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Electronic Spectra of Trivalent Metal Complexes of 3-Phenyl- and 3-Benzyl-2, 4-pentanedione*

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The 3-phenyl- and 3-benzyl-2, 4-pentanedione complexes of trivalent aluminum, chromium, iron and cobalt were prepared, and their electronic absorption spectra measured in the 220—900 mμ range. The spectral data were interpreted in detail in terms of the $\pi_3 \rightarrow \pi_4$, the electron transfer ($d_\varepsilon \rightarrow \pi_4$) and the $d \rightarrow d^*$ transitions of the various components. In this series of complexes, an inter-ring π-interaction between a phenyl ring and a chelate ring is expected to remain to a limited extent in the metal complexes of 3-phenyl-2, 4-pentanedione, although the twist of both rings from the coplanarity is significant. For the aluminum complexes, π-electrons in the ligand part remain delocalized in a manner similar to that which holds in the corresponding enolate ion. On the other hand, each kind of $\pi_3 \rightarrow \pi_4$ transition in the transition metal complexes of the 2, 4-pentanedione derivatives was found to depend on the number of d_ε electrons of the central metal ion and to appear in this increasing order of energy: $Cr < Fe < Co$. In addition, the metal-ligand π-interaction has a major effect on the $\pi_3 \rightarrow \pi_4$ transition, and it seems to increase with respect to the ligands in the order: 2, 4-pentanedione, 3-phenyl-2, 4-pentanedione, and 3-benzyl-2, 4-pentanedione. The two major substituent (at the 3-position of 2, 4-pentanedione) effects which may affect the $\pi_3 \rightarrow \pi_4$ transitions were identified.

Much work has been done on the interpretation of the absorption spectra of 2, 4-pentanedione complexes from various aspects.[1-6] In two of these studies, Barnum applied the Hückel LCAO-MO calculation to the 2, 4-pentanedione chelate systems in order to estimate the effect of metal-ligand π-bonding on the electronic transition energies; he also successfully analyzed $\pi_3 \rightarrow \pi_4$ and $d_\varepsilon \rightarrow \pi_4$ transition bands.[4,5]

In the present study, the 3-phenyl- and 3-benzyl-2, 4-pentanedione complexes of trivalent aluminum, chromium, iron and cobalt have

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[1] K. Sone, I. Miyake, H. Kuroya and K. Yamasaki, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **69**, 70 (1948).

[2] R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

[3] R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).

[4] D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).

[5] D. W. Barnum, ibid., **22**, 183 (1961).

[6] J. P. Fackler, Jr., F. A. Cotton and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963).

TABLE I. ANALYSES AND MELTING POINTS OF TRIVALENT METAL COMPLEXES OF 3-SUBSTITUTED 2,4-PENTANEDIONES

3-Substituent	Complex	Carbon,* %	Hydrogen,* %	Metal,* %	M.p., °C
Phenyl	$Al(C_{11}H_{11}O_2)_3$	71.40(71.73)	6.21(6.02)	—	268
	$Cr(C_{11}H_{11}O_2)_3$	68.59(68.62)	5.78(5.76)	—	272—273 (decomp.)
	$Fe(C_{11}H_{11}O_2)_3$	67.74(68.17)	5.85(5.72)	—	259—259.5 (decomp.)
	$Co(C_{11}H_{11}O_2)_3$	66.03(67.81)	5.68(5.69)	—	183—184 (decomp.)
Benzyl	$Al(C_{12}H_{13}O_2)_3$	72.61(72.71)	6.75(6.61)	—	165.7—166.3
	$Cr(C_{12}H_{13}O_2)_3$	70.06(69.78)	6.35(6.34)	—	174.5—175.0 (decomp.)
	$Fe(C_{12}H_{13}O_2)_3$	69.38(69.34)	6.58(6.30)	8.95(8.96)	160—161.5 (decomp.)
	$Co(C_{12}H_{13}O_2)_3$	68.74(69.00)	6.44(6.27)	9.42(9.41)	142—143.5 (decomp.)

* Calculated values for the specified formula are given in parentheses.

TABLE II. ULTRAVIOLET ABSORPTION BANDS OF 2,4-PENTANEDIONES

β-Diketone	λ_{max}(mμ); log ε		
	n-Hexane	Ethanol	Ethanol and sodium ethoxide*
3-Phenyl-2,4-pentanedione		(227—243)	
	284; 3.98	286; 3.95	306.5; 4.26
3-Benzyl-2,4-pentanedione	(262)	(261)	
	(269)	(269)	
	287; 3.80	289; 3.58	309; 4.29
3,3-Dibenzyl-2,4-pentanedione	(248)	248.5; 2.47	
	253.5; 2.56	253.3; 2.57	
	259.4; 2.68	258.9; 2.68	
	265.0; 2.62	264.7; 2.60	
	269.0; 2.44	(268.0)	
	301; 2.08	294; 2.09	
2,4-Pentanedione		274.0	294.0; 4.43
	268.8; 4.08†	272.5; 4.02†	

Shoulder bands or indistinct bands are enclosed in parentheses.

* Ethanol contains 0.022 to 0.11 N sodium exthoxide.

