Spectrochemical Study of Microscopic Crystals. VIII.[1] *Absorption Spectra of Dicyclopentadienyl-compounds of Iron and Cobalt*

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Since the first preparation of dicyclopentadienyl-iron[2], a number of reports have appeared on the dicyclopentadienyl-compounds of various metals. Although the measurement of pleochroism is expected to afford valuable information about the linkages within the complexes, none of the former investigators have dealt with this property. In this paper we will report on the quantitative dichroism measurement with crystals of dicyclopentadienyl-iron (II) and dicyclopentadienyl-cobalt (III) perchlorate, and discuss the results of the measurements.

Experimental

Materials.—Dicyclopentadienyl-iron was prepared from cyclopentadienyl-magnesium bromide and tris-(2,4-pentanediono)-iron (III) in orange, monoclinic needles elongated along the [100] m.p. 173°C. The optical measurements were made on the prism face with polarized light having its electric vector along and perpendicular to the (100)-plane.

Dicyclopentadienyl-cobalt (III) perchlorate was prepared according to the method of Wilkinson et al.[3] from tris-(2,4-pentanediono)-cobalt (III) and cyclopentadienyl-magnesium bromide. The yellow, prismatic crystals thus obtained exhibit a straight extinction on the prism face. The optical measurements were made on this face with the electric vector along the directions of extinction.

Measurements.—Quantitative dichroism measurements were performed at room temperature in the region covering from 2400 to 7000 Å by Tsuchida-Kobayashi's microscopic method[4]. The symbol, α, represents absorption coefficient per mm. of a crystal. Molecular absorption coefficients, K, were estimated from the relation, $K=10\,\alpha M/\rho$, where M and ρ denote formula weight of a compound and density of a crystal, respectively.

Results and Discussion

Dicyclopentadienyl-iron (II).—The results of the measurements are shown in Fig. 1 and Table I. The A- and B-absorption represent the absorption with the electric vector along and perpendicular to the a-plane of the crystal, respectively. Based on the

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[1] Paper VII of this series, S. Yamada, A. Nakahara, Y. Shimura and R. Tsuchida, This Bulletin, 28, 222 (1955).

[2] T. J. Kealy and P. L. Pauson, *Nature*, 168, 1039 (1951); S. A. Miller, J. A. Tebboth and J. F. Tremayne, *J. Chem. Soc.*, 1952, 632.

[3] G. Wilkinson, *J. Am. Chem. Soc.*, 74, 6148 (1952).

[4] R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds." *Zoshindo*, Osaka, 1944, p. 180. See also the previous papers of this series.

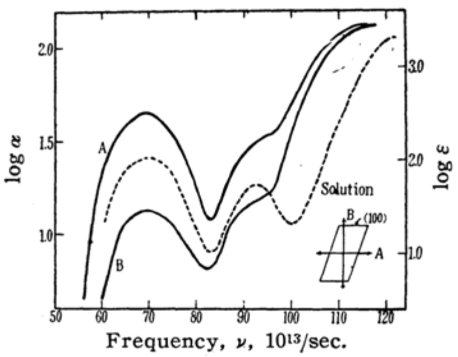

Fig. 1. Absorption spectra of $Fe(C_5H_5)_2$. The spectra of the aqueous solution (dotted curve) is taken from Ref. (7).

TABLE I

ABSORPTION MAXIMA OF DICYCLOPENTADIENYL-IRON IN THE CRYSTALLINE STATE

	Band I			Band II			Specific Badd		
	ν, 10^{13}/sec.	log α	K	ν, 10^{13}/sec.	log α	K	ν, 10^{13}/sec.	log α	K
A–abs.	69.1	1.65	558×10^2	93.4	1.47	368×10^2	117	2.15	176×10^3
B–abs.	69.6	1.14	172×10^2	93.0	1.14	172×10^2	120	2.15	176×10^3
		$\alpha_A/\alpha_B=3.24$			$\alpha_A/\alpha_B=2.14$				

crystal analysis[5,6], it is seen that the A-absorption represents the main characteristic of the component absorption of the molecule with the electric vector perpendicular to the cyclopentadienyl-rings, and the B-absorption represents the one along the pentagonal rings. Taking into consideration the orientation of the molecules in the crystal[5,6], the components of the molecular absorption coefficients (Fig. 2) were estimated, and shown in Table II. Dicyclopentadienyl-iron in the crystalline state is seen to exhibit in the region of the present measurement three band maxima at about 70, 94 and 120×10^{13}/sec., which almost correspond with the maxima observed for the solution of the compound[7]. Comparing the absorption curves of dicyclopentadienyl-iron with those of other compounds of iron[8], it is supposed that the absorption bands at 70 and 94×10^{13}/sec. should correspond to such absorption bands as would appear when the iron atom comes into co-ordinate linkage with ligands. Those bands, therefore, may be considered as due mainly to the co-ordinate linkages around the central metal atom of the complexes. Based on the former investigations on the absorption spectra of metallic complexes[9], it is also supposed that the band at about 120×10^{13}/sec. should be due to the electronic transitions in the cyclopentadienyl rings in coordination with the metal atom, being designated as a specific band.

