

**176.** *Structure of the Chromium Lakes of Dyes. Part I. Lakes of *oo'*-Dihydroxy- and *o*-Hydroxy-*o'*-carboxy-azo-compounds, including Monosulphonic Acids. The Behaviour of Azosalicylic Acids with Chromic Salts.*

By H. D. K. DREW and R. E. FAIRBAIRN.

An investigation of the chromium lakes of mordant dyes was undertaken in view of the importance of chroming processes in the dyeing of fibres, and also in order to find what effect on the structures of the lakes would result on passing from a bivalent metal (such as copper) to trivalent chromium. For comparison, some lakes of ferric iron, and of some bivalent metals also, were examined. With *oo'*-dihydroxy- and *o*-hydroxy-*o'*-carboxy-azo-compounds, the chief type of chromium or ferric lake contained one azo-residue to one metallic atom, the third valency of the metal remaining associated with an acidic radical; when, in virtue of this third valency, the metallic atom interacted with a second molecule of the same or of a similar azo-dye, a more complex type of lake, acidic in nature, was produced. The effect of introducing a sulphonic acid group into the azo-dye was, in the case of chromium, to produce water-soluble lakes retaining the same essentials of structure. The lakes, which belong to types not hitherto described, were often beautifully crystalline, and their purity was not open to doubt; they represent, essentially, structures which are actually present in chrome-dyed fibres, the primary chromium lakes of the sulphonic acid dyes being identical with those deposited in dyeings with chromium lake dyes. The chromic lakes, especially those of the *oo'*-dihydroxy-azo-dyes, were found to be much more stable to mineral acids than the ferric or copper lakes. On the other hand, a single *o*-hydroxyl group was insufficient to hold a chromium atom in stable union with an azo-dye, so that the linking of chromium with an azo-nitrogen atom may be feebler than that of copper. The

azosalicylic acids formed chromic lakes having markedly different properties from the foregoing lakes; two types were recognised, which are probably of general occurrence in the series. Some lakes of nickel, copper, and zinc are also described: with the *oo'*-dihydroxy-azo-compounds, not containing sulphonic acid groups, nickel and zinc form, like copper, monomeric complexes involving combination of the metal atom with both hydroxyl groups. Monomeric copper derivatives of the azosalicylic acids were isolated; they may be among the types of the derivatives of this series which are applied industrially.

AMONG the numerous metallic derivatives of the mordant dyes, the chromium lakes are of paramount interest, because of their exceptionally favourable properties in relation to the dyeing of fibres. It is well recognised that the chroming of many dyes greatly improves their fastness to washing and milling, and also to light, and that it has an important effect in modifying the shades. Within the last few decades there has been a tendency towards the use as dyes of the chromium lakes themselves, as a supplement to the methods of introducing the metal by the chroming process. These two methods, however, are by no means equivalent in the majority of cases: for example, in a number of instances, whilst the shade produced by dyeing with a chromium lake is the brighter, that of one or more of the chroming processes may hold the advantage in fastness. The method of dyeing with a chromium lake leads to the introduction into the fibre of a practically uniform colouring lake, so that it may be regarded as the equivalent of dyeing with a single substance; but it is nearly certain that, at least in many instances, the chroming processes lead to the deposition in the fibre of more than one colouring lake. Hardly any information is available as to the structure of any of these colouring lakes of chromium, although in some examples of the chromium lakes used as dyes an approximate ratio of the number of chromium atoms present per molecule of combined dye has been given. It would clearly be of great advantage, in considering the mechanism of dyeing on the various fibres and the factors which control the degrees of fastness to the several agencies, to have an outline of the structures and properties of the colouring lakes of chromium. The object of the work to be described in the present and later papers was to obtain information of this kind by preparing and examining pure chromium derivatives of dyes, and subsequently to compare their effects on fibres with those obtained in the chroming processes. The present paper is concerned with chromium derivatives of some of the less complex mordant azo-dyes.

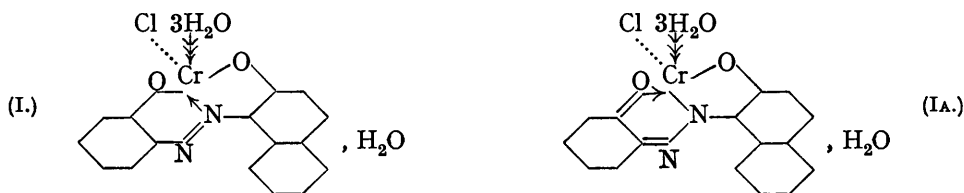
Morgan and his collaborators (Morgan and Porter, J., 1915, 107, 645; Morgan and Evens, J., 1919, 115, 1126; Morgan, *J. Soc. Dyers and Col.*, 1921, 37, 43) were the first to give close attention to the structure of the chromium lakes of azo-dyes. Morgan and Main Smith (J., 1921, 119, 704; 1922, 121, 160, 286; 1924, 128, 1731; *J. Soc. Dyers and Col.*, 1925, 41, 233; see also Morgan and King, J., 1922, 121, 1723; Morgan and Moss, *ibid.*, p. 2857) made an extensive examination of the cobaltamine lakes of azo-dyes containing three dye residues to each metallic atom bound in the inner sphere of co-ordination, and they prepared also several chromium lakes (*e.g.*, those of Diamond Black PV and of Palatine Chrome Black 6B) of analogous constitution. They recognised the union of the metallic atoms with azo-nitrogen and with a hydroxyl group in the *o*-position with respect to an azo-group. The substances described by them do not, however, overlap with any of those mentioned in the present paper.

We investigated the direct interaction of some of the simpler types of azo-compounds with chromium salts, in the absence of co-ordinating amines, with a view to extending the knowledge obtained by Morgan as to the part played by substituents ortho to the azo-group. We wished also to find how far the possession of the extra valency bond of tervalent chromium, as compared with bivalent copper, would influence the character of the metallic lakes (compare Drew and Landquist, J., 1938, 292, on the structure of the copper lakes). The following is a summary of the results obtained.

