sible to have a reaction intermediate with a broken chelate ring. The alternative explanation is a reaction intermediate with a seven coördinated iron(II) ion. Such a coördination intermediate would presumably necessitate changes in electron configuration of the complex, which would account for the slowness of its formation. Somewhere in the dissociation reaction the electronic configuration for iron(II) changes from $d^2d^2d^2D^2SP^3$ to $d^2d^1d^1d^1d^1SP^3D^2$.

It is not possible from this work to definitely establish whether the hydroxide ion effect on $FePh_3^{++}$ is due to an SN1 or an SN2 mechanism. Both mechanisms involve partially dissociated species and neither mechanism accounts for the observed $[OH^-]^3$ term without the introduction of several intermediates. However, the SN2 mechanism is the simpler of the two. It has fewer intermediates and gives a $[OH^-]^2$ dependence at low hydroxide ion concentrations without the necessity of assuming an intermediate with two activated Ph molecules. The hydroxide ion is not the only nucleophilic ion which can accelerate the dissociation of $FePh_3^{++}$. Cyanide ion and thiocyanate ion both cause faster dissociation of $FePh_3^{++}$.[14] The cyanide ion kinetics with $FePh_3^{++}$ resemble the hydroxide ion kinetics, with a reaction intermediate likely. The aqueous cyanide ion causes faster dissociation than the hydroxide ion. All of these factors contribute to the feasibility of an SN2 mechanism with reaction intermediates containing nucleophilic groups.

The fact that it is possible to bring about the rapid dissociation of $FePh_3^{++}$ should prove of value in analytical separations involving the use of 1,10-phenanthroline kinetics.[15]

It is naturally of considerable interest to know whether hydroxide ion will affect the dissociation kinetics of other 1,10-phenanthroline complexes such as nickel(II) and cobalt(III). These systems, as well as a comparison of the effect of other nucleophilic groups besides hydroxide ion, are now under investigation.

(14) P. Grimes, "Reactions of Anions with 2,2'-Bipyridine, 1,10-Phenanthroline and the Iron(II) Complexes of These Reagents," M.S. Thesis, Ames, Iowa, Iowa State College, 1956.

(15) D. W. Margerum and Charles V. Banks, *Anal. Chem.*, **26**, 200 (1954).

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF SYDNEY]

Tridentate Chelate Compounds. I

BY FRANCIS LIONS AND KENNETH V. MARTIN[1]

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New tridentate chelate compounds containing three donor nitrogen atoms and possessing structural features resembling those of terpyridine have been prepared and shown to form coördination compounds readily. Some polymers possessing recurring tridentate chelate groups also have been prepared and their capacity to combine with metal salts demonstrated. Some of the iron containing polymers have unusual magnetic properties.

2,6-Bis-(α-pyridyl)-pyridine (I), better known by its trivial name "terpyridine," is a most important tridentate chelate compound which has been extensively studied. However, it is relatively inaccessible. In 1953 one of the authors and his coworkers[2] reported briefly on the preparation and use of 8-(α-pyridylmethyleneamino)-quinoline (II) as a tridentate chelate compound with constitutional features similar to those of I and showed that it coördinated with iron(II) salts similarly to I. The present paper describes a number of new tridentate chelate compounds, each containing three donor nitrogen atoms and some possessing details of molecular structure similar to I.

2-Aminomethylpyridine (III) is available from the reduction with zinc dust and acetic acid of pyridine-2-aldoxime.[3] We have also found that it can be synthesized from the 2-chloromethylpyridine of Matsumura[4] by condensation with potassium phthalimide using Bolhofer and Sheahan's[5] modification of the Gabriel reaction, and hydrolysis of the 2-phthalimidomethylpyridine so obtained. However, the over-all yield is small and the method of Craig and Hixon is preferable.

III reacts readily with pyridine-2-aldehyde to give the Schiff base 2-(α-pyridylmethyleneaminomethyl)-pyridine (IV) as a pale yellow oil. IV might well be expected to function as a tridentate chelate compound with all three nitrogen atoms acting as donors and attaching the tridentate residue to a metal atom in two coplanar 5-membered ring "chelate loops."[6] The molecules of both I and IV possess the same sequence of atoms and bonds, *viz.*, –N=C–C=N–C–C=N–, in the donor chain, so that at least some of the possibilities which exist for double bonding and resonance must be similar for the molecules of both substances.

Addition of iron(II) sulfate to an aqueous suspension of II results in formation of an intensely red-colored solution from which bis-(2-(α-pyridylmethyleneaminomethyl) - pyridine) - iron(II) perchlorate (V) can be precipitated. This salt is diamagnetic and must apparently be an octahedral iron(II) complex salt with lower level ($3d^24s4p^3$) covalent bonds. Its complex cation must be very similar structurally to that of the bis-terpyridine iron(II) salts, each tridentate residue lying in one

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(1) University Research Fund Student of the University of Sydney.

(2) F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, THIS JOURNAL, **75**, 3834 (1953).

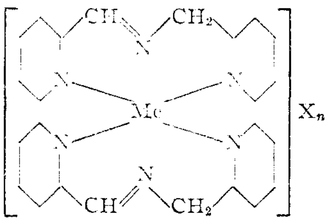
(3) L. C. Craig and R. M. Hixon, *ibid.*, **53**, 4367 (1931).

