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Quadridentate Chelate Compounds. II[1]

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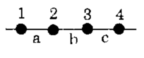
Some factors necessary for the design of linear (open-chain) quadridentate chelate groups are considered and illustrated by reference to some of the coördination chemistry of several new bases. These are 1,2-bis-(8′-quinolylmethyleneamino)-ethane, 1,2-bis-(6′-methyl-2′-pyridylmethyleneamino)-ethane, 1,6-bis-(2′-pyridyl)-2,5-diazahexane, 1,6-bis-(6′-methyl-2′-pyridyl)-2,5-diazahexane, 1,4-bis-(8′-quinolyl)-1,5-dithiapentane, 1,8-bis-(2′-pyridyl)-3,6-dithiaoctane, 2,2′-bis-(2″-pyridylmethyleneamino)-biphenyl and 2,2′-bis-(8″-quinolylmethyleneamino)-biphenyl. The manner in which these bases function as chelating agents is demonstrated by the preparation and study of the properties of several of their metal coördination derivatives.

In this preliminary paper we endeavour to point out some considerations which, in our opinion, must be taken into account in designing organic compounds that are to function as linear, or open-chain, quadridentate chelate groups.[2a] The molecules of such compounds must be capable, either with or without preliminary loss of protons, of presenting and bonding to a suitable metal atom by coördination covalences four donor atoms which are all members of a continuous chain. The architecture of the organic compound is as important as are the preferred stereochemical disposition of the metal valences and the nature of the bonds formed in the coördination process.

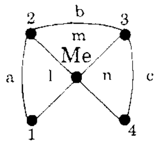
Molecules may be brought into union as quadridentates with six-covalent metal atoms which have an octahedral disposition of the covalences or with metal atoms with coördination number four. These latter may demand a tetrahedral or a square planar arrangement of their coördination covalences and the quadridentate residue must be spatially capable of presenting its four donor atoms to the metal atom from the apices of either a circumscribing tetrahedron or a square in such a way that these donors can bond themselves readily to the circumscribed metal atom.

To a six-covalent metal atom a quadridentate residue must be capable of presenting its four donor atoms spatially so that all four lie in a plane (equatorially) leaving two apices of the coördination octahedron in *trans* position to each other to be occupied by other atoms, or, alternatively, in such a way that the two apices of the coördination octahedron not occupied by the quadridentate are in *cis* positions to each other.

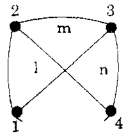
If attention be first directed to organic compounds whose molecules are capable of presenting four donor atoms to a metal atom from the corners of a circumscribing square ('planar quadridentates') it quickly becomes apparent that such substances as appear to have been thus used possesss molecules which are most frequently of the linear (open-chain) type, with the four donor atoms being members of the chain [*cf. e.g.*, 1,2-bis-(salicylideneamino)-ethane (I)], or which contain macrocyclic rings (*cf.* the porphyrins and the phthalocyanines) in which the donor atoms are ring members. In these latter the resonating molecules are necessarily flat, as are their metal derivatives.



IIa



IIb



IIc

In the linear type (IIa) the nature of the terminal donor atoms (1 and 4) of the chain is not usually of great moment stereochemically. All that is necessary is that these two terminal donor atoms and the metal atom lie in the coördination plane.

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[1] A previous paper by F. Lions and K. V. Martin, THIS JOURNAL, **79**, 1273 (1957), may be considered as Part I of this series of papers.

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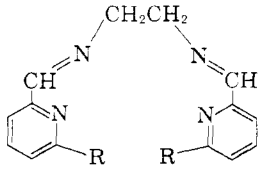
[2a] For a discussion of linear chelating agents see G. Schwarzenbach, *Experientia Supplementum*, **V**, 173–175 (1956).

The penultimate atoms in the quadridentate chain (those attached to donor atoms 1 and 4) may also lie in this plane but this is not obligatory. The nature of the central donor atoms (2 and 3) is important. In a molecule of the coördination compound these atoms must each be bonded to at least three other atoms (the metal atom being one) and they must lie in the coördination plane containing the metal atom and the two terminal donor atoms. Short lengths of the chains a, b and c (IIa; for example, 2 carbon atoms), plane chelate loops l, m and n (IIc) and coplanarity of these with the plane of coördination demand the coplanarity of donor atoms 2 and 3 and of each set of three atoms attached to them. The only common donor capable of fulfilling this condition is nitrogen, either in an azomethine structure or in an acid imide type structure (*cf.* >NH in pyrrole) after loss of a proton. Good examples of this type structure are Schiff bases derived from ethylenediamine, such as I (Type A_1).



IIIa, R = H
IIIb, R = CH_3

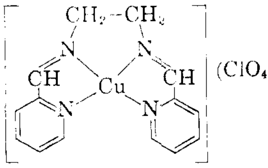
It is possible for an organic molecule to function as an open-chain planar quadridentate molecule even if the chelate loops l, m and n are small and the donor atoms 2 and 3 have a non-planar distribution of their bonds when coördinated. In the molecules of such coördination compounds some part or parts of the molecule must lie out of the plane containing the metal atom and the four attached donor atoms, as, for example, through the buckling of one or more of the chelate loops. Thus, when donor atoms 2 and 3 are sulfide sulfur or amino nitrogen (secondary or tertiary), a 2-atom link b giving a five-membered chelate loop m buckled across the line of centers of donor atoms 2 and 3 would seem not only to be possible but rather the normal strainless form (Type B). While there also exists the possibility of an alternative *trans* form of chelate loop m with one carbon atom of the b link above the plane of coordination and the other below it (also Type B), this would seem to be less likely in many coördination compounds containing quadridentate chains. Further, it is possible for loop m to be planar while loops l and n are not planar (Type C), or loops l and m planar and coplanar while loop n is not planar (Type D). Non-planar relatively strainless ring-atom distribution in coördination compounds (such as ethylenediamine in square-planar or octahedral complexes) would appear to be quite normal.[3]

It should also be remembered that increase in length of the central link b beyond three atoms between azo-methine nitrogen donors 2 and 3 creates serious steric difficulties if there is to be a planar distribution of the metal atom and its attached donor atoms. Models show, for example, that substitution of $=N-(CH_2)_n-N=$ ($n > 3$) for the $=N-CH_2-CH_2-N=$ sequence of IIIa forces apart the carbon atoms of the methylene groups attached to the nitrogen atoms in the m loop as well as these nitrogen atoms.

The environmental requirements of the donor atoms 1 and 4 in open-chain planar quadridentates must be considered. When these atoms terminate the chain of the chelate group (*e.g.* oxygen of carboxyl) there are usually no consequent difficulties in design. However, if donor atoms 1 and 4 are not the ultimate atoms in the chain then the attached terminal groups may interfere with each other spatially to such an extent that it becomes impossible to attach the whole molecule as a planar quadridentate to a 4-covalent metal atom demanding a planar bond distribution. Thus, IIIa can function as a planar quadridentate, giving with copper(II) perchlorate the non-hydrated complex salt IV. It is not possible for IIIb so to function. The size of the metal atom must influence effects of this kind. Thus, the "obstacle" effect exhibited by the methyl groups of IIIb might be expected to be greater with a metal atom of small radius than with one of large radius. However, the overlap of the terminal methyl groups would appear to be so great with IIIb that it is difficult to envisage it functioning as a planar quadridentate, and, as is mentioned later, there would appear to be difficulties even for the parent base IIIa to function as a planar quadridentate.

What has been said so far concerning the design of planar quadridentates for 4-covalent metals should apply fairly closely to the equatorial attachment of them to 6-covalent metals. However, here, quadridentates having donor atoms 2 and 3 other than azo-methine or acid-imide type nitrogens which nevertheless arrange the four donors at the corners of a square for a 4-covalent square-planar metal atom [such as palladium(II)] might coördinate more easily and naturally with a 6-covalent atom in the alternative way as non-planar quadridentates. A useful test of capacity for this latter type of behavior is reaction with ammonium tetrachloro-α,α'-bipyridineruthenate-(III), in the complex ion of which the bipyridine residue is very firmly held while the chlorine atoms are reasonably labile and able to be replaced by the quadridentate. Replacement of all four chlorines by the four donor atoms of the quadridentate is evidence of its assumption of one or other of the non-planar spatial configurations XVa-d.

In some respects it would seem easier to design open-chain quadridentates of this type. Many of these, also, should be capable of encompassing



IV

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[3] *Cf.*, *e.g.*, J. V. Quagliano and S. Mizushima, THIS JOURNAL, **75**, 6084 (1953); K. Nakatsu, M. Shiro, Y. Saito and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 158 (1957); E. J. Corey and J. C. Bailar, Jr., THIS JOURNAL, **81**, 2622 (1959).

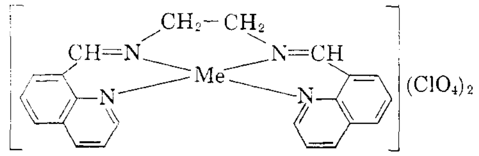
a 4-covalent metal atom and bonding to it four donor atoms located at the apices of a circumscribing tetrahedron. The chelate loops in the molecules of coördination compounds derived from such quadridentates could be disposed in three different planes if donor atoms 2 and 3 were, for example, sulfide sulfur or amine nitrogen. Any three covalences of such donor atoms are pyramidally arranged (with the atom occupying one apex of the pyramid and the three attached atoms the other apices).

