Studies on Organic Reagents for Inorganic Analysis. VI. Absorption Spectrum of Phenylfluorone-Metal Chelate and the Nature of the Chelating Bond

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For many organic dyes used for the colorimetry of metals, the color change is ascribable to the shift of the $\pi \rightarrow \pi'$ absorption spectra of the organic system caused by the chelating. With respect to the nature of such color change, there have been many papers published recently. Molecular orbital (LCAO) method was applied successfully by Belford, Martell and Calvin[1] to compute the effect of metal ion upon the β-diketone-metal chelate. The absorption spectra of metal oxalates were interpreted by Graddon[2] on the basis of a simple electrostatic effect. Dortashaeppi, Hürzeler and Treadwell[3] tried to apply a free electron gas model method to the alizarin chelates of several metals. Based on the amperometric titration data, the absorption spectra of alizarin S and its metal chelate were also discussed by Larsen and Hirozawa[4].

In the treatment of the problem, however, the effect of the nature of the chelating bond has been almost neglected, although it seems sometimes to have considerable influence on the absorption spectra. The author reported previously that the maximum wavelengths of the absorption spectra of phenylfluorone metal chelates shift toward the longer side with the decrease in the electronegativity of the metal chelated[5]. In this paper, the correlation of the maximum wavelength with the ionic character of the chelating bond was treated theoretically with the aid of the free electron gas model approximation.

Fundamental Consideration

The author has adopted Kuhn's free electron gas model method[6,7] for the present purpose, because the model can be conveniently applied to the subject although the value of the model must not be overestimated. According to Kuhn, the electron gas suffers a disturbance in the case of polyenes, unsymmetrical cyanines, etc., and the π-electrons are thought to be placed in a one-dimensional potential having a sine curve periodicity. The wavelength of absorption maximum is expressed by the following equation.

$$\frac{1}{\lambda_{\max}} = \frac{V_0}{\boldsymbol{h}\cdot\boldsymbol{c}}\left(1-\frac{1}{N}\right)+\frac{\boldsymbol{h}}{8m\boldsymbol{c}}\cdot\frac{N+1}{L^2} \qquad (1)$$

where, L is the length of the path of the free π-electron measured along the conjugated chain, N, the number of π-electrons, m, the mass of the electron, $\boldsymbol{c}$, the velocity of light, $\boldsymbol{h}$, Planck's universal constant, and V_0, the amplitude of the sine-shaped potential along the chain.

1) R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. & Nuclear Chem.*, **2**, 11 (1956).
2) D. P. Graddon, ibid., **3**, 308 (1956).
3) Y. Dortashaeppi, H. Hürzeler and W. D. Treadwell, *Helv. Chim. Acta*, **34**, 797 (1951).
4) E. M. Larsen and S. T. Hirozawa, *J. Inorg. & Nuclear Chem.*, **3**, 198 (1956).
5) Part II of this series: H. Sano, This Bulletin, **30**, 790 (1957).
6) H. Kuhn, *Helv. Chim. Acta*, **31**, 1441 (1948); *J. Chem. Phys.*, **16**, 840 (1948).
7) H. Kuhn, *Z. Elektrochem.*, **53**, 165 (1949); *J. Chem. Phys.*, **17**, 1198 (1949).

Suppose that the dye is resonating between two limiting structures Ia and Ib. When each of the two structures makes the same contribution to the normal state of the dye, as seemed to be the case for symmetrical polymethine dyes, each conjugated C–C bond should have an equal bond length*, and the value of V_0 should be zero.

$$\underset{1\ 2\ 3\ 4\ 5}{\cdots\text{C}=\text{C}-\text{C}=\text{C}-\text{C}=\cdots} \leftrightarrow \underset{1'\ 2'\ 3'\ 4'\ 5'}{\cdots=\text{C}-\text{C}=\text{C}-\text{C}=\text{C}-\cdots}$$

Ia Ib

On the other hand, when Ia and Ib do not make equal contribution to the normal state, as seemed to be the case for polyene etc., a longer C–C bond (so-called "single bond") and a shorter bond (so-called "double bond") appear alternatively along the conjugated chain, and V_0 has a definite value.

