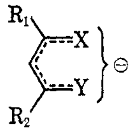
The Relative Stereochemical and Electronic Effects of Oxygen and Sulfur Donor Atoms in Planar and Tetrahedral Complexes of Nickel(II)

D. H. Gerlach[1] and R. H. Holm

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received December 19, 1968*

Abstract: Reactions of primary amines with the 3-phenyl-1,2-dithiolium cation and with O-ethyl-β-ketoamine cations have led to the synthesis of three series of α,β-unsaturated, N-substituted β-aminothiones $R_\gamma C(S)CH{=}C(NHR)R_\alpha$ (H(R–S$R_\gamma HR_\alpha$): $R_\gamma HR_\alpha$ = PhHH, PhHMe, MeHMe). Structures of the compounds of the PhHH series have been established by mass spectroscopy and synthesis; the predominant tautomer of all compounds in chloroform solution has been shown by pmr to be the aminothione form. Bis-chelate nickel(II) and zinc(II) complexes M(R–S$R_\gamma HR_\alpha$)$_2$ can be readily prepared by nonaqueous chelation reactions. Spectral, magnetic, and proton resonance studies reveal that Ni(R–S$R_\gamma HR_\alpha$)$_2$ species in chloroform and carbon tetrachloride solutions are involved in a rapid planar $\rightleftharpoons$ tetrahedral equilibrium presumably identical with that displayed by the precisely analogous bis(β-ketoamine) complexes Ni(R–$R_\gamma HR_\alpha$)$_2$. Thermodynamic data (ΔF, ΔH, ΔS) pertaining to the structural equilibria of eight pairs Ni(R–$R_\gamma HR_\alpha$)$_2$–Ni(R–S$R_\gamma HR_\alpha$)$_2$, the members of which differ only in their donor atom sets, have been obtained from analysis of the temperature dependencies of contact shifts. In all cases it is observed that the planar stereoisomer of Ni(R–S$R_\gamma HR_\alpha$)$_2$ is much more stable than that of Ni(R–$R_\gamma HR_\alpha$)$_2$. The relative equilibrium positions are shown to be controlled mainly by enthalpy effects, which in turn are ascribed to differences primarily in Ni–O and Ni–S bonding in the two stereoisomers. Contact shifts in β-ketoamine and β-aminothione complexes arise from π delocalization in the highest filled MO of the ligands produced by ligand-to-metal antiparallel spin transfer. Experimentally determined spin densities in the mixed ligand complexes Ni(*t*-Bu–PhHH)(*t*-Bu–SPhHH) and Ni(*t*-Bu–SPhHH)(Et$_2$-ati) (Et$_2$-ati = N,N′-diethylaminotroponeiminate) indicate that, with respect to tetrahedral Ni(II) as the common acceptor, the π-donor propensity of a β-aminothione is less than that of the analogous β-ketoamine ligand. Large contact shift differences between active and *meso* diastereoisomers of Ni(R–SPhHH)$_2$, R = *sec*-Bu, MeCHCH$_2$Ph (Amp), are observed, and it is shown for the R = Amp isomers that these differences arise mainly from inequalities in ΔF_{active} and ΔF_{meso}, in agreement with a previous argument.

In the course of attempting to establish the principles which govern the stereochemistry of four-coordinate metal(II) chelate complexes, two experimental approaches have been adopted. These have been designed so as to reveal the differential stabilities of the two limiting stereochemistries, planar and tetrahedral, as separate functions of metal ion and ligand structure in solutions of noncoordinating solvents, where stereochemical populations are not seriously perturbed by effects of the medium. Both approaches have involved use of the β-difunctional ligand system **1**, the basic importance of which, as recently emphasized,[2] is that donor atoms or groups X and Y may be incorporated in various combinations. In the first approach the coordinated metal ion has been varied over the Cr(II)–Zn(II) sequence in several series of complexes having constant ligand structure. The ligands thus far employed have been of the β-ketoamine type (**1**, X = O; Y = NR), and comparative stereochemical determinations and interpretations for Co(II) and Ni(II) complexes have been presented recently.[3,4] Similar information for complexes of other metal ions in the sequence will be forthcoming.[5] The second approach has been concerned with changes in stereochemical populations of complexes of a given metal ion as the ligand structure is systematically varied. In either approach the situation sought is that of a planar $\rightleftharpoons$ tetrahedral equilibrium, whose existence permits a quantitative measurement of the relative stabilities of the two stereochemical forms as a function of ligand structure or metal ion. Because this equilibrium has been established only for Co(II) and Ni(II) complexes at present, all of the quantitative determinations of stereochemical preference have been made on complexes of these metal ions.



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This investigation is concerned with the effect of ligand structural changes on the stereochemical populations of bis-chelate nickel(II) complexes derived from **1**. Previously, it has been demonstrated that the bis(β-ketoamine) complexes **2** (R = alkyl, aryl) are involved in the equilibrium[3,4,6–9]

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

which is displaced to the right as the size of the R group increases. This same effect has been observed in bis-

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[1] Petroleum Research Fund Predoctoral Fellow, 1968–1969.

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[8] S. McKinley and E. P. Dudek, *Inorg. Nucl. Chem. Lett.*, **3**, 561 (1967) (N-substituted 2-acetiminodimedone complexes).

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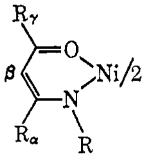
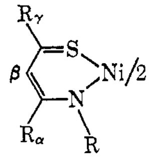
(salicylaldimino)-,[7,10] bis(pyrrole-2-aldimino)-,[11] and bis(aminotroponeimino)nickel(II)[12] complexes, as well as for bis(β-ketoamino)cobalt(II) complexes.[3,4] Of somewhat greater fundamental significance to the question of the factors affecting the relative stabilities of planar and tetrahedral structures of complexes of a given metal ion are the properties of the donor atom sets X_2Y_2. In the most meaningful situation X and Y could be varied without introducing any purely steric consequences on the position of equilibrium 1, thereby revealing their electronic effects on stereochemical populations.



2, $Ni(R\text{-}R_\gamma HR_\alpha)_2$



3, $Ni(R\text{-}SR_\gamma HR_\alpha)_2$

Of the various donor atom sets composed of X, Y = O, NR, and S, investigations of those which reveal the relative stereochemical effects of sulfur *vs.* oxygen are particularly significant for at least two reasons. First, because oxygen and sulfur donors in bis-chelate complexes derived from **1** bear no substituents, replacement of one by the other does not result in any important steric effect on the position of the equilibrium, especially if not more than two such donors are involved, the planar forms are *trans*, and the ligand structures are otherwise identical. These conditions are well satisfied by pairs of bis(β-ketoamine) and bis(β-aminothione) complexes, **2** and **3**, respectively. Second, it is becoming increasingly apparent that replacement of two or more oxygen donors by sulfur, without any other stereochemically significant alterations in ligand composition, has several important structural consequences. One of these is depolymerization. Sterically unencumbered Ni(II) β-diketonates are trimerized in solution[13a] and in the solid state,[13b] but similar $Ni\text{-}O_2S_2$,[14] $Ni\text{-}OS_3$,[14c] and $Ni\text{-}S_4$[14b,c,15,16] complexes are without present exception monomeric and planar in both phases. Likewise, polymeric Co(II) β-diketonates[17] are degraded to simple $Co\text{-}O_2S_2$ and $Co\text{-}S_4$ monomers[5,16] upon such substitution.[18] The second structural consequence appears to be the tendency of sulfur to stabilize preferentially the planar form of monomeric complexes, at least for those of cobalt(II) where the effect is clearly observable.[19] Thus, bis(dipivaloylmethanido)cobalt(II) and (monomeric) bis(acetylacetonato)cobalt(II) are tetrahedral,[17a] whereas bis(dithioacetylacetonato)cobalt(II) is planar.[16]

For the reasons just cited several series of bis(β-aminothiono)nickel(II) complexes **3** have been prepared; complexes of this type are largely unexplored, only a few nickel(II) complexes having been reported[21] prior to this work. It has been demonstrated that a number of these complexes are involved in the same structural equilibrium 1 as are their exactly analogous oxygen-containing counterparts **2**.[3,4,6,7] Complexes of types **2** and **3** exhibit proton contact shifts due to the existence of the paramagnetic tetrahedral forms, and accurate thermodynamic data for pairs of $Ni\text{-}O_2(NR)_2$ and $Ni\text{-}S_2(NR)_2$ complexes have been obtained from analysis of the temperature dependencies of these shifts. In this way the relative stereochemical effects of sulfur *vs.* oxygen on the position of equilibrium 1 have been determined. In addition, general synthetic procedures for β-aminothiones and their nickel(II) complexes are described together with information concerning the relative ligand field strengths and spin delocalization properties of β-ketoamine and β-aminothione ligand systems. Certain preliminary results and conclusions from this investigation, which is described in full here, have been presented previously.[22]

Throughout this report complexes **2** and **3** are designated as indicated above employing abbreviated notations consistent with prior usage.[2-4,6,7,22] Free ligands are represented as $H(R\text{-}R_\gamma HR_\alpha)$ (β-ketoamines) and $H(R\text{-}SR_\gamma HR_\alpha)$ (β-aminothiones). For R = $MeCHCH_2Ph$ the designation Amp (from amphetamine) is employed.

Experimental Section

Preparation of α,β-Unsaturated β-Aminothiones. These compounds may be prepared by nucleophilic reactions of primary amines with 1,2-dithiolium salts[21,23-27] or of hydrosulfide ion with O-alkylated β-ketoamine salts. The first method has been used to prepare 1-phenyl-3-amino-2-propene-1-thiones (PhHH series). The second method has been applied to the synthesis of 1-phenyl-3-amino-2-butene-1-thiones and 4-amino-3-pentene-2-thiones (PhHMe and MeHMe series, respectively). It is a modification of McGeachin's preparation of α,β-unsaturated β-iminoamines[28] and is generally a more convenient method for compounds of these series because of the ready accessibility of β-ketoamines and their ease of alkylation.