It would appear useful to us to attempt to classify open-chain quadridentate chelate groups into the eight classes listed in Table I according to the structural features of the coördination compounds they form. There should also be a proviso that each class can be subdivided into subclasses according as to whether donor atoms 1 and 4 are terminal (subclass 1), not terminal (subclass 2), or one terminal and the other not terminal (subclass 3). This table is not exhaustive but covers the types most likely to be encountered. Some chelate groups can be "facultative"— *i.e.*, able to arrange their four donor atoms in a square planar arrangement or alternatively in a tetrahedral arrangement about a metal atom according to the spatial demands of the metal atom. It should also be remembered that a quadridentate capable of having its four donor atoms take up a tetrahedral disposition about a 4-covalent metal atom should usually be readily capable of disposing the four donor atoms nonequatorially about a 6-covalent metal atom.

TABLE I

Class	Disposition of donor atoms about the central metal atom	Remarks
A	Square	All chelate loops plane and coplanar with the plane of coördination
B	Square	Loop m non-planar. Loops l and n plane and coplanar
C	Square	Loop m plane and coplanar. Loops l and n non-planar
D	Square	Loops l and m plane and coplanar. Loop n non-planar
E	Tetrahedral	All chelate loops plane
F	Tetrahedral	Loop m non-planar; loops l and n plane
G	Tetrahedral	Loops l and n non-planar; loop m plane
H	Tetrahedral	All three loops l, m and n non-planar

The experiments now described were designed to illustrate and to test some of the considerations put forward above. Thus, 1,2-bis-(8'-quinolylmethyleneamino)-ethane, readily formed by interaction of quinoline-8-aldehyde and ethylenediamine, would appear to be a planar quadridentate of Class A$_2$. However, it resembles I and differs structurally from IIIa in that coördination compounds derived from it contain two chelate loops (l and n) which are six-membered, while those derived from IIIa, such as IV, contain three five-membered chelate loops. A model shows that this leads to some "atom-crowding" of the hydrogen atoms attached to the 2-carbon atoms of the quinoline nuclei when the molecule functions as a planar quadridentate group. Nevertheless, that it does so function is shown by the ready preparation of the light-blue stable complex copper(II) perchlorate, $[Cu(Base)](ClO_4)_2$, (Va), and the cream complex palladium(II) perchlorate, $[Pd(Base)](ClO_4)_2$, (Vb).

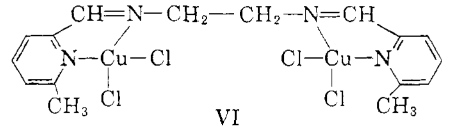


Va, Me = Cu
Vb, Me = Pd

1,2-Bis-(6'-methyl-2'-pyridylmethyleneamino)-ethane (IIIb) is readily prepared from 6-methylpyridine-2-aldehyde and ethylenediamine. As previously indicated, its molecules are so constructed with azo-methine donor nitrogen atoms 2 and 3 that coördination of all four nitrogen atoms with a metal atom would demand planar distribution of the whole organic residue about the metal atom. However, because of the spatial demands of the methyl groups attached to the pyridine rings, there is insuperable steric hindrance to such an arrangement. Moreover, as models show, distortion of the bond angles in the chelate loops is necessary to bring all four nitrogen donors of IIIa to the corners of a square from which they can conveniently bond to a square planar metal atom.

When experiments were made to study the behavior of IIIb in the presence of metal ions, some interesting phenomena were observed. Thus, with copper(II) chloride in ethanol and IIIb it is possible to obtain either a brown complex VI or, especially if the solution is heated, a bright green complex salt VIIa. Usually the brown complex VI separates first, but not always, and either product usually can be obtained as required by carrying out the reaction at the boiling point of the solvent and adding a seed of the product required.

The brown complex VI is slightly soluble in nitrobenzene but the solutions are practically non-conducting. There seems little doubt that it should be formulated containing a bis-bidentate group



VI

Analysis of the green complex salt VIIa shows that in its formation 6-methylpyridine-2-aldehyde has been lost through hydrolysis during coördination.[4] The aldehyde can be detected readily by its odor and by formation of its 2,4-dinitrophenylhydrazone from the mother liquors. An exactly analogous green complex bromide VIIb could be prepared from IIIb and copper(II) bromide in alcohol. However, it did not appear possible to

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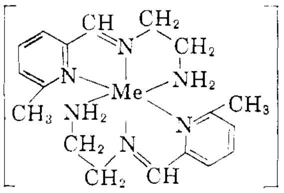
(4) *Cf.* G. L. Eichhorn and J. C. Bailar, Jr., THIS JOURNAL, **75**, 2905 (1953).

isolate any brown complex analogous to VI during this preparation.

From either VIIa or VIIb which were very soluble in cold water, giving blue solutions, it was possible with the help of sodium perchlorate to obtain a dark blue, crystalline complex perchlorate VIIc. There seems little doubt from analyses that the molecules of the salts VIIa, VIIb and VIIc contain octahedral complex cations in which there are two tridentate residues each of which has been derived from a molecule of IIIb by loss of a 6-methylpyridine-2-aldehyde fragment, and the salts are to be formulated as shown.



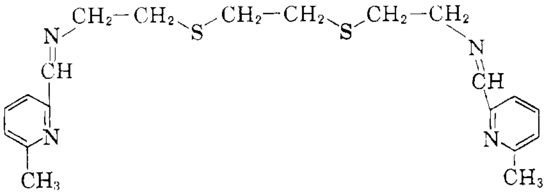
VIIa Me = Cu, X = $CuCl_4$, n = 1
VIIb Me = Cu, X = $CuBr_4$, n = 1
VIIc Me = Cu, X = ClO_4, n = 2
VIId Me = Fe, X = ClO_4, n = 2

Reaction of IIIb with aqueous iron(II) sulfate leads to rapid development of an intense violet color, and from the resulting solution sodium perchlorate precipitates the complex salt VIId. It is not particularly stable, decomposing readily in hot aqueous or alcoholic solution. During its preparation also, a 6-methylpyridine-2-aldehyde residue had been split off from each molecule of IIIb and the aldehyde could be readily detected and identified. The formation of complexes derived from ethylenediamine residues substituted on one nitrogen atom only is noteworthy as it is relatively difficult to prepare monosubstituted ethylenediamines.

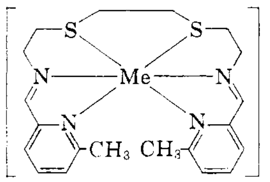
Loss of a 6-methylpyridine-2-aldehyde residue from each molecule of IIIb during the coördination process makes possible the placing of nitrogen donors in all six octahedral coördination positions by the use of the main part of each of two IIIb molecules for each metal atom. At the same time, as an accurate model shows, the spatial arrangement of each set of three nitrogen donors is better than in the molecule of IIIb. The overlap of the methyl groups attached to the pyridine rings would, in any case, prevent IIIb from functioning as a planar quadridentate. However, the positioning of the four nitrogen donors in the molecule of IIIb or the parent base IIIa is such that strain would accompany quadridentate function. It is significant that Busch and Bailar[5a] in reporting on 1,2-bis-(2'-pyridylmethyleneamino)-ethane as a quadridentate reported that iron(II) chloride, and cobalt(II) chloride reacted with IIIa to give solid products "found to be contaminated with excess metal salt." Copper(II) chloride gave green and blue products and a correct nitrogen analysis for a $[Cu(Quad)]Cl_2 \cdot 2H_2O$ compound was reported for this latter. However, it seems significant that the infrared spectrum indicated the presence of the >NH group.

We have found that IIIa can be induced to coördinate readily either in aqueous or ethanolic solution with copper(II) perchlorate 6-hydrate to give the relatively insoluble, blue-grey, crystalline, anhydrous substance IV. There seems no doubt that IIIa here functions as a quadridentate. On the other hand, condensation of IIIb with copper(II) perchlorate in ethanol leads to loss of a 6-methyl-pyridine-2-aldehyde residue from each molecule of IIIb and then coördination of two of the remaining tridentate fragments with each copper atom to give finally the complex salt VIIc. As formulated the complex cation of VIIa–c contains copper with a coördination number of six. Although the coördination number of copper is usually four, examples of complexes of six-covalent copper are known.[5b]

As further evidence of the largely steric nature of these effects, we have condensed 6-methylpyridine-2-aldehyde with 1,8-diamino-3,6-dithiaoctane ("EEE base") to obtain 1,8-bis-(6'-methyl-2'-pyridylmethyleneamino)-3,6-dithiaoctane (VIII) and have caused this to react with iron(II) sulfate, thus obtaining an intensely colored complex sulfate from which the pure, diamagnetic sparingly soluble iodide (IXa) and perchlorate (IXb) were isolated.



VIII



IXa Me = Fe, X = I, n = 2
IXb Me = Fe, X = ClO_4, n = 2
IXc Me = Co, X = I, n = 2
IXd Me = Co, X = ClO_4, n = 2

We were also able to isolate cobalt(II) complex salts (IXc and IXd) containing VIII whose magnetic moments corresponded to one unpaired electron and which are apparently low-spin octahedral complex salts. All these salts are to be formulated as containing a sexadentate residue and they are analogous to the corresponding salts derived from 1,8-bis-(2'-pyridylmethyleneamino)-3,6-dithiaoctane previously described by one of the authors and his co-workers.[6] The methyl groups attached to the pyridine rings do not interfere with each other spatially when a molecule of VIII is wrapped round a metal atom as a sexadentate chelate group, the N–N–S donor atom sequences can take up practically strainless configurations and there is little difficulty in forming the complex ions.

