[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OSAKA UNIVERSITY]

Researches on Dichroism of Planar Complexes. II. The Color and the Structure of $[Pt(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][PtBr_4]$

BY SHOICHIRO YAMADA

Dichroism of crystals of "Magnus salt type compounds," $[Pt(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][PtBr_4]$, was measured in the visible and near-ultraviolet region by the microscopic method. From comparative consideration of measurement results with dichroism of K_2PtCl_4, $K_2PtBr_4 \cdot 2H_2O$ and $Pt(NH_3)_4Cl_2 \cdot H_2O$ previously reported, the color of Magnus' salt type compounds was discussed. In these compounds, there exists direct interaction between platinum ions of planar complex ions PtX_4^{--} (X: halogens) and $Pt(NH_3)_4^{++}$, which gives rise to remarkable bathochromic effect. This interaction is supposed due to mutual disturbance between electronic clouds of d-electrons which spread above and below the central platinum ions.

On mixing a colorless aqueous solution of tetramminoplatinum(II) chloride and a red solution of potassium tetrachloroplatinate(II), a difficultly soluble green compound, $[Pt(NH_3)_4][PtCl_4]$, is formed, which is called Magnus green salt. The remarkable change of color in this reaction as well as the deep color of this compound has attracted attention of a number of investigators. No direct research on the subject, however, has been undertaken, nor any plausible explanation has been proposed about the origin of this color. This reseach was undertaken for the purpose of investigating the color of Magnus salt and its related compound, $[Pt(NH_3)_4][PtBr_4]$. These compounds are so sparingly soluble that it is impossible to measure absorption in solutions. Moreover, ordinary methods of the absorption measurement of the crystal cannot be applied since crystals large enough for the measurement are unavailable. In this work, dichroism of crystals of $[Pt(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][PtBr_4]$ was measured in the visible and the ultraviolet region by the microscopic method.[1] The result of the measurement was discussed in relation to the dichroism of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$, $K_2[PtCl_4]$ and $K_2[PtBr_4] \cdot 2H_2O$ which had been formerly reported.[2]

Experimental

Magnus green salt, $[Pt(NH_3)_4][PtCl_4]$, was obtained in green prismatic needles from aqueous solution of potassium tetrachloroplatinate(II) and that of tetramminoplatinum (II) chloride. The tetragonal crystal of this compound shows remarkable dichroism; it appears dark green by polarized light with electric vector parallel to the *c*-axis and very pale green by that perpendicular to the *c*-axis. The crystal structure was analyzed by Cox and others.[3]

Br-Magnus salt, $[Pt(NH_3)_4][PtBr_4]$, was prepared by a similar method as in the case of Magnus salt. The crystal of this compound belongs to the tetragonal system, and is dichroic, that is, dark green by polarized light parallel to the *c*-axis, and yellowish-green by that perpendicular to it.

Dichroism measurement of microcrystals was carried out with polarized light parallel and perpendicular to the *c*-axis by means of the microscopic method, as previously reported.[1,2] The results of measurement are shown in the Figs. 1 and 2. The notations "∥-absorption" and "⊥-absorption" represent absorptions by polarized lights with electric vectors parallel and perpendicular to the plane of the complex ions, respectively. α means extinction coefficient per mm. of the crystal. For comparison dichroisms of $Pt(NH_3)_4Cl_2 \cdot H_2O$, K_2PtCl_4 and $K_2PtBr_4 \cdot 2H_2O$[2] are shown in the figures.

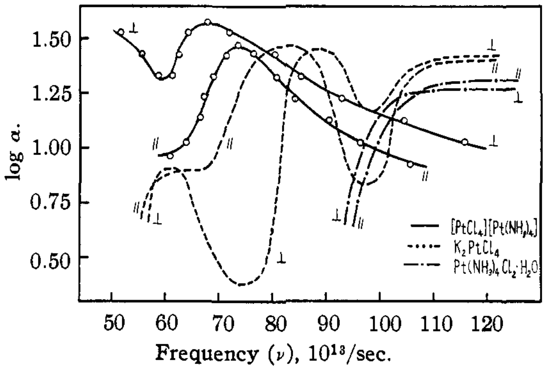

Fig. 1.—Dichroism of $[PtCl_4][Pt(NH_3)_4]$, K_2PtCl_4[a] and $Pt(NH_3)_4Cl_2 \cdot H_2O$[a].

[a] Curves of these compounds were taken for comparison from the previous report. ref. (2).

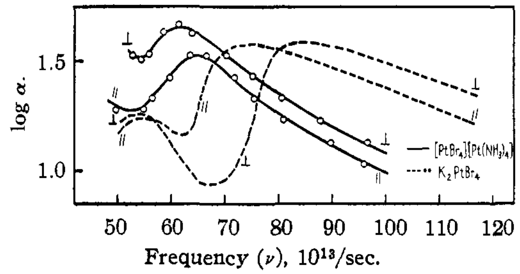

Fig. 2.—Dichroism of $[PtBr_4][Pt(NH_3)_4]$ and K_2PtBr_4[a].

[a] Curves of these compounds were taken for comparison from the previous report, ref. (2).

Discussion of Results

If both the component ions in the Magnus salt were in the state not much different from those in the crystal of K_2PtCl_4 or $Pt(NH_3)_4Cl_2 \cdot H_2O$, the crystal of the Magnus salt would show such an absorption spectrum as obtained by superposing absorption spectra of both component ions in the above mentioned compounds. The crystal of Magnus salt, however, shows different absorption spectrum from those of K_2PtCl_4 and $Pt(NH_3)_4Cl_2 \cdot H_2O$ or superposition of them. Consequently, it is evident that both complex ions in the Magnus salt are in a more unstable state and that the absorptions characterizing these ions are shifted bathochromically as compared to those in the crystals of K_2PtCl_4 and $Pt(NH_3)_4Cl_2 \cdot H_2O$. Comparative considerations on absorption spectrum of the Magnus salt with those of K_2PtCl_4 and $Pt(NH_3)_4Cl_2 \cdot H_2O$ leads to the conclusion that absorption bands of this salt with maxima $\nu = 68$ and $\nu = 74$ ($\times 10^{13}$/sec.)

