Proton Magnetic Resonance Studies of High-Spin Nickel(II) Complexes with Pentadentate Schiff Bases

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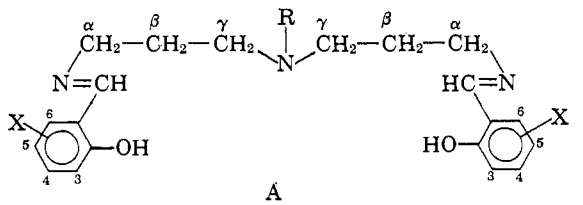
Abstract: The proton magnetic resonance spectra of two series of high-spin, five-coordinated nickel(II) complexes have been observed, where the pentadentate ligand is formed from substituted salicylaldehydes and bis(3-aminopropyl)amine or bis(3-aminopropyl)methylamine. Two sets of aromatic peaks are observed, which are interpreted as arising from the nonequivalence of the two aromatic fragments in the chelate. This extent of nonequivalence is found to depend markedly on the amino-nitrogen substituent, the solvent, and the temperature. This variable magnetic nonequivalence is related to small changes in the solution structure produced by steric effects of the aminomethyl group, with the extent of nonequivalence increasing as the structure tends toward a square pyramid with the salicylaldimine fragments bonded *cis* to each other. This tendency for these pentadentate ligands to take up a square structure with *cis* rather than *trans* aromatic rings is also evidenced for the pyridine solutions of the chelates, where some peak splitting is observed in spite of octahedral coordination. The shift patterns for the five-coordinated chelates indicate π delocalization, but other factors must be important. The shift distribution for the pyridine adducts is consistent with that of other related octahedral complexes.

Complexes of the pentadentate ligand of structure A have recently been shown[1] to produce five-coordinated 3d metal(II) complexes. Five coordination



A

in these high-spin nickel(II) complexes has been established[1,2] only very recently, though some uncharacterized complexes of this ligand has been reported earlier.[3] To date there are only a few documented examples of five-coordinated nickel(II).[4-7]

The five coordination has been established on the basis of absorption and reflectance spectra,[1] which are inconsistent with either octahedral or tetrahedral coordination, but closely resemble the spectra of [5-Cl-SALen$(C_2H_5)_2]_2Ni^{II}$ and [N-CH_3-SAL$]_2Ni^{II}$ in the lattice of its zinc analog, both of which have been shown to be five coordinated by X-ray analysis, the former in a distorted square pyramid[8] and the latter in a trigonal bipyramid.[4] The present complexes also form adducts with a single molecule of pyridine,[1] resulting in octahedral coordination, and molecular weight measurements reveal that there exist only discrete monomers in solution.

Results for a single crystal X-ray analysis on one of these complexes, NiSAL-MeDPT, carried out simultaneously with this work,[2] have proved five coordination, with a distorted trigonal bipyramidal arrangement of the five bonding atoms as shown in Figure 1. The great similarity of the reflectance and the solution absorption spectra indicates that the solution structure is essentially identical with that in the crystal.[1]

Proton magnetic resonance studies have proved extremely useful in elucidating various magnetic and structural properties of nickel(II) complexes in solution.[9-13] In view of the novel structure of these complexes, a pmr investigation was undertaken in order to determine what properties of the observed isotropic shifts can be related to their structure.

These complexes are fully paramagnetic,[1] μ_{eff} = ~3.34 BM, and give no evidence of any paramagnetic $\leftrightarrows$ diamagnetic equilibrium in solution. Their solution pmr spectra can thus be expected to display large, isotropic resonance shifts[9,10,14] for the protons from their position in the free ligand or diamagnetic zinc complex. Such shifts arise either from a proton–electron dipolar interaction or from the contact interaction resulting from the delocalization of unpaired spin onto the ligand.[14] The character of the observed shifts can thus depend on both the magnetic anisotropy and on the type of orbital containing the unpaired electron. Such investigations for tetrahedral nickel complexes with substituted salicylaldimines have demonstrated[15] that their observed shifts originate in a contact interaction with spin in the highest filled ligand π orbital. From the temperature dependence of the shifts, the square-planar $\leftrightarrows$ tetrahedral solution equilib-

(1) L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, **88**, 5180 (1966).
(2) P. L. Orioli, M. Di Vaira, and L. Sacconi, *Chem. Commun.*, 300 (1966).
(3) M. Calvin and C. H. Berkelew, *J. Am. Chem. Soc.*, **68**, 2267 (1946).
(4) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965).
(5) L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Am. Chem. Soc.*, **87**, 3102 (1965).
(6) J. Lewis, R. S. Nyholm, and S. A. Rodley, *Nature*, **207**, 72 (1965).
(7) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); M. Ciampolini and G. P. Speroni, *ibid.*, **5**, 45 (1966).
(8) L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965).
(9) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).
(10) G. N. La Mar, W. D. Horrocks, Jr., and L. C. Allen, *ibid.*, **41**, 2126 (1964).
(11) A. Chakravorty and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 3999 (1964), and references therein.
(12) A. Chakravorty, J. P. Fennessey, and R. H. Holm, *Inorg. Chem.* **4**, 26 (1965).
(13) J. D. Thwaites and L. Sacconi, *ibid.*, **5**, 1029 (1966); J. D. Thwaites, I. Bertini, and L. Sacconi, *ibid.*, **5**, 1036 (1966).
(14) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).
(15) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964).

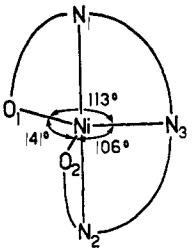


Figure 1. X-Ray structure for coordinating atoms in NiSAL–MeDPT.

rium was characterized,[15] as originally performed for aminotroponeimines.[9,16] More recently, pmr investigations have been extended to nickel chelates with N-substituted salicylaldimines, where the substituent contains a site capable of bonding to the metal.[12,13] Such chelates resulted in a complicated mixture of species in solution, either octahedral, tetrahedral, and square planar[12] or octahedral, five-coordinated, and square planar.[13] The isotropic shift patterns for the octahedral[12,13] complexes differed significantly from that observed for the tetrahedral species,[15] and the exact origin of the shifts is still in question, though π bonding seems to be primarily responsible for the spin delocalization. For the chelates giving rise to five-coordinated species in solution, as implied by their absorption spectra,[13] the character of the observed shifts could not be definitely related to the presence of the five-coordinated species, presumably because of the rapid equilibrium which averaged over the shifts of the contributing species.

We report here the pmr spectra of two series of complexes,[1] with ligand A, where X = Cl, H, CH_3, the two series differing in the R substituent. Those with R = H are designated X–NiSAL–DPT, while those with R = CH_3 are labeled X–NiSAL–MeDPT.

