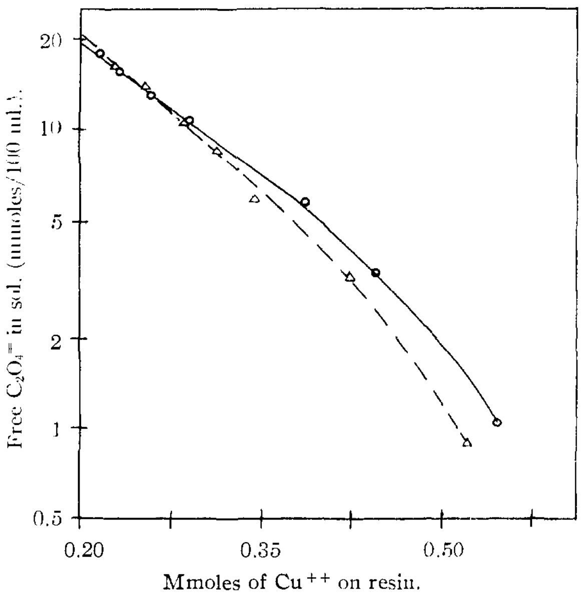

Fig. 1.—O, pH 9.00; Δ, pH 7.00.

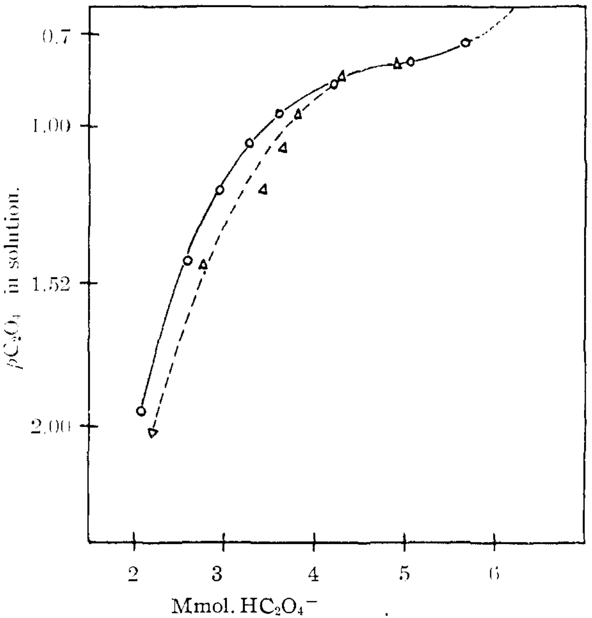

Fig. 2.—O, pH 9.00; Δ, pH 7.00.

the limited solubility of sodium oxalate in water. No attempt was made to determine the magnitude of the complexity constant because the exact amount of oxalate in the complex cannot be determined. It appears that the complex starts as $Cu(C_2O_4)_2^=$ and that the bioxalate displaces oxalate, then adds more, until eventually the complex of formula $Cu(HC_2O_4)_6^{-4}$ is produced. Whereas this anion would not be stable in solution due to electrostatic repulsions, our data indicate that it is stabilized by the resin. Since a resin has a relatively high concentration of positive charges, it can exert a screening effect which will favor and stabilize a more highly charged anion.

Acknowledgments.—The authors wish to thank the Rohm and Haas Company for supplying the resin used in this work and the Research Corporation for financial assistance.

WACO, TEXAS

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

Sexadentate Chelate Compounds.[1] X

BY FRANCIS LIONS AND KENNETH V. MARTIN[2]

RECEIVED DECEMBER 23, 1957

A number of new linear sexadentate chelate compounds and some related tridentate and quadridentate chelate compounds have been prepared and some of their coördination compounds studied. One of them—the α-pyridyl-hydrazone of pyridine-2-aldehyde—appears to be a promising reagent for the colorimetric estimation of cobalt.

In the simplest type of sexadentate chelate molecule, the six donor atoms are located successively along a chain, which, when coördination takes place, becomes wound round the coördinated metal atom in such a way as to bring the six donor atoms into positions at the apices of the coördination octahedron. The final position taken up by the chelating residue must be relatively strainless. Certain of the structural details requisite for the successful design of such molecules have been reported previously.[3] In this paper further experiments are described which also bear on this question of design.

It was pointed out in Part V of this series of papers[3] that it should be possible to substitute for the two sulfur atoms of 1,8-diamino-3,6-dithiaoctane (EEE base) two >N–CH_3 groups, which, despite the tertiary nature of the nitrogen atoms, might well be expected to function as donor atoms and thus enable 1,8-bis-(salicylideneamino)-3,6-dimethyl-3,6-diazaoctane to behave as a sexadentate chelate compound. It was considered at the time that the formation of imidazolidine rings

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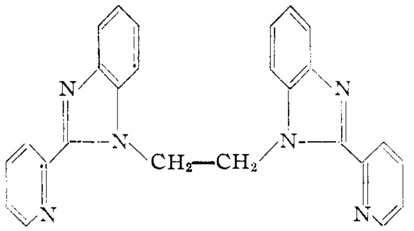
(1) The term "chelate compound" as used by the authors conforms to the original definition given by G. T. Morgan and H. D. K. Drew (*J. Chem. Soc.*, **117**, 1457 (1920), footnote) in the words "The adjective "chelate" derived from the great claw or "chela" (chely) of the lobster and other crustaceans, is suggested for *these caliper-like groups* which function as two associating units and fasten on to the central metallic atom so as to produce heterocyclic rings." Some chemists today regard the actual final coördination compound as the chelate compound. In our opinion this is wrong. We would define a chelate compound as a compound "whose molecule is capable of attaching itself either directly or after loss of a proton or protons to a suitable metal atom at more than one point."

(2) University Research Grant Student of the University of Sydney.

(3) *Cf.* F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, THIS JOURNAL, **74**, 4188 (1952); **75**, 1526, 2443 (1953); **76**, 383 (1954).

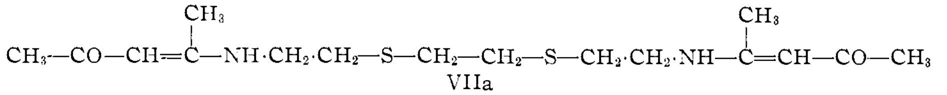
would militate against success in attempts to make and use 1,8-bis-(salicylideneamino)-3,6-diazaoctane (I) as a sexadentate chelate, in line with the experience of Diehl.[4] However, das Sarma and Bailar[5] showed recently how to obtain complexes containing I coördinated as a sexadentate chelate moiety. We now briefly report that 1,2-bis-(*o*-aminophenylamino)-ethane (II), in which the donor capacity of the imino groups might well be expected to be lower than that of the imino groups of triethylenetetramine, can be condensed with salicylaldehyde to give the yellow crystalline 1,2-bis-(*o*-salicylideneaminophenylamino)-ethane (III). This Schiff base is the nitrogen analog of the bis-salicylidene derivative of BEB base.[3] From it could be prepared the dark red diamagnetic crystalline 1,2-bis-(*o*-salicylideneaminophenylamino)-ethane cobalt(III) iodide (IV), a typical binary electrolyte. Interaction of II with pyridine-α-aldehyde (2 moles) gave an uncrystallizable yellow oil which reacted with iron(II) sulfate in aqueous ethanol to give a dark-blue solution from which ultimately diamagnetic dark-blue crystalline 1,2-bis - (*o* - α - pyridylmethyleneaminophenylamino)-ethane iron(II) perchlorate unisesquihydrate (V) was obtained. There thus seems little doubt that the bis-salicylidene and the bis-α-pyridylmethylene derivatives of II can function as sexadentate chelate compounds. The base II is readily converted by treatment with formic acid to 1,2-bis-(1′-benzimidazolyl)-ethane. Further, when the soluble complex iron salts containing the 1,2-bis-(*o*-α-pyridylmethyleneaminophenylamino)-ethane iron(II) cation are boiled with water, a colorless solid, 1,2 - bis - (2′ - α - pyridyl -1′- benzimidazolyl)- ethane (VI) is formed in good yield.



