Spectrochemical Study of Microscopic Crystals. IV. The Dichroism of the Tetrahalogeno-Complex Type[1]

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Previously the present authors[2,3] reported on the dichroism of tetra-co-ordinated planar complexes of platinum(II) and palladium(II), and reached the conclusion that the dichroisms of these planar complexes can be classified into two types; that is, the "tetrahalogeno-complex type" and the "tetracyano-complex type." Both the types have been found to show the following common rule as to the second band: the $\parallel$-absorption[4] is hyperchromic to the $\perp$-absorption[4] in palladium complexes, and the $\parallel$-and $\perp$-absorptions in platinum complexes show the band with maximum absorption coefficient of almost equal magnitude. The main difference between the two is that in the former type the second band of the $\parallel$-absorption lies in the longer wave-length than the $\perp$-absorption whereas in the latter it holds the relation reverse to the above. It seemed of interest to investigate the cases with other planar tetra-co-ordinated complexes. In the present work, the dichroisms of crystals of K_2PdI_4, $K_2Pd(SCN)_4$ and $K_2Pt(SCN)_4$ have been measured and the results of the measurements have been discussed in association with the previous data[2,3] on dichroisms of planar complexes.

Experimental

Materials.—$K_2Pd(SCN)_4$ was prepared in red hexagonal prisms from potassium tetrachloro-palladate (II) and potssium thiocyanate. The crystal shows dichroism on the prism face, i. e,, orange-red and yellow, and exhibits an oblique extinction. Dichroism measurements were made on the prism face by polarized lights with their electric vectors along the directions of extinction.

K_2PdI_4 was prepared in black, rhombic tablets with metallic lustre by adding a concentrated solution of potassium tetrachloro-palladate (II) to a hot solution of potassium iodide. The crystal exhibits a straight extinction. Dichroism can be recognized under the microscope with a thin crystal; that is, it appears brownish black and greenish black by polarized lights with their electric vectors along the c-and a-axes, respectively. Dichroism measurements were made in these directions; c-and a-absorptions represent absorptions by polarized lights with their electric vectors along the c-and a-axes, respectively.

$K_2Pt(SCN)_4$ was prepared in orange, hexagonal prisms by the method of Buckton[5]. The crystal exhibits an oblique extinction on the prism face, and appears yellow and yellowish orange by polarized light with electric vector along the directions of extinction. Dichroism measurements were performed along the directions of extinction, that is, the a-and b-directions in the figure (Fig. 3).

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

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[1] Presented in part at the Symposium on Co-ordination Compounds, Tokyo, November 13, 1951.

[2] S. Yamada, *J. Am. Chem. Soc.*, **73**, 1182 (1951).

[3] S. Yamada, H. Yoneda and R. Tsuchida, *J. Chem. Soc. Japan*, **69**, 145 (1948).

[4] $\parallel$- or $\perp$-absorption represents, respectively, absorption by polarized light with its electric vector parallel or perpendicular to the plane of the complex.

[5] G. B. Buckton, *Ann.*, **92**, 286 (1854).

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

show a marked dichroism on the prism face. Dichroism measurements were made on this face by polarized lights with electric vectors parallel and perpendicular to the principal axis. Although the dichroism of the crystal had been reported in the previous paper,[2,3] measurements in the present work have been extended to the region of longer wave-length and smaller extinction coefficients. The crystal structure of the compound has not yet been analyzed. However, we concluded in the previous report[3] that the complex ions in the crystal are arranged parallel to each other with their planes perpendicular to the c-axis. ‖ -and ⊥-absorptions are designated on the basis of the above presumption.

Measurements.—Quantitative dichroism measurements were performed by the microscopic method.[7] The crystals used in the measurements were several hundredths of mm. thick. α denotes extinction coefficient per mm. of the crystal. Molecular absorption coefficients, k, were estimated from the relation, $k=10M\alpha/\rho$, where M and ρ represent, respectively, the molecular weight of the compound and the density of the crystal. Results of the measurements are shown in the Figures 1∼4 and tabulated in the Tables I∼III.

Absorption spectra of aqueous solutions of $K_2PdBr_4.2H_2O$ and $K_2Pd(SCN)_4$ were determined by the photographic method using a sector-photometer, and that of $K_2Pt(SCN)_4$ was determined with a Beckman quartz-spectrophotometer model DU.[8]

Results and Discussion

Potassium Tetrathiocyanato-palladate (II). —A striking difference is observed between the two component absorptions in Fig. 1.