Experimental Section

The proton magnetic resonance spectra were recorded on a Varian HR-60 spectrometer, using tetramethylsilane as internal reference. All spectra were run at 27°, unless noted otherwise. The spectra for all chelates were obtained in both deuteriochloroform and pentadeuteriopyridine, at concentrations approximately 0.05 *M*, with the shifts found to be concentration independent. The pmr spectra for NiSAL–DPT and NiSAL–MeDPT, and their two methyl ring-substituted derivatives, were run over the temperature range −62 to 54° in $CDCl_3$, using a dewar probe and a liquid nitrogen cryostat as described elsewhere.[13] The pmr spectra of 0.10 *M* $CHCl_3$ solutions of NiSAL–DPT and NiSAL–MeDPT were recorded as a function of added deuteriopyridine. The diamagnetic zinc complexes were run on a Varian A-100 spectrometer.[17]

The pmr spectra of 5-CH_3–NiSAL–MeDPT and 3-CH_3–NiSAL–DPT were also recorded in the following protonless or fully deuterated solvents: carbon disulfide, carbon tetrachloride, d_6-benzene, d_6-acetone, d_4-methanol, d_3-nitromethane, and d_3-acetonitrile. These two chelates were only sparingly soluble in these solvents, 0.005–0.01 *M*, with the exception of CS_2. All other samples were either too insoluble to produce discernible spectra in more than one or two solvents, often in none, or produced cloudy solutions, which formed precipitates within a few hours. Their pmr spectra were characterized by broad, unidentifiable peaks. Only the pmr spectra are reported here for which we are reasonably certain that no decomposition occurred. A few of the solutions were too dilute to produce recognizable peaks on the DP-60 spectrometer and were thus run on the more sensitive HR-100 Varian spectrometer. A few test runs on both spectrometers verified that the observed shifts are proportional to field strength.

All shifts are reported as isotropic shifts, in cycles per second at 60 Mcps, defined as the difference in resonance position for a given proton in the paramagnetic chelate and the diamagnetic zinc complex, such that upfield shifts are considered positive.

The complexes used are those reported elsewhere.[1] The deuterated solvents were purchased from Fluka, AG, Buchs, Switzerland, except for d_3-nitromethane, d_3-acetonitrile, and d_4-methanol, which were obtained from E. Merck, Darmstadt, Germany.

An attempt was made to observe the electron spin resonance spectrum of a 0.1% solid solution of NiSAL–MeDPT in ZnSAL–MeDPT, using a Hilgher & Watts X-Band spectrometer, in order to estimate the *g*-tensor anisotropy. However, no signal attributable to the sample was located down to liquid-nitrogen temperature.

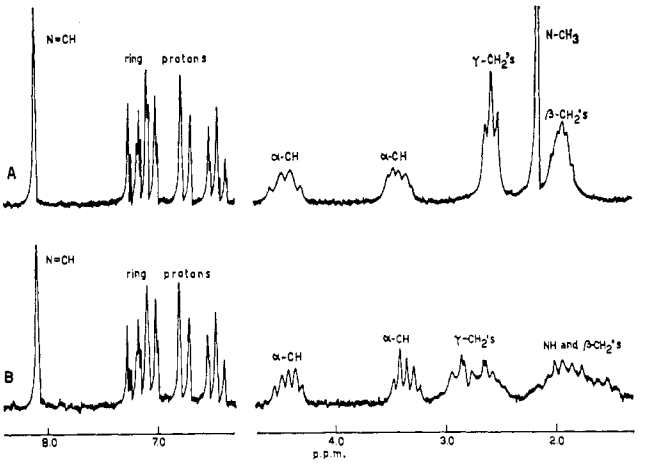


Figure 2. Pmr traces for (A) ZnSAL–MeDPT and (B) ZnSAL–DPT in $CDCl_3$.

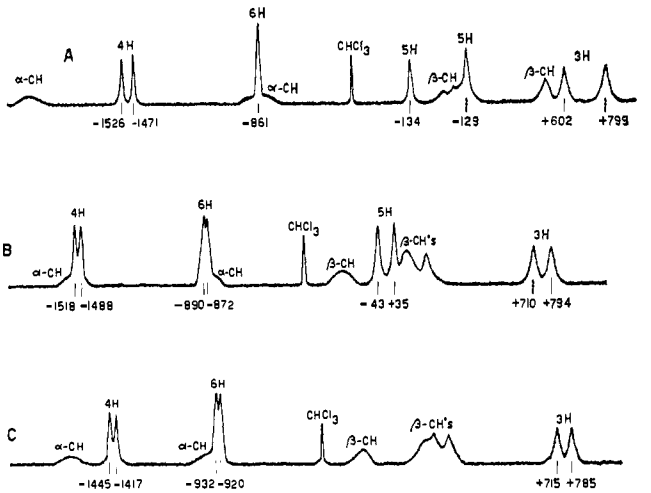


Figure 3. Pmr traces for ring protons of (A) NiSAL–DPT, (B) NiSAL–MeDPT, and (C) 5-Cl–NiSAL–MeDPT in $CDCl_3$.

Results

The pmr traces for ZnSAL–DPT and ZnSAL–MeDPT in *d*-chloroform are shown in Figure 2. The isotropic shifts for the ring protons of the complexes in *d*-chloroform are listed in Table I, and in Table II for the d_5-pyridine solutions. In both cases, the peaks are referenced against the zinc complexes. The pmr traces between −2000 and +1000 cps from TMS, the region over which all aromatic ring protons are observed, are recorded in Figure 3 for *d*-chloroform solu-

(16) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

(17) Organic Chemistry Department, Swiss Federal Institute of Technology.

Table I. Isotropic Shifts for Ring Protons of X-NiSAL-RDPT in Deuteriochloroform[a]

X	R	3 ΔH	3 δ	4 ΔH	4 δ	5 ΔH	5 δ	6 ΔH	6 δ	Δ_T
H	H	1204	197	−1096	55	516	263	−439	0	515
		1007		−1041		253				
3-Cl	H	...		−1279	54	396	152	−384	0	206
				−1225		244				
3-CH_3	H	(−230)	(72)	−1374	78	475	203	−361	0	353
		(−158)		−1296		272				
5-Cl	H	1211	196	−1015	49	...	...	−477	0	245
		1015		−966						
5-CH_3	H	1268	208	−1063	47	(−519)	(213)	−448	0	468
		1060		−1016		(−306)				
3,5-Cl_2	H	...	...	−1216	70	...	...	−429	25	95
				−1146				−404		
H	CH_3	1199	84	−1088	30	421	77	−468	18	209
		1115		−1058		344		−450		
3-Cl	CH_3	...	...	−1273	42	348	0	−414	46	86
				−1231		348		−368		
3-CH_3	CH_3	(−188)	(9)	−1375	67	399	43	−395	41	160
		(−179)		−1308		356		−354		
5-Cl	CH_3	1190	70	−1015	28	...	...	−510	12	110
		1120		−987				−498		
5-CH_3	CH_3	1246	95	−1015	22	(−422)	(70)	−470	21	208
		1151		−1033		(−350)		−449		
3,5-Cl_2	CH_3	...	...	−1201	46	...	...	−440	54	100
				−1155				−386		
4-CH_3	CH_3	−1190	97	(552)	(22)	457	72	−425	0	191
		1093		(530)		385				

[a] Shifts in cps at 60 Mcps, at 27°, referenced to the position for each proton in the diamagnetic zinc complex. Shifts in parentheses indicate methyl protons. δ denotes the splitting between two component peaks for position *i*. Δ_T denotes total ring splitting.

