II.—*On the Platino-tersulphocyanides and the Platino-bisulphocyanides, two new series of salts, and their decompositions.*

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Although the salts of platinum have been pretty closely studied by chemists, and are perhaps found to be more numerous than those of any other metal, there is some room for surprise that scarcely any attention has been paid to their action upon sulphocyanogen compounds. The only notice I have been able to find of a sulphocyanide of platinum, is that made by Grotthus, and quoted by Brande, stating it to occur as a bulky flocculent precipitate of a yellow colour, soluble in acids and in solutions of chloride of potassium and sodium, but thrown down again from these solutions by alcohol. Hitherto, I have not met with a substance answering these properties, unless it should prove to be identical with that last described in this paper.

The addition of bichloride of platinum to a cold solution of sulphocyanide of potassium alone gives rise to the ordinary double salt, chloroplatinate of potassium, with disengagement of hydrosulphocyanic acid. If on the other hand, a strong solution of sulphocyanide of potassium be previously heated to 70° or 80° C., there is no precipitation, but the liquid changes to a deep port-wine-red colour, accompanied with a rise in temperature. On standing, this solution deposits a multitude of brilliant red or gold-coloured plates, which are very soluble in hot water. By this process, much waste of sulphocyanide of potassium is unavoidable, from the presence of free hydrochloric acid, which also decomposes the new compound into a brown flocculent precipitate, if the temperature rises above a certain point.

A more profitable operation consists in dissolving in a moderate quantity of water, five parts of pure sulphocyanide of potassium, weighed in an anhydrous state, which is best obtained by fusion. Four parts of dry chloroplatinate of potassium are then added by degrees to the solution, combination with which may be promoted by a heat regulated below the boiling point. A deficiency of the sulphocyanide must be carefully avoided, as in such a case the above-mentioned brown product is an invariable result, rendering the purification of the crystals exceedingly difficult. After filtering the hot liquid, it is set apart to cool, when the new salt is deposited in beautiful and regular hexagons, often of a large size. To remove traces of chloride of potassium, one product of the reaction, the crystals may be redissolved in boiling alcohol, and passed through a filter surrounded with hot water, a necessary precaution to prevent obstruction from a too rapid crystallization. The solid salt dissolves in 12 parts of water at 60° C., but is far more soluble in boiling water, and still more so in hot alcohol. The crystals, which are of a deep carmine red, belong to the rhombohedral or three and one-membered system. From the alcoholic solution they often take the form of double six-sided pyramids, united base to base with apices truncated; but the aqueous solution usually furnishes hexagonal plates.

With access of air, this substance ignites at a very gentle heat, with a blue sulphurous flame and peculiar odour. A red heat resolves it into sulphocyanide of potassium, gaseous products, and reduced platinum. In common with all the soluble salts to be described, it has an exceedingly nauseous taste, and the colour is so intense, that one drop of a saturated solution will give a distinct yellow tinge to a gallon of water.

A pure solution does not strike a blood-red colour with sesquichloride of iron; but such a mixture becomes nearly black and opaque on heating, from the formation of a substance in heavy lustrous grains. Caustic potassa converts the red salt into a red gelatinous mass, without evolution of ammonia, which, however, is freely disengaged on ignition with soda-lime. Acted on by hydrosulphuric acid, the salt is resolved into hydrosulphocyanic acid, sulphocyanide of potassium, and bisulphide of platinum. It is also decomposed by concentrated sulphuric and hydrochloric acids. The action of nitric acid will be afterwards referred to.

The dry salt is quite permanent at ordinary temperatures; but from its inability to bear a high degree of heat without decomposition, most of the compounds to be described were dried *in vacuo* over sulphuric acid, previous to analysis.

The potassium was separated by precipitating the new acid with nitrate of silver. After removing the excess by hydrochloric acid, the alkali was weighed in the form of chloroplatinate of potassium.

The platinum was determined by igniting the bisulphide, precipitated by sulphide of ammonium.

The carbon was estimated by burning the substance in a stream of air and oxygen, observing the usual precautions for absorbing traces of nitrous and sulphurous acids.

And here I may be allowed to bear a grateful testimony to the readiness and convenience in determinations of this kind, afforded by the gas-furnace for organic analysis, lately constructed and described by Dr. Hofmann. From the abrupt decomposition and presence of both sulphur and nitrogen in the substances to be noticed, their determinations may be said to present more than usual difficulty. Attention, however, to slow burning is all that is necessary in these cases, to procure accurate results. By the simple addition of another tube and piston, nitrogen determinations may be also conducted with great neatness and accuracy.

The sulphur was determined by oxydizing the substance with chlorate of potassa and hydrochloric acid, assisted by gentle heat. Sufficient boiling water was then added to hold in solution any chloroplatinate that might be formed, and the precipitate from chloride of barium was filtered off whilst hot. This method was found to obviate the tedious washings which are necessary when fuming nitric acid or a nitrate is employed. Its substitution is strongly recommended in the analysis of volatile sulphuretted compounds.

I.	0·7554	grm. of substance gave	0·6030	grm. of	chloroplatinate of potassium.
I.	0·7050	„ „ „	0·2230	„	platinum.
II.	0·9132	„ „ „	0·2876	„	platinum.
III.	0·5980	„ „ „	0·1900	„	platinum.
I.	1·0900	„ „ „	0·4582	„	carbonic acid.
II.	1·0160	„ „ „	0·4390	„	carbonic acid.
I.	0·7264	„ „ „	1·5705	„	chloroplatinate of ammonium.
II.	1·0044	„ „ „	2·1888	„	chloroplatinate of ammonium.
III.	0·6628	„ „ „	1·4492	„	chloroplatinate of ammonium.
I.	0·5628	„ „ „	1·2600	„	sulphate of baryta.
II.	0·4030	„ „ „	0·9096	„	sulphate of baryta.