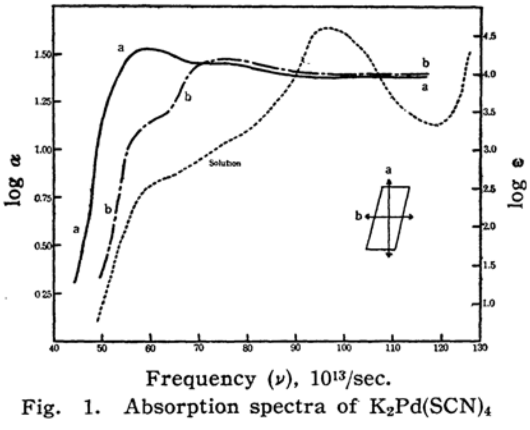

Fig. 1. Absorption spectra of $K_2Pd(SCN)_4$

Comparing the result of the present measurements with existing data on absorption spectra of other palladium complexes,[2,3] it is reasonable to suppose that in the absorption spectra of the crystal the band at $\nu=60\times10^{13}$/sec. corresponds to the second band,[9] and that the flat absorption in the shorter wavelength region consists of the third[9] and SCN-specific bands.[10] The first band[9] may be so small that it is probably covered under the large second absorption band. The rule as to the dichroism of planar complexes of palladium, which was reported previously,[2] states that the second band of the ‖ -absorption is hyperchromic to that of the ‖ -absorption. Therefore, the absorption curve "a" of the thiocyanato-complex may reasonably be assigned to the ‖ -absorption. From the absorption curves, the following conclusion may be reached for the above complex-salt; the ‖ -absorption is bathochromic to the ⊥-absorption. This is the case with the " tetrahalogeno-complex type.[2]" Consequently, tetrathioacyanatopalladium (II) complex is supposed to fall into the group of the tetrahalogeno-complex type."

Potassium Tetraiodo-palladate (II).—A rather remarkable dichroism can be recognized, as shown in Fig. 2. The band at $\nu=40$ in the c-absorption is considered to be the second band, and the broad absorption extending from $\nu=60$ to shorter wave-length region is supposed to be the superposition of the third and I-specific bands. With the a-absorption, the second band lies in the near infrared region. The broad absorption curve in the visible and shorter wave-length region consists of the third and I-specific bands. It is readily seen that for the second band the following relation exists; the a-absorption is bathochromic and hyperchromic to the c-absorption. With tetrachloro-and tetrabromopalladate (II) ions, the following rule has been established[2]: the ‖ -absorption of the second

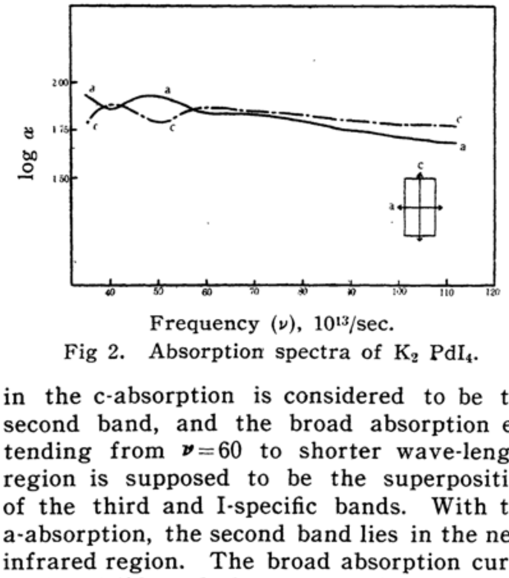

Fig 2. Absorption spectra of $K_2\,PdI_4$.

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[7] R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds," Zoshindo, Osaka, Japan, 1944, p. 180; This Bulletin, **13**, 619 (1938); *J. Chem. Soc. Japan*, **60**, 769 (1939).

