the Re–Cl_a and Re–Cl_b distances are to be regarded as indicating the existence of normal, single bonds. The Re–Cl_c distances of 2.52 Å. are about 0.15 Å. longer, however. This lengthening is definitely significant, being *much* greater than the sum of the standard deviations in the short (σ = 0.02, 0.04) and in the long (σ = 0.03) Re–Cl distances, and indicates that the Re–Cl_c bonds are weaker than the other, normal ones. This may be partly, or even entirely due to steric pressure of the Cl_a atoms on the Cl_c atom, rather than to any inherent tendency of the Re–Cl_c bond to be weaker.

All Cl–Re–Cl angles are within 1–2° of 90° except for the Cl_a–Re–Cl_c angles, which are only 80°. This, however, is due in large part at least to van der Waals repulsions between the Cl_a atoms. Thus, it is possible to describe the structure and bonding in the following way. Each rhenium atom lies in an approximately square $ReCl_4$ group, for which four of its oribitals are required. It uses an orbital on one side of this plane to bind a fifth chlorine atom, somewhat more loosely. Its remaining orbitals are used in the intermetal bonding in the Re_3 cluster.

Crystal Packing.—The crystal packing is illustrated in Fig. 2, which shows the projection down the [100] axis. All Cs···Cl distances (Table VI) are within an acceptable range, 3.3–3.9 Å. (*cf.* 3.6 in CsCl). In particular, there is no indication that any Cs···Cl interactions are seriously perturbing the $[Re_3Cl_{12}]^{3-}$ structure. The coordination numbers of the cesium atoms cannot be defined rigorously because of the range of Cs···Cl distances. If we arbitrarily select 3.9 Å. as a cut-off for the coordination sphere, the coordination numbers of Cs_I, Cs_{II}, and Cs_{III} are, respectively, 12, 11, and 10. The polyhedra so defined are all rather irregular, although the arrangement about Cs_I is somewhat similar to the 3, 6, 3 set of neighbors about a sphere which is in a close-packed structure.

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Complexes Derived from Strong Field Ligands. XVI. The Transition Metal Complexes of 2-Pyridinalhydrazones

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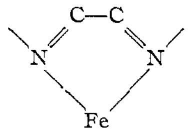
Received May 25, 1963

A variety of complexes have been synthesized with methyl and phenyl substituted 2-pyridinalhydrazones. Magnetic moments, molar conductances, and spectral data have been applied to the characterization of the compounds. The properties of the cobalt(II) and nickel(II) complexes are typical of spin-free octahedral species, while the behavior of the iron(II) complexes provides evidence for an interesting steric effect. Although all the other known complexes of iron(II) with pyridinal imines and hydrazones are spin-paired, tris-(2-pyridinaldimethylhydrazone)-iron(II) iodide is paramagnetic with a magnetic moment of 5.45 Bohr Magnetons. This is explained on the assumption that the –NNR′ group of the hydrazone group is planar. The hypothesis is supported by spectral and other results. Similar steric effects limit the number of molecules of pyridinalphenylhydrazone that may enter an octahedral coordination sphere.

Introduction

Since the first observations by Blau[1] on the complexing abilities of 2,2′-bipyridine and 1,10-phenanthroline, much interest has been found in the metal derivatives of ligands containing the –N=C—C=N– linkages. Earlier efforts centered on the original aromatic ligands and their derivatives. More recently, investigations in this series have directed attention toward the similar behavior of pyridinalimines,[3] α-diketoimines,[3] pyridinalhydrazones,[4] α-diketodihydrazones,[4] and pyridinaldazine.[5]

Typically the octahedral, tris-chelated iron(II) derivatives of these ligands exhibit spin-paired ground states and spectral properties provide evidence for extensive metal–ligand π-bonding. Infrared spectral studies have revealed that the



chelate ring is best considered to be an aromatic system.[2,4,6] Further, the characteristic low energy charge-transfer spectra of such compounds support this conclusion.[7] In contrast, the majority of the bidentate ligands of this class yield three-to-one octahedral complexes of cobalt(II) and nickel(II) which are of the high-spin type.[3–5] Infrared data indicate that the degree of metal–ligand π-bonding decreases in the order Fe(II) > Co(II) > Ni(II). In the case of tris-

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[1] F. Blau, *Ber.*, **21**, 1007 (1888); *Monatsh. Chem.*, **19**, 647 (1898).

[2] W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, **54**, 959 (1954).

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[5] W. J. Stratton and D. H. Busch, *ibid.*, **80**, 1286 (1958); *ibid.*, **80**, 3191 (1958); *ibid.*, **82**, 4834 (1960).

[6] K. Nakamoto, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 437.

[7] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **78**, 1137 (1956).

(biacetyl-bis-methylimine)-cobalt(II), and a number of closely related tridentate ligands, spin-pairing occurs and the observed values of μ_{eff} at room temperature vary from that expected for the low-spin complex (~1.9) to close to the maximum value for octahedral cobalt(II) (~5 B.M.).[8] Further investigation of the cobalt(II) complexes having intermediate values for their magnetic moments discloses a non-Curie–Weiss temperature dependence that is consistent with the coexistence of doublet and quartet states in these compounds.[9,10]

These observations establish a qualitative relationship between the parameters determining the spin multiplicity of the ground state of the first row transition element ions and the coordinating abilities of ligands of this class. Since the critical *Dq* for spin-pairing is expected to be smaller in the case of iron(II) than that for cobalt(II),[11] similar ligands of somewhat lesser ligand field strength might produce iron(II) derivatives having mixed singlet–quintet ground states. In the event that deviations from octahedral symmetry are sufficiently great, singlet–triplet equilibria might be observed in the case of nickel(II). The investigations reported here are concerned with the synthesis and characterization of complexes of 2-pyridinalmethyl-, dimethyl-, phenyl-, and diphenylhydrazones. Twenty-eight new complexes have been prepared and characterized through analysis and magnetic, conductance, and spectral measurements.

Experimental

Materials.—2-Pyridinaldehyde was obtained from the Aldrich Chemical Company and purified by distillation when necessary. Methylhydrazine was obtained from the Olin Mathieson Chemical Corporation and used without further purification. 1,1-Dimethylhydrazine, phenylhydrazine, and 1,1-diphenylhydrazine hydrochloride were obtained from Eastman Organic Chemicals and used as received.

