Diastereoisomeric Four-Coordinate Complexes. V.[1] Pseudo-Tetrahedral Complexes of Controlled Absolute Configuration. Configurational Interconversion of Nickel(II) Complexes without Racemization

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Abstract: The stereochemistry of four-coordinate metal(II) complexes derived from 2,2′-bis(salicylideneamino)-biphenyl [M(X-sal)$_2$bp, M = Co, Ni], 2,2′-bis(salicylideneamino)-6,6′-dimethylbiphenyl [M(X-sal)$_2$bmp, M = Ni, Pd, Zn], and 2,2′-bis(salicylideneamino)-1,1′-binaphthyl [Ni(X-sal)$_2$bn] has been investigated in solution. A previous claim that ligands of the first two types can, by virtue of steric constraints, form only pseudo-tetrahedral species has been vitiated by the isolation of Pd(3*s*Bu-sal)$_2$bmp and a variety of crystalline, diamagnetic Ni(II) complexes. In solution it is demonstrated by ligand-field spectral and proton contact shift studies that Ni(II) complexes of the three series undergo a planar $\rightleftharpoons$ tetrahedral equilibrium which lies heavily toward the planar side. When these complexes are prepared from the racemic diamine and racemic 3-*sec*-butyl-5-methylsalicylaldehyde, three azomethine proton and 5-methyl signals are observed in every case. By controlling the absolute configurations of the diamine and 3-*sec*-butyl group, it is shown that these signals arise from the diastereoisomers $\Delta(+,+) \equiv \Lambda(-,-)$, $\Delta(-,-) \equiv \Lambda(+,+)$ (active), and $\Delta(+,-) \equiv \Lambda(+,-)$ (*meso*) of the pseudo-tetrahedral form. The absolute configuration (Δ, Λ) at the pseudo-tetrahedral metal is controlled entirely by the configuration (*R*, *S*) of the diamine with the following stereochemical correlations operative: $R \leftrightarrow \Delta$, $S \leftrightarrow \Lambda$. Preparation of pseudo-tetrahedral complexes from resolved diamines therefore results in completely stereospecific formation of a given absolute configuration at the metal. Proton resonance measurements up to 90° reveal that the signals of the two active forms of the Ni(II) complexes (*e.g.*, $\Delta(+,+)$ and $\Lambda(+,+)$) are not averaged, indicating that the dynamic structural conversion occurs without racemization at the metal. This behavior is contrasted to that of analogous bis-chelate Ni(II) complexes for which two signals of the corresponding active isomers cannot be observed. The contribution of the entropy change to the values of ΔF for the planar $\rightarrow$ tetrahedral conversion of Ni(II) complexes is discussed.

Pseudo-tetrahedral bis-chelate metal(II) complexes of the general type M(A–B)$_2$ are enantiomeric at the metal ion and can in principle exist in two absolute configurations, Δ and Λ, which have been defined previously.[3] Despite the fact that a large number of such complexes have been prepared, at present there is a virtually complete lack of information concerning their absolute configurations. The more credible reported resolutions or preparations of diastereoisomeric salts,[4–6] principally those of Be(II) and Zn(II), invariably lead to the conclusion that the enantiomers are of very limited optical stability, thereby rendering difficult their isolation in the configurationally pure condition. Such configurational instability may be another manifestation of the now well-recognized stereochemical mobility of four-coordinate metal(II) complexes which is clearly demonstrated in several series of bis-chelate Co(II)[7,8] and Ni(II)[7–13] complexes. These species exhibit the dynamic planar $\rightleftharpoons$ tetrahedral equilibrium in solutions of noncoordinating solvents with the lifetime of the Ni(II) stereoisomers being on the order of $\sim 10^{-3}$ sec or less. Additional evidence suggestive of low configurational stability of pseudo-tetrahedral complexes follows from recent proton resonance studies.[1,3] Despite the fact that the proton contact shifts of Ni(II) complexes are highly sensitive to subtle structural differences, it has not been possible to observe separate sets of signals of bis(N-(+ or −)-(*R*)-salicylaldimino) or bis(N-(+ or −)-(*R*)-β-ketoamino) complexes,[3] even at low temperature and in the absence of a detectable amount of the planar form, although the chemical shifts of the $\Delta(+,+)$ and $\Lambda(+,+)$ or $\Delta(-,-)$ and $\Lambda(-,-)$ diastereoisomers are in principle different. Further, the chemical-shift difference between the two methyl groups in *meso*-bis(N-α-phenethylsalicylaldimino)-zinc(II) is measurable only below $\sim$20°, indicating that above this temperature a rapid $\Delta(+,-) \rightleftharpoons \Lambda(+,-)$ interconversion averages the environments of the methyl groups.[1]

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[1] Part IV: M. J. O'Connor, R. E. Ernst, J. E. Schoenborn, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 1744 (1968).

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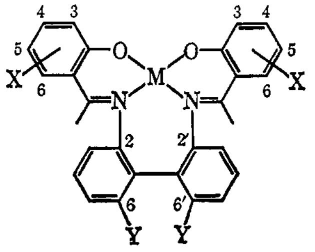
The few available measurements of racemization rates in noncoordinating solvents[5,6] indicate a first-order intramolecular path consistent with the interconversions $\Delta \rightleftarrows \Lambda$ produced by metal–ligand bond rupture or $\Delta \rightleftarrows$ planar $\rightleftarrows \Lambda$ in which no bonds need be considered formally broken, but do not distinguish between these possibilities. Regardless of the racemization mechanism, however, the foregoing observations show that even in noncoordinating solvents chelating ligands which can effect formation of the pseudo-tetrahedral structure do not simultaneously promote the stability of the absolute configuration at the metal. In connection with our present objective of attempting to detect the two absolute configurations in diastereoisomeric complexes by proton resonance and to examine their rates of interconversion, we have focused attention on the complexes of simplified general structure **1**.



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The 2,2′-bis(salicylideneamino)biphenyl ligand system in **1** potentially has two important structural consequences. First, it is able to dispose itself in a relatively strainless manner so as to form an O_2N_2 pseudo-tetrahedron, a property first recognized by Lions and Martin,[14] who prepared Be(II) and Cu(II) complexes. Second, the use of 2,2′-diamino-6,6′-dimethylbiphenyl should lead to complexes (**1**, Y = CH_3) of high configurational stability in the pseudo-tetrahedral form. This expectation is based on the very high activation energy (45 kcal/mole[15]) and the calculated rate constant of $\sim 10^{-22}$–10^{-23} sec^{-1} at 300°K for racemization of the biphenyl. Each enantiomer of the diamine should then produce a single absolute configuration at the metal. Further, because the absolute configurations of these enantiomers are known,[16] the configurations of the complexes **1** are unequivocally determined. This stereochemical correlation is illustrated in this work, and it is demonstrated that diastereoisomeric Ni(II) complexes of type **1** differing only in absolute configuration at the metal can be detected by proton resonance and do not racemize in the course of undergoing the planar $\rightleftarrows$ tetrahedral structural change. A series of new Co(II), Ni(II), Pd(II), and Zn(II), complexes of type **1** have been prepared. Throughout this report such complexes are designated as M(X-sal)$_2$B in which B = bp and bmp represent the 2,2′-biphenylyl and 6,6′-dimethyl-2,2′-biphenylyl groups, respectively. In addition several Ni(II) complexes analogous to **1** but containing a 2,2′-(1,1′-binaphthyl) bridging group (B = bn) have been prepared. M(X-sal)$_2$B complexes were prepared from inactive components unless the asymmetric (X = *sec*-Bu = *s*Bu) or dissymmetric (B) ligand portions are prefixed with (+, −) or (*R*, *S*) (equivalently,[16] +, −), respectively. The signs refer to the sign of $[\alpha]\text{D}$ of the parent salicylaldehyde or diamine. Bis(salicylaldimine)metal(II) complexes are abbreviated as M(X-R-sal)$_2$, in which R is the nitrogen substituent.

