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THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO, AND THE OLIN MATHIESON CHEMICAL CO., NEW HAVEN, CONNECTICUT

Metal Complexes Derived from Substituted Hydrazones of 2,6-Diacetylpyridine

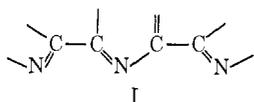
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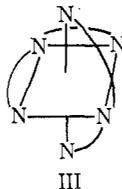
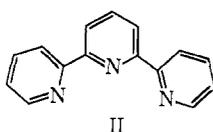
The iron(II), cobalt(II), nickel(II), and copper(II) complexes with a series of hydrazones of 2,6-diacetylpyridine have been prepared. The ligands include: 2,6-diacetylpyridinedihydrazone, H; 2,6-diacetylpyridinebis(methylhydrazone), MH; 2,6-diacetylpyridinebis(phenylhydrazone), PH; and 2,6-diacetylpyridinebis(dimethylhydrazone), dMH. From the six-coordinate nickel(II) complexes, the spectrochemical series is H ($Dq = 1258 \text{ cm}^{-1}$) \gg dMH ($Dq = 1119 \text{ cm}^{-1}$) = MH ($Dq = 1117 \text{ cm}^{-1}$) $>$ PH ($Dq = 1063 \text{ cm}^{-1}$). The variation reveals the intramolecular steric requirements in these complexes. The iron(II) complexes FeL_2^{2+} , all of the spin-paired configuration, provide an illustration of the pitfalls associated with ferromagnetic impurities. A series of one-to-one complexes may contain examples of five-coordination.

Introduction

The trimethine structural unit (I) is responsible for the powerful chelating properties of 2,6-di(2'-pyridyl)-

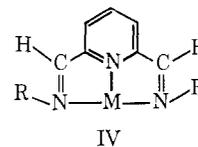


pyridine (II), more commonly called terpyridine. This



molecule behaves as a tridentate ligand (III) and has been the subject of numerous papers concerning analytical applications,²⁻⁸ as well as kinetic,⁹ synthetic,¹⁰⁻¹⁷ and infrared studies.¹⁸ The terpyridine nucleus, however, does not lend itself easily to synthetic procedures by which the effective donor ability of the trimethine group might be altered.

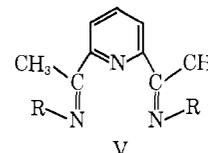
Another class of materials, containing the trimethine unit, which has been studied consists of derivatives of 2,6-pyridinedialdehyde. Stoufer and Busch^{19,20} have prepared and characterized several divalent metal complexes of 2,6-pyridinedialdihydrazone (IV, R =



NH_2). These authors have shown that the 2:1 cobalt(II) complex, *viz.*, bis(2,6-pyridinedialdihydrazone)-cobalt(II) iodide, exists at room temperature as an equilibrium mixture of species exhibiting the doublet and quartet spin states.²⁰

Various 2,6-pyridinedialbisimine complexes have also been studied. Lions and Martin²¹ have reported complexes of 2,6-pyridinedialbis(phenylimine) (IV, R = C_6H_5) and 2,6-pyridinedialbis(benzylimine) (IV, R = $\text{CH}_2\text{C}_6\text{H}_5$) with iron(II), cobalt(II), cobalt(III), and copper(II). Figgins and Busch^{22,23} have prepared and characterized the iron(II), cobalt(II), and nickel(II) complexes of 2,6-pyridinedialbis(methylimine). The lack of a suitable preparative method for the dialdehyde has curtailed these studies.

