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Ligand Field Spectra of Some Tris(1,3-diketonato)iron(III) Chelates. The Electronic Repulsion Parameters and the Nephelauxetic Effect

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The spin-forbidden transitions $^4T_{1g} \leftarrow {}^6A_{1g}$ and $^4T_{2g} \leftarrow {}^6A_{1g}$ were recorded for a series of substituted tris(1,3-diketonato)-iron(III) chelates. The transition energies were then calculated by treating the repulsion parameters B and C as adjustable parameters and Δ as a semiempirically calculated parameter. Iterative procedures were used until the calculated energies agreed with the observed to within ± 0.05 kK. The calculations were rigorous in the sense that configuration interactions were included and no assumptions were made about the relative size of B and C. Similar calculations for $FeF_6{}^{3-}$, $Fe(H_2O)_6{}^{3+}$, $Fe(urea)_6{}^{3+}$, $Fe(ox)_3{}^{3-}$, and $Fe(mal)_3{}^{3-}$ give excellent agreement between observed and calculated spectra. The ratio of C/B for the diketonates is not constant, but varies from 5.4 to 7.4 depending upon the substituent groups on the chelate rings. The C/B ratio calculated for the complex ions listed above is considerably lower. The values of B and C were used to calculate the repulsion parameters F^2 and F^4 which are proportional to the d-electron radial functions. There are systematic and opposite changes in F^2 and F^4 throughout the series of iron(III) chelates. A plausible mechanism for the trends in F^2 and F^4 is presented which involves the concept of orbital electronegativity.

Introduction

In a previous paper, we discussed the spectrochemical and nephelauxetic series for several substituted 1,3-diketonate chelates of chromium(III).[1] The values of Δ, B_{35}, and B_{55} were calculated from the spectral transition energies using the assumption that $C = 4B$. A striking feature of the values calculated is that Δ is essentially constant throughout the series, while B_{35} varies markedly. This greatly simplifies assignment and interpretation since spectra shifts in this series of closely related complexes are almost entirely attributable to changes in the values of the interelectronic repulsion parameters. The constancy of Δ for various chromium(III) 1,3-diketonates can be used in the semiempirical determination of Δ for other metal chelates of these ligands as well. The values of Δ for several 1,3-diketonates of iron(III) have been calculated in this manner.[2]

The nephelauxetic series for the chromium(III) 1,3-diketonates, determined by the values of B_{35}, was rationalized on the basis of the electronic effect of the groups substituted at the 1,3 positions on the chelate ring.[1] There is a strong correlation between the Hammett σ constants for the substituents and the value of B_{35}. One reason for undertaking this study was to determine the nephelauxetic series for the iron(III) 1,3-diketonates. This system is relatively simple since the solution spectra of high-spin iron(III) complexes can be adequately described by three parameters Δ, B, and C.[3]

Experimental Section

Synthesis of Ligands.—Most of the ligands are commercially available. The ligands not commercially available were synthesized by the condensation of an ester and a ketone according to the method of Collman.[4] Potassium *tert*-butoxide was used as the condensing agent.

Synthesis of Chelates.—Syntheses of most of the chelates have been reported. Table I contains abbreviations, melting point comparisons, and references to the original synthesis for the entire series. The preparation and analyses for the previously unreported formyl derivatives are given below.

Tris(1,3-butanedionato)iron(III), **Fe(BDO)₃**.—A 2.7-g sample

(1) A. F. Fatta and R. L. Lintvedt, *Inorg. Chem.*, **10**, 478 (1971).
(2) R. L. Lintvedt and L. K. Kernitsky, *ibid.*, **9**, 491 (1970).
(3) W. Low and G. Rosengarten, *J. Mol. Spectrosc.*, **12**, 319 (1964).
(4) J. P. Collman, E. T. Kittleman, W. S. Hurt, and N. A. Moore, *Inorg. Syn.*, **8**, 141, 144 (1966).