Experimental Section

Preparation of Compounds. (a) Biphenyldiamines. 2,2′-Diaminobiphenyl was prepared by reduction of the corresponding 2,2′-dinitro compound with powdered tin and concentrated hydrochloric acid:[17] mp 77–79°, lit.[17] 78–79°. 2,2′-Dinitro-6,6′-dimethylbiphenyl was obtained by modification of a published procedure.[18] 2-Iodo-6-nitrotoluene[18] was mixed with twice its weight of acid-washed, ignited sand. The mixture was heated to 170° and an equal weight of copper–bronze (Venus-United States Bronze Powders, Inc.) was added at a rate such that the temperature of the molten reaction mixture did not exceed 200°. When all of the copper bronze had been added, the mixture was maintained at 200° for a further 30 min; then it was cooled to room temperature. The product was extracted as previously described[18] and subjected to catalytic hydrogenation (1 atm) in ethanol over platinum black. The spent catalyst was removed by filtration and 2,2′-diamino-6,6′-dimethylbiphenyl was precipitated from the reaction mixture by addition of water. The product was obtained as white crystals from absolute ethanol, mp 136–137°, lit.[18] 136°.

The *R* and *S* enantiomers of 2,2′-diamino-6,6′-dimethylbiphenyl were resolved using (+)- and (−)-tartaric acid, respectively;[19] $[\alpha]^{23}\text{D} \pm 46°$ (*c* 2.1, absolute ethanol); lit.[16] +48°, −47° (absolute ethanol).

(b) **2,2′-Diamino-1,1′-binaphthyl.** β-Naphthylamine was converted to azo-2,2′-naphthalene,[20] which was then treated with stannous chloride and hydrogen chloride[21] to yield the diamine. Recrystallization from 95% ethanol afforded the product as white crystals, mp 190–192°; lit.[21] 193°. Resolution was effected with *d*-camphorsulfonic acid according to the method of Kuhn and Goldfinger:[22] $[\alpha]^{30}\text{D} +154°$ (*c* 3.58, pyridine); lit.[22] $[\alpha]^{21}\text{D} +145°$ (*c* 3.82, pyridine).

(c) **Substituted Salicylaldehydes.** 5-Methyl-, 3-*sec*-butyl-, 5-*sec*-butyl-, and 3-*sec*-butyl-5-methylsalicylaldehydes were prepared from the corresponding alkyl-substituted phenols by the Duff reaction.[23] (+)-3-*sec*-Butylsalicylaldehyde, $\alpha^{25}\text{D} +15.3$ (neat, 1 dm), was obtained from (+)-2-*sec*-butylphenol,[24] $[\alpha]^{25}\text{D} +17.9°$ (neat), lit.[24] +18.1°. The resolution of this phenol and the preparation of 2-*sec*-butyl-4-methylphenol will be described in detail in a forthcoming publication.[25]

(d) **2,2′-Bis(salicylideneamino)biphenyls.** These Schiff bases were prepared as yellow or orange crystalline solids by condensation of the appropriate salicylaldehyde and biphenyldiamine in refluxing ethanol[14] according to the following general procedure for racemic 2,2′-bis(3-*sec*-butylsalicylideneamino)biphenyl. Racemic 3-*sec*-butylsalicylaldehyde (1.78 g, 0.01 mole) and 2,2′-diaminobiphenyl (1.84 g, 0.01 mole) were mixed in absolute ethanol (10 ml). The solution was refluxed for 2 hr. The resultant yellow crystalline product was collected and recrystallized from absolute ethanol, mp 162–163°.

Anal. Calcd for $C_{34}H_{34}N_2O_2$: C, 80.92; H, 7.19; N, 5.55. Found: C, 80.87; H, 6.98; N, 5.48.

The remaining ligands were not analyzed but were shown to have purities in excess of 95% by pmr measurements.

(e) **Complexes.** Zinc(II) complexes were obtained by the following method. The Schiff base (0.01 mole) and anhydrous zinc chloride (0.01 mole) were stirred vigorously in 20 ml of anhydrous methanol. A solution of potassium hydroxide in anhydrous methanol (0.02 mole in 5 ml) was added dropwise over a 30-min period to produce a yellow precipitate, which was collected and recrystallized twice from *n*-heptane–chloroform to yield yellow

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Table I. Characterization of 2,2′-Bis(salicylideneamino)biphenyl–Metal(II) Complexes (**1**)[a]

Complex	X	Y	Mp, °C	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Co(sal)$_2$bp	H	H	280[b]	69.49	4.04	6.23	69.45	4.06	6.08
Ni(3*s*Bu-5Me-sal)$_2$bn[c]	3-*s*Bu-5-Me	. .	>330	76.64	6.14	4.06	76.60	6.08	4.09
Ni(sal)$_2$bp · 2CHCl$_3$[d]	H	H	303–304	48.89	2.93	4.07	49.30	2.89	4.00
Ni(3*s*Bu-sal)$_2$bp	3-*s*Bu	H	157–160[e]	72.75	6.11	4.99	72.47	6.10	5.01
Ni(5Me-sal)$_2$bp[g]	5-Me	H	207–210	70.47	4.65	5.87	69.46	4.65	5.60
Ni(3*s*Bu-5Me-sal)$_2$bp	3-*s*Bu-5-Me	H	154–157	73.36	6.50	4.75	73.68	6.35	4.84
Ni(3*s*Bu-sal)$_2$bmp	3-*s*Bu	Me	220–222[f]	73.36	6.50	4.75	73.67	6.45	4.68
Ni(5*s*Bu-sal)$_2$bmp	5-*s*Bu	Me	185–186	73.36	6.50	4.75	72.85	6.39	4.63
Ni(3*s*Bu-5Me-sal)$_2$bmp	3-*s*Bu-5-Me	Me	295–296	73.91	6.86	4.54	74.29	7.10	4.54
Pd(3*s*Bu-sal)$_2$bmp	3-*s*Bu	Me	287–289	67.87	6.01	4.40	67.81	5.96	4.61
Zn(3*s*Bu-sal)$_2$bp	3-*s*Bu	H	246	71.89	6.03	4.93	72.17	6.25	4.96
Zn(3*s*Bu-sal)$_2$bmp	3-*s*Bu	Me	239–240	72.54	6.43	4.70	72.30	6.60	4.58

