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The Synthesis, Solution Stereochemistry, and Electron Delocalization Properties of Bis(β-iminoamino)nickel(II) Complexes

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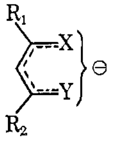
Reaction of β-ketoamines with primary amine hydrochlorides yields a series of β-iminoamines $R_\alpha C(NR){=}CHC(NHR)R_\alpha$ (R_α = H, CH_3; R = benzyl, aryl). These compounds react with nickel(II) salts under nonaqueous conditions to form bis-chelate complexes of the general type $Ni[R_\alpha C(NR)CHC(NR)R_\alpha]_2$. Magnetic, spectral, and proton resonance properties of these complexes indicate that they adopt a pseudo-tetrahedral structure with a spin-triplet ground state in chloroform solution and that no diamagnetic planar stereoisomer is present in any case. All complexes manifest large isotropic proton contact shifts in solution which have been interpreted in terms of an effective π-delocalization mechanism involving ligand→metal antiparallel spin transfer. The mode of spin transfer is considered in some detail, and experimental spin densities at several ligand positions evaluated from contact shift measurements are shown to be consistent with $\sim 1/13$ unit of free spin in the highest filled π MO of the ligand anion. Two or more of the four possible diastereoisomers of the R_α = CH_3, R = *o*-tolyl complex have been detected by proton resonance. Proton resonance spectra of the free ligands indicate that, at least on the time scale of the measurements, they exist as symmetrical hydrogen-bonded species or undergo rapid intramolecular proton transfer between the two nitrogens.

Introduction

The conjugated, monoanionic, β-difunctional ligand shown in general form 1 is among the most fundamental



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chelating systems in coordination chemistry. One of its principal advantages is found in the flexibility of synthesis such that a wide variety of terminal substituents R_1 and R_2 (usually H, alkyl, aryl) and donor atoms or groups X and Y may be incorporated in various combinations. In the past few years we have been engaged in a general investigation of the synthesis and solution stereochemistry of bis-chelate complexes derived from 1. An integral part of this work has been a study of the configurational equilibria and electron delocalization of Ni(II) complexes.

Consideration of steric and electronic factors, supported by some published information, indicates that in *strictly four-coordinate*, bis-chelate complexes variation of the donors X and Y will generally have a more pronounced effect on stereochemistry, electronic structures, and attendant electron delocalization than will variation of the groups R_1 and R_2. For this reason investigations of these properties as a function of X and Y are of particular significance. Commonly X and Y are O, S, and NR (R = H, alkyl, aryl), generating six possible sets of donor atoms in a bis-chelate system. Substantial progress has recently been made in elucidating some of the aforementioned properties of complexes with X = Y = O,[2] in particular, and those with X = O, Y = S[3] and X = O, Y = NR.[4] The chemistry of these groups of complexes derived from 1 is rather well developed. On the other hand, complexes having X = Y = S[5] and X = S, Y = NR[6] have been prepared only recently and little has been reported thus far on their structural and electronic properties. Even less is known about the remaining group of complexes, characterized by X = Y = NR, which may be considered to be derived from α,β-unsaturated β-iminoamines. Brief reports of the synthesis of Ni(II), Cu(II), and Co(II) derivatives of malondialdehyde dianil and methylmalondialdehyde dianil[7] and of a unique, completely encycled Ni(II) complex obtained by a metal template condensation of 3-formylacetylacetone and *o*-phenylenediamine[8] have been published. The only other example of a β-iminoamine chelate ring occurs in the aromatized derivative of 2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone)dioximinenickel(II) cation.[9]

By way of furthering the systematic investigation of bis-chelate complexes derived from the β-difunctional

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(1) Massachusetts Institute of Technology.

(2) For a review of β-ketoenolate complexes see J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966).

(3) β-Thioxoketone complexes: E. Uhlemann, G. Klose, and H. Muller, *Z. Naturforsch.*, **19b**, 962 (1964); S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Australian J. Chem.*, **18**, 673 (1965); R. K. Y. Ho, S. E. Livingstone, and T. N. Lockyer, *ibid.*, **18**, 1927 (1965); **19**, 1179 (1966); S. H. H. Chaston, S. E. Livingstone, and T. N. Lockyer, *ibid.*, **19**, 1401 (1966); S. H. H. Chaston and S. E. Livingstone, *ibid.*, **19**, 2035 (1966); E. Uhlemann and W. W. Suchan, *Z. Anorg. Allgem. Chem.*, **342**, 41 (1966); E. Uhlemann and P. Thomas, *J. Prakt. Chem.*, **34**, 180 (1966); A. Yokoyama, S. Kawanishi, M. Chikuma, and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **15**, 540 (1967); S. H. H. Chaston and S. E. Livingstone, *Australian J. Chem.*, **20**, 1065, 1079 (1967).

(4) β-Ketoamine complexes: (a) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2117 (1965); (b) E.-G. Jäger, *Z. Anorg. Allgem. Chem.*, **337**, 80 (1965); (c) S. Yamada, H. Nishikawa, and E. Yoshida, *Bull. Chem. Soc. Japan*, **39**, 994 (1966); (d) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **88**, 2442 (1966); *Inorg. Chem.*, **7**, 776 (1968); (e) S. Yamada and E. Yoshida, *Bull. Chem. Soc. Japan*, **40**, 1854 (1967); (f) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *J. Am. Chem. Soc.*, **89**, 6104 (1967).

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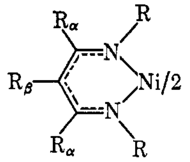
TABLE I

CHARACTERIZATION OF 2-N-ARYLAMINO-4-N-ARYLIMINO-2-PENTENES AND THEIR BIS-CHELATE Ni(II) COMPLEXES

		% ligand							% complex						
			Calcd			Found				Calcd			Found		
Rα	R	Mp,[a] °C	C	H	N	C	H	N	Mp,[a] °C	C	H	N	C	H	N
CH_3	C_6H_5[c]	50–52	81.56	7.25	11.19	81.58	7.15	11.36	162–163	73.26	6.15	10.05	73.20	6.04	9.77
CH_3	o-$C_6H_4CH_3$[c,d]	33.5–35.5	81.97	7.97	10.06	82.02	7.89	10.05	282–284	74.39	6.90	9.13	74.07	6.80	8.91
CH_3	m-$C_6H_4CH_3$[c]	53–55	81.97	7.97	10.06	81.92	8.04	9.85	143–144	74.39	6.90	9.13	73.83	6.92	8.61
CH_3	p-$C_6H_4CH_3$[c]	73–74	81.97	7.97	10.06	81.74	7.85	10.16	186–187	74.39	6.90	9.13	74.05	7.05	8.49
CH_3	p-$C_6H_4C_6H_5$[b,e]	124–125	86.53	6.51	6.96	86.59	6.54	6.92	215–216	80.84	5.85	6.50	79.36	6.07	6.18
CH_3	$CH_2C_6H_5$[c]				g				134–136	74.39	6.90	9.13	74.74	7.06	9.14
H	C_6H_5[f]				h				313–316	71.88	5.23	11.18	71.95	5.19	11.22

