378. *The Azo-group as a Chelating Group. Part I. Metallic Derivatives of* o-*Hydroxyazo-compounds.*

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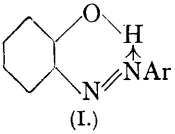
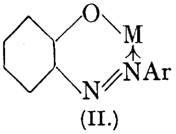
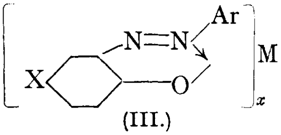
THE belief has long been held that *o*-hydroxyazo-compounds (I) and their metallic derivatives (II) have a co-ordinated structure. Sidgwick (" The Electronic Theory of Valency," 1927, p. 235) points out that among the azo-dyes those having an *o*-hydroxyl have mordant characteristics, this being due to the possibility of chelation with the mordanting metal. Morgan and Smith (J., 1924, **125**, 1732) describe a number of cobalt and chromium lakes derived from *o*-hydroxyazo-dyes, chelation being achieved as in (II). In a detailed examination of the absorption spectra of azo-dyes Blumberger (*Chem. Weekblad*, 1928, 282, 315; 1930, 190; 1932, 454; 1933, 538; 1935, 6) attributes the anomalous behaviour of *o*- and *peri*-hydroxyazo-compounds to co-ordination between the neighbouring hydroxy- and azo-groups.



(I.)



(II.)



(III.)

In the absence of boiling-point, vapour-pressure, and solubility data, evidence of co-ordination in the *o*-hydroxyazo-compounds may be sought in their melting points. Although no direct connexion between melting point and chelate structure has been established, among isomeric hydroxyazo-compounds those possessing a free *o*-hydroxyl almost invariably have the lowest melting point; *e.g.*, 4-benzeneazoresorcinol 1-methyl ether and 3-methyl ether melt at 123° and 137° respectively, and the 1-ethyl ether and 3-ethyl ether at 87° and 145° respectively. These pairs of ethers are so similar in structure that all factors other than co-ordination which may affect the melting point are virtually eliminated.

In the present investigation we have turned our attention to the metallic salts of the *o*-hydroxyazo-compounds with a view to detecting co-ordination of the type (II). A search of the literature reveals that *o*-hydroxyazobenzene forms an alcohol-soluble copper salt melting at 225° and *p*-hydroxyazobenzene forms no such salt (Bamberger, *Ber.*, 1900, **33**, 1951). Much work from Italian schools has been devoted to the preparation of metallic complexes derived from 1-arylazo-β-naphthols and -β-naphthylamines (Charrier and Beretta, *Gazzetta*, 1926, **56**, 865; Crippa, *ibid.*, 1927, **57**, 20, 497, 593; 1928, **58**, 716; Crippa and Long, *ibid.*, 1931, **61**, 99; Cremonini, *ibid.*, 1928, **58**, 372). The compounds described by these authors were prepared under conditions which would not necessarily lead to salt formation, and disagreement is expressed as to their structure. The majority are represented as containing the metal associated with the azo-compound without hydrogen replacement, though Cremonini (*loc. cit.*) formulates them as naphthoxides of the type (II). All are agreed, however, that complex formation is not extended to azo-compounds in which the coupled phenol (or amine) is a derivative of benzene.

We describe cupric, nickel, and cobaltic salts of some *o*-monohydroxyazo-compounds prepared by the action of the metallic acetates on the latter; we regard this method of preparation as likely to lead to salt formation. We find that the formation of co-ordinated salts, far from being restricted as suggested above, is common to all *o*-hydroxyazo-compounds. Indeed, we believe that the reason for the stability of these salts is to be found in their chelated structure, since the metallic salts of the corresponding *p*-hydroxyazo-compounds, if formed at all, are extremely unstable. The salts described show properties typical of co-ordinated compounds : they are insoluble in water, sparingly soluble in polar solvents, but readily in non-polar solvents; they melt in the neighbourhood of 200° to form deeply coloured liquids.

The structure assigned (III) to the metallic complexes leaves no doubt that the stereochemical arrangement of the aryl groups about the azo-nitrogen atoms is *trans*. Although this provides no positive evidence as to the geometrical configuration of the parent azo-compounds, the fact that decomposition of the metallic complexes by cold acid, in all the cases tried, yielded azo-compounds identical with the originals supports the view that all stable azo-compounds are *trans*. Dipole-moment evidence to this effect is also put forward by Bergmann, Engel, and Sandor (*Ber.*, 1930, **63**, 2572).

