TABLE IV

THERMODYNAMIC PARAMETERS FOR METAL–BIPYRIDINE[a] AND –TERPYRIDINE[b] COMPLEXES AT 25°

Metal ion	Ligand	Log K_1	$-\Delta H_1$	Log β_n[c]
Mn^{2+}	bipy	2.6	3.5	
	terpy	4.4	5.7	
Fe^{2+}	bipy	4.3	(6.0)[d]	17.5
	terpy	7.1	8.0	20.9
Co^{2+}	bipy	5.7	8.2	16.1
	terpy	8.4	10.7	18.3
Ni^{2+}	bipy	7.1	9.6	20.1
	terpy	10.7	9.5	21.8
Zn^{2+}	bipy	5.2	7.1	
	terpy	6.0	10.1	
Cd^{2+}	bipy	4.3	5.1	
	terpy	5.1	5.5	

[a] Data from ref 11 and 12. [b] $K = k_f/k_d$; $\Delta H = E_f - E_d$. [c] $\beta_n = K_1K_2K_3$ for bipy and K_1K_2 for terpy. [d] Estimated.[12]

diethylenetriamine complexes. The corresponding ratio for the zinc and cadmium complexes is only 1.2, suggesting that terpyridine chelates comparatively more weakly with these metal ions. It is unlikely, however, that they are acting as bidentate ligands only, since the structure of $Zn(terpy)Cl_2$ shows that all three nitrogens coordinate with only minor strain.[13]

Although there are puzzling features which certainly require further examination, nevertheless a good deal of understanding now exists in this particular area. We are turning our attention to solvents other than water as well as metal ions such as chromium(II) and vanadium(II), for which there is a paucity of data.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS,
AND THE UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

The Synthesis, Structures, and Solution Equilibria of Bis(pyrrole-2-aldimino)metal(II) Complexes

BY R. H. HOLM,[1] A. CHAKRAVORTY, AND L. J. THERIOT

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Synthesis of an extensive series of bis(pyrrole-2-aldimino)metal(II) complexes with M(II) = Co, Ni, Pd, Cu, and Zn and various alkyl groups (R) appended to the azomethine nitrogen has been effected by a nonaqueous chelation reaction in tetrahydrofuran. Preliminary single crystal X-ray results for complexes with R = *t*-butyl reveal that cobalt, nickel, and zinc complexes are isomorphous, but appreciable differences in the cell constants of the nickel complex indicate that it is not truly isostructural with the tetrahedral cobalt and zinc complexes. The copper complex exists in two crystalline modifications, neither of which is isomorphous with the Co–Ni–Zn series. Spectral and magnetic studies in solution show that the *t*-butyl cobalt complex is tetrahedral whereas the corresponding copper complex is distorted from planarity to an unknown extent. Copper complexes with less bulky R groups are planar. The *t*-butyl nickel complex is pseudo-tetrahedral; complexes with *sec*-alkyl groups such as isopropyl are involved in a configurational equilibrium between planar and pseudo-tetrahedral forms. The paramagnetic nickel complexes show large isotropic proton hyperfine contact shifts. Spin density calculations for the coordinated ligand system are used as the basis of proton resonance assignments. It is concluded that in the pseudo-tetrahedral form spin imbalance exists in the highest filled ligand π-MO and that in addition there is an underlying spin imbalance in the highest filled σ-MO, the result of which is observable in the proton resonance spectra. Thermodynamic parameters characterizing the structural change have been obtained for the nickel complexes from the temperature dependence of the proton contact shifts. A quantitative comparison of the stabilization of tetrahedral Ni(II) by pyrrole-2-aldimine, salicylaldimine, and β-ketoamine ligand systems is presented.

Introduction

During the past several years efforts in these laboratories have been directed toward an examination of the occurrence of conformational equilibria of metal complexes in solutions of noncoordinating solvents and evaluation of the relative stabilities of the stereoisomers involved. Particular emphasis has been placed on the planar $\rightleftharpoons$ tetrahedral equilibrium of four-coordinate nickel(II) complexes. It is now well established that this equilibrium, while still rare, does persist in four general groups of bis-bidentate nickel(II) complexes, *viz.*, salicylaldimines,[2-4] naphthaldimines,[5] β-ketoamines,[6] and aminotroponeiminates,[7] and is frequently measurably altered in position by changes in solvent, temperature, and substituents appended to the basic ligand structure. In addition to our studies, those of

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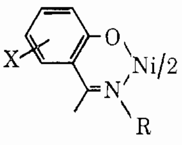
Sacconi, *et al.*,[8,9] have contributed substantially to present knowledge of conformational equilibria, including those involving five- and six-coordinate monomeric species.[4,9]

Configurational equilibria in inert solvents involving complexes other than those of nickel are little known. However, very recently cobalt(II) complexes of functionally substituted salicylaldimines have been found in equilibrium mixtures of octahedral, pyramidal, and tetrahedral structures.[10] The existence of the planar ⇌ tetrahedral equilibrium for certain bis(β-ketoamino) cobalt(II) complexes has now been established.[11]

It is clear from an examination of Stuart–Breigleb metal chelate models that the existence of the tetrahedral configurations of the salicylaldimine and β-ketoamine complexes, **1** and **2**, respectively, is due to a steric interaction of an appropriately chosen R group with the adjoining half of the molecule in the *trans*-planar arrangement. Such an interaction can be alleviated by a torsional motion about the axis bisecting the chelate rings with the consequent formation of a pseudo-tetrahedral structure. Inasmuch as all strictly four-coordinate nickel(II) complexes with common donor atoms such as oxygen, nitrogen, and sulfur are planar and diamagnetic in the absence of any appreciable steric strain, it may be safely concluded that nickel(II) in such complexes is inherently more stable in the singlet, planar configuration. It is of interest to ascertain generally whether or not the tetrahedral configuration can be stabilized relative to the planar one in nickel(II) complexes containing ligand systems quite different from those in **1** or **2** by deliberately imposing steric strain in the planar form. Accordingly, we have examined the complexes **3** (particularly the nickel(II) complexes) derived from N-substituted pyrrole-2-aldimines. In the planar form of such complexes it is readily apparent that a sufficiently bulky R group will suffer substantial steric interaction with 5-H in particular and that this interaction, similar in kind to that in **1** and **2** but necessarily different in detail, might destabilize the planar form such that the free energy difference between the two configurations could be reduced sufficiently to allow population of both at room temperature. This expectation has been realized. In this paper we report the results of detailed study of the configurational equilibria of a number of nickel(II) complexes.



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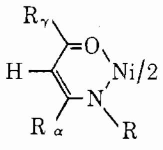

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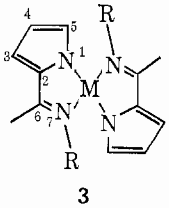

3

The chemistry of bis(pyrrole-2-aldimino) complexes has been little studied and only scant, disparate reports of synthesis exist. Pfeiffer, *et al.*,[12] have prepared the bis Ni(II) and Cu(II) complexes with R = H and the tetradentate complexes of these metals derived from the condensation products of pyrrole-2-aldehyde with ethylenediamine and *o*-phenylenediamine. Tanaka and Yamauchi[13] have reported the synthesis of a wide variety of Cu(II) complexes with R = aryl while Emmert, *et al.*,[14] have prepared the tris Co(III) complex with R = CH_3. Very recently we have reported the preparation of a number of other tris Co(III) complexes with R = alkyl and determined their geometrical configurations by proton magnetic resonance.[15] Early in the present study it was discovered that no one of the several simple synthetic procedures[12–14] was of general utility in preparing bis complexes of Co(II), Ni(II), Cu(II), and Zn(II). Here we report that the nonaqueous chelation technique previously used to prepare hydrolytically unstable complexes[6] provides a general synthetic route to these complexes, as well as those of Co(III).[15] To augment the study of the structures of the nickel complexes, we also report certain spectral, magnetic, and X-ray results on the bis complexes of the above elements. Finally, it is appropriate to point out that the results reported herein may be of some peripheral biochemical interest inasmuch as the pyrrole-2-aldimine group is an isosteric fragment of pyrromethenes and porphyrins.

