

The reaction pathway is known in terms of the chemical steps which occur in dilute solution and those steps which produce excited states. It is of particular interest that at least two reactions in the systems produce excited states. Although simple thermodynamic considerations indicate the production of an excited state in this reaction is not possible, because of the complex reaction mechanism such calculations are of questionable validity. This points out the necessity

for using thermodynamic calculations only in those situations where both the oxidant and the reductant undergo simple one-electron-transfer reactions.

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Applications of Isotropic Shifts to the Investigation of Structures and Structural Equilibria of Metal Complexes

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During the development of nuclear magnetic resonance as a spectroscopic tool for structure determination, attempts to observe the nmr spectra of paramagnetic species in solution under high-resolution conditions were occasionally unsuccessful, or at best gave broad featureless signals whose line widths rather than chemical shifts were the important characteristics. Such observations were no doubt responsible for numerous cases in the literature in which the nmr spectra of metal complexes were not recorded for the reason, stated or implied, that the complexes were paramagnetic. Although the proton resonance spectra of several paramagnetic complexes in solution had been reported¹ and the sources of the observed paramagnetic or isotropic shifts were fully realized earlier,² the potential utility of the spectra of such species did not become evident until 1960–1962, when Eaton, Phillips, and co-workers presented a detailed analysis of the ¹H and ¹⁹F spectra of a wide variety of substituted nickel(II) aminotroponiminates.³

The spectra of these complexes, which are fully tetrahedral or are involved in rapid planar ⇌ tetrahedral structural equilibria in noncoordinating solvents, revealed the isotropic shift phenomenon in the form of

large displacements of resonance frequencies upfield and downfield from their nominal diamagnetic positions, with retention of narrow line widths. For proton signals at ambient temperature these displacements, *i.e.*, isotropic shifts, cover in some cases a 310-ppm range, from -170 (downfield) to +140 ppm (upfield). Perspicacious interpretation of these spectra has provided a new and exceedingly sensitive technique for detecting delocalization of unpaired electrons, investigating pathways of spin delocalization, and obtaining accurate values of the thermodynamic parameters characterizing the structural equilibria. The aminotroponiminates provided the first practical examples of the utility of nmr spectra of paramagnetic complexes in solution, and the use of isotropic shifts in the investigation of structural and electronic properties of complexes of nickel(II) and other metal ions with favorably short electronic relaxation times has become more widespread since the first major publication²⁰ of the Du Pont group.

The total isotropic shift of the *i*th nucleus in a paramagnetic species is defined as

$$(\Delta H_i/H_0)_{\text{total}} = (\Delta H_i/H_0)_{\text{obsd}} - (\Delta H_i/H_0)_{\text{dia}} \quad (1)$$

in which $(\Delta H_i/H_0)_{\text{obsd}}$ is the observed shift and $(\Delta H_i/H_0)_{\text{dia}}$ the shift in the absence of the paramagnetic effect. Both are measured with respect to the same internal standard to avoid bulk susceptibility corrections. For paramagnetic metal complexes values of the latter shift are generally taken from the spectra of free ligands or structurally related, diamagnetic complexes such as those of zinc(II) and cobalt(III). The total isotropic shift (eq 2) is a sum of contributions from the scalar (or Fermi) isotropic hyperfine contact interaction, which arises from electron spin delocalization or spin polarization, and the nuclear-electron dipolar interaction. Derivations of equations appropriate to these

(1) H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, **27**, 314 (1957); **28**, 749 (1958); W. D. Phillips, C. E. Looney, and C. K. Ikeda, *ibid.*, **27**, 1435 (1957); A. Forman, J. N. Murrell, and L. E. Orgel, *ibid.*, **31**, 1129 (1959).

(2) For a discussion of isotropic shifts and a review of the nmr spectra of paramagnetic species, *cf.* D. R. Eaton and W. D. Phillips, *Advan. Magnetic Resonance*, **1**, 103 (1965); E. de Boer and H. van Willigen, *Progr. Nucl. Magn. Resonance Spectrosc.*, **2**, 111 (1967).

(3) (a) W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **33**, 607 (1960); (b) R. E. Benson, D. R. Eaton, A. D. Josey, and W. D. Phillips, *J. Am. Chem. Soc.*, **83**, 3714 (1961); (c) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962); (d) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Discussions Faraday Soc.*, **34**, 77 (1962); (e) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962); (f) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962).

two types of isotropic shifts have been given elsewhere.^{2,4}

$$(\Delta H_i/H_0)_{\text{total}} = (\Delta H_i/H_0)_{\text{contact}} + (\Delta H_i/H_0)_{\text{dipolar}} \quad (2)$$

The contact shift is expressed by eq 3, in which a_i is the electron-nuclear coupling constant in gauss, g is

$$\left(\frac{\Delta H_i}{H_0}\right)_{\text{contact}} = -a_i \left(\frac{\gamma_e}{\gamma_n}\right) \frac{g\beta S(S+1)}{3kT} \quad (3)$$

the average value of the principal components of the g tensor, S is the total electron spin, and γ_e and γ_n are the gyromagnetic ratios of the electron and the nucleus whose resonance is observed, respectively. Equation 3 holds only for those species which obey the Curie law.⁵ When this equation applies, the coupling constants may be evaluated from measurement of contact shifts at a given temperature or better, at a series of temperatures. If the proton contact shifts occur as a consequence of spin delocalization in a ligand π orbital, the hyperfine coupling constant from eq 3 is related to the π spin density, ρ_{C_i} , of the i th carbon atom by

$$a_i = Q_X \rho_{C_i} / 2S \quad (4)$$

in which Q_X is a proportionality constant for the appropriate structural fragment (*i.e.*, C_i-H_i , $C_i-CH_{(i)3}$). Because the magnitude and sign of a given a_i can be obtained from contact shift measurements, the sign of ρ_{C_i} can be determined. In an esr experiment the sign of the coupling constant and, hence, of the spin density is undetermined.

Dipolar shifts occur in magnetically anisotropic complexes, where the dipolar interaction between the nuclear magnetic moment and the electron spin magnetization on the metal cannot average to zero in a rapidly tumbling complex in solution. The shifts for axially symmetric systems are in general expressible by eq 5, in which the bracketed term is the geometric factor dependent upon the angle X_i between the vector of

$$\left(\frac{\Delta H_i}{H_0}\right)_{\text{dipolar}} = \frac{\beta^2 S(S+1)}{3kT} \left[\frac{3 \cos^2 X_i - 1}{R_i^3} \right] F(g) \quad (5)$$

length R_i joining the metal and the i th nucleus and the principal molecular axis; $F(g)$ is some function of the diagonal components of the g tensor appropriate to the molecular symmetry and the relative magnitudes of the tumbling time of the species in solution and the electron spin relaxation time, T_{1e} .⁴

The principal distinguishing features of contact and dipolar shifts are evident from the forms of eq 3 and 5. Contact shifts result either from spin delocalization

effected by symmetry-allowed mixing of ligand orbitals with spin-containing metal orbitals or by polarization of metal-ligand bonding orbitals by unpaired spin in metal orbitals of a different symmetry. In either case a scalar coupling between nuclear and electron spins results producing a contact shift which, from eq 3, has no explicit dependence upon molecular geometry. Dipolar shifts, or "pseudocontact shifts," arise from dipolar coupling at a distance and depend upon geometry, but require no covalent metal-ligand interactions or spin polarization effects.

