

On heating these compounds sublime or decompose without melting. They are easily soluble in organic solvents, but less soluble in methanol than in ethanol. They are almost insoluble in water but are slowly decomposed with liberation of the phosphite and formation of a green nickel(II) compound.

The compounds were found to be diamagnetic (measured on a Gouy balance at room temperature).

Molecular weight determinations were done cryoscopically in benzene.

*Tetrakis(trimethyl phosphite)nickel(0)*,  $[\text{Ni}(\text{P}(\text{OMe})_3)_4]$ . (Found: C 25.96; H 6.76. Calc for  $\text{C}_{12}\text{H}_{36}\text{NiO}_{12}\text{P}_4$ : C 25.45; H 6.49).

*Tetrakis(triethyl phosphite)nickel(0)*,  $[\text{Ni}(\text{P}(\text{OEt})_3)_4]$ . (Found: C 39.30; H 8.53; Ni 8.05, 8.20, 8.08; Mol.wt. 714. Calc. for  $\text{C}_{24}\text{H}_{60}\text{NiO}_{12}\text{P}_4$ : C 39.85; H 8.36; Ni 8.11; Mol.wt. 723).

*Tetrakis(triisopropyl phosphite)nickel(0)*,  $[\text{Ni}(\text{P}(\text{OPr})_3)_4]$ . (Found: C 48.50; H 9.34; Ni 6.67, 6.54; Mol.wt. 890. Calc. for  $\text{C}_{36}\text{H}_{84}\text{NiO}_{12}\text{P}_4$ : C 48.52; H 9.43; Ni 6.55; Mol.wt. 891).

*Tetrakis(triisopropyl phosphite)nickel(0)*,  $[\text{Ni}(\text{P}(\text{OiPr})_3)_4]$ . (Found: C 49.05; H 9.57. Calc. for  $\text{C}_{36}\text{H}_{84}\text{NiO}_{12}\text{P}_4$ : C 48.52; H 9.43).

*Tetrakis(tributyl phosphite)nickel(0)*,  $[\text{Ni}(\text{P}(\text{OBu})_3)_4]$ . (Found: C 53.90; H 10.01; Ni 5.84. Calc. for  $\text{C}_{48}\text{H}_{108}\text{NiO}_{12}\text{P}_4$ : C 54.39; H 10.20; Ni 5.55).

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Received March 23, 1965.

## On the Alleged *cis-trans*-Isomeric Forms of Bis(benzylmethylglyoximato)nickel(II)

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Sugden,<sup>1</sup> in 1931, isolated two forms of bis(benzylmethylglyoximato)nickel(II) which differed considerably in solubilities and melting points. The  $\beta$ -form (m.p. 75–77°C) was more soluble than the  $\alpha$ -form (m.p. 168°C) in cold acetone. The two forms were considered to be *cis-trans*-isomeric square-planar nickel complexes and this seemed to be corroborated by measurements of their electric dipole moments. These were found by Cavell and Sugden<sup>2</sup> to be 1.60 and 1.30 D, respectively.

During an investigation of the paper-chromatographic separation of *cis-trans*-isomeric complexes we have come to the conclusion that these two forms are not *cis-trans*-isomers. We have confirmed the existence of the two forms of this nickel compound; however, the following observations indicate that the appearance of two forms has to be interpreted in another way than as a case of *cis-trans*-isomerism.

*Paper chromatography.* On circular paper chromatography, using pentane as the eluant, both forms behaved similarly: Some of the compound dissolved and moved as a red-brown ring in the solvent front leaving an apparently immobile dark-brown spot at the starting point. However, during continued elution this spot disappeared slowly and formed a faintly yellow "tail". With other eluents and on aluminium oxide columns there was a similar indication that some transformation took place during the elution. Melting points of the products isolated from the spots varied between the m.p. of the pure  $\alpha$ - and  $\beta$ -form (see below).