In this work we wish to report the synthesis and characterization of various complexes derived from the related tridentate ligands—the 2,6-diacetylpyridinebis-hydrazones. Specifically, complexes involving divalent iron, cobalt, and copper with 2,6-diacetylpyridinedihydrazone (V, R = NH_2 , abbreviated H), 2,6-diacetylpyridinebis(methylhydrazone) (V, R = NHCH_3 , MH),



2,6-diacetylpyridinebis(phenylhydrazone) (V, R = NHC_6H_5 , PH), and 2,6-diacetylpyridinebis(dimethylhydrazone) (V, R = $\text{N}(\text{CH}_3)_2$, dMH) are reported as well as the cobalt(II) complex of 2,6-diacetylpyridinebis(2'-pyridylhydrazone) (V, R = $\text{NHC}_5\text{H}_4\text{N}$, PyH). The preparation and characterization of the imine complexes derived from 2,6-diacetylpyridine (V, R = CH_3 , CH_2CH_3 , $\text{CH}_2\text{C}_6\text{H}_5$, C_6H_5 , $p\text{-ClC}_6\text{H}_4$, $p\text{-FC}_6\text{H}_4$, $p\text{-}$

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TABLE I
ELEMENTAL ANALYSES^a

Compound	Theory				Found			
	C, %	H, %	N, %	Halide, %	C, %	H, %	N, %	Halide, %
H	56.52	6.85	36.63	...	56.57	6.89	36.49	...
[Fe(H) ₂]I ₂	31.23	3.79	20.24	36.67	56.86	7.09	37.07	...
[Fe(H) ₂]Cl ₂	42.45	5.15	27.51	...	31.07	3.97	19.76	36.35
[Co(H) ₂]I ₂	31.09	3.77	20.15	36.51	42.08	5.35	27.10	...
[Co(H) ₂]Cl ₂ ·H ₂ O	40.76	5.32	26.41	...	30.94	3.71	19.51	36.56
[Ni(H) ₂]I ₂	31.10	3.77	20.16	36.52	41.06	5.13	26.09	...
[Ni(H) ₂]Cl ₂ ·1.5H ₂ O	40.10	5.42	25.98	...	30.99	4.00	20.01	36.19
[Cu(H) ₂]Cl ₂ ·1.5H ₂ O	39.74	5.38	25.75	...	39.82	5.26	26.19	...
MH·0.5H ₂ O	57.87	7.95	30.68	...	40.03	5.22	25.50	...
Fe(MH)Cl ₂ ·0.5H ₂ O	37.21	5.11	19.73	...	57.89	8.66	29.45	...
Co(MH)Cl ₂	37.84	4.91	20.06	...	37.53	4.94	19.64	...
Ni(MH)Cl ₂	37.86	4.91	20.07	...	37.47	4.89	20.43	...
Cu(MH)Cl ₂	37.35	4.85	19.80	...	37.74	5.28	19.70	...
[Fe(MH) ₂](ClO ₄) ₂	38.11	4.94	20.20	10.22	37.09	5.26	20.10	...
					38.33	5.19	20.07	10.16
					38.00	4.90	20.76	...
[Co(MH) ₂]I ₂	35.17	4.56	18.64	33.79	34.93	4.62	18.53	33.53
[Co(MH) ₂](ClO ₄) ₂	37.94	4.92	20.11	...	38.04	5.33	19.60	...
[Ni(MH) ₂]I ₂	35.18	4.56	18.65	33.80	34.97	4.78	18.78	33.68
[Ni(MH) ₂](ClO ₄) ₂	37.95	4.92	20.12	...	37.74	4.81	20.55	...
dMH	63.12	8.56	28.32	...	63.42	8.84	28.12	...
					63.12	8.52	28.10	...
Fe(dMH)Cl ₂	41.73	5.66	18.72	...	41.50	5.83	18.73	...
Co(dMH)Cl ₂	41.39	5.61	18.57	...	41.59	5.95	18.51	...
Ni(dMH)Cl ₂ ·0.5H ₂ O	40.45	5.75	18.15	...	41.07	5.74	17.98	...
Cu(dMH)Cl ₂ ·0.5H ₂ O	39.95	5.68	17.92	...	40.20	5.67	17.92	...
[Fe(dMH) ₂](ClO ₄) ₂	41.67	5.65	18.69	9.46	41.58	5.82	18.72	9.52
[Co(dMH) ₂]I ₂	38.67	5.24	17.35	31.44	38.40	5.13	17.30	31.54
[Co(dMH) ₂](ClO ₄) ₂ ·H ₂ O	40.52	5.76	18.18	...	40.69	5.83	18.17	...
[Ni(dMH) ₂](ClO ₄) ₂	41.51	5.63	18.62	...	41.36	5.90	18.68	...
PH	73.44	6.16	20.39	...	73.55	6.41	20.10	...
Fe(PH)Cl ₂ ·H ₂ O	51.66	4.75	14.35	...	51.34	4.33	14.53	...
Co(PH)Cl ₂ ·0.5H ₂ O	52.30	4.60	14.52	...	52.69	5.00	14.53	...
Ni(PH)Cl ₂ ^b
Cu(PH)Cl ₂	52.78	4.43	14.66	...	53.38	4.85	14.64	...
[Fe(PH) ₂](ClO ₄) ₂	53.57	4.50	14.88	...	53.96	5.20	14.70	...
[Co(PH) ₂](ClO ₄) ₂	53.40	4.48	14.83	...	53.38	4.68	14.75	...
[Ni(PH) ₂](ClO ₄) ₂	53.41	4.48	14.83	...	53.60	4.70	14.88	...
PyH	66.07	5.54	28.39	...	66.26	5.56	28.20	...
Co(PyH)I ₂	34.67	2.91	14.90	38.57	34.60	2.95	14.91	38.68