VI

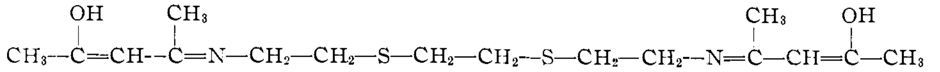
The molecule of a condensation product obtained by the interaction of a primary amine with a β-diketone possessing the $-CO-CH_2-CO-$ grouping becomes capable after loss of a proton, of attaching itself to a suitable metal atom, bonding occurring between the metal atom and the oxygen and the nitrogen atoms with formation of a six-membered chelate ring. Such amine–β-diketone condensation products are structurally similar to those obtained by interaction of primary amines with salicylaldehyde. Each contains a potential azomethine tertiary nitrogen atom capable of functioning as a donor atom and a suitably located acidic hydroxyl group. The condensation process is thus a useful one for the synthesis of chelate compounds capable of providing a donor oxygen atom and a donor nitrogen atom for each primary amino nitrogen atom in the original primary amine. Nevertheless, apart from the preparation of quadridentate chelate compounds from diamines and β-diketones, it does not appear to have been much exploited in the preparation of multidentate chelate compounds.

Condensation of acetylacetone (2 moles) with 1,8-diamino-3,6-dithiaoctane (EEE base) leads to ready formation of the condensation product VII [4,15 - dimethyl - 5,14 - diaza - 8,11 - dithia - $\Delta^{3,15}$-octadecadien-2,17-dione (VIIa), or the corresponding bis-enol, 4,15-dimethyl-5,14-diaza-,8,11-dithia-$\Delta^{2,4,14,16}$-octadecatetraen-2,17-diol (VIIb)]. VII reacts readily in methanol with cobalt(II) acetate to give a red-brown inner complex salt in solution. This is readily oxidized by hydrogen peroxide to the deep-blue complex cobalt(III) salt



$$CH_3-CO-CH=\overset{\displaystyle CH_3}{\overset{|}{C}}-NH\cdot CH_2\cdot CH_2-S-CH_2-CH_2-S-CH_2\cdot CH_2\cdot NH-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-CO-CH_3$$

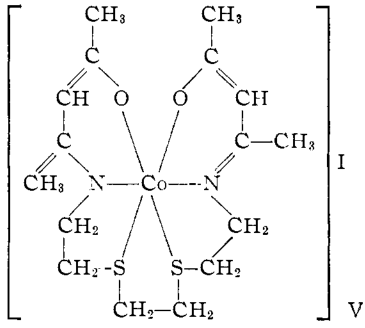
VIIa



$$CH_3-\overset{\displaystyle OH}{\overset{|}{C}}=CH-\overset{\displaystyle CH_3}{\overset{|}{C}}=N-CH_2-CH_2-S-CH_2-CH_2-S-CH_2-CH_2-N=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH=\overset{\displaystyle OH}{\overset{|}{C}}-CH_3$$

VIIb

From the solution can be precipitated the dark-blue crystalline 4,15-dimethyl-5,14-diaza-8,11-dithia-$\Delta^{2,4,14,16}$-octadecatetraen-2,17-diol cobalt(III) iodide (VIII). Conductivity measurements show this salt to be a binary electrolyte. It is diamagnetic, an indication of lower level (d^2sp^3) covalent bonding. Structurally, the complex cation must be similar to that of the corresponding 1,8-bis-(salicylideneamino)-3,6-dithiaoctane cobalt(III) ion[3] and capable of existing in one or other of two enantiomorphous forms. However, despite numerous attempts, resolution into optically active forms was not achieved.



VIII

As further examples of the value of acetylacetone in the synthesis of multidentate chelate compounds, we have condensed it with *o*-aminophenol to the 2-(*o*-hydroxyanilino)-Δ^2-penten-4-one (IX) of W. Sinda,[6] and with 8-aminoquinoline to 2-(8′-quinolylamino)-Δ^2-penten-4-one (X). Each of

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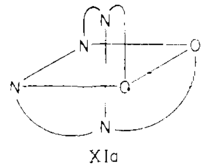
[4] H. Diehl, *et al.*, *Iowa State Coll. J. Sci.*, **22**, 110 (1947), *C. A.*, **42**, 4864 (1948).

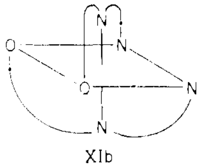
[5] B. das Sarma and J. C. Bailar, Jr., THIS JOURNAL, **77**, 5476 (1955).

[6] W. Sinda, *J. prakt. Chem.*, [2] **83**, 242 (1911).

these bases can function as a tridentate chelate compound. Thus, X reacts readily with cobalt(II) acetate in methanol to give an unstable inner complex which can be oxidized readily, and the brown crystalline bis-(2-(8′-quinolylamino)-Δ^3-penten-4-ol) cobalt(III) iodide (XI), a diamagnetic binary electrolyte, is then easily obtained. Stereochemical considerations require that its complex cations should exist in one or other of the enantiomorphous forms represented by XIa and XIb.



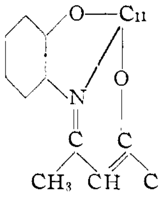
XIa



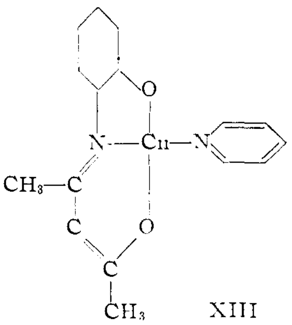
XIb

The ability of 8-aminoquinoline to form tridentate chelate compounds has been previously demonstrated by the preparation of 8-α-pyridylmethyleneaminoquinoline.[7]

The base IX reacts readily with copper(II) acetate in methanol to give the inner complex 2-(*o*-hydroxyanilino)-Δ^3-penten-4-one copper(II) (XII) a typical inner complex which is coördinatively unsaturated and, for example, can combine with pyridine to give XIII.

