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Complexes Derived from Strong Field Ligands. XVII. Electronic Spectra of Octahedral Nickel(II) Complexes with Ligands of the α -Diimine and Closely Related Classes

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The LaPorte forbidden spectra of twelve octahedral nickel(II) complexes containing ligands having the $—N=C—C=N—$ chelate rings are interpreted in terms of modern ligand field theory. The complete octahedral energy level diagram for nickel(II) is calibrated in the region of high Dq (>1200 cm^{-1}) on the basis of these results. The subject compounds exhibit Dq values spanning the range from 980 through 1280 cm^{-1} , making possible the determination of the relative energies of the 1E_g and ${}^3T_{2g}$ states at high ligand field. These data lead to clarification of uncertainties relating to the Dq values assigned to the familiar 1,10-phenanthroline and 2,2'-bipyridine complexes. The planar structure of R_1R_2N function of pyridinal-hydrazones is confirmed. The critical Dq for spin-pairing in octahedral iron(II) complexes is estimated to be 1250 ± 80 cm^{-1} (based on the spin-free state).

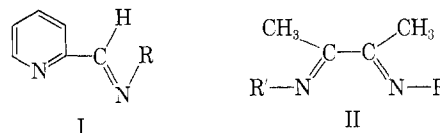
Introduction

The complexes of 1,10-phenanthroline and 2,2'-bipyridine with the transition metal ions rank among the most studied and best characterized coordination compounds containing ligands of strong bonding ability.³ The spectra of the nickel(II) complexes of these familiar ligands have previously been determined and assignments of the observed transitions have been made by Jørgensen⁴ and by Liehr and Ballhausen.⁵ The earlier investigators have indicated differences of opinion with regard to the assignments of the transitions to the 1E_g and ${}^3T_{2g}$ states. This uncertainty has remained unresolved despite the elegant and complete theory of the electronic states of d^8 in fields of O_h symmetry as presented by Liehr and Ballhausen. Clearly, the thorough testing of this detailed theory in the range of ligand field strengths around those of *o*-phenanthroline (*o*-phen) and 2,2'-bipyridine (dipy) could not be accomplished prior to the availability of more extensive data. Although Liehr and Ballhausen⁵ suggest that the 1E_g state will lie below the ${}^3T_{2g}$ state only at Dq values in excess of 1300 cm^{-1} and simultaneously assign a Dq to *o*-phen of 1155 cm^{-1} , it has been pointed out that this should be regarded as a best opinion in the absence of more extensive data.⁶

Complexes Containing Ligands of the Dimethine Class

The development of a substantial series of complexes derived from the hydrazones and imines of α -diketones and 2-pyridinaldehyde, during recent years,⁷⁻¹³ has

now made possible a detailed investigation of the electronic states of octahedral nickel(II) in the region of strong ligand fields. A variety of structural parameters may be altered in these substances, providing a range of ligand field strengths. The ligands for which data are presented here may be represented by structures I and II, where R is CH_3 , $(\text{CH}_3)_2\text{CH}$, $\text{CH}_2\text{C}_6\text{H}_5$, NH_2 , NHCH_3 , $\text{N}(\text{CH}_3)_2$, NHC_6H_5 , or $\text{N}(\text{C}_6\text{H}_5)_2$ and R' is CH_3 or NH_2 . The syntheses and properties of most of these substances have been reported earlier.⁷⁻¹³



However, 2-pyridinalisopropylimine (PiPI) and 2-pyridinalbenzylimine (PBI) and the iron(II) and nickel(II) complexes— $\text{Fe}(\text{PiPI})_3(\text{BF}_4)_2$, $\text{Ni}(\text{PiPI})_3(\text{BF}_4)_2$, $\text{Fe}(\text{PBI})_3(\text{BF}_4)_2$, and $\text{Ni}(\text{PBI})_3(\text{BF}_4)_2$ —are reported for the first time here. The molar magnetic susceptibilities and magnetic moments of these new compounds are listed in Table I. These values conform to the usual values for octahedral complexes of Fe(II) and Ni(II) with ligands of this class. It has been noted earlier¹³ that of all the known bidentate ligands derived from structure I, only 2-pyridinal-N,N-dimethylhydrazone produces a spin-free complex of the formula FeL_3^{2+} , all the other complexes of this class being spin paired.

