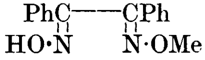
CCVII.—*The Co-ordination Compounds of Oximes.*

By OSCAR L. BRADY and MORRIS MARCUS MUERS.

THE formulation of the metallic complexes of oximes still presents difficulties and in the hope of throwing more light on this subject it was proposed to study the complex formation of the four possible *O*-monomethyl ethers of benzildioxime :

(I.)



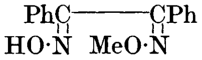
$$\begin{array}{cc}\mathrm{PhC} & \!\!\!\text{———}\mathrm{CPh}\\ \Vert & \Vert\\ \mathrm{HO{\cdot}N} & \mathrm{N{\cdot}OMe}\end{array}$$

$$\begin{array}{cc}\mathrm{PhC} & \!\!\!\text{—————}\mathrm{CPh}\\ \Vert & \Vert\\ \mathrm{N{\cdot}OH} & \mathrm{MeO{\cdot}N}\end{array}$$

(II.)

(III.)

$$\begin{array}{cc}\mathrm{PhC} & \!\!\!\text{———}\mathrm{CPh}\\ \Vert & \Vert\\ \mathrm{N{\cdot}OH} & \mathrm{N{\cdot}OMe}\end{array}$$



$$\begin{array}{cc}\mathrm{PhC} & \!\!\!\text{———}\mathrm{CPh}\\ \Vert & \Vert\\ \mathrm{HO{\cdot}N} & \mathrm{MeO{\cdot}N}\end{array}$$

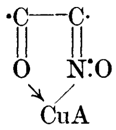
(IV.)

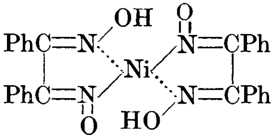
Unfortunately, in spite of many attempts, only the first three of these could be obtained (Brady and Muers, this vol., p. 216), but the study of these has given interesting results. Only *O*-monomethyl-α-benzildioxime (I) gave *complexes*, which are of the type R_3Co and R_2Ni.

The earlier formulæ for the metallic complexes of oximes involving the attachment of the metal to the oxygen of the oximino-group (Tschugaev and Lebedinski, *Z. anorg. Chem.*, 1913, **83**, 1; Taylor and Ewbank, J., 1926, 2818) were conceived with insufficient regard for stereochemical considerations. Pfeiffer and Richarz (*Ber.*, 1928, **61**, 103) corrected this and found that if the Meisenheimer configurations were correct it became necessary to adopt the nitrone structure for the oxime and attach the metal to the nitrogen atom, as, for example, in (V).

In the case of the dioximes, however, these authors do not formulate a complex and it remained for Hieber and Leutert (*Ber.*, 1929, **62**, 1839) to suggest an analogous structure for the nickel complex of α-benzildioxime (VI).

(V.)

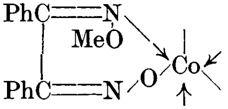




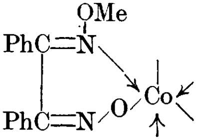
(VI.)

Our study of the behaviour of the *O*-monomethyl ethers of the benzildioximes had led us independently to a practically identical conclusion as regards the structure of complexes of this type.

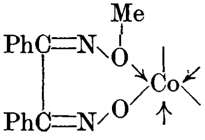
The cobalt complex formed from (I) has the composition $[\mathrm{CPh(\colon NOMe)\cdot CPh(\colon NO)}]_3\mathrm{Co}$ and if the earlier type of formula, linking cobalt to oxygen, be adopted, the compound can be represented as (VII) on the Hantzsch and as (VIII) on the Meisenheimer configuration (to save space, only one of the three oxime residues is shown).



(VII.)



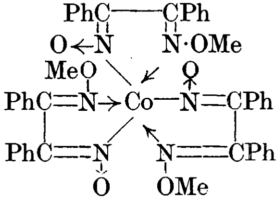
(VIII.)



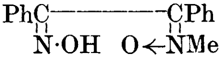
(IX.)

In view of the tetrahedral arrangement of the valency directions about the nitrogen atom (Mills and Warren, J., 1925, **127**, 2507), (VII) is stereochemically impossible. The formation of (VIII) involves a change in the configuration of the oximino-group and, although we have been unable to recover any one of the monomethylbenzildioximes from the very stable cobalt compound, we have succeeded in regenerating the original monomethyl-α-benzildioxime from the analogous but less stable nickel complex. Since this isomeride is not the stable one (Brady and Muers, *loc. cit.*), there can be no question of stereoisomeric change during the decomposition. Moreover, if this change of configuration occurred, α′-monomethyl-γ-benzildioxime (III), where the hydroxyl group is already in the right position, should give the complex more readily than monomethyl-α-benzildioxime.

The only remaining formula constructed on these lines is (IX). This necessitates the retention of the Hantzsch configuration, the formation of a seven-membered ring, and the existence of a co-ordinate link between a metal and the oxygen of a methoxyl group which does not seem to have been observed in other compounds. There seems, therefore, to be no alternative but the nitrone structure, the formula we suggest being (X). The nitrone structure using the Hantzsch configurations is open to the same criticism as (VII).


(X.)

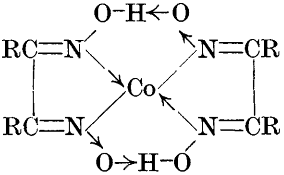

(XI.)


(XII.)

A point of interest is that neither *N*-monomethyl-α-benzildioxime (XI) nor *N*-monomethyl-β-benzildioxime (XII) (Brady and Muers, *loc. cit.*) yields a cobalt complex : here one of the nitrogen atoms is already quadrivalent and cannot therefore form the co-ordinate link.

