

Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19711

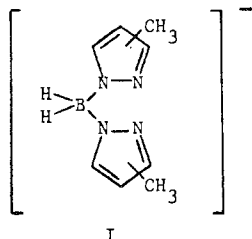
Structure Determination of Dihydrobis(1-pyrazolyl)borates by ^1H NMR of Potassium Salts and Nickel(II) Chelates

Wallace H. McCurdy, Jr.

Received February 28, 1975

AIC50152X

The series of geminal poly(1-pyrazolyl)borates, $[\text{R}_n\text{B}(\text{pz})_{(4-n)}]^-$, reported by Trofimenko¹ provides an excellent coordination system for studies of effects of bonding and structure on chemical reactivity. In order to interpret reaction enthalpy data for divalent transition metals² and acid catalyzed rates of decomposition³ observed with several dihydrobis(1-pyrazolyl)borates, it became necessary to determine the methyl position(s) in the dihydrobis[3(5)-methyl(1-pyrazolyl)]borate ion, I. Extensive ^1H NMR investigations



of *N*-substituted pyrazoles^{4,5} have shown that relative positions of 3-H and 5-H may be reversed by changing the solvent polarity. Structures were identified by observing the direction and magnitude of changes in chemical shifts of pyrazole protons in a known series of solvents. In this fashion, assignments of 3-H and 5-H doublets in alkali poly(1-pyrazolyl)borates were based on measured differences in chemical shifts with respect to 4-H (triplet) in the pyrazole ring as solvent or counterion was varied.¹ The proton displaying the largest induced shifts was correlated with the proton bearing the largest coupling constant and consequently was designated 3-H. Of interest to this study are data given for potassium dihydrobis(1-pyrazolyl)borate, $\text{KH}_2\text{B}(\text{pz})_2$, in D_2O : 7.58 ($J = 1.8$ Hz), 7.51 ($J = 2.2$ Hz), and 6.17 ppm ($J = 2.0$ Hz).¹ This order of proton assignment is followed by all symmetrical *N*-substituted pyrazoles in solvents of high dielectric constant. However, the coupling constants in these compounds are uniformly $J_{3,4} < J_{4,5}$. In specific cases, 3(5) proton and methyl group resonances in spectra of poly(1-pyrazolyl)borates have been determined by double resonance experiments on a metal complex bearing nuclear spin⁶ and by temperature dependent studies of a metal complex showing fluxional behavior.⁷ This work is concerned with application of diamagnetic shifts which appear on comparison of ^1H NMR spectra of potassium salts vs. nickel(II) chelates as a method of labeling 3(5) protons and methyl groups in dihydrobis(1-pyrazolyl)borates.

Results and Discussion

High resolution ^1H NMR spectra of potassium dihydrobis[3(5)-methyl(1-pyrazolyl)]borate, $\text{KH}_2\text{B}(\text{Mepz})_2$, (Table I) are consistent with a single isomeric structure. No resonance signals indicating a mixture of 3-methyl and 5-methyl substituted 1-pyrazolyl rings could be detected in the product prepared by reaction of potassium borohydride with excess 3(5)-methylpyrazole. Initial experiments were undertaken to identify the 1-pyrazolyl ring proton observed at 7.51 ppm ($J = 1.9$ Hz) in D_2O . Induced solvent effects, $\Delta\nu_s$, were determined from chemical shifts of $\text{KH}_2\text{B}(\text{pz})_2$, $\text{KH}_2\text{B}(\text{Mepz})_2$, and $\text{KH}_2\text{B}(\text{Me}_2\text{pz})_2$ measured in acetone- d_6 , methanol- d_4 , acetonitrile- d_3 , and D_2O (Table I). In this series of solvents, the ligands are most stable in acetonitrile and decompose most

