*Studies of the Absorption Spectra of Azo Dyes and Their Metal-complexes. VII. The Absorption Spectra of the Metal-complexes Derived from Phenolazo-α- and Phenolazo-β-naphthols**1

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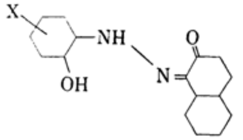
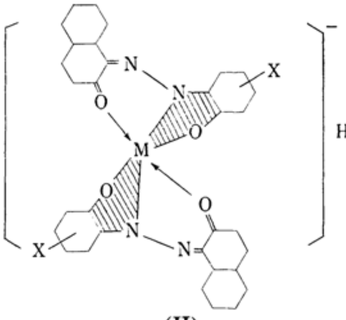
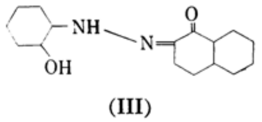
The relations between the spectral variation caused by the 2:1-metal-complex formation and the nature of the metal-ligand linkages have been investigated with respect to phenolazo-β-naphthols and phenolazo-α-naphthols.



(I)



(II)



(III)

(X : Substituent)

The derivatives of I and III in 95% methanol containing 0.1 g. of acetic acid per liter*2 exist almost exclusively in the hydrazone form, and their phenolic hydroxyls are fixed in an undissociated state.1) Most of these derivatives have weak shoulders near 400~420 mμ, shoulders which are due to the small quantity of the azo tautomer in the azo-quinonehydrazone equilibrium.2)

The 2:1-chromium(III)- and cobalt(III)-complexes of the derivatives of I and III, which have an octahedral conformation around the central metal atom,3) are considered to have the bond type as in II, as was pointed out in Parts III and IV of this study. All the complexes in this study have been purified by column chromatographic separation and by successive reprecipitation.

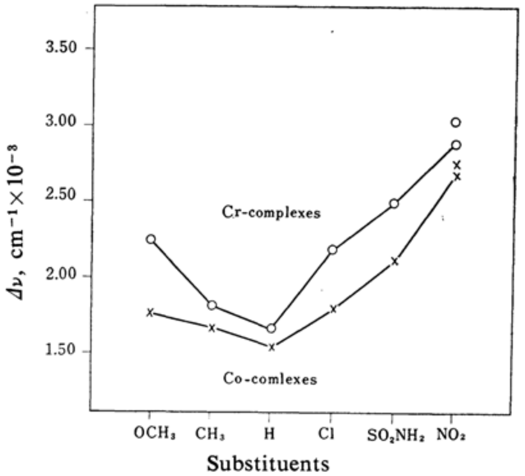


Fig. 1. Relation between the substituents and the shifts of the visible absorption bands with complex-formation ($\Delta\nu$); Single marks, 4-NO_2 substituted derivatives. Full lines, 5-substituted derivatives

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[*1] Parts I-V, This Bulletin, **36**, 487, 492, 500, 506, 512 (1963).

[*2] Such a medium-containing acid has been used to prevent the dissociation of the phenolic hydroxyl.

1) Y. Yagi, Part VI of this study This Bulletin, **37**, 1875 (1964).

2) K. Auwers et. al. *Ann.*, **378**, 210 (1911); **487**, 79 (1931); A. Burawoy et. al. ibid., **503**, 180 (1933); **504**, 71 (1933); **509**, 60 (1934); A. Burawoy et. al., *J. Chem. Soc.*, **1953**, 1443; **1952**, 3734.

3) P. Pfeiffer and S. Saure, *Ber.*, **74**, 935 (1941).

