Spectrochemical Study of Microscopic Crystals. XVIII[1]. *The Color and the Structure of Compounds of a Magnus Green Salt Type*

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Magnus green salt having an empirical formula of $[Pt(NH_3)_4][PtCl_4]$ is peculiar in that the salt in the crystalline state is colored green, whereas the separate component complex-ions in solution are colorless and red, respectively. In order to elucidate the peculiarity, the present authors[2] formerly determined the dichroism of the compound, and concluded that the unusually deep color of Magnus green salt might be due to the possible interaction between platinum atoms which are arranged in a straight line.

When the ammonia molecules in Magnus green salt are replaced by molecules of an alkylamine, the condition around the platinum atoms is supposed to change electronically as well as sterically. Therfore, it seemed to be interesting to see what change would occur in the structure of compounds of a Magnus green salt type with several alkylamines. This paper presents the results obtained concerning the above problem on the basis of dichroism measurements in the visible and ultraviolet region.

Experimental

Materials.—Tetrakis-(methylamine)-platinum(II) chloride was prepared in colorless crystals from potassium tetrachloroplatinate(II) and an excess of methylamine.

Tetrakis-(ethylamine)-platinum(II), tetrakis-(*n*-propylamine)-platinum(II) and tetrakis-(*n*-butylamine)-platinum(II) chloride were prepared in colorless crystals by the same method as in the case of methylamine. The reaction in every case proceeded in quite a similar way. The crystals were purified by repeated recrystallization from hot water. The solubility of the complex compounds in water seems to decrease as the number of carbon atom increases. All the amines used in the present work were of reagent grade.

Compounds of a Magnus green salt type, $[Pt(amine)_4][PtCl_4]$, were prepared by adding a solution of a tetramine-platinum(II) compound into a solution of potassium tetrachloroplatinate(II). The crystals of the compounds precipitated at once when the solutions of the two compounds were mixed together.

$[Pt(methylamine)_4][PtCl_4]$ forms green, needle-like crystals. The crystals show a marked dichroism on the prism face; they are dark green with polarized light having its electric vector along the needle-axis, and pale green with the electric vector perpendicular to the axis. The dichroism measurements were made on the prism face with the electric vectors along the two directions.

$[Pt(ethylamine)_4][PtCl_4]$ forms pink, needle-like crystals, which show a straight extinction and are dichroic. They are pink with the electric vector perpendicular to the needle-axis, and very pale pink with the electric vector along the needle-axis. The dichroism measurements were carried out with the electric vectors along the two directions.

$[Pt(n\text{-propylamine})_4][PtCl_4]$ and $[Pt(n\text{-butylamine})_4][PtCl_4]$ form pink, microcrystalline aggregates. The crystals obtained were so small that the dichroism measurements were not made.

Measurements.—The dichroism measurements in the visible and near-ultraviolet region of the crystals were carried out by Tsuchida-Kobayashi's microscopic method[3], as in the former papers of this series. The measurements were also made with a newly constructed apparatus, which consists in principle of a monochromator, a reflecting microscope and a photo-electric detector with a photomultiplier. Most of the parts were made by the Olympus Co.[4] The detailed description of the apparatus will be presented elsewhere.

The *c*- and *a*- absorption in the figures represent the absorption with the electric vector along and perpendicular to the needle-axis of the crystal, respectively.

Results and Discussion

The results of the measurements are shown in Fig. 1 and Fig. 2. It is seen that $[Pt(methylamine)_4][PtCl_4]$ in the crystalline state absorbs the light in a wavelength region much longer than the component complex-ions in solution (Fig. 1).

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[1] Paper XVII of this series, S. Yamada, H. Nakamura and R. Tsuchida, This Bulletin, **31**, 303 (1958).

[2] S. Yamada and R. Tsuchida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **70**, 142 (1949); S. Yamada, *J. Am. Chem. Soc.*, **73**, 1579 (1951).

[3] R. Tsuchida and M. Kobayashi, "The Color and the Structure of Metallic Compounds," Zoshindo, Osaka, 1944, p. 180.

[4] R. Tsuchida and S. Yamada, to be published later. The apparatus was constructed in co-operation with the staffs of Olympus Co., to whom we are greatly indebted.