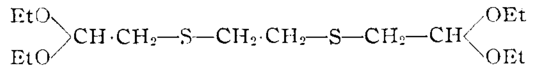


XII



XIII

Ethylene dithiol can be converted into the bis-sulfide XIV by interaction in absolute ethanol solution with bromoacetal and sodium ethoxide. The di-aldehyde XV obtained from XIV by careful acid



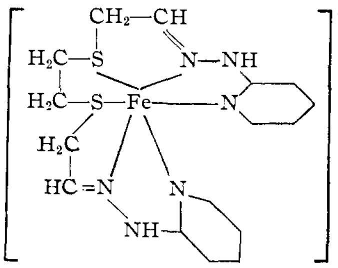
$$\begin{matrix}\mathrm{EtO}\\ \mathrm{EtO}\end{matrix}\!>\!\mathrm{CH\cdot CH_2{-}S{-}CH_2\cdot CH_2{-}S{-}CH_2{-}CH}\!<\!\begin{matrix}\mathrm{OEt}\\ \mathrm{OEt}\end{matrix}$$

XIV

$CHO\cdot CH_2-S-CH_2-CH_2-S-CH_2-CHO$

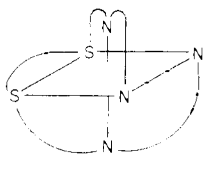
XV

hydrolysis can be condensed with primary amines to give bis-anils of the type XVI, but these were difficult to purify. This was especially true of the condensation products with *o*-aminophenol and 8-aminoquinoline which might well be expected to be capable of functioning as sexadentates. However, the bis-α-pyridyl-hydrazone of XV was crystalline and readily purified. It was found to behave as a typical sexadentate chelate compound, coördinating with iron(II) salts in aqueous dimethylformamide solution to give intensely red compounds similar in color to the tris-(*o*-phenanthroline) iron(II) salts. The complex iron(II) iodide, obtained pure in red needles which melt at 225°, was diamagnetic, indicating the d^2sp^3 bonding characteristic of lower level covalently-bonded octahedral iron(II) complex salts. Its molecular conductivity was consistent with that of a ternary electrolyte. The complex cation can be formulated two-dimensionally as XVII, the distal

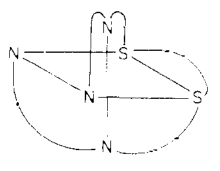


XVII

nitrogen atoms of the α-pyridylhydrazine residues being shown as donor atoms. This is justified by the previously reported demonstration that α-pyridylhydrazine can function as a bidentate *chelate compound*[8] as well as by the experiments described below. Spatially, the three atoms (Fe, N and C) attached to each of these distal donor nitrogen atoms must line in the same plane with it so that the complex ion must be formulated three-dimensionally as XVIIIa or XVIIIb.



XVIIIa



XVIIIb

Interaction of the bis-α-pyridylhydrazone of XV with cobalt(II) salts in aqueous dimethylformamide solution led to formation of the brown-pink complex cobalt(II) salts, and pure solid (3,6-dithiaoctan-1,8-dial bis-α-pyridylhydrazone) cobalt(II) perchlorate (XIX) was isolated. Attempts to oxidize the soluble complex cobalt(II) salts to the corresponding complex cobalt(III) salts led to profound decomposition.

XIX had a magnetic moment of 2.5 Bohr magnetons, suggesting strong lower level covalent bonds but not enabling a distinction to be made between a square-pyramidal (5 coördinate bonds) or a square-planar (4 coördinate bonds) arrangement. Octahedral coördination is not considered to be likely, as octahedral cobalt(II) compounds usually have magnetic moments of 1.7 to 2.0 Bohr magnetons.[9] A model shows that the organic moiety can function as a quinquedentate chelate accommodating itself to a square-pyramidal arrangement of its donor atoms if one of the terminal ring nitrogen atoms does not bond to the metal atom. The square-planar arrangement is less satisfactory and is considered to be unlikely.

When multidentate chelate molecules coördinate with metal atoms there is formed the maximum number of coördinate bonds consistent with the stereochemical arrangement of the chelate moiety and the coördination number of the metal. In

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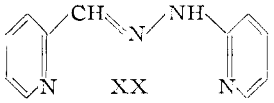
[7] F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, THIS JOURNAL, **75**, 3834 (1953).

[8] B. Emmert and O. Schneider, *Ber.*, **66**, 1875 (1933).

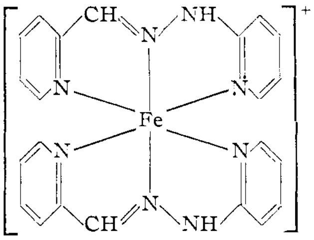
[9] B. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 12 (1954).

XIX five is the maximum number of lower level covalent bonds which can be formed without promoting an electron from a 3d to a 5s level. Formation of six octahedrally disposed coördinate bonds would require electron promotion for $3d^24s4p^3$ bonding or highly electro-negative donor atoms for $4s4p^34d^2$ bonding, and the magnetic evidence is against both these interpretations.

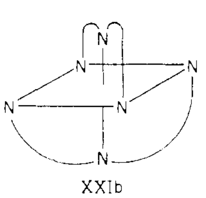
The capacity of the distal nitrogen of α-pyridylhydrazine or the derived hydrazones to function as a donor atom has been further illustrated by the synthesis of two tridentate and one quadridentate chelate compounds from it. Thus, α-pyridylhydrazine reacts readily with pyridine-2-aldehyde to form 1-(α-pyridylmethylene)-2-(α-pyridyl)-hydrazine (XX). Addition of aqueous iron(II) sulfate solution to an ethanolic solution of XX gave an intensely red solution from which sodium perchlorate precipitated red crystalline bis-(1-(α-pyridylmethylene)-2-(α-pyridyl)-hydrazine) iron(II) perchlorate (XXI), a diamagnetic ternary electrolyte and a typical octahedral iron(II) complex salt with lower level covalent bonds. The chelate compound XX thus behaves as a tridentate with three of its four nitrogen atoms functioning as donor atoms. The complex cation of XXI can be formulated two-dimensionally as XXIa and three-dimensionally (one stereoisomer) as XXIb. Structurally it is similar to the bis-terpyridine iron(II) ion and the similarity extends to the chain of atoms containing the three donor atoms (—N=C—C=N—N—C=N— in XXI and —N=C—C=N—C—C=N— in terpyridine). There should thus be similar possibilities for resonance and π-bonding.