TABLE I. VISIBLE ABSORPTION SPECTRA OF THE DERIVATIVES OF I AND THEIR METAL-COMPLEXES

	Absorption bands, λ_{max}, mμ ($\varepsilon_{max}\times10^{-4}$)		
Derivative	Ligand dyes	Chromium-complexes	Cobalt-complexes
5-OCH_3	521.4 (1.88), 389.8*(0.50)	654.6*(1.51), 590.8 (2.49), 476.3*(1.11)	574.3, 535.6*
5-CH_3	506.8 (2.15)	618.5*(1.51), 558.0 (2.63), 464.4 (1.36)	553.7 (2.79), 515.0*(2.44), 481.0*(1.76)
H	533.2*(1.75), 503.2 (2.06), 397.8*(0.72)	610.5*(1.49), 548.9 (2.52), 461.5*(1.45)	545.5 (2.74), 514.9 (2.48), 474.5*(1.80)
5-Cl	516.3 (2.08), 403.5*(0.66)	624.0*(1.35), 582.0 (2.18), 473.7*(1.13)	569.0 (2.58), 528.9*(2.24)
5-SO_2NH_2	531.0*(1.74), 501.9 (2.05), 405.0*(0.68)	618.0*(1.56), 573.8 (2.19), 456.5*(1.35)	561.4 (2.64), 522.9*(2.26), 484.6*(1.80)
5-NO_2	496.1 (2.14), 380.6*(0.72)	633.5*(1.64), 579.2 (2.04), 481.4*(1.49)	572.5 (2.61), 532.9*(2.19), 488.5*(1.78)
4-NO_2	512.9 (2.86)	662.3*(2.29), 606.8 (2.88), 500.9*(1.69)	596.0 (3.51), 555.6*(2.98)

The solvent used is 95% methanol containing 0.1 g. of acetic acid per liter.

* Inflection.

Owing to the slight solubility of the cobalt-complex of 5-OCH_3 derivative, the measurement has been made qualitatively.

TABLE II. ELECTRONIC ABSORPTION SPECTRA OF DERIVATIVES OF III AND THEIR METAL-COMPLEXES

Derivative	Metal	Absorption bands, λ_{max}, mμ ($\varepsilon_{max}\times10^{-4}$)					
5-CH_3	None	510.8*(1.70)	523.9 (2.04)	386.0 (0.67)	303.6 (1.50)	245.6*(1.56)	
	Cr		566.1 (2.79)	324.3 (3.33)	273.0*(2.67)	233.5 (5.71)	
	Co		559.8 (—)	519.1*(—)	313.0 (—)	244.8 (—)	
H	None	550.7*(1.67)	515.5 (2.05)	380.0 (0.80)	301.9 (1.52)	244.2*(1.58)	
	Cr	614.0*(1.55)	557.2 (2.44)	322.0 (2.88)	269.0*(2.51)	232.3 (4.94)	
	Co		552.3 (—)	515.0*(—)	310.7 (—)	241.7 (—)	
5-NO_2	None		506.1 (2.29)	368.5 (1.19)	291.9 (2.45)	241.*0(1.63)	
	Cr	639.2*(1.51)	565.5 (2.38)	410.0*(1.93)	330.5 (3.91)	265.5*(2.55)	233.3 (4.03)
	Co		551.1 (2.89)	475.0*(2.19)	395.5*(2.14)	311.5 (4.86)	251.7*(4.35)

The main bands in the visible region are shown in the second column.

As to the chromium(III)- and the cobalt(III)-complexes in the same solvent system as above, the visible absorption bands of the ligands undergo marked bathochromic displacements, resulting in very broad and depressed bands. Generally, the molar extinction coefficients of the complexes alter in the Cr<Co manner, and the half-value widths, in the Co<Cr manner. For instance, the visible absorption band of the chromium(III)-complex (the cobalt(III)-complexes in parenthesis) of (II, X=H) is: $\lambda_{max}=548.9(545.5)$ mμ, $\varepsilon=2.52(2.74)\times10^4$, and the half-value width, $l=6.08(4.49)\times10^3$ cm^{-1}. It is of further interest that there is an inflection at a longer or shorter wavelength side of the main visible band in the spectra of the chromium(III)- or the cobalt(III)-complexes respectively. These are not due to the polarization of the M–O (M, tervalent metal; O, phenolic oxygen) bond by a negative substituent, as was pointed out in Part V, because they show no change in relative