The corresponding percentages to these numbers are :

	I.	II.	III.
Potassium	12·73	—	—
Platinum	31·64	31·49	31·77
Carbon	11.64	11·78	—
Nitrogen	13·54	13·56	13·66
Sulphur	30·70	30·96	—

The carbon, nitrogen, and sulphur are therefore in the proportion to constitute three equivalents of sulphocyanogen. Their union with one equivalent of platinum forms the new radical, which takes up another equivalent of potassium in constructing the above salt.

The name proposed for the new substance is *platino-tersulphocyanide of potassium*, and the formula

$$KPtC_6N_3S_6, \text{ or } KPt\,3\,CyS_2.$$

The theoretical and experimental numbers are subjoined:

		Theory.		Experimental mean.
1 equiv. of	potassium	39	12·52	12·73
1 ,,	platinum	99	31·73	31·63
6 ,,	carbon	36	11·53	11·72
3 ,,	nitrogen	42	13·46	13·58
6 ,,	sulphur	96	30·76	30·83
		312	100·00	

There has been, therefore, in the reaction a simple substitution of 3 equivs. of sulphocyanogen for 3 equivs. of chlorine in the chloroplatinate of potassium employed Expressed in equation;

$$K, PtCl_3 + 3\,KCyS_2 = KPt\,3\,CyS_2 + 3\,KCl.$$

An interesting method of controlling this formula presented itself in estimating the quantity of sulphocyanogen in the compound, thus comprising in one analysis the whole of the carbon, nitrogen, and sulphur present. A solution of the salt was precipitated by sulphide of ammonium, and heated on the water-bath until all trace of free ammonia was lost. After adding acetic acid, the bisulphide of platinum was filtered off, and the clear liquid treated with nitrate of silver. The formation of acetate of silver was prevented by addition of a few drops of nitric acid.

0·7150 grms. of substance gave 1·1275 grms. of sulphocyanide of silver, equiv. to 0·3999 grms. of sulphocyanogen. Calculated for 100 parts.

	Required.	Found.
3 equivs. of sulphocyanogen	55·76	55 90

We may therefore safely infer the correctness of the following equation:

$$K, PtC_6N_3S_6 + 2\,NH_4S = PtS_2 + KCyS_2 + 2(NH_4CyS_2).$$

Subplatino-tersulphocyanide of mercury appears immediately as a copious curdy precipitate on adding nitrate of suboxide of mercury to a solution of the new potassium salt. It is of a deep orange colour, which changes to a pale primrose-yellow on raising the liquid to ebullition. After washing, it was gathered on a filter, pressed with paper, and dried *in vacuo* over sulphuric acid. Freed from water it will bear a considerable temperature without change. Heated in the air-bath to between 140° and 150° C. it suddenly swells up into a singular metallic and arborescent looking substance, showing some resemblance to coarse tea.* At the same time there is a rush of gas which spontaneously kindles.

No further change is observed up to 250°, but below redness, mercurial fumes and cyanogen gas are liberated; and finally, if exposed in an open crucible, the mass fires like tinder, leaving a residue of platinum.

I. 0·5150 grm. of substance gave 0·1076 grm. of platinum.
II. 1·0010 „ „ „ 0·2120 „ platinum.
III. 0·9734 „ „ „ 0·2052 „ platinum.
IV. 0·9024 „ „ „ 0·2534 „ carbonic acid.

which, expressed in 100 parts, give:

	I.	II.	III.	IV.
Platinum	20·87	21·19	21·08	—
Carbon	—	—	—	7·68

agreeing with the formula:

$$Hg_2\,Pt\,3(Cy\,S_2).$$

		Theory.		Experimental mean.
2 equivs. of mercury		200	42·28	—
1 „	platinum	99	20·95	21·04
6 „	carbon	36	7·61	7·68
3 „	nitrogen	42	8·87	—
6 „	sulphur	96	20·29	—
		473	100·00	

In common with all the examined salts of this series, subplatino-tersulphocyanide of mercury yields by dry distillation in a retort, the

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* I have not been able sufficiently to examine this compound or arrive at any certain formula. I will only mention that 0·7092 grm. gave by ignition 0·1662 grm. of platinum, which is equivalent to 23·49 per cent.

beak of which is placed under water, much bisulphide of carbon. This circumstance, together with the fact verified by experiment, that nitrogen also is a product, explains the brisk evolution of gas, and ready inflammation of the substance noticed above. The nitrogen gas was identified by conducting the reaction in a sealed tube, and subsequently collecting the gas over water.

Platino-tersulphocyanide of Iron.—When a slightly acid solution of sulphate of iron is added to a concentrated solution of platino-tersulphocyanide of potassium, a black crystalline substance falls, which is insoluble in water, and also in alcohol.

Under the microscope, these grains appear as shining six-sided figures with rounded edges. They are not affected by dilute sulphuric, hydrochloric, or nitric acid, but concentrated nitric acid dissolves them with formation of sulphuric acid. A cold solution of potassa converts them into sesquioxide of iron, and a yellow liquid containing platinum and sulphocyanogen.

To estimate the platinum in this salt, a weighed portion was dissolved in *aqua regia*, and after dilution with water, hydrosulphuric acid was passed in excess, and the precipitate ignited. The filtrate treated with ammonia gave the iron as sesquioxide. The other analyses were made in the usual manner, portions from different preparations being employed.

I.	0·9966	grms.	of substance	gave	0·1334	grms.	of sesquioxide of iron.
I.	"	"	"	"	0·3317	"	platinum.
II.	1·0288	"	"	"	0·1426	"	sesquioxide of iron.
II.	"	"	"	"	0·3412	"	platinum.
III.	1·0100	"	"	"	0·1448	"	sesquioxide of iron.
I.	0·9938	"	"	"	0·4321	"	carbonic acid.
II.	1·0513	"	"	"	0·4475	"	carbonic acid.
I.	1·0044	"	"	"	2·1888	"	chloroplatinate of ammonium.
II.	0·5956	"	"	"	1·3360	"	chloroplatinate of ammonium.
I.	1·07172	"	"	"	1·6775	"	sulphate of baryta.