(4) E. Matsumura, *J. Chem. Soc. Japan*, **74**, 363 (1953); *cf. C.A.* **48**, 6442b (1954).

(5) J. C. Bolhofer and W. A. Sheban, THIS JOURNAL, **72**, 2786 (1950).

(6) *Cf.* F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, *ibid.*, **74**, 4188 (1952).

or other of two equatorial planes at right angles to each other, the metal atom being in both planes



V, Me = Fe, X = (ClO_4), n = 2
VI, Me = Co, X = (ClO_4), n = 2
VII, Me = Co, X = I, n = 3.

(Fig. 1). The complex cation of V should thus exist in enantiomorphous forms.

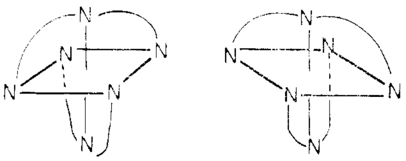
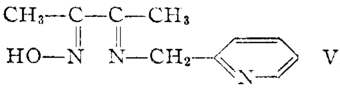


Fig. 1.

Addition of cobalt(II) chloride to an ethanolic solution of IV leads to development of a deep-blue color and blue bis-(2-(α-pyridylmethyleneaminomethyl)-pyridine)-cobalt(II) perchlorate (VI) can be precipitated. Its magnetic moment of 4·3 Bohr magnetons indicates the use of upper level (4s4p^{3}4d^2) covalent bonds. Treatment of the blue ethanolic solution of the complex cobalt(II) chloride corresponding to VI with a mild oxidising agent, such as aqueous hydrogen peroxide, changes the color to brown. After destruction of excess peroxide by boiling, addition of potassium iodide to the cooled solution leads to precipitation of diamagnetic bis-(2-(α-pyridylmethyleneaminomethyl)-pyridine)-cobalt(III) iodide (VII). Structurally, the complex cations of VI and VII must be constituted similarly to those of V.

Interaction of III and diacetyl monoxime in hot ethanol leads to formation of colorless crystalline 2-oximino-3-methyl-4-aza-5-α-pyridyl-Δ^3-pentene (VIII). VIII coördinates readily with iron(II) and cobalt salts. Thus, solid VIII readily dissolves in aqueous iron(II) sulfate solutions with development of an intense red color and diamagnetic bis-(2-oximino-3-methyl-4-aza-5-α-pyridyl-Δ^3-pentene)-iron(II) iodide (IX) readily can be precipitated by addition of a soluble iodide.

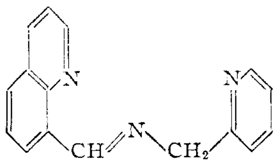


VIII

Interaction of VIII with cobalt(II) chloride in aqueous ethanol followed by oxidation with cerium(IV) nitrate leads to formation of the complex bis-(2-oximino-3-methyl-4-aza-5-α-pyridyl-Δ^3-pentene) cobalt(III) salt and the diamagnetic iodide X can be precipitated. Heating of the reaction mixture during the preparation leads to decomposition and liberation of diacetyl. In each of the complex salts IX and X the two residues of VIII function as tridentates without proton loss from the oximino group, each tridentate residue forming two coplanar 5-membered ring chelate loops with the metal atom, the structural pattern being similar to that of Fig. 1.

We have again prepared 8-(α-pyridylmethyleneamino)-quinoline[2] (II) and have found that it combines readily with cobalt(II) salts to give complex cobalt(II) salts which can be oxidized to the cobalt(III) state. Thus, bis-(8-(α-pyridylmethyleneamino)-quinoline)-cobalt(III) perchlorate can be obtained as a diamagnetic crystalline solid. The relative ease of synthesis of II and similar compounds suggests commencement of a study of the coördinating capacity of substituted derivatives of XI. It has already been amply demonstrated that substituents in the 2,2′-bipyridine or the 1,10-phenanthroline molecule can affect the chelating power, whether because of steric or electron-attracting or -repelling effects.[7] We have condensed pyridine-2-aldehyde with 8-aminoquinaldine[8] to obtain the Schiff base 8-(α-pyridylmethyleneamino)-2-methylquinoline (XII) and have found that XII coördinates readily with iron(II) salts to give diamagnetic intensely-green bis-(8-(α-pyridylmethyleneamino)-2-methylquinoline)-iron(II) salts. The intensity of the color is indistinguishable from that obtained with XI and it seems reasonable to infer that the single substituent methyl group in the quinoline nucleus does not materially affect the chelating capacity, despite its proximity to one of the donor nitrogen atoms. This is in marked contrast to the effect on the chelating power of 2,2′-bipyridine or of 1,10-phenanthroline of methyl groups similarly introduced into positions adjacent to the donor nitrogen atoms.

Quinoline-8-aldehyde[9] condenses readily with 2-aminomethylpyridine (III) to give 2-(8′-quinolylmethyleneaminomethyl)-pyridine (XVI), which coördinates readily as a tridentate chelate compound with iron(II) sulfate in aqueous solution. From the resulting intensely-green solution can be isolated green crystalline diamagnetic bis-(2-(8′-quinolylmethyleneaminomethyl)-pyridine)-iron(II) iodide (XVII). It is worth noting that of the two chelate loops formed by a molecule of XVI when it coördinates with a metal atom, one is a five-membered ring whilst the other is six-membered.



