e.g., $K_2Hg(SCN)_4$ and $K_2Pt(SCN)_6$,[17] broadening of the absorption band associated with the carbon–nitrogen stretching vibration makes exact location of the frequency difficult. The carbon–sulfur frequencies, however, remain sharp and are lowered to 716 and 694 cm.$^{-1}$, respectively, as compared to the values 780 to 810 cm.$^{-1}$ observed for those compounds with a metal to nitrogen bond.

Jeffery[18] reports X-ray evidence indicating a mercury to sulfur single bond in the compound $CoHg(SCN)_4$ and states that the cobalt is so located as to be within bonding distance of the nitrogen. The infrared spectrum of this compound shows a carbon–nitrogen stretching frequency at 2137 cm.$^{-1}$ and a carbon–sulfur stretching frequency at 793 cm.$^{-1}$. In the analogous compounds in which cobalt(II) is replaced by other divalent metals, these vibrations occur at approximately the same frequencies. The large difference between the carbon–sulfur stretching frequency in these compounds and that observed in $K_2Hg(SCN)_4$ and the close agreement with the frequency observed in the thiocyanatocobalt ammines may well imply that a structure comparable to that proposed for $[Co(NH_3)_5NCS]Cl_2$ involving a double bond between the metal and the ligand exists in these polymeric materials. Further, the bridging by thiocyanate exhibited in these compounds should be quite analogous to that proposed by Werner for the silver adducts of the thiocyanatocobalt ammines.

The Structure of the Silver(I) Adducts.—1. The adduct of $(Co(NH_3)_5NCS]^{++}$, formed on the addition of a large excess of silver nitrate or silver perchlorate, does not analyze to be the 1:1 adduct proposed by Werner. Furthermore, the C–N and the C–S stretching frequencies are almost identical with those observed in the thiocyanatocobalt ammine ion itself. The potentiometric titration of thiocyanatopentamminecobalt(III) perchlorate with silver perchlorate gave no evidence for the formation of a stable compound in solution. Thus, no evidence for the formation of a silver—thiocyanatopentammine adduct was observed.

2. The adducts of both the *cis*- and *trans*-$[Co\ en_2(NCS)_2]^+$ are apparently real compounds involving a true bridging by thiocyanate. In both cases, the analysis of these adducts indicated a 1:1 compound, potentiometric titrations gave definite evidence for complex formation in solution, and the C–N stretching frequency in the *cis*-adduct is 27 cm.$^{-1}$ higher than that observed in the simple ion. This same shift in frequency to higher wave numbers is observed when the simple $K_2Hg(SCN)_4$ spectrum is compared with the spectra of bridged $MHg(SCN)_4$ compounds and is reported by Chatt and Duncanson[19] to be observed also in platinum compounds containing a thiocyanato bridge.

Assignment of N–H Vibrations in the Spectra of Bis-ethylenediaminecobalt Complexes.—Since the *cis*- and *trans*-bisthiocyanato-bisethylenediamine cobalt(III) thiocyanates are extremely resistant to aquation, these compounds were boiled with deuterium oxide and partial replacement of the labile hydrogens on the coördinated nitrogens obtained. On comparison of the spectra of the deuterated and undeuterated complexes, it appeared that the frequencies in the regions 3000–3300 cm.$^{-1}$, 1560–1600 cm.$^{-1}$, and 1120–1150 cm.$^{-1}$ could be attributed to various modes of N–H vibrations.

Further, it was observed that only one N–H vibration frequency appeared in the 1120–1150 cm.$^{-1}$ region in the *trans*-isomer but that two appeared in the *cis*-isomer. The differentiation between the *cis*- and *trans*-isomers also was observed in other bis-acido bis-ethylenediaminecobalt(III) complexes (Table III).

Acknowledgments.—The authors wish to express their appreciation to Dr. L. H. Jones of the Los Alamos Scientific Laboratories for instructing one of us (MMC) in the application of infrared spectroscopy to the solution of problems in inorganic chemistry and for helpful discussions; to Mr. James Brader for his work in obtaining the spectra reported herein; and to the National Science Foundation and the Socony-Mobil Oil Company for financial support.

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[17] S. B. Hendricks and H. E. Merwin, *Am. J. Sci.*, **15**, 487 (1928).

[18] J. W. Jeffery, *Nature*, **159**, 610 (1947).

[19] J. Chatt and L. A. Duncanson, *ibid.*, **178**, 997 (1956).

URBANA, ILLINOIS

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

Tridentate Chelate Compounds. II[1]

BY HAROLD A. GOODWIN[2] AND FRANCIS LIONS

RECEIVED MAY 12, 1959

A series of Schiff's bases has been prepared by condensing primary amines derived from pyridine or a benzpyridine with suitable aldehydes derived from pyridine or a benzpyridine. Their molecules contain three donor nitrogen atoms spaced similarly to the nitrogen atoms in the molecule of 2,6-bis-(α-pyridyl)-pyridine ("terpyridine"). Each has been shown to function as a tridentate with copper salts but it has been found that substituents adjacent to the donor nitrogen atom sequence lower the capacity of the organic molecule to coördinate with iron salts. 2,3,5,6-Tetrakis-(α-pyridyl)-pyrazine and 2,3,5,6-tetrakis-(6′-methyl-2′-pyridyl)-pyrazine with three-nitrogen sequences similar to that in terpyridine have also been synthesized. The former is an excellent tridentate. The coördinating capacity of the latter, especially with iron salts, appears to have been markedly lowered by the substituent methyl groups adjacent to the terminal nitrogen atoms of the three donor nitrogen atom sequence.

It was reported in Part I of this series of papers that 8-(α-pyridylmethyleneamino)-2-methylquinoline (Ia) was capable of forming coördination compounds with salts of metals such as iron (iron(II))

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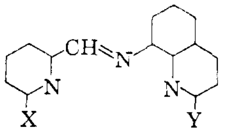
[1] For Part I of this Series see F. Lions and K. V. Martin, THIS JOURNAL, **79**, 2733 (1957).

[2] Commonwealth Research Student, University of Sydney.



Ia, X = H, Y = CH_3
Ib, X = H, Y = H

in a manner similar to the unmethylated compound Ib,[3] two molecules of the organic base coördinating as tridentates with each iron(II) ion. The intense green colors of these complex iron(II) compounds from Ia and Ib were indistinguishable and, at least, qualitatively, it did not appear as though the methyl group in Ia greatly interferes with its capacity for coördination.

