Absorption Spectra of Metallic Complexes with Aromatic Molecules

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Ever since the first preparation of bis-(benzene)-chromium[2] and confirmation with X-rays of the sandwish structure of this compound[3], a number of metallic complexes with aromatic molecules have been synthesized. The study of these compounds is thought to be interesting because of the peculiar bonding involved in the compounds which may be quite similar to that in the ferrocene-type compounds. Many articles have been presented concerning various properties of the compounds, but there have been very few reports available which discuss their absorption spectra in relation to the bonding[4].

In the present work, the authors have determined quantitatively absorption spectra of some chromium compounds containing aromatic molecules and discussed the results of the measurements in relation to the bonding involved in the metal-arenes in general.

Experimental

Materials. — Bis-(benzene)-chromium (I) iodide was prepared in yellow crystals from bis-(benzene)-chromium (0), which was obtained according to the method of Fischer[2]. Dichroism of the compound was reported in the earlier paper[4].

Bis-(toluene)-chromium (I) iodide was prepared

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

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

[4] S. Yamada, H. Nakamura and R. Tsuchida, This Bulletin, **30**, 647 (1957).

by the method of Fischer and Seus⁵⁾ from bis-(toluene)-chromium(0). The yellow, prismatic crystals of the compound show a straight extinction and a slight but definite dichroism on the well-developed prism face.

Monobenzene-chromium tricarbonyl was prepared in yellow, plate-like crystals by the method of Fischer and Öfel⁶⁾ from chromium hexacarbonyl and bis-(benzene)-chromium(0) in a sealed tube. The crystals show a slight dichroism on the face, on which the dichroism measurement was carried out.

Chromium hexacarbonyl was prepared in colorless crystals according to the method of Natta et al.⁷⁾

Measurements. — Dichroism in the visible and ultraviolet regions of $Cr(C_6H_6)(CO)_3$ was determined on the above-mentioned face with Tsuchida and Kobayashi's microscopic method⁸⁾ using polarized light.

Ultraviolet absorption spectra in solution were determined with a Beckman DU spectrophotometer.

Infrared spectra of the compounds in Nujol mulls and in potassium bromide discs were determined in the rock salt region with a Hilger H800 infrared spectrophotometer.

The notations in the present paper are the same as those used in the former papers of this series.

Results and Discussion

Ultraviolet Absorption Spectra of Metal Carbonyls. — Absorption spectra of chromium hexacarbonyl in various solvents have been determined in the present work, and are shown in Fig. 1. The present measurement indicates that there is a very weak absorption band at about 50×10^{13} sec^{-1}, which was not reported by the previous investigators⁹⁾. The weak absorption band of this sort, which is observed in the absorption spectra of $Cr(C_6H_6)(CO)_3$, $[Cr(C_6H_6)_2]^+$ and $[Cr(C_6H_5CH_3)_2]^+$, may belong to a "spin-forbidden absorption band" and is discussed in the later part of the present paper.

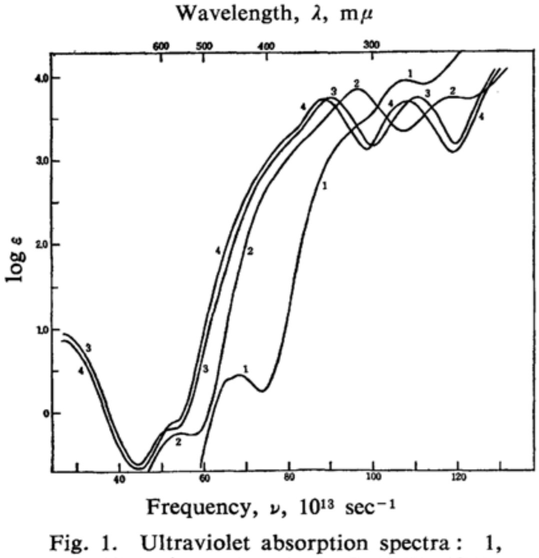

Fig. 1. Ultraviolet absorption spectra: 1, $Cr(CO)_6$ in methanol; 2, $Cr(C_6H_6)(CO)_3$ in methanol; 3, $Cr(C_6H_6)_2I$ in water; 4, $Cr(C_6H_5CH_3)_2I$ in water.

Milazzo and Scheibe⁹⁾ believed that most of the intense absorption bands of $Cr(CO)_6$ in the shorter wavelength, excepting the first inflation which they regarded as due to the carbonyl molecule itself, might be due to the decomposition products formed by photo-dissociation from the original molecule. Their conclusion was based upon the absence of a fine structure in the absorption curve. In the opinion of the present authors, however, the absence of a fine structure alone seems to be insufficient for such a conclusion. Such a flat absorption curve may be ascribed rather to the extraordinary nature of the ligand or, in other words, of the metal-to-ligand bond. Flat absorption curves similar to the spectrum of chromium hexacarbonyl are often exhibited; for example, by complexes of transition elements with ligands such as cyanide, isonitriles, ethylene, dimethylglyoxime and so forth.