Table I
Nomenclature and Melting Points

Ligand name	Complex abbreviation	Mp, °C Lit.	Mp, °C Found	Ref
1,3-Butanedione	Fe(BDO)₃		135–137	
2,4-Pentanedione	Fe(Acac)₃	189	188–189	a
4,4-Dimethyl-1,3-pentanedione	Fe(*tert*-BuPDO)₃		104	
2,2,6,6-Tetramethyl-3,5-heptanedione	Fe(DPM)₃	163	163–164	b
1,1,1-Trifluoro-2,4-pentanedione	Fe(TFAc)₃	114	116–117	c
1,1,1,5,5,5-Hexafluoro-2,4-pentanedione	Fe(HFAc)₃	47	47	d
1-Phenyl-1,3-propanedione	Fe(PhPDO)₃		171–172	
1-Phenyl-1,3-butanedione	Fe(BzAc)₃	211	210–212	e
4,4,4-Trifluoro-1-phenyl-1,3-butanedione	Fe(TFBzAc)₃	140	139–140	a
1,3-Diphenyl-1,3-propanedione	Fe(DBM)₃	265	263–265	a

a See ref 2. *b* G. S. Hammond, W. G. Nonhebel, and C. S. Wu, *Inorg. Chem.*, **2**, 73 (1963). *c* R. C. Fay and T. S. Piper, *J. Amer. Chem. Soc.*, **85**, 500 (1963). *d* H. D. Gafney, R. L. Lintvedt, and I. S. Jaworiwsky, *Inorg. Chem.*, **9**, 1728 (1970). *e* R. C. Fay and T. S. Piper, *J. Amer. Chem. Soc.*, **84**, 2303 (1962).

(0.01 mol) of ferric chloride was ground to a powder in a mortar. About 1 g of the sodium salt of 1,3-butanedione (NaBDO) was added to the mortar and the two powders were ground together until a smooth dark red paste developed. The process was repeated until a total of 3.24 g (0.03 mol) of NaBDO had been added. The paste was ground several minutes more to ensure complete mixing. The product was extracted into hexane and crystallized from that solvent. The yield was 0.31 g or 10%. A melting point determination showed the product to char at 115° and melt with decomposition at 135°. *Anal.* Calcd for Fe-(C₄H₅O₂)₃: C, 46.3; H, 4.8. Found: C, 47.3; H, 5.0.

Tris(1-phenyl-1,3-propanedionato)iron(III), **Fe(PhPDO)₃**.—To 2.70 g (0.01 mol) of ferric chloride hexahydrate dissolved in 100 ml of water was added, with stirring, 5.10 g (0.03 mol) of the sodium salt of 1-phenyl-1,3-propanedione (NaPhPDO)[1] dissolved in 100 ml of water. The mixture was stirred 10 min, and the product was filtered, washed with water, and dried. The dried crude chelate was dissolved in benzene and the solution was filtered. The volume was reduced to 50 ml, 300 ml of hexane was added, and the mixture was allowed to cool in a freezer (−18°) for several hours. The product was recovered by filtration and dried *in vacuo*. The yield was 2.0 g or 41%. The compound melts at 171–172°. *Anal.* Calcd for Fe(C₉H₇O₂)₃: C, 65.2; H, 4.2. Found: C, 65.8; H, 4.6.

Tris(4,4-dimethyl-1,3-pentanedionato)iron(III), **Fe(*tert*-Bu-PDO)₃**.—The above procedure was followed using 0.01 mol of FeCl₃·6H₂O and 0.03 mol of the sodium salt of 4,4-dimethyl-1,3-pentanedione (Na-*tert*-BuPDO).[1] The reaction mixture was al-

TABLE II
SPECTRAL TRANSITIONS AND LIGAND FIELD PARAMETERS (IN KK)[a]

	$^4T_{1g} \leftarrow {}^6A_{1g}$		$^4T_{2g} \leftarrow {}^6A_{1g}$		Δ	B	C	C/B
	Obsd	Calcd	Obsd	Calcd				
Fe(*tert*-BuPDO)₃	9.39	9.37	13.07	13.10	14.70	0.573	3.12	5.4
Fe(DPM)₃	9.81	9.80	13.42	13.40	14.60	0.554	3.21	5.8
Fe(BDO)₃	9.56	9.58	13.16	13.10	14.70	0.548	3.19	5.8
Fe(Acac)₃	9.79	9.82	13.33	13.31	14.70	0.536	3.26	6.1
Fe(TFAc)₃	9.93	9.96	13.33	13.30	14.50	0.513	3.29	6.4
Fe(TFBzAc)₂	9.74	9.73	13.07	13.07	14.40	0.503	3.25	6.5
Fe(BzAc)₃	9.74	9.77	13.07	13.06	14.60	0.503	3.29	6.5
Fe(HFA)₃	10.10	10.09	13.33	13.31	14.40	0.493	3.33	6.8
Fe(PhPDO)₃	9.80	9.82	12.99	12.99	14.70	0.483	3.35	6.9
Fe(DBM)₃	9.90	9.93	12.90	12.90	14.40	0.453	3.37	7.4