1-Phenyl-3-anilino-2-propene-1-thione was prepared according to Leaver, *et al.*[24] None of the other β-aminothiones prepared has been reported previously. General procedures for the two synthetic methods follow.

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

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(14) *Cf.* literature citations in ref 2, footnote 3, and: (a) J. Sieler, Ph. Thomas, and E. Uhlemann, *Z. Chem.*, **7**, 243 (1967); (b) E. Uhlemann and Ph. Thomas, *ibid.*, **7**, 430 (1967); (c) A. Ouchi, M. Hyodo, and Y. Takahashi, *Bull. Chem. Soc. Japan*, **40**, 2819 (1967); (d) R. K. Y. Ho, S. E. Livingstone, and T. N. Lockyer, *Aust. J. Chem.*, **21**, 103 (1968); R. K. Y. Ho and S. E. Livingstone, *ibid.*, **21**, 1781 (1968); S. L. Perry, R. S. Quinn, and E. P. Dudek, *Inorg. Chem.*, **7**, 814 (1968).

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(17) (a) Solution: F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964); (b) solid state: F. A. Cotton and R. C. Elder, *ibid.*, **4**, 1145 (1965).

(18) Note also that the order of polymerization of $Co(XYPEt_2)_2$ complexes in solution is X = Y = O > X = O, Y = S > X = Y = S: W. Kunchen and H. Hertel, *Chem. Ber.*, **101**, 1991 (1968).

(19) No stereochemical effects due to sulfur–oxygen replacement are observable for monomeric bis-chelate nickel(II) complexes derived from **1**. All such $Ni\text{-}S_4$,[14b,c,15,16] $Ni\text{-}OS_3$,[14c] $Ni\text{-}O_2S_2$,[14] and $Ni\text{-}O_4$[13a,20] complexes are diamagnetic and planar.

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Table I. Characterization of β-Aminothiones, $R_\gamma CSCHC(NHR)R_\alpha$ (**4**, **7**)

R	R_γ	R_α	Mp, °C	Calcd, %				Found, %			
				C	H	N	S	C	H	N	S
i-Pr	Ph	H	64–65	70.20	7.36	6.82	15.62	69.85	7.15	6.94	15.55
i-Bu	Ph	H	61–63	71.18	7.81	6.39	14.62	71.08	7.63	6.26	14.68
sec-Bu	Ph	H	39–39.5	71.18	7.81	6.39	14.62	71.40	7.74	6.67	14.37
t-Bu	Ph	H	54–56	71.18	7.81	6.39	14.62	71.33	7.76	6.10	14.48
$CHEt_2$	Ph	H	44–45	72.36	7.81	6.03	13.80	72.38	7.96	5.89	13.72
CH_2Ph	Ph	H	84–85	75.85	5.97	5.53	12.65	75.97	6.00	5.37	12.45
MeCHPh	Ph	H	48–49	76.36	6.41	5.24	11.99	76.13	6.26	5.37	12.18
$MeCHCH_2Ph$	Ph	H	68–69	76.82	6.81	4.98	11.39	77.18	7.04	5.58	11.33
i-Pr	Ph	Me	81–82	71.18	7.81	6.39	14.62	71.18	7.80	6.22	14.67
Me	Me	Me	89–90	55.76	8.58	10.83	. .	55.64	8.25	10.83	. . .

(a) N-Substituted 1-Phenyl-3-amino-2-propene-1-thiones. 3-Phenyl-1,2-dithiolium perchlorate[29] (10 g) was suspended in 200 ml of *n*-heptane and treated with a twofold molar excess of primary amine. The mixture was stirred at room temperature for 15 min, warmed to 40–50°, and filtered. Reduction of the filtrate volume by *ca.* one-third followed by cooling afforded the aminothiones as orange crystalline products. Final purification was achieved by recrystallization from *n*-heptane. The use of ethanol as the solvent, as in the preparation of several anilinothiones,[24] led to yields of only 5–30%, whereas the yields obtained from reactions in *n*-heptane were essentially quantitative.

(b) N-Substituted 1-Phenyl-3-amino-2-butene-1-thiones and 4-Amino-3-pentene-2-thiones. To a stirred solution of 0.053 mole of the β-ketoamine in 100 ml of dichloromethane, 10 g (0.053 mole) of triethyloxonium tetrafluoroborate in 50 ml of dichloromethane was added dropwise. The solution was stirred for 20 min at room temperature, and then a solution of sodium hydrosulfide (0.053 mole) in absolute ethanol was added. The reaction mixture was stirred for an additional 15 min and filtered, and the solvent removed *in vacuo*. The crude aminothiones were purified by vacuum distillation or recrystallization from *n*-heptane. Yields of purified products range from 30 to 60%.

Characterization data are presented in Table I. Compounds not subjected to elemental analyses and used in preparation of complexes (*vide infra*) were identified by their pmr spectra. Chemical shift data for some representative compounds are listed in Table III.

Preparation of Complexes. (a) Bis(β-ketoamino)nickel(II) Complexes. Certain of the complexes utilized in this work have been reported elsewhere.[3,4,6,7] The new complexes were prepared by a nonaqueous chelation reaction in *t*-butyl alcohol which has been described in detail previously.[6,30] *n*-Heptane or a toluene–*n*-heptane mixture was used to extract the products from the reaction mixtures and for recrystallization.

Bis(1-phenyl-3-isobutylamino-2-propen-1-ono)nickel(II), Ni(*i*-Bu–PhHH)$_2$, dark green needles, mp 119–121°. *Anal.* Calcd for $C_{26}H_{32}N_2O_2Ni$: C, 67.41; H, 6.96; N, 6.05. Found: C, 67.90; H, 6.89; N, 6.04.

Bis(1-phenyl-3-(3-pentylamino)-2-propen-1-ono)nickel(II), Ni(3-Et$_2$CH–PhHH)$_2$, golden brown microcrystals, mp 101–102°. *Anal.* Calcd for $C_{28}H_{36}N_2O_2Ni$: C, 68.45; H, 7.39; N, 5.70. Found: C, 68.98; H, 7.37; N, 5.64.

Bis(1-phenyl-3-anilino-2-propen-1-ono)nickel(II), Ni(Ph–PhHH)$_2$, green crystals, mp 211–212°. *Anal.* Calcd for $C_{32}H_{24}N_2O_2Ni$: C, 71.60; H, 4.81; N, 5.57. Found: C, 71.83; H, 4.70; N, 5.63.

(b) Bis(β-ketoamino)zinc(II) Complexes. Certain of these complexes were required as diamagnetic reference standards for the analogous nickel(II) complexes exhibiting small proton contact shifts. In general they are much less readily prepared than their nickel(II) and cobalt(II) analogs and could not be obtained by the nonaqueous chelation method in *t*-butyl alcohol. The synthetic procedure employed, which was not uniformly successful, is a modification of the nonaqueous chelation method originally reported by McClellan and Benson[31] and used recently in the preparation of bis(β-iminoamino)nickel(II) complexes.[2] Because of the considerable hydrolytic sensitivity of some of the complexes, all operations were carried out in a closed system under dry nitrogen. A solution of 0.050 mole of the β-ketoamine in 150 ml of tetrahydrofuran (distilled under nitrogen from lithium aluminum hydride) was treated dropwise with an equimolar amount of 1.6 *M* *n*-butyllithium solution in *n*-hexane. During the addition the solution was maintained at −20°. Ten minutes after the completion of the addition, 0.030 mole of tetramethylammonium tetrachlorozincate(II) was introduced and the reaction mixture stirred for 48–72 hr at room temperature. (This reaction period was required to avoid contamination of the product with free ligand or its lithium salt.) The solvent was removed under reduced pressure and the residue extracted with boiling *n*-heptane or an *n*-heptane–toluene mixture. The solid obtained upon cooling the extract solution was collected and recrystallized from the same solvent or solvent mixture. The complexes were isolated as light yellow crystalline solids.

Bis(1-phenyl-3-isopropylamino-2-buten-1-ono)zinc(II), Zn(*i*-Pr–PhHMe)$_2$, mp 192–195°. *Anal.* Calcd for $C_{26}H_{32}N_2O_2Zn$: C, 66.45; H, 6.86; N, 5.96. Found: C, 66.23; H, 6.75; N, 6.17.

Bis(4-methylamino-3-penten-2-ono)zinc(II), Zn(Me–MeHMe)$_2$, mp 164–166°. *Anal.* Calcd for $C_{12}H_{20}N_2O_2Zn$: C, 49.75; H, 6.96; N, 9.67. Found: C, 50.11; H, 7.38; N, 9.72.

The above method failed when applied to the synthesis of zinc(II) complexes of the PhHH series. Products isolated from the reaction mixtures were free ligands or their lithio derivatives, which are somewhat soluble in nonpolar solvents. One such lithio compound was characterized; pmr data are given in Table III.

1-Phenyl-3-N-isobutyl-N-lithioamino-2-propen-1-one, white crystals, mp 194–195°. *Anal.* Calcd for $C_{13}H_{16}LiNO$: C, 74.63; H, 7.70; N, 6.70. Found: C, 74.43; H, 7.78; N, 6.59.

(c) Bis(β-aminothione)nickel(II) Complexes. These compounds were prepared by the nonaqueous chelation procedure in *t*-butyl alcohol.[6,30] Extraction of the products from the residues obtained upon removal of *t*-butyl alcohol was effected by boiling *n*-heptane or an *n*-heptane–toluene mixture, and the products were recrystallized from the same solvent. The pure complexes were isolated as brown or green-brown crystalline solids. The active forms of Ni(*sec*-Bu–SPhHH)$_2$ and Ni(Amp–SPhHH)$_2$ were prepared from amines having the following rotations:[7] *sec*-butylamine, $[\alpha]^{25}D$ +7.40° (neat); amphetamine, $[\alpha]^{24}D$ +34.5° (neat). Characterization data are set out in Table II.

