# Diastereoisomeric Four-Coordinate Complexes. III.[1,2] Paramagnetic Nickel(II) Complexes with Three Asymmetric Centers

**R. E. Ernst,[3] M. J. O'Connor, and R. H. Holm[4]**

*Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin.* *Received June 12, 1967*

**Abstract:** Three series of bischelate nickel(II) complexes containing a center of asymmetry at the metal and two asymmetric ligand centers have been prepared and their proton resonance spectra at 100 Mc investigated for the purpose of detecting diastereoisomers and evaluating the energetics of their structural changes. The chelates of 5-methyl-N-substituted salicylaldimines, Ni(5-Me-R-sal)$_2$ (**1**), and of two $\beta$-ketoamines, Ni(CH$_3$C(NR)CHCOPh)$_2$ (**2**) and Ni(HC(NR)CHCOPh)$_2$ (**3**), contain unsymmetrical chelate rings, each of which has an asymmetric center (R = *sec*-Bu, CH$_3$CHCH$_2$Ph, CH$_3$CHPh). Preparation using optically active ligand components yields the active complexes $\Delta(+,+)$, $\Lambda(+,+)$ or $\Delta(-,-)$, $\Lambda(-,-)$, whereas racemic components give the active isomers plus the *meso* forms $\Delta(+,-)$, $\Lambda(+,-)$. The complexes exist in chloroform solution exclusively in the tetrahedral configuration (**2**) or in planar and tetrahedral configurations in rapid equilibrium (**1, 3**), and show separate sets of isotropic proton contact shifts for the active and *meso* isomers. The effects of the absolute configurations $\Delta$ or $\Lambda$ at the metal could not be detected in the pmr spectra. At fixed temperature contact shifts of **2** depend only on electron-nuclear coupling constants, whereas those of **1** and **3** depend on the coupling constants and $\Delta F$ for the planar-tetrahedral conversion. Because the difference in contact shift of a corresponding proton in the active and *meso* forms of **2** and **3**, which are structurally and electronically similar, are always much larger for **3**, these differences are concluded to derive primarily from unequal $\Delta F$ values of the two forms. A similar effect is inferred to account for contact-shift differences observed in the diastereoisomeric forms of **1**. The thermodynamic quantities characterizing the configurational changes of **1** and **3** have been evaluated from the temperature dependence of the contact shifts and are interpreted in terms of a small stereoselective effect favoring usually the active tetrahedral form. Ligand exchange reactions in solution between the complexes **1** (R = (+)-PhEt, (−)-PhEt; (+)-PhEt, (+)-*sec*-Bu; (−)-PhEt, (+)-*sec*-Bu) have been detected by pmr and found to proceed with no over-all stereoselectivity.

Interest in and investigations of enantiomeric and diastereoisomeric metal complexes are currently accelerating as the ORD and CD methods for establishing absolute and relative configurations are being developed and tested, and as the factors responsible for stereoselective behavior continue to come into sharper focus.[5] The classical studies of diastereoisomeric complexes, as well as investigations of a more recent or current nature, have dealt almost exclusively with nonlabile, six-coordinate species containing an asymmetric center at the metal plus one or more asymmetric centers on the chelating ligands, which are generally saturated polyamines. Various combinations of ligand and complex absolute configurations generate sets of intramolecular nonbonded interactions[6] which are often sufficiently different to facilitate separation and, thereafter, identification of the diastereoisomers.[5]

Compared to research on six-coordinate complexes, there has been relatively little activity invested in four-coordinate asymmetric complexes, particularly in diastereoisomeric complexes. This situation is very probably due to the real or assumed ease of racemization at the metal in pseudo-tetrahedral complexes by ligand exchange or rearrangement to a planar form, and the absence of an asymmetric center at the metal in strictly planar chelates. Furthermore, stereoselective effects in complexes having asymmetric ligand centers and a planar disposition of metal–ligand $\sigma$ bonds might be expected to be small or undetectable, particularly if the centers are *trans* or otherwise distant from one another. This is sometimes[7] but not always the case, and as a result there has been a recent surge of interest in diastereoisomers of four-coordinate complexes. Diastereoisomers of [Pt(olefin)(PhCH(NH$_2$)Me)Cl$_2$][8] and [Pt(RR'SO)(PhCH(NH$_2$)Me)Cl$_2$][9] have been prepared and in some instances separated, permitting a high degree of resolution of appropriate olefins and sulfoxides. Bis(*o*-hydroxyamidine)copper(II) complexes, prepared from racemic ligands, crystallize as racemic or *meso* species[10] depending upon ligand structure. Similarly, racemic and *meso* forms of Ni(II) macrocyclic tetraamine complexes have been prepared and their structures elucidated.[11,12]

---

[1] Part I: R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **85**, 821 (1963).

[2] Part II: R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **86**, 379 (1964).

[3] National Institutes of Health Predoctoral Fellow.

[4] Alfred P. Sloan Foundation Fellow; author to whom inquiries should be addressed: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

[5] For recent reviews concerning enantiomeric and diastereoisomeric complexes, *cf.*, J. H. Dunlop and R. D. Gillard, *Advan. Inorg. Chem. Radiochem.*, **9**, 185 (1966); R. D. Gillard, *Progr. Inorg. Chem.*, **7**, 215 (1966); A. M. Sargeson, *Transition Metal Chem.*, **3**, 303 (1966); R. D. Gillard and H. M. Irving, *Chem. Rev.*, **65**, 603 (1965).

[6] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[7] R. D. Gillard, H. M. Irving, R. M. Parkins, N. C. Payne, and L. D. Pettit, *J. Chem. Soc., Sect. A*, 1159 (1966).

[8] A. Panunzi and G. Paiaro, *J. Am. Chem. Soc.*, 88, 4843 (1966); P. Corradini, G. Paiaro, A. Panunzi, S. F. Mason, and G. N. Searle, *ibid.*, **88**, 2863 (1966); A. C. Cope, J. K. Hecht, H. W. Johnson, Jr., H. Keller, and H. J. S. Winkler, *ibid.*, **88**, 761 (1966); G. Paiaro, A. Panunzi, and A. DeRenzi, *Tetrahedron Letters*, 3905 (1966); A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **87**, 3644 (1965); G. Paiaro and A. Panunzi, *ibid.*, **86**, 5148 (1964); A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *ibid.*, **85**, 3276 (1963).

[9] A. C. Cope and E. C. Caress, *ibid.*, **88**, 1711 (1966).

[10] J. Iball and C. H. Morgan, *Nature*, 202, 689 (1964); *J. Chem. Soc., Sect. A*, 52 (1967).

[11] N. F. Curtis and Y. M. Curtis, *ibid.*, 1653 (1966); N. F. Curtis, *Chem. Commun.*, 881 (1966), and references therein; I. E. Maxwell and M. F. Bailey, *ibid.*, 883 (1966); R. R. Ryan, B. T. Kilbourn, and J. D. Dunitz, *ibid.*, 910 (1966).

Nuclear magnetic resonance has only recently been employed as a means of detecting components in diastereoisomeric mixtures. Evidence is now accumulating that in a number of four-[12] and six-coordinate[13] diamagnetic complexes, the chemical shift differences between diastereoisomers required in principle are often observable although not always resolvable. The situation is generally more favorable in paramagnetic complexes whose signals are not excessively broad, for contact interactions often accentuate chemical shift differences to such an extent that they are an order of magnitude or more larger than those of isostructural diamagnetic complexes.[14] Contact interactions facilitate ready detection of diastereoisomeric octahedral cobalt(II) histidine complexes[15] and certain tetrahedral bis(salicylaldimino)nickel(II) complexes[16] whose structural differences are quite subtle.

In previous proton resonance studies[1,2] of the planar $\rightleftharpoons$ tetrahedral structural equilibrium of bis(R-N-salicylaldimino)nickel(II) complexes, we have demonstrated that the diastereoisomers produced by the introduction of asymmetric R groups are readily detectable. These complexes exhibit large proton contact shifts which for certain ring substituents resulted in differences of ~1–2 ppm or more between the two detectable diastereoisomers at room temperature. Further, it was established that the energetics of structural interchange were measurably different for the two isomers. Subsequent studies have indicated that the contact interactions alone, measured by electron-nuclear coupling constants, do not necessarily account for the substantial differences in shifts.[17] In order to provide additional examples of the utility of proton resonance in detecting diastereoisomeric tetrahedral Ni(II) complexes and establishing the relative energetics of their structural interchange, we have prepared and studied several new series of bis(salicylaldimino)- and bis($\beta$-ketoamino)nickel(II) complexes. This work, which is reported here, has allowed us to refine and substantiate our previous argument[2] concerning the origin of the large chemical shift differences between diastereoisomers of these complexes. It is the first part of a series of current pmr investigations of diastereoisomeric complexes possessing three, four, and five asymmetric centers.[18]

## Experimental Section

**Preparation of Compounds.** (a) **Amines.** (+)-*sec*-Butylamine was obtained by resolution of the inactive amine with (+)-tartaric acid according to the method of Thomé[19] as improved by Bruck, *et al.*:[20] $[\alpha]^{25}\mathrm{D}$ +7.4° (neat), lit.[20] $[\alpha]\mathrm{D}$ +7.48°. $\alpha$-Phenethylamine was resolved into its (+) and (−) enantiomers using (−)-malic acid[21] and (+)-tartaric acid,[22] respectively: $[\alpha]^{25}\mathrm{D}$ +39.6° (neat); lit.[23] +39.9°, −39.5° (neat); lit.[22] $[\alpha]^{22}\mathrm{D}$ −40.3°. (+)-Amphetamine was obtained from Aldrich Chemical Co. It was distilled from potassium hydroxide: $[\alpha]^{24}\mathrm{D}$ +34.5° (neat); lit.[23] $[\alpha]^{25}\mathrm{D}$ +34.1°.

