no doubt, reflects the absence of a free acetate group in these complexes. An upper limit can be placed on this rate. Since separate peaks separated by ~10 ppm are observed for corresponding protons in *cis* isomers, the rate constant for acetate scrambling must be significantly less than 10^3 sec^{-1}.

Finally, the observation of separate peaks for complex and free excess ligand requires that the Ni–N bond lifetimes also are $<10^{-4}$ sec. Upper limits for these rates could be readily determined by using deuterated excess ligand to follow the incorporation of free ligand into the complexes.

Acknowledgment.—The authors wish to acknowledge financial support from the National Institutes of Health, Grant GM-12598, and the National Science Foundation, Grant GP-13786. We also wish to acknowledge the National Science Foundation, Grant GP-6880, for the purchase of the Varian HA-100 nmr spectrometer used in these studies.

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Syntheses and Solution Equilibria of Some Nickel(II) Chelates

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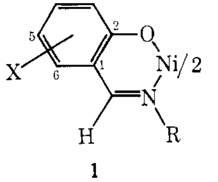
Received October 21, 1969

The syntheses of a number of nickel(II) complexes derived from various imines of 2-hydroxyacetophenone, 2-hydroxypropiophenone, and 2-hydroxybutyrophenone are described. Normally a nonaqueous chelation reaction is required for the syntheses. Unlike the salicylaldimine complexes, the present chelates do not form paramagnetic associated species in noncoordinating solvents like chloroform or benzene. In pyridine solution an equilibrium exists between a pseudooctahedral pyridine adduct and the parent planar species. This equilibrium has been thermodynamically characterized by variable-temperature spectroscopic and magnetic measurements. In several cases the paramagnetic pyridine adduct could be isolated in the crystalline state. It is concluded that steric factors are important in determining the population of the pseudooctahedral state in pyridine solution. An important conclusion is that the tendency to attain paramagnetism is uniformly less in the present complexes than in the corresponding salicylaldimine chelates. Some copper(II) complexes of the present ligands are also synthesized and examined spectroscopically. Their behavior is qualitatively similar to that of the salicylaldimines.

Introduction

The complexes derived from Schiff bases form a vast and fruitful area of research in coordination chemistry. More than one review article[1,2] concerning this general area have appeared in the last few years. The most widely investigated among Schiff base complexes are probably those derived from salicylaldimines. In particular, the bis chelates **1** show interesting stereochemical patterns. The behavior of complex **1** depends largely on the nature of group R. When R is a straight-chain alkyl group, the solids are usually diamagnetic but their solutions in, *e.g.*, chloroform and benzene, exhibit the equilibrium[3,4]



1
(R-sal)$_2$Ni

$$\underset{\text{(planar)}}{\text{monomer } (S = 0)} \rightleftharpoons \underset{\text{(pseudooctahedral)}}{\text{associated species } (S = 1)} \qquad (1)$$

When R = aryl, the solids are either diamagnetic or paramagnetic depending upon the nature of the aryl group.[5,6] In solution (*e.g.*, in chloroform) they also exhibit equilibrium 1 heavily shifted toward the right unless steric factors prevent this.[5] When R is an α-branched alkyl group, conformational equilibria involving planar (S = 0) and tetrahedral (S = 1) geometries occur in solution.[7,8]

In contrast to extensive research on the salicylaldimine chelates **1**, surprisingly little is known about the corresponding chelates, **2**. Many years ago Pfeiffer, *et al.*,[9] reported the synthesis of (H–hac)$_2$Ni. Harris, *et al.*,[10] later synthesized (Me–hac)$_2$Ni and (OH–hac)$_2$Ni. Holm and coworkers[11] recently reported the nmr data on the complex (*sec*-Bu–hac)$_2$Ni. Apart from these there are no reports on the syntheses and studies of the complexes **2**. This probably stems from problems involved in the synthesis of **2**. The simple synthetic methods[1] that are generally applicable to salicylaldimines are in many cases of no avail in the syntheses of 2-hydroxyacetophenimine and other type **2** complexes.

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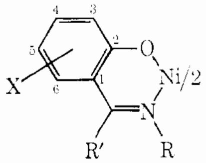
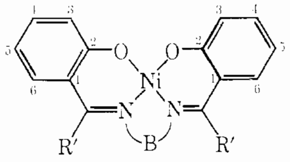
A general procedure for the syntheses of 2 (R = straight-chain alkyl or aryl) is reported in this paper.

Since **1** and **2** differ only in substituents on the azomethine carbon, the two groups of compounds may be expected to behave similarly in many respects. While this is true to a large extent, there are very significant quantitative or even qualitative differences. These constitute the major results of the present study.

Another class of compounds described in this paper are of type **3** with a bridging group B. They also show considerable difference in behavior from the corresponding salicylaldimine complexes.[12] The only compound[13] of this type reported previously appears to be ((hac)$_2$-en)Ni.



2



3

(R–hac)$_2$Ni when R′ = CH_3
(R–hpr)$_2$Ni when R′ = C_2H_5
(R–hbu)$_2$Ni when R′ = n-C_3H_7
R = straight-chain alkyl, aryl, or OH

((sal)$_2$en)Ni; ((sal)$_2$pn)Ni when R′ = H
((hac)$_2$en)Ni; ((hac)$_2$pn)Ni when R′ = CH_3
((hpr)$_2$en)Ni; ((hpr)$_2$pn)Ni when R′ = C_2H_5
((hbu)$_2$en)Ni: ((hbu)$_2$pn)Ni when R′ = n-C_3H_7
en when B = $(CH_2)_2$ and pn when B = $(CH_2)_3$

Several complexes of copper(II) corresponding to **2** and **3** were also synthesized in order to compare their crystal field spectra with those of the salicylaldimine chelates. The results do not reveal any particularly novel features and are appended only briefly in this report.

Experimental Section

Preparation of Compounds.—The 2-hydroxyarylcarbonyl compounds either were obtained from Aldrich Chemical Co. or were synthesized by Fries rearrangement[14] of the corresponding phenyl ester made from the appropriate phenol, carboxylic acid, and thionyl chloride.

The salicylaldimine complexes of nickel(II), 1 (R = alkyl and aryl), were prepared by following well-known procedures.[3,5,15] **Bis(salicylaldoximato)nickel(II), 1 (R = OH)**, was synthesized according to the method of Cox, *et al.*[16]

The bis chelate of 2-hydroxyacetophenone oxime, (OH–hac)$_2$Ni, is described in the paper of Harris, *et al.*[10] The other oxime chelates, reported for the first time in this paper, were prepared by following the same general procedure.[10] They form green needle-shaped crystals or shining green leaflets.

Bis(2-hydroxyacetopheniminato)nickel(II), (H–hac)$_2$Ni, was prepared in the form of red crystals by allowing[9] bis(2-hydroxyacetophenonato)nickel(II) dihydrate[17] to react with aqueous ammonia. **Bis(N-methyl-2-hydroxyacetopheniminato)nickel(II)**, (Me–hac)$_2$Ni, was prepared by following the published procedure.[10]

Complexes 2 having R = C_2H_5, n-C_3H_7, or n-C_4H_9 could not be synthesized by usual procedures. For example, bis(2-hydroxyacetophenonato)nickel(II) dihydrate fails to react with primary amines in boiling ethanol. The procedure[10] used for the synthesis of (Me–hac)$_2$Ni could not be successfully extended for the higher homologs. A general synthesis of these complexes could be achieved by the following nonaqueous chelation reaction.

The appropriate ketone (0.03 mol) and excess amine were heated to reflux in ethanol for 1 hr. The yellow solution was stripped of solvent and excess amine. The crude Schiff base thus obtained as a yellow crystalline solid was used without further purification. Potassium t-butoxide (0.03 mol) and $[(C_6H_5)_4N]_2[NiBr_4]$ (0.015 mol) were added to a solution of the Schiff base in dry tetrahydrofuran (80 ml). The mixture was stirred magnetically for 12 hr in a stoppered flask and then filtered. The solvent was removed from the brown filtrate (rotary evaporator) and the solid residue was repeatedly extracted (four 50-ml portions) with boiling dry toluene. The combined toluene extracts were concentrated to ~30 ml and then cooled in a stoppered flask in a refrigerator. The brown crystals with a yellow sheen were recrystallized once from dry toluene. The yield of the pure product was ~30%.

