59. *Chemical Evidence for the Planar Structure of Plato-tetrammines.*

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A PLATO-TETRAMMINE salt of the form $[Pt(a—b)_2]X_2$, where a—b is a chelate diamine of non-symmetrical outline, should occur in *cis*- and *trans*-forms if the distribution of the four valencies about the platinum atom is planar, but in only one form (resolvable) if the distribution is tetrahedral. Reihlen and Hühn (*Annalen*, 1931, **489**, 42) have investigated several substances of this nature without observing more than one form in each case, and have claimed, moreover, that the tetrammines are resolvable and therefore of tetrahedral structure. On the other hand, Tscherniaev (*Ann. Inst. Plat.*, 1926, **4**, 243) has claimed the isolation of three isomeric plato-salts of the ammine $[Pt\,am\,py(NH_2{\cdot}OH)(NO_2)]Cl$. We thought that a tetrammine of this lower type of symmetry, $[Pt\ a\ b\ c\ d]X_2$, where a b c d are four different amines, would give a more decisive result; but in view of the difficulty of preparing the necessary intermediate triammines, *e.g.*, $[Pt\ a\ b\ c\ X]X$, and of the fact that the tetrammine if planar could exist in three isomeric forms, we decided to examine a tetrammine of the intermediate type, $[Pt(a—b)c\ d]X_2$, which should give two geometrical isomerides if planar but only a racemic form if tetrahedral. *iso*Butylenediamine, $NH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}NH_2$ (designated as ib), was chosen as the chelate grouping, since it is the simplest non-symmetrical chelate diamine which is incapable of becoming dissymmetric even if regarded as co-ordinated to platinum through dissimilar links. Owing again to the difficulty of preparing mixed triammines, it was recognised that the chelate group would necessarily have to be the last to be co-ordinated to the molecule, and that therefore the initial material must be the mixed diammine, Pt c d X_2. We were already aware (J., 1932, 2328) that chelate groupings can be added only to diammines of β-form. Very little is known of mixed β-diammines, and the few representatives of this class have not yet been clearly differentiated from their α-isomerides; but it has now been confirmed that the action of amines on Cossa's potassium salt, a method due to Klason (*Ber.*, 1904, **37**, 1349), gives mixed β-diammines as main products. With ethylamine (ae), $K[Pt(NH_3)Cl_3]$ gave β-*amminoethylaminoplatinous chloride*, Pt am ae Cl_2 (am = NH_3), a well-defined substance having a definite m. p. This diammine was shown to be of β-structure by coupling it with chelate diamines, mixed tetrammines (see later) being produced, whereas the corresponding α-*amminoethylaminoplatinous chloride*, which was prepared by the action of hydrochloric acid upon β-*diamminobisethylaminoplatinous chloride*, [Pt am_2ae_2]Cl_2 (from β-Pt am_2Cl_2 and ethylamine), lost both ammonia and ethylamine when treated with a chelate diamine, giving only a bischelate tetrammine.

When β-Pt am ae Cl_2 was treated with 1 equiv. of *iso*butylenediamine, it gave a mixture of two isomeric plato-tetrammines which were separated by fractional crystallisation; analysis showed that each was anhydrous and had the formula [Pt am ae ib]Cl_2; they were sharply distinguished both in crystalline form and in solubility. The less soluble form, α-*amminoethylamino*iso*butylenediaminoplatinous chloride*, gives a *plato-salt*, α-[Pt am ae ib]$PtCl_4$, in thin silver-pink plates; the β-tetrammine, which is about four times as soluble as its α-isomeride in 96% alcohol, gives a more soluble β-*plato-salt* of chamois shade, forming bundles of woolly needles. The isomeric plato-salts, like the parent tetrammines, are readily distinguishable by inspection; they can be repeatedly crystallised without alteration from dilute hydrochloric acid, in which the α-salt forms a solution of markedly deeper colour; both plato-salts are anhydrous.