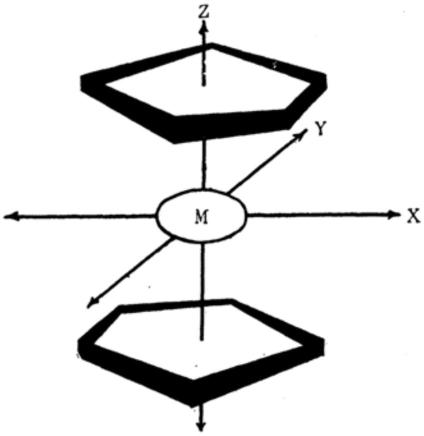

Fig. 2. Configuration of the metallic dicyclopentadienyl-compounds.

TABLE II

	Band I	Band II
K_z	94400	56400
K_x	17200	17200
K_z/K_x	5.48	3.28

For the bands at 70 and 94×14^{13}/sec., *Z-absorption, the absorption with the electric vector perpendicular to the pentagonal rings, has much larger intensity than X-absorption, absorption with the electric vector parallel to the pentagonal rings;* $K_z/K_x=5.48$ for the band at 70×10^{13}/sec., and $K_z/K_x=3.28$ for the band at 94×10^{13}/sec.

As to the specific band at about 120×10^{13}/sec., which may be ascribed to transitions in the cyclopentadienyl-radicals in coordination with the metal atom, *the absorption with electric vector along the rings is slightly hypsochromic to that perpendicular to the above.*

Dicyclopentadienyl-cobalt (III) Perchlorate.—Results of the measurements are shown in Fig. 3 and Table III. A-absorption

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[5] E. O. Fischer and W. Pfab, *Z. Naturforsch.*, 7b, 377 (1952).

[6] P. F. Eiland and R. Pepinsky, *J. Am. Chem. Soc.*, 74, 4971 (1952); J. D. Dunitz and L. E. Orgel, *Nature*, 171, 121 (1953).

[7] L. Kaplan, W. L. Kester and J. J. Katz, *J. Am. Chem. Soc.*, 74, 5531 (1952).

[8] K. Sone, This Bulletin, 25, 1 (1952), etc.

[9] Absorption bands of such a kind were previously named "specific bands." See R. Tsuchida and M. Kobayashi, This Bulletin, 13, 476 (1938).

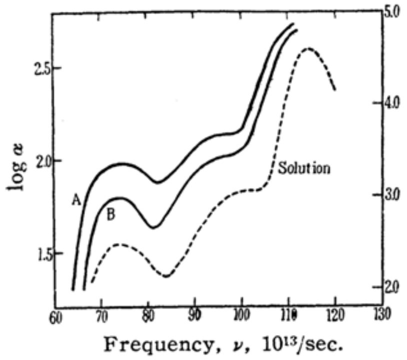

Fig. 3. Absorption spectra of $Co(C_5H_5)_2ClO_4$. The spectra of the aqueous solution (dotted curve) is taken from Ref. (3).

TABLE III

ABSORPTION MAXIMA OF DICYCLOPENTADIENYL-COBALT (III) PERCHLORATE IN THE CRYSTALLINE STATE

	Band I		Band II	
	ν, 10^{13}/sec.	log α	ν, 10^{13}/sec.	log α
A-abs.	74.4	2.0	97.0	2.2
B-abs.	74	1.79	97	2.06
	$\alpha_A/\alpha_B=1.62$.		$\alpha_A/\alpha_B=1.38$	

and B-absorption denote absorption with electric vector along and perpendicular to the direction of elongation. The compound exhibits three absorption bands at 74, 96 and about 115×10^{13}/sec., which almost coincide with the band maxima reported for the solution[10]. By analogy with dicyclopentadienyl-iron (II), the band at 115×10^{13}/sec. may be readily assigned to the specific band, which is due to the electronic transitions in the cyclopentadienyl-rings of the cobaltic compound. The two bands at the longer wave-length of dicyclopentadienyl-cobalt are supposed to be due to the electronic transitions of co-ordination electrons or electrons closely related to the co-ordinate linkages. The crystal structure of the present compound has not yet been determined. But it is reasonable that we should expect for this compound a similar rule on dichroism to that for the corresponding iron-compound. Thus, for the bands directly connected with the co-ordinate linkages in the dicyclopentadienyl-cobalt (III)-complex, the Z-absorption should be stronger than the X-absorption. The results of the present measurements, therefore, indicate that the B-absorption represents the main characteristic of the component absorption with the electric vector along the pentagonal rings. On the basis of the above assumption, the dichroism of this compound is seen to be quite similar to that of the corresponding iron-compound. Thus for both the bands, *absorption is stronger with electric vector perpendicular to eth pentagonal rings than with the vector along the cyclopentadienyl-rings.*

