33. *Studies on Alkylated Complex Cyanides. Part I. The Isomerism of the Alkylated Ferrocyanides. Part II. Hexaethylated Ferrocyanides.*

By Ernald G. J. Hartley (with crystallographic examination by H. M. Powell).

Part I.

A former investigation on the alkylation of the ferrocyanides (Hartley, J., 1910, **97**, 1725; 1912, **101**, 705; 1913, **103**, 1196; etc.) resulted in the isolation of a series of salts containing the stable bivalent cation * $[Fe(CNMe)_6]$, the chloride of which, when heated under diminished pressure, evolved methyl chloride and gave tetramethyl ferrocyanide in two varieties, described as the α- and β-form. These isomerides are stable and crystallise well, nearly always in combination with their respective solvents. Although they exhibit a general similarity in chemical behaviour, well-marked differences are apparent in their properties both in the solid state, *e.g.*, crystalline form, solubility in various liquids, etc., and in their solutions.

The experimental work has been repeated in part by Hölzl (*Monatsh.*, 1927, **48**, 72) and extended to the study of other metallic double cyanides, including the molybdenum and tungsten salts, both containing eight cyanide radicals. A number of interesting substances were thus obtained, but no cases of isomerism were observed and none of the compounds exhibited the stability of the ferrocyanides.

The results of these two investigations on the latter are mainly in agreement, but there is one important discrepancy. From the product obtained by heating the above chloride $[Fe(CNMe)_6]Cl_2$, Hölzl isolated two substances, which he regarded as being identical with the author's original α- and β-tetramethyl ferrocyanides. As far as the α-variety is concerned, he is probably correct, but in the case of the β-isomeride there is a complete lack of resemblance between the two preparations, as can be seen from the following comparison of their properties.

Hölzl's β-tetramethyl ferrocyanide (*loc. cit.*, p. 76) (i) gives with silver nitrate a precipitate of silver cyanide corresponding to two of the six cyanide groups in the molecule; (ii) gives no colour with ferric chloride solution; (iii) is more soluble in water than the isomeride; (iv) behaves as an electrolyte in aqueous solution.

Hartley's β-tetramethyl ferrocyanide (i) gives no precipitate of silver cyanide with soluble silver salts, though with silver nitrate a sparingly soluble micro-crystalline compound,

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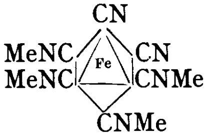
* In the original papers an old notation was employed to represent this series of compounds. It is now clearly advantageous to replace this by formulæ based on Werner's system.

$[Fe(CNMe)_4(CN)_2]AgNO_3$, is precipitated, which, unlike silver cyanide, dissolves in hot water; (ii) gives with ferric chloride a red coloration similar in intensity to that produced by the isomeride; (iii) is considerably *less* soluble in water and organic solvents than the isomeride; (iv) has the same molecular weight in solution as the isomeride.

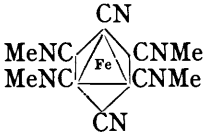
The molecular weight was determined by an osmotic method (Berkeley and Hartley, *Proc. Roy. Soc.*, 1916, **92**, 491). The measurements obtained correspond with the simple formula $[Fe(CNMe)_4(CN)_2]$ as representing both the α- and β-form and thus afford no indication of ionisation in either isomeride. From the above comparison it is clear that the author's β-compound is not identical with Hölzl's (which should therefore be otherwise described) and the latter's assumption of two different co-ordination numbers for iron (*loc. cit.*, p. 79) * to account for the properties of the isomerides is certainly not applicable to the original pair of substances. It is not now possible to explain this discrepancy in experimental results, as no substance with properties agreeing with Hölzl's β-isomeride was isolated in the original preparations. It may, however, be pointed out that the presence of a small quantity of a constituent is easily overlooked in the complex product which is obtained in a reaction of this nature.

The remainder of this section records some considerations and experiments in connexion with the structure of the original α- and β-tetramethyl ferrocyanides.

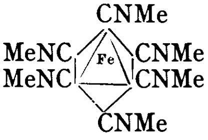
The simplest explanation of the observed isomerism was recently pointed out by Glasstone (J., 1930, 321; cf. Hölzl, *loc. cit.*, p. 80). (I) and (II) represent the isomerides



(I.) *Cis-.*



(II.) *Trans-.*



(III.)

as possessing *cis*- and *trans*-structures, in both of which the iron has the normal co-ordination number of six. Glasstone considers that the *cis*-form probably corresponds to the α-isomeride.

