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Determination of Geometrical Isomers in Schiff Base Complexes by Proton Magnetic Resonance. Tetrahedral Nickel Halide Complexes of Ligands Derived from 1,2-Diaminoethane and Aceto- and Benzophenones

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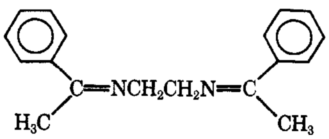
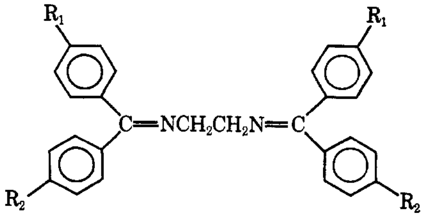
Earlier pmr studies in these laboratories of paramagnetic nickel halide complexes of chelating Schiff base ligands derived from aliphatic polyamines and benzaldehyde derivatives were aimed at establishing a criterion of stereochemistry based on the observed isotropic shift patterns.[2] The results of these investigations, together with a subsequent X-ray structure determination of one of the four-coordinate species,[3] when coupled with the findings presented here, enable us to place the pmr assignments on a firm basis and to formulate a diagnostic pmr criterion of stereochemistry in complexes of this type. The present note deals with the pmr spectra of four-coordinate nickel(II) complexes of the type $NiLX_2$ ($X = Br$, I) where L is the Schiff base formed by reaction of 1,2-diaminoethane (en) with acetophenone (Ap) or derivatives of benzophenone (Bp). The abbreviations for the ligands are indicated as



$(Ap)_2en$



$R_1 = R_2 = H$, $(Bp)_2en$; $R_1 = R_2 = CH_3$, $(4,4'\text{-}CH_3Bp)_2en$;

$R_1 = R_2 = OCH_3$, $(4,4'\text{-}OCH_3Bp)_2en$; $R_1 = X$ ($X = Cl, CH_3$),

$R_2 = H$, $(4\text{-}XBp)_2en$

Experimental Section

The ketones, 1,2-diaminoethane, and nickel salts are commercially available and were used without further purification. The ketimine ligands were isolated by the general procedure of refluxing 0.10 mol of the ketone with 0.05 mol of 1,2-diaminoethane (en) for 20–60 hr in toluene with a trace of PCl_5 added. The volume of toluene was reduced under reduced pressure at 50° and the remaining oil was allowed to stand until crystals formed, usually in less than 1 day. The product was filtered and dried *in vacuo* and recrystallized from ethanol if the product appeared impure. The complexes were prepared by combining equimolar solutions of the ligand in boiling 1-butanol and nickel halide, boiled ~10 min in the same solvent. The volume of solution was reduced by boiling, a small amount of cyclohexane was added to promote crystallization, and the product was collected by filtration under nitrogen and dried *in vacuo*.

The analyses were performed by Baron Consulting Co., Orange, Conn. Pmr spectra were recorded on a Varian A-60-A spectrometer operating at 37° with chloroform-*d* as solvent and TMS as internal reference.

Results

The analyses of the complexes are reported in Table I and they conform to the composition $NiLX_2$. They closely resemble the tetrahedral complexes previously prepared[2a,b] in their purple-violet color, solubility in polar organic solvents, and moisture sensitivity.

TABLE I

ANALYTICAL DATA FOR COMPLEXES

Compound	% carbon		% hydrogen		% nitrogen	
	Calcd	Found	Calcd	Found	Calcd	Found
$Ni[(Ap)_2en]Br_2$	44.77	44.49	4.17	4.37	5.80	5.77
$Ni[(Ap)_2en]I_2$	37.47	37.48	3.49	3.62	4.85	5.13
$Ni[(Bp)_2en]Br_2$	55.40	54.98	3.98	4.29	4.61	4.57
$Ni[(Bp)_2en]I_2$	47.97	47.83	3.45	3.66	3.99	4.10
$Ni[(4,4'\text{-}CH_3Bp)_2en]Br_2$	57.96	56.92	4.86	5.01	4.22	4.42
$Ni[(4,4'\text{-}CH_3Bp)_2en]I_2$	50.76	50.15	4.26	4.39	3.70	3.79
$Ni[(4,4'\text{-}OCH_3Bp)_2en]Br_2$	52.85	52.28	4.43	4.58	3.85	3.93
$Ni[(4\text{-}ClBp)_2en]Br_2$	49.75	49.62	3.28	3.49	4.14	4.34
$Ni[(4\text{-}CH_3Bp)_2en]Br_2$	56.73	56.44	4.44	4.49	4.41	4.48