(b) **Salicylaldimine Complexes.** 5-Methylsalicylaldehyde was prepared from *p*-cresol by the Duff reaction.[24] The complexes were obtained by refluxing bis(5-methylsalicylaldehyde)nickel(II) and the appropriate amine in 1:2 mole ratio for 1 hr in methanol or ethanol. The solvent was removed and the residue extracted with *n*-heptane (R = $PhCHCH_3$, M = Ni) or chloroform (R = *sec*-Bu; M = Pd, Zn). Reduction of solution volume afforded the first crop of crystals. Two recrystallizations from the same solvents gave pure products. The exception to this procedure was the nickel complex with R = $PhCH_2CHCH_3$. It was isolated directly from the methanol reaction mixture as the bright green solvate. This material was twice recrystallized from methanol and heated at 65° (0.05 mm) to give the yellowish brown solvent-free complex.

(c) **$\beta$-Ketoamine Complexes.** Benzoylacetaldehyde was prepared according to a published procedure[25] and isolated as the cupric complex. The free ligand was isolated by treatment of the complex with 5 *M* $H_2SO_4$ followed by ether extraction and removal of solvent from the dried ($Na_2SO_4$) organic phase, yielding a yellow oil which was not further purified. N-Substituted 3-amino-1-phenyl-2-buten-1-one and 3-amino-1-phenyl-2-propen-1-one ligands were obtained by refluxing benzoylacetone and benzoylacetaldehyde, respectively, with ~15% mole excess of amine in methanol with Drierite added. After removal of methanol *in vacuo*, the crude products were purified by vacuum distillation. Purity in excess of 95% was established in each case from the pmr spectrum; the products were not analyzed.

The bis(N-substituted 3-amino-1-phenyl-2-buten-1-one)- and bis(N-substituted 3-amino-1-phenyl-2-propen-1-one) nickel(II) complexes were prepared by a nonaqueous chelation reaction in *t*-butyl alcohol described previously.[17] Isolation of the first group of complexes follows the previous procedure. The residue after reaction, obtained by removal of *t*-butyl alcohol, was extracted with warm toluene, and the products were isolated by volume reduction of the extract and cooling. Two additional recrystallizations, from toluene–*n*-heptane, afforded the pure complexes as yellow-brown to brown crystals. Complexes of the second group were obtained by a slightly different procedure. In the preparation of the N–$CH(CH_3)CH_2Ph$ and N–$CH(CH_3)Ph$ complexes the residue was extracted with warm toluene (100 ml/10 mmoles of theoretical yield), *n*-heptane (one-half of the toluene volume) was added, and the solution was allowed to stand for ~5 hr at room temperature. During this time a brownish oil and a small amount of crystalline product formed. The solution was decanted, filtered, and reduced to one-third its volume. Upon cooling to 0° the crystalline product formed. Two additional recrystallizations from toluene–*n*-heptane yielded the complexes as yellowish green microcrystals. The N-*sec*-butyl and N-*t*-butyl complexes were obtained by extracting the residue with boiling *n*-heptane (100 ml/25 mmoles of theoretical yield). The crystalline products obtained by cooling the extract to room temperature were twice recrystallized from *n*-heptane. The *sec*-butyl and *t*-butyl complexes were obtained as yellow-green and brown crystals, respectively.

Bis(4-(+)-*sec*-butylamino-3-penten-1-onato)nickel(II) was prepared by the same procedure as that for the complex obtained from the racemic ligand,[17] mp 196–197°. Bis(5-methyl-N-(+)-*sec*-butylsalicylaldimino)nickel(II), mp 192–193°, was available from earlier work.[2]

**ORD Spectra.** Measurements were made on a Cary Model 60 spectrometer using 0.1-dm cells at 25°. Spectra of the (+,+) and (−,−) isomers of bis(5-methyl-N-$\alpha$-phenethylsalicylaldimino)nickel(II) are shown in Figure 2. Data for the (−,−) isomer in chloroform: (*c*, 0.372) $[M]_{650}$ −2160, $[M]_{589}$ −690, $[M]_{570}$ −520; (*c*, 0.0186) $[M]_{438}$ −5470, $[M]_{398}$ −1870, $[M]_{322}$ +290; (*c*, 0.0037) $[M]_{286}$ −27,000, $[M]_{280}$ −16,000.

**Other Physical Measurements.** Because of the sensitivity of bis($\beta$-ketoamino)nickel complexes to traces of water,[17] all measurements of them were carried out using solutions prepared from dried solvents and, when necessary, a dry nitrogen atmosphere or an

---

[12] L. G. Warner, N. J. Rose, and D. H. Busch, *J. Am. Chem. Soc.*, **89**, 703 (1967).

[13] R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966); D. A. Buckingham, S. F. Mason, A. M. Sargeson, and K. R. Turnbull, *ibid.*, **5**, 1649 (1966); S. T. Spees, L. J. Durham, and A. M. Sargeson, *ibid.*, **5**, 2103 (1966); D. A. Buckingham, L. J. Durham, and A. M. Sargeson, *Australian J. Chem.*, **20**, 257 (1967); R. G. Asperger and C. F. Liu, *J. Am. Chem. Soc.*, **89**, 708 (1967).

[14] F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1315 (1967).

[15] C. C. McDonald and W. D. Phillips, *J. Am. Chem. Soc.*, **85**, 3736 (1963).

[16] A. Chakravorty and R. H. Holm, *ibid.*, **86**, 3999 (1964).

[17] G. W. Everett, Jr., and R. H. Holm, *ibid.*, **87**, 2117 (1965).

[18] M. J. O'Connor, R. E. Ernst, and R. H. Holm, to be published.

[19] L. G. Thomé, *Ber.*, **36**, 582 (1903).

[20] P. Bruck, I. N. Denton, and A. H. Lamberton, *J. Chem. Soc.*, 921 (1956).

[21] A. W. Ingersoll, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 506.

[22] W. Theilacker and H. Winkler, *Ber.*, **87**, 690 (1954).

[23] H. E. Smith, S. L. Cook, and M. E. Warren, Jr., *J. Org. Chem.*, **29**, 2265 (1964).

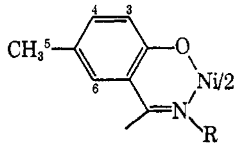
[24] J. C. Duff, *J. Chem. Soc.*, 547 (1941).

[25] C. Bulöw and W. von Sicherer, *Ber.*, **34**, 3889 (1901).

evacuated sample container. The salicylaldimine complexes are considerably more stable and required no special precautions in handling. Magnetic moments of solids and solutions at room temperature were measured by the Gouy method using aqueous nickel chloride solutions and freshly boiled and distilled water, respectively, as the calibrants. Measurements of electronic spectra were obtained using a Cary Model 14 spectrophotometer. Nmr spectra were taken on a Varian HR-100 spectrometer using $CDCl_3$ solutions with TMS as an internal reference. Solution concentrations were 0.1 $M$ or less. Chemical shifts were measured by the usual side-band technique.

## Results and Discussion

Reaction of bis(5-methylsalicylaldehyde)nickel(II) with an asymmetric primary amine yields the bis(salicylaldimino) complexes of general formulation **1**. If an optically pure amine is used only one complex, either Ni(5-Me-(+)R-sal)$_2$ or Ni(5-Me-(−)R-sal)$_2$, here-



**1**

after designated as the active forms, is produced. Use of the racemic amine results in a diastereoisomeric mixture containing the two active forms and the *meso* form, Ni(5-Me-(+)R-sal)(5-Me-(−)R-sal). If the amine is branched at the α-carbon atom, the complexes exist in both the planar and tetrahedral configurations in noncoordinating solvents at and above room temperature with the occurrence of the following dynamic equilibria.

$$\text{planar } [(+,+) \text{ or } (-,-)] \rightleftharpoons \text{tetrahedral } [(+,+) \text{ or } (-,-)] \qquad (1)$$

$$\text{planar } (+,-) \rightleftharpoons \text{tetrahedral } (+,-) \qquad (2)$$

Previous work has demonstrated that the structural interconversion is so rapid that the proton shifts are averaged over the configurations of the two structural isomers, and that for a variety of asymmetric R groups the active and *meso* complexes exhibit two well-resolved sets of shifts at virtually all temperatures of measurement.[2] These sets are unambiguously identified by measuring the pmr spectrum of the active form alone.