[a] Uncorrected. [b] Ligand recrystallized from 1:1 tetrahydrofuran–n-heptane. [c] Complex extracted from reaction mixture with n-heptane and recrystallized from n-heptane. [d] Final purification of complex by vacuum sublimation. [e] Complex extracted with 1:1 n-heptane–toluene and recrystallized from 5:1 n-heptane–toluene. [f] Extracted and purified by Soxhlet extraction with benzene. [g] Ligand previously characterized.[13] [h] 1-Phenylamino-3-phenyliminopropene; previously characterized.[14,15]

ligand **1**, we have prepared a new series of bis(β-iminoamino)nickel(II) complexes **2**. These have R = aryl or benzyl and are designated throughout as $Ni(R_2–R_\alpha R_\beta–R_\alpha)_2$,[10] using a notation of ligand positions consistent with that for β-ketoamine complexes.[4a,d,f] The complexes have been characterized by magnetic, spectral, and proton resonance measurements. Large isotropic hyperfine contact shifts have been observed whose signs and magnitudes are consistent with unpaired electron delocalization effected by ligand-to-metal antiparallel spin transfer. The complete body of results and conclusions from these investigations is reported here.



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Experimental Section

Preparation of Ligands.—Among the ligands utilized in this study, all of the N,N′-diaryl-β-iminoamines derived from acetylacetone are reported for the first time. The hydrochlorides of 2-phenylamino-4-phenylimino-2-pentene[11,12] and 2-p-tolylamino-4-p-tolylimino-2-pentene[11] have been previously reported, as have the free bases 2-benzylamino-4-benzylimino-2-pentene[13] and malondialdehyde dianil[14,15] and their hydrochlorides.

The 2-N-arylamino-4-N-arylimino-2-pentene hydrochlorides were prepared by a method reported by Schiebe.[11] The β-ketoamines were first obtained by reaction of acetylacetone and the appropriate amine[4a] and purified by distillation or recrystallization. Equimolar quantities of the β-ketoamine and amine hydrochloride were refluxed for 1 hr with enough absolute ethanol to dissolve them. The first crop of crystals was obtained by cooling of the reaction mixture; reduction of solution volume followed by cooling yielded a second crop. The β-iminoamine hydrochlorides were deprotonated by refluxing them with a twofold molar excess of triethylamine in enough dry ether to make up a thin slurry, followed by filtration to remove triethylammonium chloride, evaporation of ether, and removal of the remaining triethylamine *in vacuo*. The resultant oils were recrystallized from dry pentane, unless otherwise indicated in Table I, until a constant melting point was achieved. Compounds so obtained were analytically pure. Characterization data are given in Table I (chemical shift values are set out in Table V).

Malondialdehyde dianil monohydrochloride was obtained from Aldrich Chemical Co. and used directly. Dorman's procedure[13] was used to prepare 2-benzylamino-4-benzylimino-2-pentene.

Preparation of Complexes.—The sensitivity of the β-iminoamine complexes to hydrolytic decomposition required the use of nonaqueous chelation reactions for their preparation. Thoroughly dried solvents were employed in the extraction and recrystallization steps referred to below. Toluene and n-heptane were dried by refluxing them over sodium and phosphorus pentoxide, respectively.

$Ni(R_2–CH_3HCH_3)_2$ (R = C_6H_5, Bz) and $Ni[(C_6H_5)_2–HHH]_2$ were prepared in t-butyl alcohol by use of the nonaqueous chelation procedure described previously.[4a] After removal of the t-butyl alcohol *in vacuo*, the complexes were extracted from the solid residue using n-heptane alone or mixed with toluene, as indicated in Table I. $Ni(R_2–CH_3HCH_3)_2$ (R = PhPh, m-tol, p-tol) complexes were obtained by reaction of the ligand with n-butyllithium in tetrahydrofuran in a manner analogous to that recently employed in the synthesis of iron(II) aminotroponeiminates.[16] The ligand (0.02 mol) was dissolved in 20 ml of tetrahydrofuran (distilled from lithium aluminum hydride) and the solution was cooled to −78° under nitrogen. Then 13 ml of n-butyllithium in hexane (1.6 *N*, 0.021 mol) was added during 2 min, followed by warming of the mixture to room temperature and the addition of 7.0 ml (0.011 mol) of tetraethylammonium tetrabromonickelate.[17] The mixture was stirred vigorously under nitrogen for 2–3 hr while a greenish brown color developed. The solvent was then removed *in vacuo* and the residue was extracted by use of the solvents indicated in Table I. In both methods the complexes were first isolated by volume reduction of extract solution followed by recrystallization from the solvents noted in this table. To indicate the efficacy of either preparative method for a given complex, $Ni[(o\text{-tol})_2–CH_3HCH_3]_2$ was prepared in equally good yield and purity by both methods. Yields ranged between 50 and 70% except in the case of $Ni((C_6H_5)_2–HHH)_2$, which was obtained in 83% yield. In several cases cocrystallization of the complex and free ligand or its lithium salt, which could not be completely avoided despite several recrystallizations, led to slightly high analytical results; the presence of small amounts of ligand or its salt was indicated by the pmr spectra of these complexes. Characterization data for the complexes are found in Table I.

The complexes $Ni(R_2–CH_3HCH_3)_2$ form greenish black crystals which are readily soluble in common, weakly polar organic solvents giving very deep green solutions. The dissolved complexes are decomposed by small amounts of water or by prolonged

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(10) R = Bz, benzyl; PhPh, p-biphenylyl; o-tol, o-tolyl; m-tol, m-tolyl; p-tol, p-tolyl.

(11) G. Schiebe, *Ber.*, **56**, 137 (1923).

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heating above ~60°. $\mathrm{Ni((C_6H_5)_2\text{–}HHH)_2}$ is a reddish violet solid which is only slightly soluble in organic solvents to yield reddish orange solutions.

Magnetic Susceptibility Measurements.—Measurements of solids and solutions were made by the Gouy method using aqueous nickel chloride solutions or $\mathrm{HgCo(NCS)_4}$ and distilled water, respectively, as calibrants. Solutions were prepared in the absence of air and moisture by admission of chloroform, previously distilled from phosphorus pentoxide under nitrogen, to an evacuated sample tube containing the complex.

