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Synthesis and Proton Magnetic Resonance Studies of Paramagnetic Nickel(II) Complexes Containing Benzaldimine Groups. I. Tetrahedral Complexes[1a]

By IVANO BERTINI, DONALD L. JOHNSTON, and WILLIAM DeW. HORROCKS, Jr.[1b]

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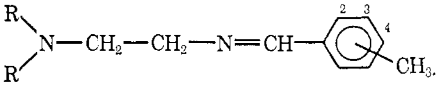
Nickel halide complexes of Schiff bases obtained from benzaldehyde derivatives and 1,2-diaminoethane (en), 1,2-diaminopropane (pn), 2,3-diaminobutane (bn), 1,3-diaminopropane (tn), 1-amino-2-dimethylaminoethane (Me_2en), and 1-amino-2-diethylaminoethane (Et_2en), of the formula $NiLX_2$ (X = Cl, Br, I), were synthesized and characterized. Most of them are pseudotetrahedral both in the solid state and in solution. The proton magnetic resonance spectra show sizable isotropic shifts. The pn derivatives give rise to doubling of the aromatic proton resonances attributable to the nonequivalence of the two aromatic groups. The multiplicity of the peaks for the tn complexes suggests the presence of several isomers. In the case of bn complexes separate resonances are observed for *meso* and racemic complexes.

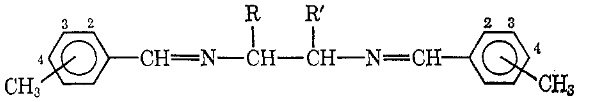
Introduction

Pmr investigations of paramagnetic nickel(II) complexes containing aromatic groups have proved useful in the study of subtle electronic and structural changes[2-4] owing to large isotropic shifts (resonance shifts from the diamagnetic positions). At the present time, there is no entirely satisfactory theory to account for the pattern of shifts, although VB and MO calculations have shown some promise in accounting for π-spin delocalization. Furthermore, only a few studies of the effect of structural changes and coordination number on spin delocalization in a particular group have been carried out.[3-6] Further experimental data are clearly necessary in order to gain a firm understanding of the spin-delocalization phenomenon in metal complexes.

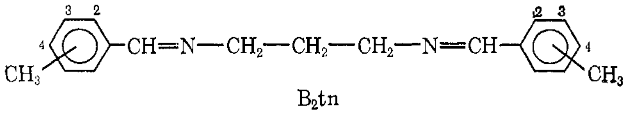
The present paper deals with spin delocalization in benzaldimine groups in pseudotetrahedral complexes and the succeeding paper treats five-coordinate complexes containing the same groups. The ligands involved in the present study are shown below. The synthesis, physical properties, and pmr spectra of complexes of the type $NiLX_2$ (X = Cl, Br, I) are reported here.[8]



R = CH_3, Me_2enB
R = C_2H_5, Et_2enB



R = R' = H, B_2en
R = CH_3, R' = H, B_2pn
R = R' = CH_3, B_2bn[7]



B_2tn

Experimental Section

All of the benzaldehyde derivatives and alkyldiamines are commercially available except 2,3-diaminobutane which was prepared according to the method of Dickey, *et al.*[9]

Preparation of the Complexes.—All of the complexes were prepared by the same general method. An *n*-butyl alcohol solution containing 5 mmol of the diamine and 11 mmol of the benzaldehyde derivative was boiled for 10 min after adding 10 ml of 2,2-dimethoxypropane. This solution was added to a boiling solution of 5 mmol of the appropriate metal salt in 30 ml of *n*-butyl alcohol. After boiling for some minutes, the solution was filtered

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(1) (a) This research was supported by the National Science Foundation through Grant GP-6321. (b) Department of Chemistry, The Pennsylvania State University, University Park, Pa. 16802.

(2) E. L. Muetterties and W. D. Phillips, *Advan. Inorg. Chem. Radiochem.*, **4**, 232 (1962); R. E. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

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(6) (a) J. D. Thwaites and L. Sacconi, *Inorg. Chem.*, **5**, 1029 (1966); (b) J. D. Thwaites, I. Bertini, and L. Sacconi, *ibid.*, **5**, 1036 (1966).

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(8) Two of these complexes had been previously reported: L. Sacconi and I. Bertini, *Inorg. Chem.*, **7**, 1178 (1968).

