MCD results on the Pd and Au halides support Jørgensen's[6] assignment of the two intense bands as $^1A_{1g} \rightarrow {}^1A_{2u} + {}^1E_u(\pi)$ and $^1A_{1g} \rightarrow {}^1E_u(\sigma)$. For $PtCl_4^{2-}$, we identify the shoulder at 43,400 cm^{-1} as the $^1A_{1g} \rightarrow {}^1A_{2u} + {}^1E_u(\pi)$ transition, but the main band at 46,200 cm^{-1} appears to be of quite different character and may well be the $5d \rightarrow a_{2u}$(metal $6p_z$) transition suggested by Cotton and Harris[21] and Anex and Takeuchi.[10]

Acknowledgments. We are deeply indebted to Drs. Jørgensen, Anex, and Gray for supplying us with chemical samples and to Drs. Anex and Takeuchi for permission to quote their reflection results prior to publication. We are also indebted to Mrs. K. Victor for help in the measurement of the absorption spectra. This work was supported in part by a grant from the National Science Foundation.

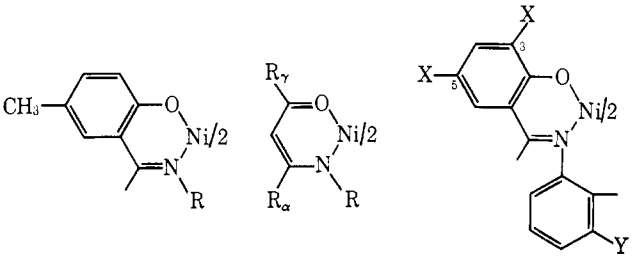
Diastereoisomeric Four-Coordinate Complexes. VI.[1] Paramagnetic Nickel(II) Complexes with Four Asymmetric Ligand Centers

R. E. Ernst,[2] M. J. O'Connor, and R. H. Holm[3]

Contribution from the Departments of Chemistry, University of Wisconsin, Madison, Wisconsin, and Massachusetts Institute of Technology, Cambridge, Massachusetts. *Received April 18, 1968*

Abstract: A series of bis-chelate nickel(II) complexes containing four asymmetric ligand centers occurring as two inequivalent pairs has been synthesized, and their proton resonance spectra have been investigated in order to determine to what extent the contact shift method can detect all possible diastereoisomers. The complexes examined are of the bis(salicylaldimine) type having the general formulation Ni(X-R-sal)$_2$, in which X = 3*s*Bu, 5Me and R = CH_3CHCH_2Ph (Amp), CH_3CHPh (PhEt), and *sec*-Bu (= *s*Bu). All complexes are shown to exist in the dynamic planar $\rightleftharpoons$ tetrahedral equilibrium in chloroform solution. It is demonstrated that, apart from the absolute configuration at the metal in the tetrahedral form, six pmr-distinguishable diastereoisomers are possible for complexes prepared from racemic ligand components. Signals corresponding to the six isomers were observed in the pmr spectra of the three groups of complexes. A general method of signal assignments for the Ni(X-R-sal)$_2$ isomers is described and applied to Ni(3*s*Bu-Amp-sal)$_2$, resulting in unequivocal assignment of certain signals to the six possible isomers. The marked sensitivity of the pmr method in detecting diastereoisomers arises from the contact interaction and the presence of the structural equilibrium, for which the ΔF value of each diastereoisomer is measurably different. These values are considered to differ principally because of inequalities in the free energies of the paramagnetic, tetrahedral forms which in turn are produced by the various sets of intramolecular (R-R, R-X) interactions. Intrinsic differences in electron-nuclear coupling constants are shown to be unimportant in producing the primary chemical shift separation between R-active and R-*meso* sets of isomers with R = Amp. The sets of thermodynamic parameters (ΔF, ΔH, ΔS) describing the planar–tetrahedral structural change of the six diastereoisomers of Ni(3*s*Bu,5Me-Amp-sal)$_2$ have been derived from the temperature dependence of the contact shifts of each isomer.

Our recent investigations of diastereoisomeric four-coordinate metal(II) complexes[1,4-6] have been undertaken with the purpose of detecting and identifying all possible isomers and determining the stabilities of the planar and tetrahedral stereoisomers and the enantiomeric configurations of the latter. This work has been principally concerned with nickel(II) complexes[1,4,5] because of the simultaneous population of both planar and tetrahedral configurations in many cases and the presence of large proton contact shifts from the tetrahedral isomers which greatly amplify the intrinsic chemical shift differences between corresponding nuclei in different diastereoisomers. Three groups of complexes have been examined in detail by proton resonance: the bis(salicylaldimines) **1**,[4,5] the bis(β-ketoamines) **2**,[5] and the 2,2′-bis(salicylideneamino)biphenyls **3**.[1]



1 **2** **3**

The tetrahedral forms of **1**, **2**, and **3** are enantiomeric, giving rise to the Δ and Λ absolute configurations, which have been defined previously[5] to possess right-handed and left-handed chirality, respectively, with reference to the C_2 axis of the molecule. The Δ and Λ configurations of **3** are formed with complete stereospecificity

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(2) National Institutes of Health Predoctoral Fellow.
(3) Author to whom correspondence should be addressed at Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139.
(4) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, 86, 379 (1964) (part II).
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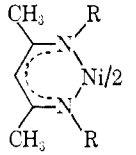
from the *R*-(+) and *S*-(−) biphenyl- (or 1,1′-binaphthyl-) diamines,[1] respectively. Diastereoisomers of **1**, **2**, and **3** are readily prepared by introducing two asymmetric ligand centers at equivalent positions in the planar and tetrahedral stereoisomers. Preparation of **1** and **2** from asymmetric primary amines results in the active [(+,+), (−,−)] and *meso* (+,−) forms of the planar isomer in which the ligand asymmetric centers occur in the nitrogen substituents R. The corresponding tetrahedral diastereoisomeric forms of **1**, **2**, and **3**, together with their enantiomers, are the following: $\Delta(+,+) \equiv \Lambda(-,-)$ $\Lambda(+,+), \equiv \Delta(-,-)$ (active); $\Delta(+,-) \equiv \Lambda(+,-)$ (*meso*). From the results presently at hand, the following principal conclusions concerning the detection of diastereoisomers by proton resonance and the configurational stability of the tetrahedral isomers may be drawn.

(i) Chemical shift differences between diastereoisomers of **1**, **2**, and **3** are composed almost entirely of *contact* shift differences,[4,5] which are usually in the range ~0.5–5 ppm.[1,4,5]

(ii) Contact shift differences are largest when measurable amounts of planar diastereoisomers are present in rapid equilibrium with the related tetrahedral diastereoisomers.[1,4,5] These differences are mainly due to nonzero $\Delta\Delta F$ values (*e.g.*, $\Delta F_{active} - \Delta F_{meso}$) for the planar → tetrahedral structural change, which in turn derive from real differences in free energies of the tetrahedral, paramagnetic diastereoisomers.[5]

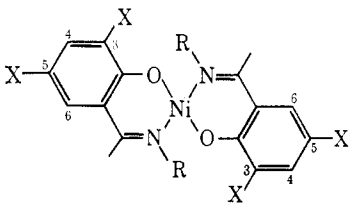
(iii) The Δ and Λ configurations of the bis-chelate complexes **1** and **2** have lifetimes of $\lesssim 10^{-3}$ sec, as inferred from the failure to detect two separate signals of an active (*e.g.*, (+,+)) form even at temperatures as low as −40° and in the absence of a detectable amount of the planar stereoisomer.[4,5] These configurations are presumably averaged by rapid racemization accompanying the structural change, and have thus far been detected in pmr experiments only for the tetrahedral diastereoisomers of **3**, which have high activation energies for racemization.[1]

From (iii) it follows that the only diastereoisomers of **1** and **2** detectable by pmr are the active and *meso* forms generated by the two asymmetric ligand centers R. Recently we have become interested in the potential of the highly sensitive contact shift method for detecting and identifying diastereoisomeric nickel(II) complexes possessing *more than two optically active ligand centers*. For example, the signal multiplicities in the pmr spectrum of tetrahedral, paramagnetic bis(2-*o*-tolylamino-4-*o*-tolylimino-2-pentenato)nickel(II) (**4**, R = *o*-tolyl)



4

require the presence of two diastereoisomers and are not inconsistent with the existence of four,[7] the maximum number possible for this complex. The diastereoisomers arise because of restricted rotation of the *o*-tolyl group with respect to the chelate ring. The individual isomers could not be identified because there is no way of deliberately controlling the absolute configurations of the active sites in the molecules. As a consequence, we have investigated a series of complexes which possess more than two asymmetric ligand centers whose configurations can be systematically varied in the manner required for identification and unequivocal assignment of pmr signals of all possible diastereoisomers. The complexes are of the bis(salicylaldimine) type and have the general structure **5**. Asymmetric ligand centers have been introduced as two inequivalent pairs of groups R



5

and 3-X, so located that they can mutually interact in the tetrahedral stereoisomers. Further, the R groups are of a steric nature such that the structural equilibrium (1) is produced. The conditions mentioned in (ii) above

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

are therefore realized, and the complexes **5** represent very favorable cases with which to assess the ability of the contact shift effect to detect isomers of quite subtle structural differences.