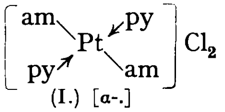
In view of this result, we re-examined Reihlen's [Pt ib_2]Cl_2, and found that here again the plato-tetrammine consisted of a mixture of two well-defined isomerides, whether it was prepared from potassium chloroplatinite and 2 mols. of base, from α-Pt am_2Cl_2 and 2 mols. of base, or from iso*butylenediaminoplatinous chloride*, Pt ib Cl_2 (from potassium chloroplatinite and the diamine), and 1 mol. of base. From 96% alcohol the less soluble isomeride, α-*di*iso*butylenediaminoplatinous chloride*, forms large rhombic tablets of the *dihydrate*; it yields a *plato-salt*, α-[Pt ib_2]$PtCl_4$, consisting of square tablets of nacreous deep-chamois shade. The β-*tetrammine*, which is about twice as soluble as its isomeride in 96% alcohol, forms woolly bundles of thin needles consisting of the monohydrate and gives a more soluble β-*plato-salt* in compact complex prismatic crystals of deep pink shade. The isomeric plato-salts are again easily distinguishable by eye, and are unaltered by repeated crystallisation; both are anhydrous.

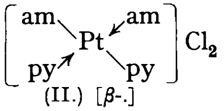
The existence of these two pairs of isomeric plato-tetrammines and of their plato-salts, already briefly reported by us (*Nature*, 1933, **132**, 210), could conceivably be explained on one of the following hypotheses as alternative to the planar theory: (*a*) that each pair of isomerides includes a planar and a tetrahedral form; (*b*) that both isomerides of a pair are either *cis*- or *trans*-planar, the isomerism being occasioned by the manner of location of the positive charges.

To test the matter, the following interactions, each of which could give a pair of isomeric tetrammines if hypothesis (*a*) were true, have been examined: (1) ethylenediamine (en) and β-Pt am ae Cl_2, which gave *amminoethylaminoethylenediaminoplatinous chloride*, [Pt am ae en]Cl_2; (2) ethylenediamine and β-Pt am py Cl_2, which gave *amminopyridinoethylenediaminoplatinous chloride*, [Pt am py en]Cl_2; (3) ethylamine and α-Pt am py Cl_2, which gave α-*amminopyridinobisethylaminoplatinous chloride*, [Pt am py ae_2]Cl_2. In each case only one tetrammine could be isolated, and the product gave a single *plato-salt* with potassium chloroplatinite. The action of *iso*butylenediamine upon β-Pt am_2Cl_2 likewise gave rise to a homogeneous product, [Pt am_2ib]Cl_2, which was characterised as its *plato-salt*. There is, therefore, good reason for rejecting hypothesis (*a*).

If hypothesis (*b*) were true, a much closer relationship than that actually found might be expected to subsist between the members of a pair of isomerides; *e.g.*, electromorphs would probably be to some extent interconvertible (whereas we have not found any signs of interconversion), and would probably also possess similar crystalline structures and solubilities (whereas marked differences were noted in these respects). Moreover, if the isomerism were due to stable and easily distinguishable electromorphs, it might be expected to be found also in some of the cases (1)—(3), above.

Still another alternative hypothesis might arise from the suggestion of Rosenblatt and Schleede (*Annalen*, 1933, **505**, 51), who postulate that [Pt en_2]Cl_2 could exist in four forms, planar with respect to the arrangement of the four nitrogen atoms about platinum, but comprising modifications of the five-membered rings on a supposed analogy with the Sachse models for *cyclo*hexane rings; in the case of [Pt ib_2]Cl_2, this would mean that eight forms are possible, four being dissymmetric. Apart from the fact that there is no evidence for the existence of this complexity of forms, we think that the hypothesis can be rejected on the ground that there is no experimental support for the occurrence of biplanar forms of five-membered ring compounds. It is concluded that the observed isomerism is due solely to the planar distribution of the amine groupings about the platinum atom. This probably means that all of the known plato-tetrammines are of planar type. It is shown in this paper that chelate diamines readily become added to β-Pt am py Cl_2 to form mixed plato-tetrammines without displacement of pyridine or ammonia, but that in the case of α-Pt am py Cl_2 complete displacement of these groups occurs with formation of bischelate plato-tetrammines. Hence it follows that α-Pt am py Cl_2 is a *trans*-compound, and since this substance is produced by removing ammonia and pyridine (by means of hydrochloric acid) from β-[Pt am_2 py_2]Cl_2, the latter must have formula (II), and its α-isomeride must thus have formula (I). These configurations, as is well known, are in agreement with the common methods of producing these tetrammines, through the action of amines (ammonia or pyridine) on the four unmixed α- and β-plato-diammines. There is analogy between (I) and (II), on the one hand, and α- and β-[Pt ib_2]Cl_2 on the other, both in the order of solubility of the plato-tetrammines and of their plato-salts and in the colour of the latter; in each pair, the more soluble plato-tetrammine forms a pink plato-salt and the less soluble a chamois-yellow plato-salt, which likewise is less soluble than its isomeride. For this reason it is concluded that formulæ (III) and (IV) represent α- and β-[Pt ib_2]Cl_2, respectively. In the case of α- and β-[Pt am ae ib]Cl_2, it is not yet possible to decide with any certainty which isomeride has formula (V) and which has (VI).


