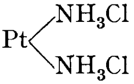
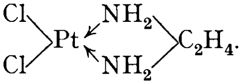
396. *Interpretation of the Phenoxtellurine Dibisulphate Reaction with Platinous Compounds. Micro-analysis of Platinum and Tellurium.*

By H. D. K. Drew.

PHENOXTELLURINE dibisulphate (I) gives intensely purple colorations with a very few plato-diammines of the β-(*cis*-)series, notably with β-diamminoplatinous chloride (Drew, Pinkard, Wardlaw, and Cox, J., 1932, 993); it gives no colour with the γ-isomeride or with α-plato-diammines; the coloration is so sensitive that as little as 0·1% of the β-dichloride can be detected in admixture with either of its isomerides. A number of β-diammino-platinous chlorides, such as those of ethylenediamine and of ethylamine, give no colorations after recrystallisation and only traces of colour when freshly prepared; that of pyridine gives a persistent feeble reddish coloration. Tress, Wyatt, and Drew (J., **1933**, 1338; this vol., p. 56) believed, chiefly for other reasons, that the β-plato-diammines were of two structural types, *e.g.*,



$Pt{<}^{NH_3Cl}_{NH_3Cl}$ and

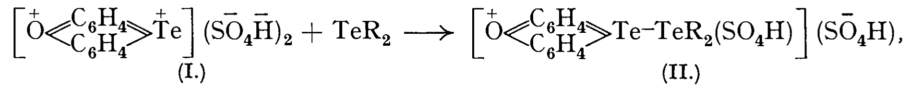


$^{Cl}_{Cl}{>}Pt{\leftleftarrows}^{NH_2}_{NH_2}{>}C_2H_4.$

If this were so, only the β-plato-diammines of the first type would be expected to give colorations with phenoxtellurine dibisulphate, since only these have formulæ completely analogous with those of the tellurides, selenides, and other substances which the author has already shown to give exactly similar colorations with the dibisulphate. Those β-plato-diammines which give only feeble colorations might well be mixtures of the two possible forms, the second form being in excess. Hence it was desirable to obtain experimental evidence of the nature of the coloured platinum complexes.

Black colorations are also given by phenoxtellurine dibisulphate with ammonium or alkali chloroplatinite, and blackish or reddish colorations with the chloroplatinites of plato-tetrammines and -triammines. Plati-ammines or platinic salts never give such colorations, showing that the lower state of valency of the metal in the reactant is essential. In the case of palladium, where the palladic state is not very stable, the ammines do not give colorations and there is only a very feeble coloration with alkali chloropalladites, indicating that a stable condition of the higher state of valency of the metal is also an essential. These facts suggested that when a coloured complex is formed the platinous atoms receive bisulphate radicals from phenoxtellurine dibisulphate and pass into a potentially platinic state by union with tellurium.

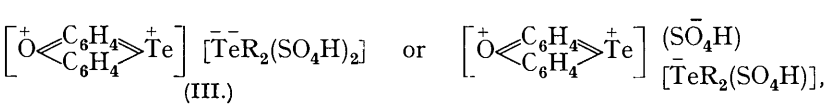
The interaction of the dibisulphate with phenoxtellurine and with other tellurides has been shown (J., 1926, 223, 3054; 1927, 116; 1928, 506, 511) to be based on the following type of reaction :



$$\left[\overset{+}{O}{<}^{C_6H_4}_{C_6H_4}{>}\overset{+}{Te}\right](\overset{-}{SO_4}\overset{-}{H})_2 + TeR_2 \longrightarrow \left[\overset{+}{O}{<}^{C_6H_4}_{C_6H_4}{>}Te{-}TeR_2(SO_4H)\right](\overset{-}{SO_4}H),$$

(I.) (II.)

the requirements for the generation of a purple complex being the lower state of valency of the metalloid in one of the reactants and the possession by at least one of them of a ring structure capable of becoming *o*-quinonoid. The bond between the two metalloid atoms of the coloured complex may be assumed to be covalent as in (II), or electrovalent, giving either



$$\left[\overset{+}{O}{<}^{C_6H_4}_{C_6H_4}{>}\overset{+}{Te}\right][\overset{-}{T}\overset{-}{e}R_2(SO_4H)_2] \quad \text{or} \quad \left[\overset{+}{O}{<}^{C_6H_4}_{C_6H_4}{>}\overset{+}{Te}\right]\begin{matrix}(\overset{-}{SO_4}H)\\ [\overset{-}{T}eR_2(SO_4H)],\end{matrix}$$

(III.)

