

### 111. *Structure of the Aluminium Lakes of Some Azo-Dyes and of Alizarin.*

By W. F. BEECH and H. D. K. DREW.

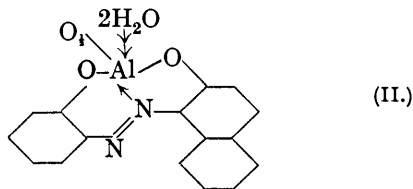
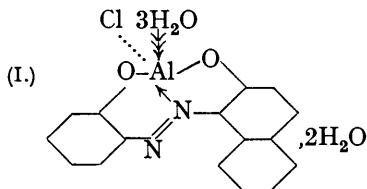
A study of the behaviour of several *oo'*-dihydroxyazo-compounds with salts of aluminium showed that the lakes produced with this metal are similar in structure to those of trivalent chromium. In general, the aluminium lakes were much less stable to acids than the corresponding chromium lakes, and, probably for this reason, they were prepared with greater difficulty. Good yields, however, were obtained from the monosulphonic acids of two azo-dyes. The degree of hydration in corresponding cases in the two series of lakes is not in general the same. The part played by a sulphonic acid group, when present in one of the aromatic nuclei of the azo-dye, is the same in the lakes of both metals, this group and the two hydroxyls serving to neutralise the three valencies of the metal. Definite aluminium lakes of alizarin were isolated; their structures and possible connexion with the Turkey-red lake are discussed.

THE object of the work was to compare the lakes of another trivalent metal with those of chromium (Drew and Fairbairn, J., 1939, 823), as regards structure, composition, and stability, in order to see if there was anything exceptional in the behaviour of chromium. Aluminium was chosen, since this metal still has a value in mordanting processes, and nothing appears to be known regarding its lakes with the azo-dyes.

As in the case of chromium, we were not able to isolate any definite lakes of aluminium with the *o*-monohydroxyazo-dyes; and it must probably be concluded that such lakes, if they can be formed, are unstable. With the *oo'*-dihydroxyazo-dyes, however, aluminium formed well-defined lakes, although not so readily as chromium. The acidity of the medium throughout the reaction seemed to be a decisive factor in the case of aluminium; and this was verified both directly and by finding that the aluminium lakes, both in substance and when present on fibres, were much less stable to mineral and organic acids than the corresponding chromium lakes.

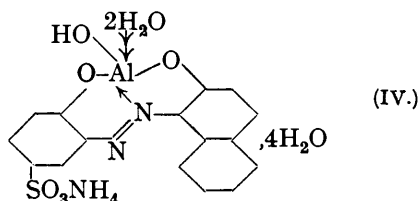
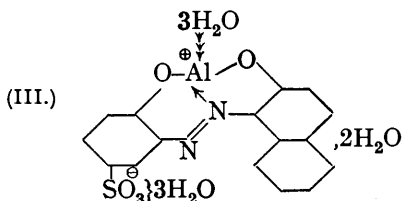
When aluminium chloride was condensed with *o*-hydroxybenzeneazo- $\beta$ -naphthol, in alcoholic solution, the chief product was the red-brown *aluminichloride pentahydrate* (I), which may be compared with the tetrahydrate, more purple in shade, formed in the case of chromium (*loc. cit.*). The alumin-complex was soluble in water, the red solution containing ionised chlorine; it was readily decomposed by mineral acids. The complex,

when partly dehydrated, became soluble also in ether and other organic solvents; when completely dehydrated, it lost part of its halogen as hydrogen chloride. Dilute aqueous ammonia or potassium chromate converted the complex into its red-brown *oxide tetrahydrate* (II), which was insoluble in water, but soluble in ether; this substance was also prepared



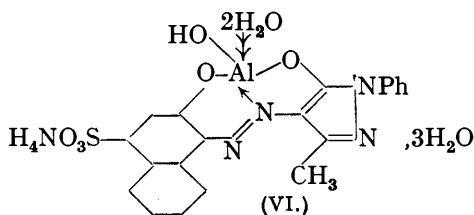
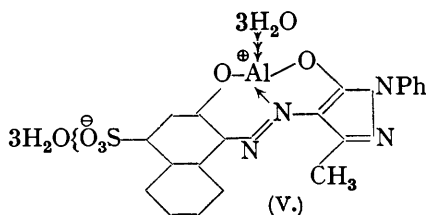
directly from the azo-dye and aluminium chloride in the presence of sodium hydroxide. A by-product, in the condensation giving rise to (I), was a reddish black-substance, soluble in aqueous ammonia, containing two dye residues per atom of aluminium; this was probably the acid alumi-complex,  $[Al(C_{16}H_{10}O_2N_2)_2]H, 2H_2O$ , corresponding with an acid complex already described (*loc. cit.*) in the case of chromium.

