202. *Complex Compounds of the Olefins with Metallic Salts. Part I. Zeise's Salt.*

By J. Stuart Anderson.

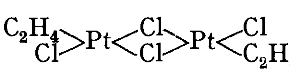
The ability of olefinic compounds to enter into complex formation with metallic salts has been known since Zeise (*Pogg. Ann.*, 1831, **21**, 497) obtained the compound $K[PtCl_3,C_2H_4],H_2O$ from the products of reduction of platinic chloride with alcohol. The number of such metal salt–olefin complexes has since been considerably extended, but the subject has received no systematic study. The literature indicates that, although the capability of combining with olefins is widely distributed among the metals [cf. Kondakov's zinc chloride–amylene compounds, $ZnCl_2,C_5H_{10}$ (*Chem. Listy*, 1930, **24**, 1), the numerous mercury salt–olefin compounds, and the work of Gangloff and Henderson (*J. Amer. Chem. Soc.*, 1917, **39**, 1420) on compounds with iron and aluminium chlorides], yet it is most strongly exhibited by platinum. In addition to Zeise's salt, homologous compounds derived from propylene and amylene $K[PtCl_3,X]$ ($X = C_3H_6$ or C_5H_{10}) were prepared by Birnbaum (*Annalen*, 1869, **145**, 67), and Chojnacki (*Jahresber.*, 1870, 510) obtained the analogous ethylenetribromoplatinite, $K[PtBr_3,C_2H_4]$.

The ability to form such compounds is not limited to hydrocarbons. Biilmann and his co-workers (*Zentr.*, 1917, I, 562) prepared a number of analogous substances containing unsaturated acids, alcohols, and aldehydes, and more recently, Pfeiffer and Hoyer (*Z. anorg. Chem.*, 1933, **211**, 241) have shown that in these substances it is actually the ethylenic linkage which is functioning, being a specific co-ordinating group for platinum. While, therefore, the property is common to all ethylenic compounds, the complexes containing the hydrocarbons are most suited for systematic study, the interpretation of their constitution being free from any ambiguity.

The interest and importance of this group of compounds lie in the fact that, while demarcated in no way chemically from other types of complex salt (cf. Jörgensen's comparison of Zeise's salt with Cossa's salt, *Z. anorg. Chem.*, 1900, **24**, 158), the mechanism of complex formation is obscure in that the co-ordinated molecule possesses no " lone pair " of electrons with which to form the co-ordinate link. Moreover, Smyth and Zahn (*J. Amer. Chem. Soc.*, 1925, **47**, 2501) found ethylene to have zero dipole moment; data for other olefins are scanty, but the moment is certainly small in all cases.

The object of this series of papers is the investigation of this structural problem, by determining the manner in which decomposition products, molecular symmetry, stability, etc., are affected by systematic variation of the olefin component. The present paper deals with the principal reactions of Zeise's salt.

Zeise considered that he had obtained the basic compound of the series, $PtCl_2,C_2H_4$, by precipitating his ammonium salt with chloroplatinic acid. His product consisted probably of the more or less decomposed acid of the series. Ethyleneplatinous chloride (I) may, however, be isolated from the solution obtained by reducing sodium chloroplatinate with alcohol by evaporation below 50° in a high vacuum. A tarry, brown, strongly acid mass is obtained, from which (I) may be separated by extraction with chloroform, followed by recrystallisation from benzene: it is thereby obtained in well-formed orange crystals, showing roughly parallel extinction. It is somewhat soluble in chloroform, but not very soluble in cold benzene (about 30 mg. in 10 c.c.). An approximate molecular-weight determination by the Barger–Rast method points to the dimeric form, in agreement with that found for $PtCl_2,P(OEt)_3$ by Rosenheim and Löwenstamm (*Z. anorg. Chem.*, 1903, **37**, 394).



$$\overset{C_2H_4}{\underset{Cl}{}}{>}Pt{<}\overset{Cl}{\underset{Cl}{}}{>}Pt{<}\overset{Cl}{\underset{C_2H_4}{}}$$

(I.)

The representation of (I) and its derivatives as compounds of bivalent platinum is justified beyond doubt by the following considerations. (*a*) Zeise's acid is formed by the direct absorption of ethylene by platinous chloride dissolved in alcoholic hydrochloric acid (Birnbaum, *loc. cit.*); moreover, the analogous compounds of olefinic alcohols, etc., were obtained by Pfeiffer and Hoyer by the direct action of the unsaturated compounds on potassium chloroplatinite. (*b*) The action of excess pyridine on Zeise's salt leads to the formation of $PtCl_2,2C_5H_5N$ (see below). (*c*) Any formulation involving quadrivalent platinum would necessarily introduce covalencies linking the hydrocarbon to the platinum atom (*i.e.*, representation as an alkylplatinum derivative); such a structure is very unlikely in view of the ready quantitative liberation of ethylene by various reagents. For the same reason, the structure advanced by Drew, Pinkard, Wardlaw, and Cox (J., 1932, 997) must be definitely eliminated.