XVI

In any consideration of design of new tridentate chelate compounds related to I cognizance must be taken of the recent availability of pyridine-2,6-dialdehyde (XVIII). XVIII will condense with primary amines (2 mols.) to give Schiff bases of the general formula XIX in which there is the same sequence of donor atoms and bonds as

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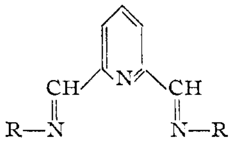
[7] *Cf. e.g.*, W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Revs.*, **54**, 991 (1954).

[8] D. L. Hammick, *J. Chem. Soc.*, 1302 (1926).

[9] R. C. Elderfield and M. Siegel, THIS JOURNAL, **73**, 5622 (1951).

in I. When R is methyl or ethyl in XIX these bases are oils. However, when R is phenyl or benzyl the compounds XIX are crystalline solids. These coördinate readily with metal salts as tridentate chelates. Thus, it is quite easy to prepare the red diamagnetic bis-(2,6-pyridylene-dimethyleneaniline)-iron(II)[10] perchlorate (XX) and bis-(2,6 - pyridylene - dimethylenebenzylamine) - iron-(II) bromide (XXI), typical octahedral iron(II) complex salts with lower level ($3d^24s4p^3$) covalent bonding. Structurally, the planar tridentate residues in a molecule of one of them must be situated in two planes at right angles, and since these residues are symmetrical, the complex ion must be identical with its mirror image so that the salts are not resolvable (Fig. 2).


XIX

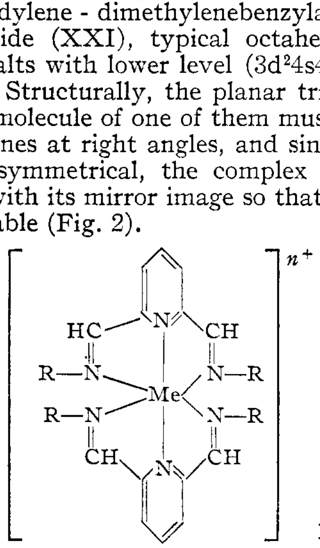


Fig. 2.

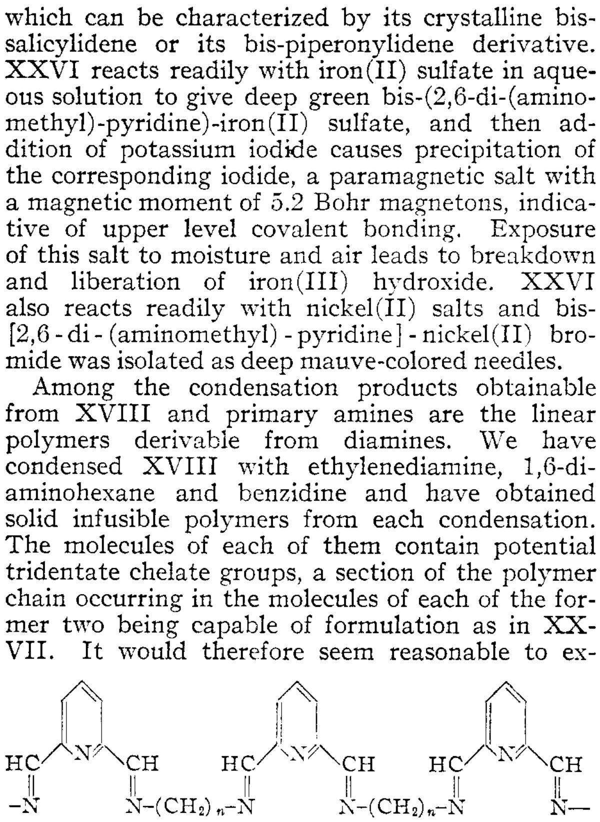
From cobalt(II) chloride and XIX (R = $-CH_2-C_6H_5$) in aqueous ethanol can be obtained in solution bis-(2,6-pyridylene-dimethylenebenzylamine)-cobalt(II) chloride. The corresponding iodide XXII, which crystallizes in dark brown needles, is paramagnetic with a magnetic moment of 3.8 Bohr magnetons. The chloride can be oxidized in solution with chlorine and, eventually, diamagnetic bis-(2,6-pyridylene-dimethylenebenzylamine)-cobalt(III) iodide can be isolated. This oxidation cannot be effected with any rapidity with cerium-(IV) nitrate in nitric acid solution, almost pure complex cobalt(II) salt being recoverable.

When copper(II) chloride is allowed to react with XIX (R = $-CH_2C_6H_5$) in ethanol a bright green color develops and a solid separates. Addition of more base results in re-solution of the solid and change of color to grey-green. From this solution perchloric acid precipitates bis-(2,6-pyridylene - dimethylenebenzylamine) - copper(II) perchlorate (XXIII). We consider this salt to be an octahedral copper(II) complex salt with $4s4p^34d^2$ upper level covalent bonds. Six-covalent copper(II) complexes are not novel.[11]

Pyridine-2,6-dialdoxime (XXIV) appears to function as a tridentate chelate compound. Thus, when it is treated in aqueous ethanol solution with iron(II) sulfate and then sodium acetate, a deep-red crystalline solid $C_{14}H_{11}N_6O_4FeNa$ (XXV) is obtained. This is a binary electrolyte with the coördinated iron atom in the anion. However, further consideration of its structure is reserved for a later paper.