Experimental Section

Preparation of Compounds.—Pyrrole-2-aldehyde was obtained from Aldrich Chemical Co.

Copper(II) complexes were prepared by the method previously described[12] for the R = H complex by substituting the appropriate primary amine for ammonia. The complexes are prepared in equally good yield by the nonaqueous method described below using $[(C_2H_5)_4N]_2CuCl_4$ as the source of metal ion. The products were purified by recrystallization from dichloromethane–*n*-hexane. All are brown or black crystalline materials except for that with R = *t*-butyl, which is dark green.

Nickel(II) complexes could not be prepared by the aqueous condensation procedure described for the R = H and tetradentate complexes.[12] The complexes with R = alkyl and (to a lesser extent) aryl are hydrolytically unstable and cannot be obtained in the presence of water and base. The complexes were prepared by a previously reported nonaqueous chelation method.[15] Pyrrole-2-aldehyde and the appropriate primary amine were condensed in absolute ethanol by allowing the solution to stand for several hours at room temperature. The solvent was then removed at reduced pressure using a rotary evapo-

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TABLE I

CHARACTERIZATION OF BIS(PYRROLE-2-ALDIMINO)METAL(II) COMPLEXES

			Calcd, %			Found, %		
M	R	Mp,[a] °C	C	H	N	C	H	N
Co	t-C_4H_9	155–157	60.49	7.33	15.68	60.73	7.31	15.79
Ni	C_2H_5[b]	161	55.86	6.03	18.61	55.79	6.06	18.46
Ni	n-C_3H_7	96–98	58.39	6.74	17.03	58.32	7.16	17.06
Ni	i-C_3H_7[c]	148–149	58.39	6.74	17.03	58.31	6.91	16.91
Ni	sec-C_4H_9	121–123	60.53	7.34	15.69	60.67	7.33	15.36
Ni	t-C_4H_9	135–136	60.53	7.34	15.69	60.59	7.32	15.67
Ni	$CH(C_2H_5)_2$[d]	103	62.36	7.85	14.55	62.21	7.96	14.59
Ni	C_6H_{11}[e]	161–162	64.57	7.39	13.69	64.69	7.39	13.79
Ni	$CH_3CHCH_2OCH_3$[f]	127–129	55.55	6.74	14.40	55.32	6.69	14.76
Ni	p-$C_6H_4CH_3$	250 dec	67.79	5.22	13.18	67.68	5.21	13.26
Ni	$CH_3CHCH(CH_3)_2$[g]	76–84	62.36	7.85	14.55	62.24	8.16	14.69
Pd	CH_3	~270	44.95	4.40	17.47	44.82	4.31	17.36
Cu	i-C_3H_7	123–124	57.55	6.64	16.78	57.60	6.73	16.90
Cu	n-C_4H_9	91–92	59.73	7.24	15.48	60.15	7.11	15.35
Cu	t-C_4H_9	155	59.73	7.24	15.48	60.18	7.18	15.43
Zn	i-C_3H_7	94–95	57.24	6.61	16.69	56.99	6.91	16.60
Zn	t-C_4H_9	159–160	59.43	7.20	15.40	58.78	7.21	15.39

[a] Uncorrected. [b] Calcd: Ni, 19.50. Found: Ni, 19.75. [c] Calcd: Ni, 17.84. Found: Ni, 18.06. [d] Calcd: Ni, 15.24. Found: Ni, 14.86. [e] Calcd: Ni, 14.35. Found: Ni, 14.19. [f] Calcd: Ni, 15.09. Found: Ni, 15.04. [g] Calcd: Ni, 15.24. Found: Ni, 14.93.

TABLE II

CRYSTALLOGRAPHIC DATA FOR BIS(N-t-BUTYLPYRROLE-2-ALDIMINO)METAL(II) COMPLEXES[a]

		Cell constants									
M(II)	Space group	a	b	c	α	β	γ	Z	ρ_{obsd}	ρ_{calcd}	V, $Å^3$
Co	Pbcn	17.20	7.18	15.23				4	1.223	1.262	1881
Ni	Pbcn	16.80	7.50	15.42				4	1.197	1.221	1943
Cu (a)	$P4_12_12$ or $P4_32_12$	9.89	9.89	19.08				4	1.280	1.287	1868
Cu (b)	$P1$ or $P\bar{1}$	7.49	11.26	11.73	81° 41′	89° 38′	76° 16′	2	1.254	1.275	950
Zn	Pbcn	17.19	7.23	15.28				4	1.254	1.272	1899

[a] Data obtained by Dr. C.-H. Wei, University of Wisconsin.

rator leaving the crude Schiff base as an oil. Exceptions to this procedure involve the N-methyl and p-tolyl bases which are solids and can be removed from the reaction mixture by filtration. The bases were not further characterized but their proton resonance spectra were in agreement with the expected Schiff base structure. The crude base, potassium t-butoxide, and $[(C_2H_5)_4N]_2(NiBr_4)$ were allowed to react in dry tetrahydrofuran in a 1:1:0.5 mole ratio. After several hours of magnetic stirring at room temperature the reaction mixture was dark brown (violet for R = t-butyl). The reaction mixture was filtered and the filtrate reduced in volume to a dark oil which was extracted several times with dry n-hexane. The extract on concentration deposited a crystalline product which was purified by recrystallization from dichloromethane–n-hexane. Brown to black crystals were obtained except for the R = t-butyl complex, which is dark violet.

Cobalt(II), zinc(II), and palladium(II) complexes were prepared by the procedure used for the nickel(II) complexes. The complexes were purified by recrystallization from dichloromethane–n-hexane. The zinc complexes tend to discolor slowly in air and should be stored under dry nitrogen.

Physical Measurements.—Magnetic susceptibilities, proton magnetic resonance spectra, and optical spectra were determined by the usual methods.[3]

Results and Discussion

Characterization data for all compounds prepared in this work are set out in Table I. With the exception of nickel(II) and copper(II) complexes with R = H, these complexes of general type **3** are rather soluble in nonpolar or weakly polar solvents such as n-hexane, chloroform, and dichloromethane. In solution, complexes of copper(II), palladium(II), and cobalt(II) are unaffected by small amounts of water, whereas the nickel(II) complexes are decomposed slowly to uncharacterized insoluble products, the apparent order of stability being R = aryl $\gg$ n-alkyl > branched alkyl. This is the same stability order found for bis(β-ketoamino)nickel(II) complexes and further illustrates the utility of nonaqueous chelation reactions effected by strong base for the preparation of hydrolytically unstable complexes. Such reactions are of course useful for hydrolytically stable and unstable complexes and have been recently employed using different solvents and bases for the preparation of a number of transition metal complexes derived from weakly acidic parent ligand systems.[6,11,15–17]

X-Ray Results and Solid-State Configurations.—A preliminary single crystal X-ray examination of the cobalt, nickel, copper, and zinc complexes with R = t-butyl has been carried out by Dr. C.-H. Wei. The results are shown in Table II and are to be compared with structural data for the salicylaldimine complexes **1** of these same metals having the bulky R groups isopropyl and t-butyl.[18,19] The cobalt, nickel, and zinc complexes are orthorhombic with space group Pbcn.

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The cobalt and zinc complexes are rigorously isomorphous and presumably have a tetrahedral structure. The clearly different cell constants of the nickel complex indicate a significantly different molecular structure, possibly manifested by a smaller dihedral angle between the (assumed) planar ligands. The copper complex was obtained in two crystalline modifications from *n*-heptane solution, neither of which is isomorphous with the other three complexes. The tetragonal form (a) consists of dark green prisms while the triclinic form (b) was isolated as delicate, light green needles.

