Teller stabilization energy that was present in the four-coordinate square-planar system is lost, and  $\Delta H$  per bond is smaller than for the planar species. On the other hand, in some cases Cu(II) does not form six-coordinate complexes with chelating ligands because of the tendency toward tetragonal distortion predicted by the Jahn-Teller theorem.<sup>16,17</sup> McIntyre et al. concluded from a study of the heats of chelation of Cu(II) with the tridentate diethylenetriamine ligand (dien) that only one of the three nitrogens of the second coordinating ligand are bonded to the metal ion, to give a four-coordinate complex.<sup>18</sup> Ciampolini et al. postulated, however, that the  $[\text{Cu}^{\text{II}}(\text{dien})_2]^{2+}$  complex was five-coordinate but that, indeed, one copper-nitrogen bond remained unformed to allow some tetragonal distortion of the complex species.<sup>19</sup> In this case the Jahn-Teller stabilization energy probably is smaller than for true tetragonal distortion but nevertheless still stabilizes the five-coordinate distorted complex compared to six-coordinate octahedral. This reasoning is also used by Jonassen to explain the entropy values for the

$[\text{Cu}^{\text{II}}(\text{dien})_2]^{2+}$  complex.<sup>20</sup> However, as we are not certain of the geometry of the complex of Cu(II) with  $\text{HB}(\text{pz})_3^-$ ,  $\Delta H$  per bond in Table I(c) is based on six-coordination.

The difference between  $\Delta H$ (overall) for reaction of the metals with  $\text{B}(\text{pz})_4^-$  and  $\text{HB}(\text{pz})_3^-$  is quite spectacular. Approximately 17–20 kcal/mol less heat is obtained in each case with the tetradentate ligand as compared to the tridentate; and, in fact, the reaction of Zn(II) with  $\text{B}(\text{pz})_4^-$  was found to be slightly endothermic. The effect on the chelation reaction of replacing the remaining boron hydrogen atom with a fourth pyrazole ring could be competition for coordination sites or steric crowding, so that some or all of the metal-ligand bonds are weakened. The surprisingly large decrease in enthalpy may also be due in part to difficulty in crystal packing caused by the large ligands. Once again it is suggested that Cu(II) may have only five metal-ligand bonds, to maintain some tetragonal distortion, or that Jahn-Teller stabilization energy is lost if the complex is octahedral. The other three metal ions are apparently octahedrally coordinated, and  $\Delta H$  per bond for all complexes with  $\text{B}(\text{pz})_4^-$  is based on six-coordination.

One further observation can be made concerning metal ion chelation in water media. The position of the enthalpy results of Zn(II) with respect to Co(II) and Ni(II) reverses on going from the four-coordinate to the six-coordinate complexes. The overall enthalpy as well as the average  $\Delta H$  per bond for reaction of Zn(II) with  $\text{H}_2\text{B}(\text{pz})_2^-$  and  $\text{H}_2\text{B}(\text{Me}(\text{pz}))_2^-$  is greater than that of Co(II) and Ni(II), while it is less for reaction with  $\text{HB}(\text{pz})_3^-$  and  $\text{B}(\text{pz})_4^-$ . This can be explained in view of the strong tendency for Zn(II) to be four-coordinate with mono- and bidentate ligands. Crystal field stabilization effects are absent and stereochemistry is determined mainly by ion size. The tetrahedral configuration is thermodynamically most stable for the fairly small Zn(II) ion.<sup>21</sup> When the metal ion is placed in a six-coordinate environment, the reaction enthalpy should decrease because the donor atoms must take up positions further away from the metal ion. On the other hand, the greater tendency of Co(II) and Ni(II) to be six-coordinate compared to Zn(II)<sup>22</sup> explains the formation of more stable complexes with  $\text{HB}(\text{pz})_3^-$  and  $\text{B}(\text{pz})_4^-$ .