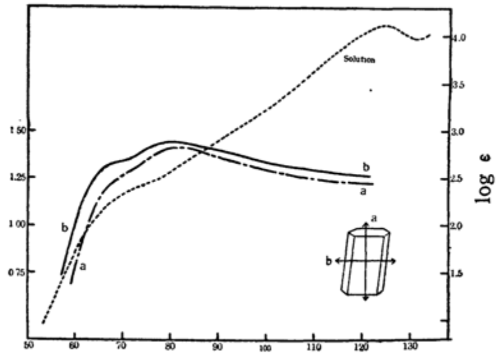
[8] The authors are indebted to the Analytical Laboratory of our department for the measurement of absorption spectra of $K_2Pt(SCN)_4$ with a Beckman spectrophotometer.

[9] About the first, second and third absorption bands, see R. Tsuchida, This Bulletin, **13**, 388 and 436 (1938).

[10] R. Tsuchida and M. Kobayashi, This Bulletin, **13**, 476 (1938).

band is bathochromic and hyperchromic to the ⊥-absorption. Since it seems reasonable to assume that the tetraiodo-palladate (II) ion shows a dichroism of the same type as those of the tetrachloro-and tetrabromo-palladate (II) ions, the following presumption may be reached that the a-absorption corresponds to the ∥-absorption and the c-absorption to the ⊥-absorption. Moreover, comparing the dichroism of potassium tetraiodo-palladate (II) with those of tetrachloro- and tetrabromo-complexes and judging from the relation between the dichroisms and the external forms with the latter two crystals, in both of which the planes of the complex ions are perpendicular to the c-axis,[3)] it may be concluded that in the crystal of potassium tetraiodo-palladate (II) the complex-ions are arranged at least almost parallel to each other with their planes perpendicular to the c-axis.

Potassium Tetrathiocyanato-platinate (II). (Fig. 3.)—In the b-absorption the small inflexion at $\nu=68$ corresponds to the second band and the broad absorption stretching over the shorter wave-length region consists of the third and SCN-specific bands. Similarly, in the a-absorption, the inflexion at $\nu=70$ corresponds to the second band and the broad absorption curve in the shorter wave-length region consists of the third and specific bands. The first band may be concealed under the large second band, as in the case of potassium tetrathiocyanato-palladate (II). No very great difference can be recognized between the a- and b-absorptions, but these absorptions seem to represent the characteristic feature of the dichroism of the planar tetrathiocyanato-complex. Thus for the second absorption band is found the following relation: the b-absorption is bathochromic and hyperchromic to the a-absorption.



Frequency (ν), 10^{13}/sec.

Fig. 3. Absorption spectra of $K_2Pt(SCN)_4$

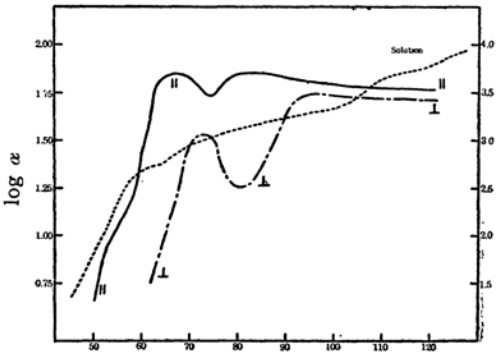
TABLE II

ABSORPTION MAXIMA OF TETRATHIOCYANATO-COMPLEX COMPOUNDS

		ν 10^{13}/sec.	log α	ν 10^{13}/sec.	log α
$K_2Pt(SCN)_5$	∥	67	1.31	80	1.44
	⊥	71	1.25	83	1.42
$K_2Pd(SCN)_4$	∥	58	1.54	73	1.44
	⊥	62	1.14	75.8	1.48

Since the tetrathiocyanato-platinate (II) ion is reasonably supposed to belong to the group of complexes which show a dichroism of the "tetrahalogeno-complex type," as in the case of the tetrathiocyanato-palladate (II) ion, it is considered that the b- and a-absorptions are abundant, respectively, with the parallel and perpendicular components of the planar complex ion, though the a- and b-absorptions may not completely coincide with the ∥-and ⊥-absorptions.

Potassium Tetrabromo-palladate (II) Dihydrate.—The absorption curve in the region for the low value of α was determined in the present measurement (Fig. 4). A slight



Frequency (ν), 10^{13}/sec.

Fig. 4. Absorption spectra of $K_2PdBr_4 \cdot 2H_2O$.