In the salicylaldimine series with R = isopropyl the cobalt, nickel, copper, and zinc complexes are isomorphous and the unit cells nearly isometric except for that of the copper complex.[19] The difference almost certainly derives from real differences in molecular configuration; the dihedral angle between ligands is 81° in the nickel complex[20] but only 60° in the copper complex.[21] Replacement of isopropyl by *t*-butyl forces the angle to 80°.[22] In both the pyrrole-2-aldimine and salicylaldimine series, the *t*-butyl group most strongly stabilizes the tetrahedral configuration. The crystal structure dissimilarity between the copper and the other three complexes in the first series is attributed to a much smaller distortion from planarity of the copper complex. Thus it appears that, with a common R group and a given metal, the salicylaldimine ligand system is intrinsically capable of stabilizing in the crystalline phase a higher degree of tetrahedrality than the pyrrole-2-aldimine system. As the following results show, this stability trend obtains in solutions of nickel complexes.

Configurations of Co(II), Ni(II), and Cu(II) Complexes in Solution.—The pyrrole-2-aldimino ligand system resembles the salicylaldimine and β-ketoamine systems in that steric strain in a *trans*-planar configuration can be readily varied by structural variation of R. The relative tendencies of these ligands to stabilize the planar and tetrahedral configurations of several metal(II) complexes, particularly those of nickel, will be considered in this and the following section. Brief comparisons of the electronic properties will also be made. For these purposes reference is made to Tables III and IV and Figures 1–3.

TABLE III

MAGNETIC MOMENTS IN SOLID AND SOLUTION PHASES[a]

		Solid[b]	Solution	
M	R	μ_{eff}, BM	Solvent	μ_{eff}, BM
Co	*t*-C_4H_9	4.67	Toluene	4.74 ± 0.04
Ni	*n*-C_3H_7	Dia	$CHCl_3$	~0
Ni	*i*-C_3H_7	Dia	$CHCl_3$	1.28 ± 0.25
Ni	*sec*-C_4H_9	Dia	$CHCl_3$	1.31 ± 0.25
Ni	*t*-C_4H_9	3.30	$CHCl_3$	3.29 ± 0.05
Ni	$CH(C_2H_5)_2$	Dia	$CHCl_3$	1.51 ± 0.15
Ni	C_6H_{11}	Dia	$CHCl_3$	0.80 ± 0.40
Ni	$CH_3CHCH_2OCH_3$	3.16	...	...
Cu	*i*-C_3H_7	1.82	$CHCl_3$	1.83 ± 0.15
Cu	*n*-C_4H_9	1.84	$CHCl_3$	1.81 ± 0.15
Cu	*t*-C_4H_9	1.98	$CHCl_3$	1.95 ± 0.15

[a] All values obtained at room temperature (23–28°). [b] Accurate susceptibilities of diamagnetic samples not measured.

TABLE IV

ELECTRONIC SPECTRA IN SOLUTION

M	R	Solvent	Frequency, cm^{-1} (extinction coeff[a])
Co	*t*-C_4H_9	Toluene	20,830 (629), 19,610 (600), 17,100 (129), 16,000 (58), 9730 (36), 8330 (28)
Ni	*n*-C_3H_7	Toluene	19,200 (190) sh
	i-C_3H_7	Toluene	18,200 (250) sh, 12,600 (4) sh, 11,000 (2) sh, 6900 (8)
	sec-C_4H_9	Toluene	~18,000 sh, 12,800 (4) sh, 11,000 (2) sh, 6710 (8)
	t-C_4H_9	Toluene	18,180 (420), 12,500 (17), 10,900 (9) sh, 6370 (32)
	$CH_3CHCH_2OCH_3$	Toluene	20,000 (150) sh, 17,700 (80) sh, 9620 (22), 6800 sh
Cu	*n*-C_4H_9	$CHCl_3$	24,400 (1100) sh, 18,940 (240)
	i-C_3H_7	$CHCl_3$	24,400 (~1100) sh, 18,600 (240)
	t-C_4H_9	$CHCl_3$	23,530 (1120), 15,500 (250)

[a] Apparent values, uncorrected for background absorption, are given; values are l. mole^{-1} cm^{-1}.

The only cobalt(II) complex which could be prepared is that with R = *t*-butyl. Reaction in air using 1:2 mole ratios of metal to ligands with less bulky R groups such as isopropyl, *sec*-butyl, and ethyl led to the tris Co(III) complexes which have been shown to exist as the *trans* stereoisomers in solution.[15] That the *t*-butyl complex has the expected tetrahedral structure in noncoordinating solvents is evidenced by the substantial orbital contribution to the magnetic moment (4.7 BM) and the electronic spectrum. The visible band, whose components lie in the 16,000–21,000 cm^{-1} region, is by virtue of its intensity and shape[23] the ν_3 transition in idealized tetrahedral symmetry ($^4A_2 \rightarrow {}^4T_1(P)$). Bands at 8330 and 9730 cm^{-1} are assigned as components of ν_2 ($^4A_2 \rightarrow {}^4T_1$), a transition frequently split even in complexes of the CoX_4^{2-} type which more closely approach T_d symmetry. The splitting of ν_2 in bis(salicylaldimine) and -(β-ketoamine) complexes (components at ~8000 and ~11,000 cm^{-1})[11,24,25] presumably reflects the lower effective ligand field symmetry of the Co–O_2N_2 *vs.* the Co–N_4 coordination sphere. The magnetic moment of the Co–N_4 complex is considerably larger than those of Co–O_2N_2 complexes (4.3–4.5 BM[11,24,26]) even though Δ_t is approximately the same for both types of complexes (estimated at 5500 ± 500 cm^{-1}), a situation not anticipated by the simple ligand field model for tetrahedral Co(II)[23] and prob-

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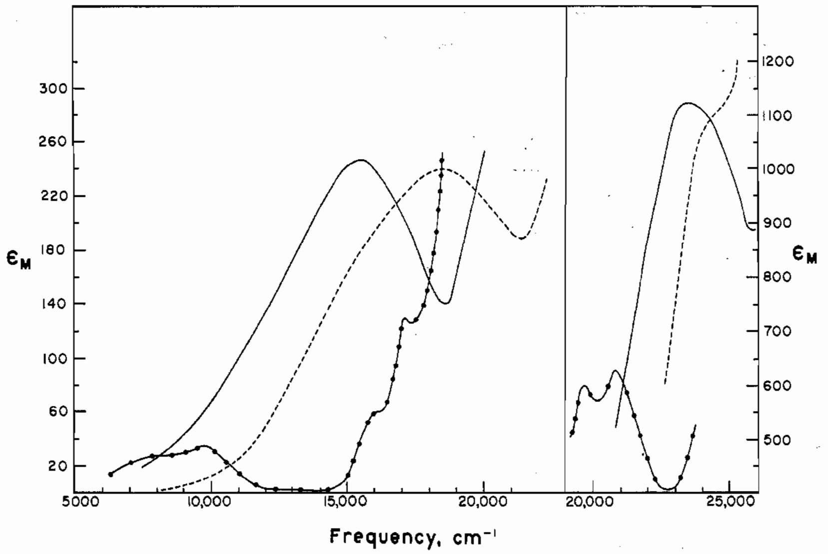

Figure 1.—Electronic spectra of bis(N-R-pyrrole-2-aldimino)metal(II) complexes in solution at 25°: ———, M = Cu(II), R = t-C_4H_9 in chloroform; ---------, M = Cu(II), R = i-C_3H_7 in chloroform; —●—●—●—, M = Co(II), R = t-C_4H_9 in toluene.

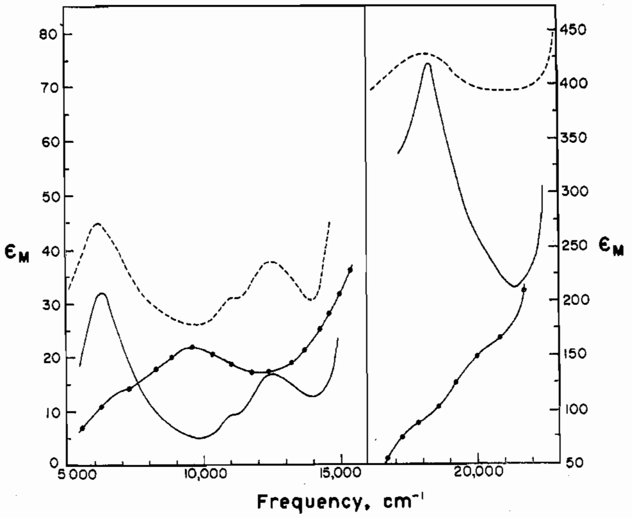

Figure 2.—Electronic spectra of bis(N-R-pyrrole-2-aldimino)-nickel(II) complexes at 25°: ———, R = t-C_4H_9 in toluene; ---------, R = t-C_4H_9 in Nujol mull (the ordinate is relative absorbance); —●—●—●—, R = $CH_3CHCH_2OCH_3$ in toluene.