The percentage composition is:

	I.	II.	III.
Iron	9·35	9·51	8·99
Platinum	33·29	33·16	—
Carbon	11·85	11·60	—
Nitrogen	13·50	13·96	—
Sulphur	32·08	—	—

The formula is:

$$FePt\,3CyS_2.$$

The theoretical and experimental numbers are:

	Theory.		Experimetal Mean.
1 equiv. of iron	28	9·30	9·28
1 „ platinum	99	32·90	33·23
6 „ carbon	36	11·96	11·73
3 „ nitrogen	42	13.95	13·73
6 „ sulphur	96	31·89	32·08
	301	100·00	

A substance exactly similar in appearance and general character is produced by substituting the salts of the sesquioxide of iron. It falls, however, only on boiling the mixed solutions. A qualitative examination is all that I have been able to bestow upon this compound.

Platino-tersulphocyanide of Silver is prepared by decomposing a solution of the potassium salt by nitrate of silver. It is a heavy curdy substance, of a deep orange colour, which shrinks and agglutinates into a tenacious mass when boiled in water, but again hardens on cooling. A gentle heat causes the dry salt to swell much, igniting with a blue flame if air be present. It is fusible by the blow-pipe into a metallic bead of platinum and silver, by which behaviour it may be readily distinguished from the mercury salt. When recently precipitated it is soluble in cold ammonia, but decomposition ensues at a higher temperature. Nitric acid also acts energetically upon it with disengagement of binoxide of nitrogen; a yellow substance is thrown down; and sulphuric acid is formed during the reaction.

The behaviour of hot caustic potassa towards the silver salt presented a convenient method of estimating the proportional quantities of the platinum and silver contained. By this treatment, 1 equiv. of platino-tersulphocyanide of silver is resolved into 3 equivs. of sulphocyanide of potassium, with precipitation of binoxide of platinum and oxide of silver in the form of a black heavy powder.

$$\mathrm{Ag, Pt\,3(CyS_2) + 3\,KO = 3\,(K, CyS_2) + PtO_2 + AgO.}$$

0·6513 grm. of substance gave by igniting the oxides:
0·3538 „ platinum and silver.
0·9038 „ substance gave by ignition in oxygen and air:
0·3061 „ of carbonic acid.

This accords with the above formula for the silver-salt, thus:

	Theory.		Found.
1 equiv. of silver	108	54·33	54·32
1 „ platinum	99		
6 „ carbon	36	9·44	9·10
3 „ nitrogen	42	11·12	—
6 „ sulphur	96	25·11	—
	381	100·00	

Here it may be mentioned that the platino-tersulphocyanides, in many respects, bear a strong resemblance to the sulphocyanides. As an example, it may be noticed that both their silver salts form double crystallizable compounds with sulphocyanide of potassium. The parallellism of these two substances is further carried out in their immediate decomposition by dilution with water. In the case of the double sulphocyanide of silver and potassium, a simple separation of the two salts takes place, every trace of silver being thrown down as sulphocyanide. In the double platinum compounds, the reaction consists in a transfer of the potassium to the platinum acid, and precipitation of the silver as sulphocyanide. This last substance (the product of the latter experiment), was identified by analysis, as well as by a careful examination of its properties.* The clear red liquid filtered from the precipitate consisted of a solution of platino-tersulphocyanide of potassium. Expressed by an equation, it stands thus:

$$\mathrm{Ag\ Pt\ 3\ (CyS_2) + KCyS_2 = AgCyS_2 + KPt\ 3\ (CyS_2).}$$

Platino-tersulphocyanide of silver is insoluble in an excess of platino-tersulphocyanide of potassium.

Platino-tersulphocyanide of Lead.—This is a remarkably beautiful substance, thrown down in the form of innumerable golden plates, on uniting the concentrated solutions of acetate of lead and platino-tersulphocyanide of potassium. The crystals, which are minute, but

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* I. 0·8594 grm. of precipitate, burnt in oxygen and air, gave:
0·2164 „ carbonic acid, or 6·87 per cent of carbon.
II. 0·8548 „ precipitate, burnt in oxygen, &c.. gave:
0·2196 „ carbonic acid, or 6·99 per cent of carbon.

Sulphocyanide of silver requires:

	Calculated.	Experimental mean.
Carbon	7·23	6·94

very regular hexagons, are soluble in alcohol, but less so in cold water, with which they should be well washed on the filter for purification, as recrystallization from a hot solution does not offer a good method, from the speedy deposition of sulphate of lead and disengagement of hydrosulphocyanic acid: an explanation of this decomposition will be offered when we treat of the salts of the next series. The general properties of platino-tersulphocyanide of lead are such as might have been anticipated from the examination of the iron and silver compounds, and leave no doubt of its composition. Attempts were made to obtain analytical numbers, but from the difficulty of procuring the substance chemically pure, they are not sufficiently accurate for insertion.

A subsalt of a brilliant red colour, insoluble in water and in alcohol, is precipitated on substituting the subacetate of lead for the neutral acetate. Its ready solubility in dilute nitric or acetic acid presented the most ready method of estimating the lead in combination, by precipitation as sulphate.

0·5000 grm. of substance gave 0·3100 grm. of sulphate of lead, equivalent to 42·36 parts of lead in 100.

If reliance may be placed upon this single analysis, it satisfactorily points to the basic sulphocyanide of lead as its analogue. The formula for the new compound thus would be:

$$\mathrm{Pb, Pt\ 3(CyS_2) + PbO}$$

which requires for:

	Theory.	Experiment.
2 equivalents of lead	43·36	43·46

A substance, similar in properties, but much paler in colour, may be procured by the addition of ammonia (not in excess) to the solution of platino-tersulphocyanide of lead.

