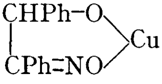
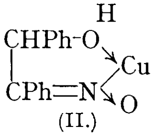
186. *Compounds of α-Benzoinoxime with Bivalent Metals.*

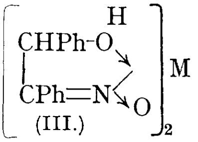
By J. S. Jennings, E. Sharratt, and W. Wardlaw.

Benzoinoxime is one of a number of organic reagents recently employed in the detection and estimation of metals. The copper derivative, discovered by Feigl (*Ber.*, 1923, **56**, 2083), is a deep green, amorphous compound which is insoluble in water and organic solvents and when dried at 105—115° contains 22·02% Cu in accordance with the formula (I) assigned to it by Feigl. This structure, however, cannot be regarded as fully established.

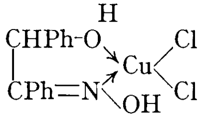
It is unusual to find the hydrogen atom of the secondary alcoholic group replaced by copper; moreover, benzoinoxime is a reducing agent and one would expect it to reduce a proportion of the cupric salt to the cuprous state. From the analytical data, structure

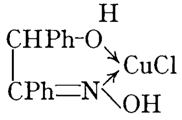

(I.)

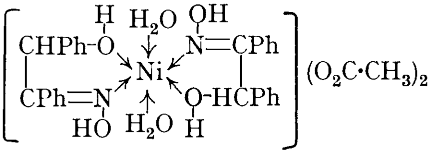

(II.)


(III.)

(II), which is that of a cuprous compound, is a possible alternative to (I). Decomposition of Feigl's compound with hydrochloric acid yielded cuprous chloride, but, as hydroxylamine hydrochloride was formed simultaneously, this is no indication of the valency state of the copper. Convincing evidence in favour of (I) has, however, been obtained by treating Feigl's compound with alcoholic hydrogen chloride; the green crystalline salt (II*a*) then separates with a molecule of alcohol of crystallisation. With hot water, two molecules of hydrogen chloride are eliminated from (II*a*) and the original compound (I) is produced. A compound of formula (II) would give the derivative (II*b*) on treatment with


(II*a*.)


(II*b*.)


(IV.)

alcoholic hydrogen chloride. Whilst Feigl's compound must have structure (I), there is, at present, no decisive evidence whether the ring is five- or six-membered.

Feigl states that nickel and cobalt salts do not give precipitates with benzoinoxime, but it is mentioned in " Organic Reagents for Metals " (1934, p. 19) that this is incorrect. We agree with the latter opinion, for we find that these metals give respectively a brown and a buff precipitate with the reagent. In addition, bivalent palladium and platinum give derivatives with benzoinoxime; the former immediately, and the latter slowly. Considerable difficulty was experienced in preparing any of these compounds pure, owing to the coprecipitation of the benzoinoxime, which is difficultly soluble in aqueous alcohol. However, pure products were obtained in all cases except that of cobalt, and these were covalent compounds of the type (III), where M = Ni, Pd, Pt. In no case, by varying the experimental conditions, could we obtain a derivative similar to that of copper.

We have also been able to show in the case of nickel that the oxime can function as a chelate group attached by two co-ordinate links. We find that, when an alcoholic solution of benzoinoxime reacts with aqueous nickel sulphate in presence of large concentrations of ammonium acetate or excess of sodium acetate and acetic acid, the usual brown precipitate of *nickel dibenzoinoxime* is first produced, but on standing at 40° for an hour, the substance changes to a brilliant green complex *salt*. It is sparingly soluble in hot water, and with dilute sulphuric acid yields acetic acid. The water of crystallisation is not removed from it on drying for 12 hours in a desiccator over phosphoric oxide. It appears to have the structure (IV), and when it is warmed with ammonia, alcohol, or acetone, the brown nickel compound of type (III) is produced.

It will be seen the α-benzoinoxime may function as a chelate group in three ways. In Feigl's formula (I), it may be attached to a copper atom by two principal valencies. With other bivalent metals it may be associated by either one principal valency and one co-ordinate link, as in (III), or by two co-ordinate links, as in (IV) and (II*a*).