^a Abbreviations used in Table I are: H = 2,6-diacetylpyridinedihydrazone, MH = 2,6-diacetylpyridinebis(methylhydrazone), dMH = 2,6-diacetylpyridinebis(dimethylhydrazone), PH = 2,6-diacetylpyridinebis(phenylhydrazone), pyH = 2,6-diacetylpyridinebis(2'-pyridylhydrazone). ^b Acceptable analyses could not be obtained.

CH₃C₆H₄, and *p*-OCH₃C₆H₄) with divalent iron, cobalt, and nickel are reported elsewhere.^{24,25}

Experimental Section

2,6-Diacetylpyridine, methylhydrazine, and dimethylhydrazine were obtained from the Aldrich Chemical Co., Milwaukee, Wis., and were used as received. All other materials were the usual reagent chemicals. Analytical results appear in Table I and were performed by the Schwarzkopf Microanalytical Laboratories.

2,6-Diacetylpyridinedihydrazone.—This material is prepared in water from the diketone and hydrazine, employing a reaction time of 1 hr. Recrystallization is effected from boiling ethanol. This white powdery material has been prepared previously by Lukes and Pergal²⁶ (mp 174–177° (apparent decomposition), lit. 181°).

Bis Complexes of 2,6-Diacetylpyridinedihydrazone.—These materials may be prepared by combining the ligand and the appropriate metal chloride hydrate in an ethanol–water mixture

(one to one by volume). Addition of an excess of potassium iodide after several minutes of stirring, followed by cooling overnight, produces the highly crystalline complex, which is then recrystallized from a warm (45°) ethanol–water mixture (1:1), collected by filtration, and dried *in vacuo* over P₄O₁₀; yields, 30–78%. The highly crystalline materials are dark brown (cobalt), light brown (nickel), and red-purple (iron). Similarly, the complexes may be prepared in methanol as the chloride salts. Finally, the metal complexes may be generated from an *in situ* preparation of the ligand from its two components in the presence of an aqueous solution of the metal chloride.

2,6-Diacetylpyridinebis(methylhydrazone).—This yellow oily solid is prepared by adding 2 moles of the hydrazine slowly with stirring to 1 mole of the diketone in methanol. After the addition is complete, the solution is refluxed for 30 min. The methanol is removed and the product is collected at 130°, 19 mm.

Bis Complexes of 2,6-Diacetylpyridinebis(methylhydrazone).—These materials may be isolated as either the purple perchlorate salt (iron) or the brown iodide salts (nickel and cobalt) by direct combination of the diketone, hydrazine, and metal chloride in water. Addition of potassium iodide led to the isolation of the iodide salts. In the case of iron(II) the isolated iodide complex was then converted to the less soluble perchlorate salt.

(24) J. A. Burke, Jr., J. D. Curry, and D. H. Busch, unpublished results.

(25) J. D. Curry and D. H. Busch, unpublished results.

