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Sexadentate Chelate Compounds. VIII[1]

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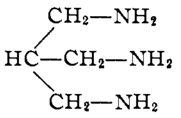
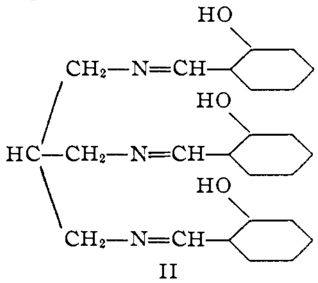
The tris-salicylidene and tris-(α-pyridylmethylene) derivatives of 2-aminomethyl-1,3-diaminopropane have been prepared and shown to function as sexadentate chelate compounds. So also does the bis-(α-pyridylmethylene) derivative of EEE base with iron(II) salts, giving stable complex iron(II) salts. With cobalt(II) salts, however, it appears to coördinate as a quinquedentate[2] chelate compound.

2-Aminomethyl-1,3-diaminopropane (I) forms a tris-salicylidene derivative II. It was pointed out in Part I[3] of this series of papers that II should be capable of functioning as a sexadentate chelate compound. This paper briefly describes the preparation of dark-red cobalt(III) and iron(III) complexes (IIIa and IIIb) from II. The iron(III) complex is obtained by interaction of solutions of either iron(II) or iron(III) salts and of II in presence of sodium acetate, whilst IIIa is obtained from cobalt(II) acetate and II followed by hydrogen peroxide oxidation. Each metal derivative is capable of sublimation *in vacuo* but there is considerable simultaneous decomposition.

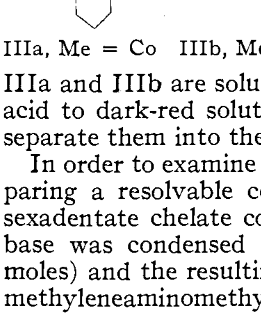


I

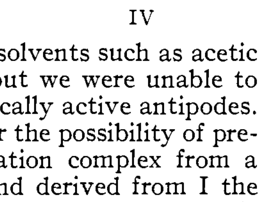


II

It was also pointed out in Part I that because of the octahedral disposition of the six metal atom valences in the inner complexes IIIa and IIIb the circumscribing organic moiety of each molecule would have to be so disposed about the central metal atom that there would be, of necessity, a partial right-hand or left-hand spiral arrangement corresponding to non-superposable enantiomorphous forms. The non-salt-like inner complexes IIIa and IIIb are soluble in solvents such as acetic acid to dark-red solutions, but we were unable to separate them into their optically active antipodes.



IIIa, Me = Co IIIb, Me = Fe



IV

In order to examine further the possibility of preparing a resolvable coördination complex from a sexadentate chelate compound derived from I the base was condensed with pyridine-2-aldehyde (3 moles) and the resulting crude oily tris-(α-pyridylmethyleneaminomethyl)-methane (IV) caused to react in solution with iron(II) sulfate. The resulting complex iron(II) salt was converted to the iodide and the perchlorate which were isolated as dihydrates. These salts are distinguished by their

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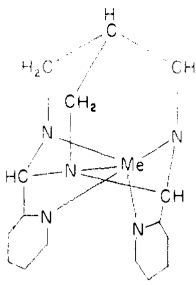
[1] For the previous communication in this series see F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, THIS JOURNAL, **76**, 383 (1954).

[2] The authors would draw attention to the lack of precision creeping into the nomenclature of multidentate chelate compounds. It is surely better to use words derived solely from Greek, or alternatively, Latin roots. Words such as multidendate or polydontate, sexadentate or hexadontate, should be permissible, but bilingual hybrids such as polydentate or hexadentate should be avoided.

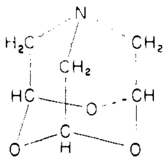
[3] F. P. Dwyer and F. Lions, THIS JOURNAL, **72**, 1545 (1950).

violet color which is so intense that their formation can be used to show the presence of iron(II) salts in concentrations as low as one part in five millions.