[a] Data refer to mixture of diastereoisomers. [b] Nitrogen atmosphere. [c] Binaphthyl derivative, Ni(3*s*Bu-5Me-sal)$_2$-*R*-bn, mp >300°. [d] *Anal.* Calcd: Cl, 30.92. Found: Cl, 30.68. [e] Ni(3-(+)-*s*Bu-sal)$_2$bp, 180°. [f] Ni(3*s*Bu-sal)$_2$-*S*-bmp, 196–198°; Ni(3-(+)-*s*Bu-sal)$_2$-*S*-bmp, 203–205°; Ni(3-(+)-*s*Bu-sal)$_2$-*R*-bmp, 206–208°; Ni(3-(+)-*s*Bu-sal)$_2$bmp, 214–215°. [g] Impure sample after four recrystallizations from toluene–*n*-heptane; could not be further purified.

crystals. The cobalt(II), nickel(II), and palladium(II) complexes were prepared by a previously described nonaqueous chelation method in dry *t*-butyl alcohol.[10] All operations in the preparation of the cobalt complex were carried out in a nitrogen atmosphere. After removal of *t*-butyl alcohol the residue was extracted with hot *n*-heptane–toluene mixtures. Volume reduction of the extracts afforded crystalline products which were further purified by recrystallization from *n*-heptane–toluene. Ni(sal)$_2$bp was recrystallized from *n*-heptane–chloroform. The following exceptions to this general procedure were used. Hot *n*-heptane was used to extract Ni(3*s*Bu-sal)$_2$bmp and Ni(3*s*Bu-5Me-sal)$_2$bmp. Ni(3*s*Bu-sal)$_2$bp and Ni(3*s*Bu-5Me-sal)$_2$bp were most conveniently obtained from their concentrated extract solutions by slow addition of pyridine. These pyridinates were then recrystallized from *n*-heptane and the pyridine was quantitatively removed from the crystalline products by heating at 100° (0.1 mm) for at least 48 hr. The palladium and cobalt complexes were orange-red while all of the nickel complexes, with the exception of yellow-brown Ni(5Me-sal)$_2$bp, were reddish brown. Characterization data for all complexes are given in Table I.

ORD Spectra and Optical Rotations. Measurements of the ORD spectra were made on a Cary Model 60 spectrometer at 25° using 0.1-dm cells and chloroform solvent which had been freed of ethanol by passage through an alumina column. Spectra of the various diastereoisomers of Ni(3*s*Bu-sal)$_2$bmp are shown in Figure 1. The following optical rotations, measured using a Perkin-Elmer Model 141 spectropolarimeter, were obtained for the optically active Ni(II) complexes in chloroform solution using 0.1-dm cells: Ni(3-(+)-*s*Bu-sal)$_2$-*R*-bmp, $[\alpha]^{24}\text{D}$ +810°, $[\alpha]^{24}{}_{546}$ +87° (*c* 0.23); Ni(3-(+)-*s*Bu-sal)$_2$-*S*-bmp, $[\alpha]^{24}\text{D}$ −590°, $[\alpha]^{24}{}_{546}$ +430° (*c* 0.14); Ni(3*s*Bu-sal)$_2$-*S*-bmp, $[\alpha]^{25}\text{D}$ −670°, $[\alpha]^{24}{}_{546}$ +720° (*c* 0.21); Ni(3*s*Bu-5Me-sal)$_2$-*R*-bn, $[\alpha]^{24}\text{D}$ +1850°, $[\alpha]^{24}{}_{546}$ −230° (*c* 0.21). Ni(3-(+)-*s*Bu-sal)$_2$bmp showed no measurable rotations at 546 and 589 mμ.

Molecular Weights. Measurements were made with a Mechrolab Model 302 osmometer at 37° using solutions prepared from dry toluene. The following average molecular weights were obtained over the indicated concentration ranges.

	Calcd	Found
Ni(3*s*Bu-5Me-sal)$_2$bp	589	589 (0.05–0.26 *m*)
Ni(3*s*Bu-5Me-sal)$_2$bmp	617	622 (0.04–0.21 *m*)
Zn(3*s*Bu-sal)$_2$bmp	596	601 (0.04–0.27 *m*)

Other Physical Measurements. Electronic spectra were recorded using a Cary Model 14 spectrometer. Optical rotations were obtained with a Perkin-Elmer Model 141 spectropolarimeter. Magnetic measurements were made by the Gouy method with aqueous nickel chloride solutions and distilled water as the calibrants for solid and solution measurements, respectively. Proton resonance spectra were obtained using a Varian HR-60 spectrometer. CDCl$_3$ solutions of ~0.3 *M* concentration or less were employed. Chemical shifts were measured by the usual side-band technique with respect to TMS as an internal reference. The line widths and chemical shifts of the azomethine proton in the Ni(II) complexes were found to be extraordinarily sensitive to very small amounts of pyridine or *t*-butyl alcohol. Consequently, all samples were rigorously desolvated before use, and the data in Table III and the spectra in Figures 3 and 4 refer to such samples, whose pmr spectral characteristics could not be changed by additional exposure to the desolvating conditions mentioned above.

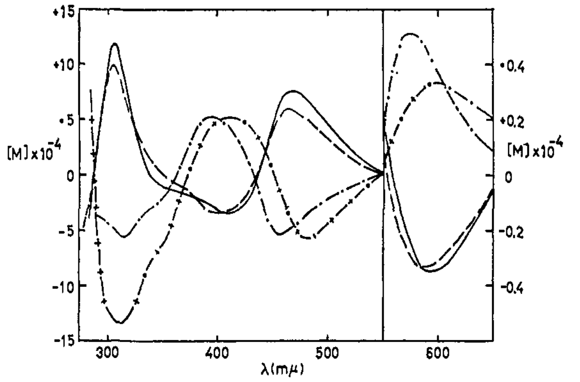

Figure 1. ORD spectra in chloroform solutions at 25°: ——, Ni(3*s*Bu-sal)$_2$-*S*-bmp; – – –, Ni(3-(+)-*s*Bu-sal)$_2$-*S*-bmp; –·–·–, Ni(3-(+)-*s*Bu-sal)$_2$-*R*-bmp; —+—+, Ni(3*s*Bu-5Me-sal)$_2$-*R*-bn ([M]/4 values shown in 550–650-mμ region).