Complexes 2, R = aryl, were obtained using the same general procedure as above but with the following modifications. The Schiff bases were prepared[18] by heating a mixture of the ketone and excess amine to reflux for 16 hr. The cooled reaction mixture was acidified with 3 N hydrochloric acid and then extracted with ether. The Schiff base was isolated by evaporating the ether layer. Since the complexes are only slightly soluble in tetrahydrofuran, a major portion accumulates in the residue during the chelation reaction. Consequently the whole reaction mixture (after magnetic stirring) was evaporated to dryness and the residue was extracted with boiling dry toluene (seven 50-ml portions). The yield of the shining brown crystals was ~20%.

Complexes 3, B = $(CH_2)_2$, were prepared by extending the straightforward procedure of Pfeiffer, *et al.*,[13] who reported ((hac)$_2$en)Ni. The tetradentate Schiff bases were made by allowing the ketone to react with the diamine in ethanol. The reaction of an ethanolic solution of the Schiff base with an aqueous solution of nickel acetate tetrahydrate furnished the crude complex which was recrystallized from chloroform or dichloromethane yielding orange-red crystals.

Complexes 3, B = $(CH_2)_3$, were best prepared by chelation reactions in tetrahydrofuran. Details are the same as those described for 2 (R = alkyl) complexes. The complex ((hac)$_2$-pn)Ni is red while the remaining compounds are brown.

The salicylaldimine complexes corresponding to **3** were prepared according to the method of Pfeiffer, *et al.*[12,13]

Crystalline pyridine adducts, (Et–hac)$_2$Ni·2py (yellowish green), (n-Pr–hac)$_2$Ni·2py (green), (OH–hac)$_2$Ni·2py (light pink), and ((hac)$_2$pn)Ni·2py (yellowish brown) resulted when the respective chelates were dissolved in hot dry pyridine and the solutions thus obtained were allowed to cool (py = pyridine). The solute concentration required for this purpose varies from one compound to another. The adducts were separated from the mother liquor by quick filtration. The adhering solvent was removed by pressing in folds of dry filter paper. The solids were quite stable at room temperature in stoppered vials but they lost pyridine when left in the air and particularly on warming. The product remaining in each case is the parent chelate. Several pyridine adducts other than those mentioned above were prepared but they were not investigated any further.

Bis(2-hydroxyacetophenonato)copper(II) was prepared as dark green crystals by mixing an aqueous solution of copper acetate with an ethanolic solution of 2-hydroxyacetophenone followed by addition of aqueous sodium hydroxide. The copper complexes, **(R–hac)$_2$Cu (R = H, CH_3, or n-C_4H_9)** and **((hac)$_2$B)Cu (B = $(CH_2)_2$ or $(CH_2)_3$)** were made in good yields from the above

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complex by treating it with the appropriate amines in absolute alcohol. They were recrystallized either from a mixture of dichloromethane and petroleum ether (bp 60–80°) or from absolute ethanol.

Bulk Susceptibility Measurements.—These were done using a sensitive Gouy balance assembled from a Varian V-4005 electromagnet (pole caps tapered to 1-in. diameter), a matching V-2900 solid-state power supply, and an Ainsworth semimicro balance. Split sample tubes were used for all measurements on solids. $CoHg(SCN)_4$ was used as the standard.[19] For solution measurements freshly boiled water was used as the standard. The pyridine used for solution measurements was distilled twice over solid sodium hydroxide. The gram susceptibility of pyridine was repeatedly found to be $-(0.610 \pm 0.002) \times 10^{-6}$. This value is slightly less than what is reported elsewhere.[3]

A double-walled jacket through which thermostated (±0.1°) water was circulated was used for variable-temperature solution measurements. The temperature within the jacket was determined with a sensitive thermometer. The temperature was stable to within ±1°. The density of solutions was determined at various temperatures with a suitably designed specific gravity bottle. Diamagnetic corrections were estimated from Pascal's constants as given by Selwood.[20]

Electronic Spectral Measurements.—A Cary 14 recording spectrophotometer was used for these measurements. Solids were examined in Nujol mulls. Variable-temperature solution measurements were done by circulating thermostated (±0.1°) water or 95% ethanol through an appropriate cell holder.

Calculation of Thermodynamic Parameters.—The equilibrium constant, K, for the reaction

$$\text{planar complex } (S = 0) + 2\text{py} \rightleftharpoons \text{adduct } (S = 1) \quad (2)$$

is

$$K = \frac{[\text{adduct}]}{[\text{planar complex}][\text{py}]^2} \quad (3)$$

The enthalpy and entropy changes, $\Delta H°$ and $\Delta S°$, are related to K by the well-known equation

$$\frac{\Delta H°}{T} - \Delta S° = -R \ln K \quad (4)$$

(a) **Spectroscopic Method.**—The oscillator strengths for the ν_1 band of the pseudooctahedral species were used to determine K. The oscillator strengths were calculated using the area under the band. Proper corrections were made for the absorption tail at the high-energy end. The limiting spectrum (100% octahedral species) was determined by cooling the solutions until there was no further increase in the oscillator strength. For complexes of type **2**, cooling to $\sim -10°$ usually sufficed. For complexes of type **3**, the limiting spectra could not be obtained within the temperature range accessible to us.

If f_0 is the limiting oscillator strength and f is the observed oscillator strength, then K becomes

$$K = \frac{[cf/f_0]}{[c - (cf/f_0)][b - (2cf/f_0)]^2} \quad (5)$$

where c is the total concentration of the solute and b is the total concentration of pyridine.

(b) **Magnetic Method.**—The equilibrium constant can be expressed in the form

$$K = \frac{[cx]}{[c - cx]\,[b - 2cx]^2} \quad (6)$$

with

$$x = (\mu_{\text{eff}}/\mu_0)^2 \quad (7)$$

where μ_0 is the magnetic moment of the pseudooctahedral species and μ_{eff} is the observed magnetic moment of the equilibrium solution.

Proton Resonance Measurements.—These were done on a Varian HR-100 spectrometer using tetramethylsilane as the internal standard.

Results and Discussion

Synthesis and Structure of the Chelates.—Characterization data for the chelates are set out in Tables I and II. The majority of the chelates of type **2** and **3** require a nonaqueous chelation reaction for synthesis. This general procedure has been found to be of great value for preparation of a variety of hydrolytically unstable chelates.[21–23] The tris chelates of cobalt(III)[21,22] corresponding to the chelates **2** also belong to this class.

No crystal structure data are available on complexes **2** or **3**. However by analogy with salicylaldimines of known structure[1] it is quite safe to attribute a planar *trans* structure to complexes **2**. On the other hand, **3** must be *cis* because of the compelling requirements of the bridging group. The complexes of types **2** and **3** are found to be uniformly diamagnetic in the solid state.

Behavior of Complexes 2 and 3 in Solution. (a) **In Chloroform, Benzene, or Toluene.**—Complexes **2** will be considered first. An immediate task is to settle whether the equilibrium 1 is important for this class of chelates. Some electronic spectral results are shown in Figures 1 and 2. It is well established[3] that for $(Me\text{–}sal)_2Ni$, a very considerable amount of the associated species ($S = 1$) contributes to the solution compositions in solvents like chloroform and benzene. The associated species is known[3] to absorb at ~9500 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{2g}$ transition in an idealized octahedral crystal field for nickel(II)). It can be seen from Figure 1a that the intensity of this band increases with decreasing temperature as would be expected if equilibrium 1 shifts to the left with increasing temperature. Also shown in the same figure is the spectrum of $(Me\text{–}hac)_2Ni$ (same solute concentration as in the $(Me\text{–}sal)_2Ni$ case). There is no trace of any band below 16,000 cm^{-1} in the temperature range −10° to +32°. $(Me\text{–}hac)_2Ni$ is too insoluble for reliable magnetic susceptibility measurements. However, we believe that the results shown in Figure 1a convincingly demonstrate that associated species with a triplet ground state are not important in the case of $(Me\text{–}hac)_2Ni$. It is suggested that for this chelate equilibrium 1 is shifted completely to the left.

