Studies of the Absorption Spectra of Azo Dyes and their Metal-complexes. IV. The Effects of Substituents on the Absorption Spectra of Chromium(III)- and Cobalt(III)-complexes of Phenolazoacetoacetanilides*[1]

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Studies of the relationships between substituents and electronic absorption spectra or stabilities have been reported1) on metal-complex azo-dyes containing functional groups ortho and ortho' to the azo linkage. Little is known, however, with respect to the 2 : 1-metal-complex monoazo dyes, for example, the chromium(III)- or cobalt(III)-complexes of phenolazoacetoacetamides*[2].

Since the chelate ring involving a phenolic oxygen, a central metal, and a hydrazone nitrogen contributes much toward the metal-ligand linkage, as has been shown in Part III2), the influence of substituents in the phenolic nucleus upon the electronic absorption spectra will be characteristic of the central metal used. Therefore, the author has investigated the metal-complexes*[3] of substituted phenolazoacetoacetanilides.

Results and Discussion

The Effects of Substituents in the Phenolic Nuclei upon the Electronic Absorption Spectra of Metallized Phenolazoacetoacetanilides.—It has been reported in this series of studies3)

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*[1] Presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

*[2] The compounds in this paper have hydrazone forms but are, for convenience, named as azo forms. α-(2-Hydroxyphenylazo)-acetoacetanilide, for example, is abbreviated as phenolazoacetoacetanilide.

1) F. A. Snavely et al., *J. Soc. Dyers Colourists*, **73**, 491 (1957); Z. Yoshida et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **60**, 1413 (1957).

*[3] The term "metal-complex" in this paper denotes the 2 : 1-metal-complex.

2) Part III, This Bulletin **36**, 500 (1963).

3) Part I, II and III, This Bulletin, **36**, 487, 492, 500 (1963).

that the electronic absorption spectra of phenolazoacetoacetanilides exhibit four groups of conjugation bands (K bands)[4] and that these bands undergo characteristic changes with complex-formation. The A ligand-band arises from a transition involving electron migration along the whole conjugate system of the ligand. The B ligand-band originates in a conjugative electronic transition between the acetyl carbonyl and the hydrazone group, the C ligand-band in a conjugative electronic transition between the phenolic nucleus and the hydrazone group and, the D ligand-band, in a conjugative electronic transition between the carboxylic acid anilide group and the hydrazone group.

Since the degree of modification of the bands expected for the partial chromophores is regarded as an indication of the extent of the electronic interaction therein[5], an investigation of the four characteristic bands of the metal-complexes will reveal useful information about the metal-ligand linkage.

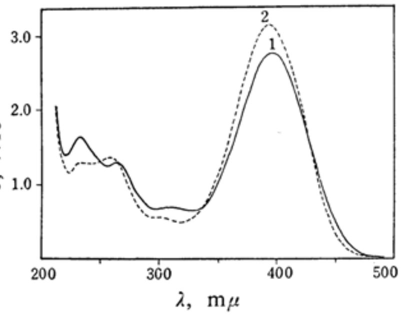


Fig. 1. Absorption spectra of 5-chloro-2-hydroxyphenylazoacetoacetanilide (1) and 2-hydroxy-4-sulfamoylphenylazoacetoacetanilide (2) in the standard solvent.

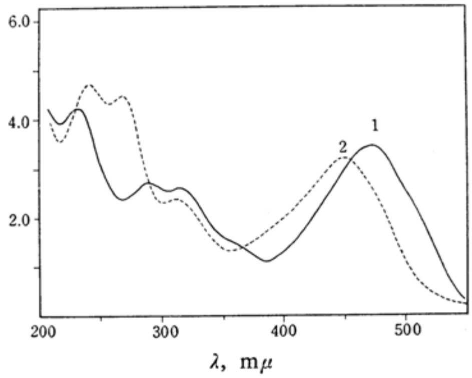


Fig. 2. Absorption spectra of chromium-(1) and cobalt-(2) complexes of 5-chloro-2-hydroxyphenylazoacetoacetanilide in the standard solvent.