At the present time isotropic shifts are being exploited in the investigation of four important aspects of the structural and electronic properties of paramagnetic metal complexes: (i) mechanisms of metal-ligand spin transfer and delocalization of spin in saturated and conjugated ligand systems; (ii) solvation behavior; (iii) ion-pair formation and structures; (iv) stereochemistry and structural equilibria. The investigation of any of these properties is feasible only if the nmr signals are not excessively broadened, for it is the isotropic shifts themselves, and in many instances the resolution of signals whose separations are unobservable in the absence of isotropic interactions, rather than line widths, which are the important spectral features. As a first approximation, line widths are dependent upon the T_{1e} value of the coordinated metal ion, and well-resolved spectra are obtained only in those cases in which the electronic relaxation times are very short. The factors effecting short T_{1e} values are not well understood, and a consideration of them² falls outside the purview of this report. Suffice to say that nmr spectra of complexes containing those ions (*e.g.*, $V^{IV}O$, sextet Mn(II) and Fe(III), Cu(II)) whose T_{1e} 's are relatively long, thereby permitting observation of their electron paramagnetic resonance at room temperature, are in general very poorly resolved or undetectable. Conversely, the spectra of complexes derived from V(III), Cr(II), Co(II), and Ni(II), in particular, with short T_{1e} 's are generally well resolved.

Our purpose in this Account is to examine the information relevant to aspect iv above, stereochemistry and structural equilibria of metal complexes, which is obtainable from isotropic shift studies. The single most important benefit from contact and dipolar interactions is that they produce, in effect, a nonlinearly expanded chemical shift scale permitting resolution of signals which are barely resolvable, or not resolvable at all, in analogous diamagnetic systems examined at 100 MHz. In certain of the examples considered, the relative contributions from contact and dipolar interactions are not of direct importance, although it has been established that the former are principally responsible for the observed isotropic shifts. Most of the results considered derive from our own investigations and are primarily concerned with complexes of nickel(II), whose stereochemical complexities are matters of continuing interest,⁶ and whose proton resonance line widths are frequently less than 10 Hz.

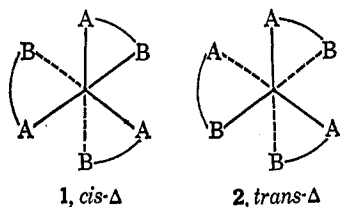
(6) L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).

(4) H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958); H. M. McConnell and R. E. Robertson, *ibid.*, **29**, 1361 (1958); G. N. LaMar, W. D. Horrocks, Jr., and L. E. Allen, *ibid.*, **41**, 2126 (1964); G. N. LaMar, *ibid.*, **43**, 1085 (1965); J. P. Jesson, *ibid.*, **47**, 579 (1967).

(5) Curie dependence of contact shifts is a special case and may not strictly hold if, among other reasons, the ground state is split by spin-orbit coupling. For derivation of the temperature dependence of contact shifts of octahedral complexes with nonzero spin-orbit matrix elements within the ground-state manifold, cf. R. M. Golding, *Mol. Phys.*, **8**, 561 (1964). Another source of departure of contact shifts from eq 3 is the existence of species with different ground-state spin multiplicities over which the contact shifts are averaged; such cases are considered in a following section.

cis-trans Isomerism in Tris-Chelate Complexes

Tris-chelate complexes containing symmetrical chelate rings possess idealized D_3 symmetry, in which case those substituents of the same type and having the same location in each ring are equivalent, as in $V(\text{acac})_3$ and $\text{Co}(\text{acac})_3$. However, if the chelate rings are unsymmetrical, *cis* or facial (**1**) and *trans* or meridional (**2**) isomers, each of which is enantiomorphous, are possible; in **1** and **2** A and B convey the ring asymmetry. Separation and subsequent identification of these isomers are not trivial matters, their electronic and vibrational spectra being very similar



and not structurally diagnostic, and the relatively time-consuming determination of dipole moments is the most reliable of the older physical methods for establishing structures. However, identification of isomers and measurement of their equilibrium concentrations are readily accomplished by nmr provided the two isomers are not rapidly interconverting. The *cis* isomer possesses a C_3 axis whereas the *trans* isomer has no symmetry at all, with the consequence that in principle a given substituent on each chelate ring in **2** will produce a separate resonance whereas in **1** only a single resonance will occur. This procedure has been applied to diamagnetic β -diketone,⁸ Schiff base,⁹ amino acid,¹⁰ and other^{9a,11} complexes, principally those of cobalt(III). The differences in chemical shifts of at least one substituent in the *trans* form are usually resolvable, allowing in favorable cases detection of this form alone or in the presence of the *cis* isomer.

The isotropic shift effect in vanadium(III) complexes of β -diketones,¹² β -keto amines,¹³ salicylaldehydes,¹⁴ and salicylaldehydes¹⁴ greatly amplifies these intrinsic chemical differences in the *trans* form and between *cis* and *trans* forms, permitting unambiguous detection of both isomers and in some instances measurement of their relative amounts. As an example, consider the

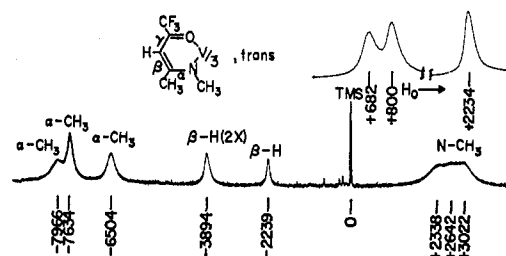
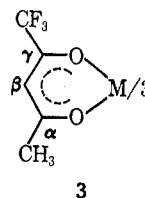
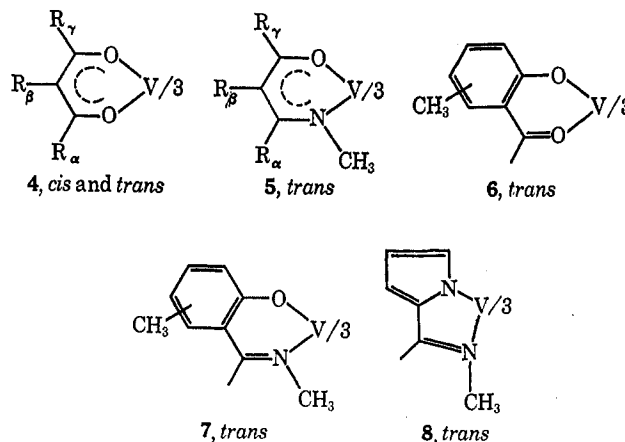


Figure 1. Nmr spectra of $V(\text{tfac})_3$ in CDCl_3 at room temperature: bottom, pmr spectrum; insert, ^{19}F spectrum. Frequencies (cps) are the chemical shifts relative to TMS.

spectrum of $V(\text{tfac})_3$ ¹² (**3**, $M = V$) (Figure 1). The



multiplicity of signals reveals the presence of both *cis* and *trans* isomers. The ^{19}F spectrum consists of four signals of relative intensity 1:1:1:0.5 with that at +2011 cps being due to the *cis* form. The *cis:trans* ratio obtained from the relative intensities is 1:6, somewhat less than the statistical value of 1:3. This information permits assignment of all signals in the pmr spectrum, as shown in Figure 1. Amplification of chemical shift differences owing to isotropic interactions is clearly illustrated by comparison of the pmr spectra of $V(\text{tfac})_3$ and $\text{Co}(\text{tfac})_3$, whose signals have been identified by chromatographic separation of the isomers.^{8b} In CDCl_3 solution at ambient temperature the total spread of the pmr spectrum of $\text{Co}(\text{tfac})_3$ is 3.68 ppm, whereas for $V(\text{tfac})_3$ it is 45.52 ppm. Further, the spread in signals of a given ring substituent for $\text{Co}(\text{tfac})_3$ and $V(\text{tfac})_3$, respectively, in their *trans* forms is as follows: $\alpha\text{-CH}_3$, 0.05, 16.73 ppm; $\beta\text{-H}$, 0.05, 32.99 ppm; $\gamma\text{-CF}_3$, 0.18, 15.4 ppm. Because of the isotropic shift effect it is possible to resolve all signals of a given substituent in the *cis* and *trans* forms of a variety of tris-chelate vanadium(III) complexes, such as **4**¹² ($R_\alpha \neq R_\gamma$), **5**,¹³ **6**,¹⁴ **7**,¹⁴ and **8**,¹³ whose structures are indicated.



