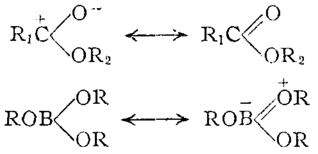
was obtained from the uncatalyzed reaction already cited, and from eleven runs involving acid concentrations between 0.0036 and 0.0421 *M*. The value of *k* in the latter case was 0.114 min.$^{-1}$.

The Reaction Mechanism.—The complete solvolysis of an alkyl borate obviously requires three steps, in which the alkoxy groups are successively replaced. We believe the first step to be practically rate-controlling. The structural studies show that a secondary borate reacts much more slowly than a primary one. The interpolation that ethyl di-*sec*-butyl borate[14] (the first intermediate in the ethanolysis of *sec*-butyl borate) reacts faster than *sec*-butyl borate, seems safe enough. Separate evidence was obtained from a mixture of esters prepared by mixing 1.5 moles *sec*-butyl alcohol with 1.0 mole of ethyl borate and distilling off the ethanol formed. The expected product would consist of a preponderance of the two mixed esters $(EtO)(BuO)_2B$ and $(EtO)_2(BuO)B$ with much smaller proportions of $(EtO)_3B$ and $(BuO)_3B$. The behavior of this mixture in the dilatometer at 0° is shown in curve B, Fig. 1. The large initial volume change, prolonged to about 50 minutes, is probably due to fairly rapid solvolysis of the mixed esters. The final slope (0.00495 at 0°, 0.0230 at 25°), in close agreement with the ethanolysis rate of pure *sec*-butyl borate, probably represents the solvolysis of this compound alone, for the molar volume change in the period of linearity is only 10% of the usual change.

The detailed mechanism of a single stage of ethanolysis was shown by Scattergood and coworkers[2] to involve fission of a boron–oxygen bond, presumably after addition of the solvent to the boron atom. Some additional evidence for such a mechanism, as opposed to a separation of a carbonium ion from the alkyl borate, is provided by our observation that the acid-catalyzed solvolysis of *t*-butyl borate produced no isobutylene; nor was ethyl *t*-butyl ether reported as a by-product of the preparation of *t*-butyl borate in boiling ethanol.[3] The mechanism of ethanolysis of the borates may therefore proceed by addition of ethanol to the borate molecule followed by loss of an alkoxide ion, with suitable modification to accommodate acid or base catalysis. This mechanism is similar to the mechanism of carboxylic ester hydrolysis, the electron-deficient boron atom taking the role of the electron-deficient carbon atom of the carbonyl group



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[14] Mixed orthoborates of this type have not yet been isolated; see L. H. Thomas, *J. Chem. Soc.*, 820 (1946).

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

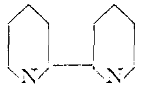
Complexes of Biacetyldihydrazone and Pyridinalhydrazones with Iron(II), Cobalt(II) and Nickel(II)

BY R. CARL STOUFER AND DARYLE H. BUSCH

RECEIVED JULY 18, 1956

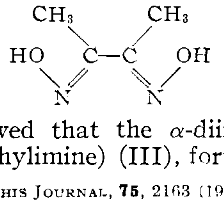
Iron(II), cobalt(II) and nickel(II) complexes have been prepared and characterized with biacetyldihydrazone (BdH), 2-pyridinalhydrazone (PAH), 2,6-pyridindialdihydrazone (PdAdH) and 2-pyridinal-*p*-tolilimine (PAT). The compounds having a metal–ligand ratio of 1:3 were isolated in all cases and the compounds having a metal–ligand ratio of 1:2 were isolated in several instances. The magnetic susceptibilities have been measured and the corrected magnetic moments of the metal ions are reported. The iron(II) complexes which contain three molecules of ligand are diamagnetic; however, the metal atoms exhibit small residual paramagnetisms. The remaining complexes are all highly paramagnetic. The colors, solubilities, magnetic moments and chemical properties indicate that the complexes are closely related to the well-known complexes with such aromatic heterocyclic diamines as 2,2'-bipyridine.

