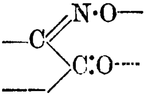
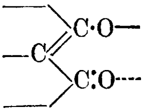
CCCXLIII.—*Researches on Residual Affinity and Co-ordination. Part XII. Cobaltammine and Ferric Lakes of Dinitrosoresorcinol.*

By Gilbert T. Morgan and John Ewart Moss.

In two earlier communications (T., 1921, **119**, 704; this vol., p. 160) on cobaltammine lakes of quinoneoxime and alizarin dyes, it was shown experimentally that these adjective dyes owe their distinctive lake-forming properties to the presence in the colour molecule of at least one unsaturated group (I or I*a*) capable of

(I.)





(I*a*.)

taking up two positions in the co-ordination complex surrounding a metallic atom so that the latter becomes finally held in a heterocyclic ring. To these unsaturated radicles, which are capable of acting as two associating units, has been given the name of chelate groups because of the tenacity of their grip on the implicated metallic atom.

The presence of chelate groups in a dye may be detected by the use of a cobaltammine reagent consisting of an ammoniacal solution of hydroxopentamminocobaltic chloride, $[HO{\cdot}Co(NH_3)_5]Cl_2$. If the dye contains one chelate group, three of these unsaturated radicles combine with one atom of tervalent cobalt, satisfying completely its principal and supplementary valencies so that the metallic atom loses completely its capacity for combining with ammonia. This central cobalt atom, which is then said to be completely chelated, has become implicated in three heterocylic rings, one arising from each of the three chelate groups.

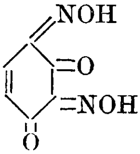
Meanwhile, the cobaltammine reagent combines with any other acidic groups present in the dye to give a pentamminocobaltic salt, so that if the resulting complex lake contains n atoms of cobalt and m molecules of ammonia the relationship between these constituents is expressed by equation (i) . . . $m = 5(n - 1)$.

If there are two or more lake-forming chelate groups present in the dye, the relationship becomes somewhat more complicated, because, owing to spatial arrangement, the second chelate group can only co-ordinate once with a tervalent cobalt atom, the latter retaining the power of association with four molecules of ammonia. The equation for a polychelate dye thus becomes

$$\text{ii} \ . \ . \ . \ m = 5\left[n - \frac{c+4}{5}\right],$$

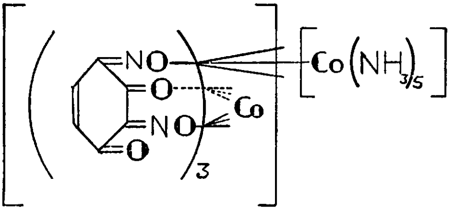
where c is the number of chelate groups. Several examples of dichelate mordant dyes have been observed in the alizarin series (*loc. cit.*).

These considerations have now been applied to the case of dinitrosoresorcinol or 1 : 2 : 3 : 4-benzodiquinone-1 : 3-dioxime (II) with the object of ascertaining the nature of the metallic lakes derived from this quinoneoxime dye, or, in other words, of finding out whether the colouring matter is a monochelate or a dichelate dye. Dinitrosoresorcinol, when precipitated on iron mordants, gives rise to fast green lakes, variously designated as resorcinol green, chlorin, resorcin green, Alsace green, fast myrtle green, etc. With chromium mordants, it furnishes fast brown lakes. These shades of colour resemble closely those derived from the 1 : 2-naphthaquinonemonoximes (Gambine or nitrosonaphthol dyes) which have been shown definitely to be monochelate dyes (*loc. cit.*).



(II.)