Hydroplatino-tersulphocyanic acid is most conveniently procured by precipitating a warm concentrated solution of platino-tersulphocyanide of lead by sulphuric acid. The filtrate, which is of a fine red colour, contains the new acid, which is capable of forming all the salts above described, and deports itself in the usual manner of a true acid. From its deep hue, it can be scarcely proved to redden litmus paper, but it presents a decided sour, and then very rough taste to the tongue. It freely displaces carbonic acid from the alkalies, and dissolves metallic zinc with liberation of hydrogen and production of a bright yellow insoluble compound hitherto unexamined. When concentrated on the water-bath, decomposition speedily commences; and on approaching dryness, a brown amorphous mass, very rich in platinum, remains in the dish. By gentle distillation, an acid liquid passes over in considerable quantity, accompanied with the odour of hydrocyanic acid. The distillate furnished with nitrate of silver a copious white precipitate, which on examination proved to be a mixture of cyanide and sulphocyanide of silver. The aqueous and alcoholic solutions of this acid undergo exactly similar reactions at ordinary temperatures, and for this reason I have hitherto failed in procuring the acid in the solid state. By rapid evaporation in the air-pump over sulphuric acid, a confused semi-crystalline mass was obtained; but this gave very little hope of furnishing numbers likely to prove the exact constitution of the acid in its solid condition.

Platino-tersulphocyanide of Barium is a deep red substance, crystallizing in long flattened prisms, or in broad laminæ, often of considerable size. Obtained by dissolving three parts of dry platino-tersulphocyanide of potassium in the solution of one part of chloride of barium in water, or, as an excess of the latter is desirable, it may be in the proportion of nine to four. After evaporation at a gentle heat, the mass may be extracted with hot alcohol, which dissolves nothing but the new salt. It does not appear to be so stable as the potassium-compound.

Platino-tersulphocyanide of Ammonium.—The preparation of this salt by direct union of the acid and base is difficult; that by double decomposition, however, is very convenient. One part of dry sulphate of ammonia may be boiled for a few minutes in a moderately strong solution of 3·5 parts of platino-tersulphocyanide of potassium. The new salt, on cooling, may be separated from the sulphate of potassa and sulphate of ammonia, the last of which is purposely in excess, by alcohol. Another solution in hot water is requisite to obtain it pure, from which the new substance is produced in beautiful crimson hexagonal plates, in figure much resembling the potassium-salt. It is quite stable at ordinary temperatures, but the odour of sulphocyanic acid is readily perceived on boiling the aqueous solution. It gives all the reactions of the potassium-salt.

0·5121 grm.	of substance,	dried *in vacuo*, gave	0·1750	grm.	of platinum.
0·8615	„	„	burnt in oxygen and air	0·3838	„	carbonic acid.
„	„	„	burnt in oxygen	0·1212	„	water.

clearly indicating the formula:

$$NH_4, Pt\,3CyS_2.$$

The theoretical and experimental numbers are :

		Theory.		Experiment.
1 equiv. of	platinum	99	34·02	34·17
6 ,,	carbon	36	12·37	12·14
4 ,,	hydrogen	4	1·38	1·56
4 ,,	nitrogen	56	19·24	—
6 ,,	sulphur	96	32·99	—
		291	100·00	

Platino-tersulphocyanide of Sodium is best procured by precipitating the lead-salt with sulphate of soda. It readily crystallizes in broad garnet-coloured tables, which are soluble in alcohol and in water.

Platino-tersulphocyanide of Copper is precipitated by mixing solutions of sulphate of copper and platino-tersulphocyanide of potassium. It first appears of a brickdust-red colour, which speedily changes at the boiling-heat of the liquid to a black insoluble powder. It gives a fine green solution with ammonia, but the addition of hydrochloric acid reproduces the copper-salt of a dark brown tint.

General remarks upon the foregoing compounds are perhaps better deferred until something has been said with reference to the members of another series which have arisen from the search after analogous compounds to be obtained from protochloride of platinum. I proceed, therefore, to the consideration of:

Platino-bisulphocyanide of Potassium.—Sulphocyanide of potassium dissolves protochloride of platinum with the production of great heat. A red liquid is formed, which by gentle evaporation yields crude crystals of a substance showing in a less marked degree the characteristics of the former group. As in the last case, the best method for procuring it consists in acting upon the double-salt of protochloride of platinum and chloride of potassium (chloroplatinite of potassium*) with sulphocyanide of potassium. They may be taken in equal parts, provided the latter contains no carbonate of potassa or other impurity. It is only necessary that it should be in excess. As the new salt is exceedingly soluble, and crystals are not well obtained by evaporation, the sulphocyanide should be used as a concentrated solution, and not too much of the platinum-salt added at a time, so as to keep the temperature within moderate limits. A

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* This is best obtained by neutralizing the hydrochloric solution of protochloride of platinum with carbonate of potassa.

mass of small needles is deposited on cooling, which should be purified from chloride of potassium by strong alcohol, from which again the salt is best recovered by spontaneous evaporation. After pressing between paper, to remove excess of sulphocyanide of potassium, the salt may be once more obtained by gentle evaporation from an aqueous solution.

The crystals appear in stellar groups, and under the microscope show tapering six-sided prisms of a fine red colour, although not so intense as is observable in the potassium-salt of the prior series. At 60° F. they readily dissolve in 2½ parts of water, but their solubility increases at a higher temperature, and in warm alcohol they are soluble to any extent. They are not deliquescent, neither are they, when perfectly dry, apparently affected by a temperature of 100° C.; nevertheless, for analysis, it was preferred to dry them over sulphuric acid in the usual manner.

Nothing worthy of remark is to be observed with reference to the method of obtaining the numerical details here appended.