If the mean bond length of the longer C–C bond and the shorter bond is represented with $\overline{R}'$ and $\overline{R}''$, respectively, the relation mentioned above is summarized as follows:

$$V_0=0, \text{ when } \overline{R}'-\overline{R}''=0 \quad (2)$$

$$V_0>0, \text{ when } \Delta R=\overline{R}'-\overline{R}''>0 \quad (3)$$

The Relation between V_0 and ΔR.—It was difficult to obtain theoretically the relation between V_0 and ΔR. Therefore, the problem was solved with the aid of empirical treatment. The difference between the mean "double-" and mean "single-" bond length in polyenes, ΔR, was obtained by calculation based on Coulson's semi-empirical theory[8], because few observed values for the bond length of polyenes were reported. The results are shown in Table I**.

TABLE I. CALCULATED VALUES OF $\overline{R}'$, $\overline{R}''$ and ΔR

j	$\overline{R}'$, Å	$\overline{R}''$, Å	ΔR, Å
1	—	1.330	—
2	1.432	1.347	0.085
3	1.424	1.356	0.068
4	1.420	1.362	0.058
5	1.415	1.365	0.050
6	1.414	1.369	0.045
7	1.412	1.371	0.041
8	1.411	1.373	0.037
9	1.410	1.375	0.034
10	1.409	1.376	0.032
11	1.408	1.377	0.030
12	1.407	1.378	0.029
—	—	—	—
22	1.402	1.384	0.017

The values of V_0 calculated from the experimentally determined absorption maxima of a number of polyenes*** have been collected in Fig. 1, which shows the relationship between V_0 and the number of conjugated double bonds. It is found that the values of V_0 distribute in a narrow range hyperbolically with the increasing number of the conjugated double bonds.

Based on the values ΔR obtained in Table I and the values of V_0 estimated from Fig. 1, an empirical equation for the ΔR-relation is derived as follows:

$$V_0=3-3\left(1-\frac{\Delta R}{0.21}\right)^5 \quad (4)$$

Fig. 2 illustrates the value of V_0 as a function of ΔR.

In practice, the small value of V_0 is useful for the following discussion, because the value of V_0 is smaller than one electron volt in the dye-metal chelate. Therefore, Eq. 4 can be reduced to

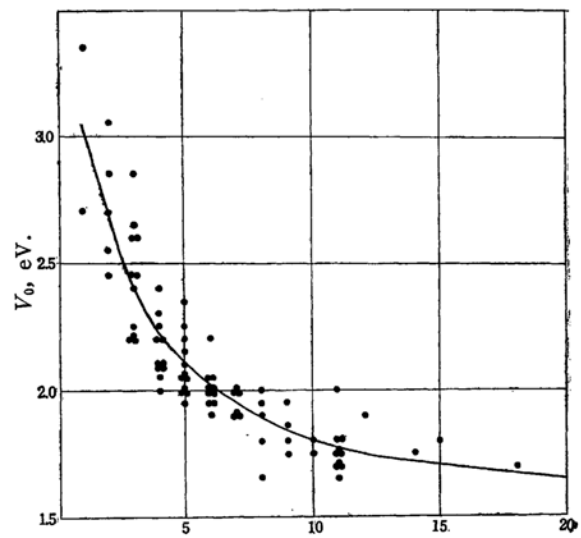


Fig. 1. Relation between V_0 and the number of conjugated double bond.

* This approximation is not strictly correct, but no objection is found in the following consideration, because the corresponding bond length in both structures strictly equal, namely, C_1-C_2, C_2-C_3, C_3-C_4,.....equal to $C_{1'}$-$C_{2'}$, $C_{2'}$-$C_{3'}$, $C_{3'}$-$C_{4'}$,....., respectively.

** The value of bond length for the "single" bond is underestimated, because the calculation used here includes no self-consistent treatment, whereas that of "double" bond is considered to be practically equal to the true value.

*** The absorption maxima were taken from the follwing: A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold Publishers, Ltd., London (1954); Y. Urushibara, "Organic Chemistry II (Yûkī Kagaku)", Kyôritsu Shuppan, Tokyo (1955).

8) C. A. Coulson, *Proc. Roy. Soc.*, **A169**, 413 (1939).

