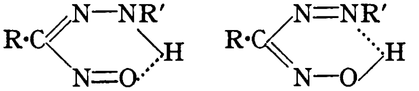
146. *The Azo-group as a Chelating Group. Part V. Metallic Derivatives of Arylazo-oximes and of Formazyl Compounds.*

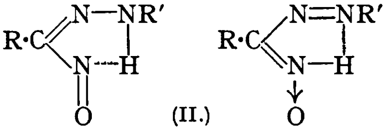
By Louis Hunter and Carl B. Roberts.

Cobaltic complexes of six arylazo-aldoximes and cupric, nickel and cobaltous complexes of six formazyl compounds are described. From their properties they are shown to be co-ordination compounds, the central metal atom deriving electrons from one of the azo-nitrogen atoms.

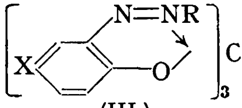
The reactivity of the methin-hydrogen atom of the aldehydearylhydrazones towards substituting agents is illustrated by the action of nitrous acid to give arylazo-oximes (Bamberger and Pemsel, *Ber.*, 1903, **36**, 62) and of diazonium salts to give formazyl compounds (v. Pechmann, *Ber.*, 1894, **27**, 1690). The products thus formed have in common their tautomeric character, and an ability to yield metallic derivatives the co-ordinated nature of which provides further examples of the electron-donor properties of the azo-group.

The Arylazo-oximes.—The preparation of the arylazo-oximes as nitroso-compounds, and their reactivity as oximes, would seem to indicate an internally co-ordinated structure (I or II). On stereochemical grounds the six-membered system in (I), involving as it does


(I.)


(II.)

the comparatively stable N–H–O bond, is probably to be preferred to the five-membered system in (II), which possesses the less stable N–H–N bond. However this may be, a co-ordinated structure for the arylazo-oximes receives support from their physical properties: they are very soluble in hydrocarbon solvents, have relatively low melting points, and in certain cases are volatile without decomposition. Above all, however, by the replacement of their acidic hydrogen atom, they yield metallic derivatives which, by their low melting points and their high solubility in organic solvents, without doubt possess a chelate structure. Six well-defined cobaltic complexes are described, and numerous impure copper and nickel derivatives were obtained but not thoroughly examined. A choice between five- and six-membered formulation of the cobaltic complexes is not possible on the existing data, but by reason of their close analogy with the cobaltic complexes of the *o*-hydroxyazo-compounds (III) described in Part I (J., 1935, 1598), we ascribe to them a similar formulation (IV).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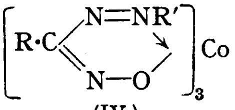
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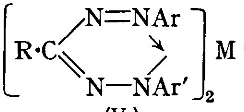
(V.)

The Formazyl Compounds.—The constitution of these compounds has been fully discussed in the preceding paper. The conclusions reached are mainly based on the isolation of metallic (copper, nickel, and cobalt) derivatives which are described in the present paper. These are highly coloured solids with definite melting points, insoluble in water, but readily soluble in organic solvents; their composition indicates replacement of the imino-hydrogen atom of the parent formazyl compounds by an equivalent of metal. From these properties we conclude that they possess the structure (V; M = metal).

Whereas the cobalt complexes (IV) derived from the arylazo-aldoximes are invariably cobaltic (even in the absence of an oxidising agent), those derived from the formazyl compounds are cobaltous (V; M = Co). There seems little doubt that the urge to acquire a rare-gas structure, satisfied in (IV), is frustrated in (V) by the steric interference of the numerous aryl groups surrounding the central metal atom. For the same reason it would appear that the distribution of the valencies around the metallic atom in (V) can scarcely be planar.

EXPERIMENTAL.

Nitrogen analyses were performed by Drs. Weiler and Strauss, Oxford. Metals were estimated, after destruction of organic matter under Kjeldahl conditions, by gravimetric analysis with the following organic precipitants : salicylaldoxime for copper; dimethylglyoxime for nickel; anthranilic acid for cobalt (Funk and Ditt, *Z. anal. Chem.*, 1933, **91**, 332; 1933, **93**, 241).

The arylazoaldoximes used in this work were prepared by the method of Bamberger and Pemsel (*loc. cit.*); the following have not previously been described : *Benzeneazopiperonaldoxime.* Piperonalphenylhydrazone (10 g.) was added to a solution of sodium (1·5 g.) in absolute alcohol (100 c.c.), amyl nitrite (12 c.c.) poured in, and the mixture refluxed for 20 minutes. After cooling and filtering, the solution was poured into ice-water (300 c.c.) containing 2N-caustic soda (20 c.c.), and kept overnight. Amyl alcohol was then removed by extraction with ether, and the aqueous liquor acidified to precipitate the crude *azo*-compound. After numerous crystallisations from alcohol (charcoal), it formed micro-crystalline, fawn nodules, m. p. 138° (decomp.) (Found : N, 15·5. $C_{14}H_{11}O_3N_3$ requires N, 15·6%). Yield, 4 g. from 45 g. of the phenylhydrazone.