Despite repeated efforts using most of the well-known resolving agents, no success was attained in attempts to resolve these salts—a result to be attributed to failure to find a suitable resolving agent. At first sight it would appear that the complex ions of these salts could be formulated as possessing a high degree of symmetry (partial formulation V). In this formulation the azomethine double bonds have been replaced by a system in which each methine carbon atom (from the aldehyde group of a pyridine-2-aldehyde residue) becomes linked to each of two of the three nitrogen atoms of I forming a cage-ring system.



V



VI

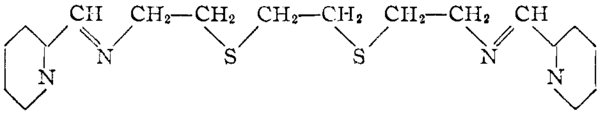
In the molecule of hexamethylenetetramine the four nitrogen atoms are linked through single carbon atoms in a very similar cage-ring structure, whilst hydrolysis of tris-acetalylamine yields not the tri-aldehyde but the very stable ring compound "trimorpholin" (VI).[4]

A model of the organic residue V without the metal atom can be readily built up strainlessly. However, it shows quite clearly that the direction to be taken up by each fourth (coördination) covalence of each of the three nitrogen atoms derived from the residue of I would then be *outward* and not toward the central point which would have to be occupied by a 6-covalent metal atom if the organic molecule were functioning as a sexadentate chelate. The potential fourth valence of each nitrogen atom of the hexamethylenetetramine molecule is similarly directed *outward* from the center of the cage. It is concluded, therefore, that IV must be formulated as a tris-azo-methine compound when it coordinates as a sexadentate chelate compound.

The complex iron(II) salts derived from IV are distinguished by their marked resistance to oxidation to the iron(III) state. Even cerium(IV) nitrate in acid solution fails to remove an electron, indicating the relatively high valence state stabilization conferred by this chelate arrangement. The three metal–pyridine–nitrogen atom bonds are arranged mutually at right angles in the complex ions, an arrangement which should lead to maximum stability according to Kimball,[5] because there is always the possibility of resonance double bonding owing to the unsaturated nature of the pyridine rings.

These complex iron(II) salts derived from IV break down when their aqueous solutions are boiled, pyridine-2-aldehyde being extruded. Bailar and Eichorn[6] have drawn attention to the role of metal ion catalysis in Schiff base hydrolysis. It is possible to obtain complex salts containing ruthenium or rhodium central metal atoms but further examination of these has been postponed.

Condensation of 1,8-diamino-3,6-dithiaoctane (EEE base; *cf.* Part III[7]) with pyridine-2-aldehyde yields 1,8-bis-(α-pyridylmethyleneamino)-3,-6-dithiaoctane (VII) which can be combined with various metal salts to give complex salts containing VII in the cation. With iron(II) salts violet complex salts are obtained of which the perchlorate $[Fe(C_{18}H_{22}N_4S_2)](ClO_4)_2$ and the iodide dihydrate $[Fe(C_{18}H_{22}N_4S_2)]I_2 \cdot 2H_2O$ were isolated pure. The complex cations of these salts exist in enantiomorphous forms and resolution was effected through the *d*-antimonyl tartrate salts. Optically active iodide dihydrates were obtained with $[\alpha]^{20}\mathrm{D}$ ±2,600° and $[M]^{20}\mathrm{D}$ ±18,300°. If the *d*-antimonyl tartrate solutions are kept warm during the resolution a second-order asymmetric transformation occurs[8] and almost all the salt is obtained as l-complex-*d*-antimony tartrate. Solutions of the optically active complex iron(II) iodides racemize readily and even at 20° racemization is almost complete within 4 hours. Heating of solutions of these salts leads to decomposition, extrusion of pyridine-2-aldehyde and precipitation of iron(III) hydroxide. The complex iron(II) salts can be oxidized in solution with cerium(IV) nitrate to a purplish-blue compound, but this is unstable and could not be isolated pure.



