194. *Quadrivalent Vanadium Lakes of Azo-dyes.*

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Lakes of quadrivalent vanadium with azo-dyes, each containing two reactive substituents (OH, NH_2, CO_2H) in the oo'-positions with respect to the azo-group, are described. The effects of introducing one or two sulpho-groups into the nuclei of the dye are examined, and also that of introducing a p-hydroxyl group. The lakes are of two kinds, *viz.*, the vanadyl lakes, which are similar in structure to the principal lakes of tervalent chromium, and the vanadi-lakes, in which the metal exerts its full quadrivalency in combination with two residues of the azo-dye. The lakes are much less stable to mineral acids than the chromium lakes. The co-ordination number of quadrivalent vanadium is six.

THE structure and properties of the lakes formed by a number of azo-dyes with copper and other bivalent metals, and with tervalent chromium, iron, and aluminium, have already been examined (Drew and Landquist, J., 1938, 292; Drew and Fairbairn, J., 1939, 823; Beech and Drew, this vol., pp. 603, 608), but lakes of this kind with quadrivalent metals have not hitherto been described in the literature. It was of interest to compare the behaviour of a metal in this state of valency with that of the metals of lower valency, and vanadium was chosen as an example, since its simple compounds have frequently been claimed as mordants. Some well-defined lakes of quadrivalent vanadium with oo'-disubstituted azo-dyes have now been prepared, the o-substituents being OH, NH_2, and CO_2H.

An attempt was made to prepare a quadrivalent vanadium lake of benzeneazo-β-naphthol, but no evidence of combination could be obtained. It is probable that, as with tervalent chromium, the presence of a single *o*-hydroxyl group in the molecule of an azo-dye is insufficient to hold a quadrivalent vanadium atom in stable combination with the azo-group.

(i) *oo′-Dihydroxy-azo-compounds.*—*o*-Hydroxybenzeneazo-β-naphthol, when condensed in alcoholic solution with vanadyl chloride, gave anhydrous, green crystals of the *bisazo-vanadi-complex* (I), which was insoluble in water and (possibly for this reason) stable towards boiling concentrated hydrochloric acid. It was soluble in benzene and other organic solvents, and was co-ordinatively saturated, dissolving in pyridine or aniline but not combining with either. Under less acid conditions, moist vanadyl hydroxide being used, the condensation in alcohol with the azo-dye gave rise to a mixture of (I) with the *hydrated vanadyl complex*, (II) or (IIA), a dark reddish-brown, crystalline powder, soluble in water or alcohol to deep brownish-red solutions, and decomposed by hydrochloric acid with regeneration of the azo-dye. On dehydration, 2 mols. of water were lost, whereas only 1 mol. was regained on exposure to moist air. When the complex was dissolved in pyridine, a crystalline *monopyridino*-derivative (III) was obtained, which lost its pyridine in dry air at 115°. These facts may perhaps be regarded as supporting formula (II), rather than (IIA).

(I.)　　　　　(II.)　　　　　(IIA.)
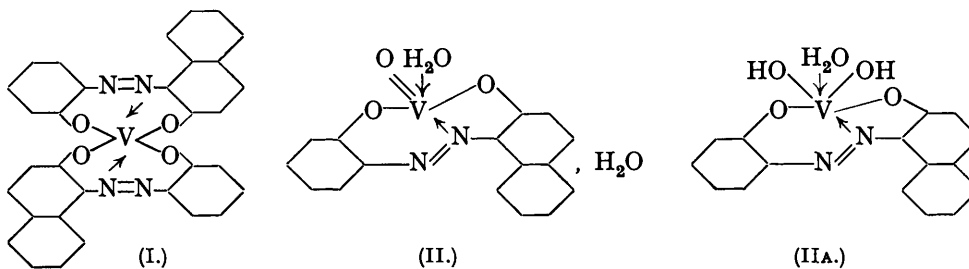
Vanadyl hydroxide and *o*-hydroxybenzeneazoresorcinol, condensed in alcoholic solution, gave only the *vanadyl complex* (IV), with $2\frac{1}{2}$ mols. of water. This substance dissolved in water, giving deep orange-red solutions; mineral acids liberated the azo-dye, but aqueous alkalis gave red solutions of their salts with the disengaged hydroxyl of the vanadyl complex.


