in the solvents used automatically keeps [L] small, the first-order dependence on carbon monoxide concentration[4] in bis(β-ethoxyethyl) ether does not rule out the possibility that this reaction has the same mechanism as the reaction of $CH_3Mn(CO)_5$ with other nucleophiles. In any event, a comparison of the observed second-order rate constants for the reaction in mesitylene of $CH_3Mn(CO)_5$ with CO ($4.49 \times 10^{-4}\ M^{-1}\ sec.^{-1}$ at 30°) and with cyclohexylamine ($1.11 \times 10^{-4}\ M^{-1}\ sec.^{-1}$ at 25°) shows that even when the rate is dependent on the concentration of the nucleophile, it is not greatly affected by a change in the nature of the nucleophile.

The reactions of manganese pentacarbonyl halides with a variety of ligands have been studied by Angelici and Basolo.[7] As in the case of $CH_3Mn(CO)_5$, the rate

$$Mn(CO)_5X + L \longrightarrow Mn(CO)_4LX + CO$$

of reaction was found to be independent of the nature and concentration of the ligand used, which caused the authors to suggest that the rate-determining step involved the loss of carbon monoxide to form an intermediate of lower coordination number. Since the reaction proceeded smoothly in nonpolar solvents, it was virtually certain that solvent did not become coordinated in the rate-determining step. The effect of changing the solvent on the rate of the reaction was far smaller than for the reactions of $CH_3Mn(CO)_5$ and was in the reverse direction; that is, the more polar solvents slowed the reaction down. This is in agreement with a transition state which is slightly less polar than the starting material, in contrast to the more polar transition state in the reactions of $CH_3Mn(CO)_5$.

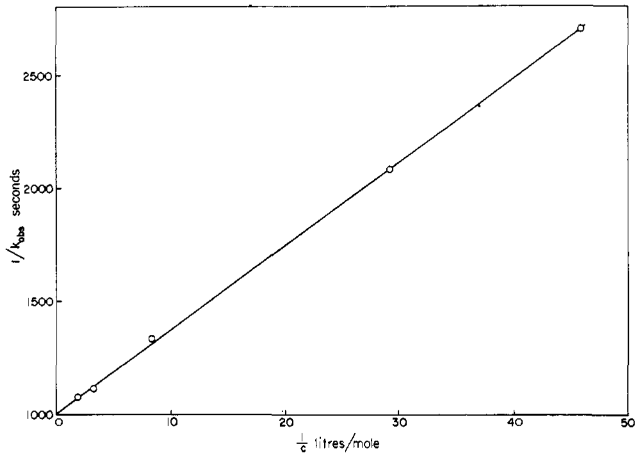

Fig. 5.—Plot of the reciprocal of observed rate constant *vs.* the reciprocal of phosphite concentration for the reaction of $CH_3Mn(CO)_5$ with triphenyl phosphite in tetrahydrofuran.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138]

Studies on Nickel(II) Complexes. VII. A Nuclear Resonance Investigation of Mixed Ligand Complexes

BY A. CHAKRAVORTY AND R. H. HOLM[1]

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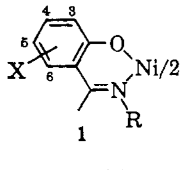
Equilibration of solutions of differently substituted bis(salicylaldimine)-Ni(II) complexes which are involved in a planar ⇌ tetrahedral conformational equilibrium results in rapid and nearly statistical ligand exchange. The mixed ligand complexes thus produced have been unambiguously identified by their proton resonance spectra which, like those of the pure complexes, exhibit characteristic isotropic proton hyperfine contact interactions. Spin densities in the mixed complexes have been measured, and comparison with the pure complexes shows that an asymmetric redistribution of spin has occurred. A recent model for the production of asymmetric spin density distributions is applied to the mixed salicylaldimine complexes. A probable mechanism for the ligand-exchange process is discussed.

Introduction

As part of a continuing series of investigations in these laboratories concerning the solution equilibria of bis(chelate)nickel(II) complexes,[2-7] we have discovered facile ligand-exchange reactions between variously substituted bis(salicylaldimine) complexes of general type 1. These exchange reactions take place rapidly in solution in the absence of any added free ligand. The mixed ligand complexes thus produced can be readily detected from measurements of their isotropic proton hyperfine contact shifts,[8] which are in most cases distinguishable from the contact shifts of the unmixed complexes, the spectra of which are unchanged. The utilization of the contact shift technique for the study of the mixed ligand complexes necessitates that at least a fraction of the unmixed and mixed complexes exist in a paramagnetic configuration. Accordingly, the complexes studied in this work have R = *sec*-alkyl and/or *t*-butyl groups. It has been previously demon-



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(1) Alfred P. Sloan Foundation Fellow.

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

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

(4) (a) R. H. Holm and K. Swaminathan, *ibid.*, **2**, 181 (1963); see also (b) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963); L. Sacconi, M. Ciampolini, and N. Nardi, *ibid.*, **86**, 819 (1964).

(5) R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **85**, 821 (1963).