VII

The constitutions to be ascribed to such complex salts as these resolvable iron(II) salts must be similar to those previously assigned to the complex cobalt(III) salts derived from the bis-salicylidene derivative of EEE base VIIII. It should, however, be noted that in the iron(II) complex salts of VII each "chelate loop"[8] is now a 5-atom chelate ring, whereas in the complexes derived from VIII chelate loops 1 and 5 each contain 6 atoms.

Addition of sodium iodide to the aqueous alcoholic solution of the complex cobalt(II) acetate, prepared by treating cobalt(II) acetate tetrahydrate with VII, causes precipitation of the stable iodide $[Co(C_{18}H_{22}N_4S_2)]I_2$ (IX). Oxidation of the complex cation of such salts is difficult and cannot be effected, for example, by the oxygen of the air, or by heating with aqueous hydrogen peroxide solution. The perchlorate can be oxidized by cerium(IV) nitrate in dilute nitric acid and a rather unstable cobalt(III) complex salt $[Co(C_{18}H_{22}N_4S_2)](ClO_4)_3$ isolated. It is instantly reduced by iodide

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[4] L. Wolff and R. Marburg, *Ann.*, **363**, 184 (1908).

[5] G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940); *cf.* also, D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

[6] G. L. Eichorn and J. C. Bailar, Jr., This Journal, **75**, 2905 (1953).

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

[8] *Cf.* E. E. Turner and M. M. Harris, *Quart. Rev.*, **1**, 299 (1948).

ion to the cobalt(II) complex with liberation of iodine. The magnetic moment of the perchlorate corresponding to IX, 1.85 Bohr magnetons, is indicative of strong covalent bonds but does not distinguish between octahedral, pyramidal-tetragonal (5-covalent) or planar (4-covalent) coördination. Models show that the organic molecule can accommodate itself to any of these configurations. Octahedral coördination would necessitate the promotion of the unpaired electron to an upper unstable orbital whence it should be detached easily by oxidation,[9] and this is at variance with the difficulty of effecting oxidation, and the reverse ease of reduction of the complex cobalt(III) salts. Since the large electronic promotional energy is a charge against the bond energy, octahedral cobalt(II) complexes involving lower orbital covalent bonds are rare. More stable complexes are usually formed by the use of upper orbital covalent bonds when the energy necessary for pairing electrons to provide vacant 3d orbitals is also obviated. If lower orbital bonds are favored by the possibility of π bonding, as in the present instance, reduction in the coördination number to 5 or 4 removes the necessity for electronic promotion. With multidentate organic molecules it would appear that in so far as the stereochemistry and the coördination number of the metal permit, the maximum number of coördinate bonds is formed. According to Daudel and Bucher[10] complexes with a central 5-covalent metal atom using $3d4s4p^3$ bonds will have a tetragonal pyramidal arrangement of the five donor atoms, with the metal atom in the plane containing four of them. A five-coördinated structure has been proposed for the complex ion of the compound $K_3Co(CN)_5$[11] whose magnetic moment also corresponds to one unpaired electron. The chelate compound VII can function as a quinquedentate with a tetragonal pyramidal arrangement of five of its donor atoms by merely leaving one of the terminal pyridine nitrogen atoms uncoördinated IX. It will be recalled that the suggestion was made in Part III[8] of this series of papers that isomerization of the green 1,10-bis-(salicylideneamino)-4,7-dithiadecane-cobalt(III) salts to the corresponding brown isomers involved preliminary breaking of the terminal oxygen–metal bonds followed by re-orientation and then re-formation of oxygen–metal bonds in alternative positions.

Formulation of the cobalt(II) complex salts derived from VII as containing a quinquedentate moiety requires that they should exist in enantiomorphous forms, but we were unable to effect resolution of them. Too much importance should not, however, be attached to this failure. We were unable previously to resolve the brown cobalt(III) salts derived from the bis-salicylidene derivative of TET base by any direct method but obtained the optically active forms by isomerization of the optically active green forms.[8] Because of π bonding sulfur forms stronger bonds to cobalt than nitrogen. Coordination with sulfur should be favored. Models show that it is not easy for VII to behave as a planar quadridentate chelate compound by leaving the terminal pyridine ring nitrogen atoms unattached, mainly because of the non-planar distribution of the three valences of 3-covalent sulfur. Finally, it should be remembered that the well-known relative instability of complexes with large rings makes it unlikely that our cobalt(II) complex should contain a quadridentate moiety with the two sulfur atoms unattached.