*o*-Hydroxy-azo-compounds. Experiments with benzeneazo- $\beta$ -naphthol, with 4'-nitro-, 4'-sulpho-, and 4'-carboxy-benzeneazo- $\beta$ -naphthol, and with benzeneazo- $\alpha$ -naphthol-4-sulphonic acid, in which attempts were made to obtain chromium derivatives involving union of chromium at the phenolic hydroxyl and co-ordination with azo-nitrogen, led to negative

results. Only salts in which chromium was combined with the carboxy- or sulpho-group could be obtained. This result tends to confirm the general impression that a single *o*-hydroxyl group is insufficient to hold a chromium atom in stable combination with azo-nitrogen, although further experiments with the azo-sulphonic acids are in progress. The co-ordinated ferric complexes were similarly either non-existent or very unstable, and those of bivalent manganese and of zinc were likewise not obtained. The behaviour of these metals, therefore, contrasts with that of bivalent copper, nickel, and cobalt, which readily form co-ordinated complexes with these *o*-hydroxyazo-compounds under suitable conditions.

*oo'*-Dihydroxy-azo-compounds. *o*-Hydroxybenzeneazo- $\beta$ -naphthol, when condensed in alcoholic solution with chromic chloride, gave as main product the dark purple, crystalline *chromi-chloride tetrahydrate* (I), which was soluble in warm water and contained the chlorine as an ion (indicated by a broken line in the formula). Three of the four water molecules are



probably co-ordinated with the chromium atom. When the tetrahydrate was caused to lose part or the whole of the attached water molecules, either by boiling its aqueous solution for some time or by drying the crystals at  $150^\circ$  and above, it became converted into a form insoluble in boiling water and not restored to the soluble condition on being kept for a long time in moist air or in water. It was found that other chromi-chlorides of the same type likewise occurred in water-soluble and -insoluble forms, the latter having a lower water content; and it seemed probable that, as soon as one or two molecules of water were lost from the tetrahydrate, the chlorine atom became covalently attached to chromium, giving a tri- or di-hydrated chromi-chloride, insoluble in water but soluble in ether. As partial loss of water from the water-soluble chromi-chlorides occurs very easily, the phenomenon is important in the preparation and use of these derivatives. The removal, above  $150^\circ$ , of the last molecule or two of water from the tetrahydrate was accompanied by loss of part of the chlorine as hydrogen chloride, probably with formation of a chromi-hydroxide or -oxide, and therefore the extent of the rehydration of the dried material, equivalent to  $2\frac{1}{2}$  molecules of water, on exposure to moist air had but little exact significance. Aqueous ammonia or potassium chromate produced from the chromi-chloride an amorphous purple precipitate, insoluble in water, but soluble in chloroform, which was shown to be the *chromi-oxide tetrahydrate* (or *chromi-hydroxide dihydrate*).

The preparation of the foregoing chromi-complexes showed without doubt that the third valency of trivalent chromium could remain, after lake-formation, as an ionised valency, or as a covalency, unassociated with the azo-dye residue, the union of the metal with the latter being constituted by the remaining two valencies of chromium and (probably) the co-ordination with azo-nitrogen. This type of lake, hitherto unobserved, was found to be of general occurrence among the *oo'*-dihydroxy- and *o*-hydroxy-*o'*-carboxy-azo-compounds, whether or not acidic groups were substituted in the aromatic nuclei of the azo-dye. It seems clear that in lakes of this type the plane of the azo-dye residue must be perpendicular to that of the three addenda co-ordinated to the chromium atom (*e.g.*,  $3\text{H}_2\text{O}$ ).

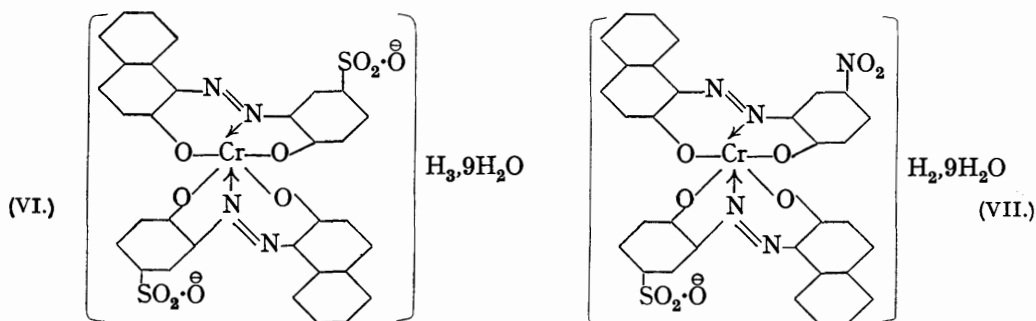
The tinctorial properties, also, suggested that these lakes were of interest in connection with the theory of chrome dyeing, and therefore attention was given to possible alternative methods of formulation. In the first place, polymeric forms of the suggested structure may be ruled out, since they would involve either (*a*) the presence of chromium bound in the external sphere, and such was shown to be absent; or (*b*) the linking of chromium atoms with two hydroxyls associated each with a different molecule of the azo-dye, a type of structure which may likewise be eliminated when the fact that the monohydroxy-azo-compounds do not form chromi-complexes is taken into consideration. There would thus appear no





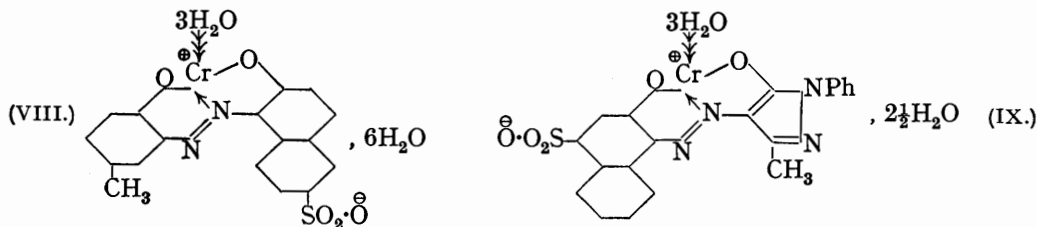
lost (see experimental section) and probably becoming a chromi-oxide of the azo-sulphonic acid; when dissolved in aqueous ammonia, it was transformed into the ammonium salt of (V). Amorphous precipitates were frequently produced in small quantities in similar condensations with other azo-dyes, but it was proved that they could not always be converted into soluble complexes in the manner described above.