(7) Abbreviations employed for β -diketonate anions: acac, acetylacetonate; tfac, trifluoroacetylacetonate.

(8) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **84**, 2303 (1962); (b) R. C. Fay and T. S. Piper, *ibid.*, **85**, 500 (1963); (c) R. A. Palmer, R. C. Fay, and T. S. Piper, *Inorg. Chem.*, **3**, 875 (1964).

(9) A. Chakravorty and R. H. Holm, *ibid.*, **3**, 1521 (1964); (b) A. Chakravorty and K. C. Kalia, *ibid.*, **6**, 690 (1967); (c) A. Chakravorty and B. Behera, *ibid.*, **6**, 1812 (1967).

(10) R. G. Denning and T. S. Piper, *ibid.*, **5**, 1056 (1966).

(11) A. Chakravorty, B. Behera, and P. S. Zacharias, *Inorg. Chim. Acta*, **2**, 85 (1968); K. C. Kalia and A. Chakravorty, *ibid.*, **2**, 154 (1968).

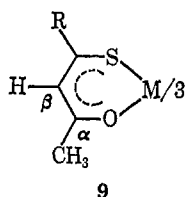
(12) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1315 (1967).

(13) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *ibid.*, **6**, 1607 (1967).

(14) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *J. Am. Chem. Soc.*, **89**, 6472 (1967).

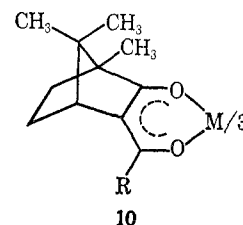
The exclusive population of the *trans* isomers of **5**, **7**, and **8** derives from strongly destabilizing steric interactions among nitrogen substituents larger than H in the *cis* isomers.^{9a} The source of the relative instability of the *cis* form of **6** is unknown.

The structural sensitivity of chemical shifts of vanadium(III) complexes has recently been employed to investigate the comparative stereochemical effects of oxygen and sulfur donor atoms in tris-chelate species.¹⁵ The tris(β -thioketonato)cobalt(III) complexes **9** ($M = \text{Co}$; $R = \text{CH}_3, \text{C}_6\text{H}_5, \text{CH}(\text{CH}_3)_2, \text{C}(\text{CH}_3)_3$) exhibit one α - CH_3 or β -H signal, consistent with exclusive population of the *cis* (C_3 or C_{3v}) isomer.



Similarly, only the *cis* form is detectable in an analogous series of vanadium(III) complexes. Chemical shift data for a typical pair of tris(β -thioketonates) ($R = \text{C}_6\text{H}_5$) are the following: α - CH_3 , $-1.41, -41.93$ ppm; β -H, $-5.95, -35.07$ ppm (Co(III) , V(III) , tetramethylsilane reference). Equilibrium constants for the *trans* \rightleftharpoons *cis* reaction of tris(β -diketonato)metal(III) complexes are usually less than statistical,^{8a,b,16} indicating preferential stability of the *trans* form. The generally rapid substitutional lability of vanadium(III) complexes ensures equilibrium isomer distribution, and the large contact shifts minimize the possibility of accidental chemical shift degeneracy and an incorrect structural assignment. Thus the *cis* isomers of the vanadium(III) complexes **9**, and presumably of the cobalt(III) complexes as well, are the thermodynamically more stable structures, an unanticipated inversion of isomer stabilities compared to the corresponding tris(β -diketonates). The source and generality of the preferential stability of the *cis* isomers of complexes of general type **9** are being further investigated.¹⁶

An additional and important complexity in stereochemistry is introduced when the ligands in structures **1** and **2** are themselves dissymmetric. If each ligand has the same absolute configuration, denoted by (+), there are two pairs of diastereoisomers, *cis*- Δ (+++), *cis*- Λ (+++), and *trans*- Δ (+++), *trans*- Λ (+++), or a total of four species, which are in principle distinguishable by nmr. Cases in point are the tris((+)-3-acetylcamphorato)- (**10**, $R = \text{CH}_3$, (+)-atc) and tris((+)-3-hydroxymethylenecamphorato)metal(III) (**10**, $R = \text{H}$, (+)-hmc) systems of complexes.^{17,18} Isomer detection by classical means involves chromatography of



reaction mixtures, which when performed on the non-labile $\text{Rh}((+)\text{-hmc})_3$ complexes yielded two isomers concluded to possess enantiomeric configurations at the metal from their ORD spectra, but to be the same geometrical isomer.¹⁷ From their pmr spectra, which exhibit four methyl signals of unequal intensity, the isomers were established to be *trans*, with *trans*- Λ more abundant than *trans*- Δ .¹⁷ No evidence for distinction between these diastereoisomers by pmr was given. In a similar manner, the two chromatographically separable isomers of $\text{Co}((+)\text{-hmc})_3$ were found to be *trans*- Λ (more abundant) and *cis*- Λ .^{17,18} Isomers of the vanadium(III) complexes $\text{V}((+)\text{-hmc})_3$ and $\text{V}((+)\text{-atc})_3$ are not amenable to chromatographic separation because of their lability and oxidative instability in solution. However, their large isotropic shifts, together with the established fact that stereoselective interactions of (+)-hmc and (+)-atc ligands in their respective complexes preferentially stabilize the Λ absolute configuration,¹⁷ permit an effective isomer assay by nmr. In $\text{V}((+)\text{-atc})_3$ the acetyl methyl resonance occurs as six resolvable signals with negative isotropic shifts having a total separation of 17.3 ppm. Three of these, with the intensity ratio 1:2:1 and shifts of $-31.0, -38.4,$ and -45.7 ppm, arise from an essentially statistical mixture of *trans*- Λ and *cis*- Λ . The remaining three signals, which are of equal intensity and have shifts of $-31.7, -33.6,$ and -48.3 ppm, must then be assigned to *trans*- Δ . Further, the ratio *trans*- Δ :*trans*- $\Lambda = 0.31$ ($29^\circ, \text{CDCl}_3$) has been obtained from signal integration. A similar isomer distribution appears to hold with $\text{V}((+)\text{-hmc})_3$.¹⁸

Structural Equilibria of Bis-Chelate Complexes

The idealized limiting stereochemistries of four-coordinate complexes are planar and tetrahedral. Clearly the most fundamental structural rearrangement of such species is interconversion between these geometries. For enantiomeric chelate complexes this process may or may not be accompanied by racemization of the absolute configuration at the metal in the tetrahedral form. It is now well recognized that a wide variety of suitably constituted nickel(II) chelate complexes^{6,19} and a smaller number of cobalt(II) complexes²⁰ may be prepared for which the free-energy differences between the two stereoisomers are suffi-

(15) R. H. Holm, D. H. Gerlach, J. G. Gordon, II, and M. G. McNamee, *J. Am. Chem. Soc.*, **90**, 4184 (1968).