Generally speaking, absorption spectra of carbonyls of transition elements may be regarded as a superposition of "ligand field absorption bands", due mainly to the metal under the field of the CO molecules, and absorption bands due to the electronic transitions which are closely related with the CO-groups under the field of the metal atom with which they are linked. Thus, the inflation at about 92×10^{13} sec^{-1} of $Cr(CO)_6$, which is found in Fig. 1, may be regarded as corresponding to a "ligand field band", and the absorption bands in shorter wavelength may be due to the electronic transitions closely related with the CO-groups under the field of the central metal. Absorption bands of the latter type, however, can not be ascribed to the CO-groups alone, since the present measurement shows that the absorption bands of $Cr(CO)_6$ undergo a slight "red shift" on changing a solvent from a less polar to a more polar one, whereas the carbonyl-group in ketones, for example, suffers a "blue shift"¹⁰⁾. The authors are inclined to assume that the bands may most probably be due to electronic transitions from a level related principally with

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5) E. O. Fischer and D. Seus, *Chem. Ber.*, **89**, 1809 (1956).

6) E. O. Fischer and K. Öfel, ibid., **90**, 2532 (1957).

7) G. Natta, R. Ercoli, F. Calderazzo and A. Rabizzoni, *J. Am. Chem. Soc.*, **79**, 3611 (1957).

8) R. Tsuchida and M. Kobayashi, This Bulletin, **13**, 619 (1938); "The Colour and the Structure of Metallic Compounds" (Kinzokukagobutsu no Iro to Kozo), Zoshindo, Osaka (1944), p. 180.

9) G. Milazzo and G. Scheibe, *Z. physhik. Chem.*, **B31**, 431 (1936).

10) G. Scheibe, *Ber.*, **58**, 587 (1925).

the metal to excited levels of the CO-groups in the metallic complex.

In connection with the chromium hexacarbonyl, it seems to be interesting to discuss here about the absorption spectrum of $Co_2(CO)_8$. Hieber et al.[11] reported the absorption spectrum of the compound in solution, only pointing out that the binuclear complex showed an absorption spectrum different from that of the corresponding mononuclear complexes. The spectra of the compound in the gaseous and solution states were later determined and discussed in combination with the infrared spectrum, the bibridged structure being regarded as most probable[12]. On re-examination of the ultraviolet spectra reported by the former investigators, it is readily recognized that $Co_2(CO)_8$ exhibits absorption in the wavelength region much longer than the corresponding mononuclear $[Co(CO)_4]^-$ ion. It is known from data so far obtained that the absorption spectrum of bibridged complexes without special interaction between the two metal atoms may be regarded as a superposition of the two mononuclear complexes of which the binuclear complex is assumed to be composed. Thus, the absorption spectrum of the bibridged, binuclear complex is known to show no greatly bathochromic displacement from the spectrum of the corresponding mononuclear complexes. This may be recognized; for example, in comparing absorption spectra of dicobalt-μ, μ'-diol, diplatinum-μ, μ'-dichloro, dipalladium-μ, μ'-dichloro and dichromium-μ,-μ'-diol complexes with the spectra of the corresponding mononuclear complexes[13]. The displacement of the absorption spectrum of $Co_2(CO)_8$ from that of $[Co(CO)_4]^-$ seems to be too great for an ordinary type of binuclear complex without special interaction. Thus, the appearance of the absorption in the enormously long wavelength region may be taken as evidence for the assumption of the direct interaction between the cobalt atoms in the $Co_2(CO)_8$.

Ultraviolet Absorption Spectra of Bis-(benzene)- and Bis-(toluene)-chromium(I) Iodide.—Ultraviolet absorption spectra of bis-(benzene)- and bis-(toluene)-chromium(I) iodide, which have been determined in the present work, are shown in Fig. 2 and Table I. The absorption spectrum of $[Cr(C_6H_6)_2]I$ in solution was formerly reported by the present authors, but the measurement has been extended to the longer wavelength region in the present work.

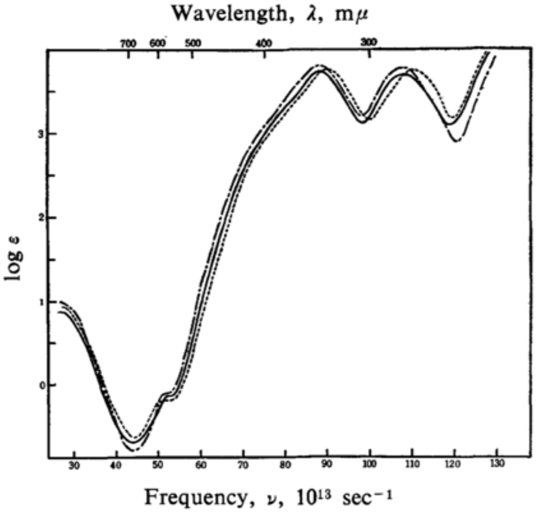

Fig. 2. Ultraviolet absorption spectra: ——, $Cr(C_6H_5CH_3)_2I$ in water; — - —, $Cr(C_6H_5CH_3)_2I$ in ethanol; ------, $Cr(C_6H_6)_2I$ in water.