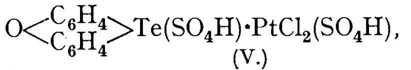
which are phenoxtellurylium salts of the hypothetical acids H_2TeCl_4 and $HTeCl_3$ respectively. The form (II) was preferred for the crystalline complex because the simple aromatic ditellurides, TeR·TeR, are themselves purple (Morgan and Drew, J., 1925, **127**, 2307), whereas the ion $\overset{+}{O}{<}^{C_6H_4}_{C_6H_4}{>}\overset{+}{Te}$ is only red; but tautomerism between the forms (II) and (III), initiated by the tendency of the Te—Te system to ionise to $\overset{+}{Te}$ - - - - - $\overset{-}{Te}$ in the presence of the bisulphate ion, must be assumed in order to account for the changes which take place in solution.

It is now found that the black substance produced when ammonium or potassium chloroplatinite is rubbed with phenoxtellurine dibisulphate is *phenoxtellurylium plato-chloride* (IV; see p. 1792). Although the reaction may be represented simply as a double decomposition (*a*), the preliminary changes of shade indicate that it is probably a complex transformation in which the bisulphate ion migrates to platinum, giving the intermediate (V), and is then replaced by chlorine (*b*) :

$$(a)\quad (\mathrm{I}) + K_2PtCl_4 = 2KHSO_4 + (\mathrm{IV}),$$

$$(b)\quad K_2PtCl_4 \rightleftharpoons 2KCl + PtCl_2,$$

$$(\mathrm{I}) + PtCl_2 =$$



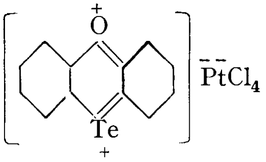
$$O\!\!<\!\!\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}\!\!>\!\!Te(SO_4H)\cdot PtCl_2(SO_4H),$$

(V.)

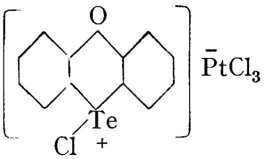
$$(\mathrm{V}) + 2KCl = (\mathrm{IV}) + 2KHSO_4.$$

The black material cannot be recrystallised, but it was shown to be a definite substance by full analysis, by several repetitions of the preparation and purification, and by semi-quantitative examination of its interaction with hydrochloric acid and with aqueous potassium chloride.

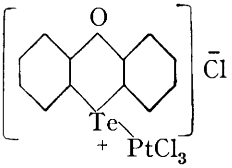
With hydrochloric acid it reacts to give phenoxtellurine dichloride and chloroplatinous acid, whilst with aqueous potassium chloride it decomposes even in the cold into phenoxtellurine dichloride and potassium chloroplatinite. These reactions seem to indicate the presence in (IV) of the ions of formula (IV*A*), but since both these ions are only red, it is difficult to account for the black colour of the solid; hence it must be assumed that this form, if present, is tautomeric with (IV*B*), which represents a salt of the unknown acid $H[PtCl_3]$; for reasons given later, it is at least possible that this acid would be black. Formula (IV*C*) represents a further possible tautomeric form which cannot be excluded; here the black colour could be attributed to the covalency linking Pt with Te (compare the tellurides of platinum).



(IV*A*.)



(IV*B*.)



(IV*C*.)

In (IV*B*) and (IV*C*) the *o*-quinonoid state is assumed absent, since it has never yet been found in the phenoxtellurine series in association with halogen ions. The chloroplatinous acid and alkali chloroplatinite produced in the above reactions gave excellent specimens of the *pink* form of Magnus's salt when treated with aqueous tetrammino-platinous chloride, even in presence of much hydrochloric acid. It is hoped to return to this point in a later paper.