Table II. Isotropic Shifts for Ring Protons of X-NiSaL-RDPT in Pentadeuteriopyridine[a]

X	R	3	4	5	6
H	H	449	−1050	37	−100
3-Cl	H	...	−1202	40	−126
3-CH_3	H	(−77)	−1339	49	−83
			−1323		
5-Cl	H	439	−950	..	−108
5-CH_3	H	448	−1037	(−66)	−74
3,5-Cl_2	H	...	−1120	..	−113
H	CH_3	462	−1072	20	−116
3-Cl	CH_3	...	−1265	32	−108
3-CH_3	CH_3	(−91)	−1342	41	−99
5-Cl	CH_3	444	−965	..	−108
5-CH_3	CH_3	454	−1030	(−55)	−95
3,5-Cl_2	CH_3	...	−1110	..	−109
4-CH_3	CH_3	465	(246)	36	−98

[a] Shifts in cps at 60 Mcps, at 27°, referenced to the position in the diamagnetic zinc complex. Parentheses denote methyl protons.

tions of NiSAL-DPT, NiSAL-MeDPT, and 5-Cl-NiSAL-MeDPT. The temperature dependence of the two unsubstituted chelates is illustrated in Figure 4.

The dependence of the positions of the ring proton resonances in *d*-chloroform solution, as d_5-pyridine is added to NiSAL-DPT and NiSAL-MeDPT, appears in Figure 5. Table III and Table IV present the isotropic shifts for the ring protons of 5-CH_3-NiSAL-MeDPT and 3-CH_3-NiSAL-DPT, respectively, in the two inorganic and six fully deuterated solvents.

Discussion

Assignment of the Peaks. The peak at −8.1 ppm belongs to the azomethine proton, and the four peaks between −6.4 and −7.3 ppm arise from the four ring protons. For the ZnSAL-MeDPT complex, the signal at −2.2 ppm must arise from the aminomethyl group.

Table III. Isotropic Shifts for Ring Protons of 5-CH_3-NiSAL-MeDPT in Various Solvents[a,b]

Solvent	3 ΔH	3 δ	4 ΔH	4 δ	5 ΔH	5 δ	6 ΔH	6 δ	Δ_T	ε[c]
Carbon tetrachloride	1142	53	−1121	37	(−324)	19	−420	38	147	2.24
	1089		−1084		(−305)		−382			
d_6-Benzene	1144	69	−1091	41	(−364)	55	−430	29	194	2.28
	1075		−1050		(−309)		−401			
Carbon disulfide	1110	66	−1080	38	(−333)	46	−386	32	182	2.64
	1044		−1042		(−287)		−354			
d-Chloroform	1245	95	−1055	22	(−422)	70	−470	21	208	4.81
	1150		−1033		(−352)		−449			
d_6-Acetone	1296	102	−1046	42	(−409)	87	−480	29	260	20.7
	1194		−1004		(−322)		−451			
d_4-Methanol	1388	53	−965	73	(−520)	189	−527	0	315	32.6
	1335		−892		(−331)					
d_3-Nitromethane	1366	113	−1034	66	(−482)	150	−505	8	337	39
	1253		−968		(−332)		−497			
d_3-Acetonitrile	844	84	−988	194	(−470)	129	−269	0	407	39
	760		−794		(−241)					

[a] See footnote *a*, Table I. [b] For 3-CH_3-NiSAL-MeDPT, Δ_T's (cps) were observed as: carbon tetrachloride, 162; carbon disulfide, 160; acetone, 193; acetonitrile 440. [c] ε denotes dielectric constant, "Handbook of Chemistry and Physics," 45th ed, The Chemical Rubber Co., Cleveland, Ohio, 1964.

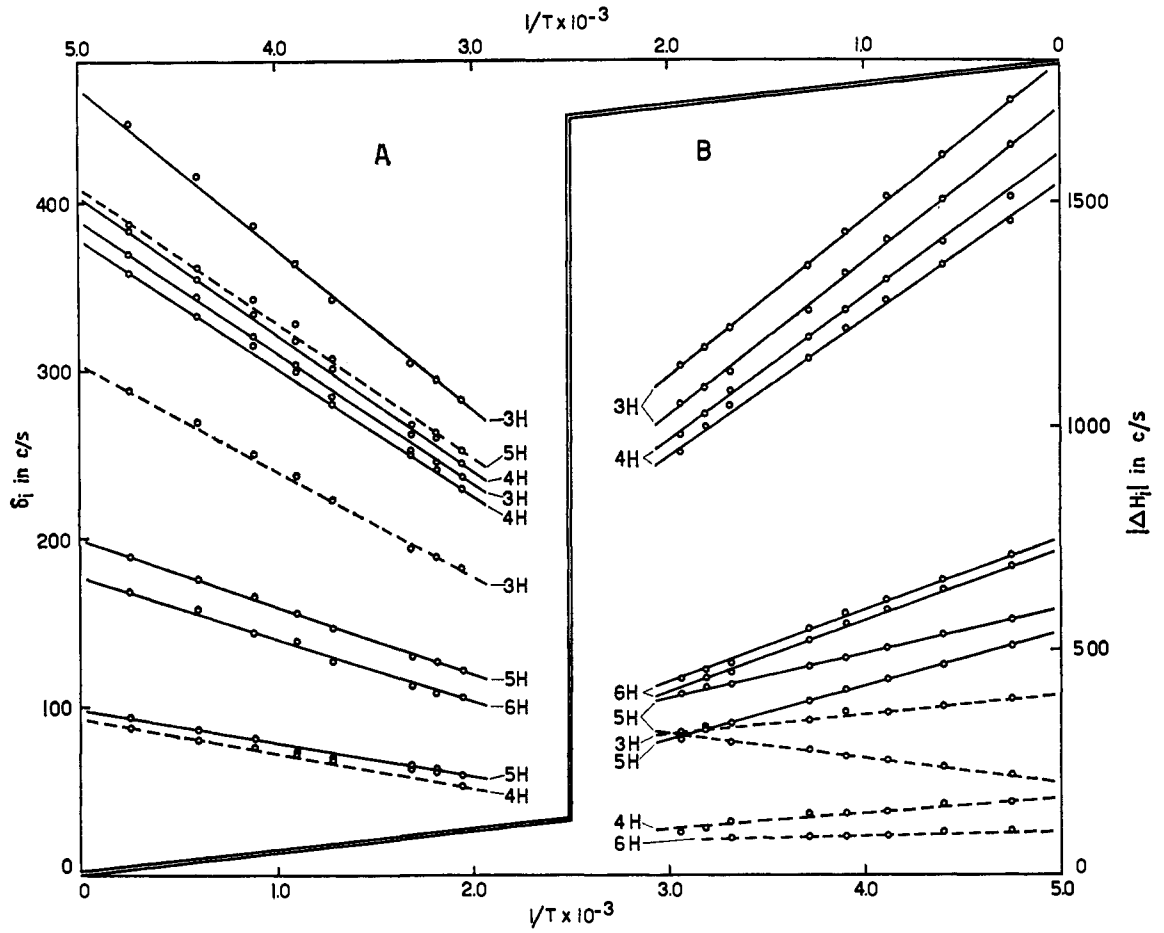


Figure 4. Temperature dependence for ring proton isotropic shifts, ΔH_1, ———; and peak splittings, δ_1, - - - -, for (A) NiSAL–DPT and (B) NiSAL–MeDPT, in $CDCl_3$.