A by-product of the condensations with the azo-sulphonic acid was usually present in the neutralised mother-liquors after the separation of (V); this substance, which was purple-black and soluble in water, was formed also on condensing (V) with a further molecular proportion of the azo-dye; it was the *nonhydrated tribasic acid chromi-complex* (VI), which formed soluble alkali salts; it was not rendered insoluble on desiccation. In the



same manner, 5'-nitro-2'-hydroxybenzeneazo- $\beta$ -naphthol combined with (V), giving the blue-black *nonhydrated dibasic acid chromi-complex* (VII). The formation of acids of this kind, on combination of the chromi-complexes with an additional molecule of the same or of another *oo'*-dihydroxyazo-dye, seems to be a general rule; it appears to be immaterial whether or not acidic substituents are present in either of the azo-residues; these chromi-acids dye animal fibres in much darker shades than do the former type of chromi-complexes (*e.g.*, V) of either of the constituent azo-dyes present, as also is the case with (VI) and its analogues.

When the sulphonic acid group in the foregoing type of dihydroxy-azo-compound was in the naphthalene instead of in the benzene nucleus, the same type of chromium complex was produced. 4'-Hydroxy-*m*-tolueneazo- $\beta$ -naphthol-6-sulphonic acid gave the crystalline



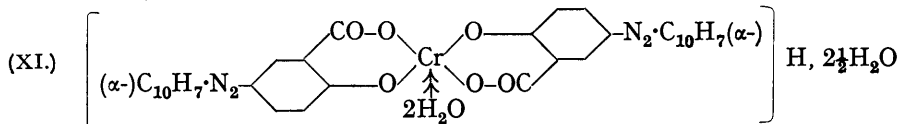
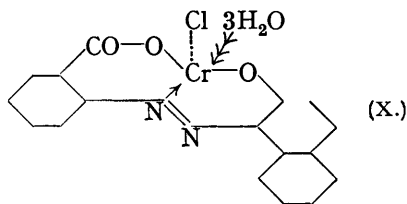
*nonhydrated chromi-sulphonate* (VIII), of a bluer shade of violet than (V), and also more difficult to obtain crystalline; on desiccation at  $150^\circ$ , it appeared to lose only eight of its nine molecules of water, and, unlike (V), it was not polymerised in the process but remained soluble in water.

Condensation of 2'-hydroxy-4'-sulphonaphthalene-1' : 4-azo-1-phenyl-3-methylpyrazol-5-one and chromic chloride in alcohol gave a crystalline red *chromi-sulphonate* (IX), which may have been a hexahydrate but appeared to contain  $5\frac{1}{2}$  molecules of water; it was only sparingly soluble in water, but formed readily soluble ammonium and alkali salts; on desiccation at  $170^\circ$ , it appeared to retain one molecule of water, but became still less soluble in water.

The examples given in the preceding paragraphs justify the conclusion that in all cases of *oo'*-dihydroxyazo-compounds the primary action of chromic salts is to insert a metal atom at the two hydroxyl groups, this atom being probably also co-ordinatively bound with

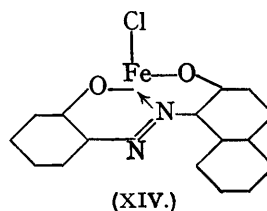
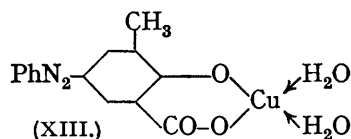
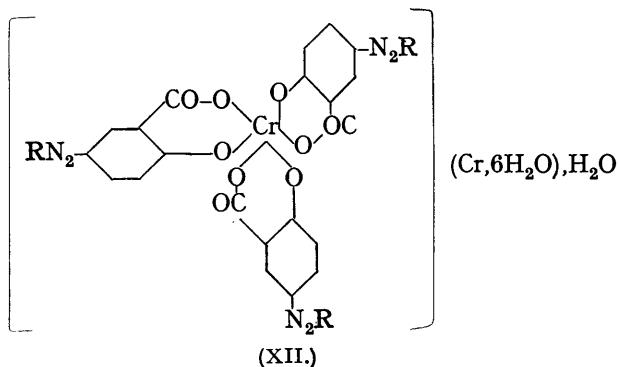
one nitrogen atom of the azo-group; and that when these complexes react with a further molecule of the azo-compound, salt-forming chromi-acids are produced.

*o*-Carboxy-*o'*-hydroxy-azo-compounds. Of these, only *o*-carboxybenzeneazo- $\beta$ -naphthol was examined. This azo-compound, when condensed with chromic chloride in alcohol, gave a red *chromi-chloride* (X), which was probably a trihydrate but was not obtained



crystalline; it contained a chloride ion and was soluble in water, the solution being deep red, but it occurred also in a less hydrated form insoluble in water. It was found in the case of copper (Drew and Landquist, *loc. cit.*) that the *o*-carboxy-*o'*-hydroxy- behaved similarly to the *oo'*-dihydroxy-azo-compounds, and the same is evidently true with respect to chromium.

*The azosalicylic acids.* The chroming of these dyes on animal fibres usually produces less change of shade than occurs with the foregoing types of mordant azo-dyes, but nevertheless the fastness is improved. With the azosalicylic acids, co-ordination of the metal with azo-nitrogen is not possible in a simple structure in which the atom of the metal is associated with the carboxy- and (or) hydroxy-group of the salicylic residue. In the only example of this type studied in detail, that of naphthalene-1'-azosalicylic acid, the two yellowish-brown *chromic complexes* isolated were very different in properties from those of the preceding azo-dyes; one of these (XI), was soluble in alcohol and in aqueous alkalis, and was a hydrated acid; but the other (XII, R =  $\alpha$ -C<sub>10</sub>H<sub>7</sub>) was insoluble in all solvents except pyridine, and was a chromic salt of a tribasic chromi-acid. It is of interest that here a tri-basic acid



can be produced, whereas with the preceding azo-compounds, such a substance, which could be formed only if the co-ordination of the metal with azo-nitrogen were broken, could not be isolated. With copper (see experimental part), the azosalicylic acid dyes formed complexes in which one azo-residue was united through the carboxy- and hydroxy-groups to one metallic atom, which was co-ordinated with two molecules of water or the like; for example, benzeneazo-*o*-cresotic acid formed with alcoholic cupric acetate the brown *cupri-complex dihydrate* (XIII).

