

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 CH₃ 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-CH₃ 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 molecule²⁸ 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

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

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Schiff bases formed from benzaldehyde derivatives and bis(2-aminoethyl)amine (DENB₂) and bis(2-aminopropyl)amine (DPNB₂) 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 paper¹ 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.

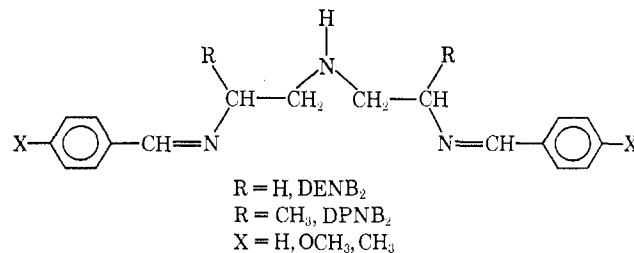
Furthermore, the pmr spectra were useful in detecting geometrical isomers and diastereoisomers in pseudo-tetrahedral complexes¹ and it was of interest to obtain corresponding structural information in the five-coordinate series.

Complexes of the type NiLX₂ where L is a Schiff base

(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.

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formed from aliphatic triamines and benzaldehyde derivatives of the type



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

TABLE I
 ANALYTICAL AND MAGNETIC DATA

Compound	% carbon		% hydrogen		% nitrogen		$\mu_{\text{eff}},^d$ BM
	Calcd	Found	Calcd	Found	Calcd	Found	
Ni[DENB ₂]Cl ₂ ^a	52.86	52.53	5.17	5.20	10.25	10.33	
Ni[DENB ₂]Br ₂	43.42	43.58	4.25	4.67	8.43	8.83	
Ni[DEN(4-CH ₃ B) ₂]Cl ₂	54.96	55.15	5.77	5.71	9.61	9.71	3.25
Ni[DEN(4-OCH ₃ B) ₂]Cl ₂ ^b	51.21	51.43	5.37	5.37	8.95	9.25	
Ni[DPNB ₂]Cl ₂ ^c	54.97	54.51	5.77	5.86	9.62	9.70	
Ni[DPNB ₂]Br ₂	45.70	45.50	4.79	4.82	8.00	8.09	3.14
Ni[DPN(4-CH ₃ B) ₂]Cl ₂	56.7	56.59	6.28	6.47	9.04	9.18	3.21
Ni[DPN(4-OCH ₃ B) ₂]Cl ₂ ^b	53.2	52.95	5.88	5.99	8.45	8.56	

^a Association degree $n = 0.97$. ^b Molar conductivity values in 1,2-dichloroethane are *ca.* $0.05 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. The molar conductivity for $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$ in the same solvent is $21 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. ^c Association degree $n = 1.01$. ^d Measured at 23° and corrected for diamagnetic contributions as indicated in ref 1.

Results

All the compounds are green, crystalline, paramagnetic ($\mu_{\text{eff}} \approx 3.2$ BM, Table I) substances decomposed by water. Their analyses (Table I) correspond to the general formula NiLX₂. Mull spectra show bands at 6000, 9000, and 16,000 cm^{-1} and some absorption at *ca.* 25,000 cm^{-1} on the tail of a charge-transfer band in the case of the chloro derivatives. Spectral data are reported in Table II and typical mull and solution spectra are shown in Figure 1. Molecular weight measurements in 1,2-dichloroethane show Ni(DENB₂)Cl₂ and Ni(DPNB₂)Cl₂ to be essentially monomeric.

The pmr spectra of chloroform-*d* solutions show large isotropic shifts. The spectra of three chloro derivatives are reported in Figure 2.

The DEN derivatives show only three reasonably sharp peaks at -30, -13, and -5 ppm from TMS assigned to the 2-, 4-, and 3-H resonances of the phenyl group, respectively, in analogy with the assignments proposed for the pseudotetrahedral complexes.¹ This is supported by the results for the substitution of 4-H by 4-CH₃ or 4-OCH₃.