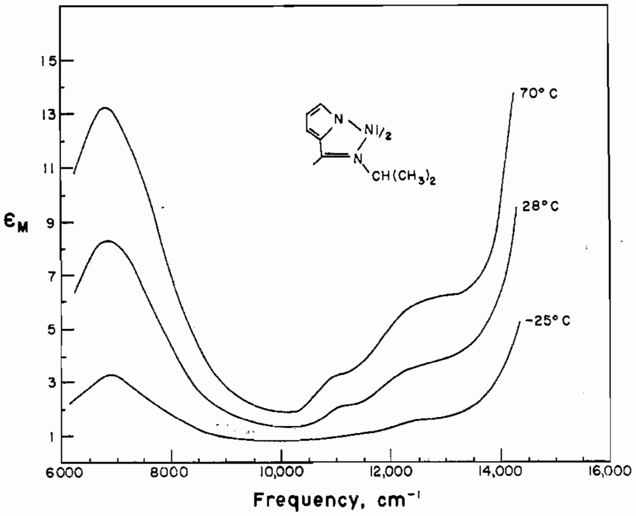

Figure 3.—Temperature dependence of the spectrum of bis(N-isopropylpyrrole-2-aldimino)nickel(II) in toluene.

ably caused by different degrees of distortion. The observed moment is very close to that (4.67 BM) of a tetrahedral bis(pyrromethene)cobalt(II) complex.[27]

The spectral and magnetic properties of the R = isopropyl and n-butyl copper(II) complexes are nearly identical and undoubtedly correspond to planar or essentially planar structures. However, in the t-butyl complex the magnetic moment is definitely larger in both the solid and solution phases, and the only absorption feature which can be assigned on the basis of its intensity as a ligand field transition undergoes a red shift of ~3000 cm^{-1}. These changes are extremely similar to those observed for salicylaldimine complexes in which R is varied in an identical manner[28] and are in the proper direction for a planar → pseudo-tetrahedral distortion. Bis(salicylaldimino)copper(II) complexes with R groups other than branched alkyl have been established to the planar, whereas the isopropyl and t-butyl complexes are increasingly distorted toward full tetrahedrality (*vide supra*). The spectral and magnetic data for the t-butyl copper complex **3** do not allow a distinction between a rapid configurational equilibrium involving planar and pseudo-tetrahedral structures, such as is found with certain nickel complexes (*vide infra*), and the presence of a single structural species. However, we have found that the isopropyl complex, brown as crystals and in solution, can be cocrystallized in small amounts with the analogous zinc complex (very light yellow crystals) to give green crystals whose color resembles that of the t-butyl copper(II) complex, which is green in both the solid and solution. The mull spectrum of the mixed crystal reveals a weak band at 15,700 cm^{-1} which is believed to be the counterpart of the 15,500 cm^{-1} band found in solutions of the t-butyl copper complex. It is concluded that the latter complex exists as one structural species in solution,

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[27] D. R. Eaton and E. A. LaLancette, *J. Chem. Phys.*, **41**, 3534 (1964).

[28] L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Inorg. Nucl. Chem.*, **19**, 73 (1963); L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, 276 (1964).

viz., pseudo-tetrahedral, and it is inferred from previous work[28] that in copper complexes of the bis-chelate type, only very large distortions from planarity, approaching a dihedral angle of 90°, can be recognized from susceptibility and spectral measurements.

The nickel(II) complexes have been the most extensively studied. The dependence of solution configurations on the steric properties of R definitely resembles the situation found in the salicylaldimine[2,3,8] complexes in that for both groups at room temperature no detectable tetrahedral form is present when R = *n*-alkyl and no detectable planar form when R = *t*-butyl. Furthermore, when R is a secondary alkyl group such as isopropyl, both configurations are measurably populated. Evidence of these solution configurations is now summarized.

Nickel complexes with R = ethyl and *n*-propyl retain their planar diamagnetic structures in solution as evidenced by magnetic susceptibility and proton measurements, the latter showing the absence of contact shifts expected for a paramagnetic nickel(II) complex.[3-7] Their solution spectra show no features in the visible region other than a shoulder at 19,200 cm^{-1}, believed to be the lowest energy spin-allowed transition, which is superimposed on a steeply rising absorption curve extending into the ultraviolet region. The properties of the *p*-tolyl complex are entirely similar and give no evidence for the strong molecular association found in solutions of the N-arylsalicylaldimine complexes.[29] The monomeric structure of the representative *n*-propyl complex was verified by osmometry in benzene at 37° (calcd mol wt 329, found 335).[30]

The *t*-butyl nickel complex **3** has in solution a magnetic moment and electronic spectrum in accord with the presence of only the tetrahedral form. The moment of 3.30 BM, while considerably lower than predicted and occasionally found for idealized tetrahedral nickel(II), is virtually identical with that of its salicylaldimine analog,[3,8] whose pseudo-tetrahedral structure is firmly established.[8] However, this moment is clearly in the range for tetragonal[31] or quasi-octahedral[8,29] structures as well. The pseudo-tetrahedral structure is readily proven by the ligand field spectra in the solid and in solution (*cf.* Figure 2). These spectra are virtually identical and consist of a band at $\sim$6400 cm^{-1} (ν_2), a very weak feature at $\sim$11,000 cm^{-1}, and at least two bands in the region 12,500–18,200 cm^{-1} (ν_3). They are convincingly similar in both band positions and relative intensities to the pseudo-tetrahedral salicylaldimine[2,8] and β-ketoamine[6] complexes and may be assigned similarly: ν_2, ${}^3T_1 \rightarrow {}^3A_2$; $\sim$11,000 cm^{-1}, ${}^3T_1 \rightarrow {}^1D$; ν_3, ${}^3T_1 \rightarrow {}^3T_1(P)$. Δ_t may be estimated[32] as 2800 cm^{-1}, compared with $\sim$3100 cm^{-1} for the salicylaldimines.[2] The pronounced splitting of ν_3 has been previously observed[2,8] and presumably arises from an effective ligand field of lower than T_d symmetry.

Turning next to the *sec*-alkyl nickel complexes, it is found that in solution their measured moments per nickel are less than 2 BM and that their absorption spectra exhibit features due to the tetrahedral form with ν_2 particularly evident but displaced $\sim$400–600 cm^{-1} toward higher energies compared to the *t*-butyl complex. The absorption feature at $\sim$19,000 cm^{-1} arising from the planar form is not readily observable in the presence of a small percentage of tetrahedral form. The presence of planar form is of course obvious from the magnetic data, which show that this form predominates at room temperature. Molecular weight measurements on the representative isopropyl complex at 37° in benzene (0.03 *M*) yielded 313 *vs.* a calculated value of 329. From these results we conclude that the bis(pyrrole-2-aldimino)nickel(II) complexes of this type are involved in the equilibrium

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

The endothermic nature of this equilibrium is shown by spectral studies of the isopropyl complex at a variety of temperatures. Illustrative results are set out in Figure 3. A temperature increase clearly displaces the equilibrium to the right as evidenced by the intensity increases of ν_2 and the lower energy component of ν_3. Parallel studies have demonstrated the presence of the configurational equilibrium for the following complexes in addition to that with R = isopropyl: *sec*-butyl, 3-pentyl, cyclohexyl, 2-(3-methyl)butyl. The complex with R = $CH_3CHCH_2OCH_3$ shows a markedly different behavior from these five complexes. Spectral and proton resonance results indicate a more complicated solution behavior than that due to equilibrium 1. The absorption maximum at 9620 cm^{-1} (*cf.* Figure 2), whose intensity decreases with increasing temperature, is not assignable to either the planar or tetrahedral forms. On the basis of a previous study of salicylaldimine complexes bearing the same R group,[4] it is concluded that the 9620 cm^{-1} feature is due to a pseudo-octahedral stereoisomer and that an equilibrium involving octahedral, planar, and tetrahedral species obtains in solution.