**Chelation in Acetonitrile Medium.** As was indicated earlier, titration of the pyrazolylborate ligands by the first-row transition metal ions in MeCN results in soluble chelate species. In most cases the stoichiometry indicated by the thermometric end point was 1:2 metal:ligand. Two exceptions to this metal:ligand ratio are discussed below.

It should be noted that both Co(II) and Ni(II) have  $\Delta H$  values much higher than those of Cu(II) and Zn(II) (Table II(a)). In these cases titration end points were observed at 1:3 metal:ligand stoichiometry. In addition, the color of the resulting solution of Ni(II) chelate was a very light blue-purple, rather than the orange expected from  $\text{Ni}[\text{H}_2\text{B}(\text{pz})_2]_2$ . These discrepancies suggest that in MeCN Co(II) and Ni(II) do not form the four-coordinate chelate species obtained in aqueous solution but rather form complexes of higher coordination number. Therefore, some spectral investigations into these chelation reactions were undertaken to identify the complex species.

Quantitative studies of the absorbance of solutions containing various mole ratios of metal to ligand, performed in the 350–700-nm region, are summarized in Table III. Only one major peak is seen in the visible region for Co(II) up to a mole ratio of 1:1 metal: $\text{BH}_2(\text{pz})_2^-$  (Table III(a)). As more ligand is added, the solution becomes a brilliant scarlet and a triplet appears which reaches maximum intensity at a ratio of 1:2. Further addition of ligand decreases the intensity of the triplet, and at a ratio of 1:4 Co(II): $\text{H}_2\text{B}(\text{pz})_2^-$  it has nearly disappeared. At this composition the color is very light pink. Tetrahedral Co(II) chelates are known to exhibit a fairly

Table II. Enthalpy of Reaction of Co(II), Ni(II), Cu(II), and Zn(II) with some Poly(1-pyrazolyl)borates in Acetonitrile Media<sup>a</sup>

| (a) H <sub>2</sub> B(pz) <sub>2</sub> <sup>-</sup> |                       |                     | (b) H <sub>2</sub> B(Me(pz)) <sub>2</sub> <sup>-</sup> |                       |                                  | (c) HB(pz) <sub>3</sub> <sup>-</sup> |                       |                                  | (d) B(pz) <sub>4</sub> <sup>-</sup> |                       |                                  |
|--|-----------------------|---------------------|--|-----------------------|----------------------------------|--------------------------------------|-----------------------|----------------------------------|-------------------------------------|-----------------------|----------------------------------|
| Metal  | Δ <i>H</i> , kcal/mol | Av Δ <i>H</i> /bond | Metal  | Δ <i>H</i> , kcal/mol | Av Δ <i>H</i> /bond <sup>c</sup> | Metal                                | Δ <i>H</i> , kcal/mol | Av Δ <i>H</i> /bond <sup>b</sup> | Metal                               | Δ <i>H</i> , kcal/mol | Av Δ <i>H</i> /bond <sup>b</sup> |
| Co(II)   | -34.66 ± 1.2          | -5.78 <sup>b</sup>  | Co(II)   | -22.25 ± 0.66         | -5.57                            | Co(II)                               | -41.97 ± 0.44         | -6.98                            | Co(II)                              | -32.82 ± 0.34         | -5.48                            |
| Ni(II)   | -36.00 ± 0.19         | -6.00 <sup>b</sup>  | Ni(II)   | -23.08 ± 0.30         | -5.77                            | Ni(II)                               | -45.93 ± 0.04         | -7.66                            | Ni(II)                              | -31.13 ± 0.44         | -5.19                            |
| Cu(II)   | -28.45 ± 1.00         | -7.12 <sup>c</sup>  | Cu(II)   | -23.93 ± 0.40         | -5.98                            | Cu(II)                               | -32.27 ± 0.16         | -5.38                            | Cu(II)                              | -27.47 ± 0.54         | -4.58                            |
| Zn(II)   | -26.98 ± 0.44         | -6.74 <sup>c</sup>  | Zn(II)   | -28.37 ± 0.20         | -7.08                            | Zn(II)                               | -36.58 ± 1.16         | -5.92                            | Zn(II)                              | -25.54 ± 0.41         | -4.26                            |