rapidly in methanol. Fairly linear graphs of proton chemical shift vs. solvent dielectric constant, ϵ , were obtained for each salt in the three oxygen-containing solvents. Least-squares slopes ($\Delta\nu_s/\Delta\epsilon$) of curves for $\text{KH}_2\text{B}(\text{pz})_2$ (Table I) show a gradual increase: low-field H < mid-field H < 4-H, which suggest the same order of solvent dependence reported previously.¹ However, in agreement with spectra of *N*-substituted pyrazoles, a larger coupling constant was always observed for the low-field proton (5-H) rather than the proton with the larger solvent shift (3-H) in $\text{KH}_2\text{B}(\text{pz})_2$. Least-squares slopes for 4-H decrease uniformly upon methyl substitution in the series of bis(1-pyrazolyl)borate salts. Assuming the decrease in $\Delta\nu_s/\Delta\epsilon$ of 3-H or 5-H is comparable with that for 4-H in $\text{KH}_2\text{B}(\text{Mepz})_2$, the least-squares slope (0.338) of the low-field proton is close to the predicted value for 5-H (0.343) and the unknown structure is potassium dihydrobis[3-methyl(1-pyrazolyl)]borate. Unfortunately the differences in $\Delta\nu_s/\Delta\epsilon$ values for these protons are approximately equal to standard deviations of the slopes and thus no meaningful conclusions may be drawn from this study.

Several unsuccessful attempts were made to prepare paramagnetic rare earth chelates and to apply a paramagnetic shift agent such as tris(dipivalomethanatoeuropium(III)) to CDCl_3 - CD_3CN solutions of the ligands. The possibility of utilizing ^1H NMR spectra of nickel(II) chelates of these salts was suggested.⁸ Nickel(II) contact shifts and paramagnetic line broadening have been employed to identify ligand structures^{9,10} and 1-methylpyrazoles.¹¹ A major obstacle to this procedure was finding a suitable solvent for both series of potassium salts and nickel(II) chelates. Although dimethyl sulfoxide and acetone meet the solubility requirement, orange crystals of nickel(II) dihydrobis(1-pyrazolyl)borate, $\text{Ni}[\text{H}_2\text{B}(\text{pz})_2]_2$, turn blue in these solvents. In contrast to sharp, ^1H NMR spectra characteristic of orange solutions of nickel(II) chelates, blue solutions yield a very broad signal about 43 ppm downfield from TMS. This behavior has been ascribed to the transformation of a square planar nickel(II) complex into an octahedral paramagnetic structure by coordination of solvent.¹² Evaporation of dimethyl sulfoxide allows recovery of the orange chelate but a green nickel salt is obtained from acetone showing that the ligand has decomposed. Protective action of methyl groups is indicated by the absence of blue color or decomposition of nickel(II) dihydrobis[3,5-dimethyl(1-pyrazolyl)]borate, $\text{Ni}[\text{H}_2\text{B}(\text{Me}_2\text{pz})_2]_2$, in these solvents. Whereas all of the nickel(II) chelates dissolve readily in chloroform, only $\text{KH}_2\text{B}(\text{Me}_2\text{pz})_2$ is appreciably soluble in this solvent. In order to evaluate inductive effects of nickel coordination on a common basis, ^1H NMR spectra of salts in D_2O were compared with corresponding spectra of chelates in CDCl_3 .

Substitution of 3-H and/or 5-H by methyl increases the shielding of 4-H in $\text{KH}_2\text{B}(\text{pz})_2$ by 0.20–0.25 ppm per methyl group (Table I) in close agreement with similar studies of 1-methylpyrazoles.¹³ A comparable diamagnetic shift of 4-H (0.21–0.33 ppm) is observed for each ligand upon decreasing solvent polarity (Table I: K, D_2O vs. K, Me_2CO) or upon converting the potassium salt into a nickel(II) chelate (Table I: K, D_2O vs. Ni, CDCl_3). This information provides a rationale for choosing 4-H as internal standard. Formation of ion pairs from potassium salts in solvents of low dielectric constant should produce approximately equal changes in shielding at 3-H and 5-H because all four nitrogens of the dihydrobis(1-pyrazolyl)borate anion will be exposed to the cation charge. However, covalent bonding of nickel(II) with 2-N should hinder rotation of the 1-pyrazolyl rings and therefore introduce different shielding effects at 3-H vs. 5-H. A chelation shift parameter may be defined

$$\Delta\nu_c = (\delta_{\text{K salt}} - \delta_{\text{Ni chelate}})_{\text{rf}}$$