Examination of Figure 1b shows that the complex $(n\text{-Bu–hac})_2Ni$ behaves in an identical fashion. On the other hand, the magnetic susceptibility measurements of Clark, *et al.*,[4] have established the increasing population of associated species with increasing solute concentration and/or decreasing temperature for the chelate $(n\text{-Bu–sal})_2Ni$. In full accord with this, the intensity of the ~9500-cm^{-1} band increases with decreasing temperature. Further, at a given concentra-

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TABLE I

CHARACTERIZATION OF NICKEL(II) AND COPPER(II) COMPOUNDS OF TYPE 2[a]

Compound						% C		% H		% N	
R′	R	X	M	Formula	Mp,[b] °C	Calcd	Found	Calcd	Found	Calcd	Found
CH_3	C_2H_5	H	Ni	$C_{20}H_{24}N_2O_2Ni$	203–204	62.70	63.10	6.31	6.60	7.31	7.60
CH_3	n-C_3H_7	H	Ni	$C_{22}H_{28}N_2O_2Ni$	215–216	64.21	64.65	6.86	6.70	6.81	7.00
CH_3	n-C_4H_9	H	Ni	$C_{24}H_{32}N_2O_2Ni$	193–194	65.60	65.49	7.35	7.29	6.38	6.50
C_2H_5	n-C_4H_9	H	Ni	$C_{26}H_{36}N_2O_2Ni$	180–181	66.83	66.80	7.77	7.37	5.99	6.15
n-C_3H_7	n-C_4H_9	H	Ni	$C_{28}H_{40}N_2O_2Ni$	130–132	67.89	68.25	8.14	8.35	5.66	5.90
CH_3	OH	5-CH_3	Ni	$C_{18}H_{20}N_2O_4Ni$	>250	55.86	55.98	5.21	5.20	7.24	7.52
C_2H_5	OH	H	Ni	$C_{18}H_{20}N_2O_4Ni$	192–194	55.86	55.64	5.21	5.24	7.24	7.11
C_2H_5	OH	5-CH_3	Ni	$C_{20}H_{24}N_2O_4Ni$	250–252	57.88	58.15	5.83	5.98	6.74	6.82
CH_3	C_6H_5	H	Ni	$C_{28}H_{24}N_2O_2Ni$	>250	70.17	69.68	5.05	5.08	5.85	5.97
CH_3	C_6H_5	5-CH_3	Ni	$C_{30}H_{28}N_2O_2Ni$	>250	71.03	71.41	5.56	5.78	5.52	5.50
CH_3	m-$C_6H_4CH_3$	H	Ni	$C_{30}H_{28}N_2O_2Ni$	>250	71.03	71.60	5.56	5.41	5.52	5.27
CH_3	m-$C_6H_4CH_3$	5-CH_3	Ni	$C_{32}H_{32}N_2O_2Ni$	>250	71.78	72.51	6.03	6.11	5.23	5.33
C_2H_5	C_6H_5	H	Ni	$C_{30}H_{28}N_2O_2Ni$	>250	71.03	71.74	5.56	5.57	5.52	5.72
C_2H_5	C_6H_5	5-CH_3	Ni	$C_{32}H_{32}N_2O_2Ni$	>250	71.78	72.04	6.03	5.95	5.23	5.16
CH_3	H	H	Cu	$C_{16}H_{16}N_2O_2Cu$	>250	57.91	57.56	4.86	4.90	8.44	8.80
CH_3	CH_3	H	Cu	$C_{18}H_{20}N_2O_2Cu$	216–217	60.07	60.02	5.60	5.70	7.80	7.90
CH_3	n-C_4H_9	H	Cu	$C_{24}H_{32}N_2O_2Cu$	97–98	64.97	64.78	7.25	7.30	6.30	6.39

[a] Refer to structure **2** in the text. [b] All melting points reported in this table are uncorrected.

TABLE II

CHARACTERIZATION OF NICKEL(II) AND COPPER(II) COMPOUNDS OF TYPE 3[a]

Compound					% C		% H		% N	
R′	B	M	Formula	Mp,[b] °C	Calcd	Found	Calcd	Found	Calcd	Found
CH_3	$(CH_2)_3$	Ni	$C_{19}H_{20}N_2O_2Ni$	250	62.16	61.60	5.50	6.01	7.63	7.30
C_2H_5	$(CH_2)_2$	Ni	$C_{20}H_{22}N_2O_2Ni$	>250	63.04	61.95	5.82	5.92	7.34	7.16
n-C_3H_7	$(CH_2)_2$	Ni	$C_{22}H_{26}N_2O_2Ni$	>250	64.46	64.59	6.40	6.56	6.84	6.76
n-C_3H_7	$(CH_2)_3$	Ni	$C_{23}H_{28}N_2O_2Ni$	219–221	65.27	65.47	6.67	6.96	6.62	6.38
CH_3	$(CH_2)_2$	Cu	$C_{18}H_{18}N_2O_2Cu$	>250	60.39	60.89	5.07	5.10	7.83	7.70
CH_3	$(CH_2)_3$	Cu	$C_{19}H_{20}N_2O_2Cu$	242–243	61.37	61.76	5.42	5.49	7.54	7.68

[a] Refer to structure **3** in the text. [b] All melting points reported in this table are uncorrected.

tion and temperature the intensity of the $\sim$9500-cm^{-1} band is in the order (Me–sal)$_2$Ni > (n-Bu–sal)$_2$Ni indicating that association is greater in the former complex.

Additional evidence in favor of the lack of association in (n-Bu–hac)$_2$Ni is provided by pmr data. The pmr spectrum of this complex is very similar to that of the corresponding free Schiff base. In particular, the azomethine methyl protons resonate at identical (2.27 ppm from tetramethylsilane at 28.5°; solute concentration in $CDCl_3$ is 0.32 M) frequencies in both compounds. In contrast to this the broad azomethine proton signal in (n-Bu–sal)$_2$Ni (solute concentration in $CDCl_3$, 0.32 M; 28.5°) is shifted downfield by $\sim$3 ppm from the corresponding free-ligand signal. This shift is undoubtedly due to contact interaction[24] in the paramagnetic associated species. It is known[25,26] that, among all the ring protons in paramagnetic salicylaldimine complexes, the one on the azomethine carbon undergoes the maximum negative contact shift. If paramagnetic molecular aggregates made appreciable contribution to the solution composition of (n-Bu–hac)$_2$Ni, a measurable contact shift would be expected for the azomethine methyl protons.

In Figure 2 are shown portions of the electronic spectra of (m-Tol–sal)$_2$Ni and (m-Tol–hac)$_2$Ni taken at the same temperature and at very similar concentrations.[27] In striking contrast to the salicylaldimine complex, the 2-hydroxyacetophenimine chelate shows complete lack of the existence of the paramagnetic pseudooctahedral associated species.

The remaining complexes of type **2** behave similarly to the three (R–hac)$_2$Ni complexes described above. *We are therefore able to make the generalization that unlike the salicylaldimine complexes, the chelates* **2** *carrying alkyl substituents on the azomethine carbon do not form measurable amounts of paramagnetic molecular aggregates in the solution phase.*

No definite and proven models exist for the associated species of salicylaldimine complexes. In the case of (Me–sal)$_2$Ni it has been speculated[3,10] that the associated species consist of units that are parallel but are laterally displaced such that the oxygen atom of one unit is vertically above or below the nickel atom of the adjacent unit. In this way, dimers or polymers can be generated. If this model is correct, the lack of association in (Me–hac)$_2$Ni may be attributed to steric hindrance created by the azomethine methyl group. In the other (R–hac)$_2$Ni (R = C_2H_5, n-C_3H_7, n-C_4H_9, etc.) complexes additional steric hindrance can arise due to preferred orientation (*vide infra*) of the R group.

In benzene or toluene solution, (alkyl–hac)$_2$Ni shows

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

[26] E. A. LaLancette, D. R. Eaton, R. E. Benson, and W. D. Phillips, *ibid.*, **84**, 3968 (1962).