It is seen in Fig. 2 and Table I that the absorption spectrum of $[Cr(C_6H_5CH_3)_2]I$ bears a close resemblance to the spectrum of $[Cr(C_6H_6)_2]I$. Thus, between the two curves there is only a very slight difference in the wavelength and the intensity of the band maxima. In addition, the solvent effect on absorption bands is also the same for the two compounds, as seen in Table I. It may safely be concluded that the $[Cr(C_6H_5CH_3)_2]^+$ ion has the same structure and bonding as the $[Cr(C_6H_6)_2]^+$ ion. Both the complex ions may most probably have the sandwich structure.

Free benzene and toluene are known to show a characteristic band at about 260 mμ with a fine structure. On the contrary, both the $[Cr(C_6H_6)_2]^+$ and the $[Cr(C_6H_5CH_3)_2]^+$ ion are found to show no absorption bands of the above sort. The absorption bands of the chromium(I)-complexes in the corresponding wavelength region are much more intense than the band of benzene or toluene, and do not show such a fine structure as is observed in the spectra of the aromatic molecules themselves. Moreover, Bands II and III of the chromium(I)-complexes undergo a slight " blue shift ", whereas the absorption band of the benzene ring with a fine structure undergoes a slight " red shift ". These facts seem to show that the electronic state of the benzene rings in the chromium(I)-complexes is quite different from that of a benzene ring in the free benzene derivatives. The dichroism of the $[Cr(C_6H_6)_2]^+$ ion also seems to be consistent with this assumption[4]. If the aromaticity of the benzene rings in the chromium(I)-complex were comparatively remarkable, a dichroism similar to the benzene rings would be observed, just as in ordinary benzene derivatives. Since a dichroism of this

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[11] W. Hieber and K. K. Hofmann, *Z. anorg. u. allgem. Chem.*, **270**, 49 (1952).

[12] R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, *J. Am. Chem. Soc.*, 77, 3951 (1955); J. W. Cable, R. S. Nyholm and R. K. Sheline, ibid., 76, 3373 (1954).

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

TABLE I. ABSORPTION MAXIMA OF CHROMIUM COMPOUNDS WITH AROMATIC MOLECULES

Compound	Solvent	Band I′ $\nu(\log \varepsilon)$	Band I $\nu(\log \varepsilon)$	Band II $\nu(\log \varepsilon)$	Band III $\nu(\log \varepsilon)$
$[Cr(C_6H_5CH_3)_2]I$[a]	water	27(0.82)	75(2.9)	88.0(3.72)	108.1(3.69)
	ethanol	27(1.00)	76(3.0)	87.6(3.80)	107.8(3.77)
	solvent effect	very slight	very slight	slight blue shift	slight blue shift
$[Cr(C_6H_6)_2]I$[a,b]	water	26(0.95)	76(2.75)	90 (3.76)	110.6(3.75)
	solvent effect	very slight	very slight	slight blue shift	slight blue shift
	stronger component		Z	Z	Z
$[Cr(C_6H_6)(CO)_3$[a]	methanol		80(3.3)	96.3(3.86)	118.3(3.74)
	ethanol		80(3.4)	96.1(3.54)	118.1(3.67)
	solvent effect		very slight	slight blue shift	slight blue shift
	stronger component		Z	Z	(Z)
$[Cr(C_6H_5 \cdot C_6H_5)_2]I$	ethanol[c]			87.7(4.01)	120(3.39)
	——[d]			86.2(3.8)	120(4.5)
$[Cr(C_6H_5 \cdot C_6H_5)_2](OC_6H_5)$	ethanol[c]			87.0(——)	121(——)
$[Cr(C_6H_6)(C_6H_5 \cdot C_6H_5)]I$	ethanol[c]			87.5(——)	111(——)

ν: $10^{13} \times sec^{-1}$

a) The present measurement.

b) Ref. 4 in the text.

c) Taken from H. H. Zeiss and M. Tsutsui, *J. Am. Chem. Soc.*, **79**, 3062 (1957).

d) Taken from Ref. 5, in which the solvent is not given. In the curve there is observed inflation at about 116×10^{13} sec^{-1} ($\log \varepsilon$ 4.3).

sort or a band with a fine structure characteristic of the free benzene derivatives is not observed, the electronic state of the benzene rings in this chromium(I)-complex seems to be comparatively far apart from the state of the free benzene molecule. It is most likely, as is shown in the later part of this paper, that the π-electrons on the benzene rings are attracted to a considerable extent toward the central chromium ion to form firm linkage with it.

The present measurement also indicates that both $[Cr(C_6H_6)_2]I$ and $[Cr(C_6H_5CH_3)_2]I$ exhibit an absorption band (Band I′) in the near-infrared region. Since it is known that neither free benzene, toluene nor iodide ion in solution has any absorption bands of this sort, Band I′ in the infrared region can be ascribed to the $[Cr(C_6H_6)_2]^+$ and $[Cr(C_6H_5CH_3)_2]^+$ ion. Band I′ may be characteristic of the chromium(I)-complexes, since the present measurement indicates that $Cr(C_6H_6)(CO)_3$ or $Cr(CO)_6$ has no absorption bands in the corresponding wavelength region.