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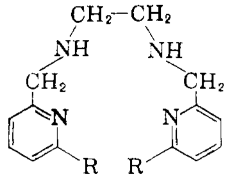
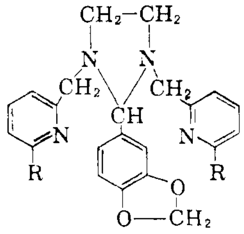
(5) (a) D. H. Busch and J. C. Bailar, Jr., THIS JOURNAL, **78**, 1138 (1956); (b) *cf.*, *e.g.*, S. Kirschner, *ibid.*, **78**, 2372 (1956).

(6) F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, *ibid.*, **79**, 1269 (1957).

It was considered that further evidence bearing on this question of steric hindrance could be obtained by the study of 1,6-bis-(2′-pyridyl)-2,5-diazahexane (Xa) (since the completion of this paper our attention has been drawn to the work of LaCoste who has determined the chelation formation constants of 1,6-bis-(2′-pyridyl)-2,5-diazahexane with several bivalent metal ions (S. Chaberek and A. E. Martell, "Organic Sequestering Agents," John Wiley and Sons, Inc., New York, 1959, p. 535) and 1,6-bis-(6′-methyl-2′-pyridyl)-2,5-diazahexane (Xb). These yellow oily bases were obtained readily by causing pyridine-2-aldehyde and 6-methylpyridine-2-aldehyde, respectively, to react with ethylenediamine in hot ethanolic acetic acid solution in the presence of dissolving zinc. Each of them could be caused to react readily with piperonal to give the corresponding imidazolidine derivative (XIa and XIb, respectively). These two bases Xa and Xb are constituted similarly in many ways to triethylene tetramine so that the stereochemistry of their coördination compounds might well be expected to be similar.[7] However, it should be remembered that in Xa and Xb the coördination covalences of the nitrogen atoms of the pyridine rings (donor atoms 1 and 4) must be directed along axes of these rings and this must certainly tend to make obligatory in their planar coördination compounds planar distribution of the chelate loops l and n. A model shows that Xa should be able to function as a planar quadridentate of Class B$_2$ provided that the two carbon atoms of chelate loop m are both above (or below) the plane of coördination.

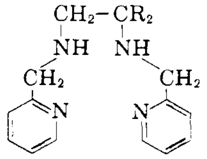


Xa R = H
Xb R = CH$_3$

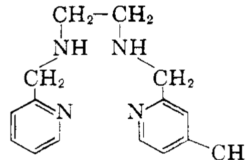


XIa R = H
XIb R = CH$_3$

Evidence of such a non-planar arrangement of chelate loop m should be obtainable by preparation and resolution of a suitable complex salt derived from a quadridentate of type Xc or Xd and we have instituted experiments along these lines.

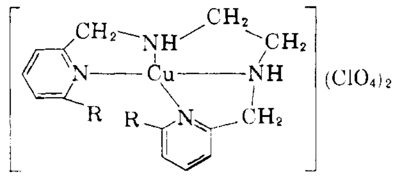


Xc



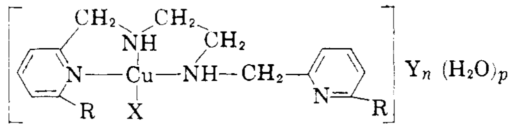
Xd

The base Xa reacted readily with copper(II) perchlorate in ethanol solution to give a deep-blue violet complex salt of the formula [Me(Base)]-(ClO$_4$)$_2$. There seems little doubt that it should be formulated as XIIa. Xb also reacted readily in ethanol solution with copper(II) perchlorate to give a deep blue solution. Addition of ether to this caused precipitation of a blue oil, which was induced to crystallize and was then found, rather surprisingly, to correspond to the formula of the anhydrous salt XIIb. In our opinion the copper–nitrogen covalences in the cation of this salt are non-planar, and there is a structural similarity to the "blocked" copper(II) dipyrrylmethine compounds.[1,8] That the copper atom *does not favor* this non-planar disposition of its covalences is shown by the fact that addition of pyridine to the ethanolic solution of XIIb leads to formation of the anhydrous salt [CuPy(quad.)]-(ClO$_4$)$_2$ which, in our opinion, must be formulated as XIIIf.



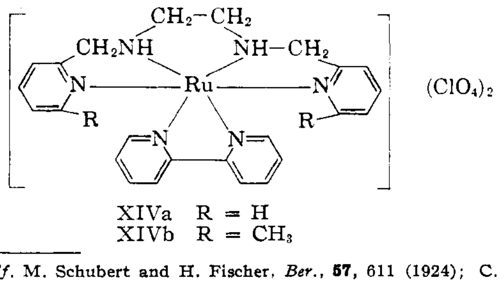
XIIa, R = H
XIIb, R = CH

Each of the bases Xa and Xb coördinates readily in ethanol solution with copper(II) halides to give complex copper(II) halides which are deep blue in color and the analyses of which show must be formulated as XIIIa, XIIIb and XIIId. These three salts react with excess sodium perchlorate in ethanol solution to give corresponding complex perchlorate salts such as XIIIc and XIIIe, respectively, in the molecules of which one halogen atom is coördinatively bound to the copper atom.



XIIIa X = Cl, R = H, Y = Cl, n = 1, p = 1.5
XIIIb X = Br, R = H, Y = Br, n = 1, p = 0
XIIIc X = Br, R = H, Y = ClO$_4$, n = 1, p = 0
XIIId X = Cl, R = CH$_3$, Y = Cl, n = 1, p = 1
XIIIe X = Cl, R = CH$_3$, Y = ClO$_4$, n = 1, p = 0
XIIIf X = C$_5$H$_5$N, R = CH$_3$, Y = ClO$_4$, n = 2, p = 0

That the bases Xa and Xb are able to function as non-planar quadridentate chelate groups, belonging probably to Class E$_2$, or possibly F$_2$, is shown by their ability to react in hot ethanol with ammonium tetrachlorobipyridine ruthenate(III) to form the corresponding orange-brown bipyridine-{1,6-bis-(2′-pyridyl)-2,5-diazahexane}-ruthenium(II) or bipyridine{1,6-bis-(6′-methyl-2′-pyridyl)-2,5-diazahexane}-ruthenium(II) salts, respectively, and from which the perchlorates (XIVa) and (XIVb)



XIVa R = H
XIVb R = CH$_3$

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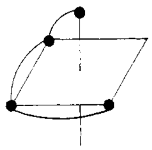
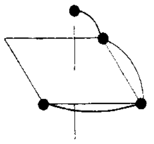
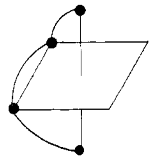
[7] *Cf.*, F. Basolo, THIS JOURNAL, **70**, 2634 (1948).

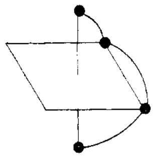
[8] *Cf.* M. Schubert and H. Fischer, *Ber.*, **57**, 611 (1924); C. R. Porter, *J. Chem. Soc.*, 368 (1938).

were obtained pure. Since in the complex cations of these salts the bipyridine residue must occupy two adjacent positions in the coördination octahedron, four configurations would seem to be possible (two pairs of enantiomorphs). These are shown in the partial diagrams XV a–d. The arrangements in XVc and XVd are axially symmetrical and there would seem to be less chance of steric interference between the bipyridine residue and the ends of the quadridentate residue in these arrangements than there would be in the less symmetrical arrangements XVa and XVb. We are therefore of the opinion that the salts XIVa and XIVb should be formulated as possessing the enantiomorphous arrangements of XVc and XVd.

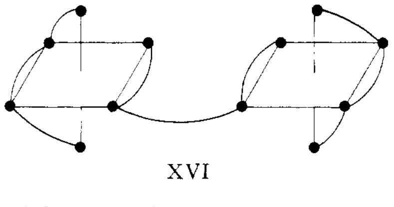

XVa


XVb


XVc

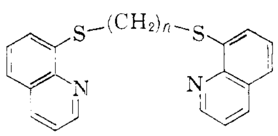

XVd

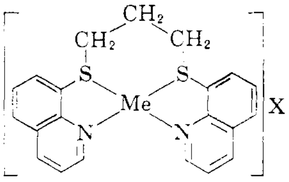
Reaction of the base Xa with ethanolic nickel(II) chloride gave a pale lilac colored solution containing a complex chloride and from which also a sparingly soluble perchlorate could be isolated after addition of sodium perchlorate. Analysis showed these salts to have the composition $[Ni_2(Base)_3]X_4$ (where X = Cl or ClO_4). They would thus appear to have complex cations containing two octahedrally disposed six-covalent nickel atoms each of which has one complete quadridentate Xa residue occupying four coördination apices about it while the third Xa residue supplies two donor nitrogen atoms to each nickel atom and acts as a bridge group to tie them into the same cation. There are many possible alternative formulations. However, using the reasoning applied to the adoption of the formulae XVc and XVd above, some such structural formula as the *meso*-form XVI or those for the corresponding *d*- and *l*-forms would appear to be most likely.