(16) J. G. Gordon, II, and R. H. Holm, unpublished results.

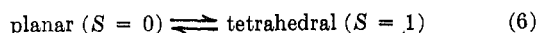
(17) J. H. Dunlap, R. D. Gillard, and R. Ugo, *J. Chem. Soc.*, **A**, 1540 (1966).

(18) Y. T. Chen and G. W. Everett, Jr., *J. Am. Chem. Soc.*, **90**, 6660 (1968).

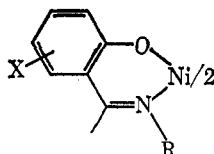
(19) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966); E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev. (London)*, **22**, 457 (1968).

(20) (a) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **88**, 2442 (1966); (b) G. W. Everett, Jr., and R. H. Holm, *Inorg. Chem.*, **7**, 776 (1968).

ciently small that both are measurably populated in noncoordinating solvents at or near room temperature. In the case of nickel(II) complexes the structural equilibrium is (6), which involves planar diamagnetic and tetrahedral paramagnetic species. This equilib-



rium was first demonstrated in detail for the bis(salicylaldimino) complexes **11**²¹ by optical spectral, magnetic susceptibility, and molecular weight measurements. The important properties of equilibrium 6 are the ligand



11, Ni(X-R-sal)₂

structural features which promote its existence and affect its position, and the attendant thermodynamic quantities ΔG , ΔH , and ΔS . While the latter can be determined by measurement of the temperature dependence of ligand field band intensities or magnetic susceptibilities, they are obtained much more easily and accurately by measurements of isotropic shifts over a temperature range coupled with measurements of magnetic moments when necessary.

The basis for the thermodynamic characterization of equilibrium 6 by the isotropic shift method is the rapid interconversion on the nmr time scale between the two isomers such that the observed chemical shifts are averaged over both. The isotropic components of these shifts, which arise only in the tetrahedral forms, have been shown in a number of cases²²⁻²⁴ to derive mainly, if not exclusively, from contact rather than dipolar interactions. Correspondingly, eq 3 is employed in the slightly modified form (7),²⁵ in which the bracketed term is readily shown to be the mole fraction

$$\left(\frac{\Delta H_t}{H_0}\right) = -a_t \left(\frac{\gamma_e}{\gamma_n}\right) \frac{g\beta S(S+1)}{3kT} [\exp(\Delta G/RT) + 1]^{-1} \quad (7)$$

of tetrahedral form, N_t . $\Delta G = -RT \ln K_{eq}$ and $K_{eq} = N_t/N_p$, with N_p the mole fraction of the planar isomer. Values of ΔG can be obtained from eq 7 by measurement of the contact shifts provided g and a_t are known. g values are readily evaluated from magnetic moments using the relation $g = \mu_{eff}[S(S+1)]^{-1/2}$ and values of μ_{eff} obtained from measurements on the solid paramagnetic form, which in a number of cases crystallizes

from the equilibrium solutions. Otherwise, a suitable, structurally analogous paramagnetic complex must be used. Independent measurement of a_t and ΔG 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. In the latter situation the contact shifts have the dependence of eq 3, thereby allowing accurate determination of coupling constants from contact shift measurements alone. These values may then be applied in the non-Curie region, represented by eq 7, and the temperature dependence of ΔG can be calculated from measured shifts. In most instances the stereochemical populations of complexes involved in equilibrium 6 are not sufficiently temperature sensitive that both Curie and non-Curie regions are demonstrably obtained within the usual experimental range of ca. -50 to 100° . Alternative procedures are required which involve, within a series of structurally related complexes, transferral of a given coupling constant a_t from a complex with $N_t = 1$ in solution (eq 3) to one whose contact shifts obey eq 7, or separate evaluation of ΔG at a given temperature from magnetic moment measurements on the equilibrium solution. In the latter case values of N_t and, thereafter, ΔG may be obtained from eq 8, in which μ_{obsd} and μ_t are the observed magnetic moment of the equilibrium mixture

$$N_t = \mu_{obsd}^2/\mu_t^2 = [\exp(\Delta G/RT) + 1]^{-1} \quad (8)$$

and the moment of the tetrahedral isomer, respectively. From eq 7 a_t values may be calculated, the temperature dependence of ΔG determined, and the standard enthalpy and entropy changes evaluated by a least-squares fit of the data to the equation $\Delta G = \Delta H - T\Delta S$. Using these procedures a large body of thermodynamic data has been obtained for extensive classes of bis-chelate nickel(II) complexes,²⁶⁻³³ including the salicylaldimines **11**,^{23, 27-29} aminotroponimines **12**,³⁰ pyrrole-2-aldimines **13**,³¹ β -keto amines **14**,^{20b, 28, 32, 33} and β -thio amines **15**.³³

Several important conclusions relevant to the structural dynamics and equilibria of the complexes **11-15** emerge from the contact shift and thermodynamic results. First, all known members of each class demonstrably involved in equilibrium 6 by virtue of

(26) Note that in several cases^{22a, 23, 27, 30, 32} eq 7 with a 3 in place of 1 in the bracketed term has been used to interpret contact shifts of complexes involved in equilibrium 6. That equation improperly takes into account electron spin degeneracy such that the free energy changes calculated from it are too large by $RT \ln 3$ and the entropy changes too low by $R \ln 3$. Coupling constants and ΔH values are unaffected. Therefore, due corrections should be applied when comparing data obtained from it and eq 7.

(27) A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1010 (1964).

(28) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *J. Am. Chem. Soc.*, **89**, 6104 (1967).

(29) M. J. O'Connor, R. E. Ernst, and R. H. Holm, *ibid.*, **90**, 4561 (1968).

(30) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *ibid.*, **85**, 397 (1963).

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

(32) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2117 (1965).

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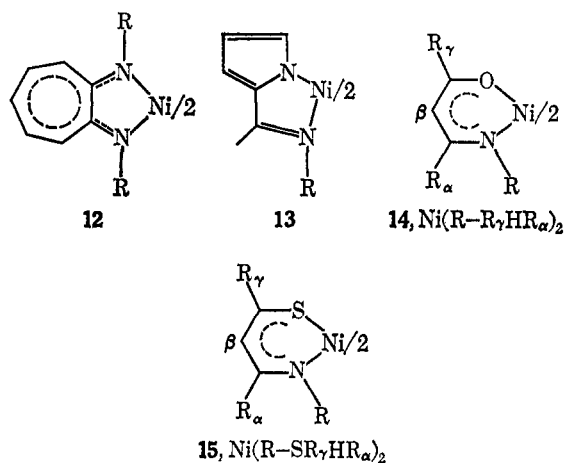
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(22) (a) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962); (b) D. R. Eaton and W. D. Phillips, *ibid.*, **43**, 392 (1965).

(23) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964).

(24) J. E. Parks and R. H. Holm, *Inorg. Chem.*, **7**, 1408 (1968).