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Table I

Analytical and Magnetic Data

Compound	% carbon		% hydrogen		% nitrogen		μ_{eff}, BM[c]
	Calcd	Found	Calcd	Found	Calcd	Found	
$Ni[Me_2enB]Cl_2$	43.31	43.59	5.29	5.34	9.18	9.20	
$Ni[Me_2enB]Br_2$	33.46	33.28	4.09	4.01	7.10	7.07	3.26
$Ni[Et_2enB]Br_2$	36.92	36.99	4.77	4.75	6.62	6.63	3.28
$Ni[B_2en]Br_2$	42.25	42.15	3.55	3.61	6.16	6.05	3.49
$Ni[B_2pn]Cl_2$	53.74	53.31	4.78	4.82	7.38	7.02	3.33
$Ni[B_2pn]Br_2$[a,b]	43.55	43.26	3.87	3.78	5.97	5.33	3.23
$Ni[B_2pn]I_2$	36.27	36.61	3.22	3.30	4.98	4.97	3.25
$Ni[B_2bn]Br_2$[a]	44.77	44.82	4.18	4.21	5.80	5.97	
$Ni[B_2$-*meso*-$bn]Br_2$	44.77	44.70	4.18	3.96	5.80	5.88	
$Ni[B_2tn]Br_2$	43.55	43.37	3.87	3.95	5.97	5.95	3.38
$Ni[Me_2en(4\text{-}CH_3B)]Br_2$	35.25	35.06	4.43	4.43	6.83	6.81	
$Ni[(4\text{-}CH_3B)_2pn]Br_2$	45.92	46.02	4.46	4.53	5.63	5.68	
$Ni[(2\text{-}CH_3B)_2pn]Br_2$	45.92	46.14	4.46	4.36	5.63	5.66	
$Ni[(3\text{-}CH_3B)_2pn]Br_2$	45.92	44.99	4.46	4.50	5.63	5.50	
$Ni[(4\text{-}OCH_3B)_2pn]Br_2$	43.14	42.83	4.19	4.01	5.30	5.29	
$Ni[(4\text{-}CH_3B)_2bn]Br_2$[a]	47.01	47.07	4.74	4.99	5.48	5.66	
$Ni[(4\text{-}CH_3B)_2$-*meso*-$bn]Br_2$	47.01	46.85	4.74	4.75	5.48	5.64	
$Ni[(4\text{-}CH_3B)_2tn]Br_2$	45.92	45.92	4.46	4.34	5.63	5.60	
$Zn[(4\text{-}CH_3B)_2pn]Cl_2$	55.03	54.92	5.35	5.56	6.76	6.62	

[a] Molar conductivity values for 10^{-3} *M* solutions of these compounds in 1,2-dichloroethane are between 0.2 and 0.02 $ohm^{-1}\ cm^2\ mol^{-1}$. The molar conductivity for $[(n\text{-}C_4H_9)_4N]Br$ in the same solvent was 21 $ohm^{-1}\ cm^2\ mol^{-1}$. [b] The association degree $n = 0.95$, as determined by molecular weight measurements in 1,2-dichloroethane. [c] Measured at room temperature (22–24°) and corrected for diamagnetic contributions as calculated from ref 10.

and concentrated, and, generally, crystals were obtained. In some cases cyclohexane was added to promote crystallization. The crystals were collected in a filter funnel under dry nitrogen and dried at 100° under vacuum. The analyses were performed by Baron Consulting Co., Orange, Conn.

Physical Measurements.—Solid-state magnetic moments were determined by the Gouy method. A Varian electromagnet, Model V-4004, and a Mettler Model H16 microbalance were used. The Gouy tube was calibrated with freshly distilled water and $Hg[Co(NCS)_4]$.[10] The susceptibility measurements in chloroform solution were taken by Evans' method.[11]

The electronic spectra were recorded in the range 5000–30,000 cm^{-1} with a Cary 14 spectrophotometer using 1-cm silica cells. Molecular weights were determined in 1,2-dichloroethane at 37° with a Mechrolab Model 301A vapor pressure osmometer calibrated with benzil. The conductivity values were measured on an ESI universal impedance bridge, Model 250 DA. The concentration of the solutions was *ca.* 10^{-3} *M*.

Pmr spectra were recorded with a Varian A-60 spectrophotometer operating at 39°. Nitromethane-d_3, dichloromethane-d_2, and chloroform-*d* were used as solvents and TMS was used as the internal reference. Some spectra were recorded also on a Varian HA-100 (operating at 27°) using the internal lock technique in order to establish the nature of the doublings. A broad resonance at *ca.* −30 ppm from TMS could be revealed only with the latter apparatus operating in high-resolution mode using a modulating frequency of 4500 cps. The agreement between the spectra recorded by the two instruments was satisfactory after correction for the difference in operating temperature.