(d) Bis(β-aminothiono)zinc(II) Complexes. Preparations were accomplished by the method described above for the β-ketoamine complexes. These compounds are more readily formed and are less hydrolytically unstable than their β-ketoamine analogs. They were isolated in pure form as yellow crystalline solids.

Bis(1-phenyl-3-isobutylamino-2-propene-1-thiono)zinc(II), Zn(*i*-Bu–SPhHH)$_2$, mp 131–133°. *Anal.* Calcd for $C_{20}H_{32}N_2S_2Zn$: C, 62.20; H, 6.43; N, 5.58. Found: C, 62.41; H, 6.63; N, 5.58.

Bis(1-phenyl-3-*n*-propylamino-2-butene-1-thiono)zinc(II), Zn(*n*-Pr–SPhHMe)$_2$, mp 177–179°. *Anal.* Calcd for $C_{26}H_{32}N_2S_2Zn$: C, 62.20; H, 6.43; N, 5.58. Found: C, 61.91; H, 6.25; N, 5.39.

Bis(4-methylamino-3-pentene-2-thiono)zinc(II), Zn(Me–SMeH-Me)$_2$, mp 210–212°. *Anal.* Calcd for $C_{12}H_{20}N_2S_2Zn$: C, 44.79; H, 6.26; N, 8.71; S, 19.93. Found: C, 44.88; H, 6.26; N, 8.82; S, 19.91.

(e) Bis(N,N′-diethylaminotroponeimino)nickel(II). The complex was prepared according to a published method.[32]

Molecular Weight Determinations.[33] The molecular weights of two representative bis(β-aminothiono)nickel(II) complexes were

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Table II. Characterization of Bis(β-aminothiono)nickel(II)Complexes, Ni(R–SR$_\gamma$HR$_\alpha$)$_2$ (3)

R	R$_\gamma$	R$_\alpha$	Mp, °C	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % S	Found, % C	Found, % H	Found, % N	Found, % S
i-Pr	Ph	H	265–267	61.94	5.63	6.02	13.78	61.68	5.87	6.16	13.73
i-Bu	Ph	H	179–181	63.04	6.51	5.65	12.94	63.22	6.47	5.68	12.67
sec-Bu[a]	Ph	H	174–176	63.04	6.51	5.65	12.94	63.05	6.73	5.76	12.93
t-Bu	Ph	H	160–161	63.04	6.51	5.65	12.94	63.15	6.57	5.60	12.61
CHEt$_2$	Ph	H	111–113	64.25	6.93	5.35	12.25	64.30	6.97	5.39	12.19
MeCHCH$_2$Ph[a,c]	Ph	H	165–167[b]	69.79	5.86	4.52	10.35	69.83	6.03	4.49	10.04
Ph	Ph	H	211–215 dec	67.21	4.52	5.23	11.98	67.21	4.56	5.04	11.49
n-Pr	Ph	Me	236–238	63.04	6.51	5.65	12.94	62.81	6.53	5.59	12.86
i-Pr	Ph	Me	186–189	63.04	6.51	5.65	12.94	63.18	6.32	5.66	12.86
Me	Me	Me	201–202	46.73	6.40	8.89	20.35	46.71	6.24	8.73	19.90
i-Pr	Me	Me	199–200	51.76	7.60	7.55	17.27	51.72	7.50	7.56	17.25

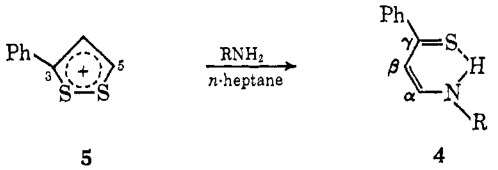
[a] Data refer to mixture of diastereoisomers. [b] Active isomer 167–168°. [c] Active (+,+) isomer, $[\alpha]^{27}{}_{\mathrm{D}}$ −233°, $[\alpha]^{27}{}_{578}$ −318°, $[\alpha]^{27}{}_{546}$ −1252° (*c* 0.0942, CHCl$_3$).

determined in dry toluene solutions at 37° using a Mechrolab osmometer: Ni(*sec*-Bu–SPhHH)$_2$, calcd mol wt 495, found 487 (av), 0.031–0.136 *m*; Ni(*t*-Bu–SPhHH)$_2$, calcd mol wt 495; found 501 (av), 0.025–0.083 *m*.

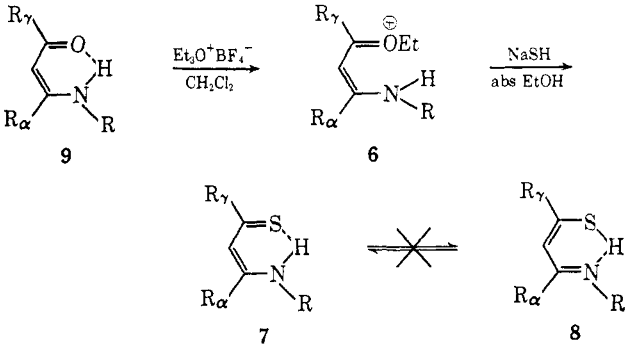
Physical Measurements. Because of the sensitivity of most of the complexes to traces of water, all measurements were carried out in rigorously dry solvents and wherever possible under a dry nitrogen atmosphere or *in vacuo*. Magnetic moments in solution were measured by an nmr method[34] using TMS signals of solvent and solution, or by the Gouy method using freshly distilled, boiled water as the calibrant. Moments of solids were obtained by the Gouy method using an aqueous nickel chloride solution as the calibrant. Electronic spectra were recorded on a Model 14 Cary spectrophotometer. Mass spectra were determined using a Hitachi Perkin-Elmer RMU-6D spectrometer operating at 70 eV. Proton resonance spectra were obtained with a Varian HA-60 or HA-100 spectrometer equipped with a variable-temperature probe accessory. Chemical shifts were measured relative to TMS as an internal standard by the usual side-band technique.

Results and Discussion

Ligand Synthesis and Structures. In order to investigate the relative stereochemical populations of pairs of complexes 2–3, it was first necessary to prepare a series of β-aminothiones strictly analogous to the β-ketoamines whose nickel(II) complexes have been previously studied in detail.[3,4,6,7] Three series of complexes, classified in terms of their ring substituents R$_\gamma$HR$_\alpha$ as the PhHH, PhHMe, and MeHMe series, have been examined. β-Aminothiones **4** of the PhHH type were prepared in high yield by reaction of the appropriate primary amine with the 3-phenyl-1,2-dithiolium cation (**5**) in an *n*-heptane slurry. Compounds of the other two series were obtained in 30–60% yield by treatment of dichloromethane solutions of O-ethyl-β-ketoamine cations **6** as their tetrafluoroborate salts with an ethanolic solution of sodium hydrosulfide. Both reactions presumably proceed by nucleophilic attack on the cations, and analogous reactions of amines with a variety of dithiolium ions have been reported.[21,23–27,35] Ions of type **6** have been previously employed in the synthesis of β-iminoamines[28] where primary amines serve as the nucleophile. Displacement of an ethoxyl grouping by hydrosulfide has also been utilized in the recent synthesis of dithiotropolone from the 1,2-diethoxytropylium ion.[36]



5 **4**



9 **6** **7** **8**

Two structural features of the products of the reactions of **5** and **6** with amines have been established. First, it has been shown by pmr that the predominant, if not exclusive, tautomeric structure in chloroform solution is that of α,β-unsaturated β-aminothiones **4** and **7** rather than that of a β-iminothiol **8**. Taking the compounds H(PhCH$_2$–PhHH) and H(PhCH$_2$–SPhHH)$_2$ as examples, both show a 7-cps splitting of the benzyl methylene signals (*cf*. Table III). A large number of condensation products of β-diketones with primary amines have conclusively been shown to possess the β-ketoamine structure **9** by a variety of physical methods including nmr.[37]

Similar splittings are observed in the spectra of β-ketoamines such as H(PhCH$_2$–MeHMe)[37b] and H-(PhCH$_2$–MeHH)[37c] and have been demonstrated to arise from H–N–CH$_2$ spin coupling. The N-methyl signals of H(Me–MeHMe) and H(Me–SMeHMe) are 5-cps doublets. Accordingly, all compounds of the PhHH, PhHMe, and MeHMe series are assigned the β-aminothione structure in chloroform solution. Similar conclusions based on synthetic and ultraviolet spectral data have been drawn for compounds of the PhHPh types.[24] Second, it has been demonstrated by mass spectroscopy and synthesis that in the preparation of β-aminothiones from **5** nucleophilic attack occurs

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[34] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

[35] For a discussion of the reactions of 1,2-dithiolium ions with nucleophilic reagents, *cf*. H. Prinzbach and E. Futterer, *Advan. Heterocyclic Chem.*, 7, 39 (1967).

[36] C. E. Forbes and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 6884 (1968).

[37] (a) G. O. Dudek and E. P. Dudek, *ibid.*, **86**, 4283 (1964); **88**, 2407 (1966); (b) G. O. Dudek and R. H. Holm, *ibid.*, **84**, 2691 (1962); (c) G. O. Dudek and G. Volpp, *ibid.*, **85**, 2697 (1963); (d) see also E. P. Dudek and G. O. Dudek, *J. Org. Chem.*, **32**, 823 (1967).

