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

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

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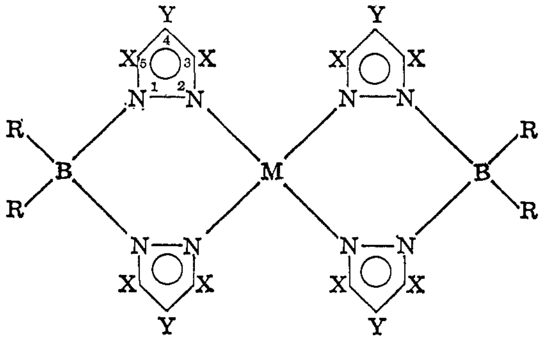
Abstract: Spectral and magnetic data are presented for a new family of transition metal chelates involving poly(1-pyrazolyl)borate ligands. These molecules behave as univalent ligands which can be either bidentate or tridentate depending on the number of pyrazolyl groups. Neutral complexes with the ions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

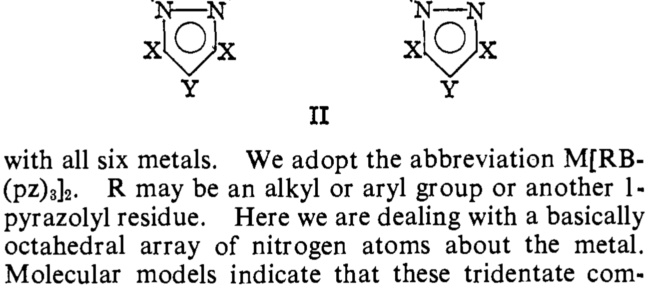
In another publication[1] the synthesis and properties of a number of poly(1-pyrazolyl)borate transition metal complexes have been reported briefly. The series of complexes with divalent transition metal ions is of particular interest in that these ligands offer the opportunity of forming chelates of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

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



I

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



II

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

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

Table I. Room-Temperature Effective Moments in Solution (BM)

	Mn	Fe	Co	Ni	Cu
M[$H_2B(pz)_2$]$_2$	5.99 ± 0.02[a]	5.20 ± 0.02[a]	4.53 ± 0.05[b]	0[b]	1.9 ± 0.1[b]
M[$HB(pz)_3$]$_2$	6.11 ± 0.05[b]	. . .[c]	5.40 ± 0.05[b]	3.24 ± 0.05[b]	2.12 ± 0.15[b]
M[$B(pz)_4$]$_2$	5.98 ± 0.05	0	5.24 ± 0.10	3.22 ± 0.05	2.05 ± 0.15

[a] Moment measured for complex I (X = CH_3, Y = H). [b] Measured in dichloromethane solution. All others measured in chloroform. [c] Moment is strongly temperature dependent.

which the individual complexes are assigned their various structures will be considered in the light of magnetic and spectral data.

The optical data have been analyzed in terms of the crystal-field theory, and consideration is given to the position of the ligands in the spectrochemical and nephelauxetic series.

Epr studies of the Co^{2+} compounds have also been made and have been reported elsewhere.[3] The evidence for the structures postulated above will first be summarized and the various physical measurements then discussed in detail.

Summary of Evidence for Geometric Structures

The assignment of octahedral geometry to complexes of the form M[$HB(pz)_3$]$_2$ and M[$B(pz)_4$]$_2$ is based on the following observations.

1. All the complexes M(HB[pz)$_3$]$_2$ have been shown to be isomorphous. They are stable, well-characterized compounds with analyses and molecular weights corresponding closely to the formulas given.
2. The room-temperature effective magnetic moments of the pairs M[$HB(pz)_3$]$_2$, M[$B(pz)_4$]$_2$ are closely similar and consistent with those found for octahedral coordination in the literature.
3. The electronic spectra of the pairs M[$HB(pz)_3$]$_2$, M[$B(pz)_4$]$_2$ are closely similar and agree well with other octahedral spectra in the literature.
4. The diamagnetism of Fe[$B(pz)_4$]$_2$ gives strong evidence for octahedral coordination. Low-spin ferrous complexes are relatively common, the six d electrons filling the t_{2g} orbitals to give a $^1A_{1g}$ ground state.
5. Proton nuclear resonance for the Co complexes shows that the six pyrazolyl residues in Co[$HB(pz)_3$]$_2$ are equivalent, and the additional two in Co[$B(pz)_4$]$_2$ are different. The resonances of the six equivalent pyrazole residues are in approximately the same positions for the two complexes.
6. Single crystal epr data for the Co^{2+} complexes can only be interpreted in terms of an axially distorted octahedral crystal field about the cobalt atom.[3] The magnetically dilute powder epr spectra of Co[$HB(pz)_3$]$_2$ and Co[$B(pz)_4$]$_2$ are very similar.
7. The fact that the tris- and tetrakis(1-pyrazolyl)-borate ions are tridentate, uninegative ligands provides a ready explanation of their inability to form neutral chelates with trivalent metal ions of the type usually found for bidentate ligands. Thus iron(III) reacts with $B(pz)_4^-$ forming the complex ion Fe[$B(pz)_4$]$_2^+$ isolable as the nitrate or hexafluorophosphate.[4]

Turning to the remaining compounds, molecular models indicate that [$H_2B(pz)_2$]$^-$ can act only as a bidentate ligand, and the complexes of the form M[$H_2B(pz)_2$]$_2$ give molecular weights and analyses corresponding closely to this formula. They are therefore four-coordinate and either tetrahedral or planar. The evidence on which decisions have been made between the alternatives is summarized below.

Ni[$H_2B(pz)_2$]$_2$. The diamagnetism of this compound is strong evidence for its planar structure. This is supported by the electronic spectral data, the longest wave transition being at 21,000 cm^{-1}. Tetrahedral Ni^{2+} complexes, which cannot be diamagnetic within the framework of simple ligand-field theory, show absorption at much longer wavelengths.

Cu[$H_2B(pz)_2$]$_2$. This compound is isomorphous with the Ni complex. The d–d transition observed in the electronic spectrum is at too high a frequency to be from a tetrahedral system. Using the electrostatic $-^4/_9$ ratio for the splitting due to a tetrahedral field relative to an octahedral field and comparing with the octahedral Δ value, a tetrahedral copper dihydrobis(1-pyrazolyl)borate would be expected to absorb at about 7000 cm^{-1}. If Jahn–Teller effects are important in the octahedral case, the predicted tetrahedral absorption would be at even longer wavelengths. The longest wavelength absorption in Cu[$H_2B(pz)_2$]$_2$ is at 18,500 cm^{-1}.

Co[$H_2B(pz)_2$]$_2$ and Zn[$H_2B(pz)_2$]$_2$. The proton nmr spectra show all four pyrazolyl residues to be equivalent with the shifts of the cobalt compound being quite different from those for the octahedral complexes. The effective magnetic moment is in the middle of the range for the tetrahedral Co(II). High-spin planar Co(II) cannot be ruled out on the basis of magnetic data, but the complex is isomorphous with Zn[$H_2B(pz)_2$]$_2$ and not with Cu[$H_2B(pz)_2$]$_2$ and Ni[$H_2B(pz)_2$]$_2$. The optical data give strong support to the assignment. All three spin-allowed transitions have been detected, and the splittings and intensities are similar to those for other tetrahedral Co(II) systems in the literature. Four-coordinate Zn(II) complexes are always tetrahedral unless steric requirements make this impossible (*e.g.*, zinc phthalocyanine).

Fe[$H_2B(pz)_2$]$_2$ and Mn[$H_2B(pz)_2$]$_2$. Optical data for the Fe(II) complex give strong evidence for tetrahedral coordination. Δ for the high-spin octahedral ferrous complexes studied is ~12,500 cm^{-1},[2] and so a Δ of ~6000 cm^{-1} would be expected for high-spin tetrahedral coordination. Absorption corresponding to the $^5T_2 \leftarrow {}^5E$ transition (separation Δ) is found at 5800 cm^{-1}. The magnetic moments are consistent with the tetrahedral assignment, but high-spin planar structures could not be ruled out on this basis. The change in the sign of the B^{11} nmr shift on passing from Mn[$B(pz)_4$]$_2$ (+1692 cps) and Mn[$HB(pz)_3$]$_2$ (+1882 cps) to Mn[$H_2B(pz)_2$]$_2$ (−2593 cps) must in any mechanism indicate a change in geometry.