Spin Delocalization and Contact Shifts in Ni(II) Complexes.—It is now well recognized that an analysis of isotropic contact shifts can yield thermodynamic data for an equilibrium such as (1) and, in the absence of pseudo-contact contributions to the total isotropic shift, provide a description of the unpaired electron spin density in the ligand system.[33] In the limit of no diamagnetic species the contact shift of Δf_i of the *i*th proton is related to the electron–nuclear coupling con-

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[29] R. H. Holm and K. Swaminathan, *Inorg. Chem.*, 1, 599 (1962).

[30] It may be of interest to point out here that we have also investigated the nickel complex **3** with R = CH_3. In chloroform solution it displays a time-dependent proton resonance spectrum with many more lines than reconcilable with a simple monomolecular species. The initial spectrum is itself quite dependent on the method of crystallization of the complex, which apparently exists in two different crystalline modifications. Associative equilibria appear to be involved because the solution obtained from one preparation yielded a molecular weight of 323 (benzene, 0.04 *M*, 37°; calcd mol wt 273). The resonance shifts observed in various solutions do not at present indicate the formation of any appreciable amount of paramagnetic solute. A thorough investigation of the solution behavior of this complex will be reported subsequently (A. Chakravorty, work in progress).

[31] A. B. P. Lever, *Inorg. Chem.*, **4**, 763 (1965).

[32] A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959).

[33] D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962), and subsequent papers.

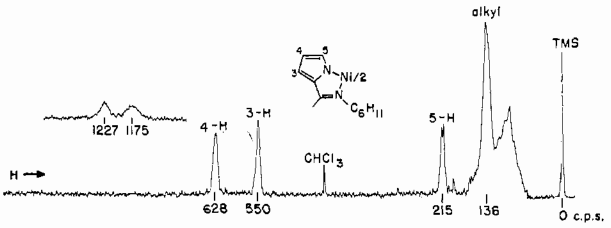

Figure 4.—Proton resonance spectrum of bis(N-cyclohexylpyrrole-2-aldimino)nickel(II) in $CDCl_3$ at 60 Mc and 25°. Frequencies are the chemical shifts.

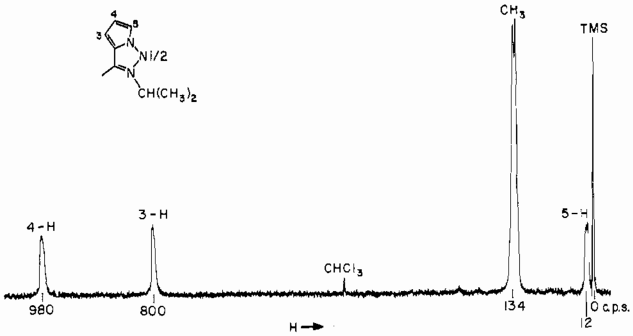

Figure 5.—Proton resonance spectrum of bis(N-isopropylpyrrole-2-aldimino)nickel(II) in $CDCl_3$ at 60 Mc and 25°. Frequencies are the chemical shifts.

stant a_i by the equation

$$\frac{\Delta f_i}{f} = -a_i\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g\beta S(S+1)}{6SKT} \qquad (2)$$

in which the remaining symbols have their usual meanings.[3,7,33] If to a good approximation the spin density exists in the π or the σ portions of the ligand system, it may be evaluated by the relations $a_i = Q^\pi{}_{CH}\cdot\rho^\pi{}_{C_i}$ or $a^\sigma{}_i \approx P_H\rho^\sigma{}_{H_i}$. For five- and six-numbered ring radicals Q_{CH} varies between -23 and -30 gauss;[34] $P_H = 508$ gauss, the hyperfine splitting constant of the hydrogen atom.[35]

Representative proton resonance spectra are shown in Figures 4 and 5. Equation 2 applies only to the *t*-butyl complex. Studies of the temperature dependences of the contact shifts of the remaining five complexes reveal a more complicated behavior than the simple Curie dependence of eq 2 and can be interpreted in terms of the presence of equilibrium 1 with a large proportion of planar form present (*vide infra*). Coupling constants for the *t*-butyl complex were calculated from the observed shifts using eq 2 and the results are set out in Table V. It is assumed that, like other pseudo-tetrahedral Ni–N_4 complexes,[33] the pyrrole-2-aldimines have negligible pseudo-contact shifts.

Considered first are the assignments of the signals of the four nonequivalent protons in **3**. Unambiguous assignment could very probably be accomplished by systematic substitution at positions 3–6 by methyl or some other group. Unfortunately, many appropriately substituted pyrrole-2-aldehydes do not readily condense with primary amines to form Schiff bases under ordinary conditions so that a chemical verification of the assignments proposed below has not been possible.[36]

TABLE V

CONTACT SHIFTS AND COUPLING CONSTANTS OF NICKEL(II) COMPLEXES IN CHLOROFORM SOLUTION

R	Position	Δf_i, cps[a]	a_i, gauss
t-C_4H_9	3	$-2{,}742$	0.394
	4	$-4{,}057$	0.583
	5	$+3{,}386$	-0.487
	6	$-10{,}350$	1.488
i-C_3H_7	3	-526	
	4	-750	
	5	$+448$	
sec-C_4H_9	3	-518	
	4	-763[b]	
	5	$+503$	
$CH(C_2H_5)_2$	3	-652	
	4	-988	
	5	$+690$	
$CH_3CHCH(CH_3)_2$	3	-290	
	4	-394	
	5	$+266$	
C_6H_{11}	3	-303	
	4	-405	
	5	$+216$	

[a] $\Delta f_i = (f_i)_{obsd} - (f_i)_{dia}$, all measurements relative to tetramethylsilane as an internal standard; $(f_i)_{dia}$ values taken from the spectrum of the R = *n*-propyl complex and are as follows: 3-H, -400; 4-H, -372, 5-H, -390; HC═N, -448 cps. All shifts obtained at 60 Mc/sec and 40° except for R = *t*-C_4H_9, which was measured at 23°. [b] Mean of signals at -747 and -778 cps.

The spectra of the nickel complexes are quite similar in general features. All complexes show a single signal with positive contact shift (upfield), which in the weakly paramagnetic complexes is observed to be split into a spin–spin doublet. In complexes with R = *sec*-alkyl four signals with negative contact shifts (downfield) are observable (*cf.* Figure 4). Counterparts of the two broad signals, which are farthest downfield, have been observed and assigned in the salicylaldimines[3] and in one β-ketoamine complex.[6] Here these features are collectively assigned as C—H (R) and HC═N (6-H) by an analogy permitted by the presence of the common structural feature CH—N—CH and based on relative line widths and large downfield shifts. The *t*-butyl complex exhibits only one such downfield signal (at $-10{,}350$ cps), which is assigned to 6-H. Other protons attached directly to the chelate ring invariably give sharper signals with much smaller contact shifts.[3-6] Accordingly, the remaining two downfield signals and the single upfield signal are assigned to the ring protons 3-H, 4-H, and 5-H in all complexes.

Specific assignment of ring proton signals is not straightforward. Because the ligand is neither even nor odd alternant, no simple valence bond description of spin density can be given other than to note that

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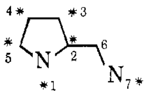
(34) R. W. Fessenden and S. Ogawa, *J. Am. Chem. Soc.*, **86**, 3591 (1964).

(35) R. Bersohn, "Determination of Organic Structures by Physical Methods," Vol. 2, Academic Press, New York, N. Y., 1962, Chapter 9. For a recent treatment of hyperfine splitting in σ radicals and a modified expression for $a^\sigma{}_i$, *cf.* W. T. Dixon, *Mol. Phys.*, **9**, 201 (1965).