For the specific band at 115×10^{13}/sec., *absorption with electric vector along the rings is slightly hypsochromic to that perpendicular to the above.*

General Rules on the Dichroism.—From what is described in the foregoing part of this paper may be derived the following rules on the dichroism which are common for dicyclopentadienyl-iron (II) and -cobalt (III) complexes: (1) *For the two bands at the longer wave-length, due mainly to the co-ordination electrons around the metal atom, Z-absorption is highly hyperchromic to X-absorption, and* (2) *for the specific band, Z-absorption is slightly bathochromic to X-absorption.*

Rule (1) means that, for the bands which are considered as due mainly to the co-ordination electrons around the metal atom, the electronic transitions occur much more readily with the electric vector along the direction binding the metal atom and the centres of the pentagonal rings than with the vector along the plane. In the previous reports on planar quadri-co-ordinate complexes[11], it was found that for the band, considered to be due to the co-ordinate linkages, the oscillator strength was much greater with the electric vector along the complex-plane in which co-ordinate linkages exist than with the vector perpendicular to the plane. Hence, the above rule (1) may be compatible with the previously derived relation[11], assuming that there should exist firm linkages between the metal atom and cyclopentadienyl-radicals. Furthermore, the remarkable difference in absorption coefficient between the Z- and X-absorption seems to indicate that the π-electrons of the cyclopentadienyl-radicals may be involved considerably in the linkages between the metal atom and the pentadienyl-rings.

Rule (2) is concerned with the specific band, which may be ascribed to transitions in the cyclopentadienyl-radicals in co-ordination with the metal atom. It may be expected that the compounds would exhibit similar dichroism to that of the benzene rings if the pentagonal rings in these compounds would hold their aromatic property. For the π-band of the benzene rings in such compounds as hexamethylbenzene, absorption with the

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[10] G. Wilkinson, *J. Am. Chem. Soc.*, **74**, 6148 (1952).

[11] S. Yamada and R. Tsuchida, This Bulletin, **26**, 489 (1953). See also S. Yamada, *J. Am. Chem. Soc.*, **73**, 1182 (1951), etc.

electric vector along the benzene rings was found to be far more hyperchromic and slightly bathochromic to that with the electric vector perpendicular to the benzene rings[12], and for the specific bands of cupric complexes with β-diketones, such as tropolone, salicylaldehyde or acetyl-acetone, each involving π-electronic systems, absorption with the electric vector along the plane of π-electronic systems was found to be far more bathochromic to the absorption with the electric vector perpendicular to the plane[13]. It is seen that the above rule (2) on the specific band of the metallic dicyclopentadienyl-compounds is not compatible with the dichroism for the π-band of the benzene rings, nor with that for the specific band of π-electronic systems within ligands in co-ordination with the metal atoms. It is supposed, therefore, that *the electronic state of the cyclopentadienyl-radicals in the above compounds differs from that of the π-electronic systems in the metallic complexes of an ordinary type as well as from that of the benzene-derivatives. Thus, as far as dichroism is concerned, the cyclopentadienyl-raaicals in the metal-compounds exhibit little aromatic property*. The above relations on the dichroism with the present metal-compounds may be comprehensible, assuming that the π-electrons in the pentagonal rings may be greatly attracted toward the metal atom to form co-ordinate linkages with the metal atom[14].

Rules (1) and (2) can be elucidated also in terms of the group theory. The details of the quantum-theoretical treatment will be submitted later.