It is 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 generally appear in the visible or near-ultraviolet region. In terms of the "ligand field theory", these absorption bands, Bands I and I′, may be ascribed to electronic transitions between the energy levels which are produced by splitting the lowest levels of the free metal ion under the field of the ligands. The chromium(I) ion with a $3d^5$ configuration has an $^2F_2$ level as its lowest level in the very strong ligand field[14]. Therefore, a few ligand field bands should appear corresponding to electronic transitions from the lowest level to the upper levels of the metal with the same multiplicity which might be regarded, in approximation, as produced by splitting from the original ^2I of the free chromium(I) ion under the very strong ligand field[14]. Band I′ in the near-infrared region and the inflation at about 76 to 78×10^{13} sec^{-1} (Band I(of $[Cr(C_6H_6)_2]^+$ and $[Cr(C_6H_5CH_3)_2]^+$ seem to belong to this sort of absorption bands.

The appearance of the ligand field bands, rather characteristic of the metal in ordinary metallic coordination compounds, seems to show

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[14] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 766 (1954).

that *the linkage between chromium and the aromatic molecules in the chromium-complexes discussed here is rather similar, at least essentially, to the linkage in complexes of transition elements of a Werner-type, so that the π-electrons on the benzene rings in these compounds are withdrawn to a considerable extent toward the central chromium.*

Bands II and III may be different in their origin from the ligand field bands, judging from their intensity, which seems to be rather too great for the ligand field bands. The two bands seem to be due most probably to electronic transitions closely related with the benzene rings, but may not be regarded as belonging to those bands that are quite identical in their origin to the typical absorption band of free benzene, since Bands II and III show a slight but definite " blue shift " when the solvent is changed from a less polar to a more polar one, whereas the band of free benzene rings is known to show a slight " red shift ". It may be assumed that Bands II and III are due to electronic transitions from the orbital principally related with the central metal ion to the excited levels of the benzene rings in the complexes. The fact that the difference $\nu_{\text{III}}-\nu_{\text{II}}$ is nearly constant for the $[Cr(C_6H_6)_2]^+$ and the $[Cr(C_6H_5CH_3)_2]^+$ ion may be consistent with the assumption presented in this paper about the origin of these absorption bands. The assumption also is borne out by the observation in the present work that the value $\nu_{\text{III}}-\nu_{\text{II}}$ for $[Cr(C_6H_6)_2]^+$ and $[Cr(C_6H_5CH_3)_2]^+$ is nearly equal to the value for $Cr(C_6H_6)(CO)_3$. This will be reported in the next paragraph of the present paper.

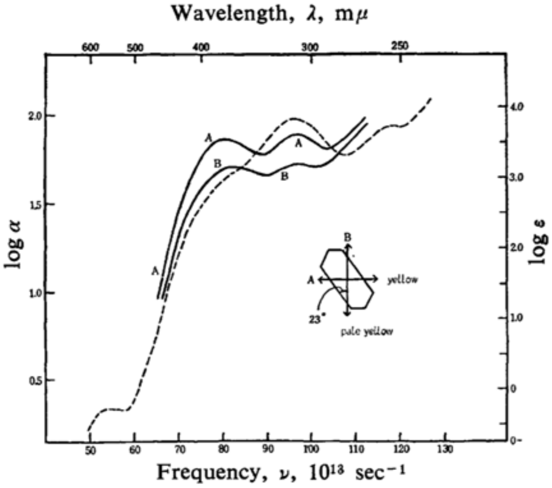

Fig. 3. Ultraviolet absorption spectra of $Cr(C_6H_6)(CO)_3$ in the crystalline state (——) and in methanol (------).

Ultraviolet Absorption Spectra of Mono-benzene-chromium(0) Tricarbonyl. — Ultraviolet absorption spectra of $Cr(C_6H_6)(CO)_3$ have been determined and are shown in Fig. 3 and Table I. Since the chromium(0) atom in $Cr(C_6H_6)(CO)_3$ with a $3d^6$ configuration has $^1A_1$ as its lowest level in the case of very strong ligand field, the chromium(0)-complexes are expected to show a few ligand field bands which are due to electronic transitions from the $^1A_1$ level to the upper levels of the metal atom with the same multiplicity. In fact, the present measurement indicates that no absorption bands of this sort are apparently observed in the absorption curve of $Cr(C_6H_6)(CO)_3$ in solution. In the opinion of the present authors, the ligand field bands of the compound are situated possibly in the comparatively short wavelength region and seem to be covered partly under the more intense absorption bands. The inflation at about 80×10^{13} sec^{-1} in the curve of the solution most probably represents a ligand field band superposed by more intense absorption bands. A distinct maximum corresponding to the ligand field band is recognized at about the same wavelength in the absorption curve of the crystal, as seen in Fig. 3.