The foregoing consecutive formula II assigned to dinitrosoresorcinol has not hitherto been demonstrated by direct proof, but nevertheless this constitution is rendered very probable by the analogies drawn from the behaviour of homologues of resorcinol towards nitrous acid. β-Orcinol [$2CH_3 : 2OH = 1 : 4 : 3 : 5$], in which one methyl group occupies the position contiguous to the two hydroxyl radicles, yields only a mononitroso-derivative even with excess of nitrous acid, whereas orcinol [$CH_3 : 2OH = 1 : 3 : 5$] and its isomeride, cresorcinol [$CH_3 : 2OH = 1 : 2 : 4$], readily furnish dinitroso-compounds even with a deficiency of nitrous acid, and in the latter instance one of the nitroso-groups must enter the position contiguous to the two hydroxyl radicles (Kostanecki, *Ber.*, 1887, **20**, 3133). The consecutive formula for dinitrosoresorcinol suggests a possibility that this substance may behave towards metallic mordants as a dichelate dye, in which contingency the cobaltammine lake should have a composition determined by the second of the foregoing equations. Putting *c* and *n* each equal to 2, the number, *m*, of ammonia molecules should be four. Experiment shows, however, that the dicobaltic lake contains not four but five molecular proportions of ammonia in accordance with equation i. Hence it follows that dinitrosoresorcinol, although a dioxime, behaves as a monochelate dye, thus falling into line with the nitrosonaphthol or 1 : 2-naphthaquinonemonoxime colouring matters. The simplest explanation of this behaviour is that the median *iso*nitroso- and carbonyl radicles form the two limbs of the chelate group, leaving to the terminal *iso*nitroso-radicle the simpler function of salt-formation. On this hypothesis, the constitution to be assigned to the cobaltammine lake is as shown in formula III.



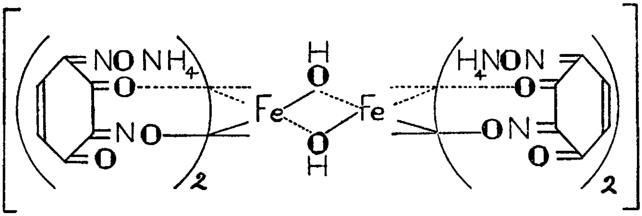
(III.)

This view of the constitution of the cobaltammine lake is confirmed by evidence derived from a study of the iron lakes of dinitrosoresorcinol.

The iron lakes of quinoneoxime dyes are almost invariably cited as ferrous compounds in the technical literature of colouring matters. There is, however, no analytical justification for this fallacious formulation, which has been advocated probably owing to two circumstances : first, these lakes are often produced either on the textile fibres or in bulk from ferrous compounds, and, secondly, the deep green colour of the lakes suggests a misleading analogy with the similar although much paler tints of many ferrous salts.

The green quinoneoxime iron lakes can be produced from either ferric or ferrous salts, but in the latter instance lake formation is accompanied by oxidation. The product contains ferric iron in both cases and the intense green colour is characteristic of the heterocyclic complex in which the tervalent iron atom has now become implicated.

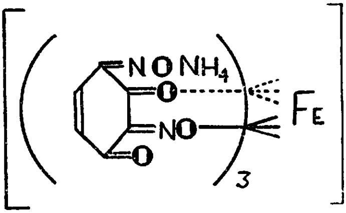
When dinitrosoresorcinol and ferrous sulphate interact in presence of ammonia under ordinary atmospheric conditions, a deep green lake is obtained. This product contains no ferrous iron, but has the composition of a basic ferric compound derived from a monochelate mordant dye (IV).



(IV.)

The formation of this basic ferric lake agrees with the analytical data obtained by O. Hoffmann in a study of the iron lakes of 2-nitroso-α-naphthol-4-sulphonic acid (Naphthol Green G), where ferrous salts gave lakes corresponding with a basic ferric constitution (*Ber.*, 1891, **24**, 3741). This investigator noticed that by repeated crystallisation the basic lakes furnished the normal ferric lake, a product which was obtained more directly by the use of a ferric salt.

The interaction of ferric alum and dinitrosoresorcinol in presence of ammonia leads similarly to the normal ferric lake containing one atomic proportion of iron combined with three molecular proportions of the monoammonium salt of the benzodiquinonedioxime radicle (V).



(V.)

The composition and properties of the cobaltammine and ferric lakes of dinitrosoresorcinol furnish corroborative evidence in support of the view that this dye contains one chelate group and one salt-forming radicle as symbolised in the foregoing constitutional formulæ.