Molecular Weights.—The molecular weight of a representative complex, $\mathrm{Ni[(C_6H_5)_2\text{–}CH_3HCH_3]_2}$, was measured by a Mechrolab osmometer in fresh, dry carbon tetrachloride solution; found, 532 (average of four determinations, 3.5–47 m*m*); calcd, 557. The slightly low result may indicate a small amount of decomposition to which molecular weight measurements by this method are quite sensitive.

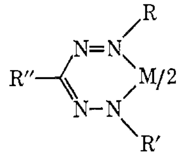
Electronic Spectra.—Solutions were prepared using dry chloroform and were recorded immediately on a Cary 14 spectrophotometer.

Proton Resonance Measurements.—Spectra of ligands and complexes were obtained on Varian A-60 and HA-100 spectrometers, respectively, equipped with a constant-temperature probe assembly. All spectra were recorded using $\mathrm{CDCl_3}$ solutions containing TMS as an internal reference. Chemical shifts were measured using the usual side-band technique. Concentrations used were ~0.1 *M* except in the case of $\mathrm{Ni((C_6H_5)_2\text{–}HHH)_2}$ for which a saturated solution ($\sim 10^{-3}$ *M*) and repetitive scan technique were required owing to low solubility.

Results and Discussion

The majority of β-iminoamines and their nickel(II) complexes **2** investigated in this work have $R_\alpha = \mathrm{CH_3}$ and R = aryl. All of these complexes have been prepared for the first time, as have the corresponding free ligands. Of the substitutional variants of **2** with R = alkyl, only $\mathrm{Ni(Bz_2\text{–}CH_3HCH_3)_2}$ has been prepared; no complexes with R = H are presently known. The nonaqueous chelation methods described here and elsewhere[4a,16] would almost certainly be applicable to the synthesis of these complexes. In this connection it is noted that $\mathrm{H[(C_2H_5)_2\text{–}CH_3HCH_3]\cdot HClO_4}$[18] as well as $\mathrm{H(H_2\text{–}C_6H_5HC_6H_5)}$, and $\mathrm{H(H_2\text{–}C_6H_5HCH_3)}$[19] have been reported. Their ligand properties have yet to be investigated.

Although the present investigation of four-coordinate, bis-chelate β-iminoamine complexes has been preceded by only one study of such complexes, which was restricted in scope,[7] six-membered chelate rings of a symmetrical, unsaturated nature with a pair of nitrogen-donor atoms are well recognized in other groups of complexes. These include the bis-[N′-(perfluoroacylimidoyl)perfluoroalkylamidine],[20] bis(pyrromethene),[21,22] bis(formazan),[23-26] and deprotonated bis(dipyridylmethane) and bis(dipyridylamine) complexes.[27] Of these, the bis(formazan) complexes (**3**) are the most closely related to the β-iminoamines and the structures of the two groups of complexes will be compared.



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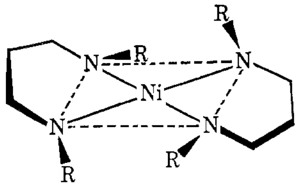
Stereochemistry in Solution.—When R is a particularly large group such as phenyl, complexes **2** cannot have a structure in which the two chelate rings and the metal are coplanar without seriously disturbing the expected trigonal-coplanar arrangement of bonds around the donor nitrogens. This situation is also encountered in the bis(formazans) **3** with R, R′ = aryl, and in bis-(β-ketoamine) and bis(salicylaldimine) complexes which possess two sterically active nitrogen substituents. On the basis of the considerable amount of X-ray structural information now at hand for bis-chelate Ni(II) complexes, two general distortions from coplanarity of the metal and chelate rings, both of which preserve the approximate planarity of the individual chelate rings (excluding the metal), may be recognized. The first of these is a simple torsional distortion so as to produce a nonzero dihedral angle between the rings. Such a structure is well established for several sterically hindered, paramagnetic, bis(salicylaldimino) complexes[28]; in these cases the dihedral angle exceeds 80°. The second distortion takes the form of a "stepped" structure in which the coordination sphere of the metal is planar and the two chelate rings are approximately planar but are offset from each other in parallel planes separated by ~1–2 Å. This structure has been found for bis(N-phenyl-N′-*p*-tolyl-C-methylformazan)nickel(II)[26] and is illustrated by **4**. At present it is not at all certain which distortion a given sterically crowded Ni(II) complex will assume inasmuch as both have been found for the bis(N-substituted salicylaldimino) complexes.[28,29] The two structures should be distinguishable by magnetic measurements because **4** will be diamagnetic whereas the torsionally distorted (pseudo-



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tetrahedral) structure will be paramagnetic provided the dihedral angle is sufficiently large.

Magnetic moments for complexes **2**, given in Table II, reveal a triplet ground state in both solid and solution phases and are consistent with a pseudo-tetrahedral structure. However, several lines of evidence indicate that the degree of distortion of the $Ni-N_4$ unit from planarity, while sufficient to stabilize a triplet ground state, does not result in the highest possible symmetry (D_{2d}) of the complex. The Curie magnetic moments of Ni(II) in a perfect or effective tetrahedral environment should fall in the 3.6–4.0-BM range at room temperature and decrease markedly with decreasing temperature.[30] Moments in this range are not usually found for bis-chelate Ni(II) complexes, although those complexes which like **2** possess an N_4 coordination sphere and potential D_{2d} symmetry, *viz.*, the bis(pyrromethenes)[21c] and bis(aminotroponeimines),[31] usually have room-temperature moments in excess of ~3.30 BM. Additionally, the observed moments of **2** fall below those of bis(β-ketoamino)- and bis(salicylaldimino)-nickel(II) complexes ($\gtrsim$3.25 BM) whose pseudo-tetrahedral structures have been established in both solution[4] and crystalline[28] phases and whose ligand field microsymmetry is ostensibly lower than that in the β-iminoamines. The Curie dependence of the proton contact shifts (*vide infra*) rules out the possibility that magnetic moments result from a significant fraction of singlet-state complexes which might arise as a consequence of a planar $\rightleftharpoons$ tetrahedral or monomer $\rightleftharpoons$ polymer (paramagnetic) equilibrium. Molecular weight measurements have shown that $Ni[(C_6H_5)_2-CH_3HCH_3]_2$ is monomeric in solution. Spectral measurements in the ligand field region are also indicative of low symmetry distortions. Data are presented in Table II and the spectrum of a typical complex is shown in Figure 1. Absorptions in the 6000–11,000-cm^{-1} region are diagnostic of pseudo-tetrahedral structures of $Ni-O_2N_2$[4] and $Ni-N_4$[21] complexes but do not usually take the form of three closely spaced, clearly observable bands. Indeed, only two are expected in this region,[4] *viz.*, ν_2 and the first singlet–triplet transition of tetrahedral Ni(II). The lowest energy feature is presumably associated with ν_2,[4] whose upper state ($^3A_2$) cannot be split by lower symmetry distortions. The remaining bands cannot be assigned with any certainty, but their presence, together with the small orbital contributions to the magnetic moments, must imply a grossly distorted pseudo-tetrahedral structure for the β-iminoamine–nickel(II) complexes.