The ultraviolet absorption curve of $Cr(C_6H_6)(CO)_3$ bears a resemblance to that of the $[Cr(C_6H_6)_2]^+$ or the $[Cr(C_6H_5CH_3)_2]^+$ ion excepting that the absorption band in the infrared region, which is observed in the latter complexes, is absent in the former. Thus, the absorption bands at about 86 and 111×10^{13} sec^{-1} of $Cr(C_6H_6)(CO)_3$ in solution apparently correspond to Bands II and III of the $[Cr(C_6H_6)_2]^+$ or the $[Cr(C_6H_5CH_3)_2]^+$ ion, and are regarded as due to the electronic transitions from a level closely related with the central metal to two excited levels of the benzene rings in combination with the metal. It is found that *the difference $\nu_{\text{III}}-\nu_{\text{II}}$ is almost constant for $[Cr(C_6H_6)_2]I$, $[Cr(C_6H_5CH_3)_2]I$ and $Cr(C_6H_6)(CO)_3$*, it being in agreement with the present assumption about the origin of Bands II and III. The fact that $Cr(C_6H_6)(CO)_3$ shows absorption bands corresponding closely to those of $[Cr(C_6H_6)_2]I$, in spite of the oxidation state of chromium in the former compound which is different from the oxidation state in the latter, seems to indicate that *the linkage of chromium with the aromatic molecule is essentially alike in the above three compounds*. In fact, a recent study with X-rays[15] indicates that a molecule of $Cr(C_6H_6)(CO)_3$ has a structure similar to that of the $[Cr(C_6H_6)_2]^+$ ion having possibly the sandwich structure, the benzene ring in the molecule being parallel to the plane in which the three oxygen atoms are contained.

On the other hand, the absorption spectrum of

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15) P. Corradini and G. Allegra, *J. Am. Chem. Soc.*, **81**, 2271 (1959).

$Cr(C_6H_6)(CO)_3$ is found to be quite different from the spectrum of $Cr(CO)_6$. Thus, the absorption bands in the ultraviolet region, which are rather characteristic of the metal carbonyls such as $Cr(CO)_6$ and may be due to the electronic transitions closely related with the excited levels of the CO molecules, are missing in $Cr(C_6H_6)(CO)_3$. This fact seems to show that *the linkage of chromium with the CO molecules in* $Cr(C_6H_6)(CO)_3$ *may be different in its nature from the corresponding linkage in* $Cr(CO)_6$. In connection with this, it may be worth noting that mixed carbonyls of wolfram and iron with some isonitriles show absorption spectra similar to those of $W(CO)_6$ and $Fe(CO)_5$, respectively. The linkage of the metal with the CO molecules in these mixed carbonyls is found to be rather similar to the linkage in the corresponding metal carbonyls.

TABLE II. CO STRETCHING FREQUENCIES

Compound	Freq. cm^{-1}
CO	2143[a]
$Cr(CO)_6$	2108, 2019, 2000[b] (1965, weak)[c]
$Cr(C_6H_6)(CO)_3$	1955[d]

a) Cf. L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Methuen & Co., London (1954).
b) N. J. Hawkins, H. C. Mattraw, W. W. Sabot and D. R. Carpenter, *J. Chem. Phys.*, **23**, 2422 (1955).
c) S. L. Shufler, H. W. Sternberg and R. A. Friedel, *J. Am. Chem. Soc.*, **78**, 2687 (1956).
d) The present measurement.

TABLE III. C–C SKELETAL VIBRATIONS OF BENZENE NUCLEUS

Compound	Skeletal vibr. cm^{-1}
$Cr(C_6H_6)(CO)_3$	1445[a]
$[Cr(C_6H_6)_2]I$	1428[b]
$Fe(C_5H_5)_2$	1410[c]
C_6H_6	1500[d]
C–C double	1600∼1680[d]
C–C single	800∼1200[d]

a) The present measurement.
b) Ref. 4 in the text.
c) 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).
d) Cf. L. J. Bellamy, loc. cit.

As seen in Table II, comparison of a CO stretching frequency of $Cr(C_6H_6)(CO)_3$ with the corresponding values of its related compounds gives the following order: free CO > $Cr(CO)_6$ > $Cr(C_6H_6)(CO)_3$. Since the stronger linkage between the carbon and the chromium atom would loosen the linkage between the carbon and the oxygen atom more greatly, the above frequency shift seems to show, at least qualitatively, that *the metal-to-carbon bond in* $Cr(C_6H_6)(CO)_3$ *may be stronger than the corresponding bond in* $Cr(CO)_6$.