The temperature dependence of the contact shift of the *i*th proton in a complex rapidly interconverting between the planar and tetrahedral configurations is given by

$$\frac{\Delta f_i}{f} = -a_i\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g\beta S(S+1)}{6SkT}[\exp(\Delta F/RT) + 1]^{-1} \qquad (3)$$

in which $\Delta f_i$ is the contact shift, $a_i$ the electron-nuclear hyperfine 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 ($S = 1$) and $N_p$ the mole fraction of the planar ($S = 0$) stereoisomer. The remaining symbols have their usual meanings.[2] The tetrahedral mole fraction may be expressed as

$$N_t = [\exp(\Delta F/RT) + 1]^{-1} = \frac{{\mu_{obsd}}^2}{{\mu_t}^2} \qquad (4)$$

where $\mu_{obsd}$ is the observed magnetic moment of the equilibrium mixture and $\mu_t$ the moment of the tetrahedral isomer. For a given proton $i$ in the active and *meso* forms of complexes such as **1**, the difference in contact shifts is expressed as

$$\Delta f_{i(\mathrm{act})} - \Delta f_{i(meso)} = \Delta\Delta f_i =$$
$$\frac{B}{T}\left[\frac{a_{i(meso)}}{\exp(\Delta F_{meso}/RT) + 1} - \frac{a_{i(\mathrm{act})}}{\exp(\Delta F_{\mathrm{act}}/RT) + 1}\right] \qquad (5)$$

where

$$B = \left(\frac{\gamma_e}{\gamma_H}\right)\frac{fg\beta S(S+1)}{6Sk}$$

Hence, the origin of nonzero $\Delta\Delta f_i$ values rests in an intrinsic difference in coupling constants, $\Delta a_i$, or free-energy changes, $\Delta\Delta F$, for the diastereoisomers or a combination of these two effects, where we define

$$\Delta a_i = a_{i(\mathrm{act})} - a_{i(meso)} \qquad (6)$$

and

$$\Delta\Delta F = \Delta F_{\mathrm{act}} - \Delta F_{meso} \qquad (7)$$

In addition, it is true that in principle $g_{\mathrm{act}} \neq g_{meso}$. However, it is known or assumed that the differences in magnetic susceptibilities of two such closely related isomers are indistinguishable by the usual techniques of bulk magnetic measurement and that the $g$ values of the two are essentially identical. Equation 5 is derived on this basis.

The present investigation represents an attempt to assess more thoroughly than was previously possible the relative contributions of $\Delta a_i$ and $\Delta\Delta F$ to $\Delta\Delta f_i$ values observed for paramagnetic Ni(II) complexes. Ideally, for each diastereoisomeric pair, measurements of $\Delta a_i$ and $\Delta\Delta F$ are required. Independent measurement of these quantities for the *same* pair can be achieved only if it is possible to reach both the non-Curie ($N_t < 1$) and Curie ($N_t \cong 1$) regions of contact shift dependence within the experimentally accessible temperature range of measurement. In the latter situation the contact shifts are given by

$$\frac{\Delta f_i}{f} = -a_i\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g\beta S(S+1)}{6SkT} \qquad (8)$$

thereby allowing accurate determination of coupling constants for each diastereoisomer from contact shift measurements alone. These values may then be applied in the non-Curie region, represented by eq 3, and the separate temperature dependences of the free energies for the active and *meso* forms calculated from the contact shifts. Unfortunately, in the present and past studies we have been unable to devise any diastereoisomeric pair of complexes whose stereochemical populations are sufficiently temperature sensitive that both the Curie and non-Curie regions are demonstrably obtained within the experimental range of −50 to 100°. Indeed, the asymmetric salicylaldimine complexes have $N_t \cong$ 0.4–0.6[26] in this range and only with an optically inactive R group (*t*-Bu) is it possible to obtain $N_t = 1$.[2,28] Because no measurement of $\Delta a_i$ was

---

[26] Note that, as pointed out elsewhere,[27] the $\Delta F$ values in ref 2 are too large by an amount $RT \ln 3$, leading to erroneously small $N_t$ values. The quoted $\Delta S$ values in this reference are too small by $R \ln 3$.

[27] R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966).

[28] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963); L. Sacconi, M. Ciampolini, and N. Nardi, *ibid.*, **86**, 819 (1964).

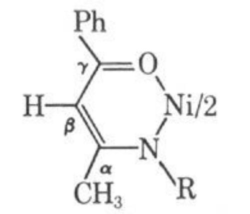
**Table I.** Characterization of Bis(5-methyl-N-R-salicylaldimino)metal(II) and Bis(β-ketoamino)nickel(II) Complexes

| R | $R_\alpha$ | Complex | Mp, °C[a] | Calcd, % C | Calcd, % H | Calcd, % N | Found, % C | Found, % H | Found, % N |
|---|---|---|---|---|---|---|---|---|---|
| | | | Salicylaldimines | | | | | | |
| $PhCHCH_3$ | | Ni(5-Me-PhEt-sal)$_2$ | 165–166[b] | 71.80 | 6.03 | 5.23 | 71.33 | 6.08 | 5.26 |
| $PhCH_2CHCH_3$ | | Ni(5-Me-Amp-sal)$_2$ | 77–80[c] | 72.48 | 6.44 | 4.97 | 72.28 | 6.52 | 4.74 |
| $CH_3CH_2CHCH_3$ | | Pd(5-Me-*sec*-Bu-sal)$_2$ | 151–152 | 59.23 | 6.63 | 5.75 | 58.95 | 6.64 | 5.80 |
| $CH_3CH_2CHCH_3$ | | Zn(5-Me-*sec*-Bu-sal)$_2$ | 187 | 64.64 | 7.23 | 6.28 | 64.71 | 7.21 | 6.36 |
| | | | β-Ketoamines | | | | | | |
| $PhCHCH_3$ | $CH_3$ | Ni(PhEt-PhHMe)$_2$ | 189[d] | 73.61 | 6.18 | 4.77 | 73.41 | 6.28 | 4.73 |
| $PhCH_2CHCH_3$ | $CH_3$ | Ni(Amp-PhHMe)$_2$ | 171 | 74.16 | 6.55 | 4.55 | 74.46 | 6.65 | 4.49 |
| $CH_3CH_2CHCH_3$ | H | Ni(*sec*-Bu-PhHH)$_2$ | 106[e,f] | 67.41 | 6.96 | 6.05 | 67.43 | 7.10 | 6.02 |
| $PhCHCH_3$ | H | Ni(PhEt-PhHH)$_2$ | 167–168[g] | 73.01 | 5.77 | 5.01 | 72.81 | 5.78 | 4.90 |
| $PhCH_2CHCH_3$ | H | Ni(Amp-PhHH)$_2$ | 120–121[h] | 73.61 | 6.18 | 4.77 | 73.75 | 6.40 | 4.65 |
| $C(CH_3)_3$ | H | Ni-(*t*-Bu-PhHH)$_2$ | 124–125 | 67.41 | 6.96 | 6.05 | 67.30 | 6.90 | 5.93 |

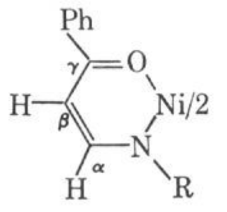
[a] Refers to mixture of diastereoisomers. [b] (−,−), (+,+) complexes, 136°. [c] After removal of methanol; (+,+) complex 87–88°. [d] (−,−) complex, 213–214°. [e] Softening at 79°, complete melting at 106°. [f] (+,+) complex, 151°. [g] (+,+) complex, 126°. [h] (+,+) complex, 118°.

possible for the Ni(II) salicylaldimines, it was necessary to assume $a_{i(\mathrm{act})} = a_{i(meso)}$ and to calculate the temperature dependences of $\Delta F$ for a given pair from a single $a_i$ value for both the active and *meso* forms. This procedure, while defensible for reasons given previously,[2] is not desirable without further justification, for it requires that a nonzero $\Delta\Delta F$ effect is the sole, or at least the predominant, contributing factor to the observed $\Delta\Delta f_i$ values.

In the absence of a diastereoisomeric pair of complexes which exhibit both Curie and non-Curie contact shift dependences, the next most favorable situation would be one involving two closely related pairs possessing structurally and electronically similar planar and tetrahedral forms, with one pair exhibiting a strict Curie dependence and the other a non-Curie behavior. This situation is believed satisfied to an entirely reasonable degree by the pair of bis(β-ketoamine) complexes **2** and **3**, whose structural and electronic similarities are obvious. Both groups of complexes can be prepared with the same asymmetric R groups as the pure active form or as a diastereoisomeric mixture of active and *meso* forms. As the following data show, the principal effect of altering $R_\alpha$ from $CH_3$ to H is to make $N_t < 1$. Characterization data for complexes of types **2** and **3** and for new salicylaldimine complexes with the same R groups are set out in Table I. β-Ketoamine complexes are abbreviated throughout as Ni(R-$R_\gamma R_\beta R_\alpha$)$_2$. Before considering the pmr results, it is first necessary to examine the spectral and magnetic data which serve to establish independently the configurations and the configurational equilibria of the complexes **1**, **2**, and **3**.