*Interconversion of the two forms.* In a sealed flask containing dry pentane and the  $\beta$ -form as the bottom phase, crystals of the  $\alpha$ -form deposited after some days on the walls of the flask. The same transformation was shown to occur in other

solvents, *e.g.* in acetone or methanol. The m.p. of the  $\alpha$ -form was usually found to be near the value given by Sugden but occasionally somewhat higher values, amounting to 180°C, have been found. The high values are obtained not by recrystallisation but by *slow* crystallisation of the  $\alpha$ -form. The  $\beta$ -form was found to be more soluble than the  $\alpha$ -form in various solvents.

According to Sugden the  $\beta$ -form on heating to 120°C is transformed into an "equilibrium mixture" of the  $\alpha$ - and  $\beta$ -form melting at 152°C. This has been found to be incorrect: When products melting on rapid heating near 150°C are kept somewhat below this temperature it can be seen under the microscope that some particles melt and resolidify and after some time the melting point will be near that of the  $\alpha$ -form. Accordingly the  $\beta$ -form is not transformed into an equilibrium mixture on heating but more or less completely into the  $\alpha$ -form.

Conversion in the opposite direction, *i.e.* from the  $\alpha$ -form to the  $\beta$ -form, can be effected in various ways:

a) On rapid evaporation of a solution of the  $\alpha$ -form. Thus a solution of the  $\alpha$ -form in benzene poured on a glass sheet, after rapid evaporation at room temperature, left a brown solid which according to its m.p. consisted mainly of the  $\beta$ -form. This also explains the varying melting points of the products isolated from the chromatograms, since the m.p. will be highly dependent upon the evaporation velocity of the solvent applied.

b) On precipitation from a benzene solution by addition of pentane. The yield of the  $\beta$ -form could be greatly increased by using a large volume of pentane and adding it as quickly as possible to a concentrated solution of the  $\alpha$ -form in benzene. When the pentane was added slowly to a dilute solution of the  $\alpha$ -form in benzene the  $\alpha$ -form, or at any rate higher melting products, separated.

c) By melting the  $\alpha$ -form and rapid cooling of the melt. In fact we found this method to give the "purest" product of the  $\beta$ -form with melting points between 76 and 77°C, when the glassy, cooled melt was stirred with pentane and filtered.

All the conversions of the  $\alpha$ -form to the  $\beta$ -form and *vice versa* have in common that the  $\alpha$ -form was obtained under conditions which favoured crystallisation and the  $\beta$ -form under conditions restraining crystallisation. This in connection with the fact

that all these transformations except the last mentioned have occurred at room temperature and in almost inert solvents makes it improbable that the  $\alpha$ - and  $\beta$ -form should be geometrical isomers. The observations described under a) and b), in fact, make it improbable that the two forms exist as individual species in solution.

*Physical properties of the solutions of the two forms.* As expected no difference could be found between the physical properties of solutions of the two forms.

The dielectric constants of equimolar solutions of the two forms in benzene were found in a series of experiments to be identical within the uncertainty limits of the experiments. This contrasts with the findings of Cavell and Sugden,<sup>2</sup> but the instrument used by us (Dipolmeter DM 01 from Wissenschaftlich-Technische Werkstätten, Weilheim) allows for higher precision than that used by Cavell and Sugden.

No differences were found between ultraviolet and visible spectra of the two forms in ethanol (absorption maxima: 210, 260, 390  $m\mu$ ), or carbon tetrachloride (absorption maxima: 267, 338, 390  $m\mu$ ), or between infrared spectra of the two forms in chloroform or carbon disulfide.

Finally molecular weight determinations in benzene solutions by the method of vapour pressure lowering have given values near 465 for both forms (calc. 441 for the monomer). This agrees with the cryoscopic measurements of Sugden.<sup>1</sup>

*Properties of the solid phases.* In Debye diagrams (taken in a Bradley camera) the  $\alpha$ -form appeared crystalline. The  $\beta$ -form gave diagrams somewhat like an amorphous compound but with weak lines due to the crystalline  $\alpha$ -form.

Under the polarization microscope the  $\alpha$ - and  $\beta$ -form appeared crystalline and amorphous, respectively. In specimens having melting points between 77 and 168°C both forms could be observed under the microscope.