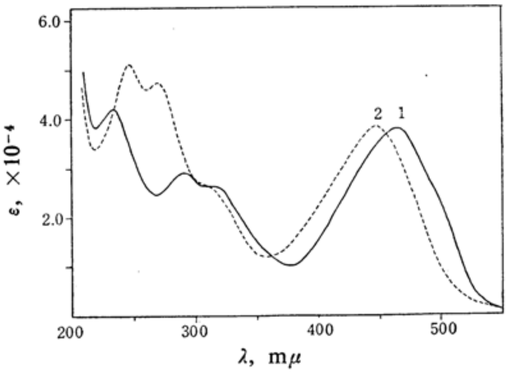
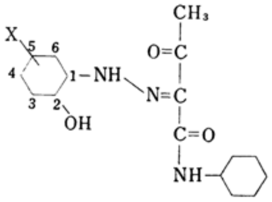
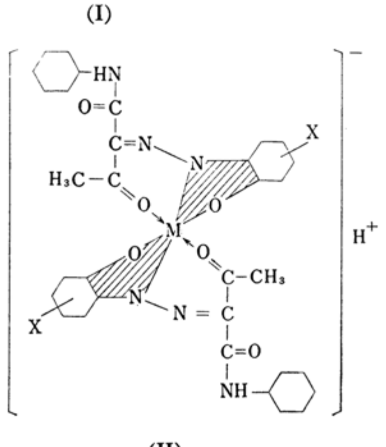


Fig. 3. Absorption spectra of chromium-(1) and cobalt-(2) complexes of 2-hydroxy-4-sulfamoylphenylazoacetoacetanilide in the standard solvent.

The electronic absorption spectra of the chromium(III)- and cobalt(III)-complexes II derived from phenolazoacetoacetanilides I in the standard solvent[*4] are illustrated in Table I (Figs. 1—3). This table shows the shift of each ligand-band with the complex-formation, i. e., $\Delta\nu$ (in cm^{-1}) = ($\nu_{\max}$ of a ligand-band) $-$ ($\nu_{\max}$ of the corresponding complex-band). The shifts of the bands vary according to the substituent, as is shown in Fig. 4, in which the substituents at abscissa are conveniently



(I)



(II)

(X, Substituent ; M, Tervalent metal)

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[4] A. Brawoy, *J. Chem. Soc.*, **1937**, 1865; **1939**, 1177; A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy", Edward Arnold Publishers, Ltd., London (1954), p. 111.

[5] E. A. Braude, *J. Chem. Soc.*, **1945**, 490.

[*4] "Standard solvent" denotes aqueous 80% methanol containing 0.1 g. of acetic acid per liter.

TABLE I. ELECTRONIC ABSORPTION SPECTRA OF THE METAL-COMPLEXES DERIVED FROM PHENOLAZOACETOACETANILIDES IN THE STANDARD SOLVENT