Reduction of XXIV with zinc dust and acetic acid leads to formation in good yield of 2,6-bis-aminomethylpyridine (XXVI), a colorless oil which absorbs carbon dioxide from the air but which can be characterized by its crystalline bis-salicylidene or its bis-piperonylidene derivative. XXVI reacts readily with iron(II) sulfate in aqueous solution to give deep green bis-(2,6-di-(aminomethyl)-pyridine)-iron(II) sulfate, and then addition of potassium iodide causes precipitation of the corresponding iodide, a paramagnetic salt with a magnetic moment of 5.2 Bohr magnetons, indicative of upper level covalent bonding. Exposure of this salt to moisture and air leads to breakdown and liberation of iron(III) hydroxide. XXVI also reacts readily with nickel(II) salts and bis-[2,6 - di - (aminomethyl) - pyridine] - nickel(II) bromide was isolated as deep mauve-colored needles.

Among the condensation products obtainable from XVIII and primary amines are the linear polymers derivable from diamines. We have condensed XVIII with ethylenediamine, 1,6-diaminohexane and benzidine and have obtained solid infusible polymers from each condensation. The molecules of each of them contain potential tridentate chelate groups, a section of the polymer chain occurring in the molecules of each of the former two being capable of formulation as in XXVII. It would therefore seem reasonable to expect them to be able to absorb certain kinds of metal salt from solution through the ability of the recurring tridentate groups to coördinate with the metal atoms. The polymer derived from benzidine apparently possesses very little capacity for coordination with ions such as iron(II) which favor an octahedral environment. However it will combine with salts such as copper(II) chloride. The polymers from ethylenediamine and hexamethylenediamine do readily combine with salts such as iron(II) sulfate, rapidly acquiring a purplish-blue color when suspended in aqueous solutions of it.


XXVII

Consideration of the spatial requirements of the various atoms in the molecule of the polymer derived from hexamethylenediamine shows that it should be possible for two successive tridentate residues in the chain to coördinate with the same six-covalent metal atom, the two planar tridentate residues becoming disposed in two planes at right angles to each other. If this process were to occur regularly along the chain the resulting giant molecule might be looked on as containing a series of sexadentate chelate residues regularly spaced along a linear molecule and each coördinated through six nitrogen atoms to a metal atom. However, it

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[10] The bivalent radical C_5H_3N is named pyridylene by analogy with phenylene.

[11] *Cf. e.g.*, G. Peyronel, *Gazz. chim. ital.*, **71**, 363 (1951); E. I. Onstott and H. A. Laitinen, THIS JOURNAL, **72**, 4724 (1950); S. Kirschner, *ibid.*, **78**, 2372 (1956).

is quite unlikely that such regularity could occur. Thus, if in a series of five successive three-nitrogen-atom groups along the chain the first and second became bonded to a metal atom (as a sexadentate) and the fourth and fifth did also, then the third group—now an isolated tridentate group—might function by bonding to a metal atom to produce cross-linking of neighboring polymer chains. It might also remain unattached. Such a process of forming recurring sexadentate coördinated ions along the chain of the polymer would involve very complicated twining and twisting and it hardly seems probable that a polymer molecule, once formed, could undergo this process.

In fact, suspension of the powdered water-insoluble 1:1 polymer obtained by condensing XVIII with hexamethylenediamine in an aqueous solution containing excess iron(II) sulfate, followed by boiling, leads to the taking up of one molecule of iron(II) sulfate for each two residues of XVIII. The suspended solid acquires a deep reddish-blue color. This iron-containing solid is insoluble in any of the common solvents and does not melt below 300°. The analytical results suggest that in its molecules each iron atom is probably bonded to the six nitrogen atoms from two tridentate residues, the results agreeing with an empirical formula $C_{26}H_{34}N_6FeSO_4 \cdot 6H_2O$. The magnetic behavior was quite unusual, the solid being ferromagnetic with a molar susceptibility (ψ_m) of $155{,}000 \times 10^{-6}$ c.g.s. unit. It is difficult, without much more evidence, to draw conclusions concerning the molecular structure. Ferromagnetism is usually observed in lattices of magnetic particles with loose interatomic bonding and with unpaired parallel spins.[12] If each iron atom were upper-level convalently bonded to the nitrogen atoms of two tridentate residues then there would be four unpaired electron spins for each iron atom. Spins of one iron atom could possibly be coupled with spins of adjacent iron atoms and this might account for the observed ferromagnetism.

When an ethanolic solution of XVIII is added to a solution of hexamethylenediamine and iron(II) sulfate in aqueous ethanol (polymer preparation in the presence of iron(II) sulfate) a small amount of an insoluble solid separates from the solution. Addition of a soluble perchlorate to the red filtrate then causes precipitation of a diamagnetic red complex iron(II) perchlorate. From its elementary composition it would appear that in this salt two iron(II) atoms are bound for every seven tridentate residues in the polymer molecule. Since the material is diamagnetic it seems probable that the immediate environment of each iron atom contains six bound nitrogen atoms (from two tridentate residues), and the solubility of the sulfate in water suggests that these are derived from successive residues in the same polymer chain and that there is no cross-linking.

Suspension of the finely ground pre-formed 1:1 polymer in an alcoholic solution of cobalt(II) chloride followed by boiling, leads to the taking up of one molecule of cobalt(II) chloride for each residue of XVIII, the polymer being converted into a brown solid. This was found to be paramagnetic (3.7 Bohr magnetons). Without further prolonged studies it is only possible to guess at its structure, but it could be that there are present chlorine bridges linking cobalt atoms in structures of the type shown in Fig. 3.