Among the best known complexing agents for iron(II), cobalt(II) and nickel(II) are the aromatic heterocyclic diamines and triamines which may be exemplified by 2,2'-bipyridine (I)



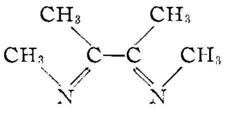
I

and the α-dioximes, of which dimethylglyoxime (II) is most familar.



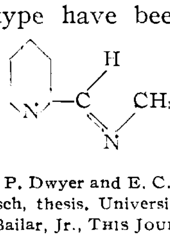
II

Krumholz[1] showed that the α-diimines, such as biacetylbis-(methylimine) (III), form iron(II) complexes which are quite similar to those of the aromatic heterocyclic diamines.



III

Recently,[2] the preparation of compounds involving functional groups of both the cyclic amine type and the imine type have been reported. This



IV

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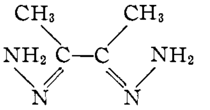
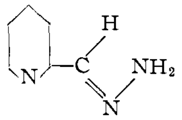
[1] P. Krumholz, THIS JOURNAL, **75**, 2163 (1953).

[2] W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Revs.*, **54**, 980 (1954); D. H. Busch, thesis, University of Illinois, Aug., 1954; D. H. Busch and J. C. Bailar, Jr., THIS JOURNAL, **78**, 1137 (1956).

class of ligand is illustrated by 2-pyridinalmethylimine (IV). All of these molecules contain the group —N=C—C=N— in their structures. It was the purpose of the work reported here to explore additional ligand types which might form complexes similar to either the aromatic heterocyclic diamines or the α-dioximes. Three new ligands have been studied. These are biacetyldihydrazone[3] (V), 2-pyridinalhydrazone (VI) and 2,6-pyridindialdihydrazone (VII). Iron(II), cobalt(II) and nickel(II) complexes with these chelating agents have been prepared and characterized, and their magnetic moments have been measured.

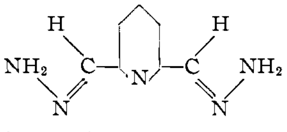


V

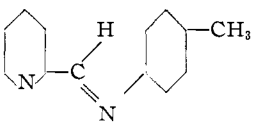


VI

VII



The magnetic moments of a series of complexes with 2-pyridinal-*p*-tolilimine (VIII) are also reported. Several of the latter group of complexes were first prepared by Bähr and Thämlitz.[4]



VIII

Experimental

Biacetyldihydrazone.—Biacetyldihydrazone was prepared by the method of Busch and Bailar,[2] m.p., 158°. *Anal.* Calcd. for $C_4H_{10}N_4$: C, 42.08; H, 8.83; N, 49.09. Found: C, 42.26, 42.22; H, 8.89, 8.97; N, 48.95, 49.03.

Tris-(biacetyldihydrazone)-iron(II) Iodide 3-Hydrate.—Two and twelve hundredths grams of iron(II) chloride 4-hydrate (0.0107 mole) was dissolved in 10 ml. of water. The solution was filtered, warmed and added to a second solution containing 4.0 g. (0.035 mole) of biacetyldihydrazone dissolved in a minimum amount of hot water. (Alternatively, dry ligand was dissolved in a warm solution of the metal salt.) The resulting solution was dark red. Approximately 1 g. of potassium iodide per ml. of solution was added and the solution cooled in an ice-bath. A dark rust-colored product crystallized. The crystals were filtered with suction and washed with a small amount of cold water. The product was recrystallized after dissolution in warm water (60°) by adding potassium iodide, as described above. The purified product was washed with small amounts of cold water, absolute ethanol and anhydrous ether, in that order, and dried *in vacuo* over P_2O_5 at room temperature; yield 82%. *Anal.* Calcd. for $[Fe(C_4H_{10}N_4)_3]I_2 \cdot 3H_2O$: C, 20.43; H, 5.14; N, 23.83. Found: C, 20.42; H, 4.92; N, 24.04.