Substituent	Metal	A					B			C			D		
		λ_{max}	ε_{max}	$\Delta\nu_A$	l	δ	λ_{max}	ε_{max}	$\Delta\nu_B$	λ_{max}	ε_{max}	$\Delta\nu_C$	λ_{max}	ε_{max}	$\Delta\nu_D$
5-CH_3	None	401.5	2.72	—	4.75	0.31	317.0	0.64	—	268.0	1.14	—	231.4	1.44	—
	Cr	474.0	3.27	3.81	5.13	0.62	314.0 (368.8*)	2.69 1.61	−0.30	292.5*	2.58	3.12	228.8	4.19	−0.49
	Co	447.2	2.79	2.55	—	—	318.2	2.33	0.12	270.3	3.92	0.31	244.9	3.83	2.39
H	None	396.0	2.81	—	4.70	0.37	279.0*	1.00	—	258.0	1.14	—	234.0	1.36	—
	Cr	466.9	3.23	3.83	5.13	0.69	310.0	2.63	3.58	(292.3*)	2.50	4.55	232.5	3.81	−0.28
	Co	442.5	3.02	2.65	6.01	1.15	315.2	2.38	4.11	269.5	4.13	1.65	241.0	3.93	1.24
5-Cl	None	396.0	2.76	—	4.63	0.31	311.0	0.68	—	262.5	1.29	—	231.5	1.64	—
	Cr	473.3	3.43	4.12	4.77	0.55	315.0 (365.0*)	2.59 1.39	0.40	289.5	2.72	3.56	230.4	4.28	−0.20
	Co	450.2	3.19	3.04	5.85	1.10	313.0	2.36	0.20	270.3	4.49	1.10	242.7	4.72	2.00
5-SO_2NH_2	None	389.5	2.81	—	4.59	0.36	303.0*	0.63	—	258.0	1.74	—	232.5	1.84	—
	Cr	460.4	3.78	3.95	4.63	0.59	319.6*	2.61	1.71	291.9	3.80	4.50	234.3	4.69	0.33
	Co	440.0	3.79	2.94	4.64	0.69	315.5*	2.58	1.30	272.5	5.95	2.06	249.0	5.57	2.85
5-NO_2	None	391.0	2.72	—	6.81	1.43	303.0	1.38	—	246.0	1.56	—	231.0	1.66	—
	Cr	463.0	4.50	3.98	5.95	1.33	—	—	1.30	315.5	3.89	8.95	241.7	3.27	1.92
	Co	449.1 401.6*	4.66 3.55	3.31	6.35	1.47	309.3	3.68	0.67	263.5	4.44	2.70	(251.0*)	4.18	3.45
4-SO_2NH_2	None	394.4	3.16	—	4.44	0.28	305.6*	0.54	—	258.3	1.37	—	231.9*	1.32	—
	Cr	463.8	3.77	3.80	4.68	0.52	322.2*	2.54	1.68	290.0	2.89	4.23	233.8	4.19	0.35
	Co	448.3	3.81	3.05	4.86	0.73	317.6*	2.48	1.23	269.3	4.74	1.58	246.6	5.11	2.57
4-NO_2	None	415.5	3.94	—	3.88	0.24	325.0	0.79	—	259.8*	1.21	—	238.4	1.46	—
	Cr	490.5	4.70	3.68	4.13	0.33	364.5	2.06	3.34	284.8*	2.63	3.38	255.0	3.14	2.72
	Co	481.2	4.23	3.29	4.86	0.53	303.7	2.83	−2.15	267.5	4.94	1.11	242.7*	4.08	0.74
3-NO_2	None	406.5	1.87	—	—	—	355.5*	1.53	—	262.7	1.64	—	234.0	1.60	—
	Cr	479.0	4.06	3.72	4.42	0.49	—	—	−5.23	299.8	3.21	4.71	237.3*	3.61	0.59
	Co	471.5	3.88	3.39	4.39	0.46	(307.0*)	3.22	−4.44	289.4*	3.76	3.52	249.9	4.86	2.71

N. B. a) Absorotion maxima (λ_{max}) in mμ, molar extinction coefficients (ε_{max}) in 10^{-4}, red-shifts of the ligand-bands with complex-formation ($\Delta\nu$) in $10^{-3}\times cm^{-1}$, half-value widths (l) and inclination parameters (δ) of the A bands in $10^{-3}\times cm^{-1}$.

b) * Inflection.

c) Absorption maximum in parenthesis denotes an indistinct location.

d) In the chromium-complexes of the 3-nitro and 5-nitro derivatives, the C band is superposed by the B band.

e) Inflections near the four main bands are shown under the respective main band.

arranged in the generally accepted order[6] of electronegativity at regular intervals.

