# 33. *The Planar Configuration of Diamagnetic Nickel Complexes. Part I. Isomeric Nickel Derivatives of Benzylmethylglyoxime.*

By SAMUEL SUGDEN.

THE theory of valency developed by Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 1367) leads in most cases to the generally accepted stereochemical configurations, *viz.*, a tetrahedral arrangement for a covalency of four, and an octahedral configuration for a covalency of six. There is, however, one important exception: if one of the vacant *d* levels in a transition element is concerned in the formation of linkages, then a configuration of four bonds at an angle of 90°

in one plane is possible. At the same time, the magnetic moment of the atom should decrease in a definite manner, since the *d* level concerned in valency formation is not available for the electrons of the incompleted sub-group. For nickel the moment should decrease from 2·83 Bohr magnetons to zero.

It has long been known that nickel carbonyl and potassium nickelicyanide are diamagnetic, but in these substances a planar configuration cannot give rise to stereoisomerism. In the course of an investigation on the magnetic properties of nickel complexes which will shortly be submitted for publication, the author found that the glyoximes of nickel are all diamagnetic. Recently Klemm, Jacobi, and Tilk (*Z. anorg. Chem.*, 1931, **201**, 1) and Cambi and Szegö (*Ber.*, 1931, **64**, 2591) have found that the nickel derivatives of dimethyl- and diphenyl-glyoxime are diamagnetic. In addition, other diamagnetic nickel complexes are described by these workers, *e.g.*, *N*-alkylthiocarbamates and *o*-phenanthroline derivatives.

It is evident that a diamagnetic nickel atom with a planar configuration should give rise to two stereoisomeric compounds when combined with two unsymmetrical chelate groups. Since nickel dimethylglyoxime has a very high melting point and is practically insoluble in most organic solvents, it is desirable in a search for isomerides of this type to use a highly substituted glyoxime. Benzylmethylglyoxime was chosen since it is readily prepared, and the difference in bulk and chemical character of the methyl and benzyl groups should produce a marked difference in the physical properties of the *cis*- and the *trans*-form.

When the *nickel* derivative of this glyoxime was examined it was found to consist of two isomeric compounds, the α-form, m. p. 168°,* and the β-form, m. p. 75—77°. These have the same nickel content and the same molecular weight. The β-isomeride is much more soluble in cold acetone than the α-form and can thus be separated; it was finally purified by solution in benzene and fractional precipitation with ligroin. The β-form is thermolabile and readily changes at 120° to a product melting at 152°. For this reason the m. p. was taken as the temperature at which complete melting took place in 30 secs. when the substance contained in a capillary tube was plunged into a previously heated bath. The product of m. p. 152° is not a third isomeride, but an equilibrium mixture of the α- and the β-form. This is shown by boiling it with acetone; on cooling, crystals of the α-form are deposited, and the mother-liquor when fractionally precipitated with water gives fractions of lower m. p. containing the β-isomeride.

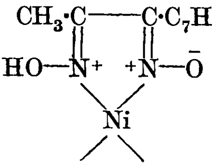
---

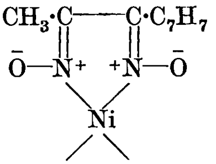
* All m. p.'s quoted are corrected for thermometer errors and for exposed stem.

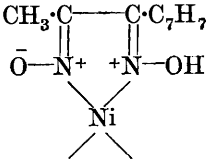
Both forms are diamagnetic and have the following susceptibilities at 18°: α-form, $\chi = -0{\cdot}44 \times 10^{-6}$, β-form $\chi = -0{\cdot}24 \times 10^{-6}$. The lower value for the β-form is possibly due to the presence of a trace of a paramagnetic green compound (see Experimental).

It is thus clear that there are two isomeric nickel benzylmethylglyoximes, but it remains to be considered whether the isomerism is due to the planar configuration of the nickel atom or whether stereoisomeric forms of the oxime are present in the two nickel compounds. The latter hypothesis seems improbable, for the parent glyoxime is only known in one form. It was found that the isomeric nickel derivatives when shaken in the cold with 15% hydrochloric acid regenerated the same glyoxime, identical with that from which they were prepared. Furthermore, acetylation of the isomeric nickel derivatives with acetic anhydride in the presence of pyridine at room temperature gave the same diacetyl derivative from both nickel derivatives, and the product was identical with that prepared from the original glyoxime. Thus the same isomeric glyoxime is present in the two nickel compounds.

Following Pfeiffer (*Ber.*, 1930, **63**, 1811; compare Tschugaev, J., 1914, **105**, 2187), the chelate ring would be formulated as in (I), and it then appears possible to write another formula (III) by transposing


(I.)

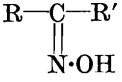

(II.)


(III.)

the $\bar{\text{O}}$ and the OH group. If these are distinguishable, then with a tetrahedral configuration of the nickel three isomerides are possible, *viz.*, one with both rings of type (I), one with both rings of type (III), and a third with one ring of each type. It is doubtful, however, whether (I) and (III) are distinguishable, for the removal of a proton by ionisation gives the anion (II), through which the two forms would be readily interconvertible. The relation between (I) and (III) closely resembles that between the oximino- and the nitrone forms of monoximes (IV and V), and it is usually considered that these represent inseparable tautomeric forms. In the author's view, the large difference in m. p. of the two nickel derivatives cannot be accounted for by structural isomerism involving the displacement of a proton as in (I) and (III). They must, therefore, be regarded as geometrical isomerides with a planar configuration of the valency linkages from the nickel. By analogy with the maleic–fumaric series, the low-melting form has most probably the *cis*-configuration;

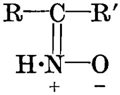
it is hoped shortly to settle this point by comparing the dipole moments of the isomerides.

