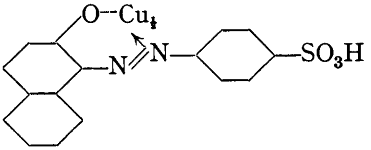
112. *Copper Lakes of Azo-dyes. Some Further Types.*

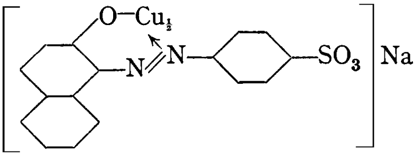
By W. F. Beech and H. D. K. Drew.

A number of copper lakes are described, in which copper is combined with azo-dyes containing reactive substituents in the *oo*'-positions (OH, CO_2H, NH_2). The effect of introducing one or two sulphonic acid groups into the aromatic nuclei of the azo-dyes has been examined. The results show that *both* nitrogen atoms of an azo-group can become co-ordinated to metal atoms, and that the aromatic nuclei can revolve to either side of the azo-chain. The azo-dyes are able to adjust their configurations to conform with the structural requirements of substituents in the nuclei and with the valency of the lake-forming metal.

In a previous study of this subject (Drew and Landquist, J., 1938, 292), it was mentioned that copper, although it readily forms lakes with mono-*o*-hydroxyazo-dyes, has not yet been induced to form such complexes when a sulphonic acid group is present in one of the aromatic nuclei of the dye, unless this group has been neutralised by entering into salt formation with another basic atom or group. For instance, in several cases examined, there was formed, from an azo-dye of this kind and a copper salt, not the internal complex, *e.g.*, (I), but merely the simple copper salt of the sulphonic acid; yet the sodium salt (II) of the internal complex could readily be prepared and could even be obtained directly from the simple copper salt of the azo-dye and sodium acetate. This behaviour, which suggested that the sulphonic acid group was too strongly acidic to allow of the retention of copper by linkings to two azo-groupings and two *o*-hydroxyls, raised some interesting questions as to what would occur when other types of azo-sulphonic acids were employed. Some of these cases are discussed in the present paper.

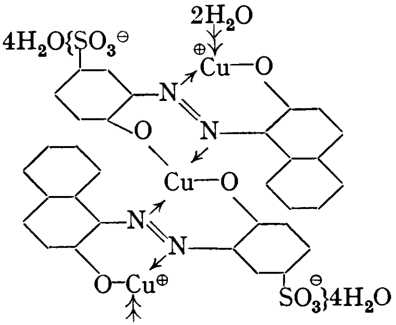
(I.)



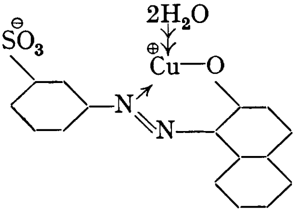


(II.)

The first point examined was as to whether the presence of a single sulphonic acid grouping in an *oo*'-dihydroxyazo-dye would be sufficient to prevent formation of an internal complex. When 2'-hydroxy-5'-sulphobenzeneazo-β-naphthol was condensed with cupric chloride, a reddish brown *cupri-complex dodecahydrate*, containing three atoms of copper to two azo-dye residues, was obtained in high yield. This substance can apparently only be formulated as (III), in which the azo-nitrogen atoms are necessarily in the *anti*-form in both of the dye residues. The substance presents the first case which demonstrates that *both* of the nitrogen atoms of an azo-grouping can be co-ordinated to metallic atoms at the same time (although, necessarily, not to a single metallic atom; compare *loc. cit.*, p. 293), or, in other words, that both nitrogen atoms of an azo-group can remain co-ordinatively saturated.



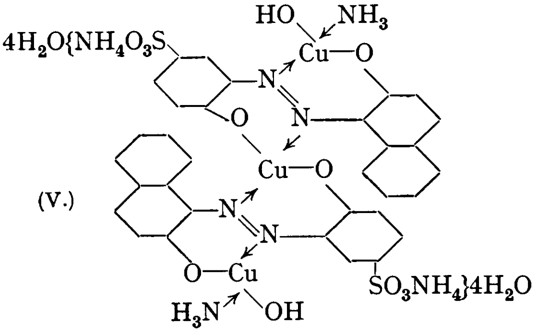
(III.)