**2**



**3**

**Configurations and Configurational Equilibria.** Bischelate complexes such as **1**, **2**, and **3**, which contain unsymmetrical chelate rings, have enantiomeric configurations at the metal when nonplanar. Following the nomenclature suggested for trigonal complexes,[29] the two absolute configurations, depicted in Figure 1, are designated as Δ and Λ, which describe the configurations without reference to any known structure. Barring complete stereoselectivity, complexes prepared from active amines will consist of the Δ(+,+), Λ(+,+) or Δ(−,−), Λ(−,−) isomers, whereas those prepared from the racemic amines will contain these active species and the *meso* forms Δ(+,−), Λ(+,−). That true enantiomeric complexes are produced by using the (+) and (−) amines is demonstrated by the exact mirror image ORD curves of the (+,+) and (−,−) forms of a typical complex, Ni(5-Me-PhEt-sal)$_2$,[30] shown in Figure 2. The *meso* form of these complexes will occur as an inactive mixture and cannot be prepared free of active isomers.

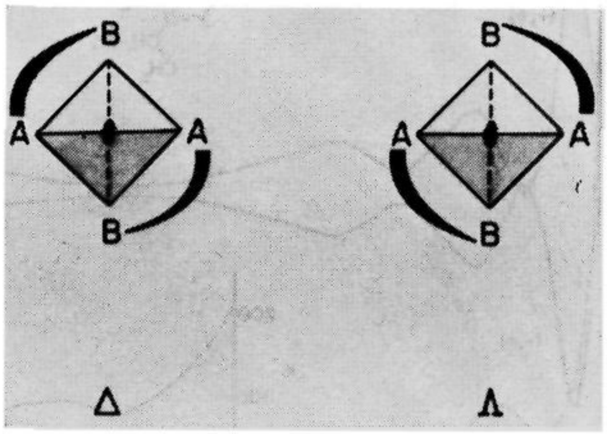


Figure 1. Absolute configurations of a bischelate complex viewed down the $C_2$ axis: Δ, right-handed helicity, Λ, left-handed helicity along principal axis. A and B convey the chelate ring asymmetry.

The establishment of the stereochemical configurations of the complexes **1**–**3** and of the existence of the configurational equilibrium from magnetic and spectral data follows directly from considerations discussed in detail elsewhere.[2,17,28,31,32] Relevant data are given in

---

(29) T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

(30) The preparation of several other substituted Ni((−)PhEt-sal)$_2$ complexes and their ORD curves in the visible region have been reported by A. P. Terent'ev, G. V. Panova, and E. G. Rukhadze, *J. Gen. Chem. USSR*, **34**, 3055 (1964).

(31) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963); A. Chakravorty and R. H. Holm, *ibid.*, **3**, 1010 (1964).

(32) For reviews of the configurations and configurational equilibria of nickel(II) salicylaldimine and β-ketoamine complexes, *cf.* R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966); L. Sacconi, *Coordination Chem. Rev.*, **1**, 126 (1966); S. Yamada, *ibid.*, **1**, 415 (1966).

Table II. Magnetic Data for Solids and Chloroform Solutions

| Complex[a] | Solid $\mu_{eff}$, BM[b] | Solution Conc, *mm*[f] | Temp, °C | $10^6 \chi^M_{cor}$ | $\mu_{eff}$, BM[b] |
|---|---|---|---|---|---|
| Ni(*sec*-Bu-PhHMe)$_2$ | 3.34[c] | 61.0 | 24 | 4690 | 3.34 ± 0.05 |
| Ni(Amp-PhHMe)$_2$ | 3.19 | 41.2 | 27 | 4230 | 3.18 ± 0.05 |
| Ni(PhEt-PhHMe)$_2$ | 3.25 | 34.3 | 27 | 4244 | 3.19 ± 0.05 |
| Ni(*t*-Bu-PhHH)$_2$ | 3.27 | 53.3 | 25 | 4409 | 3.25 ± 0.05 |
| Ni(*sec*-Bu-PhHH)$_2$ | 2.38 | 49.5 | 27 | 3673 | 2.97 ± 0.05 |
| Ni(Amp-PhHH)$_2$ | Dia | 37.0 | 26 | 3840 | 3.03 ± 0.05 |
| Ni(PhEt-PhHH)$_2$ | Dia | 11.8 | 26 | 1859 | 2.11 ± 0.20 |
| Ni(5-Me-*sec*-Bu-sal)$_2$ | 3.28 | 66.2 | 30 | 2049 | 2.23 ± 0.06[d] |
| Ni(5-Me-Amp-sal)$_2$ | ...[e] | 32.9 | 26 | 2216 | 2.30 ± 0.06 |
| Ni(5-Me-PhEt-sal)$_2$ | ...[e] | 41.8 | 25 | 522 | 1.11 ± 0.40 |

[a] Data refer to diastereoisomeric mixture of complexes (except for Ni(*t*-Bu-PhHH)$_2$): Ni(*i*-Pr-PhHH)$_2$,[33] 3.05 BM (CHCl$_3$); Ni(*i*-Pr-PhHMe)$_2$,[17] 3.35 (solid), 3.33 BM (CS$_2$). [b] Calculated from the Curie law, $\mu_{eff} = 2.83(\chi^M_{cor}T)^{1/2}$. [c] Reference 17. [d] Reference 2. [e] Not measured. [f] Molar concentration range 0.018–0.097 *M*.

Tables II and III. Previous work has shown that for salicylaldimine complexes having R = *sec*-alkyl, planar and tetrahedral forms exist in equilibrium in chloroform solution.[2] Both Ni(5-Me-*sec*-Bu-sal)$_2$ and Ni(5-Me-Amp-sal)$_2$ are involved in this equilibrium, as evidenced by the near-infrared absorption band at ~6900 cm$^{-1}$, characteristic of the pseudo-tetrahedral form and the magnetic moments in solution which are intermediate between 0 and 3.2–3.3 BM. Moments of fully tetrahedral crystalline salicylaldimines and various Ni(X-*t*-Bu-sal)$_2$ complexes in the solid and solution phases fall within the latter range.[2,28,31] On the basis of the same evidence both stereoisomers are found in solutions of Ni(5-Me-PhEt-sal)$_2$, although $N_t$ for this complex is considerably less than for the other two. Further evidence for the configurational equilibrium of this complex is shown by the temperature dependence of the intensity of the ~7000-cm$^{-1}$ band, given in Figure 3. As with other salicylaldimine complexes[32] the equilibrium is shifted toward the tetrahedral isomer with increasing temperature, and below room temperature associated species form and produce a characteristic absorption feature at ~9500 cm$^{-1}$. Existence of the associated species is also revealed by the temperature dependence of the contact shifts (*vide infra*).

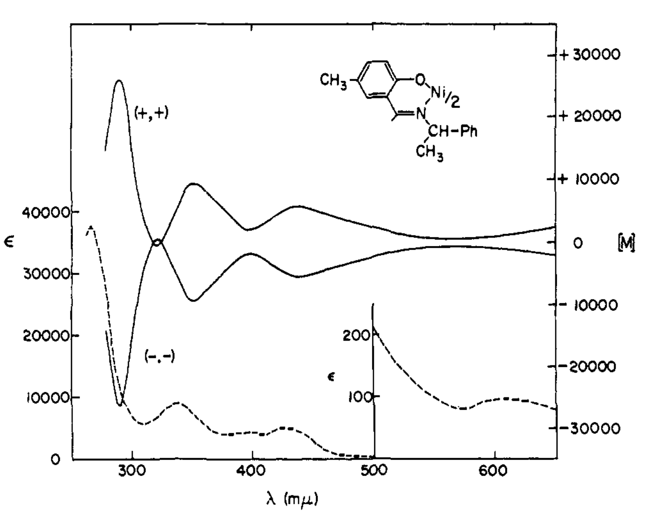


Figure 2. Electronic absorption spectrum and ORD spectra (———) of the (+,+) and (−,−) isomers of Ni(5-Me-PhEt-sal)$_2$ in chloroform solution at room temperature.

Table III. Electronic Spectral Data in Chloroform Solutions[a]

| Complex | $\lambda_{max}$, cm$^{-1}$ | ε, l. mole$^{-1}$ cm$^{-1}$[b] |
|---|---|---|
| Ni(Amp-PhHMe)$_2$ | 16,700, 14,700 (sh) | 61, 21 |
| | 10,900, 6020 | <1, 22 |
| Ni(PhEt-PhHMe)$_2$ | 17,100, 14,900 (sh) | 45, 20 |
| | ..., 5990 | ..., 18 |
| Ni(*t*-Bu-PhHH)$_2$ | 16,800, 14,700 (sh) | 50, 18 |
| | 10,700, 5920 | <1, 22 |
| Ni(*i*-Pr-PhHH)$_2$ | 16,580, 15,400 (sh) | 53, 32 |
| | 10,800, 6370 | <1, 33 |
| Ni(*sec*-Bu-PhHH)$_2$ | 16,500, 14,700 (sh) | 59, 32 |
| | 10,800, 6310 | <1, 31 |
| Ni(Amp-PhHH)$_2$ | 16,500, 14,700 (sh) | 56, 31 |
| | 10,900, 6330 | <1, 34 |
| Ni(PhEt-PhHH)$_2$ | 16,500, ... | 68, ... |
| | 10,900, 6060 | <1, 16 |
| Ni(5-Me-PhEt-sal)$_2$[c] | 37,400, 29,600 | 37,000, 8800 |
| | 24,900 (sh), 23,500 | 4240, 4900 |
| | 16,200, ... | 96, ... |
| | 11,000, 6990 | ~1, 6.0 |
| Ni(5-Me-Amp-sal)$_2$ | 16,800 (sh), 14,700 (sh) | 96, 57 |
| | 11,000, 6850 | 4, 33 |

[a] Data refer to diastereoisomeric mixtures of complexes (where appropriate) measured at ambient room temperature; spectral data for Ni(*i*-Pr-PhHMe)$_2$ and Ni(*sec*-Bu-PhHMe)$_2$ given in ref 17; all β-ketoamine complexes exhibit a broad shoulder in the 7500–8500-cm$^{-1}$ region. [b] Apparent values, uncorrected for underlying absorption. [c] Spectra of the (+,+) and (−,−) complexes are indistinguishable from that of the mixture.