Complexes of 2-Pyridinalmethylhydrazone. 2-Pyridinalmethylhydrazone.—Methylhydrazine (21.7 g., 0.47 mole) was added dropwise, with stirring, to 2-pyridinaldehyde (42.84 g., 0.40 mole). The temperature of the reaction mixture increased. After the addition was complete, the reaction mixture was stirred for an additional 30 min. The resulting solution was distilled and the fraction that came over at 116° (7 mm.) was collected; yield 78%. *Anal.* Calcd. for $C_7H_9N_3$: C, 62.20; H, 6.71; N, 31.09. Found: C, 62.01; H, 6.77; N, 31.08.

Dichlorobis-(2-pyridinalmethylhydrazone)-cobalt(II).—Cobalt(II) chloride 6-hydrate (2.38 g., 0.01 mole) was dissolved in 25 ml. of absolute ethanol. This solution was added rapidly to a solution of 2-pyridinalmethylhydrazone (2.75 g., 0.0203 mole) in 25 ml. of absolute ethanol. The solution was stirred for 30 min. and placed in a rotary evaporator to facilitate removal of the excess solvent. The brown product that was obtained was filtered, washed with small portions of cold acetone, and air dried. It was then placed in a vacuum sublimator at 120° for 24 hr. to remove any excess ligand and solvent; yield 96%. *Anal.* Calcd. for $[Co(C_7H_9N_3)_2Cl_2]$: C, 42.02; H, 4.53; N, 21.00; Cl, 17.72. Found: C, 42.14; H, 4.50; N, 21.21; Cl, 17.52.

Dichlorobis-(2-pyridinalmethylhydrazone)-nickel(II).—This complex was prepared as a green powder in the same manner as that reported for the analogous cobalt complex; yield 88%. *Anal.* Calcd. for $[Ni(C_7H_9N_3)_2Cl_2]$: C, 42.04; H, 4.54; N, 21.02; Cl, 17.73. Found: C, 41.74; H, 4.39; N, 20.9; Cl, 17.77.

Bis-(2-pyridinalmethylhydrazone)-copper(II) Chloride.—Copper(II) chloride 2-hydrate (1.71 g., 0.010 mole) was dissolved in 50 ml. of distilled water. The solution was added at a moderate rate to 2-pyridinalmethylhydrazone (2.84 g., 0.021 mole). A yellow-brown color developed immediately. The mixture was stirred for an additional 30 min. and placed in a rotary evaporator where most of the solvent was removed. The green-brown product was filtered, washed with one small portion of cold acetone (in which it is soluble), and dried *in vacuo* over P_2O_5 at room temperature. The product decomposed at elevated temperatures; yield 57%. *Anal.* Calcd. for $[Cu(C_7H_9N_3)_2]Cl_2$: C, 41.54; H, 4.48, N, 20.76; Cl, 17.51. Found: C, 40.97; H, 4.50; N, 20.88; Cl, 17.67, 17.69.

Dichloro-2-pyridinalmethylhydrazonezinc(II).—Zinc(II) chloride (1.40 g., 0.01 mole) was dissolved in 25 ml. of distilled water and added dropwise, with stirring, to 2-pyridinalmethylhydrazone (1.49 g., 0.11 mole). The solution was placed on a rotary evaporator and most of the solvent was removed. The remaining solution was placed in the refrigerator for 3 days, and a yellow solid separated. It was filtered, washed with acetone, and dried *in vacuo* over P_2O_5 at room temperature; yield 80%. *Anal.* Calcd. for $[Zn(C_7H_9N_3)Cl_2]$: C, 30.97; H, 3.34; N, 15.48; Cl, 26.12. Found: C, 30.52; H, 3.15; N, 15.53; Cl, 26.01.

Dichloro-2-pyridinalmethylhydrazonecadmium(II).—Cadmium(II) chloride (2.30 g., 0.01 mole) was dissolved in 25 ml. of distilled water. This solution was added dropwise, with stirring, to 2-pyridinalmethylhydrazone (1.49 g., 0.11 mole). A white precipitate formed immediately. After stirring for an additional 30 min., the product was filtered, washed with small portions of water and then acetone, and dried *in vacuo* over P_2O_5 at room temperature; yield 84%. *Anal.* Calcd. for $[Cd(C_7H_9N_3)Cl_2]$: C, 26.40; H, 2.85; N, 13.19; Cl, 22.27. Found: C, 26.37; H, 2.72; N, 13.12; Cl, 22.47.

Dichloro-2-pyridinalmethylhydrazonemercury(II).—This yellow complex was prepared in a manner analogous to that reported for the comparable cadmium(II) compound; yield 91%. *Anal.* Calcd. for $[Hg(C_7H_9N_3)Cl_2]$: C, 20.67; H, 2.23; N, 10.33; Cl, 17.44. Found: C, 21.01; H, 2.23; N, 10.60; Cl, 17.03.

Tris-(2-pyridinalmethylhydrazone)-cobalt(II) Iodide.—Cobalt(II) chloride 6-hydrate (2.38 g., 0.01 mole) was dissolved in 25 ml. of distilled water. This solution was added dropwise, with stirring, to 2-pyridinalmethylhydrazone (4.46 g., 0.033 mole). A red solution resulted, to which 4.0 g. of potassium iodide dissolved in 20 ml. of water was added. The mixture was stirred for an additional 5 min. and allowed to stand overnight at 0°. The resulting black crystals were filtered, washed with acetone, and recrystallized from 50 ml. of water to which 3.0 g. of potassium iodide had been added. The crystals were filtered, washed with acetone, and dried *in vacuo* over P_2O_5 at room temperature; yield 83%. *Anal.* Calcd. for $[Co(C_7H_9N_3)_3]I_2$: C, 35.11; H, 3.79; N, 17.55; I, 35.34. Found: C, 34.99; H, 3.45; N, 17.39; I, 35.32.

Tris-(2-pyridinalmethylhydrazone)-nickel(II) Iodide.—This complex was prepared as salmon-colored crystals in the same manner as reported for the cobalt analog; yield 81%. *Anal.* Calcd. for $[Ni(C_7H_9N_3)_3]I_2$: C, 35.13; H, 3.79; N, 17.56; I, 35.35. Found: C, 34.82; H, 3.84; N, 17.64; I, 35.32.