Remaining are thus four peaks with relative areas 2:2:4:4 for ZnSAL–MeDPT, and with areas 2:2:4:5 for ZnSAL–DPT, going upfield with the azomethine proton peak taken as 2. For ZnSAL–MeDPT, these four peaks arise from the 12 methylene protons, while the amino proton is apparently included in the farthest upfield peak in this set for ZnSAL–DPT. The fact that six-membered rings are formed upon coordination to the metal makes these splittings expected. The peak at −2.6 ppm is assigned to the γ-CH's, on the basis that a triplet appears for the MeDPT case due to coupling with the β-CH's, while this peak is further split by coupling to the NH proton for the DPT complex. The peak at −1.9 ppm is assigned

Table IV. Isotropic Shifts for the Ring Protons of 3-CH_3–NiSAL–DPT in Various Solvents[a,b]

Solvents	3		4		5		6			
	ΔH	δ	ΔH	δ	ΔH	δ	ΔH	δ	Δ_T	ϵ[c]
Carbon tetra-	(−258)	74	−1450	76	460	212	−361	10	372	2.24
chloride	(−184)		−1374		248		−351			
d_6-Benzene	(−252)	73	−1397	96	470	202	−366	0	371	2.28
	(−179)		−1301		268					
Carbon disulfide	(−194)	62	−1326	86	524	145	−416	0	293	2.64
	(−132)		−1240		379					
d-Chloroform	(−230)	72	−1374	78	475	203	−361	0	353	4.64
	(−158)		−1296		272					
d_6-Acetone	(−244)	62	−1370	84	436	197	−326	0	343	20.7
	(−182)		−1286		241					
d_4-Methanol	(−215)	84	−1218	65	502	96	−409	40	285	32.6
	(−131)		−1153		406		−369			
d_3-Nitromethane	(−225)	98	−1338	112	592	201	−470	0	411	39
	(−127)		−1226		391					
d_3-Acetonitrile	(−199)	94	−1124	121	394	107	−263	93	415	39
	(−105)		−1003		287		−170			

[a] See footnote *a*, Table I. [b] For 5-CH_3–NiSAL–DPT, Δ_T's (cps) were observed as: carbon disulfide, 375; acetone, 320; methanol, 432. [c] See footnote *c*, Table III.

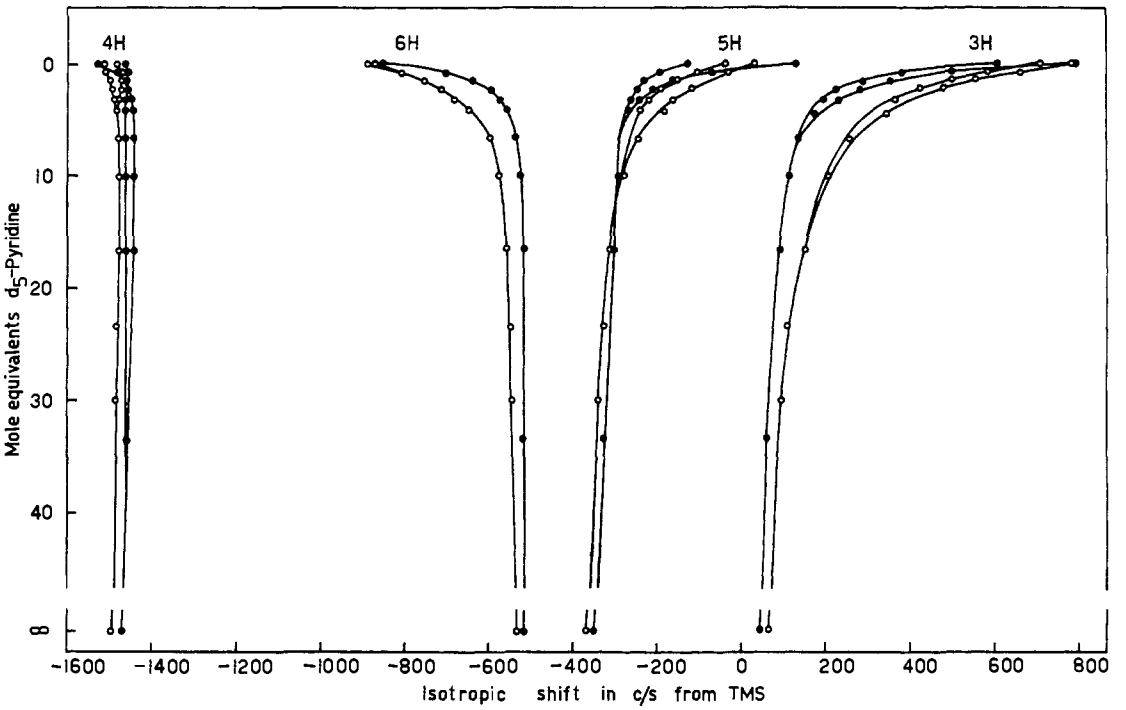


Figure 5. Plot of ring proton chemical shifts *vs.* excess molar equiv of deuteropyridine for NiSAL–DPT (●) and NiSAL–MeDPT (O) in $CDCl_3$.

to the β-CH's, as it appears as a slightly broadened quintuplet indicating more or less equal coupling to the α-CH's and γ-CH's. This peak is again more complicated in ZnSAL–DPT, presumably because of further coupling with the NH. The two smaller peaks at −2.4 and −4.4 ppm thus belong to the α-CH's, since their multiplet structure is least affected by the amino nitrogen substituent. As this group of protons lie closest to the aromatic ring, the chemical shift difference for the axial and equatorial protons would be expected to be greatest,[18] the observed difference being 2.0 ppm. The multiplet structure for the α-CH's in ZnSAL–MeDPT shows five components, with intensities 1:2:2:2:1. This is interpreted as arising from axial–equatorial coupling of 12.5 cps and coupling to the adjacent CH's of 5.5 cps. For ZnSAL–DPT, the peak at −4.4 resembles more a quartet, which could arise from equal coupling to the other α-CH and β-CH's. This would indicate that there might be some slight difference in structure, or in methylene chain configuration, between the ZnSAL–DPT and ZnSAL–MeDPT complexes (*vide infra*). However, since long-range coupling to the NH is also possible, no definite conclusions can be drawn. The assignment of the ring protons on the basis of multiplet structure and substitution is trivial. The peak locations, relative to TMS, are (in cps at 60 Mcps): 3-H, −404; 4-H, −430; 5-H, −387; 6-H, −422; 3-CH_3, −128; 4-CH_3, −130; 5-CH_3, −131.