(36) The ligand N-*n*-propyl-5-methylpyrrole-2-aldimine was prepared, but only bright green intractable oils were obtained from the nonaqueous chelation reaction.

simple contributing structures may be written placing positive spin density at the starred positions but not at 6-C in the neutral ligand radical **4**. Thus a zero or negative spin density is expected at 6-C and positive or negative spin densities at the remaining C and N positions depending on the extent of spin correlation effects at each position. This situation is entirely similar to that found in the bis(pyrromethene)nickel(II) complexes **5** (X = H, $CO_2C_2H_5$) recently investigated by Eaton and LaLancette.[27] These complexes are likewise rendered tetrahedral by steric effects and have solution moments of 3.3–3.4 BM. Our analysis of proton resonance assignments and spin density distributions is related to that used by Eaton and LaLancette for the complexes **5**. However, the conclusions reached concerning spin density distributions are different for the pyrrole-2-aldimines and pyrromethenes.



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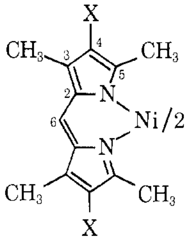

5

In the tetrahedral form two limiting cases of symmetry-allowed metal–ligand π delocalization of spin can be defined.[6,27,37,38] The first case involves donation of spin from the metal dπ orbitals to the lowest vacant MO of the ligand (metal→ligand charge transfer) while the second case requires spin donation from the highest filled ligand MO to a dπ metal orbital (ligand→metal charge transfer). A third possibility is that the donating or accepting ligand orbital be of σ symmetry, for even in idealized tetrahedral nickel(II) complexes, in which the metal has the configuration $e^4t_2^4$, the t_2 orbitals have both σ and π symmetry with respect to ligand bonding. In an actual complex several types of delocalization might be operative, symmetry properties and relative energies of metal and ligand orbitals permitting. In the tetrahedral nickel chelate complexes thus far studied metal→ligand charge transfer[27,37] or ligand→metal charge transfer[3-7,38] appear to be the dominant delocalization paths, with some evidence in β-ketoamine[6] and salicylaldimine[3] complexes of σ contributions to the shifts of HC–N and C–H (R) protons.

To assess the likelihood of the several possible spin delocalization paths, ordinary Hückel (HMO) and extended Hückel[39] (EHMO) calculations were carried out. The results are shown in Table VI. HMO calculations were performed with a set of nitrogen parameters suggested by Streitwieser[40] and with a simpler set[41] not differentiating the two nitrogen atoms and used in calculations on the pyrromethenes.[27] The EHMO parameters used are given in the table; exponents were taken from the tabulation of Clementi and Raimondi.[42] The ligand was assumed planar and the distances were taken to be those in pyrrole and an ordinary azomethine group.[43] All C–H distances were set at 1.1 A and for simplicity the EHMO calculations were performed on the ligand anion with R = H. The orbitals are numbered in the order of increasing stability. The π-electron configuration of the anion is then $\psi_7^2\psi_6^2\psi_5^2\psi_4^2$. Inspection of the eigenvectors of ψ_4 (highest filled π-MO) and ψ_3 (lowest vacant π-MO) reveals that they both have π symmetry with respect to d_{xz} and d_{yz} in the C_2 symmetry of tetrahedral form. On the basis of arguments already given in detail for pseudo-tetrahedral nickel complexes of effective C_{2v} or C_2 symmetry, it appears quite likely that the odd electrons of the metal are best described by the configuration $d_{xz}^1d_{yz}^1$.[44] In the simplest model metal–ligand π interaction will produce a predominant spin imbalance in either ψ_4 or ψ_3.

Table VI

Molecular Orbital Energies of Pyrrole-2-aldimine

HMO		EHMO	
MO	$E, -\beta^a$	MO	E, ev^b
ψ_7	−2.413	ψ_7	−15.312
ψ_6	−1.484	ψ_6	−14.427
ψ_5	−1.177	ψ_5	−12.852
ψ_4	−0.5858^c	σ_{14}	−12.724
ψ_3	0.5212^c	σ_{13}	−12.425
ψ_2	1.336	ψ_4	−12.266
ψ_1	1.803	ψ_3	−9.344
		ψ_2	−6.483
		ψ_1	−4.593

[a] Results obtained with $\alpha_{N_1} = \alpha + 1.5\beta$, $\alpha_{N_7} = \alpha + 0.5\beta$, $\beta_{CN_1} = 0.8\beta$, $\beta_{CN_7} = \beta$. [b] Results obtained with $\alpha(N2s) = -26.92$, $\alpha(N2p) = -13.40$, $\alpha(C2s) = -21.40$, $\alpha(N2p) = -11.40$, $\alpha(H1s) = -13.60$ ev; $\xi(N2s) = 1.924$, $\xi(N2p) = 1.917$, $\xi(C2s) = 1.608$, $\xi(C2p) = 1.568$, $\xi(H1s) = 1.000$. [c] Using $\alpha_N = \alpha + \beta$, $\beta_{CN} = 1.2\beta$, energies are −0.6876 (ψ_4) and 0.6807 (ψ_3).

Energy considerations do not favor delocalization involving ψ_3. The HMO energy of this orbital is -0.5212β or -0.6807β, depending on the parameters employed, and is to be compared with the energy of -0.262β for the analogous orbitals in the pyrromethenes which constitute the only known examples of nickel complexes with metal→ligand charge transfer.[27] Indeed, these energies are near that (-0.6662β[37]) of the lowest vacant MO of the aminotroponeiminates whose complexes are definitely involved in ligand→metal charge transfer. Further, the energy of ψ_4 (0.5858β or 0.6876β) appears slightly more bonding than the top bonding orbital of the aminotroponeiminates (0.3808β[37]).

For further clarification of spin density distributions and spectral assignments of the pyrrole-2-aldi-

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(37) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

(38) D. A. Levy and L. E. Orgel, *Mol. Phys.*, **3**, 583 (1960).

(39) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(40) A. Streitweiser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 5.

(41) L. E. Orgel, T. L. Coltrell, W. Dick, and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

(42) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(43) L. E. Sutton, Ed., "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1959.

(44) A. Chakravorty and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 3999 (1964); D. R. Eaton and W. D. Phillips, *J. Chem. Phys.*, **43**, 392 (1965).

TABLE VII

SPIN DENSITY CALCULATIONS ON THE PYRROLE-2-ALDIMINO GROUP

	$\psi_4{}^a$		$\psi_3{}^a$		$\psi_4{}^d$		$\psi_3{}^d$		EHMO[f]		
Position	HMO	SCF[b]	HMO	SCF[b]	HMO	SCF[b]	HMO	SCF[b]	ψ_4	ψ_3	$\sigma_{14}{}^g$
1	0.0001	−0.1431	0.0691	−0.0034	0.0009	−0.0832	0.0826	0.0818	0.0000	0.1445	. . .
2	0.2518	0.2750	0.0548	0.0122	0.3097	0.3663	0.0133	−0.0545	0.5954	0.0519	. . .
3	0.1103	0.1249	0.1789	0.2329	0.0989	0.1303	0.1512	0.1853	0.2072	0.3868	0.0033
4	0.0944	0.0845[c]	0.0002	−0.0773	0.1157	0.0785[e]	0.0223	−0.0375	0.2853	0.0051	0.0134
5	0.2622	0.3059	0.1850	0.2493	0.3008	0.3742	0.0825	0.0554	0.5710	0.2550	0.0039
6	0.0021	−0.1289	0.2613	0.2621	0.0110	−0.0435	0.4293	0.5574	0.0482	0.7848	0.1793
7	0.2792	0.4817	0.2506	0.3241	0.1629	0.1773	0.2188	0.2123	0.2929	0.3718	. . .