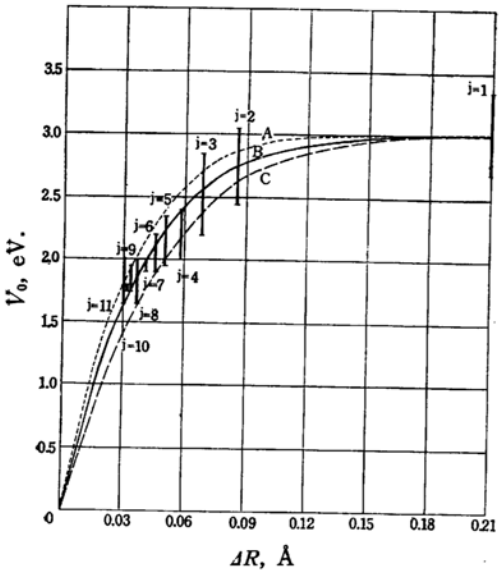


Fig. 2. Relation between V_0 and ΔR.
Curve A: $V_0=3-3(1-\Delta R/0.21)^6$
Curve B: $V_0=3-3(1-\Delta R/0.21)^5$
Curve C: $V_0=3-3(1-\Delta R/0.21)^4$

$$V_0 \simeq 71.4\Delta R - 680\Delta R^2 \qquad (5)$$

Deviation from Eq. 4 is 5%, at $\Delta R<0.03$Å, $V_0<1.8$ eV.,

or $$\Delta R \simeq \frac{V_0}{71.4}\left(1+\frac{680}{71.4^2}\cdot V_0\right) \qquad (6)$$

The Relation between V_0 and the Ionic Character of the Chelating Bond.—As is well known, a bond length, R, is expressed as follows:

$$R=R_1-(R_1-R_2)\frac{3x}{2x+1} \qquad (7)$$

where R_1 is the C–C bond length of pure single bond of ethane, R_2 is that of pure double bond of ethylene and $(1+x)$ is the bond order of the C–C bond in question based on the valence bond theory[9]. For instance, x should be expected to be 0.5 when ΔR is zero.

Suppose that $(1+x)$ represents the bond order of the "double" bond, the bond length, R'', is

$$R''=R_1-(R_1-R_2)\frac{3x}{2x+1}, \quad x>0.5 \qquad (8)$$

Similarly, the bond length corresponding to "single bond", R', is

$$R'=R_1-(R_1-R_2)\frac{3(1-x)}{3-2x} \qquad (9)$$

Then,

$$\Delta R=3(R_1-R_2)\frac{2x-1}{4-(2x-1)^2} \qquad (10)$$

substituting numerical data for R_1 and R_2 in Eq. 10, it is seen that

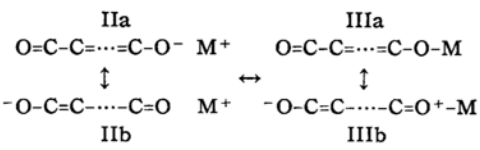
$$\Delta R=0.63\frac{2x-1}{4-(2x-1)^2}$$
$$(R_1: 1.54\text{Å}, R_2: 1.32\text{ Å}) \qquad (11)$$

By rewriting this expression it is seen that

$$x=\frac{1}{2}+\frac{2}{0.63}\Delta R-\frac{8}{0.63^3}\Delta R^3+\frac{64}{0.63^5}\Delta R^5-\cdots \qquad (12)$$

$$x\simeq\frac{1}{2}+\frac{2}{0.63}\Delta R, \qquad \Delta R<0.16\text{ Å} \qquad (12')$$

On the other hand, the value of x may be connected with the ionic character of the bond between the metal and the donor atom of the dye as follows:



In the four formulae, IIa and IIb represent two limiting structure of the metal-dye compound combined with a pure ionic bond, whereas IIIa and IIIb represent two limiting structures of compound combined with a pure covalent bond.

When the metal-donor bond has a pure covalency, the conjugated system is considered to be similar to that of polyene ($V_0=V_{0n}$, $\Delta R=\Delta R_n$, and $x=x_n$) which has the same number, N, of conjugated π-electron, whereas it becomes equal to that of symmetrical polymethine ($\Delta V_0=0$, $\Delta R=0$, $x=0.5$) when the bond is pure ionic.

