59. *Structure of the Copper Lakes of Azo-dyes.*

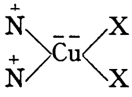
By H. D. K. Drew and J. K. Landquist.

Lake formation with copper increases the stability of azo-compounds, particularly towards light, but little is known to account for the effect. Only in a few of the less complex cases have the lakes been isolated and their structures determined. The present paper describes copper lakes of *o*-hydroxy-, *o*-carboxy-, *oo'*-dihydroxy-, *o*-hydroxy-*o'*-carboxy-, and *oo'*-dicarboxy-azo-compounds of the benzene and the naphthalene series, and some examples in which one hydroxyl group is *m*- or *p*- to the azo-group; lakes of *o*-hydroxy-azo-sulphonic acids also are described, together with some simple copper salts of these acids. The structures of the lakes and their stereochemical forms are discussed, and the general principles governing the formation of the lakes are indicated. The results of the work imply that the stability of the lakes is enhanced among those which have inner co-ordination of copper with azo-nitrogen, and that such forms arise only when copper is affixed by covalent linkings to substituents (such as OH, CO_2H, or NH_2) which are in the *o*-position to the azo-groups, *m*- or *p*-hydroxyls having little or no effect; the presence of two substituents of this kind (particularly two hydroxyl groups) in the *oo'*-positions further increases the stability, the lakes assuming fused-ring forms. The inner co-ordinated copper lakes of sulphonic and carboxylic acids of the *o*-monohydroxy-azo-series are formed only when the acid groups are neutralised by further copper atoms or by other metals or groups. Copper attached to a sulphonic acid group is capable of transference to the inner co-ordinated state under certain conditions. Some of the lakes exhibit co-ordinative unsaturation when prepared by normal means, and this property has been made use of to determine their structures.

The special properties of the metallic lakes of azo-dyes containing the hydroxyl or amino-group in an *o*-position to the azo-group have led many authors to assume co-ordination of the metallic atom with one or both nitrogen atoms of the azo-group (see, for example, Werner, *Ber.*, 1908, **41**, 1062; Baudisch, *Z. angew. Chem.*, 1917, **30**, 133; Morgan and Main Smith, J., 1924, **125**, 1731; Charrier and Beretta, *Gazzetta*, 1926, **56**, 865; Crippa, *ibid.*, 1927, **57**, 20; Cremonini, *ibid.*, 1928, **58**, 372; Elkins and Hunter, J., 1935, 1598); but so varied are the structural possibilities among the copper derivatives of the azo-compounds that principles governing the formation of these lakes have not been defined in the literature, except as regards those of mono-*o*-hydroxy- and -amino-compounds. The position with respect to the stereochemistry of the lakes is still more obscure, and is complicated by the lack of general agreement as to the space structure of tervalent nitrogen and of 4-covalent copper.

Owing to the variable co-ordination number of bivalent copper and to the uncertainty as to whether the metal is to be regarded in all cases as covalently linked with or as ionised from the oxygen of hydroxyl, carboxyl, or sulphonic acid groups in the neighbourhood of the azo-group, it was not at first possible to apply the principles of Werner; but as the work progressed, a review of the data brought us to the conclusion that the stable co-ordination compounds of cupric copper are ordinarily those in which the copper atom is associated with 35 planetary electrons (*i.e.*, the atomic number of copper, together with 6 additional electrons from attached atoms), but that in the copper lakes of azo-compounds this number of electrons may fall short of 35 by one or more pairs. When this occurs, the lake will exhibit co-ordinative unsaturation and will tend to combine with one or more molecules of water, ammonia, or the like. Further, when water and the like are present in the lake, the number of associated planetary electrons may in rarer instances be exceeded by one or more pairs, in which case the lake will tend to lose co-ordinating molecules until the number of electrons associated with the copper atom has reached 35. The azo-group of aromatic substances shows, so far as we could find, little or no co-ordinating power for a metal atom not already attached by some other group in an *o*-position to the azo-group, and therefore external molecules of the azo-dye are not combined in excess with the metal nor can azo-dye molecules be eliminated from the complex, as is the case, for example, with ammonia. There are then three ways in which an atom of bivalent copper can become saturated co-ordinatively in these lakes : it may be (1) non-ionised and co-ordinated with two nitrogen or other atoms, or (2) singly ionised and co-ordinated with three atoms, or (3) doubly ionised and co-ordinated with four atoms. Our experience has been that the second of these modes is rarely found. It happens sometimes that the lakes isolated are not co-ordinatively saturated and they may be well-defined and apparently stable substances; in these cases the degree of co-ordinative unsaturation can generally be determined by noting the number of ammonia or similar molecules which the lakes are capable of attaching in stable combination.

The structures of the co-ordinatively saturated lakes can be expressed by regarding the cupric atoms as having always a double negative charge (N here represents any co-ordinating atom) :



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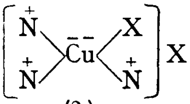

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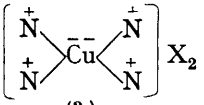
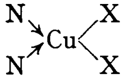
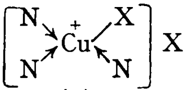


(3.)

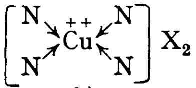
or the co-ordination bond of Sidgwick may be employed :



(1.)



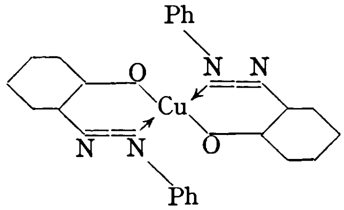
(2.)



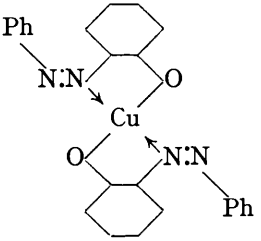
3.)

The latter system is adopted in this paper.

o-*Hydroxy-azo-compounds.*—Several authors have shown that the cupric derivatives of these substances contain one copper atom to two azo-groups. We have found that the lakes of *o*-hydroxyazobenzene, 2-hydroxy-5-methylazobenzene, 2-hydroxy-5 : 5′-dimethylazobenzene, benzeneazo-β-naphthol, and *m*-tolylazo-β-naphthol are all anhydrous. By crystallisation from pyridine, quinoline, or aniline, followed by analysis, it was shown that they are co-ordinatively saturated and do not affix further molecules of the bases. A number of structures have been attributed to this type of lake. We arrived at the general structure (as I) from the following considerations. An examination of models, from the point of view of strain, showed that a copper atom, whether planar or tetrahedral, cannot be co-ordinated with *both* nitrogen atoms of an azo-group, although such formulæ continue to appear in the literature. The copper derivatives have the characteristic properties of co-ordinated substances and are at the same time co-ordinatively saturated. They must therefore contain copper in combination with nitrogen of the azo-groups, belonging thus to type (1) above.



(I.)



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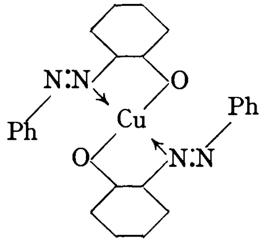
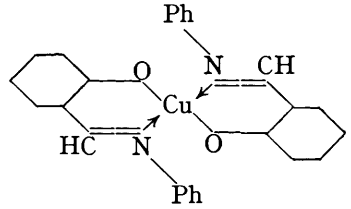
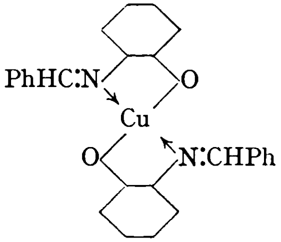


(III.)