(26) R. Lukes and M. Pergal, *Chem. Listy*, **52**, 68 (1958).

Recrystallization is from warm methanol; yields, 19–45%. The complexes were also made by reaction of the metal perchlorates with the ligand.

2,6-Diacetylpyridinebis(dimethylhydrazone).—This viscous yellow oil may be prepared in nearly quantitative yields from the diketone and hydrazine by refluxing the components in ethanol under nitrogen for 48 hr. After removal of the solvent the yellow residue is distilled using a modified Hickman still.

Bis Complexes of 2,6-Diacetylpyridinebis(dimethylhydrazone).—All three complexes may be prepared by addition of the metal perchlorate to the ligand in water. Alternatively, the iron(II) and cobalt(II) complexes were prepared from the ligand components in water and isolated as the perchlorate and iodide salts, respectively. The purple iron(II) material was recrystallized four times from ethanol–water solvent (1:1 by volume) and washed once with warm methanol. The black-brown cobalt(II) derivative was recrystallized once from methanol. The nickel(II) complex must be prepared under nitrogen as it is unstable; yields, 6–77%.

2,6-Diacetylpyridinebis(phenylhydrazone).—This material is prepared in a manner similar to that just described for 2,6-diacetylpyridinedihydrazone in 95% ethanol. Recrystallization is carried out using hot benzene or boiling ethanol. The phenylhydrazone is an off-white microcrystalline material (mp 216–217°).

Bis Complexes of 2,6-Diacetylpyridinebis(phenylhydrazone).—These complexes are prepared in acetone from the metal perchlorate and the ligand using stoichiometric amounts. Cooling produces the crystalline materials. The physical descriptions of the nickel(II) and cobalt(II) complexes are as before while the iron(II) complex is a bright red color; yields, 83–85%.

Mono Complexes of the 2,6-Diacetylpyridinebis(hydrazones).—These materials may be prepared as follows: The metal chloride and ligand are dissolved in separate methanol solutions and the ligand solution is added rapidly to the solution of metal salt with stirring. After 1 hr of stirring the solution is cooled overnight. The solid which separates is collected by filtration, washed with ether, and dried over P_4O_{10} *in vacuo* (100°).

2,6-Diacetylpyridinebis(2'-pyridylhydrazone).—This yellow solid is prepared from the diketone and the hydrazine²⁷ in ethanol. After stirring for 30 min, the solvent is removed and the residue is recrystallized from ethanol; mp 194–195°.

Iodo(2,6-Diacetylpyridinebis(2'-pyridylhydrazone))cobalt(II) Iodide.—This brown material is prepared by reaction of the metal chloride with the ligand in warm acetone. After adding a tenfold excess of water the solution is heated and filtered. Adding potassium iodide, concentrating the solution, and cooling produces the desired product. Recrystallization is carried out in methanol; yield, 61%.

Magnetic Measurements.—Magnetic measurements were made by the Gouy method using mercury(II) tetrathiocyanatocobaltate(II) as standard.

Infrared Spectra.—Infrared spectra were obtained using the potassium bromide pressed disk method (solids) and sodium chloride smear plates (liquids) with a Perkin-Elmer 337 double-beam grating spectrophotometer. The spectra were calibrated with polystyrene.

Electronic Spectra.—Solution spectra were obtained by means of a Cary Model 14 recording spectrophotometer using matched fused quartz cells.

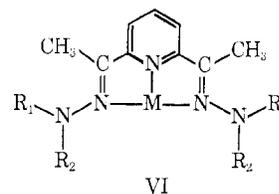
Conductivities.—Conductivities were measured in doubly distilled water or methanol using precisely determined concentrations near 10^{-1} M.

Molecular Weights.—Molecular weights were obtained in nitromethane using a Mechrolab Model 301A osmometer.

Results and Discussion

The synthesis and characterization of a series of divalent iron, cobalt, and nickel complexes with N-sub-

stituted hydrazones of 2,6-diacetylpyridine have been carried out. Molecular models reveal that these hydrazones (VI) will function as planar tridentate



ligands in much the same fashion as does terpyridine. These materials involve a further analogy to terpyridine in that both ligands contain the trimethine structural unit.