Bis-(biacetyldihydrazone)-cobalt(II) Chloride.—Two grams of cobalt(II) chloride 6-hydrate (0.0084 mole) was dissolved in 30 ml. of ethanol. This solution was warmed and added to a solution prepared by dissolving 2.0 g. of biacetyldihydrazone (0.0175 mole) in 150 ml. of boiling ethanol. The mixing resulted in a brown-red colored solution from which a maroon-colored crystalline product was isolated by filtering with suction. The crystals were washed several times with small portions of cold absolute ethanol and anhydrous ether, and dried *in vacuo* at room temperature over P_2O_5; yield 99%. *Anal.* Calcd. for $[Co(C_4H_{10}N_4)_2]Cl_2$: C, 26.80; H, 5.61; N, 31.30. Found: C, 26.75, 26.49; H, 5.81, 5.64; N, 30.58, 30.71.

Tris-(biacetyldihydrazone)-cobalt(II) Iodide.—Two grams of cobalt(II) chloride 6-hydrate (0.0084 mole) was dissolved in a minimum amount of cold water. This was added to a solution which was prepared by dissolving 2.96 g. (0.026 mole) of biacetyldihydrazone in a minimum amount of hot water. The mixing resulted in a dark red-brown solution. The solution was cooled in an ice-bath and approximately 1 g. of potassium iodide per ml. of solution was added. A dark amber, crystalline product separated. The crystals were filtered with suction and washed with cold water and absolute ethanol. The product was redissolved in a small amount of warm water, filtered and again crystallized by the addition of potassium iodide. The purified product was filtered with suction, washed with cold water, absolute ethanol and anhydrous ether, in that order, and dried *in vacuo* at room temperature; yield 73.5%. *Anal.* Calcd. for $[Co(C_4H_{10}N_4)_3]I_2$: C, 21.99; H, 4.62; N, 25.65. Found: C, 21.91, 21.83; H, 4.64, 4.70; N, 25.59, 25.42.

Bis-(biacetyldihydrazone)-nickel(II) Chloride.—This substance was prepared as a light blue powder according to the method reported for the similar cobalt compound. *Anal.* Calcd. for $[Ni(C_4H_{10}N_4)_2]Cl_2$: C, 26.85; H, 5.64; N, 31.40; Ni, 16.40; Cl, 19.80. Found: C, 26.81, 26.76; H, 5.86, 5.69; N, 31.11, 31.19; Ni, 16.55, 16.63; Cl, 19.59, 19.74.

Tris-(biacetyldihydrazone)-nickel(II) Chloride 2-Hydrate.—Two grams of nickel(II) chloride 6-hydrate (0.0086 mole) was dissolved in 50 ml. of ethanol and added with stirring to a solution of biacetyldihydrazone prepared by dissolving 3.1 g. of biacetyldihydrazone (0.027 mole) in 150 ml. of boiling ethanol. The color of the resultant solution was a dark pink. The solution was cooled in an ice-bath which resulted in the separation of a red-brown, needle-like crystalline product which was filtered with suction, washed with absolute ethanol and anhydrous ether, and dried *in vacuo* at room temperature; yield 68.7%. *Anal.* Calcd. for $[Ni(C_4H_{10}N_4)_3]Cl_2$: C, 28.40; H, 6.70; N, 33.15. Found: C, 28.37, 28.48; H, 6.67, 6.85; N, 33.12, 33.20.

