Studies of the Absorption Spectra of Azo Dyes and their Metal-complexes. III. The Electronic Absorption Spectra of Metal-complexes Derived from Phenolazoacetoacetanilides*[1]

By Yoshiharu YAGI

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Metal-complex dyes, having two molecules of such ligand dyes as *o,o'*-dihydroxymonoazo dyes per atom of chromium(III) or cobalt(III), are recognized to have superior dyeing-properties¹⁾ and are expected to develop progressively. The absorption spectra of such ligand dyes generally undego marked changes by coordination with metal atoms²⁾.

In previous papers³⁾ the author investigated the electronic absorption spectra of phenolazoacetoacetamides*[2] in order to assign the four characteristic groups of bands. With respect to the metal-complexes of these azo compounds, there are many problems deserving of further study; e. g., the cobalt(III)-complexes ordinarily have a higher fastness to light than the chromium(III)-complexes⁴⁾. The author supposed that an investigation of the spectral variations of the four characteristic bands with the complex formation would give useful information about the metal-ligand linkage. This paper deals with the absorption spectra of the metal-complexed phenolazoacetoacetanilides.

Results and Discussion

A General Survey of the Electronic Absorption Spectra of the Metal-containing Phenolazoacetoacetanilides and the Assignments of the Four Groups of Bands.—The structure of 2:1-metal-complexes of phenolazoacetoacetanilides has up to the present been represented as in I⁵⁾. Two molecules of such terdentate ligand-dyes are known to have a octahedral

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

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

1) H. Pfitzner, *Melliand Textilber.*, **35**, 649 (1954); R. Casty, *Textil-Rundschau*, **11**, 328 (1956).

2) H. Zollinger, "Chemie der Azofarbstoffe", Birkhäuser Verlag, Basel (1958), p. 245.

3) Parts I and II, This Bulletin, **36**, 487, 492 (1963).

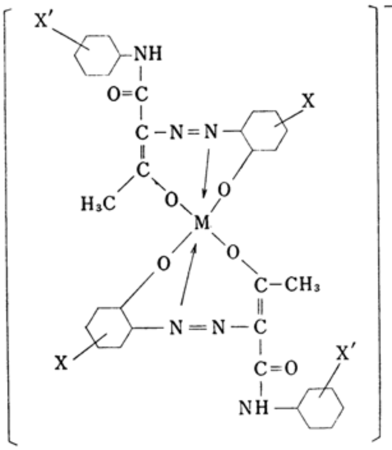
4) K. Venkataraman, *Review of Textile Progress*, **7**, 337 (1955); J. R. Geigy A.-G., Brit. Pat. 736034; E. Koike and Y. Yagi, Japanese Pat. Announced No. 36-8730.

5) H. D. K. Drew et al., *J. Chem. Soc.*, **1939**, 823.

TABLE I. ABSORPTION SPECTRA OF THE CHROMIUM(III)-COMPLEX OF 2-HYDROXY-5-(*N*-ETHYLSULFAMOYL)PHENYLAZOACETOACETANILIDE IN A VARIETY OF SOLVENTS

Solvent	A	B	C	D
Anhydrous methanol	460.8(3.67)	322.5*(2.48)	292.9(3.88)	235.0(4.72)
95% Methanol	461.0(3.64)	322.4*(2.42)	292.5(3.86)	235.2(4.64)
Standard solvent	461.0(3.74)	322.3*(2.51)	292.5(3.99)	235.0(4.81)
Aqueous 0.01N NaOH	455.0(3.53)	316.5*(2.49)	288.4(3.63)	234.0(3.56)

Wavelengths (λ) in mμ; Molar extinction coefficients (ε)$\times 10^{-4}$ in parenthesis.
* Inflection



(I)

X, X′ : Substituents
M : Tervalent metal

conformation around the central metal atom[6] and to form the penetration complex by sp^{3}d^2 hybridization[7]. It is also known[8] that the metal-complex molecule is a monobasic acid.