The question whether the azo-nitrogen atoms are of *syn*- or *anti*-form then arises. Stereochemical considerations indicate that, besides the 6-ring formula (I), which has *anti*-azo-groups and copper attached to the nitrogen atom remote from hydroxyl, there are two other possible formulæ (II and III), with 5-rings, one having *syn*- and the other *anti*-azo-groups, with copper in both cases attached to the nitrogen adjacent to hydroxyl. A decision can be reached if it can be found whether the remote or the adjacent nitrogens are co-ordinated to copper. In the salicylideneimines the adjacent nitrogen atoms of the azo-compounds are replaced by carbon, which cannot co-ordinate, but Delépine (*Bull. Soc. chim.*, 1899, **21**, 944), Barrow and Duffey (Thesis, Univ. of Lond., 1934), and others have shown that these substances form co-ordinated copper salts of composition analogous to those of the azo-compounds; thus the copper salt of salicylideneaniline cannot have a structure analogous to (II) or (III), but must be presumed to have structure (IV). For this reason structure (I) is, by analogy, preferred for the derivatives of the azo-compounds. At the same time, the 5-ring containing copper is not excluded on principle and indeed is probable in certain cases; for example, the copper derivative of benzylidene-*o*-aminophenol (Barrow and Duffey, *loc. cit.*) has presumably * structure (V). The 5-ring compounds, however, differ from the 6-ring in that they have comparatively high melting points and are insoluble in organic solvents.

(IV.)

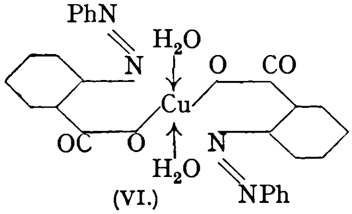




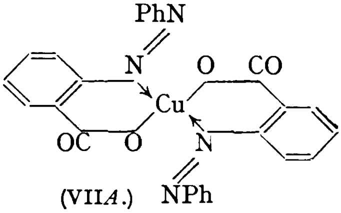
(V.)

If the quinone-hydrazone formulæ for the azo-compounds are adopted, the forms of the above structures remain unaltered, the nature of the linkings only being changed. This will be seen to hold also for certain cases mentioned later.

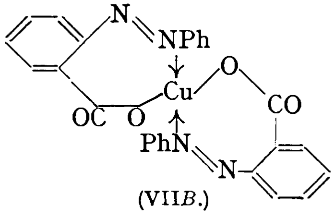
o-Carboxy-azo-compounds.—Paal (*Ber.*, 1891, **24**, 3058) obtained amorphous green precipitates from copper sulphate and ammoniacal solutions of *p*-chloro- and *p*-bromo-azobenzene-*o*′-carboxylic acids, but did not investigate them. No further work on the *o*-carboxylic acids is on record. We find that azobenzene-*o*-carboxylic acid forms the dihydrated green copper salt (VI), which is sparingly soluble in water but more soluble in benzene or chloroform. The water molecules are somewhat tenaciously held, but may be replaced by aniline or pyridine molecules. The anhydrous substance (VII), which may be obtained by boiling a benzene solution of the dihydrate to expel water and then adding petroleum, is yellow and does not crystallise from benzene or chloroform; it is soluble in many organic solvents and is rehydrated in moist air. Probably, (VII) has the co-ordinated 6-ring formula (VII*A*), where the nearer nitrogen atoms of the azo-groups, which may be either *syn* or *anti* in form, are attached to the metal; but the non-planar 7-ring form (VII*B*), in which the azo-groups have the *anti*-form, would have little strain with the double bonds in the positions shown, and cannot be excluded. The carboxyls are covalently linked to the metal in either case, and probably the unusual co-ordination with the nearer nitrogen of the azo-groups is a weak linking which is disrupted in the presence of other co-ordinating molecules, giving, for example, (VI) with water; an alternative, less likely from general considerations and in view of the properties of the substances, is that the covalency between copper and carboxyl tends to become an ionised link, the co-ordination with nitrogen being retained. It is remarkable that (VI) separates from acetone as a crystalline brownish-green *monoacetone* compound which is anhydrous; this may represent the intermediate phase as shown in (VIII). An *o*-carboxyl group in azobenzene thus resembles an *o*-hydroxyl, but occasions



(VI.)



(VII*A*.)



(VII*B*.)

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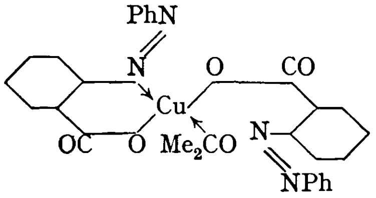
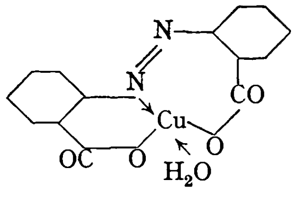
* Barrow has himself arrived at this conclusion regarding the structure of the salicylidene derivatives (private communication).

formation of a less stable link between azo-compound and metal, with the result that the copper derivative, instead of being co-ordinatively saturated, exhibits weak co-ordinating affinity, a property which may be termed pseudo-co-ordinative unsaturation.

An interesting comparison arose with azobenzene-2 : 2′-dicarboxylic acid, which formed a green copper salt, probably a dihydrate; a molecule of water was retained at 105°, the monohydrate being stable in moist air. This substance was readily decomposed by acids and by reagents which precipitate copper, and was sparingly soluble in water or in organic solvents, although it separated from pyridine as an unstable tripyridine complex. It is probable that, as in the case of the copper salt of the monocarboxylic acid, the co-ordination of the metal with nitrogen of the azo-group is feeble and is disrupted in co-ordinating solvents; it is possible also that the covalent linking between the metal and the carboxyl may become ionised in the presence of pyridine. Thus, the monohydrate may be represented by (IX); but the alternative that it is an un-co-ordinated copper salt is not entirely excluded, although the presence of the firmly bound water molecule then becomes anomalous.

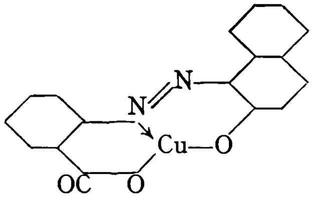
(VIII.)



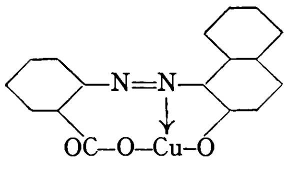


(IX.)

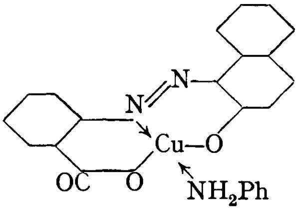
o-*Hydroxy*-o′-*carboxy-azo-compounds*.—Two azo-compounds of this type were studied : *o*-carboxybenzeneazo-*p*-cresol and *o*-carboxybenzeneazo-β-naphthol. These gave red-brown copper derivatives, alike in structure and exhibiting co-ordinative unsaturation; they were soluble in aniline or pyridine, forming crystalline derivatives with one molecule of these bases (as XI). The copper derivative from the second azo-compound was shown to have the simple molecular weight in pyridine and therefore the structure of these derivatives is as indicated in the 6-ring formula (X), which is not quite flat, the nuclei being slightly rotated about the bonds joining them to the azo-group; but formula (X*A*), though unlikely (see below), is also possible stereochemically. Barrow and Duffey (*loc. cit.*) obtained a green copper derivative of salicylideneanthranilic acid. If, as is probable, this substance is a true analogue of the above azo-derivatives, it must have structure (XII), similar to (X), a structure similar to (X*A*) being here impossible.