Table I. Chemical Shifts of Dihydrobis(1-pyrazolyl)borates, $M[H_2B(R)_2]_n^a$

M	R	Solvent	3(5)-H		4-H	3(5)-CH ₃	
K	pz	Me ₂ CO	7.43 d (1.8)	7.25 d (1.6)	5.94 t (1.8)		
		MeOD ^b	7.46 (2.0)	7.38 (1.7)	6.05 (1.9)		
		MeCN	7.43 (1.8)	7.32 (1.5)	5.99 (1.5)		
		D ₂ O	7.66 (2.1)	7.54 (1.8)	6.24 (1.9)		
Ni	pz	CDCl ₃	$0.38_s \pm 0.01_1$	$0.41_s \pm 0.03_1$	$0.45_s \pm 0.02_3$		
			7.54 d (2.0)	6.81 d (2.2)	6.03 t (2.0)		
			10.8	65.7	19.1		
K	Mepz	Me ₂ CO	7.28 d (1.8)		5.69 d (1.8)	2.12	
		MeOD ^b	7.37 (2.0)		5.85 (1.7)	2.19	
		MeCN	7.27 (1.7)		5.74 (1.3)	2.17	
		D ₂ O	7.51 (1.9)		6.01 (1.8)	2.17	
Ni	Mepz	CDCl ₃	$0.33_4 \pm 0.02_1$		$0.41_s \pm 0.04_3$		
			7.37 d (2.1)		5.69 d (2.0)	1.79	
			12.1		28.5		34.7
K	Me ₂ pz	CDCl ₃			5.65 s	2.15	2.02
		Me ₂ CO			5.50	2.20	2.03
		MeOD ^b			5.64	2.14	2.01
		D ₂ O			5.78	2.11	2.06
Ni	Me ₂ pz	CDCl ₃			$0.38_3 \pm 0.04_8$		
					5.45 s	2.26	1.76
					29.8	-13.8	27.0
					18.0	-10.1	23.2

^a Chemical shifts are reported in ppm downfield from TMS (or SDSS in D₂O): s = singlet, d = doublet, t = triplet; coupling constants, in parentheses, are in hertz. ^b Spectra were obtained at 60 MHz and 30°; all other spectra were recorded at 90 MHz and 25°. ^c Solvent dependent slopes were calculated by least-squares treatment of proton resonance (Hz) vs. solvent dielectric constant curves for pyrazolyl protons. Values of dielectric constants were taken from the "Handbook of Chemistry and Physics", 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967. ^d Chelation shifts ($\Delta\nu_c$) are differences in Hz between corresponding potassium salts in D₂O and nickel(II) chelates in chloroform-*d*. ^e Chelation shifts were measured with both potassium salt and nickel(II) chelate in chloroform-*d*.

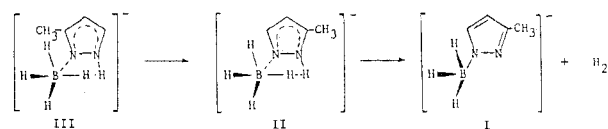
to describe relative changes in electron density at 3, 4, and 5 positions of 1-pyrazolyl rings which accompany coordination of nickel(II) and transfer of the solute from D₂O to CDCl₃.

The chelation shift for the mid-field proton in $KH_2B(pz)_2$ (7.54 ppm, $J = 1.8$ Hz in D₂O) is three times larger than $\Delta\nu_c$ of 4-H and six times larger than the low-field proton shift value. By assuming that the proton in closest proximity to the chelation site experiences the largest shielding increase in square planar complex formation, the proton at 7.54 ppm is labeled 3-H and the previous assignment is confirmed.¹ In $KH_2B(Mepz)_2$, the chelation shift of 4-H is about 10 Hz larger than the corresponding value for $KH_2B(pz)_2$ presumably as a result of methyl substitution. However, $\Delta\nu_c$ of the unidentified doublet (7.51 ppm, $J = 1.9$ Hz in D₂O) in the methyl derivative is only one fifth of the 3-H and slightly larger than the 5-H shift values in the parent compound. Furthermore, a chelation shift of +35 Hz for the methyl singlet is much larger than induced solvent effects on methyl protons and comparable with the $\Delta\nu_c$ value of 3-H in $KH_2B(pz)_2$. This evidence supports a conclusion that the ligand isomer, I, is dihydrobis[3-methyl(1-pyrazolyl)]borate. The designation of 3- and 5-methyl groups in $KH_2B(Me_2pz)_2$ presents a more difficult challenge. Although the crisscrossing of signals separated by only 0.05 ppm (D₂O) cannot be eliminated, small positive shifts of the methyl at 2.06 ppm and small negative shifts of the methyl at 2.11 ppm observed in less polar solvents than water make this event unlikely. Throughout this study, the chelation shift parameter, $\Delta\nu_c$, appears to magnify the same trends shown by solvent induced shifts, $\Delta\nu_s$. From this viewpoint, the low-field methyl is assumed to be deshielded by nickel(II) chelation in contrast to increased shielding of 3-Me in $KH_2B(Mepz)_2$ and therefore is called 5-Me. Diamagnetic shifts of the high-field methyl and 4-H in $KH_2B(Me_2pz)_2$ closely resemble the $\Delta\nu_c$ values of 3-Me and 4-H in $KH_2B(Mepz)_2$ using D₂O, MeOH, or Me₂CO as solvent for the potassium salts. Very similar, although smaller, chelation shifts were obtained when CDCl₃ was employed as solvent for both $KH_2B(Me_2pz)_2$ and $Ni[H_2B(Me_2pz)_2]_2$. Zaev et al.¹¹ reported a diamagnetic shift of 3-Me and a paramagnetic shift of 5-Me following addition of $NiBr_2 \cdot 3H_2O$ to 1,3,5-trimethylpyrazole in CDCl₃. An octahedral nickel(II)