(I) decomposes without melting at 125—130°, and does not combine with a further molecule of ethylene, unlike $PtCl_2CO$, which readily forms $PtCl_2(CO)_2$. The higher thermal stability of the carbonyl compounds is to be related to the fact that carbonyl chloride (the probable first product of decomposition of $PtCl_2CO$) itself reacts with platinum to give $PtCl_2CO$ at temperatures below 260°. With ethylene dichloride or other chlorinated compounds resulting from the breakdown of (I), this type of reaction does not occur.

The compound (I) is rapidly and quantitatively reduced by hydrogen at room temperature to platinum; the hydrogen chloride being absorbed by alkali, there was a net diminution of volume corresponding to 1 mol. of gas per formula weight of (I): $PtCl_2,C_2H_4 + 2H_2 = Pt + 2HCl + C_2H_6$. With aqueous potassium chloride, quinoline, amines, etc., (I) reacts to give compounds of the types described below.

The quinolinium salts of the olefintrichloro-platinites and -palladites are characterised by relatively high stability and low solubility. *Quinolinium ethylenetrichloroplatinite* (II) is stable enough to be recrystallised from boiling water; in presence of 1 mol. of quinoline, it passes into the non-electrolyte, *quinolinoethyleneplatinous chloride* (III),

$$\text{(II.)}\quad C_9H_7NH[PtCl_3,C_2H_4] \underset{HCl}{\overset{C_9H_7N}{\rightleftarrows}} [C_9H_7N,PtCl_2,C_2H_4]\quad \text{(III.)}$$

the reaction being reversed by hot 2*N*-hydrochloric acid. The salt (II) melts with decomposition about 130°.

There is some evidence that carbon monoxide and ethylene play exactly analogous rôles in co-ordination compounds, a fact which may have significance for the interpretation of the structure of both olefin complexes and metal carbonyls. For instance, ethylene, like carbon monoxide, forms a loose compound with ammoniacal cuprous chloride (Manchot and Brandt, *Annalen*, 1911, **370**, 286), and Reihlen (*ibid.*, 1930, **482**, 161) has reported volatile iron carbonyls in which carbon monoxide (2 mols.) is replaced by butadiene and its homologues. In agreement with this view, the reactions of $K[PtCl_3,C_2H_4],H_2O$ are the counterparts of those of the formally similar potassium carbonyltrichloroplatinite, $K[PtCl_3,CO],H_2O$ (Mylius and Foerster, *Ber.*, 1891, **24**, 2424); *e.g.*, potassium cyanide effects vigorous decomposition, ethylene being liberated quantitatively according to the equation

$$K[PtCl_3,C_2H_4] + 4KCN = K_2Pt(CN)_4 + 3KCl + C_2H_4.$$

Other reagents which can give rise to complex platinites K_2PtX_4 tend to react similarly, but the extent to which liberation of ethylene occurs at room temperature varies with the nature of the complex involved (cf. reaction with potassium nitrite, below). The reaction probably proceeds by an initial metathesis to a complex $K[PtX_3,C_2H_4]$, which may break down spontaneously or in presence of excess of reagent. For $X = CN$, breakdown is immediate and quantitative; for $X = NO_2$, however, only about 10% of the ethylene is evolved at room temperature. The reaction is completed by heating, but the volume of the gaseous products is only about 75% of the theoretical. The deficiency is accounted for, in part at least, by hydration of the ethylene, for the condensate in a trap at $-50°$ contained alcohol (iodoform test). It is possible, in view of the deficiency in the ethylene liberated by pyridine (below), that polymerisation of the ethylene, and other side reactions may also be operative. The reaction with potassium thiocyanate is intermediate between those with cyanide and with nitrite.

If ethyleneplatinous chloride is dissolved in hydrobromic acid and warmed, addition of quinoline hydrobromide gives rise to a red crystalline product having the properties expected of the quinoline salt of Chojnacki's acid (*loc. cit.*), $C_9H_7NH[PtBr_3,C_2H_4]$. This is less stable than the salt (II), and is decomposed by hot water.

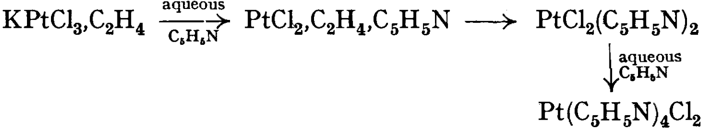
Compounds of the general type $K[PtX_3,C_2H_4]$ appear, therefore, to decrease in stability in the order $X = Cl > Br > NO_2 > CNS > CN$.

With water, Zeise's salt undergoes a reaction above 90° exactly analogous to that of $K[PtCl_3,CO]$ (Mylius and Foerster, *loc. cit.*), *viz.*, $K[PtCl_3,CO] + H_2O = KCl + 2HCl + Pt + CO_2$. In the present case, the products might be expected to contain either (*a*) ethylene glycol (possibly also ethylene chlorohydrin), if the ethylene double linkage were in some manner symmetrically co-ordinated to the platinum atom, as Pfeiffer originally suggested ("Organische Molekülverbindungen," 1922, p. 14), or (*b*) acetaldehyde, if the co-ordinate link is formed by one of the carbon atoms.