There have been many studies of the effects of substituent groups adjacent to donor atoms in bidentate molecules such as those of the 2,2′-bipyridines or the 1,10-phenanthrolines on their coördinating power.[4]

In general, it has been shown that substitution of a single group, such as methyl, in a position adjacent to a donor nitrogen atom (a 6- or 6′-position in 2,2′-bipyridine, or a 2- or 9-position in 1,10-phenanthroline) yields a compound still capable of coördination as a bidentate with iron(II) salts, but the complex salts so obtained have lower color intensity and stability than those derived from the corresponding unsubstituted parent compounds. Substitution in both 6- and 6′-positions in 2,2′-bipyridine or in both 2- and 9-positions in 1,10-phenanthroline completely prevents coördination with iron(II) salts although complex salts can be prepared with copper(II) compounds.

It appeared of interest to study, even if only briefly, some Schiff's bases potentially capable of functioning as tridentates but having more or less bulky substituent groups in positions adjacent to one or other of the terminal nitrogen donor atoms. The actual compounds employed are listed in Table I and were obtained by condensation of an aldehyde such as pyridine-2-aldehyde, 6-methylpyridine-2-aldehyde or quinoline-2-aldehyde with a primary amine such as 2-aminomethylpyridine, 6-methyl-2-aminomethylpyridine, 2-aminomethylquinoline, 8-aminoquinoline or 2-methyl-8-aminoquinoline. These Schiff's bases were prepared simply by interaction of stoichiometric amounts of reactants, with some external heating if necessary, and were then caused to react in the crude condition with the metal salt being studied.

The Schiff's bases numbered II–VI in Table I are distinguished by their possession of *one* blocking group (either a methyl group or the methine $\mathrm{CH}\begin{smallmatrix}\diagup\\ -\\ \diagdown\end{smallmatrix}$ corner of a fused benzene ring) adjacent to one of the terminal nitrogen atoms in the three-donor-nitrogen-atom chain. Each of these bases was found to coördinate with iron(II) salts to give intensely colored complex iron(II) salts of which the iodides and perchlorates (except those from V) were usually capable of ready isolation in the pure state.

The iron(II) complex salts derived from V were quite intensely green but decomposed even in cold water or alcohol. Although the water-insoluble iodide could be isolated it was not obtained analytically pure. The instability of these salts is probably not due entirely to steric effects, but depends also on the chemical make-up of the Schiff's base.

Qualitatively, the intensities of the colors of solutions of complex iron(II) salts derived from II, III, IV, V and VI suggest that one "blocking group" adjacent to a donor nitrogen atom does not greatly affect the stability of the derived iron(II) complex salts when compared with that of, say, the unsubstituted tridentate 8-(α-pyridylmethyleneamino)-quinoline (Ib). All these complex iron(II) salts were diamagnetic, indicating strong covalent lower orbital $3d^24s4p^3$ bonding.

The tridentate Schiff's bases VII, VIII, IX, and X, when added to solutions of iron(II) salts, apparently failed to react, there being either no color change or, at most, the development of a faint orange-red color. It did not prove possible to isolate any complex iron(II) salts from these.

Complex copper(II) salts containing each of the tridentates II–X could be prepared readily by adding an ethanolic solution of copper(II) chloride dihydrate slowly to an ethanolic solution of the Schiff's base. A yellow-brown complex salt of the type [Cu(tridentate)Cl]Cl crystallized out in each experiment. These complex salts were more stable in solution than the corresponding iron(II) complex salts and could be readily converted to the corresponding perchlorates, [Cu(tridentate)Cl]ClO_4 with the help of sodium perchlorate.

Japp and Wilson[5] showed that the heating together of benzoin and ammonium acetate led to formation of 2,3,5,6-tetraphenylpyrazine. Shortly afterwards Leuckart[6] reported the preparation of the same base by the heating together of benzoin and ammonium formate. We have applied these reactions to 2,2′-pyridoin and 6,6′-dimethyl-2,2′-pyridoin and have isolated readily the bases 2,3,5,6-tetrakis-(α-pyridyl)-pyrazine (XIa) and 2,3,5,6-tetrakis-(6′-methyl-2′-pyridyl)-pyrazine (XIb) in yields of up to 45%.

The molecules of these substances, as formulated, would appear, at first sight, to be symmetrical about the axis shown as a dotted line in the diagram. The six nitrogen atoms are thus divided into two groups of three, and each of these three-nitrogen-atom sequences would appear to be constituted analogously to that present in the molecule of 2,6-bis-(α-pyridyl)-pyridine (terpyridine, XII). If this were true molecules of XIa would appear to be capable of presenting their six nitrogen atoms in two planar tridentate groups of three as donor atoms to suitable acceptor metal atoms. Coördination, then, of XIa with the salt of a suitable six-covalent metal (such as iron(II)) should produce a rather curious type of elongated condensation polymer in which all the tetrakis-(α-pyridyl)-pyrazine residues in any one cation would

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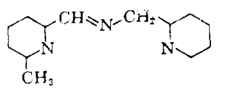
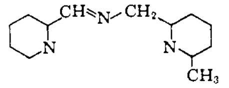
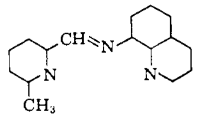
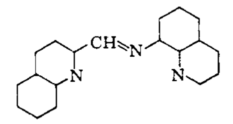
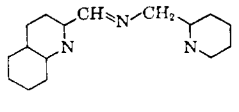
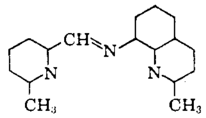
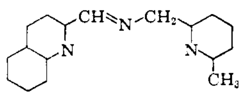
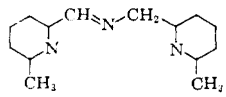
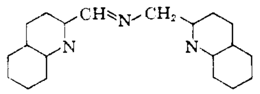
[3] *Cf.* F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, This Journal, **75**, 3834 (1953).

[4] *Cf. e.g.*, W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Revs.*, **54**, 991 (1954); F. H. Case, *et al.*, *J. Org. Chem.*, **19**, 31, 919 (1954); **20**, 1330 (1955); **21**, 1069 (1956); **22**, 390 (1957).

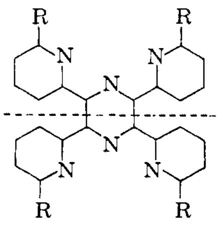
[5] F. R. Japp and W. H. Wilson, *J. Chem. Soc.*, **49**, 825 (1886).

[6] H. Leuckart, *J. prakt. Chem.*, [2] **41**, 333 (1890).