† The values are cited from J. B. Conant and A. F. Thompson, Jr., *J. Am. Chem. Soc.*, **54**, 4039 (1952).

been prepared, and their electronic spectra interpreted in terms of the $\pi_3 \rightarrow \pi_4$ transition which is characteristic of the ligand molecules and of the electron transfer transition in the chromium, iron and cobalt complexes. The $d \rightarrow d^*$ transitions characteristic of the nuclear metals have also been assigned for the transition metal complexes.

Experimental

Preparation of Materials. — 3-Phenyl-2,4-pentanedione was prepared from phenylacetone and acetic anhydride in the presence of boron trifluoride and of *p*-toluenesulfonic acid in the 0—5°C temperature range, following the method described in the literature7); b. p. 110—115°C at 17 mmHg; m. p. 58.0—59.0°C (reported7) b. p. 116—118°C at 20 mmHg; m. p. 58.5—59.5°C). 3-Benzyl-2,4-pentanedione was obtained by the reaction of sodium acetylacetonate with excess benzyl chloride8); b. p. 115—118°C at 4 mmHg; n_D^{25} 1.5236 (reported b. p. 140—146°C,8) 143—146°C9) at 10 mmHg; n_D^{25} 1.52509)); a yield of 43%.

The methods of preparation employed for the trivalent metal complexes of acetylacetonate were used in this study with some modification for the syntheses of 3-phenyl- and 3-benzyl-2,4-pentanedione complexes of the corresponding trivalent metals. The procedure has been described in detail elsewhere.10) The results of analysis, along with the values of the melting point, are listed in Table I.

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7) C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. 8, 133 (1954).

8) G. T. Morgan, *J. Chem. Soc.*, **1925**, 797.

9) R. P. Dryden and A. Winston, *J. Phys. Chem.*, **62**, 635 (1958).

10) K. Nakamura and Y. Murakami, *Tech. Reports Kyushu Univ.* (*Kyushu Daigaku Kogaku Shuho*), **38**, 329 (1965).

TABLE III. ABSORPTION BANDS IN METAL COMPLEXES OF 2, 4-PENTANEDIONES

Metal complex	λ_{max}(mμ); log ε			
	3-Phenyl-2, 4-pentanedione		3-Benzyl-2, 4-pentanedione	
	Ethanol	Chloroform	Ethanol	Chloroform
Al(III) complex	231.5; 4.10			
			(264)	(265)
			(270)	(272)
	299.0; 4.51	301.5; 4.54	301.5; 4.48	305.0; 4.57
	(314)	(314)	(318)	(318)
Cr(III) complex	(258; 4.18)	(260; 4.23)	(257; 3.98)	
			265; 4.05	266; 4.06
			270; 4.06	271; 4.06
	(289; 4.02)	(291; 4.04)	(285; 4.00)	288.5; 4.02
	(310; 3.93)	(312; 4.02)	(318; 3.92)	(320; 3.95)
	348.0; 4.10	351.0; 4.14	352; 4.11	355.5; 4.13
	(395)	(395)	(400)	(400)
	(410—440)	(410—440)	(420—445)	(420—445)
	575	575.0; 2.06	565; 2.01	565.0; 2.00
Fe(III) complex	247.0; 4.36		(240; 4.16)	
			(263)	(265)
			(270)	(271)
	284.0; 4.39	284.0; 4.36	286.0; 4.33	286.5; 4.38
			(310)	
	368.0; 3.58	372.0; 3.58	372.5; 3.56	378.0; 3.58
	445.0; 3.55	457.0; 3.65	450.0; 3.50	462.0; 3.63
Co(III) complex	228.5; 4.54		(227; 4.52)	
	253.0; 4.51	256.5; 4.71	248.5; 4.55	
	(263.5)	(264.5)	(262.5)	(264)
	(270)	(271)	(269)	(270)
	(308)	(308)	(300)	(300)
	(338; 3.82)	(340; 3.88)	341; 3.84	343; 3.88
	(410—470)	(410—470)	(410—460)	(410—460)
	608; 2.2	608; 2.35	595; 2.28	596; 2.28

Shoulder or indistinct bands are enclosed in parentheses.

Spectral Measurements.—The ultraviolet and visible spectra of the metal complexes were measured by standard methods, using a Hitachi ESP-2 type recording spectrophotometer. Ethanol, *n*-hexane and chloroform were used as solvents in this study.

Results and Assignments

The absorption spectra of 3-phenyl- and 3-benzyl-2, 4-pentanedione and of the corresponding enolate ions are illustrated in Fig. 1, along with that of 3, 3-dibenzyl-2, 4-pentanedione. The spectra of the trivalent metal complexes of 3-phenyl- and 3-benzyl-2, 4-pentanedione are shown in Figs. 2 through 5. It may be seen that these absorption spectra of metal complexes are generally similar to the corresponding 2, 4-pentanedione complexes. The significant peaks of the absorption spectra of the ligands and the metal complexes are listed in Tables II and III respectively.

Ligands.—The $\pi_3 \rightarrow \pi_4$ transition band of acetylacetone was observed to shift to a longer wavelength upon replacement of the γ-hydrogen with either phenyl or benzyl group. Besides this profound band, several indistinct shoulders, which are due to $\pi \rightarrow \pi^*$ transitions in a benzene ring system, were observed. Among several shoulders which appeared in the 249—274 mμ range in the spectrum of 3-benzyl-2, 4-pentanedione, 263 and 269 mμ bands were noticed as being most intense. On the other hand, in 3, 3-dibenzyl-2, 4-pentanedione there are three distinct bands, of nearly identical intensity, at 253.3, 258.9 and 264.7 mμ in ethanol; this is because of the absence of its enol form. These $\pi \rightarrow \pi^*$ bands are located on the longer wavelength side relative to the secondary bands (^1L_b) of benzene itself.

