Spectrochemical Study of Microscopic Crystals. XIII[1]. *The Structure of Wolffram's Red Salt*, $Pt(NH_2 \cdot C_2H_5)_4Cl_3 \cdot 2H_2O$ *and a Related Compound*[2]

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Formerly the present authors studied the polarized absorption spectra of those compounds involving apparently tervalent platinum or palladium which display extraordinarily deep colours[1,3]. It was found in the earlier studies[3] that some of the above compounds have chains consisting of platium or palladium atoms in different oxidation states connected through halide ions and that the formation of the chains gives rise to a characteristic charge transfer absorption polarized along the chains. Wolffram's red salt, $Pt(EA)_4Cl_3 \cdot 2H_2O$[4], which contains a platinum atom in an apparently tervalent state, may be supposed to belong to a similar type of compound[3]. This compound was first synthesized by Wolffram[5], who obtained the red crystals of this compound by oxidizing an aqueous solution of tetrakis-(ethylamine)-platinum(II) chloride, $Pt(EA)_4Cl_2$, with hydrogen peroxide. Much later Reihlen and Flohr[6] considered the compound as containing divalent and quadrivalent platinum atoms, and ascribed the unusually deep colour of the compound to a special structure of the crystal lattice, which, however, was not explained at all. On the contrary, Drew and Tress[7] attempted to explain the deep colour of this compound on the assumption that the compound might involve a tervalent platinum atom. Establishing the diamagnetism of this compound, Jensen showed that the compound did not involve the platinum in the tervalent state. The deep colour of this compound, however, was still left unexplained[8].

The present work was undertaken in order to explain the color of Wolffram's salt and a related compound in relation to the structure and the probable aid in the comprehension of the charge transfer spectra.

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[1] Part XII of this series, S. Yamada and R. Tsuchida, This Bulletin, 29, 694 (1956).

[2] Presented in part before the ninth annual meeting of the Japan Chemical Society, Kyoto, April 2nd, 1956.

[3] R. Tsuchida and S. Yamada, *Nature*, **174**, 1064 (1954); This Bulletin, 29, 421 (1956).

[4] The notation, A, denotes a molecule of ethylamine.

[5] H. Wolffram, Dissertation Königsberg, 1900.

[6] H. Reihlen and E. Flohr, *Ber.*, 67, 2010 (1934).

[7] H. D. K. Drew and H. J. Tress, *J. Chem. Soc.*, **1935**, 1244.

[8] K. A Jensen, *Z. anorg. allgem. Chem.*, 229, 252 (1936).

Experimental

Materials.—Tetratkis-(ethylamine)-platinum (II) chloride dihydrate was prepared according to the method of Reihlen and Flohr[6] as colourless crystals. The absorption spectrum was determined with the aqueous solution.

Dichloro-tetrakis-(ethylamine)-platinum(IV) chloride dihydrate was prepared by the method of Reihlen and Flohr[6] in pale-yellow crystals. The crystals of the compound are quite stable in the dark, but undergo decomposition on irradiation of ultra-violet light to form a red compound. The aqueous solution of the compound is rather stable in the light. The absorption spectrum was determined in an aqueous solution.

Wolffram's red salt, $Pt(ethylamine)_4Cl_3 \cdot 2H_2O$, was obtained by the method of Reihlen and Flohr[6] from $[Pt(EA)_4]Cl_2$ and $[Pt(EA)_4Cl_2]Cl_2$. Red crystals of the compound thus obtained show a striking dichroism; they are dark-red with polarized light having its electric vector along the needle axis and almost colourless with polarized light having its electric vector normal to the needle axis. The measurement of the dichroism was carried out along the above two directions.

Tribromo-tetrakis-(ethylamine)-platinum dihydrate, $Pt(EA)_4Br_3 \cdot 2H_2O$, was obtained by the method of Reihlen and Flohr from Wolffram's red salt. Green crystals thus obtained show a striking dichroism; they are dark-green with polarized light having its electric vector along the needle axis, and pale yellow with the electric vector normal to the needle axis. The measurement of the polarized absorption spectra was carried out in these two directions.

Dibromo-tetrakis-(ethylamine)-platinum (IV) bromide, $[Pt(EA)_4Br_2]Br_2$, was prepared in orange, crystalline powder by treating an aqueous solution of $[Pt(EA)_4]Cl_2$ with an excess of hydrogen peroxide and concentrated hydrobromic acid. The absorption spectrum was determined in an aqueous solution.