Tris-(2-pyridinalmethylhydrazone)-iron(II) Iodide.—This complex was prepared as red crystals in the manner previously described for the cobalt analog; yield 79%. *Anal.* Calcd. for $[Fe(C_7H_9N_3)_3]I_2$: C, 35.27; H, 3.81; N, 17.63; Fe, 7.81; I, 35.49. Found: C, 35.09; H, 4.05; N, 17.41; Fe, 7.99; I, 35.39.

Complexes of 2-Pyridinaldimethylhydrazone. 2-Pyridinaldimethylhydrazone.—2-Pyridinaldimethylhydrazone was prepared by the method of Wiley, *et al.*,[12] b.p. 128–130° (13 mm.). *Anal.*

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[8] D. H. Busch, "Cobalt, ACS Monograph 149," R. S. Young, Ed., Reinhold Publ. Corp., New York, N. Y., 1960, Chapter 6.

[9] R. C. Stoufer, D. H. Busch, and W. B. Hadley, *J. Am. Chem. Soc.*, **83**, 3732 (1961).

[10] R. C. Stoufer and D. Smith, private communication.

[11] L. Orgel, *J. Chem. Phys.*, **23**, 1819 (1955).

[12] R. H. Wiley, S. C. Slaymaker, and H. Kraus, *J. Org. Chem.*, **22**, 204 (1957).

Calcd. for $C_8H_{11}N_3$: C, 64.40; H, 7.43; N, 28.17. Found: C, 64.43; H, 7.14; N, 28.38.

Dichlorobis-(2-pyridinaldimethylhydrazone)-cobalt(II).—Cobalt(II) chloride 6-hydrate (2.38 g., 0.01 mole) was dissolved in 35 ml. of absolute ethanol. This was added rapidly to a solution of 2-pyridinaldimethylhydrazone (3.00 g., 0.022 mole) in 25 ml. of absolute ethanol. A bright red solution developed immediately. The solution was placed on a rotary evaporator and most of the solvent was removed. The red product was filtered, washed with acetone, and dried *in vacuo* over P_2O_5 at 100°; yield 89%. *Anal.* Calcd. for $[Co(C_8H_{11}N_3)_2Cl_2]$: C, 44.87; H, 5.18; N, 19.63; Co, 13.76; Cl, 16.56. Found: C, 44.78; H, 5.04; N, 19.38; Co, 13.95; Cl, 16.76. When the solvent is removed at an elevated temperature in the rotary evaporator, the complex is formed as a green product which converts to the red product on exposure to air.

Dichlorobis-(2-pyridinaldimethylhydrazone)-nickel(II).—This complex was prepared as a green powder in a manner the same as that reported for the cobalt analog; yield 81%. *Anal.* Calcd. for $[Ni(C_8H_{11}N_3)_2Cl_2]$: C, 44.90; H, 5.18; N, 19.64; Ni, 13.71; Cl, 16.57. Found: C, 45.07; H, 5.36; N, 19.35; Ni, 14.07; Cl, 16.36.

Bis-(2-pyridinaldimethylhydrazone)-copper(II) Chloride 1-Hydrate.—Copper(II) chloride 2-hydrate (1.71 g., 0.01 mole) was dissolved in 50 ml. of distilled water and added at a rapid rate to a solution of 2-pyridinaldimethylhydrazone (3.00 g., 0.0201 mole) in 25 ml. of absolute ethanol. The mixture was stirred for 30 min. after completion of addition. A small quantity of precipitate formed but the bulk of the product remained in solution. The solution was placed on a rotary evaporator in order to remove most of the solvent. The greenish brown product that resulted was filtered and dried *in vacuo* over P_2O_5 at room temperature. At elevated temperatures the complex decomposed; yield 81%. *Anal.* Calcd. for $[Cu(C_8H_{11}N_3)_2]Cl_2{\cdot}H_2O$: C, 42.62; H, 5.37; N, 18.64; Cl, 15.73. Found: C, 42.71; H, 5.32; N, 18.32; Cl, 16.36.

Dichloro-2-pyridinaldimethylhydrazonepalladium(II).—2-Pyridinaldimethylhydrazone (3.00 g., 0.0201 mole) was mixed with 25 ml. of absolute ethanol. To this, a solution of potassium tetrachloropalladate(II) (3.26 g., 0.01 mole) dissolved in 25 ml. of distilled water was added slowly, with stirring. There was immediate formation of a precipitate; however, upon further addition of the palladium(II) solution, the solid dissolved. After addition was completed, 40 ml. of 50% ethanol was added and the reaction mixture was stirred for an additional 4 hr. The solution was placed on a rotary evaporator in which the excess solvent was removed. The yellow product was filtered, washed with a small portion of cold water, and dried *in vacuo* over P_2O_5 at room temperature; yield 95%. It should be noted that the one-to-one complex formed despite the presence of a large excess of ligand. *Anal.* Calcd. for $[Pd(C_9H_{11}N_3)Cl_2]$: C, 29.40; H, 3.39; N, 12.86; Pd, 32.65; Cl, 21.70. Found: C, 29.45; H, 3.34; N, 13.06; Pd, 32.48; Cl, 22.04.

Dichloro-2-pyridinaldimethylhydrazonezinc(II).—Zinc (II) chloride (1.40 g., 0.01 mole) was dissolved in 25 ml. of distilled water and added dropwise, with stirring, to 2-pyridinaldimethylhydrazone (3.30 g., 0.0221 mole). A white precipitate formed immediately. The mixture was stirred for an additional 30 min. The precipitate was filtered, washed with cold water and absolute methanol, and dried *in vacuo* over P_2O_5 at room temperature. It is noteworthy that, although a twofold excess of ligand was employed, the one-to-one complex still formed; yield 94%. *Anal.* Calcd. for $[Zn(C_8H_{11}N_3)Cl_2]$: C, 33.66; H, 3.88; N, 14.72; Cl, 24.84. Found: C, 33.39; H, 4.10; N, 14.48; Cl, 24.70.

Dichloro-2-pyridinaldimethylhydrazonecadmium(II).—This complex was prepared as a white powder in a manner analogous to that previously described for the comparable zinc complex; yield 73%. *Anal.* Calcd. for $[Cd(C_8H_{11}N_3)Cl_2]$: C, 28.90; H, 3.34; N, 12.64; Cl, 21.33. Found: C, 29.27; H, 3.50; N, 12.78; Cl, 21.23.

