Spectrochemical Study of Microscopic Crystals. XIV[1]. *Absorption Spectra and Structure of Dibenzene-chromium(I) Iodide*

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In the course of these several years, dicyclopentadienylcompounds of various metallic elements were prepared, and their chemical and physical properties were extensively studied from various sides[2]. Recently Fischer and Hafner[3] succeeded in preparing an interesting compound with a molecular formula of $Cr(C_6H_6)_2$, which was shown through an X-ray examination[4] to consist of sandwich molecules resembling the molecule of dicyclopentadienyliron(II), $Fe(C_5H_5)_2$[5]. Preparations also were reported of several other compounds of similar structure[3,6]. Although reports have appeared concerning the properties of the compounds of this type, their electronic states are still open to question.

In order to study the linkages in the compounds of this type, the present authors have determined absorption spectra of dibenzenechromium(I) iodide, $[Cr(C_6H_6)_2]I$, in water and ethyl alcohol, and also in the crystalline state. Description and discussion of the measurements are given below.

Experimental

Material.—Crystals of dibenzene-chromium(I) iodide were kindly donated by Dr. E. O. Fischer of "Technische Hochschule, München". The yellow crystals of the compound show a well-developed prism face of a rectangular form, on which the measurement of dichroism has been made. It has been found in the course of the measurement that the crystal undergoes photodecomposition with ultra-violet light. On the contrary, the crystal is comparatively stable in the dark.

Measurement.—Visible and ultra-violet spectra of the compound in the crystalline state have been measured on the above-mentioned face using Tsuchida-Kobayashi's microscopic method[7] with polarized light having its electric vector along and perpendicular to the direction of elongation. The *c*- and the *a*-absorption refer to absorption with the electric vector along and perpendicular to the direction of elongation, respectively.

Visible and ultra-violet absorption spectra in solution and an infra-red spectrum in pressed potassium bromide have been determined with a Beckman DU spectrophotometer and a Hilger H 800 infra-red spectrophotometer, respectively. The symbols used here are the same as those in the former reports of this series.

Results and Discussion

The results of the present measurements are shown in Fig. 1, Table I, Table II and Table III.

Whereas benzene molecules in solution are known to show a characteristic absorption band at about 2600 Å which involves a distinct fine structure, the present measurement indicates that $[Cr(C_6H_6)_2]I$ shows no absorption band of the above sort. It is supposed, therefore, that the electronic state of the benzene rings

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[1] Part XIII of this series, S. Yamada and R. Tsuchida, This Bulletin, **29**, 894 (1956).

[2] See, for example, E. O. Fischer, *Angew. Chem.*, **67**, 475 (1955).

[3] E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 665 (1955).

[4] E. Weiss and E. O. Fischer, *Z. anorg. allgem. Chem.*, **286**, 142 (1956).

[5] E. O. Fischer and W. Pfab, *Z. Naturforsch.*, **7b**, 377 (1952); P. F. Eiland and R. Pepinsky, *J. Am. Chem. Soc.*, **74**, 4971 (1952); J. D. Dunitz and L. E. Orgel, *Nature*, **171**, 121 (1953).

[6] H. H. Zeiss and W. Herwig, *J. Am. Chem. Soc.*, **78**, 5959 (1956).

[7] R. Tsuchida and M. Kobayashi, "The Colour and the Structure of Metallic Compounds," Zoshindo, Osaka, 1944, p. 180 (in Japanese).

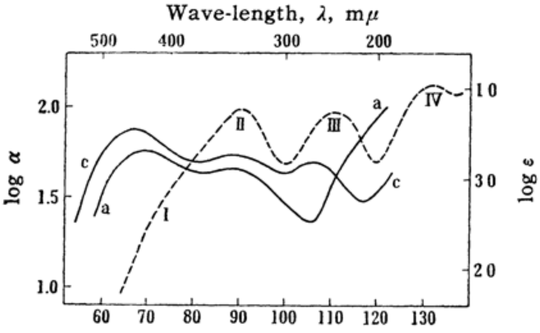

Fig. 1. Absorption spectra of $[Cr(C_6H_6)_2]I$ in the crystalline state (——) and in aqueous solution (······).

within the chromium(I) compound is quite different from that of a free benzene molecule. Thus it is most likely that the π-electrons on the benzene rings are considerably attracted toward the central chromium ion to form firm linkages with it.