Results and Discussion

Structures in the Solid and Solution Phases. The work of Lions and Martin[14] was undertaken with the purpose of preparing a quadridentate ligand of steric constraints such that only a pseudo-tetrahedral structure was possible for a complex of a divalent metal ion. There is little question that Be(sal)$_2$bmp prepared by them and the two Zn(II) complexes prepared in this work have such a structure because four-coordinate Be(II) and Zn(II) are ordinarily tetrahedral in the absence of any steric interactions which tend to force this structure. The same comments apply to Co(sal)$_2$bp whose magnetic moments in the solid (4.32 BM, 19°) and in chloroform solution (4.35 BM, 20°) and ligand-field spectral bands at 5990 and 11,100 cm^{-1} (*cf.* Table II) are in complete agreement with bissalicylaldiminocobalt(II) complexes of known pseudo-tetrahedral structure.[26] The X-ray structure[27] of

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$Cu(sal)_2bp$[14] reveals a severely distorted $Cu–O_2N_2$ pseudo-tetrahedron in which the dihedral angle between the Cu–ON planes is only 37°. This sort of distorted structure is known to occur in the $Cu(R\text{-}sal)_2$ species with R = Et (36°),[28a] *i*-Pr (60°),[28b] and *t*-Bu (54°),[28c] which possess the indicated dihedral angles. If the extent of tetrahedrality is roughly measured by these angles, it follows that the 2,2′-biphenylyl grouping is no more forcing of a tetrahedral configuration than two ethyl groups and somewhat less so than two isopropyl or *t*-butyl groups, at least with respect to Cu(II).

Table II. Electronic Spectral Data in Chloroform Solution[a]

Complex	λ_{max}, cm^{-1}	ε, l. $mole^{-1}$ cm^{-1}
$Co(sal)_2bp$	5990, 11,100, 15,600 (sh)	22.3, 51.7, 5.7
$Ni(3s\text{Bu-5Me-sal})_2bn$	8440, 9900, 15,100 (sh)	4.7, <1, 122
$Ni(sal)_2bp$	8300, 10,100, 15,200 (sh)	5.1, <1, 90
$Ni(3s\text{Bu-sal})_2bp$	8400, 10,000 15,400 (sh)	4.3, <1, 107
$Ni(5\text{Me-sal})_2bp$	8400, 10,000, 15,000 (sh)	5.1, <1, 84
$Ni(3s\text{Bu-5Me-sal})_2bp$[b]	8400, 9950, 15,300 (sh)	2.9, <1, 120
$Ni(5s\text{Bu-sal})_2bp$	8330, 10,000, 14,800 (sh)	7.0, <1, 96
$Ni(3s\text{Bu-sal})_2bmp$	8380, 10,000, 15,300 (sh)	3.8, <1, 86
$Ni(3s\text{Bu-5Me-sal})_2bmp$	8400, 9950, 15,000 (sh)	5.1, <1, 110

[a] Data refer to mixtures of diastereoisomers; all complexes show strong absorptions at >17,000 cm^{-1}. [b] In pyridine solution bands at 11,000 cm^{-1} (ε 30.4); 12,400 (sh) (ε 13.6).

In this investigation we have obtained definite evidence that 2,2′-bis(salicylideneamino)biphenyl and its 6,6′-dimethyl variant do not impose an exclusively pseudo-tetrahedral structure on metal ions which are ordinarily planar in the absence of steric strain. First, $Pd(3s\text{Bu-sal})_2bmp$ has been prepared under nonaqueous conditions. It would appear unlikely that this complex would be stable unless it possesses the approximately planar $Pd–O_2N_2$ coordination unit found in $Pd(X\text{-}R\text{-}sal)_2$ complexes with large R groups such as Et,[29a] *n*-Bu,[29b] *i*-Pr,[29c] and *t*-Bu.[29d] Second, the seven Ni(II) complexes of the bp or bmp types are all diamagnetic in the crystalline state, indicating an $Ni–O_2N_2$ coordination sphere which, if not exactly or approximately planar, is at least insufficiently distorted toward a pseudo-tetrahedral structure to stabilize the triplet ground state found for $Ni(X\text{-}R\text{-}sal)_2$ complexes with R = *i*-Pr.[30] The contention that these ligands cannot coordinate to Ni(II) because they furnish only a tetrahedral disposition of donor atoms[14] is vitiated. Indeed, our synthetic experiments indicate that the previous failure[14] to obtain Ni(II) complexes was very probably due to the lack of complete exclusion of water from the reaction mixture. These complexes are readily prepared by the nonaqueous chelation method.[10]

When dissolved in chloroform all Ni(II) complexes exhibit ligand-field spectral and proton resonance properties indicative of the formation of small fractions of pseudo-tetrahedral species. Spectral data are presented in Table II. The pattern of bands at ~8300–8700 and ~10,000 cm^{-1} is entirely typical of pseudo-tetrahedral $Ni(X\text{-}R\text{-}sal)_2$ complexes,[3,11,12,31] and is assigned similarly as ν_2 and $^3A_2(F)\text{-}^1D$ in idealized tetrahedral symmetry. The principal difference compared to the spectra of the bis-chelate complexes is the shift of ν_2 to higher energies by ~1000–2000 cm^{-1}. The shoulder at ~15,000 cm^{-1} is ascribed to the first spin-allowed transition of the diamagnetic form. The complexes display proton contact shifts, which are considered in detail in a subsequent section. Room-temperature data are given in Table III. The positive temperature coefficients of these shifts (*cf.* Figure 6) and their very small values indicate that the population of the paramagnetic species increases with increasing temperature. The spectral and pmr information, together with the demonstrated monomeric nature of several representative complexes in toluene solution, demonstrates the existence of the dynamic configurational equilibrium (eq 1) in solution for Ni(II) complexes which contain bp, bmp, and bn bridging groups.

Table III. Proton Contact Shifts of Nickel(II) Complexes in $CDCl_3$ Solution

Complex	Isomer[b]	Δf_i,[a] cps	
		HC=N	5-Me
$Ni(sal)_2bp$	Δ,Λ	−2888	...
$Ni(5\text{Me-sal})_2bp$	Δ,Λ	−3156	−182
$Ni(3s\text{Bu-sal})_2bp$[d]	Λ(+,+)	−1495	...
	(+,−)	−1406	...
	Δ(+,+)	−1271	...
$Ni(3s\text{Bu-5Me-sal})_2bp$[d]	Λ(+,+)	−1390	−96
	(+,−)	−1314	−90
	Δ(+,+)	−1207	−81
$Ni(5s\text{Bu-sal})_2bmp$	*c*	−4537	...
$Ni(3s\text{Bu-sal})_2bmp$	Λ(+,+)	−2694	...
	(+,−)	−2570	...
	Δ(+,+)	−2430	...
$Ni(3s\text{Bu-5Me-sal})_2bmp$[d]	Λ(+,+)	−2512	−154
	(+,−)	−2434	−148
	Δ(+,+)	−2351	−143
$Ni(3s\text{Bu-5Me-sal})_2bn$[d]	Λ(+,+)	−2321	−142
	(+,−)	−2233	−135
	Δ(+,+)	−2105	−127

