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Nephelauxetic and Spectrochemical Series for 1,3-Diketonates. Ligand Field Spectra of Some Tris(1,3-diketonato)chromium(III) Chelates

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A series of substituted 1,3-diketonate chelates of Cr(III) was prepared in which the 1,3 substituents are H, CH_3, CF_3, *tert*-C_4H_9, and C_6H_5. The electronic spectra were recorded and assignments of d–d, charge-transfer, and intraligand transitions were made. The ligand field parameters Δ, B_{35}, and B_{55} were calculated from the spectral data and used to determine spectrochemical and nephelauxetic series for the ligands. The values of Δ for the chelates studied are essentially constant, varying only from 17.5 to 18.0 kK. The values of B_{35} and B_{55} in the chelates are reduced very significantly from the free-ion values for Cr(III). The values of B_{55} indicate a strong π-type back-bonding mechanism for delocalization of the metal t_{2g} electrons. Trends in B_{35} and B_{55} have been interpreted in terms of the inductive and resonance effects of the chelate ring and its 1,3 substituents.

Introduction

Discussions of ligand field effects and bonding in transition metal complexes usually concern themselves with splitting energies between the metal d orbitals. The magnitude of the splitting energy, Δ, as a function of the metal ion and the ligand is reasonably well understood within the framework of the ligand field theory. Of equal importance, but less well studied, is the magnitude of the interelectronic repulsion energies, B and C, as a function of the metal ion and the ligand. The decrease in B and C in complexes from the free-ion values is termed the nephelauxetic effect. The effect has been the subject of a general review by Jørgensen[1] and a specific review of Cr(III) complexes by Forster.[2] Most of the studies of the parameters Δ, B, and C to date involve compounds which exhibit widely different values of both Δ and B (assuming $C = 4B$). In order to study the nature and origin of the nephelauxetic effect it would be useful to develop a series of compounds in which the relationship (or lack of relationship) between Δ and B is clearly evident.

In a previous paper we reported the Δ values for a series of tris(1,3-diketonato)chromium(III) chelates.[3] The striking feature of these data is that the ability of all the 1,3-diketones to split the d orbitals is approximately the same. Thus, the first spin-allowed absorption (${}^4T_{2g} \leftarrow {}^4A_{2g}$) whose energy is assumed to be equal to Δ is nearly independent of the nature of the chelate ring substituent groups. This fact makes a spectral study of an extensive series of tris(1,3-diketonato)chromium(III) chelates interesting since shifts in the other d–d absorptions throughout the series would be due to changes in the repulsion energies. Thus, these changes can be studied as a function of the electronic effect of the substituent groups without the complication of major changes in Δ taking place simultaneously. For these reasons, we have undertaken a systematic study of the spectrochemical and nephelauxetic series for the 1,3-diketonate-type ligands.

The second spin-allowed transition (${}^4T_{1g} \leftarrow {}^4A_{2g}$) whose energy depends upon Δ and B has not been definitely assigned in the tris(1,3-diketonato)chromium(III) spectra because of overlapping, intense charge-transfer bands. The assignment of this transition has been the subject of some controversy in tris(2,4-pentanedionato)chromium(III), $Cr(acac)_3$. Orgel[4] suggested that it should lie about 7.0 kK higher in energy than ${}^4T_{2g} \leftarrow {}^4A_{2g}$. Whereas this is true for the hexaaquochromium(III) ion, Piper and Carlin[5] have shown that the intense peak at this energy in the $Cr(acac)_3$ spectrum has the wrong polarization for the d–d transition. Several other workers have suggested that the ${}^4T_{1g} \leftarrow {}^4A_{2g}$ transition appears in $Cr(acac)_3$ as a shoulder at approximately 23.3 kK on the charge-transfer band.[6–8] This shoulder, although difficult to observe in $Cr(acac)_3$, is well resolved in other members of the series reported herein. The assignment of this transition along with ${}^4T_{2g} \leftarrow {}^4A_{2g}$ and ${}^2E_g \leftarrow {}^4A_{2g}$ makes it possible to extract three ligand field parameters, Δ, β_{35}, and β_{55}.