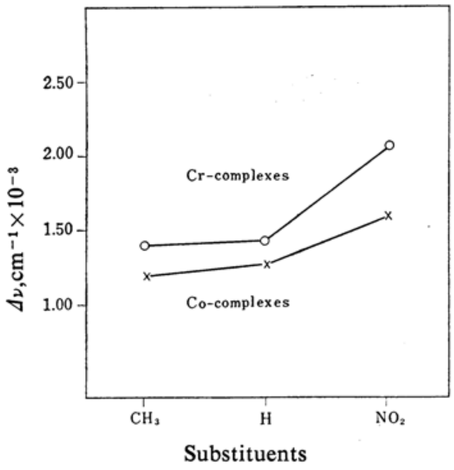

Fig. 2. Relation between the substituents and the shifts of the visible absorption bands with complex-formation; the substituents are on the 5-position of the phenolic nuclei.

intensity and/or in location as a result of the polarity change of the solvent, and because they also exist in the spectra of the complexes with no nitro group. Their origin is, at present, not known.

The bathochromic shifts of the visible absorption bands of the derivatives of I and III with the complex-formation ($\Delta\nu$, cm^{-1}: differences of absorption maxima between the ligand and the corresponding complex) are shown in Figs. 1 and 2. The substituents at abscissa are conveniently arranged in the generally accepted order[4] of electronegativity at regular intervals.

The bathochromic shifts of the bands with the complex-formation may be ascribed mainly to two factors;[5] (i) the polarity of the M–O (O, phenolic oxygen) bond; i. e., any alteration of the electronic configuration, which polarizes the bond, causes a red-shift[6] of the visible absorption band, and (ii) the perturbation of the π-electron system by the dπ-pπ interaction between the hydrazone group and the central metal, i. e., the appearance of the resonance stabilized system involving the aromatic nuclei and the chelate ring system.

In the series of complexes II if factor i is markedly dominant, as was shown in the series of complexes in Parts III–V, the 5-OCH_3 derivatives do not have such bathochromic shifts as those of the 5-Cl derivative, as is shown in Fig. 1. It is reasonable to consider that factor ii contributes much to these shifts of bands, since the ligand molecule of II has two powerful aromatic nuclei connected with the hydrazone bridge. Therefore, in the case of the complex the phenolic nucleus of which is substituted by a group of powerful resonance effects, the resonating system involving the d-electrons of the central metal is stabilized, resulting in an increase in the polarizability of the π-electron system and, hence, the bathochromic displacement of the visible absorption band. The visible absorption bands of the complexes, substituted by a nitro group in the 4-position, i. e., in the position para to the hydrazone group, are located at longer wavelength positions than those of the corresponding 5-substituted derivatives. This is presumably because of an intensified effect of factor ii.

With regard to the complexes of III in Fig. 2, however, factors i and ii are considered to be almost equally operative. The relationship between the $\Delta\nu$ and the electronegativities of the substituents if factor i should dominate will be shown in a forthcoming paper.[7]

It has previously been concluded in the series of phenolazoacetoacetamides that the chromium(III)-complex has the ionic M–O (O, phenolic oxygen) bond, whereas the cobalt(III)-complex has the covalent bond. In the II and III series, however, such a peculiarity would be relatively small, since the difference in $\Delta\nu$ between the chromium(III)- and the cobalt(III)-complex is relatively small (that is, the visible absorption positions of both complexes are close together).

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[5] Y. Yagi, This Bulletin, **36**, 506 (1963).

[6] A. Burawoy and E. Spinner, *J. Chem. Soc.*, **1955**, 2557.

[7] Y. Yagi, This Bulletin, **37**, 1881 (1964).