Dichloro-2-pyridinaldimethylhydrazonemercury(II).—This complex was prepared as a yellow powder by the method previously described for the comparable zinc compound; yield 93%. *Anal.* Calcd. for $[Hg(C_8H_{11}N_3)Cl_2]$: C, 22.84; H, 2.64; N, 9.99; Cl, 16.85. Found: C, 22.61; H, 2.50; N, 10.06; Cl, 16.56.

Tris-(2-pyridinaldimethylhydrazone)-cobalt(II) Iodide.—Cobalt(II) chloride 6-hydrate (2.38 g., 0.01 mole) was dissolved in 25 ml. of distilled water. This solution was added dropwise, with stirring, to 2-pyridinaldimethylhydrazone (4.92 g., 0.033 mole). The reaction mixture was stirred for an additional hour. A solution of 5.0 g. of potassium iodide in 25 ml. of distilled water was added rapidly and stirring was continued for several minutes. The mixture was placed in a refrigerator overnight. The red-brown crystals that formed were filtered, washed with water, and recrystallized from a 3% potassium iodide solution. The crystals were filtered, washed with a small portion of cold water, and dried *in vacuo* over P_2O_5 at room temperature; yield 64%. *Anal.* Calcd. for $[Co(C_8H_{11}N_3)_3]I_2$: C, 37.90; H, 4.37; N, 16.58; I, 33.38. Found: C, 37.79; H, 4.52; N, 16.63; I, 33.57.

Tris-(2-pyridinaldimethylhydrazone)-nickel(II) Iodide.—This substance was prepared as tan crystals by essentially the same procedure as reported for the analogous cobalt complex; yield 73%. *Anal.* Calcd. for $[Ni(C_8H_{11}N_3)_3]I_2$: C, 37.92; H, 4.38; N, 16.59; I, 33.39. Found: C, 37.74; H, 4.17; N, 16.38; I, 33.70.

Tris-(2-pyridinaldimethylhydrazone)-iron(II) Iodide 2-Hydrate.—This red brown complex was prepared by essentially the same procedure as was previously reported for the analogous cobalt compound; yield 60%. *Anal.* Calcd. for $[Fe(C_8H_{11}N_3)_3]I_2{\cdot}2H_2O$: C, 36.34; H, 4.70; N, 15.89; Fe, 7.04; I, 32.00. Found: C, 36.55, 36.77; H, 4.63, 4.77; N, 15.45, 15.66; Fe, 6.90; I, 31.58, 31.99.

Complexes of 2-Pyridinalphenylhydrazone. 2-Pyridinalphenylhydrazone.—This compound was prepared in a slightly different manner from that previously reported in the literature.[13] 2-Pyridinaldehyde (28.92 g., 0.27 mole) was mixed with 200 ml. of absolute ethanol and added dropwise, with stirring, to a solution of phenylhydrazine (27.20 g., 0.252 mole) in 100 ml. of absolute ethanol. During addition, the temperature of the solution increased and a yellow crystalline material was deposited. After the reaction was completed, the solution was placed in an ice bath for 6 hr. The yellow crystals were filtered and recrystallized from 100 ml. of hot absolute ethanol. The crystals were filtered, washed with cold ethanol, and dried *in vacuo* over P_2O_5 at 100°; yield 97%. *Anal.* Calcd. for $C_{12}H_{11}N_3$: C, 73.07; H, 5.62; N, 21.31. Found: C, 73.13; H, 5.76; N, 21.51.

Dichlorobis-(2-pyridinalphenylhydrazone)-cobalt(II).—Cobalt(II) chloride 6-hydrate (2.38 g., 0.01 mole) was dissolved in 50 ml. of warm absolute ethanol. 2-Pyridinalphenylhydrazone (4.34 g., 0.022 mole) mixed with 50 ml. of hot absolute ethanol was added dropwise with stirring to the cobalt chloride solution. After addition was completed, the reaction mixture was stirred for an additional 15 min. and then placed in an ice bath for 12 hr. The dark red material that formed was filtered, washed with small portions of cold absolute ethanol, and dried *in vacuo* over P_2O_5 at room temperature; yield 92%. *Anal.* Calcd. for $[Co(C_{12}H_{11}N_3)_2Cl_2]$: C, 54.97; H, 4.23; N, 16.03; Co, 11.24; Cl, 13.52. Found: C, 54.66; H, 4.37; N, 16.02; Co, 11.08; Cl, 13.30.

Dichlorobis-(2-pyridinalphenylhydrazone)-nickel(II).—This complex was prepared as a green-brown material in a manner similar to that reported for the analogous cobalt compound; yield 73%. *Anal.* Calcd. for $[Ni(C_{12}H_{11}N_3)_2Cl_2]$: C, 55.00; H, 4.23; N, 16.04; Ni, 11.20; Cl, 13.53. Found: C, 54.96; H, 4.48; N, 16.30; Ni, 11.50; Cl, 13.26.

Dichlorobis-(2-pyridinalphenylhydrazone)-iron(II).—This substance was prepared in a manner analogous to that previously reported for the comparable cobalt complex. However, the substance was difficult to purify. The excess ligand was removed by sublimation at 110°; yield 86%. *Anal.* Calcd. for [Fe($C_{12}H_{11}$-

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[13] A. Kaufman and L. Vallette, *Ber.*, **46**, 49 (1913).

TABLE I

DIAMAGNETIC CORRECTIONS FOR LIGANDS AND ANIONS

Ligand or anion	$\chi_M \times 10^{+6}$
2-Pyridinalmethylhydrazone	−110
2-Pyridinaldimethylhydrazone	−122
2-Pyridinalphenylhydrazone	−141
2-Pyridinaldiphenylhydrazone	−190
Chloride ion[a]	−26
Iodide ion[a]	−52
Water[a]	−13

[a] Values obtained from P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1953.