The analytical data in Table I indicate that these hydrazones may form two types of complexes with divalent iron, cobalt, copper, and nickel—*i.e.*, one-to-one and two-to-one species. The materials exhibiting a one-to-one ligand to metal ratio are generally formed by addition of equivalent amounts of metal chloride to the appropriate ligand in methanol. This procedure, while working in the case of the methylhydrazone, phenylhydrazone, and dimethylhydrazone, does not work in the case of the unsubstituted hydrazone; the two-to-one product being preferred. The two-to-one complexes are highly crystalline materials and are red-purple (iron), brown-black (cobalt), and brown (nickel).

A marked decrease in donor strength accompanies the substitution of groups for hydrogens on the amino nitrogen (Table II). The relative positions of H, MH, and PH in the spectrochemical series for nickel(II), as revealed by Table II (H > MH > PH), are completely

TABLE II
ABSORPTION BANDS OF OCTAHEDRAL NICKEL(II) COMPLEXES
WITH HYDRAZONES OF THE TRIMETHINE TYPE^a

	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (${}^3T_2 \rightarrow {}^3T_{2-g}$)		${}^3A_{2g} \rightarrow {}^1E_g(D)$ (${}^3T_2 \rightarrow {}^1T_2$)		Dq , cm^{-1}
	ν , cm^{-1}	ϵ	ν , cm^{-1}	ϵ	
[Ni(PH) ₂] ²⁺ ^b	10,630	31.5	11,380	30.4	1063
[Ni(MH) ₂] ²⁺ ^c	11,170	22.3	1117
[Ni(dMH) ₂] ²⁺ ^c	11,190	48.2	1119
[Ni(PdAdH) ₂] ²⁺ ^d	12,200	11.4	1220
[Ni(H) ₂] ²⁺ ^c	12,580	35.1	~14,494	27.3	1258

^a The double group notation is given as well as the more familiar Mulliken notation. Abbreviations used are: PH = 2,6-diacetylpyridinebis(phenylhydrazone), MH = 2,6-diacetylpyridinebis(methylhydrazone), dMH = 2,6-diacetylpyridinebis(dimethylhydrazone), PdAdH = 2,6-pyridinedialdihydrazone, H = 2,6-diacetylpyridinedihydrazone. ^b Spectrum determined in DMF. ^c Spectra determined in methanol. ^d Spectrum determined in water.

consistent with expectations derived from studies with 2-pyridinalhydrazones.²⁸ Increased steric requirement of the amino function substituents decreases the ligand field strength of the ligand molecule. Assuming that complete ligand planarity exists, the preferred configuration of the ligand molecule in the case of PH and MH is VII.

(27) J. F. Geldard and F. Lions, *Inorg. Chem.*, **2**, 270 (1963).

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TABLE III
MAGNETIC SUSCEPTIBILITIES AND MOMENTS OF METAL
COMPLEXES WITH HYDRAZONES OF THE
TRIMETHINE TYPE^a

Complex	$\chi_m \times 10^6$	Temp, °K	μ_{eff}
[Fe(H) ₂]I ₂	-177.6	302	(0.63)
[Co(H) ₂]I ₂	1733	301	2.24
	1610	304	2.19
[Ni(H) ₂]I ₂	3552	305	3.09
[Cu(H) ₂]Cl ₂ · 1.5H ₂ O	953.2	295	1.73
[Fe(MH) ₂](ClO ₄) ₂	-213.7	301	(0.58)
[Co(MH) ₂]I ₂	9044	301	4.80
[Ni(MH) ₂]I ₂	3779	299	3.17
[Fe(dMH) ₂](ClO ₄) ₂	-90.6	301	(0.87)
[Co(dMH) ₂]I ₂	3729	302	3.18
[Ni(dMH) ₂](ClO ₄) ₂	3973	306	3.28
[Fe(PH) ₂](ClO ₄) ₂	0.0	304	(1.07)
[Co(PH) ₂](ClO ₄) ₂	8587	299	4.67
[Ni(PH) ₂](ClO ₄) ₂	3986	299	3.28
Co(PyH)I ₂	7892	302	4.47

^a Molar susceptibilities for ligands and anions ($-\chi_m \times 10^6$): H, 120.3; MH, 144.0; dMH, 167.7; PH, 202.4; PyH, 216.0; I⁻, 50.6; Cl⁻, 23.4; ClO₄⁻, 32.0; and H₂O, 13.0; from J. Lewis and B. N. Figgis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.