Results

The analyses of the complexes are reported in Table I and correspond to the general formula $NiLX_2$ (X = Cl, Br, I). They are crystalline, moisture sensitive, and soluble in common polar organic solvents except for $Ni(Me_2enB)Cl_2$ which is insoluble in common solvents. They are all paramagnetic with magnetic moments ranging from 3.20 to 3.50 BM (see Table I).

Except for $Ni(Me_2enB)Cl_2$ and $Ni(Me_2enB)Br_2$ the mull electronic spectra are similar to each other and very closely resemble the solution spectra (see Figure 1) in 1,2-dichloroethane. $Ni(Me_2enB)Br_2$, which shows a mull spectrum similar to the chloride analog, changes color upon dissolution in 1,2-dichloroethane and the solution spectrum is similar to those of the other derivatives (see Figure 2). The frequencies of the absorption maxima of representative compounds are reported in Table II. The compound $Ni(B_2pn)Br_2$ does not conduct, is monomeric in 1,2-dichloroethane, and is fully paramagnetic with a magnetic moment of 3.25 BM in chloroform solution.

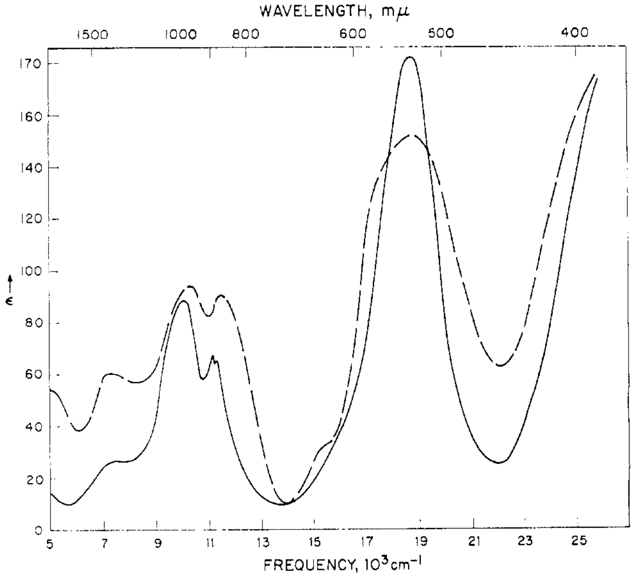

Figure 1.—Mull spectrum (- - - -) and solution spectrum in 1,2-dichloroethane (—) of $Ni[B_2pn]Br_2$.

Pmr Spectra.—Figures 3 and 4 show some representative pmr spectra. Large upfield and downfield shifts in paramagnetic complexes are evident. The spectra

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(10) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 615.

(11) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

TABLE II

SPECTROSCOPIC DATA FOR SOME COMPLEXES[a]

Compoud	Absorption max, cm^{-1} (ϵ_{molar}, for solns)				
Ni(Me$_2$enB)Cl$_2$		7330, 7800		13,700	23,000
Ni(Me$_2$enB)Br$_2$	<5000	6900	10,500 sh	13,300	19,700
		7250 (18)	10,050 (73)	11,100 (50), 11,400 (46), 15,600 sh, 17,500 sh	19,000 (181)
Ni(Et$_2$enB)Br$_2$	<5000	7300	10,200	11,200, 17,500 sh	19,000
	<5000	7140 (20)	10,000 (83)	11,100 (55), 11,300 (49), 15,600 sh, 17,400 sh	18,900 (198)
Ni(B$_2$en)Br$_2$	<5000	7500	10,200	11,350, 17,400 sh	18,600
	<5000	7150 (27)	10,100 (92)	11,200 (69), 11,500 (66), 14,900 sh, 17,500 sh	18,700 (172)
Ni((B$_2$pn)Cl$_2$	<5000	7150	10,370	11,850, 18,200 sh	19,200
	<5000	6900 (28)	10,270 (66)	11,600 (42), 11,900 (40), 15,900 sh	19,200 (123)
Ni(B$_2$pn)Br$_2$	<5000	7150	10,370	11,500 15,400 sh, 17,400 sh	18,800
	<5000	7250 (26)	10,100 (89)	11,240 (67), 11,380 (65)	18,700 (183)
Ni(B$_2$pn)I$_2$	<5000	6950	9,750	10,600, 17,100 sh	20,800, 24,500
	<5000	7300 sh (23)	9,700 (121)	10,600 (145), 17,300 sh (412)	21,550 (3185) 24,060 (2440)
Ni(B$_2$bn)Br$_2$	<5000	7300	10,100	11,400	18,500
	<5000	7550 (25)	10,150 (84)	11,230 (60), 11,430 (60), 15,500 sh	18,630 (183)
Ni(B$_2$tn)Br$_2$	<5000	6800	10,500	11,500, 17,600	19,200
	<5000	7150 (21)	10,500 (73)	11,600 (72), 17,600 (155)	19,000 sh

[a] First line Nujol mull on filter paper, second line solution in 1,2-dichloroethane.