A crystalline cobaltous complex containing two benzildioxime residues to one cobalt atom, has been obtained from α-benzildioxime.

In formulating the complexes of the dioximes we prefer a slight modification of Hieber and Leutert's structure and suggest that they should be represented as (XIII).


(XIII.)

Such a formula might account for the lack of reactivity of the hydroxyl group in compounds of this type. Tschugaev (J., 1914, **105**, 2192) records that they are not acted upon by phenylcarbimide (phenyl carbamylamine in the text is an obvious misprint) and we have found that the nickel complex of dimethylglyoxime, for example, gives no methane with magnesium methyl iodide in amyl ether. The symmetry of this formula is also some recommendation for it.

EXPERIMENTAL.

Cobalt Complex of O-*Monomethyl-α-benzildioxime.*—This compound was difficult to obtain pure, many preparations containing free oxime and free cobalt hydroxide; the former was particularly difficult to remove by crystallisation, but the following method was ultimately found to give the best results. The oxime (5 g.) was dissolved in boiling acetone (60 c.c.) and cobalt nitrate (3 g. of the hydrated salt), dissolved in a little water, was added. On addition of 2*N*-aqueous ammonia (10 c.c.) a deep red-brown colour appeared. The solution was then poured into excess of *N*/10-sodium hydroxide, the precipitate collected and extracted with the minimum amount of chloroform, and the filtered chloroform solution washed with dilute sodium hydroxide solution. As the material obtained after evaporation of the chloroform still contained oxime, it was redissolved in acetone and again poured into $N/10$-sodium hydroxide solution. The precipitated compound was thoroughly washed with water and dried in a vacuum, the *complex* being obtained as a red-brown powder, m. p. 165—169° (decomp.) (Found: C, 64·7; H, 4·9; N, 10·7; Co, 7·1. $C_{45}H_{39}O_6N_6Co$ requires C, 66·0; H, 4·8; N, 10·3; Co, 7·2%). Attempts to crystallise the compound were unsuccessful.

If cobalt acetate was used in the above preparation, some complex was formed before the addition of ammonia but the yield was not so good. Sodium hydroxide could be used in place of ammonia, indicating that the ammonia plays no essential part in the complex formation. The production of the complex depends on the presence of atmospheric oxygen; when this was excluded, on addition of aqueous ammonia, a green solution was formed which rapidly assumed the red-brown colour on being shaken with air.

Nickel Complex of O-*Monomethyl-α-benzildioxime.*—This compound was more difficult to obtain pure than the cobalt complex. Nickel nitrate solution (2 c.c. $5N$) was added to $2N$-ammonia (5 c.c.), followed by $2N$-ammonium chloride until the precipitate was dissolved, and the whole was added to a solution of the oxime (2·5 g.) in hot alcohol (100 c.c.). The dark brown solution was poured into $N/10$-sodium hydroxide (250 c.c.) and the precipitate produced was washed with $N/10$-sodium hydroxide until no more oxime was removed, then with ammonium chloride solution until no nickel could be detected in the filtrate, and finally with water. After drying in a vacuum, the *complex* was obtained as a brown powder which could not be crystallised (Found: Ni, 10·8; N, 10·1. $C_{30}H_{26}O_4N_4Ni$ requires Ni, 10·4; N, 9·9%).

The complex (0·2 g.) and potassium cyanide (0·3 g.) were boiled for 30 seconds with alcohol (5 c.c.), the brown colour then having almost disappeared, and poured into water. The precipitated oxime, crystallised from acetone, gave *O*-monomethyl-α-benzildioxime.

Copper and Ferrous Complexes of O-*Monomethyl-α-benzildioxime.*—When a solution of copper acetate was added to an acetone solution of the oxime a deep olive-green colour was produced which was destroyed on dilution. The use of chloroform and subsequent dilution gave a more stable solution, but evaporation resulted in the decomposition of the complex.

Addition of ferrous sulphate solution to a solution of the oxime in acetone, followed by aqueous ammonia, gave a violet-red colour which disappeared in a few seconds. The coloured material could be extracted with benzene, but it decomposed even in this solvent after a few minutes.

Cobalt Complex of α-Benzildioxime.—α-Benzildioxime (5 g.) was placed in the thimble of a hot-extraction pattern Soxhlet apparatus, and acetone together with cobalt acetate (2·5 g. of hydrated salt), dissolved in the minimum amount of water, in the flask. After 5 hours' boiling, the precipitate first produced by the addition of the cobalt acetate to the acetone was replaced by crystals of the *complex.* These were washed with acetone, dilute acetic acid, dilute aqueous sodium hydroxide, and with water. They consisted of well-defined, brown, diamond-shaped crystals with a small quantity of less dense, brown needles, which were removed by levigation with water (Found: Co, 10·8; N, 10·4. $C_{28}H_{22}O_4N_4Co$ requires Co, 10·9; N, 10·4%).

Cobalt Complex from γ-Benzildioxime.—A solution of the oxime (4 g.) in hot alcohol (50 c.c.) was treated with cobalt acetate (3 g.) dissolved in the minimum of water. The brown powder precipitated on cooling was washed with alcohol and dried in a vacuum. The ratio of cobalt to nitrogen (approximately 2 : 5 in atomic proportions) indicated that the product was a mixture and all attempts to purify it were unsuccessful. The solution became acid during the reaction, indicating that at least one of the hydrogen atoms of the oximino-groups had been replaced by cobalt.

THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON.
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