As seen in Table III, comparison of a skeletal C–C vibration of a benzene nucleus gives the following order: free C_6H_6 > $Cr(C_6H_6)(CO)_3$ > $[Cr(C_6H_6)_2]^+$. Since the displacement of the skeletal C–C vibration from the vibration of free C_6H_6 is less in $Cr(C_6H_6)(CO)_3$ than in $[Cr(C_6H_6)_2]^+$, *the linkage of the chromium atom with the benzene molecule may be stronger in the latter than in the former.*

The conclusion that the linkage between the chromium and the carbon of CO is stronger in $Cr(C_6H_6)(CO)_3$ than in $Cr(CO)_6$ is found to be in accordance with the fact that the Cr-C(in CO) distance is shorter in $Cr(C_6H_6)(CO)_3$[15] than in $Cr(CO)_6$[16]. It may also be worth noting that the Cr–C(in C_6H_6) distance is longer in $Cr(C_6H_6)(CO)_3$ than in the neutral molecule of $Cr(C_6H_6)_2$[17].

Dichroism of Monobenzene-chromium Tricarbonyl.—The results of the dichroism measurement are shown in Fig. 3. A preliminary report on the crystal structure of $Cr(C_6H_6)(CO)_3$ has recently been published, but the more detailed description of the crystal structure is not available. Comparison of the absorption spectra of $Cr(C_6H_6)(CO)_3$ with the spectra of $[Cr(C_6H_6)_2]I$, however, has enabled one to derive the main characteristics of the component absorptions of the former as referred to the principal axes of the molecule. Actually the molecules are not arranged in the crystal with their corresponding molecular axes completely parallel to each other. However, the dichroism of the crystal, as determined in the present work, may be thought to represent the main features of the component absorptions of the molecule.

The absorption band at about 80×10^{13} sec^{-1} of the crystal probably corresponds to the inflation at about the same frequency in the absorption curve of the compound in solution. This band may be regarded as corresponding to the absorption band at about 70×10^{13} sec^{-1} of $[Cr(C_6H_6)_2]I$ in the crystalline state, and may be assigned to one of ligand field bands. It is to be noted that Band II is found to be much weaker in the crystalline state than in solution, as was also found to be the case with $[Cr(C_6H_6)_2]I$.

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[16] L. O. Brockway, R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

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

[18] The Z-direction refers to the threefold axis of the molecule of $Cr(C_6H_6)(CO)_3$.

The dichroism for Bands I and II of $Cr(C_6H_6)(CO)_3$ is found to be quite similar to that of $[Cr(C_6H_6)_2]I$ on suitable assumption of the crystal structure. Thus, if it is assumed that A- and B- absorptions in Fig. 3 represent, respectively, the main features characteristic of Z- and X, Y-absorption of the complex-molecule[18], the dichroism of $Cr(C_6H_6)(CO)_3$ seems to be coincident with the dichroism of $[Cr(C_6H_6)_2]^+$. The following relationship may be derived on the dichroism of $[Cr(C_6H_6)_2]I$ and $Cr(C_6H_6)(CO)_3$.

Z-absorption is stronger than X, Y-absorption for Bands I and II.

The absorption spectra and the dichroism of these compounds are evidently different from those of free benzene rings. If much aromaticity were kept in the benzene rings within the chromium-complexes, a dichroism similar to the dichroism of the free benzene rings would be observed, just as in most benzene derivatives. Since the dichroism characteristic of the free benzene rings or a band with a fine structure is not observed, the electronic state of the benzene rings in these compounds seems to be far from the state of the free benzene molecule.

The observation that Z-absorption is stronger than X, or Y-absorption for Bands I and II seems to be in good agreement with the concept that *the π-electrons on the benzene rings in* $Cr(C_6H_6)(CO)_3$ *are strongly withdrawn toward the chromium atom to form linkage with it.*

A similar type of dichroism was formerly reported with bis-(cyclopentadienyl)-iron(II) and cobalt(III) complexes, where Z-absorption is stronger than X- and Y-absorptions of the complexes for the two absorption bands in the long wavelength region[19]. This relationship also was taken as evidence that the π-electrons on the pentagonal rings are withdrawn considerably toward the metal atom to form firm bonds with it.

Weak Absorption Bands in the Long Wavelength Region.—The present measurement indicates that $Cr(CO)_6$, $[Cr(C_6H_6)_2]^+$ and $[Cr(C_6H_5CH_3)_2]^+$ all display a very weak band system in the long wavelength side. A part in the shorter wavelength region of the weak band is covered by much stronger absorption bands. It is theoretically known that the electronic transitions between levels with different multiplicities are strictly forbidden, appearing in most cases as very weak absorption bands. Thus, chromium(III)-complexes are known to display a spin-forbidden band with very small intensity to the long wavelength side of the ligand field absorption band[20]. In a similar way, the very weak absorption band systems of $Cr(CO)_6$ or $[Cr(C_6H_6)_2]^+$ may most probably correspond to the spin-forbidden bands which are due principally to chromium(0) or chromium(I). The spin-forbidden bands may tentatively be assigned to electronic transitions from the ground state $^1A_1$ to $^3F_1$ and $^3F_2$ in the case of chromium(0), and to transitions from the ground state $^2F_2$ to $^4F_1$ and $^4F_2$ in the case of chromium(I).

The solvent effect upon this type of the weak absorption bands has been examined, and is shown in Table IV. It is found that the band undergoes a slight "red shift" with the compounds examined here.