When Magnus's green salt is rubbed with phenoxtellurine dibisulphate, it gives a reaction which, unlike the foregoing, depends upon the conditions; but experiments indicated that a proportion of (IV) was always present in the final product, along with reddish or purplish-red materials. The black substance probably occurs as a result of the tendency of Magnus's salt to dissociate :

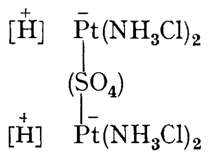
$$[Pt(NH_3)_4]PtCl_4 \rightleftharpoons [Pt(NH_3)_4]Cl_2 + PtCl_2,$$

since the presence of the plato-tetrammine could be demonstrated in the final product, although only in small proportion. A full examination of this complex reaction was not possible owing to the labile nature of the remaining coloured substances.

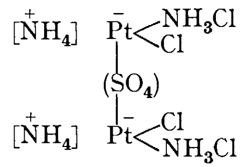
The most interesting of the coloured platinum complexes are the purple products from the β-plato-diammines. The example studied, that from the β-dichloride, proved difficult : for many months the purple complex was fugitive under all attempts to separate it from the associated products, breaking up into black, grey, or colourless materials. However, a method was at length found by which a homogeneous product could always be obtained. Finally, it was found that the purple substance could be dissolved in cold diluted sulphuric acid (75% by vol.) and reprecipitated in pure crystalline condition by cautious addition of water. It is an intensely purple-black substance, having a distinct copper-like bronze. Analysis showed the substance to be $C_{36}H_{40}O_{23}N_4Cl_4S_5Te_3Pt_2$; it was therefore formed from two molecular proportions of the ammine and three of the dibisulphate, with loss of sulphuric acid.

Its constitution was worked out by studying its decomposition with warm glacial acetic acid or, better, with cold acetic anhydride, followed by the action of water on the product. Acetic anhydride at once decomposes the purple complex practically quantitatively into a greenish- or bluish-black substance and phenoxtellurine sulphate and dibisulphate, the latter dissolving as sulphuric acid and phenoxtellurine sulphate. The black substance, when boiled with water, decomposes entirely into sulphuric acid and the original ammine. It was then found that an identical bluish-black material could be prepared by allowing acetic anhydride containing a little sulphuric acid to react upon the ammine. The analyses of these substances pointed to the formula $2Pt(NH_3)_2Cl_2,H_2SO_4$; but neither of the materials was pure, since acetic anhydride tends to abstract sulphuric acid, an equilibrium being set up. The compound was, however, prepared in a nearly pure state by the action of fairly concentrated sulphuric acid upon the ammine; it was then quite black, and when decomposed by hot water or by cold aqueous sodium chloride gave approximately the theoretical quantities of sulphuric acid and ammine. These reactions leave no doubt that the compound is *diamminodichloroplatosulphuric acid* (VI), of which the alkali salts are probably unstable, thus accounting for the decomposition in the presence of ions. The behaviour of the substance precludes the view that it is the ammonium salt of a mixed Cossa's acid (VII).

(VI.)



$$\begin{array}{ll} \overset{+}{[\mathrm{H}]} & \overset{-}{\mathrm{Pt}}(\mathrm{NH_3Cl})_2 \\ & \quad | \\ & (\mathrm{SO_4}) \\ & \quad |^{-} \\ \overset{+}{[\mathrm{H}]} & \mathrm{Pt}(\mathrm{NH_3Cl})_2 \end{array}$$