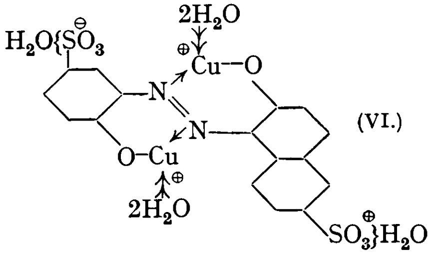


(IV.)

Another point of interest is that a copper atom is, in this instance, able to maintain its position in a lake although it is ionised from a sulphonic acid grouping. This might mean that in the *oo*'-dihydroxyazo-dyes the linkages from oxygen or from the azo-nitrogens (or both) are stronger than in the case of the mono-*o*-hydroxyazo-dyes; or, alternatively it might be assumed that such a lake as (IV) should be preparable. However, as described below, our attempts to isolate (IV) and similar lakes failed, and it therefore seems probable that each hydroxyl of the *oo*'-dihydroxyazo-dyes is in fact more acidic than the hydroxyl of the mono-*o*-hydroxyazo-dyes. Lastly, two of the copper atoms of (III) are each singly ionised and co-ordinated with three other atoms, a condition not often met with in copper lakes (*loc. cit.*, p. 293). The crystalline *ammonium salt octahydrate* (V) was prepared from (III); it retained two ammonia molecules co-ordinated to the outer copper atoms.

(V.)

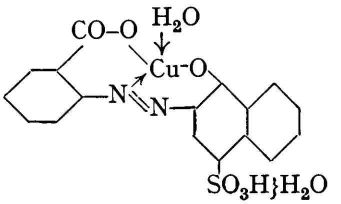


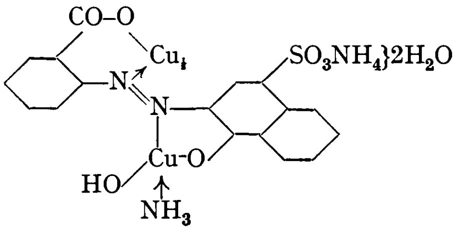


(VI.)

A second point examined was the effect of the presence of two sulphonic acid groupings in the *oo*'-dihydroxyazo-dye. From 2'-hydroxy-5'-sulphobenzeneazo-β-naphthol-6-sulphonic acid and cupric chloride in aqueous-alcoholic solution were obtained greenish-bronzed red crystals of the *cupri*-complex (VI), with 5½ or 6 H_2O; this substance was readily soluble in water. It appears to be the first case of a lake of a bivalent metal in which two atoms of the metal are combined with only one azo-dye residue. Its preparation affords indirect confirmation of the structure of (III), since the formation of a substance of structure (VI) could have been predicted from that of (III); it confirms also the principle of the co-ordinative saturation of the azo-group.

(VII.)



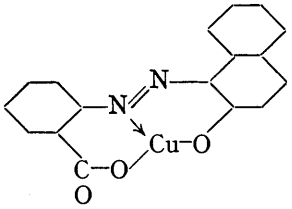


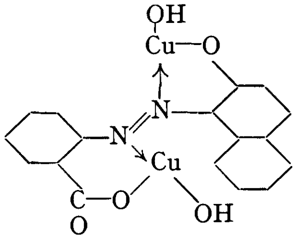
(VIII.)

In (III) and (VI) it is seen that aromatic nuclei bearing the two *o*-hydroxyl groups have become rotated so as to bring the hydroxyls on opposite sides of the azo-chain, whereas it has already been shown (Drew and Landquist, *loc. cit.*) that in *oo*'-dihydroxyazo-dyes devoid of sulphonic acid groupings simpler copper lakes are formed, with the two hydroxyls on the same side of the azo-chain. The above authors found that 2'-carboxybenzeneazo-β-naphthol gave, with alcoholic cupric chloride, brown needles of a lake of this latter type (A); but that, with alcoholic cupric acetate, the azo-dye gave a brown basic copper derivative, the analysis of which agreed closely with the empirical formula $C_{17}H_{10}O_3N_2Cu,Cu(OH)_2$. They were then unable to suggest a likely structural formula, but it seems clear, in the light of the results now described, that the substance was the *cupri-hydroxide* complex (B). This case is of interest, since it indicates that both types of lake can be prepared from the same azo-dye under different conditions of acidity of the medium.