Although 3-phenyl-2, 4-pentanedione seems to demonstrate shoulder bands due to a similar electronic transition in approximately the same range, the definite position of these bands could not be detected clearly. In 3-phenyl-2, 4-pentanedione, several indistinct shoulders were also observed in the 227—243 mμ range; they may

TABLE IV. ABSORPTION BANDS IN 2, 4-PENTANEDIONE COMPLEXES AND THEIR ASSIGNMENTS

Metal complex	λ_{max}(mμ) Ethanol This work	Ethanol Literature (4)	Ethanol Literature (3)	Chloroform This work	Chloroform Literatuer (3)	Assignment of transition
Al(III)	287.0* (300)		288			$\pi_3 \to \pi_4$
Cr(III)	256.5	255				$\pi_3(e) \to \pi_4(a_1)$
	272	270				$\pi_3(e) \to \pi_4(e)$ $\pi_3(a_2) \to \pi_4(a_1)$
	(295)	(295)				$\pi_3(a_2) \to \pi_4(e)$
	335	332	336			$d_\varepsilon(a_1) \to \pi_4(e)$ $d_\varepsilon(e) \to \pi_4(a_1)$
		380		376	374	$d_\varepsilon(e) \to \pi_4(e)$
		388		384	382	
				391	388	
		(410)		(412), (435)	410	${}^4A_{2g} \to {}^4T_{1g}$
		560		560	560	${}^4A_{2g} \to {}^4T_{2g}$
Fe(III)	237	235	237			$\pi_3(e) \to \pi_4(a_1)$
	274	272	274		273	$\pi_3(e) \to \pi_4(e)$ $\pi_3(a_2) \to \pi_4(a_1)$
	(295)					$\pi_3(a_2) \to \pi_4(e)$
	354	351	354[1)]		353	$d_\varepsilon(a_1) \to \pi_4(e)$ $d_\varepsilon(e) \to \pi_4(a_1)$
	437	431	435[1)]		437	$n \to d^*$
					725	${}^6A_{1g} \to {}^4T_{2g}$
					975	${}^6A_{1g} \to {}^4T_{1g}$
Co(III)	230	228	228			$\pi_3(e) \to \pi_4(a_1)$
	258	256	257			$\pi_3(e) \to \pi_4(e)$ $\pi_3(a_2) \to \pi_4(a_1)$
	(295)	(295)				$\pi_3(a_2) \to \pi_4(e)$
	326	323				$d_\varepsilon(a_1) \to \pi_4(e)$ $d_\varepsilon(e) \to \pi_4(a_1)$
				(405—440)	(400)	$d_\varepsilon(e) \to \pi_4(e)$ ${}^1A_{1g} \to {}^1T_{2g}$
				595	592	${}^1A_{1g} \to {}^1T_{1g}$

Shoulder bands are given in parentheses.
* log ε, 4.61

be attributed to the primary bands (${}^1L_a$) in the benzene π-system.

The $n \to \pi^*$ forbidden transition in the ketonic forms of the present ligands is expected to appear on a longer wavelength side of the $\pi \to \pi^*$ transition band. Nevertheless, this band of a rather low intensity seems to be hidden by the intense $\pi \to \pi^*$ bands. On the other hand, the $n \to \pi^*$ band with a maximum at 301 mμ in n-hexane was clearly observed in 3, 3-dibenzyl-2, 4-pentanedione, and it demonstrated a significant solvent effect, which resulted in a blue shift to 294 mμ in ethanol.

In the presence of sodium ethoxide, the enolate ions are formed, and the $\pi \to \pi^*$ transition bands shift to longer wavelengths, i. e., to 306.5 mμ in the 3-phenyl derivative and to 309 mμ in the 3-benzyl; also, their intensities increase.

Aluminum Complexes.—The general appearance of the absorption spectra is quite similar to that of the respective free ligand species. The $\pi_3 \to \pi_4$ band upon chelation shifts to a wavelength shorter by 850 cm^{-1} with respect to the enolate ion. Also, the γ-substituent tends to shift the $\pi_3 \to \pi_4$ transition band to a longer wavelength with respect to the acetylacetonate complex; 1670 cm^{-1} with a benzyl group and 1400 cm^{-1} with a phenyl, while the benzyl group obviously has a greater effect on the π-energy level. The secondary bands (${}^1L_b$) of the benzene ring appear in the 3-benzyl-2, 4-pentanedione complex as shoulders located at 264 and 270 mμ, while the phenyl derivative demonstrates in its spectrum the first primary band (${}^1L_a$) of a phenyl substituent at 231.5 mμ.