VII coördinates readily with copper(II) salts. The structure of the complex cation of the green 1,8-bis-(α-pyridylmethyleneamino)-3,6-dithiaoctane-copper(II) perchlorate (X) is of considerable interest. Das Sarma and Bailar[12] concluded from infrared studies that the organic chelate residue in the complex 1,8-bis-(salicylideneamino)-3,6-diazaoctane-copper(II) was functioning not as an octahedrally disposed sexadentate, but as a square-planar quadridentate with only four donor atoms coördinating with the metal atom. They demonstrated the existence of enantiomorphous forms, although only very low rotations were measured. It is worth pointing out that their results would accord equally well with the hypothesis that their chelate compound functions as a quinquedentate. Since all copper(II) complexes appear to be of the upper orbital type,[6] $4s4p^34d$ hybridization would be involved, and this should yield a trigonal bi-pyramidal arrangement of the bonds. This type of structure has been found to occur in terpyridine–cadmium(II) chloride and terpyridine–zinc(II) chloride and has been suggested for terpyridine–copper(II) chloride.[13] Models show that either VII or the 1,8-bis-(salicylideneamino)-3,6-diazaoctane residue of das Sarma and Bailar can be fitted practically strainlessly around either an octahedral or trigonal bipyramidal structure. In the absence of infrared data it is not possible to decide whether the complex copper(II) ion of X contains a sexadentate or a quinquedentate moiety. We do not favor a planar quadridentate arrangement.

Experimental

Tris-salicylidene-2-aminomethyl-1,3-diaminopropane(II).—To a solution of 2-aminomethyl-1,3-diaminopropane trihydrochloride[14] (5 g.) and sodium acetate (9.8 g.) in the minimum volume of warm water was added a hot solution of salicylaldehyde (8.78 g.) in ethanol. The mixture immediately became yellow and sodium chloride separated. After boiling for a few minutes sufficient water was added to dissolve the sodium chloride. The product crystallized on cooling—yellow needles, m.p. 133° (from ethanol).

Anal. Calcd. for $C_{25}H_{25}N_3O_3$: C, 72.3; H, 6.1; N, 10.1. Found: C, 72.3; H, 6.3; N, 10.2.

Tris-salicylidene-2-aminomethyl-1,3-diaminopropane-cobalt(III).—A solution of the Schiff base II (0.4 g.) in hot methanol (120 ml.) was added to a solution of cobalt(II) acetate tetrahydrate (0.2 g.) in methanol (25 ml.). The solution rapidly became dark-red in color. Hydrogen peroxide solution (5 ml. of 3%) was then added. The dark-red-brown leaflets which separated were collected and dried at 100°. This inner complex was sparingly soluble in chloroform to a pale yellow solution and dissolved in hot glacial acetic acid but was insoluble in the other common solvents. It could be sublimed at 400° at 2 mm. with partial melting and decomposition.

Anal. Calcd. for $C_{25}H_{22}N_3O_3Co$: C, 63.7; H, 4.7; N, 8.9; Co, 12.6. Found: C, 64.6; H, 4.9; N, 8.9; Co, 12.6.

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[9] *Cf.* L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1943.

[10] R. Daudel and A. Bucher, *J. chim. phys.*, **42**, 6 (1945).

[11] A. W. Adamson, THIS JOURNAL, **73**, 5710 (1951).

[12] B. das Sarma and J. C. Bailar, Jr., *ibid.*, **77**, 5476 (1955).

[13] D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1956).

[14] T. A. Geissman, M. J. Schlatter and I. D. Webb, *J. Org. Chem.*, **11**, 736 (1946).