In order to see whether the presence of an *o*-carboxylic acid grouping in the azo-dye would modify the type of lake formed in the case of a monosulphonic acid, 2'-carboxybenzeneazo-α-naphthol-4-sulphonic acid was condensed with cupric chloride in aqueous solution. The purplish-brown *cupri*-complex *dihydrate* contained one copper atom to each azo-dye residue and was sparingly soluble in water. The structure is probably (VII), but there are alternatives which cannot be eliminated. A crystalline red *ammonium* salt, probably (VIII), was obtained from (VII), but with a change of structure, involving the elimination of one-third of the azo-dye residues and also co-ordination of ammonia; on being kept for some weeks, this salt lost almost the whole of its water of crystallisation and co-ordinated ammonia.

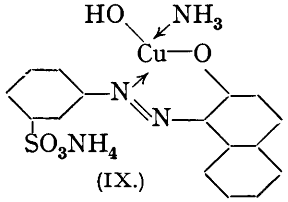
(A.)



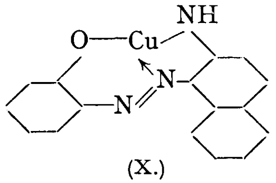


(B.)

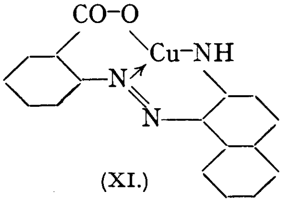
Two further *o*-hydroxyazo-monosulphonic acid dyes were examined to try to obtain a copper lake with a free sulphonic acid group (as IV). Benzeneazo-α-naphthol-4-sulphonic acid gave with aqueous cupric chloride only the simpler *copper* salt *octahydrate*; 3′-sulphobenzeneazo-β-naphthol gave a similar simple *copper* salt *octahydrate*. The action of ammonia on the latter salt was examined : the effect was, as in previous cases (*loc. cit.*), to transfer the copper to the inner complex, the *ammonium* salt of a *cupri-hydroxide* complex (IX) being isolated as red needles, the ammonia having in this instance removed one of the dye residues. The production of a salt of this type was not observed in the previous work, and it may be that the concentration of ammonia determines whether or not the cuprihydroxide stage shall be attained.



(IX.)



(X.)



(XI.)

Lakes of a kind not before described were obtained from two azo-dyes containing an *o*-amino-group. 2′-Hydroxybenzeneazo-β-naphthylamine gave a purplish-red *cupri*-complex (X), which was anhydrous, but combined with pyridine to form the well-crystallised *monopyridino*-derivative of (X); the degree of co-ordinative unsaturation of (X) is compatible only with the monomeric structure assigned to it. Similarly, 2′-carboxybenzeneazo-β-naphthylamine gave the red anhydrous *cupri*-complex (XI), which crystallised from aqueous pyridine probably as a monopyridino-derivative; but, on exposure to moist air, the pyridine was displaced by water, giving the *monohydrate* of (XI).

The lakes described in this paper illustrate the several ways in which the azo-dye molecules are able to adjust themselves in order to accommodate the varying stereochemical and structural factors brought into play by the introduction of different substituents into the aromatic nuclei. Thus, not only either but both azo-nitrogen atoms can become co-ordinated with the metal atoms, and at the same time the aromatic rings can revolve about the bonds joining them to the azo-group, bringing the reactive *o*-substituents into the most favourable positions for lake formation. If the results obtained with the copper lakes are compared with those described in the cases of chromium (Drew and Fairbairn, J., 1939, 823) and aluminium (Beech and Drew, preceding paper), it will also be manifest that similar adjustments are brought into operation to satisfy the numerical difference of valency among the lake-forming metals.

EXPERIMENTAL.