[a] Data refer to 60 Mc/sec, ~27°; $\Delta f_i = f_i(\text{complex}) - f_i(\text{dia})$. [b] Λ(+,+) ≡ Δ(−,−), Δ(+,+) ≡ Λ(−,−), (+,−) = *meso*. [c] Mixture of active and *meso* diastereoisomers. [d] Signal assignments made by analogy with those proven for $Ni(3s\text{Bu-sal})_2bmp$.

$$\text{planar } (S = 0) \rightleftharpoons \text{tetrahedral } (S = 1) \qquad (1)$$

Configurational Stability. If pseudo-tetrahedral $M(A–B)_2$ complexes possess two equivalent asymmetric ligand centers in addition to their intrinsic dissymmetry at the metal, the following diastereoisomers, shown together with their enantiomers, are possible. In the event that all three asymmetric or dissymmetric molecular sites are stable on the nmr time scale of measurement, it is possible in principle to observe separate signals from

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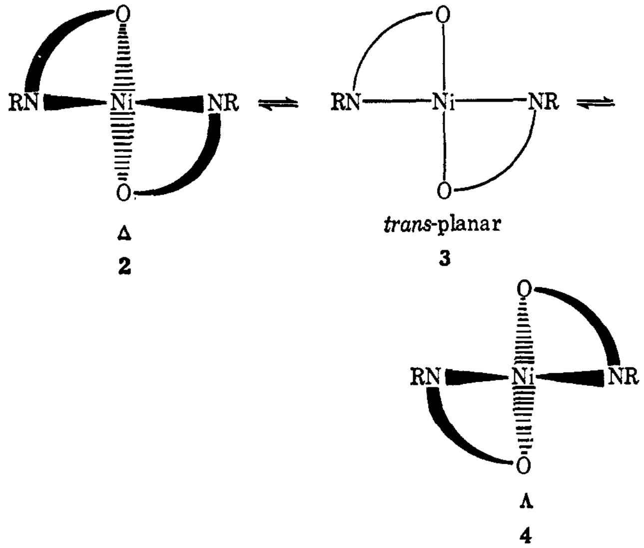
$$\left.\begin{array}{l}\Delta(+,+) \equiv \Lambda(-,-)\\ \Lambda(+,+) \equiv \Delta(-,-)\end{array}\right\}\text{active}$$

$$\Delta(+,-) \equiv \Lambda(+,-)\ \textit{meso}$$

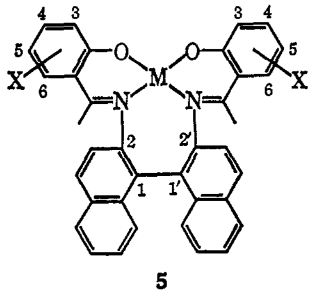
the three diastereoisomers. However, for Ni(X-R-sal)$_2$ complexes only two diastereomers can be observed, these being the active, (+,+) or (−,−), and *meso*, (+,−), forms. The absence of splitting of the active peak into signals associated with the Δ and Λ configurations has led to the conclusion that either this splitting is too small to resolve even at 100 Mc,[3] or, more likely, that the configuration at the metal is rapidly racemized by the interconversions **2** $\rightleftharpoons$ **3** $\rightleftharpoons$ **4**. This configurational mobility is to be contrasted with that in the quadridentate bp (**1**, Y = H), bmp (**1**, Y = CH$_3$), and bn (**5**) complexes. In order for these complexes to racemize, the biphenylyl or binaphthylyl groups must themselves be racemized in the course of the Δ $\rightleftharpoons$ Λ interconversion. A sufficiently high activation energy for racemization of these groups will ensure configurational stability of the complexes,[32] a point substantiated by isolation of the enantiomers of Cu(sal)$_2$-bmp.[14] The configurational interconversion (eq 1) observed for the Ni(II) complexes will then occur *without* racemization as shown schematically by the interconversion **6**$\rightleftharpoons$**7**. The *cis* structure of the diamagnetic "planar" form **7** is inferred from the structure of Cu(sal)$_2$bp[27] and from molecular models, which show that the bp, bmp, and bn groups cannot span *trans* positions.



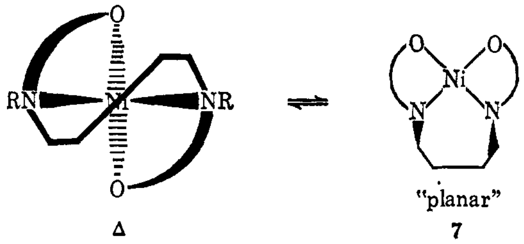
Δ
2

trans-planar
3

Λ
4



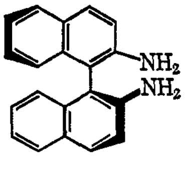
5



Δ
6

"planar"
7

Absolute Configuration at the Metal Site. In the pseudo-tetrahedral form of complexes **1** and **5** *the absolute configuration at the metal is fixed uniquely by the absolute configuration of the biphenyl or binaphthyl grouping.* The crucial stereochemical correlations between the complexes and the biaryldiamines from which they are derived can now be made with complete certainty. Very recently the first unequivocal proof of the absolute configuration of an enantiomeric biaryl by X-rays has been given.[34] (+)-2,2′-Dihydroxy-1,1′-binaphthyl-3,3′-dicarboxylic acid dimethyl ester has been shown to possess the *R* configuration and has been chemically correlated with (+)-2,2′-dihydroxy-1,1′-binaphthyl.[34] Previously, the (−)-diol had been correlated with (−)-2,2′-diamino-1,1′-binaphthyl,[35] thereby demonstrating the *S* configuration **8** of the latter. From the absolute configuration of the diamine the stereochemical correlations below follow directly and unambiguously, as can be verified from inspection of molecular models.



S-(−) **8**

$$R \longleftrightarrow \Delta$$
$$S \longleftrightarrow \Lambda$$

The configurational connection between the bn and bmp series of complexes can be made from representative ORD spectra shown in Figure 1. Ni(3*s*Bu-5Me-sal)$_2$-*R*-bn and Ni(3*s*Bu-sal)$_2$-(−)-bmp have oppositely signed Cotton effects in the visible where the optically active transition is a *ligand-field band* of the diamagnetic form.[36] Because this form of the *R*-bn complex will interconvert only with the Δ form at ordinary temperatures, the (−)-bmp complex must give rise to the op-

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(32) The facile resolutions of 2,2′-diamino-6,6′-dimethylbiphenyl[19] and 2,2′-diamino-1,1′-binaphthyl[22] at room temperature alone indicates an activation energy for racemization of 17 kcal/mole or more.[33] Note also that the activation energy in M(sal)$_2$bmp and M(sal)$_2$bn will almost certainly be higher than those of the diamines for in these cases methyl–methyl and naphthyl–naphthyl passage is required for racemization, whereas in the diamines amino–methyl and amino–naphthyl passage offers an alternative racemization route. In addition, resistivity of the coordinated metal to racemization and the required passage of 3-substituents on the benzene portion of the chelate ring, among other effects, will further increase the activation energy. The pmr detection of all three diastereoisomers of Ni(3*s*Bu-sal)$_2$bp up to 80° (*vide supra*) supports this contention; 2,2′-diaminobiphenyl cannot be resolved under ordinary conditions.