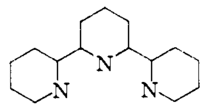
TABLE I

No.	Formula	Name	Derived from
II		2-(6'-Methyl-α-pyridylmethyleneaminomethyl)-pyridine	6-Methylpyridine-α-aldehyde and 2-aminomethylpyridine
III		6-Methyl-2-(α-pyridylmethyleneaminomethyl)-pyridine	Pyridine-2-aldehyde and 6-methyl-2-aminomethylpyridine
IV		8-(6'-Methyl-α-pyridylmethyleneamino)-quinoline	6-Methylpyridine-2-aldehyde and 8-aminoquinoline
V		8-(2'-Quinolylmethyleneamino)-quinoline	Quinoline-2-aldehyde and 8-aminoquinoline
VI		2-(2'-Quinolylmethyleneaminomethyl)-pyridine	Quinoline-2-aldehyde and 2-aminomethylpyridine
VII		2-Methyl-8-(6'-methyl-α-pyridylmethyleneamino)-quinoline	6-Methylpyridine-2-aldehyde and 8-aminoquinaldine
VIII		6-Methyl-2-(2'-quinolylmethyleneaminomethyl)-pyridine	Quinoline-2-aldehyde and 6-methyl-2-aminomethylpyridine
IX		6-Methyl-2-(6'-methyl-α-pyridylmethyleneaminomethyl)-pyridine	6-Methylpyridine-2-aldehyde and 6-methyl-2-aminomethylpyridine
X		2-(2'-Quinolylmethyleneaminomethyl)-quinoline	Quinoline-2-aldehyde and 2-aminomethylquinoline

be coaxial but alternately in planes at right angles to each other (see Fig. 1).



XIa, R = H
XIb, R = CH_3



XII

XIa was shown experimentally to coördinate with iron(II) salts to give red-violet coördination compounds (*cf.* terpyridine) the bivalent cations of which each contained two molecules of the organic base and one iron atom. The base XIa thus functions only as a tridentate and not as a bis-tridentate.

The explanation of this result would appear to be as follows: When the nitrogen atoms of the two pyridine rings attached to the pyrazine ring in the 2- and the 6-positions, together with the nitrogen atom in the 1-position of the pyrazine ring, become the three donor atoms of a tridentate group united by coördination covalences to a metal atom, these two pyridine rings become coplanar with the pyrazine ring. Such an arrangement, as a model quickly will show, makes such spatial demands that it is impossible for the pyridine rings attached to

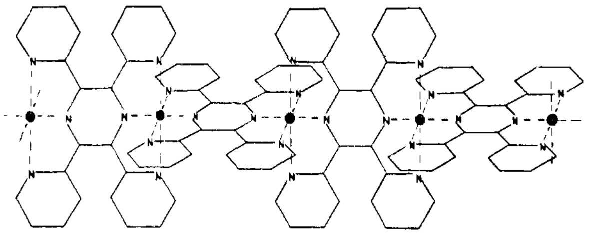


Fig. 1.

the 3- and 5-positions of the pyrazine ring to be simultaneously coplanar with it and thus to present their nitrogen atoms in such a way as to have them function as donors to the same metal atom. (Coplanarity is here essential for tridentate function.) Thus, the nitrogen atoms of these two pyridine rings and the nitrogen atom in the 4-position

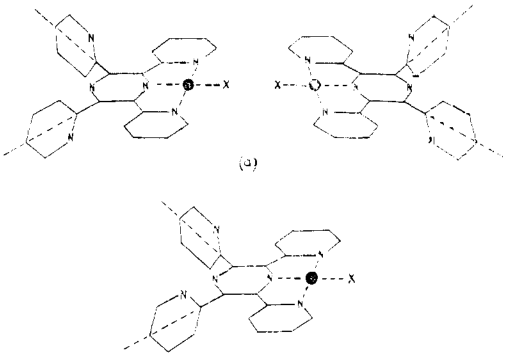
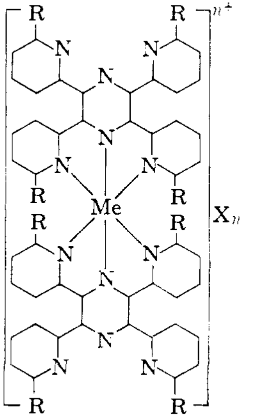


Fig. 2.

of the pyrazine ring cannot coördinate simultaneously with a second metal atom when the first-mentioned three nitrogen atoms in the molecule are coördinately bound to a metal atom in a tridentate arrangement.



XIIIa, Me = Fe, R = H, $n = 2$
XIIIb, Me = Ni, R = H, $n = 2$
XIIIc, Me = Co, R = H, $n = 3$
XIIId, Me = Ru, R = H, $n = 2$

A similar steric effect was described by Case[7] and later confirmed by Irving and Hampton[8] in the failure of 1,1′-di-isoquinolyl to coördinate as a bipyridyl with iron(II) salts.

It should also be remembered[9] that pyrazine fails to form bis-quaternary ammonium salts, quaternization of one nitrogen atom apparently rendering it impossible for the second nitrogen atom to donate a lone pair of electrons to a second positively charged alkyl radical. Coördination bonding of a pyrazine nitrogen atom to a metal atom would similarly markedly reduce any tendency of the second nitrogen atom of the pyrazine ring to indulge in coördination bonding.

The restriction of rotation of the pyridine rings attached to the pyrazine ring in the 3- and 5-positions about the respective axes of the attaching bonds, if great enough, could render possible the existence of stereoisomeric complex salts. Thus, when a molecule of Ia became attached as a tridentate to a four-covalent metal atom with planar disposition of the covalences this metal atom would lie in the plane containing the pyrazine ring, the pyridine rings in the 2- and 6-positions, and the axes of attachment of the other two pyridine rings (Fig. 2).

The nitrogen atoms of these two-extra-planar pyridine rings could be on the same side of this plane of coördination or on opposite sides. The former arrangement would possess a plane of symmetry, the latter a diad axis of symmetry only. Hence, there could be two enantiomorphous configurations corresponding to this latter arrangement. It should then be possible to prepare salts corresponding to these *meso-* and *dl-* configurations and the latter of these should be resolvable.

The stereochemistry of the complexes theoretically obtainable by coördination of salts of an octahedrally disposed six-covalent metal with two molecular proportions of Ia would be quite complex, as many stereochemical arrangements are possible. It would be out of place to discuss them exhaustively in this paper because so far no such stereoisomerism has been observed experimentally. However, it is worthwhile pointing out that one of the possible arrangements would possess the rarely designed fourfold alternating axis of symmetry. If one imagined that the complex ion formed by coordination of, say, an iron(II) atom with two molecules of Ia were rotated about the axis along which all four nitrogen atoms of the two pyrazine nuclei and the iron atom were disposed, and that the pyridine rings attached to the 3,5,3′- and 5′-positions of these nuclei were greatly restricted from free rotation about the bond attaching them to the pyrazine nuclei, then these pyridine rings would perforce move during the rotation in an edgewise fashion. The nitrogen atom of any one such pyridine ring would thus be on a "leading" edge or a "trailing" edge, according to the direction of rotation. If it so happened that all four nitrogen atoms of these pyridine rings were simultaneously on "leading" edges (or, alternatively, all on "trailing" edges), the arrangement of the whole ion would possess a fourfold alternating axis of symmetry.