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(1) Tsuchida and Kobayashi, *Bull. Chem. Soc. Japan*, **13**, 619 (1938); "The Colours and the Structures of Metallic Compounds," Osaka, Japan, 1944, p. 180.

(2) Yamada, THIS JOURNAL, **73**, 1182 (1951).

(3) Cox, Pinkard, Wardlaw and Preston, *J. Chem. Soc.*, 2527 (1932).

correspond to the third band[4] of $PtCl_4^{--}$ ion with that of $Pt(NH_3)_4^{++}$ ion partly overlapped on it.

The crystal structure of Br–Magnus salt has not been analyzed as yet. From comparison of external form and dichroism of the compound with those of Magnus salt, it can be presumed that Br-Magnus salt has the similar crystal structure to that of the Magnus salt. That is, it has such a crystal structure that planar complex ions, $PtBr_4^{--}$ and $Pt(NH_3)_4^{++}$, are piled alternatively along the *c*-axis, with the complex planes parallel to each other and perpendicular to the *c*-axis. The notations $\parallel$- and $\perp$-absorption in the Fig. 2 are based on such a crystal structure as above postulated. Thus, it is found that absorption bands of Br–Magnus salt with maxima at $\nu = 65$ and $\nu = 61$ are of similar nature to those of Magnus salt with maxima at $\nu = 74$ and $\nu = 68$, corresponding to the third absorption band of $PtBr_4^{--}$ ion.

As can be seen in the Figs. 1 and 2, the crystals of these Magnus salt type complex compounds show similar absorption curves and dichroism, with the only difference that the Br-Magnus compound has the corresponding absorption band at the longer wave length than the Magnus salt in accord with the spectrochemical series.[4b] The following regularities, which are common for both compounds, can be deduced on dichroism of the absorption band in the shorter wave length region. (1) The intensity of $\perp$-absorption is larger than that of $\parallel$-absorption, the ratio $\alpha_\perp/\alpha_\parallel$ being

$$\log (\alpha_\perp/\alpha_\parallel) = 0.1, \text{ or } \alpha_\perp/\alpha_\parallel = 1.25$$

(2) $\perp$-absorption is more bathochromic than $\parallel$-absorption.

These regularities afford some information about the state of complex ions in the crystals of "Magnus salt type compounds." It is evident that dichroism of Magnus salt type compounds is different from what should be expected from those of K_2PtCl_4, $K_2PtBr_4 \cdot 2H_2O$ and $Pt(NH_3)_4Cl_2 \cdot H_2O$. Thus, the first of those regularities in Magnus salt means that polarized light with electric vector perpendicular to the plane of complex is more easily absorbed than that parallel to the plane of complex, which is rather unusual for ordinary compounds with planar complexes. This anomaly suggests that there is some interaction between complex ions in the direction perpendicular to the plane of complex ions, which gives direct effects to absorption of complex ions.

The second regularity means that bathochromic change of $\perp$-absorption as compared with independent component complex ions is larger than that of $\parallel$-absorption and hence larger change is expected in the direction perpendicular to the plane of complex than in the parallel direction.

Taking the crystal structure of Magnus salt type compounds into consideration, it can be concluded that there exists interaction between planar complex ions perpendicular to the planes of them. One idea of such interactions would be that between chlorine ion and ammonia of the complex ions arranged above and below one another. Such an idea, however, cannot be accepted, since it would affect indirectly the linkage between platinum and chlorine or platinum and ammonia, and would have bathochromic effect to both $\parallel$- and $\perp$-absorption, but cannot explain dichroism of Magnus salt type compounds satisfactorily, which is markedly different from those of independent complex ions in intensity of the band as well as wave length. In order to satisfy such regularities as mentioned above, interaction which has direct effect to absorption of complex ions, should be expected in the direction perpendicular to the plane of complex ions.

Direct interaction between platinum ions can be mentioned as such.

As described above, two kinds of planar complex ions are arranged parallel to each other in the Magnus salt type compounds, with their planes perpendicular to the *c*-axis. On the other hand, in planar complex ions such as tetrahalogenoplatinate(II) ions, the central platinum ion is coördinated by four halogen ions at the corners of the *square* and two pairs of d-electrons above and below the central platinum ion. The interaction between platinum ions of planar complex ions above and below one another, which is responsible for the deep color, is considered to exist in the crystals of Magnus salt type compounds. Such interaction is due to a kind of mutual disturbance between electronic clouds of d-electrons spreading above and below the platinum. This bears resemblance to that which is supposed to exist in aromatic molecular compounds such as quinhydrone,[5] and is also very similar to some interaction between certain dyestuffs, which Scheibe and Kortüm reported about.[6]

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NAKANOSHIMA, OSAKA CITY, JAPAN

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[4] (a) Tsuchida and Yamada, *J. Chem. Soc., Japan*, **70**, 44 (1949); (b) about the third band, *cf.* Tsuchida, *Bull. Chem. Soc., Japan*, **13**, 388, 436 (1938).

[5] Tsuchida, Yamada and Nakamoto, unpublished.

[6] Scheibe, *Z. angew. Chem.*, **50**, 51, 212 (1937); Kortüm, *Z. physik. Chem.*, **34**, 255 (1936), etc.