Studies of the Absorption Spectra of Azo Dyes and their Metal-complexes. V. The Electronic Absorption Spectra of Metal-complexed Phenolazoacetoacetbenzylamides

By Yoshiharu YAGI

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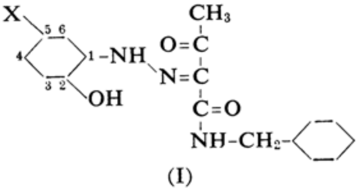
Previous studies[1)] of the electronic absorption spectra of phenolazoacetoacetanilides[*1] have shown that four groups of bands are to be expected for partial or total chromophoric systems[2)] of the respective molecules and that the interception of the π-p conjugation between the amide nitrogen and the amide aryl group, as in case of phenolazoacetoacetbenzylamide (I), causes the hypsochromic displacement of the A, B and C bands. The author has also investigated the metal-ligand linkage of the 2:1-complexes consisting of two molecules of phenolazoacetoacetanilides (II)[3a)] and a tervalent metal atom. The work described in the present paper was first undertaken to study the absorption characteristics and the metal-ligand linkage with respect to the metallized phenolazoacetoacetbenzylamides[3b)].

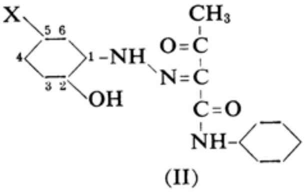
In the series of metallized phenolazoacetoacetanilides, the A band of the cobalt(III)-complex[*2] having a nitro group in the para-position to the Co–O (O, phenolic oxygen) bond has been observed to split into two peaks. The cause of such anomalous band-splitting will be investigated, together with the above-mentioned problems.

Results and Discussion

The Electronic Absorption Spectra of Chromium(III)- and Cobalt(III)-complexes Derived from Phenolazoacetoacetbenzylamides. — The electronic absorption spectra of chromium(III)- and cobalt(III)-complexes derived from 5-sulfamoyl- and 5-chloro derivatives of I in the standard solvent[*3] are illustrated in Table I (Figs. 1–3), together with the corresponding derivatives of II.



(I)



(II)

(X, Substituent)

The spectra of the metal-complexed I in the near ultraviolet and visible regions show four groups of bands, which will be identified as A, B, C and D counting from the longer

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[*1] 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) Parts II, III and IV, This Bulletin, **36**, 492, 500, 506 (1963).

2) E. A. Braude, *J. Chem. Soc.*, **1945**, 490.

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

3) a) Such metal-complexes are known as acid dyes. For example: Ciba Ltd., U. S. Pat. 2565898 (1951); Brit. Pat. 716753 (1954); J. R. Geigy A.-G., Brit. Pat. 736034 (1955); E. Koike and Y. Yagi, Japanese Pat., Announced No. 36-8730 (1961).
b) Y. Yagi and K. Kmura, Japanese Pat., Announced No. 36-11975 (1961).

[*3] The term "standared solvent" denotes aqueous 80% methanol containing 0.1 g. of acetic acid per liter.

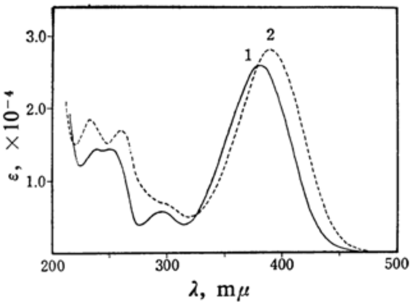


Fig. 1. Absorption spectra of 2-hydroxy-5-sulfamoylphenylazoacetoacetbenzylamide (1) and 2-hydroxy-5-sulfamoylphenylazoacetoacetanilide (2) in the standard solvent.

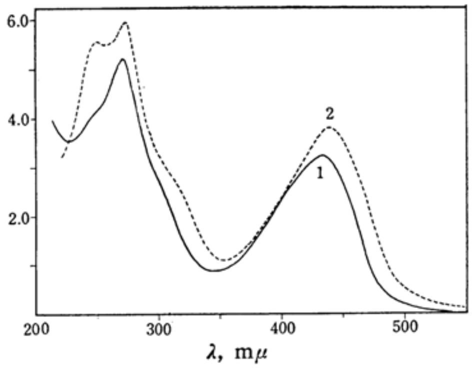


Fig. 2. Absorption spectra of cobalt-complexes derived from the ligand-dyes shown in Fig. 1 in the standard solvent; the numbering of the curves corresponds to those in Fig. 1.