0·0132 grm. of substance gave, by igniting the precipitate from sulphide of ammonium :
0·3920 „ platinum. The filtrate, evaporated with sulphuric acid, gave :
0·3455 „ sulphate of potash.
1·0055 „ substance, ignited in air and oxygen, gave :
0·3446 „ carbonic acid.
0·7060 „ substance, ignited with soda-lime, gave :
1·2000 „ chloroplatinate of ammonium.
0·5140 „ substance, digested with chlorate of potash and hydrochloric acid, gave :
0·9540 „ sulphate of baryta.

The numbers, for 100 parts, give results which agree most nearly with the formula :

$$KPtC_4N_2S_4 \text{ or } KPt\,2\,(CyS_2).$$

	Theory.		Experiment.
1 equiv. of potassium	39	15·38	15·27
1 „ platinum	99	38·98	38·78
4 „ carbon	24	9·44	9·34
2 „ nitrogen	28	11·02	10·66
4 „ sulphur	64	25·18	25·44
	254	100·00	

The constitution of this salt is therefore quite in accordance with what might be expected from the modification in its construction, and since 2 equivs. of sulphocyanogen are found to replace 2 equivs. of chlorine, the circumstance may be employed as a distinction in its name. For the compound last-described, I propose the designation *platino-bisulphocyanide of potassium*, and for its corresponding acid, *hydroplatino-bisulphocyanic acid*, which, although not euphonious, has the advantage of expressing the arrangement of its elements.

The solution of the pure salt is orange-red: a port wine colour denotes impurity. It copiously precipitates silver and copper-salts, the former of a pale yellow, the latter of a purple-black. No visible change is produced on the nitrate of the suboxide of mercury, except in giving a red tinge to the liquid; and no characteristic precipitates are formed with nitrate of lead or protosulphate of iron, which behaviour marks it off from the platino-tersulpho-cyanide of potassium, and furnishes some good distinguishing tests. It forms a yellow heavy compound with subacetate of lead, which is readily soluble in acetic and other acids.

Platino-bisulphocyanide of Silver was examined as a control to the formula of the potassium-salt. It is a curdy substance, not unlike sulphocyanide of silver, partially soluble in ammonia, with decomposition. It is soluble in sulphocyanide of potassium, which solution appears to undergo the same change on dilution with water as is observable in the corresponding silver-salt of the previous series.

I.	0·7114	grm.	of substance, dried *in vacuo* and fused with carbonate of soda, gave:
	0·4552	,,	reduced platinum and silver.
II.	0·9518	,,	substance, ignited in air and oxygen gas, gave:
	0·2324	,,	carbonic acid.
III.	1·0137	,,	substance, ignited in air and oxygen gas, gave:
	0·2595	,,	carbonic acid.
IV.	0·6106	,,	substance, ignited with soda-lime, gave:
	0·8316	,,	chloroplatinate of ammonium.
V.	0·4454	,,	substance gave, by ignition with chlorate of potash:
	0·6084	,,	sulphate of baryta.
VI.	0·4494	,,	substance gave, by ignition with chlorate of potash
	0·6360	,,	sulphate of baryta.

Expressed in percentage composition :

	I.	II.	III.	IV.	V.	VI.
Silver Platinum	63·98	—	—	—	—	—
Carbon	—	6·89	6·98	—	—	—
Nitrogen	—	—	—	8·53	—	—
Sulphur	—	—	—	—	19·38	19·41

These indicate the formula :

$$\text{Ag Pt } 2(\text{CyS}_2),$$

as may be seen by comparing the results found, with the theoretical requirements.

		Theory.		Experimental mean.
1 equiv. of silver		108	64·08	63·98
1 ,,	platinum	99		
4 ,,	carbon	24	7·45	6·94
2 ,,	nitrogen	28	8·66	8·53
4 ,,	sulphur	64	19·81	19·40
		323	100·00	

It is scarcely necessary to mention that the salts of both acids form powerful detonating mixtures with chlorate of potassa. The platinotersulphocyanide of silver in particular inflames with the slightest friction in a mortar, accompanied with a bright flame and loud report. Care is therefore necessary in preparing a mixture for analysis by a large dilution with carbonate of soda.

Hydroplatino-bisulphocyanic acid.—This is best procured by a cautious decomposition of the baryta salt with dilute sulphuric acid. The aqueous solution is speedily decomposed by evaporation, even *in vacuo*, during which process there is an oxidation of the sulphur at the expense of the water. A red or yellow insoluble deposit, rich in platinum and hydrosulphocyanic acid, are the principal bodies formed, the former of which will be noticed in treating of the action of oxidizing agents.

This tendency to absorb oxygen has been slightly touched upon whilst remarking the almost spontaneous decomposition of platinotersulphocyanide of lead into sulphate of lead and other products. Some knowledge has been also gained whilst searching for an explanation of the frequent escape of carbonic acid attending the solution of chloroplatinate of potassium in sulphocyanide of potassium.

This effervescence has been traced to the carbonate of potassa, more or less present in the last salt, even when crystallized from alcohol. It was also found that solutions of platino-tersulphocyanide of potassium, assisted by gentle heat, react in a similar manner upon the carbonate with a partial decolorization of the liquid. A red salt crystallizes out, which in no way differs from platino-bisulphocyanide of potassium, whilst the presence of both sulphate and sulphocyanide of potassium is recognized in the filtrate. The first action seems to consist in the partial abstraction of sulphocyanogen from the platino-tersulphocyanide, reducing it to that of the second series. Part of this sulphocyanogen combines with part of the potassium. The sulphur in another equivalent is acted upon by the liberated oxygen, forming sulphate of potassa, whilst the cyanogen is left to combine with the remaining potassium. The carbonic acid escapes as such. This rather complex action may be expressed in an equation which satisfies all the requirements:

$$6\,(\mathrm{K, Pt\ 3Cy\ S_2}) + 8\,(\mathrm{KCO_3}) = 6\,(\mathrm{K, Pt\ 2Cy\ S_2}) + 2\,(\mathrm{KSO_4}) \\ + 5\,(\mathrm{KCy\ S_2}) + \mathrm{KCy} + 8\,\mathrm{CO_2}.$$

A slight modification also represents the change observed in the lead-salt by ebullition with water. The sulphuric acid formed by secondary action isolates the platinum acid:

$$6\,(\mathrm{Pb, Pt\ 3Cy\ S_2}) + 8\,\mathrm{HO} = 6\,(\mathrm{Pb, Pt\ 2Cy\ S_2}) + 2\,(\mathrm{HSO_4}) \\ + 5\,(\mathrm{HCyS_2}) + \mathrm{HCy}.$$

Long-continued boiling of the aqueous solution of platino-tersulphocyanide of potassium furnishes also the same result.

