

## A New Red Platinum(II)-Platinum(IV) Compound

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A number of compounds, e. g.,  $[\text{PtBr}_2(\text{NH}_3)_2]$ - $[\text{PtBr}_4(\text{NH}_3)_2]$  and  $[\text{PtCl}_2\text{en}][\text{PtCl}_4\text{en}]$ ,<sup>1)</sup> have been known as platinum(II)-platinum(IV) compounds, which can be regarded as consisting of platinum(II) and platinum(IV) complexes. The characteristic feature of these compounds is their intense color, which can not be expected from the component complexes. This anomalous color has been believed, on the basis of X-ray<sup>2)</sup> and ultraviolet<sup>3)</sup> investigations to be due to the platinum(II)-halogene-platinum(IV) interaction. Among these compounds the red Wolfram salt,<sup>4,5)</sup>  $[\text{Pte}_4][\text{PtCl}_2\text{ea}_4]\cdot\text{Cl}_4\cdot 4\text{H}_2\text{O}$  (where "ea" denotes ethylamine), has attracted much interest; its prominent properties are its clear red color, the distinct dichroism, and the colorlessness of its aqueous solution. This compound has been believed to be unique in containing ethylamine, since, according to Reihlen and Flohr,<sup>5)</sup> the substitution of ethylamine with other amines (or ammonia) does not lead to the formation of homologue compounds.

In this paper, in spite of Reihlen's statement, a new red platinum(II)-platinum(IV) compound, which should be one of the homologues of Wolfram's salt and which yet has no ethylamine, will be reported.

This compound was obtained in the course of synthetic work on  $[\text{Pten}_3](\text{ClO}_4)_4$  (where "en" denotes ethylenediamine). Hexachloroplatinic acid was heated with an excess of ethylenediamine in 96% ethanol for 1.5 hr. The resulting light yellow precipitate was filtered and then extracted with a small amount of water. When to this solution, 60% aqueous perchloric acid was added, red crystals appeared.

This compound was found by elementary

analyses to have the formula  $\text{Pten}_2\text{Cl}(\text{ClO}_4)_2$  (Found: Pt, 35.80; C, 8.83; H, 3.13; N, 10.42; Calcd.: Pt, 35.49; C, 8.74; H, 2.93; N, 10.42%). The properties of this compound are similar to those of Wolfram's salt. The crystal shows a remarkable dichroism, is red (when parallel to the needle) and a very light yellow (when perpendicular to the needle). It is stable in the air, decomposes above 220°C, and is soluble in water, forming a colorless solution from which the red crystals can be recrystallized by adding concentrated perchloric acid.

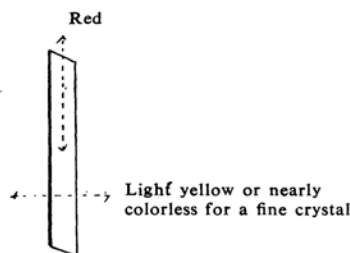


Fig. 1. Microscopic observation and dichroism of the red crystal.

The compound was directly synthesized from the colorless solution of  $[\text{Pten}_2]\text{Cl}_2$  and  $[\text{PtCl}_2\text{en}_2]\text{Cl}_2$  at an equimolar ratio by adding 60% perchloric acid. Elementary analyses, infrared spectra, and microscopic observations indicated that the two products, obtained by different methods, are the same compound.

From the above facts, a rational formula would be  $[\text{Pten}_2][\text{PtCl}_2\text{en}_2](\text{ClO}_4)_4$ ; this compound is undoubtedly one of the homologues of Wolfram's red salt.

A number of combinations of platinum(II) and platinum(IV) complexes are now being investigated in an attempt to obtain new compounds of this type.

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