As stated above, we have been unable to detect isomerism due to such steric effects. It is well known that recemization of stereoisomers whose existence depends on restricted rotation is much easier in the dipyridyl and phenylpyridyl series than in the diphenyl series. Partial rotation of a pyridine ring attached to a pyrazine ring in the 3- (or 5-) position should be relatively easy if it is the nitrogen corner of the ring (which does not carry a protruding hydrogen atom) which slips past the projecting methine corner of the adjacent pyridine nucleus in the 2- (or the 6-) position. Hence, while the "obstacle" effect is sufficiently great in Ia to prevent both ends of the molecule simultaneously behaving as tridentate groups, it is probably not great enough to enable optically stable stereoisomeric coördination compounds to be prepared from it.

It should be noted, first, that there is here an excellent suggestion for the successful design and preparation of coördination complexes containing alternating axes of symmetry and, second, that it should be possible to prepare the compound repre-

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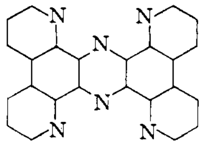
(7) F. H. Case, *J. Org. Chem.*, **17**, 471 (1952).

(8) H. Irving and A. Hampton, *J. Chem. Soc.*, 430 (1955).

(9) *Cf. e.g.*, R. C. Elderfield, "Heterocyclic Compounds," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 400.

sented by XIV whose molecules should be planar, and perhaps capable of behaving as bis-tridentates or bidentate-tridentates, and consequently of providing elongation polymer cations of the Fig. 1 type with metal ions of *suitable size.*

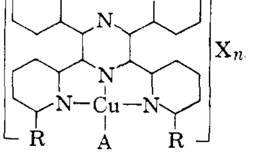


XIV

The coördination compounds derived from XIa are very similar to those derived from terpyridine, described by Morgan and Burstall.[10] The iron(II) salts have been mentioned. When added to an aqueous solution of iron(II) sulfate the base XIa gradually dissolves to an intensely red-violet solution. From this the sparingly soluble complex iron(II) perchlorate or iodide readily can be prepared. The iodide is diamagnetic ($3d^24s4p^3$ bonds). Solutions of it do not appear to decompose even on long keeping. Reaction of XIa with nickel(II) chloride in ethanol gives the yellow-brown complex nickel(II) chloride (XIIIb) and the sparingly soluble perchlorate is isolated readily. These complex salts are paramagnetic, with a magnetic moment of 3.1 B.M.

Addition of XIa to aqueous cobalt(II) chloride solution gives, ultimately, a deep brown solution and this brightens to a deep orange-red on oxidation with chlorine. From the solution sodium perchlorate causes the precipitation of the light brown diamagnetic complex cobalt(II) perchlorate(XIIIc). The complex ruthenium(II) salts (XIIId) are also prepared readily from potassium pentachlorohydroxyruthenate(IV), and are similar to the bis-terpyridine ruthenium(II) salts.[11] The perchlorate (XIIId, X = ClO_4) was a deep red-brown crystalline salt.

With copper(II) salts it was found that only one molecule of XIa was taken up by each copper(II) ion. Reaction of the base in aqueous solution with copper(II) salts gives bright green solutions from which sodium perchlorate precipitates fine green needles of aquo-tetrakis-(α-pyridyl)-pyrazine-copper(II) perchlorate trihydrate (XVa). Interaction of XIa and copper(II) chloride in dimethylformamide solution gives brown chlorotetrakis-α-pyridylpyrazine-copper(II) chloride (XVb) which dissolves readily in water giving a solution from which the corresponding perchlorate(XVc) can be precipitated.



XVa, A = H_2O, R = H, X = ClO_4, $n = 2$
XVb, A = Cl, R = H, X = Cl, $n = 1$
XVc, A = Cl, R = H, X = ClO_4, $n = 1$

The base XIb possesses substituent methyl groups in positions adjacent to the terminal nitrogen atoms of a tridentate three-donor nitrogen-atom sequence. From the experience recorded earlier for "blocked" Schiff's bases it was not anticipated that XIb would coördinate with iron(II) as easily as the unmethylated base XIa. Experiment showed that XIb forms well-defined, highly colored complex salts when reacting with iron(II) chloride, cobalt(II) chloride, nickel(II) chloride and copper(II) chloride in alcoholic solution. Each coördination compound conformed to the formula $[M(base)Cl_2]$. Each of these complex chlorides had negligible conductivity in nitrobenzene solution which would seem to preclude their formulation as $[M(base)_2][MCl_4]$. The possibility that they might be formulated as coördination polymers XVI in which each molecule of XIb functions as a bis-bidentate would seem to be precluded by the lack of ability of the pyrazine nucleus to have both its nitrogens function simultaneously as donors.

The highly crystalline nature of the complexes containing XIb would also seem to indicate that they are not polymeric. It is our belief that in these salts the organic molecules function as simple bidentate or tridentates giving complexes in which the central metal atom of each molecule is either 4-covalent or 5-covalent. Unfortunately, their low solubilities prevented determination of their molecular weights. The complexes of iron(II), cobalt(II) and nickel(II) were quite insoluble in cold water and rapidly decomposed in hot water liberating the parent base. The iron(II) complex was the least stable. The copper(II) complex seemed to be stable even after prolonged treatment with hot water. However, addition of pyridine to an aqueous solution of the copper complex led to immediate precipitation of the base XIb.

Addition of an alcoholic solution of XIb to aqueous copper(II) sulfate solution gave a deep green-brown solution from which addition of sodium perchlorate caused (XVII) an olive-green precipitate to form with the composition $[Cu(base)](ClO_4)_2 \cdot 6H_2O$. We consider that in the molecules of this substance one molecule of the base is coördinated as a tridentate to the 4-covalent copper(II) atom, the fourth coördination position being occupied by a molecule of water. Heating the substance at 95° for several hours in an external atmosphere at 2 mm. pressure causes a loss in weight equivalent to the loss of five molecules of water per molecule. XVII would thus appear to be aquo tetrakis-(6'-methyl-2'-pyridyl)-pyrazine-copper(II) perchlorate pentahydrate. The dehydrated salt is brown but it rapidly becomes green on exposure to the atmosphere. The magnetic moments found experimentally are much higher than those calculated from the spin only formula. However, it does not seem to us profitable to speculate on the reasons for this elevation along the lines of Figgis and Nyholm's work.[12] According to their arguments the observed high moment of the $[Co(base)Cl_2]$ complex would suggest that it is octahedral and such a spatial environment for the cobalt atoms would require polymer molecules.