*Benzeneazo-*p*-tolualdoxime,* prepared similarly by the nitrosation of *p*-tolualdehydephenylhydrazone, and repeatedly crystallised from alcohol, formed brick-red needles, m. p. 133° (decomp.) from benzene–petrol (Found : N, 17·6. $C_{14}H_{13}ON_3$ requires N, 17·6%). Yield, 10 g. from 70 g. of the hydrazone.

p-*Tolueneazobenzaldoxime,* prepared by the nitrosation of benzaldehyde-*p*-tolylhydrazone, formed orange-yellow needles, m. p. 111° (decomp.), from alcohol (Found : N, 17·0%).

Cobaltic Complexes of the Arylazo-oximes.—These were prepared from six parent arylazo-aldoximes by mixing a moderate excess of an aqueous alcoholic solution (filtered) of cobalt acetate with a hot alcoholic solution of the azo-compound. The complex was immediately precipitated, and after cooling the liquid was filtered; a further crop could be obtained by diluting the filtrate and keeping it overnight.

(1) The *cobaltic* complex from benzeneazoacetaldoxime formed reddish-purple needles with a green reflex, m. p. 238° (decomp.), from hot aqueous alcohol (Found : N, 23·4; Co, 10·6. $C_{24}H_{24}O_3N_9Co$ requires N, 23·1; Co, 10·8%). It was readily soluble in benzene, chloroform,

carbon tetrachloride, and acetone, less soluble in alcohol, and insoluble in water or light petroleum.

(2) The *cobaltic* complex from benzeneazobenzaldoxime formed a purple-brown amorphous powder, m. p. 133°, from cold acetone by precipitation with water (Found : N, 17·3; Co, 8·2. $C_{39}H_{30}O_3N_9Co$ requires N, 17·2; Co, 8·1%), readily soluble in benzene, chloroform and acetone, fairly soluble in alcohol, ether, or light petroleum, and insoluble in water.

(3) The *cobaltic* complex from benzeneazo-*p*-tolualdoxime formed an amorphous purple-brown powder, m. p. 149°, from alcohol (Found : N, 16·0; Co, 7·5. $C_{42}H_{36}O_3N_9Co$ requires N, 16·3; Co, 7·6%), readily soluble in benzene, chloroform, and acetone, but sparingly soluble in alcohol.

(4) The *cobaltic* complex from benzeneazoanisaldoxime formed a brownish-purple powder, m. p. 210° (decomp.) (Found : N, 15·2; Co, 7·2. $C_{42}H_{36}O_6N_9Co$ requires N, 15·3; Co, 7·2%), very soluble in benzene and acetone, sparingly in alcohol.

(5) The *cobaltic* complex from benzeneazopiperonaldoxime formed a purple-brown amorphous powder, m. p. 145° (Found : N, 14·4; Co, 6·8. $C_{42}H_{30}O_9N_9Co$ requires N, 14·6; Co, 6·8%), readily soluble in benzene, chloroform, or acetone, but almost insoluble in alcohol.

(6) The *cobaltic* complex from *p*-tolueneazobenzaldoxime formed a purple-brown amorphous powder, m. p. 145° (Found : N, 16·1; Co, 7·6. $C_{42}H_{36}O_3N_9Co$ requires N, 16·3; Co, 7·6%), readily soluble in benzene or chloroform, less soluble in acetone, and almost insoluble in alcohol.

Metallic Complexes of the Formazyl Compounds.—*Nickel complexes.* These were obtained by refluxing an acetone solution of the formazyl compound with an aqueous alcoholic solution of nickel acetate for 1—3 hours. The *complex* appeared as a precipitate, which was collected and washed with alcohol, and finally with cold dilute hydrochloric acid to remove traces of basic nickel salts. They were black substances, insoluble in water and in cold alcohol, acetone, petrol, and benzene, but moderately soluble in hot chloroform. They gave dark green solutions in concentrated sulphuric acid.

(1) Diphenylformazylbenzene gave a black crystalline solid with a greenish reflex, m. p. 300° (decomp.) (Found : N, 16·9; Ni, 8·6. $C_{38}H_{30}N_8Ni$ requires N, 17·1; Ni, 8·9%).

(2) Phenyl-*p*-tolylformazylbenzene gave black needles, m. p. 287° (decomp.) (Found : Ni, 8·5. $C_{40}H_{34}N_8Ni$ requires Ni, 8·6%).