TABLE II

MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF COMPLEXES OF N-SUBSTITUTED HYDRAZONES OF 2-PYRIDINALDEHYDE[a]

Complex	$\chi_M \times 10^{+6}$	μ_{eff} (metal ion)
$[Co(PMH)_2Cl_2]$	7471	4.35
$[Ni(PMH)_2Cl_2]$	3656	3.07
$[Fe(PMH)_3]I_2$	−210	0.69
$[Co(PMH)_3]I_2$	6891	4.21
$[Ni(PMH)_3]I_2$	3064	2.90
$[Co(PdMH)_2Cl_2]$	9542	4.88
$[Ni(PdMH)_2Cl_2]$	4083	3.26
$[Fe(PdMH)_3]I_2 \cdot 2H_2O$	11708	5.45
$[Co(PdMH)_3]I_2$	8971	4.77
$[Ni(PdMH)_3]I_2$	2607	2.93
$[Fe(PPH)_2Cl_2]$	11158	5.30
$[Co(PPH)_2Cl_2]$	9372	4.83
$[Ni(PPH)_2Cl_2]$	3264	2.95
$[Fe(PdPH)_2Cl_2]$	9764	5.00
$[Co(PdPH)_2Cl_2]$	9355	4.89
$[Ni(PdPH)_2Cl_2]$	3487	3.10

[a] Abbreviations: PMH, 2-pyridinalmethylhydrazone; PdMH, 2-pyridinaldimethylhydrazone; PPH, 2-pyridinalphenylhydrazone; PdPH, 2-pyridinaldiphenylhydrazone.

$N_3)_2Cl_2]$: C, 55.30; H, 4.26; N, 16.13; Fe, 10.72; Cl, 13.60. Found: C, 55.23; H, 4.35; N, 15.96; Fe, 10.70; Cl, 13.80.

Dichlorobis-2-pyridinalphenylhydrazonecopper(II).—Copper(II) chloride 2-hydrate (1.70 g., 0.01 mole) was dissolved in 75 ml. of acetone. This solution was added rapidly to a solution of 2-pyridinal phenylhydrazone (4.34 g., 0.022 mole) in hot acetone. Brown crystals formed immediately. They were filtered, washed with several portions of acetone followed by anhydrous ether, and dried *in vacuo* over P_2O_5 at 100°; yield 62%. *Anal.* Calcd. for $[Cu(C_{12}H_{11}N_3)Cl_2]$: C, 43.45; H, 3.34; N, 12.57; Cl, 21.38. Found: C, 43.58; H, 3.61; N, 13.00; Cl, 20.67.

Complexes of 2-Pyridinaldiphenylhydrazone. 2-Pyridinaldiphenylhydrazone.—1,1-Diphenylhydrazine hydrochloride (24.94 g., 0.113 mole) was dissolved in 100 ml. of boiling absolute ethanol. Sodium bicarbonate (25.18 g., 0.30 mole) was added, with stirring, to the boiling solution. Effervescence ensued, indicating the liberation of carbon dioxide due to the neutralization of the hydrogen chloride. After addition of the sodium bicarbonate, the reaction mixture was stirred for an additional 10 min. with boiling and then filtered hot to remove any excess solid material. 2-Pyridinaldehyde (11.46 g., 0.107 mole) was added dropwise, with stirring, to the hot diphenylhydrazine solution. After complete addition, the reaction mixture was refluxed for 1 hr. and then placed in an ice bath for 12 hr. The yellow, slightly discolored, crystals were filtered and then recrystallized from hot ethanol. The crystals were filtered, washed with cold ethanol, and air dried. The discoloration in the final product was removed by treatment with charcoal; yield 85%. *Anal.* Calcd. for $C_{18}H_{15}N_3$: C, 79.09; H, 5.53; N, 15.37. Found: C, 79.01; H, 5.31; N, 15.33.

Dichlorobis-(2-pyridinaldiphenylhydrazone)-cobalt(II).—Cobalt(II) chloride 6-hydrate (2.38 g., 0.01 mole) was dissolved in 35 ml. of warm absolute ethanol. 2-Pyridinaldehyde (6.00 g., 0.022 mole) was dissolved in 50 ml. of hot absolute ethanol and added slowly with stirring to the cobalt(II) chloride solution. The mixture was stirred for an additional 30 min. and then placed on a rotary evaporator to remove the excess solvent. The green product that was obtained after filtration was washed thoroughly with several portions of acetone and then placed in a vacuum sublimator for 12 hr. at 80° to facilitate removal of any excess ligand; yield 86%. *Anal.* Calcd. for $[Co(C_{18}H_{15}N_3)_2Cl_2]$: C, 63.91; H, 4.47; N, 12.42; Cl, 10.48. Found: C, 63.74; H, 4.61; N, 12.47; Cl, 10.60.

Dichlorobis-(2-pyridinaldiphenylhydrazone)-nickel(II).—This complex was prepared as a brown powder in a manner analogous to that previously described for the comparable cobalt compound; yield 89%. *Anal.* Calcd. for $[Ni(C_{18}H_{15}N_3)_2Cl_2]$: C, 63.93; H, 4.47; N, 12.43; Cl, 10.49. Found: C, 63.76; H, 4.61; N, 12.48; Cl, 10.38.

Dichlorobis-(2-pyridinaldiphenylhydrazone)-iron(II).—This compound was prepared as a red powder in a manner comparable to that just described for the analogous cobalt derivative; yield 80%. *Anal.* Calcd. for $[Fe(C_{18}H_{15}N_3)_2Cl_2]$: C, 64.20; H, 4.49; N, 12.48; Cl, 10.53. Found: C, 63.95; H, 4.69; N, 12.69; Cl, 10.83. It should be mentioned that these three derivatives can also be prepared by using acetone as the solvent. In this manner, the complexes precipitate more readily.

Bis-(2-pyridinaldiphenylhydrazone)-copper(II) Chloride.—Copper(II) chloride 2-hydrate (1.70 g., 0.01 mole) was dissolved in 25 ml. of hot absolute ethanol and added slowly, with stirring, to a solution of 2-pyridinaldiphenylhydrazone (6.00 g., 0.022 mole) dissolved in 50 ml. of hot ethanol. A yellow product began to precipitate almost immediately. The mixture was stirred for an additional 15 min. The product was filtered, washed with several small portions of acetone, and air dried. The excess ligand was removed by sublimation *in vacuo* at 110° for 12 hr.; yield 92%. *Anal.* Calcd. for $[Cu(C_{18}H_{15}N_3)_2]Cl_2$: C, 63.48; H, 4.44; N, 12.34; Cl, 10.41. Found: C, 63.25; H, 4.31; N, 12.58; Cl, 10.21.

Magnetic Measurements.—The magnetic moments were obtained at room temperature by the Gouy method, using ferrous ammonium sulfate 6-hydrate and mercuric tetrathiocyanatocobaltate(II) as standards. Diamagnetic corrections were made for the ligands and anions (Table I) so that the reported values are the moments attributable to the metal ions (Table II). The magnetic moments are believed accurate to within a maximum deviation of 0.1 Bohr Magneton.