Chromium Complexes.—The general appearance of the absorption spectra of transition metal complexes is quite different from those of non-transition metal complexes, such as aluminum complexes. The splittings of the $\pi \to \pi^*$ band caused by the π-interaction between metal and ligand, and the appearance of electron transfer bands ($d_\varepsilon \rightarrow \pi^*$) and of $d_\varepsilon \rightarrow d_\gamma$ bands brought about by a ligand field are characteristic of the absorption spectra of transition metal complexes. The general trend of the absorption spectra of trivalent metal complexes of the present ligands is quite similar to that of the corresponding acetylacetonate complexes. Therefore, the results of

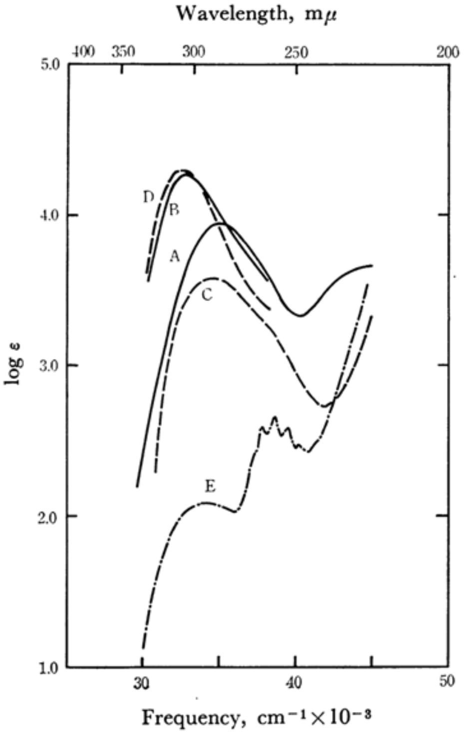

Fig. 1. Absorption spectra of 2,4-pentanediones in ethanol: A, 3-phenyl-2,4-pentanedione; B, 3-phenyl-2,4-pentanedione with sodium ethoxide; C, 3-benzyl-2,4-pentanedione; D, 3-benzyl-2,4-pentanedione with sodium ethoxide; E, 3,3-dibenzyl-2,4-pentanedione.

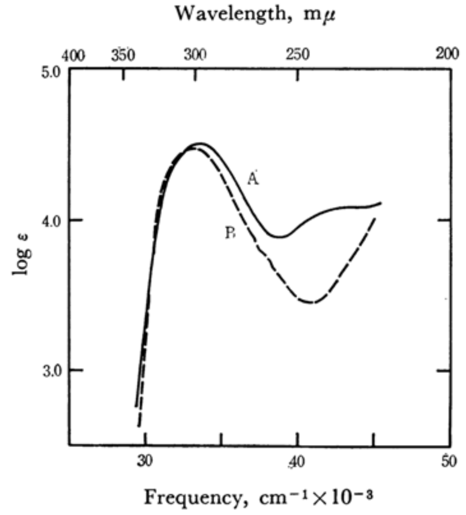

Fig. 2. Absorption spectra of aluminum(III) complexes in ethanol: A, tris(3-phenyl-2,4-pentanediono)aluminum(III); B, tris(3-benzyl-2,4-pentanediono)aluminum(III).

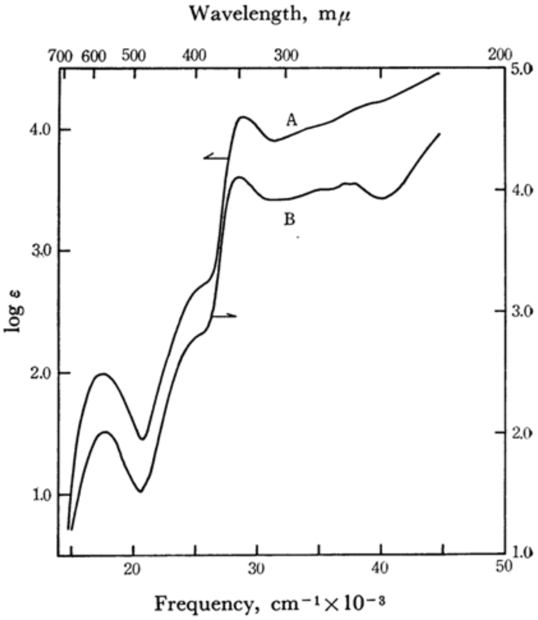

Fig. 3. Absorption spectra of chromium(III) comlexes in ethanol: A, tris(3-phenyl-2,4-pentanediono)chromium(III); B, tris(3-benzyl-2,4-pentanediono)chromium(III).

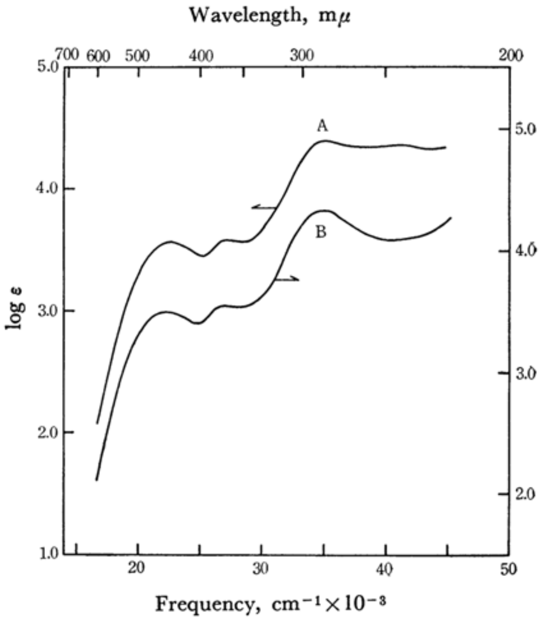

Fig. 4. Absorption spectra of iron(III) complexes in ethanol: A, tris(3-phenyl-2,4-pentanediono)-iron(III); B, tris(3-benzyl-2,4-pentanediono)iron-(III).