Cobalt(III)-complexes.—Band-shifts with substitution are the most notable in the C bands. The degree of the shifts ($\Delta\nu_C$ in cm^{-1}) with complex-formation varies according to the substituent, as is shown in Fig. 4b. Generally an electronegative substituent in para to the M–O (M, tervalent metal; O, phenolic oxygen) bond increases the red-shift of the C band in the chromium(III)- and the cobalt(III)-complexes.

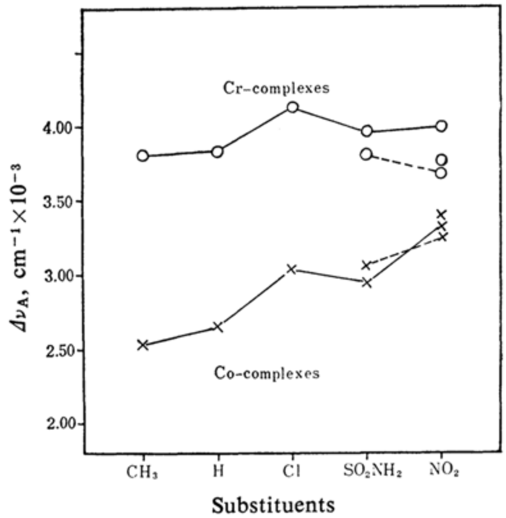

Fig. 4a. Relation between the substituents and the shifts of the A ligand-bands with complex-formation ($\Delta\nu_A$) (full lines, 5-substituted derivatives; dotted lines, 4-substituted derivatives; single marks, 3-substituted derivatives.)

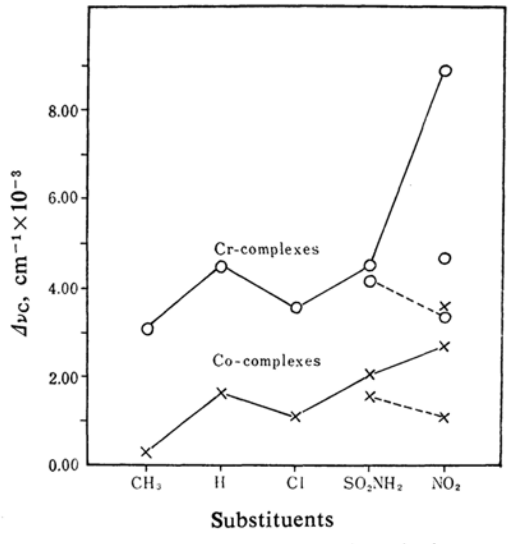

Fig. 4b. Relation between the substituents and the shifts of the C ligand-bands with complex-formation ($\Delta\nu_C$).

In Part II it was noticed how, in the spectra of phenolazoacetoacetamides, the C ligand bands are sensitive to any alteration of the electronic configuration of the system. In the metal-complexes also, the values of $\Delta\nu_C$ are considered to indicate the polarity of the M–O (O, phenolic oxygen) bond. The relatively small $\Delta\nu_C$ value of the cobalt(III)-complexes as compared with those of the chromium(III)-complexes indicate the covalent character of the Co–O (O, phenolic oxygen) bond.

Since the chromium(III)- and the cobalt(III)-complexes in this study are formed by d^2sp^3 hybridized orbitals and since their $d\pi$-orbitals[7a] have stable electronic configurations[2,7b], the $d\pi$-$p\pi$ bondings in both the complexes are considered to contribute equally to the ligand-metal linkage. A five-membered chelate ring (the shaded portions in II) is stabilized in the cobalt(III)-complexes to facilitate the transition expected for a partial chromophore involving the phenolic nucleus, i. e., to increase the intensities of the C bands. Both the half-value widths (l) and the inclination parameters (δ) of the cobalt(III)-complexes are somewhat larger than those of the corresponding chromium(III)-complex, indicating that the stable chelate ring emphasizes the perturbation of the π-electron system.