(III.)　　　　　(IV.)

(V.)　　　　　(VI.)
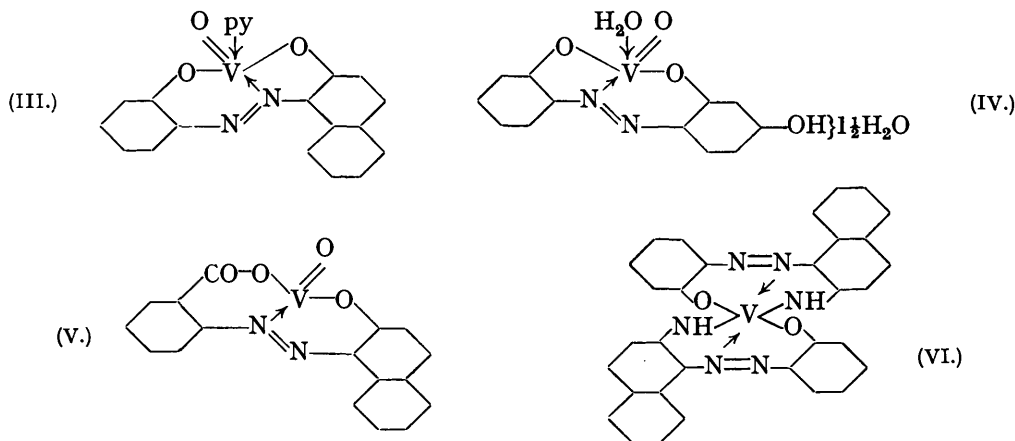
The sodium salt of *o*-carboxybenzeneazo-β-naphthol and alcoholic vanadyl chloride likewise afforded a reddish-brown *vanadyl complex*, which, however, was insoluble in water, although it dissolved in pyridine to a red solution. The complex could not be crystallised and was probably not quite homogeneous; but analysis showed that it

contained accurately one vanadium atom per azo-dye residue, so that, apart from the question of hydration, the formula must be (V).

(ii) *o*-Hydroxybenzeneazo-β-naphthylamine gave, with alcoholic vanadyl hydroxide, two lakes, as in the case of *o*-hydroxybenzeneazo-β-naphthol : (*a*) the anhydrous *bisazo-vanadi-complex* (VI), which crystallised in brown leaflets, insoluble in water, but soluble to brownish-red solutions in benzene or pyridine; it was less stable to concentrated hydrochloric acid than (I); and (*b*) the plum-coloured *vanadyl complex*, as (II), which was somewhat unstable and was not obtained in a pure state (see Experimental).

(iii) The case of salicylidene-*o*-aminophenol was examined for comparison with those of the azo-compounds. With alcoholic vanadyl hydroxide this gave brown needles of the anhydrous *vanadyl complex* (VII), insoluble in alcohol. This complex was co-ordinatively unsaturated, forming crystalline *monopyridino*- and *monoanilino*-derivatives, brown and green, respectively; it formed also a *monoacetone* derivative (indigo-blue rhombohedra), which lost the acetone, rapidly at 130° and more slowly on standing in air, reverting to (VII).