Table II

Magnetic Moments and Ligand Field Spectra of Nickel(II) Complexes

Complex	μ_{eff},[a] BM Solid	μ_{eff},[a] BM $CHCl_3$ soln[b]	λ_{max}, cm^{-1} (ϵ_M[c])
$Ni[(C_6H_5)_2-HHH]_2$	3.17	[d]	7140 (29), 9100 (28), 10,200 (19)
$Ni(Bz_2-CH_3HCH_3)_2$	3.06	3.04	7940 (32), 9440 (31), 10,400 (23), 17,220 (170)
$Ni[(C_6H_5)_2-CH_3H-CH_3]_2$[f]	3.10	3.08	7250 (63), ~8500[e] (56), 10,000 (38), 15,870 (500)
$Ni[(PhPh)_2-CH_3H-CH_3]_2$	3.11	2.97	7220 (76), 8510 (66), 10,100 (44), 15,870 (450)
Ni[(*p*-tol)$_2$–$CH_3H-CH_3]_2$	3.07	3.08	7300 (66), ~8500[e] (58), 10,000 (39), 15,390 (400)
Ni[(*m*-tol)$_2$–$CH_3H-CH_3]_2$	3.13	3.05	7270 (67), ~8500[e] (55), 10,000 (36), 15,870 (380)
Ni[(*o*-tol)$_2$–$CH_3H-CH_3]_2$	3.16	3.05	7010 (80), ~7900[e] (70), 10,150 (42), 15,730 (570)

[a] Calculated from the Curie law, $\mu_{eff} = 2.83(\chi^M_{cor}T)^{1/2}$. [b] Concentration range 0.045–0.14 *M*. [c] Apparent values in l. mole^{-1} cm^{-1}, uncorrected for overlapping absorption; chloroform solution. [d] Insufficiently soluble for measurement. [e] Shoulder on lower energy peak. [f] Spectrum in 5000–13,000-cm^{-1} region shown in Figure 1.

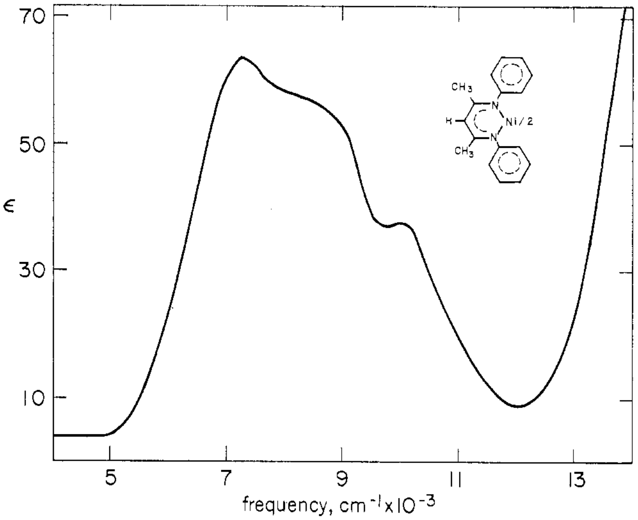

Figure 1.—Ligand field spectrum of $Ni[(C_6H_5)_2-CH_3HCH_3]_2$ in chloroform solution in the near-infrared region.

The bis(formazan)nickel(II) complexes **3** (R, R′ = aryl, R″ = CH_3, aryl) have been found to be diamagnetic in the solid state,[24,25] a behavior consistent with structure **4**. The possible similarity of steric interactions between the same set of aryl groups in **2** and **3** suggests that the structures of the two groups of nickel complexes might be closely related in solutions of noncoordinating solvents although they are different in the solid phases. Indeed, a pseudo-tetrahedral structure was proposed for bis(N-phenyl-N′-*p*-tolyl-C-methylformazan)nickel(II) on the basis of its partial resolution on (+)-quartz.[24] However, as Dale[26] has pointed out, structure **4** with identical aryl groups *cis* to each other is also enantiomeric. We have obtained the proton resonance spectrum of this compound in a saturated solution in deuteriochloroform. At 60 Mc the N-*p*-tolyl methyl and C-methyl shifts are −135 and −173 cps; corresponding signals in the free ligand occur at −137 and −143 cps, respectively. This complex exhibits no proton hyperfine contact shifts, in contrast to the β-iminoamines (*vide infra*), and therefore remains diamagnetic in solution. It is concluded that the formazan complex undergoes no significant torsional

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(30) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

(31) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

distortion and that the "stepped" *cis* structure **4** is most probably the source of the optical isomerism.[32,33]

Proton Resonance Studies.—All seven bis(β-iminoamino)nickel(II) complexes exhibit well-resolved pmr spectra whose extremely large upfield and downfield chemical shifts result from isotropic contact interactions. Spectra of representative complexes are shown in Figures 2–5. These complexes constitute the sixth general group of four-coordinate bis-chelate Ni(II) complexes in which substantial contact shifts together with favorably small signal line widths have been observed. The other groups are the bis(aminotroponeimino),[31,34] bis(salicylaldimino),[4f,35] bis(β-ketoamino),[4a,d,f] bis(pyrrole-2-aldimino),[36] and bis(pyrrometheno)[22] complexes. All of the complexes in these groups exist partially or completely in a pseudo-tetrahedral configuration, which appears to promote a sufficiently short electron spin relaxation time such that well-resolved spectra of usefully narrow line widths are obtained ($T_{1e} \ll a_i$) whether or not the complexes are involved in a rapid planar $\rightleftarrows$ tetrahedral equilibrium.[37]

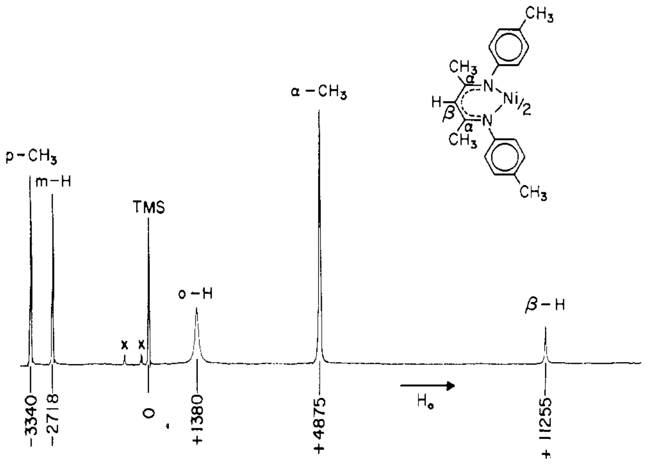

Figure 2.—Pmr spectrum (100 Mc) of Ni[(p-tol)$_2$-CH$_3$HCH$_3$]$_2$ in CDCl$_3$ solution. Frequencies (cps) are the chemical shifts. Features marked with × are due to free-ligand impurity.