Measurement.—Quantitative measurements of absorption spectra of the crystals were made by Tsuchida—Kobayashi's microscopic method[9] with polarized light in the regions covering 2400 to 7500 Å. The notation, α, represents the absorption coefficient per mm. of a crystal. The c- and a-absorption denotes absorption with the electric vector parallel and normal to the needle axis, respectively.

Absorption spectra in solution were determined with a Beckman DU quartz-spectrophotometer. The symbol, ε represents a molar extinction coefficient.

Results and Discussion

Structure of Wolffram's Red Salt.—It seems to be obvious that Wolffram's salt, $Pt(EA)_4Cl_3 \cdot 2H_2O$, contains platinum atoms in bi- and quadri-valent states, but not the tervalent state, since the compound in its crystalline state proved to be diamagnetic[8]. The compound is obtained when evaporating a mixed solution of $[Pt(EA)_4]Cl_2$ and $[Pt(EA)_4Cl_2]Cl_2$. The red crystals of the compound dissolve in water to give a colourless solution from which the red crystals of the original compound separate out on cooling. All these facts indicate that Wolffram's salt may be formulated as $[Pt(EA)_4][Pt(EA)_4Cl_2]Cl_4 \cdot 4H_2O$.

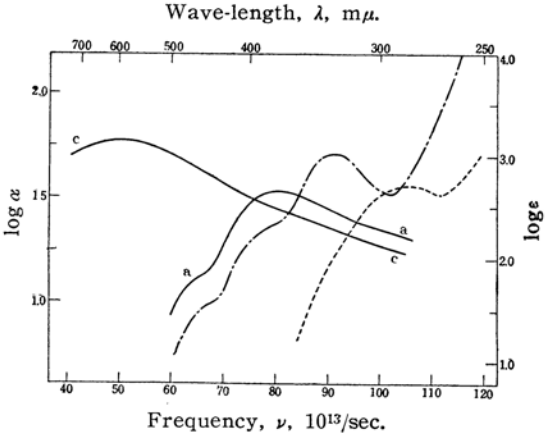

Fig. 1. Absorption spectra of $[Pt(EA)_4][Pt(EA)_4Cl_2]Cl_4 \cdot 4H_2O$ in the crystalline state (———), $[Pt(EA)_4]Cl_2$ in solution (- - - -) and $[Pt(EA)_4Cl_2]Cl_2$ in solution (·—·—).

Polarized absorption spectra of Wolffram's red salt in the crystalline state and absorption spectra of the component complexes in aqueous solution have been determined in the visible and ultra-violet region, and are shown in Fig. 1. It is seen from the curves that $[Pt(EA)_4]Cl_2$ or $[Pt(EA)_4Cl_2]Cl_2$ does not show absorption in the visible region, only the tail of the latter absorption extending into the end of the visible region. Comparison of the absorption spectra of Wolffram's salt with those of the component complexes indicates that Wolffram's salt shows to the long wavelength side a new absorption band which is not observed with either of the component complexes alone. This fact implies that the component complexes in the crystal of Wolffram's salt undergo some great effect which does not exist in either of the component complexes alone. The nature of the effect may be judged from the polarization property of the new band at the long wavelength. The present measurement shows that the absorption occurs only with the electric vector along the needle axis, and does not with the electric vector normal to the needle axis. This relationship may be readily understood on the assumption that Wolffram's salt involves infinite chains consisting of the com-

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9) R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds," Zōshindo, Osaka (1944), p. 180; This Bulletin, 13, 619 (1938).

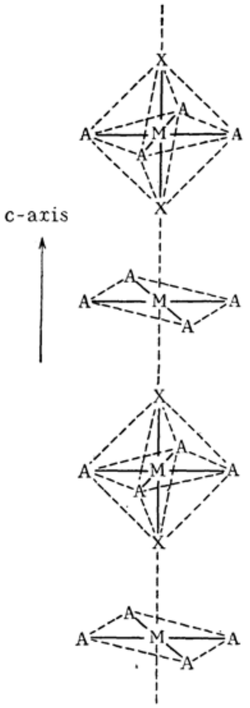

Fig. 2. Chain structure in the crystals of Wolffram's red salt and a related compound having the empirical formula, $\text{Pt(EA)}_4\text{X}_3\cdot 2\text{H}_2\text{O}$.

ponent complexes arranged so that they are piled one just above another along the needle axis (Fig. 2).