2′-Hydroxy-5′-sulphobenzeneazo-β-naphthol.—To a filtered, hot solution of the free azo-sulphonic acid (1·14 g.; 2 mols.) in water (150 c.c.) was added a solution of cupric chloride dihydrate (0·85 g.; 3 mols.) in a little cold water, whereupon a reddish precipitate separated. The mixture was boiled under reflux for one hour, and the precipitate filtered off, washed with boiling water (250 c.c.), and dried on porous tile in air (yield, 1·5 g.). When molecular proportions of dye and copper salt were employed in the preparation, the yield was only 0·8 g., and part of the dye was left unchanged in the filtrate. The product was the *cupri*-complex *dodecahydrate* (III), four molecules of water evidently being associated with two of the copper atoms (the remainder of the water has been assigned to the sulpho-groups, but, in this case and in others described in this paper, it is to be recognised that only what appears the most probable location of the water molecules has been indicated); the complex was very sparingly soluble in water but could be recrystallised from that solvent; it was soluble in basic solvents or solutions but insoluble in the common organic solvents (Found: C, 35·45; H, 3·95; Cu, 17·2, 17·3; H_2O, loss at 170°, 19·8. $C_{32}H_{18}O_{10}N_4S_2Cu_3,12H_2O$ requires C, 35·25; H, 3·85; Cu, 17·5; $12H_2O$, 19·85%); exposed to moist air, the desiccated substance rapidly regained almost the whole of the lost water. It crystallised from dilute aqueous ammonia as small red-brown needles of the *ammonium* salt *octahydrate* (V), with two further ammonia molecules co-ordinated to the outer copper atoms (Found: N, 10·35; Cu, 16·95. $C_{32}H_{34}O_{12}N_8S_2Cu_3,8H_2O$ requires N, 10·0; Cu, 17·0%). The complex (III) was stable to dilute acetic acid, but not to mineral acids.

2′-Hydroxy-5′-sulphobenzeneazo-β-naphthol-6-sulphonic Acid.—Condensation between this azo-sulphonic acid and cupric chloride occurs in aqueous solution, but the separation of the product is difficult to effect, owing to its great solubility. The following method was preferable: the azo-sulphonic acid (1·1 g.; 1 mol.) was boiled with 96% alcohol, and a little water was added so as almost to complete the dissolution of the solid; the solution was filtered hot, and to the filtrate was added cupric chloride dihydrate (0·86 g.; 2 mols.) dissolved in a little warm 96% alcohol, whereupon precipitation began and the colour changed from orange to purplish. The mixture was boiled under reflux for 2 hours, and the precipitate filtered off; from the filtrate, good crystals separated in a few days and were removed. Both products, after being dried in air, were substantially the same, the latter being rather purer. They consisted of the *cupri*-complex (VI) (Found: C, 29·6; H, 3·45; Cu, 19·5, 19·6; H_2O, loss at 170°, 15·5.

$$C_{16}H_8O_8N_2S_2Cu_2,6H_2O$$

requires C, 29·3; H, 3·05; Cu, 19·4; $6H_2O$, 16·5%); the substance was probably a hexahydrate but the analytical figures are closer to those for 5½ mols. The complex formed red plates with green reflex; it was nearly insoluble in alcohol but readily soluble in cold water; mineral acids decomposed it.

2′-Carboxybenzeneazo-α-naphthol-4-sulphonic Acid.—The dye (1·1 g.) was dissolved in boiling water (100 c.c.) and treated with cupric chloride dihydrate (0·65 g.) dissolved in a little water; there was precipitation; the mixture was boiled under reflux for one hour, and the reddish-brown precipitate was collected, washed with hot water, and dried in air [Found (two preparations): C, 44·0, 43·95; H, 3·25, 3·3; Cu, 13·2; H_2O, loss at 150°, 7·9. $C_{17}H_{10}O_6N_2SCu,2H_2O$ requires C, 43·45; H, 3·0; Cu, 13·5; $2H_2O$, 7·65%]. Formula (VII) was considered the most probable for this *cupri*-complex *dihydrate*, which was much more soluble in water than (III); it separated from hot water in an amorphous state. When crystallised from hot dilute aqueous ammonia it gave red needles of an *ammonium* salt *tetrahydrate* with two co-ordinated ammonia molecules (Found: N, 10·4; Cu, 17·4; $H_2O + NH_3$, loss at 180°, 11·75. $C_{34}H_{34}O_{14}N_8S_2Cu_3,4H_2O$ requires N, 10·1; Cu, 17·3; $5H_2O + 2NH_3$, 11·2%), for which formula (VIII) is suggested. When dried at 180°, it polymerised, apparently from a cupri-hydroxide to a polymeric cupri-oxide, the co-ordinated ammonia molecules also being lost; loss equivalent to nearly 4 mols. of water and 2 mols. of ammonia occurred even on keeping the salt in air for 2 weeks (Found: C, 40·55; H, 2·95; H_2O, loss at 180°, 2·75%). That the ammonium sulphonate group tends to lose its water of crystallisation in some cases is confirmed in the salt (IX), below.

