that it is in this region that fundamental C–H frequencies occur; also that extensive work on N–H frequencies[7,8] has shown them to occur in about the same region as those due to C–H frequencies. The line at 2795 cm.$^{-1}$ (appearing only at the high temperature) may be due to a N–H vibration. The other line (appearing at both low and high temperatures) suggests the possibility of the N–H—O bond.[9] The changes occurring with temperature as well as a recent observation in this Laboratory of a weak band in the corresponding position in the infrared absorption spectrum indicate that this is not a mercury line. Investigation is being continued to decide more definitely the nature of the bond to which this vibration must be ascribed.

Summary

1. Raman spectra have been taken of pure acetoxime at various temperatures from 70 to 130° and of carbon tetrachloride solutions of acetoxime at various concentrations at 60°.

2. Microphotometer tracings of the spectra show that the O–H band at 3400 cm.$^{-1}$ gradually changes position and shows a sharp line at temperatures greater than 100° and in dilute solutions. These changes are due to the breaking of hydrogen bonds in the acetoxime.

3. Evidence is also presented which may indicate that acetoxime exists in tautomeric forms.

SEATTLE 5, WASH. RECEIVED[10] NOVEMBER 30, 1950

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[7] Edsall, *J. Chem. Phys.*, **5**, 225 (1937).

[8] Bernstein and Martin, *Trans. Roy. Soc. Can.*, III, **31**, 95 (1937).

[9] Pauling, "The Nature of the Chemical Bond," Cornell University Press., Ithaca, N. Y., 1939.

[10] Original manuscript received June 15, 1944.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OSAKA UNIVERSITY]

Researches on Dichroism of Planar Complexes. I

BY SHOICHIRO YAMADA

Absorption spectra of crystals are very important from both the theoretical and experimental points of view. For example, since molecules or ions are considered to be fixed in the crystal, measurement of pleochroism is expected to give certain information about the difference of bonds in different directions as well as the arrangement of ions or molecules. It is due to technical difficulties that measurements of absorption spectra of crystals have been so scarce.[1] Formerly, Tsuchida invented a new method,[2,3] which enables us to make measurements of dichroism in the visible and the near ultraviolet region with microscopic crystals easily obtainable in ordinary procedures of preparation. By this method, researches on absorption spectra of crystals have been carried out, some of which were about dichroism of metallic complex compounds[3,4] and dichroism of the benzene ring.[5] The present paper deals with the dichroism measurement of compounds with planar complex ions.

Experimental

Materials.—K_2PdCl_4 was prepared according to the direction of Gutbier and Krell.[6] It forms orangish-brown, tetragonal crystals. The structure of the crystal was analyzed by R. G. Dickinson.[7]

K_2PtCl_4 was obtained as red, prismatic, tetragonal crystals by reducing K_2PtCl_6 with potassium oxalate. The crystal analysis was made by R. G. Dickinson.[7]

$K_2PdBr_4 \cdot 2H_2O$ was prepared by the method of Gutbier and Krell.[6] The brown prismatic crystals belong to the rhombic system.

$K_2PtBr_4 \cdot 2H_2O$ was prepared as purplish-red, rhombic crystals by the same method as in K_2PtCl_4.

$Pd(NH_3)_4Cl_2 \cdot H_2O$ was prepared according to the direction of Cox.[8] The crystal structure was determined by B. N. Dickinson.[9]

$Pt(NH_3)_4Cl_2 \cdot H_2O$ was prepared by the method of Cox.[8] The crystal structure analysis was carried out by Dickinson.[9]

$K_2Pd(CN)_4 \cdot 3H_2O$ was obtained from K_2PdCl_4 and KCN as colorless, triclinic prisms.

$BaNi(CN)_4 \cdot 4H_2O$ was prepared according to the method of Brasseur.[10] The crystal structure was determined by him.