The electronic absorption spectra of chromium(III)-, cobalt(III)-, iron(III)-, and aluminum-compexes of 2-hydroxy-5-(*N*-ethylsulfamoyl)phenylazoacetoacetanilide (II) in the standard solvent[*3] are shown in Fig. 2. Four groups of bands are generally observed in the visible and ultraviolet region. These bands will hereafter be referred to as A, B, C and D counting from the longer wavelength side. The absorption spectra of the chromium(III)-complex[*4] of II in a variety of solvents are illustrated in Table I. A slight intensity decrease and a small hypsochromic displacement of each band in an aqueous sodium hydroxide solution are probably due to the electrostatic interaction between inorganic ions and solvent molecules around the absorbing system, as was discussed by Klotz[9]. However, the relative positions of the four bands in each solvent are almost invariable. Provided that an anionic charge, which is generated with the ionization of the free complex-acid in a polar solvent, as in an aqueous alkaline solution, is localized in the complex-molecule, there should be appreciable band-shifts in the ultraviolet region, as has been reported in the case of ligand-dyes in Part II. Consequently, the anionic charge is considered to have a non-localized character.

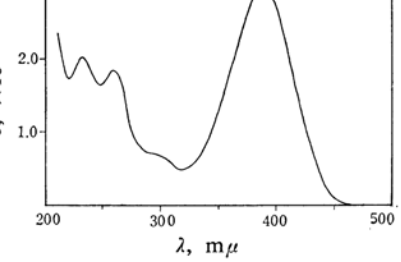


Fig. 1. Absorption spectrum of 2-hydroxy-5-(*N*-ethylsulfamoyl)-phenylazoacetoacetanilide (II) in the standard solvent.

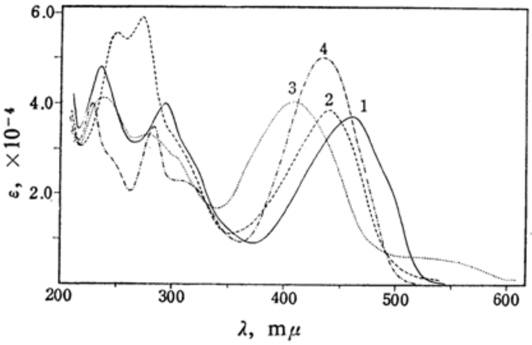


Fig. 2. Absorption spectra of the chromium-(1), cobalt- (2), iron- (3) and aluminum-(4) complexes of II in the standard solvent.

In Part II, the four characteristic groups of bands in the spectra of the ligand-dyes were assigned: the ligand-band A arises from a transition involving electron migration along the whole conjugate system. The ligand-band

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6) Pfeiffer and S. Saure, *Ber.*, **74**, 935 (1941).
7) J. C. Bailar, Jr., and C. F. Callis, *J. Am. Chem. Soc.*, **74**, 6018 (1952).
8) H. Zollinger, *Texti-Rundschau*, **13**, 217 (1958).
[*3] The term "standard solvent" denotes aqueous 80% methanol containing 0.1 g. of acetic acid per liter.
[*4] The term "metal-complex" in this paper denotes the 2 : 1-metal-complex.
9) I. M. Klotz, *Chem. Revs.*, **41**, 373 (1947).

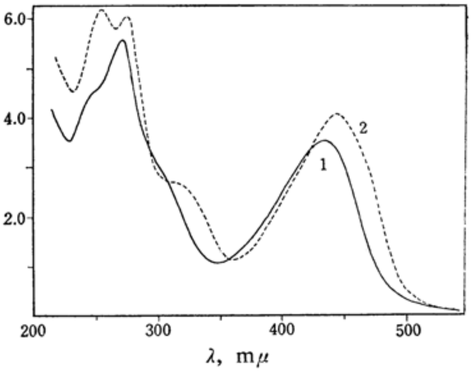
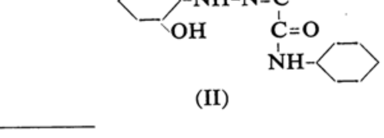


Fig. 3. The cobalt-complexes of 2-hydroxy-5-sulfamoylphenylazoacetoacet-2-chloro-6-methylanilide (1) and 2-hydroxy-5-sulfamoylphenylazoacetoacet-5-chloro-2-methoxyanilide (2) in the standard solvent.