XVI

1,4-Bis-(8′-quinolyl)-1,4-dithiabutane (XVIIa) might well be expected to coördinate with suitable metal salts as a linear tetrahedral quadridentate of Class E_2. Attempts to prepare it by treatment of the sodium salt of 8-thiolquinoline with ethylene dibromide in dry ethanol all failed, apparently because of the marked tendency of the quinoline nitrogen atom to quaternize intramolecularly immediately upon formation of the intermediate β-bromoethyl-8-quinolyl sulfide. Similar behavior is exhibited by the sodium salt of 8-hydroxyquinoline and we shall report on these quaternary salts later. 8-Thiolquinoline, incidentally, is usually described in the literature[9] as a red crystalline dihydrate or as an anhydrous purple oil. It is possible to prepare it in the anhydrous state as a blue oil which boils at 138–140° (3 mm.). On one occasion distillation of a sample which had not been completely dehydrated gave a forerun of dihydrate boiling at 174° (0.5 mm.). When this had all distilled, the temperature dropped and the pure 8-thiolquinoline distilled at the lower boiling point.

It is readily possible to prepare a homolog of XVIIa by causing trimethylene bromide to react in dry ethanol solution with the sodium salt of 8-thiolquinoline. The resultant 1,5-bis-(8′-quinolyl)-1,5-dithiapentane (XVIIb) is a facultative linear quadridentate. When functioning as a planar quadridentate it would be of Class B_2, and when tetrahedral, as Class F_2, the chelate loops l and n being always planar.


XVIIa $n = 2$
XVIIb $n = 3$


XVIIIa Me = Cu, X = $CuCl_4$, $n = 1$
XVIIIb Me = Pd, X = $PdCl_4$, $n = 1$
XVIIIc Me = Pt, X = $PtCl_4$, $n = 1$
XVIIId Me = Cu, X = ClO_4, $n = 2$
XVIIIe Me = Cu, X = ClO_4, $n = 1$

As a planar quadridentate it readily forms complex copper(II), palladium(II) and platinum(II) complex salts (XVIIIa, XVIIIb and XVIIIc, respectively). The deep-green copper(II) perchlorate (XVIIId) could be prepared readily by addition of ethanolic copper(II) perchlorate to an ethanolic solution of the base. It does not appear to be stable in aqueous solution, breaking down easily, especially on warming. When treated in ethanol solution with sulfur dioxide, the color changes rapidly to yellow and the canary-yellow 1,5-bis-(8′-quinolyl)-1,5-dithiapentane copper(I) perchlorate (XVIIIe) can be precipitated with dry ether. In this last salt there would appear to be little doubt that the base XVIIb is functioning as a linear tetrahedral quadridentate chelate group of Class F_2. Interaction of XVIIb with nickel(II) chloride in hot ethanol gave a paramagnetic product of the formula $NiCl_2$·base. It can be formulated as an octahedral complex with two chlorines coördinated to the nickel atom, $[Ni(Base)Cl_2]$, or as a tetrahedral, four-covalent nickel chloride, $[Ni(Base)]Cl_2$. It is insoluble in cold water and decomposes rapidly in hot. The complex was not sufficiently soluble in nitrobenzene to enable its conductivity in that solvent to be determined.

The base XVIIb coördinates to give complex salts in which the central (m) chelate loop is six-membered while the l and n loops are five-membered. It seemed of interest, therefore, to synthesize a

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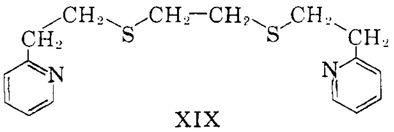
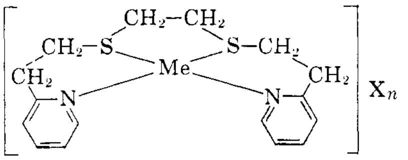
[9] A. Edinger, *Ber.*, **41**, 937 (1908); G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, 3236 (1956).

quadridentate of similar type in which the central m loop in a derived coördination compound would be five-membered and the l and n loops six-membered. Accordingly, freshly distilled 2-vinylpyridine was mixed with 1,2-dithiol-ethane. Reaction occurred with heat evolution and 1,8-bis-(2′-pyridyl)-3,6-dithiaoctane (XIX) eventually was obtained as a white crystalline solid.

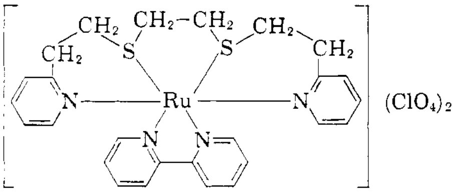


XIX



XXa Me = Cu; X = ClO_4; n = 2
XXb Me = Cu; X = ClO_4; n = 1
XXc Me = Pt; X = ClO_4; n = 2
XXd Me = Pd; X = ClO_4; n = 2

This base is again "facultative." It can function either as a planar or as a tetrahedral linear quadridentate. Thus, addition of XIX to an aqueous solution of copper(II) sulfate gives a solution with an intense royal-blue color from which the crystalline complex perchlorate (XXa) can be precipitated with the help of sodium perchlorate. This salt can be reduced with sodium hydrosulfite to the colorless diamagnetic copper(I) complex salt XXb in which the chelate group undoubtedly is arranged tetrahedrally about the metal atom. Addition of XIX to solutions of either potassium tetrachloropalladate(II) or of potassium tetrachloroplatinate(II) leads to formation of the corresponding palladium(II) and platinum(II) complex salts and the diamagnetic complex perchlorates XXd and XXc can be isolated readily:



XXI

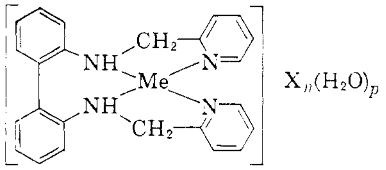
Interaction of nickel(II) chloride and XIX in ethanol gives a paramagnetic product which may be formulated as an octahedral complex salt with two chlorines coördinated to nickel or, alternatively, as a tetrahedral complex chloride. It is similar in many ways to the complex nickel(II) chloride derived from the base XVIIb described above. Reaction of XIX with ammonium bipyridine tetrachlororuthenate(III) led to replacement of the coördinated chlorines and ultimately orange-brown bipyridine-{1,8-bis-(2′-pyridyl)-3,6-dithiaoctane}-ruthenium perchlorate (XXI) was isolated. In this salt the quadridentate group is almost certainly disposed as in XVc or XVd.

It is well known that ring formation between substituents occupying the 2- and 2′-positions of a biphenyl molecule can be effected as easily as between similar substituents located in *ortho* positions of a benzene molecule. A recent example was the incorporation of 2,2′-diaminobiphenyl as a bidentate chelate group in a complex salt.[10] The seven-membered chelate ring containing the diamino-biphenyl residue and the metal atom in each cation of this salt is practically strainless and closely resembles a five-membered ethylenediamine-metal atom chelate ring (or a corresponding ring derived from *o*-phenylenediamine).

It seemed to us that some useful linear quadridentates might be derived from 2,2′-diaminobiphenyl and, indeed, attention was drawn in Part I to some 2,2′-bis-salicylideneaminobiphenyl derivatives and their ability to function only as tetrahedral quadridentate chelate groups. Models show that similar behavior could not be anticipated for 2,2′-bis-(2″-pyridylmethyleneamino)-biphenyl (XXII), because of the requirements that its coördination compounds must have plane l and n chelate loops.

However, reduction of both the azomethine double bonds of XXII would give 2,2′-bis-(2″-pyridylmethylamino)-biphenyl (XXIII) and models show that this base should be capable of functioning as a "facultative" linear quadridentate. When planar it would belong to Class B_2 and when tetrahedral to Class E_2.

Slow addition of pyridine-2-aldehyde to a hot stirred ethanolic solution of 2,2′-diaminobiphenyl containing acetic acid and dissolving zinc led to formation of XXIII, which was isolated as a colorless crystalline solid. It reacted readily with potassium tetrachloropalladate(II) and eventually pale orange 2,2′-bis-(2″-pyridylmethylamino)-biphenylpalladium(II) perchlorate (XXIVa) was isolated.



XXIVa Me = Pd, X = ClO_4, n = 2, p = 0
XXIVb Me = Cu, X = Cl, n = 2, p = 1
XXIVc Me = Cu, X = ClO_4, n = 2, p = 2

Reaction of XIII with copper(II) chloride dihydrate in hot ethanol gave the salt XXIVb and from this with the help of sodium perchlorate was prepared XXIVc. In all these salts there appears little doubt that XXIII is functioning as a planar quadridentate of Class B_2. However, XXIII reacts readily with ammonium bipyridine tetrachlororuthenate(III) to give bipyridine-{2,2′-bis-(2″-pyridylmethylamino)-biphenyl}-ruthenium(II) chloride, from which the corresponding brown perchlorate (XXV) was readily isolated. In the cations of this complex salt the molecules of XXIII must be coördinated as non-planar quadridentate groups and models show that the quadridentate group could take up any of the alternative configurations in the coördination octahedron corresponding to XVa-d. However, the more symmetrical configurations XVc and XVd would seem to make it much

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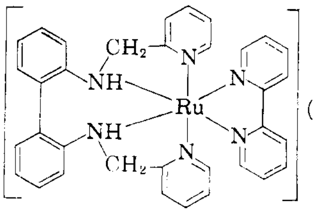
[10] F. McCullough, Jr., and J. C. Bailar, Jr., THIS JOURNAL, **78**, 714 (1956).



XXV

more easy for the bipyridine residue of XXIII to bond to the ruthenium atom.

Condensation of quinoline-8-aldehyde with 2,2′-diaminobiphenyl in hot ethanol solution leads to formation of 2,2′-bis-(8″-quinolylmethyleneamino)-biphenyl (XXVI), a yellow crystalline solid.