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(3) J. P. Jesson, *J. Chem. Phys.*, **45**, 1049 (1966).

(4) S. Trofimenko, unpublished work.

A. **Susceptibility Data**. The effective magnetic moments of the complexes measured in solution at room temperature and calculated assuming the Curie law is obeyed are given in Table I. Satisfactory measurements of the moments for $Mn[H_2B(pz)_2]_2$ and $Fe[H_2B(pz)_2]_2$ could not be obtained because of the instability of the complexes. Fe^{2+} and Mn^{2+} complexes of structure I (X = CH_3, Y = H) are more stable, and room-temperature moments for these compounds are included in the table. We shall consider the magnetic data for each metal in turn, indicating how the information supports the molecular structures which have been assigned to the compounds. It should be emphasized that the moments given are to be viewed as qualitative indicators of the gross molecular structure. The influence of low-symmetry components of the field, corrections for temperature-independent paramagnetism, and possible non-Curie law behavior have been ignored.

Mn^{2+}. High-spin Mn^{2+} has a $^6A_1$ ground state in both octahedral and tetrahedral coordination. This is the only spin sextet of the configuration, and departures from the spin-only value of the moment (5.92) due to spin–orbit mixing of higher states and low symmetry components of the crystal field are expected to be small. The measured moments are consistent with the assignment of a tetrahedral structure to $Mn[H_2B(pz)_2]_2$ and an octahedral structure to $Mn[HB(pz)_3]_2$ and $Mn[B(pz)_4]_2$. Tetrahedral and octahedral Mn^{2+} cannot, of course, be distinguished on the basis of their magnetic moments.

Fe^{2+}. High-spin octahedral Fe^{2+} has a $^5T_{2g}$ ground state and gives room-temperature moments of about 5.3 BM, which are relatively insensitive to temperature. High-spin tetrahedral Fe^{2+} has a ^5E ground state with moments in the 5.1-BM range. A distinction between the two types of coordination for high-spin cases on the basis of their moments is of dubious validity since low-symmetry components of the field can produce appreciable variations in the effective moment.

A clear distinction between tetrahedral and octahedral geometries is possible for low-spin Fe^{2+} since the octahedral low-spin ground state is $^1A_{1g}$, the t_{2g} orbitals being completely occupied, and complexes of this type are, of course, diamagnetic. The low-spin tetrahedral ground state would be $^3T_1$. The diamagnetism of $Fe[B(pz)_4]_2$ is then clear evidence for essentially octahedral coordination. Additional evidence is provided by the singlet–quintet spin equilibrium shown by $Fe[HB(pz)_3]_2$ and discussed elsewhere.[2] Octahedral Fe^{2+} is one of the most likely situations for the observation of a spin-free–spin-paired equilibrium, the required mean pairing energy being in the region of 15,000 cm^{-1} and varying according to the degree of reduction of the interelectronic repulsion integrals by covalent bonding of the ligand. Complex II (X = Y = CH_3) is completely high spin with a room-temperature moment of 5.22 BM. The moment of 5.2 BM for complex I (X = CH_3, Y = H) is consistent with the assignment of tetrahedral geometry.

Co^{2+}. Tetrahedral Co^{2+} has a $^4A_2$ ground state with a moment given approximately by

$$\mu_{\text{obsd}} = 3.87\left(1 + \frac{4\zeta}{3\Delta}\right)$$

where Δ is the one-electron crystal-field parameter, and ζ is the single-electron spin–orbit parameter. Because of the possibility of relatively large percentage changes in Δ (Δ for tetrahedral Co^{2+} being in the region 3000 cm^{-1}) and the large spin–orbit parameter (ζ = 540 cm^{-1}), μ_{obsd} can cover a quite wide range. Values have been found from ~4.2 to ~4.9 BM. The upper end of this range overlaps values found for octahedral coordination (4.7–5.4 BM), and the assignment of geometry on the basis of room-temperature moment is not always possible. The fact that $Co[H_2B(pz)_2]_2$ is isomorphous with $Zn[H_2B(pz)_2]_2$ argues strongly for tetrahedral coordination, and the moment of 4.52 BM places it right in the middle of the tetrahedral range.

The high-spin ground state in octahedral coordination is $^4T_{1g}$, and an appreciable temperature dependence of the moment is anticipated. Distortions in the octahedral field can give rise to large anisotropy in the magnetic moment and g-tensor components which would not be found for tetrahedral coordination. Magnetically dilute single-crystal epr measurements in $Co[HB(pz)_3]_2$ at 4.2°K give unambiguous evidence for an axially distorted octahedral field.[3] The magnetically dilute powder epr of $Co[HB(pz)_3]_2$ and $Co[B(pz)_4]_2$ are very similar, indicating the same geometry about Co^{2+}. The room-temperature moments of 5.40 and 5.24 BM for $Co[HB(pz)_3]_2$ and $Co[B(pz)_4]_2$ are good for octahedral coordination.

Ni^{2+}. The zero magnetic moment for $Ni[H_2B(pz)_2]_2$ provides unambiguous evidence for essentially square-planar Ni^{2+}. The electrons are paired owing to the strong antibonding character of the d orbital involved in σ bonding to the square-planar array ($d_{x^2-y^2}$ for a coordinate system in which the x and y axes pass through the nitrogen atoms). $Ni[H_2B(pz)_2]_2$ is isomorphous with $Cu[H_2B(pz)_2]_2$ which must also be planar. Octahedral Ni^{2+} gives rise to a $^3A_{2g}$ ground state. The moment is given approximately by

$$\mu_{\text{eff}} = 2.83\left(1 + \frac{2\zeta}{\Delta}\right)$$

and should be relatively insensitive to temperature and small departures from octahedral symmetry. Values of 2.9–3.3 BM have been found. Using the free ion value of ζ = 650 cm^{-1}, we would have Δ = 9400 cm^{-1}. This value is in poor agreement with the value of Δ = 12,000 cm^{-1} found from the optical data. The discrepancy is perhaps not surprising in view of the approximations involved in the formula for the effective moment, and the value of 12,000 cm^{-1} is probably closer to the true value. The room-temperature moments of 3.22 and 3.24 BM for $Ni[HB(pz)_3]_2$ and $Ni[B(pz)_4]_2$ are consistent with the postulated octahedral geometry.

Cu^{2+}. The ground state for octahedral copper, ^2E_g, consists of two noninteracting Kramer's doublets, and the moment is relatively insensitive to distortions. Similar moments are therefore found for planar and octahedral environments. Values of ~1.9 BM are usually obtained. The measurements on the Cu complexes are less accurate than those for the other metals because of the small nmr shifts involves. Jahn–Teller distortions can be important in these systems.

B. **Optical Data**. In considering the optical data, it is convenient to discuss the molecules of a given geometry collectively. After a brief consideration of the zinc complexes, first the planar, then the tetrahedral, and finally the octahedral complexes will be discussed.

1. **Zinc Complexes.** The transitions in these complexes are probably intraligand in character and set a short wavelength limit for the absorptions in the other complexes which may be assigned to the d–d and charge-transfer transitions involving the metal. The data for the three zinc complexes measured in cyclohexane solution are given in Table II. The possibility that some of the transitions are metal-to-ligand charge transfer is, of course, not completely ruled out, but the wavelengths observed are reasonable for aromatic $\pi^* \leftarrow \pi$ absorption.