In this work it is demonstrated that six diastereoisomers are possible for complexes of type **5** and that in certain cases all of them may be detected by proton resonance. The methods of signal assignment are discussed in detail and the thermodynamic parameters for the structural change (1) evaluated from the temperature dependence of the contact shifts are presented. Throughout this report complexes of types **1** and **5** are designated as Ni(3X,5X-R-sal)$_2$; X = H is not explicitly specified. These complexes were prepared from inactive components unless the asymmetric ligand portions (R, X) are prefixed with (+) or (−). The signs refer to the sign of $[\alpha]_D$ of the amine or salicylaldehyde from which the complex was derived. The following abbreviations are used for R: CH_3CHPh, PhEt; CH_3CHCH_2Ph, Amp (from amphetamine).

Experimental Section

Resolution of Amines. Racemic α-phenethylamine was resolved into its (+) and (−) enantiomers using (−)-malic acid[8] and (+)-tartaric acid,[9] respectively: $[\alpha]^{25}D$ +39.6° (neat), lit.[10] +39.9°; $[\alpha]^{25}D$ −39.5° (neat), lit.[9] −40.3°. *sec*-Butylamine was resolved into its (+) and (−) isomers using the method of Thomé[11] as improved by Bruck, *et al.*,[12] $[\alpha]^{25}D$ +7.40° (neat), lit.[12] +7.53°; $[\alpha]^{25}D$ −7.50° (neat), lit.[12] −7.64°. (+)-Amphetamine (Aldrich Chemical Co.) after drying over and distillation from potassium hydroxide gave $[\alpha]^{24}D$ +34.5° (neat), lit.[10] +34.1°. (−)-Amphetamine was liberated from its sulfate (K and K Chemicals) by treatment with sodium hydroxide solution. After purification the amine gave $[\alpha]^{25}D$ −25.8° (neat), indicating ~75° resolution.

2-*sec*-Butyl-4-methylphenol. The following procedure is more convenient than the several published[13,14] and results in comparable

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Table I. Characterization Data for Bis(salicylaldimino)nickel(II) Complexes

Complex	Mp, °C[a]	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Ni(3*s*Bu,5Me-*i*Pr-sal)$_2$[b]	159–160	68.84	8.47	5.35	68.81	8.57	5.48
Ni(5*s*Bu-*i*Pr-sal)$_2$[c]	135–136	67.89	8.14	5.65	67.77	8.18	5.78
Ni(3*s*Bu-*s*Bu-sal)$_2$[d,f]	Oil	68.84	8.47	5.35	69.45	8.67	5.61
Ni(3*s*Bu,5Me-*s*Bu-sal)$_2$[d,f]	Oil	69.70	8.77	5.08	69.82	8.89	5.20
Ni(5*s*Bu-*s*Bu-sal)$_2$[e]	145–146	68.84	8.47	5.35	69.50	8.63	5.29
Ni(3*s*Bu-PhEt-sal)$_2$[d,f]	Oil	73.68	7.16	4.52	74.10	7.20	4.55
Ni(3*s*Bu,5Me-PhEt-sal)$_2$[d,f]	129–133	74.19	7.47	4.33	74.06	7.39	4.40
Ni(3*s*Bu-Amp-sal)$_2$[d,f]	Oil	74.19	7.47	4.33	74.29	7.30	4.22
Ni(3*s*Bu,5Me-Amp-sal)$_2$[d,f]	Oil	74.67	7.76	4.15	74.90	7.75	4.25

[a] Refers to mixture of diastereoisomers. [b] Prepared by nonaqueous chelation, recrystallized from *n*-heptane. [c] Prepared from Ni(X-sal)$_2$ in chloroform, recrystallized from chloroform–*n*-heptane. [d] Prepared by nonaqueous chelation, isolated as dipyridinate. [e] Prepared from Ni(X-sal)$_2$ in *n*-heptane, recrystallized from *n*-heptane. [f] Diastereoisomers isolated were also oils.

yields; it is similar to that previously employed in the alkylation of cresols.[15] A mixture of *sec*-butyl alcohol (370 g, 5 moles), *p*-cresol (1080 g, 10 moles), and anhydrous zinc chloride (1080 g, 8 moles) was heated at 140° for 60 hr in a 3-l., three-necked flask equipped with a stirrer and reflux condenser. The solution was allowed to cool and settle for 1 day; the upper liquid layer was decanted off, washed with dilute HCl (two 500-ml portions), and vacuum distilled. After foreruns of water and *sec*-butyl alcohol, two large fractions were collected; 95–110° (10 mm) (mainly unreacted *p*-cresol) and 110–130° (10 mm). The latter fraction was redistilled and the product, a white crystalline solid (mp ~40°), was obtained from the fraction boiling at 115–121° (10 mm). In various runs the yields ranged from 20 to 30%. Purity was established from the pmr spectrum, in which the methyl signal of the product and that of *p*-cresol were separated by τ ~0.1, and was consistently greater than 95% in different preparations; phenylurethane derivative, mp 94–95°; lit.[14] 94–95°.

Alkylated Salicylaldehydes. 3-*sec*-Butyl-, 3-*sec*-butyl-5-methyl-, and 5-*sec*-butylsalicylaldehyde were prepared by the Duff reaction[16] and were purified by vacuum distillation. The previously unreported 3-*sec*-butyl-5-methylsalicylaldehyde, bp 117–120° (5 mm), was characterized as its 2,4-dinitrophenylhydrazone, mp 224–225°. *Anal.* Calcd for $C_{18}H_{20}N_4O_5$: N, 15.05. Found: N, 15.27. Conversion of (+)-2-*sec*-butylphenol (*vide infra*) to (+)-3-*sec*-butylsalicylaldehyde yielded a product with $\alpha^{25}D$ +15.3° (neat, 1 dm).

Resolution of 2-*sec*-Butylphenol. The (+) enantiomer of this compound had been previously obtained[17] by formation of a diastereoisomeric mixture of 2-*sec*-butylphenyl *d*-camphorsulfonate from reaction of *d*-camphorsulfonyl chloride and the phenol, followed by fractional recrystallization from ethanol. In our hands the initial mixture could not be induced to crystallize from ethanol. The oil recovered after stripping off the ethanol was dissolved in acetone, from which a waxy solid product was obtained after cooling the solution for 24 hr at −15°. This product was dissolved in an equal weight of hot ethanol and allowed to crystallize at room temperature. Six repetitions of this procedure yielded the resolved diastereoisomer (mp 72–73°) which when decomposed gave (+)-2-*sec*-butylphenol; $[\alpha]^{25}D$ +17.9° (neat), lit.[17] $[\alpha]^{23}D$ +18.1°.