(VII.) (VIII.) (IX.)
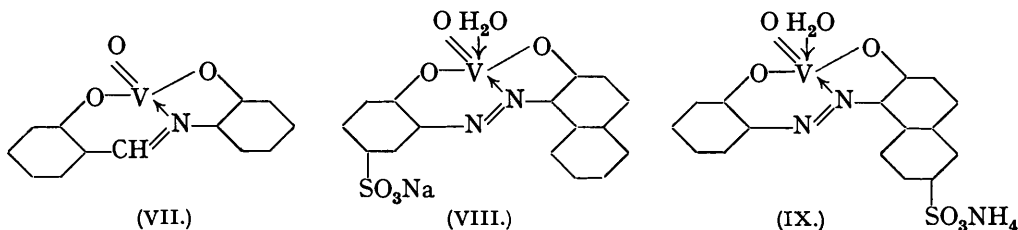
(iv) *oo'-Dihydroxyazosulphonic acids.* 2'-Hydroxy-5'-sulphobenzeneazo-β-naphthol and 2'-hydroxybenzeneazo-β-naphthol-6-sulphonic acid gave deep purple-red solutions when condensed with aqueous vanadyl hydroxide. On evaporation, the solutions left soluble, dark-red, glassy substances, which could not be purified. Analyses indicated that the glasses contained the vanadyl complexes, with the sulpho-groups partly free (*e.g.*, as in XIV) and partly combined with further vanadyl vanadium. Aqueous ammonia or sodium hydroxide set free the ionised vanadium, as vanadyl hydroxide, without affecting that of the co-ordinated group, so that the ammonium or sodium salts of the vanadyl complexes were produced; these salts could be isolated by fractional precipitation of the aqueous solution with ammonium or sodium chloride : the vanadyl hydroxide separated first, being readily distinguishable from the salts of the vanadyl complexes. In this way were obtained the crystalline hydrated *sodium* salt (VIII) of the *vanadyl complex* of the 5'-sulpho-dye, a purplish-red substance, readily soluble in water, and the hydrated *ammonium* salt (IX) of the *vanadyl complex* of the 6-sulphonic acid, which in substance was purpler in shade (browner on fibres).

(X.) (XI.)

(XII.) (XIII.)
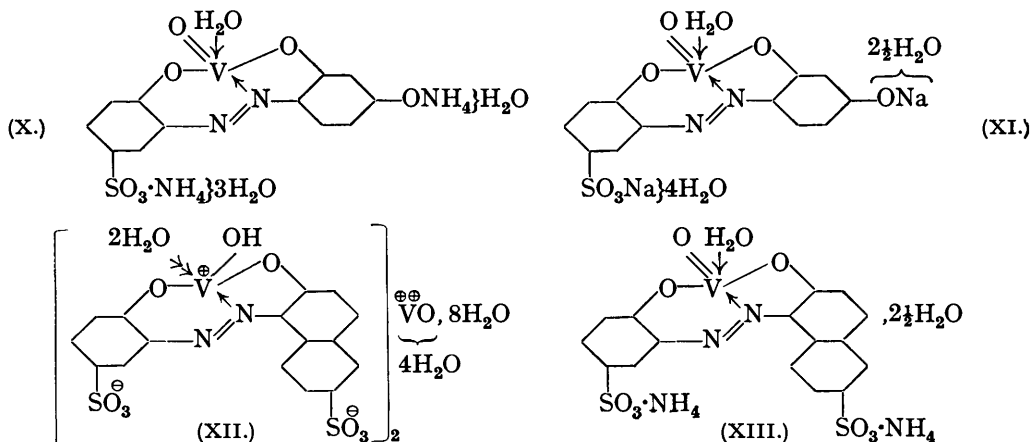
2'-Hydroxy-5'-sulphobenzeneazoresorcinol similarly gave a dark orange-red glass, from which the *diammonium* salt *pentahydrate* (X) and *disodium* salt (XI), with $7\frac{1}{2}$ H$_2$O, of the *vanadyl complex* were prepared. These salts crystallised from aqueous ammonium and sodium chloride, respectively, illustrating the interesting point that the 4-hydroxyl group of the azo-dye is considerably acidic in character. The vanadyl derivatives of this azoresorcinol all gave orange or brownish-red solutions, devoid of the purplish or rose-red tints of the derivatives of the foregoing pair of azo-β-naphthol dyes.