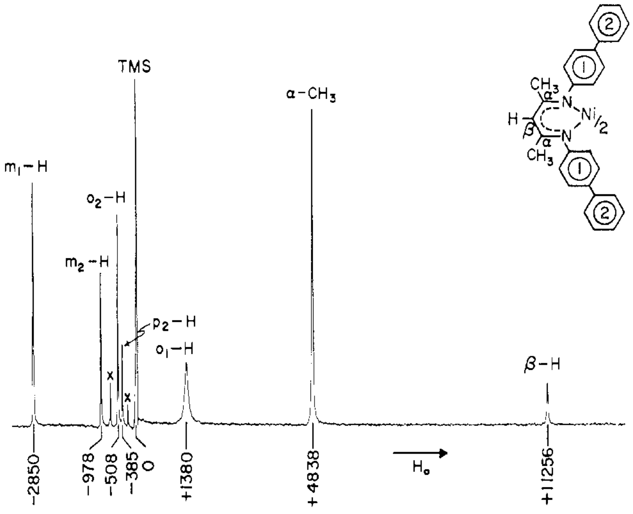

Figure 3.—Pmr spectrum (100 Mc) of Ni[(PhPh)$_2$-CH$_3$HCH$_3$]$_2$ in CDCl$_3$ solution. Frequencies (cps) are the chemical shifts. Features marked with × are due to free-ligand impurity.

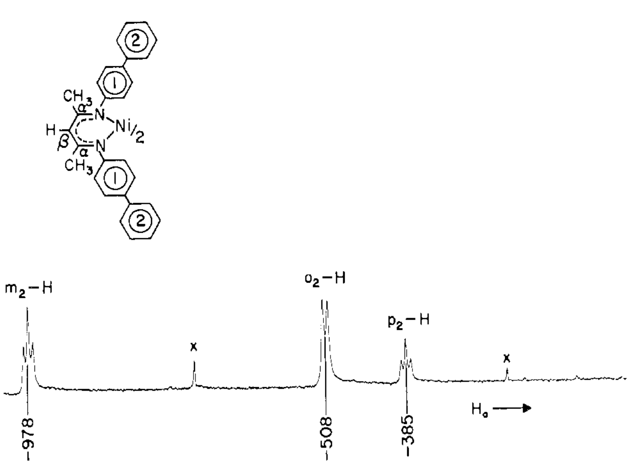

Figure 4.—Pmr spectrum (100 Mc) of the biphenylyl group of Ni[(PhPh)$_2$-CH$_3$HCH$_3$]$_2$ in CDCl$_3$ solution. Frequencies marked with × are due to free-ligand impurity.

Contact shifts of the β-iminoamine complexes are presented in Table III. Diamagnetic reference positions from which these shifts were calculated were taken from the spectra of the free ligands, which are discussed in a subsequent section. The close correspondence of contact shifts, as well as of magnetic

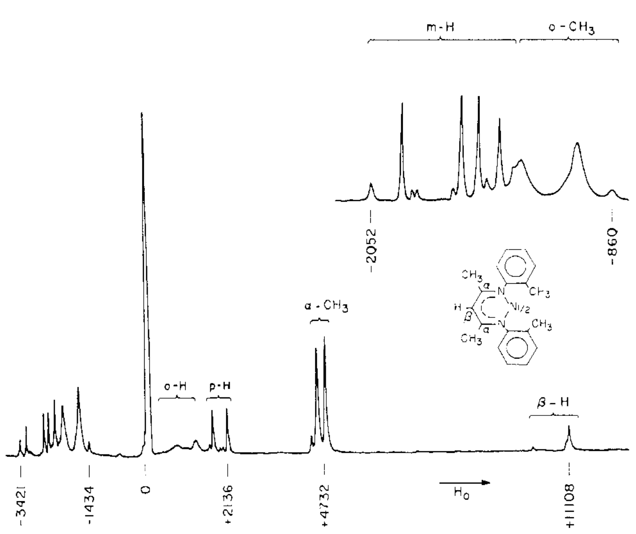

Figure 5.—Pmr spectrum of the mixture of diastereoisomers of Ni[(o-tol)$_2$-CH$_3$HCH$_3$]$_2$ in CDCl$_3$ solution: bottom, complete spectrum at 100 Mc; top, expanded spectrum in the m-H and o-CH$_3$ region at 60 Mc. Frequencies (cps) are the chemical shifts.

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(32) The decided tendency of the N,N′-diarylformazan ligand system to stabilize a planar M–N$_4$ coordination unit is evidenced by the magnetic moments (1.93–2.12 BM) of three bis-chelate Co(II) complexes.[25] Generally, Co(II) complexes of this type, such as β-ketoamines[4d,e] and pyrromethenes,[21b] which are subject to even a small amount of steric crowding in the planar form, readily assume a pseudo-tetrahedral configuration.

(33) Dale's structural results for bis(N-phenyl-N′-p-tolyl-C-methylformazan)nickel(II) make it probable that both *cis* and *trans* isomers are present in the crystalline phase.[26] The two separate isomers, whose chemical shifts are expected to differ only slightly, could not be detected in solution by proton resonance.

(34) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962), and succeeding papers.

(35) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964); A. Chakravorty and R. H. Holm, *ibid.*, **86**, 3999 (1964); *Inorg. Chem.*, **3**, 1010 (1964).

(36) R. H. Holm, A. Chakravorty, and L. J. Theriot, *ibid.*, **5**, 625 (1966).

(37) G. N. LaMar, *J. Am. Chem. Soc.*, **87**, 3567 (1965).