Typical pmr spectra and Ap and Bp complexes are illustrated in Figure 1. The acetophenone complexes exhibit four resonances, three are downfield at −15.18, −11.12, and −7.65 ppm and one is quite broad and upfield at +8.43 ppm from TMS. The upfield peak is assigned to the imine CH_3 on the basis of its broadness and its absence in the spectra of the Bp complexes (*vide infra*). The peak at −7.65 ppm is assigned to the 4-H proton on the basis of relative intensity: $^1/_2$ as compared with the other downfield resonances. Of the two remaining resonances, the one at −15.18 ppm is assigned to the 2-H proton because it is broader than that at −11.12 ppm which is hence assigned to the 3-H proton.

The spectra of the benzophenone (Bp) complexes show many resonances both up- and downfield from TMS (see Figure 1). These can be assigned by essentially superimposing the spectra of the previously reported benzaldimine (B) complexes and the acetophenone complexes discussed above (leaving out the peak assigned to the imine CH_3). With the asymmetric ($R_1 \neq R_2$) Bp complexes it is noted that 4-H and 4-CH_3 peaks occur with both Ap and B assignments. Also, many of these peaks appear as multiplets.

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[2] (a) I. Bertini, D. L. Johnson, and W. DeW. Horrocks, Jr., *Chem. Commun.*, 1471 (1969); (b) I. Bertini, D. L. Johnston, and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **9**, 693 (1970); (c) I. Bertini, D. L. Johnston, and W. DeW. Horrocks, Jr., *ibid.*, **9**, 698 (1970).