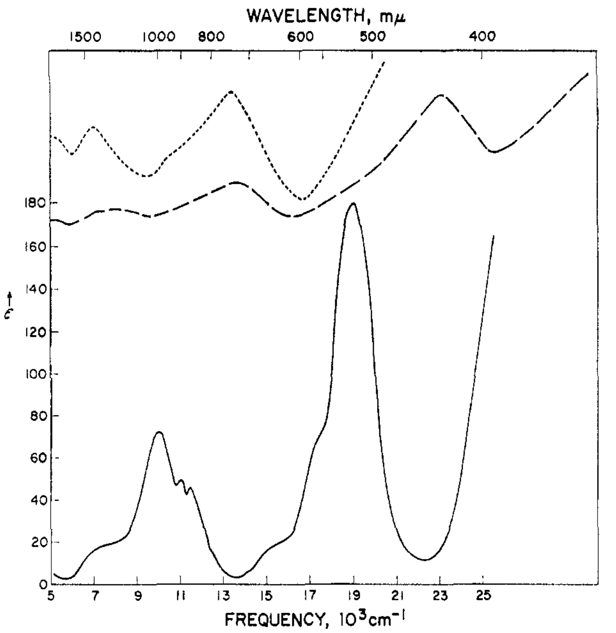

Figure 2.—Mull spectra of Ni[Me$_2$enB]Cl$_2$ (– –) and Ni[Me$_2$enB]Br$_2$ (- - - -); solution spectrum of Ni[Me$_2$enB]Br$_2$ in 1,2-dichloroethane (—).

(not shown) of the benzal(en) derivatives are the simplest, with peaks at −16 ppm (intensity 1) and −8 ppm (intensity 2) and a very broad peak at *ca.* −25 to −35 ppm from TMS as internal reference. This latter peak is difficult to observe at 60 Mc; however it is revealed in the high-resolution mode at 100 Mc.

The spectra of the pn derivatives all have a broad peak at ≃+5 ppm attributable to the aliphatic methyl group. Other absorptions occur in the same general positions as for the en derivatives but show two peaks for each one observed for the en analogs. The intensities of the two components of these pn peaks are identical for each absorption. Their splitting increases by a factor of $^{10}/_{6}$ when the spectrum is recorded at 100 Mc. This rules out the possibility that the doubling is due to first-order spin–spin coupling. Methyl derivatives were prepared in order to assign the peaks and to investigate the behavior of the methyl resonances. The methyl resonances appear as doublets in the pn derivatives while they are single in the en compounds.

The peak or double peak at *ca.* −16 ppm disappears upon substituting the 4-H by a 4-CH$_3$ or 4-OCH$_3$ while the peak at −8 ppm decreases in intensity by half upon substitution of 3-H by a 3-CH$_3$. The peak or double peak at −16 ppm is, therefore, assigned to the 4-H, that at −8 ppm is assigned to the 3-H, and that at ≃−30 ppm is assigned to the 2-H. The NCH$_2$ and the N(CH$_3$)$_2$ proton resonances were not observed and are presumably very far downfield and quite broad.[12]

The bn complexes synthesized from a mixture of racemic and *meso* bn[9] appear quite similar to the pn derivatives (Figure 4) in that all the aromatic peaks are doubled. In addition, two peaks assignable to methyl resonances of the aliphatic chain also appear. The spectra of the complexes synthesized from *meso*-bn[9] show but a single resonance for each observed position.

The complex Ni(B$_2$tn)Br$_2$ is too insoluble in chloroform-*d* or dichloromethane-d_2 for nmr purposes. The spectrum in nitromethane-d_3, where some solvolysis may occur, presents many peaks. Attempts to prepare other derivatives, apart from Ni[(4-CH$_3$-B)$_2$tn]Br$_2$, were unsuccessful. The 4-CH$_3$ derivative is soluble in chloroform-*d* and shows, apart from other peaks downfield, four peaks upfield (see Figure 3) assignable to methyl resonances.