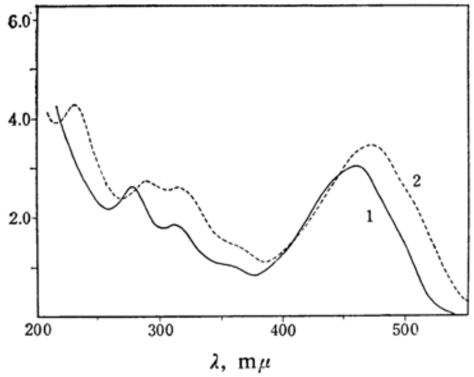
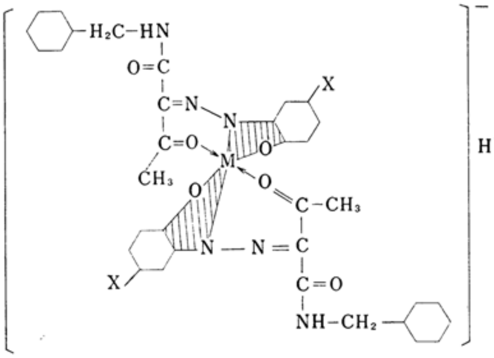


Fig. 3. Absorption spectra of chromium-complexes derived from 5-chloro-2-hydroxyphenylazoacetoacetbenzylamide (1) and 5-chloro-2-hydroxyphenylazoacetoacetanilide (2) in the standard solvent.

wavelength side. As was pointed out in Part III, these bands originate in the four conjugation bands (K bands)[4] of the respective ligand-dye. The A ligand-band arises from a transition involving electron migration along the whole conjugate system of the ligand-molecule. The B ligand-band originates in a conjugative electronic transition between the acetyl carbonyl and the hydrazone group, the C ligand-band, in one between the phenolic nucleus and the hydrazone group, and the D ligand-band, in one between the carboxylic acid amide group and the hydrazone group.

With regard to absorption spectra of the ligand-dye I, the interception of the π-p conjugation by the insertion of a methylene bridge caused a decrease in the intensity and the red-shift of the D band, resulting in the hypsochromic and hypochromic displacement of the A, B and C bands. In the spectra of metal-complexed II also, the D bands markedly decrease in intensity, as is shown in Figs. 2 and 3. For example, the D band in the chromium(III)-complex of the 5-chloro derivative is completely submerged in the other band-system and can not be detected. An absorption band due to a forbidden transition within the phenyl or the phenol nucleus (B-band)[5] should appear near the D bands, but this is considered to be submerged in such conjugation bands as the D or C bands.



(III)

A comparison of the A bands between the I and II series indicates that the elimination of the π-p conjugation causes a hypsochromic displacement of about 7 mμ in the cobalt(III)-complexes and one of 10~14 mμ in the chromium(III)-complexes, In Table I, the $\Delta\nu_A$ values (the red-shifts of A ligand-bands with complex-formation, i. e., the absorption maximum of the ligand-band A − absorption maximum of the corresponding complex-band, in cm^{-1}) of the chromium(III)-complexes are almost equal in the two series. However, the $\Delta\nu_A$ values of the cobalt(III)-complexes are larger in the I series.

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[4] A. Burawoy, *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] A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, **1952**, 2310, 3734.

TABLE I. ELECTRONIC ABSORPTION SPECTRA OF CHROMIUM(III)- AND COBALT(III)-COMPLEXES

Substituent (X)	Series of ligand	Metal	A				
			λ_{max}	ε_{max}	$\Delta\nu_A$	l	δ
$-SO_2NH_2$	I	None	380.0	2.60	—	4.57	0.31
		Cr	449.0	3.26	4.05	4.58	0.58
		Co	433.1	3.23	3.23	4.68	0.68
	II	None	389.5	2.81	—	4.59	0.36
		Cr	460.4	3.78	3.95	4.63	0.59
		Co	440.0	3.79	2.94	4.64	0.69
-Cl	I	None	387.0	2.42	—	4.70	0.27
		Cr	459.3	3.02	4.07	4.55	0.52
		Co	443.5	3.13	3.29	5.06	0.90
	II	None	396.0	2.76	—	4.63	0.31
		Cr	473.3	3.43	4.12	4.77	0.55
		Co	450.2	3.19	3.04	5.85	1.10

N.B. a) Absorption 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}.