The bathochromic shift of the A ligand-bands with the complex-formation may be ascribed mainly to two factors; (i) the polarity of the M–O (O, phenolic oxygen) bond, and (ii) the perturbation of the π-electron system by the $d\pi$-$p\pi$ interaction. Generally, influences increasing the polarity of the absorbing system displace the K band to longer wavelengths[8]. Therefore, a substituent increasing the polarity of the above mentioned M–O bond displaces the A band as well as the C band towards longer wavelengths, as is shown in Fig. 4 (i. e., factor i). That is, the more electronegative the substitutent in the 5-position, the larger the values of $\Delta\lambda_A$ and $\Delta\nu_C$. In the metal-complexes, which have larger $\Delta\lambda_A$ and $\Delta\nu_C$ values, the A bands are generally higher in intensity and smaller in l and δ (except those of the 5-nitro derivative). This suggests shat the contribution of the five-membered chelate ring slightly decreases because of the polarity increase of the M–O bond.

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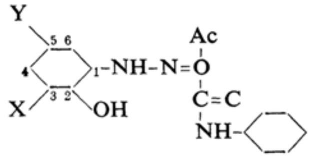
[6] L. P. Hammett, *Chem. Revs.*, **17**, 125 (1935); H. H. Jaffé, ibid., **53**, 191 (1953); H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

[7] a) D. P. Craig et at., *J. Chem. Soc.*, **1954**, 332.; b) "The Chemistry of the Coordination Compounds", Ed. by J. C. Bailar, Jr., Reinhold Publishing Corp., New York (1956), p. 185.

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

TABLE II. ABSORPTION SPECTRA OF THE METAL-COMPLEXES DERIVED FROM 3, 5-DISUBSTITUTED PHENOLAZOACETOACETANILIDES



Substituent		Metal	Band A				
3-X	5-Y		λ_{max}	ε_{max}	$\Delta\nu_A$	l	δ
NO_2	CH_3	None	410.0	1.81	—	—	—
		Cr	485.7	4.03	3.80	4.18	0.35
		Co	483.0	3.54	3.68	4.16	0.32
NO_2	Cl	None	410.0	1.96	—	—	—
		Cr	487.7	4.19	3.88	4.05	0.29
		Co	484.2	3.95	3.73	3.93	0.21
NO_2	NO_2	None	410.0 471.0*	2.11 1.00	—	—	—
		Cr	468.3	3.18	3.03	6.83	1.58
		Co	461.8	4.35	2.73	5.00	1.95
Cl	NO_2	None	382.0	2.76	—	6.52	1.22
		Cr	461.3	3.63	4.50	—	—
		Co	448.9 412.7*	4.49 3.78	3.90	6.52	1.51

All the spectra were measured in the standard solvent. But those of the ligand-dyes, except the dye ($X=NO_2$, $Y=CH_3$), were determined in aqueous 80% methanol containing 0.002 mol. of hydrochloric acid per liter.

In case of the 4-nitro and 4-sulfamoyl derivatives, the polarization of the M–O bond is not so large as those of the 5-substituted derivatives (Fig. 4b). However, the values of $\Delta\nu_A$ are almost equal to those of the 5-substituted derivatives (Fig. 4a). It is considered that an elongation[9] and a planarity increase[10] of the conjugate system upon the introduction of the substituent in the 4-position, i. e., para to the hydrazone group, result in an enhancement of the $d\pi-p\pi$ bonding (i. e., factor ii).

With regard to the 3-nitro derivative, the nitro-group in the 3-position fairly polarizes the M–O bond, resulting in the increase of both $\Delta\nu_A$ and $\Delta\nu_C$ values.

The relatively large $\Delta\nu_D$ values in the cobalt(III)-complexes indicate that the stable chelate ring emphasizes the planarity of the ligand-molecule to reduce the energy of the transition expected for the partial chromophore involving the amide group.