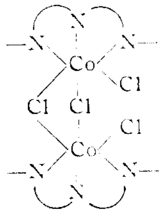

Fig. 3.

These preliminary studies with polymers are being continued.

Experimental

2-Aminomethylpyridine.—The base, best prepared by the method of Craig and Hixon,[3] was a colorless oil, b.p. 104° (20 mm.). It also was prepared as follows. 2-Picoline-N-oxide (4 g.) was added to a solution of *p*-toluenesulfonyl chloride (7 g.) in dry benzene (20 ml.). After 4 hours the benzene was removed *in vacuo* and the residue heated at 170° (oil-bath) for 1 hour. The residual thick dark oil was washed with ether, then treated with saturated aqueous sodium bicarbonate solution (20 ml.). Three extractions with ether (50 ml.) were then made and the combined extracts dried and the solvent removed. The remaining crude 2-chloromethylpyridine (3 g., picrate had m.p. 144°) was dissolved in dimethylformamide (20 ml.) and potassium phthalimide (5 g.) added. The stirred mixture was then heated at 100° for 6 hours. After cooling, aqueous potassium hydroxide solution (50 ml. of 10%) was added and two ether extractions (25 ml.) made. The combined ether extracts were washed with 5% potassium hydroxide solution, dried over solid potassium hydroxide and then the ether removed. After many recrystallizations from ethanol 2-**phthalimidomethylpyridine** (0.5 g.) was obtained in colorless plates, m.p. 125°.

Anal. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.6; H, 4.2; Found: C, 70.5; H, 4.4.

Hydrolysis of this compound to 2-aminomethylpyridine was effected by the method of Ing and Manske.

Bis-[2-(α-pyridylmethyleneaminomethyl)-pyridine]-iron-(II) Perchlorate Monohydrate (V).—Admixture of equimolecular proportions of freshly distilled pyridine-2-aldehyde and III caused immediate reaction and rise of temperature to about 60°. The condensation was completed by warming at 100° for 15 min. The yellow oily Schiff base IV could not be induced to crystallize. Addition of aqueous iron(II) sulfate (0.7 g. of the heptahydrate) to IV (1 g., 2 moles) led to formation of an intensely red solution from which saturated aqueous sodium perchlorate solution precipitated a red salt. Recrystallized from water this formed dark red plates which decomposed at 193°. The salt was diamagnetic.

Anal. Calcd. for $C_{24}H_{22}N_6FeCl_2O_8 \cdot H_2O$: C, 4.38; H, 3.7; Fe, 8.4; Found: C, 44.0; H, 4.0; Fe, 8.3.

Bis-[2-(α-pyridylmethyleneaminomethyl)-pyridine]-cobalt(II) Perchlorate Monohydrate (VI).—A solution of cobalt(II) chloride hexahydrate (0.7 g.) in water (10 ml.) was added to IV (1 g.). An immediate blue color developed and a small amount of solid separated. This was filtered off and saturated aqueous sodium perchlorate solution (5 ml.) added to the filtrate. A deep blue precipitate formed. It was collected, well washed with water and dried *in vacuo*. On exposure to air it gradually changed to a red gum.

Anal. Calcd. for $C_{24}H_{22}N_6CoCl_2O_8 \cdot H_2O$: C, 43.0; H, 3.6; Co, 8.8; Found: C, 43.1; H, 3.9; Co, 8.9.

This complex cobalt(II) salt had a magnetic moment of 4.2 Bohr magnetons at 23°.

2-Oximino-3-methyl-4-aza-5-α-pyridyl-Δ^3-pentene (VIII).—2-Aminomethylpyridine (5 g.) was added to a solution of

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(12) R. S. Nyholm, *Quart. Revs.*, **7**, [4] 377 (1953).

diacetylmonoxime (5 g.) in ethanol (20 ml.) and the mixture refluxed for 5 minutes. The product (3.5 g., 40%) crystallized on cooling, and was recrystallized from ethanol and thus obtained in colorless needles, m.p. 157°.

Anal. Calcd. for $C_{10}H_{13}N_3O$: C, 62.8; H, 6.8; Found: C, 62.6; H, 6.7.

Bis-(2-oximino-3-methyl-4-aza-5-α-pyridyl-3-pentene)-iron(II) Iodide Dihydrate (IX).—Iron(II) sulfate heptahydrate crystals (0.23 g.) were added to a stirred suspension of VIII (0.45 g.) in water (5 ml.). The solids soon dissolved to a deep red solution. Saturated aqueous potassium iodide solution (5 ml.) was then added. The complex iodide which crystallized was collected and recrystallized from an ethanol–ether mixture, being thus obtained as a diamagnetic micro-crystalline red solid which did not melt below 300°.

Anal. Calcd. for $C_{20}H_{26}N_6O_2FeI_2 \cdot 2H_2O$: C, 33.0; H, 4.1; Fe, 7.7. Found: C, 32.5; H, 4.2; Fe, 7.5.