Salicylaldimine Complexes. These were prepared from the appropriate bis(salicylaldehydato)nickel(II) complex (hydrated form) and amine by refluxing them in a 1:2.1 mole ratio in chloroform or *n*-heptane, or by a nonaqueous chelation procedure[18] employing the preformed Schiff base. In some cases oils were obtained after work-up of the reaction mixture and these were converted to the solid dipyridine adducts by the following method. The oil (0.01 mole) was dissolved in 15–20 ml of warm, dry *n*-heptane or *n*-pentane. Anhydrous pyridine (5–8 ml) was added dropwise with stirring. The bright green dipyridinate crystallized on cooling the solution to room temperature followed, when necessary, by slight volume reduction *in vacuo*. The crystallization procedure was repeated and the product collected, dried under suction for 5 min, and stored in a desiccator over pyridine for 24 hr. After this time the pyridine was removed at 100° (0.01 mm) until constant weight of the sample was achieved. Characterization data for the complexes together with further experimental details, entered as footnotes, 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-Amp-sal)$_2$ are shown in Figure 1. The following optical rotations, measured using a Perkin-

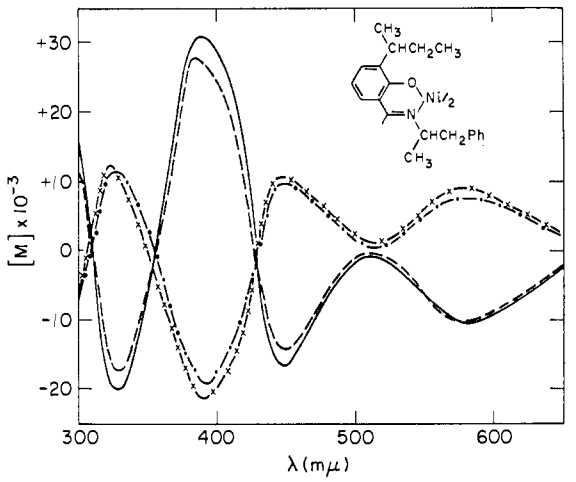

Figure 1. ORD spectra in chloroform solutions at 25°: ———, Ni(3*s*Bu-(+)-Amp-sal)$_2$; – – – –, Ni(3-(+)-*s*Bu-(+)-Amp-sal)$_2$; — · —, Ni(3*s*Bu-(−)-Amp-sal)$_2$; —×—, Ni(3-(+)-*s*Bu-(−)-Amp-sal)$_2$.

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,5Me-(+)-*s*Bu-sal)$_2$, $[\alpha]^{26}D$ −1250°, $[\alpha]^{26}_{546}$ −820° (*c* 0.44); Ni(3*s*Bu,5Me-(−)-*s*Bu-sal)$_2$, $[\alpha]^{24}D$ +1260°, $[\alpha]^{24}_{546}$ +830° (*c* 0.41); Ni(3*s*Bu,5Me-(+)-PhEt-sal)$_2$, $[\alpha]^{23}D$ +390°, $[\alpha]^{23}_{546}$ +450° (*c* 0.43); Ni(3*s*Bu,5Me-(−)-PhEt-sal)$_2$, $[\alpha]^{24}D$ −380°, $[\alpha]^{24}_{546}$ −440° (*c* 0.48); Ni(3*s*Bu-(+)-Amp-sal)$_2$, $[\alpha]^{24}D$ −1600°, $[\alpha]^{24}_{546}$ −850° (*c* 0.37); Ni(3*s*Bu-(−)-Amp-sal)$_2$, $[\alpha]^{24}D$ +1160°, $[\alpha]^{24}_{546}$ +630 (*c* 0.30); Ni(3-(+)-*s*Bu-(+)-Amp-sal)$_2$, $[\alpha]^{24}D$ −1680°, $[\alpha]^{24}_{546}$ −820° (*c* 0.42); Ni(3-(+)-*s*Bu-(−)-Amp-sal)$_2$, $[\alpha]^{23}D$ +1200°, $[\alpha]^{23}_{546}$ +700° (*c* 0.39); Ni(3*s*Bu,5Me-(+)-Amp-sal)$_2$, $[\alpha]^{27}D$ −1130°, $[\alpha]^{27}_{546}$ −640° (*c* 0.54); Ni(3*s*Bu,5Me-(−)-Amp-sal)$_2$, $[\alpha]^{26}D$ +960°, $[\alpha]^{26}_{546}$ +570° (*c* 0.38). These rotations refer to complexes prepared from optically active components (amines, 3-*sec*-butylsalicylaldehyde) with rotations given above.

Molecular Weights. Measurements were made with a Mechrolab Model 302 osmometer operating at 37° using solutions prepared from dry toluene. The following average molecular weights were obtained over a 0.03–0.20 *m* concentration range: Ni(3*s*Bu,5Me-*s*Bu-sal)$_2$, calcd 551, found 520; Ni(3*s*Bu-Amp-sal)$_2$, calcd 648, found 616.

Other Physical Measurements. Electronic spectra were recorded on a Cary Model 14 spectrometer. Magnetic measurements of

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(17) M. F. Hawthorne and D. J. Cram, *J. Am. Chem. Soc.*, 74, 5859 (1952).
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solutions were made by the Gouy method using distilled, freshly boiled water as the calibrant; magnetic moments are given in Table III. Proton resonance spectra were obtained using a Varian HR-100 or HR-60 spectrometer. $CDCl_3$ solutions of ~0.3 *M* or less were employed. Chemical shifts were measured by the usual side-band technique with respect to TMS as an internal reference.

Results and Discussion

Solution Stereochemistry. Establishment of the stereochemical configurations of the complexes **5** and the existence of equilibrium 1 in chloroform solution from magnetic and spectral data follows directly from the considerations discussed in detail elsewhere.[1,4,5,19-21] The complete set of solution magnetic data and representative ligand field spectral data are given in Tables II and III, respectively. The magnetic moments without exception are intermediate between 0 and 3.2–3.4 BM, the latter range being that expected in the event of exclusive population of the tetrahedral configuration. Moments in this range have been found for Ni(X-*t*Bu-sal)$_2$ complexes in both solution and crystalline phases;[4,19,20] these species are fully tetrahedral in both phases at room temperature. The order of increasing stabilization of the tetrahedral form by the R group,[22] Amp > secBu ~ *i*-Pr ≫ PhEt, is the same as found earlier for Ni(5Me-R-sal)$_2$ complexes in chloroform.[4,5]

Table II. Magnetic Data for Nickel(II) Complexes in Chloroform Solution

Complex[a]	Concn, *mm*[b]	Temp, °C	$10^6\chi^M_{corr}$	μ_{eff}, BM[c]
Ni(3*s*Bu,5Me-*i*Pr-sal)$_2$	80.1	24	2752	2.56
Ni(5*s*Bu-*i*-Pr-sal)$_2$	50.2	23	1753	2.04
Ni(3*s*Bu-*s*Bu-sal)$_2$	53.6	25	2796	2.58
Ni(3*s*Bu,5Me-*s*Bu-sal)$_2$	60.5	22	2808	2.58
Ni(5*s*Bu-*s*Bu-sal)$_2$	58.2	24	1391	1.86
Ni(3*s*Bu-PhEt-sal)$_2$	66.2	23	958	1.51
Ni(3*s*Bu,5Me-PhEt-sal)$_2$	60.7	24	780	1.36
Ni(3*s*Bu-Amp-sal)$_2$	59.5	25	2971	2.66
Ni(3*s*Bu,5Me-Amp-sal)$_2$	39.7	22	2972	2.65
Ni(3*s*Bu,5Me-(+)-Amp-sal)$_2$	34.8	24	2653	2.51

[a] Mixture of diastereoisomers. [b] Molar concentration range 0.050–0.104 *M*. [c] Calculated from the Curie law, $\mu_{eff} = 2.83 \cdot (\chi^M_{corr}T)^{1/2}$.

Table III. Ligand Field Spectra of Nickel(II) Complexes in Chloroform Solution

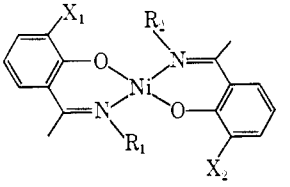
Complex	λ_{max}, cm^{-1}	ϵ, l. mole^{-1} cm^{-1}
Ni(3*s*Bu,5Me-*s*Bu-sal)$_2$[a]	14,800,[b] 11,000, 6850	92, 4, 56
Ni(3*s*Bu,5Me-PhEt-sal)$_2$[a]	15,400,[b] 11,000, 7020	114, 1, 17
Ni(3*s*Bu,5Me-Amp-sal)$_2$[a]	14,600,[b] 11,000, 6900	86, 4, 68
Ni(3*s*Bu,5Me-(+)-Amp-sal)$_2$	14,900,[b] 11,000, 6900	88, 4, 58

[a] Mixture of diastereoisomers. [b] Shoulder on absorption feature at higher energy.

The presence of the absorption feature at 6800–7000 cm^{-1}, whose intensities parallel the trend in magnetic moments, and the weak triplet–singlet band at 11,000 cm^{-1} are entirely characteristic of the tetrahedral isomer. These data together with the demonstrated lack of significant association of the representative complexes Ni(3*s*Bu,5Me-*s*Bu-sal)$_2$ and Ni(3*s*Bu-Amp-sal)$_2$ in toluene and the proton resonance results (*vide infra*) fully substantiate the existence of equilibrium 1 for all complexes of type **5**.