[a] ϵ_{max} for $^4T_{1g} \leftarrow {}^6A_{1g} \sim 0.4$; ϵ_{max} for $^4T_{2g} \leftarrow {}^6A_{1g} \sim 1.2$.

lowed to stand overnight. The product was filtered, washed with water, dried, and recrystallized from hexane (10–15 ml). The crystals were dried *in vacuo*. The yield was 3.1 g or 71%. The complex melts at 104°. *Anal.* Calcd for Fe(C₆H₁₀O₂)₃: C, 57.7; H, 7.5. Found: C, 58.7; H, 7.6.

The formyl derivatives are difficult to purify because of their great solubility and decomposition on most chromatography columns. In each case the impurity is undoubtedly the free ligand which should not interfere with the spectral results.

Tris(1-*o*-methylphenyl-2,4-butanedionato)chromium(III), Cr-(*o*-MeBzAc)₃.—This chelate was prepared by the method of Collman, *et al.*,[4] using the sodium salt of the ligand. The product was purified chromatographically using an alumina column and eluting with a 50:50 mixture of benzene and methylene chloride. The purified product melts at 148°. *Anal.* Calcd for Cr-(C₁₁H₁₁O₂)₃: C, 68.6; H, 5.7. Found: C, 68.0; H, 5.8.

Spectra were obtained in chloroform and carbon tetrachloride at 25° on a Cary 14 spectrometer using concentrated solutions (0.1–1 *M*) in 10-cm quartz cells.

Results

The generalized formula for the compounds studied is
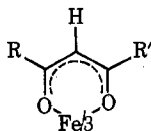
where R and R′ = H, CH₃, CF₃, *tert*-C₄H₉, or C₆H₅. The observed energies of the spin-forbidden d–d transitions, $^4T_{1g} \leftarrow {}^6A_{1g}$ and $^4T_{2g} \leftarrow {}^6A_{2g}$, for the series are listed in Table II. In addition, Table II lists the calculated values of the ligand field parameters Δ, B, and C. The calculation of Δ has been discussed previously.[2] The relationship used in this empirical calculation has been described by Jørgensen[5] as

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

Values of f(ligand) were calculated from the Δ values measured for the chromium(III) complexes of the same ligands.[2] The value of g(Fe(III)) is taken as 14.0. This is obtained from the spectra of Fe(H₂O)₆³⁺ and defining f(H₂O) as equal to 1.00.[5]

The values of B and C, shown in Table II, were determined using the Tanabe–Sugano matrices for the $^4T_{1g}$ and $^4T_{2g}$ states.[6] Each matrix is 3 × 3 and therefore contains configuration interactions from two higher states of the same symmetry and spin. The actual calculations were carried out by an IBM 360-67 computer. The procedure involved supplying values for Δ, B, and C and calculating the three roots of each matrix. The parameters were varied until the lowest energy roots of the matrices agreed with the observed

(5) C. K. Jørgenson, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, Chapter 7.
(6) Y. Tanabe and S. Sugano, *J. Phys. Soc. Jap.*, **9**, 753 (1954).

energies of the $^4T_{1g}$ and $^4T_{2g}$ states for each compound studied. The calculated energies are included in parentheses after the observed energies in Table II. In each case the value of Δ supplied was that determined by the empirical method described above. The values of B and C were allowed to vary from near zero to their free-ion values to achieve the best fit with the observed energies. By introducing the predetermined value of Δ, unique values of B and C were obtained. Assuming that the spectral transitions are known to ±0.1 kK, the values of B and C can be determined to ±0.01 and ±0.02 kK, respectively. The sensitivity of the lowest energy roots of the matrices to small changes in B and C is illustrated below by the results of three sample calculations. It should be noted that if all three parameters are allowed to vary, "fits" for the $^4T_{1g}$ and $^4T_{2g}$ energies may not be unique. However, treating Δ empirically does allow a unique fit of calculated and observed energies.