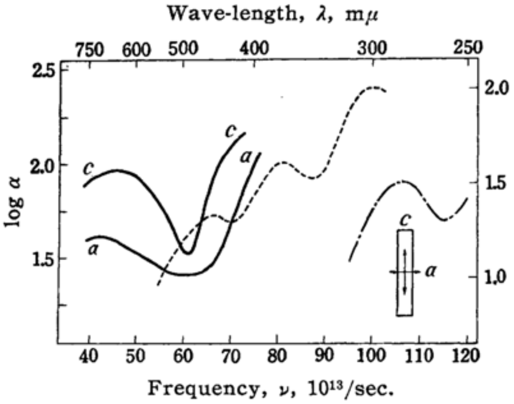

Fig. 1. Absorption spectra of [Pt(methylamine)$_4$][PtCl$_4$] in the crystalline state (——), [Pt(methylamine)$_4$]Cl$_2$ (— - —) and K$_2$[PtCl$_4$] (-----) in aqueous solution. The latter two curves are taken from H. Yoneda, This Bulletin, **30**, 130 (1957) and ref. 6, respectively.

Thus the Magnus green salt type compound of methylamine shows a band at 46.6×10^{13}/sec. (644 mμ), whereas the separate component ions are transparent in this region. It is presumed, therefore, that the complex-ions in the crystal of [Pt(methylamine)$_4$][PtCl$_4$] are under an effect, which is much stronger than that due to the crystalline field of ordinary compounds. The crystal structure analysis of the methylamine Magnus salt is not available for the present. The nature of the effect, however, may be judged from comparison of the dichroism of the compound with the dichroism of Magnus green salt, [Pt(NH$_3$)$_4$][PtCl$_4$]$^{2)}$. The comparison reveals that the dichroism of the former is quite similar to that of the latter. Therefore, the state of the component complex ions in both the compounds may be almost the same.

It would be appropriate to recall the results with the latter$^{2)}$, in the crystal of which the planar complex-ions were determined with X-rays to be arranged parallel to each other with platinum atoms disposed at an equal distance along a straight line. The crystal of [Pt(NH$_3$)$_4$][PtCl$_4$] was found to show in the longer wave-length region an absorption band of a new sort, which was not shown by either of the separate component complex-ions alone. For the new absorption band, the absorption is considerably stronger in the direction perpendicular to the planar complex-ions than along the complex-ions. This relationship, combined with the crystal structure analyses$^{5)}$, led us to the conclusion that in the crystal of Magnus green salt there would be a direct type of interaction between the platinum atoms along the direction perpendicular to the complex-plane.

Based on this result and on the close similarity in the dichroism between the two compounds, the dichroism of [Pt(methylamine)$_4$][PtCl$_4$] in the crystalline state, as has been determined in the present work, may be readily understood, when it is assumed that the *c*-absorption corresponds to the absorption with the electric vector perpendicular to the complex-plane and the *a*-absorption to the absorption with the electric vector along the complex-plane. Thus it may be most likely that the planar complex-ions in the crystal of this compound are arranged in such a way that they are piled one just above and one below another with their planes parallel to each other, and that there would exist a direct type of interaction between platinum atoms in the direction along the needle-axis.

On the contrary, the absorption spectra of [Pt(ethylamine)$_4$][PtCl$_4$] in the crystalline state may be understood in terms of the absorption spectra of the separate component ions undergoing no extraordinary effect. It is seen in Fig. 2 that the ethylamine Magnus salt does not show an absorption band in the region of longer wave-length than the region where either of the separate complex-ions alone absorbs

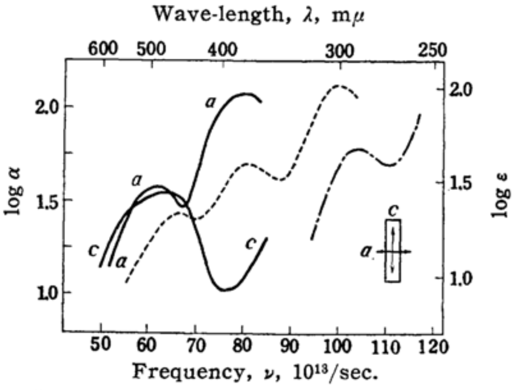

Fig. 2. Absorption spectra of [Pt(ethylamine)$_4$][PtCl$_4$] in the crystalline state (——), [Pt(ethylamine)$_4$]Cl$_2$ (— - —) and K$_2$[PtCl$_4$] (----) in aqueous solution. The last two curves are taken from the references cited in Fig. 1.