The pmr traces of three nickel chelates are illustrated in Figure 3 over the region where all the ring protons lie. What becomes immediately obvious is that there appears not a single peak per ring position, but two separate resonances. For some samples, as many as 21 peaks were observed with the complex containing a total of 23 protons. That two peaks arise per ring position was verified by the use of substituents, where peaks disappeared in pairs upon chloro substitution and shifted and tripled in intensity upon methyl substitution. The difference in resonance position for a pair of peaks is as large as 263 cps in chloroform solution. Also, the N–CH_3 peak in the MeDPT complexes illustrates that there should be two separate resonances per ring position by the fact that the intensity ratio for this methyl group to any single ring peak is only 3:1, instead of the expected 3:2. In a few cases, the 6-H peak was not split, and this resulted in the only peak attributable to this position having twice the intensity of any of the other "split" proton peaks.

Assignment was performed completely by substitution, as the line widths were too great (≥10 cps) to resolve any multiplet structure in all but a few cases. For 3-Cl–NiSAL–MeDPT, the two 4-H peaks each showed a doublet, as did the 6-H, while the 5-H exhibited a triplet, as is expected. This sample thus serves to confirm the 6-H assignment, as complexes with substituents at this position were not prepared. The peak positions are found to be quite independent of ring substituents, except that the 4-H resonated slightly further downfield upon substituting at the 3 position, as has been observed in other related chelates of nickel.[13]

The temperature dependences of the ring proton resonances of NiSAL–DPT and NiSAL–MeDPT in chloroform are plotted as a function of $1/T$ in Figure 4, and verify that the shifts generally follow a Curie law,[14] eliminating any equilibrium such as was found for a number of nickel(II) systems.[9,11–13,15,16]

Assignment of the ring protons was facilitated by the fact that they exhibited line widths significantly

(18) J. S. Waugh and R. S. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957); D. J. Wilson, D. J. V. Boekelheide, and R. W. Griffin, *ibid.*, **82**, 6302 (1960).

smaller than for the remaining protons. Because of the low solubility for most of the complexes and excessive line widths, it was possible to locate all of the nonring protons in only a very few samples. Aside from the ring proton resonances for NiSAL–DPT in chloroform, the following peaks (cps) and their relative intensities have been observed: −13,300 (1), −10,500 (1), −6500 (2), −4200 (2), −1960 (1), −850 (1), 80 (1), 146 (1), 529 (1), 780 (1), and −14,980 (1) and −16,700 (1). The four peaks between 80 and 780 cps can be confidently assigned to the four β-CH's, since only for this position do spin polarization effects predict upfield contact shifts. Both σ and π spin density result in downfield shifts for α-CH's and γ-CH's. This assignment is also consistent with the smaller line widths for these peaks, as they are one bond further removed from the nickel than the other two methylene positions. The two peaks at −14,980 and −16,700 cps can be assigned to the azomethine protons, again because of much narrower lines due to a greater distance from the metal. A large downfield shift for this position has been observed in other nickel chelates with salicylaldimines.[15] The two larger peaks at −6500 and −4200 cps can be assigned to the γ-CH's, since the N–CH_3 resonates at −4700 cps, and there would not be expected to be very much difference in the peak positions of the aminomethyl and aminomethylene groups. This leaves the four peaks at −13,300, −10,500, −1960, and −850 cps, which must arise from the α-CH's. This assignment is consistent in that the largest spread of the α-CH's was also observed in the diamagnetic zinc chelates. The presence of unpaired spin in the aromatic system just greatly amplifies the effect. The assignments for the α-CH's and γ-CH's are speculative, however, and cannot be fully justified. It will be shown later that these assignments are consistent with certain features of these complexes. This scheme of assignments holds true for all DPT complexes, as only minor differences in position occur. The N–H resonance was not found presumably because it is too close to the metal.

For the NiSAL–MeDPT series, the nonring protons are found at: −13,200 (1), −11,400 (1), −6700 (4), −4700 (3), −1630 (1), −1000 (1), −187 (1), 112 (1), 155 (1), and 227 (1), and −11,930 (1) and −13,520 (1), all in cps. The four peaks between −187 and 227 cps are assigned to the β-CH's, and those at −11,930 and −13,520 cps to the azomethine protons, on the same basis as for NiSAL–DPT. The peak at −4700 cps arises from the aminomethyl group, due to its relative intensity and its absence in the DPT chelates. The peak of intensity 4 at −6700 cps is attributed to the γ-CH's, again because of its position being so similar to the aminomethyl. The remaining peaks must belong to the four α-CH's.

As can be seen from a comparison of the assignments for the DPT and MeDPT complexes, the resonance positions are quite similar. Significant differences are noted in the spread of the β-methylene shifts, the extent of downfield shift for the azomethine protons, and the fact that the γ-methylene protons give rise to two peaks for the DPT chelates, but only a single broad resonance (800 cps) for the MeDPT complexes.

Origin of the Double Peaks. The appearance of almost twice the number of peaks expected, even after considering the nonequivalence of the methylene protons resulting from ring formation, can be considered to arise from two likely situations. One would be the presence of two distinct species in solution with differing shift patterns, the other possibility being that we have but one species, but the two salicylaldimine fragments are nonequivalent, such that their shift patterns differ.

The former case could result from two geometrical isomers or from optical isomers. There have been reported[12,15] some cases of similar "doubling" of lines where the origin was traced to the presence of optical isomers. The doubled peaks did not appear with equal intensity, and both sets of peaks were indicative of identical spin distributions, with only a small scaling in magnitude between them.[12,15] Also, the splittings[12,15] represented only a very small fraction of the total shift. In the present study, it is found that the doubled peaks always appear with equal intensity, and this observation holds true over a wide temperature range and in a number of solvents. In view of these observations, plus the fact that the crystal structure[2] showed only one geometrical isomer, the doubling could only arise from optical isomers. However, the two sets of peaks for these five-coordinated complexes display significantly different shift patterns or spin distributions, since the splitting is not at all proportional to the shift magnitude. Often the smallest shift exhibits the largest splitting and *vice versa*. Moreover, the splitting here represents up to 100% of the shift in some cases. Therefore, though these complexes possess no center of symmetry and optical isomers have been observed,[2] their presence in solution cannot explain the observed pattern of peak splittings.

It can be shown, however, that the properties of the observed splittings are consistent with the presence of only one species in solution, with such coordination of the pentadentate ligand that the two salicylaldimine fragments are nonequivalent in some major respect. In NiSAL–MeDPT, for example, the only two positions for which no splittings are observed are the N–CH_3 and the γ-CH's. If two species produced the doubling, it might be expected that these positions should also display a splitting. However, for the case where we have only one species in solution with nonequivalent aromatic fragments, it is obvious that the N–CH_3 "belongs" to both fragments, such that no splitting can be expected. Furthermore, the γ-CH's are next nearest to this equivalence point, such that it would not be unexpected that they show small or negligible splittings. For NiSAL–DPT, the γ-CH's do split, but only into two peaks. Even in this complex, however, this splitting is the smallest for the methylene protons when expressed as fraction of the total shift. It should be pointed out here that a splitting of the γ-methylene peak into two resonances can arise from the effect of ring formation upon coordination to the nickel, even though this splitting was not observed in the diamagnetic zinc complex. The reason for this is that the effect of the unpaired spin can magnify an unobservably small chemical-shift difference in the diamagnetic chelate so that it is readily seen in a paramagnetic complex. However, the splitting of any methylene group into four peaks will only arise through the additional effect of nonequivalence of the two sides of the ligand.