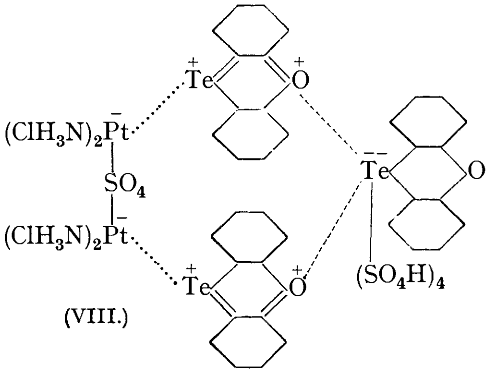


$$\begin{array}{ll} \overset{+}{[\mathrm{NH_4}]} & \overset{-}{\mathrm{Pt}}\!\begin{smallmatrix}\diagup \mathrm{NH_3Cl} \\ \diagdown \mathrm{Cl}\end{smallmatrix} \\ & \quad | \\ & (\mathrm{SO_4}) \\ & \quad |^{-} \\ \overset{+}{[\mathrm{NH_4}]} & \mathrm{Pt}\!\begin{smallmatrix}\diagup \mathrm{Cl} \\ \diagdown \mathrm{NH_3Cl}\end{smallmatrix} \end{array}$$

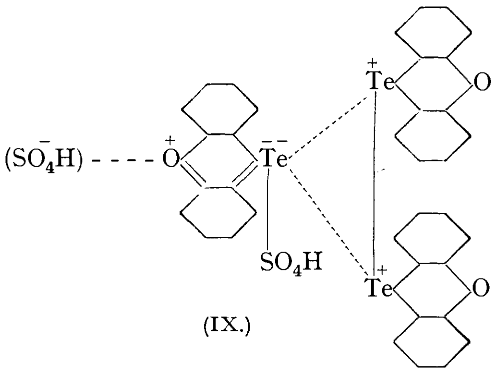
(VII.)

Tschugaev (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 213) records that β-$Pt(NH_3)_2Cl_2$, but not the α-isomeride, gives a dark green, almost black, coloration with concentrated sulphuric acid, and uses the reaction as a test for the β-dichloride. He does not seem to have determined the composition of the coloured substance, but it is evident that his product was an impure sample of (VI). It is remarkable that this substance should be black, but it may be recalled that α-$Pt\,py_2(SO_4)$ is also black in the anhydrous state (Gmelin-Kraut, "Handbuch der anorg. Chem.," Vol. V, Pt. III, p. 553). The simpler acids of this form, $HPtCl_3$ and $H_2[Pt(Cl_2)–SO_4–PtCl_2]$, are unknown; but in this paper the black colour of compound (IV) has already been tentatively ascribed to its being a salt of $HPtCl_3$ (cf. IV*B*).

It was then clear that the purple substance must be a tellurylium salt of (VI), in further combination with a molecule of phenoxtellurine dibisulphate. There are several ways in which this complex could be represented structurally, *triphenoxtellurylium tetrabisulphate diamminodichloroplatosulphate* (VIII) being the most probable. This structure agrees with both the analytical data and the semi-quantitative decomposition reactions; it represents a derivative of the acid H_2TeCl_6, and is thus in accord with the fact that free phenoxtellurine



(VIII.)



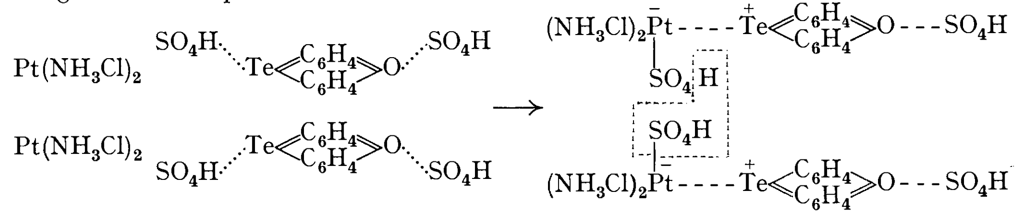
(IX.)

is never produced during the formation or decomposition of the purple substance. It is clear that the platinum atoms in (VIII) are potentially in the platinic state, since the

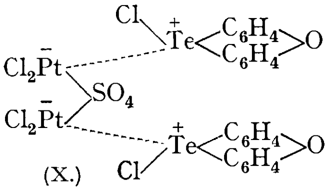
Pt–Te bonds may become covalent if the third phenoxtellurine residue (anion) becomes ionised directly from the remaining pair of tellurium atoms instead of from oxygen.