Electronic Spectra of the Nickel(II) Complexes

The spectral data reported in Table II were obtained with a Cary Model 14 recording spectrophotometer,

TABLE I
MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF SOLID COMPLEXES OF SOME SUBSTITUTED IMINES OF 2-PYRIDINALALDEHYDE

Complex	$\chi_M \times 10^4$ (complex)	μ_{eff} , B.M.
$[\text{Fe}(\text{PiPI})_3](\text{BF}_4)_2 \cdot 1.5\text{H}_2\text{O}$	—148	...
$[\text{Ni}(\text{PiPI})_3](\text{BF}_4)_2 \cdot 1.5\text{H}_2\text{O}$	3,744	3.18
$[\text{Fe}(\text{PBI})_3](\text{BF}_4)_2$	—338	...
$[\text{Ni}(\text{PBI})_3]\text{I}_2$	3,356	3.10

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(3) W. W. Brandt, F. P. Dwyer, and F. C. Gyrfas, *Chem. Rev.*, **54**, 412 (1954).(4) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).(5) A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (N.Y.)*, **6**, 134 (1959).

(6) A. D. Liehr, private communication.

(7) D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **78**, 1137 (1956).(8) R. C. Stouffer and D. H. Busch, *ibid.*, **78**, 6016 (1956).(9) P. E. Figgins and D. H. Busch, *ibid.*, **82**, 820 (1960).(10) R. C. Stouffer and D. H. Busch, *ibid.*, **82**, 3491 (1960).(11) R. C. Stouffer, D. H. Busch, and W. B. Hadley, *ibid.*, **83**, 3732 (1961).(12) P. E. Figgins and D. H. Busch, *J. Phys. Chem.*, **65**, 2236 (1961).(13) M. A. Robinson and D. H. Busch, *Inorg. Chem.*, **2**, 1171 (1963).

TABLE II
 ABSORPTION^a BANDS OF OCTAHEDRAL DIVALENT NICKEL(II) COMPLEXES WITH LIGANDS OF THE DIMETHINE TYPE

Complex ^b	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (${}^3T_g \rightarrow {}^3T_{2-3}$)		${}^3A_{2g} \rightarrow {}^1E_g(D)$ (${}^3T_g \rightarrow {}^1T_g$)		${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (${}^3T_g \rightarrow {}^3T_{1,3-3}$)		<i>Dq</i>
	cm. ⁻¹	ϵ	cm. ⁻¹	ϵ	cm. ⁻¹	ϵ	
[Ni(H ₂ O) ₆] ²⁺ ^c	8,600	(2.5)	14,500	(1.8)	13,500	(1.8)	860
[Ni(PdPH) ₂ Cl ₂]	9,850	(4.7)	12,580	(4.4)	985
[Ni(PMH) ₂ Cl ₂]	10,260	(8.1)	12,420	(4.2)	1026
[Ni(PPH) ₂ Cl ₂]	10,310	(7.4)	12,410	(3.6)	1031
[Ni(PdMH) ₃] ⁺²	10,440	(7.5)	12,180	(5.4)	17,990	(32.1)	1044
[Ni(en) ₃] ^{+2c}	11,200	(7.3)	12,400	(5.0)	19,270	(39.0)	1120
[Ni(PiPI) ₃] ⁺²	12,380	(7.2)	11,490	(7.55)	18,350	(6.7)	1120
[Ni(PBI) ₃] ^{+2d}	12,500	(7.55)	11,610	(7.4)	19,100	(10.5)	1238
[Ni(dipy) ₃] ^{+2c}	12,650	(7.1)	11,500	(5.7)	1250
[Ni(BMI) ₃] ⁺²	12,660	(11.1)	11,420	(7.15)	19,200	(11.6)	1265
[Ni(PMI) ₃] ⁺²	12,670	(8.9)	11,710	(7.3)	25,380	(102)	1266
[Ni(PMH) ₃] ⁺²	12,690	(7.5)	11,770	(6.3)	≈19,510	(14.6)	1267
					[19,840]	(21.9)	1269
					[20,830]	(23.4)	1269
[Ni(<i>o</i> -phen) ₃] ^{+2c}	12,700	(6.8)	11,550	(5.5)	19,300	(11.9)	1270
[Ni(PAH) ₃] ⁺²	12,720	(7.6)	11,850	(6.3)	≈20,880	(21.4)	1272
[Ni(BdH) ₃] ⁺²	12,800	(10.0)	11,740	(6.9)	20,260	(24.6)	1280

