

Evidence for such an intermediate has been presented by Wood and Higginson,<sup>21</sup> who proposed a similar complex as the product of the electron-transfer reaction between chromium(II) and tris(oxalato)cobaltate(III). Wood and Higginson reported that this intermediate slowly changes to the *cis*-bis(oxalato)diaquochromate(III) ion and that this change is accelerated by chromium(II). Cursory experiments in this laboratory<sup>22</sup> have produced results in agreement with the

(21) P. B. Wood and W. C. E. Higginson, *J. Chem. Soc., A.*, 1645 (1966).

(22) M. Frank, C. Pasquale, and D. H. Huchital, work in progress.

data of Wood and Higginson. Preliminary experiments have produced a rate constant for the chromium(II)-accelerated formation of *cis*-Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> of ca. 5.0 M<sup>-1</sup> sec<sup>-1</sup>. Taking this value for *k*<sub>4</sub> in eq 6 and 7 with *k*<sub>3</sub> (0.11 M<sup>-1</sup> sec<sup>-1</sup>) ≈ *k*<sub>-4</sub> (0.17 M<sup>-1</sup> sec<sup>-1</sup>) readily explains our inability to detect the intermediate (I).<sup>23</sup> Further work on the structure and reactions of the proposed intermediate is being carried out.

(23) Since *K*<sub>eq</sub> (= [*cis*]/[*trans*]) ≫ 1, as indicated by spectral measurements, *k*<sub>-3</sub> must be ≪ 1. Thus, any intermediate formed reacts rapidly with Cr<sup>2+</sup> to give the *cis* product.

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## Ligand Field Information from Charge-Transfer Spectra of Substituted Tris(1,3-diketonato)iron(III) Chelates. Spectrochemical Series for 1,3-Diketones

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Received September 29, 1969

A series of tris(1,3-diketonato)iron(III) chelates has been prepared in which the 1,3-substituents are CH<sub>3</sub>, CF<sub>3</sub>, and C<sub>6</sub>H<sub>5</sub>. The spectra of this series in the 20–38-kK region were studied in order to make assignments based on the expected electronic effect of the substituents. Three electronic transitions can be successfully treated using a simple one-electron molecular orbital scheme. The data presented support the assignment of the most intense band between 30 and 37 kK to the intraligand π→π\* transition. The other two bands in this region are assigned to a metal-to-ligand (t<sub>2g</sub> → π\*) charge transfer between 24 and 29 kK, and a ligand-to-metal (π → e<sub>g</sub>) charge transfer between 20 and 23 kK. These assignments are justified on the basis of the relative energy separations in the simplified molecular orbital diagram. In connection with these energy separations, a spectrochemical series for the substituted 1,3-diketones was developed from the visible spectra of the corresponding Cr(III) chelates. The octahedral splitting parameter, Δ, for the Fe(III) chelates was then calculated using the relationship Δ = g(metal ion)/f(ligand). The energy separations (π - t<sub>2g</sub>) and (e<sub>g</sub> - π\*) were determined from the charge-transfer spectra. The sum (π - t<sub>2g</sub>) + Δ + (e<sub>g</sub> - π\*) agrees very well with the observed π → π\* transition energy. In terms of ligand field effects, the CF<sub>3</sub> substituent on the chelate ring destabilizes all the metal levels relative to CH<sub>3</sub>. The phenyl substituent stabilizes the metal levels relative to CH<sub>3</sub>.

### Introduction

A number of studies dealing with the electronic absorption spectra of the first-row transition metal acetylacetonates have been reported. Most of the results have been reviewed by Fackler.<sup>1</sup> The electronic structure of these chelates is of sufficient interest to prompt several workers to undertake orbital calculations using various degrees of sophistication.<sup>2–4</sup> As a result of experimental and theoretical work, many spectral assignments appear certain. On the other hand, several assignments are still the subject of controversy. The spectrum of Fe(acac)<sub>3</sub> is not yet clearly understood. There is general agreement that the intense absorption at 36,600 cm<sup>-1</sup> is due to a π → π\* transition on the ligand. It is also reasonably well established that the absorption at 28,300 cm<sup>-1</sup> is a t<sub>2g</sub> → π\* charge transfer. The other intense band at 22,800 cm<sup>-1</sup> has been variously assigned to an anomalous peak,<sup>3</sup> π → t<sub>2g</sub>,<sup>4</sup> and