Quantitative Measurement of Dichroism of Microscopic Crystals.—In the present research was applied the microcrystal method,[2,3] which makes it possible to measure absorption spectra of solid substances in microcrystalline state. It is in most cases very difficult to make measurement of absorption of solid substances by ordinary methods which implies raising a considerably large, single crystal and preparing from it a thin plane-parallel section by polishing. Principal part of the apparatus consists of a quartz microscope and a quartz spectrograph with a sectorphotometer. Both spectra of light through the crystal and of light for comparison were photographed on the plate. Measurements were made in the region from about 6000 Å. to nearly 2000 Å. with linearly polarized light parallel and perpendicular to the principal axis. The extinction coefficient per mm., α, is given by the expression

$$\alpha = 0.9/d \log a_0/a$$

where d is thickness in mm. of the crystal, and a_0 and a are angles of the rotating sector for light through the crystal and the light for comparison. The results of dichroism measurement were shown in the figures 1 to 4. The $||$ or $\perp$ denotes absorption by polarized light with electric vector parallel or perpendicular to the planes of planar complex ions, respectively. Thickness of the crystals used was several hundredths of mm.

Discussion of Results

Previously Tsuchida,[11] in his general theory on the absorption bands of metallic complex compounds, explained many data by classifying four kinds of absorption bands, the first, second, third

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[1] Krishnan and Seshan, *Proc. Indian Acad. Sci.*, **8**, 487 (1938); Scheibe, *Z. angew. Chem.*, **52**, 631 (1939); Le Roux, *Compt. rend.*, **196**, 394 (1933) etc.

[2] Tsuchida and Kobayashi, *Bull. Chem. Soc. Japan*, **13**, 619 (1938); *J. Chem. Soc. Japan*, **60**, 769 (1939).

[3] Tsuchida and Kobayashi, "The Colours and the Structures of Metallic Compounds," Osaka, Japan, 1944.

[4] Tsuchida, Yamada and Yoneda, *J. Chem. Soc. Japan*, **69**, 145 (1948); Tsuchida and Yamada, *ibid.*, **70**, 44 (1949).

[5] Tsuchida, Kobayashi and Nakamoto, *ibid.*, **70**, 12 (1949).

[6] Gutbier and Krell, *Ber.*, **38**, 2385 (1905).

[7] R. G. Dickinson, THIS JOURNAL, **44**, 2404 (1922).

[8] Cox and Preston, *J. Chem. Soc.*, 1089 (1933).

[9] B. N. Dickinson, *Z. Krist.*, **88**, 281 (1934).

[10] Brasseur, De Rassenfosse and Pierard, *ibid.*, **88**, 210 (1934).

[11] Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 388, 436 (1938).

and special bands according as their origins. According to him the first absorption band is due to electron transitions in an unsaturated shell of the central ion, the second band to coördination electrons, the third band to electronegative ligands in transpositions, and the special band to the special ligand such as nitro, isothiocyanate, etc.

In the following, discussion about dichroism of planar complex ions will be made on the basis of Tsuchida's theory. From Figs. 1 to 4, it is seen that the nature of dichroism of planar complex ions is classified into two types, that is, the tetrahalogeno-complex type, to which belong $PdCl_4^{--}$, $PdBr_4^{--}$, $PtCl_4^{--}$ and $PtBr_4^{--}$ and the tetracyano-complex type, to which belong the other four. The following regularities may be found in the former type (Figs. 1 and 2). (1) The second absorption band of ||-absorption is more bathochromic than that of ⊥-absorption. (2) In palladous complex ions, the second band of ||-absorption is more hyperchromic than that of ⊥-absorption. In platinous complex ions, the second band of ||- and ⊥-absorption show about equal intensity. (3) Both ||- and ⊥-absorption spectra show the first bands at about the same wave length.

The latter type shows the following regularities (Figs. 3 and 4). (1) The second absorption band of ||-absorption is more hypsochromic than that of ⊥-absorption. (2) As to the intensity of the second band holds the same as the corresponding regularity found in the former type.

The rule on the first absorption bands confirms Tsuchida's theory of absorption spectra attributing the first band to transition electrons in the central ion, since this rule suggests that the first band is less anisotropic in spite of the external symmetry of the ion and, consequently, due to the more inner origin in the complex ion than the second band.