Table II. Ultraviolet Absorption Spectra of Zinc Complexes Measured in Cyclohexane Solution

Compound	λ, mμ	ν, cm⁻¹	ε	Comment	Assignment
$Zn[H_2B(pz)_2]_2$	218	45,900	24,000		Intraligand
	215	46,500	23,000	Shoulder	
$Zn[HB(pz)_3]_2$	216	46,300	17,000	Shoulder	Intraligand
	210	47,600	33,000		
	205	48,800	34,000		
$Zn[B(pz)_4]_2$	218	45,900	18,000	Shoulder	Intraligand
	212	47,200	30,000		
	207	48,300	31,000		

2. **Planar Complexes.** There can be little doubt that there is an essentially planar array of nitrogen atoms about the metal in these complexes. It does not follow, however, that the pyrazole rings and boron atoms, as shown in structure I, are also coplanar. In fact, molecular models indicate that the borons are probably out of the plane of the rings and that the rings may be inclined to one another. Two forms of the molecule $M[H_2B(pz)_2]_2$ could then exist: a "boat" form with both borons up and a "chair" form with one up and one down. With chelates of structure I ($X = CH_3$, $Y = H$ or any other group), only the chair form is possible for steric reasons. The molecular symmetry is therefore less than D_{4h}. However, in the present discussion it will be assumed that only nearest neighbors to the metal need be considered and that the local symmetry is D_{4h}.

The molecular orbital theory of this type of complex has been considered by Gray and Ballhausen[5] and by Liehr, *et al.*[6] A complete ligand-field calculation, including spin–orbit effects, has been made by Fenske, *et al.*,[7] for Pt^{2+}. They find the orbital ordering $d_{xz}d_{yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$. The x and y axes pass through the ligand atoms at the corners of a square array. Some confidence may be placed in this ordering for Pt^{2+}, but it could be different when other metals are considered. Gray and Ballhausen[5] suggest that the lowest unoccupied orbital which is mainly ligand in character, for systems where the ligand has a π system, will be $a_{2u}(\pi^*)$ and that the long-wavelength charge-transfer transitions in their d^8 complexes involve transfer of an electron from the metal to this orbital. The data and assignments for the two planar pyrazole complexes are given in Table III.

Table III. Electronic Absorption Spectra of Planar Complexes

Compound	λ, mμ	ν, cm⁻¹	ε	Comment	Assignment
$Ni[H_2B(pz)_2]_2$	472	21,200	72		${}^1A_{2g} \leftarrow {}^1A_{1g}$
	277	36,100	1400		${}^1B_{1u} \leftarrow {}^1A_{1g}$
	247	40,500	15,000	Shoulder	${}^1A_{2u} \leftarrow {}^1A_{1g}$
	242	41,300	21,000		${}^1E_u \leftarrow {}^1A_{1g}$
	234[a]	42,700	15,000	Shoulder	
	219[a]	45,700	12,000		Ligand ?
$Cu[H_2B(pz)_2]_2$	542	18,450	68		${}^2B_{2g} \leftarrow {}^2B_{1g}$
	328	30,500	1000		${}^2A_{2u} \leftarrow {}^2B_{1g}$
	265	37,700	1000		${}^2A_{1u} \leftarrow {}^2B_{1g}$
	219[a]	45,700	18,000		Ligand ?
	203[a]	49,300	20,000		

[a] In cyclohexane solution. Others in dichloromethane.

$Ni[H_2B(pz)_2]_2$. The first band, in view of its extinction coefficient, must be assigned to the first d–d transition $(d_{x^2-y^2})(d_{xy}) \leftarrow (d_{xy})^2$. It is somewhat stronger than the corresponding transition in the compounds studied by Gray and Ballhausen. The band is quite symmetrical, and a search to longer wavelengths with more concentrated solutions did not reveal any further absorption (such as the associated singlet–triplet transition). The first charge-transfer transition, ${}^1B_{1u} \leftarrow {}^1A_{1g}$, is orbitally forbidden and is assigned to the absorption at 277 mμ which has the reasonable extinction coefficient ε 1400. The next two charge-transfer transitions are orbitally allowed, and the transition to the ${}^1E_u$ state was found by Gray and Ballhausen to be the stronger of the two. The assignments in Table III have been completed on this basis. It is possible there is some splitting of the E_u state due to departures from D_{4h} symmetry. Neglecting exchange and Coulomb integrals between electrons centered on different atoms and evaluating those for electrons on the same atom in terms of the Slater–Condon theory for complex atoms, Gray and Ballhausen[5] found the following energies for the optical transitions.

$$
\begin{array}{ll}
{}^1A_{2g} \leftarrow {}^1A_{1g} & \Delta_1 - 35F_4 \\
{}^1B_{1u} \leftarrow {}^1A_{1g} & \Delta E({}^1B_{1u}) \\
{}^1A_{2u} \leftarrow {}^1A_{1g} & \Delta E({}^1B_{1u}) + \Delta_2 - 20F_2 + 100F_4 \\
{}^1E_{u} \leftarrow {}^1A_{1g} & \Delta E({}^1B_{1u}) + \Delta_2 + \Delta_3 - 15F_2 + 75F_4
\end{array}
$$

where Δ_1, Δ_2, and Δ_3 are the one-electron splittings $(x^2 - y^2) - (xy)$, $(xy) - (z^2)$, $(z^2) - (xz, yz)$; $\Delta E({}^1B_{1u})$ is the energy of the ${}^1B_{1u} \leftarrow {}^1A_{1g}$ transition; and F_2 and F_4 are the Slater–Condon interelectronic repulsion integrals.

Using $F_2 = 10F_4 = 700$ cm⁻¹, the assignments in Table III lead to $\Delta_1 = 23{,}700$ cm⁻¹; $\Delta E({}^1B_{1u}) = 36{,}100$ cm⁻¹; $\Delta_2 = 11{,}400$ cm⁻¹; and $\Delta_3 \approx 0$.

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(5) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

(6) J. R. Permuareddi, A. D. Liehr, and A. W. Adamson, *ibid.*, **85**, 249 (1963).

(7) R. F. Fenske, D. S. Martin, and K. Rudenberg, *Inorg. Chem.*, **1**, 441 (1962).

Table IV. Electronic Absorption Spectra of Tetrahedral Complexes

Compound	λ, mμ	ν, cm^{-1}	ε	Comment	Assignment
$Co[H_2B(pz)_2]_2$ in CH_2Cl_2	3120	3,200	7		$^4T_2 \leftarrow {}^4A_2$
	1220	8,200	97	Well-resolved doublet	$^4T_1(F) \leftarrow {}^4A_2$
	1070	9,300	92		
	585	17,100	340	Well-resolved triplet	$^4T_1(P) \leftarrow {}^4A_2$
	552	18,100	406		
	525	19,000	301		
	280	35,700	1,700		Metal–ligand
	242[a]	41,300	5,000		
	208[a]	48,100	18,000		Ligand
$Fe[H_2B(pz)_2]_2$ ($X = CH_3$, $Y = H$ in $CHCl_3$)	1730	5,800	16		$^5T_2 \leftarrow {}^5E$
	280[a]	35,700	1,500		Metal–ligand
	224[a]	44,600	12,000		Ligand

[a] Measured in cyclohexane.

As expected, Δ_1 is by far the largest of the Δ values due to the strongly antibonding character of the σ-bonding $d_{x^2-y^2}$ orbital. The value of Δ_1 is close to that found in $Ni(CN)_4^{2-}$, and the Δ_2 and Δ_3 values are also quite similar. As with most calculations of this type, the results are quite sensitive to the values of F_2 and F_4 chosen (we have used the values selected by Gray and Ballhausen), and so the final parameters, particularly Δ_2 and Δ_3, are subject to fairly large errors. From the comparison of spectra in planar d^8 complexes in cases where the ligand has no π system with those cases where a π system is present, Gray and Ballhausen were able to establish a pattern for ligand-to-metal and metal-to-ligand charge transfer. They concluded that ligand-to-metal transitions would be separated by ~10,000 cm^{-1}, while the metal-to-ligand transitions are separated by only 2000–3000 cm^{-1}. The assignments made here are consistent with this scheme.