Since most of the B bands are superposed by the C bands and present themselves as inflections, exact evaluations of them are difficult. However, the intensities of the B bands in the spectra of 3-nitro and 5-nitro derivatives are higher than those of the other derivatives. Such intensity increases agree with the finding, reported in Part II, that the electron-withdrawing group stabilizes the hydrazone structure[3,11], resulting in an enhancement of the conjugation B band.

Chromium(III)-complexes.—In the chromium(III)-complexes, the $\Delta\nu_C$ values are larger than that of the corresponding cobalt(III)-complex. That is, the Cr–O (O, phenolic oxygen) bonds have a highly ionic character. The larger shifts of the A bands as compared with those of the coblt(III)-complexes are mainly to be attributed to the ionic Cr–O bond.

In the series of 5-substituted derivatives, the $\Delta\nu_C$ values in Fig. 4b show that an electronegative group increases the polarity of the Cr–O bond. On the other hand, a variation of $\Delta\nu_A$ in Fig. 4a exhibits a gentler slope than that of the chromium(III)-complexes. Consequently, it is concluded that the influence of the i factor on the A bands is not so effectively operative as in the case of the cobalt(III)-complexes, because the Cr–O bonds originally have a highly ionic character.

In the series of 4-substituted derivatives, both $\Delta\nu_A$ and $\Delta\nu_C$ values are smaller than those of the corresponding 5-substituted derivative.

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[9] H. P. Koch, ibid., **1949**, 408; H. H. Szmant and H. J. Planinsek, *J. Am. Chem. Soc.*, 72, 4042 (1950).

[10] W. R. Brode, "The Roger Adams Symposium", John Wiley & Sons, Inc., New York (1955), p. 29.

[11] A. Burawoy, A. G. Salem and A. R. Thompson, *J. Chem. Soc.*, **1952**, 4793; H. Shingu, *J. Chem. Soc. Japan*, (*Nippon Kwagaku Kwaishi*), **60**, 542 (1939).

It is considered that the substituent in the 4-position, i. e., meta to the M–O bond, scarcely participates in the polarization of the M–O bond (smaller $\Delta\nu_C$) and that the dπ-pπ interaction also is not effectively operative, because the five-membered chelate ring is weaker than that of the 4-substitued cobalt(III)-complex (smaller $\Delta\nu_A$).

A small $\Delta\nu_A$ value in the spectrum of the 3-nitro derivative also is attributed to the same reason.

Further Observation of 3, 5-Disubstituted Derivatives.—The bathochromic displacements of the A bands due to the polarization of the M–O (O, phenolic oxygen) bond are pronounced in the cobalt(III)-complexes. As will seen in the series of 5-substituted derivatives in Table I, the A band of the cobalt(III)-complex approaches that of the corresponding chromium(III)-complex in accordance with the polarization of the Co–O bond.

In Table II are shown the visible absorption bands of the chromium(III)- and cobalt(III)-complexes of 3, 5-disubstituted phenolazoacetoacetanilides. Remarkable proximities of the absorption maxima in the two complexes produced by the introduction of electron-withdrawing groups in the 3- and 5-positions are to be seen. That is, the polarization of the Co–O bonds results in the displacement of the A bands to longer wavelengths.

In Table II, the A bands of those metal-complexes having a nitro group in the 5-position are broader than those of the other derivatives. Moreover, the cobalt(III)-complex of the 3-chloro-5-nitro derivative, as well as of the 5-nitro derivative in Table I, exhibits a weak inflection at a shorter wavelength than that of the A band. An assignment of this band will be made in the next paper.