2'-Hydroxy-5'-sulphobenzeneazo-β-naphthol-6-sulphonic acid and aqueous vanadyl hydroxide afforded a deep rose-red glass, readily soluble in cold water, consisting of the *vanadyl* salt of the *vanadyl complex* (XII), with 16 H$_2$O. When the unco-ordinated vanadium was removed from this substance by means of ammonia, the *diammonium* salt of the *vanadyl complex* (XIII), with $3\frac{1}{2}$H$_2$O, was obtained in bright-red needles, soluble in water.
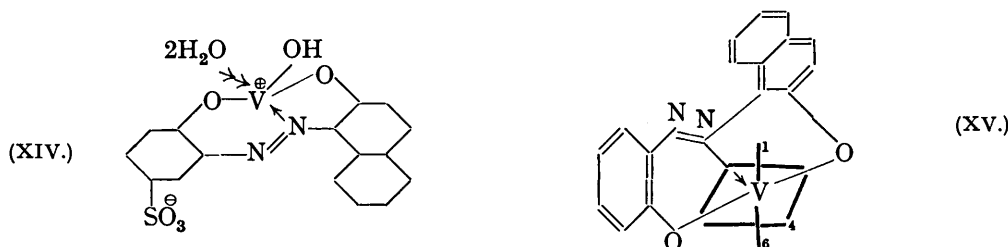
None of the foregoing vanadyl derivatives of the azo-sulphonic acids was stable towards aqueous mineral acid, and this explains why the derivatives cannot well be prepared from vanadyl chloride in the absence of bases. Vanadyl hydroxide, if present in excess, neutralised the sulpho-groups of the vanadyl lakes (*e.g.*, XIV); the crude lakes obtained were therefore, in general, mixtures of the lakes of the type of (XIV) and their vanadyl salts. Confirmatory evidence was found from experiments on the dyeing of animal fibres with the crude lakes and their salts : the salts did not dye fibres in absence of acids, but the crude lakes did so, usually in old-rose tints (except in the case of the lake of *o*-hydroxy-benzeneazoresorcinol, where the shade was orange-brown). This behaviour indicates that the lakes of type (XIV) are stable in aqueous solution in the absence of mineral acid. The fastness properties towards acids and alkalis of the dyeings with the vanadyl lakes, although superior to those of the free dyes, were much inferior to those of the corresponding chromium lakes.

The structures and chemical properties of the lakes described in this paper afford evidence that the co-ordination number of quadrivalent vanadium is six, and not five—as has sometimes been proposed. The vanadi-lakes, (I) and (VI), illustrate this point particularly clearly. There is an interesting comparison between the structures of (I) and of the acid chromi-complex of *o*-hydroxybenzeneazo-β-naphthol (Drew and Fairbairn, *loc. cit.*, p. 826) : in combination with two residues from this dye, the negatively charged tervalent chromium atom assumes identically the same state as the neutral quadrivalent vanadium atom. Thus, whilst the tervalent chromium atom associates itself with nine additional electrons, the atom of quadrivalent vanadium associates itself with eight. The stereochemistry of the vanadi- and vanadyl lakes now described may probably be regarded as identical with that suggested (*idem, ibid.*) for the chromium lakes, the vanadium atom having octahedral symmetry; *e.g.*, in (I) the median planes of the azo-dye residues are mutually perpendicular, and in (II) the median plane of the azo-dye residue is perpendicular to that containing the metallic atom, the doubly bonded oxygen atom and the co-ordinated water molecule. Thus, the component nuclei of the azo-dye not being similar, the vanadi-lakes must be dissymmetric; and the vanadyl lakes must also be dissymmetric, since the oxygen atom doubly bound to the metal can only occupy *cis*-positions of the octahedron. The skeleton (XV), where the 5-ring is arbitrarily associated with the naphthalene nucleus, shows the best positions of the double bonds, as regards freedom from strain (only one azo-dye residue is illustrated, the remaining three groups or atoms attached to vanadium occupying positions 1, 4, and 6 of the octahedron).

4 B

EXPERIMENTAL.