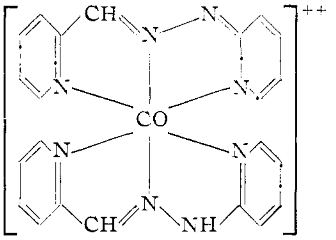
XX



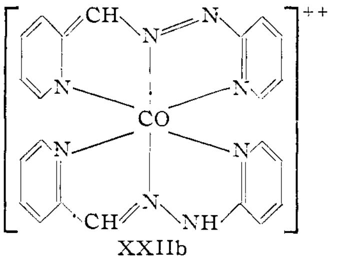
XXIa



XXIb



XXIIa



XXIIb

With ethanolic copper(II) chloride XX reacts to form green 1-(α-pyridylmethylene)-2-(α-pyridyl)-hydrazine copper(II) chloride, a compound very similar to the terpyridine copper(II) chloride of Corbridge and Cox.[10]

When XX was added to a methanolic solution of cobalt(II) acetate an intense red-brown color developed and a complex bromide $C_{22}H_{19}N_8CoBr_2$ (XXII) could be precipitated in red-brown glistening fluorescent plates. In solution the red-brown color was perceptible at concentrations as low as 0.5×10^{-7}. This complex salt was diamagnetic, the cobalt atom thus being in the tervalent state. On boiling in concentrated hydrobromic acid solution the salt dissolved, giving a green solution. Cooling of this and then neutralization with ammonia restored the red-brown color. A reasonable explanation of the formation and structure of this compound is that the initial reaction proceeds with loss of a proton from one of the tridentate residues, oxidation of the cobalt atom to the cobalt(III) state and simultaneous bonding of six nitrogen atoms to cobalt ($3d^24s4p^3$ bonds). The intense color of XXII is to be correlated with the possibilities of resonance in the highly-conjugated proton-poor tridentate residue, two of the possible bond formulations of the cation being shown in XXIIa and XXIIb.

XXII can be named as (1-(α-pyridylmethylene)-2-(α-pyridyl)-hydrazine) (1-(α-pyridylmethylene)-2-(α-pyridyl)-hydrazide)-cobalt(III) dibromide. A possible mechanism of the formation reaction is as follows. The -I effect of the pyridine ring of the pyridylhydrazine residue, which is an electron sink, lowers the electron density on its proximal nitrogen atom and the hydrogen atom attached to it tends to gain positive charge. Coördination now of two tridentate residues with a cobalt(II) ion, with formation of $3d^24s4p^3$ bonds, leads to promotion of an electron to an outer 5s orbital from which it is removed easily by oxidation. This increases the ionic charge to +3, which is sufficient for the expulsion of one of the hydrogen atoms attached to a proximal nitrogen atom as a proton. Such a mechanism explains why only one proton is lost, why no similar reaction is observed with iron(II) and copper(II) salts, their bivalent state being sufficiently stable, and why the color is discharged in conditions of high proton concentration. Dwyer and Hogarth and Block and Bailar[11] have reported examples of coördination of polyamines with metals such as osmium and gold with simultaneous proton loss.

The persistent brown color of these complex cobalt salts and the specificity of the reaction strongly suggest its use in analytical work. The maximum absorption in the visible spectrum is at 4,900 Å. Using a Spekker filter No. 603, which exhibits maximum transmission at 4,920 Å., and 1-cm. cells on a Spekker colorimeter, it was found that aqueous cobalt(II) chloride solutions (containing between

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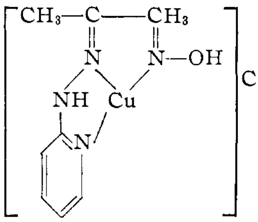
(10) D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1956).

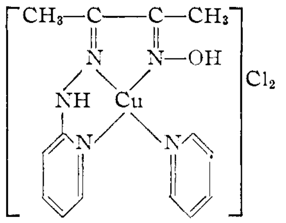
(11) F. P. Dwyer and J. W. Hogarth, THIS JOURNAL, **77**, 6152 (1955); B. P. Block and J. C. Bailar, Jr., *ibid.*, **73**, 4722 (1951).

10 and 100 micrograms of cobalt in each 25 ml.) obeyed Beer's law.

Diacetyl monoxime and α-pyridylhydrazine react together at 100° to give diacetyloxime α-pyridylhydrazone (XXIII). This reacts with copper(II) chloride in ethanol to give bright green solid diacetyloxime α-pyridylhydrazone copper(II) chloride (XXIV), a coördinatively unsaturated salt which readily coördinates further with pyridine to give XXV. XXIII thus functions as a tridentate chelate compound, the nitrogen atom of the pyridine nucleus, the distal nitrogen atom of the hydrazine side chain and the nitrogen atom of the oximino group functioning as donor atoms.



XXIV

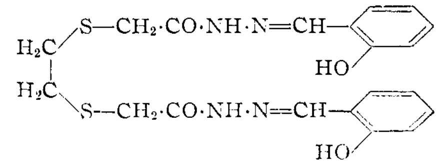


XXV

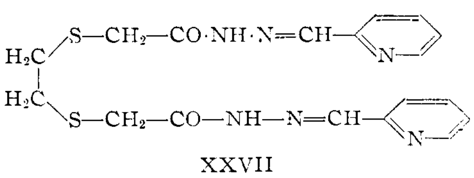
The two chelate loops of the complex ions of XXIV and XXV are five-membered. It is also worthy of note that the nitrogen atom of the oximino group acts as a donor atom without loss of a proton from the group.

With an α-diketone α-pyridylhydrazine readily yields the osazone. The osazone from diacetyl was shown to react readily in ethanol solution with copper(II) chloride to give the brown crystalline diacetyl-bis-(α-pyridyl)-hydrazone copper(II) chloride a typical ternary electrolyte in which the chelate moiety is undoubtedly functioning as a quadridentate.

Ethylene bis-thioglycolic hydrazide has been prepared and condensed with salicylaldehyde to XXVI and with pyridine-2-aldehyde to XXVII.



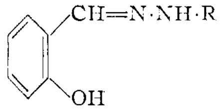
XXVI



XXVII

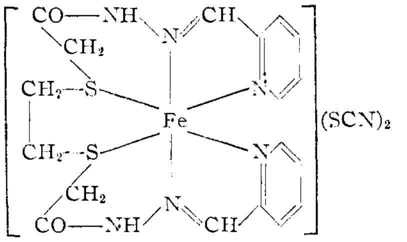
Addition of cobalt(II) acetate in acetic acid to an acetic acid solution of XXVI led to immediate precipitation of a solid orange-yellow compound $C_{20}H_{22}N_4O_4S_2Co$ (XXVIII) which was quite insoluble in the many solvents tried, did not melt below 300° and was stable to oxidizing agents. Its magnetic moment was 4.3 Bohr magnetons—indicative of upper level covalent bonding. According to Figgis and Nyholm,[9] this is indicative of a cobalt(II) complex with $4s4p^3$ (tetrahedral) bonding. Such a structural environment for each cobalt atom would be possible in XXVIII if it were a linear polymer in which each cobalt atom was bonded to each of two residues of XXVI through the terminal oxygen atom and the adjacent azomethine nitrogen atom at one end of the organic residue.

The low solubility and infusibility of XXVIII might be considered to support this view. On the other hand, the magnetic evidence might be interpreted to mean that XXVIII is a compound in which the sexadentate organic moiety is bonded to cobalt by upper level $4s4p^34d^2$ bonds. In support of this view is the fact that the salicylidene derivative of α-pyridylhydrazine forms stable very insoluble complexes, suggesting that insolubility is conferred by the grouping



Also, addition of aqueous iron(II) sulfate solution to XVII in dimethylformamide solution leads to immediate precipitation of a deep-red solid $C_{20}H_{20}N_4O_4S_2Fe$ (XXIX). This does not melt below 320°, has a magnetic moment of 4.5 Bohr magnetons, is highly insoluble and is resistant to oxidation. In our opinion, it must be formulated as an iron(II) complex with upper level $4s4p^34d^2$ covalent bonding.

