XXX.—*The Structure of the Platinicyanides: The Potential of the Platino-Platinicyanide Electrode.*

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WHEN a concentrated solution of potassium platinocyanide, $K_2Pt(CN)_4$, is anodically oxidised with a platinum electrode (preferably platinised) and a low *C.D.*, a characteristic, dark brown product separates at the anode (Wilm, *Ber.*, 1888, **21**, 1434). This compound, which has the empirical formula $K_7Pt_4(CN)_{16},6H_2O$, is generally regarded as a platinoplatinicyanide

$$3K_2Pt(CN)_4,KPt(CN)_4,6H_2O;$$

the platinicyanides would thus differ from the platini-halogen salts in containing tervalent platinum. The same compound has also been obtained by Levy (J., 1912, **101**, 1081) by the action of hydrogen peroxide (20 vol.) on a potassium platinicyanide solution. By repeated treatment of a concentrated platinocyanide solution with acidified perhydrol, Levy obtained the completely oxidised compound $\mathrm{KPt(CN)_4}$; the conditions necessary for its preparation seem to be very critical, and it was not found possible to repeat it. Moreover, a more completely oxidised compound than Wilm's salt could not be prepared electrolytically, although both high and low *C.D.*'s at different temperatures were used. From a concentrated solution the dark brown product always separated. When more dilute solutions were used, so that no solid appeared at the anode, oxidation never proceeded to a greater extent than approximately one-sixth of the platinocyanide present. In order to obtain further information on the nature of the platinicyanides, it was decided to investigate the platino–platini electrode, and in the determination of the potentials of this electrode Wilm's salt, together with pure potassium platinocyanide, was used.

When a noble-metal electrode is inserted in a solution of Wilm's salt and platinocyanide, a definite and reproducible *P.D.* is slowly set up, attaining a maximum at the end of 1—2 hours and then remaining steady for many hours. The current produced tends to flow through the electrolyte from the calomel to the platino–platini electrode.

On the assumption that the platino–platini salts are of the same type as the ferro–ferri salts (Wilm, Levy), the reaction taking place at the electrode can be represented by $\mathrm{Pt^{III}}\overset{-}{\mathrm{(CN)}}_4 + \ominus \longrightarrow \mathrm{Pt^{II}}\overset{=}{\mathrm{(CN)}}_4$. The equation for the electrode *P.D.* is thus $E = E_0 + RT/F \,.\, \log a_i/a_o$ where a_i and a_o are the activities of the platini- and platino-ions, respectively. In the presence of excess and constant amount of electrolyte (*N*-potassium chloride), one can assume that the ratio of the activities of the platinum salts is equal to the ratio of their concentrations (i and o, respectively), *i.e.*, $a_i/a_o = i/o$, and the equation takes the form $E = E_0 + RT/F \,.\, \log i/o$.

EXPERIMENTAL.

The electrode solutions were prepared by weighing out the requisite amounts of the two salts and dissolving in *N*-potassium chloride. An ordinary type half cell was used in conjunction with a normal calomel electrode. Platinised glass or platinum points were used as electrodes, although with the latter, owing to the small capacity, polarisation effects were very marked, and the determination of the null point was troublesome. The measuring apparatus consisted of a Weston standard cell, a Kohlrausch rotating bridge, and a Cambridge moving-coil galvanometer.

Results.

In Table I is shown the effect of concentration on the *E.M.F.* at 15°, the ratio platino : platini being kept constant at 3 : 1 by the use of Wilm's salt alone. It will be noticed that there is a small fall in the *E.M.F.* with decreasing total concentration.

TABLE I.

Conc. of Wilm's salt (mg./l.) ...	293·0	195·3	130·2	82·1	47·0
E.M.F. of cell	0·5898	0·5894	0·5883	0·5879	0·5852

In Table II are given the potentials of the electrode when the ratio platino : platini is changed from 3 : 1 to 53 : 1, the concentration of the latter being kept constant. In column 3 are the values of E_0 when calculated according to the last equation (above).

TABLE II.

Ratio, mols. platino : platini.	*E.M.F.* of electrode (Calomel = 0·2870 volt).	E_0, volt.	E_0', volt.
3·00	0·8748	0·9016	0·8884
4·47	0·8690	0·9054	0·8872
9·45	0·8594	0·9140	0·8867
9·86	0·8580	0·9137	0·8858
13·68	0·8542	0·9178	0·8860
52·65	0·8410	0·9374	0·8893

It will be noticed that E_0 progressively increases instead of giving the expected constant. If, however, the equation $E = E_0' + RT/2F \,.\, \log i/o$ is used, which differs only in the value of n, the values under E_0' are obtained. These are much more constant and suggest that in the conversion of the platinocyanide into the platinicyanide there is a valency change from 2 to 4 instead of from 2 to 3, although this form of equation cannot represent the electrochemical changes in these circumstances.