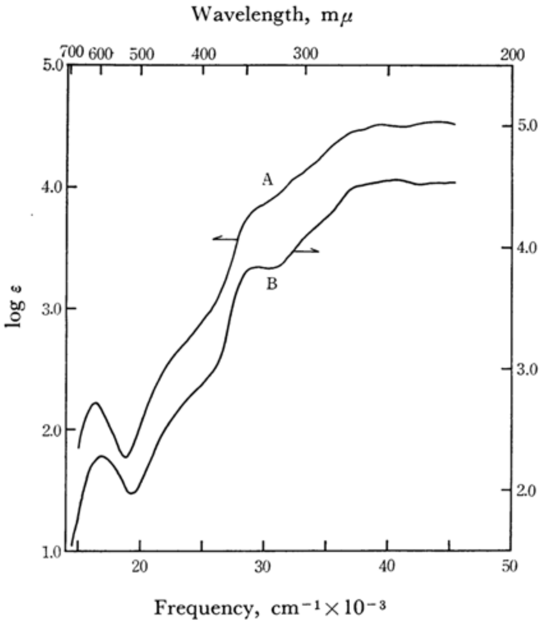

Fig. 5. Absorption spectra of cobalt(III) complexes in ethanol: A, tris(3-phenyl-2, 4-pentanediono)cobalt(III); B, tris(3-benzyl-2, 4-pentanediono)cobalt(III).

the Hückel LCAO-MO calculation carried out by Barnum$^{5)}$ are referred to in the assignment of absorption bands in this work.

The 3-phenyl derivative shows extremely broad bands in the ultraviolet region of its electronic spectrum due to the presence of $\pi\rightarrow\pi^*$ transition bands of a phenyl ring. Thus, the assignment of $\pi_3\rightarrow\pi_4$ bands would involve some uncertainty due to the lack of an exact resolution of absorption bands. The 258 mμ band in ethanol is tentatively assigned to the $\pi_3(e)\rightarrow\pi_4(a_1)$ transition. In the range of $\pi_3(e)\rightarrow\pi_4(a_1)$ transition for the 3-benzyl-2, 4-pentanedione complex, three absorption bands appeared at 257, 265 and 270 mμ; of these, the first one was found to be a weak shoulder. Some of these bands (most likely the latter two) are presumably due to the $\pi\rightarrow\pi^*$ secondary bands (^1L_b) of the benzene ring. The 289 and the 310 mμ bands in the phenyl derivative, and the 285 and the 318 mμ bands in the benzyl (when ethanol is used as a solvent), all of which appeared as shoulders, were assigned to the $\pi_3(e)\rightarrow\pi_4(e)$ overlapped with $\pi_3(a_2)\rightarrow\pi_4(a_1)$ and the $\pi_3(a_2)\rightarrow\pi_4(e)$ transitions respectively. All these $\pi_3\rightarrow\pi_4$ bands shifted to longer wavelengths upon replacement at the 3-position, with reference to those of the 2, 4-pentanedione complex.

Electron transfer ($d_\varepsilon\rightarrow\pi_4$ transition) bands were also observed to shift to longer wavelengths upon replacement of the 3-position, relative to the parent complex. The overlapping $d_\varepsilon(a_1)\rightarrow\pi_4(e)$ and $d_\varepsilon(e)\rightarrow\pi_4(a_1)$ transitions are attributed to the 348 mμ band and the 352 mμ band, while the $d_\varepsilon(e)\rightarrow\pi_4(e)$ transition are attributed to the 395 mμ shoulder band and the 400 mμ shoulder band in the phenyl and the benzyl derivative respectively.

The first $d\rightarrow d^*$ ($^4A_{2g}$—$^4T_{2g}$) transition lies at 575 and 565 mμ in the phenyl and the benzyl derivative respectively. On the other hand, a shoulder lying in 410—440 mμ for the phenyl derivative and one in 420—445 mμ for the benzyl are assigned to the second $d\rightarrow d^*$ band. Since 2, 4-pentanedione has been shown to be placed in the spectrochemical series$^{11)}$ in the neighborhood of oxalate and water, the second $d\rightarrow d^*$ ($^4A_{2g}\rightarrow{}^4T_{1g}$) transition is expected to lie close to the 416 mμ band of the oxalate complex$^{12)}$ or to the 407 mμ band of the aqueous complex.$^{12)}$ In addition, Sone$^{13)}$ suggested that the following relationship holds among the first and the second bands for the chromium(III) complex:

$$\nu_2 = 1.117\,\nu_1 + 13.06$$

where ν_1 and ν_2 represent the first and the second bands in the frequency unit (10^{13} sec^{-1}) respectively. From this equation, the second bands for both the phenyl and benzyl derivatives may be expected to appear in the vicinity of 420 mμ. Thus, the above assignment for the second $d\rightarrow d^*$ band seems reasonable.