Experimental Section

Synthesis of Ligands.—Many of the ligands are commercially available. The diketones formed from the condensation of a formyl group and a ketone were synthesized by us according to the method of Collman, *et al.*[9] Potassium *tert*-butoxide was used as the condensing agent. Attempts to condense methyl formate and trifluoroacetone by this procedure were unsuccessful.

Synthesis of Chelates.—The metal complexes were synthesized by one of several methods.[9–14] In cases where cis–trans isomerism is possible, the isomers of some complexes were separated by chromatography on alumina. The chelate was dissolved in a minimum amount of benzene, poured onto a column packed with heptane, and eluted with a 1:1 benzene–methylene chloride mixture to yield the trans isomer. The more polar cis

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TABLE I

PHYSICAL DATA AND NOMENCLATURE

Ligand name	Complex abbreviation	Mp, °C Lit.	Mp, °C Found	Anal, % C Calcd	Anal, % C Found	Anal, % H Calcd	Anal, % H Found	Ref
1,3-Propanedione	$Cr(PDO)_3$	182	181					9
1,3-Butanedione	$Cr(BDO)_3$	169 (trans)	171					
		164 (cis)	165					9
1-Phenyl-1,3-propanedione	$Cr(C_6H_5PDO)_3$	... (trans)	194	65.7	65.7	4.3	4.8	9
		... (cis)	197	65.7	66.4	4.3	4.6	
4,4-Dimethyl-1,3-pentanedione	$Cr(tert\text{-}C_4H_9PDO)_3$	...	116	58.2	58.6	7.6	7.9	9
		...	135	58.2	57.9	7.6	7.6	9
2,4-Pentanedione	$Cr(acac)_3$	216	216					10
1-Phenyl-2,4-butanedione	$Cr(BZAC)_3$	235	235					11
1,3-Diphenyl-1,3-propanedione	$Cr(DBM)_3$	>300	>300					12
1,1,1-Trifluoro-2,4-pentanedione	$Cr(TFAC)_3$	150	149					12
1,1,1,5,5,5-Hexafluoro-2,4-pentanedione	$Cr(HFAC)_3$	84	84					13
4,4,4-Trifluoro-1-phenyl-1,3-butanedione	$Cr(TFBZAC)_3$	...	150	51.65	52.70	2.58	2.93	12
1,1,1-Trifluoro-5,5-dimethyl-2,4-hexanedione	$Cr(TFDMH)_3$		56	45.21	45.62	4.71	4.54	12
2,2,6,6-Tetramethyl-3,5-heptanedione	$Cr(DPM)_3$	229	230					14

TABLE II

TRANSITION ENERGIES (kK) AND NEPHELAUXETIC PARAMETERS (CM^{-1})

Compound	$\pi_3(e) \rightarrow \pi_4(a)$	$\pi_3(e) \rightarrow \pi_4(e)$, $\pi_3(a) \rightarrow \pi_4(a)$	$\pi_3(a) \rightarrow \pi_4(e)$	$d_\epsilon(a) \rightarrow \pi_4(e)$	$d_\epsilon(e) \rightarrow \pi_4(a)$	$d_\epsilon(e) \rightarrow \pi_4(e)$	$^4A_{2g} \rightarrow {}^4T_{1g}$	$^4A_{2g} \rightarrow {}^4T_{2g}$	$^4A_{2g} \rightarrow {}^2E_2$	B_{35}	β_{35}	B_{55}	β_{55}
$Cr(PDO)_3$	37.59	35.46	32.26	29.15	28.49	25.97	22.88	18.02	12.40[a]	446	0.48	614	0.66
$Cr(BDO)_3$	38.46	36.10	32.89	29.67	29.15	25.97	23.42	17.86	12.69	522	0.57	630	0.68
$Cr(C_6H_5PDO)_3$	35.72	33.90	32.47	27.25		23.81	21.51	17.83	12.37	300	0.33	613	0.67
$Cr(tert\text{-}C_4H_9PDO)_3$	38.31	35.59	32.47	29.24		25.77	23.59	17.86	12.69	541	0.59	629	0.69
$Cr(acac)_3$	39.22	36.76	33.56	29.76		25.77	23.26	17.86	12.95	505	0.55	644	0.70
$Cr(BZAC)_3$	38.61	33.90	32.79	27.93		...	21.74	17.76	12.58	358	0.39	624	0.68
$Cr(DBM)_3$	35.01	30.77	32.47	25.91		21.98	20.83	17.48	12.13	297	0.32	601	0.65
$Cr(TFAC)_3$	37.74	35.34	32.26	28.99		25.38	22.55	17.64	12.20	453	0.49	618	0.66
$Cr(HFAC)_3$	36.36	34.33	32.89	28.27	27.78	24.69	21.68	17.45	12.56	383	0.42	624	0.68
$Cr(TFBZAC)_3$	36.36	32.26	...	27.25		...	21.42	17.54	12.28	348	0.38	608	0.66
$Cr(TFDMH)_3$	37.59	35.46	32.26	28.99		25.58	22.62	17.61	12.55	464	0.50	623	0.68
$Cr(DPM)_3$	39.37	35.56	33.06	29.41		25.71	23.26	17.70	12.96	523	0.57	644	0.70