Benzeneazo-α-naphthol-4-sulphonic Acid.—This dye gave with boiling aqueous cupric chloride only the red simple *copper* salt *octahydrate* (Found: Cu, 7·3, 7·4; H_2O, loss at 140°, 16·1. $C_{32}H_{22}O_8N_4S_2Cu,8H_2O$ requires Cu, 7·4; $8H_2O$, 16·7%); it crystallised unchanged from hot water and was nearly neutral in reaction; when desiccated, it became nearly black but was rapidly rehydrated to the red material in moist air. *3′-Sulphobenzeneazo-β-naphthol* gave in a similar way a red simple *copper* salt *octahydrate* (Found: Cu, 7·6%; empirical formula as in last case). When dissolved in hot aqueous ammonia, this simple salt was transformed into red needles of the *ammonium* salt of a *cupri*-complex (IX), of which two preparations were analysed (Found : C, 44·2, 44·25; H, 4·2, 4·25; N, 12·35; Cu, 14·4, 14·3; $H_2O + NH_3$, loss at 160°, 5·9. $C_{16}H_{18}O_5N_4SCu$ requires C, 43·5; H, 4·1; N, 12·7; Cu, 14·4; $\frac{1}{2}H_2O + NH_3$, 5·9%); evidently the cupri-oxide was here formed on desiccation. The salt (IX) was nearly insoluble in both water and aqueous ammonia.

2′-Hydroxybenzeneazo-β-naphthylamine.—The azo-dye (1·3 g.) was dissolved in boiling 96% alcohol (150 c.c.) and the solution filtered while hot; cupric acetate monohydrate (1 g.), dissolved in hot alcohol (75 c.c.) containing glacial acetic acid (2 c.c.), was then added to the boiling solution of the dye; the reddish-brown precipitate was filtered off, boiled with alcohol (50 c.c.) and again collected and dried in air on porous tile. This substance was the *anhydrous cupri*-complex (X) (Found : C, 58·9; H, 3·2; Cu, 19·7. $C_{16}H_{11}ON_3Cu$ requires C, 59·15; H, 3·4; Cu, 19·6%); there was negligible loss of weight at 130°. The complex was somewhat soluble in benzene and readily soluble in pyridine, but insoluble in water, alcohol, or ether; it was decomposed by warm hydrochloric acid. When water was cautiously added to the intensely purple concentrated solution of the complex in hot pyridine, red hexagonal plates, with green reflex, separated on partial cooling; the crystals were removed at once, since they were liable to decompose on keeping in the mother-liquor. This product was the *monopyridino*-derivative of (X), the base being co-ordinated to the copper atom (Found : C, 62·8; H, 4·3; Cu, 15·6. $C_{21}H_{16}ON_4Cu$ requires C, 62·45; H, 4·0; Cu, 15·75%); warming with aqueous sodium hydroxide set free the pyridine.

2′-Carboxybenzeneazo-β-naphthylamine.—To a hot, filtered solution of the azo-dye (1·5 g.) in 96% alcohol (200 c.c.) was added a filtered solution of cupric acetate monohydrate (1·0 g.) in hot alcohol (75 c.c.) containing glacial acetic acid (2 c.c.); a red precipitate was formed. The mixture was boiled for a few minutes, and the precipitate was collected, boiled with alcohol (100 c.c.), and again filtered off and dried in air on porous tile. The substance was the anhydrous *cupri*-complex (XI) (Found : C, 57·55; H, 3·35; Cu, 18·2. $C_{17}H_{11}O_2N_3Cu$ requires C, 57·85; H, 3·15; Cu, 18·0%); it was insoluble in water or aqueous ammonia, and was decomposed by warm dilute hydrochloric acid. It dissolved readily in pyridine, the hot solution depositing glistening red needles with strong green reflex; this substance, after being dried in air on porous tile, proved to be the *monohydrate* of (XI), a co-ordinated pyridine molecule having probably been displaced by a water molecule (Found : C, 55·05; H, 3·45; Cu, 17·4. $C_{17}H_{13}O_3N_3Cu$ requires C, 55·05; H, 3·5; Cu, 17·2%).

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