The base XXVII is a relatively insoluble substance but dissolves readily in dimethylformamide. Addition of aqueous iron(II) sulfate solution to such a solution causes it to become intensely red and [bis-(α-pyridylmethylene)-ethylene bisthioglycolic hydrazide]-iron(II) thiocyanate (XXX) can be precipitated from this solution. This salt is diamagnetic, and it would thus appear that in it the residue of XXVII functions as a sexadentate chelate residue, the iron atom being covalently attached by lower level ($3d^24s4p^3$) bonds. It is a relatively stable salt, but it cannot be recovered from boiling aqueous solutions.



XXX

It is worthy of note that in XXVIII, XXIX and XXX chelate loops 2 and 4 are six-membered, as they are in the complex cobalt(III) cations derived from the bissalicylidene derivative of TET base.[3] However, whereas a series of green and brown isomeric salts were obtained from this latter chelate compound, no such isomerism was observed with the derivatives of XXVI and XXVII.

Finally, because Mukherjee[12] made the claim in 1953 that the bissalicylidene derivative of diglycylethylene-diamine can function as a sexadentate chelate compound, we have prepared the bis-α-pyridylmethylamide of ethylene bis-thioglycolic

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(12) A. K. Mukherjee, *Science and Culture*, **19**, 107 (1953).

acid (XXXI) which is somewhat similar to XXVII. No evidence could be obtained that this amide functioned at all as a chelate compound. This is to be associated with the very low donor power of the amide nitrogen atoms. Because of the $-$I effect of the $>C{=}O$ groups, there exists a tendency for the donor pair of electrons to pass from the nitrogen atom to the $>C{=}O$ group, thus reducing the donor power to such an extent as to inhibit chelation.

Experimental

1,2-Bis-(*o*-aminophenylamino)-ethane (II).—1,2-Bis-(*o*-nitrophenylamino)-ethane[13] was reduced with tin and hydrochloric acid and the tetramine isolated in colorless tablets, m.p. 102–103° (from benzene). It absorbs carbon dioxide from the air and rapidly becomes brown. Accurate analyses could not be made, a typical result being *Anal.* Calcd. for $C_{14}H_{18}N_4$: C, 69.4; H, 7.5; N, 23.1. Found: C, 66.3; H, 7.4; N, 20.9. Crystalline derivatives could, however, be prepared and these gave the expected analytical figures.

1,2-Bis-(*o*-salicylideneaminophenylamino)-ethane (III).—A solution of salicylaldehyde (4 g.) in ethanol was added to a hot solution of II (4.0 g.) in ethanol (10 ml.) and the solution boiled for a few minutes. The golden-yellow Schiff base separated almost immediately. It was recrystallized from alcohol–ethyl acetate and obtained in golden needles, m.p. 164°.

Anal. Calcd. for $C_{28}H_{26}N_4O_2$: C, 74.6; H, 5.8. Found: C, 74.4; H, 5.8.

1,2-Bis-(1′-benzimidazolyl)-ethane.—Heating of II with 90% formic acid at 100° for 90 minutes, followed by pouring off the reaction mixture into excess 10% sodium hydroxide solution, led to separation of a white solid which was collected, washed and recrystallized from hot water and thus obtained in colorless needles, m.p. 227°.

Anal. Calcd. for $C_{16}H_{14}N_4$: C, 73.3; H, 5.4. Found: C, 72.9; H, 5.5.

1,2-Bis-(*o*-salicylideneaminophenylamino)-ethane Cobalt(III) Iodide Monohydrate (IV).—Addition of a solution of cobalt(II) acetate tetrahydrate (0.5 g.) in methanol (20 ml.) to a boiling solution of III (1 g.) in ethanol–ethyl acetate (20 ml.) gave a red-brown solution. Addition of hydrogen peroxide solution (4 ml. of 3%) caused intensification of the color. The solution was boiled for a few minutes, filtered and then treated with saturated aqueous potassium iodide solution (5 ml.). After cooling, the complex cobalt(III) iodide was induced to crystallize in red-brown shining plates. Recrystallized from boiling aqueous methanol it formed deep red plates, m.p. 305°.

Anal. Calcd. for $C_{28}H_{24}N_4O_2CoI, H_2O$: C, 51.5; H, 4.0; N, 8.6; Co, 9.0. Found: C, 51.3; H, 4.2; N, 8.7; Co, 8.8.

This diamagnetic salt was insoluble in cold water but dissolved sparingly in hot water to an intensely red-brown solution. It was insoluble in solvents such as acetone, benzene and ether.

1,2-Bis-[*o*-(α-pyridylmethyleneamino)-phenylamino]-ethane Iron(II) Perchlorate Uni-sesquihydrate (V).—Freshly distilled pyridine-2-aldehyde (1.8 g.) was added to a solution of II (2 g.) in ethanol (10 ml.) and the solution heated on the water-bath for 5 minutes. A solution of iron(II) sulfate heptahydrate (2.4 g.) in water (10 ml.) was added to the resultant intensely orange colored solution after it had been cooled. Most of the ethanol was then boiled off. Addition of saturated aqueous potassium iodide solution (5 ml.) caused a blue oil to separate. Attempts to re-dissolve it in boiling water led to separation of a colorless solid which proved to be 1,2-bis-(2′-α-pyridyl-1′-benzimidazolyl)-ethane (VI) *vide infra*. Addition of perchloric acid (5 ml. of 10%) caused a dark blue solid to separate. Recrystallized from hot water, this diamagnetic salt formed deep-blue plates which decomposed violently at 227°.

Anal. Calcd. for $C_{26}H_{24}N_6FeCl_2O_8 \cdot 1.5H_2O$: C, 44.5; H, 3.8; N, 12.0; Fe, 8.0. Found: C, 44.4; H, 3.7; N, 11.8; Fe, 7.7.

1,2-Bis-(2′-α-pyridyl-1′-benzimidazolyl)-ethane (VI).—Prolonged heating with water of the blue oily complex iodide mentioned above, led to separation in 80% yield of a colorless base which was collected and recrystallized from benzene. It was thus obtained in colorless plates, m.p. 236°.

Anal. Calcd. for $C_{26}H_{20}N_6$: C, 74.9; H, 4.9. Found: C, 74.7; H, 4.8.

4,15-Dimethyl-5,14-bis-aza-8,11-bis-thia-$\Delta^{3,15}$-octadecadien-2,17-dione (VIIa).—EEE base (7.7 g.) and freshly distilled acetylacetone (8 g.) were heated together at 100° for 90 minutes after addition of one small drop of hydrochloric acid. On cooling, a pale yellow solid (13.7 g., 100%) was obtained. Recrystallized from aqueous ethanol it formed colorless needles, m.p. 74.5°.