Tris-salicylidene-2-aminomethyl-1,3-diaminopropane-iron(III) Monohydrate.—A solution of iron(II) chloride tetrahydrate (0.23 g.) in methanol (25 ml.) was added to a hot solution of II (0.4 g.) in methanol (120 ml.). The solution became dark red. A concentrated ethanolic solution of sodium acetate trihydrate (0.5 g.) was then added, followed by water (50 ml.). On cooling, the solution deposited dark red-brown micaceous plates. The same substance was obtained when iron(III) chloride was substituted for iron(II) chloride and is undoubtedly the iron(III) complex. It was insoluble in all the common solvents except hot glacial acetic acid. After decomposition with hot 2 *N* hydrochloric acid solution iron(III) ion could be detected in the solution. It could be partially sublimed at 400° at 2 mm., some decomposition occurring simultaneously.

Anal. Calcd. for $C_{25}H_{24}N_3O_4Fe$: C, 61.7; H, 4.9; N, 8.6. Found: C, 61.5; H, 5.0; N, 8.6.

Tris-(α-pyridylmethylene)-2-aminomethyl-1,3-diaminopropane-iron(II) Iodide Trihydrate.—A solution containing redistilled pyridine-2-aldehyde (3.2 g.) and 2-aminomethyl-1,3-diaminopropane (1.03 g.) in methanol (10 ml.) was boiled gently for 2–3 minutes and then a solution of iron(II) chloride tetrahydrate (2 g.) in methanol (20 ml.) added. The intensely permanganate-colored solution was maintained at 60° for a few minutes, after which solid sodium iodide (5 g.) was added. The mixture was then cooled in ice. The precipitate of sodium chloride admixed with a little iron(III) hydroxide was filtered off and the complex iodide precipitated with ether as a black oil which solidified on scratching. It was recrystallized twice from methanol–ether and obtained in black needles extremely soluble in water and methanol but only moderately so in ethanol and acetone.

Anal. Calcd. for $[C_{22}H_{22}N_6Fe]I_2 \cdot 3H_2O$: Fe, 7.6; N, 11.4. Found: Fe, 7.7; N, 11.2.

Tris-(α-pyridylmethylene)-2-aminomethyl-1,3-diaminopropane-iron(II) Perchlorate Trihydrate.—Aqueous sodium perchlorate solution (1 ml. of 30%) was added to a solution of the above-described iodide (1 g.) in methanol (30 ml.). Ether was then added. The fine black precipitate was collected and recrystallized from warm methanol by the addition of ether and thus obtained in black needles, very soluble in water but less soluble than the above-described iodide.

Anal. Calcd. for $[C_{22}H_{22}N_6Fe](ClO_4)_2 \cdot 3H_2O$: C, 38.8; H, 4.1; N, 12.4. Found: C, 39.1; H, 4.0; N, 12.4.

1,8-Bis-(α-pyridylmethyleneamino)-3,6-dithiaoctane (VII).—Freshly-distilled pyridine-2-aldehyde (3.21 g.) was added to a solution of 1,8-diamino-3,6-dithiaoctane (2.7 g.) in ethanol (10 ml.) and the solution gently boiled for a few minutes. Some of the alcohol was allowed to evaporate and the residue allowed to stand for some days, when the product crystallized (yield 80%). It was recrystallized from ether and obtained in colorless needles, m.p. 59–60°.

Anal. Calcd. for $C_{18}H_{22}N_4S_2$: C, 60.3; H, 6.2. Found: C, 60.1; H, 6.4.