The DPN derivatives show spectra with numerous and very broad peaks (see Figure 2). They have been assigned by comparison with DEN derivatives and by their behavior as a function of temperature. With the latter method the peaks due to aromatic hydrogen

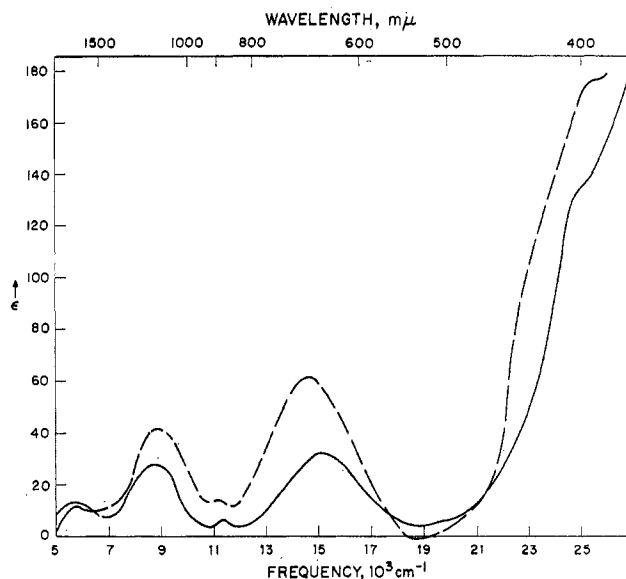


Figure 1.—Mull spectrum (----) and solution spectrum (—) in 1,2-dichloroethane of Ni[DENB₂]Cl₂.

atoms have been distinguished from those due to aliphatic ones owing to the difference in diamagnetic positions. In every DPN spectrum two or three very broad peaks of differing intensity are attributed to the aliphatic methyl groups since they are absent in the DEN spectra. The 3-H signal is always split into at

 TABLE II
 SPECTROSCOPIC DATA^a

Compound	Absorption max, cm^{-1} (ϵ_{molar} for solns)					
	5780	8850	11,230	14,700	19,700	25,200
Ni[DENB ₂]Cl ₂	5720 (13)	8700 (28)	11,370 (6)	15,160 (32)	19,800 sh	24,800 (131)
Ni[DENB ₂]Br ₂	5750	9160		14,900		
	5720 (11)	8970 (27)	11,100 (11)	15,400 (51)		
Ni[DEN(4-CH ₃ B) ₂]Cl ₂	<5000	8000	11,200	13,540	18,700	23,180, 28,200 sh
	5780 (17)	8660 (36)	11,400 (12)	15,280 (42)	20,300 sh	24,950 (124) sh, 28,800 (176)
Ni[DEN(4-OCH ₃ B) ₂]Cl ₂	5720	8850	11,230	15,150	19,950	
	5700 (14)	8660 (31)	11,300 (12)	14,900 (41)	19,700 sh	24,900 (114)
Ni[DPNB ₂]Cl ₂	5530	8700	11,300	15,000	19,850	
	5720 (14)	8580 (32)	11,370 (6)	15,000 (40)	19,900 sh	25,100 (136), 28,800 (162)
Ni[DPNB ₂]Br ₂	5680	8880	11,500	15,280	19,500	
	5670 (12)	8770 (32)		15,300 (61)		
Ni[DPN(4-CH ₃ B) ₂]Cl ₂		8550	11,400	15,400	19,900	24,950, 28,750
	5720 (13)	8620 (33)	11,380 (7)	15,170 (38)	19,800 sh	25,000 (119), 28,800 (172)
Ni[DPN(4-OCH ₃ B) ₂]Cl ₂	5780	8850	11,300	15,400	20,300	25,700
	5850 (12)	9000 (32)	11,370 (6)	15,170 (39)	19,800 sh	24,800 (121)

^a First line is for Nujol mull on filter paper; second line is for solutions in 1,2-dichloroethane.