(6) (a) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962); see also (b) L. Sacconi and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 1750 (1963); (c) E. A. LaLancette, D. R. Eaton, R. E. Benson, and W. D. Phillips, *ibid.*, **84**, 3968 (1962).

(7) R. H. Holm, *ibid.*, **83**, 4683 (1961).

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

strated[2,4] that these unmixed complexes are involved in a dynamic planar (diamagnetic) $\rightleftharpoons$ tetrahedral (paramagnetic) structural equilibrium which has been thoroughly investigated by proton magnetic resonance.[7] The process of ligand exchange in type **1** complexes was initially detected in our earlier work[5] during which it was observed that the equilibration of equimolar solutions of the (+,+) and (−,−) forms of bis(5-methyl-N-*sec*-butylsalicylaldimine)nickel(II) produced a second set of contact shifts which were unambiguously shown to arise from the (+,−)-*meso* diastereoisomer. Identical behavior has been found in a number of other complexes containing optically active R groups.[2] In the present work, mixed ligand complexes derived from **1** have been studied by equilibration of chloroform solutions of complexes with different R and/or X groups. The identification and assignment of the mixed complex spectra are discussed in detail. Spin densities in the benzene rings of the mixed complexes have been evaluated and the redistribution of spin density in the complexes compared to the unmixed components is discussed.

Experimental

All complexes utilized in this work have been previously prepared[2,4] except for the two which follow. Both of these were prepared in toluene solution following a recent procedure for the preparation of bis(N-*t*-butyl-2-hydroxy-3-naphthaldimine)-nickel(II)[3] and were isolated as brown crystals.

Bis(3-methyl-N-*t*-butylsalicylaldimine)nickel(II), m.p. 224–226°.

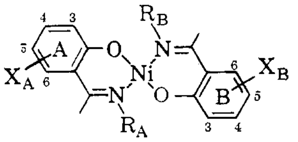
Anal. Calcd. for $C_{24}H_{32}N_2O_2Ni$: C, 65.63; H, 7.34; N, 6.38. Found: C, 65.82; H, 7.50; N, 6.34.

Bis(4-methyl-N-*t*-butylsalicylaldimine)nickel(II), m.p. 201–202°. *Anal.* Found: C, 65.44; H, 7.24; N, 6.16.

Proton resonance measurements were made as previously described.[2] In all cases, approximately or exactly equimolar quantities of the pure complexes were used. Attainment of equilibrium appeared to be complete within 5 min. after mixing so that no attempts were made to follow the rates of formation of the mixed ligand complexes. All solutions were prepared in deuteriochloroform supplied by Merck Sharp and Dohme of Canada. Solutions measured were 0.1–0.2 *M* in total solute and contained ~4% v./v. of tetramethylsilane as an internal reference.

Results and Discussion

The formation of mixed ligand bis(salicylaldimine)-nickel(II) complexes of general type **2** was observed to result from the following three equilibria produced by mixing equimolar solutions of pure type **1** complexes.



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$$R(X)R(X) + R(X')R(X') \rightleftharpoons 2R(X)R(X') \qquad (1)$$

$$R(X)R(X) + R'(X)R'(X) \rightleftharpoons 2R(X)R'(X) \qquad (2)$$

$$R(X)R(X) + R'(X')R'(X') \rightleftharpoons 2R(X)R'(X') \qquad (3)$$

In this fashion mixed complexes derived from nearly all of the pure components previously studied by proton resonance[2] have been observed. Therefore, the process of ligand exchange between complexes involved in planar–tetrahedral conformational equilibria appears to be quite general in the salicylaldimine series. However, because it was of interest in this investigation to determine spin density distributions in the mixed complexes **2**, the majority of the work has been confined to cases in which R = *t*-Bu. As the following results show, pure complexes in which R = *t*-Bu, or mixed complexes in which $R_A = R_B = t$-Bu or only $R_A = t$-Bu, exist essentially completely in the paramagnetic tetrahedral form. In this limit, the proton contact shifts are given by[8,9]

$$\frac{\Delta f_i}{f} = -a_i\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g\beta S(S+1)}{6SkT} \qquad (4)$$

in which Δf_i is the observed contact shift of the *i*th proton in c.p.s., f is the spectrometer frequency, a_i is the electron-nuclear hyperfine splitting constant in gauss for the *i*th proton, and γ_e and γ_H are the gyromagnetic ratios of the electron and proton, respectively. The *g*-value of the triplet S state was obtained from the magnetic moment of 3.30 B.M.[2] which was assumed for all complexes with R = *t*-Bu. All contact shifts were measured at 60 Mc./sec. relative to the uncomplexed ligand. As previously,[2,8] the individual spin densities ρ_{C_i} calculated from[10]

$$a_i = Q_{CH}\rho_{C_i} \qquad (5)$$

using a_i values from eq. 4 are defined such that their sum per complex is $2S$.

