

XVI.—*The Co-ordination Compounds of Oximes. Part II. Nickel and Cobalt Compounds of o-Hydroxybenzaldoxime.*

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THE use of co-ordination compound formation for the determination of the configuration of geometrical isomerides has been suggested by Hieber and Sonnehalb (*Annalen*, 1927, **456**, 86) for hydrazones, and Taylor and Ewbank (*J.*, 1926, 2821) pointed out that where the physical properties of an oxime suggested that it contained a co-ordinated ring the formation of such a ring would indicate the configuration.

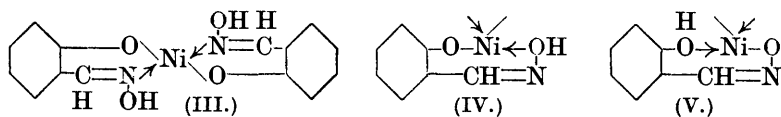
These ideas have been applied to obtain more evidence for the new configuration of aldoximes (Brady and Bishop, *J.*, 1925, **127**, 1357).

*o*-Hydroxybenzaldoxime (salicylaldoxime) has all the properties of a co-ordination compound: it is sparingly soluble in water, very soluble in organic solvents, and is more volatile than would be expected; on the other hand, the *m*- and *p*-hydroxybenzaldoximes are readily soluble in water and but moderately so in organic solvents. There seems no doubt, therefore, that this compound should be formulated as (I) or (II).



Of these, (I) is undoubtedly preferable, first because it contains a six- rather than a seven-membered ring and secondly because on treatment with acetic anhydride at room temperature *o*-hydroxybenzaldoxime gives a monoacetyl compound in which the oximino-hydroxyl is acetylated, whereas *p*-hydroxybenzaldoxime under similar conditions gives a monoacetyl compound in which the phenolic group is acetylated (Brady and Dunn, *J.*, 1914, **105**, 821).

With nickel and cobalt acetates, *o*-hydroxybenzaloxime gives co-ordination compounds of the type (III).



The results of the study of the co-ordination compounds of the dioximes (Hieber and Leutert, *Ber.*, 1929, **62**, 1839; Brady and Muers, J., 1930, 1599) strongly support formula (III) as against the alternatives (IV) and (V).

Since *o*-hydroxybenzaloxime behaves as an  $\alpha$ -aldoxime, it will be seen that the above facts support the new configurations for these compounds. Unfortunately, *o*-hydroxybenzaloxime, like all hydroxyl-substituted benzaldoximes, exists in only one form: the absence of the  $\beta$ -isomeride for comparison prevents the argument being conclusive.

Incidentally in *o*-hydroxybenzaloxime we have a compound, itself co-ordinated, which readily forms co-ordination compounds with metals. Taylor and Ewbank (*loc. cit.*) suggest that metallic complex formation in  $\alpha$ -oximino-ketones and in the benzildioximes depends on the reactivity of the carbonyl group in the first case and of the trivalent nitrogen atom of one of the oximino-groups in the second and that these groups are less reactive when the oxime itself possesses a six-membered co-ordinated ring structure. By this means they account for the failure to obtain metallic complexes from, for example,  $\beta$ -benzilmonoxime and  $\beta$ -benzildioxime. From the study of *o*-hydroxybenzaloxime it seems that the possession of a similar six-membered ring co-ordination system by the oxime is not of itself sufficient to prevent the formation of metallic complexes. This ring formation might certainly be expected to inactivate the nitrogen atom in *o*-hydroxybenzaloxime as effectively as it does in  $\beta$ -benzildioxime. If the structures of Hieber and Leutert (*Ber.*, 1929, **62**, 1839) are adopted for the metal complexes of the oximes,  $\beta$ -benzilmonoxime and  $\beta$ -benzildioxime cannot, on stereochemical grounds, form such complexes, quite apart from any question of co-ordination in the oxime.

Recently Ephraim (*Ber.*, 1930, **63**, 1928) has suggested the use of *o*-hydroxybenzaloxime as a specific reagent for the determination of copper. Under the exact conditions specified by him for the quantitative precipitation of copper, nickel salts, for example, 1% nickel chloride, give some precipitate. The addition of just enough acetic acid to redissolve the precipitate, formed by the previous addition of alkali to neutrality, is not sufficient to keep all the

nickel in solution, 5 to 10 drops more being required. The presence of salts of weak acids in any quantity would also invalidate the method.

## EXPERIMENTAL.

An alcoholic solution of *o*-hydroxybenzaloxime (5 g.) was poured into a 10% solution of nickel acetate (80 c.c.) with thorough agitation. The precipitate, after being washed with water, dried, and crystallised from chloroform, gave *nickel o*-hydroxybenzaloxime in brilliant dark green needles (Found : C, 51.1; H, 3.7; N, 8.4; Ni, 17.0; *M*, in camphor, 319.  $C_{14}H_{12}O_4N_2Ni$  requires C, 50.8; H, 3.6; N, 8.5; Ni, 17.7%; *M*, 331).

The freshly precipitated compound was suspended in water, ether and 2*N*-hydrochloric acid were added, and the mixture was shaken until the ether was colourless and no solid remained. Evaporation of the ethereal layer at room temperature gave pure  $\alpha$ -*o*-hydroxybenzaloxime, there being no indication of the formation of the missing isomeride.

The cobalt compound, prepared in an analogous way, was more difficult to purify. By dissolving it in chloroform and adding light petroleum cautiously, *cobaltous o*-hydroxybenzaloxime was obtained as a dark brown powder (Found : C, 49.4; H, 3.6; N, 8.4; Co, 17.8.  $C_{14}H_{12}O_4N_2Co$  requires C, 50.7; H, 3.6; N, 8.5; Co, 17.8%).

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