Δ, kK	B, kK	C, kK	$^4T_{1g}$, kK	$^4T_{2g}$, kK
14.14	0.720	3.00	10.67	15.17
14.14	0.720	3.02	10.78	15.29
14.14	0.740	3.00	10.86	15.47

The values of B and C reported in Table II show a considerable decrease from the free-ion values given by Low and Rosengarten,[3] *i.e.*, $B_0 = 1.10$ kK and $C_0 = 4.00$ kK. The ratio B/B_0 for the series varies from 0.52 to 0.41 in a systematic manner proceeding from Fe(*tert*-BuPDO)₃ to Fe(DBM)₃ in Table II. The values of C/C_0 vary from 0.78 to 0.84, also in a systematic manner. The trends are, however, in opposite directions. As a result, the maximum value of B and the minimum value of C occur for Fe(*tert*-BuPDO)₃, while the maximum value of C and minimum value of B occur for Fe(DBM)₃.

Several features can be noted from the data in Table II. First, the reduction in B_0 on complexation is much greater than the reduction of C_0. Second, the percentage change of B within the series is much greater than the percentage change in C within the series, approximately 20% vs. 5%. Third, the ratio C/B is not constant but has values in the range of 5.4–7.4. Fourth, the nephelauxetic series based on the values of B is exactly the same as the one determined for the analogous chromium(III) complexes.[1] This series, in order of decreasing B, is given as follows in terms of the substituent groups, R and R′, on the chelate rings: *tert*-Bu, H > *tert*-Bu, *tert*-Bu > CH₃, H > CH₃, CH₃ > CH₃, CF₃ > CF₃, C₆H₅ = CH₃, C₆H₅ > CF₃, CF₃ > C₆H₅, H > C₆H₅, C₆H₅.

For comparison, the same procedure was used to fit

TABLE III
OBSERVED AND CALCULATED TRANSITION ENERGIES AND LIGAND FIELD PARAMETERS FOR
COMPLEXES WHOSE SPECTRAL DATA ARE AVAILABLE IN THE LITERATURE (IN KK)[a]

	${}^4T_{1g}$		${}^4T_{2g}$		${}^4T_{2g}(D)$		${}^4A_{1g}, {}^4E_g$					
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Δ	B	C	C/B
$FeF_6{}^{3-}$	14.2	14.13	19.7	19.77	28.8	28.28	25.4?	23.9	12.00	1.05	2.68	2.6
$Fe(H_2O)_6{}^{3-}$	12.6	12.60	18.5	18.49		28.10	24.3, 24.6	24.2	14.00	1.01	2.82	2.8
$Fe(urea)_6{}^{3+}$	12.5	12.53	17.1	17.18		25.79	23.1, 23.4	23.8	12.95	0.78	3.02	3.9
$Fe(ox)_3{}^{3-}$	10.7	10.73	15.2	15.23		24.80	22.1	22.25	14.14	0.72	3.01	4.2
$Fe(mal)_3{}^{3-}$	11.0	11.02	15.9	15.84	25.8	25.41	22.6, 22.9	22.6	14.14	0.78	2.96	3.8

[a] The spectral peaks for these complexes as well as the analogous Cr(III) complexes are reported by C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, pp 290–292.

the observed spectra to calculate energies for a series of Fe(III) complexes whose spectra are reported in the literature. The results are presented in Table III. In each case the value of Δ was empirically determined by comparison to the analogous Cr(III) complex. The parameters B and C were then treated as adjustable parameters and a best fit between observed and calculated energies was achieved by computer techniques. The most dramatic result is for $Fe(mal)_3{}^{3-}$. Four transitions have been assigned. The first three were fitted extremely well by assigning $\Delta = 14.14$ and adjusting B and C to 0.78 and 2.96 kK, respectively. The fourth transition, ${}^4A_{1g} \leftarrow {}^6A_{1g}$, is accurately calculated using these values of B and C. The results in Table III lend strong support to the belief that the general features of octahedral Fe(III) spectra are adequately described by three parameters—Δ, B, and C.