^a The double group notation as used by Liehr and Ballhausen³ is given as is the more familiar Mulliken representation. ^b Abbreviations: PAH, 2-pyridinalhydrazone; PMH, 2-pyridinalmethylhydrazone; PdMH, 2-pyridinaldimethylhydrazone; PPH, 2-pyridinalphenylhydrazone; PdPH, 2-pyridinaldiphenylhydrazone; en, ethylenediamine; PiPI, 2-pyridinalisopropylimine; PMI, 2-pyridinalmethylimine; PBI, 2-pyridinalbenzylimine; dipy, 2,2'-bipyridine; *o*-phen, 1,10-phenanthroline; BdH, biacetyldihydrazone; BMI, biacetyl bismethylimine. ^c Values obtained from C. K. Jørgensen, *Acta Chem. Scand.*, 9, 1362 (1955). ^d DMF used as solvent.

using matched cells with fused quartz windows. The region from 0.2 to 12 μ was recorded using concentrations of the order of $2 \times 10^{-2} M$. Water was used as the solvent except where otherwise noted. The extinction coefficients listed are experimental values.

Considering only the triplet states for octahedral nickel(II), the progression of energy levels is ${}^3A_{2g} < {}^3T_{2g} < {}^3T_{1g}(F) < {}^3T_{1g}(P)$.¹⁴ For complexes containing six saturated nitrogen atoms as donors, the transitions occur in the ranges¹⁵: ${}^3A_{2g} \rightarrow {}^3T_{2g}$, 10,800–11,500 cm.⁻¹; ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, 16,500–18,900 cm.⁻¹; ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, 27,200–29,000 cm.⁻¹. On the basis of chemical behavior, the dimethine ligands are expected to exhibit greater ligand field strengths than the aliphatic amines or polyamines. Indeed, the former lead to spin pairing in the case of iron(II), while the latter do not. The proper assignment of the absorption bands of nickel(II) ions in their complexes with dimethine ligands should be consistent with the chemical facts.

The spectra of the complexes of immediate interest (Table II) reveal absorptions assignable to d-d transitions only in the first two regions, 10,000–13,000 cm.⁻¹ and $\sim 20,000$ cm.⁻¹. The third band, ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, is obscured by an intense charge-transfer absorption.¹⁶

The occurrence of the low-lying 1E_g state complicates assignments and the determination of the ligand field parameters in the case of octahedral nickel(II). Liehr and Ballhausen have shown that the occurrence of the ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ band (second band) as a double peak in the case of Ni(H₂O)₆²⁺ is probably best explained on the

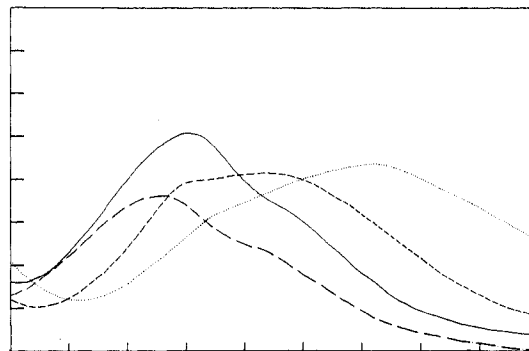


Fig. 1.—Absorption spectra of octahedral nickel(II) complexes with ligands of the dimethine type: —, $4.49 \times 10^{-2} M$ [Ni(BMI)₃]₂; - - -, $3.54 \times 10^{-2} M$ [Ni(BdH)₃]₂; ····, $1.10 \times 10^{-2} M$ [Ni(PiPI)₃](BF₄)₂⁺; ·····, $1.15 \times 10^{-2} M$ [Ni(PdMH)₃]₂.