The substance may be compared with triphenoxtellurylium dibisulphate, likewise purple, which has been shown to be the most stable of the simpler tellurylium salts and may be written as (IX), *i.e.*, as a salt of the acid H_2TeCl_4. It differs from (VIII) in that it is recrystallisable from glacial acetic acid and that when decomposed by water it gives two-thirds of its tellurium as phenoxtellurine.

The formation of (VIII) from β-$Pt(NH_3)_2Cl_2$ and phenoxtellurine dibisulphate can clearly be represented as an initial migration of a bisulphate group from tellurium to platinum in each of two molecules of the plato-diammine, these two bisulphate groups then condensing with loss of a sulphuric acid molecule; free sulphuric acid is, in fact, found among the reaction products :



The addition of the third molecule of the dibisulphate then occurs by an obvious mechanism.



(X.)

In view of the structure of the purple complex, it might be expected that the interaction of alkali chloroplatinite and phenoxtellurine dibisulphate would give rise to the analogue (X), instead of to (IV). Evidence for the presence of this substance was sought, but none was found beyond the detection of traces of sulphur in some of the samples of (IV); probably (X) is an actual intermediate which is changed into (IV) by chloride ions.

It seems clear that the results of the present work support our view that the relationship between the α- and β-plato-diammine dichlorides is not merely that between *trans-* and *cis*-isomerides but is also structural; for, if this be not the case, no explanation of the failure of the α-isomeride to form compounds of the types of (VI) and (VIII) appears possible.

In the course of the present work it was found that phenoxtellurine dibisulphate produces intensely purple complexes with tertiary aromatic phosphines, arsines, and stibines, but not with corresponding amines or bismuthines. The nature of the complexes has not yet been determined.

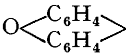
Methods of Analysis.—Owing to the cost of the initial materials, only small quantities of the coloured complexes could be prepared, and their composition had therefore to be determined by microanalysis. Methods were worked out for the determination of platinum and tellurium in the same sample, and also for the determination of chlorine and of sulphur in the presence of these elements. The determination of nitrogen and of carbon required no modification of the ordinary methods. For (VIII) the hydrogen figure was always about 1% high; no explanation of this was obtained, but it is possible that traces of sulphur trioxide may have escaped absorption in the combustion tube. Details of the methods of analysis are given on p. 1796.

[*Note.*—The dotted lines in the formulæ of this paper represent ionised linkings; in some cases the charges are also indicated.]

EXPERIMENTAL.

In all cases the phenoxtellurine dibisulphate used was freshly crystallised from concentrated sulphuric acid, collected upon sintered glass, and drained on porous tile in a desiccator for about an hour.