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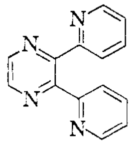
[10] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 20 (1932).

[11] G. T. Morgan and F. H. Burstall, *ibid.*, 1649 (1937).

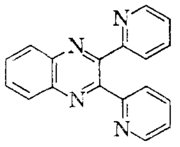
[12] *Cf.* B. T. Figgis and R. S. Nyholm, *ibid.*, 12 (1954).

Interaction of 2,2′-pyridil with ethylenediamine in alcoholic solution leads to formation of 2,3-bis-(α-pyridyl)-5,6-dihydropyrazine (XVII) which can be isolated as a colorless crystalline solid. Prolonged heat treatment of its solution in mesitylene with palladized charcoal causes loss of hydrogen and formation of 2,3-bis-(α-pyridyl)-pyrazine (XVIII). 2,2′-Pyridil can also be caused to react in alcoholic solution with *o*-phenylenediamine to give 2,3-bis-(α-pyridyl)-quinoxaline(XIX).

XVII



XVIII



XIX

XVIII and XIX are similarly constituted to XIa and XIb and study of their capacity to function as chelate groups was considered of some value. From the arguments developed earlier in this paper each of these bases might be expected to function as a bidentate, only one of the pyrazine nitrogens at a time having the capacity to function as a donor nitrogen atom. Experiment has confirmed this expectation. Addition of either XVIII or XIX to alcoholic copper(II) chloride solutions leads to formation of green crystalline compounds of formula [Cu(base)Cl$_2$].

Addition of XIX to an ethanolic solution of iron(II) chloride leads to deposition of a red-violet iron(II) complex of formula [Fe(base)Cl$_2$]. This is an unstable compound which is immediately hydrolyzed in water. It has a magnetic moment corresponding to four unpaired electrons, indicating a high-spin complex. Unfortunately, conductivities of these complexes could not be measured in nitrobenzene solution because of their insolubility in that solvent.

Addition of XVIII to aqueous iron(II) sulfate solution leads to development of a bright red color similar to that of solution of tris-bipyridine iron(II) salts. Addition of sodium perchlorate to the solution caused crystallization of a complex perchlorate [Fe(base)$_3$](ClO$_4$)$_2$. This salt is diamagnetic. Thus, XVIII which lacks a blocking group adjacent to either of the coördinating donor nitrogen atoms appears to behave very similarly to 2,2′-bipyridine. XIX, on the other hand, has a blocking group—the methine carbon atom in the 8-position of the quinoxaline nucleus—and coordinates abnormally and weakly with iron(II) salts.

The complex iron(II) salts derived from XVIII break down, with loss of color, when their aqueous solutions are heated. However, they appear to be reformed on cooling. The complex ions appear also to break down in presence of acid. Finally attention should be drawn to the very recent work of Case and Koft[13] on pyridylpyrazine compounds.

Experimental

6-Methyl-2-aminomethylpyridine.—A solution of 6-methylpyridine-2-aldehyde (60.6 g.) in ethanol (200 ml.) was added to a solution of hydroxylamine hydrochloride (34.8 g.) and potassium carbonate (80 g.) in water (400 ml.) and the mixture heated on the steam-bath for 30 minutes. The **6-methylpyridine-2-aldoxime** quickly crystallized. Recrystallized from benzene it had m.p. 165°.

Anal. Calcd. for $C_7H_8N_2O$: C, 61.8; H, 5.9. Found: C, 62.1; H, 5.8.

This oxime (45 g.) was dissolved in a mixture of acetic acid (350 ml.) and ethanol (700 ml.) and zinc dust (360 g.) added gradually with stirring over three hours. The solution was allowed to stand 24 hours, filtered free from excess zinc and the zinc acetate which had crystallized and then concentrated *in vacuo* to a sirup. The sirup was taken up in water and the solution again evaporated *in vacuo*, and the process repeated twice more in order to remove as much acetic acid as possible. Excess solid potassium hydroxide then was added and the dark oil which separated taken up in ether, dried with anhydrous sodium sulfate and finally fractionated *in vacuo*. **6-Methyl-2-aminomethylpyridine** (31 g.) was collected as a colorless oil, b.p. 78° (4 mm.). Its **5-bromosalicylidene derivative** had m.p. 77°.

Anal. Calcd. for $C_{14}H_{13}N_2OBr$: C, 55.1; H, 4.3. Found: C, 54.5; H, 4.4.

2-Aminomethylquinoline.—Quinoline-2-aldehyde was converted to **quinoline-2-aldoxime**, m.p. 183°.

Anal. Calcd. for $C_{10}H_8N_2O$: C, 69.8; H, 4.7. Found: C, 69.4; H, 4.6.

This oxime was reduced to **2-aminomethylquinoline** with zinc dust and ethanolic acetic acid as described above. It was a yellow oil, b.p. 122° (0.5 mm.). Its **5-bromosalicylidene derivative** had m.p. 144°.

Anal. Calcd. for $C_{17}H_{13}N_2OBr$: C, 59.8; H, 3.9. Found: C, 59.7; H, 4.0.

Iron(II) and copper(II) complexes from the tridentates II–X are listed in Table II. The methods employed for their preparation are illustrated by these two examples.

Bis-(6-methyl-2-(α-pyridylmethyleneaminomethyl)-pyridine-iron(II) Perchlorate Trihydrate.—A solution of 6-methyl-2-aminomethylpyridine (0.61 g.) and pyridine-2-aldehyde (0.44 g.) in ethanol (3 ml.) was refluxed gently for 10 min. A solution of iron(II) sulfate heptahydrate (1 g.) in water (20 ml.) then was added. An intense red-violet color immediately developed. After filtration sodium perchlorate was added to the filtrate. Red-violet crystals of the complex perchlorate deposited. After washing with cold water this salt was recrystallized from hot water containing a little ethanol and sodium perchlorate, then dried *in vacuo* over anhydrous calcium chloride.

Chloro-2-(2′-quinolylmethyleneaminomethyl)-quinoline-copper(II) Chloride.—A solution of copper(II) chloride dihydrate (0.34 g.) in hot ethanol (20 ml.) was added slowly with continuous stirring and scratching to a solution previously prepared by dissolving quinoline-2-aldehyde (0.32 g.) and 2-aminomethylquinoline (0.32 g.) in ethanol (10 ml.) and gently refluxing for 10 min. A dark yellow-brown crystalline precipitate of the complex chloride quickly deposited. This was washed with ethanol and dried *in vacuo*.