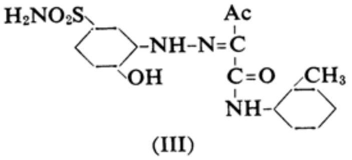
B originates in a conjugative electronic transition between the acetyl carbonyl and the hydrazone group; the ligand-band C, in a conjugative electronic transition between the phenolic nucleus and the hydrazone group, and the ligand-band D, in a conjugative electronic transition between the carboxylic acid anilide group and the hydrazone group.

From the investigation of the wavelength variations and the intensity changes as a result of substitutions, the four groups of bands in the spectra of the metal-complexes are considered to originate in the four bands of the respective ligand-molecule. For example, a marked intensity decrease of the D band in the spectrum of the 2-chloro-6-methyl derivative (Fig. 3) is similar to that of the ligand-dye itself, as has been reported in Part II. The first and the second bands[10] are thought to be submerged in these four bands. That is, these bands are the special bands[11].

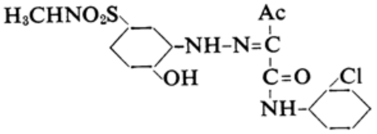
The Electronic Absorption Spectra of the Chromium(III)-, Cobalt(III)-, Iron(III)- and Aluminum-complexes.—Metal-complexes of four ligand-dyes were prepared: II, 2-hydroxy-5-sulfamoylphenylazoacetoacet-2-methylanilide (III), 2-hydroxy-5-(*N*-methylsulfamoyl)-phenylazoacetoacet-2-chloranilide (IV), and 5-chloro-2-hydroxyphenylazoacetoacetanilide (V). The electronic absorption spectra of these azo compounds and their metal-complexes are illustrated in Table II.



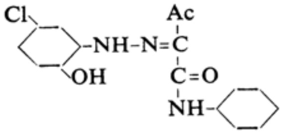
(II)



(III)



(IV)



(V)

All the A ligand-bands show red-shifts with complex-formation in the order: Cr> Co> Al > Fe. The A bands of the aluminum-complexes are sharper in shape and higher in intensity,

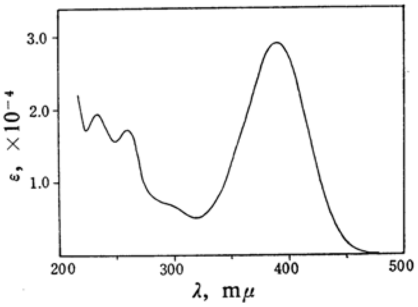


Fig. 4. Absorption spectrum of 2-hydroxy-5-(*N*-methylsulfamoyl) phenylazoacetoacet-2-chloranilide (IV) in the standard solvent.

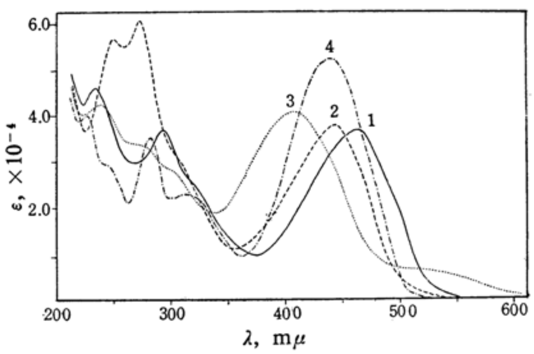


Fig. 5. Absorption spectra of the chromium- (1), cobalt- (2), iron- (3) and aluminum- (4) complexes of IV in the standard solvent.

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[10] R. Tsuchida, This Bulletin, **13**, 388, 436 (1938); *J. Chem. Soc. Japan*, (*Nippon Kwagaku Kwaishi*), **59**, 731,819 (1938): K. Sone, ibid., **71**, 270, 316 (1950).

[11] a) R. Tsuchida et al., This Bulletin, **13**, 436, 471 (1938); *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **77**, 734 (1956).
b) J. C. Bailar, Jr., ed., "The Chemistry of the Coordination Compounds", Reinhold Publishing Corp., New York (1956), p. 568.