(X.)

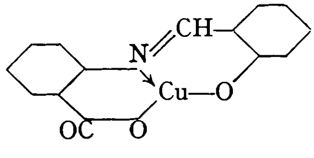


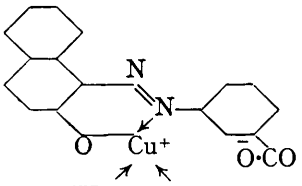
(X*A*.)



(XI.)

(XII.)

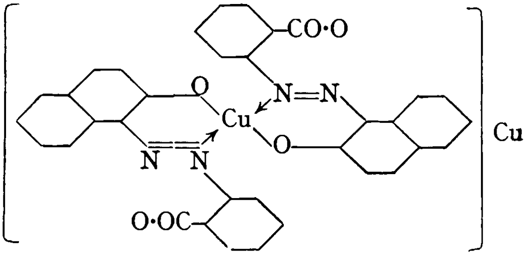




(XIII*A*.)

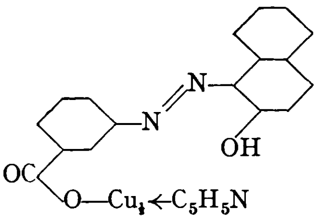
Although dimeric structures for the copper derivatives of the above azo-compounds are excluded by the molecular weight in cases where the copper is un-ionised, the structure (XIII) remains a possibility if half the copper present be considered ionised in pyridine as solvent. In that case, however, the result would be the same if the carboxyl groups were removed to *m*- or *p*-positions, and for this reason the case of benzeneazo-β-naphthol-3′-carboxylic acid was examined. The behaviour of this azo-compound with copper salts was quite different from that of the *o*-carboxylic acids. An insoluble brown copper derivative

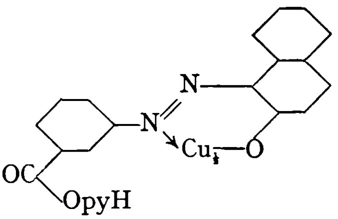
(XIII.)



was prepared from cupric chloride and the sodium salt of the azo-compound, and although this was not obtained pure, it was shown to contain one copper atom to two mols. of the azo-compound; crystallised from pyridine, this salt gave a yellow-brown *dipyridine* compound of the foregoing salt, which was obtained pure in two distinct forms differing widely in colour and in their melting points (233°; 120°). The higher-melting of these forms was probably the normal salt (XIV), and the other was possibly the pyridinium salt (XV) of the co-ordinated complex. For reasons given later, in connection with the azo-

(XIV.)



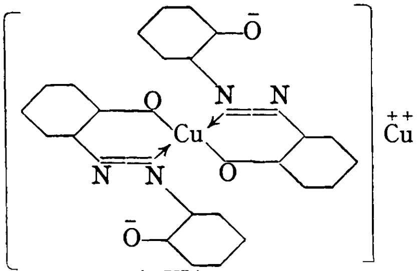


(XV.)

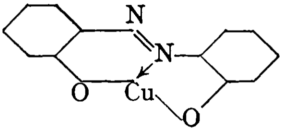
sulphonic acids, two such forms might well be interchangeable under favourable conditions. There was indication of the formation, in other circumstances, of a copper salt of structure analogous to that shown in (XIII), since the substance gave rise to a tetra-aniline compound, or, alternatively, a derivative of structure (XIII*A*); but neither of these two substances was obtained pure.

Comparison was also made with the case of benzeneazo-α-naphthol-2′-carboxylic acid. A brown copper derivative containing an atom of copper to two azo-groups was obtained in the form of a *trihydrate*; two molecules of water were tenaciously held, but were replaceable by solution in pyridine, the *dipyridine* compound being formed in red-brown crystals; aniline, however, did not combine with the copper derivative, the amorphous *anhydrous substance* separating from the hot solvent. Thus, the *p*-hydroxyl group appears to take no part in the fixation of the copper, the azo-compound behaving much like azobenzene-*o*-carboxylic acid; the dihydrated copper derivative and the dipyridine compound may therefore be regarded as similar to (VI) in structure, the anhydrous copper salt being probably like (VII*A*); in the trihydrate the loosely held third molecule of water is possibly associated with hydroxyl.

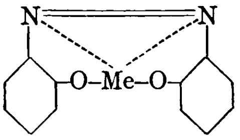
oo′-*Dihydroxy-azo-compounds.*—Although it has long been known that these substances form copper lakes, no complexes of that type have hitherto been analysed. It has been held (see, *e.g.*, Mason, *J. Soc. Dyers and Colourists*, 1932, **48**, 293) that only one hydroxyl group was in union with the metal, but the present work does not confirm this view. Both 2 : 2′-dihydroxyazobenzene and *o*-hydroxybenzeneazo-β-naphthol gave crystalline bronzed copper derivatives containing one atom of copper to one azo-group, soluble in pyridine and other organic bases to intensely purple solutions. The lakes are co-ordinatively unsaturated since they yield crystalline *monopyridine* and *monoquinoline* compounds when crystallised from these bases, although they do not combine with aniline; the combined bases are firmly held. The molecular weight of the copper lake from *o*-hydroxybenzeneazo-β-naphthol is normal in pyridine and therefore only two formulæ (XVI and XVII) are available for this type of lake. The former may be rejected for a number of reasons, *e. g.*, (a) the ionised copper atom, besides being unstably held by phenolic groups, would become co-ordinated with four molecules of pyridine or quinoline (*i.e.*, two molecules of these bases would be present per atom of copper, instead of one as actually found), and moreover (b) it should be replaceable by sodium or other ions, whereas attempts to do this lead to a mixture of sodium and copper salts, and (c) the position of the second hydroxyl group should not be material, whereas, as will be seen later, this is not the case. The lakes, therefore, have the monomeric structure (as XVII) in which only one nitrogen of the azo-group is co-ordinated, the metal being associated in a 5- and in a 6-ring. This structure is seen from models to be very little strained, the molecule being nearly flat. The azo-group is necessarily of the *anti*-form. The degree of co-ordinative unsaturation, the high stability, and the general properties of the lakes strongly support this structure. A formula (XVIII) was proposed by Boutin (Thesis, Univ. of Lyons, 1933; see Kopp, *Bull. Soc. Ind. Rouen*, 1935, **63**, 120) for lakes of this type, but, as already pointed out, the co-ordination of a metal with both azo-nitrogens is impossible on stereochemical grounds; again, such a structure would be co-ordinatively saturated.



(XVI.)



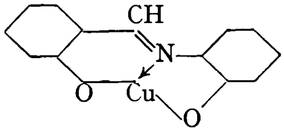
(XVII.)

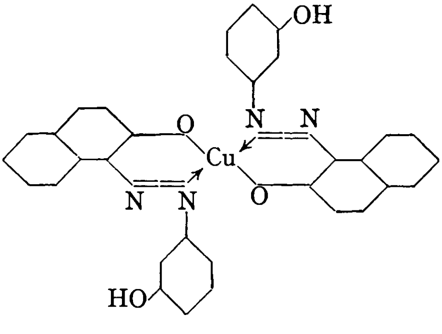


(XVIII.)