In the preparation of other complex chlorides (Table II) it was found convenient to use much less ethanol. With the bases II and III the complex chlorides were gums and it was convenient to isolate perchlorates by adding ethanolic sodium perchlorate to the ethanolic solution of the chloride, collecting the precipitate and washing it with water and ethanol.

2,3,5,6-Tetrakis-(α-pyridyl)-pyrazine IIa (R = H).—α-Pyridoin (20 g.) and ammonium acetate (90 g.) were mixed in a 250-cc. flask fitted with a reflux air condenser and slowly heated to 180° in an oil-bath. The mixture soon became molten and a very intense brown-green color developed. After about half an hour, large white crystals appeared in the melt. The heating was continued for a further 1.5 hours, with occasional shaking. The product (6.6 g., 32%) was washed with alcohol and recrystallized from pyridine; colorless plates, m.p. 284°.

Anal. Calcd. for $C_{24}H_{16}N_6$: C, 74.2; H, 4.2. Found: C, 73.9; H, 4.2.

Bis-[tetrakis-(α-pyridyl)-pyrazine]-iron(II) Perchlorate Tetrahydrate.—Tetrakis-(α-pyridyl)-pyrazine (0.22 g.) was added to a solution of iron(II) sulfate heptahydrate (0.08 g.) in water (30 ml.). The solution, which quickly became intensely blue, was heated on the steam-bath for half an hour, by which time all the base had reacted and the color had become an intense violet. The solution was filtered then and

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[13] F. H. Case and E. Koft, THIS JOURNAL, **81**, 905 (1959).

TABLE II

Tridentate	Complex	Color	Analyses, %					
			Metal		Carbon		Hydrogen	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
II	$[Fe(C_{13}H_{13}N_3)_2](ClO_4)_2 \cdot H_2O$	Violet	8.1	8.3	44.9	44.3	4.1	3.8
II	$[Cu(C_{13}H_{13}N_3)Cl]ClO_4$	Brown	15.6	15.9	38.0	38.2	3.2	3.4
III	$[Fe(C_{13}H_{13}N_3)_2](ClO_4)_2 \cdot 3H_2O$	Violet	7.7	7.5	42.7	42.4	4.4	4.1
III	$[Cu(C_{13}H_{13}N_3)Cl]ClO_4$	Brown	15.6	15.4	38.0	37.6	3.2	3.2
IV	$[Fe(C_{16}H_{13}N_3)_2]I_2 \cdot 3H_2O$	Green	6.5	6.2	44.8	44.8	3.8	3.6
IV	$[Cu(C_{16}H_{13}N_3)Cl]Cl$	Brown	16.8	16.9	50.3	49.8	3.4	3.5
V	$[Cu(C_{19}H_{13}N_3)Cl]Cl$	Brown	15.3	15.0	54.5	54.1	3.1	3.3
VI	$[Fe(C_{18}H_{13}N_3)_2]I_2$	Green	7.0	7.0	47.8	17.7	3.3	3.5
VI	$[Cu(C_{16}H_{13}N_3)Cl]Cl$	Brown	16.8	16.6	50.3	50.3	3.4	3.2
VII	$[Cu(C_{17}H_{15}N_3)Cl]Cl$	Brown	16.2	16.4	51.5	51.6	3.8	3.6
VIII	$[Cu(C_{17}H_{15}N_3)Cl]Cl$	Brown	16.2	16.0	51.5	50.5	3.8	3.6
IX	$[Cu(C_{14}H_{15}N_3)Cl]Cl$	Brown	17.8	17.8	46.7	46.3	4.2	4.2
X	$[Cu(C_{20}H_{15}N_3)Cl]Cl$	Brown	14.8	14.7	55.6	55.3	3.5	3.2

sodium perchlorate carefully added with scratching of the sides of the vessel, when the complex perchlorate crystallized, which was washed with cold water and recrystallized from methanol.

Anal. Calcd. for $[Fe(C_{24}H_{16}N_6)_2](ClO_4)_2 \cdot 4H_2O$: Fe, 5.1; C, 52.2; H, 3.7. Found: Fe, 5.1; C, 51.8; H, 3.9.

Bis-(tetrakis-(α-pyridyl)-pyrazine)-iron(II) Iodide Tetrahydrate.—To the violet solution of the complex iron(II) sulfate prepared as above sodium iodide was carefully added, when the complex iodide crystallized. This was washed with cold water and recrystallized from hot water. The complex was diamagnetic.

Anal. Calcd. for $[Fe(C_{24}H_{16}N_6)_2]I_2 \cdot 4H_2O$: Fe, 4.8; C, 49.7; H, 3.5. Found: Fe, 4.7; C, 49.3; H, 3.4.

Bis-[tetrakis-(α-pyridyl)-pyrazine]-ruthenium(II) Perchlorate Hexahydrate.—Tetrakis-(α-pyridyl)-pyrazine (0.07 g.) and potassium pentachlorohydroxyruthenate(IV) (0.03 g.) were dissolved in glycerol (5 ml.) and the dark solution heated to 180°[14] over a period of 15 min. and kept at 180–200° for 2 hr. A deep blue-violet color quickly developed which gradually changed to intense red-violet. The solution was diluted with water (20 ml.), filtered and the filtrate heated almost to boiling. To the hot solution hot sodium perchlorate solution (10%) was added slowly with scratching of the sides of the vessel. A red-violet, crystalline precipitate soon deposited. This was washed with cold water and recrystallized from methanol (in which it gave an intense orange-red solution) with the help of ether.

Anal. Calcd. for $[RuC_{48}H_{32}N_{12}](ClO_4)_2 \cdot 6H_2O$: Ru, 8.6; C, 48.6; H, 3.8. Found: Ru, 8.8; C, 48.4; H, 3,7.

Bis-[tetrakis-(α-pyridyl)-pyrazine]-nickel(II) Perchlorate Monohydrate.—A suspension of nickel(II) chloride hexahydrate (0.12 g.) and tetrakis-(α-pyridyl)-pyrazine (0.40 g.) in ethanol (7 ml.) was heated on a steam-bath. It quickly turned greenish-brown as the base dissolved, by which time the solution had become a light orange-brown. It was filtered (hot) and ether was added to the cooled filtrate, when orange-brown crystals of the complex chloride deposited. This was dissolved in cold water, in which it was very soluble, to give a light orange-brown solution. On the addition of sodium perchlorate, a yellow microcrystalline precipitate of the complex perchlorate deposited. This was washed with cold water, alcohol, and ether, and air-dried.