The bathochromic shifts of the A ligand-bands with the complex-formation are ascribed mainly to two factors: (i) the polarity of the M–O (M, tervalent metal; O, phenolic oxygen) bond; i. e., any alteration of the electronic configuration, which polarizes the bond, causes a red-shift of the A band, and (ii) the perturbation of the π-electron system by the dπ-pπ interaction between the hydrazone group and the central metal. The dπ-pπ interaction in the chromium(III)- and the cobalt(III)-complexes are considered to be equally effectively operative, because the dπ-orbitals in both the complexes by d^{2}sp^3 hybridization have stable electronic configurations$^{6)}$. Consequently, the different degrees of the bathochromic shifts of the A ligand-bands with the cobalt-complex formation are considered to depend mainly upon the polarities of the M–O bonds. The larger values of $\Delta\nu_A$ in the cobalt(III)-complexs of the I series indicate that the Co–O (O, phenolic oxygen) bond increases its ionic character. This is probably due to the stronger basicity of the phenolic hydroxyl in the I series. Further, since the substituents in the phenolic nuclei of the I series have more pronounced effects upon the absorbing systems, as was pointed out in Part II, the electronegative substituent, such as the 5-chloro or 5-sulfamoyl group, will emphasize the polarity-increase of the Co–O bond.

Since the Cr–O (O, phenolic oxygen) bond originally has a highly ionic character, the values of $\Delta\nu_A$ in the I and II series do not differ from each other.

The half-value widths (l) and the inclination parameters (δ) are generally larger in the cobalt(III)-complexes than in the chromium(III)-complexes. This suggests that the stable five-membered chelate-ring in the cobalt(III)-complexes, as shown in III (the shaded portions), emphasizes the perturbation of the π-electron system by the dπ-pπ interaction.

The C bands are closely related to the polarities of the M–O (O, phenolic oxygen) bonds, as was reported in Parts III and IV. That is, the highly ionic character of the Cr–O (O, phenolic oxygen) bond resulted in the appearance of the C bands at markedly longer wavelengths, while the highly covalent character of the Co–O (O, phenolic oxygen) bond caused the slight red-shift and the intensity increase of the C band. Such characteristic band-shifts are also observed in the I series. It is noteworthy that the $\Delta\nu_C$ values of the cobalt(III)-complexes in the I series are relatively larger than those of the corresponding chromium(III)-complexes. This confirms that the Co–O bond increases its ionic character in the I series.

The B bands run parallel to the shifts of the A bands, indicating that this group of bands is influenced by an electronic transition involving electron migration along the whole conjugate system of the molecule. The absorption intensities are almost equal in the chromium(III)- and the cobalt(III)-complexes.

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6) "The Chemistry of the Coordination Compounds", Ed. by J. C. Bailar, Jr., Reinhold Publishing Corp., New York (1956), p. 185.

OF PHENOLAZOACETOACETBENZYLAMIDES AND RELATED COMPOUNDS IN THE STANDARD SOLVENT

B			C			D		
λ_{max}	ε_{max}	$\Delta\nu_B$	λ_{max}	ε_{max}	$\Delta\nu_C$	λ_{max}	ε_{max}	$\Delta\nu_D$
296.0	0.56	—	251.7	1.43	—	239.0	1.43	—
317.0*	1.84	2.23	282.5 (264.0*)	3.39 3.07	4.33	232.8	3.60	−1.12
305.5*	2.37	1.05	271.0	5.21	2.83	243.4*	3.99	0.76
303.0*	0.63	—	258.0	1.74	—	232.5	1.84	—
319.6*	2.61	1.71	291.9	3.80	4.50	234.3	4.69	0.33
315.5*	2.58	1.30	272.5	5.95	2.06	249.0	5.57	2.85
306.0	0.53	—	264.0*	0.79	—	245.0	1.15	—
312.0 (359.0*)	1.86 0.99	0.63	278.9	2.62	2.02	—	—	—
307.5*	2.08	0.16	270.3	3.94	0.88	(236.0*)	3.96	−1.55
311.0	0.68	—	262.5	1.29	—	231.5	1.64	—
315.0 (365.0)*	2.59 1.39	0.40	289.5	2.72	3.56	230.4	4.28	−0.20
313.0	2.36	0.20	270.3	4.49	1.10	242.7	4.72	2.00

