Short Communications

Platinum Compounds of Alkadienes (Diolefins)

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Zeise\(^1\) in 1830 described some very interesting platinum compounds containing ethylene, viz. K\([\text{PtCl}_6\text{C}_2\text{H}_4]\) and PtCl\(_6\)C\(_2\)H\(_4\)\. Anderson\(^2\) in 1934 found the latter compound to be dimeric. Other alkenes have yielded analogous compounds (see the review by Keller\(^3\)), but until recently no compound containing more than one molecule of the alkene to one atom of platinum had been described. In 1950, however, Chatt and Wilkins\(^4\) succeeded in preparing the compound [PtCl\(_6\)(C\(_2\)H\(_4\)\(_2\))] which is stable below \(-10^\circ\). Their recent publication\(^5\) has prompted me to

\(^*\) It has not been generally recognised that Zeise prepared this compound. Anderson writes: "Zeise considered that he had obtained the basic compound of the series, PtCl\(_6\)C\(_2\)H\(_4\)… His product consisted probably of the more or less decomposed acid of the series". As a matter of fact, however, Zeise's analysis of his "platinum chloride inflammable" (i.e. § 39) corresponds excellently with the composition he proposed: Found (Zeise): Pt 66.53; Cl 23.88; C 8.25; H 1.34. Calc. for PtCl\(_6\)C\(_2\)H\(_4\): Pt 66.34; Cl 24.14; C 8.16; H 1.36. Also the properties described by Zeise are in agreement with those of the compound PtCl\(_6\)C\(_2\)H\(_4\), with the exception that the colour is described by Anderson as orange and by Zeise as very slightly yellow ("ciurini coloris perquam pallidii"). This may, however, simply be a question of crystal size (Anderson recrystallized his product from benzene).

mention that in 1937 I prepared some platinum compounds of alkadienes in which one molecule appears to occupy two co-ordination places. This observation was not published because I intended to investigate these compounds further but pressure of other work prevented this.

When an excess of bialyl (1,5-hexadiene), CH\(_2\) = CH–CH\(_2\)–CH\(_2\)–CH=CH\(_2\), is added to an aqueous solution of K\(_2\)PtCl\(_6\), a precipitate slowly separates. This precipitate recrystallizes from chloroform to yield a pale yellow crystalline compound of composition PtCl\(_6\)C\(_6\)H\(_{10}\) and m.p. 173\(^\circ\) (dec.). The corresponding iodide PtI\(_4\)C\(_6\)H\(_{10}\) is obtained in a similar way. The isomeric hexadiene, 2,4-hexadiene, behaves very differently: with K\(_2\)PtCl\(_6\) only free platinum is obtained and with K\(_2\)PtI\(_4\) a black precipitate consisting mainly of PtI\(_4\). Compounds derived from the lower homologue butadiene have been prepared both by Gellman\(^6\) and by Chatt and Wilkins\(^5\), but the butadiene molecule seems only to occupy one co-ordination place in these compounds.

Diallylether gives a compound, PtCl\(_6\)(C\(_6\)H\(_{10}\)O), which closely resembles the dialyl compound. Divinylether, on the other hand, reduces K\(_2\)PtCl\(_6\) to free platinum. On addition of an excess of divinylether to K\(_2\)PtCl\(_6\), a dark red precipitate (resembling CrO\(_3\)) immediately separates, but this compound is very unstable and rapidly turns brown. Analysed as soon after formation as possible, it has the composition corresponding to platinum iodide with 1/2 molecule of divinylether, but the product smells of divinylether and may
have contained 1 molecule at the beginning.

The behaviour of bialyll and diallyl ether is thus very different from that of similar compounds with smaller distances between the double bonds. It thus seems probable that both double bonds in the longer diolefin are involved in complex formation giving chelated complexes. Other compounds of the type PtCl₂, alkene are dimeric, but the compounds of bialyll and diallyl ether were found by cryoscopic measurements to be monomeric, in accordance with the view that these compounds are chelate compounds.

This conclusion is corroborated by measurement of the dipole moments of these compounds. Although the compounds are very slightly soluble in benzene it is possible to determine the order of magnitude of their dipole moments which was found to be 6—7 D. This high value is only compatible with the assumption that the compounds are cis-compounds, and this is the only possible configuration if the diolefin occupy two coordination places.

Bialyl also gives a palladium compound with the composition PdCl₂·C₄H₁₀ by reaction with the benzonitrile complex [PdCl₂(C₅H₅CN)].

An attempt to determine the structures of the bialyl compounds using X-rays was frustrated by the decomposition of the compounds. They blackened in the X-ray beam and the only identifiable reflections were due to metallic platinum and palladium.