The values of B and C can be used to calculate the more fundamental Condon–Shortley parameters, F^2 and F^4. These parameters are of theoretical interest since they could be calculated directly if the radical functions were known.[7] However, F^2 and F^4 are most often discussed as experimental parameters using the relationships $F^4 = 441C/35$ and $F^2 = 49B + 7C$. As experimental parameters they are presumed to be proportional to the radial functions for the d electrons in the complexed metal ions. The values of F^2 and F^4 for the tris(1,3-diketonato)iron(III) chelates calculated from our spectra are presented in Table IV. In addi-

TABLE IV
EXPERIMENTALLY DETERMINED VALUES OF F^2 AND F^4
FOR SEVERAL IRON(III) COMPLEXES (IN KK)

Complex	F^2	F^4	F^2/F^4
$FeF_6{}^{3-}$	70.22	33.78	2.08
$Fe(H_2O)_6{}^{3+}$	69.24	35.54	1.95
$Fe(urea)_6{}^{3+}$	59.39	38.06	1.56
$Fe(mal)_3{}^{3-}$	58.95	37.31	1.58
$Fe(ox)_3{}^{3-}$	56.35	37.93	1.45
$Fe(tert$-$BuPDO)_3$	49.93	39.29	1.27
$Fe(DPM)_3$	49.39	40.97	1.21
$Fe(BDO)_3$	49.20	40.18	1.22
$Fe(Acac)_3$	49.00	41.19	1.19
$Fe(TFAc)_3$	48.17	41.45	1.16
$Fe(TFBzAc)_3$	47.43	40.97	1.16
$Fe(BzAc)_3$	47.53	41.57	1.14
$Fe(HFAc)_3$	47.58	42.16	1.13
$Fe(PhPDO)_3$	47.09	42.16	1.12
$Fe(DBM)_3$	45.82	42.47	1.08

tion, Table IV contains F^2 and F^4 values calculated from the data in Table III.

Discussion

In the spectra of tris(1,3-diketonato)iron(III) chelates only two d–d transitions are observed. Others

(7) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, Chapter 2.

are presumably obscured by the low-energy charge-transfer bands. These two spectral bands are assigned to ${}^4T_{1g} \leftarrow {}^6A_{1g}$ and ${}^4T_{2g} \leftarrow {}^6A_{1g}$ transitions. The energies of these transitions are dependent upon Δ, B, and C. The functional relationships including configuration interactions with two higher energy states of the same symmetry and spin were given by Tanabe and Sugano.[6] With only two transition energies and three parameters it is doubtful that the observed energies can be fit with a unique set of parameters. This problem can be solved, however, with some additional experimental information. Since Δ can be measured directly in the Cr(III) chelates, the contribution of each 1,3-diketonate ligand to Δ can be evaluated. It has been found that this contribution is almost constant within the series.[1,2] It is reasonable to expect, therefore, that the contribution would be almost constant within the Fe(III) series as well. While it can be argued that calculation of Δ in this manner may not result in the correct absolute values, there seems little doubt that the values are internally consistent within the series. If such an absolute error in Δ is present, the absolute values of B and C will be affected. However, the trends within the series will not be affected by an internally consistent absolute error in Δ.

The advantage of treating the data in this manner is that it reduces the adjustable parameters to two and allows one rigorously to calculate a unique set of values of Δ, B, and C for each spectrum. The calculations have been carried out in an iterative manner in which B and C were varied from essentially zero to their free-ion values in small increments. Throughout the calculation, Δ was held constant at its empirically determined value. The results show that a unique solution is possible which reproduces the observed energies extremely well. The sensitivity of the calculated energies to small changes in B and C together with the excellent fit with observed energies lead one to the conclusion that the trends in B and C (Table II) are significant.

It should be emphasized that throughout this procedure there are no assumptions concerning the magnitude of B, C, or the ratio C/B. Since Δ is determined from the ${}^4T_{2g} \leftarrow {}^4A_{2g}$ transition in analogous Cr(III) chelates and this transition is largely independent of B and C, no assumptions are necessary. In addition, no assumptions of this type are contained in the Tanabe–Sugano matrices. Thus, both steps in the calculation are free of the usual supposition about the value of C/B.