O<sub>n</sub> → e<sub>g</sub> charge transfer.<sup>5</sup> Clearly, one problem in assigning charge-transfer transitions is the limited knowledge about the energy differences between electrons located mainly on the ligand and those mainly on the metal. This study was undertaken to make definitive assignments in the charge-transfer region for tris(1,3-diketonato)iron(III) chelates, based on the effect of systematic substitution on the 1,3-diketonate ring. Making assignments on the basis of spectral shifts would be facilitated if the ligand field splitting parameters, Δ, were known for the series. Since the spin-forbidden "d-d" transitions are not easily observed, it is difficult to determine Δ directly in these iron(III) chelates. Therefore, an initial phase of this study involved developing a spectrochemical series for substituted 1,3-diketones from which the values of Δ could be calculated.

### Experimental Section

The Fe(III) and Cr(III) chelates were synthesized using

(1) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 403 (1966).

(2) R. H. Holm and F. A. Cotton, *J. Amer. Chem. Soc.*, **80**, 5658 (1958).

(3) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 22 (1961); **22**, 183 (1961).

(4) I. Hanazaki, F. Hanazaki, and S. Nagkura, *J. Chem. Phys.*, **50**, 265, 276 (1969).

(5) Y. Murakami and K. Nakamura, *Bull. Chem. Soc. Jap.*, **39**, 901 (1966).

TABLE I  
 ANALYSES, MELTING POINTS, AND REFERENCES TO SYNTHESSES

Compound	%C		%H		Mp, °C	Ref
	Found	Calcd	Found	Calcd		
Fe(acac) <sub>3</sub>	51.35	51.0	6.07	6.0	189	6
Fe(TFA) <sub>3</sub>	35.18	35.0	2.54	2.3	114	7
Fe(HFA) <sub>3</sub>	26.3	26.6	0.73	0.4	47	10
Fe(BzA) <sub>3</sub>	66.41	66.6	5.05	5.0	218	8
Fe(DBM) <sub>3</sub>	74.39	74.5	4.55	4.5	264	8
Fe(BzTFA) <sub>3</sub>	52.24	51.4	2.83	2.6	140	8
Cr(HFA) <sub>3</sub>	26.67	26.8	0.57	0.5	84	10
Cr(BzTFA) <sub>3</sub>	52.50	51.6	3.14	2.6	169	9
Cr(acac) <sub>3</sub>	51.40	51.6	6.10	6.0	216	11

methods available in the literature. In Table I references<sup>6-11</sup> are given to actual preparations used or to preparations adapted for different ligands. The ligands used and the abbreviations employed are as follows: 2,4-pentanedione anion (acac<sup>-</sup>), 1,1,1-trifluoro-2,4-pentanedione anion (TFA<sup>-</sup>), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione anion (HFA<sup>-</sup>), 1 phenyl-1,3-butanedione anion (BzA<sup>-</sup>), 1,3-diphenyl-1,3-propanedione anion (DBM<sup>-</sup>), and 1-phenyl-4,4,4-trifluoro-1,3-butanedione anion (BzTFA<sup>-</sup>).

The spectra were recorded using a Cary 14 spectrophotometer. All solutions were prepared from spectral grade solvents.

### Results

The spectra of the iron(III) chelates in the 20–38-kK region in chloroform are shown in Table II. The spec-

 TABLE II  
 ELECTRONIC ABSORPTION SPECTRA IN THE 20–38-kK REGION  
 FOR VARIOUS TRIS(1,3-DIKETONATO)IRON(III) CHELATES  
 (IN CHLOROFORM)

Compound	Wave- number, kK	Log ε	Compound	Wave- number, kK	Log ε
	Fe(acac) <sub>3</sub>	36.6		4.5	Fe(DBM) <sub>3</sub>
	28.3	3.7		24.5	3.3
	22.9	3.7		20.5	3.1
Fe(TFA) <sub>3</sub>	36.1	4.1	Fe(BzTFA) <sub>3</sub>	32.7	4.4
	27.2	3.7		25.0	3.4
	22.8	3.6		21.7	3.4
Fe(HFA) <sub>3</sub>	35.2	4.4	Fe(3-Pacac) <sub>3</sub> <sup>a</sup>	35.2	4.4
	26.1	3.6		26.9	3.6
	22.4	3.6		21.9	3.6
Fe(BzA) <sub>3</sub>	33.3	4.2	Fe(3-Bacac) <sub>3</sub> <sup>a</sup>	35.0	4.4
	25.9	3.4		26.5	3.6
	22.2	3.1		21.6	3.6