TABLE II. ABSORPTION SPECTRA OF THE CHROMIUM-, COBALT-, IRON- AND ALUMINUM-COMPLEXES OF PHENOLAZOACETOACETANILIDES IN THE STANDARD SOLVENT

Ligand	Metal	A	B	C	D	l	δ
II	None	387.6 (2.96)	302.6* (0.71)	258.5 (1.85)	231.2 (2.03)	4.50	0.35
	Cr	461.0 (3.74)	322.3* (2.51)	292.5 (3.99)	235.0 (4.81)	4.60	0.62
	Co	440.0 (3.88)	314.5* (2.75)	272.9 (5.93)	249.5 (5.56)	4.59	0.65
	Fe	546.0* (0.56) 408.4 (4.10)	306.2* (2.69)	273.5 (3.33)	238.0 (4.19)	6.32	0.65
	Al	435.2 (5.11)	323.2* (2.08)	283.0 (3.53)	248.6*(2.71) 227.9 (4.04)	4.26	0.24
III	None	388.5 (2.76)	302.3* (0.59)	257.0 (1.63)	233.5 (1.72)	4.66	0.31
	Cr	459.0 (3.53)	321.5* (2.19)	291.7 (3.48)	232.5 (4.30)	4.50	0.58
	Co	440.4 (3.54)	317.0* (2.29)	271.5 (5.23)	251.0 (5.00)	4.55	0.81
	Fe	540.0* (0.41) 404.2 (3.79)	304.7* (2.46)	274.0*(3.07)	238.6 (4.08)	6.23	0.52
	Al	433.3 (4.71)	307.3 (2.04)	280.0 (3.01)	247.5*(2.58) 227.6*(3.89)	4.39	0.27
IV	None	389.5 (2.92)	302.3* (0.65)	259.0 (1.74)	233.2 (1.95)	4.57	0.36
	Cr	462.5 (3.68)	325.0* (2.33)	293.8 (3.69)	233.7 (4.63)	4.60	0.64
	Co	442.5 (3.78)	318.5* (2.47)	274.3 (6.09)	249.7 (5.67)	4.65	0.75
	Fe	(540.0)*(0.56) 407.2 (4.06)	305.3* (2.73)	276.0*(3.33)	240.0 (4.20)	6.73	0.77
	Al	437.0 (5.22)	312.2 (2.27)	282.9 (3.52)	248.9*(2.83) 227.6 (3.99)	4.21	0.19
V	None	396.0 (2.76)	311.0 (0.68)	262.5 (1.29)	231.5 (1.64)	4.63	0.31
	Cr	473.3 (3.43)	(365.0)*(1.39) 315.0 (2.59)	289.5 (2.72)	230.4 (4.28)	4.77	0.55
	Co	450.2 (3.19)	313.0 (2.36)	270.3 (4.49)	242.7 (4.72)	5.85	1.10
	Fe	(535.0)*(0.53) 407.2 (3.49)	309.0 (2.14)	266.5*(2.43)	235.2 (3.36)	—	—
	Al	440.0 (3.70)	325.8 (2.04)	264.8*(1.86)	239.0*(2.50)	5.55	0.49

Wavelengths in parenthesis denotes an indistinct location.

The letters, l and δ, are the half-value widths and the inclination parameters of the A bands (in $\text{cm}^{-1}\times 10^{-3}$) respectively.

indicating that these are essentially ionic complexes, as was reported by Freeman and White[12].

Shifts of the C ligand-bands with complex-formation are characteristic of the central metal atom used. Generally, red-shifts of the ligand-bands C ($\Delta\lambda_C$) with complex-formation are in the order: Cr> Al> Fe> Co.

Chromium(III)-complexes.—In the series of phenolazoacetoacetamides, it was found that the polarity increase of the phenolic O–H linkage, as in the case of the dissociation or formation of the intramolecular hydrogen bond, causes a red-shift and an intensity increase of the C band. Generally the bond formed between the phenolic oxygen and the tervalent metal is considered to be based on ion-dipole interaction, because the hydroxyl group has a strong dissociative ability[3]. The M–O (M, tervalent metal; O, phenolic oxygen) bond, therefore, is considered to have an essentially polar character. This presumably causes a displacement of the C band towards a longer wavelength. Indeed, such red-shifts of the C bands ($\Delta\lambda_C$) are the largest in the chromium(III)-complexes, indicating that the Cr–O bonds are the most ionic among the four sorts of metal-complexes.