Tsuchida's coördination theory of valency[12] assumes that, 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, with two pairs of *d*-electrons above and below. Those two pairs of electrons are supposed to be mainly responsible for the second bond of ⊥-absorption, while the second band of ||-absorption is chiefly originated from the coördination electrons in the plane of the complex ion. Therefore, the relative position of the dichroic bands of planar complex ions is determined by the relation between those special two pairs of electrons and four ligands. On the other hand, it is known that the so-called "spectrochemical series," CN^- NO_2^- NH_3 ONO^- H_2O NCS^- SO_4^{--} NO_3^- OH^- CO_3^{--} Cl^- CrO_4^{--} Br^- I^-, gives decreasing order of stability of respective ligands in coördination.[11] In consequence, it can be presumed that the second band of ||-absorption is more hypsochromic than that of ⊥-absorption in planar complexes coördinated by such ligands as NH_3 or CN^-, since these ligands, being situated considerably high in the spectrochemical series, are very stable in coördination and coördination levels in the planes of such complex ions are supposed to be more stable than those of two electron pairs. Similarly, ||-absorption is more batho-

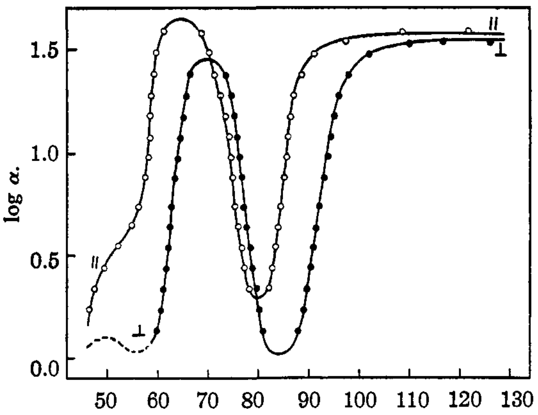

Fig. 1.—Dichroism of K_2PdCl_4.

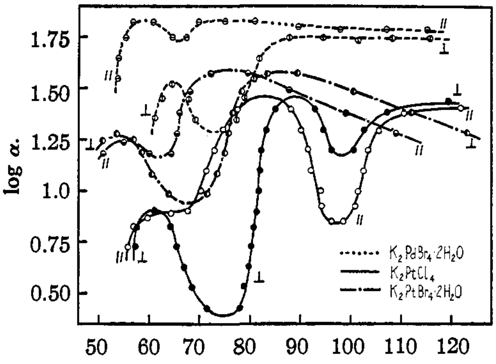

Fig. 2.—Dichroism of $K_2PdBr_4 \cdot 2H_2O$ -----, K_2PtCl_4 — and $K_2PtBr_4 \cdot 2H_2O$, —·—.

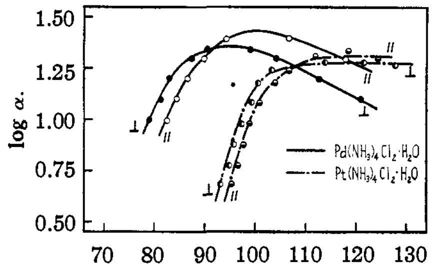

Fig. 3.—Dichroism of $Pd(NH_3)_4Cl_2 \cdot H_2O$ — and $Pt(NH_3)_4Cl_2 \cdot H_2O$ —·—.

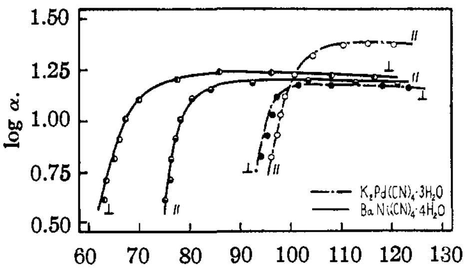

Fig. 4.—Dichroism of $K_2Pd(CN)_4 \cdot 3H_2O$ —·— and $BaNi(CN)_4 \cdot 4H_2O$ —.

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[12] Tsuchida, Kobayashi and Kuroya, *Rev. Phys. Chem. Japan*, **13**, 158 (1939).

chromic than ⊥-absorption for the second band of tetrahalogeno-complex ions, since halogens stand very low in the series. Thus two kinds of dichroism for the second band, which might seem quite different from each other, can be united by taking the spectrochemical series into consideration.

From discussion above, the general regularities of dichroism for planar complex ions can be deduced as follows: (1) The second band in ||-absorption of planar complex ions are more hypsochromic or more bathochromic than that of ⊥-absorption, according as ligands stand higher or lower in the spectrochemical series. (2) In palladous complex ions, the second bands of ||-absorption have larger intensities than those of ⊥-absorption. In platinous complex ions, the second bands of ||- and ⊥-absorptions have almost equal intensities. (3) The first absorption bands lie at about the same wave length in both ||- and ⊥-absorption.