Action of Ammonia upon the platino-sulphocyanides.—The behaviour of this alkali towards these compounds is interesting, and differs materially from that shewn by bases in general or the fixed alkalies. If carbonate of ammonia be added to a cold saturated solution of platino-tersulphocyanide of potassium, the liquid, after the lapse of a few minutes, fades in colour to a pale yellow; an effervescence sets in; and after two or three hours, a considerable quantity of yellow needles radiate in all directions. The same effect is more expeditiously obtained by using caustic ammonia; but in this case it should not be in a state of concentration, as an insoluble yellow substance generally contaminates the product, and much reduces its quantity. These crystals thrown on a filter, may be well washed in cold water, in which they are but little soluble, and dried without heat. If required of great purity, they may be again dissolved in warm alcohol, which takes up more of the substance than water. The crystals obtained by this second operation, however, are never so large, but are of a finer colour. The microscope shews them to be long rhombic prisms. Heated in a dry test-tube, they are resolved into free ammonia, hydrocyanic acid, and with access of air, sulphurous acid and metallic platinum. No trace of bisulphide of carbon could be recognized under this treatment, which is a departure from the behaviour of the platino-sulphocyanides in general, and indicates a separation from the group.

0·4885 grm. of salt dried *in vacuo* gave on ignition:
0·2772 „ platinum.
0·8092 „ salt ignited with oxygen and air gave:
0·1986 „ carbonic acid and
0·1320 „ water.
0·5137 „ salt from another sample gave with soda-lime:
1·3033 „ chloro-platinate of ammonium.
0·4578 „ salt ignited with chlorate of potassa:
0·6192 „ sulphate of baryta.

The formula deduced from the percentage composition is:

$$PtC_2\,H_3\,N_2\,S_2,$$

which requires:

	Theory.		Experiment.
1 equiv. of platinum	99	56·89	56·74
2 „ carbon	12	6·89	6·69
3 „ hydrogen	3	1·74	1·81
2 „ nitrogen	28	16·09	15·89
2 „ sulphur	32	18·39	18·55
	174	100·00	

This substance shows therefore a departure from the general series, and indicates a splitting up into compounds of a different type. An examination of the filtrate, after careful addition of hydrochloric acid, plainly proved that the decomposition so often noticed, here again takes place. It was found to contain sulphate of potassa, sulphocyanide of potassium and ammonium, and cyanide of ammonium. The change in the molecular arrangement is expressed thus:

$$6\,(K, Pt\,3\,Cy\,S_2) + 8\,NH_4\,O = 6\,(Pt\,C_2\,H_3\,N_2\,S_2) + 2\,(KSO_4)$$
$$+ 4\,(KCyS_2) + 2\,(NH_4\,Cy\,S_2) + 5\,(HCy\,S_2) + HCy.$$

The same substance is more readily formed also, by substituting platino-bisulphocyanide of potassium for platino-tersulphocyanide. As the filtrate in this case does not contain a sulphate, the action is very simple:

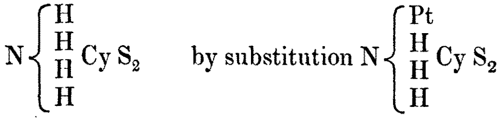
$$KPt\,2\,Cy\,S_2+NH_4\,O=PtC_2\,H_3\,N_2\,S_2+KCyS_2+HO.$$

A preparation was made after the latter method and ignited, when it was found that,

0·4100 grm. of salt gave 0·1986 grm. of platinum.

Theory requires 56·89. Experiment gave 56·68 per cent.

As the probability was against the above formula truly expressing the constitution of the substance, some light was anticipated by a regrouping of its elementary particles. An intelligible form presented itself on considering the hydrogen and part of the nitrogen as ammonia, which its behaviour at a high temperature appeared to justify, and uniting the carbon, sulphur, and the rest of the nitrogen as sulphocyanogen. Taking sulphocyanide of ammonium as the type, and substituting an equivalent of platinum for one equivalent of hydrogen, we then have the *sulphocyanide of platosammonium* (Reiset's first platinum base).



$$N\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right.Cy\,S_2 \quad \text{by substitution} \quad N\left\{\begin{matrix}Pt\\H\\H\\H\end{matrix}\right.Cy\,S_2$$

A ready proof of this supposition presented itself in the direct comparison of the two salts. The preparation of the latter by double decomposition is not difficult. One part of fused sulphocyanide of potassium may be dissolved in water, and 1·6 parts of chloride of platosammonium added. After raising the mixture nearly to the boiling point, an equal bulk of hot alcohol is shaken with the liquid to increase the solubility of the new substance, and the whole is passed, whilst hot, through a filter paper. On cooling, straw-coloured needles are deposited, which exhibit all the properties of the former compound, the identity with which was still further shown by a quantitative analysis.

0·6120 grm. by ignition gave 0·3470 grm. of platinum, representing the formula:

$$PtH_3NCyS_2.$$

The composition for 100 parts requires by theory, 56·89 of platinum; the quantity found was 56·69.