The nickel compound (III) is a buff-coloured substance, which dissolves very readily in benzene, chloroform, acetone, and carbon tetrachloride, brown solutions being produced. If the solution in the last solvent is kept in the cold for about 10 minutes, minute crystals separate, the process continuing for 2—3 days. After 12 hours, however, little of the substance remains in solution, the *product* consisting of orange-coloured crystals, $[(C_{14}H_{12}O_2N)_2Ni],CCl_4$. On standing in air for a few days, or on heating at 90° for 4—5 hours, the solvent of crystallisation is lost, and the colour of the material changes to reddish-brown. This second variety of nickel dibenzoinoxime is almost completely insoluble in all organic solvents except chloroform; evaporation of the chloroform solution gives the first variety. Thus the two forms of nickel dibenzoinoxime are interconvertible:

$$\text{First variety} \underset{\text{CHCl}_3}{\overset{\text{CCl}_4}{\rightleftarrows}} \text{second variety.}$$

Alcohol and acetone convert the first of the nickel compounds into the second variety, but the process is always accompanied by decomposition. When either variety is treated with alcohol or acetone at 40°, benzoinoxime is liberated. Benzene and ether behave similarly to carbon tetrachloride, but are less suitable for producing the second modification, the former on account of the much slower rate of the change, and the latter on account of its volatility. Phenol does not cause any change in either material below 75°, but there is a partial conversion of the second form into the first form above this temperature. The molecular weight of the first variety was therefore determined cryoscopically in phenol; the results prove it to be monomeric. No means of determining the molecular weight of the second variety could be found, since in chloroform, the only solvent for it, it reverted to the first modification.

The first *platinum* compound of type (III) is formed when potassium chloroplatinite and the oxime are kept at 40° in aqueous alcohol for 2—3 hours. The substance is dark yellow, and resembles the nickel compound in its ready solubility in organic solvents. Moreover, it reverts to a second form in carbon tetrachloride after some days. Ethyl alcohol, however, accomplishes the conversion more speedily, but even here the process is slow in comparison with the rate of change of the nickel isomerides. The second variety of the platinum benzoinoxime is pink-brown, amorphous, and soluble only in chloroform, behaving in the same manner as the second nickel compound.

The addition of benzoinoxime to potassium chloropalladite gives, immediately, a bulky primrose-yellow precipitate of *palladium dibenzoinoxime* (III). Although soluble in most of the usual organic solvents, it has not the great solubility of its nickel and platinum analogues, and it gives yellow solutions instead of the brown solutions always produced by the derivatives of these metals. In acetone, alcohol, benzene, and carbon tetrachloride, it reverts to a second variety, which has a slightly deeper yellow colour and is almost insoluble in all the usual organic reagents.

The molecular weight of the first palladium compound in phenol was determined, as was also that of the first platinum complex in chloroform; both proved to be unimolecular.

Thus, nickel, platinum, and palladium dibenzoinoximes each exist in two forms. Their m. p.'s varied with the rate of heating, owing to slow decomposition occurring before the true m. p.'s were reached. This was particularly noticeable with the first platinum benzoinoxime, which became bright red at 132°, and after being kept at this temperature for some minutes, melted at 140°, whereas the m. p. recorded in the usual way was 150—155°. Similar fluctuations were observed in the m. p.'s of the nickel and palladium derivatives.

We have no satisfactory explanation why two nickel derivatives of α-benzoinoxime exist. Professor S. Sugden very kindly examined these substances for us, and found them to be paramagnetic. This is against the idea that they have a planar configuration. On the other hand, the palladium derivatives were diamagnetic, so that the possibility that they have a planar configuration is not excluded. The two modifications in the three cases may arise from purely optical isomerism. α-Benzoinoxime is a *dl*-mixture, and when a complex compound is made with two benzoinoxime residues, there is the possibility that it may be a *meso*- or a racemic *dl*-modification. Against this view, however, is the experimental evidence that the two modifications are never present in the original preparations, and it seems most unlikely that dissolution in carbon tetrachloride would change a *meso*-form into a *dl*-mixture, or *vice versa*. Both varieties of the metallic derivatives give α-benzoinoxime when treated with cold dilute hydrochloric acid ($N/2$). The last possibility is that one form is a polymeride of the other; as the metal atoms in each case have the expected covalency of four, this does not appear probable.

EXPERIMENTAL.