(I.) [α-.]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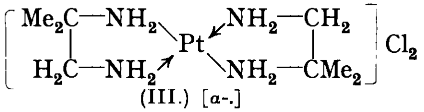
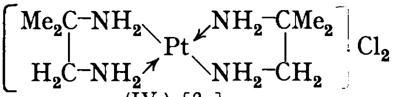

(III.) [α-.]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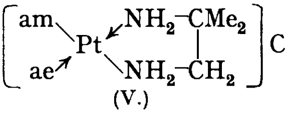
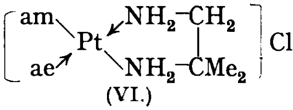

(V.)


(VI.)

In previous papers on plato- and pallado-ammines (J., 1932, 988, 1004, 1895, 2328, 2975; 1933, 1294, 1335) the stereochemical definition of the α- and β-pairs of positions was left open until more information should be available. From this and the previous paper (Drew and Wyatt, this vol., p. 56) it will be clear that the α- have now been shown to be *trans*- and the β- to be *cis*-pairs of positions in the plane of the metallic atom. In the graphical formulæ of the above series of papers, therefore, the groups shown in α-positions (written there as horizontal pairs) may now be transferred to the pairs of diagonal corners of the quadrilateral figures. In the present paper, the positive charges of the tetrammines are shown, formally, in α- (or *trans*-)positions, arbitrarily selected in some of the cases; the work here described does not bear directly on this question.

EXPERIMENTAL.

α-*Amminoethylaminoplatinous chloride*, Pt am ae Cl_2, was prepared by heating β-[Pt am_2ae_2]Cl_2 (from β-Pt am_2Cl_2 and ethylamine) with concentrated hydrochloric acid. It forms a bright yellow, crystalline powder, m. p. 215—216° (decomp.) (Found : Pt, 59·65, 59·05. $C_2H_{10}N_2Cl_2Pt$ requires Pt, 59·45%). It dissolves in hot aqueous *iso*butylenediamine with production of a mixture of α- and β-[Pt ib_2]Cl_2, ammonia and ethylamine being displaced (distinction from β-Pt am ae Cl_2). The crystals of α-Pt am ae Cl_2 are always ill-defined, and it is unusually easily soluble in water for an α-diammine; it seems probable that a proportion of γ-diammine is present.

β-*Amminoethylaminoplatinous chloride* was prepared by the action of a slight excess of aqueous ethylamine on 6·5 g. of Cossa's potassium salt, [Pt am Cl_3]K, in water (50 c.c.); after 1 day at room temperature, the precipitate was separated, dissolved in hot water, the solution filtered from a little green material, and a little hydrochloric acid added to the filtrate, from which small transparent faintly yellow rhombic plates (2·9 g., 58% yield) separated. The substance melts at 206° and at 196° when recrystallised respectively from dilute hydrochloric acid and water; admixture with the α-isomeride produces a marked depression of m. p.; it gives no coloration with phenoxtellurine dibisulphate (Found : C, 7·4; H, 3·3; N, 8·3; Pt, 59·45, 59·25, 59·45. $C_2H_{10}N_2Cl_2Pt$ requires C, 7·3; H, 3·05; N, 8·5; Pt, 59·45%). In the above reaction there is produced also another substance which is under examination.

α-*Amminoethylaminoplatinic chloride*, Pt am ae Cl_4, was obtained either by evaporating the mother-liquor from the above preparation or by oxidising the preceding compound with hydrogen peroxide and hydrochloric acid; it forms square-ended, bright yellow needles, darkening and then melting at 238° (Found : Pt, 48·1. $C_2H_{10}N_2Cl_4Pt$ requires Pt, 48·85%). This substance combines with α-Pt am ae Cl_2 at 210° to form a red crystalline substance, probably (Pt am ae Cl_3)$_2$.