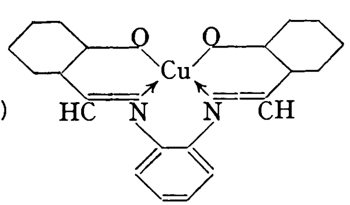
The pale green *copper* salt of salicylidene-*o*-aminophenol (XIX), in which there is only one nitrogen atom, was prepared; in confirmation of the proposed structure, it was found to possess properties similar to those of the copper lakes of the above azo-compounds. On the other hand, the copper salt of disalicylidene-*o*-phenylenediamine (XX) should be saturated co-ordinatively, a point on which no data are available.

(XIX.)





(XXI.)



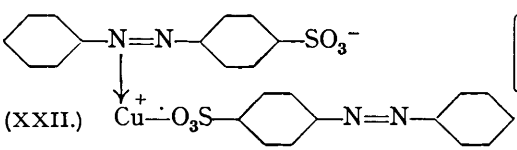
(XX.)

With the *oo′*-dihydroxy-azo-compounds may be compared the similar azo-compounds which have one of the hydroxyls in the *o*-position to the azo-group and the other removed to the *m*- or *p*-position in the second aromatic ring. Crippa (*Gazzetta*, 1928, **58**, 716) found that *p*-hydroxybenzeneazo-β-naphthol gives metallic lakes in which only the *o*-hydroxyl is involved, and it has now been found that *m*-hydroxybenzeneazo-β-naphthol behaves in a similar way, the copper derivative (XXI) containing two azo-groups to one copper atom. The behaviour of these azo-compounds is thus quite different from that of the *oo′*-dihydroxy-azo-compounds.

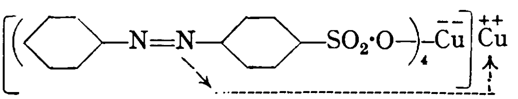
Azo-sulphonic Acids.—The sulphonic acid derivatives are among the most interesting forms of the azo-compounds, on account of their dyeing properties. Because of the great variety of forms shown by the azo-sulphonic acids and the numerous structural possibilities among their metallic derivatives, the study of these substances presents a complicated problem. So far, only a few outstanding types have been examined.

(1) Azobenzene-4-sulphonic acid formed a yellow copper salt, $(C_{12}H_9O_3N_2S)_2Cu,5H_2O$, an aqueous solution of which reacted only very slowly with hydrogen sulphide or with potassium ferrocyanide and did not react with potassium iodide in the cold; with potassium iodide in the hot, or with sodium sulphide, or with pyridine and potassium thiocyanate, it gave the reactions of an ionised copper salt. In contrast, solutions of cupric benzenesulphonate gave immediate precipitation with all the above reagents. We were unable to co-ordinate the latter salt with azobenzene. It seems probable that some kind of complex formation, accompanied by feeble co-ordination, occurs in cupric azobenzene-4-sulphonate. The ionic reactions of copper were similarly hindered in the analogous copper salts of several *o*-hydroxy-azo-compounds containing sulphonic acid groups in a *m*-, *p*-, or *peri*-position to the azo-group (see experimental section), although in each case the copper was associated with the sulphonic acid groups and not with hydroxyl.

This behaviour suggests that the cupric atoms of these salts of the sulphonic acids are in some way associated, though not strongly, with the azo-groups of the anions. This could be represented by a half ionised, half covalent structure (XXII), or by a dimeric structure (XXIII), analogous to that of $[Cu\,en_2]Cu(SO_4)_2$ and shown to be feasible from a stereochemical standpoint, in which one copper atom forms part of a complex anion and the other is a cation co-ordinated with four azo-nitrogen atoms. Neither of these formulæ seems probable, and for the present it appears best to assume that in solution the cupric ions are feebly co-ordinated with azo-nitrogen atoms of the anions. In the crystalline state this union with the azo-groups is probably disrupted, being replaced by co-ordination with water or with bases. Evidence on this point is perhaps to be found in the number of molecules of water or pyridine, or both, which are associated with the crystalline salts prepared under various conditions; for example, cupric benzeneazo-β-naphthol-4-sulphonate forms a heptahydrate, a dipyridino-pentahydrate, and a tetrapyridino-trihydrate, in each of which the copper atom may be regarded as an ion associated with four water and (or) pyridine molecules, three more water molecules being associated with the sulpho-groups.



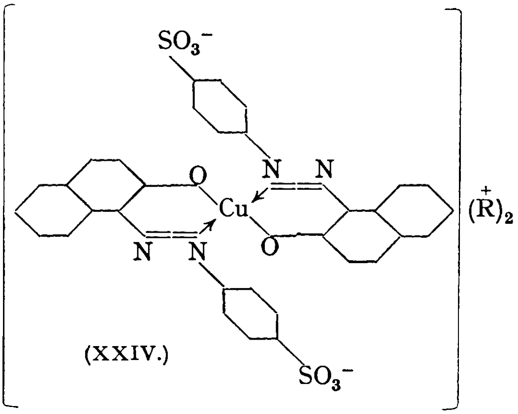
(XXII.)



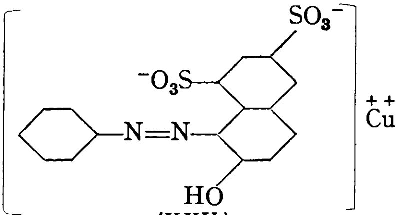
(XXIII.)

(2) o-*Hydroxy-azo-monosulphonic acids.* Of these the following were shown to form cupric salts at the sulphonic acid groups, the hydroxyls remaining free : 2-hydroxy-5-methylazobenzene-3′- and 4′-sulphonic acids, benzeneazo-β-naphthol-4′-sulphonic acid, 2-hydroxy-α-azonaphthalene-4′-sulphonic acid, and benzeneazo-β-naphthol-8-sulphonic acid. These salts, which are orange to red, are strongly hydrated and somewhat readily soluble in water.

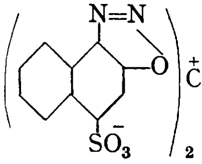
These simple copper salts undergo a remarkable change in the presence of alkali or of certain metallic salts (*e.g.*, acetates), becoming converted into brownish-red complexes in which the copper atoms have the inner type of co-ordination, *i.e.*, are associated with the oxygens of the hydroxyl groups and with azo-nitrogen atoms instead of with the sulpho-groups. For example, when a solution of the simple copper salt of benzeneazo-β-naphthol-4′-sulphonic acid is treated with sodium acetate or sodium bicarbonate, it gives the amorphous complex (XXIV, $R = Na$), which is soluble in water with a deep brown colour; with ammonium acetate, a similar but crystalline complex ($R = NH_4$) is produced; and with copper acetate, a purplish-brown complex ($R_2 = Cu$), very sparingly soluble in water but somewhat soluble in pyridine or aniline. Aqueous pyridine likewise effects the transformation of the simple into this complex copper salt, which is obtained in the form of a dipyridino-pentahydrate; a molecular proportion of the azo-compound is set free and appears as the pyridinium salt. Similar inner-complex copper derivatives were obtained from 2-hydroxy-5-methylazobenzene-3′- and 4′-sulphonic acids, 2-hydroxy-α-azonaphthalene-4′-sulphonic acid, and benzeneazo-β-naphthol-8-sulphonic acid. The change seems therefore to be a general phenomenon in the *o*-hydroxy-azo-sulphonic acid series. The inner-complex copper salts are very readily decomposed by acids (including the carboxylic and the sulphonic acid groups present in the molecule itself), and it seems to be a rule that copper cannot enter the inner-complex unless the carboxylic or the sulphonic acid groups are neutralised by copper atoms or other basic groups.