b) * Inflection

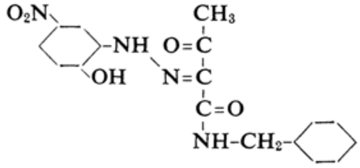
c) Absorption maximum in parenthesis denotes an indistinct location.

d) Inflections near the four main bands are shown under the corresponding main band.

However, exact evaluation is difficult, because most of these bands appear as inflection.

The D bands in the I series also often appear as inflection, because their intensities are generally low because of the interception of the π-p conjugation. Relatively longer wavelength positions and higher intensities of the D bands in the spectra of the cobalt(III)-complexes are observed than in those of the chromium(III)-complexes. This is in accord with the explanation given in the previous paper that the stable chelate ring emphasizes the planarity of the coordinated ligand-molecule, facilitating the electronic transition expected for a partial chromophore involving the amide group and resulting in an approach of the D band to the high-intensity C band.

The Splitting of the A Bands in the Spectra of Metallized 2-Hydroxy-5-nitrophenylazoacetoacetbenzylamide.—The absorption spectra of chromium(III)-, cobalt(III)-, iron(III)- and aluminum-complex of 2-hydroxy-5-nitrophenylazoacetoacetbenzylamide (IV) in a variety of solvents are shown in Table II (Figs. 4 and 5).



(IV)

Two peaks of the split A band are, for convenience, named as A_1 and A_2 counting from the longer wavelength side.

The splitting of the A bands is observed in every solvents. The D bands of these complexes decrease their intensities in a manner similar to those in Table I. For example, the D band of the cobalt(III)-complex can not be detected, as is shown in Fig. 4. Weak inflections at about 550 mμ in the spectra of the iron(III)-complex are considered to be the first absortion band⁽⁷⁾, that due to the iron(III)-ion, as was reported in Part III. The results in Part III also showed that the aluminum-complex generally shows a sharp and symmetric A band. However, all the metal-complexes of IV have broadly split A bands.

It has been reported that the absorption band of salicylaldoxime tends to split with the Ni-chelate formation⁽⁸⁾ and that such band-splitting probably arises from different bond-types, such as dsp^2 and sp^3 hybridizations. It can not, however, be thought that the A_1 and A_2 bands originate in two different bond-types, for the 2:1-chromium(III)- or cobalt(III)-complexes, such as the metal-complexes in this studies, are known to be stable penetration complexes by d^2sp^3 hybridization⁽⁹⁾; the results in the preceding papers⁽¹⁾ also confirm the above view. Nor can it be considered that the band-splitting is due to the vibrational

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7) 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).

8) K. Sone, *J. Am. Chem. Soc.*, **75**, 5207 (1953).

9) J. C. Bailar, Jr., and C. F. Callis, ibid., **74**, 6018 (1952); P. Pfeiffer and S. Saure, *Ber.*, **74**, 935 (1941).