[a] $\alpha_{N_1} = \alpha + 1.5\beta, \alpha_{N\cdot} = \alpha + 0.5\beta, \beta_{CN} = 0.8\beta, \beta_{CN_7} = \beta$. [b] $\lambda = 1.2$. [c] −0.0649 ($\lambda = 1.0$). [d] $\alpha_N = \alpha + \beta, \beta_{CN} = 1.2\beta$. [e] −0.0839 ($\lambda = 1.0$). [f] Tabulated values are the charge densities for two electrons per MO. [g] Refers to protons at the indicated positions.

mines semiquantitative estimates of spin densities in ψ_4 and ψ_3, together with their probable signs, are required. Simple HMO spin densities and HMO–SCF spin densities calculated by McLachlan's method[45] using various parameter sets are given in Table VII. HMO spin densities are of necessity positive. Electron correlation in the HMO–SCF calculations is simulated by allowing α and β spins to occupy separate Hückel orbitals whose Coulomb integrals for the rth atom differ by $2\lambda|C_{or}|^2\beta_{rs}$, in which C_{or} is the coefficient of the π-AO in the MO of the odd spin. The spin densities were calculated from

$$\rho_r = |C_{or}|^2 + \sum_{i \neq 0}(|C_{ir}|^2 - |C'_{ir}|^2) \tag{3}$$

in which C'_{ir} are coefficients of the ordinary Hückel orbitals and the C_{ir} coefficients of the orbitals obtained using the α_r values above. Values of β_{rs} are the same in both calculations. λ is an empirical parameter which has been varied from 1.0 to 1.2, a range previously employed in spin density calculations of heteroatom radicals.[27,46]

Turning to the results in Table VII, it is seen that for a given MO the relative order and signs of the calculated spin densities at some positions vary with the parameters employed. For this reason a rather complete set of calculated results is given. These results are used *only for the purpose of establishing probable relative orders and signs of spin densities in a particular MO.* The calculated spin density patterns in ψ_3 and ψ_4 are quite similar to those in the corresponding orbitals of the pyrromethenes, so that a similar mode of spin delocalization in the present complexes would be expected to lead to related spectra.

Considering calculated spin densities at carbons 3–6, spin imbalance in ψ_4 would be expected to produce a positive contact shift of 5-H and a zero or negative contact shift of 6-H. Signs of the 3-H and 4-H shifts are less reliably indicated because of the small positive values. With $\lambda = 1.0$ negative spin density appears at 4-C but not at 5-C. From these results the order of decreasing positive contact shift appears to be 5-H $\gg$ 3-H $\sim$ 4-H $>$ 6-H. Spin imbalance in ψ_3 would effect positive shifts of 3-H and 6-H and a negative shift of 4-H. Because of the sensitivity of spin density at 5-C to parameter choice, the magnitude of 5-H contact shift is uncertain but its sign appears to be positive. Thus, the observation of one positive and three negative contact shifts is in more satisfactory agreement with ligand→metal charge transfer than the reverse process, a conclusion supported by the preceding consideration of orbital energies.

It is concluded that the upfield signal is 5-H, in agreement with its doublet structure. Still to be rationalized are the downfield shifts of 3-H and 4-H and the extremely large downfield shift of 6-H, all of which are not clearly predictable from the SCF results for ψ_4. Results of an EHMO calculation of the ligand anion are helpful in seeking further clarification of the cause of these shifts. The calculations indicate that two σ-MO's, σ_{14} and σ_{13}, are interleaved in energy between the two highest occupied π-MO's.[47] The σ-MO's are heavily weighted in s, p_x, and p_y orbitals of N_1 and N_7 and can interact with the spin-containing metal orbitals. Assuming that the charge distribution in the ligand when free and complexed is not greatly different, it is seen that there is a large buildup of charge at 6-H relative to the other proton positions in the higher of these σ orbitals. Fractional spin imbalance in this orbital would produce a relatively large positive spin density at this proton and positive spin densities at the other protons as well.[48]

Noting that a unit of σ-spin density at the proton could have an $\sim$20-fold $(P^{\sigma}{}_{H}/Q^{\pi}{}_{CH})$ greater effect on the contact shift than will a unit of π-spin density at the adjoining carbon and that σ-spin densities will effect negative contact shifts, it is proposed that there exist σ contributions of varying magnitudes to the ring proton shifts. The 6-H contact shift attains its large negative value from a small π effect augmented by a large σ contribution. The 5-H shift has the largest positive contribution of any proton from a π effect and the smallest predicted σ contribution so that the net result

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

[46] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795, 2811 (1962); **39**, 609 (1963), and references therein; G. Vincow, *ibid.*, **38**, 917 (1963); W. C. Lin and C. A. McDowell, *ibid.*, **39**, 848 (1963).

[47] EHMO calculations on pyridine, methylpyridines, and certain chelating azines indicate that a σ-MO is either the highest filled or one of the two or three highest filled orbitals [R. Hoffmann, *J. Chem. Phys.*, **40**, 2745 (1964); R. H. Holm and G. W. Everett, Jr., unpublished work]. Delocalization of spin in σ-MO's is observable in tetrahedral and octahedral Ni(II) pyridine complexes [J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963); R. H. Holm, G. W. Everett, Jr., and W. DeW. Horrocks, *J. Am. Chem. Soc.*, **88**, 1071 (1966)].

[48] Squares of EHMO coefficients do not correspond to the usual definition of spin densities since their sum for a given orbital is not 1 because of the inclusion of overlap. For the present purpose we use charge densities or gross atomic populations in a given occupied MO which sum to 2 and generally run parallel to the squares of coefficients.

is a positive shift. The 3-H and 4-H protons are shifted downfield; the π-spin density at 4-C appears not to be significantly larger than that at 3-C and is rendered negative by varying λ (*cf.* Table VI) while that at 3-C remains positive. The σ contribution at 4-H appears larger than that at 3-H. Accordingly, we assign the ring proton signal farther downfield as 4-H and the remaining downfield signal as 3-H.[49,50]

Finally, it is noted that the observed spectra[27] of the pyrromethene complexes **5** are completely different from those of the pyrrole-2-aldimines. Replacing methyl by H in **5** for the purpose of comparison and noting that $Q_{\mathrm{CCH_3}}$ is positive, three positive (3-H, 5-H, 6-H) and one negative contact shifts are observed. In the pyrrole-2-aldimines just the opposite set of shifts, *viz.*, three negative and one positive, are observed, underscoring the above conclusion that the delocalization of spin follows different paths in the two groups of complexes.

Table VIII

Thermodynamic Data for the Planar → Tetrahedral Conversion of Nickel(II) Complexes in Chloroform Solution

R	Temp range, °K[a]	ΔF_{333}, cal/mole	ΔH, cal/mole	ΔS, eu
i-C_3H_7	273–373	1570	3230	5.00
sec-C_4H_9	293–373	1550	3260	5.13
$CH(C_2H_5)_2$	273–373	1360	3190	5.50
$CH_3CHCH(CH_3)_2$	313–373	1930	4350	7.25
C_6H_{11}	313–373	1900	4290	7.17
Salicylaldimines[b]				
i-C_3H_7	333–393	−27	1090	3.33
$CH(C_2H_5)_2$	333–393	231	1630	4.20
$CH_3CHCH(CH_3)_2$ active	333–393	323	1480	3.46
meso	273–393	623	2420	5.37

[a] Range of observation in which ΔF (calculated from $\Delta f_{4\mathrm{H}}$) is a linear function of temperature. [b] Bis(5-methyl-N-R-salicylaldimino)nickel(II) complexes; *cf.* ref 3; results obtained by using eq 4 and its corollary equations (*cf.* ref 3 and 51).

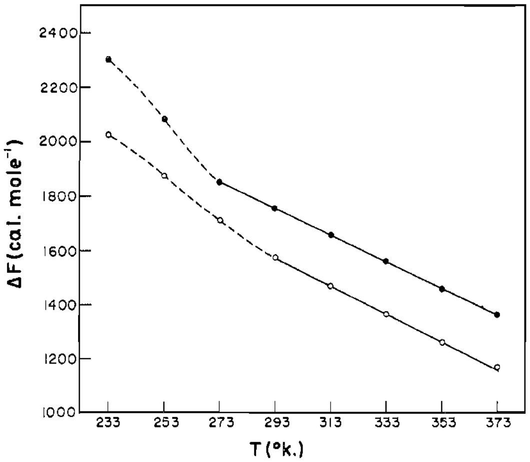

Figure 6.—Temperature dependence of the free energy changes for the planar → tetrahedral conversion of bis(N-R-pyrrole-2-aldimino)nickel(II) complexes in $CDCl_3$: —●—●—●—, R = *i*-C_3H_7; —○—○—, R = $CH(C_2H_5)_2$. Dashed lines represent regions of nonlinearity.