Accordingly, our practical results substantiate the consecutive formula for dinitrosoresorcinol (II) inasmuch as this configuration shows distinctly that the two *iso*nitroso-radicles differ fundamentally in function. The median *iso*nitroso-group alone is involved in the chelating complex, whereas the terminal *iso*nitroso-group situated in the para-position with respect to the remaining carbonyl group behaves merely as an acidic radicle. A symmetrical formulation (1 : 2 : 4 : 5) for dinitrosoresorcinol suggests on the contrary that both *iso*nitroso-groups have similar functions, thus leading to a dichelate dye. This supposition is entirely opposed to the experimental evidence.

EXPERIMENTAL.

Dinitrosoresorcinol was prepared by the method outlined in Cain and Thorpe's "Synthetic Dyestuffs," ed. 1913, page 253, and dried on porous plate over sulphuric acid under reduced pressure. The product then contained one molecule of water (Found: N = 15·08, 15·20. $C_6H_4O_4N_2,H_2O$ requires N = 15·04 per cent.) (compare Fitz, *Ber.*, 1875, **8**, 631; Kostanecki, *Ber.*, 1889, **22**, 1345; Bülow and Deiglmayr, *Ber.*, 1904, **37**, 1794). A difficulty arose in estimating ammonia in the complex cobalt-ammine lakes of dinitrosoresorcinol owing to the fact that the colouring matter itself evolved ammonia on heating with 5*N*-sodium hydroxide. The amount set free varied with the time of distillation; in three and a half hours, about one-sixth of the nitrogen present had been eliminated as ammonia and after thirteen and a half hours the proportion of nitrogen eliminated was roughly about one-fourth of the whole; there was no definite end-point. During this distillation, an unmistakably persistent odour of hydrogen cyanide was noticed, and this acid was identified in the distillate as silver cyanide. The exact nature of the decomposition was not ascertained owing to the tarry nature of the non-volatile product.

1-*Pentamminocobaltic* 3-*Cobaltic* 1 : 2 : 3 : 4-*Benzodiquinone*-1 : 3-*dioximate* (Formula III).

Dinitrosoresorcinol (5·6 grams) was added to 72 c.c. of 5*N*-ammonia, diluted with 30 c.c. of water, when a slight brownish-green precipitate was formed, which was dissolved by the further addition of 5 c.c. of 5*N*-ammonia. This solution of the diammonium salt of dinitrosoresorcinol was mixed with cobaltammine reagent, prepared by adding 2 c.c. of 5*N*-hydrogen peroxide to 20 c.c. of 2*N*-cobalt chloride diluted with 40 c.c. of 5*N*-ammonia. The resulting mixture, containing a chocolate-brown precipitate, was heated at 75° for fifteen minutes and cooled to 0°. The insoluble product, after washing with cold water, was dried over soda-lime in presence of solid ammonium carbonate for three days under 10 mm. pressure [Found: Co = 15·76, 15·83; N = 20·93. $(C_6H_2O_4N_2,H_2O)_3Co_2(NH_3)_5$ requires Co = 15·61; N = 20·38 per cent.].

The trihydrate was now dried over quicklime for three days under

10 mm. pressure [Found: Co = 16·33, 16·44; NH_3 = 11·72, 11·33; N = 22·12; another dehydrated preparation gave Co = 16·95, 16·81; N = 21·31, 21·40. $(C_6H_2O_4N_2)_3Co_2(NH_3)_5$ requires Co = 16·81; NH_3 = 12·13; N = 21·95 per cent.].

The anhydrous cobaltammine lake was a chocolate-brown, amorphous powder insoluble in water and the ordinary organic media; it evolved ammonia on heating and was decomposed by warm 5*N*-sodium hydroxide. The co-ordinated ammonia was estimated by distillation during one and three-quarters to two hours with aqueous borax (0·3 to 3 per cent.); the total nitrogen was determined by Kjeldahl's method after preliminary reduction with sodium hydrosulphite; equal weights (0·3 gram) of this reducing agent and the cobaltammine lake were digested at 100° with 6 c.c. of 2*N*-sulphuric acid. The mixture was then heated with 5 to 10 c.c. of concentrated sulphuric acid and a globule of mercury. Owing to the explosive nature of the cobaltammine lake, the metal present was estimated as anhydrous sulphate after a preliminary digestion at 100° with 2*N*-sulphuric acid followed by strong heating with concentrated acid, any separated carbon being oxidised by ammonium nitrate. With cold concentrated hydrochloric, nitric, or sulphuric acid, the anhydrous cobaltammine lake developed a reddish-brown coloration, becoming orange on dilution.