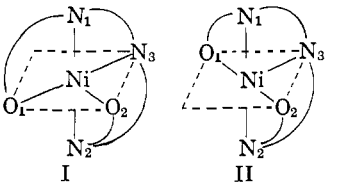
The splitting of a methylene group into four peaks is most convincingly demonstrated in the pmr trace of 5-Cl–NiSAL–DPT, where the elimination of the 5-H peaks clearly reveals two sets of split peaks. The assignment for the β-CH's is quite definite, as no spin-transfer mechanism would result in upfield shifts for the α-CH's or γ-CH's.

The observed shifts[14] must arise from either a contact interaction or from the dipolar interaction, should the nickel possess an anisotropic g tensor. In view of the similarity of the presently observed shift patterns to that observed for the tetrahedral chelates,[15] and the fact that methyl substitution always produces shifts of opposite sign to that of the proton,[9,10,19] the shifts must arise primarily from unpaired spin in the ligand highest filled π orbital. However, since the splittings are not proportional to the shift, it is indicated that the spin distribution for the two rings must differ significantly. Isotropic shifts resulting, in part, from σ density[20,21] for one of the rings could be a possibility, as would differing extents of interaction with higher ligand orbitals.[22–24] Both effects have been reported.[20–23] Because of the lack of any symmetry element for these complexes, the spin can probably be delocalized into any ligand orbital.

In order to be able to attribute the splittings to a different extent of dipolar interaction with the two rings, the two aromatic fragments must be oriented differently with respect to the major axes of the chelate; otherwise this interaction will affect both rings identically. For shift differences between the rings as large as 263 cps, the anisotropy will have to be very large, and the difference in ring orientations must represent a large deviation from equivalence. Nothing is known about the g-tensor anisotropy, due to the lack of esr data. Attempts to observe the esr signal for these complexes failed, perhaps due to large zero-field splittings. The magnetic moments for these complexes are inconsistent with sizable anisotropy, and the inverse cube of the distance dependence[14] of the dipolar interaction makes it unlikely that it could cause such large splittings. However, both the contact and dipolar interaction are thus indicated as possible origins of the double set of peaks, as long as the two salicylaldimine fragments are nonequivalent.

Such origins for the set of double peaks are quite consistent with the known structure of NiSAL–MeDPT, where the two aromatic fragments are seen to be slightly nonequivalent.[2]

The nonequivalence of the two SAL arises from the fact that the known structure lies somewhere between a trigonal bipyramid and a square pyramid. Steric effects of the methylene chains dictate that the two azomethine nitrogens tend to remain *trans* to each other, as verified in the X-ray analysis,[2] such that a trigonal bipyramidal structure would produce equivalent SAL rings. Coordination with pyridine shows that these ligands readily take up a square-pyramidal conformation,[1] as required in octahedral coordination. The two square-pyramidal structures consistent with *trans*-azomethine bonding are labeled I and II, for the SAL rings *cis* and *trans* to each other, respectively.



Of these two conformations, only I would produce nonequivalent SAL rings. It can be easily seen that for this case the two SAL rings would see radically differing ligand fields. Structure II, like the trigonal pyramidal form, would not produce splittings. It could thus be supposed that the extent of ring nonequivalence, as evidenced by the splittings, will increase with structure changes tending to approach I. The great similarity of the crystal and solution spectra indicates no major structure changes upon dissolution;[1] however, small changes in bond angles, perhaps a few degrees, cannot be precluded, as evidenced by the temperature and solvent effect on the splittings (*vide infra*).

The actual structure in any solvent is probably the result of a number of factors, such as repulsion between bonding ligand atoms, steric effects of the methylene chains and the amino nitrogen substituent, and relative crystal field stabilization energies, cfse. The atomic repulsions are likely to be insignificant, inasmuch as related salicylaldimine ligands readily form octahedral complexes.[12,13] The steric effect is definitely expected to exert a strong influence, probably favoring the trigonal bipyramidal structure, where the bands in the methylene chains are minimized. Crystal field calculations[25] have indicated that the cfse favors the square pyramid, though the high degree of covalent bonding[26] in salicylaldimine could make such calculations inapplicable in the present case. The effect of coordinating and noncoordinating solvents upon the observed splittings will be seen to shed light on the pentadentate ligand conformation in the octahedral adducts and relate to the importance of steric effects in determining the solution structure.

Pmr Spectra in Deuteriopyridine. As shown previously,[1] these five-coordinated complexes all react with 1 mole of pyridine to form the adducts, NiSAL–RDPT·py. The observed isotropic shifts in this solvent are given in Table II. As is readily observable, the shifts for the pure five-coordinated complexes and their octahedral pyridine adducts differ significantly. The shifts are much smaller in the adduct for all but the 4-H position, and the alternation of signs for adjacent positions, very obvious in chloroform solution, almost disappears in pyridine. In addition, only one peak per ring proton is now observed in each case except that of the 4-H peak in 3-CH_3–NiSAL–DPT, where a splitting of about 16 cps remains. The peaks were generally too broad (25 to 75 cps) to resolve any smaller splittings. Assignment was carried out by substitution. However, the 5-H and 6-H peaks were found so close to each other that it was necessary to verify their

(19) A. Forman, J. N. Murrell, and L. E. Orgel, *J. Chem. Phys.*, **31**, 1129 (1959).
(20) J. A. Happe and R. L. Ward, *ibid.*, **39**, 1211 (1963).
(21) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 3534 (1965).
(22) D. R. Eaton, *ibid.*, **87**, 3097 (1965).
(23) D. R. Eaton and E. A. LaLancette, *J. Chem. Phys.*, **41**, 3534 (1964).
(24) G. N. La Mar, to be published.
(25) M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).
(26) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958).

assignment by slowly adding pyridine to chloroform solutions of NiSAL–DPT and NiSAL–MeDPT. The effect on the ring resonance position as a function of excess deuteriopyridine is recorded in Figure 5.

The disappearance of the double peaks upon adduction is readily explained by the fact that, upon coordination of pyridine, the octahedral field produces more or less identical ligand fields for both SAL rings. That the ring nonequivalence has not totally disappeared is evidenced by the 16-cps splitting of the 4-H peak in 3-CH_3–NiSAL–DPT. This splitting is larger than the expected spin–spin coupling. It might thus be concluded that the ring nonequivalence in pyridine has been reduced by adduct formation, such that the splittings are very small and are probably obscured by line widths in all cases except the 3-CH_3–NiSAL–DPT.

In the pyridine adduct, the chelate must arrange itself in either conformation I or II. Of these two, only I would result in nonequivalent salicylaldimine rings such that splittings should be observed. The 16-cps splitting observed for the one complex adduct with sufficiently narrow line widths indicates that the more probable chelate arrangement is I. This conformation of the chelate in the adduct may be a bit surprising, since the largest "opening" or clearest approach to the five-coordinated complex is bisecting the O_1–Ni–O_2 angle. However, models show that the steric strain in the methylene chains resulting from structure II is quite severe and that I is more favorable.