Tris-(pyridinalhydrazone)-iron(II) Iodide.—Six and six-tenths grams of 2-pyridinaldehyde (0.061 mole) was added dropwise and with stirring to an aqueous solution containing 1.95 g. (0.061 mole) of 95% hydrazine. To this was added a second solution prepared by dissolving 4 g. of iron(II) chloride 4-hydrate (0.020 mole) in 20 ml. of water. The resulting blood-red solution was filtered and allowed to stand for 5 min. Approximately 0.5 g. of potassium iodide for each ml. of solution was added, whereupon a red-black oil-like material separated. Upon prolonged and vigorous stirring, the oil became more viscous and finally began to form small red-colored particles. After complete conversion from the oil to the solid, the product was filtered with suction and washed with water. The red-black product was redissolved in 70 ml. of water by gently warming to 40°. Again, upon the addition of potassium iodide an oil-like product began to deposit on the sides of the beaker. At this point the solution was stirred vigorously and maintained at a constant temperature of 40° until small maroon-colored crystals began to form. The oil on the sides of the beaker slowly disappeared as the volume of the crystalline product increased. The solution was cooled in an ice-bath and filtered with suction. The crystals were washed thoroughly with cold water, ethanol and absolute ether and dried *in vacuo* over P_2O_5; yield 93.5%. *Anal.* Calcd. for $[Fe(C_6H_7N_3)_3]I_2$: C, 31.27; H, 3.35; N, 18.24. Found: C, 31.10, 31.23; H, 3.67, 3.77; N, 17.90, 17.76.

Tris-(pyridinalhydrazone)-cobalt(II) Iodide and Tris-(pyridinalhydrazone)-nickel(II) Iodide.—These complexes were prepared in a manner analogous to that of the iron compound as described above (however, no difficulty was encountered in obtaining the product in a crystalline form); yield (cobalt complex), 94.0%; (nickel complex), 87.7%. *Anal.* Calcd. for $[Co(C_6H_7N_3)_3]I_2$: C, 31.97; H, 3.13; N, 18.64. Found: C, 32.00, 31.87; H, 3.31, 3.32; N, 18.29, 18.32. *Anal.* Calcd. for $[Ni(C_6H_7N_3)_3]I_2$: C, 31.98; H, 3.13; N, 18.65. Found: C, 31.69, 31.77; H, 3.32, 3.38; N, 18.51, 18.45.

2,6-Pyridindialdihydrazone.—Four grams (0.0296 mole) of 2,6-pyridindialdehyde was dissolved in 70 ml. of warm absolute ethanol. This solution was added dropwise to a second solution which had been prepared by adding 2 g. of 95% hydrazine (0.0594 mole) to 20 ml. of absolute ethanol. A crystalline product, light tan in color, was separated upon cooling the solution in an ice-bath. This product was

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(3) A preliminary report on the iron(II) complex with this ligand was included in ref. 2 (Busch and Bailar).

(4) G. Bähr and H. Thämlitz, *Z. anorg. allgem. Chem.*, **282**, 3 (1955).

filtered with suction and washed with cold absolute ethanol. The crystalline product was redissolved in 70 ml. of warm absolute ethanol and the product again separated by cooling. The crystals were filtered with suction, washed with cold absolute ethanol and anhydrous ether and dried *in vacuo* over P_2O_5; yield 56.7%. *Anal.* Calcd. for $C_7H_9N_5$: C, 51.52; H, 5.56; N, 42.92. Found: C, 51.50, 51.41; H, 5.54, 5.71; N, 42.67, 42.67.

Bis-(2,6-pyridindialdihydrazone)-iron(II) Iodide.—Four grams of iron(II) chloride 4-hydrate (0.0201 mole) was dissolved in 20 ml. of water and filtered. This was added to a second solution which was prepared by dissolving 6.56 g. of 2,6-pyridindialdihydrazine (0.0402 mole) in warm water. The black-red solution was filtered and to the filtrate was added approximately 20 g. of potassium iodide whereupon the dark maroon, crystalline product separated. The product was filtered with suction and redissolved in 300 ml. of warm water. After filtration the solution was cooled and a black needle-like product crystallized. The crystals were filtered with suction, washed with cold water, absolute alcohol and anhydrous ether and dried *in vacuo* over P_2O_5; yield 89.6%. *Anal.* Calcd. for $[Fe(C_7H_9N_5)_2]I_2$: C, 26.43; H, 2.85; N, 22.02. Found: C, 26.44, 26.56; H, 3.01, 3.02; N, 21.88, 21.94.