It is generally known that, when a metal ion having an unfilled *d*-electron shell forms a complex group with ligands, a few absorption bands of moderate intensity, rather characteristic of the metal ion, must appear in the visible or near-ultraviolet regions. To this type of absorption bands may belong the band I of the chromium(I) compound in question. When the solvent is alternated with a more polar one, this band is found to undergo only very slight solvent effect, which seems to be in agreement with the above assignment⁸⁾.

TABLE I

VISIBLE AND ULTRA-VIOLET ABSORPTION SPECTRA OF $[Cr(C_6H_6)_2]I$ IN CRYSTALLINE STATE AND IN SOLUTION

absorption band	I	II	III	IV
In crystalline state				
ν, 10^{13} sec^{-1}	67.2	86–90	105.6	>120
Δ (log α)	0.12	0.1	0.4	marked
stronger component	Z	Z	Z	X,Y
In H_2O				
ν, 10^{13} sec^{-1}	ca. 76	90	110.6	133.5
log ε	ca. 2.75	3.76	3.75	4.14
In C_2H_5OH				
ν, 10^{13} sec^{-1}	ca. 76	89.8	110.0	139.2
log ε	ca. 2.75	3.80	3.78	4.28
solvent effect	very slight	slight blue shift	slight blue shift	great red shift

The fact that the bands II and III have great intensity in solution suggests that they are different from the type I of absorption bands with much lower intensity. We suppose that these bands may be closely related with the benzene molecules. The bands show a slight but definite "blue shift" when the solvent is changed from a less polar to a more polar one. The "blue shift" indicates that the bands in question correspond to transitions of an *n*-π type, showing agreement with the above assignment. The bands II and III may not be considered as a band of such a kind that is identical in its origin with the typical absorption bands of free benzene, since the band of free benzene is known to show a "red shift".

The crystal structure of $[Cr(C_6H_6)_2]I$ is not known as yet. Although the exact arrangement of $[Cr(C_6H_6)_2]^+$ ions in the crystal can not be determined, we may be able to estimate the principal features of dichroism for the complex ion itself on a suitable assumption about the arrangement of the complex ions in the crystal. Previous studies on the dichroism of planar metallic complexes⁹⁾ indicate that for an absorption band in the longer wave-length of a planar metallic complex, which is closely related with the linkages within the complex, absorption is stronger along the direction in which the linkages exist than along the direction normal to it. Since the band I is assumed to be closely related with the linkage between the chromium ion and the benzene molecules, similar relationships to the abovementioned should hold for the band I of the chromium(I) compound.

The present dichroism measurement with the crystal indicates that the polarization for the band I is definite, though not very great. Then we may assume that the *c*-absorption in Fig. 1 may represent the main characteristics of the *z*-absorption, the *z*-absorption being absorption with polarized light having its electric vector perpendicular to the benzene rings.

If the linkages between the benzene molecules and a chromium ion were similar to those in aromatic molecular compounds such as the linkage between

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8) About the solvent effect upon absorption spectra, see, for example, M. Kasha, *Faraday Soc. Discussion*, No. 9, 14 (1950); H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952); K. Nakamoto, M. Kobayashi and R. Tsuchida, ibid., **22**, 957 (1954).

9) S. Yamada and R. Tsuchida, This Bulletin, **29**, 421 (1956); ibid., **26**, 492 (1953); *J. Am. Chem. Soc.*, **73**, 1182 (1951); *Annual Report of Scient. Works, Fac. Sci. Osaka Univ.*, **4**, 79 (1956), etc.

quinone and hydroquinone molecules in quinhydrone, there should appear on the long wave-length side a new type of absorption band which would be broad and strong, and greatly polarized along the z-direction[10]. Since this type of absorption is not observed, the linkage similar to those in aromatic molecular compounds may not be present in the chromium(I) compound.

If aromaticity of the benzene rings in this chromium(I) compound were comparatively marked, the dichroism similar to the benzene rings would be observed, just as in most benzene derivatives. The dichroism of the benzene rings, which was determined with an ordinary type of benzene derivatives, indicates that absorption is more intense along the benzene ring than along the direction normal to it[11]. Since no dichroism of the above sort or a band with a fine structure is observed, the electronic state of the benzene molecules in this chromium(I) compound seems to be far from the state of free benzene molecules. The possibility may still remain that the band with a fine structure would be very weak, being hidden by the bands of much greater intensity. This possibility, however, may be neglected, judging from the general aspect of the absorption curve with the present compound.