The detection of a typical mixed complex is considered first. Equilibration of the pure components *i*-Pr(5-CH_3) + 3-pentyl(5-CH_3) yields the *i*-Pr(5-CH_3)-3-pentyl(5-CH_3) species. The spectrum of the equilibrium mixture is given in Fig. 1 and contains the spectra of the two pure components, which have been assigned previously,[2] and the spectrum of the mixed complex. In this and succeeding cases, we shall be concerned only with the protons and methyl groups attached to rings A and B in **2**. The signs of the observed contact shifts of these substituents have been shown[2] to agree with a valence bond model of spin delocalization and may be summarized as follows: positive—3-H, 5-H, 4-CH_3; negative—4-H, 6-H, 3-CH_3, 5-CH_3. It is seen that the signals arising from the mixed complex are distinct from those of the pure components, both of which exist in *ca.* 50 mole % of the tetrahedral form. In the tetrahedral form replacement of RR by RR′ (and/or X_iX_i by X_iX_i', X_iX_j, or X_iX_j') removes the twofold rotation axis so that given numbered positions in rings A and B are distinct and two signals could in principle arise from the same substituent at each position. When eq. 4 applies, separate signals could occur if $a_i(A) \neq a_i(B)$ to an extent which would allow resolution of the two signals.

In the present system, eq. 4 does not apply and the contact shifts of all three complexes are given by[8]

$$\frac{\Delta f_i}{f} = -a_i\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g\beta S(S+1)}{2SkT}\,[e^{\Delta F/kT} + 3]^{-1} \qquad (6)$$

and thus have an explicit dependence on the free-energy change of the planar $\rightleftharpoons$ tetrahedral interconversion. This system is an example of equilibrium 2 which involves an appreciable concentration of diamagnetic forms and is quite analogous to those obtained by mixing optically active (+,+) and (−,−) complexes to produce *meso* complexes.[2,5] In Fig. 1 it is seen that

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(9) H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, **27**, 314 (1957).

(10) H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

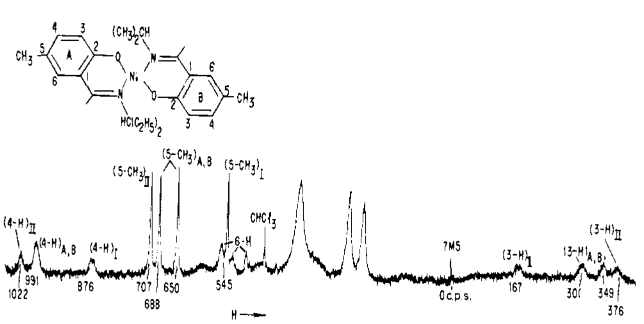

Fig. 1.— Proton resonance spectrum of the mixed complex *i*-Pr(5-CH_3)–3-pentyl(5-CH_3) and its pure components in $CDCl_3$ at 60°: frequencies are the chemical shifts; I refers to the pure 3-pentyl(5-CH_3) and II to the pure *i*-Pr(5-CH_3) complex.

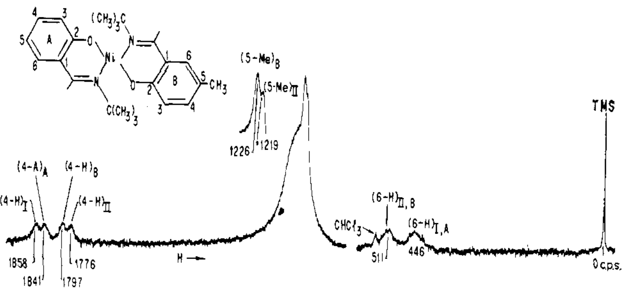

Fig. 2.—Proton resonance spectrum of the mixed complex *t*-Bu(H)–*t*-Bu(5-CH_3) and its pure components in $CDCl_3$ at 31°: the 3-H and 5-H signals, which are not shown, occur above TMS; frequencies are the chemical shifts; I refers to the pure *t*-Bu(H) and II to the pure *t*-Bu(5-CH_3) complex.

the two 3-H and 5-CH_3 signals of the mixed complex are clearly resolved; in this example, the 4-H signals are not resolved nor are those from 6-H which have very small contact shifts.[2] The temperature dependence of the contact shifts of the mixed complex from −40 to 100° show the behavior Δf_i(3-pentyl) < Δf_i(RR′) < Δf_i(*i*-Pr) and more closely parallel those of the pure *i*-Pr rather than those of the pure 3-pentyl component, which tends to indicate that ΔF(*i*-Pr) $\lesssim$ ΔF(RR′) < ΔF(3-pentyl) over this temperature range. However, as the following discussion will show, the different contact shifts of RR′ relative to the pure components at a given temperature need not be solely a consequence of the free-energy inequality, and it must be considered that in the mixed complex ΔF and a_i(A,B) may both be different compared to the RR and R′R′ complexes. For the diastereoisomeric complexes, it has been shown that $\Delta F_{\text{act}} \neq \Delta F_{meso}$,[2] but it could not be demonstrated that a_i(act) ≠ a_i(*meso*) or that for the *meso* complexes a_i(A) ≠ a_i(B). From the present mixture it is concluded (and verified in the following discussion) that for mixed complexes in which the R groups are sufficiently different, there is an intrinsic difference in the spin density distributions in rings A and B. Evaluation of spin densities in mixed complexes of this type requires determination of ΔF(RR′), a quantity which is not readily obtainable[11] for salicylaldimine complexes. The remaining portion of this work deals with mixed complexes in which R_A or R_A and R_B are *t*-Bu, thus obviating determination of ΔF(RR′). These complexes are discussed in the following sections.