*Ferric and other metallic complexes.* *o*-Hydroxybenzeneazo- $\beta$ -naphthol gave with ferric chloride in alcohol a crystalline greenish-black *ferric-chloride* (XIV), but anhydrous and with





dried in air for some weeks. Several independent preparations were analysed [Found: (1) C, 45.85; H, 4.55; Cr, 12.35; Cl, 8.75; loss at 200°, 16.7, 17.4; (2) C, 45.9; H, 4.65; Cr, 12.45; (3) C, 45.25; H, 4.35; Cr, 11.95; loss at 150°, 16.0; regain in air after 17 days, 12.9.  $C_{16}H_{10}O_2N_2ClCr \cdot 4H_2O$  requires C, 45.55; H, 4.3; Cl, 8.4; Cr, 12.35; loss of  $4H_2O$ , 17.1; regain of  $2\frac{1}{2}H_2O$ , 12.9%]. The chromi-chloride tetrahydrate was moderately readily soluble in warm water (purple-red solution), readily soluble in alcohol, very sparingly soluble in ether, and readily soluble in pyridine and other organic bases. When a solution of the chromi-chloride (2 g.) in warm water (100 c.c.) was heated with oxalic acid (1.5 g.) under reflux for 2 hours, a purplish powder separated; extraction of the dried powder with light petroleum gave crystals of the unaltered azo-compound, m. p. 192—193°. The chromi-chloride gave a *dipyridino*-compound (Found: C, 61.15; H, 4.55; Cr, 9.75.  $C_{16}H_{10}O_2N_2CrCl \cdot 2C_5H_5N$  requires C, 61.45; H, 3.9; Cr, 10.25%), a purple powder insoluble in water but soluble in chloroform; and also a similar dianilino-compound, which was not obtained pure (Found: C, 57.15; H, 5.6; Cr, 9.3%). When the chromi-chloride was dissolved in water and treated with ammonia, the *chromi-hydroxide* or *-oxide* was at once precipitated; aqueous potassium chromate gave a similar result. This substance was insoluble in water, but soluble in chloroform, from which it was obtained as a lustrous purple glass consisting of the *oxide tetrahydrate* [Found, in air-dried material: C, 53.65; H, 4.6; Cr, 13.9.  $(C_{16}H_{10}O_2N_2Cr)_2O \cdot 4H_2O$  requires C, 53.65; H, 3.9; Cr, 14.5%]; it was readily soluble in pyridine and in aniline, the bases partly replacing co-ordinated water molecules (Found, in the pyridino-compound: C, 60.85; H, 4.35; Cr, 11.95%).

The substance (b), soluble in ether as well as in alcohol, but almost insoluble in water, was kept in the air for a month [Found: C, 55.0; H, 4.5; Cr, 9.5, 9.8; loss at 140—185°, 13.15; regain in moist air, 4.9.  $(C_{16}H_{10}O_2N_2)_3Cr_2 \cdot 8H_2O$  requires C, 55.7; H, 4.45; Cr, 10.05; loss of  $8H_2O$ , 13.9%]. It was evidently a hydrated complex containing two chromium atoms to three azo-residues, probably (III).

The substance (c), insoluble in boiling alcohol, was identical with (II), mentioned under (B).

(B) The azo-dye (1 g.), dissolved in glacial acetic acid (30—90 c.c.), was mixed with a solution of chromic chloride tetrahydrate (0.7 g.) in hot glacial acetic acid (15 c.c.) and boiled under reflux (8—12 hours). A dark purple, crystalline, anhydrous precipitate separated, which was washed with acetic acid and alcohol; it was insoluble in water and in most organic solvents, including acids, but dissolved in pyridine or aqueous alkalis, yielding soluble but rather easily hydrolysable salts. Its analysis [Found: C, 66.55; H, 4.05; Cr, 8.85.  $(C_{16}H_{10}O_2N_2)_2CrH$  requires C, 66.55; H, 3.65; Cr, 9.0%] indicated that it was the *acid chromi-complex* (II). Its *pyridinium* salt was analysed [Found: C, 67.95; H, 4.45; Cr, 7.65; loss at 100°, 11.2.  $(C_{16}H_{10}O_2N_2)_2Cr \cdot C_5H_5N$  requires C, 67.7; H, 3.95; Cr, 7.95; loss of  $C_5H_5N$ , 12.05%]. When an excess of chromic chloride (1.3 g.) was used in the above preparative reaction, the product was the anhydrous *chromi-acetate* salt of (II) [Found: C, 57.7; H, 4.05; Cr, 14.55.  $\{(C_{16}H_{10}O_2N_2)_2Cr\}(C_2H_3O_2)_2Cr$  requires C, 57.9; H, 3.5; Cr, 13.95%], which was a purple crystalline substance, insoluble in all solvents, including organic and inorganic bases, and aqueous alkalis. This salt was obtained also by heating the chromi-chloride (I) in glacial acetic acid for 6 hours.

2: 2'-*Dihydroxyazobenzene*.—The azo-compound was condensed with chromic chloride in ethyl alcohol as described in the foregoing experiment (A) and the solid product obtained after spontaneous evaporation was extracted with light petroleum and then with ether; the residue was a reddish-brown solid, which was dissolved in alcohol (filtered) and recovered; it was readily soluble in water, the solution being less purple in shade than in the preceding case, and it was not precipitable by addition of hydrochloric acid (Found: C, 38.9; H, 5.0; Cr, 14.4; loss at 150°, 16.3.  $C_{12}H_8O_2N_2CrCl \cdot 4H_2O$  requires C, 38.75; H, 4.3; Cr, 14.0; loss of  $4H_2O$ , 19.4%). The substance, which contained ionisable chlorine, and did not become insoluble when dehydrated, was evidently the *chromi-chloride* (as I) of the azo-compound; ammonia or potassium chromate precipitated the insoluble *oxide dihydrate* (Found: C, 49.55; H, 3.9; Cr, 17.95, 17.7.  $C_{24}H_{16}O_5N_4Cr_2 \cdot 2H_2O$  requires C, 49.65; H, 3.45; Cr, 17.9%).