complex is probably formed in this case which precludes a comparison with square planar $Ni[H_2B(Me_2pz)_2]_2$.

Because of the small deviation of proton chemical shifts in different diamagnetic environments, interest has mainly focused on systems that involve equilibria between diamagnetic and paramagnetic species. However, Mathur and Martin¹⁴ noted unusually large diamagnetic shifts in ¹H NMR spectra of nickel(II) chelates of glycyl peptides at pH values where yellow, diamagnetic anions exist. Methylene protons adjacent to amine vs. carboxylate groups in tri- and tetraglycine were easily identified. The absence of changes in spin density of dihydrobis(1-pyrazolyl)borate ligands upon coordination with nickel(II) leads to a simple pattern of chelation shifts: 3-H > 4-H > 5-H, independent of the solvent used to dissolve the salts. At the 3 position, both methyl and proton signals undergo substantial diamagnetic shifts: 3-H > 3-Me. Small negative $\Delta\nu_c$ values are found for 5-Me in all solvents examined whereas the diamagnetic chelation shift for 5-H in D₂O decreases with decrease in polarity of the solvent used to dissolve the salts and becomes a paramagnetic shift in Me₂CO. The consistency of the graphs (Figure 1) which summarize the chelation shifts for each ligand vs. change in solvent dielectric constant, $\Delta\epsilon$ (K salt - Ni chelate), provide additional confidence in the structure assignments.

This study demonstrates the feasibility of preparing unsymmetrical (1-pyrazolyl)borates with various groups at the 3 position. Preferential attack of the 3-methylpyrazole tautomer on borohydride ion can be rationalized in terms of steric crowding of the five-center transition state proposed for these reactions. If tautomerism of III and II occurs at a faster



rate than reaction of III to liberate hydrogen, only the 3-methyl intermediate, I, will be formed. Alternatively, a dihydrobis[5-methyl(1-pyrazolyl)]borate could possibly undergo a sigmatropic shift reaction to I under the conditions of synthesis. Intramolecular 1,2 migration of *N*-trimethylsilyl¹⁵ and *N*-

