LXXXVII.—*Some Derivatives of Tetramethyl Ferrocyanide.*

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IN a recent paper on the osmotic pressure and electrical conductivity of calcium ferrocyanide solutions (Berkeley, Hartley, and Stephenson, *Phil. Trans.*, 1909, A, **209**, 319), it was shown by the authors that the usual formula given for this substance— $\text{Ca}_2\text{FeC}_6\text{N}_6$ —is not in accordance with the experimental results obtained on the assumption that Boyle's law holds good for dilute solutions, taking into consideration the fact that it is a highly ionised salt.

A double molecular weight corresponding with $\text{Ca}_4\text{Fe}_2\text{C}_{12}\text{N}_{12}$ was provisionally suggested, and it was found that the numbers obtained

from measurements of the same physical properties of potassium ferrocyanide were not incompatible with the assumption of a similar double molecule. On the other hand, it was pointed out that there is some evidence from Buchbock's work on the freezing points of solutions of tetraethyl ferrocyanide (*Zeitsch. physikal. Chem.*, 1897, **23**, 157) that the simple formula is the correct one.

Tetraethyl ferrocyanide is prepared from silver ferrocyanide and ethyl iodide, and it is possible that the radicle FeC_6N_6 may have a different constitution in a derivative of this salt from that which it has in potassium or calcium ferrocyanides, just as the nitriles and isonitriles are produced from potassium and silver cyanides respectively.

It seemed therefore desirable to prepare if possible some derivative of potassium or calcium ferrocyanide not ionised in solution, and to determine whether its molecular weight agreed with the simple or the double formula.

In the original paper on the preparation of tetraethyl ferrocyanide (*Ber.*, 1888, **21**, 935), Freund showed that this substance is not formed by the usual process of passing hydrogen chloride into a mixture of the acid and alcohol, the result being in this case an imido-ether, which is very unstable, and consequently unsuitable for a molecular weight determination. With the view of obtaining the lower homologue, tetramethyl ferrocyanide, another fairly general way of preparing methyl esters was therefore tried, namely, the action of methyl sulphate on a salt of the acid. This method can be applied in two ways. In one, methyl sulphate is simply distilled with the dry salt when the ester passes over; for example, the chloride, formate, and benzoate have been so prepared. A second means of effecting the reaction is to treat an aqueous solution of the salt with methyl sulphate.

Werner and Seybold recently (*Ber.*, 1904, **37**, 3658) thus prepared several esters, which cannot be formed directly from the acid and alcohol. After trying the second method unsuccessfully, it was found that dry potassium ferrocyanide is capable of reacting with methyl sulphate at a moderate temperature, and although tetramethyl ferrocyanide itself is not one of the products of the reaction, several compounds closely related to this are formed, an account of the preparation and properties of which seems to be of sufficient interest to be communicated to the Society.

The operation was carried out in the following manner. Fifteen grams of very finely powdered anhydrous potassium ferrocyanide were added to an excess (70 c.c.) of methyl sulphate in a flask connected with an air condenser and a calcium chloride tube to exclude moisture. The flask and its contents were heated in a

water-bath at about 80—90° for from four to six hours with frequent shaking. The solid matter had then changed to a more bulky, whitish substance (A),* usually tinged with blue. The contents of the flask were brought on to a hot filter, a hardened paper being used and suction applied until as much liquid as possible had been extracted, when the solid matter was washed with 25 c.c. of methyl sulphate, the filtrate being received in another vessel and used for further preparations.

The liquid portion, on cooling, deposited a small crop of white crystals, often slightly coloured blue (B). The liquid from the crystals was poured into a distilling flask fitted to a second similar flask in the usual way for distilling under diminished pressure. When a very low pressure had been obtained, the contents of the flask were heated in a boiling-water bath. In this way the excess of methyl sulphate distilled off fairly rapidly, leaving a brown liquid which, on cooling, solidified to a crystalline mass (C).

The three products of the reaction, A, B, and C, were examined, with the following results.