^a Measurements involve 5-cm. cell (all others measured with 1-cm. cells).

basis of spin-orbit splitting on the ${}^3T_{1g}(F)$ state. However, these same authors point out the fact that this splitting depends on *Dq* (decreasing as *Dq* increases) and that the spin-orbit components of the first excited triplet state are not sufficiently far apart to produce doubling, even at low *Dq*. Now at *Dq* values substantially in excess of 1000 cm.⁻¹, the first absorption band (${}^3A_{2g} \rightarrow {}^3T_{2g}$) is either split or exhibits a pronounced shoulder. Further, the lower intensity component appears to approach the band from higher energies, pass through it, and finally appear at lower energies as *Dq* increases. This is illustrated by Fig. 1. From the theory of Liehr and Ballhausen, it appears that the original mechanism of Jørgensen⁴ must be invoked to explain the doubling of the first band in octahedral nickel(II) complexes with ligands of high field strength. With these considerations at hand, additional criteria have been assumed in the assigning

(14) C. J. Ballhausen, *Kgl. Danske Videnskab. Selskab., Mat.-Fys. Medd.*, 24, No. 8 (1955).

(15) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, p. 296.

(16) The value of the Racah parameter *B* cannot be accurately assessed in the absence of the transition to ${}^3T_{1g}(P)$. This absorption is covered by an intense absorption which also limits the certainty of the positioning of the ${}^3T_{1g}(F)$ term. The best estimate of *B* on this limited basis is 1150 ± 25 cm.⁻¹ for seven of the compounds of principal interest.

of the components of the first band in these complexes. In general, the complex spin-orbit composition of the ${}^3T_{2g}$ band would be expected to produce a band of considerable breadth. Further, except when the states are in close proximity or in coincidence, the transition to ${}^3T_{2g}$ would be expected to exhibit a greater intensity than to the 1E_g state, although spin-orbit interaction should permit the latter state to share intensity with the former. A comparison of the data of Table II with the sample spectra contained in Fig. 1 reveals that the assignments derived from these criteria offer satisfying self-consistency. On this basis the ligands 2,2'-bipyridine, biacetylismethylimine, 2-pyridinalmethylimine, 2-pyridinalmethylhydrazine, 1,10-phenanthroline, and 2-pyridinalhydrazine all exhibit Dq values in the range 1265–1272 cm^{-1} , while the electron-rich ligand biacetyldihydrazine exhibits a greater value, 1280 cm^{-1} , some 15 cm^{-1} greater than dipyrindyl. On the same basis, 2-pyridinalbenzylimine and 2-pyridinalisopropylimine are of measurably lower Dq , about 1240 cm^{-1} . The latter ligands are associated with imine functions bearing bulky alkyl groups. If one chose arbitrarily to reverse the assignments made to the transitions to ${}^3T_{2g}$ and 2E_g , no equally appropriate accounting for the variation in intensity of the two components of the first band could be offered. Also, these ligands would be placed inappropriately close to ethylenediamine in ligand field strength.

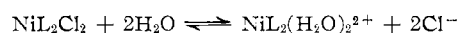
On the basis of the assignments made, it should be pointed out that the 1E_g state is expected to lie lower in energy than the ${}^3T_{2g}$ state for Dq values in excess of 1200 cm^{-1} . This constitutes only a slight modification of the energy level pattern derived from theory by Liehr and Ballhausen.⁵