The infrared spectra of the two forms in KBr discs were found to be identical between 400 and 3000  $cm^{-1}$ . However, the infrared spectra of *cis*- and *trans*-forms of the alleged type would probably not be different.

*Conclusion.* The observations reported here are inconsistent with the assumption that the two forms of bis(benzylmethylglyoximato)-nickel(II) are *cis-trans*-isomers but indicate that they are a crystalline and a disordered solid containing the same molecular species.

Cavell and Sugden have also reported a few other cases where glyoxime-nickel-complexes could be isolated in two forms with different melting points, but otherwise differing even less than the benzylmethylglyoxime compounds. In these cases both forms were crystalline and for the reasons given here they must be considered as polymorphous forms and not as stereoisomers.

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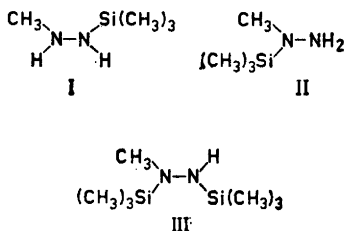
Received March 23, 1965.

### On the Structure of Trimethylsilylmethylhydrazine

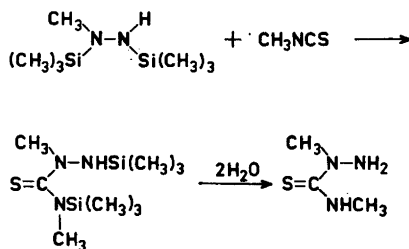
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During an investigation on thiosemicarbazides<sup>1</sup> it was our intention to prepare the hitherto unknown 1,4-dimethylthiosemicarbazide by protecting the methyl-bearing nitrogen in methylhydrazine with a trimethylsilyl group and reacting it with methyl isothiocyanate. A methyl-trimethylsilylhydrazine has been described by Wannagat and Liehr,<sup>2</sup> but was formulated as 1-methyl-2-trimethylsilylhydrazine (I). Since this compound was prepared from trimethylsilyl chloride and methylhydrazine it would rather be ex-



pected to be 1-methyl-1-trimethylsilylhydrazine (II), the methyl-bearing nitrogen being the most nucleophilic one and a methyl group exerting no steric hindrance. However, when this compound was reacted with methyl isothiocyanate 2,4-dimethylthiosemicarbazide was formed. This at first seemed to confirm the formula given to this compound by Wannagat. However, when we then carried out a reaction between methyl isothiocyanate and methyl bis(trimethylsilyl)hydrazine we again obtained 2,4-dimethylthiosemicarbazide. Since the bis(trimethylsilyl) derivative cannot for steric reasons contain the two trimethylsilyl groups at the same nitrogen atom (*cf.* Wannagat and Liehr<sup>3</sup>) it must be 1-methyl-1,2-bis(trimethylsilyl)hydrazine (III) and the reaction with methyl isothiocyanate can only be explained by assuming that a trimethylsilyl group has been displaced by the reaction with methyl isothiocyanate:



With dimethylthiocarbonyl chloride the bis(trimethylsilyl) derivative of methylhydrazine also formed 2,4,4-trimethylthiosemicarbazide and not the 1,4,4-isomer.

Such displacement reactions have been shown by Fink<sup>4</sup> to occur also in the case of silyl-substituted amines, *e.g.* in the reaction between bis(trimethylsilyl)amine and phenyl isocyanate.

Accordingly it seemed very probable that such a displacement also took place when the mono(trimethylsilyl) derivative of methylhydrazine was reacted with methyl isothiocyanate, *i.e.* that it has the structure II. The presence of an  $\text{NH}_2$  group cannot, as usual, be proved by the formation of hydrazones because an *N*-trimethylsilyl group is split off very easily hydrolytically. However, the infrared spectrum of the mono(trimethylsilyl) derivative exhibits an  $\text{NH}_2$  deformation band at  $1600\text{ cm}^{-1}$ , which is missing in the spectrum of the bis(trimethylsilyl) derivative. Furthermore the