In our former studies on the compounds of apparently tervalent platinum and palladium which display unusually deep colours, it was shown that some of those compounds involve infinite chains consisting of the metal atoms in two different oxidation states connected through halogen atoms, and that the chains give rise to a new kind of absorption polarized along the chains. This is quite similar to the relationships which are obtained with Wolffram's salt in the present work. Thus we are led to the conclusion that *the extraordinarily deep colour of Wolffram's salt in the crystalline state is due to the structure containing the infinite chains,* $---\text{Cl}-\text{Pt}^{\text{IV}}-\text{Cl}---\text{Pt}^{\text{II}}---\text{Cl}-\text{Pt}^{\text{IV}}-\text{Cl}---$.

The new absorption observed with Wolffram's red salt at the longer wave-length, which has been assumed to be originated from the infinite chains, as shown above, may be considered as due to a charge transfer along the chains.

It was concluded in our former researches[3] that the crystal of $[\text{Pt en Cl}_2][\text{Pt en Cl}_4]$[10], which has an unusually deep colour as compared with the colours of its component complexes, involves similar chains of $---\text{Cl}-\text{Pt}^{\text{IV}}-\text{Cl}---\text{Pt}^{\text{II}}---\text{Cl}-\text{Pt}^{\text{IV}}-\text{Cl}---$, along which the crystals show a characteristic charge transfer band at about 59×10^{13}/sec. Wolffram's salt involving similar chains shows a charge transfer band at about 58×10^{13}/sec. Comparing the two compounds, the platinum atoms are co-ordinated through chloride ions and/or nitrogen atoms in both the compounds, and the difference between the two may be expected to be rather small, as far as the electronic state along the infinite chains is concerned. In fact, the charge transfer absorption characteristic of the infinite chains are observed at about the same wave-length. This also seems to support the above assumption of the chain structure.

It was formerly proposed that the compounds with apparently tervalent platinum and palladium which are dealt with in the present and former papers of this series might be dinuclear complexes of such a type as are represented by (1)[11]:

$$\left[\text{A}_4\text{Pt}^{\text{II}}\begin{matrix}\text{X}\\ \\ \text{X}\end{matrix}\text{Pt}^{\text{IV}}\text{A}_4\right]^{4+} \rightleftarrows \left[\text{A}_4\text{Pt}^{\text{IV}}\begin{matrix}\text{X}\\ \\ \text{X}\end{matrix}\text{Pt}^{\text{II}}\text{A}_4\right]^{4+}. \qquad (1)$$

The evidence for this view, however, seems to be very insufficient. Since bivalent platinum usually assumes planar co-ordination, the supposed 6-co-ordination of the bivalent platinum is unusual. It may be impossible to suppose that the bivalent platinum should take octahedral 6-co-ordination which is equivalent to the octahedral co-ordination around the quadrivalent platinum so that the above resonance (1) might be allowed. The spectroscopic studies into polynuclear complexes, which will be reported elsewhere[12], indicate that the dibridged polynuclear complexes in general do not show their absorption in the wave-length regions much longer than the related monomeric compounds. Nor do they show any charge transfer band of the above sort. All these considerations, together with the X-ray structure analysis of a similar compound of tervalent platinum, $\text{Pt(NH}_3)_2\text{Br}_3$,

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[10] The notation, en, denotes a molecule of ethylenediamine.

[11] See, for example, N. V. Sidgwick, "The Chemical Elements and Their Compounds. Vol. II". Oxford Univ. Press, London (1952), p. 1605, etc.

[12] The work is concerned with halogen-bridged complexes: R. Tsuchida and S. Yamada, To be submitted soon.

seem to support our view that the appearance of a new absorption band at the long wavelength and the remarkable polarization of this new band along the *c*-axis in the crystal of Wolffram's red salt may be explained by the assumption of the infinite chains much better than by the model of the dinuclear complex.