The maintenance of the B ligand-bands, even in the coordinated state, suggests that the double bond character of >C=O in the acetyl group is not eliminated with the complex-formation. The lone pair electrons of the carbonyl oxygen will coordinate with the metal atom to form a σ bond. When the same ligand is used, the B bands of the four metal-complexes are almost equal in intensity and show only small displacements. The shifted order of the B bands as shown in Fig. 6 is probably due to the effect of an electronic transition along the whole conjugate system of the respective ligand-molecule.

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[12] D. C. Freeman, Jr., and C. E. White, *J. Am. Chem. Soc.*, 78, 2678 (1956).

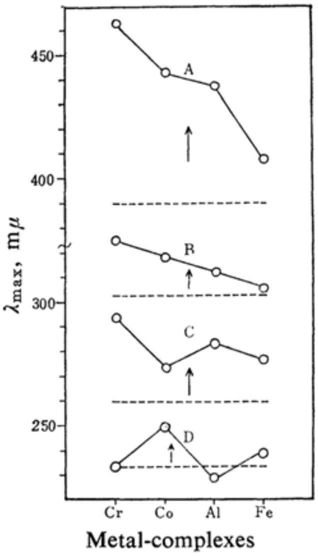
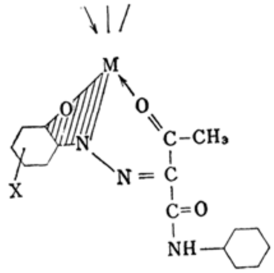


Fig. 6. Absorption maxima of the four bands in the spectra of metallized IV; dotted lines show absorption maxima of the four ligand-bands.

Therefore, the nature of the M–O (O, carbonyl oxygen) bonds are thought to be independent of the central metal used.



(VI)

(X, Substituent)

The above explanations lead to the conclusion that the structure shown in VI contributes much to the matal-ligand linkage. An imino group in the hydrazone group will coordinate with a metal atom, with a splitting off of a proton. Craig and his co-workers[13] suggested that the nitrogen lone pair has the ability to enter the π-electron orbital and that, therefore, the π-electrons of the system will be distributed over the whole conjugate system of the ligand. Thus, the overlap of the dπ-orbitals[13] of the metal with the nitrogen π-orbital will form the dπ-pπ bonding.

Cobalt(III)-complexes.—The maximum wavelengths of the A bands are always about 20 mμ shorter than those of the chromium(III)-complexes. Generally the values of $\Delta\lambda_C$ are the smallest among the four kinds of the metal-complexes, indicating the highly covalent character of the Co–O (O, phenolic oxygen) bonds.

Since the chromium(III)- and the cobalt(III)-complexes in this study are formed by d^2sp^3 hybridized orbitals, their electronic configurations are:

	3d				4s	4p
Cr:	d^1	d^1	d^1	D^2	S	P^3
Co:	d^2	d^2	d^2	D^2	S	P^3

Such completely filled or half-filled dπ-orbitals are known to be the most stable electronic configurations[14]. Consequently, the dπ-pπ bonds are considered to be almost equally operative in the chromium(III)- and the cobalt(III)-complexes. In such a case, the bathochromic shifts of the A bands with complex-formation are ascribed mainly to two causes: (i) the polarity of the M–O (O, phenolic oxygen) bond, and (ii) the perturbation of the π-electron system by the dπ-pπ interaction, serving to increase the electronic polarizability of the system. The shorter wavelength positions of the A bands in the cobalt-(III)-complexes are attributed to the highly covalent character of the Co–O bonds. Thus, a chelate ring (the shaded portion in VI) is stabilized, resulting in a facilitation of an electronic transition which will increase the intensity of the C band.

In the ligand-dye V, $\Delta\lambda_C$ decreases in the order: Cr$\gg$Co$>$Fe$>$Al. An electronegative subsutituent in the para position with regard to the hydroxyl will increase the polarity of the M–O (O, phenolic oxygen) bond. Thus, the polarity order of the bond may be somewhat different from those of the metallized II, III and IV.