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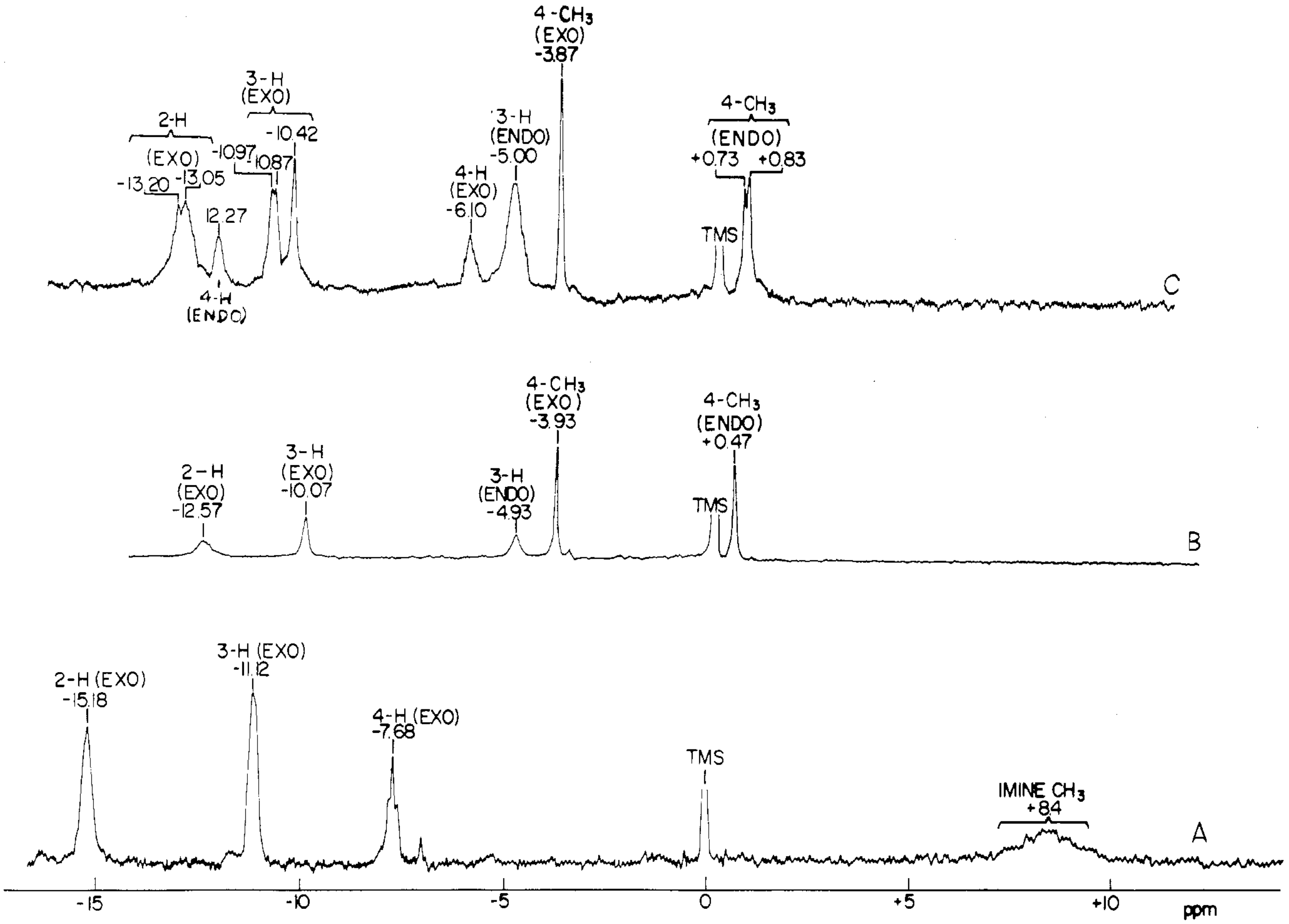


Figure 1.—Pmr spectra in chloroform-*d* at 37° (ppm from TMS as internal reference): A, Ni[$(Ap)_2$en]Br_2; B, Ni[$(4,4'\text{-}CH_3Bp)_2$en]Br_2; C, Ni[$(4\text{-}CH_3Bp)_2$en]Br_2.

Table II

Isotropic Shifts (ppm)[a,b]

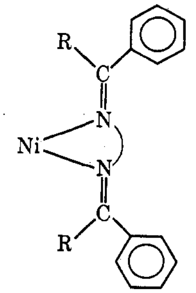
	Ring position						
	Endo phenyl			Exo phenyl			
Compound	2	3	4	2	3	4	Imine CH_3
Ni[$(Ap)_2$en]Br_2				−7.56	−3.98	+0.31	+11
Ni[$(Ap)_2$en]I_2				−5.98	−3.69	−0.20	+24
Ni[$(Bp)_2$en]Br_2[c]		+2.19	−5.18	−5.70	−3.78	+1.04	
Ni[$(Bp)_2$en]I_2[d]		+3.82	−2.98	−3.93	−3.21	+1.69	
Ni[$(4,4'\text{-}CH_3Bp)_2$en]Br_2		+2.21	(+2.77)	−4.95	−2.93	(−1.63)	
Ni[$(4,4'\text{-}CH_3Bp)_2$en]I_2	−18 vb	+3.69	(+3.15)	−4.21	−3.24	(−1.80)	
Ni[$(4,4'\text{-}OCH_3Bp)_2$en]Br_2	−26 vb	+1.57	(+0.21)	−5.41	−2.64	(−0.41)	
Ni[$(4\text{-}ClBp)_2$en]Br_2		+2.01	−5.13	−5.53 −5.41	−3.89 −3.84 −3.36	+1.10	
Ni[$(4\text{-}CH_3Bp)_2$en]Br_2		+2.14	(+3.13 +3.03) −4.90	−5.60 −5.43	−3.83 −3.73 −3.28	(−1.57) +1.27	

[a] Measured from diamagnetic chemical shifts from TMS: 2-H, −7.62; 3-H, −7.14; 4-H, −7.37; 4-CH_3, −2.30; 4-OCH_3, −3.87; CH_3 of Ap, −2.13. [b] Values in parentheses are for CH_3 protons attached to the aromatic ring. [c] Additional peak at −7.55 ppm from TMS, possibly decomposition product. [d] Additional peak at −1.53 ppm from TMS.