<sup>a</sup> Stoichiometry of all complexes 1:2 metal:ligand, except that for Co(II) and Ni(II) with H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup> which was 1:3; error limits are average deviations. <sup>b</sup> Based on six-coordination. <sup>c</sup> Based on four-coordination.

intense triplet in the visible region, while six-coordinated complexes have only one very broad peak of much lower intensity.<sup>23</sup> Jesson et al. reported the same triplet for Co-[H<sub>2</sub>B(pz)<sub>2</sub>]<sub>2</sub>.<sup>3</sup> The geometry of the Co(II) ion environment apparently shifts from octahedral in the absence of chelating ligand (six-coordinated with solvent) to tetrahedral at a mole ratio of about 1:2 metal:ligand and back to octahedral again in excess ligand. The approximate molar absorbance values (in the metal-ligand mixture indicated) show that the triplet peaks are about 10 times as intense as the octahedral band. Cabral et al. have observed similar behavior for the tetrahedral tetrakis(pyridine)cobalt(II) complex.<sup>24</sup> They reported that the octahedral configuration is assumed in the presence of excess pyridine and that the color becomes very light pink.

In the chelation of Ni(II) with H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup> in MeCN (Table III(b)) the solution is turquoise and yields two absorption peaks up to a 1:1 ratio of metal to ligand. As the mole ratio decreases below 1:1, a new band at 450 nm and the orange color appear simultaneously. This new band, observed by Jessen et al. for Ni[H<sub>2</sub>B(pz)<sub>2</sub>]<sub>2</sub>,<sup>3</sup> disappears at a mole ratio of about 1:3, and the intensity of the two remaining bands decreases nearly twofold. The solution also changes to the same blue-purple color mentioned earlier.

Nelson and Shepherd reported a molar absorptivity of 8 for the octahedral nickel(II)-pyridine complex,<sup>22</sup> which compares favorably with the value of 10 calculated in this study for solutions having the 1:3 Ni(II):H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup> ratio. It is important to note that the two bands observed for the anionic 1:3 complex of Ni(II) with H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup> (560 and 356 nm) agree nearly exactly with those reported by Daugherty and Swisher<sup>25</sup> for the 1:6 complex of Ni(II) with pyrazole in MeCN medium.

Three metal-ligand species are apparently formed successively, with 1:1, 1:2, and 1:3 metal:ligand ratios. The 1:3 chelate must therefore be an anionic species. Formation of these six-coordinate anionic complexes where precipitation is absent is not too startling. Nelson and Shepherd reported that Ni(II) (and evidently Co(II) also) shows a marked preference for octahedral coordination as long as steric effects are absent.<sup>22</sup> The fully coordinated 1:3 species is formed directly in the titration because metal ion is delivered into a solution of excess ligand (Table II(a)).

It is interesting that a blue-purple solid, stoichiometrically K<sup>+</sup>Ni[H<sub>2</sub>B(pz)<sub>2</sub>]<sub>3</sub><sup>-</sup>, is isolable from a MeCN solution containing a 1:3 mole ratio of Ni(NO<sub>3</sub>)<sub>2</sub> to K<sup>+</sup>H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup> with slow evaporation of solvent. This solid is stable in the absence of water, for example, over silica gel in a desiccator. When added to water, however, the solid nearly instantaneously changes to the orange Ni[H<sub>2</sub>B(pz)<sub>2</sub>] precipitate. It appears that the water strongly competes with the metal ion for H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup> anions, effectively removing the third ligand from the octahedral species to give the four-coordinate complex. A transformation which appears to be the same occurs if the blue-purple solid is exposed to moist air for several days.