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(36) Only a small percentage of pseudo-tetrahedral form is present under conditions of measurement (*cf.* Table IV). Recent work has demonstrated that the analogous ligand-field transition in *cis*-planar Ni(II) salicylaldimine complexes is rendered optically active by the presence of an asymmetric center in the group bridging the two nitrogen atoms: B. Bosnich, *J. Am. Chem. Soc.*, **90**, 627 (1968).

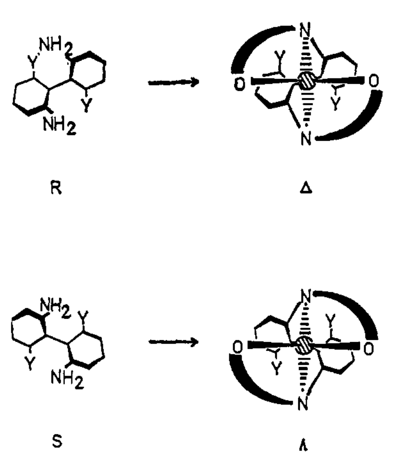

Figure 2. Correlation of the absolute configurations of biphenyl-2,2′-diamines (Y = H, CH_3) with those of the complexes $M(X\text{-sal})_2bp$ and $M(X\text{-sal})_2bmp$ in their pseudo-tetrahedral forms. Exactly the same correlation holds between (*R*)- and (*S*)-2,2′-diamino-1,1′-binaphthyl and Δ- and Λ-$M(X\text{-sal})_2bn$.

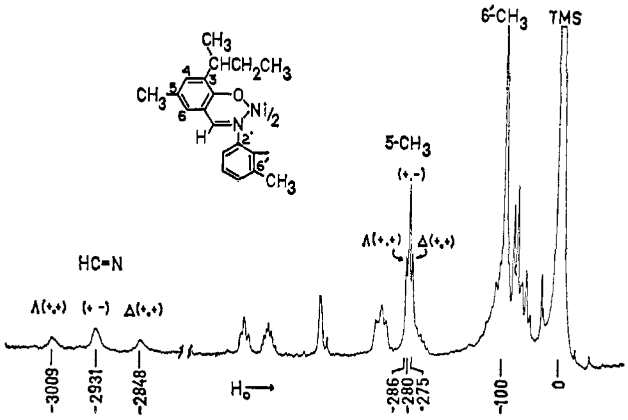

Figure 3. Complete 60-Mc pmr spectrum of a mixture of the active and *meso* diastereoisomers of $Ni(3sBu\text{-}5Me\text{-sal})_2bmp$ in $CDCl_3$ solution at ~27°. Frequencies (cps) are the chemical shifts.

posite, or Λ, configuration when pseudo-tetrahedral. Hence, the (+)- or (−)-diamine of the two series has the same absolute configuration, in complete agreement with the assignments of the *R* and *S* configurations to (+)- and (−)-2,2′-diamino-6,6′-dimethylbiphenyl, respectively, by McGinn, *et al.*,[16] on purely chemical grounds. The stereochemical correlations for the biphenyl series of compounds[37] are set out in Figure 2.

Proton Resonance Results. The pmr spectra of the Ni(II) complexes are of primary importance. In order to investigate the stabilization of the absolute configuration at the metal, it is necessary to introduce one or more asymmetric ligand centers so as to generate diastereoisomers. This was most simply accomplished synthetically by placing two X = *sec*-Bu groups at the 3 positions in **1** and **5**. The spectrum of the total isomeric mixture of $Ni(3sBu\text{-}5Me\text{-sal})_2bmp$ is shown in Figure 3. The downfield displacement of the 5-Me and azomethine signals from their diamagnetic positions in the free ligand (−132 and −497 cps, respectively)

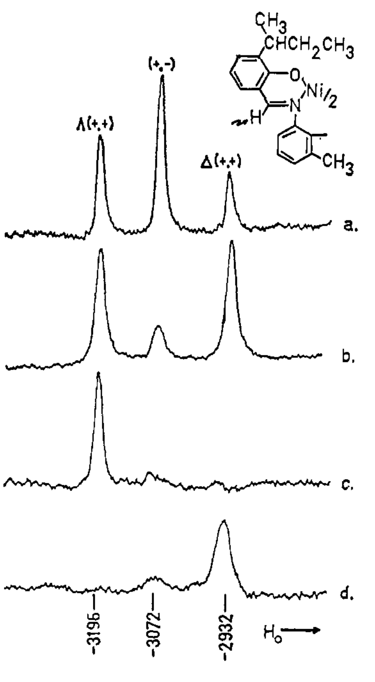

Figure 4. Pmr spectra of $Ni(3sBu\text{-sal})_2bmp$ in the azomethine region demonstrating the signal assignments for the diastereoisomers: (a) total mixture; (b) $Ni(3\text{-}(+)\text{-}sBu\text{-sal})_2\text{-}RS\text{-}bmp$; (c) $Ni(3\text{-}(+)\text{-}sBu\text{-sal})_2\text{-}S\text{-}bmp$; (d) $Ni(3\text{-}(+)\text{-}sBu\text{-sal})_2\text{-}R\text{-}bmp$.

indicates a small proportion of pseudo-tetrahedral forms present in rapid equilibrium with diamagnetic isomers. The spectra of all other Ni(II) complexes reveal azomethine and 5-Me shifts of roughly the same magnitude; room-temperature contact shifts of these groups in eight complexes are collected in Table III. Aside from the 6′-Me signals (bmp complexes), which show almost no contact shifts, only the azomethine and 5-Me shifts could be identified with certainty.

The feature of greatest interest in the spectra of the diastereoisomeric mixtures is the consistent splitting of the azomethine and 5-Me signals into three components of approximate 1:2:1 intensity ratio. In order to assign these signals the following procedure was employed. $Ni(3sBu\text{-sal})_2bmp$ was prepared from racemic components; its spectrum in the azomethine region is shown in Figure 4a. Next, $Ni(3\text{-}(+)\text{-}sBu\text{-sal})_2bmp$ was prepared from racemic amine and (+)-3-*sec*-butylsalicylaldehyde, which in turn was obtained by formylation of (+)-2-*sec*-butylphenol.[24] The marked decrease in intensity of the −3072 signal (Figure 4b) proves that this signal must arise from the *meso* diastereoisomer, Δ(+,−) ≡ Λ(+,−). Preparation of $Ni(3\text{-}(+)\text{-}sBu\text{-sal})_2\text{-}S\text{-}bmp$ from the *S*-diamine removes the signal at −2932 cps (Figure 4c); using the preceding stereochemical correlation this result shows that the −2932- and −3196-cps signals are associated with the Δ(+,+) and Λ(+,+) isomers, respectively. Finally, $Ni(3\text{-}(+)\text{-}sBu\text{-sal})_2\text{-}R\text{-}bmp$ was obtained from the *R*-diamine and displayed the required spectrum (Figure 4d) complemental to that in Figure 4c. These results are summarized schematically in Figure 5, in which the two different types of diastereoisomeric interactions are separated. The interaction between the two 3*s*Bu groups results in separation of signals of active and *meso* isomers, similar to the *R*-(+,−)-*R*-(+,−) interactions in $Ni(X\text{-}R\text{-sal})_2$.[3,12] Unlike the bis-chelate

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[37] McGinn, *et al.*,[16] have previously designated the configuration of $Cu(sal)_2\text{-}(+)\text{-}bmp$ as *R*, which is equivalent to Δ in the present notation.