Phenoxtellurylium Platochloride (IV).—The following is the best method of preparation and purification. Phenoxtellurine dibisulphate (0·6 g.) and potassium chloroplatinite (0·46 g.; 1 mol.) were ground in an agate mortar at intervals during 18 hrs. The mixture became red, maroon, and finally a black paste, containing free sulphuric acid; it was triturated with cold water (7 c.c.) to remove potassium sulphate, chloride, and unchanged chloroplatinite, as well as a little phenoxtellurine sulphate (all of which were identified in the pale yellow washings), and filtered through hardened paper; the black solid was dried over phosphoric oxide (yield 0·65 g.), ground, triturated with concentrated sulphuric acid (5 c.c.) to remove phenoxtellurine dibisulphate, and filtered through alundum; it was then triturated and washed with cold water (9 c.c.), filtered through hardened paper, dried, again ground, and then extracted with boiling glacial acetic acid (40 c.c.) in three portions, with filtration through hardened paper, the acetic acid removing phenoxtellurine dichloride. It was finally dried over powdered sodium hydroxide and phosphoric oxide, ground, and dried in an air stream at 105° to remove traces of acetic acid. An identical product resulted when ammonium chloroplatinite was used (Found: C, 22·85, 22·65, 22·9; H, 1·7, 1·5, 1·6; Cl, 22·65, 22·85; Te, 19·5, 19·4, 19·65, 19·45, 19·3; Pt, 31·25, 31·0, 31·25, 30·85, 30·7, 31·0; C : H : O : Cl : Te : Pt = 12 : 10·1 : 1·02 : 4·04 : 0·965 : 1·00. $C_{12}H_8OCl_4TePt$ requires C, 22·75; H, 1·3; Cl, 22·45; Te, 20·15; Pt, 30·85%). It is a quite black powder, insoluble in acetic anhydride, insoluble in cold concentrated sulphuric acid but decomposed on warming (yellow solution), very sparingly soluble in hot glacial acetic acid (yellow solution), and soluble in but decomposed by acetone (deep yellow solution). Cold water decomposes it only very slowly, but boiling water soon partially decomposes it into platinous chloride, a little hydrochloric acid, and phenoxtellurine dichloride and oxide. Aqueous sodium or potassium chloride decomposes it in the cold, almost quantitatively into phenoxtellurine dichloride and alkali chloroplatinite; use of only 1 mol. of the former in an attempt to obtain $KPtCl_3$ gave instead K_2PtCl_4 and $PtCl_2$. With warm dilute or cold concentrated hydrochloric acid it decomposed into phenoxtellurine dichloride (73·84 mg. gave 42·5 mgm. Calc.: 42·8 mgm.) and chloroplatinous acid [giving 66·9 mgm. of Magnus's salt (Calc.: 70·1 mgm.) when precipitated with $Pt(NH_3)_4Cl_2$]; however, the phenoxtellurine dichloride produced in this and similar experiments was always reddish and impure, but became colourless on recrystallisation from toluene (charcoal), having then the correct m. p. and mixed m. p. (265°, decomp.); on reduction it gave pure phenoxtellurine, m. p. and mixed m. p., 78—79°.

Phenoxtellurine oxide,  $O{<}\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}{>}TeO$, was prepared by grinding the dichloride with excess of silver oxide and water in a mortar for several days; the solid was extracted with boiling water, the extract giving colourless fluffy masses of thin needles which give no coloration with phenoxtellurine dibisulphate (Found: C, 45·65; H, 2·7. $C_{12}H_8O_2Te$ requires C, 46·2; H, 2·6%). When heated it gives phenoxtellurine and, apparently, diphenyl ether.

Preparation of Phenoxtellurine Diacetate.—The following is an improved method: phenoxtellurine (3 g.), dissolved in hot glacial acetic acid (11 c.c.), is treated with 3·4 g. of 10% hydrogen peroxide; heat is liberated and the solution becomes nearly colourless. On cooling, the pure diacetate separates (3·4 g.); a further crop can be obtained from the filtrate. The diacetate was converted into dibisulphate in the way already described (*loc. cit.*).

Triphenoxtellurylium Tetrabisulphate Diamminodichloroplatosulphate (VIII).—Attempts to prepare this substance in the wet way failed or gave rise only to fugitive products. The following method was reproducible: phenoxtellurine dibisulphate (0·5 g.) and β-$Pt(NH_3)_2Cl_2$ (0·25 g.; 1 mol.) were ground in an agate mortar for about 1 hr.; a very dark purple paste was obtained, which was rubbed with about 10 c.c. of cold sulphuric acid (75% by vol.) and filtered through sintered glass to remove grey solid; the clear deep-red filtrate was cautiously treated drop by drop with water, with shaking and cooling, till a purple precipitate commenced to form; it was then set aside in a closed vessel for some hours; the precipitate of minute purple needles was collected on glass or porous porcelain, dried on tile in air (yield, 0·46 g.), and then in a glass dish over phosphoric oxide for some days. At this stage, the substance was sometimes nearly pure (*e.g.*, Found: C, 22·4; H, 2·8; N, 2·9; Te, 19·85; Pt, 19·9%), and sometimes impure (*e.g.*, Found: C, 20·1; H, 2·6; Pt, 21·3%). Final purification was effected by dissolving the substance (0·3 g.) in sulphuric acid (about 5 c.c.; concentration as above), and reprecipitating, collecting, and drying it as before (Found: C, 21·4, 22·15; H, 3·0, 3·1; N, 2·8; Cl, 7·75; S, 8·45; Te, 19·0; Pt, 19·4, 19·15. $C_{36}H_{40}O_{23}N_4Cl_4S_5Te_3Pt_2$ requires C, 21·9; H, 2·05; N, 2·8; Cl, 7·2; S, 8·1; Te, 19·4; Pt, 19·8%). It is a deep purple crystalline substance, appearing almost black when quite dry; it is stable in air when on tile, or in a vacuum over phosphoric oxide when on glass but not when on porous tile. It is hygroscopic; when warmed with water it at once decomposes into phenoxtellurine salts, sulphuric acid, and the original β-ammine, but gives no trace of free phenoxtellurine. With warm glacial acetic acid or with cold acetic anhydride it decomposes rapidly, leaving a greenish- or bluish-black precipitate