$Cu[H_2B(pz)_2]_2$. The assignments in Table III for the copper complex have been made in the same way. The d–d transition $(x^2 - y^2)^2(xy) \leftarrow (x^2 - y^2)(xy)^2$ is of similar intensity to the corresponding transition in the nickel complex, and again it must be assumed that the remaining d–d transitions are obscured by charge-transfer absorption. For copper, again assuming charge transfer to the low-lying $a_{2u}(\pi^*)$ orbital, the first two charge-transfer transitions are forbidden. The assigned transitions have similar intensity to the forbidden charge-transfer transition in the nickel example. It would be dangerous to assign the absorptions at 219 and 203 mμ to particular metal-to-ligand transitions since they may be intraligand in character. The energy of the d–d transition $(b_{1g})^2(b_{2g}) \leftarrow (b_{1g})(b_{2g})^2$ is Δ_1. Denoting the energy of the first charge-transfer transition as $\Delta E(^2A_{2u})$, an estimate of the interelectronic repulsion correction for the A_{1u} transition is required. The configuration $(b_{2g})(b_{1g})(a_{2u})\ldots$ gives rise to two doublet states and a quartet. The important doublet for our purposes may be written in the form

$$(^1/_2)^{1/2}[\,|\ldots(xy)(\bar{a}_{2u})(x^2 - y^2)| - \\ |\ldots(\overline{xy})(a_{2u})(x^2 - y^2)|\,]$$

Using the approximation of neglecting repulsion integrals between ao's on different centers, the energy of the $^2A_{1g}$ transition is

$$\Delta E(^2A_{2u}) = \Delta_1 - 175F_4/2$$

The final parameters for the copper complex are therefore $\Delta_1 = 18{,}450$ and $\Delta E(^2A_{2u}) = 30{,}500$.

The expression for $\Delta E(^2A_{1u})$ would require $F_4 \sim 20$ cm^{-1}. In view of the approximations involved, this result cannot be viewed as a determination of F_4, and the true value is almost certainly larger. Δ_1 appears to be significantly lower for Cu than for Ni.

The spectra described above provide strong support for the structures assigned on the basis of the magnetic data and rule out the possibility of tetrahedral coordination in either of the complexes.

3. Tetrahedral Complexes, $M[H_2B(pz)_2]_2$ ($M = Zn^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}$). Data for the Zn^{2+} complex have been presented in Table II. The Fe^{2+} and Mn^{2+} complexes derived from dihydrobis(3,5-dimethyl-1-pyrazolyl)borate were used in the study because of their enhanced stability over the unsubstituted compounds. No d–d transitions were observed for the Mn^{2+} complex for the path lengths and concentrations available. Data for the remaining two complexes are given in Table IV.

$Co[H_2B(pz)_2]_2$. There are many optical studies of tetrahedral Co(II) complexes in the literature. The most detailed work has been carried out by Ferguson[8] using low-temperature and polarized-single-crystal techniques. Cotton[9] has studied a variety of tetrahedral Co(II) compounds both in solution and as mulls. In these studies it has been assumed that the first spin-allowed transition $^4T_1 \leftarrow {}^4A_2$ lies in the 3-μ region, outside the spectral range covered, giving a Δ of 3000–4000 cm^{-1}. Transitions to the $^4T_1(^4F)$ and $^4T_1(^4P)$ states then lie at ~5500 and ~15,000 cm^{-1}. Because of the absence of a center of symmetry and consequent mixing of d and p orbitals in these systems, the d–d transitions are commonly 100–200 times more intense than for octahedral coordination. In the present case, the transition in the 3-μ region has been observed by comparing the infrared spectra of $Zn[H_2B(pz)_2]_2$ and $Co[H_2B(pz)_2]_2$ in CCl_4 solution at the same concentration.

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[8] J. Ferguson, *J. Chem. Phys.*, **39**, 116 (1961).

[9] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

The spectra are shown in Figure 1. The sharp vibrational structure and CCl_4 absorption (there was no balancing solvent cell) are quite similar in the two cases, but there is an underlying broad absorption in the Co(II) compound due to the $^4T_2 \leftarrow {}^4A_2$ transition.

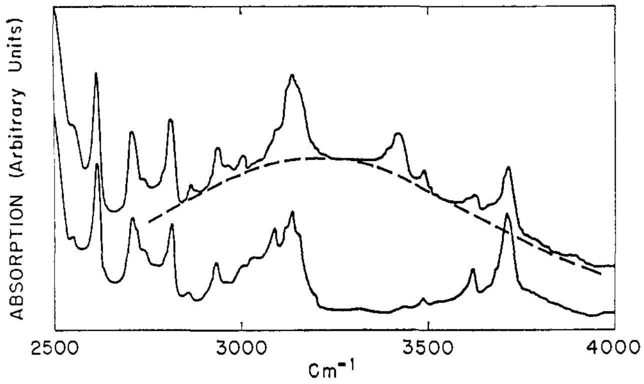

Figure 1. Absorption spectra (3 μ) of $Zn[H_2B(pz)_2]_2$ and $Co[H_2B(pz)_2]_2$ in CCl_4.

The spectrum in the 17,000–3500-A region is shown in Figure 2. Large splittings are observed in the $^4T_1(F) \leftarrow {}^4A_2$ and $^4T_1(P) \leftarrow {}^4A_2$ transitions and are attributed to the effect of spin–orbit coupling and low-symmetry components in the crystal field. Jahn–Teller effects in the excited states are theoretically possible, but they are probably small in view of the large spin–orbit contribution. Three well-resolved maxima are found for the $^4T_1(P)$ transition. The $^4T_1$ components are probably quite strongly mixed with components of the ^2G state which occur in the same region, and the triplet splitting observed is quite characteristic of Co^{2+} in tetrahedral coordination.[10–13] The two bidentate chelate residues in $Co[H_2B(pz)_2]_2$ would be expected to give rise to a low-symmetry component in the crystal field of approximately D_{2d} symmetry. It is possible that the well-resolved doublet structure in the transition to the $^4T_1(^4T)$ state can be accounted for as the splitting $T_1 \rightarrow A_2 + E$.

Since the $^4T_2 \leftarrow {}^4A_2$ transition should occur at a frequency Δ cm^{-1}, the infrared measurement indicates $\Delta = 3200$ cm^{-1}. However, the transition $^4T_1(^4F) \leftarrow {}^4A_2$ should lie at approximately 1.8Δ, and based on this assignment a value of $\Delta \sim 4800$ cm^{-1} is obtained. A possible explanation of this discrepancy is that, in view of the intrinsic weakness of the transition to the $^4T_2$ state, only the transition to the E component is observed, the B_2 component being forbidden. The measured magnetic moment corresponds to a ζ/Δ value of approximately 0.13. Combination of this value with the known free ion spin–orbit coupling constant gives $\Delta \sim 4100$ cm^{-1}. A further 10% reduction in ζ due to covalency effects would give $\Delta \sim 3700$ cm^{-1}. It does not, therefore, seem possible to choose between the alternate Δ values on the basis of the magnetic data. Just as for the planar complexes, it is probable that the boron atoms lie out of the plane of the pyrazole rings, and the rings may be inclined to one another. Two optically isomeric forms of the molecule would be possible, provided there is no rapid N–B–N inversion.

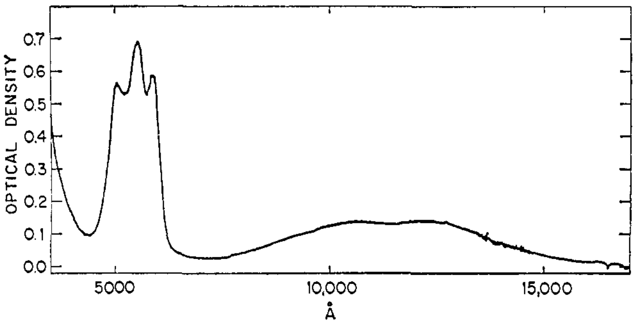

Figure 2. Absorption spectrum of $Co[H_2B(pz)_2]_2$, 3500–17,000 A, measured in $CHCl_3$ solution.