2'-Hydroxy-5'-sulphobenzeneazo- $\beta$ -naphthol condensed with aqueous aluminium sulphate in the presence of sodium hydroxide, giving lustrous red needles of the *aluminium-sulphonate octahydrate* (III), soluble in hot water and in basic solvents, but not in the common neutral organic solvents. This substance, like the corresponding chromi-sulphonate hexahydrate, became almost insoluble in water when desiccated. With ammonia, it



gave the purplish red, glassy *ammonium hexahydrate* (IV), which was freely soluble in water. The conversion into (IV) without loss of aluminium demonstrates the structure of (III). The complex (III) had considerable affinity for fibres, but lacked the stability of its chromi-analogue. In the case of this azo-dye the lake with chromium was again much purpler in hue than the aluminium lake.

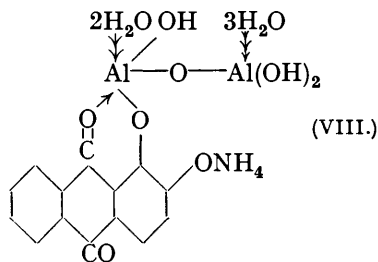
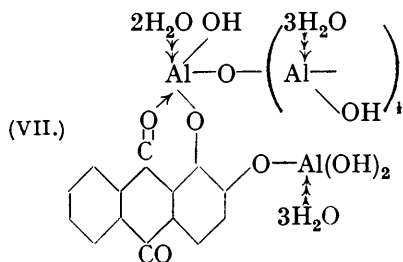
When 2'-hydroxy-4'-sulphonaphthalene-1': 4-azo-1-phenyl-3-methylpyrazol-5-one was condensed with aluminium chloride in dilute aqueous solution, red needles of the *aluminium-sulphonate hexahydrate* (V) were produced. This substance, like its chromi-analogue, was only sparingly soluble in hot water, but the purplish, glassy *ammonium pentahydrate*



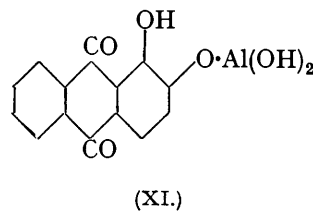
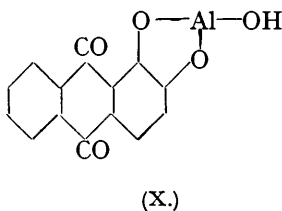
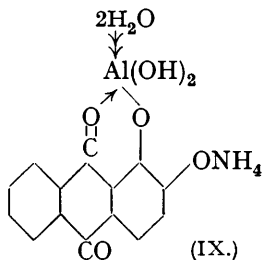
(VI) was readily soluble in water. On desiccation at  $180^\circ$ , (V) still retained  $1H_2O$ , as also does the chromi-analogue; on exposure to moist air, it regained two more molecules of water. In the case of this azo-dye, there is less difference of colour, as between the lakes with chromium and aluminium, than in the cases previously mentioned.

A pure aluminium lake was not obtained either from *o*-carboxybenzeneazo- $\beta$ -naphthol or from benzeneazosalicylic acid, but in both instances there was evidence that a lake could be prepared containing one metallic atom to each dye residue, involving union of the metallic atom with both the carboxyl and the hydroxyl grouping.

The case of alizarin has a special interest in connexion with the use of aluminium mordants. When a dilute alcoholic solution of alizarin was treated with excess over 1 mol. of sodium hydroxide and then with aluminium chloride, and the mixture boiled and afterwards filtered, the filtrate contained an *aluminium lake*, which, when freed from alizarin,



had a composition indicating a possible structure (VII), although this is only conjectural. This substance dissolved in dilute aqueous ammonia, with conversion into an insoluble substance and a soluble *red lake*; the latter contained two aluminium atoms per residue of dye, its composition suggesting the formula (VIII). Substance (VII) dissolved in concentrated aqueous ammonia with further loss of alumina, giving a dark red glassy substance