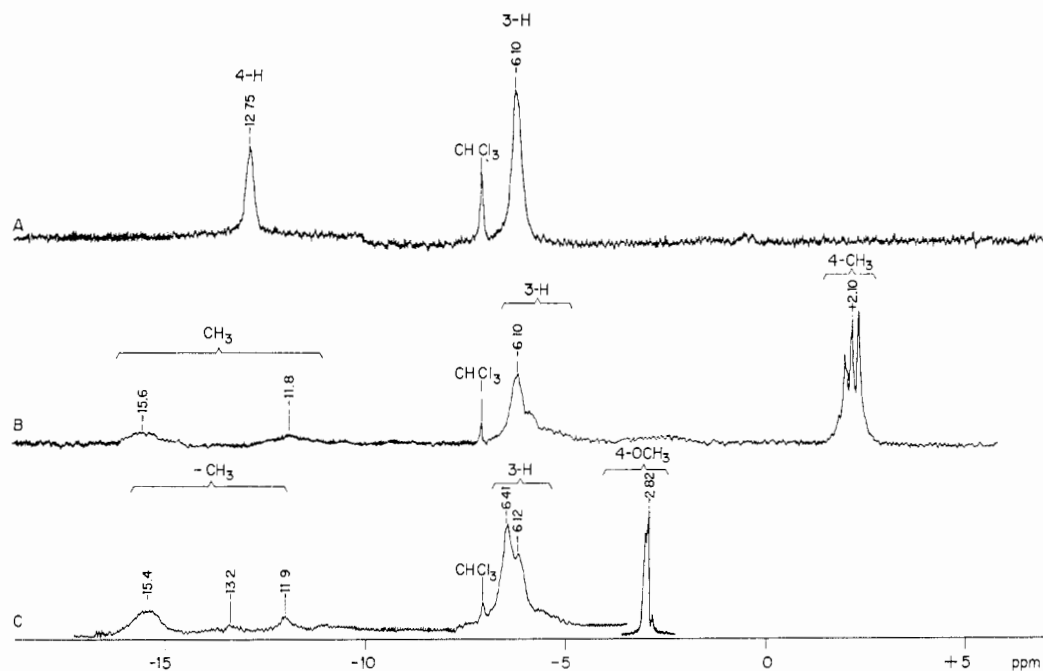


Figure 2—Pmr spectra in chloroform-*d* at 39° (ppm from TMS as internal reference): A, Ni[DENB₂]Cl₂; B, Ni[DPN(4-CH₃B)₂]Cl₂; C, Ni[DPN(4-OCH₃B)₂]Cl₂ (the -OCH₃ peak is recorded at a lower amplitude).

least two components while no splitting is observable for the broad 4-H resonance. The 2-H peak is located at *ca.* -30 ppm but is extremely broad so that no splitting can be detected. At -60° the 4-OCH₃ peaks remain unaltered while a broad absorption with two principal peaks is observed for 4-CH₃ resonance. In Table III the isotropic shifts at 39° for both the DEN and DPN compounds are reported.

Discussion

Stereochemistry of the Complexes.—The molecular weight and conductivity results indicate that the complexes are monomeric and undissociated eliminating the possibility of six-coordination. Also, the molar extinction coefficients are unreasonably large for an octahedral geometry.³ Were one nitrogen uncoordinated to produce a tetrahedral structure, no bands at frequencies as high as 25,000 cm⁻¹ would be expected.⁴ The electronic spectra may be explained on a basis of a five-coordinate structure.⁵ The bands at 6000, 9000, 16,000, and 24,000 cm⁻¹ observed for these complexes correlate well with those at 5000, 8500, and 16,400 cm⁻¹ found for NiSALMeDPT⁶ for which a five-coordinate structure with a chromophore of C_{2v} symmetry has been verified through X-ray analysis.⁷ The spectrum also corresponds closely to that of bis(pyridine-2-ethyl)aminenickel(II) complexes⁸ with bands at 9000, 15,000, and 24,000 cm⁻¹ which has been assigned a five-coordinate structure with an analogous NiN₃X₂

chromophore. On this basis the three bands between 6000 and 16,000 cm⁻¹ are assigned to transitions between levels arising from the ³F free-ion term and the band at 24,000 cm⁻¹ is assigned to ³F → ³P transitions.^{9,10}