TABLE III

PROTON CONTACT SHIFTS AND SPIN DENSITIES OF BIS(β-IMINOAMINO)NICKEL(II) COMPLEXES[a]

Complex	Substituent	Δf_i, cps[b]	ρ_{Ci}[d]
$Ni[(C_6H_5)_2-HHH]_2$	α-H[c]	−5143	−0.0208
	β-H	+12,078	+0.0488
	o-H	+1601	+0.0065
	m-H	−1975	−0.0080
	p-H	+2029	+0.0082
$Ni(Bz_2-CH_3HCH_3)_2$	α-CH_3	+5237	e
	β-H	+12,051	+0.0508
	CH_2	−828	
	o-H	−276	
	m-H	−184	
	p-H	−281	
$Ni[(C_6H_5)_2-CH_3HCH_3]_2$	α-CH_3	+5066	e
	β-H	+11,766	+0.0489
	o-H	+2082	+0.0087
	m-H	−2031	−0.0084
	p-H	+2632	+0.0109
$Ni[(PhPh)_2-CH_3HCH_3]_2$	α-CH_3	+5045	e
	β-H	+11,748	+0.0507
	o-H_1	+2110	+0.0091
	m-H_1	−2120	−0.0091
	o-H_2	+218	+0.00094
	m-H_2	−250	−0.0011
	p-H_2	+342	+0.0015
$Ni[(p\text{-tol})_2-CH_3HCH_3]_2$	α-CH_3	+5073	
	β-H	+11,742	+0.0488
	o-H	+2080	+0.0086
	m-H	−2018	−0.0084
	p-CH_3	−3109	f
$Ni[(m\text{-tol})_2-CH_3HCH_3]_2$	α-CH_3	+5044	e
	β-H	+11,824	+0.0496
	o-H	+1980, +2154	+0.0083 +0.0090
	m-H	−2078	−0.0087
	m-CH_3	+786	f
	p-H	+2594	+0.0109
$Ni[(o\text{-tol})_2-CH_3HCH_3]_2$[g]	α-CH_3	+4917, +4886,[g] +4687, +4532	
	β-H	+11,594,[g] +11,523, +10,621	
	o-H	+1986,[g] +1752, +1498[g]	
	o-CH_3	−1260, −1559,[g] −1645, −1977[g]	
	m-H	−1602, −1706,[g] −1799, −1868,[g] −1944,[g] −2060, −2326, −2374, −2460,[g] −2726	
	p-H	+2831,[g] +2714, +2655, +2452,[g] +2361	

[a] Data refer to 34°, 100 Mcps, and $CDCl_3$ solution. [b] $\Delta f_i = f_{i(complex)} - f_{i(dia)}$; values of $f_{i(dia)}$ taken from the chemical shifts of the free ligands (Table V). [c] Signal detected in a saturated solution by use of a Varian CAT. [d] All values obtained using $Q_{CH} = -23$ G. [e] Apparent $Q_{CCH_3} = +23-24$ G if $\rho_\alpha = \rho_\alpha$ in $Ni[(C_6H_5)_2-HHH]_2$. [f] Apparent $Q_{CCH_3} = +9.0$ (m), +27 (p) G if $\rho_{m,p\text{-}C} = \rho_{m,p\text{-}C}$ in $Ni[(C_6H_5)_2-CH_3HCH_3]_2$. [g] Signals of higher intensity within each group; spin densities not calculated.

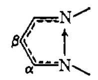
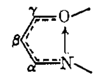
moments and ligand field spectra, indicates essentially identical electronic and geometrical structures of all complexes in solution. Contact shifts of two complexes, $Ni(Bz_2-CH_3HCH_3)_2$ and $Ni[(C_6H_5)_2-CH_3HCH_3]_2$, obey the Curie law in the temperature interval −60 to +60°, indicating that the shifts of all complexes may be treated in terms of eq 1, in which the symbols have their usual meanings.[34]

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

The signs and magnitudes of the contact shifts reveal that they are effected by ligand→metal spin transfer resulting in a net spin imbalance of sense α, parallel to the electron spin polarization of the metal, in the highest filled π MO (HFMO) of the individual ligands. Coupling constants a_i are related to aromatic carbon pπ spin densities ρ_{Ci} by the familiar relation $a_i = Q_X\rho_{Ci}$ in which Q_X is the hyperfine splitting constant for an aromatic fragment X and is negative for $\dot{C}-H$ and positive for $\dot{C}-CH_3$. Evidence for π-spin delocalization is derived from the following results. First, the qualitative observation that the signs of the α-H and α-CH_3 shifts in $Ni[(C_6H_5)_2-HHH]_2$ and $Ni[(C_6H_5)_2-CH_3HCH_3]_2$ and those of phenyl protons and methyl groups in a given position in the N-aryl substituents are of opposite sign is consistent with the opposite sign of Q_{CH} and Q_{CCH_3}. Second, the shifts of the chelate ring protons of $Ni((C_6H_5)_2-HHH)_2$ and of the N-aryl protons in other complexes alternate in sign, as expected for an odd-alternant π-electron free radical. It is noted that in $Ni[(PhPh)_2-CH_3HCH_3]_2$ the alternation of sign persists in the second ring of the p-biphenyl group where the retention of first-order nuclear spin–spin coupling (see

Table IV

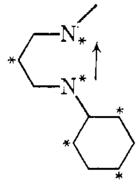
Comparison of Calculated Spin Densities for β-Iminoamine and β-Ketoamine π-Radicals

		π-Electron configuration					
		$\psi_1^2\psi_2^2\psi_3^1$			$\psi_1^2\psi_2^2\psi_3^2\psi_4^1$		
Radical	Method	$\rho\alpha$	$\rho\beta$	$\rho\gamma$	$\rho\alpha$	$\rho\beta$	$\rho\gamma$
	HMO[a]	+0.034	+0.464	...	+0.346	0.000	...
	McL[b]	−0.0750	+0.626	...	...	...	...
	VB[c]	−0.278	+0.656	...	...	...	...
	HMO[d,e]	+0.032	+0.508	+0.055	+0.381	+0.003	+0.326
	VB[d]	−0.282	+0.697	−0.249	...	...	...

[a] $\beta_{CN} = 1.2\beta$, $\alpha_N = \alpha + \beta$; $\rho_N = +0.234(\psi_3)$; $E_3 = 0.542\beta$; $E_4 = -0.800\beta$. [b] HMO results including spin correlation according to the method of A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960), using polarizabilities and $\lambda = 1.2$; $\rho_N = +0.262(\psi_3)$. [c] $\gamma_{CN} = 1.2\gamma$; $\rho_N = +0.450$. [d] Results from ref 4a. [e] $E_3 = 0.580\beta$, $E_4 = -0.860\beta$.

Figure 4) leaves no doubt as to signal assignments. Third, chelate ring spin densities calculated from the observed contact shifts using eq 1 and $a_i = Q_{CH}\rho_{Ci}$ are in excellent agreement with those calculated assuming one free spin on each ligand.

