Researches on Dichroism of Planar Complexes. III. The Color and the Structure of the Crystals of Tetracyanoplatinates (II)

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Crystals of some tetracyanoplatinates (II) have been known to show unusually deep colors. For example, crystals of the barium and calcium salts are yellow, and those of the magnesium salt orange red; they show different colors for different degrees of hydration of the same cations, whose aqueous solutions are all colorless. Such unusual colors of the salts, which seem closely related to the anisotropic character of the planar tetracyanoplatinates (II), indicate that planar complexes in these crystals are in a condition quite different from their state in solution. On the colored crystals of tetracyanoplatinates (II) there have been reported several researches, which, however, have scarcely dealt with the relation between absorption and structure or bonding; nor has any plausible explanation as to the colors of the crystals of these compounds been presented.

This research was undertaken for the purpose of investigating the problem of the colors of magnesium, calcium and barium tetracyanoplatinates (II) in the crystalline state. In this work the dichroism of the crystals of $BaPt(CN)_4 \cdot 4H_2O$, $CaPt(CN)_4 \cdot 5H_2O$ and $MgPt(CN)_4 \cdot 7H_2O$ was measured, and this phenomenon is discussed in relation to the crystal structure.

Experimental

Measurement.—Quantitative dichroism measurements of the crystals were carried out by the microscopic method with microcrystals, as described in the previous report⁽¹⁾. α denotes absorption coefficient per mm. of the crystal, and //- or ⊥-absorption represents that of polarized light with electric vector parallel or perpendicular, respectively, to the complex plane.

Extinction coefficients, ε, of barium tetracyanoplatinate (II) in aqueous solution were determined by the photographic method using a sector photometer⁽²⁾. Aqueous solutions of the complex salt were 3.3×10^{-3}, 1.3×10^{-4} and 3.3×10^{-5} molar. Measurements were made at room temperature.

Materials.—$BaPt(CN)_4 \cdot 4H_2O$. The pure yellow compound was obtained as monoclinic prisms by recrystallizing a sample of the compound of commercial reagent grade. The crystal structure has been studied by Brasseur and de Rassenfosse⁽³⁾.

$CaPt(CN)_4 \cdot 5H_2O$. It was prepared from aqueous solutions of barium tetracyanoplatinate (II) and calcium sulfate as yellow, orthorhombic, prismatic crystals. The crystal structure has not been completely analyzed, although the lattice constants and the unit cell have been determined⁽⁴⁾.

$MgPt(CN)_4 \cdot 7H_2O$. It was prepared from aqueous solutions of the barium salt and magnesium sulfate. Red, tetragonal, prismatic crystals with green metallic luster were obtained. The crystal structure has been studied by Pauling and Bozorth⁽⁵⁾.

Results and Discussion

The Crystal Structure of $CaPt(CN)_4 \cdot 5H_2O$.—The crystal structure of the calcium salt has not been determined as yet. Absorption spectrum of this crystal by polarized light perpendicular to the c-axis, however, bears a striking resemblance to //-absorptions of both barium and magnesium salts, each of them showing a sharp, characteristic absorption band

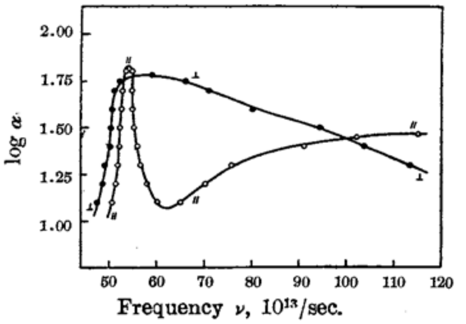

Fig. 1.—Dichroism of $MgPt(CN)_4 \cdot 7H_2O$.

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(1) S. Yamada, *J. Am. Chem. Soc.* **73**, 1182 (1951)

(2) The study of J. A. Khvostikov (*Physik. Z. Sowjetunion*, **9**, 211 (1936)) states that aqueous solutions of magnesium, barium and potassium salts show the same absorption spectra.

(3) H. Brasseur and A. de Rassenfosse, *Z. Krist.*, **88**, 210, 221 (1934).

(4) H. Brasseur and A. de Rassenfosse, *Bull. soc. roy. sci. Liège*, **4**, 24 (1935).

(5) R. M. Bozorth and L. Pauling, *Phys. Rev.*, **39**, 538 (1932).

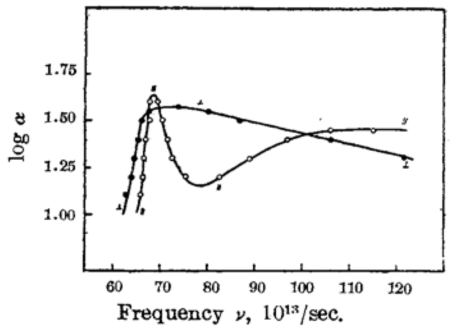

Fig. 2.—Dichroism of $CaPt(CN)_4 \cdot 5H_2O$.