(Found: H, 2·75; N, 8·4; Pt, 57·4%) consisting of (VI) mixed or combined with free β-ammine salt; *e.g.*, 79·2 mgm. of air-dried substance gave 23·48 mgm. of the bluish-black substance, and the orange filtrate contained sulphuric acid and phenoxtellurine sulphate. An exactly similar blue-black material was prepared from finely ground β-$Pt(NH_3)_2Cl_2$ and cold acetic anhydride (2 c.c.) to which three drops of concentrated sulphuric acid had been added; it was washed with ether and dried (Found: H, 2·85, 2·55; Cl, 21·3; S, 3·7; Pt, 57·25, 57·85, 57·6, 58·4%); when treated with boiling water or with cold aqueous sodium chloride it decomposed into pure β-ammino-chloride and sulphuric acid [11·7 mgm. required 1·7 c.c. 0·01*N*-Na_2CO_3 (methyl-red). Calc.: 3·4 c.c.]; these results led to the ratios Pt : Cl : N = 1 : 2 : 2, showing that the substance contained about equimolecular proportions of (VI), probably as dihydrate, and β-ammino-chloride. The substance was obtained in a much purer condition as described below, and it was then found to lose sulphuric acid somewhat readily.

Diamminodichloroplatosulphuric acid (VI) was obtained in the form of a black powder when powdered β-$Pt(NH_3)_2Cl_2$ was cautiously warmed with somewhat diluted sulphuric acid, kept under the acid, collected upon glass, and dried upon porous tile over phosphoric oxide. If the acid be too strong, oxidation sets in (odour of sulphur dioxide) and a yellow platinic salt (see below) is produced; the same is true when acetic anhydride is used. However, it has not been possible to obtain the material quite free from the original ammine. After being dried for 2 hrs., it was hygroscopic and then gave: Pt, 52·0%; 58·48 mgm. when decomposed with aqueous sodium chloride gave 37·5 mgm. of analytically pure β-$Pt(NH_3)_2Cl_2$ apart from that dissolved in the filtrate; the filtrate required 13·5 c.c. of 0·01*N*-Na_2CO_3 (Calc.: 15·5 c.c.); after a further 2 days' drying, it gave: H, 2·5; Pt, 53·0%; the dihydrate of (VI) (*i.e.*, $H_{18}O_6N_4Cl_4SPt_2$) requires H, 2·45; Pt, 53·2%; 53·26 mgm. required 11·95 c.c. of 0·01*N*-Na_2CO_3 (Calc.: 14·15 c.c.). These data indicate that some 15% of free β-$Pt(NH_3)_2Cl_2$ was still present in the purest specimen; but the fact that water or the ions of sodium chloride decompose the substance into mineral acid and only the β-plato-diammine proves that no other impurity was present in appreciable amount.

The yellow oxidation product (above) was probably the mixed plati-diammine, $Pt(NH_3)_2Cl_2(SO_4)$ (Found, in crude product: Pt, 50·9. Calc.: Pt, 49·25%). However, on recrystallisation from water, a rearrangement of the acid radicals occurs and β-$Pt(NH_3)_2Cl_4$ separates, probably leaving the plati-sulphate in solution.