5'-*Nitro-2'-hydroxybenzeneazo-β-naphthol*.—The azo-compound (4 g.), in boiling ethyl alcohol (120 c.c.), was mixed with a solution of chromic chloride tetrahydrate (2.05 g.) in warm alcohol (80 c.c.) and boiled under reflux for 12 hours. After removal of the alcohol at room temperature from the filtered solution, a purple solid remained, which was drained from a little water and hydrochloric acid, dried in air, and ground (4.45 g.). It was then extracted (Soxhlet) with petroleum (b. p. 80—100°) and afterwards with ether. The residue was dissolved in alcohol, and recovered from the filtered solution; it consisted of the hydrated *chromi-chloride* of the azo-compound. To get a specimen for analysis, 1 g. was dissolved in 165 c.c. of hot water

containing 1 c.c. of concentrated hydrochloric acid, the solution filtered hot, and 16.5 c.c. of concentrated hydrochloric acid added; the solution slowly deposited 0.7 g. of small, lustrous, rhomboidal prisms, violet-red by transmitted light, of the *hexahydrate* (IV) (Found: C, 38.25; H, 4.15; Cr, 10.2, 10.45; loss at 140—160°, 23.2; regain in air in 6 days, 20.55.  $C_{16}H_9O_4N_3ClCr \cdot 6H_2O$  requires C, 38.2; H, 4.2; Cr, 10.35; loss of  $6H_2O$ , 21.5; regain of  $4\frac{1}{2}H_2O$ , 20.5%). During desiccation, some hydrogen chloride was lost, and the rehydrated substance was not completely soluble in hot water. The hexahydrate formed the *oxide*, insoluble in water but soluble in chloroform, when treated with aqueous ammonia or potassium chromate (Found: C, 42.5; H, 4.2%); it was probably an *octahydrate*.

The substance recovered from the ethereal extract (above) consisted of purple scales, less soluble in water than the hexahydrated chromi-chloride; it contained un-ionised chlorine and was probably the *pentahydrate* of the chromi-chloride (Found: C, 39.9; H, 4.15; Cr, 9.9; loss at 140—160°, 20.75; regain in air, 12.65.  $C_{16}H_9O_4N_3ClCr \cdot 5H_2O$  requires C, 39.6; H, 3.9; Cr, 10.7; loss of  $5H_2O$ , 18.6; regain of  $3\frac{1}{2}H_2O$ , 15.95%); the rehydrated substance was almost insoluble in hot water. When an aqueous solution of the hexahydrate was boiled for some time, an insoluble substance (Found: C, 45.3; H, 3.85; Cr, 11.75%) was precipitated; this material, which was soluble in alcohol, was probably the dihydrate with a covalently attached chlorine atom.

*2'-Hydroxy-5'-sulphobenzeneazo-β-naphthol*.—The azo-compound (3 g.) was boiled under reflux with water (300 c.c.) containing anhydrous chromic sulphate (3 g.) for 8 hours, and the solution filtered hot from a trace of solid and kept overnight; the dark purple, bronzed needles (2.9 g.) that had separated were dried in air; a further crop (0.3 g.) was obtained from the mother-liquor. The same substance was obtained when chromic chloride was used instead of the sulphate, and also, though in lower yield, when potassium dichromate (made slightly acid with sulphuric acid) was employed; when half the proportion of chromic sulphate was used, the product was crystalline but less pure. The product was the *hexahydrated chromi-sulphonate* of the azo-compound (V) (Found, in two preparations: C, 38.1, 37.9; H, 4.4, 4.6; Cr, 10.2, 10.35; loss at 140—150°, 21.55, 21.65; regain in air after 1 month, 3.6, 3.65.  $C_{16}H_9O_5N_2SCr \cdot 6H_2O$  requires C, 38.35; H, 4.2; Cr, 10.4; loss of  $6H_2O$ , 21.55; regain of  $1H_2O$ , 4.6%); it was fairly readily soluble in water and in alcohol, but insoluble in ether or chloroform. On desiccation, even when heat was not used, the substance was transformed into smaller crystals which were insoluble in all solvents, including organic bases and aqueous alkalis, and it could not again be restored to the soluble state (Found for the desiccated but not rehydrated substance: C, 48.7; H, 2.35; Cr, 13.4.  $C_{16}H_9O_5N_2SCr$  requires C, 48.85; H, 2.3; Cr, 13.25%). The rehydrated substance gave C, 46.4; H, 2.95; Cr, 12.5%, indicating a gain of over  $\frac{1}{2}H_2O$ ). The hexahydrated chromi-sulphonate gave a purple, glassy *ammonium* salt when treated with an excess of aqueous ammonia; this was extremely soluble in water and was markedly saltatory when desiccated and exposed to air, the particles continuing to jump for some time; its ammonia was easily expelled by means of aqueous sodium hydroxide or by neutralisation with acids [Found for a specimen dried over calcium chloride: C, 39.6; H, 4.2; Cr, 10.45.  $(C_{16}H_9O_5N_2S \cdot CrOH)NH_4 \cdot 3H_2O$  requires C, 39.85; H, 4.15; Cr, 10.8%]. When the ammonium salt was heated at 150°, it did not become transformed into an insoluble material. Evaporated at room temperature with pyridine, it gave a complex *pyridine* salt (Found: C, 50.85; H, 3.95; Cr, 8.45; loss at 150°, 12.05%).

When less water (150 c.c.) and a greater proportion of chromium sulphate (4.2 g.) were used in the above condensation with the azo-compound (3 g.), much insoluble amorphous material was precipitated as a purplish powder (about 4 g.), and the yield of crystals of the hexahydrate from the filtrate was diminished (1 g.). The amorphous material had the composition of a *tetrahydrate* of the foregoing chromi-sulphonate (Found: C, 41.8; H, 3.75; Cr, 11.4; loss at 140—170°, 13.55; regain in air after 1 month, 16.45.  $C_{16}H_9O_5N_2SCr \cdot 4H_2O$  requires C, 41.3; H, 3.65; Cr, 11.2; loss of  $3\frac{1}{2}H_2O$ , 13.55; regain of  $4H_2O$ , 17.9%). The desiccated and rehydrated substance was moderately readily soluble in boiling water and readily soluble in aqueous ammonia, and was therefore not the same as the desiccated and rehydrated hexahydrate, as is shown also by the large regain of moisture on exposure to air. It was clear that the tetrahydrate was a polymerised substance, probably depolymerising to the chromi-oxide of the sulphonic acid, which then became rehydrated. The tetrahydrate was likewise depolymerised on boiling with aqueous ammonia, giving a solution of the same ammonium salt (above) as the hexahydrate.