(XXIV.)



(XXV.)



(XXVI.)

(3) *Benzeneazo-β-naphthol-6 : 8-disulphonic acid.* This azo-compound gave a red copper salt (XXV), which was very soluble in water. The barium salt was similar; both are octahydrated. The inner-complex salts have not yet been examined in detail.

(4) *4-Sulphonaphthalene-1 : 2-diazo-oxide.* The hexahydrated brownish-purple copper salt of this light-sensitive diazo-compound was examined, since Battegay and Schmidt (*Bull. Soc. chim.*, 1927, **41**, 205) considered it to be a co-ordinated salt, although Schmidt and Maier (*Ber.*, 1931, **64**, 767) dissented. The salt had the properties of a simple copper salt (XXVI), and treatment with the reagents noted above failed to bring about inner co-ordination of the metal. This is not unexpected, since a co-ordinated copper compound would here necessarily be the salt of a diazonium hydroxide.

Experimental.

(a) *o-Hydroxy-azo-compounds.*—[All copper derivatives as (I).] *o*-Hydroxyazobenzene, m. p. 83°, was prepared by Bamberger's method (*Ber.*, 1900, **33**, 1947, 3188), purified through its copper salt, and crystallised from alcohol. Its copper salt, prepared in alcoholic solution by means of cupric acetate, or cupric chloride and sodium ethoxide, formed silky brown needles from alcohol or benzene, m. p. 222° (corr.), or from pyridine (m. p. 223°) (Found: C, 63·0; H, 4·05; Cu, 13·85. Calc.: C, 62·95; H, 3·95; Cu, 13·85%). It was stable to cold alkali, but unstable to hot alkali, mineral acid, or aqueous sodium sulphide. We were unable to cause *p*-hydroxyazobenzene to combine with copper, nor could we obtain copper salts from either of the isomeric 2-hydroxy-5-methylazoxybenzenes.

2-Hydroxy-5-methylazobenzene, m. p. 107°, gave, with alcoholic copper acetate, the copper salt, which formed lustrous bronzed-brown needles, m. p. 232°, from benzene or alcohol (Found: Cu, 13·15. Calc.: Cu, 13·1%).

2-Hydroxy-5 : 5′-dimethylazobenzene, m. p. 95°, was light reddish-brown; its copper salt, prepared as above, formed purplish-brown needles, m. p. 225°, from xylene (Found: Cu, 12·85. Calc.: Cu, 12·4%).

Benzeneazo-β-naphthol gave its dark-maroon bronzed copper salt, m. p. 292°, crystallised from nitrobenzene, which did not combine with ammonia or pyridine (Found: Cu, 11·4. Calc.: Cu, 11·35%).

m-Tolylazo-β-naphthol formed red plates with golden lustre, m. p. 141—142°, from alcohol. With alcoholic cupric acetate it gave *cupric* m-*tolylazo-β-naphthoxide*, which formed light red-brown needles, m. p. 240—241°, from alcohol (Found: C, 69·6; H, 4·7; Cu, 11·3. $C_{34}H_{26}O_2N_4Cu$ requires C, 69·7; H, 4·45; Cu, 10·85%).

(b) *Azobenzene*-o-*carboxylic Acid.*—The azo-compound, prepared from nitrosobenzene and methyl anthranilate (Freundler, *Bull. Soc. chim.*, 1907, **1**, 219), formed orange plates, m. p. 97—98° (Found: C, 68·95; H, 4·95. Calc. for $C_{13}H_{10}O_2N_2$: C, 69·05; H, 4·45%). The red acid of the literature contains an unidentified substance which forms bright red needles, m. p. 225—229°, from acetic acid (Found: C, 66·15; H, 4·5; N, 11·75%).

Cupric azobenzene-o-*carboxylate* was precipitated as a dark oil when the azo-compound (1·7 g.) in alcohol (20 c.c.) was treated with 0·15 N-sodium hydroxide (1 equiv.), and an aqueous solution of cupric chloride dihydrate (1·28 g.) slowly stirred in. It soon solidified and then crystallised from chloroform in bright green prisms of the *dihydrate* (VI), m. p. 141—144°, which retained the water when dried for a short time over phosphoric oxide (Found: C, 56·8; H, 4·2; Cu, 11·6. $C_{26}H_{18}O_4N_4Cu,2H_2O$ requires C, 56·75; H, 4·0; Cu, 11·6%); an air-dried sample gave the same analysis. The dihydrate was very sparingly soluble in water, and was somewhat soluble to greenish-yellow solutions in chloroform, benzene, and pyridine, with loss of water when the solutions were heated (change of colour), but the anhydrous substance did not crystallise; on exposure to air, the dihydrate slowly separated. The impure anhydrous substance, m. p. 120—126° (decomp.), was prepared as a yellow powder by dissolving the dihydrate in benzene, boiling the solution to expel water, and precipitating the salt with light petroleum (Found: C, 59·4; H, 4·15; Cu, 13·85. $C_{26}H_{18}O_4N_4Cu$ requires C, 60·75; H, 3·5; Cu, 12·4%); it was hygroscopic but was liable to become hydrolysed to the free azo-compound and copper hydroxide. The dihydrate was completely hydrolysed on solution in glacial acetic acid and addition of water. Crystallised from aniline, the dihydrate gave a *dianiline* compound, yellowish-brown needles, m. p. 142° (Found: C, 65·45; H, 4·8; Cu, 9·65. $C_{26}H_{18}O_4N_4Cu,2C_6H_5{\cdot}NH_2$ requires C, 65·2; H, 4·6; Cu, 9·1%). From pyridine, in which it dissolved very readily, the dihydrate gave minute olive-green plates, m. p. 145—148° (decomp.), which still had a faint odour of pyridine after exposure to air for 18 hours; this appeared to be a *tripyridine* compound (Found: C, 65·65; H, 4·4; N, 13·35; Cu, 8·6. $C_{26}H_{18}O_4N_4Cu,3C_5H_5N$ requires C, 65·55; H, 4·4; N, 13·05; Cu, 8·5%); on being kept until all odour of pyridine was absent, the above gave a *dipyridine* compound (Found: C, 64·4; H, 4·8. $C_{26}H_{18}O_4N_4Cu,2C_5H_5N$ requires C, 64·3; H, 4·2%), which lost all its pyridine in 1 hour in a stream of dry air at 105° (Found: loss, 23·5. Calc.: loss for $2C_5H_5N$, 23·5%). When the tripyridine compound was dissolved in chloroform, precipitation with light petroleum gave yellowish-green stout needles, m. p. 183—184° (decomp.), of what is probably a *hemipyridine* compound (Found: C, 61·7; H, 4·05; Cu, 11·45. $C_{26}H_{18}O_4N_4Cu,\frac{1}{2}C_5H_5N$ requires C, 61·85; H, 3·7; Cu, 11·5%).

The *monoacetone* compound (VIII) separated from a solution of the dihydrate in acetone, as brownish-green hexagonal plates, m. p. 142° (decomp.) [Found: C, 60·55; H, 4·5; Cu, 11·15. $C_{26}H_{18}O_4N_4Cu,(CH_3)_2CO$ requires C, 60·9; H, 4·2; Cu, 11·1%]; this substance slowly lost acetone at 115° (Found: loss, 8·5. Calc.: loss, 10·2%).