Bis-(2,6-pyridindialdihydrazone)-cobalt(II) Iodide and Bis-(2,6-pyridindialdihydrazone)-nickel(II) Iodide.—These complexes were prepared in a manner analogous to that of the bis-(2,6-pyridindialdihydrazone)-iron(II) iodide. The cobalt complex was isolated in the form of black needle-like crystals which became brown upon crushing; yield 86.3%. The nickel complex was separated as a tan-colored powder; yield 79.6%. *Anal.* Calcd. for $[Co(C_7H_9N_5)_2]I_2$: C, 26.31; H, 2.84; N, 21.92. Found: C, 26.21, 26.43; H, 2.79, 2.88; N, 21.98, 21.83. *Anal.* Calcd. for $[Ni(C_7H_9N_5)_2]I_2$: C, 26.32; H, 2.84; N, 21.93. Found: C, 26.20, 26.47; H, 3.09, 2.99; N, 21.86, 21.75.

2-Pyridinal-*p*-tolilimine.—This product was prepared essentially in the manner given by G. Bähr and H. Thämlitz[4] except that the product was not fractionally distilled but merely crystallized from ligroin; m.p. cited[4] 58.5°; found, 57–58°; yield 63.0%. *Anal.* Calcd. for $C_{13}H_{12}N_2$: C, 79.56; H, 6.12; N, 14.28. Found: C, 79.67, 79.45; H, 6.19, 6.23; N, 14.35, 14.18.

Tris-(2-pyridinal-*p*-tolilimine)-cobalt(II) Iodide 3-Hydrate.—Six and six-tenths grams of 2-pyridinal-*p*-tolilimine (0.0336 mole) was added to a solution prepared by dissolving 2.67 g. of cobalt(II) chloride 6-hydrate (0.0112 mole) in 20 ml. of water. The resultant solution, which was dark red in color, was filtered to remove excess ligand. This filtrate was added with vigorous stirring to a saturated potassium iodide solution (50 ml.) (mixing of the solutions in this order prevents the formation of a putty-like mass of product which is handled with difficulty). The product separated as small orange particles which were filtered with suction. The product was washed thoroughly with water and permitted to dry on the filter. It was then dried *in vacuo* over P_2O_5; yield 72.1%. *Anal.* Calcd. for $[Co(C_{13}H_{12}N_2)_3]I_2 \cdot 3H_2O$: C, 49.02; H, 4.41; N, 8.80. Found: C, 48.15, 48.28; H, 4.20, 4.12; N, 8.72, 8.50.

Table I

Molar Susceptibilities and Magnetic Moments of Complexes

Compound[a]	$\chi_M \times 10^6$ (complex)	μ_{eff} (metal ion)
$[Fe(BdH)_3]I_2$	−225 ± 5	0.62
$[Co(BdH)_2]Cl_2$	9740 ± 110	4.91
$[Co(BdH)_3]I_2$	7090 ± 170	4.26
$[Ni(BdH)_2]Cl_2$	3720 ± 30	3.10
$[Ni(BdH)_3]Cl_2$	3675 ± 15	3.10
$[Fe(PAH)_3]I_2$	−15 ± 5	0.94
$[Co(PAH)_3]I_2$	8450 ± 10	4.63
$[Ni(PAH)_3]I_2$	3720 ± 10	3.15
$[Fe(PdAdH)_2]I_2$	−19 ± 3	0.86
$[Co(PdAdH)_2]I_2$	3180 ± 60	2.90
$[Ni(PdAdH)_2]I_2$	4020 ± 30	3.24
$[Fe(PAT)_2]Cl_2$	11600 ± 200	5.34
$[Fe(PAT)_3]I_2 \cdot 2H_2O$	−30 ± 10	0.80
$[Co(PAT)_3]I_2 \cdot 3H_2O$	10200 ± 400	5.06
$[Ni(PAT)_2](ClO_4)_2 \cdot H_2O$	3480 ± 40	2.98
$[Ni(PAT)_2]Cl_2 \cdot 2H_2O$	4440 ± 10	3.35
$[Ni(PAT)_3]I_2 \cdot 2H_2O$	4060 ± 40	3.24

[a] The following abbreviations are used: biacetyldihydrazone, BdH; 2-pyridinalhydrazone, PAH; 2,6-pyridindialdihydrazone, PdAdH; and 2-pyridinal-*p*-tolilimine, PAT.