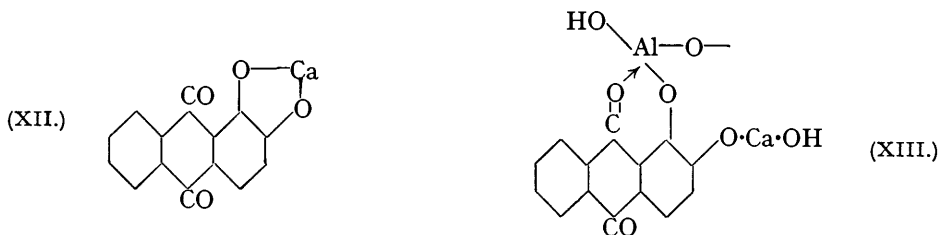


which contained one aluminium atom and one dye residue, together with a molecule of ammonia and two molecules of water, indicating the structure (IX) of the *ammonium salt of aluminium alizarate dihydrate*.

Liebermann (1893) suggested for the aluminium derivative of alizarin a formula (X), but he does not seem to have obtained any substances of this kind at all; and a number of subsequent authors appear to have adopted his proposal without making any experiments. It is clear, particularly from its behaviour in the presence of ammonia, that the substance to which we assign formula (IX) could not be represented as the ammonium derivative either of (X) or of the remaining possible structure (XI), for in the cases of such structures it would be expected that the metallic atom, not being co-ordinatively attached to the organic residue, would be removable by concentrated ammonia. There seems, therefore, every reason to suppose that in the aluminium lake of alizarin the metal is attached at a carbonyl grouping and the neighbouring hydroxyl group; the remaining hydroxyl is sufficiently acidic to attach further metal under suitable conditions, but this is more easily removed.

The opinion seems to be fairly general that, in the brightest Turkey-red dyeings, both aluminium and calcium are present in the lake (although the calcium can be replaced by other metals, including further aluminium). Numerous compositions and structures have been proposed for the hypothetical complex aluminium-calcium lake, some of the formulæ being based on analyses of dyed fibre; but it seems clear, from the wide divergence of the findings, and from the fact that a pure lake has never been isolated, that the matter is still open to much doubt. For this reason, we attempted to ascertain whether chalk would interact with alizarin in the presence of water under conditions similar to those in the Turkey-red dyebath: a substance was isolated which appeared to be identical with the already known calcium alizarate (usually prepared from an alkali alizarate and calcium chloride), to which the structure (XII) had been assigned. It seems not improbable,

therefore, that the complex aluminium-calcium lake of the Turkey-red process, if it actually occurs, is based upon a structure of type (XIII). If this be so, the lake might be derived from either (VII), (VIII), or (IX), in which case the probable ratios of alizarin



residues : aluminium atoms : calcium atoms would be 2 : 3 : 2, 1 : 2 : 1, or 1 : 1 : 1. It must be noted, however, that the aluminium lakes described above are unstable to mineral acids *in vitro*, whereas the Turkey-red dyeings are fairly stable, although this difference might possibly be connected with the manner in which the lake is attached to the fibre. No aluminium or calcium derivative of alizarin, stable *in vitro* to mineral acid, seems to be known, and the present results suggest that such is unlikely to occur.

#### EXPERIMENTAL.

*o*-Hydroxybenzeneazo- $\beta$ -naphthol.—The azo-dye (3.18 g.; 2 mols.), dissolved in warm 96% ethyl alcohol (250—300 c.c.), was mixed with a solution of aluminium chloride hexahydrate (1.44 g.; 1 mol.) in the same solvent (30 c.c.), and the mixture boiled under reflux for 8 hours, and then filtered whilst hot. The solvent was removed at room temperature, and the residue ground and extracted with ether (Soxhlet) until the extract (A) was nearly colourless. The residual solid (from the thimble) was then extracted with boiling 96% alcohol, the filtered extract allowed to evaporate, and the residue exposed to moist air on porous tile for some days; the solid so obtained was a red-brown powder consisting of the *aluminumchloride pentahydrate* (I) (Found : C, 46.1; H, 5.1; Cl, 8.9; Al, 6.7.  $C_{16}H_{20}O_7N_2ClAl$  requires C, 46.3; H, 4.85; Cl, 8.55; Al, 6.5%). This complex was soluble in water to a red solution, from which the free azo-dye separated on warming with dilute hydrochloric acid; it was almost insoluble in light petroleum, but dissolved freely in pyridine, aniline, and acetone; on being dried at 150°, the water of crystallisation was lost, together with part of the chlorine as hydrogen chloride. Dilute aqueous ammonia or potassium chromate gave the oxide, which was also prepared from the azo-dye, as described above in the preparation of (I) but with the further addition of sodium hydroxide (0.72 g.; 3 mols.) to the mixture before heating under reflux, the residue from the alcoholic filtrate being finally ground and extracted with light petroleum (b. p. 60—80°; Soxhlet) to remove soluble impurities, the residue dissolved in ether and recovered from the filtrate, and lastly dissolved in boiling 96% alcohol, and again recovered from the filtrate; after exposure to the atmosphere, the product, which was insoluble in water but soluble in ether, appeared to be the *oxide tetrahydrate* (II) (Found : C, 57.9; H, 4.4; Al, 7.8;  $H_2O$ , loss at 120°, 8.6.  $C_{32}H_{28}O_9N_4Al_2$  requires C, 57.7; H, 4.2; Al, 8.1;  $3H_2O$ , 8.25%); the last analytical figure suggests that the anhydrous hydroxide is formed on desiccation at 120°.