(a) **Mode of Spin Delocalization.**—The existence of spin density in the HFMO's of ligands rather than in the lowest unoccupied π MO (LUMO) is readily demonstrated by a simple Hückel calculation. Complexes 2 contain, formally, Ni(II) and two ligand monoanions. Removal of one electron from the ligand yields the neutral odd-alternant π-radical **5**. Hückel spin densities, which of necessity are positive, are large at the starred positions and small at the unstarred positions. Spin correlation effects are expected to render these small values negative. Because of steric effects the phenyl rings in **5** are unlikely to be strongly conjugated to the chelate ring; the Hückel spin densities given in Table IV for an odd electron in the HFMO $(\ldots\psi_3^1)$ or the LUMO $(\ldots\psi_4^1)$ refer to the isolated chelate ring. The observation $|\Delta f_{\beta\text{-H}}| > |\Delta f_{\alpha\text{-H}}|$ for $Ni[(C_6H_5)_2\text{-HHH}]_2$ is consistent only with the first of these possibilities. Further, transfer of a fraction of β spin from the HFMO to the spin-containing metal orbitals, which is symmetry allowed, will lead to *positive* contact shifts for β-, *o*-, *p*-H, and α-, *m*-CH_3, and *negative* contact shifts for α-, *m*-H and *o*-, *p*-CH_3, as observed. An entirely equivalent pattern of contact shifts has been previously found[4a,f] for the bis(β-ketoamine) complexes **6** (R_α = H, CH_3; R_γ = C_6H_5, CH_3), indicating that the predominant mode of spin delocalization and distribution of spin are closely related in the two groups of complexes.



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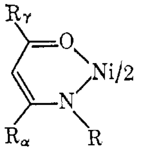

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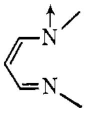
For the purpose of a semiquantitative assessment of the extent of spin delocalization in the β-iminoamine complexes, valence bond (VB) calculations, which include the effects of spin correlation, have been carried out for the chelate ring portion of the ligand. The VB approach has been exceptionally successful in reproducing observed spin densities in the nickel(II) aminotroponeiminates.[34] The ground-state wave function of the neutral radical was taken as a combination of the bond eigenfunctions **7**, **8**, and **9**. By including only contiguous exchange integrals, eigenvectors and eigenvalues were obtained by standard procedures,[38] leading to the spin densities in Table IV. The experimental values for $Ni[(C_6H_5)_2\text{-HHH}]_2$, calculated from the observed contact shifts on the assumption that $Q_{CH} = -23$ G for both α and β positions, are set out in **10** and are to be compared with the values shown in **11**, which are the theoretical spin densities for delocalization of a full spin scaled down by $^1/_{13}$ at each position. The values in **10** and **11** agree to within ~3%; the ratios of the scaled calculated values to those observed are undoubtedly more significant than the values themselves. This remarkable agreement, while certainly fortuitous in part, nonetheless strongly supports the π-delocalization model and provides the best available evidence that the contact shifts of the β-iminoamine complexes are essentially free of pseudo-contact contributions.



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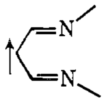

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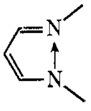

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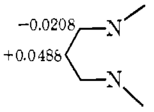

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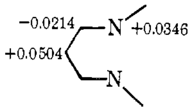

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The complete set of spin densities for all complexes calculated from the contact shifts is given in Table III.

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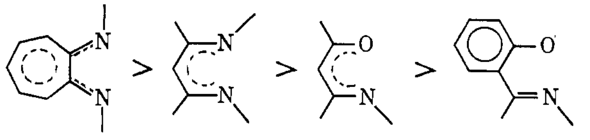
[38] H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, Chapter XIII; L. Pauling, *J. Chem. Phys.*, **1**, 280 (1933).

Values of ρ_β fall in the narrow range 0.0488–0.0507 indicating that practically the same amount of unpaired spin, $\sim^1/_{13}$, is present in all chelate rings regardless of R. Ratios of ρ_m/ρ_p and ρ_o/ρ_p of the N-aryl groups are in fair to excellent agreement with those ratios found in various N,N′-disubstituted and γ-substituted nickel(II) aminotroponeiminates[34,39] where π delocalization has been definitely established.

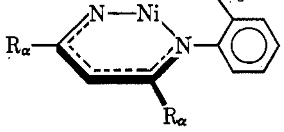
(b) **Relative π-Spin Delocalization in Bis-Chelate Ni(II) Complexes.**—The foregoing considerations show that the nickel(II) β-iminoamines closely resemble the aminotroponeimine,[34,40] salicylaldimine,[35] and β-ketoamine[4a,f] Ni(II) complexes in that the predominant mode of spin delocalization involves fractional β-spin transfer from the HFMO of each ligand to the half-filled d orbitals of Ni(II) which contain α spin. The metal orbitals, which are of the e (D_{2d}) or b (C_2) symmetry types, may be considered as effectively dπ orbitals with respect to the HFMO's of the ligands, although there is of course no symmetry separation of σ and π bonding in these pseudo-tetrahedral complexes. The metal–ligand dπ–pπ interaction in the β-iminoamines results in a total of ~0.15 unit of β spin transferred to the metal leaving $\sim^1/_{13}$ unit of α spin on each ligand.[41]

In order to investigate the relative π-bonding tendencies of the β-iminoamine and β-ketoamine ligand systems, the contact shifts of **6** ($R_\alpha = R_\gamma = CH_3$; R = i-C_3H_7) have been measured over a temperature interval in deuteriochloroform solution. The shifts possess a Curie dependence in the interval +30 to −30°. For this complex $\rho_\beta = +0.0310$ was obtained which, when compared to the value calculated by the VB method (*cf.* Table IV), indicates $\sim^1/_{22}$ of α spin in each chelate ring. Similar comparisons of VB-calculated to observed spin densities have led to estimates of $\sim^1/_{10}$ and $\sim^1/_{30}$ of α spin delocalized in the chelate rings of aminotroponeimine[34] and salicylaldimine[35] complexes, respectively. Hence, these ligands may be ordered with respect to their relative π-bonding tendencies to the same π-acceptor, pseudo-tetrahedral Ni(II), as



The principal conclusion is that an N_4 donor atom set is more effective than an O_2N_2 set in delocalizing π-spin density, as is best illustrated by the β-iminoamine–β-ketoamine comparison. A similar situation has been found in pπ–pπ spin transmission of a related mechanism in the sense that spin density is placed on the heteroatom (O, N) without change in sign. Interposition of NH and O groups between two phenyl rings results in a much more effective spin transfer through NH, as reflected by a comparison of spin densities in the appropriate N,N′-disubstituted aminotroponeiminonickel(II) complexes.[34] Finally, the above order of π-bonding of the ligands L was obtained from measurements of the complexes NiL_2 in their most stable pseudo-tetrahedral forms, which may differ somewhat in geometry, particularly with respect to the dihedral angle between the chelate rings. The comparison therefore may not be normalized to an effectively constant geometry, but could be checked by contact shift measurement of a series of mixed-ligand complexes NiLL′ followed by a comparison of experimental spin densities in L and L′ with those of the unmixed complexes. Previous results show that mixed-ligand complexes of Ni(II) can be prepared in solution and that their spin densities differ from those of the unmixed species.[22,35,40]