$Fe[H_2B(pz)_2]_2$. The tetrahedral ferrous complexes are very easily oxidized in solution. Studies were made with the more stable chelate derived from dihydrobis(3,5-dimethyl-1-pyrazolyl)borate. A single band corresponding to the expected $^5T_2 \leftarrow {}^5E$ transition is found at 5800 cm^{-1}. The separation of these energy levels is Δ on the crystal-field model, and $\Delta = 5800$ cm^{-1} is very close to $^4/_9$ the Δ for the octahedral systems (~12,500 cm^{-1}).[2]

Tetrahedral Fe^{2+} complexes reported in the literature have no d–d absorption between 500 and 2000 mμ.[14,15] It seems unlikely that the $^5T_2 \leftarrow {}^5E$ transition would be too weak to be observed, and probably Δ is less than 5000 cm^{-1} for these systems.

4. Octahedral Complexes, $M[HB(pz)_3]_2$ and $M[B(pz)_4]_2$ ($M = Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}$). The optical spectra of complexes $M[HB(pz)_3]_2$ and $M[B(pz)_4]_2$ are almost identical except for the ferrous compounds where a spin equilibrium is present in the first compound. The two types of complex will therefore be considered together. Results have already been given for the Zn complexes (Table II), and the absorption in the octahedral Mn^{2+} complexes was too weak to be detected in the effective concentrations available. Results for a variety of Fe(II) complexes are given in the following paper.[2] The results for the remaining complexes are given in Table V.

$Cu[HB(pz)_3]_2$ and $Cu[B(pz)_4]_2$. Both complexes give one very broad transition in the 16,500-cm^{-1} region which may be assigned to the expected $^2T_{2g} \leftarrow {}^2E_g$ transition. In both cases extended and very pronounced long-wavelength shoulders are found. There is some evidence of structure in the main absorption. Splittings are expected owing to the trigonal component of the field, spin–orbit coupling, and possible Jahn–Teller distortions. The apparent octahedral splitting parameter Δ, neglecting Jahn–Teller effects, is ~16,000 cm^{-1}, indicating a relatively strong ligand field. There is an increase by a factor of 3 in extinction

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(10) D. L. Wood and A. A. Ballman, *Am. Mineralogist*, 51, 216 (1966).

(11) C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, 9, 397 (1955).

(12) R. Pappalardo, D. L. Ward, and R. C. Linares, Jr., *J. Chem. Phys.*, 35, 2041 (1961).

(13) J. Ferguson, *ibid.*, 32, 528 (1960).

(14) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, 2, 1158 (1963).

(15) N. S. Gill, *J. Chem. Soc.*, 3512 (1961).

Table V. Electronic Spectra of Octahedral Complexes

Compound	λ, mμ	ν, cm^{-1}	ε	Comment	Assignment
$Cu[HB(pz)_3]_2$ in CH_2Cl_2	620	16,100	19	Pronounced long wave tail	$^2T_{2g} \leftarrow {}^2E_g$
	272	36,700	1,000		Metal–ligand
	210[a]	47,600	51,000		Ligand
	205[a]	48,800	51,000		
$Cu[B(pz)_4]_2$ in CH_2Cl_2	595	16,800	60	Pronounced long wave tail	$^2T_{2g} \leftarrow {}^2E_g$
	307	32,600	600		Metal–ligand
	263	38,000	600		
	215[a]	46,500	50,000		Ligand
$Ni[HB(pz)_3]_2$ in CH_2Cl_2	849	11,800	4.8		$^3T_{2g} \leftarrow {}^3A_{2g}$
	760	13,150	2.9	Shoulder	
	570	17,500	3.4	Shoulder	$^3T_{1g} \leftarrow {}^3A_{2g}$
	522	19,150	4.8		
	450	22,200	0.5	Shoulder	$^1A_{1g} \leftarrow {}^3A_{2g}$
	339	29,500	7.8		$^3T_{1g} \leftarrow {}^3A_{2g}$
	210[a]	47,600	39,000		Ligand
	205[a]	48,800	39,000		
$Ni[B(pz)_4]_2$ in $CHCl_3$	820	12,200	5.2		$^3T_{2g} \leftarrow {}^3A_{2g}$
	750	13,300	4.0	Shoulder	
	570	17,500	4.3	Shoulder	$^3T_{1g} \leftarrow {}^3A_{2g}$
	520	19,200	5.8		
	459	21,800	1.5	Shoulder	$^1A_{1g} \leftarrow {}^3A_{2g}$
	334	29,900	7.7		$^3T_{1g} \leftarrow {}^3A_{2g}$
	210[a]	47,600	30,000		Ligand
$Co[HB(pz)_3]_2$ in CH_2Cl_2	1100	9,100	0.4		$^2E_g \leftarrow {}^4T_{1g}$
	901	11,100	3.4		$^4T_{2g} \leftarrow {}^4T_{1g}$
	641	15,600	0.1		$^2T_{1g}, {}^2T_{2g} \leftarrow {}^4T_{1g}$
	515	19,400	1.3	Shoulder	$^4A_{2g} \leftarrow {}^4T_{1g}$
	459	21,800	13.4		$^4T_{1g} \leftarrow {}^4T_{1g}$
	284	35,300	1,300		Metal–ligand
	244	41,000	3,900		
	207[a]	48,300	26,000		Ligand
	202[a]	49,500	26,000		
$Co[B(pz)_4]_2$ in $CHCl_3$	1100	9,000	0.3		$^2E_g \leftarrow {}^4T_{1g}$
	877	11,400	3.0		$^4T_{2g} \leftarrow {}^4T_{1g}$
	645	15,500	0.1		$^2T_{1g}, {}^2T_{2g} \leftarrow {}^4T_{1g}$
	502	19,900	1.5	Shoulder	$^4A_{2g} \leftarrow {}^4T_{1g}$
	454	22,000	13.1		$^4T_{1g} \leftarrow {}^4T_{1g}$
	280	35,700	1,500		Metal–ligand
	250[a]	40,000	3,800	Shoulder	
	210[a]	47,600	20,000		Ligand

[a] Measured in cyclohexane solution.

coefficient with the substitution of the fourth pyrazole residue which is perhaps a little surprising. In the corresponding nickel and cobalt complexes there is essentially no change in extinction coefficient on substitution.

$Ni[HB(pz)_3]_2$ and $Ni[B(pz)_4]_2$. Calculations have been made for these complexes using the "complete" ligand-field matrices of Liehr and Ballhausen[16] for Ni^{2+} in an octahedral environment. The results must be viewed with some caution since it is probable there is a pronounced trigonal component in the crystal field. The calculated energy scheme as a function of Δ is shown in Figure 3. λ has been taken as -285 cm^{-1} and F_4 as 90 cm^{-1}. The relation $F_2 = 14F_4$ has been assumed. The measured transition frequencies for $Ni[HB(pz)_3]_2$ are shown in the diagram as horizontal bars, and it is seen that there is good agreement with the calculated values for $\Delta \approx 12{,}000$ cm^{-1}. The transition frequencies of $Ni[B(pz)_4]_2$ are very similar, and Δ must also be close to 12,000 cm^{-1} in this case. The assignments given in Table V are based on this calculation. Jørgensen[17] has suggested that, in $Ni(H_2O)_6{}^{2+}$, the doubling of the absorption in the 13,500-cm^{-1} region is due to spin–orbit coupling between $^3T_{1g}(^3F)$ and $^1E_g(^1D)$, giving rise to appreciable intensity for transitions to the latter state. The calculation of Liehr and Ballhausen[16] argues against this since the two states in question do not approach closely for the parameter values they have assumed. The energy scheme, however, depends quite sensitively on the values of F_2 and F_4 chosen, and the Jørgensen assignment cannot be completely ruled out. We have used the same F_2 and F_4 values as Liehr and Ballhausen, and, for the Δ value established for polypyrazolylborates, the ^1E state should be close to the $^3T_{2g}$ state. This may account for the splitting of the absorption peak. [The spin–orbit splitting in the $^3T_2$ state is much less than for $^3T_1(^3F)$.]