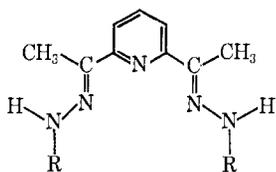
first substituent on the acetyl derivative causes a decrease similar to that of the second substituent added to the amino function of the monoaldehyde derivative. Further, inspection of Table II shows an apparent anomaly—dMH. Its position in the spectrochemical series is equivalent to that of the methylhydrazone. This position of unexpected high *Dq* may be explained by assuming that with the incorporation of the second methyl group the hydrazone function twists slightly (indeed molecular models reveal that a planar dimethylhydrazone ligand would be highly strained). Thus the steric requirement of the twisted dimethylhydrazone is equivalent to that of the rigid methylhydrazone. That the weakening of the ligand field strength of the hydrazones concomitant with amino function substitution is not a bulk effect is shown by the fact that the bulk equivalent of the methylhydrazones and phenylhydrazones, *i.e.*, the ethylimine and benzylimine, exhibit *Dq* values much greater than the corresponding hydrazones, being 1244 and 1233 cm⁻¹, respectively.

The results of the magnetic measurements on the series of hydrazone complexes appear in Table III.

TABLE IV
ASSIGNMENTS OF INFRARED BANDS FOR TRIMETHINE LIGANDS AND THEIR METAL COMPLEXES^a

Species	Assignment				
	py band I	py band II	py band III	py band IV	C=N str
H	1600 mw	...	1460 s, x	1440 sh	1570 s, x
[Fe(H) ₂]I ₂	1600 vs	...	1470 m	1450 x	1510 s
[Co(H) ₂]I ₂	1600 vs	...	1480 s	1440 ms, vx	1560 x
[Ni(H) ₂]I ₂	1600 vs	...	1470 s, x	1450 m	1530 s, x
PH	1590 sh	...	1490 s	1430 s?	1540 s
[Fe(PH) ₂](ClO ₄) ₂	1600 s	1430 m	1560 s
[Co(PH) ₂](ClO ₄) ₂	1610 vs	...	1470 w	...	1570 w?
[Ni(PH) ₂](ClO ₄) ₂	1600 vs	...	1490 m	1430 s	1540 ms
[Fe(MH) ₂](ClO ₄) ₂	1600 s	...	1480 sh	...	1520 m, x
[Co(MH) ₂]I ₂	1600 vs	...	1470 s	1460 sh	1550 sh
[Ni(MH) ₂]I ₂	1590 s	1585 sh	1470 s	1460 sh	1520 s, x
dMH	1610 mw	1560 sh?	1470 s	1430 sh	1540 sh
[Fe(dMH) ₂](ClO ₄) ₂	1600 w	...	1460 sh	...	1520 vs
[Co(dMH) ₂]I ₂	1580 sh	...	1450 s	1440 s	1570 s
[Ni(dMH) ₂](ClO ₄) ₂	1600 ms	1580 sh	1450 s, vx	1450 s	1540 sh
					1560 s
					1540 sh
					1560 m

^a Abbreviations used include: w, weak; m, medium; s, strong; x, wide; sh, shoulder; v, very; ?, questionable assignments; and py, pyridine.