Designation of Diastereoisomers. Complexes of general formulation **5** in which X = 3*s*Bu and R = *s*Bu, PhEt, and Amp possess four asymmetric ligand centers. These are present as two inequivalent pairs represented as R_1, R_2 and X_1, X_2 in the structure in Table IV. As pointed out above, the complexes when tetrahedral possess a fifth site of asymmetry, the absolute configuration (Δ,Λ) at the nickel. However, as results to be cited show, these configurations are averaged within the pmr time scale of measurement by racemization occurring as a result of structural interconversion[5] (1) or ligand exchange[5,22] and are of no further consequence in the

Table IV. Enantiomers and Diastereoisomers of a Complex with Two Inequivalent Pairs of Ligand Asymmetric Centers



R_1	R_2	X_1	X_2	Distinct isomers	Diastereoisomers[a]
+	+	+	+	a	1′*
+	+	+	−	b	2′
+	+	−	+		2′
+	+	−	−	c	3′
+	−	−	+		6
+	−	+	−		5
+	−	+	+		4′**
+	−	−	−	g	4′′
				f	4
				e	5**
				d	6
−	+	−	−		4′′
−	+	+	+		4′**
−	+	−	+		5
−	+	+	−		6
−	−	+	+	h	3′′*
−	−	+	−	i	2′′
−	−	−	+		2′′
−	−	−	−	l	1′′

[a] Isomers denoted with a single asterisk are those which were separately prepared in the Ni(3*s*Bu-Amp-sal)$_2$ series of complexes; those denoted with a double asterisk were obtained in solution by ligand exchange reactions.

(19) (a) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963); (b) A. Chakravorty and R. H. Holm, *ibid.*, **3**, 1010 (1964).
(20) (a) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963); (b) L. Sacconi, M. Ciampolini, and N. Nardi, *ibid.*, **86**, 819 (1964).
(21) For reviews of the configurations and configurational equilibria of Ni(II) salicylaldimine 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).
(22) A. Chakravorty and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 3999 (1964).

consideration of isomers detectable by proton resonance.

There are $2^4 = 16$ possible combinations of the ligand asymmetric centers, whose relative configurations are represented by (+) or (−). These are set out in the left-hand column of Table IV. Not all of these combinations represent distinct isomers inasmuch as rotation about the C_2 axis present in the planar and tetrahedral configurations of complexes with no asymmetric centers renders certain pairs of combinations identical. For example, rotation about the *pseudo*-C_2 axis interconverts the second and third species in Table IV, and, accordingly, these are labeled together as isomer b. In this way six pairs of the 16 possible combinations are found to contain species identical with each other, thus leaving ten unique isomers, which are labeled a–j. Because it is not possible to distinguish (in a nonasymmetric solvent) the components of an enantiomeric pair, these pairs have been classified together in the right-hand portion of Table IV. As a case in point, isomer a (all sites (+)) and isomer j (all sites (−)) are enantiomers and are designated collectively as isomer 1. There are four such enantiomeric pairs, or pairs of pairs, thereby reducing to six the total number of isomers which are in principle observable by proton resonance. These diastereoisomers are labeled 1–6 in the table; their enantiomers are designated by single or double primes. Diastereoisomers 5 and 6 are not enantiomeric.

The ORD spectra of several of the diastereoisomers are shown in Figure 1. It is clear that the pair Ni(3-(+)-*s*Bu-(+)-Amp-sal)$_2$ (isomer 1′) and Ni(3-(+)-*s*Bu-(−)-Amp-sal)$_2$ (isomer 3′′) gives detectably different spectra even when account is taken of the incomplete resolution of the (−)-amphetamine (~75% optically pure) used in the synthesis. The spectra of the enantiomeric mixture of complexes prepared from racemic 3-*sec*-butylsalicylaldehyde with (−)-amphetamine (isomers 1′′, 2′′, 3′′) and (+)-amphetamine (isomers 1′, 2′, 3′) bear the required mirror-image relationship after allowing for incomplete resolution of the (−)-amine.

Identification of Diastereoisomers. Assuming that diastereoisomers 1–6 are in fact separately observable in the pmr spectrum of a given complex **5**, an assignment of the signals of each isomer is required. To obtain a complete assignment of signals observed in the total mixture, it is necessary to prepare several of the isomers in their optically pure or enriched forms. Below a general method of unambiguous signal assignment is outlined for a diastereoisomeric mixture of complexes of type **5**.

The absolute configurations of the R_1 and R_2 substituents are readily controlled by use of an optically active amine in the synthesis.[4-6] Reaction of the resolved amine with the appropriately substituted salicylaldehyde followed by complexation, or with the appropriate bis(salicylaldehydato) complex, will result in a mixture, R-active, which will contain only isomers 1, 2, and 3 (specifically 1′, 2′, and 3′ or 1′′, 2′′, and 3′′ if the (+)- or (−)-amine, respectively, is used in the synthesis; *cf.* Table IV). In order to carry the assignment beyond the separation of signals for isomers 1, 2, and 3 from those for isomers 4, 5, and 6, described collectively as R-*meso*, it is necessary to control the absolute configuration of the X_1 and X_2 substituents. In the cases studied here, $X_1 = X_2 =$ *sec*-Bu and only the (+)-X form could be obtained. The use of (+)-3-*sec*-butylsalicylaldehyde with the (+)- or (−)-amine in the synthesis yields the isomers 1′ or 3′′, respectively. The signal assignments for isomers 1 and 3 then follow directly. The signals of isomer 2, which cannot be prepared separately, are assigned by elimination.

Because it is not possible to prepare each of the diastereoisomers 4, 5, and 6 separately, an alternative means of signal identification is required. The assignment of signals of these isomers has been accomplished by a series of ligand exchange reactions. It has been shown previously that Ni(X-R-sal)$_2$ complexes which are at least partially tetrahedral in chloroform solution undergo facile, essentially statistical, intermolecular ligand exchange.[5,22] Because of the sensitivity of proton contact shifts to small structural differences, the signals of the mixed ligand complex are resolvably different from those of the reactants and can be identified with certainty. In the present work the ligand exchange reactions used for signal assignments involved (+)-X species as reactants and are the following, in which the reactants and products are represented by

$$ {}^{X_1}_{R_1}(\text{no.})^{X_2}_{R_2} $$

The enclosed numbers refer to the designation of isomers in Table IV.

$$ {}^{+}_{+}(1')^{+}_{+} + {}^{+}_{-}(3'')^{+}_{-} \rightleftharpoons 2\,{}^{+}_{+}(4')^{+}_{-} \qquad (2) $$

$$ 4\,{}^{+}_{+}(1')^{+}_{+} + [{}^{-}_{-}(1'')^{-}_{-} + 2\,{}^{-}_{-}(2'')^{+}_{-} + {}^{+}_{-}(3'')^{+}_{-}] \rightleftharpoons 4\,{}^{+}_{+}(5)^{-}_{-} + 4\,{}^{+}_{+}(4')^{+}_{-} \qquad (3) $$

From eq 2 it is seen that when equimolar amounts of isomers 1′ and 3′′ are allowed to react, the spectrum of the resulting solution will exhibit signals from diastereoisomers 1, 3, and 4. Because the signals of 1 and 3 have already been assigned, those of 4 are readily identified. Similarly, when isomer 1′ is allowed to react with the mixture of isomers prepared from racemic X and (−)-R ligand components (1′′, 2′′, 3′′), the spectrum of the resulting solution will contain signals from diastereoisomers 1–5 (eq 3). Previous assignment of signals from isomers 1–4 permits identification of the signals from isomer 5. The assignment of the signals of isomer 6 in the total mixture is then made by elimination. Hence, a complete assignment of all signals in the inactive total mixture of six diastereoisomers is possible.[23]

Proton Resonance Results. Three series of complexes of type **5** were examined, each of which is considered separately below. The X substituents are 3-*s*Bu with and without 5-Me. As in previous work[4,5] the 5-Me group was introduced to provide narrow, intense signals having appreciable contact shifts which are more conveniently followed over a temperature range than are the

(23) It is relevant to point out that if the (−)-X ligand component of **5** were available, it would have been possible to perform the ligand exchange reactions indicated in eq 4 and 5. Isomers 1′′ and 3′ would be separately preparable and diastereoisomers 5 and 6 would be the only products of these reactions, thereby providing an alternative identification of their pmr signals.