In Table III the isotropic shifts from the diamagnetic positions are reported. The diamagnetic chemical shifts of the benzaldehyde derivatives and of the diamines are reported in footnote *a* of Table III. The ligand spectra agree satisfactorily with the shifts observed for Zn[(4-CH$_3$B)$_2$pn]Cl$_2$ whose spectrum is shown in Figure 3. Doublings are not evident in the diamagnetic complex.

Discussion

Stereochemistry of the Complexes.—The molecular weight, conductivity measurements, magnetic moments,[13] and electronic spectra[14] indicate that all the

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(12) R. J. Fitzgerald and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 2523 (1968).

(13) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *ibid.*, **83**, 4161 (1961).

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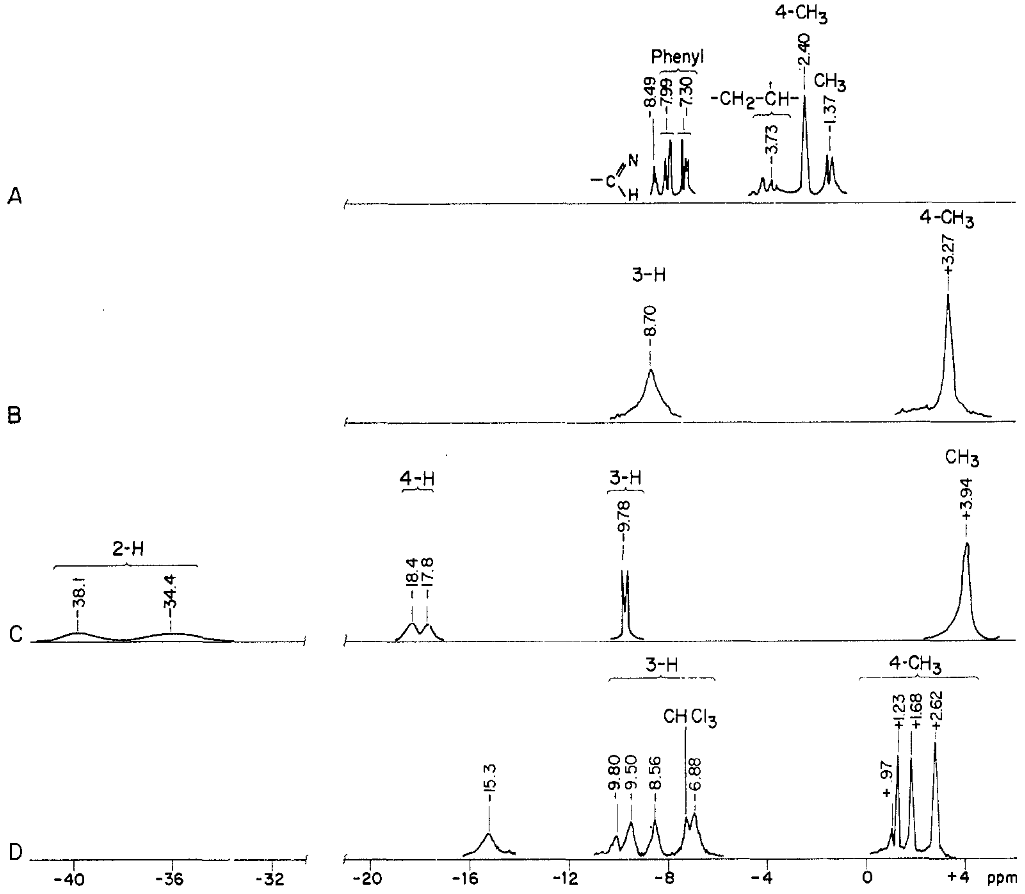

Figure 3.—Pmr spectra in chloroform-*d* at 39° (ppm from TMS as internal reference): A, $Zn[(4\text{-}CH_3B)_2pn]Cl_2$; B, $Ni[(4\text{-}CH_3B)_2en]Br_2$; C, $Ni[B_2pn]Cl_2$; D, $Ni[(4\text{-}CH_3B)_2tn]Br_2$.