The Steric Effect in Pyridinalhydrazine Complexes

The effect of substituting the amino function of pyridinalhydrazine is quite interesting. Both pyridinalhydrazine and pyridinalmethylhydrazine exhibit large Dq values, 1272 and 1264 cm^{-1} , respectively. This shows that the electron-releasing effect of the methyl group has relatively little influence on the complexing ability of these ligands. The substitution of a second methyl group on the amino group, forming 2-pyridinaldimethylhydrazine, results in an extreme decrease in the field strength of the ligand, the Dq value falling at 1044 cm^{-1} in the three-to-one octahedral nickel(II) complex. Such an effect is clearly not explainable on the basis of electronic effects; however, it is readily understood on the basis of a hypothesis set forth earlier¹³ to account for the anomalous nature of the iron(II) complex of 2-pyridinaldimethylhydrazine. It was found that the iron(II) complex $\text{Fe}(\text{PdMH})_3\text{I}_2$ exhibits the full paramagnetism of the spin-free state ($\mu_{\text{eff}} = 5.45$ B.M.) while all other complexes of the formula $[\text{FeL}_3]\text{X}_2$ with bidentate ligands of this type are spin paired. The possibility of a steric effect related to the bulk of a pyramidal $-\text{N}(\text{CH}_3)_2$ group may be eliminated on the basis of the behavior of the 2-pyridinalisopropyl-

imine (PiPI) complex, for the isopropyl function would then be the steric equivalent of the dimethylamino group. However, the iron(II) complex is spin paired. Further, the value of Dq for $\text{Ni}(\text{PiPI})_3^{2+}$, 1238 cm^{-1} , is only moderately lower than that for dipyrindyl (1265 cm^{-1}). The most probable explanation for the unusually low value of Dq in the case of the nickel complex of 2-pyridinaldimethylhydrazine may still be derived from steric considerations. In the event that the methyl groups in the $-\text{N}(\text{CH}_3)_2$ function were coplanar with the remainder of the ligand molecule, the addition of the second methyl group should result in an interligand repulsion (as revealed by models) that would cause an increase in the metal-donor bond distance with an accompanying decrease in ligand field strength. The near equivalence of Dq for PMH and PAH may be rationalized on the basis that the methyl group in the former may be directed away from the other ligands within the coordination sphere. The expected consequences of planarity of $-\text{NR}_1\text{R}_2$ on the properties of the hydrazones and their complexes have been verified by infrared spectral studies.¹⁸ The knowledge gained in these studies on interligand repulsions is being applied to the design of ligands of donor abilities intermediate between PdMH and PiPI.

The steric requirements of the phenyl group are so great in complexes containing substituted pyridinalhydrazones that 2-pyridinalphenylhydrazine and 2-pyridinaldiphenylhydrazine are limited to the formation of bis complexes with nickel(II). This stands in contrast to the behavior of 2-pyridinalbenzylimine, again providing evidence for the planarity of the group $-\text{NR}_1\text{R}_2$. The low values for Dq for the complexes containing only two moles of bidentate ligand are readily understood in terms of the concept of average environment.¹⁷ In water the dihalo compounds should aquate rapidly and the weak Dq of water would lower the average Dq of the complex.



The Critical Dq for Spin-Pairing among Octahedral Iron(II) Complexes

The information at hand facilitates a substantial improvement in the estimation of the critical value for Dq for the pairing of electrons among complexes of iron(II). From spectral data, it is possible to assign approximate values for the ligand field splitting parameter, Dq , for the octahedral iron(II) complexes of chloride,¹⁸ water,^{18,19} PdMH (this work), ammonia,¹⁸ and ethylenediamine.^{19,20} These values are compared in Table III with the corresponding values for octahedral Ni^{2+} . It is seen that for the spin-free octahedral complexes the ratio $Dq_{\text{Fe}^{2+}}/Dq_{\text{Ni}^{2+}}$ has a mean value of 1.11 with a mean deviation of about ± 0.07 . If this value of the ratio is taken as a basis for extrapolation, an estimate may be made of the

(17) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 887 (1956).

(18) C. Furlani, *Gazz. chim. ital.*, **87**, 371 (1957).

(19) F. A. Cotton and M. D. Meyers, *J. Am. Chem. Soc.*, **82**, 5023 (1960).

(20) M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 4553 (1960).

lower limit of the value of Dq for iron(II) in complexes of dimethine ligands in which the electrons of the iron atom are completely spin paired. On this basis the value for the weakest ligand of the series producing spin pairing (see Table II) is estimated to be 1374 cm.^{-1} . This value would be most appropriate for a spin-free iron(II) complex by virtue of the manner of estimation.