The enthalpy per metal-donor bond was calculated employing six-coordination for the chelates of Co(II) and Ni(II) with H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup> in MeCN and four-coordination for those of Cu(II) and Zn(II). A comparison of Δ*H* values is not strictly valid, of course, since it is made between chelates of different

Table III. Visible Absorption Spectral Data from a Mole Ratio Study of Co(II) and Ni(II) with H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup> Ligand in Acetonitrile

| Mole ratio M(II):L <sup>-</sup> | Color of soln    | λ <sub>max</sub> , nm (absorbance)    | Molar absorptivity |             |
|---------------------------------|------------------|---------------------------------------|--------------------|-------------|
| (a) M(II) = Co(II)              |                  |                                       |                    |             |
| 1:0.0                           | Light pink       | 515 (0.250)                           | 57.6               |             |
| 1:0.25                          | Light pink       | 517 (0.310)                           |                    |             |
| 1:0.5                           | Darker pink      | 517 (0.423)                           |                    |             |
| 1:0.75                          | Darker pink      | 517 (0.520)                           |                    |             |
| 1:1.00                          | Darker pink      | 519 (0.660)                           |                    |             |
| 1:1.25                          | Becoming scarlet | 575 (0.42), 525 (0.78)                |                    |             |
| 1:1.5                           | More scarlet     | 575 (0.695), 543 (0.980), 493 (0.88)  | 20.0 (490 nm)      |             |
| 1:2.0                           | Scarlet          | 577 (1.160), 543 (1.385), 497 (1.113) |                    |             |
| 4:2.5                           | Lighter scarlet  | 577 (0.941), 544 (1.088), 498 (0.902) |                    |             |
| 1:3.0                           | Pink             | 577 (0.532), 543 (0.640), 498 (0.555) |                    |             |
| 1:3.5                           | Lighter pink     | 577 (0.200), 540 (0.253), 497 (0.270) | 17 (640 nm)        |             |
| 1:4.0                           | Very light pink  | 577 (0.090), 525 (0.100), 493 (0.175) |                    |             |
| (b) M(II) = Ni(II)              |                  |                                       |                    |             |
| 1:0                             | Turquoise        | 640 (0.075), 386 (0.133)              |                    | 21 (593 nm) |
| 1:0.5                           | Turquoise        | 620 (0.08), 378 (0.152)               |                    |             |
| 1:1.0                           | Turquoise        | 593 (0.095), 375 (0.175)              | 25 (450 nm)        |             |
| 1:1.5                           | Yellow-green     | 593 (0.095), 475 (0.075), 370 (0.180) |                    |             |
| 1:2.0                           | Orange-green     | 593 (0.095), 450 (0.105), 370 (0.180) |                    |             |
| 1:2.5                           | Orange           | 593 (0.095), 450 (0.110), 370 (0.180) |                    |             |
| 1:3.0                           | Light-purple     | 560 (0.090), 450 (0.092), 362 (0.110) | 10 (560 nm)        |             |
| 1:3.5                           | Purple           | 560 (0.055), 356 (0.100)              |                    |             |
| 1:4.0                           | Purple           | 560 (0.055), 356 (0.100)              |                    |             |

geometries and different coordination numbers and also since the Co(II) and Ni(II) chelates carry a negative charge. Nevertheless, Cu(II) appears to exhibit the most stable metal-ligand bonds.

A stoichiometry of 1:2 metal:ligand was observed for *all* the metal ions with H<sub>2</sub>B(Me(pz))<sub>2</sub><sup>-</sup>. In addition, the enthalpy of reaction for Co(II) and Ni(II) is smaller than those of Cu(II) and Zn(II) (Table II(b)), in contrast to reaction with H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup>. These results indicate that the methyl group in the 3 position of the pyrazole rings introduces a steric effect which prevents octahedral complex formation such as occurred for Co(II) and Ni(II) with H<sub>2</sub>B(pz)<sub>2</sub><sup>-</sup>. Similar behavior has been discussed by Nelson and Shepherd.<sup>22</sup> Likewise Forster et al. observed that Ni(II), which is capable of coordination with six molecules of pyridine or β- and γ-picoline, can only accommodate four α-picoline groups because of the steric effect of the α-methyl group.<sup>26</sup>