Bis-(2-oximino-3-methyl-4-aza-5-α-pyridyl-Δ^3-pentene)-cobalt(III) Iodide (X).—A solution of cobalt(II) chloride hexahydrate (0.2 g.) in water (5 ml.) was added to a solution of VIII (0.3 g.) in ethanol (10 ml.). A solution of cerium(IV) ammonium nitrate (0.2 g.) in nitric acid (10 ml. of *N*) was then added to the brown solution, followed eventually by saturated aqueous potassium iodide solution (3 ml.). The diamagnetic complex cobalt(III) iodide crystallized and was collected and dried *in vacuo*. Heating of the reaction mixture during the preparation led to liberation of diacetyl.

Anal. Calcd. for $C_{20}H_{26}N_6O_2CoI_3$: C, 29.2; H, 3.2; Co, 7.2. Found: C, 28.7; H, 3.1; Co, 7.0.

Bis-[8-(α-pyridylmethyleneamino)-quinoline]-cobalt-(III) Perchlorate.—8-(α-Pyridylmethyleneamino)-quinoline[2] (XI) was prepared precisely as follows. Freshly redistilled pyridine-2-aldehyde (5.35 g.) was added to a solution of recrystallized 8-aminoquinoline (7 g.) in ethanol (6 ml.) and the mixture warmed at 100° for 1 minute. It was then cooled and dry ether (15 ml.) added. Vigorous scratching induced crystallization of the Schiff base in yellow needles which were collected and washed with dry ether, m.p. 139–140°. Recrystallization from ethanol, as previously reported, leads to some decomposition.

Anal. Calcd. for $C_{15}H_{11}N_3$: C, 77.2; H, 4.8; Found: C, 76.2; H, 5.1.

A solution of cobalt(II) acetate tetrahydrate (0.55 g.) in methanol (15 ml.) was added to a solution of XI (0.95 g.) in ethanol (5 ml.). Hydrogen peroxide solution (5 ml. of 3%) was then added and the solution evaporated to a volume of approximately 5 ml. Addition of saturated aqueous sodium perchlorate solution (5 ml.) caused precipitation of the diamagnetic brown cobalt(III) perchlorate which was collected, washed and dried *in vacuo*. It decomposed above 265°.

Anal. Calcd. for $C_{30}H_{22}N_6CoCl_3O_{12}$: C, 43.7; H, 2.7; Co, 7.2. Found: C, 43.5; H, 2.8; Co, 7.2.

Bis-[8-(α-pyridylmethyleneamino)-quinaldine]-iron(II) Iodide Dihydrate.—Solutions of 8-aminoquinaldine (3.06 g.) in ethanol (5 ml.) and pyridine-2-aldehyde (2.14 g.) in ethanol (5 ml.) were mixed and gently refluxed for 5 min. After cooling, a solution of iron(II) sulfate heptahydrate (2.4 g.) in water (10 ml.) was added. An intense green color developed. Saturated aqueous potassium iodide solution (5 ml.) was added. The complex iron(II) salt which separated was collected and recrystallized from aqueous ethanol. It was obtained in black prisms which decomposed above 250°.

Anal. Calcd. for $C_{32}H_{26}N_6FeI_2 \cdot 2H_2O$: C, 46.7; H, 3.7; Fe, 6.8. Found: C, 46.3; H, 3.4; Fe, 6.6.

Bis-(8-quinolylmethylene-α-aminomethylpyridine)-iron-(II) Iodide Trihydrate (XVII).—Admixture of hot solutions of quinoline-8-aldehyde[9] (0.8 g.) in ethanol (3 ml.) and 2-aminomethylpyridine (0.55 g.) in ethanol (2 ml.) gave an orange solution. Addition of a solution of iron(II) sulfate heptahydrate (0.6 g.) in water (5 ml.) gave an intense green solution from which saturated aqueous potassium iodide solution precipitated the dimagnetic complex iron(II) salt.

Anal. Calcd. for $C_{32}H_{26}N_6FeI_2 \cdot 3H_2O$: C, 44.6; H, 3.7; Fe, 6.5. Found: C, 44.5; H, 3.5; Fe, 6.5.

2,6-Pyridylene-bis-methyleneaniline (XIX, R = C_6H_5).—Freshly distilled aniline (8 g.) was added to a solution of pyridine-2,6-dialdehyde (5.8 g.) in ethanol (30 ml.) and the solution boiled under reflux for 30 minutes. On cooling, the Schiff base crystallized. Recrystallized from ethanol it formed colorless needles, m.p. 98°.

Anal. Calcd. for $C_{19}H_{15}N_3$: C, 80.0; H, 5.3; Found: C, 79.6; H, 5.5.

Bis-[2,6-pyridylene-bis-methyleneaniline]-iron(II) Perchlorate Dihydrate.—A solution of iron(II) sulfate heptahydrate (1 g.) in water (10 ml.) was added to a solution of XIX (R = C_6H_5) (2 g.) in ethanol (10 ml.). An intensely red solution resulted. Ethanol was removed by evaporation from a water-bath and perchloric acid solution (5 ml. of 5%) added. The complex iron(II) perchlorate which precipitated was collected and recrystallized from ethanol and obtained in red plates which decompose violently at 215°.

Anal. Calcd. for $C_{38}H_{30}N_6FeCl_2O_8 \cdot 2H_2O$: C, 52.4; H, 3.9; Fe, 6.5; Found: C, 52.7; H, 4.0; Fe, 6.3.

Boiling of aqueous solutions of this salt caused some decomposition.