Tris-(2-pyridinal-*p*-tolilimine)-nickel(II) Iodide.—This complex was prepared in the same manner as the cobalt complex. The product was separated as a fine, orange colored solid (slightly different color from that of the cobalt); yield 90.60%. *Anal.* Calcd. for $[Ni(C_{13}H_{12}N_2)_3]I_2 \cdot 2H_2O$: C, 49.97; H, 4.30; N, 8.98. Found: C, 49.50, 49.30; H, 3.92, 4.15; N, 8.91, 8.86.

Bis-(2-pyridinal-*p*-tolilimine)-iron(II) Chloride, Tris-(2-pyridinal-*p*-tolilimine)-iron(II) Iodide and Bis-(2-pyridinal-*p*-tolilimine)-nickel(II) Chloride.—These complexes were prepared after the manner of Bähr and Thämlitz,[4] and their compositions were confirmed by analysis.

Magnetic Measurements.—All magnetic measurements were made on solid samples by the Gouy method using Mohr salt, ferrous ammonium sulfate 6-hydrate, and water as standards. Diamagnetic corrections were made for the ligand and anion so that the values reported in column 3 of Table I are the moments attributable to the metal ion. The values used in correcting for the molar susceptibilities of the free ligands are given in Table II. along with the values used in correcting for the anions.

Table II

Molar Susceptibilities of Ligands and Anions

Ligand or anion	$\chi_M \times 10^6$
Biacetyldihydrazone	− 92 ± 22
2-Pyridanalhydrazone[a]	− 98 ± 19
2,6-Pyridindialdihydrazone	−113 ± 19
2-Pyridinal-*p*-tolilimine	− 60 ± 20
Iodide ion[b]	− 50.6 ± 1.6
Chloride ion[b]	− 23.4 ± 1.3
Perchlorate ion[b]	− 30.2 (derived)
Water[b]	− 13

[a] Value calculated from that of 2,6-pyridindialdihydrazone and Pascal's atomic susceptibilities as given by reference cited below, p. 51. [b] Values from P. W. Selwood, "Magneto Chemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 36.

Discussion

Complexes of Biacetyldihydrazone (Structure V).—It was pointed out in an earlier article[2] that the iron(II) complex of biacetyldihydrazone does not have the same spectral properties as the compounds containing 2,2-bipyridine, *o*-phenanthroline, 2-pyridinalmethylimine and biacetylbis-(methylimine). A single compound, formulated as [Fe(biacetyldihydrazone)$_3$] [$FeCl_4$], was reported, and it was shown that the magnetic moment could be interpreted on the assumption that the complex cation was diamagnetic and the complex anion paramagnetic. The isolation of diamagnetic salts containing simple anions and the same cation confirms this conclusion. The composition of the complex cation, three molecules of ligand coördinated to each metal ion, indicates that this donor molecule more nearly resembles biacetylbis-(methylimine) (structure III) than dimethylglyoxime (structure II) in its complexing reaction with iron(II). In contrast, dimethylglyoxime has been shown to coördinate with iron(II) in the ratio of two to one.[5]

The similarity of biacetyldihydrazone to the α-diimines and the aromatic heterocyclic amines is more striking in the case of nickel(II). Whereas