(25) W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **87**, 3779 (1965).



their non-Curie contact shift dependence interconvert rapidly on the pmr time scale (at temperatures as low -60°), as required for application of eq 7. An upper limit on the lifetime of either stereoisomer may be estimated as *ca.* 10^{-3} – 10^{-4} sec, inasmuch as equilibrium between the two different spin states is established in a time short compared to the reciprocal of the contact shifts in hertz, and a lower limit may be estimated as *ca.* 10^{-12} – 10^{-13} sec since both forms are detectable in the electronic spectra. Second, within each group the stereochemical populations are primarily a function of the steric properties of the nitrogen substituent R and the nature of the donor atom set. The basis for this conclusion can be seen from some representative data for complexes **14** and **15**, which are collected in Table I. The key structural feature of R which promotes the relative stability of the tetrahedral isomer is branching of the alkyl chain at the α carbon. This effect surely arises from steric interactions between R and the adjacent chelate ring which may be alleviated by torsional distortion around the coordinated metal to produce the tetrahedral form. For the complexes **11** and **13–15** the population of the tetrahedral isomer as a function of R increases in the order *t*-butyl \gtrsim α -branched alkyl $>$ *n*-alkyl $>$ aryl \gtrsim CH₃ \gggg H at ordinary temperatures. The enthalpy changes for the planar \rightarrow tetrahedral conversion are, with only a few exceptions,^{21c,23,33} endothermic and, consequently, equilibrium 6 is displaced to the right with increasing temperature. Effects of the donor

atom set on the equilibrium position can at present be assessed meaningfully only by comparisons of thermodynamic data for pairs of complexes **14–15** (*cf.* Table I) which are identical except for replacement of oxygen with sulfur. Analysis of thermodynamic data for eight such pairs which have $N_t < 1$ in chloroform or carbon tetrachloride solution has shown that, within the interval -40 to 70° , (i) $\Delta G_s - \Delta G_0 = \Delta \Delta G > 0$, demonstrating that sulfur effects greater stabilization of planar stereochemistry than oxygen, and (ii) $|\Delta \Delta H| > |T \Delta \Delta S|$, indicating that inequalities in stereochemical populations are due to enthalpy rather than entropy effects.³³ On the basis of arguments developed elsewhere,^{20b} differences in metal–ligand bonding in the two stereoisomers are considered principally responsible, with an appreciable extent of π bonding in the planar thio complexes a plausible source of the stability differences.

The preceding examples together with the indicated references are cited in order to demonstrate the efficacy of the isotropic shift method in carrying out a detailed analysis of structural equilibrium 6. The same general procedure can be applied to any rapid isomerization reaction involving species with different magnetic ground states provided that electron spin relaxation in the paramagnetic species is sufficiently fast and that, ideally, the isotropic shifts of these species are wholly contact or dipolar in origin. Finally, the extreme sensitivity of the isotropic shift method should be pointed out. As an example, note that Ni(CH₃-SCH₃HCH₃)₂ has $N_t^{323} = 0.04$ (Table I). This small amount of tetrahedral isomer is readily detected by the contact shift of ~ 1 ppm but is not detectable by electronic spectral or bulk susceptibility measurements. Likewise, because no contact shifts of **14** and **15** with R = H are observable, it is safely estimated that at 300°K $K_{eq} < 0.01$ and $\Delta G > 2.8$ kcal/mole, placing hydrogen at the end of the above series of nitrogen substituents which affect population of the tetrahedral isomer.

Diastereoisomeric Complexes

If a tetrahedral complex M(A–B)₂ possesses two positionally equivalent asymmetric ligand centers in addition to its intrinsic dissymmetry at the metal, the following diastereoisomers, shown together with

Table I
Representative Stereochemical Data for Bis-Chelate Nickel(II) Complexes 14 and 15 in CDCl₃ Solutions^a

Complex	β -H contact shift, ppm (30°)	ΔH , kcal mole ⁻¹	ΔS , eu	ΔG^{323} , kcal mole ⁻¹	N_t^{323}
Ni((CH ₃) ₂ C–C ₆ H ₅ HH) ₂	+97.13				1.0
Ni((C ₂ H ₅) ₂ CH–C ₆ H ₅ HH) ₂	+85.77	0.06	3.74	–1.15	0.86
Ni((CH ₃) ₂ CHCH ₂ –C ₆ H ₅ HH) ₂	+1.53	4.98	8.19	+2.33	0.03
Ni((CH ₃) ₂ C–SC ₆ H ₅ HH) ₂	+76.55				1.0
Ni((C ₂ H ₅) ₂ CH–SC ₆ H ₅ HH) ₂	+16.44	4.28	11.7	+0.51	0.31
Ni(<i>n</i> -C ₃ H ₇ –C ₆ H ₅ HCH ₃) ₂	+20.42	2.99	7.57	+0.54	0.30
Ni(CH ₃ –CH ₃ HCH ₃) ₂	+4.70	3.62	6.28	+1.60	0.08
Ni(CH ₃ –SCH ₃ HCH ₃) ₂	+1.08	5.37	10.1	+2.10	0.04

^a Data from ref 33.

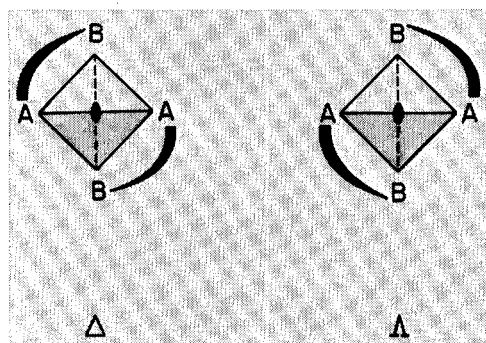


Figure 2. Absolute configurations of a bis-chelate complex viewed down the C_2 axis: Δ , right-handed, Λ , left-handed helicity along principal axis. A and B convey the chelate ring asymmetry.

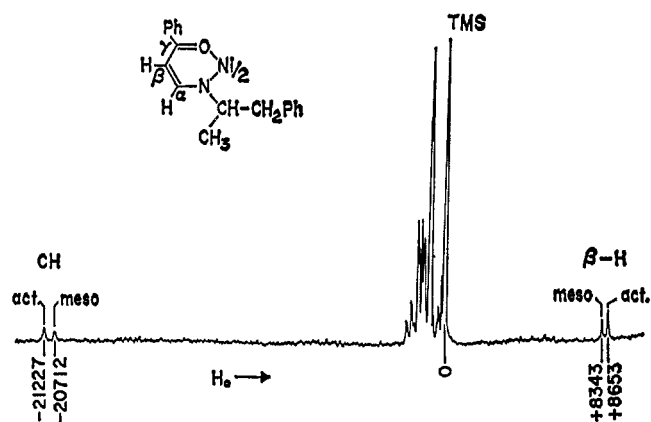


Figure 3. PMR spectrum (100 MHz) of a mixture of active and *meso* forms of $Ni(Amp-C_6H_5HH)_2$ in $CDCl_3$ solution at $\sim 30^\circ$. Frequencies (cps) are the chemical shifts.