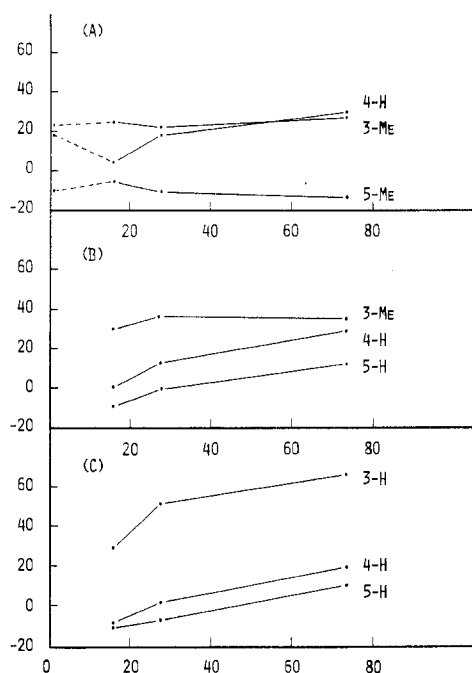


Figure 1. Comparison of dihydrobis(1-pyrazolyl)borate chelation shifts. Chelation shift ($\delta_{\text{K salt}} - \delta_{\text{Ni chelate}}$), Hz (ordinate) vs. $\Delta\epsilon(\text{K salt} - \text{Ni chelate})$ (abscissa). (A) $\text{KH}_2\text{B}(\text{Me}_2\text{pz})_2$, (B) $\text{KH}_2\text{B}(\text{Mepz})_2$, (C) $\text{KH}_2\text{B}(\text{pz})_2$ in D_2O , MeOH, and Me_2CO ; all nickel(II) chelates in CDCl_3 . $\text{KH}_2\text{B}(\text{Me}_2\text{pz})_2$ data also obtained in CDCl_3 .

trimethylgermyl¹⁶ groups in substituted pyrazoles has been reported at temperatures above 100°

Experimental Section

Potassium dihydrobis(1-pyrazolyl)borate and potassium dihydrobis[3,5-dimethyl(1-pyrazolyl)]borate were prepared by published procedures.^{1,17} Potassium dihydrobis[3-methyl(1-pyrazolyl)]borate¹⁸ was obtained by heating 26.3 g (0.32 mol) of 3(5)-methylpyrazole with 4.3 g (0.08 mol) of KBH_4 at 110° for 3 hr. A 45% yield of product was obtained with a mp of 204–206° after recrystallization from anisole.

Nickel(II) chelates were prepared by mixing nickel(II) chloride with excess ligand in water. Precipitates were air dried and recrystallized from methylcyclohexane (or benzene) after passing the solution through an aluminum oxide column. Solutions for ^1H NMR examination were obtained by ultrasonic agitation of 5–10 mg samples in 0.50 ml of deuterated solvent. Undissolved particles were removed by filtration and the solution was collected in a clean, 5 mm, NMR tube. Chloroform-*d* was passed through a 5 cm column of dry calcium carbonate immediately before use to remove impurities.

All ^1H NMR spectra at 90 MHz were obtained at 25° with a Bruker HFX-11 spectrometer equipped with a Fabritek 1074 time averaging computer. With organic solvents, 0.025 ml of tetramethylsilane was used as internal lock; in D_2O , sodium disilapentane sulfonate was employed as internal reference. Data in methanol-*d*₄ were recorded at 60 MHz and 30° using a Perkin-Elmer R-12B spectrometer. Standard deviations of ± 0.4 and ± 0.7 Hz were secured in the measurement of resonance frequencies of potassium salts and nickel(II) chelates, respectively.

Acknowledgment. The author expresses thanks to the National Bureau of Standards, Gaithersburg, Md. for a research fellowship (1971) and to Bruce Coxon for instruction in high resolution NMR. Appreciation is also extended to Clarisse L. Habraken and David L. Dalrymple for helpful discussions.

Registry No. $\text{KH}_2\text{B}(\text{pz})_2$, 18583-59-0; $\text{Ni}[\text{H}_2\text{B}(\text{pz})_2]_2$, 18131-13-0; $\text{KH}_2\text{B}(\text{Mepz})_2$, 55701-51-4; $\text{Ni}[\text{H}_2\text{B}(\text{Mepz})_2]_2$, 55701-52-5; $\text{KH}_2\text{B}(\text{Me}_2\text{pz})_2$, 53241-68-2; $\text{Ni}[\text{H}_2\text{B}(\text{Me}_2\text{pz})_2]_2$, 55722-67-3.

References and Notes

- S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3170 (1967).
- J. R. Jezorek and W. H. McCurdy, Jr., *Inorg. Chem.*, **14**, 1939 (1975).