The evaluation of the two 3 × 3 matrices resulted in the calculation of four unobserved transition energies as well as the two observed energies. These transitions and their energy ranges for the series are as follows: ${}^4T_{2g}(D) \leftarrow {}^6A_{1g}$, 22.9–23.5 kK; ${}^4T_{1g}(P) \leftarrow {}^6A_{1g}$, 32.1–32.8 kK; ${}^4T_{1g}(F) \leftarrow {}^6A_{1g}$, 39.7–40.2 kK; ${}^4T_{2g}(F) \leftarrow$

$^6A_{1g}$, 43.7–44.9 kK. Even the lowest energy $^4T_{2g}(D)$ state would be a shoulder on the high-intensity charge-transfer bonds.[2] Under normal conditions the chances of observing this transition are slim indeed.

In the terminology of the strong-field treatment, the values of B derived from the observed transitions are a function of repulsions in both the e_g and t_{2g} subsets. In this respect they are similar to the B_{35} values reported for the Cr(III) series.[1] It is satisfying, then, that the nephelauxetic series for the ligands derived from the Fe(III) chelates exactly parallels that based on B_{35} in the Cr(III) chelates. The Fe(III) series strengthens the observations made earlier that substituent groups considered to be electron donors, e.g., tert-C_4H_9 and CH_3, increases B, while electron-withdrawing groups, e.g., CF_3 and C_6H_5, decrease B. Unlike the Cr(III) series, the values of C for the Fe(III) series can be calculated without any simplifying assumptions. It is interesting that the substituent groups have the opposite effect on C; i.e., tert-C_4H_9 and CH_3 decrease C while CF_3 and C_6H_5 increase C. The change in C throughout the series is small; however, the sensitivity of the calculated energies to small variations in C leaves little doubt that the differences are significant. At present, the authors are not aware of any theoretical explanation for the different trends observed for B and C.

Within the series the different trends for B and C suggest that a discussion of the more fundamental Condon–Shortley repulsion parameters F^2 and F^4 may be informative. While C is simply related to F^4, $C = 35F^4/441$, B is a more complex function of both F^2 and F^4, $B = F^2/49 - 5F^4/441$. Thus, B is composed of two parameters which are varying in opposite directions going down the series presented in Table II. Therefore, the values of F^2 and F^4 themselves give a simpler representation of the trends in electronic repulsions. In addition, the numerical values of F^2 and F^4 are presumably proportional to the radial functions for the d electrons.[8] This, of course, has direct application to bonding discussions inasmuch as a decrease in F^2 and F^4 in complexes as compared to the free-ion values is generally explained in terms of expanded radial functions for the d electrons. Based on the results of Low and Rosengarten,[3] the free-ion values of F^2 and F^4 for Fe(III) are 80.93 and 50.27 kK, respectively. From the data presented in Table IV it is obvious that in every case the values of F^2 and F^4 are significantly reduced from the free-ion values. Two mechanisms for this expansion have been postulated: (1) central field covalency in which ligand electrons penetrate the metal core and shield the outer d electrons from the nuclear attraction and (2) symmetry-restricted covalency in which ligand orbitals of proper symmetry and energy overlap with metal d orbitals resulting in a delocalizing effect. Both mechanisms appear feasible in the 1,3-diketonato chelates due to the well-developed π system in the chelated ring of the enolate diketone. Evidence for long-range electronic effects comes from the work of Eaton,[9] who has detected unpaired spin density several bonds away from the metal. Overlap of metal t_{2g} electrons with the π^* orbitals of the ligand has been postulated to explain the delocalization. Regardless of the mechanism, unpaired spin density on the ligand would

result in significant decreases in the interelectronic repulsions on the metal ion. The 1,3-diketonates are particularly interesting since changes in the interelectronic repulsions appear quite unrelated to Δ.

The actual mechanism for the change in F^2 and F^4 is, of course, not known. The data contained in Table IV can, however, be rationalized to some extent on the basis of simple bonding arguments. For example, complexes in which the ligands contain no π^* orbitals, FeF_6^{3-} and $Fe(H_2O)_6^{3+}$, have F^2/F^4 ratios of about 2.0; complexes whose ligands contain π^* orbitals but no conjugated π system have F^2/F^4 ratios of about 1.5; complexes whose ligands contain both π^* orbitals and conjugated π systems have F^2/F^4 ratios of 1.1–1.3. In this respect, the F^2/F^4 ratios appear to be reflecting a differential expansion of σ- and π-type d electrons.