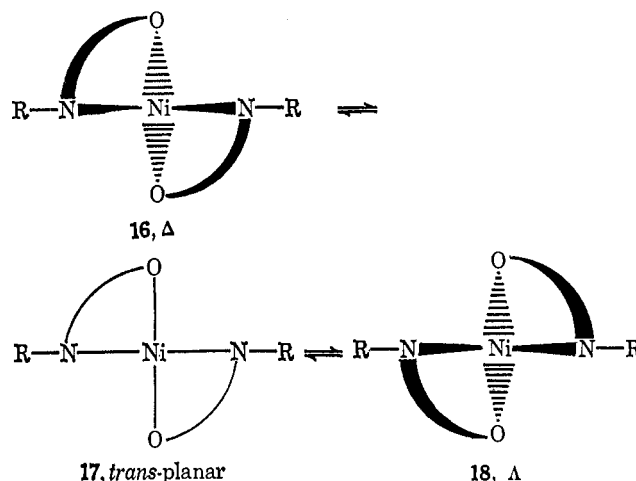
their enantiomers, are possible. Δ and Λ are the two

$$\left. \begin{aligned} \Delta(+,+) &= \Lambda(-,-) \\ \Lambda(+,+) &= \Delta(-,-) \end{aligned} \right\} \text{active}$$

$$\Delta(+,-) = \Lambda(+,-) \text{ meso}$$

absolute configurations at the metal which have been arbitrarily defined to possess right- and left-handed helicity with respect to the twofold axis (*cf.* Figure 2). In the event that all three dissymmetric molecular sites are stable on the nmr time scale of measurement, it is possible in principle to observe separate signals from the three diastereoisomers. As a case in point, consider the pmr spectrum of $Ni(Amp-C_6H_5HH)_2$ ²⁸ (Amp = $CH_3CHCH_2C_6H_5$) shown in Figure 3. This complex is derived from the racemic condensation product of benzoylacetaldehyde and amphetamine and has N_t ^{32,33} $\cong 0.85$ in chloroform solution. It exists as a mixture of planar and tetrahedral diastereoisomers in rapid equilibrium. The features of interest in the spectrum are the splittings of the β -H and CH signals by 3.10 and 5.15 ppm, respectively. The origin of the doubled signals can be unequivocally demonstrated to arise from $(+,+) \equiv (-,-)$ and $(+,-)$ isomers by

preparation of the active isomer using resolved amphetamine. This species shows only one β -H and CH signal, labeled "act." in Figure 3, thereby demonstrating that the missing signals arise from the *meso* isomer, which cannot be prepared separately. Equivalent observations have been made for the complexes **11**,^{23,28} **13**,³¹ **14**,²⁸ and **15**,³³ which possess asymmetric R groups and are involved in equilibrium 6. The failure to observe three signals arises from rapid racemization of the Δ and Λ configurations accompanying the structural change, as illustrated by the interconversion sequence **16** \rightleftharpoons **17** \rightleftharpoons **18** for $Ni-O_2N_2$ complexes.



The source of the chemical shift difference between the diastereoisomers is a matter of considerable importance. Spectra of diastereoisomeric mixtures of tetrahedral, diamagnetic zinc(II) complexes with the same ligands reveal unresolvable or extremely small³⁴ chemical shift differences between isomers, demonstrating that it is the contact shifts of the nickel(II) isomers which differ. Differences between these shifts are largest when both planar and tetrahedral forms of each diastereoisomer are present to a measurable extent. This point is illustrated by the spectrum of the diastereoisomeric mixture of $Ni(Amp-C_6H_5HCH_3)_2$ ²⁸ shown in Figure 4. This complex varies from that in Figure 3 by replacement of α -H with α - CH_3 , the only important effect of which is to displace the structural equilibrium essentially completely toward the tetrahedral form such that the isotropic shifts exhibit the Curie dependence of eq 3 whereas those of $Ni(Amp-C_6H_5HH)_2$ can be interpreted in terms of eq 7. Inspection of eq 7 reveals that the contact shift differences between diastereoisomers will arise from intrinsic inequalities of their a_i and ΔG values. The failure to resolve the β -H isotropic shifts of the isomers of $Ni(Amp-C_6H_5HCH_3)_2$, which have no free energy dependence, together with the clear structural and electronic similarities of the paramagnetic forms of this complex and $Ni(Amp-C_6H_5HH)_2$, has led to the conclusion that significant inequalities in the ΔG values for the structural change of the individual diastereoisomers are

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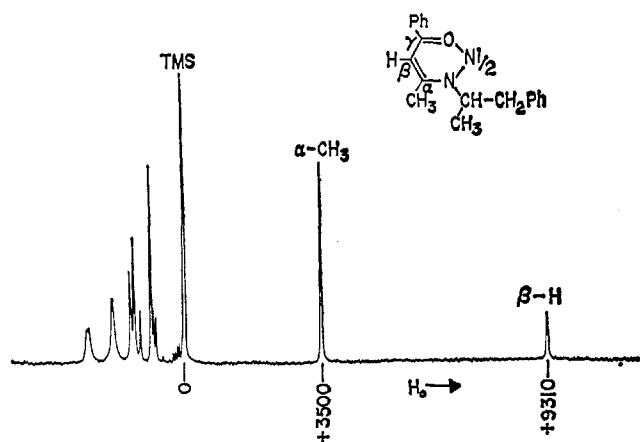
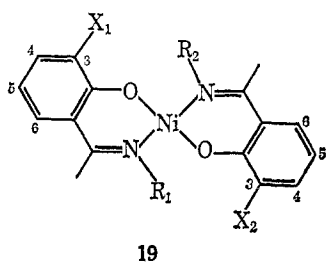


Figure 4. Pmr spectrum (100 MHz) of a mixture of active and *meso* forms of $\text{Ni}(\text{Amp}-\text{C}_6\text{H}_5\text{HMe})_2$ in CDCl_3 solution at $\sim 30^\circ$. Frequencies (cps) are the chemical shifts.

principally responsible for the large contact shift differences.²² Further, it has been concluded that the inequality in ΔG values for a given diastereoisomeric pair derives from a real difference in the free energies of the tetrahedral, paramagnetic active and *meso* forms. The stable planar forms are undoubtedly *trans*, thereby reducing to a minimum mutual interaction of R groups. In the tetrahedral form these groups are in close proximity, with the consequence that the nonbonded interactions (+)-(+) (or (-)-(-)) and (+)-(-) will differ to a much greater extent than in the planar isomers. More detailed considerations and demonstrations of the origin of contact shift differences between diastereoisomers are given elsewhere.^{23,33,35}

The foregoing conclusions indicate that the maximum contact shift resolution between diastereoisomeric bis-chelate nickel(II) complexes will occur when these shifts are averaged over planar and tetrahedral forms. To examine further the sensitivity of the isotropic shift method to the detection of diastereoisomers, a series of salicylaldimine complexes of general type **19** has been prepared.³⁵ These complexes are involved in equilibrium **6** and contain four asymmetric ligand centers introduced as two inequivalent pairs of groups R



and 3-X, so located that they can mutually interact in the tetrahedral stereoisomers. There are 16 possible combinations of asymmetric centers, of which ten are unique and six are diastereoisomers; these are labeled I-VI in Table II. A complete tabulation of various

(35) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 5735 (1968).