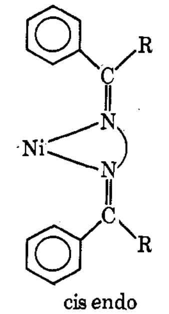
The isotropic shifts from the diamagnetic positions are reported in Table II.

Discussion

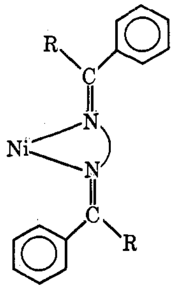
Acetophenone Complexes.—A comparison of the isotropic shift patterns for the aromatic protons of the Ap and B complexes shows these to be very different. In the B complexes,[2] the 2-H proton resonance is very broad (spreading over 6–8 ppm) and the isotropic shift is far downfield (~25–30 ppm) while in the Ap complexes the 2-H isotropic shift occurs much less downfield (~7 ppm) and is comparatively sharp ($\Delta\nu_{1/2}$ ~0.25 ppm). The 3-H proton resonance shift in the four-coordinate B complexes is slightly downfield (~2 ppm) (this resonance is found slightly upfield in the case of the five-coordinate species) while the Ap 3-H shift is downfield 3–4 ppm. The 4-H isotropic shift of the B complexes is downfield ~10 ppm while the Ap 4-H resonance is essentially unshifted from its diamagnetic position. These spectral differences provide direct evidence for different geometrical environments for the phenyl groups of the Ap and B complexes. The isomers previously discussed[2b] (**1**–**3**) would be consistent with this requirement. The number and multiplicity of the observed peaks in the pmr spectra of the en Schiff base complexes for both the B and Ap systems rule out possibility **3** (trans). The Bp complexes, wherein one phenyl must be exo and one endo, have spectra interpretable as the sum of B and Ap spectra. This supports the hypothesis that the Ap complexes have only been prepared in one of the forms **1** or **2** while the B complexes studied are only of the other structure.



cis exo
1



cis endo
2

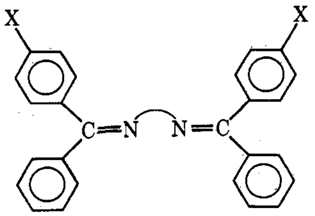


trans
3

A recent X-ray structure determination shows that $Ni[(4-CH_3B)_2$-*meso*-bn$]Br_2$ has the configuration **2** (cis endo).[3] Because of the similarity of the pmr spectra of the en–, pn–, and bn–B complexes[2] it follows that the en derivatives of benzaldehyde are also cis endo. Hence the Ap complexes are assigned configuration **1** (cis exo).

It is noted that the assignments of these conformations are generally consistent with the modes of spin delocalization used to describe pmr contact shifts. The plane of the endo-phenyl group has been shown to be roughly parallel to the C—C═N plane.[3] This would make conjugation and hence π delocalization very likely for the endo phenyl. This is generally confirmed by the alternation of the isotropic shifts noted with the B complexes. For the exo phenyl, interactions with chelate ring hydrogen and endo-methyl groups ($(Ap)_2$en complexes) or ring hydrogens and endo-phenyl groups ($(Bp)_2$en complexes) would tend to prevent this phenyl from conjugating with the C—C═N moiety. Hence σ delocalization might be expected to dominate the exo phenyl; the decreasing negative shifts observed as one goes farther from the metal[4] tends to support this mechanism.