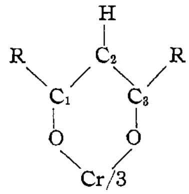
[a] Value estimated from emission data of L. S. Forster and K. deArmond, *Proc. Int. Conf. Coord. Chem., 7th, 1962*, 20 (1962), adding 200 cm^{-1}.

isomer was then eluted with acetone. In many cases the amount of cis isomer recovered was minimal. The complexes of the formyl ketones showed a marked ease of separation.

Table I lists the series of compounds along with their melting points and names. Analyses are shown for compounds not previously reported in the literature.

The spectra were recorded in chloroform, ethanol, benzene, and dixoane at 25° using a Cary 14 spectrophotometer. Reagent grade solvents were used and no attempt was made to remove the ethanol stabilizer from the chloroform. Since the spectra are unchanged in these different solvents, within experimental error, it was concluded that there is no solvent dependence. Therefore, only the energies obtained from chloroform solution spectra are reported here.

Results



R, R′ = H, CH_3, CF_3, C_6H_5, *tert*-C_4H_9

A series of 12 substituted 1,3-diketonates of Cr(III) was prepared and their electronic absorption spectra were recorded. The generalized formula for the series is given below. Spectral assignments and nephelauxetic parameters are recorded in Table II. For the solution data presented in Table II, notation indicating octahedral symmetry is used although the molecular symmetry is significantly lower. Splitting of d–d transitions due to lower symmetry is observed in the single-crystal spectra but not in solution spectra. The spectral assignments are based on the energy level splittings originally proposed by Barnum.[6] The values of B were calculated from standard equations which include configuration interactions

$$E(^4T_{1g} \leftarrow {}^4A_{2g}) = 7.5B_{35} + 15Dq - {}^1/_2[225B_{35}^2 + 100(Dq)^2 - 180DqB_{35}]^{1/2}$$

$$E(^2E_g \leftarrow {}^4A_{2g}) = 9B_{55} + 3C - \frac{50B_{55}^2}{10Dq}$$

The controversy which has surrounded the assignment of the $^4T_{1g} \leftarrow {}^4A_{2g}$ transition is largely the result of the difficulty in resolving this absorption in the most familiar member of the series, $Cr(acac)_3$. In the spectra of other members of the series this peak is readily resolvable with $\epsilon_{max} \simeq 60$. The solution spectrum of $Cr(BDO)_3$ shows this absorption clearly (Figure 1).

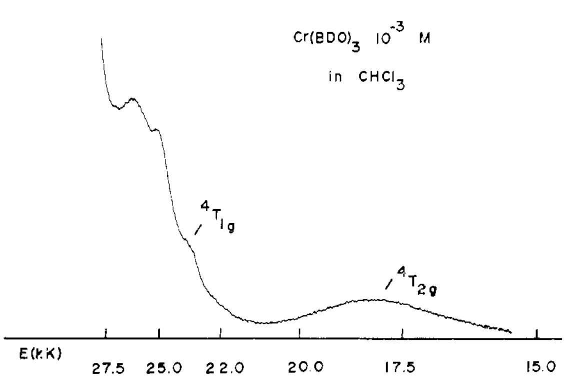


Figure 1.—Visible spectrum of $Cr(BDO)_3$.