A partly chelated lake was obtained by adding slowly a solution of 5·6 grams of dinitrosoresorcinol in 110 c.c. of 15*N*-ammonia to 20 c.c. of 2*N*-cobaltic chloride, dissolved in 55 c.c. of 5*N*-ammonia and 4 c.c. of hydrogen peroxide. A brown, gelatinous precipitate was formed, and after adding 15 c.c. of 15*N*-ammonia the mixture was heated at 60°. The insoluble product, washed successively with water, alcohol, and ether, was dried for four days over soda-lime under 10 mm. pressure in presence of ammonium carbonate [Found: Co = 15·10, 14·89; N = 21·94, 22·63.

$$(C_6H_2O_4N_2,H_2O)_3Co_2(NH_3)_7$$

requires Co = 14·90; N = 23·05 per cent.].

Ferric Ammonium Lakes of Dinitrosoresorcinol.

1. *Basic Ferric Lake*: 1-*Ammonium* 3-*Hydroxoferric* 1 : 2 : 3 : 4-*Benzodiquinone*-1 : 3-*dioximate* (Formula IV).

Ferrous ammonium sulphate (7·82 grams), dissolved in the least amount of water, was added to 500 c.c. of water and 30 c.c. of 18*N*-ammonia containing 13 grams of dissolved dinitrosoresorcinol, when an intense green coloration was produced. The solution was concentrated on the water-bath to 350 c.c. and cooled. The precipitated lake, after washing with 5*N*-ammonia, was dried for four days in a vacuum desiccator over soda-lime [Found : C = 33·07, 33·12; H = 3·45, 3·36; N = 19·05 (Kjeldahl), 19·60 (Dumas); Fe = 12·87, 12·92. $(C_6H_2O_4N_2,NH_4)_2Fe{\cdot}OH$ requires C = 32·74; H = 2·97; N = 19·04; Fe = 12·65 per cent.].

The basic ferric ammonium lake of dinitrosoresorcinol was a black amorphous powder dissolving in water to a dark green solution; its solubility decreased considerably on drying and it dissolved sparingly in alcohol or pyridine; it was insoluble in other organic media, but dissolved readily in aqueous sodium hydroxide or 18*N*-ammonia. With concentrated nitric or sulphuric acid, this lake developed a reddish-brown coloration, becoming orange on dilution. On boiling with concentrated hydrochloric acid to remove dinitrosoresorcinol, the filtrate on dilution gave all the reactions for ferric iron and showed no indication of the ferrous condition. The foregoing results proved conclusively that the lake produced from dinitrosoresorcinol and a ferrous salt in ammoniacal solution exposed to air was entirely a basic ferric compound.

2. *Normal Ferric Lake*: 1-*Ammonium* 3-*Ferric* 1 : 2 : 3 : 4-*Benzodiquinone*-1 : 3-*dioximate* (Formula V).

Ferric alum (9·6 grams), dissolved in 100 c.c. of cold water, was added to a solution of 11·2 grams of dinitrosoresorcinol in 450 c.c. of water and 25 c.c. of 15*N*-ammonia. The solution was concentrated in three different experiments to 300, 400, and 500 c.c. of liquid, the yields of green lake being, respectively, 6·9, 8, and 1·4 grams. The precipitates were washed successively with alcohol and ether and dried for five days over concentrated sulphuric acid under 10 mm. pressure [Found : Fe = 9·92, 10·39, 10·44; N = 20·73, 20·11, 20·42. $(C_6H_2O_4N_2,NH_4)_3Fe$ requires Fe = 9·17; N = 20·71 per cent.]. These results agree best with the composition of a normal ferric lake. The product is a bluish-black powder soluble in water or pyridine to a dark green solution, but insoluble in neutral ordinary organic media.