$Co[HB(pz)_3]_2$ and $Co[B(pz)_4]_2$. Most of the data for these compounds have been given in a publication describing paramagnetic resonance absorption in these systems.[3] Despite the large trigonal component in the crystal field indicated by the resonance data, there are no observable splittings of the orbital triplets in the optical spectrum. Koide[18] has shown that the transition to the $^4A_{2g}$ state should be weak. It is a two-electron transition, and his theoretical oscillator strengths are in

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(16) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 124 (1959).

(17) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

(18) S. Koide, *Phil. Mag.*, **4**, 243 (1959).

reasonable agreement with those found experimentally for the assignments given. Δ is found to be ~10,000 cm^{-1}.

C. Nuclear Magnetic Resonance Spectra. Proton magnetic resonance data obtained at 30° are given in Table VI. Shifts are in cycles per second from TMS as internal standard. The octahedral Fe(II) complexes are considered in the following paper.[2]

Table VI. Proton Nuclear Resonance Chemical Shifts

Compound	δ, cps	J, cps	Comment	Assignment
			Zn^{2+} Complexes	
Zn[$H_2B(pz)_2$]$_2$ in $CDCl_3$	−463	2.1	Doublet of doublets (0.5 cps)	3- and 5-H
	−453	2.2	Doublet of doublets (0.5 cps)	
	−375	2.1	Triplet	4-H
	~−250		Very broad	H_2 on boron
Zn[HB(pz)$_3$]$_2$ in CH_2Cl_2	−463	2.2	Doublet of doublets (0.6 cps)	3- and 5-H
	−425	1.9	Doublet	
	−361	2.1	Triplet	4-H
	~−250			H on boron
Zn[B(pz)$_4$]$_2$ in $CDCl_3$	−466	2.4	Doublet	3- and 5-H
	−444	1.6	Doublet	
	−376	2.1	Triplet	4-H

Compound	Shift	Assignment
	Co^{2+} Complexes	
Co[HB(pz)$_3$]$_2$ in $CDCl_3$	−6875	H on boron
	−5370	5-H
	−2430	4-H
	+6260	3-H
Co[B(pz)$_4$]$_2$ in $CDCl_3$	−5500	5-H
	−3630	pz (5)
	−2270	4-H
	−1910	pz (3)(4)
	−1760	pz
	+6960	3-H
Co[HB(pz)$_3$]$_2$, X = CH_3, Y = H, in $CDCl_3$	−6,450	H on boron
	−2,670	4-H
	−2,560	5-Me
	+4,700	3-Me
Co[$H_2B(pz)_2$]$_2$ in $CDCl_3$	−7,910	H_2 on boron
	−2,900	4-H
	−1,950	5-H
	+525	3-H
Co[$H_2B(pz)_2$]$_2$, X = CH_3, Y = H, in $CDCl_3$	−11,400	H_2 on boron
	−3,205	5-Me
	−2,785	4-H
	+400	3-Me
	Tetrahedral Fe Complexes	
Fe[$H_2B(pz)_2$]$_2$ in $CDCl_3$	−6,935	H_2 on boron
	−2,425	4-H
	−1,370	3-H
	+480	5-H
Fe[$H_2B(pz)_2$]$_2$, X = CH_3, Y = H, in $CDCl_3$	−12,925	H_2 on boron
	−3,290	3- and 5-Me
	−2,695	4-H
	Ni Complexes	
Ni[$H_2B(pz)_2$]$_2$ in $CDCl_3$	−470	3-, 4-, 5-H
	−419	
	−378	
Ni[HB(pz)$_3$]$_2$ in $CDCl_3$	−2,875	3-, 4-, 5-H
	+560	H on boron
Ni[B(pz)$_4$]$_2$ in $CDCl_3$	−3,230	3-, 4-, 5-H
	−2,860	
	−480	pz
	−439	
	−396	

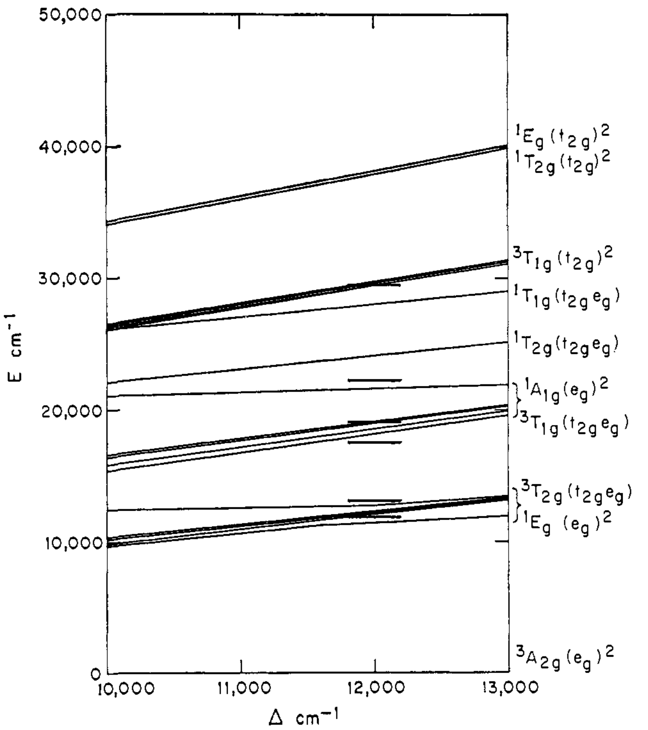

Figure 3. Energy-level diagram for octahedral Ni(II) complexes as a function of Δ. Measured Ni[HB(pz)$_3$]$_2$ transitions shown as horizontal bars.

The zinc complexes are, of course, diamagnetic and show well-resolved spin–spin splittings. The resonance of the 4-H is a triplet (see structure I for numbering) and gives an unambiguous assignment. Assignments cannot be made for the 3- and 5-H with the data available. The resonances for the hydrogen on boron are very broad. Their centers have been established by integration. The line widths of nuclear resonance spectra in paramagnetic systems are determined by the effects of dipolar and scalar coupling of the nucleus with the unpaired electrons in the molecule.[19] Appreciable scalar coupling will often broaden the resonances beyond detectability unless the electron spin–lattice relaxation time is very short. For the ions involved in the present study, rapid spin–lattice relaxation is usually found for Co^{2+} and Fe^{2+} in octahedral coordination. (Liquid helium temperatures are usually required for the observation of paramagnetic resonance in these systems.) The Co^{2+} and Fe^{2+} complexes are the only octahedral poly(1-pyrazolyl)borates which give rise to well-resolved nmr spectra. The octahedral Ni^{2+} complexes represent an intermediate case where some information can be obtained from the nmr (liquid nitrogen temperatures are usually needed to observe epr in these systems), and the Cu^{2+} and Mn^{2+} nmr spectra are too broad to provide useful information (epr can be observed at room temperature). Well-resolved proton resonance spectra are also found for the tetrahedral Fe^{2+} and Co^{2+} complexes. The tetrahedral Co^{2+} ground state is orbitally nondegenerate, and the relaxation mechanism must involve coupling of the zero-field splitting to the lattice modes.

Cobalt Complexes. The Co^{2+} complexes provide the most direct structural information since the spectra

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(19) N. Bloembergen, *J. Chem. Phys.*, 27, 572, 595 (1957).