Equilibrium 1. $R_A = R_B =$ *t*-Bu.—For pure and mixed complexes of this type eq. 4 holds. Three mixtures were investigated: X_A = H, X_B = 5-CH_3 or 4-CH_3; X_A = 4-CH_3, X_B = 5-CH_3. The spectrum of the (H, 5-CH_3) mixture is shown in Fig. 2. The two 4-H signals of the mixed complex are clearly resolved with respect to each other and the pure components; two 5-CH_3 signals are discernible although superimposed on the *t*-Bu signal. The 3-H, 5-H, and 6-H signals in this mixed complex have unresolvably small separations from the corresponding signals of the pure components. The (H, 4-CH_3) mixed complex can be detected by the 15-c.p.s. separation of 4-H from the pure complex; all other signals are unresolvably close to the pure component signals. The (4-CH_3, 5-CH_3) mixture yields no separate signals for the mixed complex, but there seems no reason to doubt that exchange has occurred. The results of the (H, 5-CH_3) mixture present a clear observation of the inequality of certain a_i(A) and a_i(B) values when R_A and R_B are identical but the complex is otherwise asymmetric, and the intermediate position of the $(4\text{-H})_{A,B}$ signals indicates that spin density is increased in one ring and decreased in the other compared to the pure components. The latter effect is larger and more general in complexes in which $R_A \neq R_B$ and is discussed more fully below.

Equilibria 2 and 3. R_A = *t*-Bu and R_B = *i*-Pr.—At and above room temperature eq. 4 is valid for complexes in which R = *t*-Bu, and eq. 6 applies when R ≠ *t*-Bu and, *e.g.*, is *i*-Pr.[2] In the *t*-Bu–*i*-Pr mixed species, we have found that eq. 4 holds at and above room temperature regardless of the nature or position of X. This is demonstrated for one representative case, the *t*-Bu(5-CH_3)–*i*-Pr(5-CH_3) mixed complex, in Fig. 3. The room temperature spectrum of this complex is shown in Fig. 6. The linear dependence of Δf_i with $1/T$ is observed from 0 to 100° for the 5-CH_3 signals; other signals have the same dependence. In general, coupling constants obtained from measurement of the mixed or pure *t*-Bu complexes at room temperature agree to within 1% of those derived from least mean squares fit of the temperature dependence of Δf_i. The small negative deviations of the contact shifts at the lower temperatures are believed due to a small concentration of paramagnetic associated species over which the contact shifts are also averaged.[12] Table I lists the contact shifts measured at room temperature of unmixed R = *t*-Bu complexes and the spin densities calculated from these data using eq. 4 with $Q_{CH} = -22.5$ gauss.

The spectrum of the parent mixed complex of the *t*-Bu–*i*-Pr series is shown in Fig. 4 and contains a number of spectral features which are found generally in this series. This spectrum is also the most difficult of any to assign and the method of assignment will be briefly discussed. The signals of pure components are easily identified by their known frequencies or by adding excess of one to the 1:1 equilibrium mixture. This

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(11) For mixed complexes, ΔF can be determined by evaluating a_i values in a temperature range in which eq. 4 applies and then calculating ΔF from contact shift measurements in a range in which eq. 6 applies. In cases where neither R group is *t*-Bu, those high temperatures at which eq. 4 applies cannot be obtained in the n.m.r. experiments. When R is *t*-Bu, lowering of temperature shifts the equilibrium only very slightly toward the diamagnetic side and also produces small concentrations of associated species[2,6,7] which tend to vitiate[2] contact shift measurements made to determine ΔF.

(12) The contact shifts of fully paramagnetic associated Ni(II)–salicylaldimine complexes are apparently somewhat less at room temperature then those of the tetrahedral complexes[6c]; much smaller contact shifts are also exhibited by monomeric octahedral Ni(II)–salicyaldimine complexes (A. Chakravorty, J. Fennessey, and R. H. Holm, *Inorg. Chem.*, in press).