Models show that the molecule of XXVI can function as a linear quadridentate only if it disposes its four donor nitrogen atoms tetrahedrally (Class E_2). In many ways the spacing of these closely resembles the corresponding spacing of the donor atoms (two oxygens and two nitrogens) in a molecule of a coördination compound derived from 2,2′-bis-salicylideneaminobiphenyl.[1] However, whereas this latter Schiff base gives non-valent inner complexes when coördinated with bivalent metals XXVI should give rise to salts containing bivalent complex cations when coördinated with salts of bivalent metals. Provided that there is sufficient metal-atom-donor-atom bond stability in such compounds, it would appear possible to prepare and resolve suitable optically active tetrahedral complex salts, and it is worth noting that racemization of an optical isomer would necessitate quite an involved intramolecular process. XXVI combines readily with copper(II) perchlorate in ethanol to give the stable complex perchlorate (XXVII). However, in view of the inability of one of us (H.A.G.) to continue with this work, and its importance, further discussion of the copper(II) and nickel(II) complex salts[11] is reserved for a later paper.

Experimental

1,2-Bis-(8′-quinolylmethyleneamino)-ethane.—Solutions of quinoline-8-aldehyde[12] (13 g.) in ethanol (15 ml.) and ethylenediamine (2.9 g.) in ethanol (5 ml.) were carefully mixed. Heat was evolved. The solution was boiled gently for 2–3 minutes then cooled. A portion was rubbed with ether, when the product crystallized; colorless needles from ethanol, m.p. 142°.

Anal. Calcd. for $C_{22}H_{18}N_4$: C, 78.1; H, 5.4. Found: C, 77.6; H, 5.3.

1,2-Bis-(8′-quinolylmethyleneamino)-ethane Copper(II) Perchlorate-1-hydrate.—A solution of copper(II) chloride-2-hydrate (0.43 g.) in hot ethanol (5 ml.) was slowly added to a solution of the above Schiff's base (0.85 g.) in ethanol (15 ml.). An ethanol solution of sodium perchlorate was added to the resultant blue-green solution when light blue-grey crystals of the complex perchlorate deposited. They were washed with ethanol and dried *in vacuo*. The salt was *paramagnetic* (moment 1.9 B.M. at 24°).

Anal. Calcd. for $[CuC_{22}H_{18}N_4](ClO_4)_2 \cdot H_2O$: C, 42.7; H, 3.3; Cu, 10.3. Found: C, 42.9; H, 3.2; Cu, 10.4.

1,2-Bis-(8′-quinolylmethyleneamino)-ethane Palladium (II) Perchlorate.—A solution of potassium tetrachloropalladate(II) (0.32 g.) in water (12 ml.) was slowly stirred into a solution of the above-described Schiff's base (0.34 g.) in ethanol (3 ml.). Careful addition of sodium perchlorate then caused the cream-colored crystalline complex perchlorate to separate. The crystals were washed with water and ethanol, then dried *in vacuo*.

Anal. Calcd. for $[PdC_{22}H_{18}N_4](ClO_4)_2$: C, 41.0; H, 2.8; Pd, 16.6. Found: C, 40.9; H, 3.1; Pd, 16.6.

1,2-Bis-(6′-methyl-2′-pyridylmethyleneamino)-ethane-(IIIb).—Solutions of ethylenediamine (3 g.) in ethanol (10 ml.) and 6-methylpyridine-2-aldehyde (12.1 g.) in ethanol (10 ml.) were mixed. Heat was evolved. The color darkened. The solution was boiled gently for a few minutes, cooled, water (100 ml.) added and crystallization induced. The solid was recrystallized from light petroleum, m.p. 80°.

Anal. Calcd. for $C_{16}H_{18}N_4$: C, 72.2; H, 6.8. Found: C, 71.8; H, 6.8.

Tetrachloro-{1,2-bis-(6′-methyl-2′-pyridylmethyleneamino)-ethane}-di-copper(II).—A solution of copper(II) chloride-2-hydrate (0.34 g.) in ethanol (10 ml.) was added to a hot solution of IIIb (0.53 g.) in ethanol (10 ml.). Scratching the sides of the vessel containing the resultant deep blue-green solution caused the separation of a light yellow-brown crystalline solid which was separated, washed with ethanol and dried *in vacuo*. This compound was slightly soluble in nitrobenzene in which the conductivity of an 0.001 *M* solution was 1.0 mho. It was *paramagnetic* with a magnetic moment corresponding to 1.8 Bohr magnetons per copper atom.

Anal. Calcd. for $[Cu_2C_{16}H_{18}N_4Cl_4]$: C, 35.8; H, 3.4; Cl, 26.5; Cu, 23.9. Found: C, 36.0; H, 3.7; Cl, 26.1; Cu, 23.5.

Bis-{1-(6′-methyl-2′-pyridylmethyleneamino)-2-amino-ethane}-copper(II)tetrachlorocuprate(II) (VIIa).—Heat treatment for a few minutes of the filtrate obtained after removal of the above-described complex led to separation of a light green crystalline product. It was collected, washed with ethanol and dried *in vacuo*. It was *paramagnetic* with a moment of 1.9 B.M. per copper atom at 27°.

Anal. Calcd. for $[CuC_{18}H_{26}N_6][CuCl_4]$: C, 36.2; H, 4.4; Cl, 23.8; Cu, 21.5. Found: C, 36.4; H, 4.3; Cl, 23.4; Cu, 21.5.

The odor of 6-methylpyridine-2-aldehyde could be readily detected in the filtrate left after removal of this salt. It was identified by formation of its *2,4-dinitrophenylhydrazone*, m.p. 224–226°.

Anal. Calcd. for $C_{13}H_{11}N_5O_4$: C, 51.8; H, 3.7. Found: C, 51.5; H, 3.8.

Bis-{1-(6′-methyl-2′-pyridylmethyleneamino)-2-amino-ethane}-copper(II) Perchlorate-1-hydrate (VIIc).—(a) Addition of sodium perchlorate to an aqueous solution of VIIa caused bright blue crystals to separate. These were collected, washed with water and ethanol then dried *in vacuo*.

Anal. Calcd. for $[Cu(C_{18}H_{26}N_6)](ClO_4)_2 \cdot H_2O$: C, 35.6; H, 4.6; Cu, 10.5. Found: C, 35.0; H, 4.5; Cu, 10.7.

(b) Hot ethanolic solutions of IIIb (0.27 g.) and copper-(II) perchlorate-6-hydrate (0.37 g.) were mixed and heated. A blue oil precipitated. The supernatant liquid was decanted and the oil induced to crystallize. The crystals were thoroughly washed with ethanol and dried *in vacuo*.

Anal. Found: C, 35.3; H, 4.5; Cu, 10.4.

Bis-{1-(6′-methyl-2′-pyridylmethyleneamino)-2-amino-ethane}-copper(II) Tetrabromocuprate(II) (VIIb).—A solution of copper(II) bromide (0.45 g.) in hot ethanol (10 ml.) was added to a hot solution of IIIb (0.53 g.) in ethanol (5 ml.). A deep green color developed and bright green crystals separated. These were collected, washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $[CuC_{18}H_{26}N_6][CuBr_4]$: C, 27.9; H, 3.4; N, 10.9; Cu, 16.5; Br, 41.3. Found: C, 28.2; H, 3.4; N, 11.1; Cu, 16.4; Br, 41.2.

Bis-{1-(6′-methyl-2′-pyridylmethyleneamino)-2-amino-ethane}-iron(II) Perchlorate-1-hydrate (VIId).—A solution of iron(II) sulfate-7-hydrate (0.28 g.) in water (5 ml.) was added to a suspension of IIIb in water (15 ml.). An intense blue violet color developed. The mixture was warmed gently and stirred until all the base had dissolved. It was then cooled, sodium perchlorate was added and crystallization

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(11) *Cf.* R. S. Nyholm, *Chem. Revs.*, **53**, 263 (1953); L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).

(12) V. M. Rodionov and M. A. Berkengein, *J. Gen. Chem.* (*U.S.S.R.*), **14**, 330 (1944) [*C. A.*, **39**, 4076 (1945)]. R. C. Elderfield and M. Siegel, THIS JOURNAL, **73**, 5622 (1951).

induced. The product was recrystallized from ethanol and obtained in very dark purple plates.

Anal. Calcd. for $[FeC_{18}H_{26}N_6](ClO_4)_2\cdot H_2O$: C, 36.1; H, 4.7; Fe, 9.4. Found: C, 36.5; H, 4.7; Fe, 9.7.

1,2-Bis-(2′-pyridylmethyleneamino)-ethane Copper(II) Perchlorate (IV).—Admixture of solutions of IIIa (0.24 g.) and copper(II) perchlorate-6-hydrate (0.37 g.) in either water or ethanol (10 ml.) led to separation of fine dark blue-grey crystals of the complex perchlorate which were then filtered, washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $[CuC_{14}H_{14}N_4](ClO_4)_2$: C, 33.6; H, 2.8; Cu, 12.7. Found: C, 33.5; H, 3.0; Cu, 12.4.