The substance A was soluble in water. It gave a precipitate of Prussian blue with ferric chloride and a white precipitate with barium chloride, and the characteristic potassium platinichloride with platinic chloride. It was almost completely soluble in hot methyl alcohol, the insoluble portion which alone gave the first two above reactions being evidently some unchanged potassium ferrocyanide and some potassium sulphate. The methyl-alcoholic solution deposited white crystals on cooling, having the appearance of potassium methyl sulphate.

An estimation of the potassium as platinic chloride (Found, K=25.98. Calc., K=26.03 per cent.) and also the quantitative conversion of the salt into potassium sulphate (Found, K=25.84; and 26.06. Calc., K=26.03 per cent.) confirmed this.

The substance B deposited from the liquid was freed from methyl sulphate as far as possible by spreading on a porous plate, and was then dried in an exhausted desiccator over sulphuric acid.

It is very soluble in water, moderately so in methyl alcohol, and practically insoluble in ethyl alcohol and all the ordinary organic solvents. The solution in water has an acid reaction, and gives a white precipitate with barium salts, evidently of barium sulphate. It gives none of the usual reactions for iron salts, nor for ferro- or ferri-cyanides. On boiling with potash it is decomposed, giving an odour of *isocyanides*, and a brown precipitate is formed, which

* As a suitable nomenclature for some of the substances formed has not yet been definitely decided on, they will be referred to through this paper, for convenience, as A, B, C, etc.

dissolves in hydrochloric acid and gives a precipitate of Prussian blue with potassium ferrocyanide. Platinic chloride gives a precipitate, which, examined under the microscope, is seen to consist of non-isotropic crystals of a fern-like appearance, when formed from a concentrated solution. The substance itself was readily crystallised from hot methyl alcohol. The crystals so obtained are quite stable in the air, and lose no weight at 100° . They begin to show signs of softening at about 220° and then gradually decompose, but no sharply defined melting point could be obtained. On ignition, a residue of practically pure ferric oxide is left, and a complete analysis of the salt, in which the iron was determined by igniting the substance, dissolving the ferric oxide in concentrated hydrochloric acid, and reprecipitating with ammonia in the usual way, showed that no iron is lost by volatilisation.

The whole of the SO_4 is precipitated by barium chloride. The analytical results, carried out with material recrystallised twice, are as follows:

0.4984 gave 0.0822 Fe_2O_3 . $\text{Fe} = 11.54$.

0.3449 „ 0.3222 BaSO_4 . $\text{SO}_4 = 38.44$.

0.2216 „ 30.03 c.c. N_2 at N.T.P. $\text{N} = 16.99$.

0.2543 „ 0.2734 CO_2 and 0.0941 H_2O . $\text{C} = 29.34$; $\text{H} = 4.14$.

Total found = 100.45.

Another preparation recrystallised three times from methyl alcohol gave $\text{SO}_4 = 38.35$; $\text{Fe} = 11.46$ per cent. The consideration of the formula to be deduced from these numbers will be dealt with later on in the paper.

The substance C, which was evidently the main product of the reaction, was freed from liquid as far as possible by spreading it on a porous plate and keeping in a vacuum over sulphuric acid. It is readily soluble in water, methyl and ethyl alcohols, but not in other ordinary solvents. It gives a similar platinichloride to the substance B, but differs from this in its extreme solubility in ethyl alcohol and also in that it gives no precipitate with barium chloride.

On keeping it for several days in a vacuum, it became partly converted into a form which is insoluble in ethyl alcohol and gives a precipitate of barium sulphate with barium chloride.

An attempt was made to recrystallise it from ethyl alcohol, but the solution was unstable, and a considerable quantity of the insoluble form was soon deposited. An analysis of the insoluble variety purified by washing several times with ethyl alcohol gave the following result:

0.4151 gave 0.3827 BaSO_4 . $\text{SO}_4 = 37.94$.

0.5163 „ 0.0868 Fe_2O_3 . $\text{Fe} = 11.76$.

As these numbers agree pretty closely with those found in the analysis of B, a complete analysis was made of the substance purified by recrystallisation from methyl alcohol. The results were as follows:

0.5000 gave 0.0822 Fe_2O_3 . $\text{Fe} = 11.51$.

0.5120 „ 0.4763 BaSO_4 . $\text{SO}_4 = 38.27$.