(c) *Azobenzene-2 : 2′-dicarboxylic Acid.*—The azo-compound was prepared by reducing *o*-nitrobenzoic acid (Griess, *Ber.*, 1877, **10**, 1869) and purified through the barium salt: it formed orange crystals, m. p. 238—239° (Found: C, 62·35; H, 3·9. Calc.: C, 62·2; H, 3·7%).

Cupric azobenzene-2 : 2′-dicarboxylate was obtained, by the interaction in aqueous solution of cupric chloride and the sodium salt of the azo-compound, as bright green micro-needles, sparingly soluble in water and almost insoluble in benzene; analyses for the air-dried substance were inexact, but indicated a dihydrate. This salt, when dried at 110°, retained, or rapidly reabsorbed from the air, 1 mol. of water, the *monohydrate* (IX) being stable in air (Found: C, 48·3; H, 3·5; Cu, 18·15. $C_{14}H_8O_4N_2Cu,H_2O$ requires C, 48·05; H, 2·85; Cu, 18·2%); it decomposed at a higher temperature or when heated with water; mineral acids or aqueous sodium bicarbonate decomposed it, and potassium iodide or ferrocyanide gave reactions as for cupric ions. When freshly crystallised from pyridine, in which it was only moderately soluble, it gave a green crystalline powder, probably a tripyridine-monohydrate, which lost pyridine slowly in air, becoming probably a monopyridine-monohydrate; the latter was soluble in boiling water without decomposition, but liberated pyridine on addition of sodium carbonate. Analyses for the last two complexes were inexact, owing to the instability of the pyridine compounds.

(d) o-*Hydroxy*-o′-*carboxy-azo-compounds.*—*o*-Carboxybenzeneazo-*p*-cresol, dark-red crystals, m. p. 186°, gave with boiling alcoholic cupric chloride the purplish red-brown *cupric* derivative (as X), which was purified by extraction with hot alcohol to remove free azo-compound (Found: C, 52·9; H, 3·7; Cu, 19·45. $C_{14}H_{10}O_3N_2Cu$ requires C, 52·9; H, 3·15; Cu, 20·0%); it was insoluble in benzene or alcohol, but soluble in aniline or pyridine. From the former it gave the *monoaniline* compound as brown needles with faint green reflex (Found : C, 58·55; H, 4·5; Cu, 15·4. $C_{14}H_{10}O_3N_2Cu,C_6H_5\cdot NH_2$ requires C, 58·45; H, 4·15; Cu, 15·5%); and from pyridine, a monopyridine compound, brown needles, for which an inexact analysis was obtained owing to its tendency to lose pyridine.

o-Carboxybenzeneazo-β-naphthol formed bright red needles, m. p. 268° (decomp.), from nitrobenzene, and gave, as in the preceding case, the *copper* derivative (X) in brown needles with strong green reflex (Found : C, 57·95; H, 3·15; Cu, 17·9; M, in boiling pyridine, 328, 385, 347. $C_{17}H_{10}O_3N_2Cu$ requires C, 57·7; H, 2·85; Cu, 18·0%; M, 353·6), soluble in aniline or pyridine, but sparingly soluble in alcohol and insoluble in water. The *monoaniline* compound (XI), a brown powder, was prepared as before (Found : C, 62·2; H, 4·15; Cu, 14·45. $C_{17}H_{10}O_3N_2Cu,C_6H_5\cdot NH_2$ requires C, 61·8; H, 3·8; Cu, 14·25%), and also the *monopyridine* complex, brown needles (Found : C, 60·95; H, 3·75; Cu, 14·8. $C_{17}H_{10}O_3N_2Cu,C_5H_5N$ requires C, 61·05; H, 3·45; Cu, 14·7%).

The action of cupric acetate on the azo-compound gave a brown basic copper derivative for which analyses (Found: C, 45·15; H, 3·25; Cu, 28·0%) indicated the formula $C_{17}H_{10}O_3N_2Cu,Cu(OH)_2$; this gave the same derivatives as the foregoing with aniline and pyridine.

(e) Benzeneazo-β-naphthol-3′-carboxylic acid, which formed a dark scarlet powder, m. p. 236—239°, from alcohol, gave with alcoholic cupric chloride (½ mol.), on gradual addition of aqueous sodium hydroxide (1 mol.), a brown precipitate of the normal copper carboxylate, but this was contaminated with cupric hydroxide; recrystallisation from pyridine gave a pure dipyridine compound (see below), but when the pyridine was removed by boiling with water hydrolysis again occurred, an impure salt being again obtained (Found : C, 61·8; H, 3·7; Cu, 10·4. $C_{34}H_{22}O_6N_4Cu$ requires C, 63·2; H, 3·4; Cu, 9·85%). Recrystallisation of the salt from aniline gave reddish-brown needles containing 3 or 4 aniline molecules, two of which appeared to be more firmly combined, but analyses varied with the method of drying (*e.g.*, a sample heated at 110° gave C, 66·85; H, 4·75; Cu, 7·65; whereas a sample dried over sulphuric acid gave C, 67·7; H, 5·15; Cu, 6·7. $C_{34}H_{22}O_6N_4Cu,2C_6H_5\cdot NH_2$ requires C, 66·4; H, 4·4; Cu, 7·65%. $C_{34}H_{22}O_6N_4Cu,3C_6H_5\cdot NH_2$ requires C, 67·5; H, 4·65; Cu, 6·85%).

The *dipyridine* compound separated slowly from a solution of the copper salt in pyridine; two forms were obtained : (i) (possibly XV) massive brown crystals with strong green reflex, m. p. 115—120° (Found : C, 65·45; H, 4·65; Cu, 7·1%), and (ii) (possibly XIV) golden-orange needles, m. p. 233—234° (darkening at 170°) (Found: C, 65·75; H, 4·45; Cu, 7·9. $C_{34}H_{22}O_6N_4,2C_5H_5N$ requires C, 65·7; H, 4·0; Cu, 7·9%). Both forms evolved pyridine when boiled with water. With alcoholic cupric acetate the azo-compound gave a brown powder which appeared from analysis to consist of the impure, partly co-ordinated copper salt, $C_{34}H_{20}O_6N_4Cu_2$ (Found : Cu, 20·5%), insoluble in water or benzene but soluble in and combining with pyridine or aniline; the solution of this substance in hot aniline deposited, on cooling, an amorphous brown powder (Found : C, 63·6; H, 4·6; N, 10·4; Cu, 13·05%) which may have been the compound $[C_{34}H_{20}O_6N_4Cu][Cu(C_6H_5\cdot NH_2)_4]$ contaminated with copper oxide.

(f) Benzeneazo-α-naphthol-2′-carboxylic acid, which formed purplish-red crystals, m. p. 245—246°, from acetic acid, was purified through its sodium salt. The addition of an equivalent of aqueous sodium hydroxide to a solution of the azo-compound (1 g.) and cupric chloride dihydrate (0·3 g.) in boiling alcohol (500 c.c.) gave brownish-red *cupric benzeneazo-α-naphthol-2′-carboxylate*, obtained as the dihydrate (as VI) after drying at 105° (Found : C, 59·85; H, 3·6; Cu, 9·6. $C_{34}H_{22}O_6N_4Cu,2H_2O$ requires C, 59·85; H, 3·6; Cu, 9·35%); this was insoluble in most solvents, but dissolved in hot aniline, the *anhydrous salt* (probably as VII A) separating as a brown powder (Found : C, 63·5; H, 4·0; Cu, 10·65. $C_{34}H_{22}O_6N_4Cu$ requires C, 63·2; H, 3·4; Cu, 9·85%). From pyridine, it separated in reddish-brown needles, m. p. 199°, of the *dipyridine compound* (Found : C, 65·85; H, 4·5; Cu, 8·05. $C_{34}H_{22}O_6N_4Cu,2C_5H_5N$ requires C, 65·7; H, 4·0; Cu, 7·9%); this lost the pyridine when boiled with water, giving the *trihydrate* of the above copper salt (Found : C, 58·55; H, 4·1; Cu, 9·4. $C_{34}H_{22}O_6N_4Cu,3H_2O$ requires C, 58·3; H, 4·0; Cu, 9·1%), which was converted into the dihydrate at 105° (Found : loss, 2·05. Calc. for loss of 1 H_2O, 2·55%).