Copper Benzoinoxime.—An aqueous solution of cupric chloride (1·5 g.; 200 c.c.) was mixed with an alcoholic solution of α-benzoinoxime (2 g.; 100 c.c.), the mixture being rendered faintly ammoniacal by the careful addition of aqueous ammonia (3*N*). A dark green precipitate formed immediately. This was washed with hot 1% aqueous ammonia, alcohol, and hot water and dried at 110—115° (Found: Cu, 21·95. Calc. for $C_{14}H_{11}O_2NCu$: Cu, 22·0%).

Copper Benzoinoxime Dichloride.—Copper benzoinoxime (1 g.) was dissolved in hot alcoholic hydrogen chloride (20 c.c.). The filtered solution, on cooling, deposited bright emerald-green crystals of *copper benzoinoxime dichloride* containing one molecule of alcohol of crystallisation. These were removed, washed with alcohol (10 c.c.), and air-dried [Found: Cu, 15·56, 15·55; Cl, 17·31. $(C_{14}H_{13}O_2N)CuCl_2,C_2H_5{\cdot}OH$ requires Cu, 15·57; Cl, 17·38%]. After some days these crystals lost their alcohol of crystallisation. They were readily soluble in alcohol and acetone, but were decomposed by water, yielding the original green copper benzoinoxime and free hydrogen chloride.

Nickel Dibenzoinoxime.—*First form.* Nickel sulphate (2 g.; $NiSO_4,7H_2O$) and ammonium chloride (5 g.) were dissolved in water (180 c.c.). Aqueous ammonia (20 c.c.; 3*N*) was then added, and the mixture heated to 65—70°. α-Benzoinoxime (1 g.) dissolved in alcohol (100 c.c.) was added. A buff-coloured precipitate formed immediately, and was filtered off after 10 minutes. The product was extracted twice with 30% aqueous alcohol (300 c.c.) at 60° to remove unchanged benzoinoxime, and then washed with hot water till free from inorganic impurities. The material was dried in a desiccator over phosphoric oxide for 3 days or placed in an oven at 90° for 5 hours [Found: Ni, 11·52; N, 5·37. $(C_{14}H_{12}O_2N)_2Ni$ requires Ni, 11·49; N, 5·48%].

In this preparation, concentrations of alcohol greater than 35% must be avoided, since this may cause some decomposition or effect a partial transformation to the second variety, whilst with low concentrations of alcohol much benzoinoxime is always precipitated, particularly at low temperatures. Analysis of the product is best effected by warming with *N*-hydrochloric acid, the precipitated oxime being filtered off, and the nickel estimated as the dimethylglyoxime compound. Complete decomposition of the substance with concentrated nitric acid causes the formation of benzaldehyde which is most undesirable.

Second form. The first variety (1 g.) was dissolved in carbon tetrachloride (40 c.c.), an intense brown colour being produced. The solution was filtered as rapidly as possible. After 10 minutes' standing, the formation of a precipitate began and continued for 2 or 3 days. At the end of the first day, the orange-coloured crystalline product was removed. Analysis showed that it contained one molecule of carbon tetrachloride of crystallisation [Found: Ni, 8·82, 8·88. $Ni(C_{14}H_{12}O_2N)_2,CCl_4$ requires Ni, 8·83%]. This was removed by 5 hours' heating at 90°, the colour of the substance becoming reddish-brown (Found: Ni, 11·37, 11·38; N, 5·46%).

Nickel Dibenzoinoxime Diacetate.—Nickel sulphate (12 g.; hydrated salt) and ammonium acetate (20 g.) were dissolved in water (200 c.c.) and heated to 40°. Benzoinoxime (4 g.), dissolved in alcohol (100 c.c.) and heated to 40°, was added to the aqueous solution and the mixture maintained at this temperature for 1 hour. The brown nickel dibenzoinoxime dissolved slowly, and an emerald-green precipitate formed. This was filtered off, extracted with warm 50% aqueous alcohol, washed with water, and dried in a desiccator {Found: Ni, 8·74; N, 4·43. $[Ni(C_{14}H_{13}O_2N)_2](CH_3{\cdot}CO_2)_2,2H_2O$ requires Ni, 8·80; N, 4·20%}.

This substance was also prepared by the following method. Nickel sulphate (2 g., hydrated salt) and sodium acetate (10 g.) were dissolved in water (200 c.c.) at 40°, and a solution of benzoinoxime (2 g.) in alcohol (100 c.c.), also at 40°, was added. Brown nickel benzoinoxime was precipitated immediately. *N*-Acetic acid (25 c.c.) was then added slowly with stirring. The brown precipitate dissolved rapidly, and the green *nickel dibenzoinoxime diacetate* crystallised gradually during 1½ hours. The product was removed, washed twice with 50% aqueous alcohol (100 c.c.) at 40°, and with hot water. It was then dried in a desiccator (Found: Ni, 8·78; N, 4·20%).