TABLE I

ABSORPTION BANDS OF TETRAHALOGENO-COMPLEX COMPOUNDS

Compond		1st band		2nd Band		3rd Band	
		ν 10^{13}/sec.	log α	ν 10^{13}/sec.	log α	ν 10^{13}/sec.	log α
K_2PdCl_4	∥	51	0.45	64.0	1.68	(98)	(1.54)
	⊥	51	0.45	68.9	1,49	(108)	(1.51)
$K_2PdBr_4 \cdot 2H_2O$	∥	(48)	(1.0)	58.8	1.85	(75)	(1.83)
	⊥	—	—	65.0	1.52	(90)	(1.75)
K_2PdI_4	∥	—	—	—	—	48.4	1.93
	⊥	—	—	40.4	1.88	(60)	1.86
K_2PtCl_4	∥	60.6	0.9	82.6	1.50	—	—
	⊥	60.6	0.9	89.1	1.45	—	—
$K_2PtBr_4 \cdot 2H_2O$	∥	54.8	1.15	74	1.48	—	—
	⊥	54.8	1.15	84	1.43	—	—

inflexion is recognized in the longer wave-length part at a low value of α and at $\nu=$ about 53. This inflexion is supposed to correspond to the first absorption band. As in the case of the tetrachloro-complex, the first absorption band is found to be much week as compared with the other bands.

Comparison of Dichroisms of Planar Tetrahalogeno-Complexes.—Numerical data of the present measurements as to the dichroisms of the tetrahalogeno-complex type are tabulated in Tables I and III along with the other available data. For the tetrahalogeno-complexes of both palladium and platinum, the following relations are found to hold for the corresponding absorption bands: (1) $\nu_{\mathrm{Cl}} > \nu_{\mathrm{Br}} > \nu_{\mathrm{I}}$ and $k_{\mathrm{Cl}} < k_{\mathrm{Br}} < k_{\mathrm{I}}$;[11] (2) especially for the second band, the oscillator strength increases in the order, chloride<bromide< iodide.[12]

These tendencies are in accordance with those of cobaltic and chromic complexes, and they could be explained mostly in terms of the difference between the halogen atoms in their polarizability and, therefore, in the covalent character of the metal-halogen linkage

TABLE III

SECOND ABSORPTION BANDS OF TETRAHALOGENO-COMPLEX COMPOUNDS

		ν 10^{13}/sec.	half width 10^{13}/sec.	α	k
K_2PdCl_4	$\parallel$	64	12.2	47.8	57800
	$\perp$	68.6	10.4	30.9	37400
$K_2PdBr_4\cdot 2H_2O$	$\parallel$	58.8	12	70.8	
	$\perp$	65.0	9	33.1	
K_2PdI_4	$\parallel$	—	—	—	
	$\perp$	40.4	—	76	
K_2PtCl_4	$\parallel$	82.6	18	31.6	38800
	$\perp$	89.1	14.4	28.2	34600
$K_2PtBr_4\cdot 2H_2O$	$\parallel$	74	—	30.2	50700
	$\perp$	84	—	26.9	45200

Absorption Curves of $K_2Pd(SCN)_4$ and K_2Pt $(SCN)_4$.—Absorption curves of both the compounds show similar features. It is also found from the curves that the tetrathiocyanato-complexes show their absorption bands in the longer wave-length region, as compared with complexes of the same metals with other ligands; for example, they are bathochromic to the dioxalato-complexes[13] and show absorption in the longer wave-length region, comparable even to the tetrabromo- as well as tetrachloro-complexes. A similar tendency can also be noticed between potassium hexachloroplatinate (IV) and potassium hexathiocyanato-platinate (IV),[14] the former being hopsochromic to the latter. This fact seems, at first sight, inconsistent with the spectrochemical series for cobaltic complexes. Such anomalies might be attributed to the difference in the mode of co-ordination linkage between these complexes of platinum and palladium and of cobalt, and also possibly to the difference in the atom species which is bound to the central matallic ion. It may be assumed that in cobaltic and chromic complexes the thiocyanate ions co-ordinate with the metallic ion by means of the nitrogen atoms, while in the palladium and platinum complexes they co-ordinate by the sulphur atoms, since the complex, in which a thiocyanate ion co-ordinates with the central metal by its sulphur atom and which should consequently be called thiocyanato-complex, would be bathochromic to the complex, in which a thiocyanate ion coordinates by its nitrogen atom and which should consequently be called isothiocyanato-complex.[15]

The Dichroism of the Tetrahalogeno-Complex Type.—For all the planar tetrahalogeno-and tetrathiocyanato-palladium complexes shown in the table hold the following common rules.