In general, all the visible spectra have the features shown in Figure 1. The ϵ_{max} values for $Cr(BDO)_3$ are 80 at 17.9 kK, 60 at 23.4 kK, 100 at 24.6 kK, and 320 at 26.0 kK. These intensities are representative of the entire series. The characteristics of the band at 23.4 kK in $Cr(BDO)_3$ are being investigated in our laboratory by single-crystal techniques. Preliminary results with polarized light show that a component of the $^4T_1$ state is observed under both $\|$ and $\perp$ light even though the transition to the ^4E component is forbidden under $\perp$ light and the transition to the $^4A_2$ component is forbidden under both $\|$ and $\perp$ light. These selection rules are valid in all trigonal point groups except C_{3v} and C_3. The presence of vibrational fine structure in the $\perp$ spectrum with spacing of 260 cm^{-1} may point to a vibrational coupling mechanism for gaining intensity. The value of 260 cm^{-1} is reasonable for a Cr–O vibration. Therefore, the electronic transition in question may be a d–d transition coupling with a metal–oxygen vibration. Similar splittings of 260 ± 40 cm^{-1} have been observed in the low-energy spin-forbidden transition ($^2E \leftarrow {}^4A_2$) in single crystals of $Cr(acac)_3$.[5] The similar vibrational structure between these two bands lends further support to the assignment of the 23.4-kK absorption to a d–d transition.

The values of β ($\beta = B_{complex}/B_0$) were calculated for both B_{35} and B_{55} using the free-ion value of 920 cm^{-1} for B_0. The values are reported in Table II under the headings β_{35} and β_{55}. The ligands are listed in order of decreasing β_{35}, as *tert*-C_4H_9PDO > DPM > BDO > acac > TFDMH > TFAC > PDO > HFAC > BZAC > TFBZAC > C_6H_5PDO > DBM. A trend of this type is usually considered to indicate increasing ability of the ligands to expand the d orbitals. In general, the effect of the substituent groups with respect to their ability to "expand the d orbitals" is as follows: $C_6H_5 > CF_3 > H > CH_3 >$ *tert*-C_4H_9.

In the calculation of β_{55} from the spin-forbidden transition, the assumption is made that $C = 4B$. The correctness of this assumption affects the absolute value of β_{55}, but it is reasonable to believe that the ratio C/B is relatively constant throughout the series. As a result, the relative ordering within the series should be unaffected by the assumption. The variation in $^2E \leftarrow {}^4A_2$ energies, and therefore in β_{55}, is quite small for the chelates studied. However, the energies can be accurately measured and the overall trend is believed to be real. The effect of the substituent groups with respect to their ability to decrease B_{55} (determined from the symmetrically substituted chelates) is as follows: $C_6H_5 > H > CF_3 > CH_3 \simeq$ *tert*-C_4H_9.

Discussion

It is possible to assign two spin-allowed transitions and one spin-forbidden d–d transition in the tris(1,3-diketonato)chromium(III) chelates. As a result, the energies Δ, B_{35}, and B_{55} can be evaluated and the ratios β_{35} and β_{55} calculated. The current interpretation of β_{55} values significantly less than unity is that this indicates π-type interactions between the metal and the ligand. Since B_{35} is determined by repulsions in both t_{2g}^3 and $t_{2g}^2e_g^1$ strong-field configurations, low values of β_{35} are believed to be indicative by both π- and σ-type delocalizations. This implies that a differential expansion of the $\pi(t_{2g})$ and $\sigma(e_g)$ metal orbitals exists which is a function of the difference between β_{35} and β_{55}. This difference is sometimes expressed as a covalancy parameter, $1 - \epsilon = \beta_{35}/\beta_{55}$.[1,2] In the series presented herein, the chelate $Cr(PDO)_3$ can be considered the parent compound since it has hydrogens substituted in the 1, 2, and 3 positions. Many of the trends observed in the values of B_{35} and B_{55} can be interpreted in terms of the electronic effects of the substituents which replace the hydrogens in the 1 and 3 positions.