On the whole, therefore, each of two structures, II and III, contributes to the normal state of the dye-metal compound, in proportion to the ionic character and covalent character, respectively. The mean bond order for "double" bonds of the dye-metal chelate, $1+x$, will be expressed as follows:

$$1+x=(1-i)(1+x_n)+1.5i \qquad (13)$$

where i is the ionic character. The value of x_n, the mean bond order of the polyene, is obtained from Table 1, Eq. 9 or 10, and the mean bond length $\overline{R'}$ or $\overline{R''}$ of the polyene, which possesses the same number of conjugated π-electron as the system. Based on Eqs. 6, 12′ and 13, the relation between i and V_0 can be derived as follows:

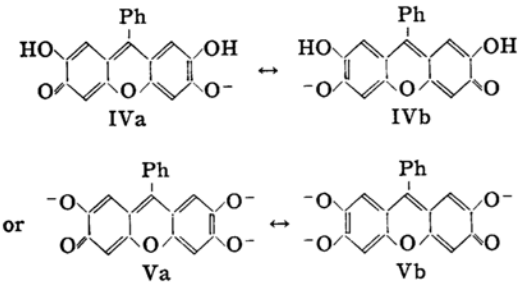
9) L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, N. Y. (1939).

$$1-i=(0.044\,V_0+0.006\,V_0^2)/(x_n-0.5) \quad (14)$$

The absorption maximum of the dye-metal complex is also connected with the ionic character of the dye-metal bond through V_0 in Eqs. 1 and 14.

Application to Experimental Results

It is necessary to know the conjugated system responsible for the absorption maximum of the dye anion to calculate the length of the conjugated chain, L, based on the number of π-electrons in the system. The phenylfluorone anion is considered to be resonating between IVa and IVb or Va and Vb, each of which makes the same contribution to the normal state of the anion, because of its symmetrical structure.

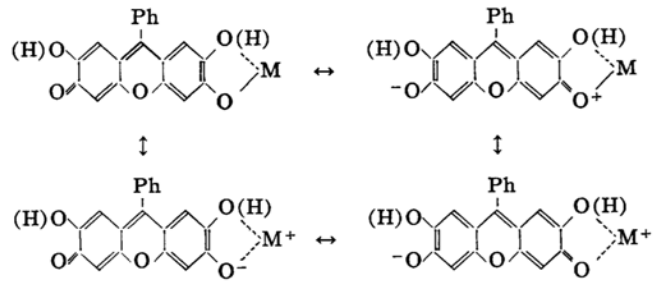


In the present study, L was calculated from the observed wavelength of the absorption maximum of the phenylfluorone anion ($N=12$, and $V_0=0$ based on the following equation,

$$\lambda_{max}=\frac{8mc}{h}\cdot\frac{L^2}{N+1} \quad (1')$$

and this value was used in calculating the value of V_0 for the metal chelates.

The possible structures of phenylfluorone metal chelate**** are



The wavelength of absorption maxima of the 2,3,7-trihydroxy-9-phenylfluorone chelates were shown in Table II together with other properties.

As is found in Table II, the shift of the absorption maximum is rather independent of the ionic radii of metals. This suggests that the electrostatic effect on the shift is not predominant in this case.

In the previous work[5] the author showed empirically that V_0 of each phenylfluoronate increased with the decrease in the ionic character estimated from the difference of electronegativity between metal and oxygen atoms. The value of the ionic character obtained through the process

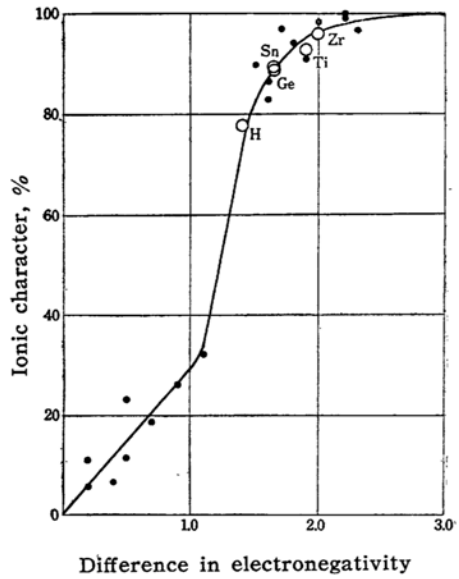


Fig. 3[10]. Relation between electronegativity difference and ionic character in the chelating bond.
○ Data obtained from metal phenylfluoronate.
● Values obtained from nuclear quadrupole coupling data by Dailey and Townes.