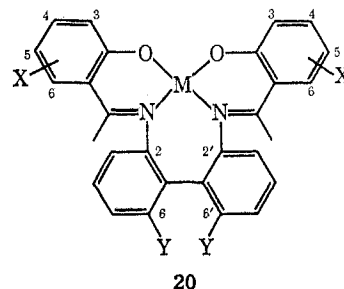
Table II
Partial Representation of the Diastereoisomers of a Complex with Two Inequivalent Pairs of Ligand Asymmetric Centers^a

Diastereoisomer	R ₁	X ₁	R ₂	X ₂	Chemical shift, ppm	N _t ^{29b}
I	+	+	+	+	-23.90	0.577
II	+	+	+	-	-23.35	0.569
III	+	-	+	-	-22.98	0.560
IV	+	+	-	+	-27.90	0.726
V	+	+	-	-	-28.17	0.734
VI	+	-	-	+	-27.52	0.715

^a 4-H chemical shifts of $\text{Ni}(\text{3-sec-C}_4\text{H}_9\text{-Amp-sal})_2$ and tetrahedral mole fractions of $\text{Ni}(\text{3-sec-C}_4\text{H}_9, 5\text{CH}_3\text{-Amp-sal})_2$ (CDCl_3 solution, $\sim 30^\circ$); data are from ref 35.

degenerate representations of the diastereoisomers is given elsewhere.³⁵ The pmr spectra of $\text{Ni}(\text{3-sec-C}_4\text{H}_9\text{-Amp-sal})_2$ and its 5-CH₃ variant have been analyzed in greatest detail.³⁵ The spectrum of the 4-H region of the former compound, prepared from racemic ligand components, is shown in Figure 5a. Six 4-H signals are clearly resolvable. The use of (+)-3-sec-butylsalicylaldehyde and (+)- and (-)-amine in the ligand preparation has permitted the synthesis of isomers I and III. Their spectra in conjunction with those of isomeric mixtures generated by the facile ligand exchange reactions of paramagnetic nickel(II) salicylaldimines^{28,36} leads to an unambiguous assignment of each signal to a particular diastereoisomer.³⁵ The assignments and the procedure by which they were obtained are given in Figure 5. These same assignments extend to the diastereoisomers of $\text{Ni}(\text{3-sec-C}_4\text{H}_9, 5\text{CH}_3\text{-Amp-sal})_2$, whose sharp 5-CH₃ signals are readily followed over a temperature range. Each diastereoisomer is found to possess a characteristic temperature dependence of its isotropic shifts from which the thermodynamic values of the planar \rightleftharpoons tetrahedral structural change can be obtained with the assumption that the values of $\alpha_{5\text{-CH}_3}$ are negligibly different for the six isomers.³⁵ Chemical shift data and tetrahedral mole fractions of the isomers are given in Table II in order to indicate the sensitivity of the method.

As a final example of the extreme sensitivity of isotropic shifts to subtle structural differences, consider the complexes $\text{M}(\text{X-sal})_2\text{bmp}$ (**20**, Y = CH₃) derived from the condensation of 2,2'-diamino-6,6'-dimethylbiphenyl with substituted salicylaldehydes.²⁹ The Schiff base ligand has the significant structural consequences of (i) disposing itself in a nearly strainless



(36) A. Chakravorty and R. H. Holm, *ibid.*, **86**, 3999 (1964).

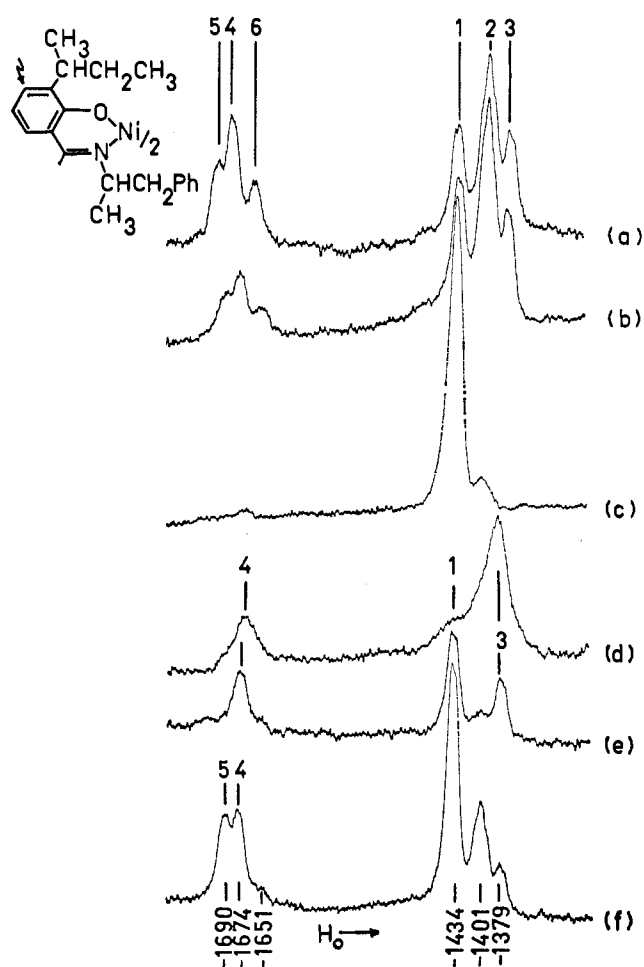


Figure 5. PMR spectra (60 MHz) of the 4-H region of Ni(3-*sec*-C₄H₉-Amp-sal)₂ in CDCl₃ solution at ~27°: (a) total mixture containing diastereoisomers I-VI; (b) mixture of Ni(3-*sec*-C₄H₉-(-)-Amp-sal)₂ complexes, enriched in isomers I, II, and III; (c) Ni(3-(+)-*sec*-C₄H₉-(+)-Amp-sal)₂, isomer I; (d) Ni(3-(+)-*sec*-C₄H₉-(-)-Amp-sal)₂, isomer III; (e) equilibrium mixture resulting from the ligand exchange reaction I + II ⇌ 2IV; (f) equilibrium mixture resulting from the ligand exchange reaction 4I + [I + II + III] ⇌ 4V + 4IV. Frequencies (cps) are the chemical shifts. For a more detailed representation of the ligand exchange reactions, consult eq 2 and 3 and Table IV of ref 35.

manner to form an O₂N₂ tetrahedron; (ii) forming complexes resistant to racemization of the absolute configuration (Δ,Δ) at the metal due to the high activation energy (45 kcal/mole) for racemization of the parent diamine; (iii) producing tetrahedral complexes of known absolute configuration because the chirality of the complex is necessarily that of the diamine. The correlation of the known absolute configurations of the diamine^{28,37} with those of the complexes illustrated in Figure 6 has recently been further confirmed by the X-ray structural determination of Co(sal)₂-R-bmp, which has the predicted Δ configuration.³⁸ The nickel(II) complexes investigated have the

(37) F. A. McGinn, A. K. Lazarus, M. Siegel, J. E. Ricci, and K. Mislow, *J. Am. Chem. Soc.*, **80**, 476 (1958).

(38) L. H. Pignolet, R. P. Taylor, and W. D. Horrocks, Jr., *Chem. Commun.*, 1443 (1968).

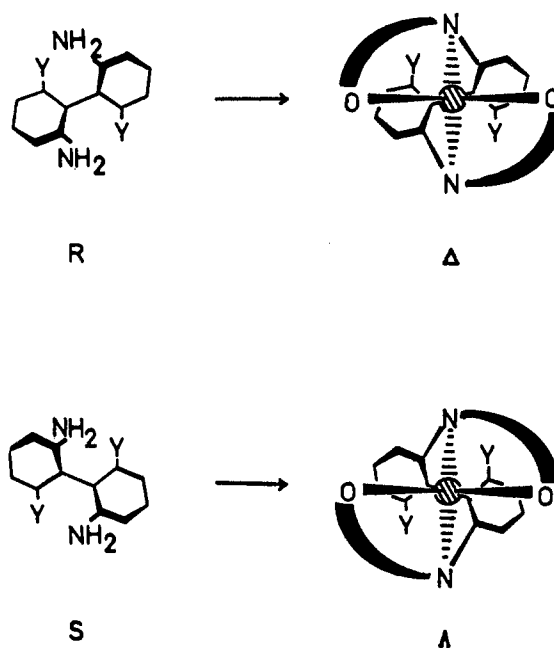


Figure 6. Correlation of the absolute configurations of biphenyl-2,2'-diamines (Y = H, CH₃) with those of the complexes M(X-sal)₂bp (Y = H) and M(X-sal)₂bmp (Y = CH₃) in their tetrahedral forms.

