

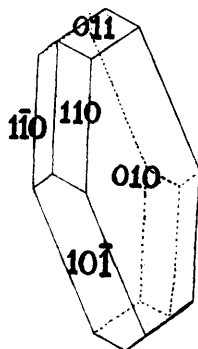
XLII.—*The Crystal Form and Isomerism of Some Ferrocyanides.*

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THE present investigation originated in the examination of an unusual crop of crystals of a ferrocyanide, which had occurred in technical practice, and were handed to me by Mr. A. Hutchinson for crystallographic examination. They proved to be sodium ferrocyanide, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$. (Found, $\text{Fe}=11.7$; $\text{H}_2\text{O}=36.9$. Calc., $\text{Fe}=11.6$; $\text{H}_2\text{O}=37.2$ per cent.) As several of the crystals were interpenetration twins of an interesting type, whilst no twinning had hitherto been observed with this salt, they were examined in detail.

The crystals, which are monosymmetric, show an unusual development of faces (Fig. 1). Adopting the setting of Bunsen (*Ann.*

FIG. 1.



Phys. Chem., 1835, [ii], **36**, 413), the forms present are $b\{010\}$, $q\{011\}$, $m\{110\}$, and $\rho\{10\bar{1}\}$, with ρ and b elongated to produce a flat prism. The following measurements were made:

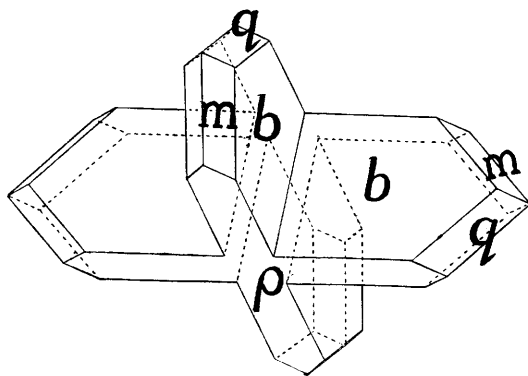
Angle.	No. of observations.	Mean.	Bunsen.
$110 : 010$	8	$49^{\circ}37'$	$49^{\circ}50'$
$011 : 010$	14	$51^{\circ}55'$	$52^{\circ}0'$
$110 : 011$	14	$61^{\circ}24'$	$61^{\circ}25'$
$011 : 10\bar{1}$	8	$56^{\circ}57'$	$57^{\circ}0'$
$110 : 10\bar{1}$	7	$61^{\circ}31'$	$61^{\circ}38'$
$110 : 1\bar{1}0$	8	$80^{\circ}43'$	$80^{\circ}20'$
$011 : 0\bar{1}1$	6	$76^{\circ}2'$	$76^{\circ}0'$

In the interpenetration twins (Fig. 2) the faces $\rho(10\bar{1})$ and $(\bar{1}01)$ of the two individuals are coplanar, whilst the mean observed value

of the angle bb' was $84^{\circ}59'$. The twin axis is the edge ρm , which requires that ρ and ρ' shall be coplanar and $bb' = 85^{\circ}2'$. There is no twin plane a possible face of the crystal. The conditions for the production of these twins could not be discovered.

While examining these crystals, which at first sight appeared to be a quite distinct crystallographic variety of sodium ferrocyanide, the possibility was considered of their being one of the isomeric forms described by Briggs (T., 1911, **99**, 1019), but the evidence adduced seems insufficient to establish the existence of isomeric forms of these salts. With reference to the α - and β -forms of potassium ferrocyanide Briggs says: "As the salts crystallise together in all proportions and are generally so very similar in

FIG. 2.



properties, marked crystallographic differences are not to be expected." Now two substances which crystallise together in all proportions are isomorphous, and therefore, as isomorphous stereo-isomerides are inconceivable, the reality of the isomerism he describes appeared doubtful. As, however, this case of isomerism had been generally accepted for several years, and was supported by other evidence, some of which was not immediately explicable, it seemed worth while to examine some pairs of the salts in question. The " α - and β -forms" of sodium and potassium ferrocyanides and of the double salt of ammonium ferrocyanide with ammonium chloride were therefore prepared according to the directions given by Briggs, and subjected to goniometric examination in order to determine whether or not they are distinct chemical individuals.

Sodium Ferrocyanide, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$.

The " α - and β -forms" show differences of colour as described by Briggs and small differences of habit, but the following measurements show that they are crystallographically identical:

Angle.	α .		β .	
	No. of observations.	Mean.	No. of observations.	Mean.
$\bar{1}10 : \bar{1}\bar{1}0$	6	$80^\circ 36'$	9	$80^\circ 32'$
$110 : 010$	11	$49^\circ 43'$	19	$49^\circ 44'$
$011 : 110$	11	$61^\circ 26'$	6	$61^\circ 30'$
$110 : 101$	8	$61^\circ 38'$	7	$61^\circ 32'$
$011 : \bar{1}01$	7	$57^\circ 0'$	5	$56^\circ 59'$
$010 : 011$	8	$51^\circ 55'$	—	—
$011 : \bar{1}\bar{1}0$	5	$71^\circ 17'$	8	$71^\circ 20'$
$011 : 01\bar{1}$	4	$76^\circ 10'$	—	—
$101 : 011$	4	$52^\circ 29'$	6	$52^\circ 26'$
$100 : 010$	6	$89^\circ 59'$	6	$90^\circ 0'$
$101 : 110$	—	—	10	$56^\circ 10'$

Potassium Ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$.