Benzophenone Complexes.—As was noted above, the pmr spectra of the Bp complexes can be interpreted as a combination of the B and Ap spectra with protons assigned similarly. Since one phenyl on Bp must be exo and the other endo, this is consistent with the assignment of Ap and B complexes to isomers **1** and **2**. It is noted that the 4-H exo-phenyl isotropic shift is slightly positive (~1 ppm). One may invoke a σ–π spin polarization mechanism to explain this, since the σ delocalization would be expected to be small this far from the metal and hence a small π delocalization may dominate. However, it is noted that, even in such strictly σ-delocalizing systems as quinuclidine, a positive shift is observed for atoms removed five bonds from the metal.[5] Also, the slightly positive isotropic shifts of the endo 3-H proton of Bp, where the B complexes had slightly negative shifts, can be attributed to the difference in the ligands.



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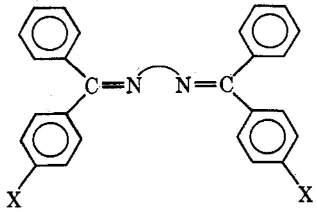

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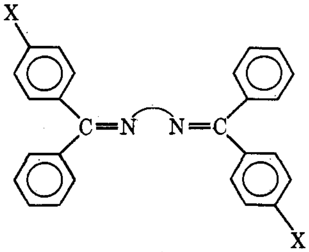

6

In the case of the asymmetric Bp complexes $(4-XBp)_2$en (X = Cl, CH_3), three isomers of types **4**–**6** must be considered. Isomers **4** and **5** should give rise to two resonances for each aromatic ring position—one for a proton on the endo phenyl and one for the proton on the exo phenyl. Isomer **6** would be expected to give rise to four resonances for each ring position—two for a proton on the endo phenyl since they are no longer equivalent and likewise two resonances for the exo-phenyl proton. The exo and endo protons are separated and assigned as with the symmetrical Bp complexes. The spectrum of the $4-CH_3Bp$ complex shows three CH_3 peaks: one of intensity ~2 corresponding to the exo CH_3 and two of intensity 1 corresponding to the endo CH_3. This is diagnositic of a mixture of isomers **4**–**6** in an almost statistical ratio (1:1:2), the two exo-CH_3 peaks being presumably not resolved. Three peaks of intensity 2:1:1 for the exo 3-H support this hypothesis. For the other peaks only partial or no resolution occurs. Variable-temperature pmr measurements show no appreciable change in the intensity of the peaks between +40 and −40°. For the $4-CH_3Bp$ complex there is no collapse of the two endo-CH_3 resonances even at 150° in nitrobenzene. This indicates that there is no rapid rotation about the C═N bond on the nmr time scale. The possibility of a slow equilibrium between conformers **4** and **6** cannot be completely

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ruled out by variable-temperature measurements because the isomer distribution may be relatively insensitive to small differences in temperature.

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Reaction Mechanism of Cyclopentadienyliron Tricarbonyl Cation with Cyanate Ion[1]

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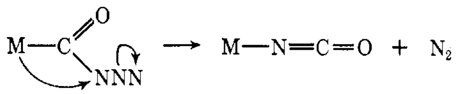
The reaction of metal carbonyl compounds with azide ion to yield isocyanato complexes was first reported[3] for $W(CO)_6$

$$W(CO)_6 + N_3^- \longrightarrow W(CO)_5(NCO)^- + N_2$$

Since that time similar reactions of $Mo(CO)_6$,[4] $Cr(CO)_6$,[4] $C_5H_5Fe(CO)_3^+$,[5] $C_5H_5Ru(CO)_3^+$,[6] and $Re(CO)_5(NH_2CH_3)^+$[7] have been carried out. Kinetic studies[4] suggest that the first step of the reaction is N_3^- attack at a carbonyl carbon atom. The resulting intermediate then rearranges with loss of N_2 to form the isocyanate product