TABLE III
THE LIGAND FIELD SPLITTING PARAMETER FOR OCTAHEDRAL IRON(II)

Ligand	Dq		$Dq_{\text{Fe}^{2+}}/Dq_{\text{Ni}^{2+}}$
	Ni^{2+}	Fe^{2+}	
Cl^-	720	860	1.19
H_2O	860	1040	1.21
PdMH	1044	1163	1.11
NH_3	1080	1115	1.03
en	1120	1140	1.02

Since the formation of the spin-paired state should result in a diminished metal-donor atom distance, the actual value for the iron(II) atom in diamagnetic $\text{Fe}(\text{PiPI})_3^{2+}$ should be somewhat larger. However, a second consideration limits the magnitude of the value. As the data in Table III reveal, the ratio $Dq_{\text{Fe}^{2+}}/Dq_{\text{Ni}^{2+}}$ decreases with increasing Dq , having an average value of 1.05 for the three stronger ligands (PdMH, NH_3 , en). Using this value, the Dq value for the hypothetical spin-free analog of the iron(II) complex with PiPI is 1300 cm.^{-1} . Since the actual ratio $Dq_{\text{Fe}^{2+}}/Dq_{\text{Ni}^{2+}}$ may diminish even further among spin-free complexes of still greater Dq , it would be surprising if Dq for the weakest ligand from the series known to produce spin pairing in Fe(II) exceeds a value intermediate between the estimates stated (1300 – 1374 cm.^{-1}); choosing 1340 cm.^{-1} as a reasonable magnitude for Dq for the hypothetical spin-free $\text{Fe}(\text{PiPI})_3^{2+}$, the critical Dq must lie between this value and that for the strongest ligand known to produce spin-free iron(II), PdMH. This limits the critical Dq to the range 1160 – 1340 cm.^{-1} , or $1250 \pm 80 \text{ cm.}^{-1}$. The synthesis of ligands within this range of Dq values should lead to a reduction in these limits and to the discovery of complexes in which Dq falls sufficiently close to the critical value to permit the thermal population of both the spin-free and the spin-paired states for octahedral iron(II).

Experimental

2-Pyridinalisopropylimine.—Freshly distilled 2-pyridinaldehyde (10.71 g. , 0.10 mole) is added dropwise with stirring to isopropylamine (6.50 g. , 0.110 mole). The mixture is stirred for 30 min. and then fractionated, keeping that portion which comes over at 78 – 80° (2 mm.); yield 77% . *Anal.* Calcd. for $\text{C}_9\text{H}_{12}\text{N}_2$: C, 72.97 ; H, 8.11 ; N, 18.92 . Found: C, 72.99 ; H, 8.01 ; N, 18.87 .

Tris-(2-pyridinalisopropylimine)-iron(II) Fluoroborate 1.5-Hydrate.—Iron(II) chloride 4-hydrate (2.00 g. , 0.01 mole) is dis-

solved in 40 ml. of distilled water and added slowly to 2-pyridinalisopropylimine (4.90 g. , 0.033 mole). After stirring for 30 min., 4.0 g. of sodium fluoroborate in 20 ml. of distilled water is added. The volume is reduced by means of a rotary evaporator and the solution is placed in a refrigerator overnight. The purple solid thus obtained is filtered, washed with a small amount of cold water, and recrystallized from 25 ml. of water at 50° by cooling to 0° . The crystals are dried *in vacuo* over P_2O_5 at room temperature; yield 90% . *Anal.* Calcd. for $[\text{Fe}(\text{C}_9\text{H}_{12}\text{N}_2)_3](\text{BF}_4)_2 \cdot 1.5\text{H}_2\text{O}$: C, 46.22 ; H, 5.56 ; N, 12.00 . Found: C, 45.79 ; H, 5.60 ; N, 12.40 .

Tris-(2-pyridinalisopropylimine)-nickel(II) Fluoroborate 1.5-Hydrate.—This compound is prepared in an analogous manner to that reported for the iron(II) counterpart; yield 73% . *Anal.* Calcd. for $[\text{Ni}(\text{C}_9\text{H}_{12}\text{N}_2)_3](\text{BF}_4)_2 \cdot 1.5\text{H}_2\text{O}$: C, 46.02 ; H, 5.54 ; N, 11.93 . Found: C, 46.01 ; H, 5.30 ; N, 12.25 .