The author wishes to express his sincere thanks to Professor R. Tsuchida for his kind suggestions and encouragement throughout this work.

Summary

Dichroism of microscopic crystals of compounds with planar complex ions were measured in the region from visible to near-ultraviolet by the microscopic method. It was found that dichroism of planar complexes can be classified into two types, the tetrahalogeno-type and the tetracyano-type. Discussion was made on these two types of dichroism from standpoints of the theory of absorption spectra for metallic compounds and the new coördination theory of valency, which had been proposed by Tsuchida. From comparative consideration about results of the measurements, general regularities were deduced on dichroism of planar complexes.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

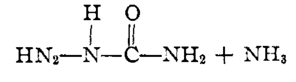
The Reduction of Carbohydrazide. The Acidity of Carbohydrazide, Semicarbazide and Urea[1]

BY ALSOPH H. CORWIN AND JOHN D. REINHEIMER

In a previous paper, Corwin and Jackson[2] found that 1,5-diphenylthiocarbazide could be reduced to 1-phenylthiosemicarbazide, and no further. Since the 1,5-diphenylthiocarbazide is symmetrical, the hydrogenolysis of one N-N bond but not the other is surprising. The reduction of the parent compound, carbohydrazide, was therefore indicated in order to ascertain whether this compound showed the same resistance toward hydrogenation.

Another method of showing that a fundamental difference between the ease of reduction of the carbohydrazide and the semicarbazide should exist is a determination of the relative acidity of these compounds. If one assumes that reduction is essentially an addition of electrons, the more acidic of these two compounds should be more easily reduced.

The carbohydrazide was reduced catalytically with Raney nickel in a low pressure hydrogenation apparatus. The theoretical amount of hydrogen was absorbed after 8 hours and no further change in pressure noted after 24 hours. The course of the reaction is given by the equation



$$H_2 + H_2N{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}NH_2 \longrightarrow HN_2{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}NH_2 + NH_3$$

The presence of ammonia was shown by its odor and no further test was run. Semicarbazide was identified by two derivatives, the white benzaldehyde derivative, d.p. 208–210° and a decomposition product of d.p. 243–245°. The literature values for these derivatives are 214° and 245–246°.[3] Chemical reduction was attempted but with no success. The reaction had to be run in the cold, for the carbohydrazide is unstable in the presence of acids or base when heated.

The acidity of very weak acids in ether and benzene has been determined by Conant and Wheland[4] and McEwen.[5] Since the solubility of urea in ether is very small,[6] liquid ammonia was used as the solvent for the acidity determination. The indicators developed by Conant were used. The results are recorded in Table I.

TABLE I

Sample	Indene pK 21	Fluorene pK 25	$(C_6H_5)_3CH$ pK 33	pK_a
Urea		Yellow	Colorless	25–33
Semicarbazide		Yellow	Colorless	25–33
Carbohydrazide	Yellow	Colorless	Colorless	21–25

Experimental

I. **Reduction of Carbohydrazide.**—Four grams of carbohydrazide[7] was dissolved in 100 ml. of commercial absolute alcohol and 2 ml. of Raney nickel was added. (Activity of catalyst was checked by reducing p-nitroaniline just prior to its use.) The calculated pressure drop for 1 mole of hydrogen was 3.7 pounds gage, and the observed drop after 24 hours shaking was 3.8 pounds gage. A strong odor of ammonia was observed when the bottle was opened. The solution was filtered, hydrochloric acid added, and the sol-

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[1] This paper is from the Doctoral Dissertation of John D. Reinheimer, The Johns Hopkins University, 1948.

[2] Corwin and Jackson, THIS JOURNAL, **71**, 3698 (1949).

[3] Curtius and Heidenreich, *J. prakt. Chem.*, **52**, 466 (1895).

[4] Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

[5] McEwen, *ibid.*, **58**, 1124 (1936).

[6] Seidell, "Solubilities of Organic Compounds," 3rd Ed., D. Van Nostrand and Co., New York, N. Y., Vol. II, p. 61.

[7] Prepared by method of Cazeneuve and Moreau, *Comp. rend.*, **129**, 1255 (1899).