Conductivity Measurements.—Molar conductances were measured using an Industrial Instruments, Inc., Model RC-16B conductivity bridge and a cell with a constant of 2.159 cm.$^{-1}$. The measurements were made at 25° by employing 10^{-3} M solutions and a bridge frequency of 1000 c.p.s. The absolute methanol used for these measurements was protected from the atmosphere and had a specific conductance of less than 10^{-7} ohm^{-1}. The results are listed in Table III.

Spectra.—Ultraviolet and visible spectra were obtained using a Cary Model 14 recording spectrophotometer and matched cells with fused quartz windows. All extinction coefficients (Tables IV and V) are on the molar basis. The infrared spectra were obtained with a Perkin-Elmer Model 21 recording spectrophotometer equipped with sodium chloride optics. The pressed pellet technique was used.

Results

The complexes of N-methyl and N-phenyl mono- and disubstituted 2-pyridinalhydrazones with iron(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), and mercury(II) have been synthesized and characterized through analysis and magnetic, conductance, and spectral measurements. Ions commonly associated with octahedral coordination (Fe(II), Co(II), Ni(II)) form two groups of solid complexes with these ligands, $[M^{II}L_2X_2]$ and $[M^{II}L_3]X_2$, where L represents the bidentate ligand and X a univalent anion. The *tetrahedral ions* Zn(II), Cd(II), and Hg(II) are best characterized in their one-to-one complexes with these ligands. These are formulated arbitrarily as emphasis has been centered on the compounds of the stoichiometry $[M^{II}L_3]X_2$.

Compounds of the Stoichiometry $[M^{II}L_2X_2]$.—These substances generally exhibit magnetic moments characteristic of typical spin-free octahedral coordination (Table II). It might be argued that the magnetic moment of $[Co(PMH)_2Cl_2]$ is anomalously low since common experience and naïve theories have led to the expectation that moments for octahedral cobalt(II) will normally be found in the range from 4.8 to 5.2 B.M. However, it has recently become clear that the magnetic properties of cobalt(II) complexes present a wide variety of behaviors of substantially more complication than, for example, the well behaved nickel(II) ion.[8-10]

The molar conductances (Table III) of these complex compounds exhibit a pattern consistent with their proposed structures. The values observed in methanol are consistent with solvolysis to produce uni-univalent electrolytes, or mixtures of uni-uni and uni-divalent electrolytes, in that solvent. This is in agreement with the behavior of similar substances as observed by Stoufer[14] and may be explained by the reactions

$$[ML_2Cl_2] + CH_3OH \rightleftharpoons [ML_2(CH_3OH)Cl]^+ + Cl^-$$

$$[ML_2(CH_3OH)Cl]^+ + CH_3OH \rightleftharpoons [ML_2(CH_3OH)_2]^{2+} + Cl^-$$

The behavior of the copper(II) ion is interesting in this regard, for the values reported in Table III indicate considerable association between the chloride ion and the copper.

The cobalt(II) and nickel(II) complexes $[Co(PMH)_2Cl_2]$, $[Co(PdMH)_2Cl_2]$, $[Ni(PMH)_2Cl_2]$, and $[Ni(PdMH)_2Cl_2]$ disproportionate upon dissolution in water forming the more stable three-to-one compounds, $M^{II}L_3{}^{2+}$. The greater stability of the three-to-one complexes is further demonstrated by the fact that with PMH and PdMH iron(II) forms only the species $Fe^{II}(L)_3{}^{2+}$, regardless of the stoichiometry of the system, under conditions used to produce the analogous two-to-one cobalt(II) and nickel(II) complexes.

The behavior of the N-phenyl-substituted ligands stands in sharp contrast to that of the unsubstituted or methyl-substituted ligands. Regardless of the conditions of the experiment, no more than two moles of 2-pyridinalphenylhydrazone and 2-pyridinaldiphenylhydrazone will combine with a single Fe(II), Co(II), or Ni(II) ion. It is particularly significant that iron(II) fails to form the usual tris-bidentate complexes with these ligands. Further, the dissolution of the complexes $[M^{II}L_2X_2]$ in water results in precipitation of free ligand and formation of the hydrated metal ion.

Compounds of the Stoichiometry $[M^{II}L_3]X_2$.—Nickel(II) and cobalt(II) complexes of the general formula $[M^{II}L_3]X_2$ form with 2-pyridinalhydrazone and the N-mono- and dimethyl derivatives. Within the limitations stated earlier, these materials exhibit magnetic moments typical of spin-free octahedral structures (Table II). The iron(II) complexes with 2-pyridinalhydrazone and 2-pyridinalmethylhydrazone, $[Fe(PAH)_3]^{2+}$ and $[Fe(PMH)_3]^{2+}$, follow the usual pattern of such complexes of ligands of the dimethine class. They are diamagnetic and contain spin-paired octahedral iron(II) (Table II). In contrast, the iron(II) complex of 2-pyridinaldimethylhydrazone, $[Fe(PdMH)_3]^{2+}$, is spin-free, $\mu_{eff} = 5.45$ B.M. This is the first case of a tris complex from the pyridinalimine or pyridinalhydrazone class in which the electrons of the iron(II) ion are not fully spin paired. The molar conductances (Table III) of all complexes of this group are in the range accepted for di-univalent electrolytes. It is therefore concluded that all contain the expected octahedral cations.

TABLE III

MOLAR CONDUCTANCES OF THE COMPLEXES OF N-SUBSTITUTED DERIVATIVES OF 2-PYRIDINALHYDRAZONES

Complex	Λ_M, ohm^{-1}
$[Co(PMH)_2Cl_2]$	118.6
$[Ni(PMH)_2Cl_2]$	81.5
$[Cu(PMH)_2]Cl_2$	102.8
$[Fe(PMH)_3]I_2$	182.9
$[Co(PMH)_3]I_2$	180.7
$[Ni(PMH)_3]I_2$	186.9
$[Co(PdMH)_2Cl_2]$	145.4
$[Ni(PdMH)_2Cl_2]$	143.5
$[Cu(PdMH)_2]Cl_2$	108.5
$[Fe(PdMH)_3]I_2\cdot 2H_2O$[a]	200.9
$[Co(PdMH)_3]I_2$	189.4
$[Ni(PdMH)_3]I_2$	186.1
$[Fe(PPH)_2Cl_2]$	142.0
$[Co(PPH)_2Cl_2]$	145.9
$[Ni(PPH)_2Cl_2]$	125.5
$[Cu(PPH)Cl_2]$	83.7
$[Fe(PdPH)_2Cl_2]$	142.7
$[Co(PdPH)_2Cl_2]$	149.9
$[Ni(PdPH)_2Cl_2]$	118.0
$[Cu(PdPH)_2]Cl_2$	100.0

[a] Limited solubility in methanol.