Anal. Calcd. for $[NiC_{48}H_{32}N_{12}](ClO_4)_2 \cdot H_2O$: Ni, 5.6; C, 54.8; H, 3.3. Found: Ni, 5.8; C, 54.7; H, 3.4.

Aquo-[tetrakis-(α-pyridyl)-pyrazine]-copper(II) Perchlorate Trihydrate.—Copper(II) chloride dihydrate (0.09 g.) was dissolved in water (20 ml.) and heated on the steam-bath for 1 hour with tetrakis-(α-pyridylpyrazine) (0.2 g.). The base slowly dissolved and a bright green solution developed. This was filtered and sodium perchlorate carefully added to the filtrate. Fine, green feathery needles of the complex perchlorate deposited. These were washed with cold water and recrystallized from hot water.

Anal. Calcd. for $[Cu_{24}H_{16}N_6 \cdot H_2O](ClO_4)_2 \cdot 3H_2O$: Cu, 8.9; C, 39.8; H, 3.4. Found: Cu, 8.6; C, 39.6: H, 3.1.

Chloro-[tetrakis-(α-pyridyl)-pyrazine]-copper(II) Chloride Monohydrate.—Copper(II) chloride dihydrate (0.34 g.) in dimethylformamide (5 ml.) was added to a hot solution of tetrakis-(α-pyridyl)-pyrazine (0.78 g.) in dimethylformamide (15 ml.). A deep green color developed and on cooling bright green crystals deposited. These were washed with a little cold ethanol and dried *in vacuo.*

Anal. Calcd. for $[CuC_{24}H_{16}N_6Cl]Cl \cdot H_2O$: C, 53.3; H, 3.4; Cl, 13.1. Found: C, 53.7; H, 3.3; Cl, 13.3.

Chloro-[tetrakis-(α-pyridyl)-pyrazine]-copper(II) Perchlorate.—Chloro-[tetrakis-(α-pyridyl)-pyrazine]-copper(II) chloride (0.5 g.) was dissolved in hot ethanol (20 ml.) and an ethanolic solution of sodium perchlorate slowly added with stirring. Light green microcrystals of the complex perchlorate deposited. These were washed with alcohol, water, alcohol again and finally ether and dried *in vacuo.*

Anal. Calcd. for $[CuC_{24}H_{16}N_6Cl]ClO_4$: Cu, 10.9; C, 49.1; H, 2.8. Found: Cu, 10.8; C, 49.6; H, 2.7.

Bis-[tetrakis-(α-pyridyl)-pyrazine]-cobalt(III) Perchlorate Dihydrate.—Tetrakis-(α-pyridyl)-pyrazine (0.39 g.) was added to a solution of cobalt(II) chloride hexahydrate (0.14 g.) in water (10 ml.) and the mixture heated on the steam-bath until all the base had dissolved, giving a deep brown solution. Chlorine gas then was passed through the solution for a few minutes, when the color quickly lightened to a bright orange-red. The solution was filtered and sodium perchlorate added to the filtrate. Yellow-brown crystals of the complex perchlorate separated. These were washed with cold water, recrystallized from hot water and dried *in vacuo.*

Anal. Calcd. for $[Co(C_{48}H_{32}N_{12})](ClO_4)_3 \cdot 2H_2O$: Co, 5.1; C, 49.3; H, 3.1. Found: Co, 5.1; C, 49.4; H, 3.2.

2,3,5,6-Tetrakis-(α-picolyl)-pyrazine (XIb, R = CH_3).—6,6′-Dimethyl-α-pyridoin (8.6 g.) and ammonium acetate (35 g.) were heated together, the temperature being brought gradually to 180° over a period of 30 min., and then kept at 180–200° for three hours. On cooling, the mixture set to a solid, crystalline mass. The product (3.6 g., 46%) was obtained in colorless rods, m.p. 227° on recrystallization from ethanol.

Anal. Calcd. for $C_{28}H_{24}N_6$: C, 75.7; H, 5.5. Found: C, 75.1; H, 5.4.

Dichloro-[tetrakis-(α-picolyl)-pyrazine]-iron(II).—A solution of iron(II) chloride tetrahydrate (0.4 g.) in ethanol (6 ml.) was added to a hot solution of tetrakis-(α-picolyl)-pyrazine (0.9 g.) in ethanol (15 ml.). An intense green color quickly developed and lustrous green plates of the iron(II) complex soon deposited. These were washed with alcohol and dried *in vacuo.*

Anal. Calcd. for $[FeC_{28}H_{24}N_6Cl_2]$: Fe, 9.8; C, 58.8; H, 4.2; Cl, 12.4. Found: Fe, 9.8; C, 58.8; H, 4.4; Cl, 12.4.

The conductivity of an $M/1000$ solution in nitrobenzene was 0.6 reciprocal ohm.

The complex was paramagnetic with a moment of 5.4 B.M. at 20°.

Dichloro-[tetrakis-(α-picolyl)-pyrazine]-cobalt(II).—A solution of cobalt(II) chloride hexahydrate (0.24 g.) in ethanol (5 ml.) was added to a hot solution of tetrakis-(α-

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[14] This method of reaction for preparing complex ruthenium compounds was elaborated by Dr. F. P. Dwyer (private communication).

picolyl)-pyrazine (0.45 g.) in ethanol (8 ml.). A dark brown-green color immediately developed. The mixture was heated on the water-bath for a few minutes and glistening, brown crystals of the product soon deposited. After cooling these were filtered, washed with ethanol and then dried *in vacuo*.

Anal. Calcd. for $[CoC_{28}H_{24}N_6Cl_2]$: Co, 10.3; C, 58.5; H, 4.2; Cl, 12.4. Found: Co, 10.1; C, 58.3; H, 4.1; Cl, 12.5.

The conductivity of an *M*/1000 solution in nitrobenzene was 0.6 reciprocal ohm.

The complex was paramagnetic with a moment of 5.1 B.M. at 20°.

Dichloro-[tetrakis-(α-picolyl)-pyrazine]-nickel(II).—A solution of nickel(II) chloride hexahydrate (0.24 g.) in ethanol (5 ml.) was added to a hot solution of tetrakis-(α-picolyl)-pyrazine (0.45 g.) in ethanol (10 ml.). A deep brown color immediately developed. The mixture was heated on the water-bath for a few minutes and golden needles of the nickel complex soon deposited. These were collected, washed with cold ethanol and dried *in vacuo*.