TABLE II. ABSORPTION SPECTRA OF METALLIZED 2-HYDROXY-5-NITROPHENYLAZOACETOACETBENZYLAMIDE IN A VARIETY OF SOLVENTS

Metal	Solvent	A			B	C	D
			A_1	A_2			
None	S			376.0 (2.46)	302.0 (1.18)	246.0 (1.38)	(232.3*) (1.21)
Cr	S		451.8(4.05)	(424.7*) (3.78)	—	307.7 (3.06)	246.0 (2.48)
	N		452.8(4.13)	(425.0*) (3.88)	—	307.4 (2.84) (267.2*) (2.22)	245.0 (2.42)
	P		466.6(4.39)	(432.4*) (4.11)	—	315.3 (2.75) (351.7*) (1.80)	—
Co	S		439.5(4.10)	414.2 (3.99)	297.6* (3.13)	266.5 (3.81)	not detected
	M		440.9(4.04)	414.6 (4.02)	296.2* (2.94)	265.9 (3.52)	not detected
	N		442.7(4.04)	416.5 (4.06)	295.0* (2.96)	266.5 (3.53)	not detected
	P		457.2(4.61)	421.7 (4.34)	(341.7*) (2.08)	—	not detected
Fe	S	(544.5*) (0.47)	418.1(3.96)	(376.0*) (3.52)	305.5 (2.51)	382.3 (2.49)	254.0* (2.33)
	P	(552.4*) (0.53)	438.4(4.48)	(407.5*) (3.92) (377.0*) (3.26)	312.5 (2.36)	—	—
Al	S		437.0(4.56)	(408.0*) (4.34)	318.8 (2.53)	267.0 (1.63)	248.2 (1.64)
	P		453.0(4.91)	417.1 (4.61)	323.0 (2.48)	—	—

N.B. a) Wavelengths (λ_{max}) in mμ, molar extinction coefficients (ε_{max}) $\times 10^{-4}$ in parenthesis.
b) S, Standard solvent; N, Aqueous 50% methanol containing 0.01 mol. of NaOH per liter; M, Aqueous 50% methanol; P, Pyridine
c) In the chromium-complex, the B band is superposed by the C band.

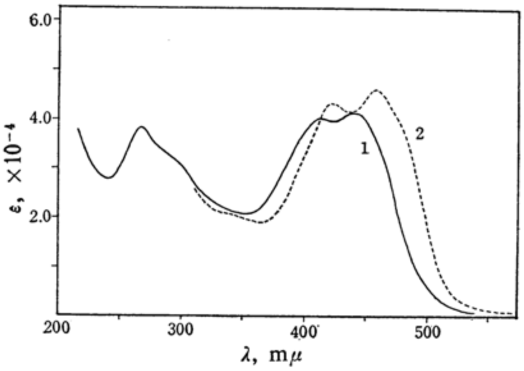

Fig. 4. Cobalt-complex of IV in the standard solvent (1) and in pyridine (2).

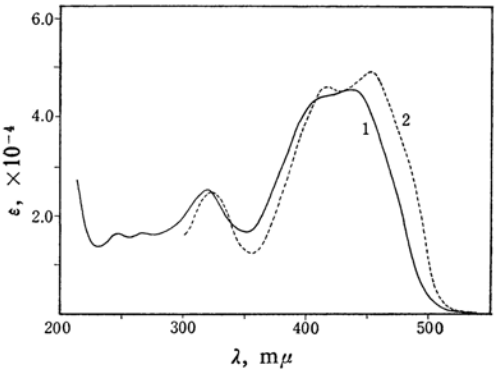

Fig. 5. Aluminum-complex of IV in the standard solvent (1) and in pyridine (2).

structure, as has been reported on metal-chelates of α, α'-dipyridyl[10].

In the cobalt(III)-complex of IV, a comparison of the absorption maxima of the A_1 and A_2 bands in pyridine with those in the standard solvent shows that the A_1 and A_2 bands undergo bathochromic shifts of 0.89×10^3 and 0.42×10^3 (in cm^{-1}) respectively when measured in pyridine. The batho- and hyperchromic displacement is more pronounced in the A_1 band (Fig. 4). Such a tendency is also observed in the other metal-complexes of IV, as is shown in Fig. 5. Generally, the increase in the polarity due to the solute-solvent interaction, and thus the magnitude of the solvent effect, is enhanced with the polar character of the absorbing molecules[11]. Although various causes are conceivable for such band-splitting, the following explanation is thought to be the most reasonable; one of the two M–O (O, phenolic oxygen) bonds which form the chelate-rings of the 2:1-metal-complex III is markedly polarized by the *p*-substituted nitro group, and thus an electronic transition along the conjugate system of the coordinated ligand-molecule involving the polarized M–O bond exhibits the A_1 band.

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[10] K. Sone, P. Krumholz and H. Stammreich, *J. Am. Chem. Soc.*, **77**, 777 (1955).