Sulphocyanide of platosammonium is indifferent to the action of dilute sulphuric or hydrochloric acid. The aqueous solution does not affect salts of copper, lead, or mercury, but precipitates nitrate of sulphate of silver as a bulky and pale yellow compound, which is rich in platinum. This precipitate requires more study than has as yet been bestowed upon it. The aqueous solution by long boiling liberates ammonia, and deposits the yellow insoluble substance above alluded to, the composition of which is yet uncertain.* Caustic potassa appears to effect the same change. A temperature between 100° and 110° C. causes the salt to fuse into a clear garnet-coloured syrup, which hardens on cooling, and does not appear to be further affected by a rise to 180° C.

Before dismissing this portion of the subject, there appears to be yet another point of view from which the salt might be regarded. Although no doubt was entertained of the correctness of the last formula, some interest seemed to be attached to the circumstance of its polymerism with another body not hitherto prepared. I have recently had occasion to show that cyanogen gas, acting on oxide of diplatosammonium, produces the platinocyanide of that base, the formula of which is double that assigned by Reiset to the decomposition. The true cyanide of platosammonium, further, may be obtained from the corresponding chloride, by acting with cyanide of potassium. Just in the same manner we might expect a parallelism between platino-bisulphocyanide of diplatosammonium and sulphocyanide of platosammonium. This may be more readily intelligible thus:

$$\underbrace{2(PtH_3N, Cy)}_{\text{Cyanide of platosammonium.}} = \underbrace{PtH_6N_2, PtCy_2}_{\text{Platinocyanide of diplatosammonium.}} \text{ and } \underbrace{2PtH_3N, CyS_2}_{\text{Sulphocyanide of platosammonium.}} = \underbrace{PtH_6N_2, Pt2CyS_2}_{\text{Platino-bisulphocyanide of diplatosammonium.}}$$

Platino-bisulphocyanide of diplatosammonium falls as a voluminous flesh-coloured precipitate, on decomposing the chloride of the base by a soluble platino-bisulphocyanide. It is quite insoluble in water, and also in alcohol. Dilute hydrochloric acid dissolves it rather freely. When heated on platinum foil, it liberates ammoniacal gas, fuses into a black bubbling mass, and then burns tinder-like to a bright platinum sponge.

0·8576 grm. of substance ignited, gave 0·4896 grm. of platinum.
" " " ignited in oxygen " 0·2090 " carbonic acid.
" " " ignited in oxygen " 0·1460 " water.
0·2656 " " ignited with chlorate of potassa and carbonate of soda . . " { 0·1512 " platinum.
" 0·3617 " sulphate of baryta.

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* A well-washed sample gave on ignition as much as 92·27 per cent of platinum. It contains sulphur and the elements of ammonia.

leading to the formula :

$$PtH_6N_2, Pt\,2(CyS_2).$$

The theoretical and experimental numbers are appended.

	Theory.		Mean found.
2 equivs. of platinum	198	56·90	56·94
4 „ carbon	24	6·90	6·65
6 „ hydrogen	6	1·72	1·89
4 „ nitrogen	56	16·09	—
4 „ sulphur	64	18·39	18·62
	348	100·00	

On the action of Chlorine Gas and Nitric Acid upon the Platino-sulphocyanides.—An examination in this direction seemed to be desirable, from the belief that the above decomposition did not show the full extent of oxidation, to which the salts of either series might be carried. When commenting upon the acids, it was mentioned that their aqueous solutions were resolved by heat into a red or brown amorphous substance, hydrosulphocyanic and sulphuric acids. The same brown compound is formed by pouring warm concentrated nitric acid on the powdered potassium salts. Experiment also proved that if a warm and rather concentrated solution of platino-tersulphocyanide of potassium be subjected to a stream of chlorine, the temperature rises considerably during the absorption of the gas. By decomposition of water, the chlorine passes into hydrochloric acid, and the liberated oxygen converts the greater part of the sulphur into sulphuric acid. The first of these acids may be removed by evaporation on the water-bath, and the latter, after careful neutralization with carbonate of soda, by a thorough washing with hot water, which at the same time carries off the whole of the potassa as bisulphate.

During evaporation, the odour of hydrocyanic acid is very perceptible. The new substance on the filter appears of all shades of colour, from a bright red to a dirty brown. It may be dried at a gentle heat, and then has the form of a light non-crystalline powder, strongly soiling the hands, insoluble in water and in alcohol, but before drying slightly soluble in hydrochloric acid. It is unaffected by a solution of potassa, but ammonia changes its colour to a yellow hue.

When ignited in a close crucible, vapours of bisulphide of carbon and cyanogen gas are disengaged, and the solid residue consists of bisulphide of platinum. The action of concentrated nitric acid is quite similar. Hydrocyanic acid and nitrous fumes are given off, and in general the insoluble residue is produced of a brighter colour.

The following numbers were obtained on its analysis:

0·3700	grm. of substance	ignited	gave	0·2304	grm. of	platinum.
0·8964	„	burnt in oxygen	„	0·2800	„	carbonic acid.
„	„	burnt in oxygen	„	0·0320	„	water.
0·7334	„	burnt with soda-lime	„	1·1600	„	chloroplatinate of ammonium.
0·5146	„	burnt with chlor. of potassa	„	0·7048	„	sulphate of baryta.
1·0704	„	a different sample	„	0·6639	„	platinum.
„	„	burnt with oxygen	„	0·3426	„	carbonic acid.
„	„	burnt with oxygen	„	0·0448	„	water.

