310. *Platinum with a Covalency of Four: Diquinolinoplatinous Chlorides.*

By E. Gordon Cox, H. Saenger, and W. Wardlaw.

It has been deduced from *X*-ray measurements that in the salts K_2PtCl_4 (Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 2404) and $[Pt,4NH_3]Cl_2,H_2O$ (Cox, this vol., p. 1912) the four associated chlorine atoms and the four associated molecules of ammonia are in one plane which also contains the platinum atom. These results are naturally of interest in view of Werner's conclusion that the isomerism of the diammines and tetrammines of platinous chloride is due to the planar distribution of the units about the platinum atom when it has a covalency of four. No compound of the type PtA_2B_2, however, has yet been investigated by *X*-ray methods, so it still remains undecided whether in 4-covalent platinum the stereochemical disposition of the units is always planar. The experimental data available seem to indicate that in certain circumstances the four co-ordinated units are grouped tetrahedrally about the platinum atom. Reihlen (*Annalen*, 1926, **448**, 312) has emphasised that in the ββ′β″-triamminotriethylaminoplatinous iodide of Pope and Mann (*Proc. Roy. Soc.*, 1925, **109**, *A*, 444) and also in the corresponding dinickel compound, the four nitrogens cannot be distributed in a plane around the central metallic atom. The possibility that platinum in its 4-covalent compounds can give rise to both tetrahedral and planar configurations becomes increasingly probable.

To investigate further the influence of the co-ordinated groups on the reactions of the diammino- and tetrammino-platinous chlorides, we have prepared for the first time in a pure condition α- and β-diquinolinoplatinous chlorides (Williams, *J. pr. Chem.*, 1859, **76**, 251). These substances show the substantial differences in properties which have already been pointed out (J., 1930, 349; this vol., p. 988) amongst similarly related members of a series. For example, the β-compound readily gives with silver oxide a β-*base* $Pt(qu)_2(OH)_2$, whilst only traces of an alkaline solution result when the α-derivative is similarly treated. Again, the α- is generally much less reactive than the β-compound. This is seen particularly well in the reactions with pyridine. With either pure or aqueous pyridine, the α- reacts very slowly with the formation of the tetrapyridino- and the α-dipyridino-platinous chloride. The β-, on the other hand, reacts much more rapidly. The products depend upon the temperature of the reaction and the concentration of the pyridine. With pure pyridine a quantitative formation of tetrapyridinoplatinous chloride is obtained. With aqueous pyridine, varying proportions of $[Pt(py)_4]Cl_2$ and $[Pt(py)_2(qu)_2]Cl_2$ are isolated. The formation of the tetrapyridino-salt is particularly interesting, for it indicates that the nature of the co-ordinated groups can greatly modify the usual course of these reactions. Generally, and in accordance with Werner's theory, the sole product of a reaction between a diammine of platinous chloride and a different amine should be the mixed salt $PtA_2B_2Cl_2$. In this particular case, however, the pyridine has replaced the quinoline in a secondary reaction.

The wide differences in stability of the tetrammines of platinous chloride are emphasised by the fact that, whereas in the preparation of the tetrapyridino-salt this product is always accompanied by a certain amount of α-$Pt(py)_2Cl_2$, yet under similar experimental conditions the mixed salt $[Pt(py)_2(qu)_2]Cl_2$ is never associated with the mixed diammine, $Pt\,py,qu,Cl_2$. One must deduce that in aqueous solution the mixed tetrammine is more stable than the simple tetrammine. The least stable tetrammine of this series is the tetraquinolino-salt. Although β-$Pt(qu)_2Cl_2$ is readily soluble in excess of warm quinoline, yet a tetrammine cannot be isolated.

Instead, on cooling, a yellow solid separates with quite different properties from the β-dichloride: it is, in fact, the *α-diquinolinoplatinous chloride.* It is a peculiar observation that the β-dichloride will not react with ammonia and the α-, as expected, is also unreactive.

The curious differences that exist between related series of the diammines is well shown by the solubility relationships in chloroform of the α- and β-$Pt(py)_2Cl_2$ and α- and β-$Pt(qu)_2Cl_2$. The α-$Pt(py)_2Cl_2$ is readily soluble and the β- insoluble. Where, however, the α-$Pt(qu)_2Cl_2$ is insoluble in chloroform, the β- recrystallises with $2CHCl_3$ in characteristic crystals (see p. 2219), which slowly lose chloroform when removed from the solution. *X*-Ray photographs showed that after several days the main body of the crystal was still unchanged, so that loss of chloroform by the surface layers sufficed to cause the considerable opacity and distortion noticed: apparently a crystal of *ca.* 2 mm. diameter takes many days to lose all its chloroform. The crystals can be preserved indefinitely in an atmosphere of chloroform. Since this compound β-$Pt(qu)_2Cl_2,2CHCl_3$ parts with its chloroform so reluctantly, it would be considered on Werner's theory to represent a six-point system, such as $[Pt(NH_3)_2Cl_4]$.