<sup>a</sup> Fe(3-Pacac)<sub>3</sub> is tris(3-phenyl-2,4-pentanedionato)iron(III). Fe(3-Bacac)<sub>3</sub> is tris(3-benzyl-2,4-pentanedionato)iron(III). These spectra were reported by Murakami and Nakamura.<sup>5</sup>

tra in this region consist of three well-resolved bands. The most intense absorption occurs at energies greater than 30 kK. This absorption is assigned to a  $\pi \rightarrow \pi^*$  transition that is located largely on the ligands. The two lower energy bands, assigned to charge-transfer transitions, have almost equal extinction coefficients, but differ markedly in band widths. Of these two, the higher energy band (24–28 kK) has a width at half-height of about 2.6 kK. This absorption has been

assigned to a  $t_{2g} \rightarrow \pi^*$  charge transfer in Fe(acac)<sub>3</sub>.<sup>3</sup> The data presented in this paper are consistent with this  $t_{2g} \rightarrow \pi^*$  assignment. The width at half-height of the lower energy charge-transfer band (20–23 kK) is about 6.3 kK. This absorption is assigned to a transition from the  $\pi$ -bonding level to the antibonding metal  $e_g$  level.

According to the simple one-electron molecular orbital treatment, the sum of  $(\pi - t_{2g}) + (t_{2g} - e_g) + (e_g - \pi^*)$ , in kilokaisers, should equal the energy of the  $\pi \rightarrow \pi^*$  transition. If the assignments of the charge-transfer transitions are correct, the sum of  $(\pi - t_{2g}) + (t_{2g} - e_g) + (e_g - \pi^*)$  can be determined from the spectral data, provided the  $(t_{2g} - e_g)$  energy is known. The values of  $(t_{2g} - e_g)$ , more commonly known as  $\Delta$ , were determined indirectly since the low-energy spin-forbidden "d-d" transitions were not observed. The relationship used is described by Jørgensen<sup>12</sup>

$$\Delta = f(\text{ligand})g(\text{metal ion})$$

The  $f(\text{ligand})$  values for this series of substituted 1,3-diketones were derived from the spectra of the tris-(1,3-diketonato)chromium chelates. Inasmuch as the  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  transition in Cr(III) compounds is a direct measure of  $\Delta$ , the  $f(\text{ligand})$  value for each ligand can be calculated directly. All  $f(\text{ligand})$  values are compared to H<sub>2</sub>O which has been assigned a value of 1.00. A spectrochemical series for the substituted 1,3-diketones is presented in Table III. In this connection,

 TABLE III  
 SPECTROCHEMICAL SERIES FOR SUBSTITUTED  
 1,3-DIKETONATE LIGANDS (IN kK)

Compound	<sup>4</sup> T <sub>2g</sub> ← <sup>4</sup> A <sub>2g</sub> (Δ)	g[Cr(III)] <sup>13</sup>	Calcd	Ref
	f(ligand)		for spectra	
Cr(acac) <sub>3</sub>	17.86	17.0	1.05	This paper
Cr(TFA) <sub>3</sub>	17.75	17.0	1.04	9
Cr(HFA) <sub>3</sub>	17.48	17.0	1.03	This paper
Cr(BzA) <sub>3</sub>	17.80	17.0	1.05	8
Cr(DBM) <sub>3</sub>	17.70	17.0	1.04	9
Cr(BzTFA) <sub>3</sub>	17.55	17.0	1.03	This paper
Cr(3-Pacac) <sub>3</sub>	17.39	17.0	1.02	5
Cr(3-Bacac) <sub>3</sub>	17.70	17.0	1.04	5

the value given by Figgis for acac<sup>-</sup>,  $f(\text{ligand}) = 1.2$ , is much too large.<sup>13</sup> After computing the values of  $\Delta$ , the energies  $(\pi - t_{2g})$  and  $(e_g - \pi^*)$  can be determined from the energies of the observed transitions using the relationships

$$(\pi \rightarrow e_g) - \Delta = (\pi - t_{2g}) \text{ in kK}$$

$$(t_{2g} \rightarrow \pi^*) - \Delta = (e_g - \pi^*) \text{ in kK}$$

The results of summing  $(\pi - t_{2g}) + \Delta + (e_g - \pi^*)$  are shown in Table IV.