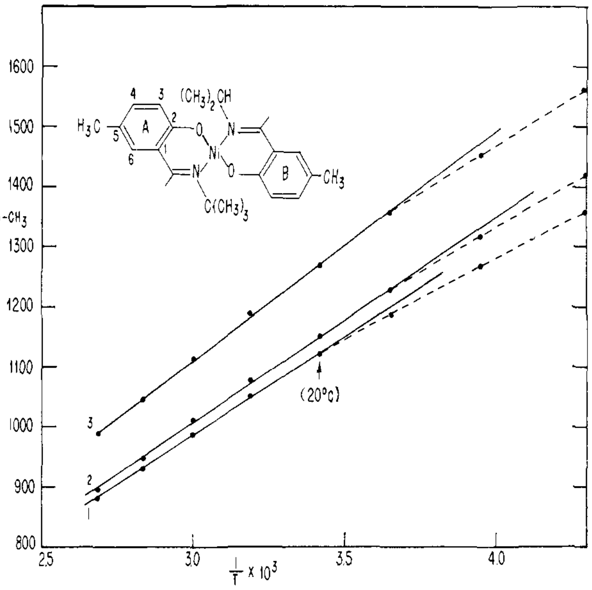

Fig. 3.—Plot of the temperature dependence of the contact shifts of the 5-CH_3 groups in the pure *t*-Bu(5-CH_3) complex (1) and the mixed *t*-Bu(5-CH_3)–*i*-Pr(5-CH_3) complex (2, ring A; 3, ring B) from −40 to 100° in $CDCl_3$.

leaves the assignment of the remaining signals to the individual rings A and B. From an examination of a large number of mixed complexes, it has been definitely established that methyl substitution on A has little effect on the contact shifts of B but a marked effect on the shifts of A, and *vice versa*. This behavior has allowed the asssignment of all signals (except 6-H[13]) in all mixtures to be made with confidence by means of a coordinated comparison with the spectra of variously substituted mixtures. In the present example, examination of *t*-Bu(4-CH_3)-*i*-Pr(H) permits ready assignment of $(4\text{-H})_A$ and $(4\text{-H})_B$. The remaining unassigned features of the mixed complex are present in an upfield group of four resolved bands. The first of these (equivalent to that at 1227 c.p.s.) is absent in the spectrum of *t*-Bu(5-CH_3)-*i*-Pr(H) and is assigned to $(5\text{-H})_A$. In the spectrum of *t*-Bu(H)-*i*-Pr(5-CH_3) the most upfield feature (equivalent to that at 1358 c.p.s.) persists but is revealed as a broad (width at half-height ~15 c.p.s.) signal decreased in intensity. The 1358 c.p.s. signal therefore contains $(5\text{-H})_B$ and one 3-H signal, which is broadened by its proximity to the metal. The spectrum of *t*-Bu(3-CH_3)-*i*-Pr(H) shows that the A signals are displaced to ~100 c.p.s. higher field (in that mixture) than the B signals, which are resolvable with a separation of 13 c.p.s. This shows that $(3\text{-H})_B$ and $(5\text{-H})_B$ have nearly the same chemical shifts and are assigned at 1358 c.p.s. in the present case. The remaining signal, $(3\text{-H})_A$, may be observed under high resolution as a broad shoulder at 1250 c.p.s. These assignments can be confirmed by examining the spectrum of *t*-Bu(H)-*i*-Pr(3-CH_3). The spectra of the methylated mixed complexes are considerably easier to assign and examples are given in Fig. 5 and 6. The assignments of the spectra of other mixed complexes were made by an analogous procedure of comparison and are given in Table II. Not all of the mixed complexes required for these assignments are included, however.

Table I

Contact Shifts and Spin Densities in Bis(N-*t*-butylsalicylaldimine) Complexes[a]

X	Position	Contact shift, c.p.s.[b]	Spin density
H	3	+1711	+0.0110
	4	−1437	−0.00943
	5	+1668	+0.0107
3-CH_3	3	−1143	
	4	−1690	−0.0111
	5	+1826	+0.0117
4-CH_3	3	+1625	+0.0104
	4	+ 795	
	5	+1749	+0.0112
5-CH_3	3	+1758	+0.0113
	4	−1357	−0.00891
	5	−1079	

[a] Data for 6-H are not included separately; in each case $\Delta f_{6H} \leq 80$ c.p.s. giving $\rho_{6C} \leq -0.0005$. [b] Positive contact shifts measured at 24°, negative shifts at 31°, in $CDCl_3$ solution.

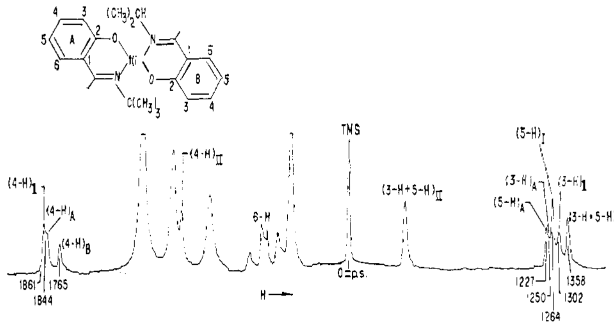

Fig. 4.—Proton resonance spectrum of the mixed complex *t*-Bu(H)–*i*-Pr(H) and its pure components in $CDCl_3$ at 25°: frequencies are the chemical shifts; I refers to the pure *t*-Bu(H) and II to the pure *i*-Pr(H) complex.