Cobalt Complexes.—The $\pi_3(e)\rightarrow\pi_4(a_1)$, $\pi_3(e)\rightarrow\pi_4(e)$ overlapped with $\pi_3(a_2)\rightarrow\pi_4(a_1)$, and the $\pi_3(a_2)\rightarrow\pi_4(e)$ transitions are believed to lie, respectively, at 228.5, 253, and 308 mμ (as a slight shoulder) in the phenyl derivative, and at 227, 248.5, and 300 mμ (as a slight shoulder) in the benzyl derivative. The first and second transition bands are shifted to shorter wavelengths with reference to those of the 2, 4-pentanedione complex. On the longer wavelength side of the $\pi_3(e)\rightarrow\pi_4(e)$ and $\pi_3(a_2)\rightarrow\pi_4(a_1)$ bands in both complexes, there exist several shoulder bands, among which the 263 mμ and the 270 mμ band are most likely to be ascribed to the secondary band (^1L_b) of a benzene.

The $d_\varepsilon\rightarrow\pi_4$ ($a_1\rightarrow e$, $e\rightarrow a_1$) band in the phenyl and benzyl derivatives shifted to longer wavelengths, at 338 (shoulder) and 341 mμ respectively, with reference to that in the 2, 4-pentanedione complex. On the longer wavelength side of these $d_\varepsilon\rightarrow\pi_4$ bands, there were observed very broad shoulders in which the $d_\varepsilon(e)\rightarrow\pi_4(e)$ charge transfer band and the second $d\rightarrow d^*$ ($^1A_{1g}\rightarrow{}^1T_{2g}$) band are expected to be involved. According to the LCAO-MO calculation for the 2, 4-pentanedione complex,$^{5)}$ the $d_\varepsilon(e)\rightarrow\pi_4(e)$ band for this complex

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11) Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).

12) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge (1961), p. 425.

13) K. Sone, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **71**, 271, 316 (1950).

is expected to lie around 400 mμ, although only a shoulder was observed in this range. Meanwhile, Shimura and Tsuchida[11] assigned the 405 mμ band in the 2, 4-pentanedione complex to the second $d \to d^*$ transition. On the other hand, Sone[13] has proposed a relationship which may correlate the first $d \to d^*$ band with the second:

$$\nu_2 = 1.189\,\nu_1 + 13.31$$

(ν_1 and ν_2: frequency in 10^{13} sec^{-1} unit)

The first band ($^1A_{1g} \to {}^1T_{1g}$) for the 2, 4-pentanedione complex, and the 3-phenyl- and 3-benzyl-2, 4-pentanedione complexes were observed at 595, 608 and 596 mμ (in chloroform) respectively. Thus, the second bands for these complexes are expected to lie in the 410—420 mμ range. Nevertheless, no unambiguous assignment was made because of the broadness of the absorption spectra in this range, as has been mentioned above.

Iron Complexes.—All the absorption bands in the 3-phenyl- and the 3-benzyl-2, 4-pentanedione complexes were observed to shift to longer wavelengths with reference to the corresponding bands in the 2, 4-pentanedione complex, as is shown in Table III and Fig. 4. The $\pi_3(e) \to \pi_4(a_1)$ and the $\pi_3(e) \to \pi_4(e)$ and $\pi_3(a_2) \to \pi_4(a_1)$ bands are believed to be located at 247 and 284 mμ in the phenyl derivative, and at 240 (shoulder) and 286 mμ in the benzyl derivative, respectively. Two distinct bands appear in the visible region for each iron complex of 2, 4-pentanedione derivatives. The absorption bands lying around the 370 mμ range are assigned to the $d_\varepsilon(a_1) \to \pi_4(e)$ and $d_\varepsilon(e) \to \pi_4(a_1)$ transitions. Barnum[4,5] has not made any assignment for the 437 mμ band in the 2, 4-pentanedione complex. The corresponding bands in the phenyl and benzyl derivatives are, respectively, at 445 and 450 mμ in ethanol. The magnitudes of these spectral shifts from the corresponding band in the 2, 4-pentanedione complex are 400 and 700 cm^{-1} for the phenyl and the benzyl derivatives respectively. Although the direction of the band shift is the same as that of the $d \to \pi^*$ bands, its magnitude is smaller than that of the latter (1100 cm^{-1} for the phenyl derivative, and 1400 cm^{-1} for the benzyl). In addition, as the polarity of a solvent increases, the band tends to shift to a shorter wavelength; there is also a decrease in its intensity. This solvent effect seems to be, in general, characteristic of an electronic transition involving a nonbonding electron, while $d \to \pi$ bands do not show such a strong solvent-dependency. Thus, a band appearing in the 450 mμ range is considered to be due to the $n \to d_\gamma$ transition, in which oxygen n-electrons are involved.

The $d \to d^*$ transitions ($^6A_{1g} \to {}^4T_{1g}$, and $^6A_{1g} \to {}^4T_{2g}$) are expected to lie in a region with much longer wavelengths; they were not observed in the present measurements.

Discussion

Ligands.—An absorption band characteristic of β-diketones is generally subject to the solvent effect which controls their keto-enol isomerism. This absorption band consists of two components: a $\pi \to \pi^*$ transition of an enol form, and a $n \to \pi^*$ forbidden transition of the corresponding keto-form, which appears on the longer-wavelength side of the former. 3-Phenyl-2, 4-pentanedione shows an absorption band at 284 mμ in n-hexane which shifts to a slightly longer wavelength with a somewhat decreased intensity in ethanol. As far as the spectral shift is concerned, the same solvent-dependency was observed for 3-benzyl-2, 4-pentanedione. However, the absorption intensity for this ligand decreases in ethanol to a greater extent than for 3-phenyl-2, 4-pentanedione. This suggests that the enol component of the latter diketone may be predominant in ethanol,* though in general polar solvents stabilize a keto-form. On the other hand, the 3-benzyl derivative increases its keto component when the solvent is changed from n-hexane to ethanol.