TABLE IV. SPIN-FORBIDDEN ABSORPTION BANDS

Compounds	Solvent	ν	log ε
$[Cr(C_6H_6)_2]I$	water	52	$\bar{1}.80$
$[Cr(C_6H_5CH_3)_2]I$	water	52.5	$\bar{1}.90$
	ethanol	53	$\bar{1}.90$
$Cr(C_6H_6)(CO)_3$	methanol	53–4	$\bar{1}.8$
	ethanol	55–6	—
$Cr(CO)_6$	methanol	67.5	0.47
	ethanol	68.5	0.45

ν: 10^{13} sec^{-1}

The present measurement also indicates that the spin-forbidden bands are displaced to the shorter wavelength region, as the ligand field bands are displaced to the same direction in the following series: $[Cr(C_6H_6)_2]^+$, $Cr(C_6H_6)(CO)_3$, $Cr(CO)_6$.

Ultraviolet Absorption Spectra of Hein's Polyphenyl-chromium Compounds.— Hein[21] reported a number of polyphenyl chromium compounds with general composition of $Cr(C_6H_5)_n$ and $Cr(C_6H_5)_n X$, where n is equal to 3 or 4, and X denotes an anion such as iodide and anthranilate. It was only after the discovery of numerous compounds with a ferrocene-like structure that the suggestion was presented that Hein's compounds might contain chromium(I)-complexes having a sandwich structure with benzene, biphenyl, terphenyl or similar aromatic molecules[22]. Identificaion of one of Hein's compounds, $Cr(C_6H_5)_4I$, with the complex $[Cr(C_6H_5 \cdot C_6H_5)_2]I$, which was prepared from chromium(III) chloride, aluminum and biphenyl as starting materials, was made by comparison of their infrared and ultraviolet absorption spectra, X-ray absorption edges and magnetic properties[5]. Absorption spectra as well as other properties

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of Hein's compounds were formerly reported, but the detailed discussion about ultraviolet spectra of the compounds has not been presented up to the present. In the following, a brief discussion will be given about the absorption spectra of these compounds on the basis of the relationships which have been obtained in the present work.

It was reported in the earlier part of the present paper that the benzene rings in combination with chromium in the compounds having linkage characteristic of the sandwich molecules show two absorption bands, which are due presumably to electronic transitions from an orbital concerned mainly with the central chromium to the two excited levels of the benzene rings. In support of this idea seems to be the fact that the frequency difference between two such transitions is nearly constant for the chromium compounds with benzene rings.

When benzene is replaced by biphenyl in a similar type of compound, a similar type of relationship may exist about the frequency difference, if the sandwich structure is kept in the biphenyl-compounds. Thus, the magnitude of the corresponding frequency difference may be constant for the compounds of chromium with biphenyl, but different from the magnitude in the case of the chromium(I)-compounds with benzene rings. Based on the concept presented here, absorption spectra of Hein's polyphenyl compounds of chromium(I) seem to be understood well if it is assumed that they contain chromium(I)-complexes with aromatic molecules, having the sandwich structure of a ferrocene-type.

In the case of $[Cr(C_6H_6)(C_6H_5 \cdot C_6H_5)]^+$, for example, which has both benzene and biphenyl in combination with chromium(I), electronic transitions to the two excited levels of benzene and to a few levels of biphenyl may be possible, their superposition being observed in the absorption curve of this compound. In fact, $\nu_{III}-\nu_{II}$ obtained from the observed curve[22] of $[Cr(C_6H_6)(C_6H_5 \cdot C_6H_5)]^+$ is found to be nearly equal to the value for $[Cr(C_6H_6)_2]^+$, as seen in Table I. This observation may be readily understandable on the basis of the assumption presented in this paper. Thus, if it is assumed that the maximum frequency of Band III, ν_{III}, of the chromium compound is greater with biphenyl than with benzene rings, the difference $\nu_{III}-\nu_{II}$, which is obtained directly from the absorption spectrum of $[Cr(C_6H_6)(C_6H_5 \cdot C_6H_5)]^+$, may correspond to the frequency difference between the two excited levels of the benzene ring in combination with the chromium. This is in agreement with the above-mentioned observation. The observation that $[Cr(C_6H_5 \cdot C_6H_5)_2]^+$ shows larger $\nu_{III}-\nu_{II}$ than $[Cr(C_6H_6)_2]^+$ does may be understood in a similar way.

The fact that the absorption spectra of Hein's compounds may be explained in this way seems to indicate that *Hein's polyphenyl chromium(I)-compounds have complex-ions with a sandwich structure similar to that of* $[Cr(C_6H_6)_2]^+$ *or* $[Cr(C_6H_5CH_3)_2]^+$.