Experiments in which Zeise's salt was heated with water in a sealed tube led to rapid and complete deposition of platinum, and the recovery of about 60% of the ethylene as such, indicating that the first product of the hydrolytic fission possessed reducing properties, attacking undecomposed salt. The aqueous solution reduced cold alkaline permanganate, but yielded no oxalate. When, however, the aqueous solution of Zeise's salt was heated at 100° in a stream of nitrogen, and the gases were bubbled through saturated aqueous dimethyldihydroresorcinol, the characteristic dimethone of acetaldehyde (m. p. 139°) was deposited. The reaction is therefore :

$$K[PtCl_3,C_2H_4] + H_2O = KCl + 2HCl + Pt + CH_3{\cdot}CHO$$

Pyridine reacts with Zeise's salt, causing immediate, almost quantitative evolution of ethylene, and forming dipyridinoplatinous chloride. The extreme insolubility of the product would indicate it to be the β-compound of Drew, Pinkard, Wardlaw, and Cox (J., 1932, 1000). Excess of aqueous pyridine also brings about the slow liberation of ethylene, leaving ultimately a colourless solution of tetrapyridinoplatinous chloride.



$$\begin{tikzcd} KPtCl_3,C_2H_4 \arrow[r, "aqueous", "C_5H_5N"'] \arrow[rr, bend left, "anhydrous\ C_5H_5N"] & PtCl_2,C_2H_4,C_5H_5N \arrow[r] & PtCl_2(C_5H_5N)_2 \arrow[d, "aqueous\ C_5H_5N"] \\ & & Pt(C_5H_5N)_4Cl_2 \end{tikzcd}$$

EXPERIMENTAL.

Ethyleneplatinous Chloride.—Pure sodium chloroplatinate (10 g.) was refluxed with alcohol (70—100 c.c.) until a test portion no longer gave a precipitate with ammonium chloride. Purity of the chloroplatinate seems to be an important factor in minimising the deposition of platinum during the reduction. The solution was filtered from deposited sodium chloride, and evaporated as far as possible in a vacuum below 50°. Soluble matter was extracted with chloroform from the strongly acid residue, which tended to crystallise slowly on keeping, the solution evaporated, and the process repeated. The product was dissolved in the minimum quantity of hot benzene, decanted from an aqueous tarry sludge, and crystallised. Recrystallisation from benzene gave pure material (Found : Pt, 66·2; Cl, 24·4. Calc. for $C_2H_4Cl_2Pt$: Pt, 66·4; Cl, 24·1%). The aqueous sludge contained much $H[PtCl_3,C_2H_4]$, together with organic matter derived from condensation of the acetaldehyde produced in the reduction.

Reduction of Ethyleneplatinous Chloride.—A weighed quantity of pure material was exposed to hydrogen, in presence of a pellet of potassium hydroxide to absorb hydrogen chloride. The hydrogen absorption was measured manometrically : 18·79 mg. absorbed 1·45 c.c. at *N.T.P.*, *i.e.*, 1·014 mols. per formula-weight (see p. 972).

Zeise's salt, $K[PtCl_3,C_2H_4],H_2O$, was prepared from the alcoholic solution from the reduction process (above) by Jörgensen's method (*loc. cit.*), and recrystallised from dilute hydrochloric acid.

Quinolinium ethylenetrichloroplatinite was precipitated from solutions of Zeise's salt by addition of an excess of quinoline, dissolved in hydrochloric acid. Recrystallisation from acidified water gave long, lemon-yellow, rhombic needles (Found : Pt, 42·2; Cl, 23·0; N, 3·2. $C_9H_8N[PtCl_3,C_2H_4]$ requires Pt, 42·5; Cl, 23·1; N, 3·1%). An identical product (Found : Pt, 42·5; Cl, 23·05%) was obtained by dissolving the following compound in hot 2*N*-hydrochloric acid.

Quinolinoethyleneplatinous chloride was obtained by the action of aqueous quinoline on solutions of Zeise's salt. Recrystallisation from much hot water yielded a pale yellow microcrystalline powder (Found : Pt, 46·2; Cl, 17·2, N, 3·4. $C_9H_7N,PtCl_2,C_2H_4$ requires Pt, 46·1; Cl, 16·8; N, 3·3%).

Reactions of Zeise's Salt.—Weighed quantities of salt were treated with concentrated aqueous solutions of potassium cyanide, nitrite, or thiocyanate in a reaction flask connected through a trap at $-50°$ to a Toepler pump. Gaseous products were pumped out and measured, and the condensate in the trap tested for alcohol. Potassium cyanide liberated 7·5% of ethylene (calc. for $K[PtCl_3,C_2H_4],H_2O$: 7·2%). Pyridine yielded ethylene and dipyridinoplatinous chloride (Found : Pt, 45·9; N, 6·7. Calc. : Pt, 46·0; N, 6·6%).

The author is indebted to the Chemical Society for a grant.

IMPERIAL COLLEGE, LONDON, S.W. 7. [*Received, May 17th,* 1934.]