The difference between the sum of  $\Delta + (\pi - t_{2g}) + (e_g - \pi^*)$  and the observed  $\pi \rightarrow \pi^*$  transition energy is 1.5 kK or less. Thus, the calculated and observed  $\pi \rightarrow \pi^*$  energies are in good agreement. A probable

(12) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 113.

(13) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y., 1966, p 244.

(6) H. S. Booth and G. G. Torrey, *J. Phys. Chem.*, **35**, 2471 (1931).

(7) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 500 (1963).

(8) R. C. Fay and T. S. Piper, *ibid.*, **84**, 2303 (1962).

(9) R. Charles, *Inorg. Syn.*, **8**, 135 (1966).

(10) M. L. Morris, R. W. Moshier, and R. E. Sievers, *Inorg. Chem.*, **2**, 411 (1963).

(11) W. C. Ferneitus and J. E. Blanch, *Inorg. Syn.*, **5**, 130 (1957).

TABLE IV  
RELATIVE DIFFERENCES BETWEEN ENERGY LEVELS IN  
TRIS(1,3-DIKETONATO)IRON CHELATES (IN kK)

	$\Delta$	$\pi - t_{2g}$	$e_g - \pi^*$	Sum of $\Delta +$ $(\pi - t_{2g})$ $+ (e_g - \pi^*)$	Obsd $\pi - \pi^*$	Diff.
Fe(acac) <sub>3</sub>	14.70	8.2	13.6	36.5	36.6	0.1
Fe(TFA) <sub>3</sub>	14.62	8.2	12.6	35.4	36.1	0.7
Fe(HFA) <sub>3</sub>	14.40	8.0	11.7	34.1	35.2	1.1
Fe(BzA) <sub>3</sub>	14.66	7.5	11.3	33.5	33.3	-0.2
Fe(DBM) <sub>3</sub>	14.57	5.9	9.8	30.3	30.0	-0.3
Fe(BzTFA) <sub>3</sub>	14.45	7.2	10.6	32.3	32.7	0.4
Fe(3-Pacac) <sub>3</sub>	14.32	7.6	12.6	34.5	35.2	0.7
Fe(3-Bacac) <sub>3</sub>	14.57	7.0	11.9	33.5	35.0	1.5

reason for the difference is that the  $\pi \rightarrow e_g$  is not simple, but involves the oxygen nonbonding electrons as well. Some observations of solvent shifts for this band indicate a contribution from nonbonding electrons.<sup>5</sup> The energy values lend convincing evidence that one charge-transfer transition is a  $t_{2g} \rightarrow \pi^*$  and the other originates in the ligand  $\pi$  level (with possible contribution from  $O_n$ ) and involves the  $e_g$  level in the excited state.

There are no split bands; however, the broadness of the bands is most probably due to molecular symmetry lower than the octahedral site symmetry of the metal ion. For the purposes of this paper, however, the approximation of octahedral symmetry is used. In Figure 1, the relative positions of ligand  $\pi$ ,  $\pi^*$ , and  $O_n$  and the metal levels are presented for the symmetrically substituted compounds. In terms of ligand field effects, the phenyl groups stabilize all metal electrons equivalently. The  $CF_3$  groups destabilize all metal levels equivalently.

### Discussion

**$\pi - \pi^*$  Intraligand Transitions.**—The most intense absorption in this spectral region ( $\log \epsilon = 4.5-4.1$ ) is assigned to the intraligand  $\pi \rightarrow \pi^*$  transition. There is general agreement in the literature concerning the assignment of this absorption. The effect of the substituents at the 1, 2, or 3 position is to decrease the energy of the  $\pi \rightarrow \pi^*$  transition. This decrease is observed even though the electronic effect of the various substituent groups is expected to be considerably different. The low energy of the  $\pi \rightarrow \pi^*$  transition in the phenyl-substituted compounds may be partially explained by raising the  $\pi$  level due to the conjugative substituent. However, lowering the  $\pi^*$  level in all complexes, relative to Fe(acac)<sub>3</sub>, is undoubtedly more important. Allinger, Tai, and Miller<sup>14</sup> have explained similar energy shifts in  $n \rightarrow \pi^*$  transitions in  $\alpha$ -substituted ketones on the basis of a steric-type interaction between empty levels on the substituent and the  $\pi^*$  level of the carbonyl group. They propose this as an alternate explanation to the so-called hyperconjugation effect. The effect of the interaction is to decrease the energy of the  $\pi^*$  level. Similar shifts have been observed for phenyl

