

137. The Planar Configuration of Diamagnetic Nickel Complexes.
Part II.

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IN continuation of the work described in Part I (J., 1932, 246) the nickel derivatives of methyl-*n*-propyl- and -*n*-butyl-glyoximes have been found to be diamagnetic and to occur in isomeric forms which are readily interconvertible. The m. p.'s of these substances and of the isomeric nickel benzylmethylglyoximes are collected below :

Isomeric Nickel Glyoximes.

Glyoxime.	M. p., α -form.	M. p., β -form.	M. p., equilibrium mixture.
Methyl- <i>n</i> -propyl.....	165°	133°	124°
Methyl- <i>n</i> -butyl	150	86	80
Benzylmethyl	168	76	150

To these may be added the two forms of the nickel derivative of methylglyoxal described by Tschugaev (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1466). This substance was obtained in a dark red unstable form and in an orange stable form, but the former is too unstable to give an m. p.

Details of the separation of the propyl and the butyl compounds are given in the experimental part of this paper. The chief difference between these isomerides and the benzyl compounds is the high proportion of the β -form found in the equilibrium mixture produced by fusion. The propyl derivatives crystallise well from acetone on a microscope slide, and the two forms have markedly different crystal habits: the α -form gives loose bundles of long blunt-ended prisms, the β -form rosettes of deeper coloured fine needles.

The occurrence of pairs of isomerides, therefore, seems general for the unsymmetrical nickel glyoximes. As a further test of Pauling's theory (*J. Amer. Chem. Soc.*, 1931, **53**, 1367) that 4-covalent nickel complexes which are diamagnetic may have a planar configuration, we have sought for other compounds of this type. The magnetic data will be published in another paper; the only compounds found which are diamagnetic and sufficiently soluble in organic solvents to enable a search for isomerides to be made are the *NN*-dialkyldithiocarbamates. The *n*-propyl and the *n*-butyl compound have been prepared, and isomerides sought by fusing these substances and fractionally crystallising the products. Each of the dithiocarbamates gave only one form.

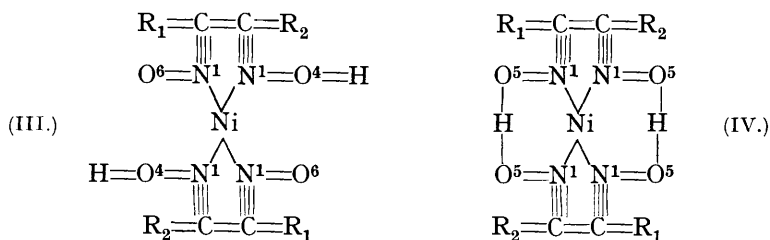
The constitution of these complexes may be written with the nickel atom co-ordinated to two sulphur atoms, as in the electronic formula (I), or to sulphur and nitrogen, as in (II).



The symmetrical formula (I) seems more probable, and would not give isomeric forms even if the links to the nickel atom had a planar configuration. The failure to find isomerides

may perhaps be taken as negative evidence in favour of (I) rather than (II). Molecular-weight measurements in benzene show that these substances have the formula $[\text{Ni}, 2\text{X}]$, where X is the dithiocarbamic acid residue.

As a further test of the theory of planar configuration of the nickel glyoximes, we have determined their dipole moments, with the results shown in Table I. Their most probable structure is represented by (III), or by (IV) if the view of Brady and Muers (J., 1930, 1601) is adopted, *viz.*, that the hydrogen atoms of the NOH groups are also co-ordinated. These formulæ show the *trans*-isomerides; the structure for the *cis*-form is obtained by interchanging the groups R_1 and R_2 in one half of the molecule. Since the central portion of



the molecule is symmetrical, the moments should be small if the bonds to nickel are in one plane and the groups R_1 and R_2 are alkyl or aryl radicals. Furthermore, the *cis*- and *trans*-forms should have nearly the same moments.

Owing to experimental difficulties, the moments recorded in Table I can be regarded only as approximate values. They are rather larger than would be expected from (IV), but not larger than might be expected from the rotation of the hydroxyl groups in (III). It will be seen that the α - and β -forms have nearly the same moment.