**** The infrared spectrum data of germanium phenylfluoronate support this structure: M. Shima, *J. Chem. Soc. Japan, Pure Chem. Soc.* (*Nippon Kagaku Zasshi*), **79**, 1049 (1958).

TABLE II

Metal	λ_{max} Å	Reagent/Metal	V_0 (eV.)	i	Ionic radius[a] Å	Electronegativity[b]
H	4680	—	0.473	0.77_7	—	2.1
Ge	5080	2 : 1	0.246	0.88_8	0.53～0.52	1.8～1.9
Si	5100	—	0.236	0.89_2	0.71	1.8～1.9
Ti	5250	2 : 1	0.160	0.92_3	0.68	1.6
Zr	5400	4 : 1	0.0891	0.95_8	0.80～0.828	1.5
Ionic	5600	—	0	1.00_0	—	—

a) L. Pauling, *J. Am. Chem. Soc.*, **49**, 765 (1927); E. Kordes, *Z. physik. Chem.*, **B48**, 91 (1941).
b) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

mentioned above is shown in Fig. 3, together with the results obtained from the nuclear quadrupole coupling data by Dailey and Townes[11], for comparison.

The agreement between two independent results is too close to be accidental. This will be due to the fact that the metal-dye chelate has the structure in which the electrostatic effect by metal is negligibly small, and the effect of the perturbation caused by metal is predominant.

Some phenylfluorone derivatives which possess some substituent in the phenyl group react with metals, and the relationship among the absorption maxima of the metal chelates is similar to that in the phenylfluorone metal chelates[12].

Experimental

Metal solutions were prepared from metal oxides (germanium, titanium), chloride (tin), or oxychloride (zirconium), and standardized gravimetrically. These stock solutions contain sufficient amounts of hydrochloric acid to prevent the hydrolysis of metals, being free from foreign ions. A working solution was prepared by dilution of an aliquot of each stock solution with water or dilute hydrochloric acid.

Phenylfluorone solution was prepared by dissolving 0.120 g. of phenylfluorone in 150 ml. of ethanol containing 1 ml. of 5.0 N hydrochloric acid, and the resulting solution was diluted to 200 ml. with ethanol.

Absorbance values of the sample and the blank solution were measured with a Beckman Model DU spectrophotometer, using 1 cm. glass cells. Distilled water or blank solution was used as a reference solution. The absorption maxima show practically no variation with the change in the acidity of the solution or the amount of the dyes and metals in solution[14].

Summary

The absorption spectra of phenylfluorone-fourth group metal chelates were investigated by the acid of Kuhn's free electron gas model method. If the chelating bond formation does not cause an essential change in the π-electron system of the dye molecule, in the more ionic chelating bond, the absorption maximum of the chelate must be closer to the maximum wavelength of the dye anion. Based on the conception in valence-bond method and ionic-covalent resonance, it was theoretically and experimentaly shown that there was a certain relationship between the absorption maximum wavelength of the chelate and the ionicity of the chelating bond. (The ionicity of the bond was estimated from the difference of electronegativity between the metal and the terminal oxygen atom). The results obtained here for the relationship between the ionicity and the electronegativity difference show too close an agreement with the results obtained from the nuclear quadrupole coupling data by Dailey and Townes.

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10) As the value of electronegativity, Dailey and Townes adopted the value reported by Huggins[13], but the author adopted here the value reported by Pritchard and Skinner as "best value" (see Table II). The value of electronegativity for the quadrupole spectrum data in Fig. 3 was rearranged in accordance with Pritchard and Skinner's scale.
11) B. P. Dailey and C. H. Townes, *J. Chem. Phys.*, **23**, 118 (1955).
12) H. Sano, This Bulletin, **30**, 672 (1957); **31**, 974 (1958).
13) M. J. Huggins, *J. Am. Chem. Soc.* **75**, 4123 (1953).
14) For other detailed procedures and experimental descriptions, see previous work of the present author[5].