The pale lemon-yellow (α) and the amber-coloured specimens (β) showed even less difference of habit than with the sodium salt. Both crystallised in the monosymmetric system. The crystals were square plates developed on the plane $b(010)$ with $m\{110\}$ and $q\{011\}$ as bevelled edges, the form $\{101\}$ occurring occasionally with the α -crystals; but as all were obtained necessarily in the presence of impurities (potassium cyanide or a trace of acid) satisfactory measurements were not easily made, vicinal faces and the lamellar twinning making the matter more difficult. The salt is pseudo-tetragonal (Dufet, *Compt rend.*, 1895, **120**, 377), and the divergence from true tetragonal symmetry was too small to be noticed in these circumstances, the angles bm and bq being indistinguishable. The values found for bm or bq were:

α (mean of 19 measurements), $67^\circ 50'$; β (mean of 11), $68^\circ 0'$. Moreover, both showed the very characteristic and marked cleavage in the plane $b(010)$, so that there can be no doubt of their crystallographic identity.

Double Salt of Ammonium Ferrocyanide and Ammonium Chloride, $(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 2\text{NH}_4\text{Cl}$.

The difference of colour was here the most marked of all. With care the " α -salt" was obtained in pale lemon-yellow crystals, whilst the β -crystals were of a deep amber or brown colour. Both crystallised in the trigonal system and commonly showed only the primary

rhombohedron, $r\{100\}$, but other forms occasionally appeared. The following angles were observed:

Angle.	α .		β .	
	No. of observations.	Mean.	No. of observations.	Mean.
100 : 010	14	82°49'	10	82°50'
$\bar{1}00$: 010:	14	97°10'	10	97°6'
100 : 111	19	52°53'	7	52°58'
111 : $\bar{1}11$	10	74°11'	4	74°12'

These are therefore also identical in crystalline form.

The crystallographic evidence thus decidedly negatives the idea of stereoisomerism. The other evidence adduced by Briggs consists of (a) the differences in the colour of the solids, (b) a slight difference in the densities of the solids, (c) a similarly slight difference in their solubilities in water, and (d) a marked difference in the optical rotatory power of two alcoholic solutions supposed to contain the *l*-menthylamine α - and β -ferrocyanides. Taking these points in succession: (a) The ease with which such colour differences may be produced, and are frequently observed, in nature when due to infinitesimal traces of impurities is well known. The true colour of these ferrocyanides is, no doubt, lemon-yellow, the " β "-crystals containing a trace of impurity, which may arise from the slight decomposition which acids produce in them. It is significant that the most striking difference of colour is observed precisely in that instance in which the salt is the most unstable, namely, with the ammonium salt, ammonium ferrocyanide being decomposed very easily by warming its aqueous solution.

(b) and (c) The differences of density and solubility recorded by Briggs are of the same order as the experimental error. It is notoriously difficult to determine the density of a crystalline powder accurately to the third decimal place (see Tutton, "Crystallography," 1911, p. 527). Finally, we have the measurements of specific rotation of the menthylamine salts. The figures quoted by Briggs are such that the differences could scarcely be due to experimental error, although the observations of rotation were made with difficulty and on very dilute solutions. Yet the crystallographic evidence proves conclusively that isomeric ferrocyanides are not in question, so that there must be some other explanation. The point remains obscure.

The possibility of real isomerism being discovered among the ferrocyanides must, of course, remain; it is only certain that the pairs of salts described by Briggs are identical. Indeed, a case of true isomerism has been realised with the tetramethyl ferrocyanides, $(\text{CH}_3)_4\text{Fe}(\text{CN})_6$, by Hartley (T., 1913, 103, 1196), although these are presumably different in being non-electrolytes.

It may be noted that this supposed isomerism among the ferrocyanides of the metals was relegated by Werner in his "Neuere Anschauungen, etc." (1913), to the section entitled "Unaufgeklärte Isomerieerscheinungen." In the same category he placed the isomeric potassium ferricyanides of Locke and Edwards (*Amer. Chem. J.*, 1899, **21**, 193, 413), and recent observations (Hauser and Biesalski, *Ber.*, 1912, **45**, 3516; Piutti, *ibid.*, 1830; Wells, *Amer. Chem. J.*, 1913, **49**, 205) leave the impression that these two salts are also identical except for a trace of impurity in one of them. In any case their existence as stereoisomerides should not be considered as established until they have been shown, by actual measurement, to have distinct crystalline forms.

Lastly, the case of Levy's yellow and green platinocyanides (T., 1908, **93**, 1446), which is cited by Briggs as a further case of stereoisomerism, is certainly nothing of the kind, for the communication in which they are described contains goniometric data showing that the two are crystallographically and therefore chemically identical.

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