Table III. Chemical Shifts of Free Ligands and Zinc(II) Complexes at 100 MHz

Compound	Chemical shifts,[a] cps: R_α	β-H	R_γ[b]	R
$H(PhCH_2$–PhHH)[e]	−688 (2d, 7, 12)	−570 (d, 7)	−750	−430[c] (d, 6), −720[d]
$H(PhCH_2$–SPhHH)[f]	∼−750[g]	−650 (d, 7)	−750	−480[c] (d, 6), −733[d]
Li(*i*-Bu–PhHH)	−737 (d, 5)	−549 (d, 5)	−750	. . .
H(*i*-Bu–PhHH)	−681 (2d, 7, 12)	−563 (d, 7)	−750	. . .
Zn(*i*-Bu–SPhHH)$_2$	−725	−630 (d, 6)	−750	. . .
H(*i*-Bu–SPhHH)	∼−750[g]	−644 (d, 7)	−750	. . .
Zn(*i*-Pr–PhHMe)$_2$	−212	−550	−760	. . .
H(*i*-Pr–PhHMe)	−203	−560	−760	. . .
Zn(*n*-Pr–SPhHMe)$_2$	−215	−635	−750	. . .
H(*n*-Pr–SPhHMe)	−207	−650	−750	. . .
Zn(Me–MeHMe)$_2$	−191	−480	−191	−301
H(Me–MeHMe)[h]	−187	−496	−193	−289 (d, 5)
Zn(Me–SMeHMe)$_2$	−202	−604	−229	−311
H(Me–SMeHMe)[i]	−207	−613	−250	−306 (d, 5)

[a] $CDCl_3$ solution, TMS reference, 0.1–0.2 *M*, 30°; d, doublet; coupling constants given in parentheses. [b] Approximate center of multiplet structures given for Ph. [c] CH_2. [d] Ph. [e] NH −1130 cps. [f] NH −1408 cps. [g] Partially obscured by Ph signal. [h] NH −1060 cps. [i] NH −1390 cps.

Table IV. Electronic Spectral Data[a]

Complex	Soln structure[b]	λ_{max}, cm^{-1}	ε,[c] l. $mole^{-1}$ cm^{-1}
Ni(*t*-Bu–PhHH)$_2$	T	16,800; 14,700 (sh); 10,700; 8330 (sh); 5920	50, 18, <1, 17, 22
Ni(*t*-Bu–SPhHH)$_2$	T	8000 (sh); 7770, 6900	33, 56, 53
Ni(*i*-Bu–PhHH)$_2$	P	16,000	93
Ni(*i*-Bu–SPhHH)$_2$	P	13,330 (sh)	160
Ni(*i*-Pr–PhHMe)$_2$[d]	T	16,800; 14,500; 10,900; 6060	20, 10, <1, 20
Ni(*i*-Pr–SPhHMe)$_2$	T–P	15,400 (sh); 8800 (sh), 7840, 7140	320, 19, 22, 22
Ni(Me–PhHMe)$_2$	P	16,500	117
Ni(Me–SPhHMe)$_2$	P	15,600 (sh)	170
Ni(*i*-Pr–MeHMe)$_2$[e]	T	19,200; 16,800; 14,800; 11,000; 6060	14, 20, 11, <1, 19
Ni(*i*-Pr–SMeHMe)$_2$	T–P	8510 (sh), 7480, 7020	14, 18, 17
Ni(Me–MeHMe)$_2$[e]	P	20,200; 17,100	60, 50
Ni(Me–SMeHMe)$_2$	P	15,630	144

[a] Chloroform solution unless otherwise indicated. [b] Predominant isomer, T tetrahedral, P planar, T–P mixture; see data in Table V. [c] Apparent values, uncorrected for underlying absorption. [d] CS_2 solution, data from ref 6. [e] CCl_4 solution, data from ref 6.

at C-5 rather than C-3. The mass spectra of four compounds of the PhHH series (R = *i*-Pr, *sec*-Bu, *t*-Bu, Amp) reveal prominent peaks at *m/e* 121 which are assigned to $PhCS^+$. In this regard the spectra are similar to those of 3-mercapto-1-phenyl-2-butene-1-one[38a] and N,N′-bis[3-(1-phenyl-2-buten-1-one)]ethylenediamine,[38b] whose structures have been substantiated by observation of $PhCO^+$ fragments. Reaction of 3-pentylamine with **5** or of sodium hydrosulfide with **6** (R = $CHEt_2$) leads to products shown to be identical by their pmr spectra. These results establish structure **4** for the β-aminothiones prepared from the 3-phenyl-1,2-dithiolium ion.

Stereochemistry in Solution. Identification of the structures of bis(β-aminothiono)- and several previously unreported bis(β-ketoamino)nickel(II) complexes together with demonstration of equilibrium 1 for both in chloroform solution may be made from the magnetic and representative spectral data presented in Tables IV and V. The arguments used are entirely analogous to those employed in interpreting the solution stereochemistry of β-ketoamine[6,7] and salicylaldimine[7,10] complexes. Of all the β-aminothione complexes only Ni(*t*-Bu–SPhHH)$_2$ possesses magnetic moments in the crystalline and the solution phase, where it is monomeric, which are the same within experimental error. This being the criterion for dissolution without structural change, the complex is considered to be wholly tetrahedral in solution, and in this respect is identical with Ni(*t*-Bu–PhHH)$_2$.[7] The absorption spectrum of Ni(*t*-Bu–SPhHH)$_2$, shown in Figure 1, is rather similar to its oxygen analog and displays the near-infrared features diagnostic of tetrahedral bis-chelate Ni(II) complexes.[2,6,7,10,11] The remaining β-aminothione complexes, all of which have

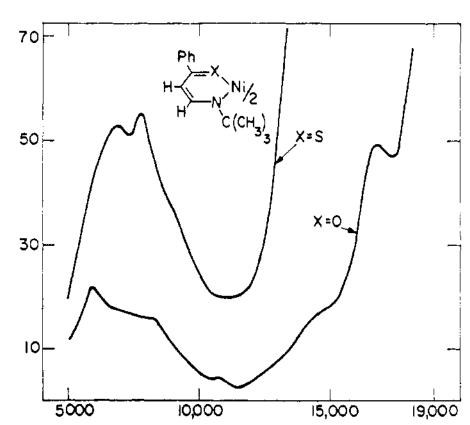

Figure 1. Electronic absorption spectra of Ni(*t*-Bu–PhHH)$_2$ and Ni(*t*-Bu–SPhHH)$_2$ in chloroform solution at 25°.

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(38) (a) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Aust. J. Chem.*, **18**, 673 (1965); (b) S. H. H. Chaston, S. E. Livingstone, T. N, Lockyer, and J. S. Shannon, *ibid.*, **18**, 1539 (1965).

Table V. Magnetic Moments in Solid and Solution Phases

		Solution			
Complex	Solid μ_{eff}, BM[a]	Solvent	Temp, °C	Concn, m*m*	μ_{eff}, BM[a]
Ni(*t*-Bu–PhHH)$_2$[b]	3.27	$CHCl_3$	25	53.3	3.25
		CCl_4	24	21.3	3.26
Ni(*t*-Bu–SPhHH)$_2$	3.20	$CHCl_3$	24	34.2	3.18
		CCl_4–TMS	30	39.7	3.17
Ni(*sec*-Bu–PhHH)$_2$[b,e]	2.38	$CHCl_3$	27	49.5	2.97
Ni(*sec*-Bu–SPhHH)$_2$[e]	3.13	$CHCl_3$–TMS	30	63.8	1.70
Ni(Amp–PhHH)$_2$[b,c]	Dia	$CHCl_3$	26	37.0	3.03
Ni(Amp–SPhHH)$_2$[e]	*j*	$CHCl_3$–TMS	31	37.7	2.06
		CCl_4–TMS	30	15.2	2.40
Ni((+)-Amp–SPhHH)$_2$	*j*	CCl_4–TMS	30	17.2	2.08
		$CHCl_3$–TMS	30	44.0	1.89
Ni(Et_2CH–PhHH)$_2$	3.22	$CHCl_3$	23	46.8	3.02
Ni(Et_2CH–SPhHH)$_2$	Dia	$CHCl_3$–TMS	23	69.1	1.41
Ni(*i*-Pr–PhHH)$_2$[c]	*g*	$CHCl_3$	*f*	. . .	3.05
Ni(*i*-Pr–SPhHH)$_2$	3.26				*h*
Ni(*n*-Pr–PhHMe)$_2$[d]	Dia	$CHCl_3$	*f*	. . .	1.58
Ni(*n*-Pr–SPhHMe)$_2$	Dia				*i*
Ni(*i*-Pr–PhHMe)$_2$[d]	3.35	CS_2	*f*	. . .	3.33
Ni(*i*-Pr–SPhHMe)$_2$	Dia	$CHCl_3$–TMS	33	40.7	2.18
Ni(*i*-Pr–MeHMe)$_2$[d]	3.37	CCl_4	*f*	. . .	3.36
Ni(*i*-Pr–SMeHMe)$_2$	Dia	$CHCl_3$–TMS	30	69.3	2.35

[a] Calculated from the Curie law, $\mu_{eff} = 2.83(\chi_{cor}{}^{M}T)^{1/2}$. [b] Data from ref 7. [c] Data from ref 4. [d] Data from ref 6. [e] Data refer to mixture of diastereoisomers. [f] 20–26°. [g] Isolated in diamagnetic and paramagnetic forms.[4] [h] Insufficiently soluble for measurement. [i] Insufficiently paramagnetic for measurement. [j] Not measured.

smaller R groups, possess solution moments considerably less than 3.2 BM where measurable. This behavior, together with the proven monomerism of a typical complex, Ni(*sec*-Bu–SPhHH)$_2$, and the marked decrease in intensity of the bands in the 6000–11,000-cm^{-1} region, is consistent only with the existence of both planar and tetrahedral forms. The magnetic data collected in Table V for a series of pairs **2**–**3** reveal that the effect of sulfur compared to oxygen donors is to decrease the mole fraction of tetrahedral species where comparisons can be made from solution moments. A more extensive and quantitative evaluation of stereochemical populations for the pairs **2**–**3** is presented in a following section.