**Experimental**

*Bialyl-dichloroplatinum(II)*. Bialyl (1 ml) was added to a solution of K₂PtCl₄ (2 g) in water (10 ml) and the mixture shaken vigorously for a few minutes. On standing a precipitate slowly separated, and after 2 days it was filtered off (yield 1.3—1.5 g). Further addition of bialyl caused the separation of a little more of the same compound and the yield was almost quantitative (calc. 1.7 g) the filtrate from the last precipitate was almost colourless. At 50° the reaction occurred more rapidly but the result was essentially the same. The compound was recrystallized from chloroform and obtained in pale yellow crystals, m.p. 172—73° (benzene gives a better recovery but more recrystallizations are necessary to obtain the pure compound); it was rather soluble in chloroform, less so in benzene and almost insoluble in ether. It dissolved somewhat in boiling water but soon decomposed with the separation of a brown precipitate. The melting point was sharp, and under the microscope the melting was seen to occur without decomposition, but the melt soon turned black. Found: C 20.51; H 3.05; Pt 58.1; Cl 20.17. Calc. for [PtCl₃(C₅H₁₀)], (348.3): C 20.69; H 2.89; Pt 58.0; Cl 20.36. Molecular weight (cryoscopically in bromoform solution): 369, 382, 364. Dipole moment, μ = 6.1 (ε = 0.00385 molar in benzene, Δε = 0.0180).

According to Gelman⁷ bialyl can replace ethylene from K²[PtCl₆C₅H₄], probably with the formation of the compound K₂[PtCl₆C₅H₄PtCl₂]. This compound was also formed as an intermediate in the preparation of the compound [PtCl₆C₅H₄], especially when the reaction took place in acid solution or when no excess of bialyl was used.

Bialyl (1 ml) and 4 N hydrochloric acid (0.5 ml) were added to a solution of K₂PtCl₄ (2 g) in water (10 ml). A crystalline mustard-yellow precipitate soon began to separate. After two hours it was filtered off (yield 0.7 g). It was almost completely soluble in water at room temperature; on longer standing the yield was larger but more of the insoluble compound [PtCl₆C₅H₄] was formed. The water-soluble substance could not be crystallized from water because it was partly decomposed in boiling water or by evaporation of an aqueous solution. The product was purified by extraction with boiling chloroform which dissolves [PtCl₆C₅H₄]. The yellow crystals have the composition K₂[PtCl₆C₅H₄]: Found: C 9.73; H 1.42. Calc. C 9.43; H 1.31. By addition of [Pt(NH₃)₄] to an aqueous solution of this compound an insoluble cream-coloured precipitate, consisting of [Pt(NH₃)₄][PtCl₆C₅H₄], was formed. Found: C 7.59; H 2.32; N 5.96; Pt 61.73. Calc. C 7.72; H 2.49; N 6.04; Pt 62.75.

*Bialyl-di-iodoplatinum(II)*. Bialyl (0.5 ml) was added to a solution of K₂PtCl₄ (1 g) and KI (1.5 g) in tepid water (10 ml). After 1 hour the precipitate was filtered off (yield 0.8 g), washed with water, dried and recrystallized from chloroform. The compound forms orange-red crystals; on heating it turns black without melting. Found: C 13.24; H 2.06;
Platinum Compounds of Cyclo-octatetraene

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In the preceding article platinin complexes of some alkadienes were described. I have prepared similar derivatives of cyclooctatetraene. A compound of composition close to PtCl₂₂₆₃H₅ separates as an orange-yellow precipitate when cyclooctatetraene is added to an aqueous solution of K₂PtCl₄. It is insoluble in water and organic solvents and therefore could not be purified. However, the corresponding iodide could be recrystallised from chloroform and was obtained as a beautiful orange-red (dichromate-coloured) crystalline powder of the exact composition PtI₂₂₆₃H₅.

The platinum atom in these compounds is certainly co-ordinated to one or more double bonds. The unlikely possibility that the platinum atom be bound to all 4 double bonds is definitely ruled out because compounds of the type [Pt₄(a)₂Cl₈] are generally colourless, easily soluble in water, and contain iodised chlorine. This is not the case with the cyclooctatetraene compound. Neither can the platinum atom be bound to only one double bond because the compound would then be dimeric, as is generally true of platinum compounds of the type PtCl₄₂a (a = amine, phosphine, alkyl sulphide, etc.). A cryoscopic determination of the molecular weight in chloroform solution shows that PtCl₂₂₆₃H₅ is monomeric; thus it seems that cyclooctatetraene occupies two co-ordination places, in the same way as diallyl. According to the preceding paper a certain distance between the double bonds is necessary for the formation of chelate compounds by

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1. Zeise, W. C. De chlorido platinae et alcohol et vinis invicem permutandis nec non de novis substantiis inde oriundis. Anniversary Volume of the University of Copenhagen, 1830. Complete German translations of this paper appeared in: J. Physik und Chemie (Schweigger-Steidel) 62 (1831) 309; 63 (1831) 121; Ann. Physik und Chemie (Poggendorf) 21 (1831) 497. A short summary of the last translation appeared in: Magazin für Pharmacie 35 (1831) 105. (In Keller’s review this article is erroneously cited as Zeise’s original paper).


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