2,6-Pyridylene-bis-(methylenebenzylamine) (XIX, R = $-CH_2C_6H_5$).—A solution of benzylamine (4.36 g.) and pyridine-2,6-dialdehyde (2.7 g.) in ethanol (20 ml.) was heated under reflux for 40 minutes. After concentration and cooling a colorless solid (6.2 g.) was deposited. Recrystallized from ethanol it formed colorless tablets, m.p. 80°.

Anal. Calcd. for $C_{21}H_{19}N_3$: C, 80.5; H, 6.1. Found: C, 80.3; H, 6.3.

Bis-(2,6-pyridylene-bis-methylenebenzylamine)-iron(II) Bromide Bi-sesquihydrate (XXI).—Saturated aqueous potassium bromide solution (10 ml.) was added to the intensely red solution obtained by mixing solutions of XIX (R = $CH_2C_6H_5$) (1.25 g.) in ethanol (10 ml.) and iron(II) sulfate heptahydrate (0.55 g.) in water (10 ml.). The precipitate was collected and recrystallized from water. Dark red diamagnetic needles, m.p. 265° (with previous softening at 165°), were thus obtained.

Anal. Calcd. for $C_{42}H_{38}N_6FeBr_2 \cdot 2.5H_2O$: C, 56.9; H, 4.9; Fe, 6.3. Found: C, 56.7; H, 4.8; Fe, 6.2.

Bis-(2,5-pyridylene-bis-methylenebenzylamine)-cobalt(II) Iodide.—Addition of a solution of cobalt(II) chloride tetrahydrate (0.7 g.) in water (10 ml.) to a solution of XIX (R = $CH_2C_6H_5$) (2 g.) in ethanol (10 ml.) caused a yellow solid to separate from the solution. It redissolved on addition of water (10 ml.). Addition of saturated aqueous potassium iodide solution then caused the complex cobalt(II) iodide to separate. It was collected and recrystallized from ethanol, and was thus obtained in dark brown needles, m.p. 251°.

Anal. Calcd. for $C_{42}H_{38}N_6CoI_2$: C, 53.7; H, 4.0; Co, 6.3. Found: C, 53.6; H, 4.0; Co, 6.1.

The molar conductance of this salt in 10 *M* aqueous solution was 255 ohms^{-1}. The salt was paramagnetic with a moment of 3.8 Bohr magnetons.

Bis-(2,6-pyridylene-bis-methylenebenzylamine)-cobalt-(III) Iodide Dihydrate.—A solution of cobalt(II) chloride hexahydrate (0.6 g.) in water (20 ml.) was added to a solution of XIX (R = $CH_2C_6H_5$) (1.5 g.) in ethanol (10 ml.). Chlorine was then bubbled through the solution for 10 minutes, the intense red-brown color changing to brown. Eventually, saturated aqueous potassium iodide solution (10 ml.) was added. The solid salt which separated was collected, washed well with water and ethanol and dried *in vacuo*. It was a micro-crystalline, relatively insoluble diamagnetic solid, m.p. 212°.

Anal. Calcd. for $C_{42}H_{38}N_6CoI_3 \cdot 2H_2O$: C, 45.7; H, 3.8; Co, 5.4. Found: C, 45.8; H, 3.7; Co, 5.1.

Bis-(2,6-pyridylene-bis-methylenebenzylamine)-copper-(II) Perchlorate.—A solution of the base XIX (R = CH_2-C_6H_5) (0.63 g.) in ethanol (10 ml.) was added to a solution of copper(II) chloride dihydrate (0.17 g.) in ethanol (10 ml.). A bright green solid separated at once. On warming it dissolved and the color changed to gray-green. Perchloric acid (5 ml. of 5%) was added. The complex copper(II) perchlorate crystallized in grey-green plates which were collected, washed and dried *in vacuo*.

Anal. Calcd. for $C_{42}H_{38}N_6CuCl_2O_8$: C, 86.7; H, 4.3; N, 9.5; Cu, 7.2. Found: C, 56.3; H, 4.4; N, 9.3; Cu, 7.0.

Pyridine-2,6-dialdoxime was obtained in colorless needles, m.p. 216° (from ethanol).

Anal. Calcd. for $C_7H_7N_3O_2$: C, 50.9; H, 4.2. Found: C, 50.9; H, 4.5.

Addition of an aqueous solution of iron(II) sulfate heptahydrate (0.59 g.) to a solution of this pyridine-2,6-dialdoxime (0.7 g.) in ethanol (10 ml.) caused development of an intense red color. Addition of sodium acetate solution caused a deep red solid to crystallize. It was recrystallized several times from hot water.

Anal. Calcd. for $C_{14}H_{11}N_6O_4FeNa$: C, 41.4; H, 2.7; Fe, 13.8; Found: C, 41.5; H, 3.2; Fe 13.1.

The equivalent conductivity at 23° was 124 ohms^{-1} indicating the salt to be a binary electrolyte.

2,6-Bis-(aminomethyl)-pyridine.—Glacial acetic acid (500 ml.) and zinc dust (400 g.) were added over a period of 2 hours to a stirred solution of pyridine-2,6-dialdoxime (25 g.) in ethanol (100 ml.). After standing overnight the solids were separated by filtration and well washed with ethanol and these washings added to the filtrate which was then evaporated almost to dryness *in vacuo*. A considerable excess of strong potassium hydroxide solution was then added and the oil which separated was taken up in ether (4 lots of 500 ml.). After removal of the ether the residual oil was distilled *in vacuo* and obtained colorless, b.p. 112° (1.2 mm.), (13 g., 63%). It solidified on standing but was difficult to handle because of its tendency to carbonate.