Spin Density Distributions.—An accurate comparison of spin densities of the *t*-Bu–*i*-Pr mixed complexes with those of both pure components is not possible due to the experimental errors inherent in the determination of spin densities (estimated error ±5%) in the *i*-Pr series,[2] and the small spin density changes in the mixed complexes. Meaningful comparisons can be made between the pure *t*-Bu and mixed complexes since the errors in these cases are no larger than errors (<1%) in the contact shift measurements. Data for the pure *t*-Bu complexes are given in Table I. Results of individual spin density determinations in the mixed complexes are found in Table II together with the contact shifts of protons and methyl groups at the 3-, 4-, and 5- positions of rings A and B. Table III lists the *estimated* total spin densities per ring together with the sum total of these per complex. The 6-H signals could not be accurately assigned[13] and, consequently, an upper limit of −100 c.p.s. was assumed in every case resulting in the inclusion of $\rho_{6C} = -0.0006$ in the totals for each ring.

The mixture with $X_A = X_B = H$ is considered first. It is seen that the spin density has redistributed itself such that positive spin density is definitely lost on ring A and probably gained on ring B (*cf.* ref. 2) compared to the pure components, but that the total spin density is, within experimental error, between the totals of the pure components. These results tend to indicate that the total amount of spin delocalized over the two rings by metal–ligand π-bonding is approximately the same

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[13] The contact shifts of 6-H are so small in pure[2] and mixed complexes that it is difficult to distinguish the signals for RR and R'R' from those for RR'.

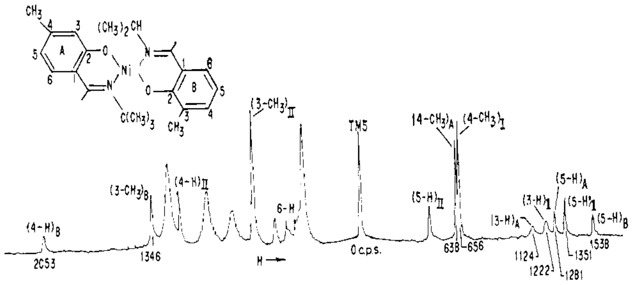
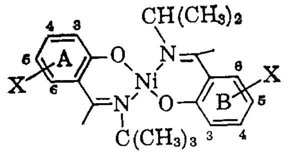


Fig. 5.—Proton resonance spectrum of the mixed complex *t*-Bu(4-CH_3)–*i*-Pr(3-CH_3) and its pure components in $CDCl_3$ at 25°: frequencies are the chemical shifts; I refers to the pure *t*-Bu(4-CH_3) and II to the pure *i*-Pr(3-CH_3) complex.

as in the pure complexes ($\sim ^1/_{15}$ of an unpaired spin[2]), and only the distribution per ring has been altered.

TABLE II

CONTACT SHIFTS AND SPIN DENSITIES IN MIXED ISOPROPYL–*t*-BUTYL COMPLEXES[a]



X_A	X_B	Position	Contact shift, c.p.s. A	Contact shift, c.p.s. B	Spin density A	Spin density B
H	H	3	+1660	+1768	+0.0106	+0.0113
		4	−1420	−1341	−0.00931	−0.00880
		5	+1631	+1762	+0.0105	+0.0113
3-CH_3	H	3	−1150	+1719		+0.0111
		4	−1738	−1310	−0.0114	−0.00859
		5	+1816	+1729	+0.0116	+0.0111
4-CH_3	H	3	+1581	+1751	+0.0101	+0.0112
		4	+ 783	−1327		−0.00871
		5	+1715	+1749	+0.0110	+0.0112
5-CH_3	H	3	+1719	+1758	+0.0111	+0.0113
		4	−1357	−1327	−0.00890	−0.00871
		5	−1123	+1751		+0.0112
H	3-CH_3	3	+1607	−1215	+0.0103	
		4	−1372	−1642	−0.00900	−0.0108
		5	+1601	+1955	+0.0103	+0.0125
H	4-CH_3	3	+1640	+1705	+0.0105	+0.0109
		4	−1400	+ 901	−0.00918	
		5	+1617	+1831	+0.0104	+0.0117
H	5-CH_3	3	+1636	+1836	+0.0105	+0.0118
		4	−1397	−1294	−0.00916	−0.00849
		5	+1617	−1238	+0.0104	
3-CH_3	3-CH_3	3	−1143	−1206		
		4	−1670	−1590	−0.0110	−0.0104
		5	+1766	+1909	+0.0113	+0.0122
4-CH_3	4-CH_3	3	+1566	+1694	+0.0100	+0.0109
		4	+ 781	+ 898		
		5	+1704	+1820	+0.0109	+0.0117
5-CH_3	5-CH_3	3	+1702	+1821	+0.0109	+0.0117
		4	−1344	−1275	−0.00881	−0.00836
		5	−1113	−1225		

[a] Positive contact shifts measured at 24°, negative shifts at 31°, in $CDCl_3$ solution.