Anal. Calcd. for $C_{16}H_{28}N_2O_2S_2$: C, 55.9; H, 8.1. Found: C, 55.9; H, 8.2.

4,15-Dimethyl-5,14-bis-aza-8,11-bis-thia-$\Delta^{2,4,14,16}$-octadecatetraen-2,17-diol Cobalt(III) Iodide (VIII).—A solution of cobalt(II) acetate tetrahydrate (4 g.) in hot methanol (100 ml.) was added to a solution of VIIIa (4 g.) in ethanol (15 ml.). The solution changed color to brown-red. Immediately afterwards hydrogen peroxide (5 ml. of 3%) was added, the color altering to deep green. After evaporation from a water-bath to a volume of about 40 ml., saturated aqueous potassium iodide solution (20 ml.) was added. The precipitate of complex cobalt(III) iodide (5 g.) was collected and recrystallized from hot water. It formed shining dark prisms, m.p. 200–201°.

Anal. Calcd. for $C_{16}H_{26}N_2O_2S_2CoI$: C, 36.4; H, 5.0; N, 5.3; Co, 11.2. Found: C, 36.4; H, 5.0; N, 5.1; Co, 11.0.

This salt was diamagnetic and had a molar conductance in 10^{-3} *M* aqueous solution of 126 ohms^{-1}.

2-(*o*-Hydroxyanilino)-Δ^2-penten-4-one Copper(II) (XII).—A solution of copper(II) acetate monohydrate (1.5 g.) in methanol (30 ml.) was added to a solution of 2-(*o*-hydroxyanilino)-Δ^2-penten-4-one[6] (2 g.) in methanol (15 ml.). The color changed to deep green and a solid separated. Recrystallized fron dioxane–ethanol it formed black plates, m.p. 295°.

Anal. Calcd. for $C_{11}H_{11}NO_2Cu$: C, 52.2; H, 4.4; Cu, 25.2. Found: C, 52.1; H, 4.6; Cu, 24.9.

2-(*o*-Hydroxyanilino)-Δ^2-penten-4-one pyridine Copper(II) (XIII).—Addition of pyridine (3 ml.) to a suspension of XII (0.15 g.) in ethanol (10 ml.) followed by warming on a water-bath for 10 minutes led to solution of the solid. Water and chloroform (2 lots of 15 ml.) were added and the combined chloroform extracts well washed with water, dried and the solvent removed. The residual solid was recrystallized several times from chloroform–petroleum ether and obtained in green needles which sinter at 280°.

Anal. Calcd. for $C_{16}H_{16}N_2O_2Cu$: C, 57.9; H, 4.9; Cu, 19.2. Found: C, 58.1; H, 4.9; Cu, 18.9.

1,1,8,8-Tetra-ethoxy-3,6-dithiaoctane (XIV).—To a solution of sodium (4.6 g.) in absolute ethanol (250 ml.) were added successively ethylene dithiol (9.4 g.) and bromoacetal (40 g.). The solution was then heated under reflux for 8 hours, sodium bromide being precipitated and a brown color developing. Most of the ethanol was distilled off, water added and the bis-acetal extracted with ether (3 lots of 200 ml.). The ether extracts were dried with potassium carbonate, the ether removed and the residual oil distilled *in vacuo* (24 g., 80%) b.p. 162° (0.5 mm.). It had a characteristic intense odor.

Anal. Calcd. for $C_{14}H_{30}O_4S_2$: C, 51.5; H, 9.2. Found: C, 51.2; H, 8.9.

3,6-Dithiaoctane-1,8-dial (XV).—The acetal XIV was hydrolyzed by a method substantially similar to that described by Alexander.[14] Dioxane (14 ml.), hydrochloric acid (2 ml. of 10*N*), water (7 ml.) and XIV (15 g.) were stirred together vigorously for 10 minutes at 100°, by which time the liquid had become homogeneous. It was cooled and extracted with ether (3 lots of 50 ml.). The combined extracts were washed with water, dried with anhydrous sodium sulfate and the solvent removed. The residual pale yellow oily aldehyde (XV, 7 g., 80%) was characterized as its **bis-(2,4-dinitrophenylhydrazone)**, orange needles, m.p. 203°.

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(13) F. Linsker and R. L. Evans, *J. Org. Chem.*, **10**, 283 (1945).

(14) E. R. Alexander, THIS JOURNAL, **70**, 2592 (1948).

Anal. Calcd. for $C_{18}H_{18}N_8O_8S_2$: C, 40.2; H, 3.4. Found: C, 40.4; H, 3.6.

Interaction with α-pyridylhydrazine (2 mols.) in dry ethereal solution, followed by removal of the solvent, left the solid bis-(α-pyridylhydrazone) of XV (100%). It was obtained from ethanol as a colorless powder, m.p. 174°.

Anal. Calcd. for $C_{18}H_{20}N_6O_2S_2$: C, 53.3; H, 5.7. Found: C, 53.3; H, 5.6.

1,12-Bis-(α-pyridyl)-1,2,11,12-tetrakis-aza-5,8-dithia-$\Delta^{2,10}$-dodecadiene Cobalt(II) Perchlorate.—A solution of cobalt(II) chloride hexahydrate (0.7 g.) in water (5 ml.) was added to a solution of the above-described bis-(α-pyridylhydrazone) (1 g.) in dimethylformamide (4 ml.), the solution becoming red-brown in color. After filtration saturated aqueous sodium perchlorate solution (4 ml.) was added. The deep pink solid which precipitated was collected and well washed with water.

Anal. Calcd. for $C_{16}H_{20}N_6S_2CO \cdot Cl_2O_8$: C, 31.1; H, 3.2; N, 13.6; Co, 9.5. Found: C, 30.8; H, 3.3; N, 13.5; Co, 9.2.

The salt decomposed above 200° and was paramagnetic, with a magnetic moment of 2.5 Bohr magnetons. Attempted oxidation to the cobalt(III) complex always led to profound decomposition.

1,12-Bis-(α-pyridyl)-1,2,11,12-tetrakis-aza-5,8-bis-thia-$\Delta^{2,10}$-dodecadiene Iron(II) Iodide Dihydrate.—A solution of iron(II) sulfate heptahydrate (0.54 g.) in water (10 ml.) was added to a solution of the bis-(α-pyridylhydrazone) of XV (0.7 g.) in dimethylformamide (5 ml.). The solution acquired an intense red color and a few drops of a dark-red oil separated. However, it went into solution on addition of more water (10 ml.). Saturated aqueous potassium iodide solution (3 ml.) was added. The dull-red precipitate which separated was crystallized from hot water and obtained in long dull-red needles, m.p. 225° (with decomp.).

Anal. Calcd. for $C_{16}H_{20}N_6S_2FeI_2$, $2H_2O$: C, 27.2; H, 3.4; Fe, 7.9. Found: C, 27.2; H, 3.6; Fe, 7.8.

This diamagnetic solid decomposes when its aqueous solutions are boiled for some time.