[27] The electronic spectrum of (m-Tol–sal)$_2$Ni was reported by Holm, *et al.*,[5] in chloroform at 25°. Their solute concentration was 0.0300 M. Much lower concentration ($\sim 2 \times 10^{-3}$ M) had to be chosen in the present study because of the low solubility of (m-Tol–hac)$_2$Ni. Further, toluene is a better solvent for this complex.

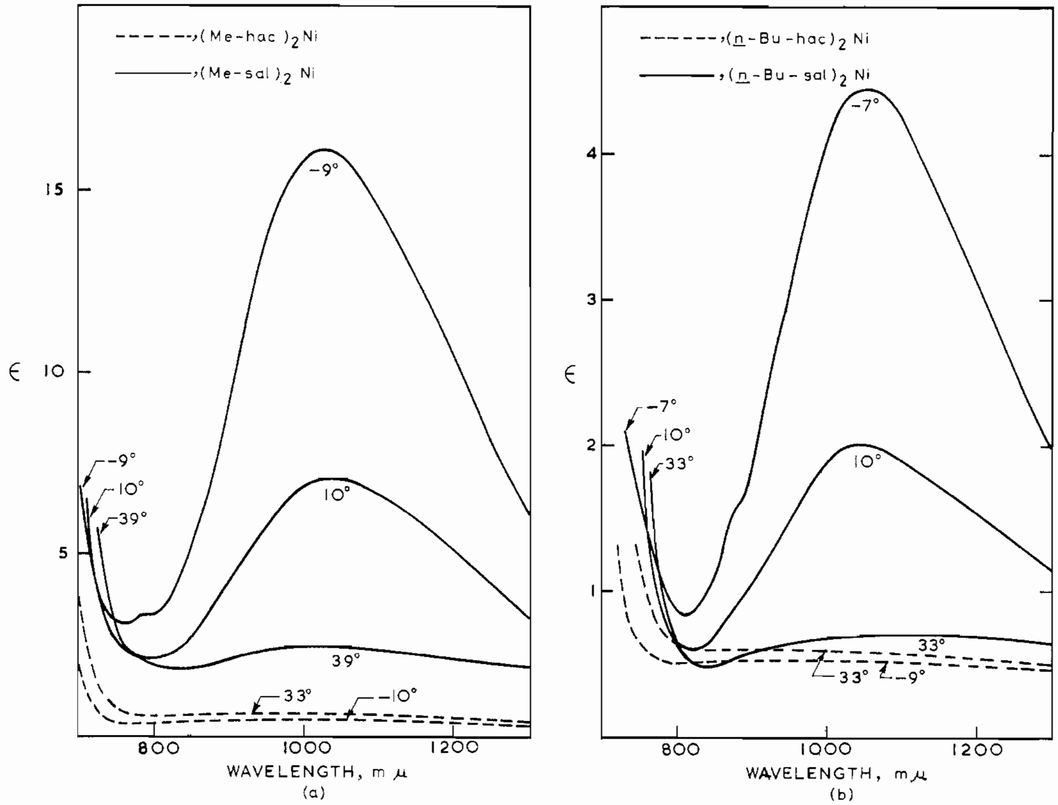

Figure 1.—Variable-temperature electronic spectra of some salicylaldimine and 2-hydroxyacetophenimine complexes in chloroform: (a) (Me–sal)$_2$Ni and (Me–hac)$_2$Ni (solute concentrations are $\sim 10^{-2}$ *M*); (b) (*n*-Bu–sal)$_2$Ni and (*n*-Bu–hac)$_2$Ni (solute concentrations are ~ 0.15 *M*).

a prominant electronic band in the region 17,500–18,200 cm^{-1} (molar extinction coefficient ε 120–160). The R = aryl or OH complexes absorb at slightly lower energies (16,400–16,700 cm^{-1}; ε 104–145). Some representative data are shown in Table III. In line with the observations on salicylaldimines,[28] this band may be assigned[29,30] to the transition $^1A_g \rightarrow {}^1B_{1g}$ ($d_{xy} \rightarrow d_{x^2-y^2}$) in idealized D_{2h} symmetry. The corresponding transition in the $-(CH_2)_2-$ bridged complexes **3** (symmetry C_{2v}) is of the type $^1A_1 \rightarrow {}^1B_1$ and it appears at $\sim$18,180 cm^{-1} (Table III). The $-(CH_2)_3-$ bridged complexes show[31] a feeble shoulder at $\sim$17,500 cm^{-1}.

TABLE III[a]

FREQUENCIES (ν_p, CM^{-1}) AND EXTINCTION COEFFICIENTS (ε, L. MOL CM^{-1}) OF ELECTRONIC BANDS OF NICKEL(II) COMPLEXES OF TYPES **2**[b] AND **3**[b] IN TOLUENE OR CHLOROFORM AT ROOM TEMPERATURE (298–303°K)

Compound				
R′	R or B	X	Solvent	ν_p (ε)
CH_3	H	H	Toluene	18,520 (103)
CH_3	n-C_4H_9	H	Toluene	17,860 (156)
C_2H_5	n-C_4H_9	H	Toluene	18,020 (142)
n-C_3H_7	n-C_4H_9	H	Toluene	18,180 (122)
CH_3	OH	H	Toluene	16,670 (120)
C_2H_5	OH	5-CH_3	Toluene	16,530 (146)
CH_3	m-$C_6H_4CH_3$	H	Toluene	16,670 (104)
C_2H_5	C_6H_5	H	Toluene	16,670 (107)
CH_3	$(CH_2)_2$	H	Chloroform	18,020 (212)
CH_3	$(CH_2)_3$	H	Chloroform	17,500[c]
n-C_3H_7	$(CH_2)_2$	H	Chloroform	18,020 (184)
n-C_3H_7	$(CH_2)_3$	H	Chloroform	17,540 (85)[c]

[a] Solute concentration $\sim 10^{-3}$ *M*. [b] Refer to the structures in the text. [c] Shoulder.

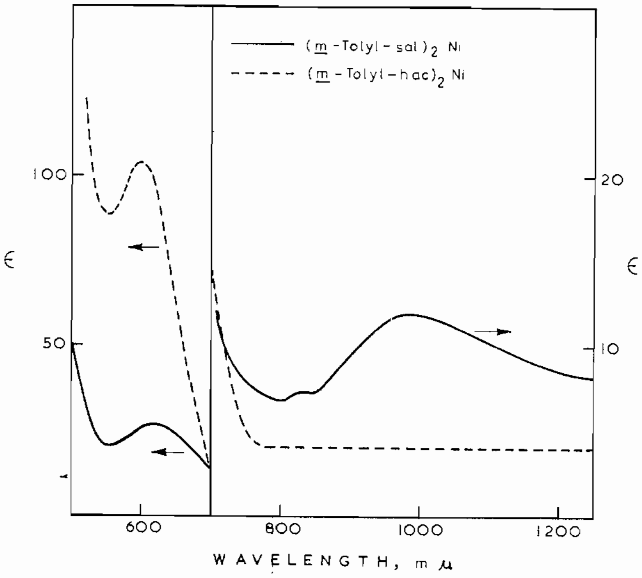

Figure 2.—Electronic spectra of (m-Tol–sal)$_2$Ni and (*m*-Tol–hac)$_2$-Ni in toluene. Solute concentrations are $\sim 10^{-3}$ *M*.

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(28) For salicylaldimines, the absorption frequencies (in chloroform or benzene) are slightly less: N-alkyl, 16,300–16,400 cm^{-1}; N-aryl, 16,100–16,400 cm^{-1}.

(29) J. Ferguson, *J. Chem. Phys.*, **34,** 611 (1961).

(30) B. Bosnich, *J. Am. Chem. Soc.*, **90,** 627 (1968).

(31) It is known[12] that the intensity of the visible band of ((sal)$_2$pn)Ni is considerably less than that of ((sal)$_2$en)Ni. A similar trend is operative in complexes **3**.