VII

The presence of the acetyl methyl group seems sterically equivalent to an amino methyl group. Thus, the

The magnetic behavior of the nickel(II) complexes is typical, falling in the range normally expected for octahedral nickel(II). The temperature dependence of the susceptibility for all of the two-to-one cobalt(II) complexes has been measured and discussed elsewhere.²⁴

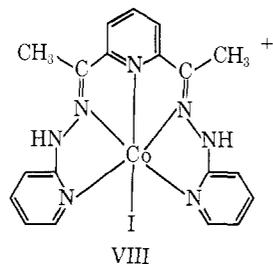
The magnetic behavior of the iron(II) complexes is interesting. All of the *bis* complexes are diamagnetic; however, these divalent iron complexes were characterized by their ability to retain trace amounts of ferro-

magnetic impurities. Thus, moments of 7.49, 7.63, 2.51, 5.22, 5.31, 1.7, 5.65, 2.90, and 3.51 BM were observed for highly crystalline analytically acceptable "diamagnetic" samples. The method used to obtain magnetic purity with these complexes was to keep recrystallizing until a constant moment was observed and then either to form another salt by a metathesis reaction or to switch to a different recrystallizing medium and continue. These materials are, in general, *not* thermally stable in solution above 45°, so care must be taken when recrystallizing them.

Since the occurrence of impurities might lead to erroneous moments among other iron(II) compounds, the preparation of bis(2-acetylpyridine-2'-pyridylhydrazone)iron(II) perchlorate was undertaken. This material has been reported to have a moment of 1.90 BM.²⁷ Our results show, however, a value after extensive purification of $\mu_{\text{eff}} = 0.68$ BM (300°K).

The assignment of pyridine bands^{23,29-31} and that of the methine absorptions^{32,33} in the infrared spectra is consistent with other work on similar systems (see Table IV).

The results of conductivity measurements on the two-to-one complexes appear in Table V. The values, while scattered, support the formulation as ternary electrolytes. The conductivity of Co(PhH)I₂ suggests a two-to-one formulation; however, the displacement of a coordinated halide by methanol commonly occurs.³² The compound is formulated as containing a six-coordinate cobalt atom (VIII).



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TABLE V
MOLAR CONDUCTANCES OF METAL COMPLEXES
WITH HYDRAZONES OF THE TRIMETHINE TYPE^a

Compound	Δ , cm ² mole ⁻¹ ohm ⁻¹	
	H ₂ O	CH ₃ OH
[Fe(H) ₂]Cl ₂	204	163
[Co(H) ₂]Cl ₂ ·H ₂ O	217	160
[Ni(H) ₂]Cl ₂ ·1.5H ₂ O	227	151
[Cu(H) ₂]Cl ₂ ·1.5H ₂ O	227	144
[Fe(MH) ₂](ClO ₄) ₂	208	181
[Co(MH) ₂](ClO ₄) ₂	196	188
[Ni(MH) ₂](ClO ₄) ₂	212	194
[Fe(dMH) ₂](ClO ₄) ₂	153	158
[Co(dMH) ₂](ClO ₄) ₂ ·H ₂ O	147	128
[Ni(dMH) ₂](ClO ₄) ₂	92	175
[Co(PH) ₂](ClO ₄) ₂	...	253
[Ni(PH) ₂](ClO ₄) ₂	...	261
[Fe(PH) ₂](ClO ₄) ₂	...	201
[Co(PyH)I]I	...	178

^a Measured at $\sim 10^{-3}$ M at 25°.

The remarkable fact that spin pairing occurs for all the iron(II) complexes while Dq toward nickel(II) spans the broad range from 1063 to 1258 cm⁻¹ requires consideration. Though no direct evidence is at hand, it is suggested that this paradox is traceable to the behavior of the uncoordinated amino functions of the hydrazone. Although the relative planarity of this group must be assumed to account for the properties of the nickel complexes, it seems likely that the iron(II) ion serves to uncouple the amino group-pyridine ring resonance, thereby permitting the folding of the amino group into the sterically less demanding pyramidal structure.

The structure of the one-to-one complexes poses an interesting problem. Molecular weight studies, in all cases studied except two, proved inconclusive. These two materials, which show negligible conductance in nitromethane, are Cu(dMH)Cl₂ (mol wt 382) and Co(dMH)Cl₂ (mol wt 377). The observed values of 327 and 386, respectively, militate against the formulation of these materials as halide-bridged polymers. The conductance values indicate that a species of the type [ML₂][MCl₄] is not present. A five-coordinate metal atom is indicated.