α-Diamminobisethylaminoplatinous chloroplatinite (from α-Pt am_2Cl_2, ethylamine, and then potassium chloroplatinite) formed long, flat, dichroic (blue-green) needles from dilute hydrochloric acid, m. p. 211° (decomp.). The β-plato-salt, similarly obtained from β-Pt am_2Cl_2, formed very long, dull-green needles, m. p. 202° (decomp.), from dilute hydrochloric acid (Found : Pt, 59·3. Calc. : Pt, 59·45%).

iso*Butylenediamine and* β-*Amminoethylaminoplatinous Chloride*.—A number of experiments were carried out, all giving similar results; *e.g.*, 4·0 g. of β-Pt am ae Cl_2 were suspended in water and treated with 3·5 c.c. of 40% *iso*butylenediamine solution, the volume being made up to 40 c.c. with water; the solid dissolved during 12 days at room temperature; the solution was allowed to evaporate over phosphoric oxide, and the residue extracted with hot alcohol, which effected a rough separation of α- and β-[Pt am ae ib]Cl_2, the former being much less soluble. The residue from the extraction was fractionated from alcohol–water, giving finally the pure α-isomeride, and the residue obtained on evaporating the alcoholic extract (above) gave the pure β-isomeride when crystallised repeatedly from 96% alcohol. The isomerides appeared to be present in nearly equal proportion, but the α-isomeride, owing to its smaller solubility, was usually isolated in larger yield (25—45%) than the β-isomeride (20—25%). The total yield of the mixture was nearly quantitative. Analysis of the various fractions for platinum showed that the composition remained unaltered throughout.

α-*Amminoethylamino*iso*butylenediaminoplatinous chloride* (V or VI) separates from 96% ethyl alcohol in colourless glassy crystals, which often appear as square blocks or as hexagonal tablets, but may develop to a more complex form. Like its isomeride, it is anhydrous and it dissolves readily in cold water (Found : C, 17·5; H, 5·45; N, 13·45; Cl, 16·9, 16·75; Pt, 46·65, 46·7. $C_6H_{22}N_4Cl_2Pt$ requires C, 17·3; H, 5·3; N, 13·45; Cl, 17·05; Pt, 46·9%). It forms a *plato-salt*, which separates from dilute hydrochloric acid in thin nacreous silver-pink rhombic or hexagonal plates which appear to be dichroic (Found : C, 10·6; H, 3·35; Pt, 56·7. $C_6H_{22}N_4Cl_4Pt_2$ requires C, 10·55; H, 3·25; Pt, 57·2%).

β-*Amminoethylamino*iso*butylenediaminoplatinous chloride* (VI or V) separates from 96% ethyl alcohol, in which it is about four times as soluble as the α-isomeride, in colourless, spear-shaped, rhombic crystals which may develop to forms with hexagonal or octagonal outlines; more perfect crystals seem to be rectangular prisms terminating in truncated square pyramids (Found : C, 17·45; H, 5·5; N, 13·6; Cl, 16·7, 17·0, 17·0; Pt, 46·8. $C_6H_{22}N_4Cl_2Pt$ requires C, 17·3; H, 5·3; N, 13·45; Cl, 17·05; Pt, 46·9%). Its *plato-salt* separates from dilute hydrochloric acid, in which its solution is markedly less coloured than an equivalent solution of the α-isomeride, in woolly masses of long thin chamois-coloured needles (Found : C, 10·6; H, 3·5; Pt, 56·75, 56·8. $C_6H_{22}N_4Cl_4Pt_2$ requires C, 10·55; H, 3·25; Pt, 57·2%). Like its isomeride, this plato-salt is unchanged in colour when dried at 115° during several hours. Both of these isomeric plato-salts have marked solubility in hot water but tend to decompose unless a trace of hydrochloric acid is present.

Amminoethylaminoethylenediaminoplatinous chloride, [Pt am ae en]Cl_2, was prepared by the action of aqueous ethylenediamine on β-Pt am ae Cl_2 at room temperature (6 days); fractionation showed that only one tetrammine was present (Found : Pt, 50·3. $C_4H_{18}N_4Cl_2Pt$ requires Pt, 50·25%); it formed prismatic needles and gave a plato-salt in bundles of small violet needles.