This work is being extended to other diamagnetic nickel complexes. In particular, nickel complexes of imines of oximino-ketones (VI) are under investigation, as these substances cannot exhibit the type of tautomerism discussed above.



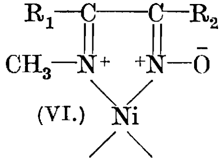
$$\begin{array}{c}\mathrm{R{-}C{-}R'}\\ \|\\ \mathrm{N{\cdot}OH}\end{array}$$

(IV.)



$$\begin{array}{c}\mathrm{R{-}C{-}R'}\\ \|\\ \mathrm{H{\cdot}\underset{+}{N}{-}\underset{-}{O}}\end{array}$$

(V.)



(VI.)

## EXPERIMENTAL.

The monoxime of benzylmethylglyoxal was prepared by adding concentrated hydrochloric acid to benzylacetoacetic ester (1 mol.) and sodium nitrite (1·1 mols.) dissolved in 10% caustic soda (1·2 mols.), the temperature being kept below 10°. The crude solid product was drained from oily material on a tile, and crystallised from dilute alcohol; m. p. 81° (Ceresole, *Ber.*, 1882, **15**, 1876, gives m. p. 80°). The second oxime group was introduced by heating together on the water-bath the monoxime (1 mol.), hydroxylamine hydrochloride (1·2 mols.), and 20% caustic soda (2·5 mols.), and was precipitated by adding acetic acid. It crystallised from 80% acetic acid as a colourless product, m. p. 194°. This is considerably higher than the m. p. given by Schramm (*Ber.*, 1883, **16**, 181, 2184), *viz.*, 180—181°.

Since preliminary experiments showed that the low-melting isomeride was easily transformed by heat into a higher-melting mixture, the precipitation of the nickel complex was carried out in the cold. The glyoxime (50 g., 2 mols.), dissolved in acetone or alcohol, was added to a cold aqueous solution of nickel chloride free from iron and cobalt (1·1 mols.), and sodium acetate (2·5 mols.). The bright orange precipitate was filtered off, washed, and air-dried; it had an indefinite m. p., 75—100°.

*Separation of Isomerides.*—The dry powdered substance was added to 15 times its weight of cold acetone. It usually dissolved completely but quickly deposited a crystalline precipitate which was filtered off; the mother-liquor was then fractionally precipitated with water. The first crop usually melted at 152°, and subsequent crops from 130° to 90°. Fractions melting below 120° were collected and shaken with 5—10 times their weight of benzene at room temperature. A small, greenish, insoluble residue was sometimes obtained which contained nickel and was paramagnetic (Found : Ni, 6·7%; $\chi_{18^\circ} = +1{\cdot}94 \times 10^{-6}$). The benzene solution was fractionally precipitated with ligroin; the earlier fractions were red oils which crystallised on standing or on rubbing with ligroin and melted at 75—77°, and later fractions showed a progressively higher m. p. In this separation it is essential to determine the m. p. of a fraction by plunging the capillary tube in a previously heated bath, otherwise interconversion occurs and the only m. p. observed is that of the equilibrium mixture, 152°. Until this was realised, fractions containing considerable quantities of the β-form were discarded. Repetition of the benzene–ligroin precipitation gave no further change in m. p. The α-form is readily obtained from the product of m. p. 152° by boiling with acetone; on cooling, orange-brown plates are deposited of m. p. 168°, unchanged on further crystallisation from acetone or benzene.

*Analyses and Molecular Weights.*—Nickel was determined by decomposing the substance in a silica crucible with concentrated sulphuric acid and roasting to oxide. This change was hastened by occasionally moistening the residue with nitric acid (Found: for α-form, Ni, 13·4; for β-form, 13·2. $C_{20}H_{22}O_4N_4Ni$ requires Ni, 13·3%). The method was checked on pure $NiSO_4,(NH_4)_2SO_4,6H_2O$ (Found: Ni, 14·84. Calc.: Ni, 14·87%). Molecular weights were determined by the freezing-point method in benzene; the moisture content of the solvent was controlled by adding a little anhydrous magnesium sulphate. The freezing-point depression constant was taken as 5·07°/1000 g. The following results were obtained ($M$, calc., 441).

| | α-Form. | | | β-Form. | |
|---|---|---|---|---|---|
| $c$, g./1000 g. | 6·21 | 10·4 | 15·0 | 7·77 | 15·1 |
| $\Delta t$ | 0·070° | 0·100° | 0·134° | 0·097° | 0·168° |
| $M$ | 450 | 527 | 567 | 406 | 456 |

*Regeneration of Glyoxime and of Diacetylglyoxime.*—1 G. of each isomeric nickel compound was shaken with 20 c.c. of 15% hydrochloric acid and 10 c.c. of ether until the orange colour disappeared. The ether was separated and allowed to evaporate at room temperature. The residue from both forms melted at 194° and did not depress the m. p. of the parent glyoxime.

To a mixture of 1 g. of acetic anhydride and 10 g. of pyridine, 1 g. of the nickel salt was added; after 20 mins. the bright green liquid was diluted with water. An oil separated which soon solidified, and was filtered off and air-dried; m. p. from both forms 73°, raised to 79° by one crystallisation from alcohol. The glyoxime warmed with acetic anhydride gave the diacetyl derivative, m. p. 80°, which did not depress the m. p. of the substance obtained from its nickel derivatives. Schramm (*loc. cit.*) gives m. p. 80°.

BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
FETTER LANE, E.C. 4. [*Received, December* 16*th*, 1931.]