In the coure of the present study, we have found that the crystal of $[Pt(EA)_4Cl_2]Cl_2 \cdot 2H_2O$ undergoes photo-decomposition with ultraviolet light. Thus on evaporating spontaneously an aqueous solution of $[Pt(EA)_4Cl_2]Cl_2$ in a sunny room, a small amount of Wolffram's salt is formed besides the crystals of the original compound. The compound, however, is quite stable to the visible light. On irradiating the crystal with a powerful tungsten lamp at a close distance, no decomposition has been observed. On the contrary, when the crystal was put into the light beam from the iron arc, photo-decomposition was found to take place in a few minutes, the crystal beginning to turn red. Observed under the microscope, red spots are formed here and there in the crystal, the spots getting larger and the number of the spots increasing. The red spots might possibly be due to the photo-reduction of the compound, followed by formation of the chain structure, which would be similar to Wolffram's salt. Thus we suppose the main change might be what follows:

$$[Pt(EA)_4Cl_2]^{2+} \xrightarrow{h\nu} [Pt(EA)_4]^{2+} + Cl_2. \qquad (2)$$

This change seems to be rather incomplete in an aqueous solution. After the aqueous solution of the compound is exposed to the sun for scores of hours, the absorption spectrum is found to be slightly different from the absorption of the original compound before the irradiation. Thus the absorption at 76.8×10^{13}/sec. diminishes its intensity. This may be explained as due to the decomposition of $[Pt(EA)_4Cl_2]^{2+}$ and subsequent formation of the $[Pt(EA)_4]^{2+}$ ion, since the former has an absorption band at this wave-length whereas the latter shows no absorption at the same wave-length. A rough estimation indicates that about twenty percent of the original compound has undergone the photoreduction after the exposure of the solution to the sun for about one hundred hours.

It was suggested in the former papers[3] that the formation of the infinite chains as assumed for Wolffram's salt would stabilize some complex radicals which would other-wise be rather unstable. In fact, the complex ion, $[Pt(EA)_4Cl_2]^{2+}$, in the crystal of Wolffram's salt is far more stable to the photo-decomposition than in the crystal of dichloro-tetrakis-(ethylamine)-platinum (IV) chloride. Thus Wolffram's salt does not undergo any change after irradiation with the iron arc for many hours. In the crystal of Wolffram's salt, the approach of the chloride ion in $[Pt(EA)_4Cl_2]^{2+}$ to the platinum(II) ion of an adjacent complex radical may partly diminish the negative charge on the chloride ion, suppressing the charge transfer from the chloride to the platinum(IV) ion, which is the reaction represented by (2). This also is an example of the stabilization of the otherwise unstable complex ions due to their incorporation into the chain structure[3].

There is known a similar type of compounds, such as $Pt(NH_3)pyCl_3$[13], $Pt(NH_3)(EA)Br_3$ and $Pt(NH_3)(EA)Cl_3$[14]. These compounds, which contain apparently tervalent platinum and show quite deep colours, may be believed to have a chain structure similar to that of Wolffram's salt. The unusually deep colour of those compounds may probably be due to the infinite chains in the crystalline state.

Structure of Reihlen's Green Salt.—On adding potassium bromide to a luke-warm, aqueous solution of Wolffram's salt, there are formed slender, green needles[6,15], which have an empirical formula, $Pt(EA)_4Br_3 \cdot 2H_2O$, analogous to that of Wolffram's red salt. Just as in the case of Wolffram's red salt, the crystals of the compound, Reihlen's green salt, dissolve in water to give an orangish-yellow solution, from which the green crystals of the original compound separate out on cooling. From these facts, it is supposed that this compound in the crystalline state may involve a structure similar to that of Wolffram's red salt, being formulated as $[Pt(EA)_4][Pt(EA)_4Br_2]Br_4 \cdot 4H_2O$.

Polarized absorption spectra of this compound have been determined, and shown in Fig. 3. It is seen from this measurement that this compound in the crystalline state shows to the long wave-length side a new absorption band, which may not be observed with the component complex ions alone. This shows that the complex ions in this crystal are subject to some effect. The present measurement also indicates that the new absorption band at the long wave length occurs only with the electric vector along the needle-axis, and not with the electric vector normal to the needle-axis. These re-

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[13] H. D. K. Drew, F. W. Pinkard, W. Wardlaw and E. G. Cox, *J Chem. Soc.*, **1932**, 1004. The symbol, py, denotes a molecule of pyridine.