A reasonable approach to understanding the trends presented in Table IV may be to use the concept of orbital electronegativity proposed by Hinze and Jaffé.[10] In the 1,3-diketonato series, changes in B and F^2 can be explained in the following manner. For chelates in which the substituent groups have no extended π system the changes in B and F^2 may be partially understood by simple inductive arguments. For example, the electron-withdrawing CF_3 group will place a slight negative charge in the σ orbitals of the oxygen atoms. This is consistent with alternating inductive polarization. In addition, polarization occurs within the π orbitals of the chelate ring, but in the opposite direction. Hence, a slight positive charge is placed in the pπ orbitals of oxygen. It is these orbitals with which the metal t_{2g} electrons interact. The presence of the decreased density will increase the electronegativity of the π orbitals and result in expansion of the metal t_{2g} orbitals. The values of B and F^2 for the series $Fe(Acac)_3$, $Fe(TFAc)_3$, and $Fe(HFAc)_3$ are consistent with this orbital electronegativity explanation. Similar arguments can be developed for inductive electron-donating substituent groups such as tert-C_4H_9. In this case, the polarizations are in the opposite direction which decreases the pπ oxygen orbital electronegativity and increases B and F^2.

The effect of phenyl groups is similar to the CF_3 groups. They are apparently slightly stronger electron-withdrawing groups than CF_3 judging from the values of B. The very large effect of the phenyls on B is believed to be due to resonance. Electron withdrawal through resonance apparently produces the most electronegative pπ oxygen orbitals of the entire series. Single-crystal structural studies have shown that the phenyl ring and the chelate ring are sufficiently coplanar to allow resonance interaction between the two rings.[11] Preliminary verification of the importance of coplanarity between the phenyl and chelate rings has come from the spectra of Cr(III) chelates in which the phenyl group is substituted in the ortho position. Substitution of a methyl group at the ortho phenyl position in the ligand benzoylacetone will destroy the coplanarity of the phenyl and chelate rings and, hence, the resonance interaction. Solution spectra of Cr(o-MeBzAc)$_3$ show transitions to the $^4T_{2g}$ and $^4T_{1g}$ states at 17.85 and 22.72 kK, respectively. Based on these values, Δ and B_{35} are

(8) E. U. Condon and G. H. Shortley, "Theory of Atomic Spectra," 2nd ed, University Press, Cambridge, 1953.

(9) D. R. Eaton, *J. Amer. Chem. Soc.*, **87**, 3097 (1965).

(10) J. M. Hinze and H. H. Jaffé, *ibid.*, **84**, 540 (1962); *Can. J. Chem.*, **41**, 1315 (1963); *J. Phys. Chem.*, **67**, 1501 (1963).

(11) See, for example, R. K. Hon, C. E. Pfluger, and R. L. Belford, *Inorg. Chem.*, **5**, 516 (1966).

calculated to be 18.1 and 0.439 kK. The value of B_{35} is significantly greater than that for $Cr(BzAc)_3$, 0.358 kK.[1] The increase in B_{35} for $Cr(o\text{-}MeBzAc)_3$ compared to $Cr(BzAc)_3$ is attributed to the loss of resonance interaction between the phenyl ring and the chelate ring. In view of these data, it is reasonable to assume that the phenyl group is acting as an electron withdrawer and that the effect is greatly enhanced by resonance.

For complexes with no π^* orbitals, $FeF_6{}^{3-}$ and $Fe(H_2O)_6{}^{3+}$, the electronegativity of the π orbitals is, of course, undefined. It is, therefore, consistent with the above argument that B and F^2 for these complex ions are very close to the free-ion values. The presence or absence of t_{2g}–π type interaction between the metal and ligands appears very critical in determining the values B and F^2. In this respect, the mechanism for reduction

of B and F^2 from the free-ion values is closely related to the symmetry-restricted covalency discussed by Jørgensen.[5]

Attaching a physical significance to the trend in F^4 is more difficult. It is tempting to postulate that F^4 is a function of repulsions in the e_g subset and that σ-orbital electronegativity is greatest for $Fe(tert\text{-}BuPDO)_3$ and least for $Fe(DBM)_3$. In light of the value of F^4 for $FeF_6{}^{3-}$, however, this approach is undoubtedly overly simplistic.