If the group R_1 has a considerable dipole moment in a definite geometrical position with respect to the nickel atom, then it is clear that the moments of the two R_1 groups would

TABLE I.

Dipole Moments of Nickel Glyoximes.

Glyoxime.	Dipole moment, in Debye units.		Glyoxime.	Dipole moment, in Debye units.	
	α -Form.	β -Form.		α -Form.	β -Form.
Methyl- <i>n</i> -propyl	1.4	1.5	Benzylmethyl	1.3	1.6
Methyl- <i>n</i> -butyl	1.3	1.3	<i>p</i> -Chlorophenyl- <i>n</i> -butyl ...	1.8	—

be opposed in the *trans*-form and would reinforce one another in the *cis*-form. Dipole-moment determinations would then give a definite test of the planar hypothesis.

The most suitable group to use in synthesising glyoximes appeared to be *p*-chlorophenyl. *p*-Chlorophenylmethylglyoxime was therefore prepared, but its *nickel* derivative proved to be almost insoluble in benzene. *p*-Chlorophenyl-*n*-butylglyoxime gave a more soluble *nickel* derivative, but difficulties in the synthesis of this oxime have so far prevented the isolation of the lower-melting form, although indications of its existence have been obtained. The higher-melting form gave a dipole moment which is nearly the same as that of nickel glyoximes not containing a polar substituent in the group R_1 . This result gives strong support to the view that the nickel glyoximes have a planar configuration, and that the higher-melting forms have the *trans*-configuration. It is difficult to account for the disappearance of the dipole moment of the two C-Cl linkages on any other hypothesis.

EXPERIMENTAL.

Methyl-n-propylglyoxime.—*n*-Propylacetoacetic ester (1 mol.) was dissolved in 10% sodium hydroxide solution, and sodium nitrite (1 mol.) added. Excess of hydrochloric acid was run slowly into the chilled solution with vigorous stirring, and the oximino-ketone separated as an oil. This was converted without further purification into the glyoxime, which was crystallised from aqueous alcohol; m.p. 175° (Tschugaev, *Z. anorg. Chem.*, 1905, **46**, 147, gives 168°). The nickel derivative was prepared by adding an alcoholic solution of the glyoxime to a cold aqueous solution of excess of nickel chloride and sodium acetate. The red precipitate was well washed

and air-dried; it was moderately soluble in benzene and acetone and less soluble in alcohol and ligroin.

Separation of isomerides. 15 G. of the nickel derivatives were dissolved in the least quantity of cold acetone, and water added slowly. The first precipitate was mostly the α -form, m. p. 160°; after recrystallisation from acetone, it had m. p. 165°, unchanged by further crystallisation. (These and other m. p.'s recorded for nickel glyoximes were determined by plunging the m.-p. tube in a preheated bath and observing whether fusion occurred in 30 secs. The ready interconversion of the isomerides makes m. p.'s meaningless if the specimen is heated slowly.) Tschugaev (*loc. cit.*) gives 144°, and Ponzio (*Gazzetta*, 1921, **51**, 213) 160°, for the m. p.

The separation of the β -form gave difficulty until it was noted that fusion gave a product of m. p. 124°, which contained a large amount of the lower-melting form. The pure β -isomeride, m. p. 133°, was obtained as the first precipitate when this equilibrium mixture was dissolved in acetone and fractionally precipitated with water; the m. p. was unchanged by repetition of this process. Microscopic examination of crystals deposited by evaporation from acetone showed that the product of m. p. 133° was homogeneous, but that of m. p. 122° gave a mixture of crystals exhibiting the habits of the typical α - and β -forms. The α -form could also be obtained from the equilibrium mixture by fractional precipitation of the benzene solution with ligroin.

Both forms gave the same equilibrium mixture on fusion, and regenerated the parent glyoxime when shaken with cold hydrochloric acid (m. p. of glyoxime from α -form 174°, from β -form 175°) (Found, for α -form: Ni, 16.8; for β -form: Ni, 16.5. Calc. for $C_{12}H_{22}O_4N_4Ni$: Ni, 17.0%).