1,8-Bis-(6′-methyl-2′-pyridylmethyleneamino)-3,6-dithiaoctane Iron(II) Iodide (IXa).—The solution obtained by admixture of solutions of 1,8-diamino-3,6-dithiaoctane[13] (1.25 g.) in ethanol (5 ml.) and 6-methylpyridine-2-aldehyde (1.7 g.) in ethanol (5 ml.) and then gently boiling for 20 minutes was added to a solution of iron(II) sulfate-7-hydrate (1.9 g.) in water (40 ml.). An intense red-violet color developed immediately. The solution was boiled, filtered and divided into halves (a) and (b). Sodium iodide was added to (a). The complex iodide crystallized at once. It was recrystallized from hot water and dried *in vacuo*. It was *diamagnetic*.

Anal. Calcd. for $[FeC_{20}H_{26}N_4S_2]I_2$: C, 34.5; H, 3.8; Fe, 8.0; I, 36.5. Found: C, 34.3; H, 3.6; Fe, 8.0; I, 36.5.

1,8-Bis-(6′-methyl-2′-pyridylmethyleneamino)-3,6-dithiaoctane Iron(II) Perchlorate-1-hydrate (IXb).—Sodium perchlorate was added to the above-mentioned filtrate (b). The complex perchlorate which separated was recrystallized from hot water and dried *in vacuo*.

Anal. Calcd. for $[FeC_{20}H_{26}N_4S_2](ClO_4)_2\cdot H_2O$: C, 36.4; H, 4.3; Fe, 8.5. Found: C, 36.2; H, 4.3; Fe, 8.4.

1,8-Bis-(6′-methyl-2′-pyridylmethyleneamino)-3,6-dithiaoctane Cobalt(II) Iodide-2-hydrate (IXc) and Perchlorate (IXd).—These two salts were prepared in a manner exactly analogous to those just described for IXa and IXb. The complex *iodide-2-hydrate* (IXd) was *paramagnetic* (2 B.M. at 27°).

Anal. Calcd. for $[CoC_{20}H_{26}N_4S_2]I_2\cdot 2H_2O$: C, 32.7; H, 4.1; Co, 8.0; I, 34.6. Found: C, 32.6; H, 3.9; Co, 8.3; I, 34.6.

The complex *perchlorate* (IXd) had a magnetic moment of 2.3 B.M. at 27°.

Anal. Calcd. for $[CoC_{20}H_{26}N_4S_2](ClO_4)_2$: C, 37.3; H, 4.1; Co, 9.2. Found: C, 37.0; H, 4.2; Co, 9.2.

1,6-Bis-(2′-pyridyl)-2,5-diazahexane (Xa).—Zinc dust (100 g.) was stirred vigorously in a solution of ethylene-diamine (15 g.) in 95% ethanol (500 ml.) and glacial acetic acid (100 ml.) at 60–70° and a solution of pyridine-2-aldehyde (53.5 g.) in ethanol (250 ml.) gradually added (1.5–2 hr.). Zinc dust and glacial acetic acid were added at intervals until a further 200 grams of each had been added. Stirring at 60–70° was continued for 5 hr. The mixture was allowed to stand overnight and was then filtered free from zinc acetate, zinc dust, etc. The filtrate was evaporated to a sirupy residue under reduced pressure and then made strongly alkaline with sodium hydroxide. The light brown oil which separated was collected and dried in ether with anhydrous sodium sulfate. It was then fractionally distilled *in vacuo*. A pale yellow oil (42 g.) b.p. 186–190° (1 mm.) was collected. The oil (0.24 g.) and piperonal (0.15 g.) were heated together strongly for a few minutes. Water was extruded. The product crystallized on cooling and was recrystallized from ethanol. This **1,3-bis-(2′-pyridylmethyl)-2-(3″,4″-methylene-dioxyphenyl)-imidazolidine (XIa)** had m.p. 109.5°.

Anal. Calcd. for $C_{22}H_{22}N_4O_2$: C, 70.6; H, 5.9. Found: C, 70.6; H, 5.9.

1,6-Bis-(6′-methyl-2′-pyridyl)-2,5-diazahexane (Xb) was prepared from 6-methylpyridine-2-aldehyde and ethylenediamine by an exactly similar method. It was a yellow oil, b.p. 188–190° (1 mm.). Its piperonylidine derivative **1,3-bis-(6′-methyl-2′-pyridylmethyl)-2-(3″,4″-methylenedioxyphenyl)-imidazolidine (XIb)**, crystallized from aqueous ethanol had m.p. 125°.

Anal. Calcd. for $C_{24}H_{26}N_4O_2$: C, 71.7; H, 6.5. Found: C, 71.0; H, 6.4.

Chloro-{1,6-bis-(2′-pyridyl)-2,5-diazahexane}-copper(II) Chloride-1.5-hydrate (XIIIa).—A solution of copper(II) chloride-2-hydrate (0.34 g.) in ethanol (5 ml.) was added to a hot solution of Xa (0.48 g.) in ethanol (5 ml.). The deep blue solution was warmed for a few minutes. On cooling bright blue crystals separated. They were washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $[CuC_{14}H_{18}N_4Cl]Cl\cdot 1^1/_2H_2O$: C, 41.6; H, 5.2; Cl, 17.6; Cu, 15.8. Found: C, 41.7; H, 5.2; Cl, 17.6; Cu, 15.8.

Bromo-{1,6-bis-(2′-pyridyl)-2,5-diazahexane}-copper(II) Bromide (XIIIb).—This salt was prepared similarly to XIIIa. It was *paramagnetic* with a magnetic moment of 1.7 B.M. at 27°.

Anal. Calcd. for $[CuC_{14}H_{18}N_4Br]Br$: C, 36.1; H, 3.9; Br, 34.3; Cu, 13.7. Found: C, 36.8; H, 4.2; Br, 34.4; Cu, 13.4.

Bromo-{1,6-bis-(2′-pyridyl)-2,5-diazahexane}-copper(II) Perchlorate (XIIIc.).—An ethanolic solution of sodium perchlorate was added to a hot solution of the salt XIIIb (0.2 g.) in ethanol (15 ml.). On cooling bright blue crystals of the complex perchlorate separated. They were washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $[CuC_{14}H_{18}N_4Br]ClO_4$: C, 34.6; H, 3.8; Cu, 13.2. Found: C, 34.9; H, 4.1; Cu, 13.0.

Tris-{1,6-bis-(2′-pyridyl)-2,5-diazahexane}-dinickel(II) Chloride-6-hydrate (XVI).—A solution of Xa (7.26 g.) in ethanol (15 ml.) was added to a suspension of nickel(II) chloride-6-hydrate (4.76 g.) in ethanol (15 ml.). Heat was evolved and the salt rapidly dissolved giving a red-violet solution which was heated on a water-bath for 0.5 hr. After cooling excess ether was added carefully when pale lilac crystals of the complex salt separated. They were recrystallized from a methanol–ether mixture. The salt was *paramagnetic* with a magnetic moment of 2.9 B.M. at 27° per nickel atom.

Anal. Calcd. for $[Ni_2C_{42}H_{54}N_{12}]Cl_4\cdot 6H_2O$: C, 46.1; H, 6.1; Cl, 13.0; Ni, 10.8. Found: C, 45.9; H, 5.9; Cl, 12.7; Ni, 10.5.

Tris-{1,6-bis-(2′-pyridyl)-2,5-diazahexane}-dinickel(II) Perchlorate.—Addition of sodium perchlorate to an aqueous solution of the above-described complex chloride caused the lilac complex perchlorate to separate. It was recrystallized from hot water and was *paramagnetic* with a magnetic moment of 3.0 B.M. at 27° per nickel atom.

Anal. Calcd. for $[Ni_2C_{42}H_{54}N_{12}](ClO_4)_2$: C, 40.6; H, 4.4; Ni, 9.5. Found: C, 40.7; H, 4.5; Ni, 9.8.

{1,6-Bis-(2′-pyridyl)-2,5-diazahexane}-*α,α′*-bipyridine ruthenium (II) Perchlorate-2-hydrate (XIVa).—A solution of Xa (0.3 g.) in ethanol (3 ml.) was added to a hot solution of ammonium tetrachlorobipyridineruthenate(III) (0.3 g.) in water (12 ml.). An intense red-brown color developed immediately. The mixture was heated on a boiling water-bath for 1 hr. Sodium perchlorate was then added. A light orange precipitate separated on cooling. This was collected and recrystallized from hot water.

Anal. Calcd. for $[RuC_{24}H_{26}N_6](ClO_4)_2\cdot 2H_2O$: C, 39.2; H, 4.1; Ru, 13.8. Found: C, 38.7; H, 3.9; Ru, 14.0.

Chloro-{1,6-bis-(6′-methyl-2′-pyridyl)-2,5-diazahexane}-copper(II) Chloride-1-hydrate (XIIId).—A solution of copper(II) chloride-2-hydrate (0.85 g.) in ethanol (8 ml.) was added to a solution of Xb (1.35 g.) in ethanol (10 ml.). A deep royal blue color developed immediately. Ether (15 ml.) was slowly added and bright blue crystals of the complex chloride separated.

Anal. Calcd. for $[CuC_{16}H_{22}N_4Cl]Cl\cdot H_2O$: C, 45.4; H, 5.7; Cu, 15.1. Found: C, 44.9; H, 5.5; Cu, 15.3.

Chloro-{1,6-bis-(6′-methyl-2′-pyridyl)-2,5-diazahexane}-copper(II) Perchlorate (XIIIe).—Sodium perchlorate solution was carefully added to a warm aqueous solution of XIIId. Deep blue crystals of the complex perchlorate separated. They were washed with cold water and dried *in vacuo*.