The ethereal extract (A) was allowed to evaporate, and the residual solid extracted with light petroleum (b. p. 60—80°; Soxhlet); the residue, exposed to the air, was an almost black powder, insoluble in water but soluble in aqueous ammonia or pyridine (Found : Al, 4.8;  $H_2O$ , loss at 120°, 6.6.  $C_{32}H_{28}O_8N_4Al$  requires Al, 4.6;  $2H_2O$ , 6.1%). This *substance*, the yield of which was very small, was probably the acid complex  $[Al(C_{16}H_{10}O_2N_2)_2]H_2O$ .

*2'*-Hydroxy-5'-sulphobenzeneazo- $\beta$ -naphthol.—To a solution of the free azo-sulphonic acid (5 g.) in water (750 c.c.) was added a solution of sodium hydroxide (1.75 g.; 3 mols.) in a little water. The violet mixture was warmed, and to it was added a solution of hydrated (+  $18H_2O$ ) aluminium sulphate (5 g.) in a little water; the whole was then boiled under reflux for 6 hours, a few c.c. of alcohol having been added to prevent frothing. The solution was filtered hot, and the filtrate set aside in a wide, open dish; after some hours, red needles of the *aluminium-sulphonate octahydrate* (III) separated (yield, about 5 g.); for analysis, it was recrystallised from hot water and dried in air on porous tile (Found : C, 37.6; H, 5.4; Al, 5.6;  $H_2O$ , loss at 150°, 24.1.  $C_{16}H_{25}O_{13}N_2SA$  requires C, 37.5; H 4.9; Al, 5.3;  $7H_2O$ , 24.6%); when heated at 180°, the loss of water was 26.0%, or about  $7\frac{1}{2}$  mols. The hydrated complex was soluble in cold water and much more so in hot, but on dehydration it became almost insoluble (polymerisation);

it was insoluble in neutral organic solvents (ether, benzene). The hydrated complex was readily decomposed by dilute hydrochloric acid, with regeneration of the azo-dye; it was freely soluble in basic solutions or solvents, forming purplish salts. The *ammonium* salt *hexahydrate* (IV) was a purplish-red glass (Found: N, 7.8; Al, 5.5; H<sub>2</sub>O, loss at 170°, 20.4. C<sub>16</sub>H<sub>26</sub>O<sub>12</sub>N<sub>3</sub>SAI requires N, 8.2; Al, 5.3; 6H<sub>2</sub>O, 21.1%); it readily evolved ammonia when warmed with alkalis.

2'-Hydroxy-4'-sulphonaphthalene-1':4-azo-1-phenyl-3-methylpyrazol-5-one.—The azo-sulphonic acid (3 g.; not quite free from its sodium salt) was dissolved in boiling water (1½ l.) and a solution of hexahydrated aluminium chloride (2 g.) in a little water was added; there was a red precipitate (probably, of a simple salt), but this gave place to a deposit of red needles when the mixture was boiled under reflux for some 16 hours. The crystals, collected, washed with water, and exposed on porous tile in air, consisted of the *aluminium-sulphonate hexahydrate* (V) (Found: C, 43.4; H, 4.7; Al, 4.7; H<sub>2</sub>O, loss at 180°, 15.8. C<sub>20</sub>H<sub>28</sub>O<sub>11</sub>N<sub>4</sub>SAI requires C, 43.2; H, 4.5; Al, 4.8; 5H<sub>2</sub>O, 16.1%); the desiccated substance regained 2H<sub>2</sub>O on exposure to moist air (Found: gain, 7.9. Calc.: 7.7%). The complex was sparingly soluble in hot water, but readily soluble in bases with formation of salts. The purplish red, glassy, *ammonium* salt *pentahydrate* (VI) was prepared (Found: N, 12.0; Al, 4.6; H<sub>2</sub>O, loss at 170°, 16.7. C<sub>20</sub>H<sub>28</sub>O<sub>11</sub>N<sub>5</sub>SAI requires N, 12.2; Al, 4.7; 5H<sub>2</sub>O, 15.7%).