Pmr Spectra.—The pmr spectra of these five-coordinate complexes, apart from the band multiplicities, are similar to those of the tetrahedral complexes,¹ but the 3-H peak exhibits a positive isotropic shift. At least qualitatively the benzaldimine resonance shifts are alternant. Unlike the aliphatic methyl resonances of the tetrahedral complexes which were shifted upfield, those of the DPN complexes are downfield (-11 to -15 ppm). A dominant dipolar interaction may account for the upfield shift in the former complexes.^{1,11} The two series have quite different geometries and magnetic anisotropy properties.

The multiplicity of peaks observed in the DPN (R = CH₃) complexes may be taken as evidence for the existence of different isomers or conformers in solution. The 4-OCH₃ and 4-CH₃ peaks are relatively sharp. The former resonance is split into three components while the 4-CH₃ resonance, which exhibits a large isotropic shift and is therefore quite sensitive to structural changes, is split into seven components. The other signals generally show lesser multiplicities owing to their smaller shifts, greater breadth, and possibly to coincidences. The intensities of the observed multiplets are generally different and are observed to change to some extent with temperature suggesting a change in relative populations of various species. For DPN complexes three isomers (1-3) are expected. When

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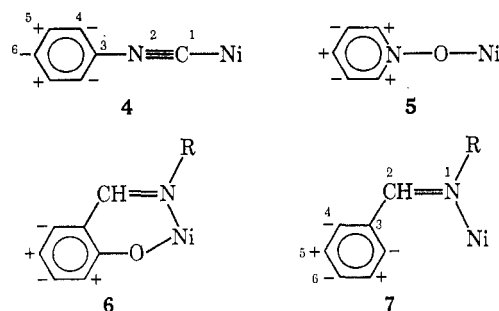
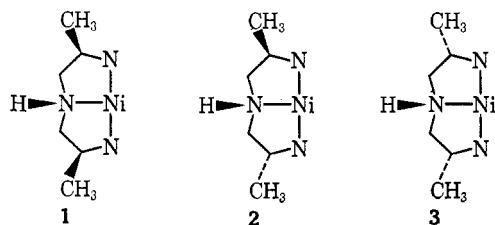
(10) C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1967).

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TABLE III
 ISOTROPIC SHIFTS OF FIVE-COORDINATE BENZALDIMINE-NICKEL COMPLEXES^{a,b}

Compound	Ring position			Aliphatic CH ₃
	2	3	4	
Ni[DENB ₂]Cl ₂	-23 vb	+1.03	-5.38	
Ni[DEN(4-CH ₃ B) ₂]Cl ₂		+1.28	(+4.75)	
Ni[DEN(4-OCH ₃ B) ₂]Cl ₂	-22 vb	+0.98	(+1.18)	
Ni[DENB ₂]Br ₂		+0.65	-5.95	
Ni[DPNB ₂]Cl ₂		+0.97, +1.30	-5.50	-14.8, -11.4
Ni[DPN(4-CH ₃ B) ₂]Cl ₂		+1.03, +1.28, +1.73	(+4.05, +4.20, +4.27, +4.40, +4.55, +4.62, +4.70)	-14.3, -10.8 vb
Ni[DPN(4-OCH ₃ B) ₂]Cl ₂		+0.72, +1.02	(+0.98, +1.05, +1.18)	-14.4, -12.2, -11.1
Ni[DPNB ₂]Br ₂		+1.33 b	-5.22	-15.0, -12.0

^a Measured from diamagnetic chemical shifts from TMS: 2-H, -7.62; 3-H, -7.14; 4-H, -7.37; 4-CH₃, -2.30; 4-OCH₃, -3.87; CH₃ of DPT, -1.02. ^b Values in parentheses are for 4-CH₃ protons of the aromatic ring.



aliphatic chelate chain conformations and, less likely, geometrical isomerism associated with the N=C bond are considered, there are more than sufficient possibilities to account for the observed signal multiplicities. An explicit assignment of the peaks is impossible; nevertheless the results provide evidence for the existence of several isomers or conformers in solution.