(1) The first band: α is much smaller than that of the second or third band. $\nu_{\parallel}$ and $\nu_{\perp}$ are not greatly different from each other.

(2) The second band: $\parallel$-absorption is bathochromic and hyperchromic to $\perp$-absorption, the oscillator strength being larger for $\parallel$-ab-sorption than for $\perp$-absorption.

(3) The third band: $\alpha_{\parallel}$ is almost equal to $\alpha_{\perp}$ $\parallel$-absorption is bathochromic to $\perp$-absorption, $\nu_3-\nu_2$ being larger for $\parallel$-absorption than for $\perp$-absorption.

For the planar platinum complexes hold similar rules to those for palladium complexes, but the former differ from the latter in the facts (1) that the second band of the $\parallel$-absorption has almost as strong intensity as that of the $\perp$-absorption, and (2) that in the $\parallel$ absorption its third band commences in almost the same wave-length region as in the $\perp$-absorption.

The fact that both $\parallel$-and $\perp$-absorptions show their first bands at almost the same wave-length suggests that the band is due to isotropic transitions. As such may be cited electronic transitions of *d*-electrons in the unsaturated shell of the central metal. The smaller value of α for the first band favours this view, suggesting that the transitions are forbidden ones. This agrees well with the idea on the origins of the bands, as advanced previously by one of the authors.[9]

The second absorption band is considered by the present authors to be originate from transitions of the electrons forming the co-ordination linkages. Therefore, in the planar

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[11] ν_x and k_x denotes, respectively, frequency and molecular absorption coefficient at maxima of the absorption bands of the tetrahalogeno-complex. Although the densities of the crystals $K_2PdBr_4\cdot 2H_2O$ and K_2PdI_4 are not available, judging from the order of their magnitude and the values of α for the compounds, it seems quite clear that the above relation should hold.

[12] Judging from the magnitude of k and the shape of the absorption bands, this relation seems evident.

[13] R. Tsuchida and S. Yamada, unpublished.

[14] H. Kuroya, unpublished.

[15] The more detailed discussion related to such discrepancies will be submitted later.

complex, the electric moment responsible for the second should be larger in the direction along the plane of the complex than in the direction perpendicular to the plane. This accords well with the above rule that the oscillator strength of the second absorption band is greater in the ∥-absorption than in the ⊥-absorption. (Table III).

Diffierences between the platinum and palladium complexes are observed with respect to the second and third bands. Thus, in the palladium complexes the second band of ∥-absorption is very hyperchromic compared to that of ⊥-absorption, whereas in the platinum complexes they have almost equal magnitudes of absorption coefficients, and the oscillator strength of ∥-absorption is not so much larger than that of ⊥-absorption in the platinum complexes as in the corresponding palladium complexes. This tendency seems related to a similar discrepancy in the birefringence between complexes of the two metals, which was observed by Mellor and Quodling,[16] who reported that planar tetra-co-ordinated compounds of platinum showed smaller double refraction than the corresponding palladium compounds. A completely explanation for the above fact can not be given for the present, but this phenomenon might be ascribed principally to the difference between the two metals in their polarizing powers and also in their polarizabilities.

Summary

(1) Dichroisms of K_2PdI_4, $K_2Pd(SCN)_4$ and $K_2Pt(SCN)_4$ have been quantitatively determined by the microscopic method, and it has been found that all of them belong to the group which exhibits the dichroism of the "tetrahalogeno-complex type."

(2) For the tetrahalogeno-complexes, the following rules have been found: $\nu_{Cl}>\nu_{Br}>\nu_{I}$ and $k_{Cl}<k_{Br}<k_{I}$ for the corresponding absorption band, and the oscillator strength of the second band is larger for ∥-absorption than for ⊥-absorption.

(3) For tetrahalogeno- and tetrathiocyanato-complexes of platinum (II) and palladium (II), common regularities have been induced on the dichroisms of the tetrahalogeno-complex type.

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[16] D. P. Mellor and F. M. Quodling, *J. Proc. Roy. Soc. New South Wales*, **69**, 167 (1936); ibid., **70**, 205 (1936).