(c) **Isomerism in Ni[(o-tol)$_2$-CH_3HCH_3]$_2$.**—The pmr spectrum of this complex, which is shown in Figure 5, is clearly more complicated than those of other complexes because of the occurrence of more than one signal for a given substituent. When the spectrum was recorded under conditions of optimum resolution, three β-H, four α-CH_3, three o-H, four o-CH_3, ten m-H, and five p-H signals were identifiable and are listed in Table III. Because molecular weight measurements indicate that the compound is not associated, the multiplicity of signals must arise from isomers of the monomer. The origin of the isomerism is considered to be due to restricted rotation about the N–C bonds involving the four o-tolyl groups, which presumably adopt an orientation roughly perpendicular to the chelate ring. This arrangement is indicated by **12** and is analogous to a hindered biphenyl. As a result each o-tolyl group becomes part of an asymmetric unit, four of which per molecule generate four diastereoisomers. Three of these are of C_1, idealized C_2, and idealized D_2 symmetry and are enantiomeric; the fourth isomer is optically inactive with idealized C_2 symmetry and is designated as C_2'. For a mixture of all four isomers the maximum number of signals is 9 for α-CH_3, o-CH_3, o-H, p-H, 18 for m-H, and 6 for β-H. The observation of ten m-H signals excludes the two-component mixtures $D_2 + C_2$, $D_2 + C_2'$, and $C_2 + C_2'$, but this and the other observed signal multiplicities cannot specify further the isomeric composition of the mixture. Indeed, the multiplicities can be accounted for by as few as two of the isomers ($C_1 + C_2$) or by all four in the event that some of the chemical shift differences which exist in principle are too small to resolve.



12

The isomeric potentialities of Ni[(o-tol)$_2$-CH_3HCH_3]$_2$ are related to those of other pseudo-tetrahedral Ni(II) complexes with two, three, or four asymmetric centers whose diastereoisomers have been detected by proton

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[39] E. A. LaLancette and D. R. Eaton, *J. Am. Chem. Soc.*, **86**, 5145 (1964).

[40] D. R. Eaton and W. D. Phillips, *J. Chem. Phys.*, **43**, 392 (1965).

[41] It should be noted that $\Sigma_i\rho_{C_i} = 2S$ for the spin densities calculated using the hyperfine coupling constants obtained from eq 1.

resonance.[4f,35,42] Unlike those cases, however, there is no way of deliberately controlling the absolute configuration of the dissymmetric or asymmetric units. Hence the observed signals cannot be assigned to particular diastereoisomers of $Ni[(o\text{-tol})_2\text{-}CH_3HCH_3]_2$. Unfavorable signal overlap has prevented any partial assignment based upon relative intensities of a set of signals of a given isomer. An equivalent case of isomerism has been encountered with bis(N,N′-di-α-naphthylaminotroponeiminato)nickel(II), whose pmr spectrum has been discussed in some detail elsewhere.[31]

Structure of the Ligands.—The free ligand structures in deuteriochloroform solution have been investigated by pmr; chemical shift data are given in Table V.

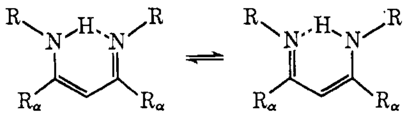
Table V

Proton Chemical Shifts of β-Iminoamines, $H(R_2\text{-}R_\alpha R_\beta R_\alpha)$, in $CDCl_3$ Solution

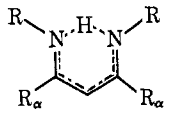
Compound	Chemical shift,[a] ppm α-H, CH_3	β-H	R^b	N-H
$H[(C_6H_5)_2\text{-}HHH]$	7.56	5.02	7.03	11.97
$H(Bz_2\text{-}CH_3HCH_3)$	1.80	4.44	4.34,[c] 7.09[d]	11.50
$H[(C_6H_5)_2\text{-}CH_3HCH_3]$	2.02	4.92	7.08	12.86
$H[(PhPh)_2\text{-}CH_3HCH_3]$	2.07	4.92	7.30	12.43
$H[(p\text{-tol})_2\text{-}CH_3HCH_3]$	1.98	4.87	2.31,[e] 7.00	12.62
$H[(m\text{-tol})_2\text{-}CH_3HCH_3]$	1.95	4.83	2.23,[f] 6.80	12.67
$H[(o\text{-tol})_2\text{-}CH_3HCH_3]$	1.87	4.86	2.18,[g] 6.95	12.43

[a] 34–35°, downfield relative to TMS. [b] Aromatic protons occur as multiplets, the center of which is given. [c] CH_2. [d] Sharp singlet. [e] $p\text{-}CH_3$. [f] $m\text{-}CH_3$. [g] $o\text{-}CH_3$.

The spectra, which are very similar to those of malondialdehyde dianils[15] and $H(Bz_2\text{-}CH_3HCH_3)$[13] in other solvents, establish the structure as a hydrogen-bonded chelate form on the basis of the large low-field shifts of the N-H protons. The diimino tautomeric structure is clearly inconsistent with the 6:1 intensity of methyl to β-H signals in $H(R_2\text{-}CH_3HCH_3)$ and with the AX_2 spectrum of α- and β-H in $H[(C_6H_5)_2\text{-}HHH]$.[15] The chemical shift equivalence of the two R_α groups in all molecules and of the two benzyl groups in $H(Bz_2\text{-}CH_3HCH_3)$ is accommodated either by a rapid tautomeric conversion **13** ⇌ **14** or by a symmetrically hydrogen-bonded structure **15**. These situations are distinguished physically by a double- or single-well potential function for the hydrogen-bonded proton but cannot be differentiated for the cases at hand by pmr. However, entirely equivalent observations have been reported for N,N′-dimethylaminotroponeimine by Brasen, *et al.*,[42] who rationalized their pmr, infrared, and dipole moment results in terms of an aromatic ten-π-electron system corresponding to a structure of effective C_{2v} symmetry similar to **15**. This "nonclassical" aromatic structure is supported by a recent X-ray structural determination[43] of the compound. The "nonclassical" structure **15** was proposed by Dorman[13] for $H(Bz_2\text{-}CH_3HCH_3)$ and, on the basis of structural analogy with the aminotroponeimines, it would appear to be a satisfactory representation of this and other compounds in Table V, which, however, have been referred to throughout this paper as β-iminoamines for the purpose of simple nomenclature.



13 **14**



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