***dl*-Bis-(α-pyridylmethyleneamino)-3,6-dithiaoctane-iron(II) Iodide Dihydrate.**—A solution of iron(II) sulfate heptahydrate (2.48 g.) in water (50 ml.) at 40° was treated with a solution of the base VII (3.6 g.) in ethanol (10 ml.). The resulting intensely reddish-purple solution was filtered free from a small amount of iron(III) hydroxide and solid potassium iodide (10 g.) added. The very dark-brown microcrystalline precipitate was collected, washed with a little ice-water and recrystallized from hot water to which potassium iodide was added. It came out in black prisms readily soluble in water or ethanol to intensely reddish-purple solutions. On boiling, these gave an odor of pyridine-2-aldehyde and deposited iron(III) hydroxide. The solutions are much more stable in presence of dilute acid. Thus, there was no evidence of decomposition after a week in 0.1 *N* hydrochloric acid. The substance was diamagnetic (*cf.* tris-(α,α'-dipyridyl)–iron(II) salts), indicating strong lower level covalent bonds.

Anal. Calcd. for $[C_{18}H_{22}N_4S_2Fe]I_2 \cdot 2H_2O$: C, 30.7; H, 3.7; N, 7.9; Fe, 7.9. Found: C, 30.7; H, 3.7; N, 7.9; Fe, 8.0.

***dl*-1,8-Bis-(α-pyridylmethyleneamino)-3,6-dithiaoctane-iron(II) Perchlorate Dihydrate.**—Addition of 10% aqueous sodium perchlorate solution to a warm moderately concentrated solution of the above-described iodide led to separation of the perchlorate, which, after recrystallization from hot water to which sodium perchlorate was added, formed very dark-red to black needles.

Anal. Calcd. for $[C_{18}H_{22}N_4S_2Fe](ClO_4)_2 \cdot 2H_2O$: Fe, 8.6; N, 8.6. Found: Fe, 8.7; N, 8.7.

A solution of this substance in *N* nitric acid when treated with cerium(IV) nitrate developed a deep-blue color, due, presumably, to formation of an unstable iron(III) complex. This could not be isolated. Addition of reducing agents restored the original reddish-purple color.

***l*-1,8-Bis-(α-pyridylmethyleneamino)-3,6-dithiaoctane-iron(II) Iodide Dihydrate.**—A solution of the above-described *dl*-complex iodide (2 g.) in warm water (50 ml.) was shaken for 15 minutes with silver *d*-antimonyl tartrate (2.1 g.) and the precipitated silver iodide removed by filtration. The filtrate was cooled to 10° and absolute ethanol gradually added whilst the sides of the vessel were vigorously scratched with a glass rod. The *l*-complex–*d*-antimonyl tartrate separated in fine red needles. Examination of subsequent crops of crystals showed them to contain more and more of the *d*-complex–*d*-antimonyltartrate. However, if the solution were kept between 30 and 35° all the salt deposited was the *l*-complex–*d*-antimonyl tartrate. The first fractions were dissolved in water at 20° and potassium iodide was added. The solid complex iodide which came out was collected and purified by taking up in cold methanol and reprecipitating with dry ether, the process being repeated many times. The salt obtained in the first fractions eventually was pure.

Anal. Found: C, 30.5; H, 3.8; N, 7.9.

A 0.01% solution in water at 20° in a 1 dm. tube gave α_D −0.26°, whence $[\alpha]^{20}D$ −2600° and $[M]^{20}D$ −18,300°. The aqueous solution still showed a slight rotation after 4 hours at 20° but was zero rotatory after 24 hours.

***d*-1,8-Bis-(α-pyridylmethyleneamino)-3,6-dithiaoctane-iron(II) Iodide Dihydrate.**—The salt recovered from the most soluble fractions in the fractional crystallization of the complex *d*-antimony tartrate salt from cold solution was converted to the iodide and crystallized several times from methanol–ether as described above for the isomer. Only a small amount of the *d*-complex–*d*-antimony tartrate was obtained.

Anal. Found: C, 30.4; H, 3.9; N, 7.8.

A 0.01 aqueous solution at 20° gave α_D 0.20° whence $[\alpha]^{20}{}_D$ 2,000° and $[M]^{20}D$ 14,100°.