Anal. Calcd. for $[NiC_{28}H_{24}N_6Cl_2]$: Ni, 10.3; C, 58.5; H, 4.2; Cl, 12.4. Found: Ni, 10.2; C, 58.3; H, 4.2; Cl, 12.2.

The conductivity of an *M*/1000 solution in nitrobenzene was 0.6 reciprocal ohm.

The complex was paramagnetic with a moment of 3.3 B.M. at 20°.

Dichloro-[tetrakis-(α-picolyl)-pyrazine]-copper(II).—A solution of copper(II) chloride dihydrate (0.17 g.) in hot ethanol (5 ml.) was added to a hot solution of tetrakis-(α-picolyl)-pyrazine (0.45 g.) in ethanol (10 ml.). A deep-brown color immediately developed and on scratching the sides of the vessel fine, yellow-brown needles of the copper complex deposited. These were collected, washed with cold ethanol and dried *in vacuo*.

Anal. Calcd. for $[CuC_{28}H_{24}N_6Cl_2]$: Cu, 11.1; C, 58.0; H, 4.2; Cl, 12.3. Found: Cu, 10.9; C, 58.0; H, 4.1; Cl, 12.2.

The conductivity of an *M*/1000 solution in nitrobenzene was 0.7 reciprocal ohms.

The complex was paramagnetic with a moment of 2.1 B.M. at 20°.

Aquo-[tetrakis-(α-picolyl)-pyrazine]-copper(II) Perchlorate Pentahydrate.—A solution of tetrakis-(α-picolyl)-pyrazine (0.45 g.) in ethanol (5 ml.) was added to a hot solution of copper(II) sulfate pentahydrate (0.25 g.) in water (10 ml.). A deep green-brown color developed. The mixture was heated on the water-bath for 15 min., then sodium perchlorate was added. On cooling olive green crystals of the complex perchlorate deposited. These were washed with cold water and ethanol, then dried *in vacuo*.

Anal. Calcd. for $[CuC_{28}H_{24}N_6H_2O](ClO_4)_2\cdot5H_2O$: Cu, 7.9; C, 41.2; H, 4.5; H_2O, 11.0. Found: Cu, 7.6; C, 41.6; H, 4.4; H_2O, 10.8.

2,3-Bis-(2′-pyridyl)-5,6-dihydropyrazine.—A solution of ethylenediamine (1.2 g.) in ethanol (5 ml.) was added slowly to a solution of 2,2′-pyridil (4.2 g.) in ethanol (30 ml.). Heat was generated and the solution darkened in color. The mixture was refluxed for one hour. Pale yellow crystals separated on cooling. These were obtained colorless by recrystallization from ethanol; m.p. 188° (2.5 g.).

Anal. Calcd. for $C_{14}H_{12}N_4$: C, 71.2; H, 5.1. Found: C, 71.0; H, 5.0.

2,3-Bis-(2′-pyridyl)-pyrazine.—A solution of the above-described dihydropyrazine (2 g.) in mesitylene (25 ml.) was refluxed with palladium/charcoal catalyst (0.2 g.) for 20 hr. The mixture was filtered while hot. The product separated on cooling in dark brown needles and was obtained colorless by recrystallization from a small volume of ethanol; m.p. 167°.

Anal. Calcd. for $C_{14}H_{10}N_4$: C, 71.8; H, 4.3. Found: C, 71.6; H, 4.5.

Tris-[2,3-bis-(2′-pyridyl)-pyrazine]-iron(II) Perchlorate Pentahydrate.—2,3-Bis-(2′-pyridyl)-pyrazine (0.7 g.) was added to a solution of iron(II) sulfate heptahydrate (0.28 g.) in water (15 ml.). A bright red color immediately developed. On the addition of sodium perchlorate red crystals of the diamagnetic complex perchlorate separated. These were recrystallized from hot water.

Anal. Calcd. for $[FeC_{42}H_{30}N_{12}](ClO_4)_2\cdot5H_2O$: Fe, 5.4; C, 48.1; H, 3.9. Found: Fe, 5.3; C, 47.7; H, 3.7.

Dichloro-[2,3-bis-(2′-pyridyl)-pyrazine]-copper(II).—A solution of copper(II) chloride dihydrate (0.17 g.) in ethanol (5 ml.) was added to a hot solution of 2,3-bis-(2′-pyridyl)-pyrazine (0.23 g.) in ethanol (10 ml.). Boiling the bright green solution for a few minutes caused green crystals to deposit. These were washed with alcohol and dried *in vacuo*.

Anal. Calcd. for $[CuC_{14}H_{10}N_4Cl_2]$: Cu, 17.4; C, 45.5; H, 2.7; Cl, 19.2. Found: Cu, 17.2; C, 45.5; H, 2.8; Cl, 19.2.

2,3-Bis-(2′-pyridyl)-quinoxaline.—A solution of *o*-phenylenediamine (1.08 g.) in ethanol (8 ml.) was added to a solution of 2,2′-pyridil (2.12 g.) in ethanol (12 ml.) and the mixture refluxed for 30 min. On cooling, light brown cubes of the product separated. These were obtained colorless, m.p. 180°, from ethanol.

Anal. Calcd. for $C_{18}H_{12}N_4$: C, 76.1; H, 4.3. Found: C, 75.5; H, 4.4.

Dichloro-[2,3-bis-(2′-pyridyl)-quinoxaline]-iron(II).—A solution of iron(II) chloride tetrahydrate (0.2 g.) in ethanol (3 ml.) was added to 2,3-bis-(2′-pyridyl)-quinoxaline (0.28 g.) in hot ethanol (10 ml.). A deep violet color developed immediately and red-violet crystals separated. These were washed with ethanol and dried *in vacuo*. The complex was *paramagnetic* with a moment of 5.4 B.M. at 27°.

Anal. Calcd. for $[FeC_{18}H_{12}N_4Cl_2]$: Fe, 13.6; C, 52.6; H, 3.0; Cl, 17.3. Found: Fe, 13.9; C, 51.9; H, 3.0; Cl, 17.2.

Dichloro-(2,3-bis-(2′-pyridyl)-quinoxaline)-copper(II).—A solution of copper(II) chloride dihydrate (0.17 g.) in ethanol (5 ml.) was added to a hot solution of 2,3-bis-(2′-pyridyl)-quinoxaline) (0.28 g.) in ethanol (10 ml.). A bright green color developed and blue-green crystals of the copper(II) complex separated. These were washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $[CuC_{18}H_{12}N_4Cl_2]$: Cu, 15.3; C, 51.6; H, 2.9; Cl, 16.9. Found: Cu, 15.3; C, 51.6; H, 3.3; Cl, 16.6.

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