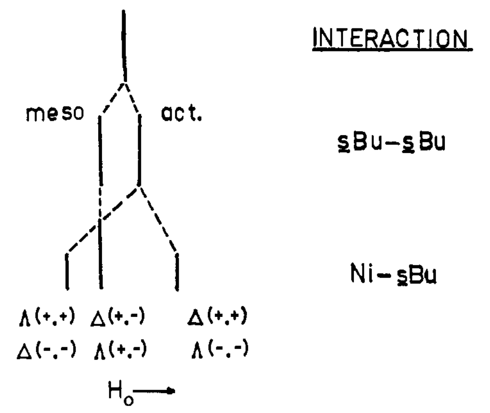

Figure 5. Schematic representation of the origin of the chemical shift separations between the three diastereoisomers of Ni(3*s*Bu-X′-sal)$_2$B (X′ = H, 5-Me; B = bp, bmp, bn).

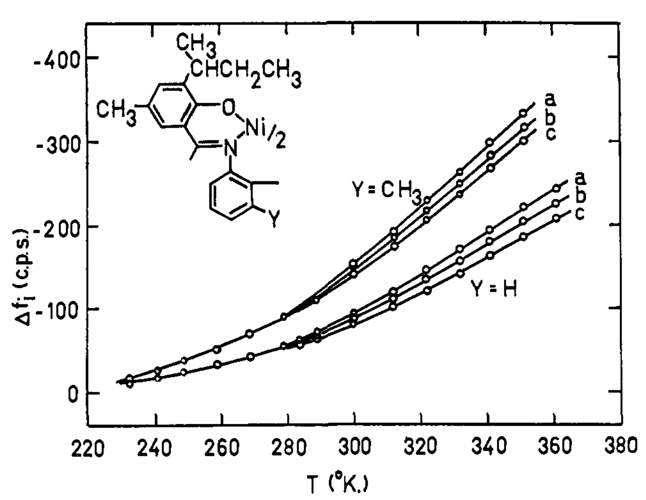

Figure 6. Temperature dependence of the 5-CH$_3$ contact shifts of Ni(3*s*Bu-5Me-sal)$_2$bp (Y = H) and Ni(3*s*Bu-5Me-sal)$_2$bmp (Y = CH$_3$) in CDCl$_3$ solution: (a) Λ(+,+), (b) (+,−), (c) Δ(+,+).

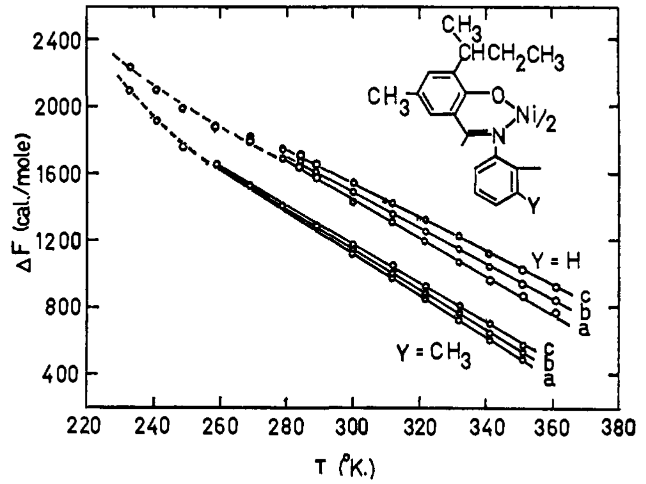

Figure 7. Temperature dependence of the free-energy changes for the planar → tetrahedral structural change of Ni(3*s*Bu-5Me-sal)$_2$bp (Y = H) and Ni(3*s*Bu-5Me-sal)$_2$bmp (Y = CH$_3$) in CDCl$_3$ solution: (a) Λ(+,+), (b) (+,−), (c) Δ(+,+).

complexes, however, a second interaction, that between the 3-*s*Bu groups and the dissymmetric metal configuration, is not time-averaged and leads to a further splitting of the active signal into its Δ and Λ components.

Signal assignments similar to those proven for Ni(3*s*Bu-sal)$_2$bmp are assumed to apply to those complexes having X = *sec*-Bu, with or without 5-Me, and B = bp, bn and are given in Table III. The same procedure leading to unequivocal signal assignments could not be applied in most of these cases because 2,2′-diaminobiphenyl cannot be resolved, and we have been unable to resolve even partially 2-*sec*-butyl-4-methylphenol, the logical precursor to active 3-*sec*-butyl-5-methylsalicylaldehyde. Complexes of the bn type were not studied in detail.

The temperature dependence of the contact shifts of the three diastereoisomers of Ni(3*s*Bu-5Me-sal)$_2$B, B = bp, bmp, in chloroform solution are shown in Figure 6. The 5-Me signals were followed owing to their extreme sharpness over the temperature interval; the azomethine signals broaden excessively with increasing temperature and their shifts are not accurately measurable at higher temperatures. Two properties of the temperature-dependent shifts are of importance. First, the contact shifts closely approach zero at the lower temperatures, indicating a shift of equilibrium to the left and a positive enthalpy of conversion to the pseudo-tetrahedral form of all diastereoisomers. Second, at no temperature up to ~360°K is there evidence of broadening of the Δ(+,+) and Λ(+,+) signals due to the onset of the Δ $\rightleftharpoons$ Λ interconversion. In fact, these signals *diverge* slightly with increasing temperature. Hence, the complexes display the configurational integrity expected, at least up to ~360°K. Maintenance of Ni(3-(+)-*s*Bu-sal)$_2$-*S*-bmp in chloroform solution at 85° for 65 hr resulted in no observable conversion to the Δ form, as indicated by the absence of an azomethine signal at −2932 cps.