(3) Phenyl-*p*-methoxyphenylformazylbenzene gave black needles with a green reflex, m. p. 273° (decomp.) (Found : Ni, 8·1. $C_{40}H_{34}O_2N_8Ni$ requires Ni, 8·2%).

(4) Phenyl-*p*-bromophenylformazylbenzene prepared by both methods (see preceding paper) yielded identical *nickel* complexes as a black crystalline solid with a green reflex, m. p. 278° (decomp.) (Found : Ni, 7·1, 7 3. $C_{38}H_{28}N_8Br_2Ni$ requires Ni, 7·2%).

(5) Phenyl-α-naphthylformazylbenzene prepared by both methods (see preceding paper) yielded identical *nickel* complexes as a black micro-crystalline powder, m. p. 262° (decomp.) (Found : Ni, 7·8, 7·8. $C_{46}H_{34}N_8Ni$ requires Ni, 7·75%).

(6) Phenyl-β-naphthylformazylbenzene prepared by both methods (see preceding paper) yielded identical *nickel* complexes as a black microcrystalline powder, m. p. 277° (Found : Ni, 7·7, 7·8%).

Cobaltous complexes. These were obtained from hot solutions of the formazyl compounds and cobalt acetate, exactly as for the nickel complexes. They were black substances, insoluble in water, alcohol, or light petroleum, but soluble in benzene, chloroform, or pyridine to yield brown solutions.

(1) Diphenylformazylbenzene gave black needles with a green reflex, m. p. 228—230°, from acetone by precipitation with water (Found : N, 17·3; Co, 9·1. $C_{38}H_{30}N_8Co$ requires N, 17·1; Co, 9·0%).

(2) Phenyl-*p*-tolylformazylbenzene gave black needles, m. p. 238° (Found : N, 16·0; Co, 8·5. $C_{40}H_{34}N_8Co$ requires N, 16·4; Co, 8·6%).

(3) Phenyl-*p*-methoxyphenylformazylbenzene gave black crystals with a green reflex, m. p. 233° (decomp.) (Found : N, 15·4; Co, 8·2. $C_{40}H_{34}O_2N_8Co$ requires N, 15·6; Co, 8·2%).

(4) Phenyl-*p*-bromophenylformazylbenzene prepared by both methods (see preceding paper) yielded identical *cobalt* complexes as black crystals, m. p. 192° (decomp.) (Found : Co, 7·0. $C_{38}H_{28}N_8Br_2Co$ requires Co, 7·2%).

(5) Phenyl-α-naphthylformazylbenzene prepared by both methods (see preceding paper) yielded identical *cobalt* complexes as a black microcrystalline powder, m. p. 190° (decomp.), from chloroform–light petroleum (Found : N, 14·4; Co, 7·5. $C_{46}H_{34}N_8Co$ requires N, 14·8; Co, 7·7%).

(6) Phenyl-β-naphthylformazylbenzene prepared by both methods (see preceding paper) yielded identical *cobalt* complexes as a black microcrystalline powder, m. p. 186° (decomp.), from chloroform–light petroleum (Found : N, 14·6; Co, 7·6%).

Cupric complexes. These were obtained by mixing a warm solution of the formazyl compound in acetone with a slight excess of cupric acetate in hot aqueous alcohol. The *complex* was immediately precipitated and after short standing was separated and washed with aqueous alcohol and finally with water.

(1) Diphenylformazylbenzene gave black needles with a green reflex, m. p. 158°, readily soluble in benzene, chloroform, and acetone, but less soluble in alcohol and light petroleum (Found : N, 16·9; Cu, 10·1. $C_{38}H_{30}N_8Cu$ requires N, 16·9; Cu, 9·6%).

(2) Phenyl-*p*-tolylformazylbenzene gave black needles, m. p. 156° (Found : Cu, 9·4. $C_{40}H_{34}N_8Cu$ requires Cu, 9·2%).

(3) Phenyl-*p*-methoxyphenylformazylbenzene gave a black crystalline solid with a green reflex, m. p. 163° (Found : Cu, 8·7. $C_{40}H_{34}O_2N_8Cu$ requires Cu, 8·8%).

(4) Phenyl-*p*-bromophenylformazylbenzene prepared by both methods (see preceding paper) yielded identical *cupric* complexes as a black crystalline solid with a green reflex, m. p. 140° (Found : Cu, 7·9. $C_{38}H_{28}N_8Br_2Cu$ requires Cu, 7·8%).

The cupric complexes obtained from phenyl-α- and -β-naphthylformazylbenzene were not pure substances, owing partly to the difficulty of their separation from unchanged parent formazyl, with which their solubilities in organic solvents were closely similar.

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