XV.—*Some New Platinocyanides.*

By LEONARD ANGELO LEVY and HENRY ARNOTT SISSON.

CONSIDERING the comparatively advanced state of our knowledge of the constitution of organic substances possessing the property of fluorescence, it is remarkable that so little should be known about this phenomenon as exhibited by platinocyanides. We were accordingly led to investigate the effect of the basic radicle and also such conditions as hydration, purity, state of division, &c., on the character of the fluorescence. For example, the lithium salt has a red fluorescence, whilst the sodium and barium salts exhibit yellow and green colorations respectively, these being the colours of the characteristic lines in the spectra of these metals.

In the course of our researches, we have prepared several platinocyanides, including the hydrazine and hydroxylamine salts, of which we can find no account in the literature. These substances showed remarkable colour changes on a very slight alteration of temperature, and as these properties appeared interesting and uncommon we have investigated them further.

Hydrazine platinocyanide, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$, is prepared by double decomposition between equivalent quantities of hydrazine sulphate and barium platinocyanide; the solution thus obtained, when allowed to evaporate spontaneously, deposits red crystals, showing blue and purple colours by reflected light.

These crystals are unstable under ordinary atmospheric conditions, and, when air-dried, become partially or completely light yellow and opaque, according to the hygrometric state of the atmosphere. The transformation can always be completed by passing dry nitrogen over

them. We analysed this light yellow modification, this being the most stable in air.

0.1300 gave 24.43 c.c. nitrogen at 16° and 748 mm. $N = 21.56$.

0.2471 „ 0.1246 Pt. $Pt = 50.42$.

0.3807 „ 0.1730 CO_2 and 0.1049 H_2O . $C = 12.39$; $H = 3.07$.

0.2269, after heating for several hours at 100°, left a dull olive-green powder, the loss of weight being 0.0309. $H_2O = 13.6$ per cent.

$C_4H_6N_6Pt, 3H_2O$ requires $C = 12.40$; $H = 3.12$; $N = 21.77$; $Pt = 50.34$; $H_2O = 13.9$ per cent.

Hydrates.—The damp red crystals become white when slightly warmed, as when a tube containing them is held in the hand, and they recover their original colour on cooling. This transformation occurs at about 28° and appears to be due to loss of water.

We arrived at this conclusion from the following facts:

(i) The red crystals, when partly exposed to air, pass through the white form before becoming yellow.

(ii) The red modification becomes white when dry nitrogen is passed over it.

(iii) Methyl alcohol turns the red crystals white before dissolving them.

This white modification is very unstable at the ordinary temperature, and rapidly becomes red and yellow on exposure to air. No determination of the percentage of water is possible owing to the rapidity with which this change occurs. The state of hydration of the red salt cannot be accurately estimated, as it is very unstable when dry. This red salt may be kept in a damp atmosphere, but the amount of adherent water would vitiate any analysis.

When pure dry nitrogen is passed over the red salt, its colour changes in succession to white, then light yellow, dark yellow, brown, and olive-green. An approximate estimation of the water in the red modification was obtained by passing dry nitrogen over the salt until it became yellow.

0.1500 gram, when so treated, gave 0.1409 gram of yellow salt.

The loss of one and two molecules of H_2O require respectively 0.1432 and 0.1366 gram of the yellow salt.

Hence this hydrate probably contains four molecules of water. The slightly greater loss of water is probably due to dampness of the red salt. The latter fluoresces faintly under radium, but no more brightly than does glass under similar conditions.

All modifications are readily soluble in methyl alcohol, from which they are wholly precipitated by ether. The colour of the precipitate varies according to the amount of water present and may be red, purple, orange, yellow, or white. If the process is repeated once

or twice on the precipitate, a pure white, crystalline salt can always be produced. When thus obtained, it is even more unstable than when prepared by the method already described.

Action of Light.—Hydrazine platinumcyanide is affected by light. A print can be obtained from a negative by placing it over a sheet of paper soaked in the methyl-alcoholic solution and allowed to dry. The print thus obtained is yellow and grey and shows details fairly well. We have not yet been able to fix this image, which is destroyed by damp, but can be reprinted when dry. The paper is also attacked and becomes brittle.

If hydrazine platinumcyanide is prepared with excess of barium platinumcyanide, fine red crystals are obtained together with some normal salt. These are permanent in air, contain barium, and, on heating to about 60° , or when placed in a vacuum desiccator, become opaque and assume a lustrous, beetle-green colour. We intend to pursue the investigation of these substances.

Hydroxylamine Platinumcyanide, $(\text{NH}_2\text{OH})_2\text{H}_2\text{Pt}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$.—This salt is prepared by double decomposition between barium platinumcyanide and hydroxylamine sulphate. The solution thus obtained, when allowed to evaporate spontaneously, leaves very soluble red crystals stable in air at the ordinary temperature.

0.1475 gave 26.1 c.c. nitrogen at 17° and 751 mm. $\text{N} = 20.3$.

0.2338 „ 0.1132 Pt. $\text{Pt} = 48.42$.

0.2387, after remaining in a vacuum desiccator over sulphuric acid, gave a black powder, the loss of weight being 0.0217; $\text{H}_2\text{O} = 9.09$ per cent.

$\text{C}_4\text{H}_8\text{N}_6\text{Pt} \cdot 2\text{H}_2\text{O}$ requires $\text{N} = 20.8$; $\text{Pt} = 48.39$; $\text{H}_2\text{O} = 8.93$ per cent.

Hydrates.—The red crystals become bright yellow when slightly warmed, and this is exactly analogous to the colour variations occurring with the hydrazine salt and takes place quite as readily. These yellow crystals again become red on cooling; the salt is soluble in methyl alcohol, but is not satisfactorily precipitated by ether. The change from red to yellow is accompanied by loss of weight.

The foregoing salts are the first members of a series of platinumcyanides which we hope shortly to prepare in the course of our investigations on the effect of the molecular weight of the base on the character of the fluorescence. We propose to prepare platinumcyanides of alkyl-substituted hydrazines, hydroxylamines, and other bases, thus obtaining a series of platinumcyanides the molecular weights of which differ by equal or known increments. The more common aromatic bases, such as phenylhydrazine, do not yield the well-crystallised salts so essential for the purpose of comparing their fluorescence.

Platinumcyanides of fluorescent bases or radioactive substances should

prove of special interest. The radium salt should be self-luminous, and an investigation of its fluorescent properties might throw some light on the origin of the fluorescence conferred by the platinocyanide group on its salts.

Most of the materials necessary for the foregoing researches have been purchased by means of funds kindly supplied by the Government Grant Committee of the Royal Society.

Our thanks are due to Dr. H. J. H. Fenton, F.R.S., for valuable advice.

CHEMICAL LABORATORY,
CAMBRIDGE UNIVERSITY.