Both stereoisomers of Ni(R-PhHMe)$_2$ are simultaneously populated in solution only when R = CH$_3$, *n*-alkyl, or aryl.[17,33] Complexes with R = *sec*-Bu, Amp, and PhEt possess the same Curie magnetic moments within experimental error in the solid phase and in chloroform solution, which is the criterion for assigning $N_t$ = 1 in solution. Additionally, the ligand field spectra in the visible and infrared regions are characteristic of pseudo-tetrahedral β-ketoamine complexes of this type.[17] Turning next to Ni(R-PhHH)$_2$, only the R = *t*-Bu complex has $N_t$ = 1. Taking the limiting moment $\mu_t$ of the other four complexes of this type to be 3.27 BM (*cf.* Table II) and assuming only planar and tetrahedral complexes to be present, the following $N_t$ values are obtained: 0.87 (*i*-Pr), 0.86 (Amp), 0.83 (*sec*-Bu), 0.42 (PhEt). The absorption spectra of all Ni(R-PhHH)$_2$ complexes exhibit the broad near-infrared absorption band maximizing in the range (5900–6400 cm$^{-1}$) where a corresponding

---

(33) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, 88, 2442 (1966), and unpublished work.

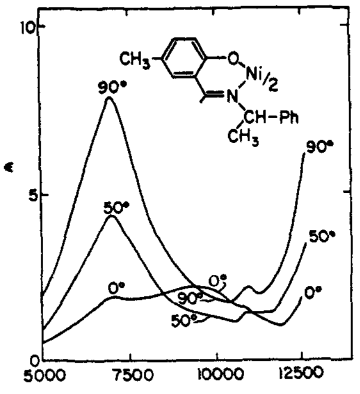


Figure 3. Ligand field spectrum of the diastereoisomeric mixture of $Ni(5\text{-}Me\text{-}PhEt\text{-}sal)_2$ complexes in toluene solution as a function of temperature in the near-infrared region.

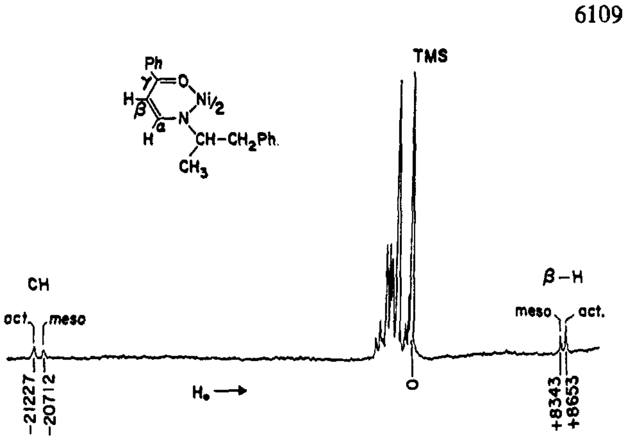


Figure 5. 100-Mc proton resonance spectrum of a mixture of active and *meso* forms of $Ni(Amp\text{-}PhHH)_2$ in $CDCl_3$ solution at ~30°. Frequencies (cps) are the chemical shifts.

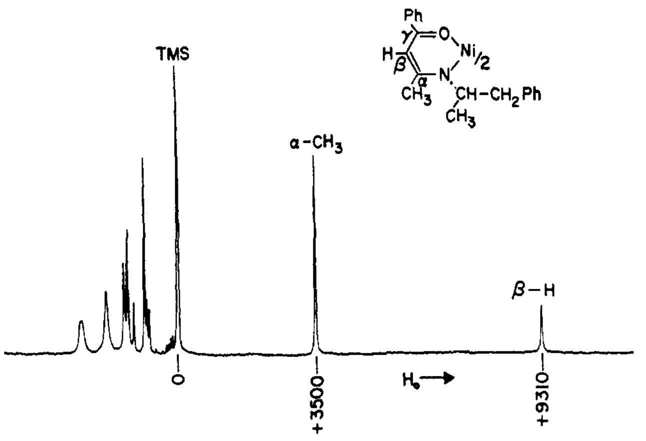


Figure 4. 100-Mc proton resonance spectrum of a mixture of active and *meso* forms of $Ni(Amp\text{-}PhHMe)_2$ in $CDCl_3$ solution at ~30°. Frequencies (cps) are the chemical shifts.

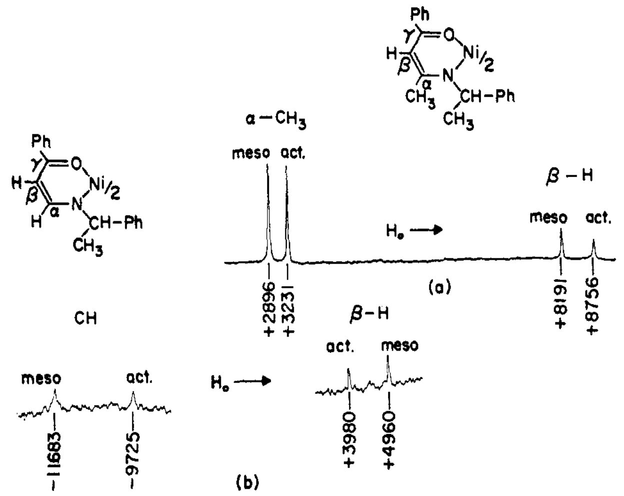


Figure 6. Portions of the 100-Mc proton resonance spectra of mixtures of the active and *meso* forms of (a) $Ni(PhEt\text{-}PhHMe)_2$ and (b) $Ni(PhEt\text{-}PhHH)_2$ in $CDCl_3$ solution at ~30°. Frequencies (cps) are the chemical shifts.

feature in the spectra of the $Ni(R\text{-}PhHMe)_2$ complexes occurs, and it is therefore attributed to the pseudotetrahedral form. It is noted that neither $\epsilon_{max}$ of these bands (*cf.* Table III) nor their integrated areas can be considered reliable guides to $N_t$ because of pronounced width and diffuseness of these absorption features.

It is concluded that the principal difference between diastereoisomeric mixtures of complexes of types **2** and **3** with the same R group is the position of the configurational equilibrium. Evidently the greater degree of motional freedom imparted to R by α-H in **3** compared to $\alpha\text{-}CH_3$ in **2** results in decreased steric interaction in the planar form, with the consequence that this stereoisomer of **3** is measurably populated. It is also observed that the tendency of R groups, as measured by magnetic moments, to destabilize the planar form in the complexes **1**[2] and **3** runs parallel, the order of increasing $N_t$ in chloroform being PhEt < *sec*-Bu $\lesssim$ *i*-Pr ~ Amp < *t*-Bu.

The peculiar magnetic moment of $Ni(sec\text{-}Bu\text{-}PhHH)_2$ in the solid phase deserves comment. The value of 2.38 BM refers to a solid containing active and *meso* forms. If $\mu_t$ = 3.27 BM for both forms, then $N_t \sim 0.5$ and it is concluded the solid contains a 1:1 mixture of planar and tetrahedral isomers. Certain bis(phosphine)dihalonickel(II) complexes can be isolated as crystalline solids in one configuration or the other,[34] but the occurrence of both configurations in the *same* crystalline phase has been demonstrated only in the case of $Ni(Ph_2(PhCH_2)P)_2Br_2$.[35] Whether or not this situation obtains here can only be determined by an X-ray investigation.

**Pmr Spectra and Contact Shifts.** Spectra of the active and *meso* forms of several β-ketoamine complexes are shown in Figures 4–6. Those of active and *meso*-salicylaldimine complexes are quite similar to spectra already published.[1,2] Contact shifts, coupling constants of interest, and $\Delta\Delta f_t$ values are given in Table IV. Assignments of sets of signals to the active and *meso* forms follows unambiguously from the spectra of the active forms alone. Individual signal assignments are the same as in previous work.[2,17] The α-H and CH(R) resonances in **3** were differentiated by use of the spectrum of $Ni(t\text{-}Bu\text{-}PhHH)_2$, which lacks the latter feature. α-H signals are very broad with extremely large negative contact shifts and were not measured for the other $Ni(R\text{-}PhHH)_2$ complexes. For **1**, **2**, and **3** the signs and magnitudes of the contact

---

(34) R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, 4, 1701 (1965).

(35) B. T. Kilbourn, H. M. Powell, and J. A. C. Darbyshire, *Proc. Chem. Soc.*, 207 (1963).