If these formulæ are correct it is apparent that by the addition of methyl to the two nitrogen atoms of the CN radicals in (I) and (II) the difference in configuration is eliminated and identical hexamethylated compounds containing the group (III) will result. This group, of course, constitutes the cation occurring in the original compound, $[Fe(CNMe)_6]Cl_2$, from which the isomerides were derived. The above structure thus accounts satisfactorily for the fact that no case of isomerism was detected among any of the salts containing this ion, and it is in agreement with the experimental observation that all the methyl groups are directly attached to nitrogen (Hartley, J., 1911, **101**, 1552).

If a similar addition is made to (I) and (II) of radicals other than methyl, *e.g.*, ethyl, there should result a pair of compounds containing the cation $[Fe(CNMe)_4(CNEt)_2]$ in two different forms in which CN·Et groups occupy the positions held by CN in the parent substances. This pair should thus exhibit properties capable of being distinguished.

In order to obtain compounds containing the ions to illustrate these points, direct combination of the tetramethyl ferrocyanides with alkyl iodides was impracticable, since the β-, unlike the α-form, scarcely reacts directly with either methyl or ethyl iodide.†

Advantage was therefore taken of the influence of mercuric iodide in promoting the formation of the required substances (see Hartley, J., 1916, **109**, 1304). In the presence of

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* Hölzl's explanation of the cause of this isomerism is given in Gmelin's " Handbuch der Anorganischen Chemie," 8, Auflage No. 59, 1930, Eisen, Teil B, s. 619.

† In the original description of these isomerides (J., 1913, **103**, 1199) it was stated that β-tetramethyl ferrocyanide does not react appreciably with methyl iodide at about 100°, at which temperature the α-isomeride forms the compound $[Fe(CNMe)_6]I_2$. Later experiments have shown that at a higher temperature combination takes place, though very slowly. With ethyl iodide the α-isomeride combines readily at 100°, but the β- not at all, even when the temperature is gradually raised to about 135°, at which point incipient decomposition sets in.

this salt, combination takes place easily with either isomeride, a mercuri-iodide being formed :

$$(\alpha\text{- or }\beta\text{-})\mathrm{Fe(CNMe)_4(CN)_2 + 2MeI + 2HgI_2 = [Fe(CNMe)_6]I_2,2HgI_2},$$
$$(\alpha\text{- or }\beta\text{-})\mathrm{Fe(CNMe)_4(CN)_2 + 2EtI + 2HgI_2 = [Fe(CNMe)_4(CNEt)_2]I_2,2HgI_2}.$$

EXPERIMENTAL.

The material used consisted of some of the original specimens of the isomerides, of which about 250 g. of the α- and 50 g. of the β- had been obtained and carefully purified by repeated crystn. from $CHCl_3$ and MeOH respectively. Both substances had remained practically pure, but the β-variety, being slightly discoloured, was crystallised once more from MeOH.

Weighed portions of the ferrocyanide with rather more HgI_2 than is required by the above equation, together with considerable excess of the alkyl iodide, were heated in sealed tubes at about 95° for 8—18 hr., the β-isomeride requiring a longer time than the α- to complete the combination. (An excess of HgI_2 is necessary in order to avoid the partial formation of mercuri-iodides of the formula $[Fe(CNR)_6]I_2,HgI_2$, which are difficult to separate.)

The increase of weight after evaporation of the alkyl iodide corresponded closely with the addition of 2 mols. of alkyl iodide per mol. of the ferrocyanide in every case.

The excess of HgI_2 was removed by solution in warm EtOH, and the salts were dissolved in boiling acetone, from which they all separated on cooling in well-formed crystals containing no solvent of crystn. They were purified by recrystn. from the same solvent.

The results were in accordance with expectation, the two methylated *products* being identical, and the methylethyl compounds differing from one another definitely. The proof of this was established mainly by crystallographic examination (see below).

The analytical figures for the first pair are in agreement with one another {Found, for α-compound : Fe, 3·9; Hg, 27·4; I, 52·2; for β-compound : Fe, 3·8; Hg, 27·4; I, 52·0. $[Fe(CNMe)_6]I_2,2HgI_2$ requires Fe, 3·8; Hg, 27·4; I, 52·0%}.

As a further proof of their constitution, the characteristic chloroplatinate and hydrogen sulphate of the hexamethylated ion, which were described in detail in the original papers, were prepared from the two nitrates, which were themselves obtained from the mercuri-iodides by the action of $AgNO_3$:

$$(\alpha\text{- or }\beta\text{-})\mathrm{[Fe(CNR)_6]I_2,2HgI_2 + 6AgNO_3 = [Fe(CNR)_6](NO_3)_2 + 2Hg(NO_3)_2 + 6AgI}.$$

Hg and excess of Ag were removed by H_2S, and the filtrate evaporated, finally in vac. over soda–lime to remove free HNO_3. No differences were observed in the respective properties of these salts whether derived from the α- or the β-ferrocyanide.