A rigorous comparison of the enthalpy of chelation of Co(II)

and Ni(II) by  $\text{H}_2\text{B}(\text{Me}(\text{pz}))_2^-$  and by  $\text{H}_2\text{B}(\text{pz})_2^-$  is not feasible because of the difference in coordination numbers obtained with the two ligands in MeCN. It is seen that for Cu(II)  $\Delta H$  of chelation is several kilocalories per mole lower for the methylated ligand than for the unmethylated one. The fact that Zn(II) chelation shows a slight increase with the methylated ligand may indicate that the inductive effect of the methyl group is important here, providing increased electron density at the bonding nitrogen atom. Steric hindrance in the tetrahedral Zn(II) chelate is not expected to be as extensive as in the planar Cu(II) species. Also, the steric effect of the methyl groups probably lowers  $\Delta H$  of chelation of the planar  $\text{Ni}[\text{H}_2\text{B}(\text{Me}(\text{pz}))_2]_2$  so that the total is only slightly larger than that for formation of the tetrahedral Co(II) chelate, where, again, a smaller steric effect would be expected. Since the overall steric effect in MeCN media is smaller than in aqueous solution, it would seem that the methyl groups of the ligand cause crystal packing difficulties, as well as steric strain in complex molecule formation. These packing difficulties are, of course, not present in the MeCN enthalpies.

Data for the reaction of the metal ions with  $\text{HB}(\text{pz})_3^-$  (Table II(c)) show that the enthalpy value for Cu(II) chelation is lower than those of the other three ions studied. Again it seems reasonable to postulate a tetragonal distorted structure for  $\text{Cu}[\text{HB}(\text{pz})_3]_2$ , as was done in aqueous media. Still the average  $\Delta H$  per bond is based on six-coordination as definite evidence of geometry is lacking.

A valid comparison can be made between six-coordinate chelation of Co(II) and Ni(II) with  $\text{H}_2\text{B}(\text{pz})_2^-$  and  $\text{HB}(\text{pz})_3^-$ . The reaction enthalpy for two  $\text{HB}(\text{pz})_3^-$  ligands is considerably greater than for three  $\text{H}_2\text{B}(\text{pz})_2^-$ , even though the end result is the same, except for the charge. Interligand repulsion is of less consequence for complex formation with  $\text{HB}(\text{pz})_3^-$ , where only two ligand molecules and two negative charges must be brought together in the chelate molecule, than for  $\text{H}_2\text{B}(\text{pz})_2^-$ , where three separate molecules and negative charges must be brought up to the metal ion. Energy is consumed in overcoming the ligand-ligand repulsive forces, and a smaller enthalpy change results for formation of the anionic complex than for the neutral one.

Reaction of the metal ions with  $\text{B}(\text{pz})_4^-$  results in enthalpy values about 10 kcal/mol lower than for reaction with  $\text{HB}(\text{pz})_3^-$  (Table II(d)). The Cu(II) enthalpy, however, is only about 5 kcal/mol smaller. The decreased  $\Delta H$  of reaction for all the metal ions compared to chelation with  $\text{HB}(\text{pz})_3^-$  indicates that one or more processes are interfering with formation of the molecular chelate (steric problems or coordination competition). The aqueous heats of reaction do not indicate clearly whether the reduced enthalpy occurs because of coordination or crystal packing effects. However, in view of the considerably smaller enthalpy decrease in MeCN as compared to that in water (17–20 kcal/mol), it seems reasonable to postulate the existence of steric difficulties associated with crystal packing in the aqueous precipitation reaction, as well as in formation of the chelate molecule itself. The enthalpy results in MeCN also lend credence to the postulate that one or more of the Cu(II) axial ligands are unbonded. Steric crowding or coordination competition resulting from the extra two pyrazole groups would be expected to be of more significance for octahedral complexation than for planar or tetragonal geometries which are spatially more open. The enthalpy is therefore not decreased as much as that of the other three metals by addition of the fourth pyrazole ring into the ligand. This same situation obtains for the Cu(II) reactions in aqueous solution.