Table IV. Contact Shifts and Coupling Constants

| Complex | Position | $\Delta f_i$,[a] cps | | | $\Delta\Delta f_i$,[b] cps | $a_i$, gauss | | |
|---|---|---|---|---|---|---|---|---|
| | | Active | | *meso* | | Active | | *meso* |
| Ni(*i*-Pr-PhHMe)$_2$[c] | $\alpha$ | | +3,739 | | ... | | −0.318 | |
| | $\beta$ | | +10,157 | | ... | | −0.865 | |
| Ni(*sec*-Bu-PhHMe)$_2$ | $\alpha$ | +3,477 | | +3,445 | 32 | −0.303 | | −0.300 |
| | $\beta$ | +9,549 | | +9,549 | 0 | −0.831 | | −0.831 |
| Ni(Amp-PhHMe)$_2$ | $\alpha$ | +3,667 | | +3,667 | 0 | −0.335 | | −0.335 |
| | $\beta$ | +9,862 | | +9,862 | 0 | −0.902 | | −0.902 |
| Ni(PhEt-PhHMe)$_2$ | $\alpha$ | +3,416 | | +3,081 | 335 | −0.306 | | −0.276 |
| | $\beta$ | +9,323 | | +8,758 | 565 | −0.834 | | −0.783 |
| Ni(*t*-Bu-PhHH)$_2$ | $\alpha$ | | −33,910 | | ... | | +3.01 | |
| | $\beta$ | | +9,713 | | ... | | −0.863 | |
| Ni(*i*-Pr-PhHH)$_2$ | $\beta$ | | +8,436 | | ... | | −0.862[e] | |
| | CH | | −18,610 | | ... | | ... | |
| Ni(*sec*-Bu-PhHH)$_2$ | $\beta$ | +8,563 | | +8,446 | 117 | −0.917[e,f] | | −0.917[e,f] |
| | CH | −19,206 | | −18,760 | 446 | ... | | ... |
| Ni(Amp-PhHH)$_2$ | $\beta$ | +9,206 | | +8,896 | 310 | −0.937[e,f] | | −0.937[e,f] |
| | CH | −20,894 | | −20,379 | 515 | ... | | ... |
| Ni(PhEt-PhHH)$_2$ | $\beta$ | +4,548 | | +5,528 | −980 | −1.08[e,g] | | −1.08[e,g] |
| | CH | −9,380 | | −11,338 | −1958 | ... | | ... |
| Ni(5-Me-*sec*-Bu-sal)$_2$[d] | 3 | +1,260 | | +1,140 | 120 | | ... | |
| | 4 | −947 | | −853 | 94 | | ... | |
| | 5 | −907 | | −810 | 97 | +0.170[h] | (+0.166)[e] | +0.170[h] |
| Ni(5-Me-Amp-sal)$_2$ | 3 | +1,444 | | +1,270 | 174 | | ... | |
| | 4 | −1,125 | | −979 | 146 | | ... | |
| | 5 | −1,090 | | −959 | 131 | +0.170[h] | (+0.186)[e] | +0.170[h] |
| Ni(5-Me-PhEt-sal)$_2$ | 3 | +325 | | +359 | −34 | | ... | |
| | 4 | −208 | | −240 | −32 | | ... | |
| | 5 | −188 | | −215 | −27 | +0.170[h] | (+0.157)[e] | +1.170[h] |

[a] Data refer to $CDCl_3$ solution, 100 Mc/sec, 30°, unless otherwise noted. [b] $\Delta f_i$(active) − $\Delta f_i$(*meso*). [c] Data from ref 17 in $CS_2$ solution converted to 100-Mc basis. [d] Spectrum (60 Mc) shown in ref 1. [e] Calculated from averaged contact shifts and solution magnetic data in Table II. [f] ±0.031 gauss. [g] ±0.25 gauss. [h] Assumed values; *cf.* text and ref 2.

shifts are the same as found previously,[2,17] indicating that spin imbalance in the ligands is affected mainly by ligand-to-metal antiparallel ($\beta$) spin transfer *via* $\pi$ bonding involving, formally, the highest filled $\pi$ MO of the ligand anion and the $d_{xz}$ and $d_{yz}$ metal orbitals.[16]

Several important results are immediately forthcoming from the spectra and contact shifts. First, the absolute configuration at the metal is of no consequence. The two isomers of the *meso* form are enantiomeric and can give only a single set of signals, but those of the active form, *e.g.*, Δ(+,+) and Λ(+,+), are diastereoisomeric and should in principle give two sets of resonances. These have never been observed for any active isomer of **1**, **2**, and **3**, presumably because of rapid racemization rates. This situation appears especially likely for the salicylaldimines, which have been shown to undergo facile ligand exchange[1,16] (*vide infra*). Second, nonzero values of $\Delta\Delta f_i$ are observed for all ring substituent signals in **1** and **3**, and for the CH signals in **3**. (The corresponding CH signals in **1** and **2** were not measured.) Particularly relevant to the source of $\Delta\Delta f_i$ values is the consistent observation for $\beta$-ketoamine complexes with the same R group that $|\Delta\Delta f_{\beta H}(\mathbf{3})| \gg |\Delta\Delta f_{\beta H}(\mathbf{2})|$, using the shifts of a chelate ring substituent common to both. The case of the R = Amp complexes is especially simple. At 30° the sets of $\alpha$-Me and $\beta$-H signals of the active and *meso* forms of Ni(Amp-PhHMe)$_2$ are coincident (Figure 4), whereas the $\beta$-H signals of Ni(Amp-PhHH)$_2$ are separated by 310 cps (Figure 5). A substantial value of $\Delta\Delta f_{\beta H}$ is observed for Ni(PhEt-PhHMe)$_2$, but this shift difference is ~1.7 times larger in Ni(PhEt-PhHH)$_2$ although of opposite sign (Figure 6).

**Origin of Contact Shift Differences in Diastereoisomers.** The contact shifts in Table IV have been calculated from the relation $\Delta f_i = f_{i(\text{complex})} - f_{i(\text{dia})}$, in which the $f_{i(\text{dia})}$ values have for convenience been taken from the free ligand spectra. Although the corresponding tetrahedral diastereoisomeric Zn(II) complexes are more suitable diamagnetic references, the very small errors in $\Delta f_i$ and $\Delta\Delta f_i$ from the use of ligand shifts are inconsequential in the argument which follows.[36]

Considering first the diastereoisomeric Ni(R-Ph-HMe)$_2$ complexes, the $\alpha$-Me contact shifts of each are observed to possess a Curie dependence from *ca.* −40 to 90°, supporting the conclusion from the magnetic susceptibility data that $N_t = 1$. Equation 8 applies, in which case the difference in contact shifts would be given by

$$\Delta\Delta f_i = -\frac{B}{T}\Delta a_i \qquad (9)$$

accepting $g_{\text{act}} = g_{meso}$. Values of $\Delta\Delta f_{\alpha\text{Me}}$ for Ni(*sec*-Bu-PhHMe)$_2$ and Ni(PhEt-PhHMe)$_2$ (*cf.* Figure 7) do decrease with increasing temperature, in agreement with eq 9 and temperature-independent $\Delta a_i$ quantities. The coupling constants for this group of complexes given in Table IV have been calculated from measured contact shifts at ~30° and exhibit a small but real de-

---

(36) Our study of the pmr spectra of diastereoisomeric Zn(II) complexes of types 1, 2, and 3 is at present incomplete (R. H. Holm, R. E. Ernst, D. H. Gerlach, M. J. O'Connor, J. Schoenborn, work in progress) but does support the appropriateness of using the free ligands as diamagnetic references on the basis of the following observations at 100 Mc: (i) chemical shifts of ligands and their complexes differ by no more than ~±15 cps and frequently by less; (ii) active and *meso* forms have been distinguished only in R = PhEt complexes. The signal separations of $\beta$-H in Zn(PhEt-PhHMe)$_2$ and Zn(PhEt-PhHH)$_2$ amount to no more than 15–30 cps, with even smaller values for the 5-Me separations in the analogous zinc(II) salicylaldimines. These values of $\Delta f_{i(\text{dia})}$ are very small compared to $\Delta\Delta f_i$ values calculated from ligand shifts.

pendence on R. Values of $\Delta a_i$, as reflected by $\Delta\Delta f_i$, are decidedly variant with R, being zero for $\alpha$-Me and $\beta$-H when R = Amp and quite substantial when R = PhEt.[37]

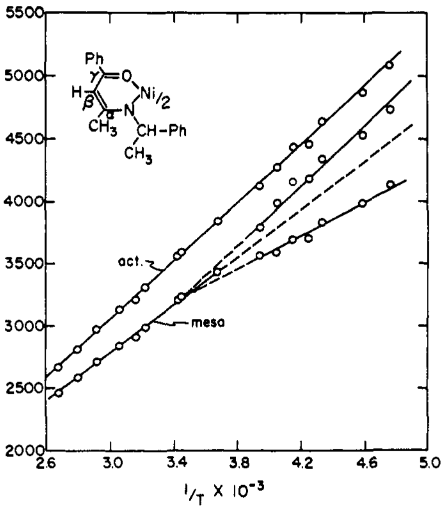
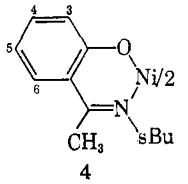


Figure 7. Temperature dependence of the contact shifts of the active and *meso* forms of Ni(PhEt-PhHMe)$_2$ in CDCl$_3$ solution.