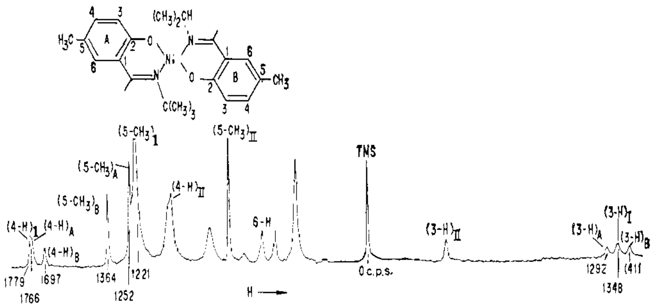


Fig. 6.—Proton resonance spectrum of the mixed complex *t*-Bu(5-CH_3)–*i*-Pr(5-CH_3) and its pure components in $CDCl_3$ at 25°: frequencies are the chemical shifts; I refers to the pure *t*-Bu(5-CH_3) and II to the pure *i*-Pr(5-CH_3) complex.

Similar conclusions are reached by comparisons involving the symmetrically substituted X = 3-, 4-, and 5-CH_3 mixed complexes. Methyl substitution on one ring has a negligible effect on the spin densities in the other ring, but clearly perturbs the distribution in the substituted ring. This situation makes highly improbable a correct evaluation of Q_{CCH_3}, which is needed to obtain the total spin density in the substituted ring, by assuming that $\rho_C(C\text{–}CH_3)$ is the same as $\rho_C(C\text{–}H)$. In the pure complexes $a_{CH_3}(i\text{-Pr}) > a_{CH_3}(t\text{-Bu})$ although $a_H(i\text{-Pr}) \cong a_H(t\text{-Bu})$, indicating a real dependence of the methyl coupling constants of the R group. We have attempted to estimate total spin densities in ring-substituted mixed complexes as follows. In the pure complexes with X = CH_3 or H the total spin density per ring was assumed the same. Values of ρ_C at the substituted positions were calculated and Q values obtained from the measured coupling constants. The Q_{CCH_3} values used for the mixed complexes were taken to be the means of the Q values for the pure complexes obtained in this way, and were applied at corresponding positions in rings A and B. While this procedure is only approximate it does show that the asymmetry in spin density distributions is maintained in the substituted derivatives and that spin is consistently lost from ring A. Indeed, the use of the same Q_{CCH_3} values for A and B will tend to minimize real differences in the total spin densities of the two. It is concluded that the individual and total changes in spin densities in the mixed complexes compared to the pure components is a real and general effect.

TABLE III

ESTIMATED TOTAL SPIN DENSITIES IN RINGS A AND B OF MIXED ISOPROPYL–*t*-BUTYL COMPLEXES

X_A	X_B	$\Sigma\rho_A$[a]	$\Sigma\rho_B$[a]	$\Sigma(\rho_A + \rho_B)$
H	H	+0.0112	+0.0132	+0.0244
3-CH_3	H	0.0105	0.0130	0.0235
4-CH_3	H	0.0112	0.0131	0.0243
5-CH_3	H	0.0113	0.0132	0.0245
H	3-CH_3	0.0110	0.0126	0.0236
H	4-CH_3	0.0111	0.0113	0.0224
H	5-CH_3	0.0111	0.0132	0.0243
3-CH_3	3-CH_3	0.0105	0.0126	0.0231
4-CH_3	4-CH_3	0.0111	0.0114	0.0225
5-CH_3	5-CH_3	0.0109	0.0131	0.0240
R = $CH(CH_3)_2$, X = H		0.0105	0.0105	0.0210 ± 0.0040[b]
R = $C(CH_3)_3$, X = H		0.0116	0.0116	0.0232 ± 0.0010[b]

[a] Includes estimated upper limit of −0.0006 for ρ_{6C}. [b] Estimated uncertainty due to experimental error.

A mixed ligand-Ni(II) complex of the aminotroponeiminates has been obtained by Eaton, *et al.*,[14] in which the nitrogen substituents are ethyl and *p*-chlorophenyl. Contact shift studies of this species have shown that the spin density distributions in the two seven-membered rings are asymmetric, and that the spin density decrease on one ring is equal to the increase on the other with the total spin density nearly the same as for the pure components. They estimate 0.11 unit of spin on one ring and 0.09 unit on the other. The behavior of this mixed complex is therefore similar to that of mixed

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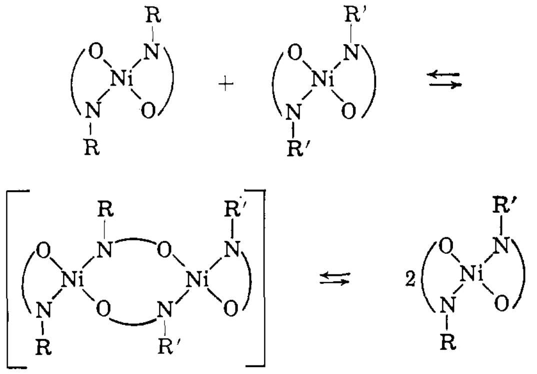
(14) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Discussions Faraday Soc.*, **34**, 77 (1962).

salicylaldimine complexes. The small spin density redistributions in the latter complexes prevent a meaningful evaluation of the fractional unpaired spin per ring.