The methylethyl *compounds* gave analytical data which are sufficiently in agreement with one another and with the proposed formula {Found, for α-compound : Fe, 3·9; Hg, 26·7; I, 51·2; for β-compound : Fe, 3·9; Hg, 27·1; I, 51·3. $[Fe(CNMe)_4(CNEt)_2]I_2,2HgI_2$ requires Fe, 3·75; Hg, 27·0; I, 51·0%}. The differences between the isomerides were most marked in (i) the cryst. form (see p. 104); (ii) the relative solubilities in dry acetone, the α-variety being approx. 11 times as sol. as the β- at room temp.

Chloroplatinates were prepared as above, but appeared under the microscope to be almost identical with one another and with the corresponding hexamethylated compound.

Crystallographic Measurements (by H. M. POWELL).

Four series of crystals were investigated. All were obtained from acetone solutions by cooling or evapn. The crystal descriptions are in accordance with the rules of T. V. Barker (" Systematic Crystallography," 1930) and a glance at the classification angles shows that the crystals of the α- and the β-tetramethyldiethyl compound are different. Fragments of the less soluble β-form did not induce crystn. of a sat. solution of the α- compound, and both cryst. varieties may be obtained from a solution made up from a mixture of the two. The two cryst. forms, therefore, represent different isomerides and not polymorphs.

Crystals of the hexamethyl compound derived from either α- or β-tetramethyl ferrocyanide proved to be identical in angular measurements and in optical properties.

β-*Tetramethyldiethylferrocyanogen mercuri-iodide* (Fig. 1). Pale yellow crystals. System : anorthic. Axial ratios $a : b : c = 1{\cdot}3137 : 1 : 1{\cdot}0464$; $\alpha = 95°48'$, $\beta = 117°35'$, $\gamma = 88°8'$.

The following table gives the mean values of the angles for seven crystals measured on a two-circle goniometer. The figures in parenthesis are to be added to give the calc. values.

	b(010).	*a*(100).	*M*(1$\bar{1}$0).	*c*(001).	*q*(011).	*Q*(0$\bar{1}$1).	*R*($\bar{1}$01).
ϕ	0° 0′	89° 3′*	139° 3′ (4′)	78° 6′*	24° 4′ (9′)	150° 46′ (15′)	284° 24′ (−10′)
ρ	90 0	90 0	89 56 (4′)	28 6*	51 52*	47 9 (1′)	21 12*

Barker classification angles : *cr* 27°13′, *ra* 35°15′, *am* 49°56′, *mb* 39°7′, *bq* 44°9′, *qc* 40°18′.

Optics. A partial biaxial figure with one optic axis slightly inclined to the normal is seen through *a*(100). The double refraction is strong and negative, and there is marked crossed dispersion.

α-Tetramethyldiethylferrocyanogen mercuri-iodide (Fig. 2). Bright yellow crystals of this substance obtained by evapn. of acetone solutions were badly formed, being turbid and having imperfect faces. System : anorthic. Forms developed : *a*(100), *m*(110), *b*(010), *M*(1$\bar{1}$0), *q*(011), *p*($\bar{1}$11), *P*($\bar{1}\bar{1}$1). Measurements on the two-circle goniometer gave inaccurate results owing to the lack of faces suitable for the original adjustment. Mean values for the interfacial angles of five crystals were obtained by the single-circle method. Since none of the angles is known with an accuracy much greater than ± 20′, the usual crystallographic consts. are not recorded, but for comparison with the β-compound the complete Barker description is given. The angles are calc. from the fundamentals, *am* 46°11′, *mb* 67°34′, *b′P* 66°39′, *Pp* 64°49′, *mp* 85°49′.

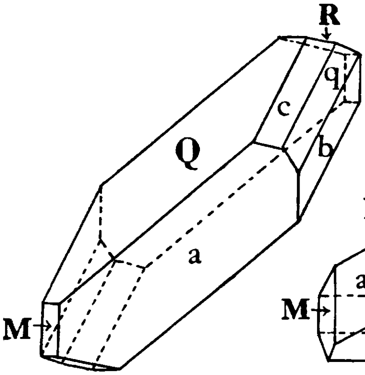

FIG. 1.

β-Tetramethyldiethylferrocyanogen mercuri-iodide.

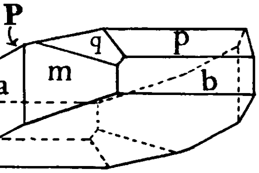

FIG. 2.

α-Tetramethyldiethylferrocyanogen mercuri-iodide.