[11] A. Burawoy, M. Cais., J. T. Chamberlain, F. Liversedge and A. R. Thompson, *J. Chem., Soc.*, **1955**, 3721.

Though an anionic charge of the 2:1-complex is generally considered to have a non-localized character, as has been pointed out in Part III, this will be localized at the polarized M–O bond in the metal-complexed IV. To confirm this explanation on other metal-complex systems, further studies are now in progress.

If the metal-complex molecule of IV involves the two M–O bonds of different polarities as explained above, the C bands expected for the partial chromophore involving the phenolic nucleus will split to two peaks. In fact, the C band of the chromium(III)-complex in an alkaline solution splits and forms an inflection near 267 mμ. No such band-splitting, however, can be detected in the other complexes of IV.

That the A_2 band of the cobalt(III)-complex has a relatively higher intensity as compared with that of the A_1 band, as is shown in Table II, agrees with the finding in Parts III and IV that the metal-ligand linkage is the most stable in the cobalt(III)-complexes. Since the M–O bonds of the chromium(III)-, iron(III), and aluminum-complexes are essentially ionic, the A_2 bands of these complexes are low in intensity. A fine structure of the A_2 band in the spectrum of the iron(III)-complex in pyridine may support the deduction in Part III that the iron(III)-complex is a mixture of different bond types.

Experimental

The Preparation of Metal-complexes of Phenolazoacetoacetbenzylamides.—*Metal-complexes of 5-Chloro-2-hydroxyphenylazoacetoacetbenzylamide. — (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 10 hr. The reaction mixture was poured into a dilute aqueous solution of hydrochloric acid to yield a yellow-brown precipitate. This complex-acid was filtered off, washed with water, and dried in vacuo. The crude complex-acid (300 mg.) was dissolved in 95% ethanol, added to an adsorption-column of activated alumina, and developed with 95% ethanol. The brown zone of the complex was separated and eluted with 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 and the successive addition of sodium chloride to this gave reddish brown prisms. This product was filtered off, washed with water, and dried in vacuo, yielding 230 mg. of the pure chromium(III)-complex.

Found: C, 54.70; H, 4.02; N, 11.41. Calcd. for $C_{34}H_{29}O_6N_6Cl_2Cr$: C, 55.14; H, 3.94; N, 11.34%.

(ii) Cobalt(III)-complex. — The ligand-dye (0.02 mol.) was suspended in an aqueous alkaline solution containing sodium hydroxide (0.05 mol.) and tartaric acid (0.005 mol.) and treated with cobalt(II) sulfate (0.01 mol.) at 60°C for 1 hr. The reaction mixture was made into a solution by the addition of ethanol and was acidified (pH 2.70) with hydrochloric acid. The precipitated complex-acid was filtered off, washed with water, and dried in vacuo. The chromatographic purification of the product (200 mg.) was carried out in the same manner as with the chromium(III)-complex, giving yellow-brown needles (150 mg.).

Found: C, 54.23; H, 4.18; N, 10.98. Calcd. for $C_{34}H_{29}O_6N_6Cl_2Co$: C, 54.64; H, 3.91; N, 11.24%.

Metal-complexes of the Other Phenolazoacetoacetbenzylamides.—These complexes were also prepared in the manner described above. The iron(III)- and aluminum-complexes of IV were prepared in a method similar to that described in Part III. 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 concentrations of 1.6×10^{-5} M (metal-complexes) and 2.5×10^{-5} M (ligand-dyes).

Summary

The absorption spectra of metallized phenolazoacetoacetbenzylamides were investigated.

The isolation of the electronic effect of the amide phenyl ring by the insertion of the methylene bridge decreases the intensity of the D band, resulting in the hypso- and hypochromic displacement of the A, B and C bands.

The red-shifts of the A and C ligand-bands with the complex-formation indicate that the Co–O (O, phenolic oxygen) bonds increase their ionic character as compared with those of the metallized phenolazoacetoacetanilides.

The splitting of the A band in the spectra of metallized 2-hydroxy-5-nitrophenylazoacetoacetbenzylamide is possibly to be attributed to the polarization of the M–O (O, phenolic oxygen) bond by the electron-withdrawing nitro group.

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Sumitomo Chemical Co., Ltd.
Osaka Works
Konohana-ku, Osaka