TABLE IV
VARIABLE-TEMPERATURE FREQUENCIES (ν, CM^{-1}) AND EXTINCTION COEFFICIENTS (ϵ, L. MOL^{-1} CM^{-1}) OF THE BANDS IN THE VISIBLE REGION FOR SOME COMPLEXES IN PYRIDINE SOLUTION[a]

Compound	T, °K	ν_1[b]	ϵ_1[b]	ν_2 and ν_p[b]	$\epsilon_2 + \epsilon_p$[b,c]
(Et–hac)$_2$Ni	260	10,150	12.4	17,240	15.3
	298	10,100	12.0	17,240	17.8
	323	10,050	10.8	17,390	25.6
	343	9,900	9.3	17,700	42.1
(n-Pr–hac)$_2$Ni	260	10,100	11.7	17,240	14.7
	288	10,050	11.6	17,240	17.2
	313	10,000	10.6	17,390	27.2
	323	9,900	10.1	17,540	34.0
	343	9,850	7.8	17,700	54.3

[a] Solute concentrations used were in the range (6–8) × 10^{-3} M. [b] Meaning of subscripts is as in the text. [c] Uncorrected for the tail absorption from the ultraviolet region.

(b) **In Pyridine.**[32]—The salicylaldimine complexes **1**, with R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, etc., are known to become fully paramagnetic ($\mu_{eff} \approx 3.1$ BM) in pyridine solution at room temperature.[15,33] The paramagnetic species is pseudooctahedral[34] (R–sal)$_2$Ni·2py. Several pyridine adducts of this composition were isolated in the solid state.[35] In contrast to the above examples, the complex (H–sal)$_2$Ni dissolves in pyridine to give a partially paramagnetic solution[3] (1.75 BM at 25°). The higher strength[36] of the in-plane ligand field is probably responsible for this.[3,37]

The behavior of complexes **2** in pyridine is more interesting. (H–hac)$_2$Ni gives brown solutions in both toluene and pyridine. Both solutions show a singlet–singlet crystal field band at 18,520 cm^{-1} (ϵ ~100). No trace of any pseudooctahedral bands could be detected in the pyridine solution. On the other hand, (Me–hac)$_2$Ni forms a green solution in pyridine which shows a typically octahedral spectrum.[32] There is little variation of band intensities in the temperature range 25–70°.[38] The same comment applies[32,38] to the salicylaldimine complexes (Me–sal)$_2$Ni and (n-Bu–sal)$_2$Ni. It is concluded[32,39] that in all the above three cases, the formation of the paramagnetic pseudooctahedral adducts is essentially complete in the solution phase.

Complexes **2** with R = C_2H_5, n-C_3H_7, or n-C_4H_9 produce greenish brown solutions in pyridine in which equilibrium 2 exists. The spectral evidence for this equilibrium was briefly cited earlier[32] in the specific case of (n-Bu–hac)$_2$Ni. Variable-temperature spectral data for two complexes are shown in Table IV. In general, the higher the solution temperature the lesser is the intensity of the $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1) transition and the higher is the intensity of the ~17,200-cm^{-1} band. Both octahedral $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_2) and planar $^1A_g \rightarrow {}^1B_{1g}$ (ν_p) bands contribute to the latter intensity. With increasing temperature, equilibrium 2 shifts to the left. Consequently, the intensities due to ν_1 and ν_2 decrease and that due to ν_p increases. The increase due to ν_p more than offsets the decrease due to ν_2. A representative variable-temperature spectrum is shown in Figure 3.

Before we proceed further, one feature of the variable-temperature spectra will be pointed out. In general, for the complexes studied, the position of the ν_1 band shifted systematically to lower energies on increasing the temperature. Further there is a discernible increase in band width with increasing temperature (Table IV and Figure 3). We have noticed the same behavior (25–70°) in pyridine solutions of (R–sal)$_2$Ni[40] and bis(acetylacetonato)nickel(II).[41] In these two cases there is little doubt that only pseudooctahedral pyridine adducts[42] are present in the solution over the measured range of temperature. Thus the shift of ν_1 with temperature is a property of the paramagnetic pseudooctahedral adduct in the solution phase.[43] A probable reason for this shift is the decrease in the effective average[44] ligand field strength with increasing Ni–py distance (increasing volume of the solution) with temperature. Similar shifts are known to occur in the optical spectra of hydrated ions in the crystalline state.[45]

Returning to the question of equilibrium 2, the variable-temperature bulk susceptibility data are presented in Table V. (n-Bu–sal)$_2$Ni remains fully paramagnetic in the temperature range 19–60°. In contrast, the other n-butyl complexes show a systematic decrease of the magnetic moment with increasing temperature. This confirms that equilibrium 2 exists in the pyridine solutions at and above room temperature and that it is shifted toward the left with increasing temperature.

The bridged complexes **3** will now be considered. In line with ((sal)$_2$en)Ni,[37] complexes **3** with B = –$(CH_2)_2$– do not show any sign of the formation of paramagnetic pseudooctahedral species in pyridine solution. The electronic spectra in the visible region in toluene and in pyridine are essentially identical.

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(32) Preliminary communication: A. Chakravorty, T. S. Kannan, and S. Gupta, *Inorg. Nucl. Chem. Letters*, **4**, 139 (1968).

(33) H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 3431 (1955).

(34) The ligand field spectrum for, *e.g.*, (n-Bu–sal)$_2$Ni in pyridine (28°) consists of the following bands which are assigned in the idealized point group O_h: $^3A_{2g} \rightarrow {}^3T_{2g}$, 10,150 cm^{-1}; $\rightarrow {}^3T_{1g}(F)$, 17,240 cm^{-1}; $\rightarrow {}^1E_g(D)$, 12,740 cm^{-1}. The molar extinction coefficients for these bands are, respectively, 14.0, 11.8, and 3.2. These figures are 15% less than those reported in ref 32. This stems from an error in calculation. However, the conclusions reached in ref 32 are not affected by this change.

(35) F. Basolo and W. Matoush, *J. Am. Chem. Soc.*, **75**, 5663 (1953).

(36) The singlet–singlet ligand field band for this complex in chloroform solution is at 18,180 cm^{-1}. The band is at considerably lower energies in the N-alkyl complexes.[22]

(37) G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).

(38) In ref 32 intensity results are reported in the range 28–50°. Heating the solutions to 70° does not bring any further changes.

(39) Ideally this conclusion should be checked by magnetic measurements. However, the solubility of (Me–hac)$_2$Ni in pyridine is very limited due to the formation of a green insoluble pyridine adduct and reliable solution magnetic moments could not be determined.

(40) The band positions expressed in wavelengths for (n-Bu–sal)$_2$Ni are: 28°, 985 and 580 mμ; 50°, 990 and 585 mμ; 70°, 1010 and 590 mμ.

(41) The band positions expressed in wavelengths are: 10°, 990 and 587 mμ; 30°, 995 and 590 mμ; 57°, 1000 and 592 mμ; 68°, 1005 and 595 mμ.

(42) J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **84**, 24 (1962); J. T. Hashagen and J. P. Fackler, Jr., *ibid.*, **87**, 2821 (1965).

(43) Paralleling the shift of ν_2, ν_1 also shifts to lower energies with increasing temperature in the case of (R–sal)$_2$Ni and bis(acetylacetonato)nickel(II). The shift of the ~17,000-cm^{-1} band in the case of complexes **2** is in the reverse direction (Table IV, Figure 3). Careful examination of spectra reveals that this is due to the movement of the center of gravity of the band toward ν_p with increasing temperature. ν_p is known (Table III) to be at slightly higher energy than ν_2.

(44) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y., 1966, p 236.

(45) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957); H. Hartmann and H. Müller, *Trans. Faraday Soc.*, **26**, 49 (1958).