In subsequent parts of this series we hope to extend the work to other examples of the electron-donor properties of the azo-group.

EXPERIMENTAL.

Only one typical preparation will be described under each metal. The yield of metallic complexes, except in the case of some of the nickel and cobalt compounds, was practically theoretical.

Cupric Complexes.—These were dark brown, crystalline substances, insoluble in water, but soluble in benzene, toluene, xylene, and chloroform to give red-brown solutions, which were too highly coloured to allow of molecular-weight determinations. In alcohol, acetone, ether, and light petroleum, the compounds were sparingly soluble to give yellow or light brown solutions. Acetic acid and dilute mineral acids, especially on warming, caused decomposition into the original azo-compounds; the complexes show considerable stability towards aqueous alkali, but are decomposed into copper oxide and the salt of the original azo-compound after some minutes' boiling.

Cupric 3-*benzeneazo*-p-*tolyloxide*. To a hot, nearly saturated, alcoholic solution of benzeneazo-*p*-cresol (1 mol.), a solution of copper acetate (excess, 1 mol.) in 50% aqueous alcohol was added dropwise; the *copper* complex was precipitated immediately as a fine brown powder. This was collected after several hours, washed successively with alcohol and water, and purified by precipitation from benzene solution by the addition of light petroleum, forming a brown crystalline powder, m. p. 230° (Found: N, 11·2; Cu, 13·0. $C_{26}H_{22}O_2N_4Cu$ requires N, 11·5; Cu, 13·1%).

Cupric 3-p'-*tolueneazo*-p-*tolyloxide*, prepared from *p*'-tolueneazo-*p*-cresol in the same way, was a red-brown, crystalline powder, m. p. 242° (Found: N, 10·9; Cu, 12·5. $C_{28}H_{26}O_2N_4Cu$ requires N, 10·9; Cu, 12·4%).

Cupric 3-m'-*tolueneazo*-p-*tolyloxide*, prepared from *m*'-tolueneazo-*p*-cresol, formed dark red-brown, micro-crystals from benzene, m. p. 221° (Found: N, 10·7; Cu, 12·6%).

Cupric 2 : 4-*bisbenzeneazophenoxide* was obtained from bisbenzeneazophenol as a chocolate-brown powder, m. p. 243° (Found: N, 16·5; Cu, 9·3. $C_{36}H_{26}O_2N_8Cu$ requires N, 16·8; Cu, 9·5%).

Cupric 1-*benzeneazo*-β-*naphthoxide*, prepared from benzeneazo-β-naphthol, formed a red-brown crystalline powder from toluene, m. p. 295° (Found: N, 10·1; Cu, 11·4. $C_{32}H_{22}O_2N_4Cu$ requires N, 10·1; Cu, 11·4%).

Cupric 2-*benzeneazo*-α-*naphthoxide*, prepared from β-naphthaquinonephenylhydrazone, formed dark brown, crystalline plates, m. p. 237° (Found: N, 10·1; Cu, 11·3%).

Nickel Complexes.—These compounds were prepared as described under the cupric complexes, except that it was usually found necessary to dilute the mixture with water to bring about their precipitation, their solubility in alcohol and acetone being usually much higher than is the case with the cupric complexes. This resulted in a diminution of yield and, in some cases, a loss of purity of the product. The presence of ammonia often facilitated the formation of the nickel complexes. They form dark olive-green needles, insoluble in water, slightly soluble in alcohol, acetone, ether, and ligroin, but soluble in benzene, toluene, and chloroform with dark green colour. In polar solvents, and especially when warm, hydrolysis frequently occurs with deposition of nickel hydroxide, the solution changing colour from green to brown. The nickel complexes are more stable to dilute acid than are the copper compounds, but eventually decompose in a similar way.

Nickel 3-*benzeneazo*-p-*tolyloxide*. To a well-stirred solution of benzeneazo-*p*-cresol (1 mol.) in hot acetone, a little aqueous ammonia (*d* 0·880) was added, followed by a solution of nickel acetate (excess, 1 mol.) in 50% aqueous acetone. The *nickel* complex was precipitated in an impure form by the careful addition of water. By solution in chloroform and precipitation with light petroleum, it formed a black crystalline powder with a green reflex, m. p. 216° (Found: N, 11·5; Ni, 12·5. $C_{26}H_{22}O_2N_4Ni$ requires N, 11·6; Ni, 12·2%).