Ligand Field Spectra. Comparison of spectra of the closely related pairs of complexes **2**–**3** offers an opportunity to assess the relative ligand field strengths of oxygen and sulfur in planar and tetrahedral complexes. This is a matter of some interest because of the paucity of such comparisons and the marked variability in the position of sulfur in the octahedral spectrochemical series, which cannot usually be transferred to planar complexes.[39] For the tetrahedral species Ni(*t*-Bu–PhHH)$_2$ and Ni(*t*-Bu–SPhHH)$_2$ the spectra (Figure 1) are unfortunately too complex to permit certain assignment of ν_2 ($^3T_1 \rightarrow {}^3A_2$ in tetrahedral symmetry) from which the tetrahedral ligand field splitting parameter Δ_t can be immediately derived. While we have in the past favored assignment of ν_2 to the most intense feature in the 5000–10,000-cm^{-1} region,[6,10] it has also been pointed out[6] that this assignment is uncertain due to the appearance of a shoulder or separate peak on the high-energy side of this feature. These bands, which are quite prominent in the spectra shown in Figure 1, obviously cannot arise from low-symmetry splitting of ν_2 and the proposal[40] that they are components of the tetrahedral ν_1 absorption ($^3T_1 \rightarrow {}^3T_2(F)$) cannot be discounted. However, for planar nickel(II) complexes derived from **1**, the data from this and other investigations, taken where possible for complexes with $R_1 = R_2 =$ Me, permit the formulation of a spectrochemical series based on the positions of the lowest energy spin-allowed absorptions. Provided these absorptions arise from a common transition, which is most likely $\ldots (d_{x^2-y^2})^2 \rightarrow (d_{x^2-y^2})^1, (d_{xy})^1$, the series is the following: $(NH)_4$[28] ~ O_4[13a] > $O_2(NR)_2$ (R = Me, H[41a]) > $S_2(NMe)_2$ ~ S_2O_2[14c] > S_4.[14c] This series clearly reveals the low ligand field position of planar, sulfur-containing Ni(II) chromophores and, on the basis of recent data summarized by Furlani and Luciani,[41b] may be extended so as to include other Ni–S_4 complexes.

Analysis of Contact Shift Data. The contact shift of the *i*th nucleus in complexes such as **2** and **3**, which are rapidly interconverting between the planar and tetrahedral configurations, is given by

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

in which Δf_i is the contact shift, a_i the electron-nuclear hyperfine coupling constant in gauss, and g the g value of the paramagnetic form. $\Delta F = -RT \ln K_{eq}$ and $K_{eq} = N_t/N_p$, with N_t the mole fraction of the tetrahedral and N_p the mole fraction of the planar stereoisomer. The remaining symbols have their usual significance.[6] The tetrahedral mole fraction is expressible as

$$N_t = [\exp(\Delta F/RT) + 1]^{-1} = \frac{\mu_{obsd}{}^2}{\mu_t{}^2} \quad (3)$$

in which μ_{obsd} is the measured magnetic moment of the equilibrium mixture and μ_t the moment of the tetrahedral isomer. Representative pmr spectra for several

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(39) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

(40) D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, **4**, 139 (1965).

(41) (a) R. D. Archer, *ibid.*, **2**, 292 (1963); (b) C. Furlani and M. Luciani, *ibid.*, **7**, 1586 (1968).

Table VI. Contact Shifts, Coupling Constants, and Thermodynamic Data

Complex	Solvent	Δf_i,[a] cps		a_i,[b] G	Temp,[c] °K	ΔH, cal/mole	ΔS, eu	$\Delta F^{323°}$, cal/mole	$N_t^{323°}$
		α	β						
Ni(*t*-Bu–PhHH)$_2$	CDCl$_3$	−33,910	+9,713	−0.863	. . .	. . .	. . .	. . .	1.0
	CCl$_4$	*d*	+9,963	−0.884	. . .	. . .	. . .	. . .	1.0
Ni(*t*-Bu–SPhHH)$_2$	CDCl$_3$	−28,373	+7,655	−0.683	. . .	. . .	. . .	. . .	1.0
	CCl$_4$	−28,768	+7,907	−0.717	. . .	. . .	. . .	. . .	1.0
Ni(*sec*-Bu–PhHH)$_2$ active	CDCl$_3$[e]	*d*	+8,563	−0.917	230–355	103	3.51	−1030	0.83
	CCl$_4$	*d*	+8,135	−0.884	250–350	892	5.98	−1040	0.83
Ni(*sec*-Bu–SPhHH)$_2$ active	CDCl$_3$	−9,520	+2,193	−0.683	260–370	4000	11.5	+287	0.39
	CCl$_4$	*d*	+2,567	−0.717	260–330	3490	10.1	+221	0.41
Ni(*sec*-Bu–PhHH)$_2$ *meso*	CDCl$_3$[e]	*d*	+8,446	−0.917	230–355	312	4.04	−992	0.82
	CCl$_4$	*d*	+7,918	−0.884	250–355	1230	6.82	−969	0.82
Ni(*sec*-Bu–SPhHH)$_2$ *meso*	CDCl$_3$	−13,930	+3,160	−0.683	240–370	3560	11.2	−50	0.52
	CCl$_4$	*d*	+3,584	−0.717	260–330	3120	9.98	−106	0.54
Ni(Amp–PhHH)$_2$ active	CDCl$_3$[e]	*d*	+9,206	−0.937	300–360	−953	0.67	−1170	0.86
	CCl$_4$	*d*	+8,802	−0.884	250–360	−320	3.06	−1310	0.88
Ni(Amp–SPhHH)$_2$ active	CDCl$_3$	*d*	+2,967	−0.683	240–370	4110	12.7	+13	0.49
	CCl$_4$	*d*	+3,517	−0.717	250–360	3570	11.4	−98	0.54
Ni(Amp–PhHH)$_2$ *meso*	CDCl$_3$[e]	*d*	+8,896	−0.937	300–360	−491	1.74	−1050	0.84
	CCl$_4$	*d*	+8,402	−0.884	250–360	399	4.70	−1120	0.85
Ni(Amp–SPhHH)$_2$ *meso*	CDCl$_3$	*d*	+5,234	−0.683	240–370	3470	13.2	−791	0.77
	CCl$_4$	*d*	+5,601	−0.717	250–360	2900	11.4	−784	0.77
Ni(Et$_2$CH–PhHH)$_2$	CDCl$_3$	*d*	+8,577	−0.888	230–370	55	3.74	−1150	0.86
Ni(Et$_2$CH–SPhHH)$_2$	CDCl$_3$	−3,189	+1,644	−0.683	270–370	4280	11.7	+507	0.31
Ni(*i*-Bu–PhHH)$_2$	CDCl$_3$	−542	+153	−0.863	300–350	4980	8.19	+2330	0.03
Ni(*i*-Bu–SPhHH)$_2$	CDCl$_3$	−83	+35	−0.683	250–370	6100	9.62	+2990	0.01
Ni(*i*-Pr–PhHH)$_2$[f]	CDCl$_3$	*d*	+8,436	−0.862	. . .	. . .	. . .	−1170[g]	0.87[g]
Ni(*i*-Pr–SPhHH)$_2$[f]	CDCl$_3$	*d*	+3,238	−0.683	. . .	. . .	. . .	+167[g]	0.43[g]
Ni(Ph–PhHH)$_2$[f]	CDCl$_3$	*d*	+548	−0.863	. . .	. . .	. . .	+1690[g]	0.06[g]
Ni(Ph–SPhHH)$_2$[f]	CDCl$_3$	−310	+167	−0.683	. . .	. . .	. . .	+2280[g]	0.02[g]
Ni(*i*-Pr–PhHMe)$_2$[h]	CS$_2$	+3,739	+10,157	−0.318[i]	. . .	. . .	. . .	. . .	1.0
Ni(*i*-Pr–SPhHMe)$_2$[f]	CDCl$_3$	+1,822	+4,185	−0.354[i]	. . .	. . .	. . .	+73[o]	0.47[o]
Ni(*n*-Pr–PhHMe)$_2$[h,j]	CDCl$_3$	+905	+2,042	−0.330[i]	230–310	2990	7.57	+543	0.30
Ni(*n*-Pr–SPhHMe)$_2$[k]	CDCl$_3$	+65	+86	−0.417[i]	270–380	4470	6.65	+2330	0.03
Ni(*i*-Pr–MeHMe)$_2$[h]	CCl$_4$	+3,558	+9,730	−0.301[i]	. . .	. . .	. . .	. . .	1.0
Ni(*i*-Pr–SMeHMe)$_2$[f,l]	CDCl$_3$	+1,950	+4,637	−0.326[i]	. . .	. . .	. . .	−111[g]	0.55[g]
Ni(Me–MeHMe)$_2$[k,m]	CDCl$_3$	+199	+470	−0.301[i]	320–370	3620	6.28	+1600	0.08
Ni(Me–SMeHMe)$_2$[k,n]	CDCl$_3$	+66	+108	−0.326[i]	270–370	5370	10.1	+2100	0.04

[a] 100 MHz, 30°; $\Delta f_i = f_i(\text{complex}) - f_i(\text{dia})$ where $f_i(\text{dia})$ values are taken from free ligands unless otherwise indicated. [b] $a_{\beta\text{-H}}$ unless otherwise noted. [c] Range of measurement in which ΔF varies linearly with temperature. [d] Not measured. [e] Data from ref 7. [f] Contact shifts not measured over temperature range because of low solubility or $N_t = 1$ for one member of comparative pair (**2**, **3**). [g] 303°K. [h] Data from ref 6. [i] $a_{\alpha\text{-Me}}$. [j] Diamagnetic reference Zn(*i*-Pr–PhHMe)$_2$, resulting in slightly different thermodynamic data than previously reported.[6] [k] Diamagnetic reference analogous zinc complex. [l] $\Delta f_{\gamma\text{-Me}} = +652$ cps. [m] $\Delta F = 2950 - 3.98T$ previously determined[3] from β-H contact shifts. [n] $\Delta f_{\gamma\text{-Me}} = +133$ cps. [o] 306°K.

pairs **2–3** of the PhHH series are shown in Figures 2 and 3. Assignment of signals is straightforward and follows from previous work on β-ketoamine complexes.[6,7] That the rapid structural interconversion required for the application of eq 2 to the contact shifts of β-aminothione complexes obtains may be observed in the spectrum of the diastereoisomeric mixture (*vide infra*) of Ni(*sec*-Bu–SPhHH)$_2$ complexes (Figure 3). The chemical shifts of the signals are averaged over the planar and tetrahedral forms, as is the case for the analogous oxygen-containing complexes and for all known bis-chelate nickel(II) species involved in equilibrium 1. In these cases, lifetime of either stereoisomer is $\lesssim 10^{-3}$ sec.