Anal. Calcd. for $[CuC_{16}H_{22}N_4Cl]ClO_4$: C, 40.9; H, 4.7; Cu, 13.6. Found: C, 40.8; H, 4.6; Cu, 13.5.

{1,6-(6′-Methyl-2′-pyridyl)-2,5-diazahexane}-*αα′*-bipyridine Ruthenium(II) Perchlorate-2-hydrate.—This complex salt was prepared by a method exactly similar to that used to obtain the corresponding complex salt with Xa.

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(13) F. P. Dwyer and F. Lions, THIS JOURNAL, **72**, 1545 (1950).

Anal. Calcd. for $[RuC_{25}H_{30}N_6](ClO_4)_2 \cdot 2H_2O$: C, 40.9; H, 4.5; Ru, 13.3. Found: C, 40.7; H, 4.2; Ru, 13.1.

1,6-Bis-(2′-pyridyl)-2,5-diazahexane Copper(II) Perchlorate (XIIa).—Hot solutions of Xa (0.48 g.) in ethanol (10 ml.) and copper(II) perchlorate-6-hydrate (0.74 g.) in ethanol were mixed and the resultant deep blue-violet solution boiled for a few minutes. On cooling deep blue-violet crystals of the complex salt separated. They were washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $[CuC_{14}H_{18}N_4](ClO_4)_2$: C, 33.3; H, 3.6. Found: C, 32.8; H, 3.7.

1,6-Bis-(6′-methyl-2′-pyridyl)-2,5-diazahexane Copper (II) Perchlorate (XIIb).—Hot solutions of Xb (0.68 g.) in ethanol (5 ml.) and copper(II) perchlorate-6-hydrate (0.93 g.) in ethanol (15 ml.) were mixed. A very dark blue color developed and on cooling dark blue needles deposited. After washing with ethanol they were dried *in vacuo*.

Anal. Calcd. for $[CuC_{16}H_{22}N_4](ClO_4)_2$: C, 36.0; H, 4.1; Cu, 12.0. Found: C, 35.8; H, 4.2; Cu, 11.7.

{1,6-Bis-(6′-methyl-2′-pyridyl)-2,5-diazahexane}-pyridine Copper(II) Perchlorate (XIIIf).—Addition of dry pyridine in excess to the hot solution of XIIb prepared above led to separation of a less soluble somewhat lighter blue complex salt. The crystals were washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $[CuC_{21}H_{27}N_5](ClO_4)_2$: C, 41.2; H, 4.4; Cu, 10.4. Found: C, 41.1; H, 4.5; Cu, 10.3.

1,5-Bis-(8′-quinolyl)-1,5-dithiapentane (XVIIb).—A solution of 8-thiolquinoline (8 g.) in absolute ethanol (15 ml.) was added with stirring to a solution of sodium ethoxide [from sodium (1.2 g.) and absolute ethanol (25 ml.)]. The yellow sodium salt of the thiol separated at once. 1,3-Dibromopropane (5.1 g.) was then added. Heat was evolved and sodium bromide deposited. The mixture was heated under reflux for 1 hr., then filtered. The product crystallized from the filtrate on cooling. It was washed with water and recrystallized from hot ethanol (6 g.). It melted at 68°.

Anal. Calcd. for $C_{21}H_{18}N_2S_2$: C, 69.6; H, 5.0. Found: C, 69.0; H, 4.9.

1,5-Bis-(8′-quinolyl)-1,5-dithiapentane Copper(II) Tetrachlorocuprate(II) (XVIIIa).—A solution of copper(II) chloride-2-hydrate (0.68 g.) in ethanol (10 ml.) was carefully added to a solution of XVIIb (0.72 g.) in ethanol (15 ml.). A bright green color developed and the product crystallized. It was collected, washed with ethanol and then recrystallized from a dimethylformamide–ethanol mixture. The complex salt was *paramagnetic* with a magnetic moment of 1.8 B.M. per copper atom at 20°.

Anal. Calcd. for $[CuC_{21}H_{18}N_2S_2][CuCl_4]$: C, 39.9; H, 2.9; N, 4.4; Cu, 20.3. Found: C, 40.1; H, 3.0; N, 4.5; Cu, 20.2.

1,5-Bis-(8′-quinolyl)-1,5-dithiapentane Copper(II) Perchlorate-1-hydrate (XVIIId).—A solution of copper(II) perchlorate-6-hydrate (0.37 g.) in hot ethanol (10 ml.) was added to a hot solution of XVIIb (0.36 g.). A bright green solution was obtained and green crystals of the complex salt soon separated. They were washed with alcohol and dried *in vacuo*. The salt dissolved slightly in water to a green solution but gradual decomposition occurred.

Anal. Calcd. for $[CuC_{21}H_{18}N_2S_2](ClO_4)_2 \cdot H_2O$: C, 39.2; H, 3.1. Found: C, 39.0; H, 3.1.

1,5-Bis-(8′-quinolyl)-1,5-dithiapentane Copper(I) Perchlorate (XVIIIe).—Sulfur dioxide was bubbled through a suspension of XVIIId in ethanol until a yellow solution was obtained. It was filtered and dry ether added to the filtrate when the product crystallized. It was recrystallized from a dimethylformamide–ether mixture.

Anal. Calcd. for $[CuC_{21}H_{18}N_2S_2]ClO_4$: C, 48.0; H, 3.5. Found: C, 47.7; H, 3.7.

1,5-Bis-(8′-quinolyl)-1,5-dithiapentane Platinum(II) Tetrachloroplatinate(II)-1-hydrate (XVIIIc).—A solution of potassium tetrachloroplatinate(II) (0.42 g.) in water (5 ml.) was slowly added to a solution of (XVIIb) (0.18 g.) in ethanol (18 ml.). The solution immediately became cloudy and on boiling small yellow prisms separated. They were washed with ethanol and water, then air dried.

Anal. Calcd. for $[PtC_{21}H_{18}N_2S_2][PtCl_4] \cdot H_2O$: C, 27.6; H, 2.2; Pt, 42.8; N, 3.1. Found: C, 27.9; H, 2.5; Pt, 42.9; N, 3.1.

1,5-Bis-(8′-quinolyl)-1,5-dithiapentanepalladium(II) Tetrachloropalladate(II) (XVIIIb).—This salt was prepared by a method exactly similar to that used for XVIIIc.

Anal. Calcd. for $[PdC_{21}H_{18}N_2S_2][PdCl_4]$: C, 35.1; H, 2.5; Pd, 29.8; N, 3.9. Found: C, 35.7; H, 2.7; Pd, 29.6; N, 3.6.

Dichloro-{1,5-bis-(8′-quinolyl)-1,5-dithiapentane}-nickel (II).—A solution of the base XVIIb (0.36 g.) in ethanol (15 ml.) was added to a solution of nickel(II) chloride-6-hydrate (0.24 g.) in ethanol (5 ml.), the mixture heated under reflux for 1 hr. and then evaporated to a volume of about 8 ml. On cooling light brown-green crystals separated. They were collected, washed with alcohol and ether and air dried. They were *paramagnetic* with a magnetic moment of 3.2 B.M. at 24°.

Anal. Calcd. for $[NiC_{21}H_{18}N_2S_2Cl_2]$: C, 51.2; H, 3.7; Ni, 12.0. Found: C, 50.5; H, 3.7; Ni, 12.0.

1,8-Bis-(2′-pyridyl)-3,6-Dithiaoctane (XIX).—At room temperature ethylene dithiol (14.1 g.) was added to freshly distilled 2-vinylpyridine (31 g.) and the flask stoppered. The colorless mixture gradually became hot (temperature rise to about 80°) and acquired a pale yellow color. It set to a solid crystalline mass on being allowed to stand overnight. Recrystallized from petroleum ether it formed elongated needles, m.p. 51–52°.

Anal. Calcd. for $C_{16}H_{20}N_2S_2$: C, 63.2; H, 6.6. Found: C, 62.9; H, 6.4.

The *di-picrate* formed yellow prisms, m.p. 149–150°, from ethanol. *Anal.* Calcd. for $C_{28}H_{26}N_5O_7S_2$: C, 44.1; H, 3.5. Found: C, 43.9; H, 3.4.

1,8-Bis-(2′-pyridyl)-3,6-dithiaoctane Copper(II) Perchlorate-1-hydrate (XXa).—A solution of XIX (1.3 g.) in ethanol (4 ml.) was added to a solution of copper(II) sulfate-5-hydrate (1.3 g.) in water (20 ml.). A deep royal blue color developed. The solution was warmed for a few minutes, filtered and sodium perchlorate solution carefully added to the filtrate. Deep blue crystals of the complex salt deposited. They were collected, washed with cold water and then recrystallized from hot water.

Anal. Calcd. for $[Cu(C_{16}H_{20}N_2S_2)](ClO_4)_2 \cdot H_2O$: C, 32.8; H, 3.8; Cu, 10.9. Found: C, 33.1; H, 3.6; Cu, 10.9.

This complex salt was *paramagnetic* with a magnetic moment of 1.82 B.M. at 24°. Its molecular conductivity in water was 220 mhos (0.001*M* solution).

1,8-Bis-(2′-pyridyl)-3,6-dithiaoctane Copper(I) Perchlorate (XXb).—Sodium hydrosulfite solution was carefully added to a solution of the complex copper(II) perchlorate just described (0.2 g. in 20 ml.), the sides of the container being scratched the while. The blue color faded and a white crystalline precipitate of the *diamagnetic* complex copper(I) perchlorate was deposited. It was collected, washed with cold water and dried *in vacuo*.