An interesting explanation of the cause of the asymmetric spin density distributions in the above mixed ligand aminotroponeiminate has recently been proposed by Lin and Orgel.[15] They find that in order to explain this effect, it is necessary to assume that, of the two possible ground states, ^3E (configuration $e^3b_2^1$) and $^3A_2$-($b_2^2e^2$), the doubly degenerate ^3E state is lowest in the pure complexes (symmetry D_{2d}), and in the mixed complex (symmetry C_{2v}) is reduced to the nondegenerate $^3B_1(b_2^2b_1^1a_1^1)$ ground state. The $a_1(d_{x^2-y^2})$ orbital is σ-bonding only and the $b_1(d_{xz})$ orbital can π-bond with only one chelate ring. The spin density asymmetry is partially averaged to the observed values by the rapid structural change and the effect of spin-orbit coupling which mixes in a fraction of the $^3B_2(b_2^1b_1^2a_1^1)$ state. If this explanation is correct for the aminotroponeiminates, the salicylaldimines offer an interesting extension of its applicability. In the tetrahedral form these pure complexes have only C_2 (pseudo-C_{2v}) symmetry, and the spin density distribution over both rings is symmetric. In the present model this result argues in favor of the $^3A_2$ ground state rater than ^3E, since both b_1- and b_2-orbitals (d_{xz} and d_{yz}) can π-bond equally with the chelate rings in the *yz* and *xz* planes, respectively. In the mixed salicylaldimine complexes the spin density asymmetry must have a different origin, however, since degeneracy of π-bonding metal orbitals is already absent in the pure complexes. The origin of the observed asymmetry is undoubtedly complex but may arise in part from what is most simply described as a steric interaction between the *t*-Bu and *i*-Pr groups and the adjacent halves of the molecule. Such an interaction in the planar configuration is most unfavorable when R = *t*-Bu (>95% tetrahedral form at room temperature) and is believed responsible for the existence of the tetrahedral form.[4a] In the *t*-Bu–*i*-Pr mixed complexes, these interactions may further persist in that range of dihedral angle between the chelate rings in which the triplet state is lowest and can be expected to be slightly different for R_A and R_B. It is observed that spin density is lost from ring A and (presumably) gained by ring B, and it is inferred that the *t*-Bu interaction disposes its chelate ring less favorably for spin transfer *via* π-bonding with one of the b-orbitals than does the *i*-Pr interaction. Examination of other mixed complexes with R_B = 3-pentyl, *sec*-butyl, 3-methyl-2-butyl, reveals the same direction of spin density asymmetry.

Process of Ligand Exchange.—The exchange of coordinated and free ligands[16–21] as well as the exchange of coordinated and free metal ions[22] has been observed in four-coordinate chelate complexes, most of which are of the salicylaldimine type.[17–22] However, ligand-exchange reactions in these and other[23] cases have consistently been studied in systems containing the complex and the free ligand, and in the presence of solvents which are themselves capable of coordination. The exchange reactions observed here are unique in that they occur in the absence of any added ligand and in solvents (chloroform and toluene) of low dielectric constant which are devoid of any significant coordinating ability. Mechanisms requiring solvent assisted ligand dissociation and solvation of intermediates are unlikely.

The rate of ligand exchange is too rapid ($t_{1/2}$ < 3 min.) to permit accurate rate measurements by n.m.r. However, several observations have been made which are suggestive of the mechanism of exchange. Ligand exchange has been observed to occur at approximately the same rate and to the same extent between any pair of bis(salicylaldimine)nickel(II) complexes[2,4a] which are wholly or partially in the tetrahedral form. Greatly reduced ligand exchange is observed between any one of these complexes and a planar essentially diamagnetic complex[7,24]; for example, the complexes *t*-Bu(5-CH_3) and *n*-Pr(5-CH_3) exhibited negligible exchange in 60 min., during which time ligand exchange between tetrahedral complexes is complete. This observation of increased ligand lability in paramagnetic over diamagnetic complexes has been made previously with respect to octahedral and planar nickel complexes.[19] A proton-catalyzed exchange process of the type $NiL_2 + HL' \rightleftharpoons NiLL' + HL$ cannot be completely eliminated, but is rendered highly unlikely since the same rate and extent of exchange was observed in rigorously dry toluene as in commercial $CDCl_3$. The facilitation of exchange by the presence of associated species is ruled out by the occurrence of exchange at 100° as well as 25°. It is concluded that the primary path of exchange involves the direct bimolecular collision of two



paramagnetic tetrahedral complexes. The activated complex may rupture two Ni–N or two Ni–O bonds giving the mixed complex or the pure components, respectively. Since the same number of these bonds are made and broken in the formation of the mixed complex, $\Delta H \sim 0$ and $\Delta F \cong -T\Delta S$. The equilibrium position will depend principally on the entropy of mixing, which for equimolar concentrations of the pure components at 25° leads to $\Delta F = -828$ kcal./mole and $K = 4$. Equilibrium concentrations in several typical mixtures measured by integration of proton resonance signals are in agreement with this treatment.

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