Palladium Dibenzoinoxime.—*First form.* To potassium chloropalladite (1·5 g.), dissolved in water (200 c.c.), an alcoholic solution of benzoinoxime (2·5 g., 100 c.c.) was added, and the mixture warmed at 60° for about 20 minutes. The very pale primrose-yellow precipitate, which formed immediately, was removed, extracted twice with 33% aqueous alcohol, washed thoroughly with hot water, and finally dried in a desiccator over phosphoric anhydride [Found: Pd, 19·10; N, 4·85. $Pd(C_{14}H_{12}O_2N)_2$ requires Pd, 19·10; N, 5·01%]. Excess of chloropalladite must be avoided in this preparation, or the product will be contaminated with another substance of higher palladium content.

Second form. The above *palladium dibenzoinoxime* (1 g.) was dissolved in chloroform (50 c.c.) and filtered as quickly as possible. After 10 minutes, a precipitate had formed, but the process of separation was allowed to continue for 24 hours, whereupon the pale primrose-yellow solid was removed, and dried in a desiccator. Carbon tetrachloride, acetone, or alcohol may be used instead of chloroform with equally good results (Found, in product from $CHCl_3$: Pd, 19·10; N, 5·01%).

Platinum Dibenzoinoxime.—First form. Potassium chloroplatinite (1 g.) was dissolved in water at 45°. Benzoinoxime (1 g.), dissolved in alcohol, was added to the solution, and the mixture maintained at 40—45° for 3 hours, while the *platinum dibenzoinoxime* formed slowly. This ochre-coloured material was filtered off, extracted twice with 33% alcohol (100 c.c.) at 40°, and washed with warm water. It was then dried in a desiccator with phosphoric oxide [Found : Pt, 30·12; N, 4·36. $Pt(C_{14}H_{12}O_2N)_2$ requires Pt, 30·15; N, 4·35%]. If, during this preparation, the temperature of the mixture is allowed to rise above 50°, intensely reddish-brown impurities result, and above 70°, the product melts to a separate layer which solidifies on cooling to an intensely brown mass of high platinum content. Attempts to accelerate the reaction by the addition of sodium acetate were unsuccessful; the presence of free mineral acid apparently has no effect on the reaction.

Second form. The foregoing product (1 g.) was dissolved in carbon tetrachloride (50 c.c.), filtered, and the intensely brown solution set aside. A precipitate formed very slowly, and after 3 weeks, the pink-brown deposit was removed, and dried in a desiccator. Alternatively, the first variety (1 g.) is dissolved in alcohol (100 c.c.), and the solution filtered; after 2 days, the pink-brown precipitate is removed and dried (Found, using carbon tetrachloride : Pt, 29·93; using alcohol : Pt, 30·21; N, 4·32%).

Molecular-weight Determinations.

Below are recorded the results from the molecular-weight determinations with the first forms of the metallic derivatives of α-benzoinoxime.

Cryoscopic determinations in phenol (constant = 7·27° per 1000 g.).

	Concn. (g./1000 g.).	Δ*t*.	*M.* Found.	*M.* Calc.
$Ni(C_{14}H_{12}O_2N)_2$	11·21	0·165°	494	511
	20·05	0·295	494	511
$Pd(C_{14}H_{12}O_2N)_2$	9·80	0·126	565	559

Ebullioscopic determinations in chloroform (constant = 2·6° per 1000 c.c.).

	(g./1000 c.c.).	Δ*t*.	*M.* Found.	*M.* Calc.
$Ni(C_{14}H_{12}O_2N)_2$	17·91	0·091	512	511
	20·71	0·105	513	511
$Pt(C_{14}H_{12}O_2N)_2$	23·29	0·095	637	647
	31·58	0·128	641	647

The authors are greatly indebted to Mr. T. W. J. Taylor for helpful discussion, and to the Department of Scientific and Industrial Research for a maintenance grant to one of them (E. S.).

UNIVERSITY OF BIRMINGHAM, EDGBASTON. [*Received, April 11th*, 1935.]