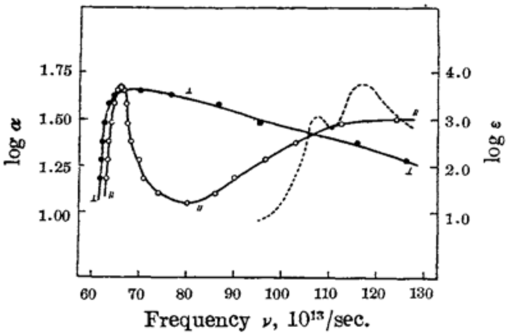

Fig. 3.—Dichroism of $BaPt(CN)_4 \cdot 4H_2O$ and absorption spectrum of aqueous solution (dotted curve).

of the same kind, which has scarcely ever been found in the crystals previously measured. On the other hand, the absorption spectrum of the calcium salt by polarized light parallel to the c-axis is similar to ⊥-absorption of the other salts. Now, according to the hypotheses that absorption by the calcium salt of polarized light perpendicular to the c-axis corresponds to //-absorption and that the other absorption corresponds to ⊥-absorption, its dichroism seems quite similar to that of the other salts. In consequence, tetracyanoplatinate (II) ions in the crystal of calcium salt are assumed to be arranged in the same way as in those of the barium or magnesium salt, in which planar ions, $Pt(CN)_4^{--}$, are oriented parallel to each other and perpendicular to the c-axis, with platinum ions disposed in equal distances on straight lines parallel to the c-axis. On the basis of the above presumption was designated //-or ⊥-absorption for $CaPt(CN)_4 \cdot 5H_2O$ in Fig. 2.

The State of the Complex Ions in Crystals.—First, the fact that the crystals of these three compounds show similar dichroism, different from each other only in the position of the absorption band, suggests that the complex ions undergo quite similar effects in these three compounds(6). Secondly, it is recognized from the figures that ⊥-absorption is both more bathochromic and more hyperchromic than //-absorption in all of these compounds, showing that the complex ion in the crystalline state is influenced more effectively in the direction perpendicular to the complex plane than in the plane, and that the force is exerted perpendicularly upon it. Thirdly, the order of bathochromicity for the sharp bands of the //-absorptions (Table 1) indicates that the effect upon the complex ion increases in the order Ca, Ba and Mg salts, since the larger the effect on the complex ion, the more bathochromically the absorption would be displaced. This order is in conformity with the increasing order of sharpness of the characteristic band (Table 1), but differs from the order of strength of the cations expected from the periodic table.

Table 1

Characteristic Bands of //-Absorption

	Shortest dist. between Pt ions	Frequency at abs. max. sec^{-1}	Half width, sec^{-1}.
$MgPt(CN)_4 \cdot 7H_2O$	3.13(a) Å.	54.0×10^{13}	2.8×10^{13}
$CaPt(CN)_4 \cdot 5H_2O$	3.32(b) Å.	68.6	5.4
$BaPt(CN)_4 \cdot 4H_2O$	3.27(c) Å.	65.8	4.6
$[Pt(NH_3)_4][PtCl_4]$	3.21(d) Å.		

(a) Ref. 5.

(b) This value was estimated on the basis of the crystal structure assumed in this report and from the data given in Ref. 3.

(c) Ref. 4.

(d) E. G. Cox, F. W. Pinkard, W. Wardlaw and G. H. Preston, *J. Chem. Soc.*, **1932**, 2527.

From the foregoing considerations, it is concluded that the force on the complex ions in the crystal differs from the Coulombic force between the cation and the complex anion. As to the force in these crystals, direct interaction between complex ions, of the same kind as was suggested for Magnus' salt in the previous report(7), is proposed. Thus, in these crystals, the mutual interaction between central platinum ions of planar complex ions is supposed to be exerted upon one another, where the pairs of electrons in coordination above and below the central platinum would contribute in a considerable degree. The considerably smaller interplatinic distance for the magnesium salt as compared with that for

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(6) It is quite clear from comparison of the absorption spectra of the crystals and of the solution that complex ions in the crystals are in a condition quite different from their state in solution.

(7) S. Yamada, *J. Am. Chem. Soc.*, **73**, 1579 (1951)

Magnus' salt would allow us to expect larger interaction between complex ions in the former than in the latter. The distances in cases of both barium and calcium salts are considered to be short enough for direct interaction to be expected between complex ions.

Thus, it is concluded that, as the distance between platinum ions becomes smaller and, in consequence, the interaction stronger in the order of Ca, Ba and Mg salts (Table 1), the absorption is displaced toward longer wave-length and the characteristic band of //-absorption becomes sharper. It may be supposed that, as the interaction between platinum ions increases in the order Ca, Ba and Mg salts, the prismatic aggregates of $Pt(CN)_4^{--}$ ions are more firmly connected together through platinum ions, with the result that a new electronic system is formed and the absorption suffers bathochromic effects, the characteristic band of //-absorption increasing in sharpness. The interaction between platinum ions in these tetracyanoplatinates (II) is extraordinary as compared to that in Magnus' salt; in the latter the interaction is reinforced by Coulombic attraction between complex ions of opposite electrical charges, while in the former there must be instead a repulsion between complex anions of the same sign.

Summary

The dichroism of crystals of $BaPt(CN)_4\cdot 4H_2O$, $CaPt(CN)_4\cdot 5H_2O$ and $MgPt(CN)_4\cdot 7H_2O$ has been measured in the visible and the near-ultraviolet region, and with the aid of results of this measurement, the state of the complex ions in the crystals has been discussed in relation to their crystal structures. These crystals show similar dichroism, with the characteristic sharp absorption band for //-absorption. It has been concluded that beween adjacent tetragonal complex ions piled upon one another along the c-axis in these crystals there exists a sort of direct interaction, which is supposed to be related to the unusual colors of these compounds. It has been found that as the distance between platinums decreases in the order of Ca, Ba and Mg salts, the interaction between platinum ions becomes stronger, and that the characteristic band becomes sharper and is displaced towards longer wave-length. The interaction in these crystals is regarded as more remarkable than that in Magnus' salt.

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