- D. R. Wilkinson, Ph.D. Thesis, University of Delaware, 1972.
- J. Elguero and R. Jacquier, *J. Chim. Phys., Phys. Chim. Biol.*, **63**, 1242 (1966).
- J. Elguero, R. Jacquier, and H. C. N. Tien Duc, *Bull. Soc. Chim. Fr.*, 3727 (1966).
- H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **13**, 1291 (1974).
- S. Trofimenko, *Inorg. Chem.*, **9**, 2493 (1970).
- S. Trofimenko, private communication.
- D. R. Eaton and W. D. Phillips, *Adv. Magn. Reson.*, **1**, 103 (1965).
- P. S. Zacharias and A. Chakravorty, *Inorg. Nucl. Chem. Lett.*, **8**, 203 (1972).
- E. E. Zaev, V. K. Voronov, M. B. Shvartsberg, S. F. Vasilevsky, Yu. N. Molin, and I. L. Kotljarevsky, *Tetrahedron Lett.*, **5**, 617 (1968).
- D. Nicholls in "Comprehensive Inorganic Chemistry", Vol. 3, J. C. Bailar, H. J. Emeléus, R. Nyholm, and A. F. Trotman-Dickenson, Eds., Pergamon Press, New York, N.Y., 1973, p 1147.
- L. G. Tensmeyer and C. Ainsworth, *J. Org. Chem.*, **31**, 1878 (1966).
- R. Mathur and R. B. Martin, *J. Phys. Chem.*, **69**, 688 (1965).
- D. H. O'Brien and C. P. Hrunig, *J. Organomet. Chem.*, **27**, 185 (1971).
- F. A. Cotton and D. J. Ciappenelli, *Synth. Inorg. Met. Org. Chem.*, **2**, 197 (1972).
- S. Trofimenko, *Inorg. Chem.*, **9**, 2493 (1970).
- This compound was first prepared by Sylvan Hersh who kindly supplied the procedure and analytical data. Calcd for $\text{KC}_8\text{H}_{12}\text{N}_4\text{B}$: C, 44.87; H, 5.65; N, 26.17. Found: C, 44.46; H, 5.50; N, 25.90. Infrared and NMR spectra are similar to other dihydrobis(1-pyrazolyl)borates. Bis chelates of dihydrobis[3-methyl(1-pyrazolyl)]borate with nickel(II), cobalt(II), copper(II), and zinc(II) were obtained by direct mixing of reagents in water. The products after recrystallization from ligroin or heptane yielded CHN analysis within 0.3% of theory. Results on the nickel(II) chelate are pertinent to this investigation. Calcd for $\text{NiC}_{16}\text{H}_{24}\text{N}_8\text{B}_2$: C, 47.02; H, 5.92; N, 27.41; Ni, 14.36. Found: C, 47.05; H, 6.07; N, 27.35; Ni, 13.98.

Contribution from the Physical and Chemical Sciences Laboratory, Webster Research Center, Xerox Corporation, Webster, New York 14580, and the Department of Chemistry, University of Rochester, Rochester, New York 14627

Synthesis and Characterization of Bis(diphenylglyoximate) Complexes of Platinum

Joel S. Miller* and Stephen Z. Goldberg

Received March 4, 1975

AIC50159E

Upon reviewing the critical features necessary for a new material to exhibit unusual electrical properties^{1b} arising from intermolecular interactions in the solid, two prominent features surface: namely, partial oxidation of the metal and close intermolecular spacings.¹⁻⁶ The larger spatial extent of the $5d_{z^2}$ orbital of Ir^{I} and Pt^{II} than the first- and second-row congeners allows these metals to form in some cases partially oxidized one-dimensional complexes which exhibit unusual anisotropic physical properties, e.g., high dc conductivity.

In 1950 Edelman reported on the oxidation of bis(diphenylglyoximate)nickel(II), $\text{Ni}(\text{HDPG})_2$, with bromine and iodine forming a formally trivalent nickel complex, $\text{Ni}(\text{HDPG})_2\text{X}$, $\text{X} = \text{Br}, \text{I}$.⁷ Subsequently, such reactions were effected on the palladium analogs.^{8,9} Preliminary data indicate that upon oxidation the metal-metal distance decreases by 0.19–0.27 Å⁸ and the dc conductivity increases by 5 orders of magnitude.^{8,10} Because of these observations and because platinum exhibits a greater spatial extension of the d_{z^2} orbital than either the second- or the first-row congeners, metal-metal overlap and stronger intermolecular interactions occur to form more pronounced anisotropic properties.¹⁻⁶ For these reasons it seemed appropriate to investigate the chemistry of bis(diphenylglyoximate)platinum(II).¹¹

Experimental Section

Physical Measurements. Electronic spectra were recorded on a Cary 15 spectrometer and infrared spectra were taken with a Beckman

* To whom correspondence should be addressed at the Xerox Corp.