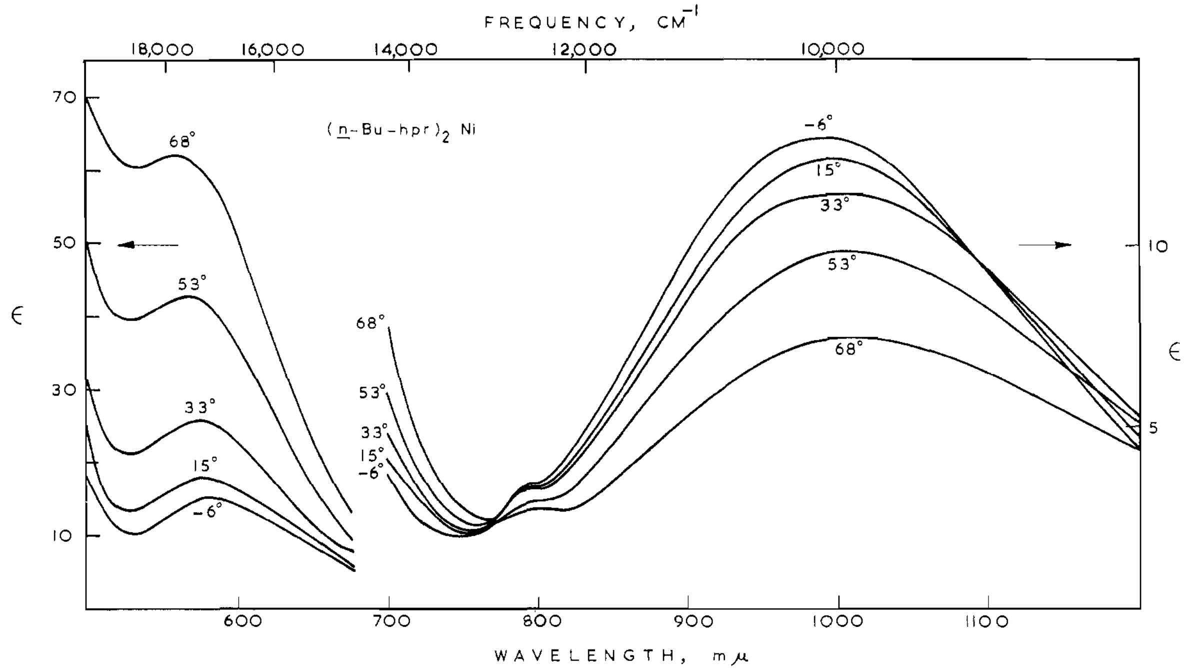

Figure 3.—Variable-temperature electronic spectral data for (n-Bu–hpr)$_2$Ni in pyridine. Solute concentration is ~7 × 10^{-3} M.

TABLE V[a]
VARIABLE-TEMPERATURE MAGNETIC SUSCEPTIBILITY DATA IN PYRIDINE FOR COMPLEXES **1**[b] AND **2**[b]

Compound	T, °K	μ_{eff},[c] BM	Compound	T, °K	μ_{eff},[c] BM
(n-Bu–sal)$_2$Ni	292	3.15[d]	(n-Bu–hpr)$_2$Ni	291	3.08
	313	3.16		303	3.05
	333	3.15		313	3.02
(OH–5-Me–hac)$_2$Ni[e]	292	3.21		323	2.95
(OH–5-Me–hpr)$_2$Ni[e]	294	3.21		333	2.85
(n-Bu–hac)$_2$Ni	295	3.18		343	2.74
	303	3.14	(n-Bu–hbu)$_2$Ni	303	3.11
	313	3.07		313	3.03
	323	3.02		323	2.92
	333	2.92		333	2.78
	343	2.88		343	2.64
				353	2.52

[a] Solute concentration (3–6) × 10^{-2} M. [b] Refer to the structures in the text. [c] Calculated by the Curie law: $\mu_{\text{eff}} = 2.84\sqrt{\chi_M T}$. [d] Lit.[15] value 3.14 BM at 293°K. [e] The unsubstituted compounds (OH–hac)$_2$Ni and (OH–hpr)$_2$Ni are unsuitable for magnetic measurements owing to the separation of insoluble pyridine adducts.

Whether this is due to blocking[37] of the approaching pyridine molecules by the bridging group[46] or to electronic factors (*e.g.*, high in-plane ligand field strength[47]) or to both is not clearly known. More fascinating is the behavior of the complexes with B = –(CH$_2$)$_3$–. Relevant spectral and magnetic data are set out in Tables VI and VII, respectively. On examination of this, one concludes that while the salicylaldimine complex is fully paramagnetic up to 80° the other complexes carrying alkyl substituents on the azomethine carbon are only partially paramagnetic and are subject to equilibrium process 2.

TABLE VI[a]
FREQUENCIES (ν, CM^{-1}) AND EXTINCTION COEFFICIENTS (ϵ, L. MOL^{-1} CM^{-1}) OF ELECTRONIC BANDS OF NICKEL(II) COMPLEXES OF TYPE **3**[b] IN PYRIDINE

T, °K	ν_1 (ϵ_1)	ν_2 (ϵ_2)
	((sal)$_2$pn)Ni	
268	11,430 (19.7)	18,180 (19.7)
307	11,430 (19.3)	18,180 (19.7)
327	11,360 (19.0)	18,180 (20.2)
344	11,300 (18.5)	18,180 (21.4)
	((hac)$_2$pn)Ni	
261	10,750 (9.7)	c
288	10,700 (5.8)	
305	10,640 (3.8)	
317	10,640 (2.8)	
344	10,580 (1.6)	

[a] Solute concentration (2–5) × 10^{-3} M. [b] Refer to structure **3** in the text. [c] The ν_2 (or ν_p) band is not very clearly recognizable due to the steeply rising ultraviolet tail.

TABLE VII[a]
VARIABLE-TEMPERATURE MAGNETIC SUSCEPTIBILITY DATA IN PYRIDINE FOR NICKEL COMPLEXES OF TYPE **3**[b]

Compound	T, °K	μ_{eff},[c] BM	Compound	T, °K	μ_{eff},[c] BM
((sal)$_2$pn)Ni	301	3.18	((hac)$_2$pn)Ni	343	1.34
	313	3.19		353	1.28
	333	3.19	((hbu)$_2$pn)Ni	294	1.88
	353	3.18		303	1.70
((hac)$_2$pn)Ni	291	2.03		313	1.52
	303	1.86		323	1.44
	313	1.61		333	1.34
	323	1.56		343	1.24
	333	1.42		353	1.18

[a] Solute concentration (4–8) × 10^{-2} M. [b] Refer to structure **3** in the text. [c] Calculated from the Curie law: $\mu_{\text{eff}} = 2.84\sqrt{\chi_M T}$.

The complexes of type **2** with R = OH are fully paramagnetic (Table V) in pyridine at room temperature. The electronic spectra of the solutions are typical of pseudooctahedral nickel(II) complexes. The last comment also applies to the R = aryl complexes. In this case magnetic measurements were not possible due to solubility limitations.

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[46] The bridging –(CH$_2$)$_2$– group is known to be in the out-of-plane (*gauche*) configuration in several related complexes.[1]

[47] It may be noted that the singlet–singlet crystal field bands in, *e.g.*, (H–hac)$_2$Ni and ((hac)$_2$en)Ni are very near to each other in energy.

Crystalline Pyridine Adducts.—Until now the major evidence in favor of the coordination of two pyridine molecules per molecule of the complex (equilibrium 2) has been the observation of pseudooctahedral crystal field spectra of the adducts in solution. An important confirmation comes from the isolation of crystalline adducts which uniformly showed the composition **2**·2py or **3**·2py. The characterization data and magnetic moments of a few crystalline adducts and the typically pseudooctahedral electronic spectrum of crystalline (Et–hac)$_2$Ni·2py are set out in Table VIII.

Table VIII
Some Data on Pyridine Adducts

Compound	% py Calcd	% py Found[a]	μ_{eff}, BM (T, °K)
(Et–hac)$_2$Ni·2py[b]	29.20	28.80	3.22 (300)
(n-Pr–hac)$_2$Ni·2py	27.80	27.50	3.18 (300)
((hac)$_2$pn)Ni·2py	30.12	28.50[c]	3.20 (294)
(OH–hac)$_2$Ni·2py	30.59	30.75[d]	e

[a] The experiment was done by heating weighed samples of the adduct under vacuum (5 mm) at 115° until the final weight became constant. [b] Electronic spectrum in Nujol mull: $^3A_{2g} \rightarrow {}^3T_{2g}$, 10,420 cm^{-1} (broad and unsymmetrical); $\rightarrow {}^1D$, 12,580 cm^{-1}; $\rightarrow {}^3T_{1g}$, 16,670 cm^{-1} (shoulder) and 17,550 cm^{-1}. The observed splitting of this last band may be due to low symmetry. [c] The low value may be due to the fact that the adduct loses pyridine very readily even at room temperature. [d] An automatic-recording thermogravimetric experiment (heating rate 10°/min) showed that the whole of pyridine is lost in a single step. [e] Not measured.