$\pi \to \pi^*$ Bands.—The spatial configuration of a phenyl ring relative to the chelate ring in a 3-phenyl-2, 4-pentanedione complex seems to control the extent of π-interaction among these groups. Such a π-interaction among these two groups would not be as strong as among the two phenyl groups in biphenyl, or as among olefinic and phenyl groups in styrene, since the latter two molecules show an absorption band in the range around 250 mμ,[14] while in a 3-phenyl-2, 4-pentanedione complex no such band exists in that range. In 2, 6-dimethylbiphenyl the inter-ring resonance may be reduced to a certain extent by the twist of both rings from coplanarity. Such a diminished π-interaction makes the absorption band appear in the 240 mμ range[15] as a shoulder, which is assigned to the first primary band (^1L_a) of a benzene ring in this substituted biphenyl. Meanwhile, in the aluminum complex of 3-phenyl-2, 4-pentanedione the steric interaction among a phenyl ring and two methyl groups on the chelate ring tends to twist both phenyl and chelate rings. However, such a fairly large deviation from coplanarity will not destroy all of the inter-ring resonance interaction, since the aluminum complex shows a $\pi \to \pi^*$ transition band at 231.5 mμ. In other transition metal complexes of the same ligand, absorption bands are broad and intense in the 240—250 mμ range in comparison with those of the corresponding metal complexes of 2, 4-pentanedione and of 3-benzyl-2, 4-pentanedione. The breadth of absorption bands in such a range

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* This keto-enol isomerism was studied in this laboratory by means of infrared and NMR spectroscopies. These results will be described in a forthcoming paper.

[14] H. E. Ungnarde, Ed., " Organic Electronic Spectral Data," Vol. II, Interscience Publishers, New York (1957), pp. 130, 295.

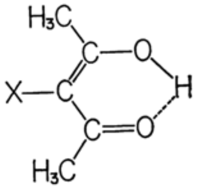
may be ascribed to the existence of the primary band (^1L_a) of a benzene ring in addition to the $\pi\rightarrow\pi^*$ bands of the chelate ring. From the observations mentioned above, the inter-ring π-interaction remains to a limited extent in the metal complexes of 3-phenyl-2, 4-pentanedione. Meanwhile, this inter-ring π-interaction may help to raise the π_3 orbital of the chelate ring to a higher energy, thus shifting the $\pi_3\rightarrow\pi_4$ band to a longer wavelength.

In the metal complexes of 3-benzyl-2, 4-pentanedione, both the hyperconjugation and inductive effects of the methylene group may raise the π_3 level to a higher energy.

The enolate ions of β-diketones decrease their delocalization energy upon chelation with either hydrogen or aluminum. The enol-forms of β-diketones show their $\pi\rightarrow\pi^*$ band at shorter wavelengths relative to the corresponding enolate ions. The magnitude of such a spectral shift follows the sequence:

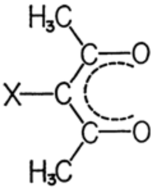
2, 4-pentanedione > 3-phenyl-2, 4-pentanedione >
2700 cm^{-1} 2400 cm^{-1}
3-benzyl-2, 4-pentanedione
2250 cm^{-1}

Such a great loss of delocalization energy in the enol forms of β-diketones (structure I) is consistent with the fact that an enolic proton is located closer to one oxygen than the other, that the two C–C bonds are not equivalent to each other in bonding character, and that neither are the two C–O bonds. Meanwhile, an identical bond character is expected for the C–C bonds and also for the C–O bonds in the enolate ion, as is illustrated by structure II.



(I)

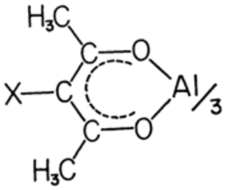
X = H, phenyl, benzyl



(II)

X = H, phenyl, benzyl

On the other hand, upon chelation with the aluminum ion, the $\pi\rightarrow\pi^*$ band shifts to a wavelength lower by 850 cm^{-1} than that of the corresponding enolate ion, regardless of the ligand species. The substituent effect on the chelate ring, therefore, seems parallel to that on the enolate ion. This leads one to the conclusion that π-electrons in the ligand part remain delocalized much like those in the corresponding enolate ion, even when the coordinate bonds are formed among an aluminum ion and carbonyl oxygens. The structure of such a chelate ring of the aluminum complexes may be represented by III.