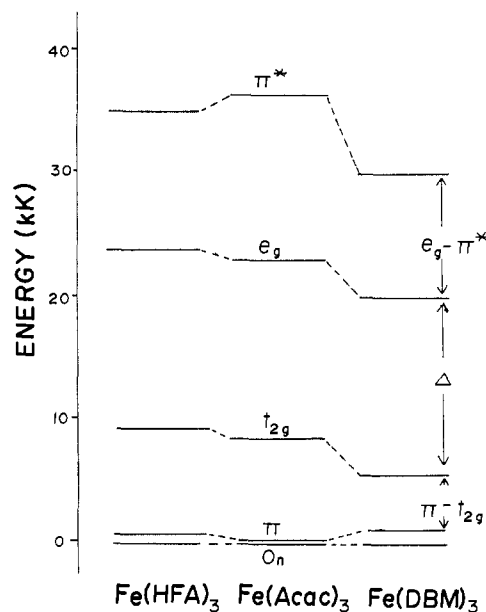


Figure 1.—Crude molecular orbital diagram of the symmetrically substituted chelates.

groups substituted  $\alpha$  to a carbonyl group.<sup>16</sup> The two  $\pi^*$  molecular orbitals in the conjugated 1,3-diketone ring can interact with substituents (in the 1, 2, or 3 position) in a similar manner, since they concentrate electron density at the five atom positions. The effect of the interaction is to lower the  $\pi^*$  energy. Thus, the calculations and observations made by Allinger, Tai, and Miller are consistent with the fact that both  $CF_3$  and  $C_6H_5$  shift the  $\pi \rightarrow \pi^*$  transition to lower energy although they are expected to have much different electronic effects on the chelate ring. The influence of the substituents is approximately additive.

**$t_{2g} \rightarrow \pi^*$  Metal-to-Ligand Charge Transfer.**—Barnum<sup>3</sup> has given convincing arguments in assigning the band at 28.3 kK in Fe(acac)<sub>3</sub> to a  $t_{2g} \rightarrow \pi^*$  metal-to-ligand charge-transfer transition. In all the spectra of chelates reported herein, this band is quite narrow (width at half-height is about 2.6 kK) indicating a transition involving relatively nonbonding electrons. It is easily observable in all spectra and is assigned, according to Barnum, to the  $t_{2g} \rightarrow \pi^*$  charge transfer. Shifts in this charge transfer as a function of ligand substitution are quite marked. An important aspect of the spectral shifts is the lowering of the  $\pi^*$  energy by the substituents. However, examination of energies of the  $\pi \rightarrow \pi^*$  and  $t_{2g} \rightarrow \pi^*$  transitions (when  $CF_3$  is substituted for methyl) shows that these two bands are shifting in the same direction, but at different rates ( $cm^{-1}/CF_3$  group). To account for different rates, one must conclude that the fluorinated ligands slightly increase the energy of the  $t_{2g}$  level relative to Fe(acac)<sub>3</sub>. Thus, two effects can account for the spectral shifts of the M-L charge transfer upon substitution of  $CH_3$  for  $CF_3$ : (1) lower energy of the  $\pi^*$  level and (2) higher energy of the  $t_{2g}$  level. In the case of the phenyl

(14) N. L. Allinger, J. C. Tai, and M. A. Miller, *J. Amer. Chem. Soc.*, **88**, 4495 (1966).

(15) (a) H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959); (b) S. MacKenzie, S. F. Marsocci, and H. C. Lampe, *J. Org. Chem.*, **30**, 3328 (1965); (c) R. C. Cookson and J. Hudec, *J. Chem. Soc.*, 429 (1962).