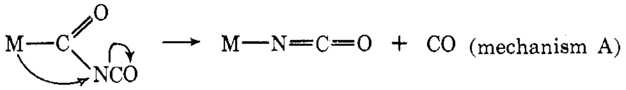
By analogy the reaction of $C_5H_5Fe(CO)_3^+$ with azide

$$C_5H_5Fe(CO)_3^+ + N_3^- \longrightarrow C_5H_5Fe(CO)_2(NCO) + N_2$$

was postulated to proceed by the same mechanism.[5] The isoelectronic cyanate ion also reacts with the cation to yield the isocyanato product. There are two possible mechanisms by which this reaction

$$C_5H_5Fe(CO)_3^+ + NCO^- \longrightarrow C_5H_5Fe(CO)_2(NCO) + CO \quad (1)$$

could occur. Mechanism A is analogous to that suggested for the azide reaction; *i.e.*, NCO^- attack occurs at the carbonyl carbon to give an intermediate which rearranges with loss of CO to give the product

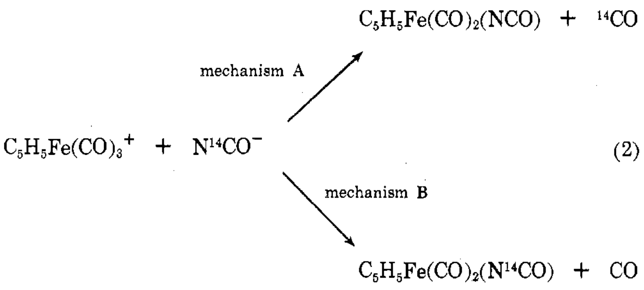


In this mechanism, it is the CO which was originally in the NCO^- ion that is evolved.

The second mechanism, B, is the simple substitution of a CO ligand by the NCO^- ligand. This might occur by direct attack of NCO^- on the metal or by dissociation of a CO group from the complex followed by rapid coordination of NCO^-. In either case it is a CO group on the metal which is evolved. Mechanism B must operate, *e.g.*, in the reactions of $C_5H_5Fe(CO)_3^+$ with Cl^-, Br^-, I^-, CN^-, and NCS^-, to give $C_5H_5Fe(CO)_2X$ accompanied by CO evolution.[5,8] In an attempt to determine whether these reactions proceeded by an associative or dissociative mechanism, the reactions with Cl^-, Br^-, and I^- were examined kinetically.[9] Unfortunately the reactions were all too fast to follow at 25° in acetone solvent.

Since NCO^- is similar to the other ions reacting by mechanism B, it appeared likely that it too would react by this general pathway. On the other hand, it is isoelectronic with N_3^- and like N_3^- has a possibility of reacting by mechanism A.

The purpose of the studies reported in this note was to establish the mode of reaction. This was accomplished by carrying out reaction 1 using ^{14}C-labeled NCO^-. The ^{14}C label would be found in the evolved CO if reaction 1 proceeded by mechanism A and in the $C_5H_5Fe(CO)_2(NCO)$ if by mechanism B. (See eq 2.) The results indicate that the reaction proceeds by mechanism B.



To eliminate the possibility that $C_5H_5Fe(CO)_2(NCO)$ is formed by some entirely different pathway and then exchanges its isocyanate group with free $N^{14}CO^-$, the exchange reaction

$$C_5H_5Fe(CO)_2(NCO) + N^{14}CO^- \longrightarrow C_5H_5Fe(CO)_2(N^{14}CO) + NCO^- \quad (3)$$

was also examined. It was found that very little exchange had occurred during the time used for reaction 2.

Experimental Section

Materials.—The $[C_5H_5Fe(CO)_3]PF_6$ was synthesized as described previously.[10] Copper(I) sulfate–β-naphthol solution was prepared according to the literature.[11] The $C_5H_5Fe(CO)_2(NCO)$ was synthesized from $[C_5H_5Fe(CO)_3]PF_6$ and KNCO as described previously[5] except THF instead of acetone was used as the solvent. The $KN^{14}CO$ was used as obtained from the New England Nuclear Corp. All solvents used were reagent grade. The

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] Fellow of the Alfred P. Sloan Foundation, 1970–1972.

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