$$ {}^{+}_{+}(1')^{+}_{+} + {}^{-}_{-}(1'')^{-}_{-} \rightleftharpoons 2\,{}^{+}_{+}(5)^{-}_{-} \qquad (4) $$

$$ {}^{-}_{+}(3')^{-}_{+} + {}^{+}_{-}(3'')^{+}_{-} \rightleftharpoons 2\,{}^{+}_{-}(6)^{-}_{+} \qquad (5) $$

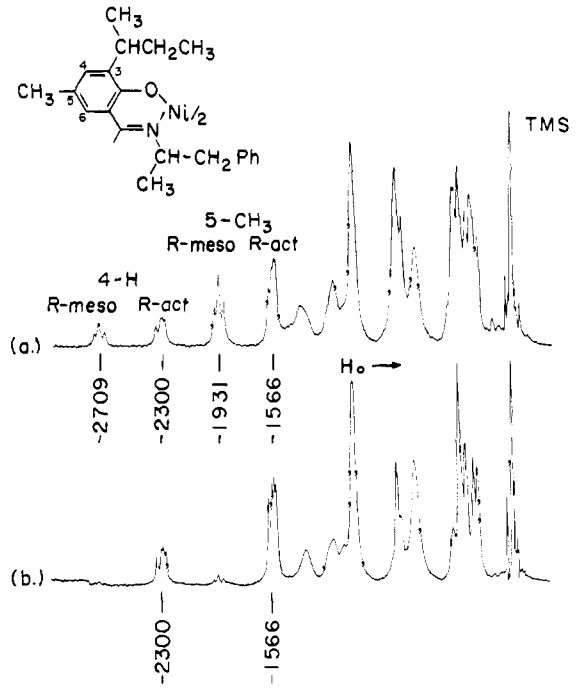


Figure 2. 100-Mc pmr spectra of Ni(3*s*Bu,5Me-Amp-sal)$_2$ in $CDCl_3$ solution at ~27°: (a) total mixture containing diastereoisomers 1-6; (b) mixture of Ni(3*s*Bu,5Me-(+)-Amp-sal)$_2$ complexes, diastereoisomers 1, 2, 3. R-act refers to isomers 1, 2, 3; R-*meso* to isomers 4, 5, 6. Frequencies (cps) are the chemical shifts.

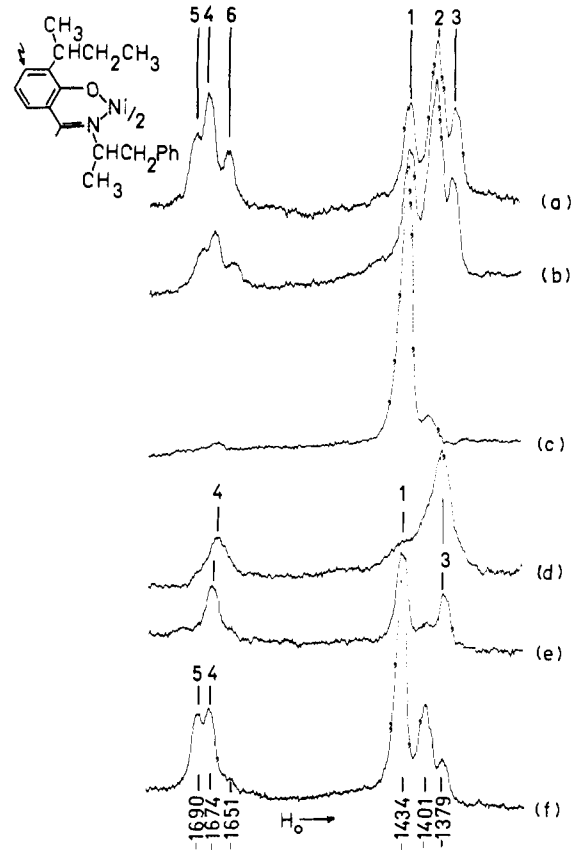


Figure 3. 60-Mc pmr spectra of the 4-H region of Ni(3*s*Bu-Amp-sal)$_2$ in $CDCl_3$ solution at ~27°: (a) total mixture containing diastereoisomers 1-6; (b) mixture of Ni(3*s*Bu-(−)-Amp-sal)$_2$ complexes, diastereoisomers 1, 2, 3; (c) Ni(3-(+)-*s*Bu-(+)-Amp-sal)$_2$, diastereoisomer 1; (d) Ni(3-(+)-*s*Bu-(−)-Amp-sal)$_2$, diastereoisomer 3; (e) equilibrium mixture from the ligand exchange reaction shown in eq 2; (f) equilibrium mixture from the ligand exchange reaction shown in eq 3. Frequencies (cps) are the chemical shifts.

broader and less intense ring proton signals. The patterns of contact shifts observed in the three series are the same as those for Ni(X-R-sal)$_2$ complexes with no asymmetric centers. The mode of unpaired spin delocalization which gives rise to the proton contact shifts and the assignment of the signals of chelate ring substituents have been discussed in detail elsewhere.[4]

The Ni(X-Amp-sal)$_2$ Series. The 100-Mc pmr spectrum of Ni(3*s*Bu,5Me-Amp-sal)$_2$ prepared from racemic ligand components is presented in Figure 2a. The features of principal interest are the seven 5-Me and seven 4-H signals, which are separated into two groups of three and four signals. The spectrum of the mixture of complexes prepared from (+)-amphetamine (Figure 2b) is simpler in that the downfield sets of 5-Me and 4-H signals are greatly reduced in intensity, thereby identifying them as belonging to diastereoisomers 4, 5, and 6. The remaining signals arise from diastereoisomers 1, 2, and 3. The principal separation of the signals of the total mixture arises from the mutual interactions of the R groups, producing R-active and R-*meso* isomers similar to those observed when 3-*s*Bu is replaced by H.[4,5] The origin of the "extra" R-active signal is considered below.

A complete assignment of signals in Figure 2 requires the deliberate introduction of a (+)- (or (−)-) 3-*s*Bu group. Because we have been unable to resolve 2-*sec*-butyl-4-methylphenol, the logical precursor to active 3-*sec*-butyl-5-methylsalicylaldehyde, the signal assignments have been carried out using Ni(3*s*Bu-Amp-sal)$_2$, the 1′ and 3′′ isomers of which can be separately prepared. The 60-Mc spectrum of the total mixture of isomers of this complex in the 4-H region is shown in Figure 3a. The marked similarity between the 4-H signals of this complex and those of Ni(3*s*Bu,5Me-Amp-sal)$_2$ clearly shows that the contact interactions at the 4 position are little affected by the interchange of 5-Me and 5-H.

Signal assignments were made by the procedure described above. The spectrum of the complex prepared from partially resolved (−)-amphetamine is given in Figure 3b. As was the case for Ni(3*s*Bu,5Me-(+)-Amp-sal)$_2$, the downfield trio of 4-H peaks is reduced in relative intensity, thereby distinguishing the signals of diastereoisomers 1, 2, and 3 from those of 4, 5, and 6. In Figures 3c and 3d are shown the spectra of complexes resulting from preparations involving (+)-3-*sec*-butylsalicylaldehyde with (+)- and incompletely resolved (−)-amphetamine, respectively.[24] The assignment of the signals due to isomers 1 (−1434 cps), 3 (−1379 cps), and, by elimination, 2 (−1401 cps) follows directly from these spectra. The peak at −1674 cps in Figure 3d arises from the use of optically impure (−)-amine in the preparation. The spectrum in Figure 3e is that of the equilibrium mixture of complexes resulting from the ligand exchange reaction between isomers 1′ and 3′′ (eq 2). The signal at −1674 cps is conclusively identified as that of diastereoisomer 4. Ligand exchange between isomer 1′ and a mixture of isomers 1′′, 2′′, and

(24) Note that in the spectrum of the pure diastereoisomer, Ni(3-(+)-*s*Bu-(+)-Amp-sal)$_2$ (Figure 3c), the occurrence of a single 4-H signal indicates the indistinguishability of the Δ and Λ isomers by pmr measurements.