Anal. Calcd. for $[CuC_{16}H_{20}N_2S_2]ClO_4$: C, 41.0; H, 4.3; Cu, 13.7; Found: C, 41.5; H, 4.1; Cu, 13.9.

Dichloro-{1,8-bis-(2′-pyridyl)-3,6-dithiaoctane}-nickel (II).—A solution of XIX (0.3 g.) in ethanol (5 ml.) was added to a solution of nickel(II) chloride-6-hydrate (0.23 g.) in ethanol (5 ml.). The solution quickly turned red-brown and then, ultimately, green. The product crystallized on addition of a small amount of ether. It was washed with a little ethanol and dried *in vacuo*.

Anal. Calcd. for $[NiC_{16}H_{20}N_2S_2Cl_2]$: C, 44.2; H, 4.7; Ni, 13.6. Found: C, 43.6; H, 4.6; Ni, 13.7.

This salt was *paramagnetic* with a moment of 3.1 B.M. at 24°. It was soluble in organic solvents but rapidly decomposed in water liberating the organic base.

1,8-Bis-(2′-pyridyl)-3,6-dithiaoctane Platinum(II) Perchlorate (XXc).—A solution of potassium tetrachloroplatinate(II) (0.41 g.) in water (15 ml.) was added to a solution of XIX (0.3 g.) in ethanol (3 ml.). A dark oily precipitate quickly separated, but this dissolved to a clear yellow solution on gentle warming and stirring. Addition of sodium perchlorate then caused separation of cream colored crystals of the product which were washed with cold water and dried *in vacuo*. The salt was *diamagnetic*.

Anal. Calcd. for $[PtC_{16}H_{20}N_2S_2](ClO_4)_2$: C, 27.5; H, 2.9; Pt, 27.9. Found: C, 27.8; H, 3.2; Pt, 27.6.

1,8-Bis-(2′-pyridyl)-3,6-dithiaoctane Palladium(II) Perchlorate (XXd).—This bright yellow *diamagnetic* salt was prepared exactly similarly to XXc.

Anal. Calcd. for $[PdC_{16}H_{20}N_2S_2](ClO_4)_2$: C, 31.5; H, 3.3; Pd, 17.5. Found: C, 31.1; H, 3.3; Pd, 17.4.

[1,8-Bis-(2′-pyridyl)-3,6-dithiaoctane]-αα′-bipyridine Ruthenium(II) Perchlorate-4-hydrate (XXI).—A solution of XIX (0.08 g.) in ethanol (5 ml.) was added to a solution of ammonium tetrachloro-αα′-bipyridine ruthenate(III) (0.11 g.) in hot water (10 ml.) and the mixture heated on a water-bath for several hours. The color changed gradually from deep-green to light orange brown. Addition of sodium perchlorate then caused separation of the light-brown crystalline complex perchlorate. It was washed with cold water and recrystallized from ethanol–ether.

Anal. Calcd. for $[RuC_{26}H_{28}N_4S_2](ClO_4)_2 \cdot 4H_2O$: C, 37.5; H, 4.4; Ru, 12.2. Found: C, 37.8; H, 4.2; Ru, 12.0.

2,2′-Bis-(2″-pyridylmethylamino)-biphenyl (XXIII).—A solution of pyridine-2-aldehyde (10.7 g.) in ethanol (5 ml.) was gradually added to a vigorously stirred hot solution of 2,2′-diaminobiphenyl (9.2 g.) in ethanol (200 ml.) and glacial acetic acid (100 ml.) in which zinc dust (100 g.) was dissolving. Further additions of ethanol, acetic acid and zinc dust were made during the course of 3 hr. The hot solution was then filtered rapidly and ethanol and excess acetic acid removed by repeated dilution with water and evaporation under reduced pressure. Some crystalline zinc acetate was also removed. Eventually, excess of cold concentrated sodium hydroxide solution was added. The heavy oil which separated was induced to crystallize by the addition of ether. It was recrystallized from ethanol as colorless prisms, m.p. 137°.

Anal. Calcd. for $C_{24}H_{22}N_4$: C, 78.7; H, 6.1. Found: C, 78.3; H, 6.1.

2,2′-Bis-(2″-pyridylmethylamino)-biphenyl Palladium(II) Perchlorate (XXIVa).—A solution of potassium tetrachloropalladate(II) (0.33 g.) in water (15 ml.) was stirred into a solution of XXIII (0.37 g.) in hot ethanol (5 ml.). The bright orange solution obtained was heated to boiling and filtered. Sodium perchlorate was added to the filtrate which was then cooled. The light orange crystals which separated were collected, washed with cold water and dried *in vacuo*.

Anal. Calcd. for $[PdC_{24}H_{22}N_4](ClO_4)_2$: C, 42.9; H, 3.3. Found: C, 42.5; H, 3.4.

2,2′-Bis-(2″-pyridylmethylamino)-biphenyl Copper(II) Chloride-1-hydrate (XXIVb).—A solution of copper(II) chloride-2-hydrate (0.34 g.) in ethanol (8 ml.) was gradually stirred into a solution of XXIII (0.74 g.) in hot ethanol (12 ml.). A deep green solution was obtained from which green crystals deposited on cooling. These were collected, washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $[CuC_{24}H_{22}N_4]Cl_2 \cdot H_2O$: C, 55.5; H, 4.7. Found: C, 55.8; H, 4.6.

2,2′-Bis-(2″-pyridylmethylamino)-biphenyl Copper(II) Perchlorate-2-hydrate (XXIVc).—Sodium perchlorate was added to a warm aqueous solution of XXIVb. Dark green crystals separated. They were collected, washed with water and dried *in vacuo*. When tested they were found to be quite free from chloride ion.

Anal. Calcd. for $[CuC_{24}H_{22}N_4](ClO_4)_2 \cdot 2H_2O$: C, 43.3; H, 3.9. Found: C, 43.3; H, 3.6.

{2,2′-Bis-(2″-pyridylmethylamino)-biphenyl}-α,α′-bipyridine Ruthenium(II) Perchlorate (XXV).—A solution of XXIII (0.37 g.) in ethanol (5 ml.) was added to a solution of ammonium α,α′-bipyridine tetrachlororuthenate(III) (0.42 g.) in hot water (15 ml.). An intense red-violet color quickly developed. The mixture was heated on a water-bath for 1 hr., the color gradually changing to a deep orange-brown. Addition of sodium perchlorate and cooling caused separation of a crystalline precipitate. This was recrystallized from methanol and dried *in vacuo*.

Anal. Calcd. for $[RuC_{34}H_{30}N_6](ClO_4)_2$: C, 49.6; H, 3.7. Found: C, 49.7; H, 3.8.

2,2′-Bis-(8″-quinolylmethyleneamino)-biphenyl (XXVI).—Hot solutions in ethanol of quinoline-8-aldehyde[12] (6 g. in 10 ml.) and 2,2′-diaminobiphenyl (3.5 g. in 10 ml.) were mixed and gently boiled for a few minutes. The product crystallized on cooling. Recrystallized from much ethanol it had m.p. 187°.

Anal. Calcd. for $C_{32}H_{22}N_4$: C, 83.1; H, 4.8. Found: C, 82.5; H, 4.8.

2,2′-Bis-(8″-quinolylmethyleneamino)-biphenyl Copper (II) Perchlorate (XXVII).—A solution of copper(II) perchlorate-6-hydrate (0.37 g.) in ethanol (5 ml.) was added to a hot solution of XXVI (0.46 g.) in ethanol (15 ml.). A deep brown solution resulted. On cooling and scratching the dark-brown crystalline complex perchlorate separated. It was washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $[CuC_{32}H_{22}N_4](ClO_4)_2$: C, 53.0; H, 3.1. Found: C, 53.0; H, 3.5.

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Magnetic and Spectral Properties of the Spin-Free 3d^6 Systems Iron(II) and Cobalt(III) in Cobalt(III) Hexafluoride Ion: Probable Observation of Dynamic Jahn–Teller Effects

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The electronic (d–d) absorption spectra of the 3d^6 systems in several salts containing either $[Fe(H_2O)_6]^{+2}$ or $[CoF_6]^{-3}$ have been studied. In all cases this is a distorted or double absorption band contrary to what would be expected assuming Russell–Saunders coupling and ligand fields of regular octahedral symmetry. It is concluded that spin-orbit coupling effects are an order of magnitude too small to account for the observed splittings and that in only a few cases might the splittings be attributable to permanent, ground-state distortion of the octahedra. It is proposed that in most cases these splittings are due to a dynamic Jahn–Teller effect in the electronic excited states. The order of magnitude of the splittings agrees well with a prior theoretical estimate made by Liehr and Ballhausen. The magnetic behavior of Co(III) in K_3CoF_6 is shown to agree well with theoretical predictions contrary to the implication of earlier data.

Introduction

The electronic state and the consequent spectral and magnetic properties of the cobalt ion (Co^{3+}) when octahedrally coördinated and spin-free (*i.e.*, with four unpaired electrons) are of considerable interest. Such ions are known to occur in a few oxide systems. Thus, for example, in the spinels, $MnCo_2O_4$ and $ZnCo_2O_4$, Lotgering has concluded that 5.5 and 15.5%, respectively, of the cobaltic ions are in the spin-free state,[1] and Jonker and van Santen find spin-free cobaltic ions in the perovskite

[1] F. K. Lotgering, *Philips Research Rept.*, **11**, 337 (1956).