1-(α-Pyridylmethylene)-2-(α-pyridyl)-hydrazine (XX).—A solution of pyridine-2-aldehyde (1 g.) and α-pyridylhydrazine (1 g.) in ethanol (10 ml.) was heated under reflux for 10 minutes. The pale yellow solid which separated on cooling (yield 100%) was recrystallized from ethanol and obtained in yellow needles, m.p. 179–180°.

Anal. Calcd. for $C_{11}H_{10}N_4$: C, 66.6; H, 5.1. Found: C, 66.5; H, 5.2.

Bis-[1-(α-pyridylmethylene)-2-(α-pyridyl)-hydrazine] Iron(II) Perchlorate Dihydrate (XXI).—A solution of iron(II) sulfate heptahydrate (0.6 g.) in water (5 ml.) was added to a solution of XX (1.05 g.) in aqueous ethanol (10 ml. of 50%), the color immediately becoming intensely red. Addition of saturated aqueous sodium perchlorate solution (5 ml.) caused precipitation of the complex perchlorate. It was recrystallized from hot water and obtained in dark-red plates which decompose at 213°. The salt was diamagnetic.

Anal. Calcd. for $C_{22}H_{20}O_8FeCl_2O_8 \cdot 2H_2O$: C, .38.5; H, 3.5; Fe, 8.2. Found: C, 38.6; H, 3.7; Fe, 8.0.

1-[α-Pyridylmethylene)-2-(α-pyridyl)-hydrazine] Copper(II) Chloride.—An ethanolic solution of copper(II) chloride dihydrate (1 g.) was added to a solution of XX (1 g.) in ethanol (10 ml.). An olive-green solid at once crystallized from the solution. It was collected, thoroughly washed with hot ethanol and dried *in vacuo*. It melted at 225–226° and was insoluble in ordinary solvents except water, from solutions in which it could not be recovered.

Anal. Calcd. for $C_{11}H_{10}O_4CuCl_2$: C, 39.7; H, 3.0; Cu, 18.9. Found: C, 39.3; H, 3.1; Cu, 18.9.

[1-(α-Pyridylmethylene)-2-(α-pyridyl)-hydrazine]-[1′-(α-pyridylmethylene)-2′-(α-pyridyl)-hydrazide] Cobalt(III) Bromide (XXII).—Solutions of XX (2 g.) in ethanol (10 ml.) and cobalt(II) acetate tetrahydrate (1.4 g.) in methanol (10 ml.) were mixed, an intense red-brown color developing. Addition of saturated aqueous potassium bromide solution (5 ml.) caused precipitation of the complex bromide, which was recrystallized from hot water and obtained in fluorescent red-brown plates, m.p. 303°.

Anal. Calcd. for $C_{22}H_{19}N_8COBr_2$: C, 43.0; H, 3.1; N, 18.2; Co, 9.6. Found: C, 43.3; H. 3.5; N, 18.6; Co, 9.2.

This complex salt was diamagnetic.

The corresponding complex *iodide*, m.p. 275°, crystallized in greenish-brown needles from alcohol–ether.

Anal. Calcd. for $C_{22}H_{19}N_8CoI_2$: C, 37.3; H, 2.7; Co, 8.3. Found: C, 37.7; H, 3.1; Co, 8.1.

This salt was also diamagnetic.

Diacetyl Oxime α-Pyridylhydrazone (XXIII).—Concentrated hydrochloric acid (one drop) was added to a mixture of diacetylmonoxime (4 g.) and α-pyridylhydrazine (4 g.) which was then heated at 100° for 10 minutes. The resultant solid (6.5 g., 90%) was recrystallized from ethanol and formed colorless needles, m.p. 214°.

Anal. Calcd. for $C_9H_{12}N_4O$: C, 56.3; H, 6.2. Found: C, 56.3; H, 6.2.

(Diacetyl Oxime-α-Pyridylhydrazone) Copper(II) Chloride (XXIV).—A solution of copper(II) chloride dihydrate (0.3 g.) in ethanol was added to a solution of XXIII (0.3 g.) in ethanol (20 ml.). A bright green precipitate was formed immediately. It was washed several times with ethanol and dried *in vacuo* and then had m.p. 240°.

Anal. Calcd. for $C_9H_{12}N_4OCuCl_2$: C, 33.0; H, 3.8; Cu, 21.9. Found: C, 33.1; H, 3.7; Cu, 21.7.

(Diacetyl Oxime α-Pyridylhydrazone-pyridine) Copper(II) Chloride (XXV).—Pyridine (0.1 ml.) was added to the mother liquor obtained when preparing XXIV. A light blue solid separated from this solution. It was recrystallized from an ethanol–ether mixture and obtained in blue needles, m.p. 264°.

Anal. Calcd. for $C_{14}H_{17}N_5OCuCl_2$: C, 41.4; H. 4.2; Cu, 15.8. Found: C, 40.9; H, 3.9; Cu, 15.4.

Diacetyl-bis-(α-pyridylhydrazone).—Ice-cold redistilled diacetyl (2.6 g.) and α-pyridylhydrazine (6.5 g.) were mixed. After the exothermic reaction which occurred, the reaction mixture solidified and was then recrystallized from ethanol; colorless needles, m.p. 214°.

Anal. Calcd. for $C_{14}H_{16}N_6$: C, 62.7; H, 6.0. Found: C, 62.8; H, 5.9.

Diacetyl Bis-(α-pyridylhydrazone) Copper(II) Chloride.—Ethanolic solutions of the above-described osazone (0.6 g. in 10 ml.) and copper(II) chloride dihydrate (0.5 in 10 ml.) were mixed and warmed for 5 minutes. On cooling a brown microcrystalline solid, m.p. 209–210°, separated. It was washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $C_{11}H_{16}N_6CuCl_2$: C, 41.8; H, 4.0; Cu, 15.8. Found: C, 41.4; H, 3.6; Cu, 15.4.

The molar conductance in 10^{-3} *M* aqueous solution was 230 ohms^{-1}.

Ethylene Bis-(thioglycolic Hydrazide).—Hydrazine hydrate (10 g. of 100%) and diethyl ethylene-bis-(thioglycolate) (b.p. 152° (0.7 mm.), 4 g.) were dissolved in ethanol (25 ml.) and the solution heated under reflux for 3 hours. The hydrazide (3.6 g.) crystallized on cooling. After recrystallization from ethanol it had m.p. 136–137°.

Anal. Calcd. for $C_6H_{14}N_4S_2O_2$: C, 30.2; H, 5.9. Found: C, 30.4; H, 5.8.

Bis-salicylidene Ethylene Bis-(thioglycolic Hydrazide) (XXVI).—A solution of salicylaldehyde (1.7 g.) and the above-described bis-hydrazide (1.5 g.) in ethanol (50 ml.) was boiled under reflux for 5 minutes. On cooling, a white solid separated and after recrystallization from ethanol it had m.p. 215°.

Anal. Calcd. for $C_{20}H_{22}N_4O_4S_2$: C, 53.8; H, 5.0. Found: C, 53.8; H, 5.1.