The $\Delta\Delta f_{\beta\text{-H}}$ values of Ni(R-PhHH)$_2$ complexes, which are a factor of 3 or 4 to orders of magnitude larger than those of Ni(R-PhHMe)$_2$ with the same R group, can arise from both $\Delta a_{\beta\text{-H}}$ and $\Delta\Delta F$ contributions. Reference to Table IV reveals that $a_{\beta\text{-H}}$ values for complexes of both types with inactive R groups are virtually identical. Separate $a_{\beta\text{-H}}$ values for the active and *meso* forms of Ni(R-PhHH)$_2$ cannot be directly determined from eq 3 and 4 because the magnetic moments of the two forms are experimentally indistinguishable. The tabulated coupling constants are mean values obtained from the measured moments of the diastereoisomeric mixtures and averaged contact shifts. Excepting Ni(PhEt-PhHH)$_2$, whose mean $a_{\beta\text{-H}}$ value is subject to considerable error, it is observed that the mean coupling constants are within experimental error[38] of each other and are relatively close to, though slightly beyond experimental error of, $a_{\beta\text{-H}}$ values of the corresponding Ni(R-PhHMe)$_2$ complexes. Because the coupling constants will be sensitive to the exact structure of the tetrahedral form and the corresponding extent of metal–ligand $\pi$ bonding, the tetrahedral isomers of the two groups are structurally and electronically very similar. There is no obvious reason to assume that $\Delta a_{\beta\text{-H}}$ for active and *meso* Ni(R-PhHH)$_2$ would be substantially different from that for the corresponding Ni(R-PhHMe)$_2$ complex. Therefore, it is concluded that the predominant contribution to the observed $\Delta\Delta f_{\beta\text{-H}}$ values of **3** is $\Delta\Delta F$, and that in two cases (R = *sec*-Bu, Amp) contributions from a $\Delta a_{\beta\text{-H}}$ effect are essentially zero.

It is likely to be generally true that any observed $\Delta\Delta f_i$ value will be only a small fraction of $\Delta f_i$ for each diastereoisomer and, therefore, will be affected by correspondingly small $\Delta a_i$ and/or $\Delta\Delta F$ values (*cf.* eq 5). For this reason a separate assessment of these contributions to contact shift differences would probably have to be made for each group of diastereoisomeric complexes with related ligand structure. In an attempt to assess the contributions of $\Delta a_i$ and $\Delta\Delta F$ to the observed shift differences of diastereoisomeric salicylaldimine complexes **1**, whose contact shifts are given in Table IV and ref 2, the complex **4** was prepared. Surprisingly and unfortunately, the effect on the stereochemical populations by replacing the azomethine proton in **1** with methyl is the opposite of that of the analogous substitution for $\alpha$-H in **3**. Although separate contact shifts of the diastereoisomers of **4** are resolvable for some signals, the contact shifts are very small, indicating that equilibria 1 and 2 lie heavily to the left.[39] From the results on Ni(R-PhHH)$_2$ complexes with the same set of R groups and $N_t < 1$ over the temperature range of measurement, we infer, but cannot definitely prove, that $\Delta\Delta F$ is the principal contributing factor to the observed $\Delta\Delta f_i$ values for each diastereoisomeric pair of salicylaldimine complexes **1**.



**4**

**Thermodynamics of the Configurational Change.** The temperature dependences of the free-energy changes in reactions 1 and 2 were obtained from eq 3 using the coupling constants in Table IV and the $\beta$-H and 5-Me contact shifts of Ni(R-PhHH)$_2$ and Ni(5-Me-R-sal)$_2$, respectively. The linear variation required by eq 10 was satisfied over at least part of the temperature

$$\Delta F = \Delta H - T\Delta S \qquad (10)$$

range. The thermodynamic results given in Table V were obtained from a least-squares fit of the data in the range where $\Delta F$ varies linearly with temperature. Ni(PhEt-PhHH)$_2$ is insufficiently soluble for measurement over a temperature range. The planar-tetrahedral conversion is endothermic for all complexes except Ni(Amp-PhHH)$_2$, whose $\Delta H$ and $\Delta S$ values lie somewhat outside the ranges of values (0.5–4.8 kcal/mole and 2.8–8.4 eu, respectively) found previously for the same process in CDCl$_3$ solution.[2,17,27,31,33] The entropy changes, which in all cases favor the tetrahedral form, contain a substantial contribution from the electronic entropy change $R \ln 3 = 2.18$ eu.

Deviations of calculated $\Delta F$ values from eq 10 frequently occur at lower temperatures. This effect is strongly dependent upon ligand structure and is undoubtedly due to the formation of paramagnetic associated species over which the contact shifts are also averaged.[2] For example, both diastereoisomers of Ni-

---

[37] No splitting of the $\alpha$-Me signals of Ni(Amp-PhHMe)$_2$ could be detected from −40 to 90°. The observation of the largest contact shift differences with Ni(PhEt-PhHMe)$_2$ is consistent with the observation that diastereoisomers are observable in the spectra of the (diamagnetic) Zn(II) complexes.[36] Contact interactions usually amplify the chemical shift differences of analogous diamagnetic molecules.[14]

[38] The limits of error of the $a_{\beta\text{-H}}$ values for Ni(R-PhHH)$_2$ complexes in Table IV were obtained by considering experimental errors in solution magnetic measurements only.

[39] The following contact shifts have been observed for **4** at 100 Mc and ~30° in CDCl$_3$ solution: 3-H, 5-H, +360; 4-H, −325; 6-H, −75; C–CH$_3$, +249, +257; C–H, −2075, −2167 cps. The corresponding *n*-Bu complex is diamagnetic in solution (A. Chakravorty and K. C. Kalia, *Inorg. Chem.*, **6**, 690 (1967)). The signs and magnitudes of the contact shifts of the paramagnetic species are in agreement with those of pseudo-tetrahedral salicylaldimines (ref 2 and Table IV) but do not rule out the presence of molecular aggregates.

Table V. Thermodynamic Values for the Planar-Tetrahedral Conversion of Diastereoisomeric β-Ketoamine and Salicylaldiminenickel(II) Complexes in Chloroform Solution

| Complex | Isomer | Temp, °K[a] | $\Delta H$, cal/mole | $\Delta S$, eu | $\Delta F^{323°}$, cal/mole | $N_t^{323°}$ |
|---|---|---|---|---|---|---|
| Ni(*sec*-Bu-PhHH)$_2$ | Active | 230–355 | 103 | 3.51 | −1030 | 0.83 |
|  | *meso* |  | 312 | 4.04 | −992 | 0.82 |
| Ni(Amp-PhHH)$_2$ | Active | 300–360 | −952 | 0.67 | −1170 | 0.86 |
|  | *meso* |  | −491 | 1.74 | −1050 | 0.84 |
| Ni(5-Me-*sec*-Bu-sal)$_2$ | Active | 320–370 | 1090 | 3.26 | +39 | 0.48 |
|  | *meso* |  | 1410 | 3.94 | +140 | 0.44 |
| Ni(5-Me-Amp-sal)$_2$ | Active | 265–365 | 658 | 2.70 | −215 | 0.58 |
|  | *meso* |  | 1040 | 3.43 | −68 | 0.53 |
| Ni(5-Me-PhEt-sal)$_2$ | Active | 290–360 | 2810 | 4.83 | +1250 | 0.12 |
|  | *meso* |  | 2560 | 4.32 | +1170 | 0.14 |
| Ni(5-Me-(+)PhEt-sal)(5-Me-(+)*sec*-Bu-sal)[b] |  | 300–345 | 2030 | 4.69 | +514 | 0.31 |
| Ni(5-Me-(−)PhEt-sal)(5-Me-(+)*sec*-Bu-sal)[b] |  | 285–345 | 2000 | 4.36 | +590 | 0.28 |

[a] Temperature range of measurement in which $\Delta F$ is a linear function of temperature. [b] Obtained by ligand exchange reaction.

(5-Me-*sec*-Bu-sal)$_2$ follow eq 10 only above ~50°. The presence of associated forms of Ni(5-Me-PhEt-sal)$_2$ is evident in the electronic spectrum at 0° (Figure 3); accordingly, deviations of calculated free-energy changes of both isomers from eq 10 are observable below ~20°. In contrast, both isomers of Ni(*sec*-Bu-PhHH)$_2$ exhibit a strict adherence to eq 10 from −40 to 90°.

In Table V $\Delta F$ and $N_t$ values are compared at the lowest common temperature at which eq 10 is obeyed. The influence on the stereochemical populations of the basic ligand structure of complexes **1** and **3** is clearly observable, with $N_t(\mathbf{3}) > N_t(\mathbf{1})$ for a common R substituent. For both groups of complexes, $N_t$ increases with the size of R, the order being PhEt < *sec*-Bu < Amp.