The pattern of the isotropic shifts for the pyridine adducts closely resembles that observed for other octahedrally coordinated nickel(II) complexes with related ligands.[12,13] The shifts display some characteristics resulting from spin in the π-ligand orbitals, since alternation does exist, and protons and methyl groups produce shifts of opposite sign for any position.[9,10,19] However, the distribution is inconsistent[15] with that expected for delocalization into the top bonding ligand orbital, and therefore other interaction may well be important. This problem will be treated elsewhere.[24]

The Effect of Noncoordinating Solvents. Although the isotropic shifts for both the NiSAL–MeDPT and NiSAL–DPT chelates exhibit quite similar patterns, one characteristic difference between the two series of complexes is readily observed. In Table I, in addition to the isotropic shifts, we list also for each ring position the difference, or splitting, between the two peaks, denoting it δ. From a comparison of the analogous complexes, one with R = H, the other with R = CH_3, it is revealed that the splittings, δ, are always larger for the former than for the latter complex, sometimes by a factor of 2–3. This is true for every position save 6-H, where no splittings appeared for the DPT complexes at room temperature and only very small ones for the MeDPT series. The splittings for any given ring position do not vary significantly upon substitution at another ring position. The methyl splittings for any position are always smaller than for the proton.

The conclusion which appears most evident is that if these splittings can be interpreted as arising from nonequivalence of the two aromatic parts of the chelate, then the extent of this nonequivalence is significantly greater for the NiSAL–DPT than for the NiSAL–MeDPT complexes in chloroform. The splitting for any one position should not be taken indiscriminately as an index of this nonequivalence, since the electronic origin of the splittings in all probability does not affect all ring positions identically. However, if we sum over all the ring positions, we obtain the total splitting parameter, Δ_T, which should be a reasonable measure of the extent of nonequivalence. This splitting parameter, Δ_T, is also given for each complex in Table I. Comparing this parameter for any two complexes differing only in R, we find Δ_T for the NiSAL–DPT consistently larger by a factor 2.2–2.5 than for the NiSAL–MeDPT complex. This ratio of parameters is remarkably constant for all complexes where Δ_T can be summed over at least three ring positions.

Within the supposition that the solution structure does not deviate appreciably from that observed in the solid, and that the extent of ring nonequivalence increases as the structure deviates slightly in the direction of structure I, the difference in Δ_T between the DPT and MeDPT complexes in chloroform indicates that their structures differ slightly, with the former complexes displaying a structure slightly closer to I than the latter. This difference in proton splittings between the two series was also observed for the methylene protons. As indicated earlier, the β-CH's are spread over $\simeq$420 cps and $\simeq$700 cps for the MeDPT and DPT chelates, respectively. Similarly, the γ-CH's produced but a single peak in NiSAL–MeDPT, while NiSAL–DPT showed two peaks. These methylene proton splittings are consistent with the ring Δ_T parameters for the two series, and verify their apparent difference in ring nonequivalence, and thus structure. Unfortunately, nothing definite can be stated about the magnitude of the differences in structure between the two series, since it is not known how the splittings depend upon small variations of the bonding angles. However, changes of just a few degrees could be considered quite consistent with the observed changes in view of the high sensitivity of pmr measurements.

The difference in structures for these complexes depending on the R substituent seems to reflect steric effects.[27] As indicated above, these structures are probably determined by a compromise between the steric effect, probably favoring a trigonal bipyramid, and the cfse, which favor a square pyramid.[26] Since the relatively more bulky methyl group will increase the steric effect in the NiSAL–MeDPT chelates more than the proton in the NiSAL–DPT series,[27] a structure for the former complexes tending more toward I should not be unexpected. That the steric effect of the methyl group influences the structure draws support from the equilibrium constant data for these complexes with pyridine.[1] As shown in Figure 5, for any given excess of pyridine in the two equally concentrated solutions of NiSAL–DPT and NiSAL–MeDPT, the extent of octahedral coordination, as determined by the pmr shift, is always greater for the former chelate. This indicates that the aminomethyl group must provide some steric inhibition[1] toward six coordination for NiSAL–MeDPT. This characteristic difference in equilibrium constants for the two series is observed also for all the ring-substituted isomers.

In order to determine if the solution structure for these complexes is dependent upon solvent, the isotropic shifts were measured in seven other solvents.

(27) F. G. Mann and R. H. Watson, *J. Chem. Soc.*, 2772 (1958).

In Tables III and IV we list the observed shifts, the splitting, δ, and the total splitting parameter, Δ_T, for 5-CH_3–NiSAL–MeDPT and 3-CH_3–NiSAL–DPT, respectively, in each of eight noncoordinating solvents.

Tables III and IV clearly indicate that the splittings are indeed sensitive to the solvent, particularly for 5-CH_3–NiSAL–MeDPT. Again, the δ's should not be taken individually as indications of the extent of ring nonequivalence, but the sum over the four ring positions, Δ_T. It is readily observed that the four ring positions are affected differently by the various solvents in some cases. For the MeDPT chelate, Δ_T varies over the range 147–407 cps, while the DPT complex shows much less variation. The isotropic shift patterns are essentially identical in all the solvents. In none of the solvents listed in Tables III and IV does any additional coordination of the five-coordinated species occur. This was verified by studying the pmr lines of the solvent.

The dependence of Δ_T on the solvent indicates that the extent of ring nonequivalence, and hence the structure, are also a function of the solvent. Since there exists no direct bonding between these solvents and the five-coordinated chelates, the solvent sensitivity of the splittings and structure must reflect some sort of variable solvation effect. The observed splitting parameter, Δ_T, increases for these solvents in the order $CCl_4 < CS_2 \simeq C_6D_6 < CDCl_3 < CD_3COCD_3 < CD_3OD < CD_3NO_2 < CD_3CN$, for the 5-$CH_3$–NiSAL–MeDPT complex. This apparent increase in ring nonequivalence, as indicated by Δ_T, correlates very well with the dielectric constants for these solvents, also included in Table III under ϵ. Since the ring nonequivalence increases as I is approached, the correlation between the parameter Δ_T and dielectric strength implies that increasing solvating power tends to stabilize the square-pyramidal structure (I) over the more trigonal bipyramidal one in solution for the MeDPT complex, or that the square-pyramidal structure is more highly solvated than the trigonal bipyramid. A very similar solvation effect has been observed[16] for the nickel(II) chelates of aminotroponeimine, where the sensitive solvent dependence of the square-planar, diamagnetic $\leftrightarrows$ tetrahedral, paramagnetic forms was explained by the higher solvation of the square-planar form. Such solvation may be considered analogous to the microcrystalline ordering postulated[28,29] to explain the linewidth differences for the hyperfine components in the esr spectra of square-planar complexes. The extent of stabilization of the square pyramid over the trigonal bipyramid forms by this mechanism could be expected to increase with the solvent dielectric strength, though solvent shape and size probably also play an important part.