Several adducts of (R–sal)$_2$Ni were characterized long ago.[35]

Thermodynamic Characterization of Equilibria.—All spectral and magnetic data presented in Tables IV–VII are strictly reversible with respect to temperature. The enthalpy and entropy changes characterizing equilibrium process 2 can be calculated using spectroscopic and magnetic data.

Since the position and the width of the ν_1 band changes with temperature (*vide supra*), the calculations of K (spectroscopic method) were based on oscillator strengths (Table IX) rather than extinction coefficients at band maxima. In calculations of equilibrium constants using magnetic data, the limiting magnetic moment (μ_0 of eq 7) was taken as 3.2 BM on the basis of the moments observed for the crystalline pyridine adducts (Table VIII) and for the fully paramagnetic solutions of **2** (R = OH) in pyridine (Table V). The agreement between the spectral and the magnetic results is good. Some plots of log K *vs.* T^{-1} are shown in Figure 4. The plots are not strictly linear and the slopes tend to decrease with temperature. Probably the enthalpy change, $\Delta H°$, for reaction 2 is temperature dependent. Assuming linearity in the limited temperature range 40–70°, values of $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept, respectively (least-squares fit). The results are shown in Table X.

Table IX
Variable-Temperature Oscillator Strengths (f)
of the ν_1 Band for Two Complexes

(n-Bu–hac)$_2$Ni ($f_0{}^a = 1.70 \times 10^{-4}$)		(n-Bu–hpr)$_2$Ni ($f_0{}^a = 1.75 \times 10^{-4}$)	
T, °K	10^4f	T, °K	10^4f
298	1.69	306	1.61
313	1.64	317	1.57
323	1.58	326	1.43
333	1.44	335	1.31
343	1.29	341	1.19

[a] Limiting oscillator strength reached at ~265°K.

Table X[a]
Enthalpy and Entropy Changes in
Adduct Formation with Pyridine

Compound	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, eu
(n-Bu–hac)$_2$Ni[b]	−11	−39
(n-Bu–hpr)$_2$Ni[b]	−8	−33
(n-Bu–hbu)$_2$Ni[c]	−10	−37
((hac)$_2$pn)Ni[b,d]	−5	−27
((hbu)$_2$pn)Ni[c]	−4	−25

[a] $\Delta H°$ and $\Delta S°$ are reliable to ±1 kcal mol^{-1} and ±5 eu, respectively. [b] Data obtained from a least-squares fit of magnetic and spectral results taken collectively. [c] Data obtained from magnetic measurements only. [d] The limiting spectrum could not be obtained at the lowest temperature accessible. Calculations were made on the basis of the limiting oscillator strength obtained for the ((sal)$_2$pn)Ni complex.

An interesting feature is that, in the bridged compounds **3** the enthalpy and entropy changes are considerably smaller[48,49] than those for complexes **2**. In all cases adduct formation is favored by the enthalpy change ($\Delta H°$) and opposed by the entropy term ($\Delta S°$).

Model for Adduct Formation.—Nothing definite is known about the detailed structure of any of the adducts described in the above sections except that they have a gross octahedral structure. It is known that bis(acetylacetonato)nickel(II)–bispyridine has a *trans* octahedral structure in the crystalline state.[50] However, the corresponding pyridine N-oxide adduct is *cis*.[51] We shall assume that the pyridine adducts we are dealing with have a *trans* octahedral structure in the solution phase. For the adducts of bridged complexes **3** the *trans* structure is guaranteed by the bridge.

Equilibrium process 2 is intimately related to steric factors, at least in complexes of type **2**. Examination of models shows that the R′ group in **2** offers considerable steric blockade to the free movement of the R group. As a result those conformations in which part of the R group (starting from the carbon atom β with respect to nitrogen) projects approximately above or below the molecular plane are preferred. This can hinder the *trans* axial approach of pyridine molecules resulting in equilibrium 2. This steric model clearly requires that when R = CH$_3$, adduct formation should proceed to completion. This does happen as in the case of (Me–hac)$_2$Ni. In the (R–sal)$_2$Ni chelates the azomethine proton creates no effective hindrance to

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(48) It is tempting to suggest that for these chelates the adduct is effectively five-coordinate involving a single Ni–py bond. However, the electronic spectra are very similar to those of **2** in pyridine and distinctly different from the spectra of high-spin five-coordinate species.[49]

(49) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965).

(50) R. C. Elder, *ibid.*, **7**, 1117 (1968).

(51) W. DeW. Horrocks, Jr., D. H. Templeton, and A. Zalkin, *ibid.*, **7**, 1552 (1968).

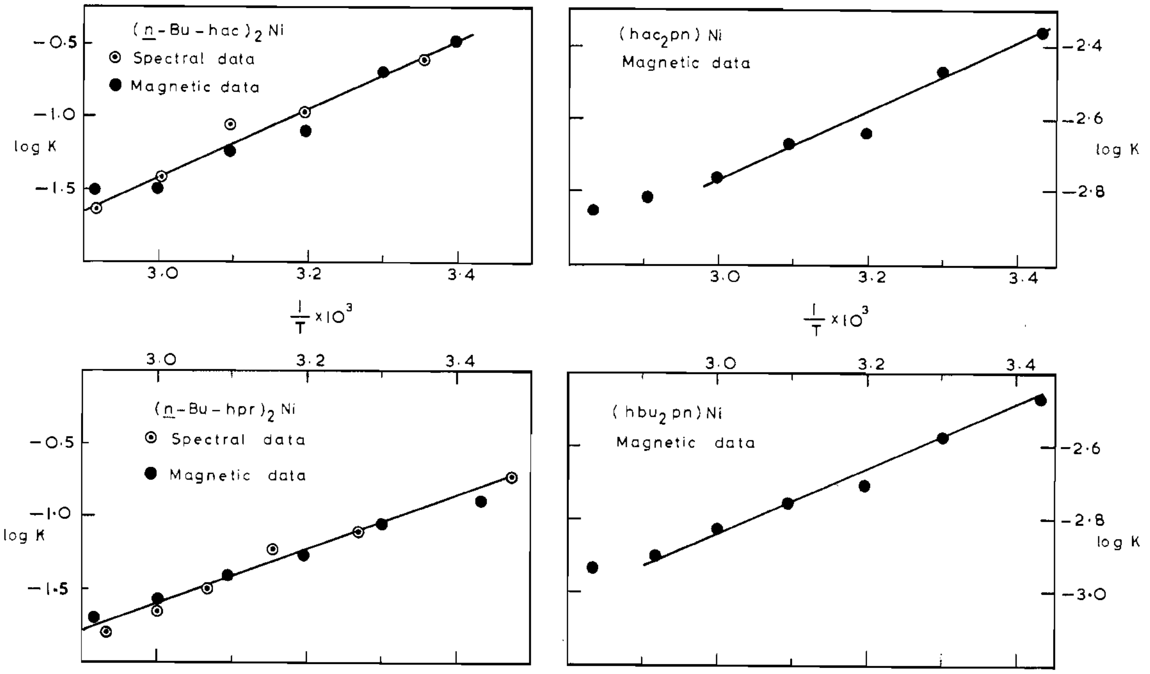

Figure 4.—Some log K vs. T^{-1} plots using magnetic and spectral data in pyridine. The full lines were obtained by the method of least squares.

the rotation of the R group. Accordingly for these complexes, equilibrium 2 is shifted completely to the right in pure pyridine.[52,53] The same steric consideration explains an observation relating to the relative population of tetrahedral species in solutions of (R–sal)$_2$Ni and (R–hac)$_2$Ni having an α-branched R (*e.g.*, *sec*-C_4H_9) group.[32]

Concerning the bridged complexes, one interesting observation is the limiting behaviors of ((sal)$_2$en)Ni (complete lack of paramagnetism) and ((sal)$_2$pn)Ni (complete paramagnetism) in pyridine solution. The in-plane ligand field is weaker in the latter complex.[12] It also has the more flexible six-membered bridging chelate ring which may conceivably be sterically more favorable than the five-membered ring in ((sal)$_2$en)Ni to axial approach of pyridine. One or both of these factors may be responsible for the observed trend in solution paramagnetism. We believe that the incomplete paramagnetism of **3** (B = $(CH_2)_3$) in pyridine also results at least partly from steric effects. Models show that the alkyl group on the azomethine carbon can interact with the bridge such that in preferred conformations the middle CH_2 group of the bridge hinders axial approach of pyridine.