Materials.—The vanadyl hydroxide employed was obtained by nearly neutralising an aqueous solution of vanadyl chloride with aqueous ammonia (d 0·88); the green precipitate was washed with hot water, drained, and used in a moist condition. It reacted readily with the azo-dyes in aqueous or alcoholic solution, but, if it was dried, the hydroxide became a much less reactive indigo-blue mass. Vanadyl chloride was used in 50% aqueous solution.

o-Hydroxybenzeneazo-β-naphthol.—(i) The dye (1 g.) in alcohol (200 c.c.) and the 50% vanadyl chloride solution (1 c.c.) were mixed and boiled under reflux for 3 hours. Well-defined, green plates of the *complex* (I) separated, and were washed with water, alcohol, and ether, and dried in air (yield, 0·35 g.) (Found : C, 66·4; H, 3·8; V, 8·9. $C_{32}H_{20}O_4N_4V$ requires C, 66·75; H, 3·5; V, 8·85%); the powdered crystals did not lose weight at 170°. The complex was insoluble in water and stable to hot concentrated hydrochloric acid; it was recovered unchanged from its brown solutions in benzene, pyridine, and aniline.

(ii) When the dye (1 g.) and moist vanadyl hydroxide (1 g.) were added to alcohol (150 c.c.) and the mixture boiled under reflux for 5 hours, the hydroxide slowly dissolved; the dark reddish-brown liquid was filtered from (I) and a little undissolved vanadyl hydroxide, and allowed to evaporate : the residue was a brown crystalline powder, which was extracted with ether, to remove any unchanged dye, and recrystallised from alcohol, affording brown micro-crystals (yield, 0·4 g.) of the *vanadyl complex*, (II) or (IIA), soluble in water and in most other solvents (except ether) to red or reddish-brown solutions (Found : C, 52·4; H, 3·9; V, 13·7; loss at 130°, 9·95. $C_{16}H_{10}O_3N_2V,2H_2O$ requires C, 52·6; H, 3·85; V, 13·95; $2H_2O$, 9·85%); the desiccated material regained $1H_2O$ in moist air (Found : regain of 4·95% of weight of anhydrous substance. Calc. : 5·45%). It separated from hot water in small plates; and from pyridine in bronzed crystals of its *monopyridino*-derivative (III) (Found : loss of pyridine at 115°, 19·7. $C_{16}H_{10}O_3N_2V,C_5H_5N$ requires C_5H_5N, 19·4%). Even dilute hydrochloric acid soon decomposed (II), liberating the original azo-dye.

o-Hydroxybenzeneazoresorcinol.—To an alcoholic solution (1 g. in 200 c.c.) of the dye (m. p. 184°, decomp.) was added moist vanadium hydroxide (1 g.), and the whole boiled under reflux for 6 hours. The filtered, dark brown solution left, on evaporation, a sticky, black material, possibly an alcoholate; but if water was added to the solution before evaporation, brown crystals were obtained. These were extracted with ether, and the residue recrystallised from 75% alcohol : the *vanadyl complex* (IV) separated as an almost black powder (0·2 g.), which was dried in air (Found : C, 42·7; H, 3·7; V, 14·7; loss at 130°, 12·9. $C_{12}H_8O_4N_2V,2\frac{1}{2}H_2O$ requires C, 42·4; H, 3·8; V, 15·0; $2\frac{1}{2}H_2O$, 13·2%); it was soluble in water to an orange-red solution, and in alkalis to red solutions; aqueous acids liberated the original azo-dye.

o-Carboxybenzeneazo-β-naphthol.—The sodium salt (red needles) prepared from 0·5 g. of the dye was refluxed with alcohol (200 c.c.) and 50% vanadyl chloride solution (0·3 c.c.) for 3 hours, a brick-red powder separating; more of the same powder was obtained on evaporating the filtrate. The product was extracted with ether and then with water to remove impurities; it was now insoluble in water and sparingly soluble in alcohol, but soluble in pyridine to a deep red solution. Analysis of the powder (Found : C, 53·1; H, 3·9; V, 13·3. $C_{17}H_{10}O_4N_2V,1\frac{1}{2}H_2O$ requires C, 53·15; H, 3·4; V, 13·3%) showed that it contained 17 carbon atoms per atom of vanadium as would be required for the *vanadyl complex* (V), but only 1·5% loss of water was found on dehydration; the substance could not be recrystallised, and it must be concluded that it was probably not homogeneous.