Table VII. B^{11} Shifts Relative to Trimethyl Borate External Standard (14.2 Mcps)

	Mn	Fe	Co	Ni	Cu	Zn
$M[H_2B(pz)_2]_2$	-2590^a	-2130	-5400	$+360$	$+670$	$+360^a$
$M[HB(pz)_3]_2$	$+1880$	$+790$	-3410	$+780$	$+640$	$+330$
$M[B(pz)_4]_2$	$+1690^a$	$+270$	-3460^a	$+940^a$	$+730$	$+260^a$

[a] In $CHCl_3$ solution; others in CH_2Cl_2.

are not complicated by the presence of a spin equilibrium as is the case for Fe^{2+}. The first three Co^{2+} complexes in Table VI are octahedral and are sufficient to establish the assignments given. The assignments have been made on the basis of intensity, the effects of substitution, and from line widths and ease of saturation. In the limit of short electron spin-lattice relaxation times, the nuclear T_2 values and hence line widths are usually determined by dipolar terms which depend on the inverse of the sixth power of the distance of the proton from the electronic dipole, and so protons closest to the metal have the greatest half-widths. Direct evidence for the tridentate nature of the $HB(pz)_3^-$ and $B(pz)_4^-$ ligands is provided by comparison of the nmr spectra of $Co[HB(pz)_3]_2$ and $Co[B(pz)_4]_2$. In the former complex the six pyrazolyl residues giving rise to three separate proton resonances are all equivalent. The proton resonance spectrum of $Co[B(pz)_4]_2$ is shown in Figure 4. The addition of the fourth pyrazolyl residue gives rise to three new resonances of one-third the intensity of the main three resonances, and, of course, the resonance due to the proton on boron is no longer present. Assignments for the tetrahedral complexes $Co[H_2B(pz)_2]_2$ and I (M = Co, X = CH_3, Y = H), given in Table VI, have been made in the same way.

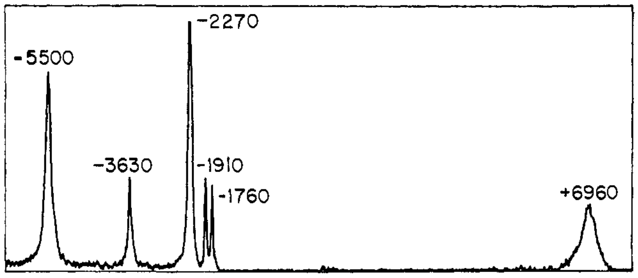

Figure 4. Proton resonance spectrum of $Co[B(pz)_4]_2$ in $CDCl_3$. Shifts from TMS at 60 Mcps.

The isotropic shifts in the octahedral compounds are determined predominantly by pseudo-contact interactions. A detailed analysis of these shifts together with complementary epr data will be published elsewhere.[20]

Ni^{2+} Complexes. Results for the Ni^{2+} complexes are given in Table VI. $Ni[H_2B(pz)_2]_2$, which is diamagnetic, gives resonances in roughly the same positions as those of the zinc complexes or of the free ligand. In $Ni[HB(pz)_3]_2$ only one resonance is observed due to the three ring protons. In $Ni[B(pz)_4]_2$ the resonance for the ring protons splits into two components, and it seems likely that the third resonance is also present in this grouping. The resonance due to H on boron is replaced by three resonances in essentially the positions for a free pyrazole residue, showing there is effectively no spin delocalization to this ring. Any appreciable dipolar shift is also ruled out. This is in harmony with the fact that the ground state is $^3A_2$, and the electronic moment would be expected to be isotropic.

Boron Nuclear Resonances. B^{11} resonance shifts measured from trimethyl borate as an external standard at 14.2 Mcps are given in Table VII. Susceptibility corrections have been applied to the shifts. The Zn complexes provide diamagnetic reference points. For the $M[HB(pz)_3]_2$ and $M[B(pz)_4]_2$ complexes of the same metal the shifts are approximately the same except for the Fe^{2+} case where the spin equilibrium is present. The shifts for the $M[H_2B(pz)_2]_2$ systems are in general quite different, the large low-field shifts in the Mn and Fe complexes providing additional evidence for the assumed geometrical differences.

Discussion

The magnitude of Δ for a given metal ion determines the position of a ligand in the spectrochemical series. Jørgensen[21] has suggested that Δ may be represented as a product of two factors, one for the ligand and one for the central ion.

$$\Delta = f(\text{ligand}) \times g(\text{central ion})$$

The position of a ligand in the nephelauxetic series is determined by the reduction of the interelectronic repulsion integrals from the values in the free ion, the parameter β being defined by

$$B(\text{complex}) = \beta B(\text{free ion})$$

Again Jørgensen has suggested that this parameter may be split into a quantity characteristic of the ligand and one characteristic of the metal

$$1 - \beta = hk$$

where h refers to the ligand and k to the metal.

Values of Δ, B, and β for the complexes studied are given in Table VIII. B values for the free ion are given in parentheses. Values of the corresponding quantities for the hexaaquo ions are given beneath the octahedral parameters for comparison. For the octahedral Ni(II) complexes the calculated transitions, using the undistorted octahedral model, are in very good agreement

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(20) J. P. Jesson, to be published.

(21) C. K. Jørgensen, *Discussions Faraday Soc.*, **26**, 110 (1958).

with the experimental values (see Figure 3). All the triplet states are reproduced closely. The high-spin states for Co(II) are not reproduced so well. This is probably due to the effect of the trigonal component in the field perturbing the postions of the ${}^4A_2$ and ${}^4T_1({}^4P)$ transitions which lie close together. In the Ni(II) case all the high-spin states are well separated. In establishing Δ and *B* for the Ni(II) case, we have used the results of the ligand-field calculation which indicates $\Delta \approx 12{,}000$ cm^{-1} and the relationship

$$\delta(T_1) = (225B^2 - 18B\Delta + \Delta^2)^{1/2}$$

where $\delta(T_1)$ is the separation between the two T_1 states.

Table VIII. Spectral Parameters for High-Spin Octahedral and Tetrahedral Complexes[a]

	Octahedral				Tetrahedral	
	Fe	Co	Ni	Cu	Fe	Co
Δ	12,500	10,000	12,000	16,000	5800	4500
B	. . .	830 (980)	850 (1040)	. . .	. . .	. . .
β	. . .	0.85	0.82	. . .	. . .	. . .
Δ (6H_2O)	10,400	7,900	8,500	12,600		
B (6H_2O)	. . .	880	890	. . .		
β (6H_2O)	. . .	0.90	0.89	. . .		

[a] Δ and *B* values in cm^{-1}.

The relevant parameters for establishing the position of the hydrotris(1-pyrazolyl)borate ligand in the spectrochemical and nephelauxetic series using the Ni(II) data are then $\Delta = 12{,}000$ cm^{-1} and $\beta = 0.82$. These values lead to the final quantities $f = 1.35$ and $h = 1.5$. The *h* value is quite sensitive to $\delta(T_1)$, and, because of the splittings of the ${}^3T_2({}^3F)$ state, $\delta(T_1)$ cannot be estimated accurately. The *h* value should therefore be accepted with some reservation. A value of $\delta(T_1) = 11{,}100$ cm^{-1} has been used in the calculation. The *B* value is reasonably close to that assumed in the original energy level calculation ($F_2 = 14F_4$; $F_4 = 90$ corresponds to $B = 810$ cm^{-1}). $h = 1.5$ gives the ligand about the same position in the nephelauxetic series as ethylenediamine, which is not unreasonable. The *f* value of 1.35 places the anion at about the same position in the spectrochemical series as *o*-phenanthroline. It should be noted that the ferrous complex of *o*-phenanthroline is low spin, as are some of the poly(1-pyrazolyl)borates.

The Δ value for the octahedral Co(II) complexes has been taken from a previous publication[3] and was obtained as a best fit to the spectrum using matrices for the trigonal potential. The Δ value obtained is quite different from the ${}^4T_2$–${}^4A_2$ separation, and, as pointed out above, this difference is probably due to the ${}^4A_2$–${}^4T_1({}^4P)$ interaction under the low symmetry component of the field. *B* has been calculated from the estimated ${}^4P$–${}^4F$ separation in the complex[3] (= 15*B*).