Because the principal experimental purpose of this work has been the evaluation of thermodynamic data for the planar–tetrahedral conversion of various pairs of complexes **2–3** set out in Table VI which are suitable for quantitative comparison, we wish to make clear the procedures and assumptions involved. These data have been obtained from analysis of the temperature dependencies of contact shifts of three series of pairs by use of eq 2.[3,4,6,7] Contact shifts are defined as $\Delta f_i = f_{i(\text{complex})} - f_{i(\text{dia})}$, and choice of diamagnetic reference as either free ligand or a derivative metal complex is unimportant so long as the contact shifts used in eq 2 are definitely larger than several hundred cycles per second. The data in Table III show that chemical shift differences for a given proton in the free ligand and its zinc(II) complex may be as large as 10–20 cps, and the choice of one or the other as the diamagnetic reference is important for the several pairs of complexes in Table VI with contact shifts under ~200 cps. In these cases zinc(II) complexes are considered to be the more realistic diamagnetic references, and where feasible their chemical shifts were used in calculating contact shifts. The use of eq 2 requires for each complex a value of a_i which was obtained in one of two ways. The first and more direct method involves evaluation of N_t at a given temperature from eq 3 followed by calculation of a_i from eq 2 using contact shifts measured at the same temperature. The limiting μ_t and g values for the tetrahedral form are taken from an appropriate complex of the same series with $N_t = 1$. This method has been applied to those complexes with $N_t < 1$ whose solution moments are sufficiently large to be accurately measured ($\mu_{\text{obsd}} \gtrsim 2.20 \pm 0.06$ BM). For Ni(R–RγHRα)$_2$ complexes these values are taken as those of Ni(*t*-Bu–PhHH)$_2$,[7] Ni(*i*-Pr–PhHMe)$_2$,[6] and Ni(*i*-Pr–MeHMe)$_2$.[6] In the second method a_i values

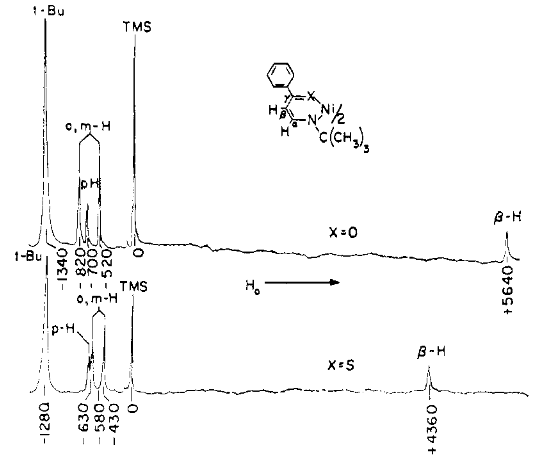

Figure 2. Pmr spectra (60 MHz) of Ni(t-Bu–PhHH)$_2$ and Ni(t-Bu–SPhHH)$_2$ in CCl$_4$ solution at ~30° (α-H signals not shown).

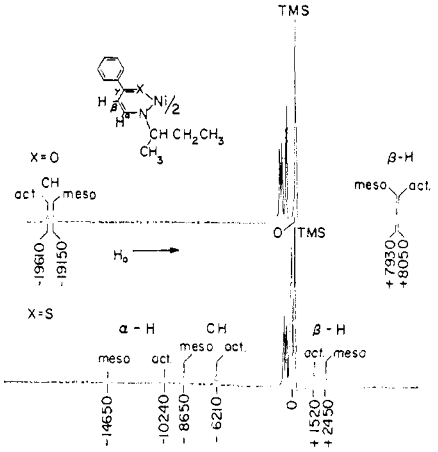

Figure 3. Pmr spectra (100 MHz) of mixtures of active and *meso* isomers of Ni(sec-Bu–PhHH)$_2$ and Ni(sec-Bu–SPhHH)$_2$ in CDCl$_3$ solution at ~30° (α-H signals of the former not shown).

are transferred from a tetrahedral model complex to those of the same series with $N_t < 1$ whose solution moments are too small to be measured with the required accuracy ($\mu_{\text{obsd}} < 2.2$ BM). In dealing with the β-aminothione complexes it was necessary to use μ_t of Ni(t-Bu–SPhHH)$_2$ as the limiting tetrahedral moment for all three series because it is the only type **3** complex with $N_t = 1$ which could be prepared. Previous demonstrations[6,7,42] that coupling constants of ring substituents in complexes of a given series are not in general sensitive functions of the nitrogen substituent R provide justification for the second method. The coupling constants in Table VI suffice to indicate which method was used for each complex.

The tetrahedral forms of complexes with asymmetric R groups (*sec*-Bu, Amp) when prepared from optically active amines will consist of the $\Delta(+,+)$, $\Lambda(+,+)$ or $\Delta(-,-)$, $\Lambda(-,-)$ isomers while those obtained from the racemic amines contain these active species and the *meso* isomers $\Delta(+,-) \equiv \Lambda(+,-)$. Δ and Λ refer to the absolute configuration at the metal and have been defined elsewhere.[7] The spectra of Ni(sec-Bu–SPhHH)$_2$ (Figure 3) and Ni(Amp–SPhHH)$_2$ prepared from racemic amines reveal the splittings between sets of signals of the active and *meso* diastereoisomers similar to those found for the analogous β-ketoamine complexes[7] and other nickel(II) complexes with $N_t < 1$.[7,10a] It is observed that in the spectra of the active isomers, *e.g.*, Ni((+)-R-SPhHH)$_2$, only one set of signals is found, indicating that the chemical shift difference between the Δ and Λ forms is averaged on the pmr time scale by rapid racemization accompanying the structural interconversion. Δ and Λ configurations are likewise racemized in bis-chelate β-ketoamine[7] and salicylaldimine[7,10a,42] nickel(II) complexes. Recent arguments that the differences in contact shifts of diastereoisomers, $\Delta\Delta f_i = \Delta f_{i(\text{act})} - \Delta f_{i(\text{meso})}$, arise principally from differences in ΔF values for the isomers rather than from differences in a_i[7] may be further supported from the magnetic moment and contact shift data for Ni(Amp–SPhHH)$_2$. The moment of an equimolar mixture of active and *meso* diastereoisomers in carbon tetrachloride solution (30°) is 2.40 BM, and that of the active isomer is 2.08 BM. From these data the moment of the *meso* isomer, which cannot be prepared separately, is 2.68 ± 0.12 BM. Coupling constants calculated from these moments and $\mu_t = 3.17$ BM using eq 2 and 3 are $a_{\beta\text{-H}(meso)} = -0.718$ G and $a_{\beta\text{-H(act)}} = -0.751$ G, which differ by ~4% whereas the β-H contact shifts (30°) differ by ~37%. The average $a_{\beta\text{-H}}$ value, -0.735 G, compares closely with $a_{\beta\text{-H}} = -0.717$ G for Ni(t-Bu–SPhHH)$_2$, the value used in obtaining the thermodynamic data for both isomers, and provides additional evidence that coupling constants are not strongly affected by the nature of R within complexes of the same R$_\gamma$HR$_\alpha$ series.

The temperature dependence of ΔF for the planar–tetrahedral conversion was obtained from the measured contact shifts and eq 2 for each β-aminothione complex, solubility permitting, whose β-ketoamine analog has $N_t < 1$. Contact shifts of the same α or β substituent were followed in a given series of both types of complexes in an attempt to render the data as meaningful as possible in a comparative sense. ΔH and ΔS values were obtained from $\Delta F = \Delta H - T\Delta S$ by a least-squares procedure. The complete set of thermodynamic data for the pairs **2**–**3** is presented in Table VI; data for certain of the β-ketoamine complexes have also been reported elsewhere.[6,7]

Thermodynamic Results and Relative Stereochemical Populations. Complete sets of thermodynamic data pertaining to equilibrium 1 were obtained for eight pairs of complexes **2**–**3** whose members have $N_t < 1$ in chloroform or carbon tetrachloride solution. Six of these pairs belong to the PhHH series and include active and *meso* diastereoisomers; the remaining two fall in the PhHMe and MeHMe series. Of the other six pairs in Table VI ΔF and N_t values were obtained at 30° only. For one of these pairs, Ni(t-Bu–PhHH)$_2$–Ni(t-BuSPhHH)$_2$, the tetrahedral mole fraction of each complex is 1 in solution; therefore, $-\Delta F^{300°} > 2.8$ kcal/mole for each, and no stereochemical differences are observable. The following principal results and conclusions apply to those pairs for which ΔF, ΔH, and ΔS data were evaluated.