Iron(II) and Iron(III) Complexes of Penicillamine[1]

BY LEON G. STADTHERR AND R. BRUCE MARTIN*

Admission of oxygen to neutral solutions containing Fe(II) and excess penicillamine yields a bis red complex that is relatively stable in aqueous solutions at room temperature. Quantitative determination shows that 1 mol of H_2O_2 as the oxidizing agent is required for each Fe(II) for maximal development of the red color in solutions containing 3 equiv of penicillamine. This result indicates that for each mole of Fe(II) 1 mol of sulfhydryl compound also undergoes oxidation and suggests a link with the Fe(III) catalyzed oxidation of sulfhydryl compounds by oxygen. The red complex may also be formed by direct addition of Fe(III) to penicillamine in neutral solutions. It disappears more quickly in the presence of O_2 or H_2O_2 than with a N_2 atmosphere. A less stable blue complex is formed in acidic solutions containing equimolar amounts of Fe(III) and penicillamine.

Nonheme iron proteins frequently contain iron–divalent sulfur linkages. Attempts to employ cysteine as a model compound for the sulfhydryl group of proteins in interactions with iron require nonaqueous solvents and low temperatures in order to inhibit rapid oxidation–reduction reactions in these systems.[2] A blue complex exhibiting an absorption maximum at 620 nm with no optical activity is formed upon mixing equimolar amounts of $FeCl_3$ and cysteine in acidic solutions of 90% ethanol at $-78°$. The blue color was shown to be due to a 1:1 complex, and it was concluded that chelation occurs through S and O donor atoms. An optically active red complex absorbing at 525 nm was prepared at $-78°$ in water-free ethanol and assigned as a bis-Fe(III) complex with chelation through S and O donors.[2]

In earlier work from this laboratory it was reported that the fleeting violet color formed upon mixing Cu(II) and cysteine is stable for hours when penicillamine is employed as a ligand.[3] The two β-methyl groups in penicillamine inhibit oxidation–reduction reactions and polynuclear complex formation. This paper describes the behavior of penicillamine with both

Fe(II) and Fe(III) at several pH values in aqueous solutions at room temperature. Blue and red complexes of Fe(III) and penicillamine are easily observable under these conditions.

Polynuclear complex formation is also inhibited in formation of Co(II)[4] and Ni(II)[4,5] complexes of penicillamine compared to cysteine. With Ni(II) both ligands form bis, diamagnetic, tetragonal, red complexes in neutral or basic aqueous solutions.[6] A strong absorption peak at 375 nm, perhaps indicative of polynuclear complex formation, occurs more easily with cysteine than with penicillamine at nonintegral molar ratios of ligand to Ni(II). In basic solutions, Co(II) forms a well-defined, bis, hexacoordinate, pink-purple

(1) This research was supported by a grant from the National Science Foundation.

(2) A. Tomita, H. Hirai, and S. Makishima, *Inorg. Chem.*, **7**, 760 (1968); **6**, 1746 (1967).

(3) E. W. Wilson, Jr., and R. B. Martin, *Arch. Biochem. Biophys.*, **142**, 445 (1971).

(4) Unpublished work performed in this laboratory by Dr. Peter Morris, who initiated the experiments described in this paper.

(5) D. D. Perrin and I. G. Sayce, *J. Chem. Soc. A*, 53 (1968). Reduction of the number of coordinating groups from six in the aqueous ions to four in the cysteine and penicillamine complexes of Zn(II) and Ni(II) is the major factor in the greater magnitude of the second formation constants compared to the first in each case. The tendency of at least the intrinsic formation constants to exhibit this order is generally observed for Zn(II). The inverse order occurs with Ni(II) for ligands such as sulfur that stabilize tetragonal, low-spin complexes.[6] The low spin state of Ni(II) requires two sulfur atoms for stabilization giving rise to a cooperative effect which further increases the relative magnitude of the second formation constant.

(6) J. W. Chang and R. B. Martin, *J. Phys. Chem.*, **73**, 4277 (1969). Solutions containing 1:1:1 molar ratios of Ni(II), cysteine (or its methyl ester), and ethylenediamine disproportionate to give 2:1 complexes of each ligand with Ni(II); the complex with two sulfur atoms is tetragonal and the other complex octahedral.