Iron Compexes.—The absorption spectra of the iron(III)-complexes have some peculiarity. If the penetration complexes (a) are formed, the contribution of the dπ-pπ interaction upon the metal-ligand linkage will be small.

	3d				4s	4p	4d
(a)	d^2	d^2	d^1	D^2	S	P^3	
(b)	d^1	d^1	d^1	d^1d^1	D^2	S	P^3

If the iron(III)-complexes formed are the normal complexes (b), the distribution of the bonding electrons will be biased in the direction of the ligand in order to increase the metal-ligand

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[13] D. P. Craig et al., *J. Chem. Soc.*, **1954**, 332.

[14] Cf. Ref. 11b, p. 185.

distance.[15] The relatively small shifts of the C bands with the complex-formation may indicate the covalent charactr of the Fe–O (O, phenolic oxygen) bonds. However, the A bands are broader than those of the chromium(III)- and cobalt(III)-complexes, in which the dπ-pπ bondings are effectively operative. Moreover, the C bands of the iron(III)-complexes are also broadened, mostly as shoulders. It may consequently be postulated that the iron(III)-cmplexes are a mixture of different bond types, as is shown in a and b.

The weak shoulders are located in the $535\sim545$ mμ region. Their true absorption intensities are about $(2\sim3)\times10^3$, since these shoulders are superposed by the slopes of the A bands. These may probably be ascribed to the first absorption bands[16] due to the iron(III)-ion, because similar weak bands in the spectra of copper- and nickel-chelates of salicylaldoxime were reported[17] to be due to the metal ions.

Aluminum-complexes. — Aluminum-complexes are ordinarily recognized to be essentially ion-dipole aggregates, as was pointed out by Craig et al.[13]

As is shown in Fig. 6, the values of $\Delta\lambda_C$ are next larger to those of the chromium(III)-complexes, indicating the high polarity of the Al–O (O, phenolic oxygen) bonds. The A bands are sharp and symmetrical; i. e., both the half-value widths (l) and the inclination parameters (δ) are smaller than those of the respective ligand-dye. This indicates that the aluminum-complexes are ionic complexes. The shifts of the A ligand-bands with complex-formation are mainly to be attributed to the polarity of the Al–O (O, phenolic oxygen) bonds.

Experimental

Syntheses of the Metal-complexes of Phenolazoacetoacetanilides.—*Metal-complexes of 2-Hydroxy-5-(N-ethylsulfamoyl)-phenylazoacetoacetanilide (II).*—(*i*) *Chromium(III)-complex.*—The ligand-dye (0.02 mol.) in formamide was treated with chromium(III) formate (0.01 mol.) at 120°C for 10 hr. The reaction mixture was poured into a dilute solution of hydrochloric acid to yield a yellow-brown precipitate of the complex-acid. A small portion of the crude product was dissolved in 95% ethanol, added to a column of activated alumina, and developed with 95% ethanol. A yellow-brown zone was separated and eluted with the same solvent.

After evaporation of the eluted solution to dryness under reduced pressure, a residue was dissolved in dry acetone, filtered, and diluted with hot benzene. Orange-brown needles were obtained.

Found: C, 50.15; H, 4.56; N, 13.33. Calcd. for $C_{36}H_{37}O_{10}N_8S_2Cr$: C, 50.04; H, 4.34; N, 13.06%.

(*ii*) *Cobalt(III)-complex.*—The ligand-dye (0.02 mol.) was suspended in a dilute solution of sodium hydroxide and treated at 80°C with cobalt(II) sulfate (0.01 mol.) to yield a brown precipitate. This precipitate was dissolved in aqueous ethanol containing sodium hydroxide, and the solution was then acidified with hydrochloric acid to precipitate the complex-acid. Purification was performed in the same manner as the chromium(III)-complex. A yellow-brown precipitate was obtained.

Found: C, 49.36; H, 4.51; N, 12.68. Calcd. for $C_{36}H_{37}O_{10}N_8S_2Co$: C, 49.90; H, 4.30; N, 12.98%.