Observations concerning the magnitude of the enthalpies of chelation of Zn(II) relative to those of Co(II) and Ni(II) such as were made for water medium can also be made for

MeCN solvent. Again Zn(II) exhibits the largest  $\Delta H$  value where four-coordinate complexes of  $\text{H}_2\text{B}(\text{pz})_2^-$  and  $\text{H}_2\text{B}(\text{Me}(\text{pz}))_2^-$  occur and the smallest value for the six-coordinate chelates of  $\text{HB}(\text{pz})_3^-$  and  $\text{B}(\text{pz})_4^-$ , for the same reasons advanced earlier.

For the entire series of complexes studied the only apparent change in chelate geometry that occurs on changing the reaction medium from water to MeCN is that, rather than four-coordinate complexes, six-coordination results with  $\text{H}_2\text{B}(\text{pz})_2^-$ . Because the chelates do not precipitate from the nonaqueous solvent, open coordination sites are available for further reaction even after two bidentate ligands have neutralized the charge on the metals. Weak solvation of both the ligands as well as the neutral complex species then permits addition of a third bidentate ligand to the coordination sphere.

Precipitation of the pyrazolylborate chelates from aqueous solution is probably the result of the repulsion of water by the large hydrocarbon-like chelate molecules, in which the ionic charges are deeply buried and in which donor atoms are directed inward. Even though this presumably exothermic contribution from precipitation of the chelates is absent in MeCN, the enthalpy of reaction is much larger than for the corresponding reaction in water. This is probably because of the much weaker solvation of the metal ions by MeCN than by water<sup>23</sup> and, even more importantly, the weaker solvation of ligand anions. As stated earlier, the nitrogens of the pyrazolylborate species can probably take part in hydrogen bonding with water molecules, while this interaction is absent or much weaker in MeCN. Hence the endothermic contribution to  $\Delta H$  (overall) from removal of solvent molecules prior to chelation is much smaller in MeCN, and the end result is a considerably larger enthalpy of reaction.

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**Registry No.**  $\text{Co}[\text{H}_2\text{B}(\text{pz})_2]_2$ , 37668-73-8;  $\text{Co}[\text{H}_2\text{B}(\text{pz})_2]_3^-$ , 55236-43-6;  $\text{Ni}[\text{H}_2\text{B}(\text{pz})_2]_2$ , 18131-13-0;  $\text{Ni}[\text{H}_2\text{B}(\text{pz})_2]_3^-$ , 55236-44-7;  $\text{Cu}[\text{H}_2\text{B}(\text{pz})_2]_2$ , 18131-14-1;  $\text{Zn}[\text{H}_2\text{B}(\text{pz})_2]_2$ , 18131-19-6;  $\text{Co}[\text{H}_2\text{B}(\text{Me}(\text{pz}))_2]_2$ , 55237-01-9;  $\text{Ni}[\text{H}_2\text{B}(\text{Me}(\text{pz}))_2]_2$ , 55236-99-2;  $\text{Cu}[\text{H}_2\text{B}(\text{Me}(\text{pz}))_2]_2$ , 55267-62-4;  $\text{Zn}[\text{H}_2\text{B}(\text{Me}(\text{pz}))_2]_2$ , 55237-00-8;  $\text{Co}[\text{HB}(\text{pz})_3]_2$ , 16842-05-0;  $\text{Ni}[\text{HB}(\text{pz})_3]_2$ , 16842-13-0;  $\text{Cu}[\text{HB}(\text{pz})_3]_2$ , 18117-13-0;  $\text{Zn}[\text{HB}(\text{pz})_3]_2$ , 16842-11-8;  $\text{Co}[\text{B}(\text{pz})_4]_2$ , 15650-36-9;  $\text{Ni}[\text{B}(\text{pz})_4]_2$ , 14728-60-0;  $\text{Cu}[\text{B}(\text{pz})_4]_2$ , 14782-57-1;  $\text{Zn}[\text{B}(\text{pz})_4]_2$ , 14728-61-1.