Inasmuch as pyridine was one of the few organic solvents in which dinitrosoresorcinol dissolved, an attempt was made to obtain a crystalline ferric pyridine lake. Anhydrous ferric chloride (1·5 grams, 1 mol.), dissolved in 7 grams of pyridine, was added to a solution of 5·35 grams (3 mols.) of dinitrosoresorcinol in 20 grams of the same solvent. Heat was evolved and a dark green coloration developed, but there was no precipitate until 40 c.c. of absolute alcohol were added, when a dark green substance was deposited, which, after washing with alcohol and drying over quicklime in a vacuum desiccator, weighed 3·3 grams. The compound gave a distinct iodoform test for alcohol (Found : C = 48·87; H = 4·44;

N (Dumas) = 11·99, N (Kjeldahl) = 11·41; Fe = 7·62. These analytical data indicate a basic ferric pyridine lake,

$\{C_5H_6N\cdot NO{:}C_6H_2O_2{:}NO\}_2Fe\cdot OH,4C_2H_6O$,

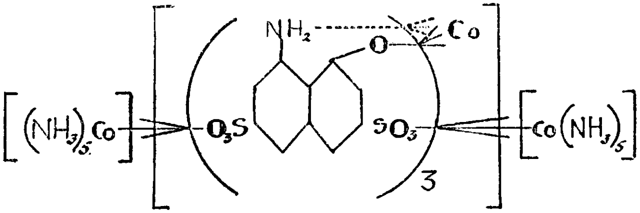
requiring C = 48·18; H = 5·50; N = 11·19; Fe = 7·44; or $[\{C_5H_6\cdot N\cdot ON{:}C_6H_2O_2{:}NO\}_2Fe]_2O,8C_2H_6O$, requiring C = 48·75; H = 5·43; N = 11·32; Fe = 7·52 per cent. It was, however, impossible to ascertain precisely by analysis the degree of hydration. This ferric pyridine lake was sparingly soluble in water, alcohol, or ether, but dissolved readily in pyridine to a deep green solution.

Cobaltammine Salts of Colour-producing Intermediates.

In connexion with an investigation still in progress on synthetic mordant azo-dyes, it became of interest to examine the behaviour of the generators of these colouring matters towards the cobaltammine reagent, especially when it was found that complete chelation of the cobaltic complex took place less readily in the benzene than in the naphthalene series.

8-Amino-α-naphthol-3 : 6-disulphonic acid (H acid) yields a cobaltammine salt (VI) containing a threefold chelated complex, whereas 2-aminophenol-4-sulphonic acid gives only a partly chelated compound even at 75°, and repeated attempts up to 100° have failed to produce more than twofold chelation (formula VII). The case of anthranilic acid is even more exceptional. The cobaltammine reagent gives an insoluble cobaltous anthranilate, which is also formed more simply with ammoniacal cobalt chloride in the absence of hydrogen peroxide. The determining factor in this reaction is in all probability the sparing solubility of cobaltous anthranilate, this salt being removed from the sphere of action before oxidation can occur. The cobalt atom, which exhibits its lower valency, has also the lower co-ordination number of 4 as in the cobaltous α-oximinoketones recently described by Ponzio (*Gazzetta*, 1922, **52**, i, 285).

3 : 6-*Dipentamminocobaltic* 1-*Cobaltic* 8-*Amino*-1-*oxynaphthalene*-3 : 6-*disulphonate* (Formula VI).

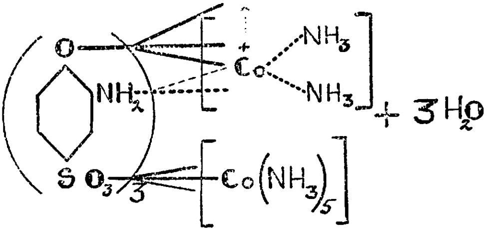


(VI.)

A specially purified specimen of the monosodium salt of H acid, obtained from Dr. de Mouilpied of the British Dyestuffs Corporation, gave Na = 6·08, 6·12; S = 17·91, 17·32 per cent., these numbers corresponding with the acid sodium salt with $1\frac{1}{2}H_2O$ (compare Dressel and Kothe, *Ber.*, 1894, **27**, 2137).