2-Pyridinalbenzylimine.—Freshly distilled 2-pyridinaldehyde (10.70 g. , 0.10 mole) is added dropwise to a solution of benzylamine (11.80 g. , 0.110 mole) in 50 ml. of absolute ethanol. The solution is stirred for 30 min. and fractionated, keeping the 165 – 166° (5 mm.) portion; yield 78% . *Anal.* Calcd. for $\text{C}_{13}\text{H}_{12}\text{N}_2$: C, 79.59 ; H, 6.12 ; N, 14.29 . Found: C, 79.52 ; H, 5.98 ; N, 14.37 .

Tris-(2-pyridinalbenzylimine)-iron(II) Fluoroborate.—Iron(II) chloride 4-hydrate (2.00 g. , 0.01 mole) is dissolved in 40 ml. of distilled water, and the solution is added dropwise with stirring to 2-pyridinalbenzylimine (6.90 g. , 0.033 mole). The mixture is stirred for 30 min. followed by the addition of a solution of 3.3 g. of sodium fluoroborate in 20 ml. of distilled water. The reaction mixture is placed in a refrigerator overnight and then filtered. The purple crystals thus obtained are washed with a small amount of cold water and recrystallized from a 50% acetone-water solution; yield 77% . *Anal.* Calcd. for $[\text{Fe}(\text{C}_{13}\text{H}_{12}\text{N}_2)_3](\text{BF}_4)_2$: C, 57.21 ; H, 4.40 ; N, 10.27 . Found: C, 57.10 ; H, 4.60 ; N, 10.35 .

Tris-(2-pyridinalbenzylimine)-nickel(II) Fluoroborate.—This complex exists as tan crystals and is formed in a manner analogous to the iron(II) derivative; the one exception being that the crude material must be crushed before recrystallization; yield 58% . *Anal.* Calcd. for $[\text{Ni}(\text{C}_{13}\text{H}_{12}\text{N}_2)_3](\text{BF}_4)_2$: C, 57.00 ; H, 4.38 ; N, 10.23 . Found: C, 56.78 ; H, 4.64 ; N, 10.20 .

Tris-(2-pyridinalbenzylimine)-nickel(II) Iodide.—2-Pyridinaldehyde (5.36 g. , 0.05 mole) is added with stirring to a solution previously made by dissolving $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (3.92 g. , 0.0165 mole) in 15 ml. of distilled water and adding benzylamine (8.04 g. , 0.075 mole) with stirring. After several minutes, the brown solution is filtered and the residue is washed several times with distilled water. The excess benzylamine is removed at reduced pressures and 6.0 g. of potassium iodide is added with stirring. The brown oil obtained after cooling by decantation of the supernatant liquid is recrystallized twice in the same manner as the fluoroborate salt. The crystals are washed with cold distilled water, methanol, and ethanol (in that order) and dried *in vacuo* over P_2O_5 overnight; yield 46.5% . *Anal.* Calcd. for $[\text{Ni}(\text{C}_{13}\text{H}_{12}\text{N}_2)_3]\text{I}_2$: C, 51.97 ; H, 4.03 ; I, 28.17 ; N, 9.32 . Found: C, 52.04 ; H, 4.02 ; I, 27.94 ; N, 9.12 .

Magnetic Measurements.—All magnetic measurements were made at room temperature by the Gouy method using ferrous ammonium sulfate 6-hydrate and mercury(II) tetrathiocyanatocobaltate(II) as standards. In Table I are listed the molar susceptibilities and the corrected values for the imine complexes under consideration. The molar diamagnetic corrections used in calculating μ_{eff} are: for 2-pyridinalisopropylimine (PiPI), -129×10^{-6} ; for 2-pyridinalbenzylimine (PBI), -179×10^{-6} ; for fluoroborate anion, -39×10^{-6} ; and for water, -13×10^{-6} c.g.s. unit.