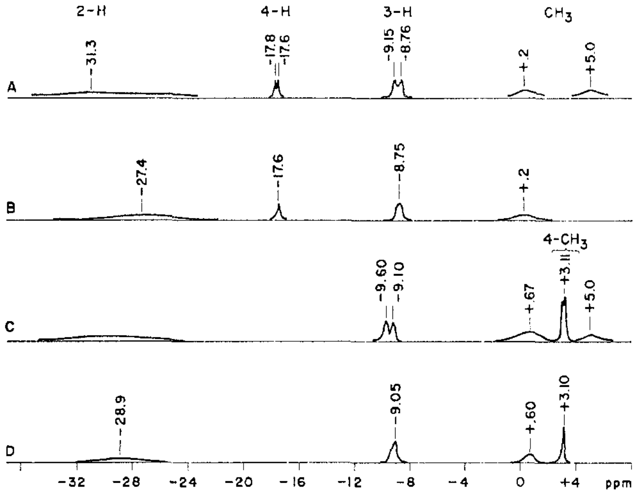

Figure 4.—Pmr spectra in chloroform-*d* at 39° (ppm from TMS as internal reference): A, $Ni[B_2bn]Br_2$; B, $Ni[B_2\text{-}meso\text{-}bn]Br_2$; C, $Ni[(4\text{-}CH_3B)_2bn]Br_2$; D, $Ni[(4\text{-}CH_3B)_2\text{-}meso\text{-}bn]Br_2$.

complexes are pseudotetrahedral in solution and, except for $Ni(Me_2enB)X_2$ (X = Cl, Br), are pseudotetrahedral in the solid state.[15] The exceptional complexes are presumably polymeric and hexacoordinate in the solid state as shown by the mull spectra.[16] The bromide derivative gives rise to pseudotetrahedral species upon dissolution. For comparison purposes, it is noteworthy to recall that Me_4en[17] (N,N,N′,N′-tetramethyl-1,2-diaminoethane) gives rise to a polymeric associated complex with nickel chloride and a monomeric tetrahedral complex with nickel bromide. The donor and steric properties of the groups $-CH_2N(CH_3)_2$ and $-CH_2N{=}CHC_6H_5$ appear to be very similar. These two types of substituents are the only ones which give rise to pseudotetrahedral complexes among the substituted ethylenediamines.[15]

Nature of the Isotropic Pmr Shifts.—The three resonances assigned to the aromatic protons are all downfield from the diamagnetic positions but by different magnitudes. However, the aromatic $3\text{-}CH_3$ resonances are downfield while the $4\text{-}CH_3$ resonances are upfield. The $2\text{-}CH_3$ peak is only slightly upfield while the 2-H is far downfield. This alternation in the behavior of the methyl resonances is characteristic of some contribution to the shifts by unpaired electron spin density located in the π system of the aromatic moiety.[2,18,19]

The observed shifts of the aliphatic methyl groups are perhaps indicative of the presence of a significant

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[16] A. B. P. Lever, S. M. Nelson, and T. M. Shepherd, *Inorg. Chem.*, **4**, 810 (1965).

[17] L. Sacconi and I. Bertini, *Inorg. Nucl. Chem. Letters*, **2**, 29 (1966); L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, **6**, 626 (1967).

[18] H. M. McConnell and D. C. Chestnut, *J. Chem. Phys.*, **28**, 107 (1958); A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

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TABLE III

ISOTROPIC SHIFTS OF TETRAHEDRAL BENZALDIMINE NICKEL COMPLEXES[a,b]

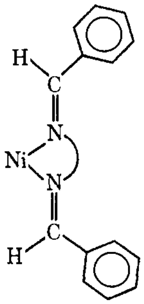
		Ring positions			
Compound	Solvent	2	3	4	Aliphatic CH_3
Ni[Me_2enB]Br_2	$CDCl_3$		−2.84	−10.2	
	CD_3NO_2		−4.08	−10.8	
Ni[Et_2enB]Br_2	$CDCl_3$	−25.9	−2.96	−10.4	−4.51
	CD_3NO_2		−3.70	−10.5	−5.17
Ni[B_2pn]Cl_2	$CDCl_3$	−26.7	−2.65, −2.87	−10.4, −11.1	+4.83
Ni[B_2pn]Br_2	$CDCl_3$	−18.7	−1.50[c]	−9.76, −10.4	+3.00
Ni[B_2pn]I_2	CD_2Cl_2		0.0	−8.34, −9.00	0.0
Ni[B_2bn]Br_2	$CDCl_3$	−23.7	−2.01, −1.62	−10.4, −10.2	+1.20, +6.0
Ni[B_2-*meso*-bn]Br_2	$CDCl_3$	−19.8	−1.61	−10.2	+1.20
Ni[Me_2en(4-CH_3B)]Br_2	$CDCl_3$		−3.08	(+4.50)	
Ni[(4-CH_3B)$_2$en]Br_2	$CDCl_3$		−1.56	(+5.57)	
Ni[(4-CH_3B)$_2$pn]Br_2	$CDCl_3$		−1.80, −2.05	(+5.50, +5.58)	+3.33
Ni[(3-CH_3B)$_2$pn]Br_2	$CDCl_3$		(−3.99, −3.44) −0.97	−10.1, −10.6	+3.00
Ni[(2-CH_3B)$_2$pn]Br_2	CD_3NO_2	(+0.25, +0.59)	*d*	−6.75, −7.34	+4.33
Ni[(4-CH_3B)$_2$bn]Br_2	$CDCl_3$		−2.46, 1.96	(+5.37, +5.45)	+1.67, +6.0
Ni[(4-CH_3B)$_2$-*meso*-bn]Br_2	$CDCl_3$		−1.91	(+5.40)	+1.60
Ni[(4-CH_3B)$_2$tn]Br_2	$CDCl_3$		−2.66, −2.36, −1.42, +0.26[e]	(+3.27, +3.54, +3.99, +4.92)	
Ni[(4-OCH_3B)$_2$pn]Br_2	$CDCl_3$	−19.2	−3.00, −2.67	(+0.17, +0.33)	+3.59