The Δ value for Cu^{2+} is, of course, uncorrected for any Jahn–Teller effect, and the "true" Δ is probably somewhat lower. The effects of the trigonal component of the field are probably comparable to any Jahn–Teller effect and have also been neglected. There is considerable uncertainty in the value of Δ given for Co(II) in tetrahedral coordination. The Δ values for the tetrahedral complexes are quite close to $^4/_9$ times the Δ for the octahedral cases.

The nuclear resonance shifts in the paramagnetic systems relative to the corresponding diamagnetic species must be ascribed to either dipolar or scalar coupling between the electron and nuclear spins. A scalar contribution to the shift requires unpaired spin density in a σ orbital on the proton in question. Four separate mechanisms giving rise to resonance shifts may be identified: (1) delocalization in the π system through dπ–pπ bonding with polarization of the spin in the σ orbital on the proton by unpaired pπ spin density, (2) delocalization in the σ system, (3) polarization of metal–ligand bonding orbitals by unpaired spin in metal orbitals of a different symmetry, and (4) the pseudo-contact or dipolar interaction.

It is apparent that the interpretation of these shifts can be a matter of some complexity, and a complete analysis is not possible with the present state of the art. Usually firm conclusions can only be obtained when one of the mechanisms predominates. With the exception of the shifts in the octahedral Co(II) complexes, which are determined largely by the pseudo-contact effect, this is apparently not the case for the present series of compounds. However, the following observations can be made for the data in this paper.

In the complex $Ni[B(pz)_4]_2$, the proton resonances in the pyrazolyl residue not bonded to the metal are close to those for the diamagnetic zinc complex. The ground state for this complex is ${}^3A_2$, and even quite large trigonal distortions in the crystal field would not be expected to give rise to large *g*-tensor anisotropies. Dipolar contributions to the shifts are therefore expected to be negligible. The scalar contribution to the shifts on the fourth pyrazolyl residue must also be negligible, indicating that the saturated boron atom is effective in insulating the terminal substituent from the unpaired spin on the metal. The fourth pyrazolyl residue in the corresponding Co^{2+} complex shows large downfield shifts. The ground state here is ${}^4T_1$, and large anisotropies in the electron moment have been shown to arise from the trigonal component in the field. The shifts in the fourth pyrazolyl residue are therefore due to the dipolar coupling between the proton and electron moments.

An appreciable dipolar contribution for the octahedral ferrous system is also anticipated. This expectation receives some support from the shift to high field of the H on boron in the hydrotris(3,4,5-trimethyl-1-pyrazolyl)borates and hydrotris(3,5-dimethyl-1-pyrazolyl)borates.[2] It is, however, still possible that the shift could arise from spin polarization through the boron. Unfortunately, the $Fe[B(pz)_4]_2$ compound, which would give the best test of this point, is diamagnetic. If the high-field shift of the terminal proton is due to the dipolar interaction, the over-all anisotropy for the Fe^{2+} system is indicated to be of the opposite sign to that for Co^{2+} where the proton on boron shifts to low field. Interpretations involving the protons attached directly to boron should be viewed with caution since large shifts are found for these protons in the tetrahedral cobaltous complexes where little *g* anisotropy is expected.

In conclusion, it may be stated that the optical and magnetic properties of this series of compounds fall into a consistent pattern. The nmr shifts of the paramagnetic compounds on the other hand do not show pronounced regularities even in such a series of closely related compounds, and it is apparent that several of the possible mechanisms for producing these shifts are combining to give a complex pattern.

Experimental Section

A. **Susceptibility Measurements.** Susceptibility measurements have been made in solution using an nmr method.[22] Measurements were made in $CHCl_3$ or CH_2Cl_2 depending on the solubility. The effective moments have been calculated using room-temperature data and assuming the Curie law is obeyed. The assumption is reasonable for all cases except the octahedrally coordinated Co complexes where a pronounced temperature dependence of effective moment is anticipated. The accuracy of the measurements varies because of the differing solubilities and susceptibilities involved. The variation of susceptibility with temperature could not be measured with sufficient accuracy to permit a meaningful verification of the Curie law behavior because of the limited temperature range which could be investigated.

B. **Optical Measurements.** Optical absorption studies were made in the region 17,000 to 2000 A using a Cary 14 recording spectrophotometer. Measurements at short wavelengths were made in hexane solution, and the remaining measurements were made in chloroform or dichloromethane. Infrared spectra were obtained using a Perkin-Elmer Model 21 spectrophotometer.

C. **Nmr Spectra.** The nmr spectra were recorded using a Varian HR-60 spectrometer for proton resonance studies of the paramagnetic species and an A-60 for the diamagnetic species. A 14.2-Mcps radiofrequency unit and probe were used for the boron studies. Measurements were made in deuteriochloroform except as noted. The proton shifts are measured *vs.* tetramethylsilane as an internal standard. The boron shifts are measured *vs.* trimethyl borate as an external standard.

D. **Synthesis of Compounds.** The synthesis of transition metal complexes with unsubstituted poly(1-pyrazolyl)borates[23] and poly(1-pyrazolyl)borates containing substituents on carbon or boron[24] will be published elsewhere.

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[22] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

[23] S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3165 (1967).

[24] Part IV: S. Trofimenko, submitted for publication.

Spin Equilibria in Octahedral Iron(II) Poly(1-pyrazolyl)borates

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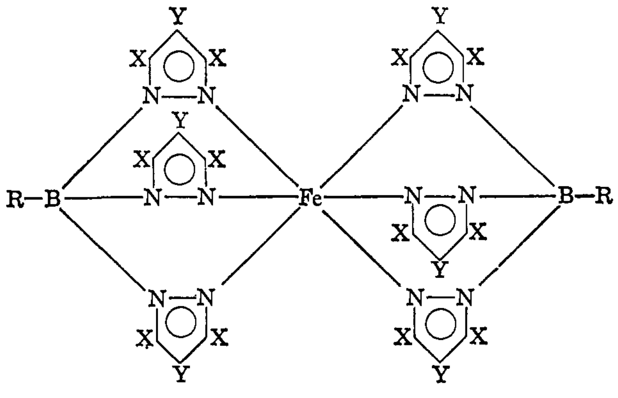
Abstract: The Fe^{2+} complexes based on the hydrotris(1-pyrazolyl)borate ligand provide an example of a "spin equilibrium" between high- and low-spin forms. Fully high-spin, fully low-spin, and complexes of intermediate spin can be produced by appropriate substitution. Optical spectra, susceptibility data, and magnetic resonance experiments leading to the characterization of these equilibria are presented.

The possibility of the occurrence of a thermally accessible electronic state of different multiplicity from the ground state has long been recognized for d^4, d^5, d^6, and d^7 ions in octahedral environments.[1] The experimental realization of an equilibrium of this type is determined by the availability of a complex for which the low-spin and high-spin ground states are separated by only a few hundred reciprocal centimeters. Since the energies involved in changes in chemical binding are in general much larger than this, the requirement is very restrictive and accounts for the fact that there are few, if any, well-documented cases of equilibria of this type.

For the d^5 and d^6 configurations, the susceptibility may be taken as the population weighted-average of the susceptibilities of the two terms of different multiplicity. For d^4 and d^7 the situation is more complicated as the spin–orbit coupling connects the two states involved. The presence of low-symmetry components in the crystal field is another factor which must also be considered.

The most favorable case for an unambiguous experimental observation of this type of equilibrium is the d^6 configuration where the low-spin system is diamagnetic and the change in the number of unpaired electrons is four.

The ferrous compounds of structures I–V present such an unambiguous example of a system in which both high- and low-spin ground states are thermally ac-



I, R = 1-pyrazolyl (pz); X = Y = H
II, R = C_6H_5; X = Y = H
III, R = H; X = Y = H
IV, R = H; X = CH_3; Y = H
V, R = H; X = Y = CH_3

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[1] L. E. Orgel, 10th Conseil Institute Chemie Solvay, Brussels, 1956.