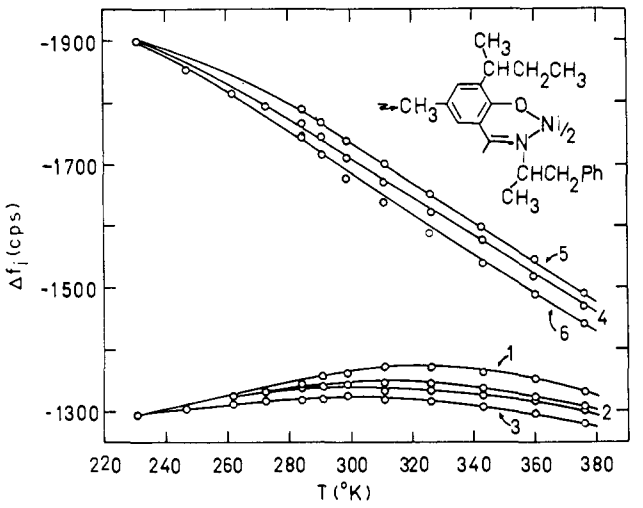


Figure 4. Temperature dependence of the 5-Me contact shifts of the diastereoisomers of Ni(3*s*Bu,5Me-Amp-sal)$_2$ in $CDCl_3$ solution at 100 Mc. Numbers 1–6 refer to the designation of diastereoisomers in Table IV.

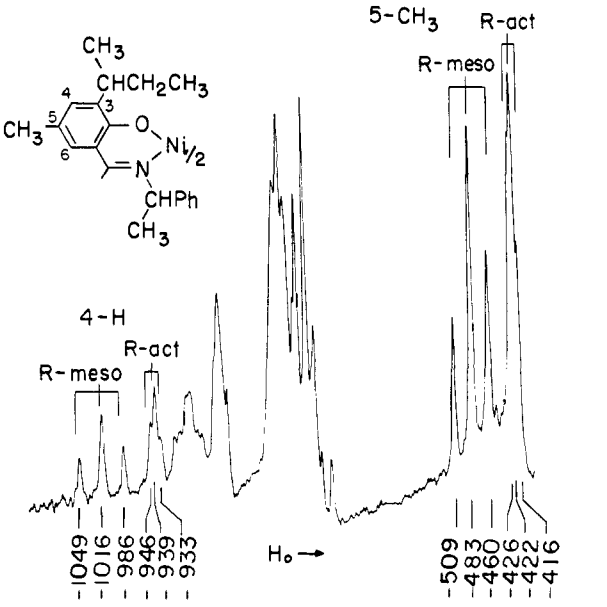


Figure 5. 100-Mc pmr spectrum of Ni(3*s*Bu,5Me-PhEt-sal)$_2$ in $CDCl_3$ solution at 0°. R-act refers to diastereoisomers 1, 2, 3; R-*meso* to diastereoisomers 4, 5, 6. Frequencies (cps) are the chemical shifts.

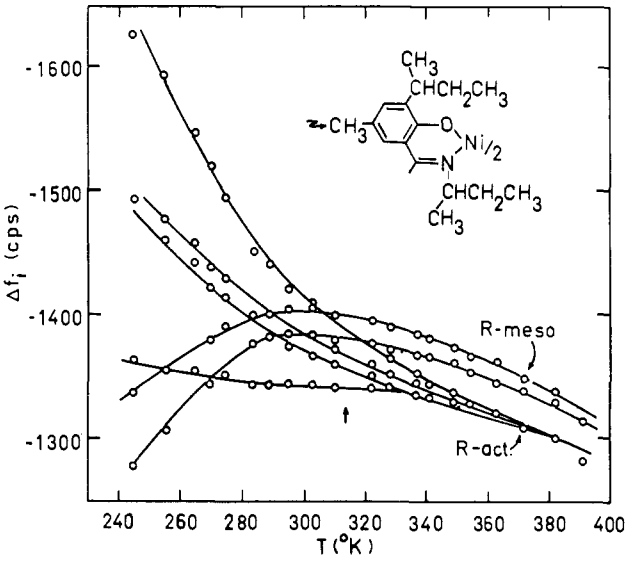


Figure 6. Temperature dependence of the 5-Me contact shifts of the diastereoisomers of Ni(3*s*Bu,5Me-*s*Bu-sal)$_2$ in $CDCl_3$ solution at 100 Mc. R-act refers to diastereoisomers 1, 2, 3; R-*meso* to diastereoisomers 4, 5, 6. The arrow indicates the temperature at which the spectrum in Figure 7 was recorded.

3′′ results in an equilibrium mixture whose spectrum is shown in Figure 3f. The −1690-cps signal is conclusively identified with diastereoisomer 5, resulting in the assignment of the 4-H feature at −1651 cps in the total mixture to diastereoisomer 6.

The assignment of signals of Ni(3*s*Bu,5Me-Amp-sal)$_2$ is assumed to parallel exactly that proven for Ni(3*s*Bu-Amp-sal)$_2$. The only important spectral difference between the two compounds is the resolution of seven 4-H and 5-Me signals, mentioned previously, in the 27° spectrum of the former compound (Figure 2). The "extra" signal arises from a doubling of the 4-H and 5-Me signals which at 27° are centered at −2303 at −1573 cps, respectively, and are assigned to diastereoisomer 2. The doublings amount to 12 (4-H) and 14 cps (5-Me) at this temperature. The temperature dependence of the 5-Me contact shifts, set out in Figure 4, shows that the splitting is detectable over a considerable temperature interval. The origin of the doubling follows from the structure of isomer 2, which lacks an authentic C_2 axis because of the opposite absolute configurations of the two 3-*s*Bu groups. The two 5-Me and 4-H groups are therefore magnetically inequivalent to a resolvable extent. Note that the absence of a C_2 axis is a necessary but not sufficient criterion for chelate ring *magnetic* inequivalence. In isomers 5 and 6 (R groups + and −) corresponding substituents (*e.g.*, 4-H, 5-Me) of the two rings are in enantiomeric environments whereas in isomer 4, as in isomer 2, they are in diastereoisomeric environments. Such magnetic inequivalence in isomer 4 is apparently too slight to be resolved. In only one other case (*vide infra*) was the splitting in isomer 2 large enough to be resolvable at 100 Mc.

The Ni(X-PhEt-sal)$_2$ Series. The pmr results for this series are similar to those for Ni(X-Amp-sal)$_2$. The 100-Mc pmr spectrum is shown in Figure 5. Six signals are observed for both 4-H and 5-CH_3. The upfield set of three for both substituents was shown to arise from the R-active diastereoisomers by preparation of isomers 1–3 using optically pure α-phenethylamine. No further signal assignments were made in this series because of the small contact shifts and attendant slight separations of signals of the components of the R-active and R-*meso* groups of diastereoisomers.

The Ni(X-*s*Bu-sal)$_2$ Series. The pmr spectra of this series were more difficult to interpret than those of the preceding two series because of overlap between the sets of R-active and R-*meso* signals and small contact shift differences between a number of signals. The temperature dependence of the 5-Me signals of Ni(3*s*Bu,5Me-*s*Bu-sal)$_2$ is given in Figure 6. Assignment of the R-active and R-*meso* signals is based upon comparison with the spectrum of diastereoisomers 1, 2, 3 prepared using optically pure *sec*-butylamine. The spectrum of this compound in the 5-Me region is shown in Figure 7; at 41° six signals are resolvable. The ori-

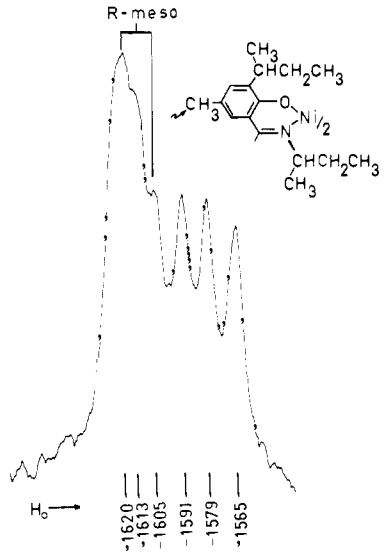


Figure 7. 100-Mc pmr spectrum of the 5-Me region of Ni(3*s*Bu,-5Me-*s*Bu-sal)$_2$ in $CDCl_3$ solution at 41°. R-*meso* refers to diastereoisomers 4, 5, 6. The unlabeled signals are due to the R-active diastereoisomers 1, 2, 3.