(g) oo′-*Dihydroxy-azo-compounds*.—2 : 2′-Dihydroxyazobenzene, brownish-yellow plates, m. p. 171—172°, was prepared by fusing *o*-nitrophenol with potassium hydroxide (Willstätter and Benz, *Ber.*, 1906, **39**, 3492); Hunter and Barnes (J., 1928, 2051) regard this as the *trans*-form. The *copper* derivative (XVII) was obtained as a brown gelatinous precipitate when the azo-compound was treated with an excess of cupric acetate or chloride in alcoholic solution; it separated from aniline in copper-coloured needles, m. p. 346—347° (decomp.) (Found : C, 52·15; H, 3·45; Cu, 22·9. $C_{12}H_8O_2N_2Cu$ requires C, 52·25; H, 2·9; Cu, 23·1%). The *monopyridine* compound formed brown micro-needles with greenish lustre, becoming discoloured above 205° and blackening at 323° (Found: Cu, 18·05. $C_{12}H_8O_2N_2Cu,C_5H_5N$ requires Cu, 17·95%). The *monoquinoline* compound formed brown needles (Found: C, 62·45; H, 3·95; Cu, 16·2. $C_{12}H_8O_2N_2Cu,C_9H_7N$ requires C, 62·3; H, 3·7; Cu, 15·7%).

o-Hydroxybenzeneazo-β-naphthol was prepared from *o*-aminophenol and β-naphthol; it separated in bronzed-violet plates, m. p. 192°, from alcohol. The *copper* derivative (as XVII) separated from aniline in reddish-brown needles, stable and unmelted at 365° (Found: C, 58·85; H, 3·35; Cu, 19·6; *M*, in boiling pyridine, 336, 318. $C_{16}H_{10}O_2N_2Cu$ requires C, 58·95; H, 3·05; Cu, 19·55%; *M*, 325·6); it was decomposed by hydrochloric acid in presence of alcohol or ether, the azo-dye being recovered as red plates with greenish-gold lustre, m. p. 192°.

The *monopyridine* compound of the copper salt was purplish-red (green lustre), and decomposed above 200° (Found: C, 62·8; H, 4·1; Cu, 15·7. $C_{16}H_{10}O_2N_2Cu,C_5H_5N$ requires C, 62·3; H, 3·7; Cu, 15·6%); its pyridine was not lost at 110° in a stream of dry air, but was removed on boiling with alcohol.

The *monoquinoline* compound formed dark red needles with green lustre, decomposing above 200° (Found: Cu, 13·55. $C_{16}H_{10}O_2N_2Cu,C_9H_7N$ requires Cu, 14·0%).

Salicylidene-*o*-aminophenol (orange-red needles, m. p. 183°) gave with alcoholic cupric acetate the pale green *cupric* derivative (XIX), insoluble in water or benzene (Found: Cu, 23·6. $C_{13}H_9O_2NCu$ requires Cu, 23·15%); it crystallised in green needles from dimethylaniline, and dissolved to brownish-yellow solutions in pyridine, piperidine, and aniline.

(h) m-*Hydroxybenzeneazo*-β-*naphthol* was prepared from *m*-aminophenol and β-naphthol, as a reddish-brown powder, m. p. 231—233°, which may perhaps be a hemihydrate (Found: C, 70·5, 70·3; H, 4·7, 5·25. $C_{16}H_{12}O_2N_2,\frac{1}{2}H_2O$ requires C, 70·3; H, 4·85%). Its alcoholic solution was treated with cupric acetate, and water added; a dark brown precipitate was then obtained; this was extracted with boiling alcohol. The concentrated extract gave the *copper* derivative (XXI) as dark brown needles with strong green reflex, m. p. 237° to 244° according to the rate of heating; it was rather soluble in organic solvents; analysis of two preparations (Found: C, 62·05, 61·95; H, 4·8, 4·9; Cu, 10·55, 10·65. $C_{32}H_{22}O_4N_4Cu,1\frac{1}{2}H_2O$ requires C, 62·25; H, 4·05; Cu, 10·3%) showed that one copper atom was present to 32 carbon atoms, but the degree of hydration remained uncertain.

(i) *Azo-sulphonic Acids.*—Azobenzene-4-sulphonic acid was obtained as the trihydrate, orange plates, m. p. 130° from water. An aqueous solution of the acid reacted with cupric chloride to give the sparingly soluble *pentahydrate* of the cupric salt in orange-yellow plates (Found: C, 42·4; H, 4·55; Cu, 9·5. $C_{24}H_{18}O_6N_4S_2Cu,5H_2O$ requires C, 42·65; H, 4·15; Cu, 9·4%). This separated from pyridine in yellowish-brown crystals, which, when dried in air for a day, appeared to be a *tripyridine* compound (Found: C, 56·8; H, 4·75; Cu, 7·95. $C_{24}H_{18}O_6N_4S_2Cu,3C_5H_5N$ requires C, 56·9; H, 4·0; Cu, 7·75%). If moisture was excluded, a pyridine solution, treated with benzene, gave brown hexagonal plates of an unstable penta- or hexa-pyridine compound (Found: C, 59·5; H, 4·95; N, 13·9; Cu, 5·8%); but if the benzene was moist, a substance containing both water and pyridine molecules was obtained (Found: C, 55·85; H, 4·95; N, 11·5; Cu, 6·25%). When exposed to moist air, the pyridine compounds all slowly revert to the pentahydrate. The addition of pyridine to a hot aqueous solution of the latter gave an insoluble yellow basic salt.

Benzeneazo-β-naphthol-4′-sulphonic acid was obtained from its sodium salt (" Orange II ") in dark red needles, m. p. 139—140°. The *cupric* salt, prepared as above, formed light reddish-orange needles of the *heptahydrate*, soluble in hot water (Found: C, 45·7; H, 4·65; Cu, 7·65. $C_{32}H_{22}O_8N_4S_2Cu,7H_2O$ requires C, 45·5; H, 4·25; Cu, 7·55%); it lost $5H_2O$ (Found: loss, 10·9. Calc., 10·65%) when dried over phosphoric oxide in a vacuum, giving the hygroscopic brown *dihydrate* (Found: C, 50·9; H, 3·95; Cu, 9·2. $C_{32}H_{22}O_8N_4S_2Cu,2H_2O$ requires C, 50·95; H, 3·45; Cu, 8·45%). When the heptahydrate or the dipyridine pentahydrate (below) was dissolved in pyridine, and benzene added, golden-red needles of a *tetrapyridine trihydrate* were obtained (Found: C, 57·5; H, 4·45; N, 10·15; Cu, 6·05. $C_{32}H_{22}O_8N_4S_2Cu,4C_5H_5N,3H_2O$ requires C, 57·35; H, 4·4; N, 10·3; Cu, 5·85%).