Electronic State of the Cyclopentadienyl-groups in the Metallic Complexes.—The electronic state of the cyclopentadienyl-groups in the metallic compounds of the above type may be judged also from the wave-length at the maxima of the specific band. When one metal atom in some compound of the above type is replaced by another, the electronic state of the cyclopentadienyl-radicals would change to a greater or less extent according to the change in the linkages between the metal atom and ligands. At the same time, as the π-electrons of the pentagonal rings are attracted toward the metal atom more strongly, π-bond character of the pentagonal rings would be lost more and more, the specific band being displaced hypsochromically corresponding to the change in the electronic state of the cyclopentadienyl-radicals. Thus it is seen from the data reported by former investigators that the Fe(II)- and Co(III)-comlexes exhibit their specific bands at a much shorter wave-length than the Ni(II)-compound (Table IV). This fact suggests that the π-electrons in the former two compounds would be attracted toward the metal atom more strongly than in the Ni(II)-compound. Such a presumption seems to be in good agreement with the order in stability of the compounds: the Fe(II)- and Co(III)-compounds are far more stable than the Ni(II)-compound. According to the same criterion, the π-electrons are supposed to be attracted rather firmly toward the metal atom in the Ru(II)-compound, which is known, as would be expected, to be very stable. It may be supposed from the above consideration that the electronic state of the cyclopentadienyl-radicals would change greatly from a compound of one metal to that of another. Moreover, there might be some possibility that the linkages or bonding orbitals in the compounds of the above type would change essentially with changing the central metal atom.

TABLE IV

MAXIMA OF SPECIFIC BANDS OF DICYCLOPENTADIENYL-COMPOUNDS IN SOLUTION

	ν, 10^{13}/sec.	log ε
$Fe(C_5H_5)_2$(a)	120	3.08
$Co(C_5H_5)_2ClO_4$(b)	114.5	4.6
$Ni(C_5H_5)_2$(c)	97.5	4.0
$Ru(C_5H_5)_2$(d)	142.9	3.5

(a) Ref. 7. (b) Ref. 3.
(c) E. O. Fischer, *Z. Naturforsch.*, 8b, 217 (1953).
(d) G. Wilkinson, *J. Am. Chem. Soc.*, 74, 6146 (1952).

As described above, the pentagonal rings in the above compounds would involve a different electronic state from the benzene rings. Their electronic state, however, would not be quite identical with those of cycloparaffines either. Thus the fact that the metal compounds in question exhibit their specific bands in the region between 2500 and 3000 Å might be taken as indicating that the cyclopentadienyl-radicals in the above compound would involve some π-electronic character, since the ordinary cycloparaffines would show no such specific bands in the corresponding region. The dichroism, reverse to that of the ordinary benzene rings, was also observed with aromatic molecular compounds, in which π-π interaction is supposed to exist between benzene rings in the direc-

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[12] R. Tsuchida, M. Kobayashi and K. Nakamoto, *J. Chem. Soc. Japan*, 70, 12 (1949); K. Nakamoto, *J. Am. Chem. Soc.*, 74, 390 (1952), etc.; G. Scheibe, S. Hartwig and H. Müller, *Z. Elektrochem.*, 49, 372 (1943).

[13] R. Tsuchida and S. Yamada, read before the sixth annual meeting of the Chemical Society of Japan, Kyoto, April, 1953; to be published soon.

[14] S. Yamada, A. Nakahara and R. Tsuchida, *J. Chem. phys.*, 22, 1620 (1954).

tion perpendicular to the benzene plane[15]. By assuming a similar effect, the dichroism of the present compounds may be understood in the same way, if the π-electrons of the pentagonal rings would be attracted toward the metal atom.

It is interesting to note that the absorption spectra of dicyclopentadienyl-iron (II) and cobalt (III) bear a close resemblance to those of tris (acetylacetono) iron (III) and cobalt (III)[16] in which π-electrons of the ligands are supposed to be involved in the co-ordinate linkages with the metal atoms. This fact, which seems to indicate similarity in linkages between the metal atom and ligands in the complexes of the above two types, may be in harmony with the above presumption that the π-electrons of the cyclopentadienyl-radicals should be greatly involved in the metal-ligand linkages.

Summary

Dichroisms of dicyclopentadienyl-iron (II) and dicyclopentadienyl-cobalt (III) perchlorate in the crystalline state have been quantitatively determined. For the two compounds, the common rules on the dichroism have been obtained. (1) For the two bands at the longer wave-length, absorption perpendicular to the pentagonal rings is very hyperchromic to absorption parallel to the rings. (2) For the specific band, absorption perpendicular to the rings is slightly bathochromic to absorption parallel to the rings.

Consideration of the results has led us to the conclusion that the cyclopentadienyl-radicals in these compounds may be different from the π-electronic systems of ordinary benzene rings, suggesting that the π-electrons would be greatly attracted toward the metal atom to form co-ordinate linkages.

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[15] R. Tsuchida, M. Kobayashi and K. Nakamoto, *Nature*, **167**, 726 (1951); K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 1739 (1952), etc.

[16] K. Sone, I. Miyake, K. Yamasaki and H. Kuroya, *J. Chem. Soc. Japan*, 69, 70 (1948).