In all cases, especially when the azo-compound was used in excess, the aqueous mother-liquor from the hexahydrate contained a more complex substance with two azo-residues to one

chromium atom; this was shown to be formed also on condensing the above hexahydrate (1.4 g.), dissolved in *N*-sodium hydroxide (15 c.c.), with the sodium salt of the azo-compound (1.2 g.) in water (15 c.c.); after being boiled for 30 minutes, the solution was treated with 5*N*-hydrochloric acid (14 c.c.) and kept, purple-black crystals (1.85 g.) separating (VI). This was dissolved in cold water (80 c.c.), and the filtered solution slowly treated with concentrated hydrochloric acid (25 c.c.); the precipitate obtained was ground and air-dried on tile (14 days) (Found: C, 42.9; H, 4.5; Cr, 5.5; loss at 140—150°, 17.45; regain in air, 15.15.  $C_{32}H_{21}O_{10}N_4S_2Cr_9H_2O$  requires C, 42.7; H, 4.35; Cr, 5.8; loss of  $9H_2O$ , 18.0%). The desiccated and rehydrated substance was still readily soluble in water; it formed a sparingly soluble di- and a tri-sodium salt.

In the same way, the hexahydrate (0.5 g.) combined with 5'-nitro-2'-hydroxybenzeneazo- $\beta$ -naphthol (0.38 g.), in presence of water (50 c.c.) and *N*-sodium hydroxide (5 c.c.); the boiled liquid, acidified with hydrochloric acid, gave a bronzed bluish-black substance of analogous composition (VII) (Found for a sample reprecipitated from water by means of hydrochloric acid and exposed to air: C, 44.8; H, 4.45; Cr, 6.35.  $C_{32}H_{20}O_9N_5SCr_9H_2O$  requires C, 44.45; H, 4.4; Cr, 6.0%), together with a purplish-black substance, insoluble in water, which was probably the chromi-azo-sulphonic acid salt (as III) of the acid complex (VII) (Found: C, 42.6; H, 4.6; Cr, 8.15.  $C_{48}H_{29}O_{14}N_7S_2Cr_2,14H_2O$  requires C, 42.75; H, 4.25; Cr, 7.7%).

*4'-Hydroxy-m-tolueneazo- $\beta$ -naphthol-6-sulphonic Acid.*—The following methods of condensation gave appreciably different results: (1) The azo-compound (3 g., containing a little of the sodium salt) in water (300 c.c.) was heated under reflux with anhydrous chromic sulphate (3 g.) for 6 hours; the initially formed precipitate seemed gradually to dissolve, the liquid becoming deep purple, but a new dark precipitate slowly formed. This was collected and dried in air (1.4 g.); it was an amorphous powder (Found: Cr, 3.6%), soluble in hot aqueous ammonia and reprecipitated unchanged by mineral acid; it did not form the same ammonium salt as the following complex (contrast the corresponding amorphous precipitate formed in the case of the preceding azo-sulphonic acid), and had no affinity for fibres; its composition was not determined. The purple aqueous filtrate gave only 0.15 g. of crystalline powder on standing, but, on addition of sodium chloride, thin, lustrous, purple plates were slowly deposited (0.4 g., dried in air); this complex, which was soluble in water to a purple solution and readily formed soluble alkali salts, was the *nonahydrate* of the *chromi-sulphonate* (VIII) (Found: C, 35.65; H, 5.0; Cr, 9.0, 9.05; loss at 140—150°, 24.7; regain in air in 2 days, 18.15.  $C_{17}H_{11}O_5N_2SCr_9H_2O$  requires C, 35.85; H, 5.1; Cr, 9.15; loss of  $8H_2O$ , 25.3; regain of  $4\frac{1}{2}H_2O$ , 19.0%). The desiccated and rehydrated material was still crystalline and soluble in water, showing that polymerisation did not occur in this case (contrast that of the chromi-sulphonate of the foregoing azo-compound). When only 1.3 g. of chromic sulphate was used in the above condensation, a similar result was obtained.

(2) The azo-compound (8.8 g.) in ethyl alcohol (250 c.c.) was mixed with chromic chloride tetrahydrate (4.5 g.) in ethyl alcohol (150 c.c.), the mixture boiled under reflux for 6½ hours, and the violet-blue liquid filtered from a black powder (0.17 g.) and a little sodium chloride; alcohol (250 c.c.) was distilled from the filtrate, and the remainder allowed to evaporate in air, leaving the chromium complex as a crystalline mass. This was drained, ground, and air-dried (8.7 g.); it was identical with the foregoing nonhydrated chromi-sulphonate.

*2'-Hydroxy-4'-sulphonaphthalene-1' : 4-azo-1-phenyl-3-methylpyrazol-5-one.*—Condensation between the azo-compound and chromic sulphate in water proceeded only to a small extent on prolonged boiling, but condensation with chromic chloride in alcohol was favourable: The azo-compound (6.4 g., not quite free from the sodium salt) was suspended and partly dissolved in boiling ethyl alcohol (320 c.c.), a solution of chromic chloride tetrahydrate (3.47 g.) in ethyl alcohol (100 c.c.) added, and the mixture boiled under reflux for 8 hours. The solid dissolved slowly to a rich deep-red solution, which was filtered hot from sodium chloride (0.46 g.) and distilled (260 c.c. of alcohol recovered). The residual liquid, after 1 day, was filtered from a dark red, crystalline powder (0.65 g.), apparently the sodium salt of the following complex, and allowed to evaporate; the residue was drained, ground, washed with cold water (30 c.c.), and extracted with two portions (500 c.c. each) of boiling water. The air-dried *chromi-sulphonate* (5.9 g.) (IX) was very sparingly soluble in water, but rather more soluble in dilute mineral acids and readily soluble in aqueous ammonia or alkalis, forming salts (Found: C, 41.6; H, 4.5; Cr, 9.3; loss at 140—170°, 14.25; regain in air in 10 days, 10.35.  $C_{20}H_{13}O_5N_4SCr_5\frac{1}{2}H_2O$  requires C, 41.95; H, 4.2; Cr, 9.1; loss of  $4\frac{1}{2}H_2O$ , 14.15; regain of  $3H_2O$ , 11.0%). The desiccated and rehydrated material was less soluble in water than the original.