Methyl-n-butylglyoxime.—The intermediate oximino-ketone was prepared from *n*-butylacetoacetic ester in the same manner as the propyl compound; after crystallisation from ether, it melted at 60°. Oximation gave the glyoxime, which was crystallised from aqueous alcohol and melted at 173°. The *nickel* complex was precipitated in cold solutions and melted between 143° and 145°. It was very soluble in benzene and acetone, and part of it readily soluble in ligroin. By recrystallisation from this solvent, the α -form, m. p. 150°, was isolated.

Separation of the isomerides. This was attempted by fractional precipitation with water of solutions of the crude product in acetone, but only mixtures were obtained, varying in m. p. from 100° to 143°. It was then found that fusion of any of these mixtures or of the pure α -form gave an equilibrium mixture of m. p. 80° which was rich in the β -form. This mixture readily gave the β -form of m. p. 86° in the earlier fractions resulting from precipitation by water from acetone solution. The α -form was also isolated from the equilibrium mixture by several recrystallisations from ligroin. Both isomerides gave the same equilibrium mixture on fusion and regenerated the parent glyoxime when shaken with cold hydrochloric acid (Found, for α -form: Ni, 15.6; for β -form: Ni, 15.7. $C_{14}H_{26}O_4N_4Ni$ requires Ni, 15.7%). Molecular weights (cryoscopic) in benzene, at concentrations ranging from 14 to 20 g. per 1000 g. of solvent: α -form, $M = 477, 494$; β -form, $M = 466, 478$ (Calc.: $M = 373$). Both forms show marked association in benzene solution but have the same molecular weight. Similar association was found with the isomeric nickel benzylmethylglyoximes (Sugden, *loc. cit.*).

p-Chlorophenylmethylglyoxime.—*p*-Chloropropiophenone, m. p. 35°, was prepared by the Friedel-Crafts reaction from propionyl chloride and chlorobenzene. From this, the *isonitroso*-ketone was made by the method of Hartung and Munch (*J. Amer. Chem. Soc.*, 1929, **51**, 2262) and melted at 119° after crystallisation from alcohol. Oximation gave the glyoxime, which crystallised from alcohol and had m. p. 223°. The *nickel* derivative, prepared in the usual manner, had m. p. 283° (Found: Ni, 11.5. $C_{18}H_{16}O_4N_4Cl_2Ni$ requires Ni, 12.2%). It was very sparingly soluble in hot benzene, chlorobenzene, and chloroform, and insoluble in ligroin. Its low solubility made it unsuitable for the separation of isomerides or the measurement of dipole moments, so further work on this substance was abandoned.

p-Chlorophenyl-n-butylglyoxime.—*p*-Chlorophenyl *n*-amyl ketone was prepared by the Friedel-Crafts reaction from chlorobenzene and hexoyl chloride. The yield was improved, and the separation of the product facilitated, by using 1 mol. of hexoyl chloride, 1.1 mols. of aluminium chloride (Al_2Cl_6), and 3 mols. of chlorobenzene. When the reaction was complete, the product was poured into cold water to decompose the excess of aluminium chloride. This gave an emulsion owing to the separation of solid chloro-ketone. When this emulsion was warmed to 60°, the chloro-ketone dissolved, and the chlorobenzene layer could readily be separated. On cooling, this layer deposited part of the desired product, and the remainder was obtained by removing two-thirds of the chlorobenzene under diminished pressure. The ketone was purified by distillation at 20 mm. and by recrystallisation from alcohol; b. p. 165°/20 mm., m. p. 64°.

The preparation of the isonitrosoketone met with great difficulties. Hartung and Munch's method (*loc. cit.*) gave a very small yield of an oily product; when sodium ethoxide was used to catalyse the reaction between the chloro-ketone and alkyl nitrite, a violent reaction occurred, but the main product was *p*-chlorobenzoic acid, m. p. 243°. Attempts to prepare the diketone, and from it the glyoxime by oxidation of the chloro-ketone with selenium dioxide, were also unsuccessful. Finally, the method of Semon and Damerell ("Organic Syntheses," Vol. 10) gave a small yield of the desired product and much unchanged chloro-ketone; the latter was recovered and worked up until sufficient of the oximino-ketone had been accumulated. *p*-Chlorophenyl isonitroso-*n*-amyl ketone melted at 42° after crystallisation from ligroin. Oximation gave a nearly quantitative yield of the glyoxime, which, when crystallised from alcohol, melted at 206°.