0.2023 „ 27.04 c.c. N_2 at N.T.P. $\text{N} = 16.76$.

0.2382 „ 0.2565 CO_2 and 0.0871 H_2O . $\text{C} = 29.39$; $\text{H} = 4.09$.

$\text{C}_{12}\text{H}_{20}\text{O}_8\text{N}_6\text{S}_2\text{Fe}$ requires $\text{Fe} = 11.28$; $\text{SO}_4 = 38.68$; $\text{N} = 16.95$;
 $\text{C} = 29.02$; $\text{H} = 4.07$ per cent.

The composition of the substance (which may be written $\text{FeC}_{12}\text{H}_{20}\text{N}_6(\text{SO}_4)_2$ or $\text{FeC}_6\text{N}_6\text{Me}_6\text{H}_2(\text{SO}_4)_2$) is thus identical with that of the compound B. The properties of the compound C, and its gradual conversion into a sulphate having the above composition, can be best explained by assuming the reaction to take place in the following way.

First, tetramethyl ferrocyanide and potassium methyl sulphate are formed by the interaction of potassium ferrocyanide and methyl sulphate, and the former, behaving as a basic substance, can combine either with an acid or with methyl sulphate, just as ammonia and amines generally can combine with both the above.

The analytical numbers obtained for B point to its being a compound of one molecule of tetramethyl ferrocyanide with one molecule of methyl sulphate and one of sulphuric acid, which may be represented provisionally by (I) writing for convenience the ferrocyanogen molecule as being composed of two tricyanogen rings:

(I) B.

(II) C.

There is at present no evidence as to which of the six nitrogen atoms is in combination with these two groups.

The substance C, which is soluble in ethyl alcohol, can then be represented by (II).

On keeping for a long time in a vacuum, it gives off the two molecules of methyl sulphate enclosed by the dotted lines, and then becomes converted into B. This is confirmed by the fact that on heating the compound C by means of an oil-bath to about 150° , methyl sulphate (Found, $\text{C} = 18.65$; $\text{H} = 4.96$. Calc., $\text{C} = 19.04$;

H=4.79 per cent.) distils over, and the insoluble variety B is at once produced.

A determination of the SO_4 in a portion of B prepared in this way, and recrystallised three times from methyl alcohol gave the following numbers:

0.4122 gave 0.3856 BaSO_4 . $\text{SO}_4 = 38.49$.

The same conversion into a sulphate is effected by adding concentrated sulphuric acid drop by drop to a solution of C in ethyl alcohol, when crystals of B are immediately deposited. A determination of SO_4 in these crystals, washed with ethyl alcohol, and dried in a vacuum, but not recrystallised, gave these numbers:

0.3910 gave 0.3602 BaSO_4 . $\text{SO}_4 = 37.90$.

$\text{C}_{12}\text{H}_{20}\text{O}_8\text{N}_6\text{S}_2\text{Fe}$ requires $\text{SO}_4 = 38.68$ per cent.

A further confirmation of the above formula for C is given by a determination of the iron made on a portion of the substance, purified as far as possible by spreading on a porous plate, and keeping for a few hours in a vacuum over sulphuric acid:

1.0172 gave 0.1126 Fe_2O_3 . $\text{Fe} = 7.75$.

$\text{C}_{16}\text{H}_{32}\text{O}_{16}\text{N}_6\text{S}_4\text{Fe}$ requires $\text{Fe} = 7.48$ per cent.

Lastly, the two formulæ proposed explain why a precipitate with barium chloride is produced with B but not with C, the former being the sulphate, the latter the methosulphate of a base.

Preparation and Analysis of the Platinichloride.

Two specimens of the above were prepared from the substances B and C respectively by precipitating a fairly strong aqueous solution with a slight excess of hydrogen platinichloride. The crystalline precipitate was washed and dried at 100° . It can be obtained in small but well-formed crystals by dissolving in a large quantity of boiling water and allowing the solution to cool slowly.