Tschugaev and Tschernjaev (J., 1918, **113**, 884) have isolated the double compound α-$[Pt,2NH_2OH,Cl_2],2CsCl$, which they formulate as $[Pt,2NH_2OH,Cl_4]Cs_2$. It is possible in the case of the compound $Pt(qu)_2Cl_2,2CHCl_3$ that the chloroform molecules may be co-ordinated through the hydrogen atom, but when hydrogen is attached to carbon such a formulation is almost unknown (Sidgwick, "Theory of Valency," p. 117). It is more probable that the co-ordination is through the chlorine atom.

EXPERIMENTAL.

Preparation of the Isomeric Dichlorides.—To cold K_2PtCl_4 aq. (5 g.; 20 c.c.), quinoline (2·8 c.c.) was added. After some time a yellow solid separated, which was extracted (Soxhlet) with $CHCl_3$. From the solution produced, yellow prismatic crystals A (Fig. 1) separated, consisting of the *β-dichloride* with $2CHCl_3$ [Found: Pt, 25·6. $(C_9H_7N)_2PtCl_2,2CHCl_3$ requires Pt, 25·6%]. When the crude product from the initial reaction contained a little C_9H_7N, the crystals obtained from the $CHCl_3$ extract were of type B (Fig. 2), terminated by domatic faces. These, after being washed with cold $CHCl_3$, were similar in composition to the crystals A.

To prepare the *α-dichloride,* the β-compound was dissolved in boiling C_9H_7N. From the reddish-brown solution, the crude yellow α-dichloride separated on cooling. This was washed with Et_2O, air-dried, and recrystallised from *m*-cresol. After a final washing with Et_2O, the crystals were dried in vac. over P_2O_5 and solid NaOH [Found: Pt, 37·3. $(C_9H_7N)_2PtCl_2$ requires Pt, 37·2%].

Crystallographic Investigation (by E. G. Cox).—The β-dichloride crystallises with $2CHCl_3$ in highly refringent, greenish-yellow prisms, which appear to be monoclinic prismatic with axial ratios $a : b : c = 0{\cdot}73 : 1 : 0{\cdot}76$; $\beta = 98°$; *d* 1·96. When recryst. from $CHCl_3$, the β-dichloride gives crystals which exhibit a combination of {010} and {110} in the prism zone terminated by {001} (Fig. 1).

On crystals from solutions containing C_9H_7N, however, {001} is very small or absent entirely, the form {011} appearing in its place, whilst forms which seem to be {210} and {101} sometimes occur, the latter being very small (Fig. 2). The crystals commence to lose $CHCl_3$ soon after removal from the solution, becoming semi-opaque and distorted. On this account the values given above are only approx. Heating to 80° causes rapid loss of $CHCl_3$ and formation of β-Pt qu_2Cl_2 (Found: Pt, 37·1. Calc.: Pt, 37·2%). This compound is sol. in MeCN but sparingly sol. in EtOH and in C_6H_6. The α-dichloride is a bright yellow powder, insol. in H_2O and very sparingly sol. in $CHCl_3$.

FIG. 1.

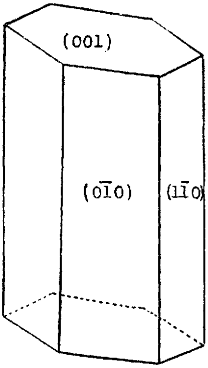
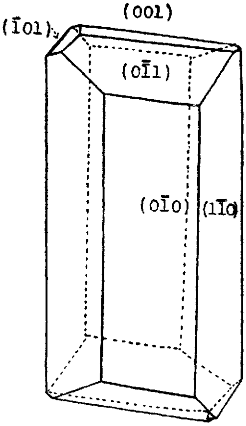


FIG. 2.



The specimen examined (E. G. Cox) seems to consist of two distinct types of crystal: (*a*) Almost colourless needles forming radiated growths; nearly all the crystals were tapered at both ends; all showed straight extinction between crossed Nicols; high refringence. (*b*) Yellow plates, mostly aggregates; the plates are six-sided, the angles between the sides being approx. 47°, 62°, and 71°; high refringence; extinction directions inclined at approx. 5° to the bisectors of the 47° angle.

The differences between the types (*a*) and (*b*) seem to be too great to be accounted for by difference of habit, since all the crystals are of one crystallisation. Assuming that the specimen is chemically homogeneous, the substance appears to be dimorphous.

Action of Moist Silver Oxide on the Isomeric Dichlorides.—(1) When the β-dichloride is ground in a tube with excess of Ag_2O and a little H_2O, no appreciable reaction takes place. On warming, however, on a water-bath, the chloride is decomposed and the filtrate, which reacts alkaline to litmus, yields, on conc. in vac. over P_2O_5, the *β-base*, Pt $qu_2(OH)_2$ [Found: Pt, 40·1.