The *dipyridine pentahydrate*, which is soluble in water without loss of pyridine, was obtained in lustrous orange needles by dissolving the copper salt (0·25 g.) and the free acid (0·2 g.) in hot water (15 c.c.), adding an excess of pyridine, and concentrating the solution to 5 c.c. (Found: C, 52·9; H, 4·6; N, 8·2; Cu, 6·65. $C_{32}H_{22}O_8N_4S_2Cu,2C_5H_5N,5H_2O$ requires C, 52·2; H, 4·35; N, 8·7; Cu, 6·6%).

Formation of inner co-ordinated complexes occurred in the following circumstances: (i)

When pyridine was added to an aqueous solution of the simple cupric salt, purplish-brown microcrystals separated; these were recrystallised from water containing a little pyridine (Found : C, 50·45; H, 4·15; N, 9·15; Cu, 12·35. $[C_{32}H_{20}O_8N_4S_2Cu][Cu(C_5H_5N)_2(H_2O)_2],3H_2O$ requires C, 50·1; H, 4·05; N, 8·35; Cu, 12·65%). The *substance* may be regarded as (XXIV) in which R_2 is a cupric ion associated with two pyridine and two water molecules. The mother-liquor gave the simple cupric dipyridine pentahydrate of the azo-dye (above) and the copper-free orange-red pyridinium salt of the azo-dye. (ii) When aqueous cupric acetate was added to an aqueous solution of the simple cupric salt, dark purplish-brown micro-needles (reddish-brown streak) of the inner-complex salt (XXIV; R_2 = Cu) separated as the hexa- or hepta-hydrate (Found : C, 43·05, 44·1; H, 3·75, 4·1; Cu, 14·8, 13·85. $[C_{32}H_{20}O_8N_4S_2Cu]Cu,6H_2O$ requires C, 43·3; H, 3·6; Cu, 14·35; whereas the heptahydrate requires C, 42·8; H, 3·75; Cu, 14·05%); it was very sparingly soluble in water and insoluble in most organic solvents, but soluble in aniline, pyridine, and benzonitrile; it was decomposed by acids, but reacted only slowly with the common reagents for copper. (iii) The action of an excess of sodium acetate or sodium bicarbonate on a solution of the simple cupric salt gave a brown amorphous solid, readily soluble in water (Found : Cu, 7·3, 7·5%); this was probably (XXIV; R = Na). (iv) When a solution of the simple cupric salt (0·5 g.) in water (25 c.c.) was treated with a concentrated aqueous solution of ammonium acetate (2—3 g.), deep brown, rectangular prisms of the *ammonium* salt of the cupric complex (XXIV; R = NH_4) separated, probably as the *hexahydrate* (Found : C, 44·85; H, 5·05; Cu, 7·15. $[C_{32}H_{20}O_8N_4S_2Cu](NH_4)_2,6H_2O$ requires C, 44·65; H. 4·65; Cu, 7·4%). (v) When the simple cupric salt was dissolved in hot water and treated with dilute aqueous ammonia, a sparingly soluble, brown copper derivative was precipitated, and a similar substance was obtained by the action of copper acetate and ammonia on the free azo-dye (Found : C, 43·2; H, 4·35; Cu, 14·9%); this substance may be an ammino-analogue of the pyridino-compound described in (i).

Benzeneazo-β-naphthol-8-sulphonic acid, crystallised from alcohol and concentrated hydrochloric acid, formed deep reddish-purple needles with strong green reflex, m. p. 202° (decomp.). The simple *cupric* salt was a *tetrahydrate,* a bright red, crystalline powder (Found : C, 48·95; H, 4·0; Cu, 7·8. $C_{32}H_{22}O_8N_4S_2Cu,4H_2O$ requires C, 48·65; H, 3·8; Cu, 8·05%), which lost $2H_2O$ on being dried over phosphoric oxide (Found : loss, 4·85. Calc., 4·55%); crystallisation of this salt from pyridine with addition of benzene gave deep red, rhombic plates of the *tetrapyridine* derivative (Found : C, 60·6; H, 4·6; Cu, 6·0. $C_{32}H_{22}O_8N_4S_2Cu,4C_5H_5N$ requires C, 60·4; H, 4·05; Cu, 6·15%). Brown salts containing copper in the inner-complex condition are produced by acting upon an aqueous solution of the simple salt with sodium acetate (Found : Cu, 7·75%) or cupric acetate (Found : Cu, 14·15%).

2-Hydroxy-5-methylazobenzene-4′-sulphonic acid was prepared as the yellow sodium salt (hydrated), which crystallised from hydrochloric or acetic acid without loss of the metal. The simple *cupric* salt crystallised from water in flat brownish-orange needles of the hexa- or hepta-hydrate (Found : C, 41·05; H, 4·65; Cu, 8·1, 8·35. $C_{26}H_{22}O_8N_4S_2Cu,6H_2O$ requires C, 41·4; H, 4·5; Cu, 8·45%. $C_{26}H_{22}O_8N_4S_2Cu,7H_2O$ requires C, 40·45; H, 4·65; Cu, 8·25%). Dried over phosphoric oxide, it gave the dark brown *trihydrate* (Found : C, 45·1; H, 4·0; Cu, 9·15; loss of H_2O, 9·0. $C_{26}H_{22}O_8N_4S_2Cu,3H_2O$ requires C, 44·6; H, 4·0; Cu, 9·1; loss of $4H_2O$ from heptahydrate, 9·35%). Sodium acetate gave an amorphous brown sodium salt of the inner-coordinated complex (Found : Cu, 7·4%), and ammonium acetate gave reddish-brown rhombic plates of the corresponding *ammonium cupric* salt (Found : C, 40·55; H, 4·9; Cu, 7·85, 8·2%), apparently a penta- or tetra-hydrate and soluble in water to a red solution.

2-Hydroxy-5-methylazobenzene-3′-sulphonic acid was prepared as its hydrated orange sodium salt, which separated from dilute hydrochloric acid in purplish flakes. The simple *cupric* salt crystallised from water in orange-red plates, with golden lustre, of the *heptahydrate* (Found : C, 39·95; H, 4·9; Cu, 8·65. $C_{26}H_{22}O_8N_4S_2Cu,7H_2O$ requires C, 40·45; H, 4·65; Cu, 8·25%). Sodium acetate gave an amorphous brown sodium cupric salt (Found : Cu, 7·65%), and ammonium acetate gave a crystalline salt.

2-Hydroxy-α-azonaphthalene-4′-sulphonic acid, which formed purplish-red needles from alcohol and hydrochloric acid, gave the simple *cupric* salt in purplish-brown needles, sparingly soluble in water (Found, in two preparations : C, 50·1, 50·75; H, 4·8, 4·45; Cu, 7·8, 8·6%), indicating a hepta- or an octa-hydrate. With this salt sodium acetate gave a purplish-brown sodium cupric salt containing two sodium atoms to each copper atom (Found: Cu, 6·3; Na, 4·8%).

Benzeneazo-β-naphthol-6 : 8-disulphonic acid formed deep red needles, with green reflex. Its *barium* salt formed red needles, with greenish-gold reflex, of the *octahydrate* (Found : Ba, 19·8. $C_{16}H_{10}O_7N_2S_2Ba,8H_2O$ requires Ba, 20·0%); and its simple *cupric* salt formed red needles, also an *octahydrate* (Found: C, 31·3; H, 4·35; Cu, 10·3. $C_{16}H_{10}O_7N_2S_2Cu,8H_2O$ requires C, 31·3; H, 4·25; Cu, 10·35%). The brown inner-co-ordinated salts were not examined.

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