***dl*-1,8-Bis-(α-pyridylmethyleneamino)-3,6-dithiaoctane-cobalt(II) Iodide Dihydrate.**—A solution of VII (1.5 g.) in methanol (5 ml.) was added to a solution of cobalt(II) acetate tetrahydrate (1 g.) in water (30 ml.) and the resulting deep-brown solution warmed at 50–60° for 5 minutes. Aeration or addition of hydrogen peroxide solution did not apparently effect any change when added to this solution. Addition of potassium iodide led to crystallization of a brown complex iodide which could be recrystallized from methanol with the help of ether or from warm water to which potassium iodide was added, and thus obtained in brown needles or prisms. Attempts to prepare optically active salts with the help of potassium antimonyl tartrate were unsuccessful.

Anal. Calcd. for $[C_{18}H_{22}N_4S_2Co]I_2 \cdot 2H_2O$: C, 30.6; H, 3.7; N, 8.0; Co, 8.3. Found: C, 30.4; H, 3.9; N, 8.1; Co, 8.2.

***dl*-1,8-Bis-(α-pyridylmethyleneamino)-3,6-dithiaoctane-cobalt(II) Perchlorate.**—An aqueous solution of the above described iodide was treated with 10% sodium perchlorate solution. Fine brown needles separated. They were collected and recrystallized from warm water. Hot aqueous solutions of this salt resisted oxidation by hydrogen peroxide, and the unchanged salt could be recovered after cooling.

Anal. Calcd. for $[C_{18}H_{22}N_4S_2Co](ClO_4)_2$: C, 35.1; H, 3.6; N, 9.1. Found: C, 35.1; H, 3.6; N, 9.0.

This salt is paramagnetic (1.85 Bohr magnetons).

1,8-Bis-(α-pyridylmethyleneamino)-3,6-dithiaoctane-cobalt(III) Perchlorate.—The above-described brown cobalt (II) complex salt (0.5 g.) was suspended in nitric acid (20 ml. of 0.1 *N*) and ammonium cerium(IV) nitrate (0.5 g.) added. Most of the substance dissolved on vigorous shaking to an orange-yellow solution which was rapidly filtered and treated with solid sodium perchlorate (2 g.). The orange-yellow crystalline precipitate which separated was collected and washed with ice-cold 2% perchloric acid solution, then ether, and finally dried under an infrared lamp. It was reduced easily by alcohol or by iodide ion, the brown cobalt(II) complex salt being regenerated.

Anal. Calcd. for $[C_{18}H_{22}N_4S_2Co](ClO_4)_3$: C, 28.1; H, 3.7; N, 7.3. Found: C, 28.9; H, 3.9; N, 7.1.

1,8-Bis-(α-pyridylmethyleneamino)-3,6-dithiaoctane-nickel(II) Perchlorate.—A solution of the base VII (0.75 g.) in methanol (5 ml.) was added to a solution of nickel(II) acetate tetrahydrate (0.5 g.) in water (50 ml.), the mixture rapidly boiled and then immediately cooled and filtered. Ten per cent. sodium perchlorate solution was then added to the brownish-red filtrate. The pink, silky precipitate which separated was recrystallized from warm water to which additions of sodium perchlorate were made and obtained in paramagnetic red needles (magnetic moment, 2.99 Bohr magnetons).

Anal. Calcd. for $[C_{18}H_{22}N_4S_2Ni](ClO_4)_2$: C, 35.1; H, 3.6; N, 9.1. Found: C, 35.3; H, 3.6; N, 9.2.

1,8-Bis-(α-pyridylmethyleneamino)-3,6-dithiaoctane-copper(II) Perchlorate.—A solution of the base VII (0.7 g.) in methanol (8 ml.) was added to a solution of copper(II) sulfate pentahydrate (0.7 g.) in water (10 ml.). Addition of 10% aqueous sodium perchlorate solution to the resultant green solution precipitated a green oil which solidified on scratching. It was purified by two rapid recrystallizations from hot water and obtained in green needles. Prolonged heating with water causes hydrolysis of the Schiff base.

Anal. Calcd. for $[C_{18}H_{22}N_4S_2Cu](ClO_4)_2$: C, 34.8; H, 3.6; N, 9.0; Cu, 10.2. Found: C, 34.6; H, 3.7; N, 9.0; Cu, 10.4.