β-Amminopyridinoplatinous chloride was prepared by the action of 1 equiv. of aqueous pyridine (1) on K[Pt am Cl_3] at room temperature (1 day), the precipitate being purified by crystallisation from hot water (yield of pure substance usually 20—25%); or, less suitably, (2) on Pt am Cl_2 (see later) in hot aqueous suspension. The diammine separates from water in yellow ill-defined crystals, which give only a very feeble brownish coloration with phenoxtellurine dibisulphate (Found : C, 17·1, 17·0; H, 2·25, 2·3; Pt, 53·95, 53·7. Calc. : C, 16·6; H, 2·2; Pt, 53·9%).

Amminopyridinoethylenediaminoplatinous chloride, [Pt am py en]Cl_2, from aqueous ethylenediamine and β-Pt am py Cl_2, crystallised as *monohydrate* from aqueous alcohol in rectangular prisms (Found : Pt, 44·4, 44·5. $C_7H_{18}ON_4Cl_2Pt$ requires Pt, 44·3%). It gives a *plato-salt*, which crystallises from water in large red rectangular plates (+ $1H_2O$) (Found, in hydrated salt : Pt, 55·5. $C_7H_{18}ON_4Cl_4Pt_2$ requires Pt, 55·25%. Found, in dried salt : Pt, 56·5. $C_7H_{16}N_4Cl_4Pt_2$ requires Pt, 56·7%). The above tetrammine was always accompanied by a small proportion of [Pt en_2]Cl_2, either through a displacement reaction or owing to the presence of some α-Pt am py Cl_2 in the initial material. A separate experiment showed that the action of ethylenediamine on α-Pt am py Cl_2 liberates pyridine and ammonia, giving [Pt en_2]Cl_2 (Found : Pt, 50·7. Calc. : Pt, 50·5%), even when only 1 mol. of ethylenediamine is used (in which case part of the diammine remains unaffected).

α-Amminopyridinobisethylaminoplatinous chloride, [Pt am py ae_2]Cl_2, was prepared from α-Pt am py Cl_2 and aqueous ethylamine (8 days at room temperature); it forms colourless complex prismatic crystals from 96% alcohol or from a little water (Found : Pt, 43·6. $C_9H_{22}N_4Cl_2Pt$ requires Pt, 43·15%). The *plato-salt* forms both a monohydrate, rose-pink, rectangular and hexagonal prisms (Found : Pt, 52·45, 52·5, 52·4. $C_9H_{24}ON_4Cl_4Pt_2$ requires Pt, 52·9%), and anhydrous salmon-pink polyhedral crystals (Found : Pt, 54·0, 54·05. $C_9H_{22}N_4Cl_4Pt_2$ requires Pt, 54·3%), which can be hydrated to the rose form. The case is probably similar to that of β-[Pt am_2dm_2]$PtCl_4$ (see Drew and Wyatt, J., 1932, 2975), in which the physical conditions determine which form is stable; sometimes both forms are initially produced together.

Amminotripyridinoplatinous chloride was obtained, as colourless square or oblong plates (Found : Pt, 36·25. $C_{15}H_{20}ON_4Cl_2$ requires Pt, 36·25%) of the *monohydrate*, by the action of 2 mols. of pyridine on α-Pt am py Cl_2; its plato-salt (+ $1H_2O$) formed very pale pink square plates (see J., 1932, 1014). When only 1 mol. of pyridine was used, the triammine was not obtained, but only the tetrammine together with unchanged diammine.

Isomeric Tetrammines of Formula [Pt ib_2]Cl_2.—A mixture of the two salts was prepared by the action of aqueous *iso*butylenediamine upon (1) α-Pt am_2Cl_2, (2) Pt ib Cl_2, or (3) potassium chloroplatinite. In reaction (1), ammonia was expelled; by fractionation from aqueous alcohol the product was separated into the α- (yield, 27%) and β-tetrammine (yield, 19%); incidentally, β-Pt am_2Cl_2 dissolves in aqueous ib without loss of ammonia, giving a tetrammine which forms a plato-salt, [Pt am_2ib]Pt Cl_4, crystallising in orange-red rhombic plates. Methods (2) and (3), which are similar in effect, are better than (1). The following is one of a number of experiments made : potassium chloroplatinite (5·0 g.), *iso*butylenediamine dihydrochloride (3·88 g.), and the equivalent of potassium hydroxide, were brought together in water (60 c.c.); after 20 hours at room temperature, dissolution of the precipitated Pt ib Cl_2 was effected by heating under reflux (2 hours); the solution was evaporated in a vacuum, and the residue extracted three times with alcohol (50 c.c.). The extracted material, which contained some potassium chloride, was fractionated from alcohol and from various mixtures of alcohol and water, the progress of the separation being followed by observing the crystal forms and the character of the plato-salts prepared from samples of the fractions; in this way, there were obtained the α- (1·79 g. of dihydrate; yield, 31%) and the β-tetrammine (2·0 g. of monohydrate; yield, 36°%); the isomerides are probably present in nearly equal quantities (total yield nearly theoretical). Final purification of the β-form is best effected from 85% alcohol.