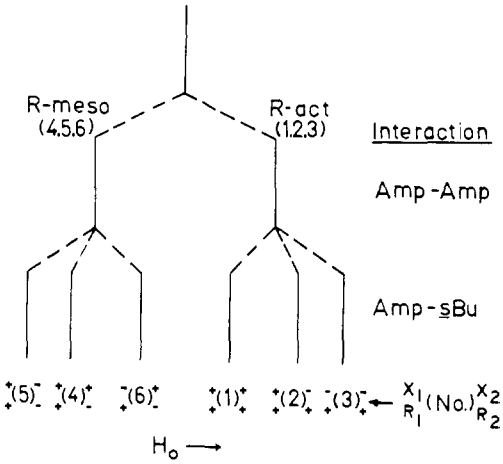


Figure 8. Schematic representation of the interaction pattern in Ni(3*s*Bu-Amp-sal)$_2$ and its 5-Me analog. Numbers 1–6 refer to the designation of diastereoisomers in Table IV. The particular representations of the diastereoisomers are chosen to emphasize the symmetries of the crossed interactions in pairs of isomers (see text).

gin of the *four* R-active signals is assumed to be the same as for Ni(3*s*Bu,5Me-Amp-sal)$_2$. Two of the R-*meso* signals are evidently coincident in chemical shift throughout the temperature range of measurement. A complete identification of all resolvable 4-H or 5-Me signals with the various diastereoisomers was not carried out.

Origin of Signal Separations among Diastereoisomers. The detection of five or six diastereoisomers in the preceding three series of complexes by pmr derives from the existence of contact interactions, which are extraordinarily sensitive to small changes in molecular structure. According to arguments developed in a recent study of Ni(II) complexes with two asymmetric R groups,[5] the intrinsic difference in contact shift between active and *meso* diastereoisomers is amplified by the involvement of the isomers in the structural equilibrium (eq 1). These arguments strongly suggest that the intramolecular interactions R_1–R_2 of each diastereoisomer produce measurably different free energies of the tetrahedral forms of the isomers, thereby leading to different contact shifts of each isomer. The dependence of the contact shift of the ith proton, Δf_i, of a particular isomer on ΔF for the structural change is given by eq 6, in which the symbols have their usual meanings.[4,5]

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

In the complexes with four asymmetric centers the three types of nonbonded interactions which affect the free energies of the tetrahedral forms and render them distinct are R_1–R_2, X_1–X_2, and R_1–X_2 (or R_2–X_1).[25] At least one of these interactions must be different for each diastereoisomer and removal of one or more of them by elimination of asymmetric groups or different placement of these groups in the molecule results in simpler spectra. The spectrum of Ni(5*s*Bu-*s*Bu-sal)$_2$ contains a doubled set of signals for 3-H, 4-H, and 6-H, indicating that only the R_1–R_2 interaction is operative and that the two 5-*s*Bu groups are too remote from R_1 and R_2 and from each other to interact effectively. As a consequence only the R-active and R-*meso* sets of isomers are distinguishable. Similarly, the removal of the R_1–R_2 interactions, as in Ni(5*s*Bu-*i*Pr-sal)$_2$ and Ni(3*s*Bu,-5Me-*i*Pr-sal)$_2$, results in spectra having no isomer splittings of any signal. All three compounds are implicated in equilibrium 1 (*cf.* Table II) and were measured as mixtures of diastereoisomers. The absence of any splittings in the spectrum of Ni(3*s*Bu,5Me-*i*Pr-sal)$_2$ indicates that the X_1–X_2 interaction alone is insufficient to produce observable effects. The isomer splittings are therefore considered in terms of the R_1–R_2 and crossed interactions.

The observed interaction pattern for Ni(3*s*Bu-Amp-sal)$_2$ and its 5-Me analog is illustrated schematically in Figure 8. The interaction between the two Amp groups results in a primary separation of signals into those of the R-active and R-*meso* sets of isomers. The Amp-3*s*Bu crossed interactions contribute a further splitting into two sets of three signals each. Evidence presented in the following section shows that the primary splitting arises principally as a consequence of free energy effects. We assume but cannot prove that the secondary splittings have a similar origin and take the isomer splittings as a manifestation of different positions of equilibrium 1 for the six diastereoisomers. These positions are in turn functions of the different set of interactions in each tetrahedral diastereoisomer. For the ideal case in which each interaction is strictly independent, a repetition of patterns in R-active and R-*meso* sets of signals in a given field direction is expected. Further, because of the similarity of the R–X interactions in the pairs of iso-

(25) The R_1–X_2 and R_2–X_1 or "crossed" interactions can also affect the free energies of the *trans*-planar forms. The argument that chemical shift differences between any two diastereoisomers whose contact shifts follow eq 6 are principally a consequence of nonzero $\Delta\Delta F$ values does not require that *only* their tetrahedral forms have different free energies. Evidence that the chemical shift differences observed for the Ni(II) complexes are in fact contact shift differences follows from the spectrum of planar diamagnetic Pd(3*s*Bu,5Me-*s*Bu-sal)$_2$, in which the 5-Me signal shows no isomer splittings. The corresponding tetrahedral Zn(II) complexes could not be prepared in the pure state, but, from observations on Zn(5Me-R-sal)$_2$ species,[5] no resolvable isomer splittings of the 5-Me signals are expected.

mers 1 and 6 (both "active"), 2 and 4 (one "active" and one "*meso*"), and 3 and 5 (both "*meso*") (*cf.* Figure 8), it is predicted that these pairs would give signals in the same relative order within each set, *i.e.*, 3, 2, 1 and 5, 4, 6. The experimentally observed order (3, 2, 1 and 6, 4, 5 with decreasing field) and the absence of duplication of patterns indicate that the various interactions are not effectively independent over the temperature interval of measurement. A similar interaction pattern would appear to apply to Ni(3*s*Bu,5Me-PhEt-sal)$_2$[26] (*cf.* Figure 5).

Thermodynamics of the Configurational Change. The thermodynamic parameters describing the planar–tetrahedral structural change for the six diastereoisomers of Ni(3*s*Bu,5Me-Amp-sal)$_2$ were obtained by a procedure similar to that previously described for complexes with two asymmetric R groups.[4,5] For the latter complexes the magnetic moment of an active isomer and the average magnetic moment per nickel of a mixture of active and *meso* isomers are not measurably different. As a result the coupling constants obtained were mean values derived from the measured solution magnetic moments of diastereoisomeric mixtures and averaged contact shifts.[5] A more desirable procedure is to evaluate the ΔF value for each isomer from measured magnetic moments according to eq 7, in which N_t is the mole fraction of tetrahedral form, μ_{obsd} is the observed mag-

$$N_t = [\exp(\Delta F/RT) + 1]^{-1} = \frac{\mu_{obsd}^2}{\mu_t^2} \qquad (7)$$

netic moment, and μ_t is the moment of the tetrahedral isomer. ΔF values together with contact shifts obtained at the same temperature can then be used to evaluate the electron-nuclear coupling constant a_i in eq 6. Thereafter, measurement of the contact shifts as a function of temperature permits determination of the temperature dependence of ΔF, and evaluation of ΔH and ΔS from $\Delta F = \Delta H - T\Delta S$.

Although the magnetic moments of all diastereoisomers of Ni(3*s*Bu,5Me-Amp-sal)$_2$ cannot be separately obtained, the average moments of the R-active set of isomers and of the total mixture of isomers were found to be measurably different and to have the values of 2.51 ± 0.05 and 2.65 ± 0.05 BM, respectively, in chloroform solution.[27] From these data the mean moment of the R-*meso* set is calculated to be 2.79 ± 0.10 BM. Coupling constants a_{5Me} calculated from these data, average contact shifts, and μ_t = 3.3 BM[1,4,5] are +0.202 ± 0.009 G for the R-active and +0.208 ± 0.015 G for the R-*meso* set of isomers. The identity of these values within experimental error[28] strongly supports our previous argument that the difference between contact shifts of diastereoisomers of the R-active and R-*meso* type is due primarily to differences in ΔF for the isomers rather than a difference in a_i.[5] It is assumed that the isomer splittings *within* the R-active and R-*meso* sets are also due to free energy inequalities and that the average value, a_{5Me} = +0.205 G, is applicable to all isomers. Using this value the temperature dependences of ΔF for all six diastereoisomers of Ni(3*s*Bu,5Me-Amp-sal)$_2$ were obtained and found to vary linearly with temperature above ~280°K as shown in Figure 9. The complete set of thermodynamic data is entered in Table V.[29]

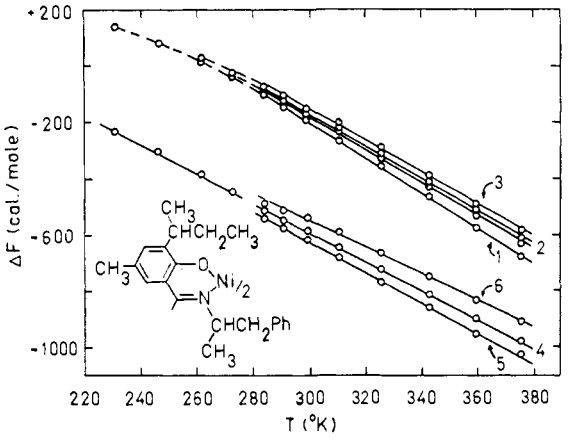


Figure 9. Temperature dependence of ΔF of the diastereoisomers of Ni(3*s*Bu,5Me-Amp-sal)$_2$ in $CDCl_3$ solution. Numbers 1–6 refer to the designation of isomers in Table IV.