Methods of Micro-analysis of Compounds containing Both Platinum and Tellurium.—The Carius method was unsuitable for the determination of either tellurium or platinum, whether silver nitrate was used to remove halogen or not: in the absence of silver nitrate, platinum was partly in solution with the tellurium; in its presence, most of the tellurium remained with platinum in the silver precipitate. In addition, part of the solid material may become firmly attached to the tube and may even colour the glass.

Chlorine may be estimated in these substances by the Carius method, a good excess of silver nitrate being used and the precipitate, tube, glass capsule, and residue from the evaporated liquid being well extracted with ammonia (Drew, Tress, and Wyatt, this vol., p. 1788). No other element was determined simultaneously with chlorine.

Platinum and tellurium were determined simultaneously (compare Scott, "Standard Methods of Chemical Analysis") by mixing the substance in an acorn-sized porcelain crucible with sodium carbonate (2 parts) and sodium nitrate (1 part), surrounding the mass with fusion mixture, placing the crucible on a clean platinum sheet, adjusting the lid, and fusing for ½ hr. to a red heat. After cooling, the fused mass was extracted with warm water, which was then acidified with nitric acid, becoming quite clear; platinum was filtered off on a weighed micro-Gooch filter which had been washed on the same day with hot concentrated nitric acid, and was then washed with 3 c.c. of that reagent. The filtrate was evaporated to dryness on a water-bath in a 50 c.c. beaker protected from dust, the residue dissolved in 10% hydrochloric acid, and 15 c.c. of freshly distilled concentrated acid added, the liquid being then heated during 1 hr. on the water-bath in the covered beaker to reduce the tellurium to the tellurous state, and then again evaporated to dryness; the residue was again dissolved in 10% hydrochloric acid and filtered through filter-paper to remove the bulk of the silica derived from the crucible; the filtrate was again evaporated, the residue dissolved in 10% hydrochloric acid, and tellurium precipitated and collected (see Drew and Porter, J., 1929, 2091) upon another micro-Gooch filter (stabilised by nitric acid, as above) which was dried and weighed; the tellurium carries down with it considerable silica, and is therefore dissolved out with warm concentrated nitric acid (3 c.c.), the filter being re-weighed. The tellurium can be determined from the loss in weight, or reprecipitated from the filtrate after removal of nitric acid; as these methods give sensibly the same result, the second procedure is unnecessary. If a small platinum crucible and lid are used instead of porcelain, together with resistance-glass vessels and freshly distilled acids, there is no silica and both methods give the same result. Experience showed that no platinum was removed from or attached itself to the crucible and that no tellurium stained it; the usually not extensive dark stains on the crucible are due to a very thin layer of oxide (produced by the nitrate) which disappears at once when the crucible is heated to whiteness after the experiment.

Platinum, sulphur, and tellurium were determined simultaneously by fusion as above in the platinum crucible. The platinum was filtered off without acidification and finally washed by hot concentrated nitric acid; or, better, it was filtered off after acidification with nitric acid and the filtrate completely evaporated on a water-bath. In either case nitrous and any nitric acid were completely removed by evaporation with 10 c.c. of distilled concentrated hydrochloric acid; barium sulphate was precipitated in a Schott dish from a small volume (3—5 c.c.) of liquid only weakly acid with a few drops of hydrochloric acid; the suspension was heated for 1 hr., cooled, and filtered through a micro-Neubauer crucible (Pregl). The filtrate from barium sulphate was precipitated by a slight excess of sulphuric acid and filtered, the filtrate evaporated to dryness with concentrated hydrochloric acid, and tellurium determined as before. Platinum and sulphur were also estimated similarly in absence of tellurium.

The methods gave concordant results (see under the various compounds) on 5—20 mgm. of substance; in several cases the values have been checked against those obtained for carbon in the same sample. No standard substances containing both platinum and tellurium are available for a check of the absolute figures, and it is doubtful if mixtures would answer the same purpose.

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