Experimental

Syntheses and Purifications of Metal-complexes Derived from Phenolazoacetoacetanilides.—*Metal-complexes of Phenolazoacetoacetanilide.*—(*i*) *Chromium(III)-complex.*—The ligand-dye (0.02 mol.) was treated with chromium(III) formate (0.01 mol.) in formamide at 120°C for 12 hr. The reaction mixture was poured into a dilute aqueous solution of hydrochloric acid to yield a precipitate of the complex-acid. This complex-acid was then filtered off, washed with water, and dried in vacuo. Purification was carried out by column-chromatography. The crude complex-acid (200 mg.) was dissolved in 95% ethanol, added to an adsorption-column of activated alumina, and developed with 95% ethanol. A brown zone of the metal-complex was extruded, separated, and eluted with 95% ethanol. The eluted solution was evaporated to dryness under reduced pressure. The residue obtained was dissolved in aqueous ethanol containing sodium hydroxide. The neutralization of the solution with dilute hydrochloric acid at 50°C and the successive addition of sodium chloride to this gave a brown-yellow precipitate. The precipitate was filtered off, washed with water, and dried in vacuo, yielding 140 mg. of the pure chromium(III)-complex.

Found: C, 59.56; H, 4.26; N, 13.09. Calcd. for $C_{32}H_{27}O_6N_6Cr$: C, 59.71; H, 4.23; N, 13.05%.

(ii) Cobalt(III)-complex.—A suspension of the ligand-dye (0.02 mol.) in a dilute aqueous solution of sodium hydroxide was treated at 80°C with cobalt(II) sulfate (0.01 mol.). The sodium-salt of the cobalt-complex crystallized out as fine flakes in the reaction mixture. The reaction mixture was made into a solution by adding ethanol and then acidified (pH 2.40) by the addition of hydrochloric acid. The precipitated complex-acid was filtered off, washed with water, and dried in vacuo. Chromatographic purification of the crude product (200 mg.) was performed in the same manner as with the chromium(III)-complex to yield 150 mg. of a brown-yellow precipitate.

Found: C, 58.86; H, 4.32; N, 12.62. Calcd. for $C_{32}H_{27}O_6N_6Co$: C, 59.08; H, 4.18; N, 12.91%.

Metal-complexes of 2-Hydroxy-5-methylphenylazoacetoacetanilide.—*(i) Chromium(III)-complex.*—The pure chromium-complex was obtained as yellow-brown precipitate.

Found: C, 60.94; H, 4.83; N, 12.49. Calcd. for $C_{34}H_{31}O_6N_6Cr$: C, 60.80; H, 4.65; N, 12.51%.

(ii) Cobalt(III)-complex.—The purified product was in the form of yellow-brown needles.

Found: C, 59.85; H, 4.59; N, 12.25. Calcd. for $C_{34}H_{31}O_6N_6Co$: C, 60.19; H, 4.60; N, 12.38%.

Metal-complexes of the Other Phenolazoacetoacetanilides.—These also wese prepared in the manner described above. Their purities were checked by elemental analysis.

Measurements of the Electronic Absorption Spectra.—The absorption spectra were measured by two recording spectrophotometers, a Beckman model DK-2 and a Shimadzu model RS-27. All the spectra were determined at a concentration of 1.6×10^{-5} M. Beer's law is valid in this dilution. The qualities of the solvents were of spectral grades.

Summary

The electronic absorption spectra of the series of metallized phenolazoacetoacetanilides have been investigated.

The substituent, in the *o*- or *p*- position to the M–O (M, central metal; O, phenolic oxygen) bond, generally alters the polarity of the M–O bond. On the other hand, the substituent, in the *m*-position to the M–O bond, i. e., the *p*-position to the hydrazone group, mainly contributes to the dπ-pπ interaction between the hydrazone group and the central metal atom.

The effects of such substituents upon the shifts of the A bands are more pronounced in the cobalt(III)-complexes than in the chromium(III)-complexes, because the former complexes have the stable five-membered chelate rings

involving the highly covalent Co–O (O, phenolic oxygen) bonds.

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