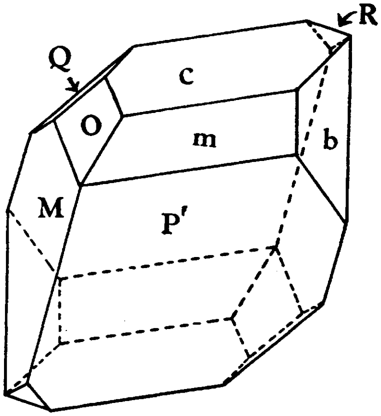

FIG. 3.

Hexamethylferrocyanogen mercuri-iodide.

Barker classification angles : *cr* 26°31′, *ra* 36°7′, *am* 46°11′, *mb* 67°34′, *bq* 63°11′, *qc* 32°50′.

Optics. Double refraction strong. In crushed fragments a partial negative biaxial figure was seen. Observed through *P*($\bar{1}\bar{1}$1), the crystals show pleochroism. For light vibration at 35° to the edge *Pp*, which has the lower refractive index, pale yellow-green is transmitted, and for the vibration at right angles bright greenish-yellow.

Hexamethylferrocyanogen mercuri-iodide (Fig. 3). Pale yellow crystals. System : anorthic. Axial ratios *a* : *b* : *c* = 1·2675 : 1 : 1·1897; α = 104°55′, β = 107°28′, γ = 98°24′.

Two-circle measurements for six crystals gave

	b(010).	*m*(110).	*M*(1$\bar{1}$0).	*c*(001).
ϕ	0° 0′	34° 12′ (−29′)	135° 30′*	41° 45′ (0′)
ρ	90 0	90 2 (−2′)	90 0	25 8 (−5′)
	R($\bar{1}$01).	*Q*(0$\bar{1}$1).	*O*(1$\bar{1}$1).	*P*($\bar{1}\bar{1}$1).
ϕ	278° 58′ (−50′)	161° 36′ (7′)	117° 40′*	210° 39′*
ρ	36 8 (−18′)	44 55 (10′)	56 46 *	54 24 *

Optics. Through *M*(1$\bar{1}$0) a partial biaxial figure with one optic axis nearly perpendicular is seen. Double refraction is strong and negative. Pleochroism is observed. Extinction on *P* is nearly parallel to the edge *QP*. For the vibration in this direction, which has the greater refractive index, the colour transmitted is yellow, and for that at right angles pale green.

PART II.

The reaction between silver ferrocyanide and ethyl iodide was first investigated by Freund (*Ber.*, 1888, **21**, 931). His experiments were carried out at the boiling point of ethyl iodide, tetraethyl ferrocyanide, but no more highly ethylated products, being obtained. The same substance has since been prepared by Buchbock, Browning, and Hölzl, all using similar methods.

When the reaction takes place at room temperature, however, ethylation proceeds further.

10·17 G. of $Ag_4FeC_6N_6$, after being in contact with excess EtI for 6 weeks, had increased in wt. to 22·46 g., corresponding to addition of *ca.* 5 mols. C_2H_5I to 1 mol. of $Ag_4FeC_6N_6$.

Extraction of the product with EtOH and $CHCl_3$ removed a very small amount of the tetraethyl compound, and a more or less cryst. mass (A) remained, insol. in H_2O and all the usual org. solvents.

This insolubility suggested the formation of a complex salt with a constitution similar to that of the hexamethylated compound $[Fe(CNMe_6)]I_2,4AgI$ previously described (Hartley, J., 1912, **101**, 707). In order to break up the substance (A) it was treated with $AgNO_3$; AgI was pptd., and the nitrate of a base remained in solution, from which a cryst. residue was obtained by evapn. to dryness. This nitrate, however, was too sol. in H_2O or EtOH to be readily purified, and it was therefore converted into an acid sulphate, since the corresponding methyl compound had proved easy to purify.

The solid nitrate was dissolved in dry EtOH, and conc. H_2SO_4 added drop by drop. No pptn. took place, but on the addition of dry Et_2O a salt was pptd., which after drying crystallised well from EtOH; after several recrystns., it was analysed {Found : Fe, 9·7; SO_4, 33·0; H_2SO_4, 16·6 (by titration with 0·1*N*-NaOH and methyl-orange). $[Fe(CNEt)_6](HSO_4)_2$ requires Fe, 9·65; SO_4, 33·1; H_2SO_4, 16·9%}. Apart from its much greater solubility in EtOH, this *substance* is very similar in its properties to the corresponding methyl compound, *e.g.*, in aq. solution it gives a white insol. mercuri-iodide and a very insol. chloroplatinate.

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[*Received, November 30th,* 1932.]