There is little doubt that the empirical formula of Wilm's salt is best represented by $K_7Pt_4(CN)_{16},6H_2O$, as is evident from the author's analyses and those of Wilm and Levy :

	K.	Pt.	CN.	H_2O.	Iodine liberated per g. of salt.
Theory	17·34	49·46	26·4	6·86	0·0804 g.
Wilm	17·2	49·4	—	6·96	—
Levy	17·1	49·2	24·9	6·9	0·0800
Author	17·1	49·6	27·0	7·1	0·0821

If electrolytic oxidation of potassium platinocyanide is carried out in the presence of hydrochloric acid, a chloro-compound similar in properties to Wilm's salt is obtained. This has the composition $[3K_2Pt(CN)_4]Cl,9H_2O$ (Hadow, J., 1861, **13**, 106; Wilm, *loc. cit.*). If oxidation with metallic peroxides is carried out in the presence of sulphuric acid, a sulphate is obtained with the composition

$[xK_2Pt(CN)_4]SO_4$, x being probably 9. The latter behaves as the sulphate of a feebly electronegative metal, undergoing decomposition with barium salts. With barium platinocyanide it gives a platinocyanide of the type $[xK_2Pt(CN)_4]Pt(CN)_4$ (Levy, *loc. cit.*).

The halogen compounds can also be prepared by mixing potassium platinocyanide with the corresponding per-halogen salt $K_2Pt(CN)_4X_2$. This indicates that these complexes are best represented by the formula $[xK_2Pt(CN)_4]KPt(CN)_4X_2$; Wilm's measurements of the molecular weight in acetic acid show that in solution they are dissociated into the simple salts (*Ber.*, 1889, **22**, 1546).

In view of the potential measurements, the so-called completely oxidised platinocyanide product is better represented by the formula $K_2Pt^{IV}(CN)_4,Pt^{II}(CN)_4$ than by the simple formula

$$KPt^{III}(CN)_4.$$

This compound is thus analogous to the perchloro-salt $K_2Pt^{IV}(CN)_4Cl_2$, the radical $Pt^{II}(CN)_4$ having replaced 2 atoms of chlorine, and is a derivative of the true platinicyanides $K_2Pt^{IV}(CN)_6$ in which a molecule of cyanogen has been replaced by $Pt^{II}(CN)_4$.

Further evidence in support of this view of the structure of the platinicyanides is given by the behaviour of Wilm's salt towards acids and alkalis and halogens.

In solution, Wilm's salt adds on 2 mols. of halogen acid or alkali chloride. Considering only the oxidised part of Wilm's salt, this addition is most easily explained as follows: In solution the salt is hydrolysed with the production of a hydroxy-compound:

$$K_2Pt^{IV}(CN)_4,Pt^{II}(CN)_4+H_2O \longrightarrow H_2Pt^{IV}(CN)_4(OH)_2+K_2Pt^{II}(CN)_4;$$

this hydroxy-compound may be compared with the corresponding chloro-derivative $H_2Pt^{IV}(Cl_4)(OH)_2$. The cyano-hydroxy-compound behaves in the same way towards halogen acids and alkali halides, forming the chloro-cyano-compound, *e.g.*, $H_2Pt^{IV}(CN)_4(OH)_2 + 2HCl = H_2Pt^{IV}(CN)_4Cl_2 + 2H_2O$. Halogens convert Wilm's salt into the corresponding per-halogen derivative. Levy explains this action on the supposition that the halogen reduces the platinicyanide to the platino-salt, which is then halogenated:

$$KPt(CN)_4 \longrightarrow KHPt(CN)_4 \longrightarrow KHPt(CN)_4X_2.$$

It is difficult to see why halogens should act here as reducing agents. The halogenation of the hydroxy-compound is, however, simple to follow. If Wilm's salt is regarded as

$$6K_2Pt^{II}(CN)_4,K_2Pt^{IV}(CN)_4Pt^{II}(CN)_4,$$

it is seen that the ratio platino : platini is 7 : 1. In the potential measurements the reaction of the cell is given by the equation $K_2Pt^{IV}(CN)_4Cl_2 + 2Hg \rightleftharpoons 2HgCl + K_2Pt^{II}(CN)_4$ [since dissolution of Wilm's salt in potassium chloride gives rise to $K_2Pt(CN)_4Cl_2]$. The electrode reaction is $[Pt(CN)_4Cl_2]^{--} + 2e = [Pt(CN)_4]^{--} + 2\overline{Cl}$, and the *E.M.F.* is given by $E = E_0 + RT/2F \,.\, \log a_y/a_z a^2_{Cl}$, where a_y = activity of chlorocyanide $[Pt(CN)_4Cl_2]$ ion; a_z = activity of platinocyanide $[Pt(CN)_4]$ ion; a_{Cl} = activity of the chlorine ion. In the presence of excess and constant amount of electrolyte, this leads to the expression $E = E_0 + RT/2F \,.\, \log c_y/c_z a^2_{Cl}$, where c_y and c_z are the concentrations of the platinichlorocyanide and platinocyanide, respectively.

Table III shows the value of E_0 calculated according to the above expression from measurements at 13°, the value of a_{Cl} in *N*-potassium chloride being taken as 0·634. The values are reasonably constant, and the slight fall may be due to incomplete splitting of Wilm's salt in the presence of a large excess of platinocyanide.

TABLE III.

Ratio, platini : platino.	Reduction potential of electrode.	E_0.
1 : 7	0·8749	0·8881
1 : 9·95	0·8690	0·8865
1 : 19·90	0·8594	0·8860
1 : 21·51	0·8580	0·8856
1 : 28·40	0·8542	0·8854
1 : 69·40	0·8410	0·8840

Summary.

From measurements of the potential of the platini–platino electrode, it is shown that in the so-called platinicyanides part of the platinum is present in the quadrivalent state and not in the tervalent state.

These salts are more correctly represented by the formula $K_2Pt^{IV}(CN)_4Pt^{II}(CN)_4$ than by $KPt^{III}(CN)_4$.

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