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(5) K. Sone, *Bull. Chem. Soc. Japan*, **25,** 1 (1952); L. Tschugaeff, *Z. anorg. Chem.*, **46**, 160 (1905); L. Tschugaeff, *Ber.*, **41**, 1678 (1908)

dimethylglyoxime(II) forms the familiar diamagnetic, water-insoluble red complex containing two molecules of ligand for each metal ion, nickel(II) complexes with 2,2′-bipyridine have been prepared containing both two and three molecules of bipyridine for each metal ion.[6] In the latter case, the three to one complex is the more stable despite the fact that it is paramagnetic[7] while the two to one complex is diamagnetic.[8] The biacetyldihydrazone complexes of nickel(II) follow this pattern fairly closely; however, both the two to one and the three to one complexes are paramagnetic, (Table I). Also, from the color of the solutions, the two to one complex appears to disproportionate when dissolved in water, yielding the tris-(biacetyldihydrazone)–nickel(II) ion. This is analogous to the behavior of the 2,2′-bipyridine complex.[6] The colors of these compounds are similar to the corresponding 2,2′-bipyridine compounds. The bis complexes are blue and green, respectively, and the tris compounds are copper-colored and pink.

The cobalt(II) complexes of biacetyldihydrazone bear corresponding resemblances to those of 2,2′-bipyridine. In this case, all the complexes are highly paramagnetic and no great color change accompanies a change in the number of bidentate chelating agents present.

Complexes of the Pyridinalhydrazones.—The complexing reactions of 2-pyridinalhydrazone and 2,6-pyridindialdihydrazone are closely related to those of biacetyldihydrazone. The tris-(2-pyridinalhydrazone) and the bis-(2,6-pyridindialdihydrazone) complex cations are readily formed with cobalt(II), nickel(II) and iron(II) in aqueous solutions, and the magnetic moments of the solid compounds (Table I) and the solubilities of their salts are comparable to those of the analogous 2,2′-bipyridine derivatives. The chlorides are very soluble; the iodides, moderately soluble and the perchlorates, only slightly soluble. The complex ions of coördination number four have not been obtained by the techniques which yielded the corresponding biacetyldihydrazone complexes. The cobalt(II) complex with 2,6-pyridindialdihydrazone exhibits a magnetic moment of 2.90 Bohr Magnetons. This value is close to that anticipated for two unpaired electrons (2.83). Since the commonly occurring electronic configurations of cobalt(II) permit either one or three unpaired electrons, this result is quite interesting. The value has been reproduced for two different samples in several determinations. It is within the realm of possibility that this moment might be the result of a single electron, having associated with it a large orbital contribution. This explanation has been applied to other cobalt(II) compounds which have moments around 2.5 Bohr magnetons.[9] This point is being investigated further.

Complexes of 2-Pyridinal-*p*-tolilimine.—The complexes of this class also bear close resemblance to the aromatic heterocyclic diamines as is expected because of the similarity of this ligand to 2-pyridinalmethylimine (IV). The tris complex of iron (II) is diamagnetic and the bis complex is paramagnetic, as are the remaining complexes with this ligand (Table I). A single anomaly appears in the case of bis-(2-pyridinal-*p*-tolilimine)–nickel(II) chloride, which is paramagnetic. This may be a consequence of the great steric requirements of the chelating agent.

The small positive magnetic moments of the six-coördinate iron(II) complexes with all of the ligands probably represent a residual paramagnetism of the type discussed by Sienko and co-workers,[10,11] for cobalt(III) and rhodium(III). This is indicated by the similar magnitudes of the quantities.

The spectral properties and solution behavior of these complex compounds are presently under investigation.

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(6) W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Revs.*, **54**, 970 (1954).

(7) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

(8) L. Cambi and A. Cagnasso, *Atti. accad. nazl. Lincei*, **19**, 458 (1934).

(9) M. Calvin and C. H. Barkelew, THIS JOURNAL, **68**, 2268 (1946).

(10) J. L. Kernahan and M. J. Sienko, *ibid.*, **77**, 1978 (1955).

(11) J. Gavis and M. J. Sienko, *ibid.*, **77**, 4983 (1955).