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## Magnetic Exchange Interactions in Transition Metal Dimers. IV. High-Spin Cobalt(II)-2,2',2''-Triaminotriethylamine Complexes with Oxalate Inner-Sphere and Cyanate, Thiocyanate, Chloride, and Azide Outer-Sphere Bridges

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Infrared, electronic absorption, electron paramagnetic resonance (X and Q band), and variable-temperature magnetic susceptibility data are presented for the high-spin Co(II) complexes of the composition  $[\text{Co}_2(\text{tren})_2\text{X}_2](\text{BPh}_4)_2$ , where  $\text{X}^- = \text{OCN}^-$ ,  $\text{SCN}^-$ ,  $\text{Cl}^-$ ,  $\text{N}_3^-$ , and  $\text{Ox}^{2-}/2$  ( $\text{Ox} = \text{oxalate}$ ), and *tren* is 2,2',2''-triaminotriethylamine. Infrared and electronic measurements show that in the oxalate case the cobalt ions are octahedrally coordinated by virtue of a bis-bidentate oxalate bridge. In the other cases the cobalt ions are (five-coordinate) trigonal-bipyramidally coordinated, and apparently each cobalt trigonal bipyramid is outer-sphere associated, probably via hydrogen bonding, with a second five-coordinate cobalt complex. Analysis of the electronic spectra of the five-coordinate complexes gives *D*<sub>s</sub> and *D*<sub>t</sub> values which are used in the analysis of the susceptibility. The susceptibility data (maximum in  $\chi$  at  $\sim 10^\circ\text{K}$ ) for the oxalate compound are least-squares fit to spin-only (i.e.,  $-2J\hat{S}_1\cdot\hat{S}_2$ ) equations to give  $J = -3.1 \text{ cm}^{-1}$  and  $g = 2.21$ . Indications of very weak ( $|J| < 0.5 \text{ cm}^{-1}$ ) antiferromagnetic interactions ( $\text{N}_3^- > \text{OCN}^- > \text{Cl}^- \approx \text{NCS}^-$ ) are found in the susceptibility curves for the other compounds through fitting to two different theoretical models, one for a monomeric *D*<sub>3h</sub>-symmetry high-spin cobalt(II) complex and the other for a cobalt(II) dimer including single-ion zero-field splitting and isotropic exchange interaction. The dimeric nature of these complexes is further substantiated by the complexity (easily nine maxima in the 0-10-kG range for a spectrum showing *no* hyperfine) of the  $\sim 12^\circ\text{K}$  X-band EPR spectra of powdered samples. A qualitative discussion of the many features and temperature dependence of the  $\sim 90$  and  $4.2^\circ\text{K}$  Q-band (0-15-kG range) spectra for the complexes is presented. An interesting power saturation effect is noted.