*o-Carboxybenzeneazo- $\beta$ -naphthol.*—The azo-compound (0.5 g.) was boiled under reflux with chromic chloride tetrahydrate (1 g.) in ethyl alcohol (100 c.c.) for 12 hours, and the liquid

allowed to evaporate to dryness; the residue was washed with 10% hydrochloric acid and dried over solid sodium hydroxide. It consisted of a mixture of water-soluble and -insoluble chromi-complexes (probably different hydrates of the same complex); to isolate the former, the mixture was shaken with water, the filtered solution allowed to evaporate to dryness, and the dark red residue (X) washed with a little water and dried over calcium chloride (Found : C, 48.4; H, 4.35; Cr, 12.5; loss at 130°, 11.1.  $C_{17}H_{10}O_3N_2ClCr, 2\frac{1}{2}H_2O$  requires C, 48.3; H, 3.6; Cr, 12.3; loss of  $2\frac{1}{2}H_2O$ , 10.65%), but it was doubtful whether a definite hydrate had been isolated. It readily lost water, being transformed into an insoluble chromi-chloride. The deep carmine-red aqueous solution of the soluble chromi-chloride contained ionised chlorine; on boiling, hydrolysis to the reddish-purple *oxide tetrahydrate* took place, with precipitation (Found for a specimen dried over calcium chloride : C, 52.9; H, 4.3; Cr, 13.4.  $C_{34}H_{20}O_7N_4Cr_2, 4H_2O$  requires C, 52.85; H, 3.7; Cr, 13.5%). Aqueous ammonia or potassium chromate likewise gave the oxide.

*Naphthalene-1'-azosalicylic Acid.*—The sodium salt of the azo-compound (1 g.) in boiling water (150 c.c.) was mixed with chromic chloride tetrahydrate (0.7 g.) dissolved in water (50 c.c.); a yellow precipitate formed at once. The mixture was boiled under reflux for 4 hours, and the liquid filtered hot from the precipitate (0.75 g.), which was now olive-brown. The dried, ground substance was extracted (Soxhlet) with benzene, and the residue with ethyl alcohol. The alcoholic extract, on evaporation, left a pale greenish-brown powder (substance a). The residue from the alcoholic extraction was a yellow powder, which was dissolved in chloroform, and the filtered solution evaporated, leaving a lustrous, black, glassy material (0.3 g.), powdering to yellowish-brown, but red by transmitted light; this material (XII) was insoluble in water, dilute mineral acids, alkalis, aqueous ammonia, or alcohol, but soluble in pyridine (deep orange-yellow solutions) (Found : C, 55.45; H, 4.6; Cr, 9.75, 9.9, 10.05; loss at 120°, 8.25; regain in air, 4.2.  $C_{51}H_{30}O_9N_6Cr_2, 7H_2O$  requires C, 55.6; H, 4.0; Cr, 9.45; loss of  $5H_2O$ , 8.2; regain of  $2\frac{1}{2}H_2O$ , 4.45%). The substance (a) (XI) was soluble in cold alcohol (golden-yellow solution) and in aqueous alkalis (Found for the air-dried substance : C, 57.35; H, 4.7; Cr, 6.5; loss at 140°, 10.45; regain in air, 3.15.  $C_{34}H_{21}O_6N_4Cr, 4\frac{1}{2}H_2O$  requires C, 57.15; H, 4.2; Cr, 7.3; loss of  $4H_2O$ , 10.1; regain of  $1H_2O$ , 2.8%).

#### Ferric Lakes.

*o*-Carboxybenzeneazo- $\beta$ -naphthol (1 g.) in ethyl alcohol (300 c.c.) was mixed with ferric chloride dihydrate (1 g.) in alcohol (50 c.c.) and boiled for 5 minutes; when the brownish-green solution was poured into water, a dark brown solid was precipitated (filtrate, dark green). The dried solid (XVI) was insoluble in water, but soluble in chloroform (Found : C, 60.95; H, 3.75; Fe, 8.7.  $[(C_{17}H_{10}O_3N_2)_2Fe]H, 2H_2O$  requires C, 60.65; H, 3.75; Fe, 8.3%). An alcoholic solution of the *complex* was readily decomposed on being warmed with alkalis or with strong acids, alkalis removing one molecule of dye. The simpler complex (as X) was probably present in the green filtrate (above), but it could not be isolated owing to its sensitiveness to acids and alkalis.

*p*-Carboxybenzeneazo- $\beta$ -naphthol in pyridine-alcohol (1 : 3) gave with ferric chloride a light red precipitate of a simple basic *ferric* salt, which was reprecipitated from pyridine with water and dried in a vacuum [Found : N, 7.85; Fe, 14.55.  $(C_{17}H_{11}O_3N_2)Fe(OH)_2$  requires N, 7.35; Fe, 14.7%].

*o*-Hydroxybenzeneazo- $\beta$ -naphthol (1 g.) and ferric chloride dihydrate (1 g.) in alcohol gave, after removal of most of the alcohol by boiling, lustrous greenish-black crystals (brownish streak) of a *ferric-chloride* (XIV), insoluble in water (Found for a sample dried in a vacuum : C, 54.2; H, 3.5; Cl, 10.0; Fe, 15.55.  $C_{16}H_{10}O_2N_2ClFe$  requires C, 54.35; H, 2.9; Cl, 10.05; Fe, 15.75%); the greenish-yellow solution in alcohol gave no reaction for ionised chlorine. When the complex was dissolved in pyridine, and the solution mixed with water, a greenish-black *pyridine complex* of the *ferric-hydroxide* was obtained [Found : C, 61.05; H, 4.5; N, 9.85; Fe, 13.4.  $(C_{16}H_{10}O_2N_2)Fe \cdot OH, C_5H_5N$  requires C, 60.9; H, 3.85; N, 10.15; Fe, 13.5%].

2'-Hydroxy-5'-sulphobenzeneazo- $\beta$ -naphthol, boiled with aqueous ferric chloride for 12 hours, gave a micro-crystalline, dark brown *ferric complex* (structure as V) with greenish reflex, which was insoluble in water or chloroform but soluble in aqueous alkalis to reddish-black solutions (Found : C, 42.95; H, 3.65; Fe, 12.1.  $C_{16}H_9O_6N_2SFe, 3H_2O$  requires C, 42.6; H, 3.35; Fe, 12.4%); it was readily decomposed by dilute mineral acids.

#### Other Lakes and Simple Salts.

*Chromic p-carboxybenzeneazo- $\beta$ -naphthol* was obtained, from an aqueous solution of the sodium salt of the dye (1 g.) and chrome alum (0.57 g.), as a bright red powder [Found : C, 62.15; H, 4.05; N, 8.9; Cr, 5.7.  $(C_{17}H_{11}O_3N_2)_3Cr, 3H_2O$  requires C, 62.5; H, 4.0; N, 8.55; Cr, 5.3%]. Warming with aqueous ammonia eliminated the chromium atom as hydroxide.