*α-Bis*iso*butylenediaminoplatinous chloride* (III) separates from 96% alcohol or from water in large colourless rectangular tablets of the *dihydrate* (Found : Pt, 40·9, 40·8, 40·9; loss at 110°, 7·4. $C_8H_{24}N_4Cl_2Pt,2H_2O$ requires Pt, 40·8; $2H_2O$, 7·5%). The *anhydrous* substance was very sparingly soluble in pure alcohol (Found : C, 21·5; H, 5·5; Pt, 44·55. $C_8H_{24}N_4Cl_2Pt$ requires C, 21·7; H, 5·45; Pt, 44·1%); it was hygroscopic, being converted in air into the monohydrate (1 hour) and then more slowly (12 hours) into the dihydrate. The *plato-salt*, α-[Pt ib_2]$PtCl_4$, separates from hot water containing a little hydrochloric acid in glistening, deep chamois-yellow, square or rectangular plates (Found : C, 13·55; H, 3·5; Pt, 55·05, 55·1. $C_8H_{24}N_4Cl_4Pt_2$ requires C, 13·55; H, 3·4; Pt, 55·1%); like its β-isomeride, it is unchanged by further crystallisation.

β-*Bis*iso*butylenediaminoplatinous chloride* (IV) separates from 96% or 85% alcohol in woolly masses of thin colourless needles of the *monohydrate* (Found : Pt, 42·7; loss at 110°, 3·7, 3·65. $C_8H_{24}N_4Cl_2Pt,H_2O$ requires Pt, 42·4; H_2O, 3·9%). From water it forms a *dihydrate* (Found : loss at 110°, 7·03. $2H_2O$ requires loss, 7·5%). The *anhydrous* substance remained crystalline when obtained from the monohydrate (Found : C, 21·75; H, 5·7; Pt, 44·4. $C_8H_{24}N_4Cl_2Pt$ requires C, 21·7; H, 5·45; Pt, 44·1%); on standing in air, it becomes rehydrated to the monohydrate only (distinction from the α-isomeride). The substance is about twice as soluble as its α-isomeride in 96% alcohol at 15°. The *plato-salt*, β-[Pt ib_2]$PtCl_4$, separates in compact complex polyhedral crystals, which frequently show hexagonal outlines (Found : C, 13·65; H, 3·65; Pt, 55·45, 54·95, 55·1. $C_8H_{24}N_4Cl_4Pt_2$ requires C, 13·55; H, 3·4; Pt, 55·1%); it is rose-pink, and is more soluble than the α-form.

iso*Butylenediaminoplatinous chloride*, Pt ib Cl_2, was prepared by the action of a slight excess of *iso*butylenediamine on aqueous potassium chloroplatinite at room temperature. The substance separated in admixture with the above plato-salts of the bisdiamine, from which it was separated by flotation and then by crystallisation from water. It forms large, sulphur-yellow, square-ended tablets, sometimes with facets (Found : C, 13·7; H, 3·45; Pt, 55·1. $C_4H_{12}N_2Cl_2Pt$ requires C, 13·55; H, 3·4; Pt, 55·1); it is moderately soluble in hot water, and gives no coloration with phenoxtellurine dibisulphate.

Klason's salt, Pt am Cl_2, was prepared as described by him from K[Pt am Cl_3] by means of chloroplatinic acid, and was obtained (yield, 57%) as minute irregular brown dendritic crystals, insoluble in hot water and not purifiable (Found : Pt, 68·15. Calc. : Pt, 68·9%). When dissolved in hot ammonia, it gave β-Pt am_2Cl_2 and [Pt am_4]Cl_2.

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