[a] Measured from diamagnetic chemical shifts from TMS: 2-H, −7.62, 3-H, −7.14; 4-H, −7.37; 2-CH_3, −2.59; 3-CH_3, −2.30; 4-CH_3, −2.30; 4-OCH_3, −3.87; CH_3 of pn and bn, −1.00; CH_3 of Et_2en, −1.02. [b] Values in parentheses are for CH_3 protons attached to the aromatic ring. [c] Splitting of this peak is observed at lower temperatures and at 100 Mc (room temperature). [d] Some solvolysis occurs; other peaks are −11.7, −10.8, and −3.84 ppm from TMS. [e] The assignment of these peaks to 3-H is tentative; another peak occurs at −15.3 ppm from TMS.

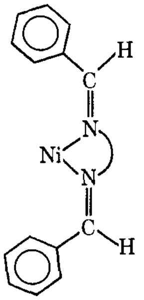
dipolar interaction.[20] Furthermore, the splitting of the OCH_3 signal in the pn derivatives of the same order of magnitude as the total isotropic shift is in agreement with the hypothesis that the splitting is due to a dipolar interaction *via* a difference in geometrical coordinates. Some σ delocalization may also contribute to the downfield bias of aromatic proton shifts.[21] Finally, it is interesting to note that the isotropic shifts of the aromatic protons which are all negative decrease in absolute value going from Cl to I. It has been found that the shifts decrease going from Cl to I when they are either up or downfield as in dihalobis(triphenylphosphine)nickel(II) complexes.[6a,22] In the latter case, a decrease in π-spin density contribution was proposed to explain the behavior of the shifts although there has been some controversy in this regard.[23] If only π-spin delocalization decreased, going from the chloride to the iodide derivatives, an increase of the negative value of the 3-H isotropic shift for the present benzaldimine derivatives would be expected. The present results suggest that changes in σ or dipolar contributions in this series of halides may also be important. Further discussion of the mode of spin delocalization in coordinated benzaldimine groups is deferred to the following paper.

Multiplicity of Resonances.—Although the en complexes show a single resonance for each aromatic proton, a doubling is observed in the case of the pn and bn derivatives and four peaks are observed for the 4-CH_3 of Ni[(4-CH_3B)$_2$tn]Br_2.

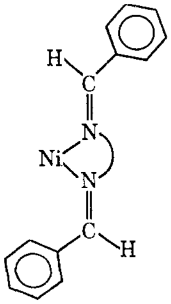
In principle, geometrical isomers are possible with respect to the carbon–nitrogen double bond. Studies on N-methylbenzaldimine[24a] showed a single isomer in solution (phenyl presumed *trans* to the methyl) while with triarylimines two isomers have been detected with barriers of the order 13–21 kcal/mol.[24] In the present case, three isomers are possible



cis-exo
1



cis-endo
2



trans
3

The fact that the en derivatives do not show any splitting of the peaks between −65 and +77° in $CDCl_3$ solutions suggests that only one isomer is present. A probable form based on molecular models is type 1 (*cis-exo*).

A doubling of the peaks in the pn derivatives is in principle expected even for a single isomer such as 1 since the pn ligand does not possess a C_2 axis. The observed inequivalence of the two aromatic moieties may be explained by subtle electronic or structural differences.