*Copper Compounds of p-Carboxybenzeneazo-β-naphthol.*—The simple *copper* salt was obtained from aqueous cupric chloride and the sodium salt of the dye as a red-brown powder, with green reflex [Found for a sample dried at 110°: Cu, 9.85.  $(C_{17}H_{11}O_3N_2)_2Cu$  requires Cu, 9.9%]; it was insoluble in most solvents, but aqueous ammonia dissolved it, with conversion into the ammonium salt of the following inner-complex copper derivative.

*Cupric cupri-p-carboxybenzeneazo-β-naphthol.* Addition of copper sulphate (1.25 g.) in aqueous ammonia to a solution of the azo-compound (1.5 g.) in aqueous ammonia produced a deep brown precipitate, which was filtered off after  $\frac{1}{4}$  hour at 100° [Found for a sample dried over calcium chloride: N, 8.4; Cu, 15.35; loss at 150°, 15.25.  $\{(C_{17}H_{10}O_3N_2)_2Cu\}Cu, NH_3, 6H_2O$  requires N, 8.45; Cu, 15.3; loss, 15.0%]. Unlike the simple copper salt (above), it was readily soluble in hot pyridine. When desiccated as above and then exposed to air, it regained  $5H_2O$  in less than 2 hours [Found for the rehydrated substance: C, 51.3; H, 4.8; Cu, 16.25.  $\{(C_{17}H_{10}O_3N_2)_2Cu\}Cu, 5H_2O$  requires C, 51.2; H, 3.75; Cu, 15.95%]. The *dipyridino*-complex was obtained in brown needles from cupric acetate (0.34 g.) and the azo-compound (0.5 g.) in alcohol-pyridine [Found: C, 61.45; H, 4.1; N, 10.05; Cu, 15.0.  $\{(C_{17}H_{10}O_3N_2)_2Cu\}Cu, 2C_5H_5N$  requires C, 61.05; H, 3.5; N, 9.7; Cu, 14.7%]. The same substance was obtained by dissolving the above pentahydrated complex in pyridine.

The *nickel* complex of *o*-hydroxybenzeneazo-β-naphthol was formed on heating to boiling a solution of nickel acetate and the azo-compound in alcohol; it was a brown powder, insoluble in water or alcohol (Found: C, 59.85; H, 3.65; Ni, 18.45.  $C_{16}H_{10}O_2N_2Ni$  requires C, 59.9; H, 3.15; Ni, 18.35%). When dissolved in pyridine, it formed a brown *pyridino*-complex (XV), isolated by addition of a little alcohol and pouring into water (Found: C, 62.85; H, 3.45.  $C_{16}H_{10}O_2N_2Ni, C_5H_5N$  requires C, 63.1; H, 3.75%).

The zinc complex of the same azo-compound was similarly obtained; it was a red powder, insoluble in water but soluble in pyridine (rose-coloured solution) with formation of the *pyridine* complex (Found: C, 62.2; H, 4.1; N, 10.8.  $C_{16}H_{10}O_2N_2Zn, C_5H_5N$  requires C, 62.25; H, 3.7; N, 10.35%).

The *nickel* complex (XVII) of *o*-carboxybenzeneazo-β-naphthol was prepared from the azo-compound (1 g.) in alcohol (500 c.c.) and nickel acetate (1 g.), the solution (purple-brown) being boiled for a few minutes and then poured into an excess of water; lustrous brown plates, with golden-green reflex, separated (Found: C, 53.4; H, 4.2; Ni, 14.4.  $C_{17}H_{10}O_3N_2Ni, 2H_2O$  requires C, 53.3; H, 3.65; Ni, 15.25%); the water was removed on drying at 110° (Found: Ni, 17.1.  $C_{17}H_{10}O_3N_2Ni$  requires Ni, 16.85%). Solution of the dihydrate in pyridine and evaporation over sulphuric acid gave a *dipyridino*-compound (Found for a sample dried over calcium chloride: C, 63.05; H, 4.45; N, 11.45; Ni, 11.65.  $C_{17}H_{10}O_3N_2Ni, 2C_5H_5N$  requires C, 63.95; H, 3.95; N, 11.05; Ni, 11.6%). Only the simple nickel salt (red) was obtained from the sodium salt of the azo-dye and aqueous nickel sulphate in the cold, but the complex salt was produced on boiling.

Zinc acetate and the azo-dye in alcohol gave a scarlet simple *salt* [Found: Zn, 10.25.  $(C_{17}H_{10}O_3N_2)_2Zn$  requires Zn, 10.1%].

The *copper* complex of benzeneazosalicylic acid (from alcoholic copper acetate and the azo-dye) was red-brown (Found: Cu, 18.75; loss at 150°, 8.7.  $C_{13}H_9O_3N_2Cu, 2H_2O$  requires Cu, 18.7; loss of  $2H_2O$ , 10.6%). When prepared from ammoniacal copper sulphate, the *complex* was green; it retained 2 mols. of ammonia when dried over calcium chloride (Found: C, 45.15; H, 4.3; N, 15.65; Cu, 17.55%).

Alcoholic nickel acetate and the azo-dye gave a brilliant yellow simple *nickel* salt [Found: Ni, 10.4.  $(C_{13}H_9O_3N_2)_2Ni, 2H_2O$  requires Ni, 10.2%], together with a less soluble brown substance which appeared to be a mixture of complexes.

Benzeneazo-*o*-cresotic acid behaved like the foregoing azo-compound, giving with alcoholic copper acetate a deep brown *copper* complex (XIII) (Found: C, 47.6; H, 3.55; Cu, 17.75.  $C_{14}H_{10}O_3N_2Cu, 2H_2O$  requires C, 47.5; H, 3.95; Cu, 17.95%), whereas cuprammonium sulphate gave pale green needles of the *diammino*-compound (Found: C, 46.8; H, 5.5; Cu, 17.05%), which, when crystallised from pyridine, was converted into a *dipyridino*-compound (Found: C, 59.95; H, 3.65.  $C_{14}H_{10}O_3N_2Cu, 2C_5H_5N$  requires C, 60.55; H, 4.2%).

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