The nickel derivative, prepared in the usual manner, was brown and only moderately soluble in benzene. Recrystallisation from this solvent gave a product of m. p. 266° which was regarded as the α -form (Found: Ni, 10.7; Cl, 12.2. $C_{24}H_{28}O_4N_4Cl_2Ni$ requires Ni, 10.4; Cl, 12.5%). The mother-liquor when precipitated with ligroin gave a product of m. p. 243°, indicating that a lower-melting isomeride was present. The amount of this product was too small to permit of further fractionation.

Nickel NN-Di-n-propyldithiocarbamate.—20% Potassium hydroxide solution (1 mol.) was shaken with carbon disulphide (1 mol.), and di-*n*-propylamine added slowly with cooling. The solution was then added to an aqueous solution of nickel chloride (1 mol.) and sodium acetate (3 mols.). The greenish-black nickel complex was extracted with acetone and recrystallised from this solvent; m. p. 135° (Found: Ni, 14.0; *M*, ebullioscopic in benzene, 447, 456. $C_{14}H_{28}N_2S_4Ni$ requires Ni 14.3%; *M*, 411).

Nickel NN-di-n-butyldithiocarbamate, m. p. 91°, was similarly prepared from di-*n*-butylamine (Found: Ni, 12.7; *M*, ebullioscopic in benzene, 469, 454. $C_{18}H_{36}N_2S_4Ni$ requires Ni, 12.6%; *M*, 467).

Specimens of these dithiocarbamates were heated to 20° above the m. p. for 10 minutes. The products were dissolved in cold acetone and fractionally precipitated with water. None of the fractions showed any appreciable change in m. p.; hence a second form does not appear to be produced by fusion.

Determination of Dipole Moments.—The dielectric constants of benzene solutions of the nickel complexes were determined by a resonance method with the apparatus described by Sugden (J., 1933, 769). In Table II, *w* is the weight fraction of solute, *d* the density, and ϵ the dielectric constant of the solution, and P_2 the total polarisation calculated in the usual manner. Owing to the low solubility and the small amount available of some of the substances examined, the values of P_2 are subject to a rather large error, and no attempt has been made to extrapolate to infinite dilution before calculating the dipole moment. The deep colour of the solutions made it impossible to obtain accurate measurements of refractive index; the value of P_E was therefore calculated from the usual refraction constants for the Na-*D* line, and no allowance made for atom polarisation or for the contribution of the nickel atom to the distortion polarisation. This will partly compensate for the neglect to extrapolate to infinite dilution. The benzene used as solvent had \bar{n}_D^{25} 0.8734, ϵ_{25} 2.273.

TABLE II.

Dipole moments in benzene at 25°.

Nickel glyoxime.	<i>w</i> .	<i>d</i> .	ϵ .	P_2 .	P_E (calc.).	μ .	Mean.
Methyl- <i>n</i> -propyl (α -form)	0.02424	0.8810	2.294	120	82	1.35	1.4
" "	0.03130	0.8822	2.294	124	"	1.42	
Methyl- <i>n</i> -propyl (β -form)	0.01812	0.8809	2.292	130	"	1.52	1.5
" "	0.02049	0.8811	2.294	133	"	1.57	
Methyl- <i>n</i> -butyl (α -form)	0.02089	0.8792	2.285	127	91	1.32	1.3
" "	0.03628	0.8833	2.293	126	"	1.30	
Methyl- <i>n</i> -butyl (β -form)	0.01581	0.8790	2.285	129	"	1.35	1.3
" "	0.03822	0.8844	2.296	128	"	1.34	
Methylbenzyl (α -form)	0.01895	0.8795	2.285	148	113	1.30	1.3
Methylbenzyl (β -form)	0.01841	0.8790	2.288	166	"	1.60	1.6
" "	0.03042	0.8839	2.301	168	"	1.63	
<i>p</i> -Chlorophenyl- <i>n</i> -butyl (α -form)	0.01425	0.8782	2.283	193	130	1.74	1.8
" " " "	0.01460	0.8788	2.285	199	"	1.82	