o-Hydroxybenzeneazo-β-naphthylamine.—The dye (1 g.; m. p. 192—193°) was dissolved in alcohol (150 c.c.), and moist vanadyl hydroxide (0·75 g.) added; when the mixture was boiled under reflux (3 hours), brown leaflets of the *bisazo-vanadi-complex* (VI) separated (yield, 0·4 g.) (Found : C, 66·4; H, 4·3; V, 9·0. $C_{32}H_{22}O_2N_6V$ requires C, 67·0; H, 3·85; V, 8·9%), which did not alter in weight at 115°. It was soluble in benzene and in pyridine (brownish-red solutions); concentrated hydrochloric acid slowly decomposed it. The alcoholic filtrate from (VI), when allowed to evaporate, deposited a reddish-brown solid, which was extracted with ether to remove unchanged dye and then recrystallised from alcohol; the plum-coloured solid which separated consisted of the *vanadyl complex*, as (II), but was not obtained pure (Found : C, 52·2; H, 4·3; V, 12·6. $C_{16}H_{11}O_2N_3V,2H_2O$ requires C, 52·6; H, 4·1; V, 14·0%); the complex appeared to be oxidised on standing in air.

Salicylidene-o-aminophenol.—The azomethine (1 g.; m. p. 183°), moist vanadyl hydroxide (0·75 g.), and alcohol (200 c.c.) were boiled under reflux for 3 hours; brown, tabular crystals

(0·4 g.) of the *vanadyl complex* (VII) separated, and were washed with alcohol and dried in air (Found : C, 55·95; H, 3·25; V, 18·15. $C_{13}H_9O_3NV$ requires C, 56·1; H, 3·25; V, 18·3%); there was no loss in weight at 140°. The complex dissolved in hot pyridine to an almost black solution, from which, on dilution with 5 vols. of water, the *monopyridino*-derivative, as (III), separated in pale-brown needles (Found : C, 60·0; H, 4·0; V, 14·75. $C_{13}H_9O_3NV,C_5H_5N$ requires C, 60·5; H, 3·9; V, 14·3%); it was soluble in alcohol to a yellow solution. The brown solution of (VII) in aniline gave, on being kept, small, bright green needles of the *monoanilino*-derivative, which were dried in air (Found : C, 61·3; H, 4·6; V, 13·3. $C_{13}H_9O_3NV,C_6H_5\cdot NH_2$ requires C, 61·45; H, 4·3; V, 13·7%); the aniline mother-liquor later gave a crop of dark brown, silky needles, which, when washed with a little alcohol and dried in air, gave an analysis suggesting that the *substance* was a polyanilino-derivative of (VII) (Found : C, 68·0; H, 5·15; V, 5·9. $C_{13}H_9O_3NV,6C_6H_5\cdot NH_2$ requires C, 70·3; H, 6·1; V, 6·1%). When the above preparation of (VII) was repeated in acetone as solvent, with the addition of concentrated aqueous ammonia (0·5 c.c.), the *monoacetone* derivative of (VII) separated in small indigo-blue rhombohedra (0·1 g.), insoluble in acetone and at once decomposed by other solvents; on being heated at 130° it lost the acetone (Found : $COMe_2$, 14·25. $C_{13}H_9O_3NV,C_3H_6O$ requires $COMe_2$, 17·25%), which was identified as the 2 : 4-dinitrophenylhydrazone.

2'-Hydroxy-5'-sulphobenzeneazo-β-naphthol.—The dye (1 g.) in water (150 c.c.) was mixed with moist vanadyl hydroxide, and the whole refluxed (6 hours), the colour of the solution becoming deep purplish-red. The filtered liquid was allowed to evaporate to dryness, and left a dark red, glassy solid; solution of this in ammonia afforded thin, red-brown plates of the ammonium salt of the vanadyl complex (XIV). The *sodium* salt (VIII) was analysed (Found : C, 35·25; H, 3·4; V, 9·6; loss at 150°, 21·8. $C_{16}H_9O_6N_2SNaV,6\frac{1}{2}H_2O$ requires C, 35·05; H, 4·0; V, 9·3; $6\frac{1}{2}H_2O$, 21·35%); the salt was almost black, with purplish-red streak; after being desiccated, it regained in moist air about $2\frac{1}{2}$ mols. of water (2 days).