Table V. Thermodynamic Data for the Planar–Tetrahedral Conversion of Diastereoisomeric Ni(3*s*Bu,5Me-Amp-sal)$_2$ Complexes in Chloroform Solution[a]

Isomer[b]	ΔH, cal/mole	ΔS, eu	$\Delta F^{298°}$, cal/mole	$N_t^{298°}$
1	1690	6.3	−180	0.57_7
2a[c]	1580	5.9	−170	0.57_0
2b[c]	1540	5.7	−160	0.56_8
3	1500	5.5	−140	0.56_0
4	970	5.2	−580	0.72_6
5	1080	5.6	−600	0.73_4
6	830	4.6	−540	0.71_5

[a] Data obtained from measurement of 5-Me contact shifts in the 280–380°K range, in which ΔF values vary linearly with temperature (*cf.* Figure 9). [b] Numbers refer to Table IV. [c] Split signals of isomer 2.

It is observed that ΔS values for all diastereoisomers are in the 4.6–6.3-eu range, but that ΔH values fall into two distinct ranges, 800–1100 cal/mole for the R-*meso* set and 1500–1700 cal/mole for the R-active set of isomers. The primary separation of signals mentioned earlier arises from this considerable difference in ΔH values for the two sets of isomers. The range of ΔS values is slightly higher than that found previously for the related complexes with X = 3-H and is probably due

(26) It is to be emphasized that for the complexes **5** the pattern in Figure 8 need not hold generally, and clearly will not if the chemical shift separations produced by the R_1–R_2 interaction are less than or approximately the same as those effected by the crossed interactions. As can be seen in Figure 6, separation of the R-*meso* and R-active signals in Ni(3*s*Bu,5Me-*s*Bu-sal)$_2$ occurs only above ~50°, and the splittings within each set become less than this separation only above ~75°. Finally, in that temperature interval where the primary splitting does result from R_1–R_2 interaction, the relative order of chemical shifts cannot necessarily be expected to be that shown in Figure 8.

(27) The difference in equilibrium position reflected by these moments is also observable in the electronic spectra (*cf.* Table III). In particular, the absorption feature at 6900 cm^{-1}, characteristic of the tetrahedral form only, has a greater extinction coefficient for the total mixture than for the R-active set of isomers, indicating that N_t(R-*meso*) > N_t(R-active) (assuming that the extinction coefficients of these two sets of isomers are the same).

(28) Error estimates for a_{5Me} values are derived from uncertainties in solution magnetic moment values only.

(29) Similar evaluations of thermodynamic data for Ni(3*s*Bu,5Me-R-sal)$_2$, R = *s*Bu, PhEt, were not carried out completely due to overlapping signals and limited regions of linear ΔF dependence within the temperature range of measurement. Approximate calculations for these two complexes gave for the R-active and R-*meso* sets of isomers ΔS values in the same range as those for R = Amp and ΔH values which indicated the order Amp < *s*Bu << PhEt.

to restricted motional freedom of the R groups in the *trans*-planar form due to their interactions with the 3-*s*Bu substituents. The difference in weighted average $N_t^{298°}$ values for the R-active and R-*meso* sets of isomers (0.16) is much larger than that for Ni(5Me-Amp-sal)$_2$[5] (0.07), consistent with the observably different magnetic moments and electronic spectra for the R-active set of isomers and the total mixture of isomers of Ni(3*s*Bu, 5Me-Amp-sal)$_2$. Differences in these properties of active and racemic Ni(5Me-Amp-sal)$_2$ could not be detected. Finally, confirmatory evidence that the "extra" 5-Me and 4-H signals in the pmr spectrum of Ni(3*s*Bu-5Me-Amp-sal)$_2$ derive from a splitting of these signals in isomer 2 is provided by the virtually identical temperature dependence of ΔF calculated from the two signals (*cf.* Figure 9) using the same coupling constant for both. Because the two signals arise from one molecular species rather than two distinct isomers, the splitting in this case must be attributed to a very small inequivalence in a_{5Me} and a_{4H} coupling constants in the two rings.

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Isomerization, Solvolysis, Ion Association, and Solvation of *cis*- and *trans*-Dichlorobis(ethylenediamine)cobalt(III) Cations in Protic and in Dipolar Aprotic Solvents

W. R. Fitzgerald, A. J. Parker,[1] and D. W. Watts[2]

Contribution from the School of Chemistry, The University of Western Australia, Nedlands, Australia 6009. *Received April 9, 1968*

Abstract: Solubilities of the chlorides and perchlorates of the *cis*- and *trans*-$[CoCl_2(en)_2]^+$ cations in the protic solvents water and methanol and in the dipolar aprotic solvents dimethylformamide (DMF), dimethylacetamide (DMA), tetramethylene sulfone (TMS), and dimethyl sulfoxide (DMSO) have been measured. The solvent activity coefficients, for transfer of these isomeric cations from DMA to other solvents, have been calculated in terms of a reasonable extrathermodynamic assumption. It has thus been possible to calculate solvent activity coefficients for ion pairs and for model transition states, which are based on a dissociative mechanism for isomerization and solvolysis. A different model must be used for the transition states for at least some solvolysis reactions. The isomerization equilibrium constants in water and in methanol, in which solvents it cannot be measured directly, have been estimated from the observed value in DMA.

It is now possible to assign solvent activity coefficients to individual anions and cations with some confidence.[3] These are invaluable for the interpretation of solvent effects on rates, equilibria, and mechanism.[4] We now apply them to some reactions of coordination compounds.

The solvent activity coefficients ${}^0\gamma_i^S$ are defined by eq 1, which expresses the change in the standard chemical potential of the solute, i, in a unimolar solution, hypothetically ideal with respect to Henry's law, on transfer from a reference solvent (superscript 0) to another solvent (superscript S) at a temperature T.

$$\bar{\mu}_i^S = \bar{\mu}_i^0 + RT \ln {}^0\gamma_i^S \quad (1)$$

In this paper, we consider the effect of solvent transfer on the standard chemical potential of the *cis*- and *trans*-$[CoCl_2(en)_2]^+$ cations, of their ion pairs with chloride ion, and of possible rate-determining transition states for their isomerization (eq 2) and solvolysis (eq 3 and 4). The significance of (3) and (4) in rate-determining isomerization in solvents other than TMS and MeOH is discussed elsewhere.[5]

$$cis\text{-}[CoCl_2(en)_2]^+ \underset{k_t}{\overset{k_c}{\rightleftharpoons}} trans\text{-}[CoCl_2(en)_2]^+ \quad (2)$$

$$cis\text{-}[CoCl_2(en)_2]^+ + \text{sol} \longrightarrow cis\text{-}[CoCl(\text{sol})(en)_2]^{2+} + Cl^- \quad (3)$$

$$trans\text{-}[CoCl_2(en)_2]^+ + \text{sol} \longrightarrow cis\text{-}[CoCl(\text{sol})(en)_2]^{2+} + Cl^- \quad (4)$$

The equilibrium constant ($K = k_c/k_t$) for isomerization (2) is strongly influenced by ion association and by solvent transfer.[6-10] These strong medium effects have been attributed qualitatively to the dipolar nature of the *cis* isomer,[5-9,11,12] which also appears to be a stronger hydrogen-bond donor than the symmetrical *trans* isomer. The *trans* isomer thus associates with anions and interacts with polar solvents less strongly than the *cis* isomer.[12] The role of hydrogen bonding in accentuating ion association in these cations is comparable to the role of the nitrogen proton

(1) Author to whom inquiries should be addressed at the School of Chemistry, University of Western Australia, Nedlands, Western Australia 6009.
(2) Visiting Scientist, University of Southern California, Sept. 1967–May 1968.
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