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5) E. G. Cox, F. W. Pinkard, W. Wardlaw and G. H. Preston, *J. Chem. Soc.*, **1932**, 2527; M. Atoji, J. W. Richardson and R. E. Rundle, *J. Am. Chem. Soc.*, **79**, 3017 (1957).

in solution. Moreover, the dichroism as well as the absorption spectrum of the crystal closely resembles that of $K_2[PtCl_4]$ in the crystalline state[6]. Thus it may be assumed that the *c*-absorption of the former represents the feature of the $\perp$-absorption and the *a*-absorption the $\parallel$-absorption of the latter, where the $\parallel$- and the $\perp$-absorption denote the absorption with the electric vector parallel and perpendicular to the plane of the complex-ion. The crystal structure analysis has not yet been reported with this salt. The above consideration indicates, however, that between platinum atoms in the crystal of $[Pt(ethylamine)_4][PtCl_4]$ there is no interaction of such a sort as exists in the crystal of Magnus green salt and the corresponding compound of methylamine.

Summarizing the results obtained in the present and former reports, we may derive the following presumption. *The compound of a Magnus salt type, which is represented by $[Pt(amine)_4][PtCl_4]$, may be classified into two kinds. One is colored green, involving a direct type of metal-to-metal interaction. The other is pink and involves no interaction of the above kind.*

The above conclusion may be used for differentiating the two types. In fact, this criterion has been applied in the present work to the case of higher alkylamines. The Magnus salt type compound of *n*-propylamine is obtained in pink microcrystals by the same method as in the case of Magnus green salt. Thus a difficultly soluble precipitate of $[Pt(n\text{-}propylamine)_4][PtCl_4]$ is formed at once, when an aqueous solution of $[Pt(n\text{-}propylamine)_4]Cl_2$ is added to a solution of $K_2[PtCl_4]$. The pink color of the salt may be regarded on the basis of the above-mentioned criterion as showing that the compound involves no metal-to-metal interaction. It is concluded in a similar way that no metal-to-metal interaction is operative in the crystal of $[Pt(n\text{-}butylamine)_4][PtCl_4]$.

It may well be presumed further that *no metal-to-metal interaction would be present in the crystals of the compounds of a Magnus salt type with higher homologues of alkylamines.* The conclusion which has been obtained up to the present is shown in Table I. It is worth noting that the drastic change from methylamine to ethylamine or higher alkylamines is found.

TABLE I

THE METAL-TO-METAL INTERACTION IN THE COMPOUNDS OF A MAGNUS SALT TYPE, $[Pt(amine)_4][PtCl_4]$

Amine	Color	Pt-to-Pt interaction
NH_3	green	present
CH_3NH_2	green	present
$C_2H_5NH_2$	pink	absent
$n\text{-}C_3H_7NH_2$	pink	absent
$n\text{-}C_4H_9NH_2$	pink	absent

This result may be explained tentatively in terms of the following two effects. One is due to the change in the inductive effect of the alkyl-group upon the nitrogen atom, and the other to the change in the steric condition around the platinum atom.

The inductive effect, on the one hand, seems to be inadequate for explaining the transition as mentioned above. The tendency of the alkyl-group to push the electronic density toward the nitrogen atom becomes greater as we go from methyl- to higher alkyl-groups. Since higher electronic density on the platinum atom would be favorable for the metal-to-metal interaction, the tendency, as is observed in Table I, can not be explained as due to the inductive effect of the alkyl-group.

On the other hand, the steric condition is considered to become less favorable for the suitable arrangement of the planar complexes, as the alkyl-groups become more bulky. Although increasing number of carbon atoms would not absolutely prevent the platinum atoms from approaching each other so closely that the metal-to-metal interaction might result, it would certainly make difficult the formation of the crystal lattice consisting of series of platinum atoms which are arranged along straight lines.

We have also found that the direct type of interaction between platinum atoms is not present in the crystals of $[Pt\,en_2][PtCl_4]$ or $[Pt(pyridine)_4][PtCl_4]$[7]. This conclusion may be understood in terms of the steric factor, similarly to the case of alkylamines.

Summary

The color and the structure of the compounds of a Magnus green salt type, $[Pt(amine)_4][PtCl_4]$, have been studied. The dichroism with crystals of $[Pt(methylamine)_4][PtCl_4]$ and $[Pt(ethylamine)_4][PtCl_4]$ has been quantitatively determined

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[6] S. Yamada, H. Yoneda and R. Tsuchida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **69**, 145 (1948).

[7] S. Yamada and R. Tsuchida, to be published later.

at room temperature in the visible and ultraviolet region by the microscopic method. From the measurements, the unusually deep color of the former has been shown to be ascribed to a direct type of interaction between platinum atoms. No interaction of this sort is present in the crystal of the latter, which is pink in color.

It is suggested that the compounds having a formula of $[Pt(alkylamine)_4][PtCl_4]$ may generally be classified into two kinds, one being colored green and the other pink. In the crystals of the former there is a direct type of interaction between platinum atoms at the center of the planar complexes, but no interaction of such a sort is operative in the crystals of the latter.

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