(i) For every complex except active and *meso*-Ni(Amp–PhHH)$_2$, ΔH is positive, showing that on en-

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

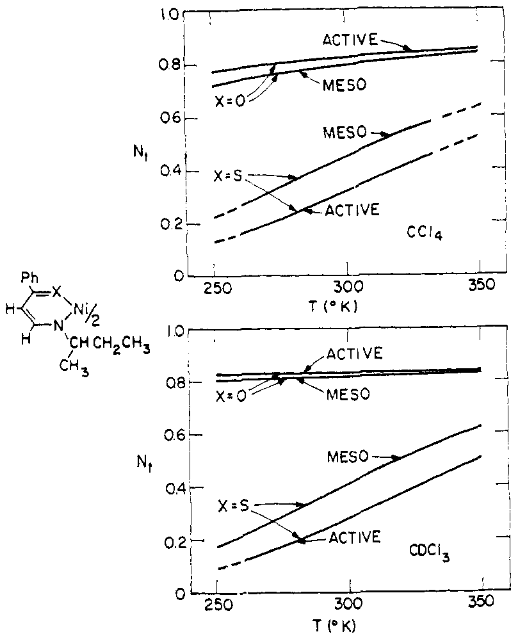


Figure 4. Temperature dependence of the tetrahedral mole fractions of the diastereoisomers of Ni(*sec*-Bu-PhHH)$_2$ and Ni(*sec*-Bu-SPhHH)$_2$ in carbon tetrachloride and chloroform solutions evaluated from data in Table VI.

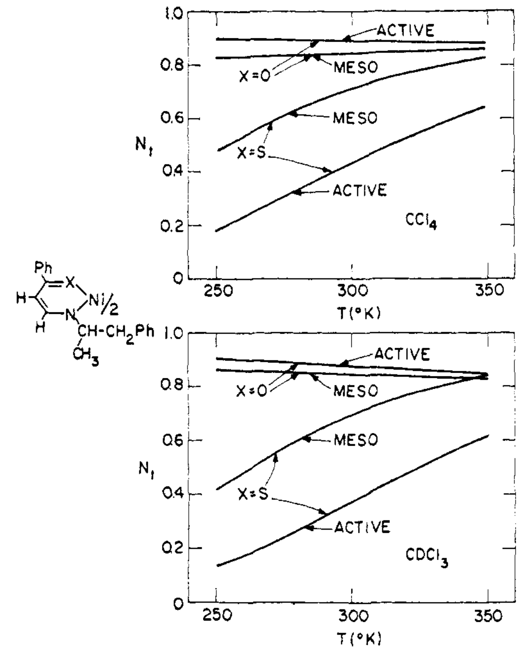


Figure 5. Temperature dependence of the tetrahedral mole fractions of the diastereoisomers of Ni(Amp-PhHH)$_2$ and Ni(Amp-SPhHH)$_2$ in carbon tetrachloride and chloroform solutions evaluated from data in Table VI.

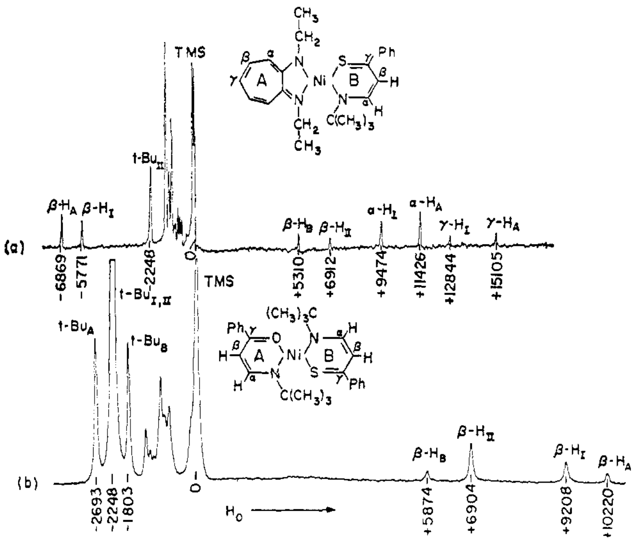


Figure 6. Pmr spectra (100 MHz) at ~30° in CDCl$_3$ solution: (a) mixed ligand complex formed by Ni(Et$_2$-ati)$_2$ (I) and Ni(*t*-Bu-SPhHH)$_2$ (II); (b) mixed ligand complex formed by Ni(*t*-Bu-PhHH)$_2$ (I) and Ni(*t*-Bu-SPhHH)$_2$ (II).

thalpy grounds the planar isomer is more stable; additionally, for every pair $\Delta\Delta H = \Delta H_S - \Delta H_O > 0$ indicating that enthalpy differences favor the planar isomer of **3** relative to that of **2**.

(ii) Positive ΔS values for every complex reveal that entropy effects alone favor the tetrahedral isomers of both **2** and **3**; further $\Delta\Delta S = \Delta S_S - \Delta S_O > 0$ for all pairs except Ni(*n*-Pr-PhHMe)$_2$–Ni(*n*-Pr-SPhHMe)$_2$ demonstrating that entropy changes produce a relative preference for the tetrahedral form of **3** over that of **2** in all pairs but one.

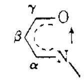
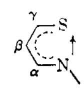
(iii) Within and below the temperature interval of measurement (maximum range *ca.* 230–370°K) $\Delta\Delta F = \Delta F_S - \Delta F_O > 0$ in all cases, revealing that in their respective ligands *sulfur exerts a relatively greater stabilization of planar stereochemistry than does oxygen.* This point is illustrated graphically by plots of mole fraction tetrahedral, calculated from the data in Table VI, *vs.* temperature shown in Figures 4 and 5 for four pairs of complexes of the PhHH series. Only in the cases of active and *meso*-Ni(Amp-PhHH)$_2$ and *meso*-Ni(Amp-SPhHH)$_2$ in chloroform solution do the stereochemical populations become nearly equal or invert from the usual order (*cf.* Figure 5), an effect associated with the large entropy change of the latter complex compared to the quite small ΔS and negative ΔH values of the former.

(iv) Change of solvent from chloroform to carbon tetrachloride does not produce any large changes in thermodynamic values of the four pairs examined in the two solvents (*cf.* Figures 4 and 5). Because carbon tetrachloride lacks the hydrogen-bonding properties by which chloroform may affect the position of equilibrium 1 in other cases[6,10] and is otherwise only weakly interacting, differential solute–solvent effects as reflected in the entropy terms in the two solvents cannot be large. The observation that $\Delta\Delta H_{CCl_4} < \Delta\Delta H_{CDCl_3}$ and $\Delta\Delta S_{CCl_4} < \Delta\Delta S_{CDCl_3}$ for the four pairs is indicative of less specific interaction between the complexes in their two forms and solvent in carbon tetrachloride solution, but the roughly proportional decrease of ΔH and ΔS results in no important difference in N_t(CCl$_4$) compared to N_t(CDCl$_3$).

(v) At *ca.* 340°K and below, $|\Delta\Delta H| > |T\Delta\Delta S|$, indicating that in this temperature range *inequalities in stereochemical populations have as their basis enthalpy rather than entropy effects.*

(vi) Diastereoisomers of the complexes **3** with R = *sec*-Bu and Amp show much greater differences in stereochemical populations within the temperature

Table VII. Calculated and Experimental Spin Densities. β-Ketoamine and β-Aminothione π Radicals and Ni(II) Complexes

Radical/complex	Method	HFMO					
		ρ_α	ρ_β	ρ_γ	ρ_N	$\rho_{O,S}$	$E_{HFMO}(\beta)$
	HMO^{a,b}	+0.032	+0.508	+0.055	+0.258	+0.147	0.580
	McL^{a-c}	−0.086	+0.686	−0.029	+0.290	+0.140	...
	HMO^{b,d,e}	+0.011	+0.339	+0.093	+0.180	+0.377	0.703
	HMO^{b,d,f}	+0.018	+0.388	+0.068	+0.200	+0.327	0.636
	McL^{b-e}	−0.067	+0.444	−0.014	+0.221	+0.416	...
	McL$^{b-d,f}$	−0.070	+0.518	−0.054	+0.239	+0.367	...
Ni(*t*-Bu–PhHH)$_2$	...		+0.038^g				
Ni(*t*-Bu–SPhHH)$_2$	...		+0.030^g				
Ni(*i*-Pr–PhHMe)$_2$	...		+0.038^g				
Ni(*i*-Pr–SPhHMe)$_2$	...		+0.035^g				
Ni(*i*-Pr–MeHMe)$_2$	...		+0.036^g				
Ni(*i*-Pr–SMeHMe)$_2$	...		+0.034^g				

[a] Data from ref 6, $\beta_{CO} = 1.5\beta$, $\alpha_O = \alpha + 1.5\beta$. [b] $\beta_{CN} = 1.2\beta$, $\alpha_N = \alpha + \beta$. [c] $\lambda = 1.2$. [d] $\alpha_S = \alpha + \beta$. [e] $\beta_{CS} = 0.6\beta$. [f] $\beta_{CS} = 0.8\beta$. [g] Calculated from experimental $a_{\beta\text{-H}}$ value (Table VI) using $Q_{CH} = -23$ G.

range of measurement than do those of **2**;[43] *i.e.*, $N_{t_{S(active)}} < N_{t_{S(meso)}}$, whereas $N_{t_{O(active)}} \gtrsim N_{t_{O(meso)}}$.