2'-Hydroxybenzeneazo-β-naphthol-6-sulphonic Acid.—The complex was prepared as in the last case. The glassy product was purpler in shade than that from the previous azo-dye. It was dissolved in a little water, and a slight excess of aqueous ammonia added; the filtered liquid was gradually precipitated by adding solid ammonium chloride, vanadyl hydroxide separating in the first crops and then the reddish-black ammonium salt (IX), which did not crystallise (Found : C, 34·5; H, 5·1; V, 7·9; loss at 170°, 18·9. $C_{16}H_{13}O_6N_3SV,7\frac{1}{2}H_2O$ requires C, 34·2; H, 5·0; V, 9·1; $6\frac{1}{2}H_2O$, 20·85%).

2'-Hydroxy-5'-sulphobenzeneazoresorcinol.—Condensation with vanadyl hydroxide, as above, afforded a very dark red glassy mass, easily soluble in cold water, which appeared to be a vanadyl salt of the vanadyl complex (Found : C, 24·25; H, 3·4; V, 16·55; loss at 170°, 16·1%); it could not be purified. When the orange-red aqueous solution of the glassy salt was treated with ammonia, and the filtered liquid fractionally precipitated with ammonium chloride, dark red needles of the *diammonium* salt *pentahydrate* of the *vanadyl complex* (X) were obtained (Found : C, 29·1; H, 4·6; V, 10·15; loss at 145°, 18·35. $C_{12}H_{14}O_7N_4SV,5H_2O$ requires C, 28·85; H, 4·8; V, 10·2; $5H_2O$, 18·05%); the desiccated salt regained $2H_2O$ in moist air. The *disodium* salt (with $7\frac{1}{2}H_2O$) of the *vanadyl complex* (XI) was also obtained (Found : C, 26·2; H, 3·5; V, 9·0, 9·25; loss at 140°, 18·65. $C_{12}H_6O_7N_2SNa_2V,7\frac{1}{2}H_2O$ requires C, 26·0; H, 3·8; V, 9·2; loss of $7H_2O$ and gain of $\frac{1}{2}CO_2$, 18·75%); it formed dark red, rectangular needles, with green reflex, soluble in water to an orange-red solution. (The disodium and the diammonium salt of the vanadyl complex of this dye were decomposed when desiccated at 140—150° in a stream of air, dried by means of phosphoric oxide but containing carbon dioxide, the ammonium group or sodium atom at the 4-hydroxyl being set free as carbonate. Allowance has been made for this in the case of the desiccation of the disodium salt, but not in that of the diammonium salt, because the ammonium carbonate formed was there partly volatilised.)

2'-Hydroxy-5'-sulphobenzeneazo-β-naphthol-6-sulphonic Acid.—Condensation, as above, of the dye and moist vanadyl hydroxide in aqueous solution, gave a purplish-red solution, affording a deep red glassy mass which, recovered from its filtered aqueous solution, was probably the hydrated *vanadyl* salt of the *vanadyl complex* (XII) (Found : C, 28·8; H, 3·75; V, 12·1; loss at 160°, 19·2. $C_{32}H_{18}O_{19}N_4S_4V_3,16H_2O$ requires C, 28·85; H, 3·75; V, 11·5; $16H_2O$, 21·65%). The salt was readily soluble in water to a deep rose-red solution, which, on treatment with ammonia as above, yielded the hydrated *diammonium* salt of the *vanadyl complex* (XIII), as small, bright red needles (Found : C, 32·65; H, 4·65; V, 8·6; loss at 170°, 9·9. $C_{16}H_{16}O_9N_4S_2V,3\frac{1}{2}H_2O$ requires C, 32·75; H, 3·95; V, 8·7; $3\frac{1}{2}H_2O$, 10·75%); the desiccated salt regained $1\frac{1}{2}$ mols. of water in moist air.

Analysis.—In the analysis of the sodium salts of the vanadyl complexes by ignition in a

micro-muffle with sulphuric acid, the residue consisted of sodium sulphate and vanadium pentoxide, sodium vanadate not apparently being formed at a low-red heat.