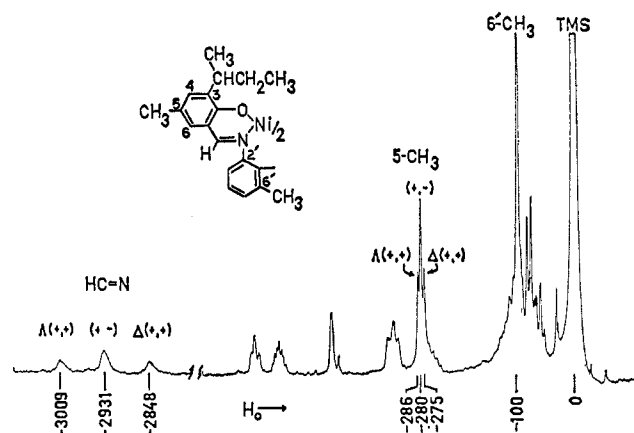


Figure 7. Complete 60-MHz pmr spectrum of a mixture of active and *meso* diastereoisomers of Ni(3-*sec*-C₄H₉,5-CH₃-sal)₂-bmp in CDCl₃ solution at ~27°. Frequencies (cps) are the chemical shifts.

favorable property of $N_t = 0.06-0.15$ in chloroform solution and contain X = 3-*sec*-C₄H₉ groups in order to produce the three possible tetrahedral diastereoisomers specified above. The spectrum of Ni(3-*sec*-C₄H₉,5-CH₃-sal)₂bmp, prepared from racemic ligand components, is shown in Figure 7. Three 5-CH₃ and azomethine signals are well resolved. The origin of these signals has been proven for the closely related complex Ni(3-*sec*-C₄H₉-sal)₂bmp through the synthesis of the separate diastereoisomers, as set out in Figure 8. Each diastereoisomer shows a separate temperature dependence of its isotropic shifts. At all temperatures up to 90°, the upper limit of measurement, there is no evidence of broadening of the Δ(+,+) and

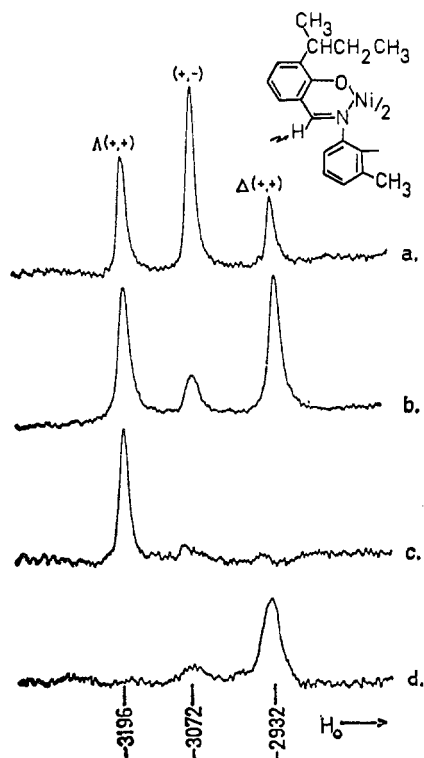
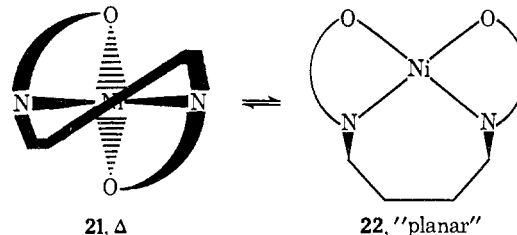


Figure 8. Pmr spectra (60 MHz) of $\text{Ni}(3\text{-sec-C}_4\text{H}_9\text{-sal})_2\text{bmp}$ in the azomethine region demonstrating the signal assignments for the diastereoisomers: (a) total mixture; (b) $\text{Ni}(3\text{-(+)-sec-C}_4\text{H}_9\text{-sal})_2\text{-RS-bmp}$; (c) $\text{Ni}(3\text{-(+)-sec-C}_4\text{H}_9\text{-sal})_2\text{-S-bmp}$; (d) $\text{Ni}(3\text{-(+)-sec-C}_4\text{H}_9\text{-sal})_2\text{-R-bmp}$.

$\Lambda(+,+)$ signals due to the onset of the $\Delta \rightleftharpoons \Lambda$ interconversion. Hence, the complexes exhibit the stereochemical integrity anticipated, at least up to 90° . Because their contact shifts are decidedly non-Curie in behavior, equilibrium 6 obtains and structural

rearrangement occurs without racemization at the metal. The interconversion sequence $21 \rightleftharpoons 22 \rightleftharpoons 21$, for example, is to be contrasted with $16 \rightleftharpoons 17 \rightleftharpoons 18$, which invariably occurs with bis-chelate complexes and produces structural rearrangement and racemization. The complete set of thermodynamic and contact shift data for nickel(II) complexes of type 20 is available



elsewhere.²⁹

The foregoing examples have been considered in order to provide at least a partial indication of the extreme sensitivity of isotropic shifts to subtle structural differences and their consequent utility in the study of the stereochemistry and structural equilibria of paramagnetic metal complexes. Use of the isotropic shift method in the investigation of structural and electronic properties of transition metal complexes is very rapidly increasing, and it may be safely anticipated that significant and new applications of the method will be forthcoming in the near future.

I wish to acknowledge support of a portion of the work described herein by the National Science Foundation and the National Institutes of Health and the valuable contributions of my coworkers whose names are to be found in the references.

Some Aspects of the Chemistry of Polythionates and Selenopolythionates

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In 1841 the French chemist Langlois heated a saturated solution of potassium bisulfite with elemental sulfur for a long time and obtained a salt which differed in properties from salts of sulfur acids known at that time. Unlike the expected product, thiosulfate, this salt did not decompose in dilute acids and gave no precipitate with barium salts. Analysis showed it to have the composition $\text{K}_2\text{S}_3\text{O}_6$. By treating it with HClO_4 , which precipitated the potassium ion as KClO_4 ,

(1) *Chemical Abstracts* sometimes cites the author as I. V. Yanitskii, German sources as J. Janitzki.

Langlois obtained in solution the first polythionic acid, the trithionic. Langlois studied the decomposition of the new acid and found that upon warming it produced sulfuric acid, sulfur dioxide, and elemental sulfur.

A year later Fordos and Gelis discovered the tetrathionic acid $\text{H}_2\text{S}_4\text{O}_6$, obtained by oxidation of thiosulfate with iodine—a reaction now familiar to every chemist. They obtained crystalline sodium and barium tetrathionates and from the latter, after precipitation of barium with sulfuric acid, solutions of tetrathionic acid. Its properties proved to be like those of Langlois'