$Pt(C_9H_7N)_2(OH)_2$ requires Pt, 40·1%]. This base is a yellow varnish, very sol. in H_2O to yield an alk. solution which absorbs CO_2 if exposed to air. When neutralised with dil. HCl aq., the pure β-dichloride is obtained, while with HBr aq. the pure *β-dibromide* separates [Found: Pt, 31·9. $Pt(C_9H_7N)_2Br_2$ requires Pt, 31·8%].

(2) The α-dichloride reacts extremely slowly when treated with Ag_2O in the same manner. Even after 24 hrs. the filtrate is only faintly alk. to litmus, and on conc. gives a trace of solid. An indication that the solution contains an α-base was obtained by neutralising it with dil. HCl aq., a small yield of a white solid insol. in NH_3 aq. being obtained.

Action of Pyridine on the β-Dichloride.—(*a*) When the β-dichloride was dissolved in boiling C_5H_5N and the satd. light-yellow filtrate concentrated in vac. over P_2O_5, a white cryst. solid, mixed with a small amount of yellow powder was obtained. The white solid was extracted with cold H_2O, and from this aq. solution white crystals of tetrapyridinoplatinous chloride were obtained [Found: Pt, 32·5. Calc. for $Pt(C_5H_5N)_4Cl_2,2H_2O$: Pt, 32·5%]. The yellow powder, insol. in H_2O, proved to be α-Pt py_2Cl_2 (Found: Pt, 46·0. Calc.: Pt, 46·0%). The formation of the tetrapyridinoplatinous chloride was further confirmed by (i) isolating and analysing the plato-salt [Pt py_4][$PtCl_4$], (ii) decomposing it with HCl aq., and isolating α-Pt py_2Cl_2.

(*b*) If the β-dichloride was treated similarly with C_5H_5N aq. instead of C_5H_5N, a pale yellow solution resulted, which, on concn. in vac. over $CaCl_2$, gave a white solid associated with a minute trace of a yellow powder. On extraction with a small vol. of cold H_2O, the white solid readily dissolved and the yellow powder remained. On concentrating the filtrate over $CaCl_2$ in vac., the white solid was recovered. This proved to be a mixture of two salts, which were separated by extraction with $CHCl_3$. The $CHCl_3$-sol. portion was *β-dipyridinodiquinolinoplatinous chloride* [Found: Pt, 28·6. $Pt(C_5H_5N)_2(C_9H_7N)_2Cl_2$ requires Pt, 28·6%] and the insol. part [Pt py_4]Cl_2,H_2O (Found: Pt, 32·4%). The proportions of the two tetrammines depended upon the concn. of the C_5H_5N solution and the temp. of the reaction.

The β-[Pt py_2qu_2]Cl_2 is a white powder sol. in H_2O, $CHCl_3$, and EtOH. On treatment with K_2PtCl_4 aq., a salmon-pink plato-salt results [Found: Pt, 41·3. $Pt(C_5H_5N)_2(C_9H_7N)_2(PtCl_4)$ requires Pt, 41·2%]. This *salt* is slightly sol. in H_2O. When the aq. solution of β-[Pt py_2qu_2]Cl_2 is warmed with dil. HCl aq., *α-pyridinoquinolinoplatinous chloride* separates [Found: Pt, 41·2. $Pt(C_5H_5N)(C_9H_7N)Cl_2$ requires Pt, 41·2%]. It is sol. in $CHCl_3$ and its formation is typical of the decomp. of β-mixed tetrammines.

Action of Pyridine on the α-Dihalide.—The α-dihalide shows a marked contrast to the β-isomeride in its reactivity to C_5H_5N. After several days' heating with C_5H_5N on a water-bath, only a faintly yellow solution is obtained. On concentration of this in vac. over H_2SO_4, the tetrapyridinoplatinous salt (Found: Pt, 32·6%), mixed with α-dipyridinoplatinous chloride (Found: Pt, 46·1%), separates. The formation of the former was again confirmed by (*a*) the isolation of the plato-salt (Found: Pt, 46·0. Calc.: Pt, 46·0%), and (*b*) the recovery of the α-dichloride (Found: Pt, 46·2. Calc.: Pt, 46·0%). With C_5H_5N aq. the reaction is still slower, with similar formation of tetrapyridinoplatinous chloride (Found: Pt, 32·6%). The absence of the mixed tetra-salt is probably due to the change of concn. of the C_5H_5N solution after long heating. However, the *α-dipyridinodiquinolinoplatinous chloride* is readily formed by heating the α-dipyridino-salt with C_9H_7N. White crystals of the required chloride are obtained on cooling the conc. solution (Found: Pt, 28·5%). This mixed tetrammine is sol. in H_2O, EtOH, or $CHCl_3$. It gives with K_2PtCl_4 a pale pink *plato*-salt, $[Pt\,qu_2py_2][PtCl_4]$ (Found: Pt, 41·1%).

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