### Introduction

In view of the large number and detailed character of the chemical, magnetic, and spectroscopic studies that have been carried out on divalent copper and nickel coordination compounds, it is surprising that few such in-depth attacks have been launched on cobalt(II) complexes. In the past few years, the discovery that certain *low-spin* cobalt(II) complexes will bind molecular oxygen has led to detailed crystallographic<sup>3</sup> and spectroscopic<sup>4</sup> studies of these systems. In contrast *high-spin* cobalt(II) complexes have not been as thoroughly studied except perhaps in the area of electronic absorption spectroscopy<sup>5</sup> where the optical characteristics of Co(II) in various environments have been set out. Even though magnetic susceptibility and EPR are potentially of greater sensitivity with respect to electronic structure, they have been all but overlooked for high-spin cobalt(II) systems probably because of the very low temperatures that are required. Very recently Ball and Blake<sup>6</sup> have reported the variable-temperature (80-400°K) magnetic susceptibilities of a series of high-spin octahedral Co(II) dimers. They found, in comparison to the analogous nickel(II) complexes,<sup>7</sup> a decreased exchange interaction in the cobalt complexes and concluded that the *t*<sub>2g</sub> spin of  $\text{Co}^{2+}$  probably makes a ferromagnetic contribution to the exchange interaction. As pointed out by Ball and Blake, any analysis of the magnetism of exchange-interacting Co(II) dimers needs to take into account spin-orbit coupling such as can be seen in the treatment by Lines.<sup>8</sup>

In this paper the results of a variable-temperature magnetic susceptibility and EPR study of the series  $[\text{Co}_2(\text{tren})_2\text{X}_2](\text{BPh}_4)_2$ , where  $\text{X}^- = \text{N}_3^-$ ,  $\text{OCN}^-$ ,  $\text{SCN}^-$ ,  $\text{Cl}^-$ , and  $\text{Ox}^{2-}/2$  and *tren* is 2,2',2''-triaminotriethylamine, are reported. The complexes will be shown to be dimeric, inner-sphere bridged

in the oxalate ( $\text{Ox}$ ) case and (most probably) outer-sphere bridged in the cases of the other X groups. Outer-sphere bridging where metal ions are associated via two hydrogen-bonding contacts of the type  $\text{Cu-X}\cdots\text{HN-Cu}$  has been found<sup>9-12</sup> to propagate an exchange interaction in the series  $[\text{Cu}_2(\text{tren})_2\text{X}_2](\text{BPh}_4)_2$  with  $\text{X}^- = \text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{OCN}^-$ ,  $\text{SCN}^-$ , and  $\text{CN}^-$ . One point which adds to the worth of the material to be presented is that spectroscopic and crystallographic studies of Co<sup>II</sup>-tren compounds are in the first case infrequent and of low level and in the second case nonexistent. Magnetic susceptibility data at room temperature for  $\text{Co}(\text{tren})(\text{NCS})_2$  and  $\text{Co}(\text{tren})\text{I}_2$  were reported<sup>13</sup> in 1958 and a solution moment for aqueous  $\text{Co}(\text{tren})^{2+}$  was available<sup>14</sup> in 1963, all of which indicated the metal ion to be high spin with a moment near 4.7 BM. The electronic spectrum of aqueous  $\text{Co}(\text{tren})^{2+}$  was also reported<sup>14</sup> and it was shown to contrast with that for the  $\text{Co}(\text{dien})_2^{2+}$  octahedral system (*dien* is diethylenetriamine). At the time, however, no conclusive evidence for the structure of these tren molecules was presented. At most it could be concluded that the coordination number was probably 5. Very recent work<sup>15</sup> with the five-coordinate high-spin Co(II) complexes of hexamethylated tren, i.e.,  $\text{Co}(\text{Me}_6\text{tren})\text{X}^+$ , has provided spectral characteristics that will be of use in the present study. The X-ray structure has been reported for trigonal-bipyramidal  $[\text{Co}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$ .<sup>16</sup>

### Experimental Section

**Compound Preparation.** All of the manipulations in the preparation of a  $[\text{Co}_2(\text{tren})_2\text{X}_2](\text{BPh}_4)_2$  compound were carried out in the following manner using a Schlenk-type apparatus as shown in Figure 1. Single-necked flasks are charged with the following solutions:  $\sim 1.5 \text{ ml}$  of tren dissolved in  $\sim 50 \text{ ml}$  of water; 0.01 mol of the sodium salt of the bridging anion (e.g.,  $\text{N}_3^-$ ,  $\text{Cl}^-$ ,  $\text{CN}^-$ ,  $\text{OCN}^-$ ,  $\text{SCN}^-$ , or