Configurational Equilibria of Ni(II) Complexes.—The temperature dependences of the contact shifts of the five complexes having *sec*-alkyl R groups show that in each case the shifts increase with increasing temperature. The ring-proton signals of each complex were measured at 20° intervals from −40 to 100° in chloroform solution; shifts at 40° are given in Table V. The positive temperature coefficients of all shifts are compatible with eq 4,[51] in which ΔF is a positive quantity decreasing with increasing temperature. Free energy changes

$$\frac{\Delta f_i}{f} = -a_i\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g\beta S(S+1)}{6SKT}[e^{\Delta F/RT} + 1]^{-1} \qquad (4)$$

for process 1 were calculated from measured shifts at the various temperatures using eq 4 and assuming that the coupling constants a_i are the same as those for the *t*-butyl complex. For all complexes at all but the lowest temperature of measurement the shifts of 4-H were larger than those of the other ring protons. Therefore, these shifts were used in calculating the thermodynamic data given in Table VIII. Over a portion of the temperature range of measurement the linear variation of ΔF required by

$$\Delta F = \Delta H - T\Delta S \qquad (5)$$

was satisfied; ΔF *vs.* T plots for two of the complexes are shown in Figure 6. Use of the 3-H and 5-H shifts gave ΔF values which agreed to within ±8% of those in the table, which must be considered uncertain to this extent. Values of ΔS are reliable to ±5%, the maximum variability of the slopes of the least-mean-squares portions of the plots for the three signals of a given complex.

Below room temperature and particularly below ~0°, the line widths increase markedly and the calculated free energies do not vary linearly with temperature (*cf.* Figure 6) for any of the five complexes

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(49) On the basis of calculation, spin imbalance in σ_{13} would have a lesser effect on the shifts of protons 3–6 inasmuch as the total charge density at those protons is 0.083 compared with 0.200 in σ_{14}. The largest charge density is at 5-H (0.0650); if significant spin imbalance exists in this MO, the effect is not nearly large enough to compensate for the predicted positive contact shift of 5-H due to π-spin imbalance in ψ_4.

(50) The signal assigned as that of 4-H is slightly but consistently broader than either of the other two ring signals. This appearance may be due to an unresolved triplet structure; repeated scans of this signal in the weakly paramagnetic complexes under the optimum resolution conditions available to us yielded only signal envelopes identical with that in Figures 4 and 5 with no resolvable fine structure. It might be argued that this signal is broadened by quadrupolar relaxation of the nitrogen nucleus and dipolar interaction with the electron spin and is thus due to that proton nearest nickel, *viz.*, 5-H. (Similar broadening effects have been observed for protons proximal to the metal; see, *e.g.*, ref 33; D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **39**, 3513 (1963); G. N. Lamar, W. DeW. Horrocks, and L. C. Allen, *ibid.*, **41**, 2126 (1964).) However, we feel that an argument based on theoretical spin densities at four ligand positions is more secure than conjecture about relative line widths of one signal compared to two others when the peak widths at half-height of the three differ by no more than ~7 cps.

(51) W. DeW. Horrocks, Jr., *J. Am. Chem. Soc.*, **87**, 3779 (1965). Horrocks has shown that the equation identical with (4) except for a 3 in place of 1 in the bracketed term and previously used (*cf.*, *e.g.*, ref 3, 7, and 33) is not strictly correct. We concur with his analysis and augment it by pointing out that the quantity J appearing in the equation for the magnetic susceptibility of a mixture of complexes having singlet and triplet ground states (his eq 9) is actually an internal energy difference ΔE [J. H. Van Vleck, "Electric and Magnetic Susceptibilities," Oxford Press, 1932, p 182). Since at fixed temperature and pressure $\Delta E - \Delta F = T\Delta S - P\Delta V$ and $\Delta S = R \ln 3$,[3] not zero, for the singlet → triplet magnetic change, it follows that the use of eq 4 containing 3 rather than 1 yields a free energy change too large by $RT \ln 3$ at given temperature and an entropy change too small by $R \ln 3$ at all temperatures (assuming $P\Delta V << T\Delta S$).

which follow eq 5 at higher temperatures. This general behavior reveals the onset of another equilibrium (in addition to (1)) and has been observed previously.[3,5,6] Unlike previous cases, however, the direction of deviation of ΔF from linearity, at least down to $-40°$, indicates that the new, presumably associated, solute species are either diamagnetic or less, rather than more,[3,5,6] paramagnetic than the planar–tetrahedral equilibrium mixture at the same temperature. The cause of the unexpected line broadening at the lower temperatures is currently being investigated. Despite the uncertainty in solution composition at the lower temperatures, the linear variation of ΔF with temperature above room temperature is believed to provide substantial verification of the predominance, if not the exclusiveness, of the configurational equilibrium in the temperature ranges shown in Table VIII.

The thermodynamic data obtained allow the first quantitative comparison of the energetics of stabilization of tetrahedral nickel(II) by a series of bidentate ligand systems in solution. Using an R group (isopropyl), solvent ($CDCl_3$), and temperature (60°) common to all, the order of increasing stabilization of the tetrahedral form is pyrrole-2-aldimine (**3**, 8.5% tetrahedral) < salicylaldimine (**1**, X = 5-CH_3, 51% tetrahedral) < β-ketoamine (**2**, $R_\alpha = R_\gamma = CH_3$, ~100% tetrahedral). This order in chloroform solution is borne out by additional observations made at room temperature which also fortify the conclusion that in each group steric effects are mainly responsible for the destabilization of the planar form. With R = H the complexes of each group are wholly planar in solution. When R is increased in size to methyl, the tetrahedral form has been detected only in the β-ketoamine complex ($R_\alpha = R_\gamma = CH_3$) where it is present in barely detectable concentration (~2%).[6,11] With R = *n*-alkyl the tetrahedral form is present only in the β-ketoamine complexes ($R_\alpha = CH_3$, $R_\gamma = C_6H_5$, R = ethyl, propyl, butyl) and to an extent of 18–30%. In the absence of complete X-ray structural results on either the planar or tetrahedral forms of the pyrrole-2-aldimine or β-ketoamine complexes, it is not yet possible to detail the nature of the steric interactions stabilizing the two forms. A discussion of the stereochemistry of salicylaldimine complexes is given elsewhere.[18] The stabilization of the planar and tetrahedral structures of complexes of these three basic ligand systems with other divalent metals is being actively investigated.

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The Electronic Spectra of Some Six-Coordinate Complexes of Iron(II) with Heterocyclic Amines

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The preparations are reported of the compounds: $Fe(isoquinoline)_4X_2$ (X = Cl, Br, I), $Fe(\beta\text{-picoline})_4Br_2$, $Fe(\gamma\text{-picoline})_4Br_2$, FeL_2X_2 (L = 4-cyanopyridine, 3,5-dichloropyridine; X = Cl, Br), and $Fe(py)Cl_2$. The electronic spectra of these compounds and some previously known complexes with pyridine are in accord with tetragonally distorted octahedral structures. The splitting of the ^5E_g level is discussed in terms of the McClure theory.[1]

Introduction

There is relatively little information available concerning the electronic spectra of high-spin six-coordinate iron(II) complexes. In ligand fields of O_h symmetry the ^5D free ion ground state splits into a $^5T_{2g}$ ground state and a ^5E_g excited state. Accordingly, the spectra of such compounds should show one spin-allowed band, expected to be in the visible or near-infrared region.

It has been observed, however, that, even when the six ligands bonded to iron(II) are identical, *e.g.*, $Fe(H_2O)_6^{2+}$ or $Fe(NCSe)_6^{4-}$, this band often suffers appreciable broadening or is split into two maxima.[2–5] Such splittings can arise from a dynamic Jahn–Teller effect or from static, tetragonal (D_{4h}) or rhombic (D_{2h}) distortions of the primary coordination sphere. Cotton and Meyers have discussed the probable causes for the

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