Spin Density Distributions and π Bonding. From the data presented in Table VI together with eq 2, it is observed that for the β-aminothione complexes values of $a_{\alpha\text{-Me}}$, $a_{\beta\text{-H}}$, and $a_{\gamma\text{-Me}}$ are negative and $a_{\alpha\text{-H}}$ values are positive. Exactly the same pattern of a_i signs, or, equivalently, contact shifts, has been found for the related β-ketoamine complexes.[3,4,6,7] In those cases it has been shown that the contact shifts arise primarily by delocalization of α spin in the ligand π orbitals, effected by ligand-to-metal antiparallel (β) spin transfer from the highest filled MO (HFMO) of the ligand anion to the d_{xz}, d_{yz} metal orbitals each containing α spin.[6] The creation of spin imbalance in the ligands results from ligand→metal π bonding in the tetrahedral form which produces, in effect, delocalization of a fraction of metal α spin in the ligand HFMO's. Comparison of theoretical spin densities for one full spin in the HFMO with measured values obtained from the experimental coupling constant of β-H and the relation $a_{\beta\text{-H}} = -23\rho_{C_\beta}$ leads to an estimate of $\sim$1/20 α spin delocalized on each β-ketoamine ligand.[6]

Contact shift data for pairs of complexes **2**–**3** provide a previously unavailable opportunity to assess the relative π-bonding (here π-donor) tendencies of oxygen and sulfur, when implicated in otherwise identical ligands, with respect to a common acceptor, tetrahedral nickel(II). Spin densities calculated by simple HMO theory and the McLachlan procedure,[45] which allows rough estimation of negative spin densities by including electron correlation, are shown in Table VII for the β-ketoamine and β-aminothione radicals ($R_\alpha = R_\gamma = R = H$). Spin distributions in the two cases are qualitatively similar and are in agreement with π-electron delocalization in the HFMO of the β-aminothione ligands. Experimental evaluation of π-spin densities from measured coupling constants is considered most reliable at β-C[46] and ρ_{C_β} values are given in Table VII. For the three pairs compared, $\rho_{C_\beta(S)} < \rho_{C_\beta(O)}$. Normalization of these values with theoretical β-C spin densities in order to obtain the relative amounts of spin delocalized in the β-ketoamine and β-aminothione ligands is not considered a reliable procedure because of the uncertainty in the best choice of sulfur parameters[47] in particular, and the effect of the coordinated metal ion on them. The values of Coulomb and resonance integrals used to obtain the results in Table VII are within the range of those required to fit theoretical and experimental spin densities determined by esr for certain sulfur-containing aromatic radicals.[48] The effect of varying β_{CS} only from 0.6 to 0.8 is clearly evident; indeed, in one radical a β_{CS} value of $\sim$1.5 was required for an acceptable fit.[49]

Relative spin densities in complexes **2** and **3** have been investigated by a more direct experimental approach. Of the experimental spin densities listed in Table VII, those of Ni(*t*-Bu–SPhHH)$_2$ (**10**) and Ni(*t*-Bu–PhHH)$_2$ (**11**) are considered the most accurate for

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(43) We are unable to offer a definite explanation of these effects. If, as proposed elsewhere,[7] stereochemical populations of active and *meso* diastereoisomers differ principally because of varying degrees of interaction between R(+)–R(+) (or R(−)–R(−)) and R(+)–R(−) groups in the *tetrahedral* configurations, one possibility is that the β-aminothione complexes possess a greater degree of tetrahedrality, *i.e.*, possess a larger dihedral angle between the mean planes of the chelate rings than do their β-ketoamine analogs. This structural feature would lead to larger nonbonded interactions in the former relative to the latter complexes. A second possibility is that the chemical shifts of the β-aminothione complexes are averaged to a different extent over a diamagnetic form which approaches a "*cis*-planar" structure than are those of the β-ketoamines. It is noted that a structural equilibrium involving as the *only* diamagnetic form such a "*cis*-planar" species is unlikely for both groups of complexes with R = Amp and *sec*-Bu. The steric demands of these groups could lead to rapid structural conversion but to slow racemization,[44] contrary to the averaging of the Δ and Λ forms observed for all active isomers of complexes with these R groups. Additionally, the bulkiness of these groups would favor the *trans* form, as has been consistently found for a number of diamagnetic bis(N-substituted salicylaldimino)nickel(II) complexes in the crystalline state.[4] In the absence of information to the contrary, we tend to favor the first possibility.

(44) M. J. O'Connor, R. E. Ernst, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 4561 (1968).

(45) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

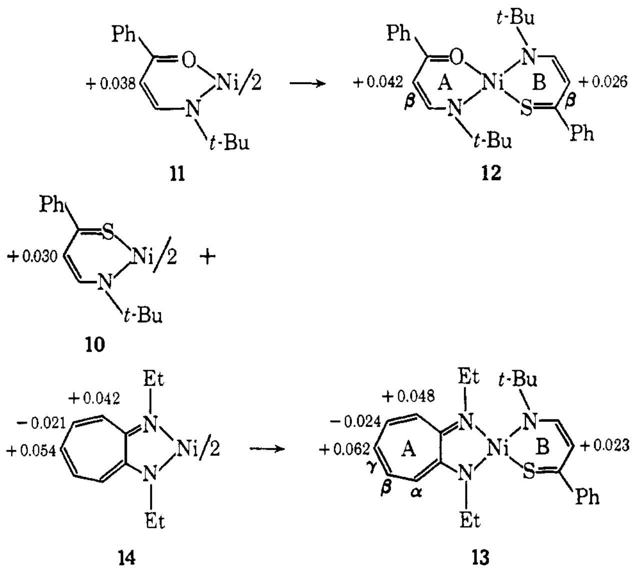
(46) Note that $\Delta f_{\alpha\text{-H}}$ values for the PhHH complexes, although negative in sign and thus consistent with the negative ρ_{C_α} values obtained by McLachlan calculations, are much too large to arise from only π-electron delocalization at the α position. This enhancement of the negative contact shifts of α-H has also been observed for Ni(*i*-Pr-MeHH)$_2$,[6] and for that complex, as well as those considered here, some delocalization of α spin in the σ system is considered responsible. Attenuation effects would be expected to make any contribution from σ delocalization of spin very small at β-H. Spin density evaluations at methyl-substituted α- and γ-C are much less certain than at β-C because of the much larger variations possible for Q_{CCH_3} than for Q_{CH}.[6]

(47) For a discussion of these parameters, *cf.* R. Zahradník, *Advan. Heterocyclic Chem.*, **5**, 1 (1965); R. Mayer, W. Bray, and R. Zahradník, *ibid.*, **8**, 219 (1967).

(48) E. A. C. Lucken, *Theor. Chim. Acta*, **1**, 397 (1963); E. T. Strom and G. A. Russell, *J. Am. Chem. Soc.*, **87**, 3326 (1965).

(49) R. Gerdil and E. A. C. Lucken, *ibid.*, **87**, 213 (1965).

any pair. Because for both complexes $N_t = 1$, $a_{\beta\text{-H}}$ values can be accurately measured directly from contact shifts (eq 2) in the same solvents and are not dependent upon ancillary measurements of N_t from solution magnetic moments. In order to gauge the relative π-bonding effects of sulfur and oxygen *in their respective ligands*, the mixed ligand complexes **12** and **13** were produced by the following exchange reactions which were allowed to proceed for *ca.* 3 days in chloroform solution at ambient temperature. Ligand-exchange reactions of bis(N,N′-diethylaminotroponeamino)-nickel(II) (**14**) have been observed previously.[50]



For both **12** and **13** $N_t = 1$; in the latter case this was substantiated by the observation of a Curie dependence of contact shifts in the range −50 to 90°. Spin densities calculated from measured contact shifts and coupling constants are shown above for **10–14**. In the case of **14** the spin densities were scaled from $\rho_{C_\beta} = -0.021$ as done previously.[32] *g* values of **12** and **13** were taken as the mean of those of the pure components. It is observed that the spin density distribution in **12** is measurably asymmetric and that in both **12** and **13** the spin densities in ring B are decreased relative to those in ring A. Provided that the total spin density in rings A and B of the mixed species equals or nearly equals the sum of the spin densities in one ligand of each of the pure components, the results for **12** and **13** demonstrate that a β-aminothione ligand π-bonds somewhat less effectively than a β-ketoamine or aminotroponeimine. Previous estimates of the fractional spin delocalization in a β-ketoamine[6] and aminotroponeimine[32] ligand as $\sim{}^1/_{20}$ and $\sim{}^1/_{10}$, respectively, lead to the following order of increasing π-bonding tendencies of the ligands with respect to tetrahedral nickel(II): aminotroponeimine > β-ketoamine > β-aminothione. Reaction of **11** and **14** in chloroform produced pmr signals indicative of the formation of a mixed ligand species analogous to **13** but with virtually no differences in contact shifts relative to the pure components. Hence, in mixed ligand complexes the π-bonding propensities of aminotroponeimine and β-ketoamine ligands are more nearly the same than are those of a β-aminothione ligand and either of the former.

On the basis of result v above and a previous analysis of the thermodynamic factors involved in the relative stabilities of planar and tetrahedral stereoisomers,[4] it is concluded that differences in metal–ligand bonding are principally responsible for the grossly unequal stereochemical populations of members of the pairs **2–3**. Because metal–ligand π bonding in the tetrahedral isomers is a stabilizing interaction, the somewhat larger amount of π bonding in the β-ketoamine complexes is consistent with the finding that their tetrahedral form is more stable than that of the β-aminothiones. It is emphasized, however, that the π-bonding properties of the magnetic electrons only can be assessed by contact shifts and that the quite small amount of ligand→metal electron transfer, probably less than $\sim{}^1/_{20}$ of an electron in both types of complexes, may not result in a significant difference in bond energies. Electron distribution in the diamagnetic planar forms of **2** and **3** cannot of course be investigated by the contact shift method. A plausible source of the stability differences of these isomers is considered to be a larger extent of metal–ligand π bonding in the β-aminothiones which can occur *via* ligand→metal ($\text{HFMO}\rightarrow p_z$) and/or metal→ligand ($d_{xz}{}^2d_{yz}{}^2\rightarrow\text{LUMO}$, $\text{Sd}\pi$) electron transfer superimposed on the (unknown) relative σ-bond strengths.

Finally, it is relevant to point out that the recent synthesis of thiosalicylaldiminenickel(II) complexes,[51] together with presently available data for salicylaldimine complexes,[10a] should permit a further assessment of the relative effects of sulfur and oxygen donor atoms on stereochemical populations and spin density distributions.

Acknowledgment. This research was supported by the National Science Foundation under Grant GP-7576X. We are indebted to M. G. McNamee for valuable experimental assistance and to Dr. R. E. Benson for a gift of the cycloheptatriene precursors of compound **14**.

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(50) D. R. Eaton and E. A. LaLancette, *J. Chem. Phys.*, **41**, 3534 (1964); D. R. Eaton and W. D. Phillips, *ibid.*, **43**, 392 (1965).

(51) E. Hoyer and B. Lorenz, *Z. Chem.*, **8**, 28 (1968).