The relative stabilities of the diastereoisomers of a given complex can be obtained from the temperature dependence of the contact shifts. The contact shifts of complexes involved in the dynamic equilibrium 1 are given by eq 2, in which Δf_i is the contact shift of the

$$\frac{\Delta f_i}{f} = -a_i\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g\beta S(S+1)}{6SkT}[\exp(\Delta F/RT) + 1]^{-1} \quad (2)$$

*i*th proton, a_i the electron–nuclear coupling constant in gauss, and *g* the *g* value of the paramagnetic form. $\Delta F = -RT \ln K_{eq}$ and $K_{eq} = N_t/N_p$, with N_t the mole fraction of the tetrahedral and N_p the mole fraction of the planar form. The remaining symbols have their usual meanings. Treatment of the contact shift data requires two assumptions. The value $a_{5Me} = +0.170$ G was assumed because it was not possible to evaluate this quantity from magnetic moment and contact shift measurements at the same temperature.[3] The concentration of paramagnetic species is too small to permit determination of ΔF from measured moments. The value chosen was taken from past work on Ni(X-R-sal)$_2$ complexes in which a_{5Me} could be accurately measured and was found to be approximately independent of R.[3,12] Further, the same value of a_{5Me} was assumed for all diastereoisomers of a given complex. This assumption is supported by recent work on bis-chelate Ni(II) complexes which has demonstrated that contact shift differences between diastereoisomers are principally due to nonzero values of $\Delta\Delta F$,[3] *e.g.*, $\Delta F_{\Delta(+,+)} - \Delta F_{(+,-)}$

Table IV. Thermodynamic Values for the Planar–Tetrahedral Conversion of Diastereoisomeric Ni(II) Complexes[a]

Complex	Isomer	Temp, °K[b]	ΔH, cal/mole[c]	ΔS, eu[c]	ΔF^{298}, cal/mole[c]	N_t^{298} [c]
Ni(3*s*Bu-5Me-sal)$_2$bp	$\Delta(+,+)$	280–360	4570	10.1	1560	0.066
	$\Lambda(+,+)$		4950	11.7	1480	0.076
	$(+,-)$		4650	10.6	1500	0.073
Ni(3*s*Bu-5Me-sal)$_2$bmp	$\Delta(+,+)$	260–350	4620	11.5	1200	0.116
	$\Lambda(+,+)$		5000	12.9	1160	0.124
	$(+,-)$		4820	12.2	1180	0.120
Ni(5Me-sal)$_2$bp	Δ,Λ	270–350	4430	11.4	1040	0.147

[a] $CDCl_3$ solution. [b] Temperature range of measurement in which ΔF is a linear function of temperature. [c] Estimates of uncertainties in the thermodynamic quantities based on calculations with $a_{5Me} = +0.170 \pm 0.020$ G are as follows: $\Delta H = \mp 130$ cal/mole; $\Delta S = \mp 0.7$ eu; ΔF, $= \pm 100$ cal/mole; and $N_t = \mp 0.020$. The relative order of values for the isomers of any compound does not change.

in the present case. With these assumptions the temperature dependences of the free-energy changes in reactions 3, 4, and 5 were obtained from eq 2. The linear variation of ΔF with temperature required by $\Delta F = \Delta H - T\Delta S$ and shown in Figure 7 was satisfied except at the lower temperatures where the effects of slight molecular association[3,12] and very small contact shifts may contribute to the apparent deviation from linearity. The full set of thermodynamic data is given in Table IV.[38] For Ni(3*s*Bu-sal)$_2$B (B = bp, bmp) the relative order of stability of the pseudo-tetrahedral form is $\Lambda(+,+) >$ *meso* $> \Delta(+,+)$.

$$\text{planar } (R\text{-}(+,+)) \rightleftharpoons \Delta(+,+) \qquad (3)$$

$$\text{planar } (S\text{-}(+,+)) \rightleftharpoons \Lambda(+,+) \qquad (4)$$

$$\text{planar } (R,S\text{-}(+,-)) \rightleftharpoons \Delta,\Lambda(+,-) \qquad (5)$$

In order to investigate the origin of the chemical shift distinctions among the diastereoisomers of the Ni(II) complexes, the pmr spectra of several other complexes, all prepared from racemic components, were examined. The azomethine signals of tetrahedral, diamagnetic Zn(3*s*Bu-sal)$_2$bp (−492 cps) and Zn(3*s*Bu-sal)$_2$bmp (−496 cps) occurred as sharp singlets; the only observable splitting was a 2-cps separation of two $-CHCH_3$ methyl doublets of the *sec*-butyl groups. A slight splitting (6 cps) of the azomethine signal was observed with "planar," diamagnetic Pd(3*s*Bu-sal)$_2$bmp, which is very small compared to that observed in the corresponding Ni(II) complex. The spectrum of Ni(5*s*Bu-sal)$_2$bmp revealed no splittings of any signal, indicating that the two *sec*-butyl groups in the 5 position of **1** are too remote from each other to interact effectively. These results support the previous contention[3] that chemical shift differences between diastereoisomeric Ni(II) complexes are essentially contact shift differences which arise from observable inequalities in the free energy changes for the planar–tetrahedral interconversion of the active and *meso* isomers.

Entropy Changes in the Structural Conversion. For three Ni(II) complexes of type **1** values of ΔS for the planar → tetrahedral change in chloroform solution lie in the 10–13 eu range (*cf.* Table IV). These values are surprisingly different from and much larger than those (2.7–5.4 eu) for the corresponding structural change of Ni(X-R-sal)$_2$ in the same solvent. Common to both the quadridentate and bis-chelate complexes is the entropy increase, $\Delta S_{elec} = R \ln 3 = 2.2$ eu, due to a change in the ground-state spin multiplicity. The remaining principal contributions to ΔS are expected to be changes in rotational motions of groups (R, X) attached to the chelate ring and solvation differences.[12] From the data of Table IV it is evident that ΔS is not strongly dependent upon either B or X in the quadridentates. The lack of any important decrease in ΔS upon replacing 3-*sec*-Bu with H in the bp complexes signifies that the principal source of the large ΔS values arises from much stronger solvation of the planar form; diamagnetic Ni(sal)$_2$bp·2$CHCl_3$ has been isolated and could not be desolvated by heating *in vacuo* at 160° for 48 hr. The relative contributions of changes in rotational motions of chelate ring substituents and solvation differences between the structural isomers cannot be satisfactorily assessed at present for the bis-chelate complexes.

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(38) The use of $a_{5Me} = +0.170$ G is strictly correct only if the extent of spin delocalization and distribution of spin density in the pseudo-tetrahedral form of Ni(X-sal)$_2$B and the Ni(X-R-sal)$_2$ complexes are the same. It is to be emphasized that the correspondence of these properties between the two types of complexes, which can be expected only if the geometries of the pseudo-tetrahedral forms are closely similar, cannot be demonstrated in this work. However, independent support for the use of this value can be obtained from the ligand-field spectra. Taking $\epsilon \sim 40$, the extinction coefficient of ν_2 in fully tetrahedral Ni(*t*-Bu-sal)$_2$,[31] as the limiting value of $\epsilon(\nu_2)$ in the tetradentate complexes and the observed intensities in Table II, the following N_t values at ~30° were calculated: Ni(3*s*-Bu-5Me-sal)$_2$bp, ~0.07; Ni(3*s*Bu-5Me-sal)$_2$bmp, ~0.13; Ni(5Me-sal)$_2$bp, ~0.13. Previously it had been shown[31] that N_t values calculated from molar extinction coefficients and magnetic moments are in good agreement. These values are averages for the mixtures of diastereoisomers and agree well with the average N_t^{298} data in Table IV for each complex.