Another possible mechanism which would stabilize I and would be expected to produce the observed dependence on the dielectric strength is that of solvation of the complex as a whole, without any ordering of solvent molecules, which decreases the repulsion between the oxygens, thereby allowing them to take up a more *cis* position. Either mechanism would account for the increased stabilization of the square-pyramidal structure with solvent dielectric strength, but *only* if the conformation of the square-based structure approaches I. The observed changes in Δ_T with solvents are quite inconsistent with structure II as a limit.

For the 3-CH_3–NiSAL–DPT complex, the variation in Δ_T with solvent is much smaller than that for the DPT complex and does not seem to indicate any significant dependence on dielectric constant, except that the splittings are again largest in nitromethane and acetonitrile. The variations in Δ_T with solvent represent only a 10–20% deviation from the average, implying that the extent of nonequivalence of the two aromatic rings, and hence the solution structure, is more or less independent, or at least does not demonstrate the striking dependence noted for 5-CH_3–NiSAL–MeDPT.

Though the pmr spectra of the two other methyl-substituted chelates are available for only a very few solvents due to insolubility, as indicated at the bottom of Tables III and IV, it is observed that the available data are consistent with the above conclusions.

From Table I, we note for the DPT series, where it appears that the ring substituent does not significantly influence the splittings and thus the structure, that the 5-CH_3 derivative produces a $\Delta_T \simeq 1.3$ times that for the 3-CH_3 isomer. This ratio of $\simeq$1.3 for the two methyl-substituted isomers holds also for the MeDPT series. It can therefore be concluded that if the structures of 5-CH_3–NiSAL–MeDPT and 3-CH_3–NiSAL–DPT were identical in any given solvent, then their ratio of Δ_T's should also be $\simeq$1.3. From a comparison of Δ_T's for the same solvent in Tables III and IV, it is observed that this ratio is about 0.5 for the solvents of low dielectric strength and increases to 1.0 for solvents with high dielectric constant. This implies that the structures of the DPT and MeDPT complexes, or their extents of ring nonequivalence, differ, with the former chelate possessing a more nonequivalent pair of SAL fragments, but with the *difference* between the two series of complexes decreasing as the solvent dielectric strength increases. As a strong solvent effect was observed only for the MeDPT chelates, and since the difference in solution structure for the DPT and MeDPT complexes was attributed to the steric effect of the aminomethyl group, it appears that solvation tends to diminish the importance of this steric effect.

This difference between the two series of complexes is also evidenced in the temperature dependence of the ring proton shifts and serves to support the supposition that steric effects account for the difference in structure, as indexed by the splitting term, Δ_T. As illustrated in Figure 4, the isotropic shifts for NiSAL–DPT follow the Curie law exactly, and hence so do the splittings, δ, as expected. For the NiSAL–MeDPT chelate, however, though the shifts generally follow the Curie law, it is noticed, particularly for 3-H and 5-H, that the two peaks for each position diverge much more than predicted by a Curie behavior. This is demonstrated in the temperature dependence of the splittings, δ. It clearly shows that δ for 3-H decreases with temperature much more slowly than predicted while δ for 5-H actually *increases* with temperature, opposite to expectations. This effect can be interpreted such that if the smaller splittings for the MeDPT series arise because steric effects tend to stabilize a more trigonal-bipyramidal-like structure, where the extent of ring nonequivalence is less than in the DPT series, then in-

(28) H. M. McConnell, *J. Chem. Phys.*, **25**, 709 (1956).
(29) R. N. Rogers and G. E. Pake, *ibid.*, **33**, 1107 (1960).

creasing temperature would counter the steric effect through thermal motion, making the structures of the two series more nearly identical. This minute change in structure is manifested in increasing δ, though the over-all shift still follows the Curie law. This characteristic difference in the temperature dependence of the splittings between the DPT and MeDPT chelates is also observed for their two methyl-substituted isomers. The temperature data are thus consistent with the relative solvent sensitivities and splittings for the two series of complexes.

In all the foregoing discussions on differences in structure, and the resemblance of the actual structure to I or II, it was never possible to specify any exact structure but only relative tendencies. Perhaps when the electronic origin of the nonequivalence and its effect on the isotropic shifts are better understood, it will be possible to make the presently qualitative results more quantitative.

The absorption spectra indicate no significant changes with solvent,[1] but it is not known what the limits are on slight changes in coordination geometry before they manifest themselves in the optical spectrum. It could be that the changes in the O_1–Ni–O_2 angle, for example, which produce the differences in splittings between the DPT and MeDPT complexes, and in the various solvents, are so small that absorption spectra could not be expected to display observable differences. In view of the extreme sensitivity of pmr in detecting differences in magnetic environment, this may well be the case. This further demonstrates the versatility and sensitivity of pmr studies on paramagnetic complexes and indicates that this technique could prove valuable in studying the conformation of multidentate ligands in complexes with unpaired spins.

Summary

The observed "doubling" of the pmr peaks in the five-coordinated complexes is attributed to the presence of a single species in solution which possesses nonequivalent salicylaldimine fragments. The magnetic nonequivalence arises from the fact that the two aromatic fragments see slightly different ligand fields, as indicated in the known X-ray structure. The pmr spectra in pyridine are consistent with octahedral coordination, and the splitting of peaks disappears or is greatly reduced. The appearance of a 16-cps splitting in one case indicates that the conformation of the pentadentate ligand in the pyridine adduct has the salicylaldimine fragments bonded *cis* to each other.

Changes in the observed splittings are related to slight changes in solution structure. Small deviations from the crystal structure in the direction of a square pyramid with the aromatic rings *cis* to each other increase the extent of nonequivalence of the aromatic rings, giving rise to larger splittings. The sum of the splittings for the four ring positions indicates that the extent of ring nonequivalence is greater for the DPT than the MeDPT complexes and is attributed to the steric effect of the aminomethyl group which tends to favor a more trigonal-bipyramidal structure. The splittings for the methylene protons are consistent with these conclusions, as are the equilibrium constant data for the pyridine adduct formation and the temperature dependence of the ring splittings for the two series of complexes.

The magnitude of the splitting parameter and hence solution structure are shown to be very solvent sensitive for the MeDPT chelates and correlate well with solvent dielectric strength. The increase of splittings with solvent strength indicates that the structure tends to approach a square-pyramidal structure with the SAL *cis* to each other. The solvent effect is interpreted as arising from preferred solvation of the square-pyramidal over the trigonal-bipyramidal structure, apparently working to counter the steric effect of the aminomethyl group. The temperature dependence of the splittings confirms this assumption. For the DPT chelates, the splittings and solution structure are insignificantly affected by either solvent or temperature. The ability to observe these changes, in spite of the fact that absorption spectra are essentially independent of substituents or solvent, is related to the much greater sensitivity of the pmr method.

Acknowledgments. G. N. L. thanks the National Science Foundation for a postdoctoral fellowship, during whose tenure this work was performed, and also expresses his appreciation to Professors H. H. Günthard and H. Primas for their hospitality during the stay at the Swiss Federal Institute of Technology. The authors also thank Professor W. von Philipsborn, Zurich University, for running a number of pmr spectra on his Varian HR-100 spectrometer and Dr. G. Rist for attempting to obtain the esr spectrum of one of our complexes. Useful discussions with Dr. P. L. Orioli and Professor W. Schneider are gratefully acknowledged.