*Alizarin*.—Powdered alizarin (3 g.; 2 mols.) was dissolved in boiling 96% alcohol (350 c.c.), and an alcoholic solution of sodium hydroxide (0.6 g.; 2.7 mols.) added, and then a solution of aluminium chloride hexahydrate (1.5 g.; 1 mol.) in a little warm alcohol, a red substance being precipitated; the whole was boiled under reflux for 6 hours, and filtered while hot; the residue contained much alumina, and was neglected; the filtrate was allowed to concentrate nearly to dryness, and the red solid which separated was collected, dried in the air, ground, and extracted with ether (Soxhlet; 4 days) to remove free alizarin. Finally, the undissolved solid was freed from ether, boiled with water (some 400 c.c. in all) until the washings were free from halogen, washed with alcohol, and dried in air. This *substance*, which was only slightly soluble in alcohol, dissolved more readily in aqueous ammonia or pyridine, though not without chemical change; its aluminium content and chemical behaviour suggested formula (VII) (Found: Al, 13.2. C<sub>28</sub>H<sub>19</sub>O<sub>17</sub>Al<sub>2</sub>·13H<sub>2</sub>O requires Al, 13.6%). Since this substance could not be recrystallised, it was dissolved in dilute aqueous ammonia, the solution filtered, and the filtrate allowed to evaporate: the red *substance* so obtained contained two aluminium atoms to each alizarin residue, and the analytical data suggested the structure (VIII) (Found: C, 35.75; H, 5.2; Al, 11.5. C<sub>14</sub>H<sub>21</sub>O<sub>12</sub>NAl<sub>2</sub> requires C, 35.95; H, 4.95; Al, 11.6%). This substance was only rather sparingly soluble in dilute aqueous ammonia, but much more soluble in concentrated ammonia. A further portion of (VII) was accordingly dissolved in cold aqueous ammonia (*d* 0.88) by shaking, and the solution filtered; the filtrate was allowed to evaporate, and the dark red, glassy residue ground and dried in air (yield, 0.5 g.) (Found: C, 47.55; H, 4.75; N, 3.8; Al, 7.45; H<sub>2</sub>O + NH<sub>3</sub>, loss at 170°, 18.1. C<sub>14</sub>H<sub>16</sub>O<sub>8</sub>NAl requires C, 47.6; H, 4.6; N, 3.95; Al, 7.65; 3H<sub>2</sub>O + 1NH<sub>3</sub>, 20.1%). There seems little doubt that this substance was *ammonium aluminium alizarate dihydrate* (IX); the substance, like alumina itself, was probably not quite fully dehydrated, at 170°, with respect to its two hydroxyl groups. It was soluble in aqueous ammonia and to some extent also in boiling water; but it was decomposed, with regeneration of alizarin, by hydrochloric acid, although in extremely dilute cold hydrochloric acid it dissolved to a red solution (probably of the dichloride).

Calcium alizarate dihydrate was prepared as follows: alizarin (2.4 g.) and precipitated chalk (1.0 g.) were boiled under reflux with 250 c.c. of water for a day, and the mixture filtered while hot. The solid was extracted with boiling water, dried, then extracted for a long time with ether (Soxhlet) to remove free alizarin. The dried residue contained free calcium carbonate and was therefore extracted with hot pyridine and filtered; the purple filtrate was allowed to evaporate to dryness. The residue still contained pyridine; this was driven off by heating at 180° in an air stream, and the purplish-red material was then allowed to become rehydrated in the atmosphere [Found: C, 54.2; H, 4.2; Ca, 11.3; H<sub>2</sub>O, loss at 180°, 11.2. Calc. for (XII): C, 53.5; H, 3.2; Ca, 12.7; 2H<sub>2</sub>O, 11.5%]. Evidently this material still retained a little free alizarin, but the analytical figures show that it contained an atom of calcium to each alizarin residue.

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