(III)

X = H, phenyl, benzyl

The metal-ligand π-interaction in transition metal complexes results in a splitting of the $\pi_3\rightarrow\pi_4$ band, and in a shift of these $\pi_3\rightarrow\pi_4$ transitions to higher energies. The magnitude of the spectral shift to a lower wavelength was found to depend on the number of d_ε electrons that the central metal ion possesses, as has been observed in the 2, 4-pentanedione complexes.[4,5] Thus, the $\pi_3\rightarrow\pi_4$ transitions in the trivalent metal complexes of the present 2, 4-pentanedione derivatives have been found to appear in this increasing order of energy:

$$\mathrm{Cr} < \mathrm{Fe} < \mathrm{Co}$$

In the iron and chromium complexes, each $\pi_3\rightarrow\pi_4$ transition band was observed to shift to a longer wavelength as the ligand varies in this order: 2,4-pentanedione, 3-phenyl-2, 4-pentanedione, and 3-benzyl-2, 4-pentanedione. On the other hand, both the $\pi_3(e)\rightarrow\pi_4(a_1)$ band, and the $\pi_3(e)\rightarrow\pi_4(e)$ combined with $\pi_3(a_2)\rightarrow\pi_4(a_1)$ band in the cobalt complexes shift in the reverse direction in the same order. In the transition metal complexes, the metal-ligand π-interaction has a major effect on the $\pi_3\rightarrow\pi_4$ transition, and it seems to increase with respect to the ligands in this order: 2, 4-pentanedione, 3-phenyl-2, 4-pentanedione, and 3-benzyl-2, 4-pentanedione. As each $\pi_3\rightarrow\pi_4$ transition band in a complex shifts to a shorter wavelength with reference to the enolate ion of the corresponding ligand, the comparison of the size of these spectral shifts may give the extent of metal-ligand π-interaction. Thus, a 3-benzyl-2, 4-pentanedione complex in general shows the greatest spectral shift among the corresponding metal complexes of three different 2, 4-pentanediones, while a metal complex of the 3-phenyl derivative comes next. For example, the $\pi_3(e)\rightarrow\pi_4(a_1)$ band in cobalt complexes shifts to a wavelength shorter from the

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[15] G. H. Beaven, "Steric Effects in Conjugated Systems," Butterworths, London (1958), Chapter 3.

enolate ion by 9500 cm^{-1} with 2, 4-pentanedione as the ligand, by 11000 cm^{-1} with 3-phenyl-2, 4-pentanedione, and by 12000 cm^{-1} with the 3-benzyl derivative.

It may be concluded that the $\pi_3 \rightarrow \pi_4$ transition is affected by either or both of the two major effects of a substituent at the 3-position of 2, 4-pentanedione:

(1) A substituent tends to raise the π_3 level of the chelate π-orbitals to a higher energy, either through the π-interaction with the chelate ring or its inductive effect on the chelate ring. As a result, a $\pi_3 \rightarrow \pi_4$ band shifts to a longer wavelength.

(2) Such π_3-orbitals that were raised to a higher energy may interact with the d_ε-orbitals. This interaction lowers the energy of the π_3-orbitals on the one hand and raises that of the d_ε-orbitals on the other. This effect results in a shift of the $\pi_3 \rightarrow \pi_4$ transition to a higher energy.

In the transition metal complexes, both of the substituent effects may come into play in the $\pi_3 \rightarrow \pi_4$ transitions, while the first effect is expected to be predominant in the aluminum complexes and the enolate ions. Upon substitution at the 3-position of 2, 4-pentanedione, the spectral shift toward a longer wavelength was observed to be greater in the aluminum complexes and the enolate ions than in the transition metal complexes. This experimental fact can be understood from the above point of view.

Meanwhile, the greatest metal-ligand π-interaction is expected in the cobalt complexes as a result of the presence of the largest number of d_ε electrons. In this instance, the second substituent effect may prevail over the first one and $\pi_3 \rightarrow \pi_4$ transition bands may tend to shift to a lower wavelength upon substitution.

In general, the solvent effect tends to shift the $\pi \rightarrow \pi^*$ band to a longer wavelength in a solvent with a higher polarity. In fact, the $\pi \rightarrow \pi^*$ bands of the ligands (the enol form) appear on the longer wavelength side in ethanol relative to those measured in *n*-hexane, as is shown in Table II. On the other hand, it is interesting to note that the reverse spectral shifts were observed in the metal complexes when the solvent was changed from chloroform to ethanol.

$d_\varepsilon \rightarrow \pi_4$ Bands.—These transition bands tend to shift to lower energies upon substitution at the 3-position of 2, 4-pentanedione. The magnitudes of such spectral shifts in metal complexes are approximately 1100 cm^{-1} with a phenyl group and 1350—1450 cm^{-1} with a benzyl with reference to the corresponding bands in 2, 4-pentanedione complexes, regardless of the metal ions employed. These phenomena are most likely caused by electronic interaction among d_ε and π_3 orbitals, which raises d_ε orbitals to a higher energy. As for the metal species concerned, the $d_\varepsilon \rightarrow \pi_4$ transition energy is greatest for the cobalt complexes and least for the iron complexes.

$d \rightarrow d^*$ Bands.—From the first $d \rightarrow d^*$ bands observed for the cobalt and chromium complexes, 2, 4-pentanedione and its 3-benzyl derivative may be inferred to occupy a higher position relative to 3-phenyl-2, 4-pentanedione in the spectrochemical series. However, the strength of the coordinate bonds may not be directly related to the value of Δ, the energy difference between the d_ε and the d_γ orbitals, as the crystal field theory would predict. Since the metal-ligand π-interactions are involved[4,5] in these transition metal complexes, it is rather difficult to estimate the hypothetical crystal field effects of these ligands which may be expected in the absence of π-interaction.

Infrared and NMR studies of these trivalent metal complexes, as well as similar spectroscopic studies of some divalent metal complexes, are now in progress in this laboratory; these results will be described in a forthcoming paper.