Nickel 3-p'-*tolueneazo*-p-*tolyloxide* formed dark olive-green crystals, m. p. 242—243° (Found: N, 10·7; Ni, 11·7. $C_{28}H_{26}O_2N_4Ni$ requires N, 11·0; Ni, 11·5%).

Nickel 3-*m*'-tolueneazo-*p*-tolyloxide was obtained in an impure condition as small, dark green crystals, m. p. 214° after softening at about 200°. Low nitrogen and high nickel analyses indicated the presence of nickel oxide.

Nickel 2 : 4-*bisbenzeneazophenoxide* was obtained in an impure condition as small black crystals, decomposing without melting between 295° and 310° (Found: N, 16·2; Ni, 8·3. $C_{36}H_{26}O_2N_8Ni$ requires N, 16·9; Ni, 8·9%).

Nickel 1-*benzeneazo*-β-*naphthoxide* was formed in excellent yield without dilution, as described under cupric complexes, as a very dark green, crystalline powder, m. p. 290° (Found: N, 10·1; Ni, 10·2. $C_{32}H_{22}O_2N_4Ni$ requires N, 10·1; Ni, 10·6%). Unlike the foregoing nickel complexes, this substance dissolved in benzene, toluene, and chloroform to give brown solutions.

Nickel 2-*benzeneazo*-α-*naphthoxide*, prepared as the isomeride above, formed light olive-green crystals, m. p. 293°, soluble in benzene, toluene, and chloroform to give brown solutions (Found: N, 10·3; Ni, 10·7%).

Cobaltic Complexes.—These are obtained by the addition of an aqueous-alcoholic solution of cobaltous acetate to an alcoholic solution of the azo-compound. The yield is poor unless hydrogen peroxide is present, though the products are identical in both cases. They form very dark brown or black crystals, insoluble in water, but more soluble in other solvents than the cupric or nickel complexes. The solutions are orange to dark red-brown and show no tendency to hydrolyse. This stability is also maintained towards dilute mineral acid, the compounds being only incompletely decomposed even on prolonged boiling.

Cobaltic 3-*benzeneazo*-p-*tolyloxide*. To a solution of benzeneazo-*p*-cresol (4 g.) in hot alcohol (300 c.c.) was added dropwise a solution of cobalt acetate (6 g.) in 50% alcohol (80 c.c.) to which had been added 20 vol. hydrogen peroxide (5 c.c.). The black precipitate which formed on standing crystallised from acetone as a dull black, microcrystalline powder, m. p. 202° (Found: N, 12·4;* Co, 8·6. $C_{39}H_{33}O_3N_6Co$ requires N, 12·1; Co, 8·5%).

Cobaltic 3-p′-*tolueneazo*-p-*tolyloxide* formed a jet black, crystalline powder, m. p. 200—201° (Found: N, 11·6;* Co, 8·4. $C_{42}H_{39}O_3N_6Co$ requires N, 11·4; Co, 8·0%).

Cobaltic 3-m′-*tolueneazo*-p-*tolyloxide* was obtained as a black crystalline powder, m. p. 187° (Found: N, 11·4;* Co, 7·9%).

Cobaltic 2 : 4-*bisbenzeneazophenoxide* crystallised from alcohol as a black crystalline powder, m. p. 180—185° (Found: N, 17·6;* Co, 6·3. $C_{54}H_{39}O_3N_{12}Co$ requires N, 17·5; Co, 6·1%).

Cobaltic 1-*benzeneazo*-β-*naphthoxide* was obtained from benzeneazo-β-naphthol by the usual method with or without the use of hydrogen peroxide, and formed a brownish-black amorphous powder, m. p. 221° (Found: N, 10·7;* Co, 7·6. $C_{48}H_{33}O_3N_6Co$ requires N, 10·5; Co, 7·4%).

Cobaltic 2-*benzeneazo*-α-*naphthoxide* crystallised from acetone as very dark purplish-brown crystals, m. p. 199° (Found: N, 10·3;* Co, 7·2%).

The addition of metallic acetates to solutions of *p*-hydroxyazo-compounds (*e.g.*, *p*-hydroxyazobenzene, benzeneazo-*o*-cresol, 4-benzeneazo-α-naphthol) under conditions similar to those described above did not give rise to metallic derivatives. As the addition proceeded, there was no darkening of colour characteristic of the formation of chelate compounds, and the azo-compounds could eventually be recovered unchanged.

The nitrogen analyses denoted by asterisks were carried out by Dr. A. Schoeller.

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