The profound difference between PdMH and the other ligands of immediate interest is also manifested in the energy associated with the metal–ligand charge-transfer absorption for the iron(II) complexes as shown in Table IV. The occurrence of this band at substantially higher energy in the case of $Fe(PdMH)_3{}^{2+}$, as contrasted to $Fe(PMH)_3{}^{2+}$ and $Fe(PAH)_3{}^{2+}$, is taken as an indication that the extent of metal–ligand π-bonding is much less than usual in the former case.

TABLE IV

CHARGE-TRANSFER SPECTRA OF THE COMPLEXES OF IRON(II) WITH PYRIDINALHYDRAZONES[a]

Complex	λ, mμ	$\epsilon \times 10^{-4}$
$[Fe(PAH)_3]I_2$	480	0.74
$[Fe(PMH)_3]I_2$	460	.64
$[Fe(PdMH)_3]I_2$	375	.46

[a] Abbreviations: PAH, 2-pyridinalhydrazone; PMH, 2-pyridinalmethylhydrazone; PdMH, 2-pyridinaldimethylhydrazone.

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(14) R. C. Stoufer, Thesis, The Ohio State University, 1958.

Discussion

The anomalous magnetic and spectral properties of the iron(II) complex of PdMH indicate that a diminution in donor strength is related to the substitution of methyl groups for both of the hydrogens of the amino group. This conclusion contradicts the expectation that the electron-donating effects of the methyl groups should tend to enhance the donor strengths of the adjacent coordinated nitrogen atoms. Further, as shown in Table V, the ultraviolet spectra of the free ligands reveal that N-alkylation increases the resonance interaction of the electron pair of the amino groups with the π-electron system of the molecule. This is reflected by a shift of the absorption band to lower energies. Since the inductive effect of the methyl groups should also enhance the electron densities on the coordinated nitrogen atoms, these results appear to contradict the observed order of complexing ability of the ligands.

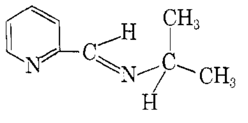
TABLE V

ABSORPTION MAXIMA IN THE ULTRAVIOLET SPECTRA OF N-SUBSTITUTED DERIVATIVES OF 2-PYRIDINALHYDRAZONE[a]

Compound	λ, mμ	$\epsilon \times 10^{-4}$	λ, mμ	$\epsilon \times 10^{-4}$	λ, mμ	$\epsilon \times 10^{-4}$	λ, mμ	$\epsilon \times 10^{-4}$
PAH	...	...	286	0.78	259	0.60	...	...
PMH	...	...	305	1.46	...	...	...	...
PdMH	...	...	315	1.90	...	...	...	...
PPH	355	2.60	299	0.83	...	...	232	1.42
PdPH	348	2.37	300	0.90	...	...	234	1.61

[a] Abbreviations: PAH, 2-pyridinalhydrazone; PMH, 2-pyridinalmethylhydrazone; PdMH, 2-pyridinaldimethylhydrazone; PPH, 2-pyridinalphenylhydrazone; PdPH, 2-pyridinaldiphenylhydrazone.

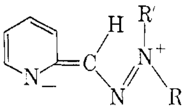
The steric requirements of the N-substituted hydrazones provide an obvious possibility as a source of reduced coordinating ability. If it is tacitly assumed that the hydrazone amine group remains pyramidal in configuration, the steric requirements of the dimethyl amino groups closely resemble those of 2-pyridinalisopropylimine (PiPI) (structure I).



I

However, the ligand field strength of PiPI has been shown to be only slightly less than that of 2,2'-bipyridine, in contrast to the low value for the splitting parameter of PdMH.[15] In addition, the three-to-one iron(II) complex of PiPI is diamagnetic as compared to the paramagnetism of the analogous iron(II) complex of PdMH. Further, the steric requirements of 2-pyridinalbenzylimine (PBI) should be similar to those of 2-pyridinalphenylhydrazone (PPH). Yet no difficulty was encountered in the synthesis of $[\mathrm{Fe(PBI)_3}](\mathrm{BF_4})_2$, whereas the comparable iron(II) complex with PPH had been unobtainable under similar experimental conditions.[14] Consequently, the enhanced steric requirements of the pyramidal dimethylamino function cannot account for the decreased complexing tendency of the corresponding hydrazones.

Consideration of the infrared spectra of the compounds in question as well as those of their complexes provides a satisfactory explanation of the aforementioned behavior pattern. The imines provide a model for the expected character of the spectrum in the double bond region[3,4,6] and assignments of the vibrations of interest are based on the general constancy of the absorption pattern of the pyridine ring.[16] As listed in Table VI, the acyclic $\mathrm{C{=}N}$ function appears as an unambiguous absorption band on the high-frequency side of the first pyridine ring band. This band falls in the 1649–1639 cm.$^{-1}$ region for the various imines.[3] However, this simple behavior vanishes in the spectra of the hydrazones. The simple high-frequency acyclic $\mathrm{C{=}N}$ band does not appear, but is replaced by an intense band in the 1570 cm.$^{-1}$ region. Although not clearly a simple group frequency, the band will be referred to as the $\mathrm{C{=}N}$ vibrational mode. The generality of this alteration suggests that the conjugative interaction between the electron pair of the amino nitrogen atom and the continued π-electron system of the molecule occurs in all of the hydrazones irrespective of the number of methyl groups that are associated with the amino function. This is the most important effect and far overshadows the electromeric effect due to substitution of methyl groups on the terminal nitrogen atom. A typical canonical form that arises as a result of this conjugative interaction is depicted in structure II.