In the first two analyses the iron was separated from the platinum by precipitating the latter as sulphide in an acid solution of the residue obtained by ignition of the salt. As the platinum was found to carry down traces of iron, in the third analysis the separation was more thoroughly effected by redissolving the impure platinum and reprecipitating as ammonium platinichloride. The analytical results were as follows:

(a) Platinichloride prepared from C:

0.5813 gave 0.1626 Pt. $\text{Pt} = 27.97$.

0.5813 „ 0.0660 Fe. $\text{Fe} = 7.94$.

(b) Platinichloride prepared from B :

0.4969 gave 0.1393 Pt. Pt = 28.03.

0.4969 „ 0.0577 Fe₂O₃. Fe = 8.14.

0.3440 „ 0.2598 CO₂ and 0.0841 H₂O. C = 20.61 ; H = 2.73.*

(c) A mixture of above recrystallised from water :

0.5260 gave 0.1457 Pt. Pt = 27.70.

0.3320 „ 0.2443 CO₂ and 0.0764 H₂O. C = 20.08 ; H = 2.57.

C₁₂H₁₈N₆Cl₆FePt requires Pt = 27.45 ; Fe = 7.89 ; C = 20.30 ;

H = 2.55 per cent.

The substance may be graphically represented as follows :

Comparing this with the formula given to B, it will be seen that the H₂SO₄ group is split off, and PtCl₆ has replaced the other SO₄ radicle.

It must clearly be understood that this structure is not considered adequate to represent completely the reactions involved in the formation and properties of these compounds, since it would be necessary to show the three pairs of nitrogen atoms unsymmetrically placed with regard to each other. It is hoped, however, that further experiments with these and the ferricyanides† will throw considerably more light on the structure of the ferrocyanogen radicle.

It has not at present been found possible to give a quite definite explanation of one step in the reaction that has been described, namely, the formation of two MeHSO₄ groups in the substance C.

It seems likely that it is due to moisture introduced at some time during the experiment, in all probability mainly in the filtration.

Water reacts very readily with methyl sulphate to form methyl hydrogen sulphate, and it is extremely difficult to ensure the complete absence of its vapour during the whole course of operations. Some experiments have been carried out, using very carefully dried materials, and filtering without exposing the liquid to the outside air by means of a porcelain filtering tube fitted in

* In this analysis, lead chromate was used, and for decomposing the oxides of nitrogen, a silver spiral, which appears not to have been quite efficient as the water was slightly acid. This accounts for the carbon and hydrogen being rather too high. In the subsequent analysis, lead chromate and a reduced copper spiral were employed, which proved quite satisfactory.

† A preliminary experiment has shown that potassium ferricyanide reacts in a similar way with methyl sulphate.

the neck of the flask in which the reaction took place, but so far definite results have not been obtained, the products being in part the same as before. It is hoped, however, that further experiments will clear up this point.

A suitable nomenclature for these substances is desirable; at present it is proposed to describe B as hexamethyl ferrocyanogen dihydrogen sulphate, and the platinum derivative as hexamethyl ferrocyanogen platinichloride.

An attempt was made to prepare the free base from hexamethyl ferrocyanogen dihydrogen sulphate by precipitating the whole of the SO_4 radicle with baryta. The experiment was carried out both with aqueous and methyl-alcoholic solutions, the baryta being added gradually from a burette until nearly the whole of the SO_4 was precipitated.

The liquid was then filtered and evaporated in a vacuum over sulphuric acid. In both cases the only product was a brown, semi-liquid mass, which could not be obtained in a crystalline form, and decomposed rapidly in aqueous solution, giving a precipitate apparently of ferric hydroxide. It was alkaline to litmus, and had an unbearable odour. It was not found possible to obtain it in a sufficiently pure condition for analysis.

I am glad to take the opportunity to express my sincerest thanks to Lord Berkeley for placing at my disposal his laboratory and all the chemicals and apparatus for this research, and for much assistance and advice during its progress. Also to his assistant, Mr. Frederick Carter, for his most valuable help in carrying out a great part of the preparations and analyses recorded in this paper; also to Mr. H. B. Hartley and Mr. D. H. Nagel, of Balliol and Trinity Colleges, Oxford, for their kindness in giving me permission to use their laboratory and apparatus for all the combustions required.

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