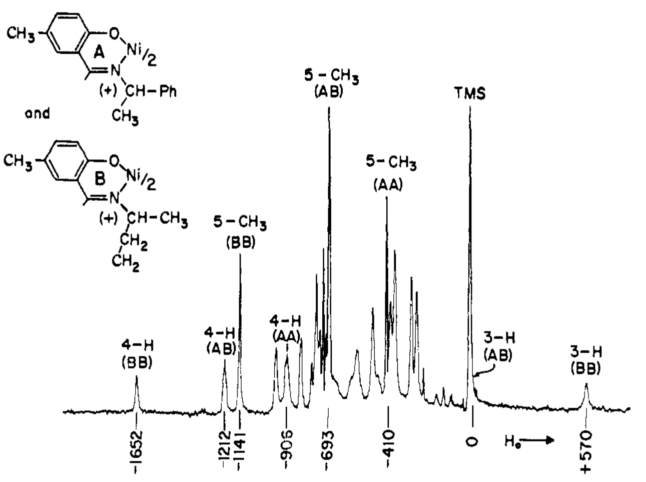


Figure 8. 100-Mc pmr spectrum of the equilibrium CDCl$_3$ solution at ~30° containing the mixed ligand complex Ni(5-Me-(+)PhEt-sal)(5-Me-(+)*sec*-Bu-sal) (AB) and the pure components Ni-(5-Me-(+)PhEt-sal)$_2$ (AA) and Ni(5-Me-(+)*sec*-Bu-sal)$_2$ (BB).

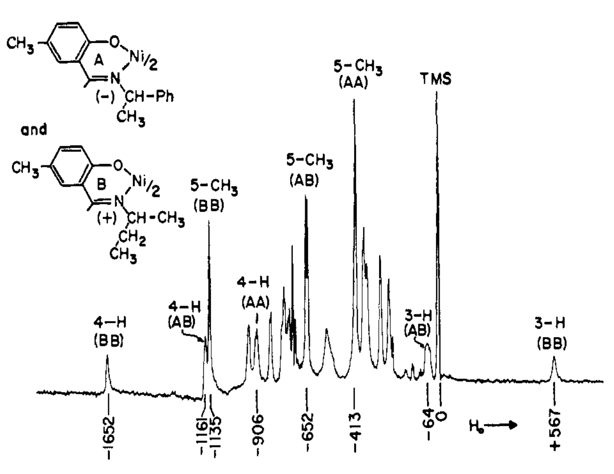


Figure 9. 100-Mc pmr spectrum of the equilibrium CDCl$_3$ solution at ~30° containing the mixed ligand complex Ni(5-Me-(−)PhEt-sal)(5-Me-(+)*sec*-Bu-sal) (AB) and the pure components Ni(5-Me-(−)PhEt-sal)$_2$ (AA) and Ni(5-Me-(+)*sec*-Bu-sal)$_2$ (BB).

**Mixed Ligand Complexes and Stereoselectivity.** By way of illustrating further the sensitivity of contact shift measurements in detecting diastereoisomeric complexes and differentiating the energetics of their structural changes, ligand exchange reactions 11–13 have been observed when chloroform solutions of the pure components in 1:1 mole ratio are mixed. These reactions reach equilibrium within several minutes of mixing. The exchange presumably occurs through a bimolecular path involving the more labile tetrahedral

$$\text{Ni(5-Me-(+)PhEt-sal)}_2 + \text{Ni(5-Me-(−)PhEt-sal)}_2 = 2\text{Ni(5-Me-(+)PhEt-sal)(5-Me-(−)PhEt-sal)} \quad (11)$$

$$\text{Ni(5-Me-(+)PhEt-sal)}_2 + \text{Ni(5-Me-(+)}sec\text{-Bu-sal)}_2 = 2\text{Ni(5-Me-(+)PhEt-sal)(5-Me-(+)}sec\text{-Bu-sal)} \quad (12)$$

$$\text{Ni(5-Me-(−)PhEt-sal)}_2 + \text{Ni(5-Me-(+)-}sec\text{-Bu-sal)}_2 = 2\text{Ni(5-Me-(−)PhEt-sal)(5-Me-(+)-}sec\text{-Bu-sal)} \quad (13)$$

species.[16] The product of reaction 11 has a pmr spectrum which is identical with that of the *meso* isomer prepared together with the active form by use of racemic α-phenethylamine in the synthesis. The products of reactions 12 and 13 are diastereoisomers, and the spectra of the equilibrium solutions in which these complexes are present are shown in Figures 8 and 9. It is evident that the contact shifts of these diastereoisomers are sufficiently different to distinguish one from the other and from the pure components in the same solution. The two chelate rings in the *meso* and mixed ligand complexes are nonequivalent, for these complexes lack the C$_2$ axis present in the active isomers. This nonequivalence has never been detected in the spectrum of any *meso* form of **1**, **2**, and **3**, except possibly that of Ni(PhEt-PhHMe)$_2$ (*vide infra*), but is observable in that of Ni(5-Me-(−)PhEt-sal)(5-Me-(+)*sec*-Bu-sal)

(Figure 9) whose 5-Me signals are split by 7 cps, further confirming the existence of this mixed ligand species.

It is observed from signal intensities that reactions 11, 12, and 13 proceed with no *over-all* stereoselectivity, *i.e.*, the concentration of the product in its planar and tetrahedral forms is twice the sum of the concentration of either pure component in both of its forms. However, the $\Delta F$ and $N_t$ data in Table IV reveal a small degree of stereoselectivity in the planar-tetrahedral conversion of the diastereoisomeric products of reactions 12 and 13 and in the conversions eq 1 and 2. The mere existence of nonzero $\Delta\Delta F$ values for the diastereoisomers of **1** and **3**, by which the contact shifts of the active and *meso* forms are mainly differentiated, does not, of course, specify the source of the free-energy differences. On the basis of the reasons which follow, it is concluded that the principal source of $\Delta\Delta F$ for a given diastereoisomeric pair derives from a real difference in free energies of the *tetrahedral*, *paramagnetic* active, and *meso* forms.

(i) The planar forms undoubtedly have the *trans* structure,[32] in which case the mutual interaction of R groups must be very slight. It is only by virtue of this interaction that the free energies of the active and *meso* isomers can differ.

(ii) The R groups in the tetrahedral forms are in close proximity with the attendant likelihood that $(+)$-$(+)$ (or $(-)$-$(-)$) and $(+)$-$(-)$ nonbonded interactions will differ to a far more pronounced extent than in the planar forms.

(iii) The differences in the total *chemical* shifts of the active and *meso* forms far exceed any such values observed for closely related diamagnetic planar or tetrahedral diastereoisomers,[36] indicating that it is the *contact* shifts which differ. Indeed, it is usually true that separate signals of active and *meso* isomers of planar Pd(II) or tetrahedral Zn(II) complexes of **1**, **2**, and **3** cannot be resolved at 100 Mc. Cases in point are Pd(5-Me-*sec*-Bu-sal)$_2$ and Zn(5-Me-*sec*-Bu-sal)$_2$, which exhibit a single set of signals, whereas the analogous Ni(II) diastereoisomers show substantial $\Delta\Delta f_i$ values. In particular, the 5-Me substituent is especially remote from the asymmetric center and the substantial $\Delta\Delta f_{5\text{Me}}$ value observed cannot arise from different shielding effects in diamagnetic diastereoisomers.

Using the preceding argument and the observation that, usually, $\Delta F_{\text{act}} < \Delta F_{meso}$, the stereoselective effects on the conversions 1 and 2 induced by the asymmetric R groups result in a slight relative stabilization of the active tetrahedral form. Of the complexes whose thermodynamic quantities have been evaluated, Ni(5-Me-PhEt-sal)$_2$ is the only exception;[40] its tetrahedral *meso* isomer is slightly more stable. The diastereoisomeric interactions in tetrahedral complexes of types **1**, **2**, and **3** with R = PhEt will be considered in more detail in forthcoming publications.

**Hindered Rotation of R groups.** The temperature dependence of the contact shifts of Ni(PhEt-PhHMe)$_2$, shown in Figure 7, reveals an unexpected behavior. Above $\sim -10°$ a simple Curie dependence of the $\alpha$-Me signal of both diastereoisomers is observed. However, below this temperature the signal of one isomer is split into two components of equal intensity which follow eq 8 to $-60°$, the limit of measurement. Because this splitting occurs only with the *meso* isomer, whose $\Delta$-$(+,-)$ and $\Lambda(+,-)$ forms are enantiomeric, it appears likely that the separate signals are due to rotameric effects arising from hindered rotation about the N–C bond, the effects of which become noticeable at the lower temperatures. The equal intensities suggest but do not prove that one molecular type is involved, having two differently averaged orientations of the PhEt groups relative to their own chelate rings. A similar effect has not been observed for complexes with other R groups or for Ni(PhEt–PhHH)$_2$ and Ni(5-Me-PhEt-sal)$_2$, whose rapid configurational interchange effectively averages out any such rotameric effects in the tetrahedral configurations.

**Acknowledgment.** This research was supported by the U. S. Public Health Service through National Institutes of Health Grant GM 12920.

---

(40) If the contact shifts of Ni(PhEt-PhHH)$_2$ at $\sim$30° are assumed to be due entirely to tetrahedral species, this complex represents a second case in which the tetrahedral *meso* isomer is the more stable. Using the data in Table IV, it is estimated that $\Delta F_{\text{act}} \cong +130$ and $\Delta F_{meso} \cong +50$ cal/mole.