Spin Delocalization.—Although dipolar shifts and σ -spin delocalization very likely contribute to the shifts observed here and in the previous paper, there is definite evidence for π -spin delocalization.¹² For the five-coordinate complexes the isotropic shifts observed for the protons of the aromatic group alternate such that the 2-H and 4-H signals are shifted downfield while the 3-H is shifted upfield. The reverse is true for the methyl substitution at the same positions.

Paramagnetic nickel complexes containing aromatic six-membered rings which give evidence for π -spin delocalization from their isotropic shifts contain ligands such as aryl isocyanides,¹³ heterocyclic amine N-oxides,¹⁴ salicylaldimines,¹⁵ and arylimines. Prototype structures 4–7 are shown for these systems. The signs indicate the direction of the observed shifts of the resonance of a proton attached to the various aromatic carbon atoms (upfield positive) and, hence, the experimental sign of the spin density present at each aromatic carbon atom.

In the case of salicylaldimine complexes 6, both the valence bond (VB)^{15a} and the McLachlan-Hückel molecular orbital (MHMO)¹⁶ are in apparently reasonable agreement with the observed spin delocalization,

that is, if one assumes some fraction of α spin (electron aligned with applied magnetic field) resides in the highest filled π MO (HFMO). Likewise good qualitative agreement was obtained for the pyridine N-oxide¹⁷ systems 5 with simple Hückel MO calculations for α -spin delocalization in the HFMO.¹⁸

Unfortunately, the apparent satisfactory agreement between theory and experiment does not extend to the remaining systems—MHMO calculations for aryl isocyanides 4 and the present arylimines 7 are in complete disagreement with α -spin delocalization in either the HFMO or the lowest vacant MO (LVMO), as shown in Table IV. The predicted shifts have exactly the opposite signs in every case. Qualitative agreement between calculation and experiment can be achieved if β -spin density is delocalized on the aromatic fragment (the unpaired electrons on Ni having α spin). This *could* occur through a σ - π correlation, *i.e.*, assuming that some unpaired electron of spin α in the Ni-N σ bond induces β -spin density on the π orbital on nitrogen which is then delocalized into the aromatic fragment. That this is not an altogether satisfying explanation is illustrated by a comparison of salicylaldimines with arylimines (structures 6 and 7). If the point of attachment of the imine substituent common to both is used as a point of reference, the observed isotropic shift patterns are identical. Indeed at room temperature the isotropic shifts of the present arylimine ligands 7 are only slightly smaller and show a downfield bias when

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(16) G. N. La Mar, *Mol. Phys.*, **12**, 427 (1967).

(17) R. W. Kluiber and W. DeW. Horrocks, Jr., *J. Am. Chem. Soc.*, **88**, 1399 (1966).

(18) A tacit assumption of such a calculation is that the spin arises on the ligand through a direct metal-ligand interaction and exists in a particular π MO (generally the HFMO). For π -spin density which occurs via σ - π nonorthogonality [see R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, **6**, 430 (1967); R. S. Fitzgerald and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 2879 (1967)] such an assumption is not necessarily warranted and calculations so based may be invalid.