The present measurement also indicates that with respect to the band IV absorption is much more intense along the plane of the benzene rings than along the direction normal to the benzene rings. From analogy with the dichroism of the benzene rings[11], it is suggested that the band IV is closely connected with the linkages within the benzene rings.

A marked "red shift" has been observed for the band IV, showing that the band corresponds to a "π-π" transition. The band IV does not correspond to the band at 2600 Å of free benzene, since both the magnitude of the red shift and the intensity seem to be too great, as compared with the values for the band at 2600 Å of free benzene.

Infra-red absorption bands of the chromium(I) compound are shown in Table II and Table III together with corresponding values of related compounds. The chromium(I) compound has an absorption band at 1428 cm.$^{-1}$ for a C–C stretching vibration in the benzene plane. It is seen that the C–C vibration in the chromium(I) compound is displaced from the original position of free benzene to a considerably smaller wave-number, being very close to the corresponding values[12] for dicyclopentadienyl-iron. From mutual comparison of the values in Table III, the electronic state of the benzene rings in $[Cr(C_6H_6)_2]I$ may be concluded to be between the states of ordinary aromatic and aliphatic carbon atoms, and to resemble the state of cyclopentadienyl-radicals in dicyclopentadienyl-iron(II). Thus the benzene rings in the chromium (I) compound may have less aromaticity than free benzene, though they still keep some of their unsaturated character.

TABLE II

INFRA-RED ABSORPTION BANDS OF $[Cr(C_6H_6)_2]I$ IN PRESSED POTASSIUM BROMIDE

freq. cm.$^{-1}$	intensity	freq. cm.$^{-1}$	intensity
795	v. str.	1145	m.
890	w.	1385	w.
974	str.	1428	str.
995 1005 (double)	m.	3025	m.

TABLE III

SKELETAL C–C VIBRATION

compound	skeletal vibr. cm^{-1}	ref.
$Fe(C_5H_5)_2$	1410	12
$Cr(C_6H_6)_2$	1428	3
$[Cr(C_6H_6)_2]I$	1428	
C_6H_6	1500	a)
C–C double	1600–1680	a)
C–C single	800–1200	a)

a) See, for example, J. L. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co., London, 1954.

Summarizing all the facts as described above, absorption spectra in the infra-red, the visible and the ultra-violet region seems to be understandable on the basis of the following assumption about the electronic state and linkages within the chromium(I) compound in question.

The benzene rings in $[Cr(C_6H_6)_2]I$ *have an electronic state which deviates* ***greatly*** ***from the state of the ordinary benzene rings,*** ***involving very little aromaticity.***

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

[11] R. Tsuchida, M. Kobayashi and K. Nakamoto, *J. Chem. Soc. Japan*, **70**, 12 (1949); K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 390 (1952); G. Scheibe, S. Hartwig and H. Müller, *Z. Elektrochem.*, **49**, 372 (1943); D. P. Craig and L. E. Lyons, *Nature*, **169**, 1102 (1952), *etc*.

[12] L. Kaplan, W. L. Kester and J. Katz, *J. Am. Chem. Soc.*, **74** 5531 (1952); E. R. Lippincott and R. D. Nelson, *J. Chem. Phys.*, **21**, 1307 (1953).

Thus we are inclined to conclude that π-electrons of the benzene rings in $[Cr(C_6H_6)_2]I$ may be strongly attracted so that the electronic state of the benzene rings is far from the state of the ordinary benzene rings and somewhat near the state of the cyclopentadienyl-radicals in dicyclopentadienyl-iron(II)[13].

Summary

Polarized absorption spectra of $[Cr(C_6H_6)_2]I$ in the visible and the ultraviolet region were quantitatively determined by Tsuchida-Kobayashi's microscopic method using a single crystal. Visible and ultraviolet absorption spectra in solution and an infra-red spectrum in potassium bromide disks were also determined.

From the results of the measurements, it was concluded that the electronic state of the benzene rings in $[Cr(C_6H_6)_2]I$ deviates greatly from the state of free benzene and that the π-electrons of the benzene rings are attracted remarkably toward the chromium ion to form firm linkages.

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[13] S. Yamada, A. Nakahara and R. Tsuchida, *J. Chem. Phys.*, **22**, 1620 (1954); This Bulletin, **28**, 465 (1955).