The doubling observed for the complexes synthesized from a mixture of *meso* and racemic bn provides an example of diastereoisomeric doubling in pseudotetrahedral complexes, not involving a planar–tetrahedral equilibrium.[25,26] The magnetic moment of Ni[B_2bn]Br_2 in chloroform-*d* solution was found to be 3.28 BM and the isotropic proton shifts follow the Curie law between −50 and +40°. Assignment of the peaks is provided by the spectra of complexes synthesized from

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meso-bn. In Figure 4 it is seen that the peaks of the *meso* isomer have smaller isotropic shifts than do the racemic complexes. In the absence of a planar–tetrahedral equilibrium, the difference in shifts between racemic and *meso* must be attributed to a difference in phenomenological hyperfine interaction constants, Δa_i,[25] which may contain both Fermi contact and dipolar contributions.[27]

The splitting of the aliphatic CH_3 resonances is up to 4 times the total isotropic shift for the aliphatic methyl groups of the *meso* complexes while the splitting of the 4-CH_3 and aromatic proton resonances is very small, as found for other fully tetrahedral diastereoisomers.[25,26] This can be accounted for by considering the two possible *gauche* conformations of the diamine molecule[28] which give different positions, axial and equatorial, to the methyl substituents. For the racemic forms both methyl groups must be in either equatorial or in axial positions but for the *meso* forms, one methyl is always axial and the other equatorial. For the racemic forms, the equatorial positions of the methyl groups presumably predominate, as has been suggested for pn complexes.[28] A rapid interconversion on the nmr time scale between the two *meso-gauche* forms would average the resonances of the equatorial and axial positions. If dipolar shifts are operative, as has been suggested in the previous section, the average geometrical factors of the aliphatic methyl groups will be different for the racemic and *meso* forms. Therefore, two different dipolar contributions to the total methyl isotropic shifts occur. The present results demonstrate that diastereoisomeric pmr splitting may be large even in the absence of a planar–tetrahedral equilibrium, particularly if a significant dipolar interaction is present.

Assignment to specific isomers or conformers of the numerous peaks found for the tn complexes is not possible. However, the present results demonstrate the sensitivity of the pmr method for detection of these species in solution.

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Contribution from the Frick Chemical Laboratory
Princeton University, Princeton, New Jersey 08540

Synthesis and Proton Magnetic Resonance Studies of Paramagnetic Nickel(II) Complexes Containing Benzaldimine Groups. II.[1] Five-Coordinate Complexes

By Ivano Bertini, Donald L. Johnston, and William DeW. Horrocks, Jr.[2]

Received August 20, 1969

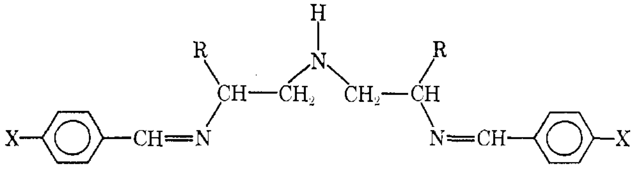
Schiff bases formed from benzaldehyde derivatives and bis(2-aminoethyl)amine ($DENB_2$) and bis(2-aminopropyl)amine ($DPNB_2$) give rise to high-spin five-coordinate nickel(II) complexes. The pmr spectra of these compounds show upfield and downfield isotropic shifts. In the case of DPN complexes, a splitting of the resonances is observed and is attributed to the existence of diastereoisomers. The spin-delocalization mechanism is discussed on the basis of MacLachlan–Hückel molecular orbital calculations and through a comparison with similar systems. Minor effects on the shift patterns caused by changes in coordination number are noted.

Introduction

In the preceding paper[1] pmr spectra and properties of tetrahedral complexes containing benzaldimine groups were reported. In the present work five-coordinate complexes containing the same groups have been studied in order to assess the effect of coordination number and stereochemistry on the isotropic shift patterns.

Furthermore, the pmr spectra were useful in detecting geometrical isomers and diastereoisomers in pseudotetrahedral complexes[1] and it was of interest to obtain corresponding structural information in the five-coordinate series.

Complexes of the type $NiLX_2$ where L is a Schiff base formed from aliphatic triamines and benzaldehyde derivatives of the type



R = H, $DENB_2$
R = CH_3, $DPNB_2$
X = H, OCH_3, CH_3

are reported.

Experimental Section

Bis(2-aminoethyl)amine was obtained from Aldrich Chemical Co. as diethylenetriamine, DEN, and bis(2-aminopropyl)amine was purchased from K & K Laboratories as dipropylenetriamine, DPN, and its constitution verified from its pmr spectrum. The complexes were prepared and physical measurements made as described for the analogous four-coordinate complexes.[1]

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(1) Part I: I. Bertini, D. L. Johnston, and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **9**, 693 (1970). This research was supported by the National Science Foundation through Grant GP-6321.

(2) Department of Chemistry, The Pennsylvania State University, University Park, Pa. 16802.