It is to be noted that Hein's chromium(I)-complexes all show Band II at about 86 to 88×10^{13} sec^{-1}, which is very close to the value for Band II of $[Cr(C_6H_6)_2]^+$, $[Cr(C_6H_5CH_3)_2]^+$ and $Cr(C_6H_6)(CO)_3$. This seems to indicate that *the linkage of the aromatic molecules with the central chromium is remarkably alike in these complexes.*

It was found in the preceding part of the present paper that the chromium(I)-complexes with aromatic molecules exhibit a very weak absorption band, due possibly to spin-forbidden transitions, in the long wavelength region and one of the ligand field bands in the near-infrared. The former investigators did not report a very weak absorption band in the visible or an absorption band in the infrared region for Hein's polyphenyl compounds of chromium(I). In the opinion of the present authors, however, there is good reason to expect that the "polyphenyl compounds of chromium(I)" show a spin-forbidden absorption band at about 50 to 55×10^{13} sec^{-1}, and two of the ligand field bands, one in the infrared and the other as inflation at about 80×10^{13} sec^{-1}, just like the bis-(benzene)- and bis-(toluene)-chromium(I) complexes.

General Aspects of Absorption Spectra of Metal-arenes.—In the next place, the authors will discuss the general aspects of absorption spectra of metallic complexes with aromatic molecules and related compounds on the basis of these measurements with the aid of the data by the former investigators. It may be assumed that these compounds in general display "ligand field absorption bands", due mainly to the central metal under the strong ligand field surrounding it, and absorption bands corresponding to the electronic transitions to the excited levels of the ligand groups in combination with the metal. A part of the former is often covered by more intense absorption of the latter type. The absorption bands of the latter type seem to be rather dependent upon the ligand and sensitive to the nature of its linkage with the metal. Thus, in the case of the cyclopentadienyl-radical, the latter bands are found to undergo a marked shift as the central metal is exchanged, while little change in this type of bands is given rise to when a benzene molecule combined with chromium is replaced by a biphenyl molecule in the chromium-arenes.

Besides these two types of absorption bands, there is usually observed a very weak absorption band system in the long wavelength region, corresponding to spin-forbidden bands due mainly to the central metal. A part of this band system is also covered by the other absorption bands with much greater intensity.

With an ordinary type of metallic complex, the order of ligands is known as the "spectrochemical series"[23], which represent the decreasing order as to the magnitude of their hypsochromic effect on the ligand field bands of the metallic complexes. In the following, discussion will be undertaken concerning metallic compounds with ligands which are coordinated to a metal atom through their carbon atom. Unambiguous assignments of absorption bands to particular electronic transitions are sometimes quite difficult, but a general trend concerning the above effect may be readily derived. Thus reviewing a series of compounds, $Cr(CO)_6$, $Cr(C_6H_6)(CO)_3$ and $Cr(C_6H_6)_2$, the authors may be able to obtain the following order as to the hypsochromic effect of the ligands: $CO > C_6H_6$. In a similar way, it is easily shown that CO has a greater hypsochromic effect than a cyclopentadienyl-radical: $CO > C_5H_5^-$. It is thus seen that CO stands extremely high in the spectrochemical series, probably even higher than CN^-. Comparison also reveals that $C_5H_5^-$ is very close to, but only a little higher than, C_6H_6 in the spectrochemical series. In summary, the following order may be derived: $CO > C_5H_5^- > C_6H_6$.

It is interesting to note that the following order also is derived from the previous data[24] about mixed carbonyls of iron and wolfram: $CO > CN{\cdot}CH_3 > CN{\cdot}C_6H_5$. Comparison of the isonitriles with C_6H_6 and $C_5H_5^-$ as to their hypsochromic effect seems to be difficult for the present.

With the same ligands, the order of transition metal elements as to their hypsochromic effect may also be derived in a similar way. With ligands such as CO, $C_5H_5^-$ and C_6H_6, light absorption is found to be displaced to a shorter wavelength, as the authors go down the periodic table for elements belonging to one and the same sub-group. More or less marked hypsochromic shift is observed when a metal atom is replaced by another which stands lower in the same sub-group for a series of elements such as (Cr, Mo, W), (Fe, Ru, Os) and (Co, Rh, Ir). Absorption maxima of all these compounds are not reported, but a difference in color seems to indicate the above trend without exception. The same trend was reported with many other ligands of an ordinary type[25].

Summary

Ultraviolet absorption spectra of $Cr(CO)_6$, $Cr(C_6H_6)(CO)_3$, $[Cr(C_6H_6)_2]I$ and $[Cr(C_6H_5CH_3)_2]I$ have been determined in various solvents. Dichroism in the visible and ultraviolet region of $Cr(C_6H_6)(CO)_3$ has been determined at room temperature by Tsuchida and Kobayashi's microscopic method with a single crystal of the compound.

The absorption spectrum of $Cr(C_6H_6)(CO)_3$ shows main features similar to those of the spectrum of the $[Cr(C_6H_6)_2]^+$ ion.

These compounds all show a weak absorption band to the long wavelength side of the intense absorption bands.

The results of the measurements have been discussed in relation to the bonding involved in these compounds. Discussion also has been undertaken about Hein's polyphenyl-compounds of chromium(I) on the basis of the present measurements. Absorption spectra of Hein's compounds of chromium(I) seem to be in agreement with the assumption of the sandwich structure.

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