[14] S. M. Jörgensen, *J. prakt. Chem.*, 33, 489 (1886), etc.

[15] The green compound is referred to tentatively as Reihlen's green salt in the present paper.

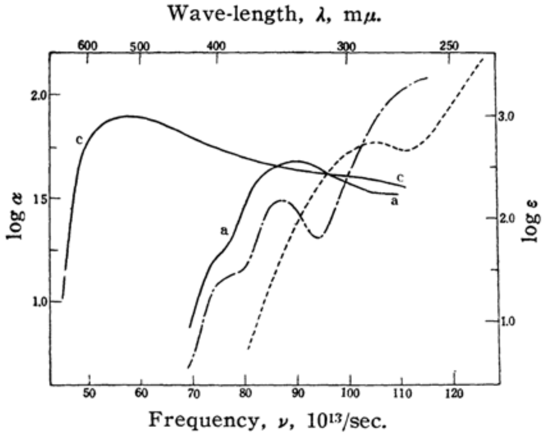

Fig. 3. Absorption spectra of $[Pt(EA)_4][Pt(EA)_4Br_2]Br_4 \cdot 4H_2O$ in the crystalline state (———), $[Pt(EA)_4]Cl_2$ in solution (- - - -) and $[Pt(EA)_4Br_2]Br_2$ in solution (·—·—).

lationships, which are quite similar to those obtained with Wolffram's red salt, may be understood if we assume that the crystal of this compound involves a structure similar to Wolffram's red salt. Thus we are led to the presumption that the compound in the crystalline state contains infinite chains of $---Br—Pt^{IV}—Br---Pt^{II}---Br—Pt^{IV}—Br---$. The absorption at about 51×10^{13}/sec. may possibly be due to the charge transfer along the infinite chains. It is concluded that *the deep colour of this compound is due to the formation of the infinite chains which are similar to those in the crystal of Wolffram's red salt.*

Charge Transfer Spectra.—It has been shown in the above discussion that the compounds with infinite chains of the above kind exhibit in the long wave-length regions charge transfer spectra which are polarized along the chains. Reviewing the data so far obtained, the following relationships on the charge transfer spectra may be derived. (1) *The charge transfer spectrum seems to be unrelated to the spectrum of both the components alone.* (2) *The spectrum is rather intense and broad.* (3) *The spectrum is strongly polarized along the infinite chains. That is, the spectrum is observed only with the electric vector along the infinite chains.*

These relationships are found to be consistent with the theory of the charge transfer spectra recently developed by Mulliken[16].

It is to be noted that the absorption normal to the infinite chains has in the long wave-length a shape similar to the superposition of the absorption spectra of the component complexes in solution. This fact seems to indicate that the absorption normal to the infinite chains may be more closely related to the linkages in the complex radicals.

Comparing the two compounds dealt with in the present work, it is seen that Reihlen's green salt shows its charge transfer band in the longer wave-length regions than the chlorine analogue, Wolffram's red salt. The difference in the wave-length of the charge transfer band between the two is found to be nearly equal to the difference in the ionization potential between the chlorine and bromine. This may also be explained on the basis of the assumption that the charge transfer takes place from the halide to platinum(II) ions.

Summary

Polarized absorption spectra of Wolffram's red salt, $Pt(EA)_4Cl_3 \cdot 2H_2O$, and a related compound, $Pt(EA)_4Br_3 \cdot 2H_2O$, EA being ethylamine, have been determined by Tsuchida-Kobayashi's microscopic method in the regions covering from 2400 to 7500 Å.

Both the compounds, which are supposed to be formulated by $[Pt(EA)_4][Pt(EA)_4X_2]X_4 \cdot 4H_2O$, have been found to show an absorption band that has not been observed with either of the components alone. Moreover, this band is strongly polarized along the needle axis. These relationships may be understood on the assumption that the crystals of these compounds involve infinite chains of $---X—Pt^{IV}—X---Pt^{II}---X—Pt^{IV}—X---$ along the needle axis, X being chlorine or bromine.

The new absorption at the longer wave-length may be considered as a charge transfer band along the infinite chains as assumed above.

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[16] R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950); **74**, 811 (1952). *J. Phys. Chem.*, **56**, 801 (1952).