I regret that I have been unable to prepare this substance in such a state of purity as to place its true composition beyond all doubt. I had anticipated from its mode of formation a substance which bears towards the platino-sulphocyanides, the same relation which the so-called solid sulphocyanogen bears towards the sulphocyanides. If, however, we calculate the water as such, it will give an excess in the experiments of more than 3 parts in the 100 taken; and the discrepancies between the other constituents will be found as great. I am therefore inclined to suppose that the hydrogen is partly accidental, and that as the formula adopted has the recommendation of great simplicity, and satisfies all the conditions observed in the reaction, it will ultimately prove to be correct. I have thought it better, in addition to the theoretical and experimental numbers, to give the ratio in parts of a unit between the component parts, which places their relation in a clearer point of view. The formula of protosulphocyanide of platinum is:

$$PtCyS_2.$$

		Theory.		Found.		Mean.	Ratio.
1 equiv. of	platinum	99	63·05	62·27	62·02	62·14	1·0
1 „	carbon	12	7·64	8·53	8·72	8·62	2·3
1 „	nitrogen	14	8·93	9·92	—	9·92	1·1
2 „	sulphur	32	20·38	18·77	—	18·77	1·9
		157	100·00				
	Hydrogen	.	.	. 0·39	0·15	0·42	0·6
						99·87	

There remains only to show by equation this decomposition by chlorine gas. The reaction is strictly in character with those before noticed.

$$K, Pt\,3\,CyS_2 + 11Cl + 16\,HO = PtCyS_2 + \left.\begin{matrix}K\\H\end{matrix}\right\}2\,SO_4 + 2\,HSO_4$$
$$+ 11HCl + 2\,HCy.$$

The platino-sulphocyanides possess characters so distinct from other salts, that there is no likelihood of confounding them with other known compounds. They are all highly coloured, and take all gradations from pale and bright yellow to deep red. This colour appears attendant, in a great measure, upon the quantity of sulphur combined with the platinum, since the intensity is more remarkable in the first than in the latter series, and is nearly lost in the sulphocyanide of platosammonium.

Their ready inflammability, and peculiar odour when gently heated, may also be considered as characteristic. The separation of the two series is well marked by their different action on reagents, which for better illustration has been arranged in the following table, representing the precipitation or non-precipitation of a soluble salt of each series.

Reagents.	Platino-tersulphocyanides.	Platino-bisulphocyanides.
Subsalts of mercury . . .	Orange precipitate . . .	No precipitate, liquid changes colour on heating.
Salts of silver	Red or orange precipitate	Pale yellow precipitate.
Protosalts of iron	Black shining grains . .	No change.
Salts of copper	Brick-red precipitate . .	Purplish-black precipitate.
Subsalts of copper . . .	Rich brown precipitate .	Purplish-black precipitate.
Salts of cobalt	Orange-red precipitate .	No change.
Salts of lead	Soluble golden laminæ .	No change.
Basic salts of lead . . .	Fine red precipitate . .	Pale yellow precipitate.
Persalts of gold	Salmon-coloured precipitate	Salmon precipitate.
Ferrocyanide of potassium .	Prussian blue formed on boiling	A nearly white precipitate on boiling.
Chromic acid	No precipitate	A copious reddish precipitate, with evolution of hydrocyanic acid.
Salts of platosamine . . .	Copious orange precipitate	Fine yellow precipitate.
Salts of diplatosamine . .	Fine vermilion-red precipitate.	Flesh-coloured precipitate.

The ready conversion of the sulphur in these compounds into sulphuric acid, in presence of water, is shown in an interesting manner by their action upon metallic zinc. Aqueous solutions of the potassa salt are resolved into platinum black, hydrosulphocyanic acid, sulphate of potassa, and free sulphuric acid, which, acting upon the zinc, liberates a considerable quantity of hydrogen gas.

A few general remarks upon the constitution of the platino-sulphocyanides may not be considered here misplaced. Viewing them according to Berzelius's explanation of the ferrocyanides, they must be taken as double compounds of protosulphocyanide and bisulphocyanides of platinum with a metallic sulphocyanide, or hydrosulphocyanic acid;

$$\overbrace{M\ Cy + Pt\ Cy}^{\text{Platino-cyanides.}} \qquad \overbrace{M\ Cy\ S_2 + Pt\ Cy\ S_2}^{\text{Platino-bisulphocyanides.}} \qquad \overbrace{M\ Cy\ S_2 + Pt\ 2\ Cy\ S_2}^{\text{Platino-tersulphocyanides.}}$$

whilst, on the more generally received idea, they contain two separate radicals of acid character, forming salts upon the hydrochloric acid type. The similarity of action between sulphur, oxygen, chlorine, cyanogen, &c., in combination has been frequently remarked. Instances of substitution of sulphur for chlorine may be seen in the reactions of sulphide of potassium upon hydrochloric ether and Dutch liquid.

Throughout this Paper, I have assumed the existence of chloroplatinous and chloroplatinic acids, from the close similarity they bear towards the platino-sulphocyanides; and I think an argument in favour of their existence may be found in the construction of the latter from the former by simple substitution of sulphocyanogen for chlorine. In the same manner we construct the platino-cyanides, by exchanging chlorine for cyanogen, although at present we want the higher number in the series. This will, doubtless, turn up upon a careful search. We have thus:

$$\begin{array}{ccc}
\overbrace{\text{Platino-chlorides or chloro-platinides.}} & \overbrace{\text{Platino-cyanides.}} & \overbrace{\text{Platino-sulpho-cyanides.}} \\
M,\ Pt\ Cl_3 & \text{missing} & M,\ Pt\ 3\ Cy\ S_2 \\
M,\ Pt\ Cl_2 & M,\ Pt\ Cy_2 & M,\ Pt\ 2\ Cy\ S_2
\end{array}$$

Some interest attaches to the new acids from the large number of sulphur-atoms they contain.

Platino-tersulphocyanide of potassium presents, I believe, the first instance of the union of sulphur with the triple cyanogen group, represented by the cyanurates, in which all the oxygen is replaced by sulphur. The analogy is not, however, strict between them, since it will be seen that in the new compounds only 2 equivs. of hydrogen are replaced by metals. The same objection does not apply with reference to the fulminates.

In conclusion, notice should be taken of a crystalline compound described by Claus, which is prepared by acting upon bisulphocyanide of mercury with sulphocyanide of potassium. From the formula given, which is $K\,Cy\,S_2 + 2\,Hg\,Cy\,S_2$, it is clearly a double compound, and therefore has but little resemblance or connection with the substances above described.