One-third of the cobaltammine reagent from 30 c.c. of 2*N*-cobalt chloride, 45 c.c. of 5*N*-ammonia, and 6 c.c of 5*N*-hydrogen peroxide was added to a solution of 10·8 grams of this acid sodium salt dissolved in 8 c.c. of 15*N*-ammonia and 10 c.c. of water, and after heating at 100° the mixture was allowed to cool. Following the addition of the remaining two-thirds of cobaltammine reagent, the dark brown, viscid liquid was heated at 60°, the cobaltammine compound being subsequently precipitated by the addition of 150 c.c. of absolute alcohol. The chocolate-brown product after washing with alcohol and ether was dried for a week over soda-lime [Found: Co = 13·45; NH_3 = 13·60; N = 14·0; S = 13·35. $(C_{10}H_4ONH_2{\cdot}S_2O_6)_3Co_3(NH_3)_{10}$ requires Co = 13·63; NH_3 = 13·13; N = 14·05; S = 14·84 per cent.]. The cobaltammine compound of H acid dissolved in water to a reddish-brown solution, changing to carmine on adding caustic alkali or to yellow on acidifying. It was insoluble in organic media, evolved ammonia on heating, and developed a heliotrope coloration, changing to carmine, with concentrated sulphuric acid.

Cobaltammine Salt of 2-*Aminophenol*-4-*sulphonic Acid*,

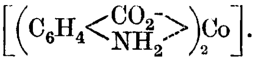


(VII.)

A solution of 11·5 grams of 2-aminophenol-4-sulphonic acid in 20 c.c. of 15*N*-ammonia and 50 c.c. of water was added to sufficient cobaltammine reagent (see preceding preparation) to furnish sufficient cobalt for a dicobaltic salt. The purplish-brown liquid was heated at 60°, cooled, treated with 30 c.c. of alcohol, filtered, and diluted with 250 c.c. of alcohol. The brown precipitate after washing with alcohol and ether was dried for a week over soda-lime under 10 mm. pressure: found Co = 13·75; NH_3 = 13·66. This preparation, redissolved in dilute ammonia and heated again at 60°, gave, after similar treatment, Co = 13·52; NH_3 = 14·00. Another specimen, after heating at 75°, gave Co = 14·54; NH_3 = 13·62. These analyses give the ratio, Co atoms : NH_3 molecules = 2 : 7, corresponding with the partially chelated compound

$(C_6H_3ONH_2{\cdot}SO_3{\cdot}H_2O)_3Co_2(NH_3)_7$, which requires Co = 13·82; NH_3 = 13·96 per cent.

Cobaltous Anthranilate,



$$\left[\left(C_6H_4{<}{\genfrac{}{}{0pt}{}{CO_2^-}{NH_2}}{>}\right)_2Co\right].$$

To 8·2 grams of anthranilic acid (3 mols.), dissolved in 15 c.c. of 5*N*-ammonia, was added the following cobaltammine reagent (1 mol.): 20 c.c. of 2*N*-cobaltous chloride, 22 c.c. of 10*N*-ammonia, and 4 c.c. of 6*N*-hydrogen peroxide. On warming at 80°, the solution yielded a dark brown precipitate which assumed a light grey colour after washing with alcohol and ether [Found: Co = 17·45; N = 9·40. $(C_7H_6O_2N)_2Co$ requires Co = 17·77; N = 8·45 per cent.]. The product contained 1·62 per cent. of ammonia. The preparation was repeated with two molecular proportions of anthranilic acid; the grey product contained Co = 17·47; N = 8·70; and only 0·83 per cent. of ammonia.

These results showed that the foregoing product was essentially cobaltous anthranilate, and not a cobaltammine salt. The preparation was now modified by using ammoniacal cobaltous chloride (1 mol.) to two molecular proportions of anthranilic acid but no hydrogen peroxide. The cobaltous anthranilate, an amorphous, grey powder insoluble in water and the ordinary organic media, gave Co = 17·60; N = 9·10; and only 0·68 per cent. of ammonia. Anthranilic acid, melting at 141°, was set free either by hydrochloric acid or on prolonged digestion with boiling water.

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