A Generalization.—In conclusion we note that a generalization is possible on the basis of our results. The tendency to attain paramagnetism is uniformly less in complexes **2** and **3** than that in the corresponding salicylaldimine chelates. This generalization applies whether the paramagnetism arises from solute association or from solute–solvent interaction. In fact it also applies when the paramagnetism is due to planar (S = 0) ⇄ tetrahedral (S = 1) equilibrium. At least a major part of this generalization is rooted in steric factors. At present we are investigating steric effects in complexes which have the same basic structure as **2** except that the R group carries an additional coordination position (*e.g.*, R = $CH_2CH_2OCH_3$).

Copper Complexes.—Only complexes derived from Schiff bases of 2-hydroxyacetophenone were examined spectroscopically. The results are shown in Table XI.

TABLE XI
FREQUENCIES (ν, CM^{-1}) AND EXTINCTION COEFFICIENTS (ϵ, L. MOL^{-1} CM^{-1}) OF ELECTRONIC BANDS OF COPPER(II) COMPLEXES OF TYPE 2[a] AND 3[a] IN CHLOROFORM AND PYRIDINE AT ROOM TEMPERATURE (303°K)

Compound R or B	ν (ϵ) Chloroform[c]	Pyridine[d]
H	17,540 (70)	17,540 (95)
CH_3	17,240 (150)[b]	16,130 (162)
n-C_4H_9	17,240 (154)[b]	16,130 (190)
–$(CH_2)_2$–	18,180 (315)	17,540 (292)
–$(CH_2)_3$–	18,180 (258)[b]	16,950 (222)

[a] Refer to the structures in the text. [b] Shoulder. [c] Solute concentration (1–7) × 10^{-3} M. [d] Solute concentration (1–4) × 10^{-3} M.

In the visible region all complexes show one broad feature in the frequency range 17,500–18,200 cm^{-1} in chloroform solution. In pyridine solution, the general nature of the spectrum remains the same. However, the bands become more well defined and undergo small red shifts with concomitant intensity changes. Presumably pyridine coordination does take place.

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(52) It is reported[53] that equilibria similar to (2) exist in solutions of (R–sal)$_2$Ni in mixtures of chloroform and pyridine. The equilibrium constant decreases with the length of the alkyl chain. This has been attributed to inductive and hyperconjugative effects of the alkyl groups. Variations of these effects among different alkyl groups are likely to be small and accordingly the complexes become fully paramagnetic in pyridine irrespective of the length of the R group. We do not believe that these electronic factors make any significant contributions to the large differences in equilibrium positions of, *e.g.*, (Me–hac)$_2$Ni and (n-Bu–hac)$_2$Ni.

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Whether this proceeds completely or equilibria similar to (2) exist in the solutions cannot be decided on the basis of the present results.

The spectral behavior is qualitatively similar to that of the salicylaldimines.[12,54–56] Interestingly, whereas $((sal)_2en)Cu$ exists as a dark green dimer[57,58] in the crystalline state and gives violet monomeric solutions in, *e.g.*, chloroform, the complex $((hac)_2en)Cu$ is violet both in the solid state and in solution. Electronic spectra are very similar in both phases. Apparently solid-state dimerization does not occur in the case of $((hac)_2en)Cu$.

Acknowledgments.—Thanks are due to the Council of Scientific and Industrial Research for a senior fellowship to T. S. K. The help received from Mr. S. Gupta of this laboratory during early stages of this research is gratefully acknowledged. Thanks are due to Dr. D. Devaprabhakara for helpful discussions. Microanalyses were done by Mr. A. H. Siddiqui of this department.

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Electrochemistry of Transition Metal Dithienes. I. Bis(maleonitriledithiolate)nickel(II) in Acetonitrile

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Received December 1, 1969

Chronopotentiometry and linear-scan voltammetry are used to demonstrate that the oxidation of $Ni(mnt)_2^{2-}$ and the reduction of $Ni(mnt)_2^-$ are diffusion controlled in acetonitrile in the presence of $(C_2H_5)_4NClO_4$ and that neither species is electroactively adsorbed onto platinum. Electron transfer is exceedingly rapid, $k_{s,h} > 1$ cm sec^{-1}. The substantial decrease in anionic mobility with increasing negative charge is attributed to the electrostriction effect. Vapor pressure osmometry demonstrates that $Ni(mnt)_2^{2-}$ but not $Ni(mnt)_2^-$ is ion paired, $K_f \approx 500\ M^{-1}$. After correction for ion-pair formation and changes in activity coefficients, $E° = -(0.17 \pm 0.01)$ V *vs.* $Ag^+(0.01\ M)|Ag$.

Introduction

Voltammetric and polarographic current–potential curves proved to be exceedingly useful for demonstrating the existence and interconversion of the several members of particular transition metal 1,2-dithiene oxidation–reduction series. Such experiments have also demonstrated ligand exchange between complexes and the dimeric nature of certain iron and cobalt bis complexes in dichloromethane. Half-wave potentials have guided synthetic work and served for the comparison of relative thermodynamic stabilities.[1,2] We are investigating the kinetics of the electrochemical interconversion of representative dithiene complexes and in this communication we present our results for nickel complexes with the maleonitriledithiolate ligand in acetonitrile. We have demonstrated that the electron-transfer step for the oxidation of bis(maleonitriledithiolate)nickel(II), $Ni(mnt)_2^{2-}$, is exceedingly rapid at platinum and is uncomplicated by electrochemically significant solution reactions. This complex and its one-electron oxidation product $Ni(mnt)_2^-$ are not adsorbed onto platinum. $Ni(mnt)_2^{2-}$ but not $Ni(mnt)_2^-$ is ion paired with the supporting electrolyte cation. Activity coefficient and ion-pairing corrections accurately reproduce the shift of half-wave potential with supporting electrolyte concentration. The fortuitous use of larger cation electrolytes and/or a single electrolyte concentration doubtless prevented the earlier observation of this ion-pairing phenomenon.

Experimental Section

The synthesis of transition metal dithiolates has been reviewed.[3] The salts $[(CH_3)_4N]_2Ni(mnt)_2$, $[(C_2H_5)_4N]_2Ni(mnt)_2$, $[(C_2H_5)_4N]_2$-$Pt(mnt)_2$, and $[(C_2H_5)_4N]Ni(mnt)_2$ were prepared as previously described;[4] elemental analyses were in excellent agreement with the theoretical stoichiometries.

This system appears to be insensitive to small amine and unsaturated nitrile impurities in the acetonitrile since no differences were observed using Eastman practical grade acetonitrile purified by method F of Forcier and Olver,[5] the second distillation being from sulfuric acid, as compared with Matheson Coleman and Bell Spectro Grade solvent. Water content is also relatively unimportant since the deliberate addition of 1% water does not affect the position or shape of linear-scan voltammograms.

Tetraethylammonium perchlorate was obtained from Eastman Chemical Co. (White Label) and was recrystallized from water and dried at room temperature in a vacuum desiccator. Benzil of unknown origin was recrystallized three times from ethanol–water.

The $Ag–Ag^+(0.01\ M),(C_2H_5)_4NClO_4(0.1\ M)$ electrode in acetonitrile solvent was used as the reference electrode in order to avoid any possible difficulties in reproducing the liquid junction

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