Bis-salicylidene-ethylene-bis-(thioglycolic Hydrazide) Cobalt(II).—Acetic acid solutions of XXVI (1.5 g. in 20 ml.) and cobalt(II) acetate tetrahydrate (0.5 g. in 5 ml.) were mixed. The orange cobalt(II) complex was precipitated immediately. It was insoluble in all the ordinary solvents and did not melt below 320°.

Anal. Calcd. for $C_{20}H_{20}N_4O_4S_2CO$: C, 47.7; H, 4.0; Co, 11.7. Found: C, 47.4; H, 4.1; Co, 11.5.

The substance was paramagnetic, with a magnetic moment of 4.3 Bohr magnetons at 24°.

Bis-salicylidene-ethylene-bis-(thioglycolic Hydrazide) Iron(II).—Admixture of solutions of XXVI (1.5 g.) in dimethylformamide (5 ml.) and iron(II) sulfate heptahydrate (0.93 g.) in water (5 ml.) led to immediate precipitation of the red-violet iron(II) complex. It was well washed with dimethylformamide and water and dried, being insoluble in all the solvents tried. It did not melt below 320° and was paramagnetic, with a magnetic moment of 4.5 Bohr magnetons at 24°.

Anal. Calcd. for $C_{20}H_{20}N_4O_4S_2Fe$: C, 48.0; H, 4.0; Fe, 11.2. Found: C, 47.7; H, 4.2; Fe, 11.0.

Bis-(α-pyridylmethylene)-ethylene-bis-(thioglycolic Hydrazide (XXVII).—Freshly distilled pyridine-2-aldehyde (2.2 g.) was added to a warmed suspension of ethylene bis-thioglycolic hydrazide (2.4 g.) in ethanol (20 ml.). The solid soon dissolved and then after a few minutes the crystalline product separated. It was recrystallized from much ethanol and thus obtained as a white powder, m.p. 190°.

Anal. Calcd. for $C_{18}H_{20}N_6O_2S_2$: C, 51.9; H, 4.8. Found: C, 51.7; H, 4.9.

Bis-(α-pyridylmethylene-(ethylene-bis-(thioglycolic Hydrazide) Iron(II) Thiocyanate Dihydrate (XXX).—A solution of iron(II) sulfate heptahydrate (0.2 g.) in a little water was added to a solution of XXVII (0.3 g.) in dimethylformamide (10 ml.). Addition of saturated aqueous potassium thiocyanate solution (5 ml.) to the intensely red colored solution led to precipitation of a solid which was recrystallized from ethanol and thus obtained in dark red needles, m.p. 210°.

Anal. Calcd. for $C_{20}H_{20}N_8O_2S_4Fe \cdot 2H_2O$: C, 38.5; H, 3.8; Fe, 9.0. Found: C, 38.3; H, 3.5; Fe, 8.6.

Ethylene-bis-(thioglycolic-α-pyridylmethylamide) (XXXI).—Ethyl thioglycolate (5.32 g.) and 2-aminomethylpyridine (4.32 g.) were heated together at 180° for 6 hours. The solid which separated on cooling (80%) was recrystallized several times from ethanol and obtained in colorless needles, m.p. 155°.

Anal. Calcd. for $C_{18}H_{22}N_4O_2S_2$: C, 55.4; H, 5.6. Found: C, 55.4; H, 5.8.

Acknowledgment.—The authors gratefully acknowledge the assistance of Miss B. Stevenson who carried out all the C, H and N microanalyses recorded in this paper.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Photochemistry of Complex Ions. I. Some Photochemical Reactions of Aqueous $PtBr_6^{-2}$, $Mo(CN)_8^{-4}$ and Various Co(III) and Cr(III) Complex Ions

BY ARTHUR W. ADAMSON AND A. H. SPORER

RECEIVED NOVEMBER 4, 1957

Studies have been made of the photochemistry of aqueous $Co(NH_3)_6^{+3}$, $Co(NH_3)_5X^{+2}$ (X = SCN, Cl, I), $Co(CN)_5X^{-3}$ (X = CN, Cl, Br, I), $Co(C_2O_4)_3^{-3}$, $Cr(NH_3)_5SCN^{+2}$, $Cr(NH_3)_2(SCN)_4^{-}$, $Cr(C_2O_4)_3^{-3}$, $Mo(CN)_8^{-4}$, and the exchange system $PtBr_6^{-2}$–Br^-. Quantum yields were obtained for the oxidation–reduction decompositions, aquation, racemization or exchange reactions that occurred, usually for two wave lengths, one in the ligand field band region and one in the electron transfer band region of the absorption spectra. The results are interpreted to indicate that the chemical nature of the excited state is qualitatively independent of the wave length of the light used. On the other hand, the net consequence of light absorption depends upon which of several possible courses is taken subsequent to the formation of the primary excited state.

The present investigation represents the initial effort of a program to develop a more quantitative understanding of the photochemistry of complex ions, and of its relationship to the thermal reactions of such ions and to the current interpretations of their spectra.

The general photosensitivity of Werner type complex ions is well known, of course, although only a scattering of quantitative observations appear in the literature. These include the reports of Linhard and of Schwartz and co-workers[1,2] on certain acido-amines of Co(III) and Cr(III), and on various hexacyano complexes. Recent investigations of the photochemical aquation of ferrocyanide ion have been made by Emschwiller.[3] Vranek[4] has studied the photo-decomposition of $Co(C_2O_4)_3^{-3}$, Taube[5] noted the photochemical exchange of Cl^- with $PtCl_6^{-2}$, and Plane and Hunt[6] recently found very low quantum yields for the photochemical exchange of H_2O^{18} with hexaaquochromic ion. Finally, fairly extensive studies have been made of the photochemical decomposition of the uranyl oxalate, ferric oxalate and mercuric oxalate complexes.[7,8]

Linhard, *et al.*,[1] observing that light of 366 mμ led to production of I_2 and of Na from the corresponding acidopentaminecobaltic complexes, concluded that the primary act involved an electron transfer from ligand to metal, in accord with the general interpretation of the near ultraviolet, high-intensity bands as being electron transfer in type. Williams[9] has similarly interpreted such bands in the case of Fe(II) and Fe(III) complexes.

On the other hand, the low intensity bands, usually in the visible, observed with most first row transition metal complexes are interpreted in terms of transitions between 3d levels whose degeneracy has been partially removed by the ligand field.[10,11] Thus, for an octahedral field, the d_{xy}, d_{xz} and d_{yz} orbitals, whose electron density is directed away from the ligand positions, are lowered in energy relative to the d_{x^2} and $d_{x^2-y^2}$ orbitals, whose electron density is directed toward ligand positions. The absorption of light in the ligand field band is thus thought to involve promotion of an electron from a T_{2g} to an E_{2g} 3d orbital, and might be expected to lead to a repulsion between the ligand and the metal ion.

Qualitatively, then, it might be expected that absorption in the region of an electron transfer band should lead to a oxidation–reduction process, and absorption in the region of a ligand field band, to a displacement of the ligand and hence to a sub-

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[4] J. Vranek, *Z. Elektrochem.*, **23**, 336 (1939).

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