(*iii*) *Iron(III)-complex.*—The ligand was treated with iron(III) chloride in formamide. The reaction mixture was poured into a dilute aqueous solution of acetic acid to yield a brown precipitate. After an aqueous ethanolic solution of the precipitate had been acidified with acetic acid, the complex-acid obtained was purified by chromatographic adsorption, as has been shown above. After removal of the solvent from an eluted solution, a residue was dissolved in dry ethanol and diluted with hot benzene to crystallize brown needles.

Found: C, 49.83; H, 4.45; N, 12.93. Calcd. for $C_{36}H_{37}O_{10}N_8S_2Fe$: C, 50.19; H, 4.30; N, 13.01%.

(*iv*) *Aluminum-complex.*—Reaction was carried out in the same manner as with the iron(III)-complex, except that aluminum sulfate was used instead of iron(III) chloride. The purification procedures were the same as that for the iron(III)-complex. Yellow needles were obtained.

Found: C, 51.38; H, 4.39; N,13.28. Calcd. for $C_{36}H_{37}O_{10}N_8S_2Al$: C, 51.91; H, 4.38; N, 13.46%.

Metal-complexes of 5-Chloro-2-hydroxyphenylazoacetoacetanilide(V). — (*i*) *Chromium(III)-complex.* —The reaction and the chromatographic separation procedures were the same as have been shown for the *N*-ethylsulfamoyl derivative. A residue obtained by the evaporation of an eluted solution was dissolved in aqueous ethanol containing sodium hydroxide. Neutralization of the solution with hydrochloric acid and the addition of sodium chloride to this gave red-brown prisms.

Found: C, 54.09; H, 3.63; N, 11.74. Calcd. for $C_{32}H_{25}O_6N_6Cl_2Cr$: C, 53.94; H, 3.54; N, 11.78%.

(*ii*) *Cobalt(III)-complex.*—Purification was carried out in the same way as with the above-mentioned chromium(III)-complex.

Found: C, 52.92; H, 3.73; N, 11.39. Calcd. for $C_{32}H_{25}O_6N_6Cl_2Co$: C, 53.42; H, 3.50; N, 11.68%.

(*iii*) *Iron(III)-complex.*—A mixture of 95% ethanol and pyridine was used as a developer liquid in chromatographic adsorption. The dilution of a dry-ethanolic solution of the separated complex-acid with hot *n*-hexane gave red-brown needles.

Found: C, 53.24; H, 3.38; 11.58. Calcd. for $C_{32}H_{25}O_6N_6Cl_2Fe$: C, 53.65; H, 3.52; N, 11.73%.

(*iv*) *Aluminum-complex.* — Yellow needles were obtained in the same manner as has been described

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[15] E. Cartmell and G. W. A. Fowles, "Valency and Molecular Structure", Butterworths Scientific Publications, London (1956).

[16] L. E. Orgel, *J. Chem. Soc.*, **1952**, 4756; *J. Chem. Phys.*, **23**, 1004 (1955).

[17] K. Sone, *J. Am. Chem. Soc.*, **75**, 5207 (1953).

in the case of *N*-ethylsulfamoyl derivative.

Found: C, 55.38; H, 3.81; N, 12.49. Calcd. for $C_{32}H_{25}O_6N_6Cl_2Al$: C, 55.90; H, 3.67; N, 12.22%.

Metal-complexes of the Other Ligand-dyes.—These were also prepared in the manner described above. The 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. The solvents used had the qualities of spectral grades.

Summary

1) The electronic absorption spectra of metallized phenolazoacetoacetanilides exhibit four characteristic groups of bands—A, B, C and D. These groups of bands originate in the band of the respective ligand-dye.

2) The metal-complexes have the structure shown in formula VI.

3) The bathochromic shifts of the A ligand-bands with complex-formation are ascribed to two causes: (i) the polarity of the M–O (M, tervalent metal; O, phenolic oxygen) bond, and (ii) the perturbation of the π-electron system by the dπ-pπ interaction. The shifts of the C ligand bands with the complex-formation are closely related to the polarity of the above-mentioned M–O bond. The cobalt(III)-complex has the covalent M–O bond with which to form a stable chelate ring, whereas the chromium(III)-complex has the ionic M–O bond.

4) The absorption characteristics of the iron(III)- and the aluminum-complexes have been discussed.

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