derivatives, the  $\pi \rightarrow \pi^*$  transition decreases rapidly with increased phenyl substitution. The  $t_{2g} \rightarrow \pi^*$  transition also decreases in energy; however, the decrease is smaller than in the  $\pi \rightarrow \pi^*$  transition. Thus, the effects of substituting phenyls for methyl groups are (1) to lower the energy of the  $\pi^*$  levels and (2) to lower the energy of the  $t_{2g}$  level. The lowering of the  $t_{2g}$  level may be caused by an enhanced  $t_{2g}-\pi^*$  interaction. This may be caused by the much lower energy of the  $\pi^*$  level in the phenyl-substituted chelates than in the  $\text{CH}_3$  or  $\text{CF}_3$  derivatives. These data are interpreted as indicating that the phenyl derivatives are  $\pi$  acceptors and the  $\text{CF}_3$  derivatives are  $\pi$  donors relative to acetylacetonate. For  $\text{Fe}(\text{HFA})_3$ , the  $t_{2g}$  level is destabilized by 0.6 kK ( $\pm \sim 0.15$  kK) relative to  $\text{Fe}(\text{acac})_3$ . For  $\text{Fe}(\text{DBM})_3$ , the  $t_{2g}$  level is stabilized by  $-2.5$  kK ( $\pm \sim 0.15$  kK) relative to  $\text{Fe}(\text{acac})_3$ .

$\pi \rightarrow e_g$  Ligand-to-Metal Charge Transfer.—Many pieces of experimental data support the assignment of the band at 20–23 kK to a ligand-to-metal charge transfer. The intensity and energy of the absorption clearly indicate a charge-transfer transition. The band width at half-height is about 6.3 kK, or approximately 2.5 times the width of the  $t_{2g} \rightarrow \pi^*$  absorption. This is consistent with a transition into an antibonding level, *i.e.*,  $e_g$ .<sup>16</sup> Finally, the transition energies for the series reported herein conform very well to the crude molecular orbital diagram for pseudooctahedral complexes if the assignment  $\pi \rightarrow e_g$  is made (see Table IV). The last consideration can be used to eliminate its assignment to a  $\pi \rightarrow t_{2g}$  transition, inasmuch as the sum (in kK) of  $(\pi \rightarrow t_{2g}) + (t_{2g} \rightarrow \pi^*) \equiv (\pi \rightarrow \pi^*)$ . This is clearly not the case in any of the complexes.

On the basis of solvent shifts, Murakami and Nakamura<sup>5</sup> have assigned this band in  $\text{Fe}(\text{3-Pacac})_2$  and  $\text{Fe}(\text{3-Bacac})_3$  to a  $O_n \rightarrow e_g$  charge transfer. This is a reasonable assignment, since qualitatively one would expect similar  $O_n$  and  $\pi$  energies. It is, however, unlikely that they would be so nearly equienergetic as required by the results shown in Table IV. All the

experimental observations can be rationalized if the transition is assumed to contain both  $\pi$  and  $O_n$  components in its ground state. In addition, a more complicated transition can account for the difference (Table IV) between the calculated and observed  $\pi \rightarrow \pi^*$  energies.

The effect of ligand substituents on the  $e_g$  level can be treated similarly to their effect on the  $t_{2g}$  level. The trends observed are: (1)  $\text{CF}_3$  groups destabilize the  $e_g$  level relative to  $\text{Fe}(\text{acac})_3$  and (2) the phenyl groups stabilize the  $e_g$  level relative to  $\text{Fe}(\text{acac})_3$ . The trends are in the same direction and of the same magnitude as the effect of the substituents on the  $t_{2g}$  level. This is consistent with the extremely small variation in  $\Delta$  among the 1,3-diketones (Table III) of a given metal ion.

**Ligand Field Aspects.**—Perhaps the most surprising ligand field aspect is the small variation in the spectrochemical series of substituted 1,3-diketones. There is very little difference in the splitting parameter,  $\Delta$ , for the chelates studied. It is not true, however, that the effect of each ligand on the metal ion is the same. Rather, the difference appears to be in the coulombic attraction portion of the ligand field potential. That is, the  $\text{CF}_3$  group increases the energy of all "metal levels" with respect to the  $\text{CH}_3$  group, while the phenyl group decreases the energy of all "metal levels." For this reason, it appears that the only significant difference in bonding within the series arises because of different charge densities on the oxygens. The differences can be explained by the electronic effect of the substituents. Initial bond formation will be the ionic attraction of the mononegative ligands for the metal ion, causing a low-energy attractive state to be stabilized. Superimposed upon this attractive force is the electron-withdrawing ability of the  $\text{CF}_3$  group in the fluorinated ligands. The effect is less negative oxygens and a general destabilization of the "ionic" levels. In the phenyl-substituted compounds, the phenyl groups act as electron suppliers relative to the  $\text{CH}_3$  group. The effect is a stabilization of the "ionic" levels relative to the  $\text{CH}_3$ - and  $\text{CF}_3$ -substituted compounds.

(16) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 100.