Anal. Calcd. for $C_7H_{11}N_3$: C, 61.3; H, 8.0; Found: C, 60.0; H, 7.9.

For analysis it was much better to prepare derivatives such as 2,6-bis-(piperonylideneaminomethyl)-pyridine colorless needles, from pyridine–ethyl acetate, m.p. 179°.

Anal. Calcd. for $C_{23}H_{19}N_3O_4$: C, 68.8; H, 4.8; Found: C, 68.7; H, 4.9.

2,6-Bis-(salicylideneaminomethyl)-pyridine, almost colorless needles (from ethanol), had m.p. 120°.

Anal. Calcd. for $C_{21}H_{19}H_3O_2$: C, 73.1; H, 5.5; Found: C, 72.9; H, 5.5.

Bis-[2,6-di-(aminomethyl)-pyridine] iron(II) Iodide.—The base XXVI (0.9 g.) was added to a solution of iron(II) sulfate heptahydrate (0.7 g.) in water (10 ml.). After filtration the resulting deep green solution was treated with saturated aqueous potassium iodide solution (5 ml.). The green complex iodide which separated was collected, washed and dried *in vacuo*. It did not melt below 300°.

Anal. Calcd. for $C_{14}H_{22}N_6FeI_2$; C, 28.8; H, 3.8; Fe, 9.6. Found: C, 28.6; H, 3.8; Fe, 9.6.

Allowing aqueous solutions of this salt to stand in air leads to decomposition and iron(III) hydroxide is deposited. The salt has a magnetic moment of 5.24 Bohr magnetons (23°).

Bis-(2,6-(diaminomethyl)-pyridine)-nickel(II) Bromide. (XXVI).—(0.6 g.) was added to a solution of nickel(II) sulfate sexahydrate (0.5 g.) in water (10 ml.). Addition of saturated aqueous potassium bromide solution (5 ml.) to the resulting deep mauve solution caused the complex nickel(II) bromide to separate. It crystallized from hot water in mauve needles which did not melt below 300°.

Anal. Calcd. for $C_{14}H_{22}N_6NiBr_2$: C, 34.1; H, 4.5; Ni, 12.0; Found: C, 33.8; H, 4.6; Ni, 11.7.

Condensation of Pyridine-2,6-dialdehyde with 1,6-Diaminohexane.—The following experiment was typical. A hot solution of pyridine-2,6-dialdehyde (3.5 g., 1 mole) in ethanol (20 ml.) was added to a hot solution of 1,6-diaminohexane (3 g., 1 mole) in ethanol (20 ml.) and the mixture boiled. Within 20 sec. a white solid had separated from the hot solution. It was collected and washed with hot ethanol. It was insoluble in most solvents but did dissolve on warming in dimethylformamide. However, this solution soon redeposited solid, probably because of molecular weight increase due to further condensation. The solid did not melt but decomposed when very strongly heated.

Anal. Calcd. for $(C_{13}H_{17}N_3)_n$: C, 72.6; H, 7.9; Found: C, 72.0; H, 7.9.

Addition of this dried, finely ground white polymer (0.65 g.) to a boiling solution of iron(II) sulfate heptahydrate (1.8 g., excess) in water (25 ml.) caused its transformation to a deep red powder. This was collected and well washed with water. It was insoluble in any of the common solvents.

Anal. Calcd. for $(C_{13}H_{17}N_3)_2 \cdot FeSO_4 \cdot 6H_2O$; C, 45.2; H, 6.7; Fe, 8.1. Found: C, 45.6; H, 6.5; Fe, 8.1.

This solid was found to be ferromagnetic with a molar susceptibility at 24° of 155,000 × 10^{-6} c.g.s. unit.

The finely ground polymer (0.5 g.) was suspended in ethanol (15 ml.) and a solution of cobalt(II) chloride sexahydrate in ethanol (50 ml.) added. The liquid was then gently refluxed. The white polymer gradually changed in color to deep brown but the solution was still a blue color after one hour. The solid polymer was again ground and reheated with the solution which eventually became colorless. The solid was then collected, well washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $C_{13}H_{17}N_3CoCl_2$; C, 45.2; H, 5.0; Co, 14.2. Found: C, 44.9; H, 5.4; Co, 13.8.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY AT HARVARD UNIVERSITY]

Vinyl Derivatives of the Metals. IV. The Preparation of Vinylgermanium Compounds by the Grignard Method[1]

BY DIETMAR SEYFERTH

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The addition of germanium(IV) chloride to vinylmagnesium bromide in tetrahydrofuran solution results in moderate yields of hexavinyldigermane in addition to tetravinylgermane. Diethyldivinylgermane and ethyltrivinylgermane have also been prepared. Hexavinyldigermane is cleaved by bromine and by iodine to give trivinylgermanium bromide and iodide, respectively.

The use of the vinyl Grignard reagent in tetrahydrofuran solution for the preparation of vinyltin compounds[2] and vinylsilanes[3] has been reported recently. In the examples where tin(IV) chloride and tetrachlorosilane were vinylated only tetravinyltin and tetravinylsilane, respectively, were isolated.

We have now investigated the reaction of vinylmagnesium bromide[4] in tetrahydrofuran solution

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