II

As a major consequence of the preceding considerations, it is necessary to assume that the configuration of the groups about the amino nitrogen is trigonal planar, and that this trigonal array is essentially coplanar with the rest of the ligand molecule. The steric requirements of the ligands must therefore be evaluated on this basis. It follows that group R (structure II) will be directed into close proximity to the other ligands bound to the central metal ion upon coordination. Molecular models reveal that such a molecule may readily chelate so long as R is a hydrogen atom (*i.e.*, PAH, PMH), but that the presence of a methyl group in this position (*i.e.*, PdMH) causes extreme crowding. In consequence, the metal–nitrogen bond (at the methine nitrogen) is substantially lengthened in the dimethylhydrazone complex. Such a forced extension of the bond distance should certainly result in a decreased ligand field strength. This is in agreement with results presented elsewhere.[15] This problem does not arise with the isopropylimine derivative because of less restricted rotation which permits rotation of the methyl groups out of the plane of the remainder of the molecule.

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(15) M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, **2**, 1178 (1963).

(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

TABLE VI

INFRARED ABSORPTION BANDS[a] IN THE 1670–1400 CM.$^{-1}$ REGION FOR 2-PYRIDINALHYDRAZONES AND THEIR COMPLEXES

Compound	d—NH	st C=N	py ring 1[b]	py ring 2[b]	py ring 3[b]	py ring 4[b]
PAH[4]	1633 sh	1566 sh	1584 s	. . .	1475 s	1436 s
PMH	1661 w	1573 vs	1593 sh	1566 sh	1467 s	1435 s
PdMH	. . .	1571 vs	1595 sh	1566 sh	1468 s	1437 s
PiPI	. . .	1648 s	1591 m	1569 m	1473 s	1440 m
PMI	. . .	1634 s	1587 s	1567 s	1468 s	1435 s
PBI	. . .	1649 s	1595 s	1574 m	1475 m	1437 s
$[Fe(PAH)_3]I_2$[4]	. . .	1541 m	1608 s	1580 m	1477 s	1445 m
$[Co(PAH)_3]I_2$[4]	1631 sh	1558 m	1608 s	1576 sh	1481 s	1447 w
$[Ni(PAH)_3]I_2$[4]	1631 sh	1555 s	1608 s	1576 sh	1479 s	1443 m
$[Fe(PMH)_3]I_2$	1635 sh	1538 w	1604 s	1575 w	1478 vs, x	1439 sh
$[Co(PMH)_3]I_2$	1655 w	1553 m	1608 s	1589 sh	1473 m	1443 m
$[Ni(PMH)_3]I_2$	. . .	1553 m	1605 s	1582 sh	1481 vs	1443 m
$[Zn(PMH)Cl_2]$	. . .	1558 m	1609 s	1589 sh	1485 s	1444 m
$[Co(PMH)Cl_2]$	. . .	1557 s	1608 s	1584 sh	1479 s	1440 m
$[Hg(PMH)Cl_2]$	. . .	1558 m	1609 s	1584 sh	1482 s	1443 s
$[Cu(PMH)_2]Cl_2$	1643 m	1556 m	1608 s	1587 sh	1482 s	1447 m
$[Fe(PdMH)_3]I_2 \cdot 2H_2O$	. . .	1530 s	1601 s	1572 w	1477 s	1442 s
$[Co(PdMH)_3]I_2$	. . .	1536 s	1605 s	1572 w	1476 w	1440 s
$[Ni(PdMH)_3]I_2$	. . .	1538 s	1607 s	1574 w	1478 s	1443 m

[a] Abbreviations: st, bond stretching vibration; d, deformation vibration; py, pyridine; s, strong; vs, very strong; m, medium; w, weak; sh, shoulder; x, wide. [b] C. H. Kline, Jr., and J. Turkevich, *J. Chem. Phys.*, **12**, 300 (1944).

The influence of coordination to metal ions on the infrared spectra of the pyridinalhydrazones provides further support for this point of view. The canonical forms which are customarily envoked to describe resonance interaction of the type proposed here predict an accumulation of charge on the nitrogen atom of the pyridine ring. Such an electron distribution should be enhanced by the formation of coordinate bond to the metal atoms, with a resultant shift of the characteristic absorption band to still lower frequencies. This expectation is fully supported by the data of Table VI, where it is shown that this band may be shifted to lower frequencies by as much as 27 cm.$^{-1}$ upon coordination. A second factor contributing to the lowering of this band is associated with metal–ligand π-bonding and is responsible for the variation from metal ion to metal ion.[3,4] The importance of the $d\pi$–$p\pi$ interaction appears to vary as follows: Hg(II) $\simeq$ Cd(II) $\simeq$ Zn(II) $\simeq$ Cu(II) $<$ Ni(II) $<$ Co(II) $<<$ Fe(II). In the ions that have d^9 or d^{10} configurations, this effect is presumed to be relatively insignificant. In the cases of the nickel(II) and cobalt(II) ions, the presence of σ-antibonding d-electrons greatly lessens the importance of metal–ligand π-bonding. However, with iron(II) there are no antibonding σ-electrons present, and the phenomenon is maximized in that instance.

The failure of experiments designed to produce the three-to-one complex of iron(II) with PPH[3] can be understood on the basis of the preceding discussion. Realization that the amine nitrogen should be treated in terms of a trigonal planar configuration which is coplanar with the remainder of the molecule prompted a detailed study of molecular models. This revealed that the phenyl groups in the three-to-one complex are mutually hindered to such an extent that only a single arrangement permits an octahedral array of the three ligands. In this arrangement the phenyl groups are forced into an unusual proximity. Therefore, it is concluded that the steric effect associated with the restricted trigonal configuration of the amine nitrogen atom does not permit the entrance of a third such ligand molecule in a single octahedral coordination sphere. Thus, in the case of the phenyl derivatives, the interligand crowding precludes the synthesis of the three-to-one complex, while the unusual properties associated with tris-(pyridinaldimethylhydrazone)-iron(II) are derived from a less extreme effect of the same type.

In conclusion, the anomalous properties associated with several substituted hydrazone complexes have been explained on the basis of steric considerations. The studies reported here provide an example of the conversion of spin-paired iron(II) into the corresponding spin-free species as a consequence of the variation of structural parameters. However, it has been demonstrated that this change does not come about as a result of a gradual smooth alteration in the coordinating ability of the ligand. The effect is derived from a sharp alteration in the complexing ability of the ligand which accompanies an added steric requirement.

Acknowledgment.—The financial support of Battelle Memorial Institute is gratefully acknowledged.