TABLE IV
CALCULATED SPIN DENSITIES^a

Position	LVMO		HFMO	
	HMO	MHMO	HMO	MHMO
	Benzaldimine ^b			
1	0.257	0.291	0.264	0.378
2	0.219	0.207	0.027	-0.070
3	0.106	0.097	0.221	0.267
4	0.111	0.133	0.084	0.066
5	0.015	-0.041	0.045	0.001
6	0.166	0.221	0.229	0.291
	Phenylisonitrile ^c			
1	0.485	0.718	0.238	0.312
2	0.164	0.013	0.128	0.075
3	0.067	0.068	0.164	0.179
4	0.077	0.067	0.107	0.115
5	0.009	-0.029	0.027	-0.028
6	0.112	0.125	0.201	0.261

^a Spin densities were calculated with a Hückel molecular orbital calculation (HMO) and then spin correlation (MHMO) was introduced through polarizability according to McLachlan ($\lambda = 1.2$): A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960). ^b See structure 7. ^c See structure 4.

compared to the salicylaldimine complexes 6. Nevertheless, an application of MHMO theory requires β -spin delocalization *via* an indirect mechanism in the former and α -spin delocalization for the latter class of compounds. It is clear from the above discussion that it is possible to obtain agreement between theory and experiment for almost any observed shift pattern. The conclusion must be that at present such agreement must be taken *cum grano salis*.

Effect of Coordination Number.—A comparison of

the isotropic shift patterns for the four- and five-coordinate complexes containing benzaldimine groups shows a similarity between the two systems with the former exhibiting the larger downfield shifts. The alternation expected for π -spin delocalization is more evident in the five-coordinate complexes, *viz.*, the upfield shift of the 3-H resonance. Table V shows a

TABLE V
ISOTROPIC SHIFT PATTERNS OF BENZALDIMINE PROTONS
IN FOUR-, FIVE-, AND SIX-COORDINATE COMPLEXES^a

Position	Isotropic shifts		
	Four	Five	Six
2	-4.6	-5.0	-7.7
3	-0.5	+0.2	+2.2
4	-1.8	-1.1	-0.6
4-CH ₃	+1.0	+1.0	+1.0

^a The isotropic shifts are normalized to 4-CH₃ isotropic shifts.

comparison of the isotropic shifts (normalized to the 4-CH₃) for the present four- and five-coordinate complexes as well as six-coordinate complexes obtained as adducts of benzaldimine with nickel acetylacetonate.¹⁹ A minor effect on the isotropic shift patterns of changes in coordination number is evident, as was found for salicylaldimine systems.^{15,16} This minor effect may be indicative of the stereochemistry of the complexes.

Acknowledgment.—We wish to thank Peter Kollman for assistance with computer calculations.

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Novel Polynuclear Iron Carbonyl Complexes Containing Phosphorus and Arsenic

By W. R. CULLEN, D. A. HARBOURNE, B. V. LIENGME, AND J. R. SAMS

Received October 9, 1969

Novel polynuclear iron carbonyl complexes have been isolated from the reactions between the iron carbonyls and the ligands

$DC=CD(CF_2)_nCF_2$ ($D = As(CH_3)_2$, $n = 1$, $fars$; $D = (C_6H_5)_2P$, $n = 2$, f_6fos). The complexes have been found to possess the stoichiometry $farsFe_3(CO)_{10}$, $farsFe_3(CO)_9$, $As_2(CH_3)_2CH_2Fe_3(CO)_9$, and $f_6fosFe_3(CO)_7$ and their structures have been investigated using various spectroscopic techniques. Some attempt has been made to assign lines in the complicated Mössbauer spectra of $farsFe_3(CO)_9$ and $As_2(CH_3)_2CH_2Fe_3(CO)_9$.

Introduction

There has been, in recent times, considerable interest in the polynuclear metal carbonyl species from the point of view of structure, stability of metal-metal bonds, and carbonyl displacement.¹ In most cases replacement of carbonyls has led to a degradation of the metal atom arrangement although some ligands have been able to

replace carbonyl groups and leave the rest of the molecule intact. The examination of the features and stabilities of these complexes so formed is not only of intrinsic interest but can be valuable in obtaining information about the parent compound.

In the case of the group VIII carbonyls of iron, ruthenium, and osmium the iron-iron bond is weak² and at the time this work started only one derivative of

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