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

A Four-coördinated Copper(II) Complex with a Tetrahedral Disposition of the Copper Valences

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The 4-coördinated copper(II) complexes of *dl*-, *d*- and *l*-2,2′-bis-(salicylideneamino)-6,6′-dimethyldiphenyl and of 2,2′-bis-(salicylideneamino)-diphenyl have been prepared. In them the four copper covalences must be tetrahedrally disposed.

With the single exception of cesium chlorocuprate, Cs_2CuCl_4, all X-ray analyses so far carried out of 4-covalent copper(II) complexes have shown them to have a square planar arrangement of the donor atoms about the metal atom. Helmholz and Kruh[2] considered from their studies of cesium chlorocuprate that in the crystal the complex ion was in the form of a tetrahedron distorted by flattening. On the other hand, spectral analysis showed that in solution the structure of the aquated ion is probably not the same as in the crystal and the tetrahedral configuration may be due to the exigencies of crystal packing.

Mills and Gott[3] claimed the preparation of a tetrahedral copper(II) complex in 1926—the copper derivative of benzoylpyruvic acid. However, many chemists have found it difficult to concede this claim.

Pauling,[4] on the basis of the X-ray results, proposed that the bonding orbitals used by copper in these 4-covalent complexes were $3d4s4p^2$, the unpaired electron being promoted to an outer 4p orbital. Such a promoted electron should be easily removed by oxidation and this behavior is not observed. Further, electronegative donor atoms are more likely to bond with 4d than with 3d orbitals. At the present time many chemists consider that 4-covalent copper(II) complexes involve the use of $4s4p^24d$ orbitals. This accounts satisfactorily for their stability to oxidation, their square planar arrangement, and the rapid interchange in solution of their donor molecules, behavior characteristic of upper level covalent bonds.

It seems surprising that tetrahedral 4-covalent copper(II) complexes do not seem so far to have been observed because the $4s4p^3$ bonding required for the tetrahedral arrangement is energetically feasible. There is some evidence which can be interpreted as showing that the spatial arrangement of organic chelate molecules about a central copper(II) atom can compel a tetrahedral arrangement of the four donor atoms. Thus Porter[5] has shown that 3,3′,5,5′-tetramethyl-4,4′-dicarbethoxy-dipyrrylmethene (I) functions as a bidentate chelate compound with many metals, coördinating with loss of a proton. In the copper(II) complex (II), first prepared by Schubert and Fischer,[6] the methyl groups in the 5- or 5′-positions of the dipyrrylmethene residues would clash very seriously in any attempt at a planar arrangement of this complex and Porter concluded that its configuration was non-planar and probably tetrahedral.

It occurred to us to design a quadridentate chelate compound with a molecule capable of presenting four donor atoms to a copper atom from the apices of a circumscribing tetrahedron but being incapable of functioning as a quadridentate in any other way. The first substance to be chosen was 2,2′-bis-(salicylideneamino)-6,6′-dimethyldiphenyl (III). Meisenheimer and Horing[7] have shown that the parent base 2,2′-diamino-6,6′-dimethyldiphenyl (IV) can be resolved into enantiomers and Kistiakowsky and Smith[8] have shown that these can be racemized only at relatively high temperatures and with difficulty. There is thus no possibility of the two benzene rings of the diphenyl system of IV or III being at any time coplanar under

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[2] L. Helmholz and R. F. Kruh, THIS JOURNAL, **74**, 1176 (1952).

[3] W. H. Mills and R. A. Gott, *J. Chem. Soc.*, 3121 (1926).

[4] L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 104.

[5] C. R. Porter, *J. Chem. Soc.*, 368 (1938).

[6] M. Schubert and H. Fischer, *Ber.*, **57**, 611 (1924).

[7] J. Meisenheimer and M. Horing, *ibid.*, **60**, 1425 (1927).

[8] G. B. Kistiakowsky and W. R. Smith, THIS JOURNAL, **58**, 1043 (1936).