β_{55}.—The results presented in Table II show that the value of β_{55} is considerably less than unity in all the chelates studied. These data are indicative of considerable π-type delocalization of the metal electrons. The most reasonable mechanism for t_{2g} electron delocalization is through the π^* orbitals of the ligands. This type of backbonding is considered to be important in complexes such as $Cr(CN)_6^{3-}$. It is interesting to note that the 1,3-diketonates exhibit a degree of backbonding similar to that of cyanide, as evidenced by the values of β_{55}, although the ligand field splitting energies are vastly different. These values are $\Delta = 26.7$ kK and $\beta_{55} = 0.69$ cm^{-1} for $Cr(CN)_6^{3-}$ and $\Delta = 18.0$ kK and $\beta_{55} = 0.66$ cm^{-1} for $Cr(PDO)_3$. This is unusual since the back-bonding of cyanide through $t_{2g} \rightarrow \pi^*$ interaction is generally invoked to explain the large value of Δ. Clearly, the same reasoning extended to the 1,3-diketonates is not valid. Within the 1,3-diketonates certain values of β_{55} are explainable on the basis of enhanced π-bonding possibilities. In general, β_{55} can be correlated to the energy separation between the t_{2g} and π^* levels. The metal-to-ligand charge transfers give this energy directly. If, for example, one compares $Cr(DBM)_3$ and $Cr(acac)_3$, it is apparent from the charge-transfer energies that the π^* level in $Cr(DBM)_3$ is more able to interact with metal electrons than the π^* level in $Cr(acac)_3$. The hydrogen-substituted parent ligand PDO^- has a relatively strong effect which reduces β_{55} significantly. Substitution of phenyl groups on the chelate rings produces a further reduction of β_{55}, presumably because of the lower π^* energy. Substitution of aliphatic electron-supplying groups such as CH_3 and *tert*-C_4H_9 produces an increase in β_{55} relative to that of $Cr(PDO)_3$. Trends within the aliphatic substituted chelates appear to be related to inductive effects even though induction is presumed to take place through the σ-bonding system. Ordering the 1,3-diketonates in a nephelauxetic series based on B_{55} is at this point of questionable utility since the energy differences are not great. However, the differences between the compounds at the extreme ends of the series, $Cr(DBM)_3$ and $Cr(DPM)_3$, are real and explainable on the basis of a π-back-bonding mechanism. Emission spectra should be useful in determining the trend in compounds where the differences are small.

β_{35}.—The spin-allowed transitions from which B_{35} values are calculated take place between the strong-field configurations $t_{2g}{}^3$ and $t_{2g}{}^2e_g{}^1$. Therefore, repulsions within both the π- and σ-bonding subsets are believed to determine the value of B_{35}. For this reason B_{35} is usually reduced more by complexation than B_{55}. The difference between B_{35} and B_{55} is assumed to be a function of the σ bonding in the complex. The fact that β_{35} changes markedly with changes in the R groups leads one to conclude that induction has its main effects through the σ-bonding system. Jørgensen[1] describes the nephelauxetic effect as arising from two simultaneous effects, covalent overlap of metal and ligand orbitals (symmetry restricted covalency, SRC) and partial screening of the metal nuclear charge by ligand electrons (central field covalency, CFC). The two effects are not easily separable without detailed calculations which are at best approximate. However, within the series presented a phenomenological approach can be used qualitatively to separate the two. One expects that a *tert*-C_4H_9 group will release electrons relative to H. In terms of the CFC mechanism, this should have the effect of further screening the metal d electrons, decreasing the effective nuclear charge, and, therefore, decreasing β_{35}. The same argument can be applied to groups with opposite induction, *e.g.*, CF_3, which should increase β_{35} by the CFC mechanism. Since this is not the effect observed, it points to the fact that SRC may be the predominant mechanism. This can be rationalized by considering that electron-withdrawing groups are removing density from a metal–oxygen molecular orbital, thereby decreasing repulsions. Electron-releasing groups would have the opposite effect and increase β_{35}. This is observed. The same phenomenological approach using two mechanisms which operate in opposite directions is useful in explaining the seemingly anomalous variation in β_{35} in the series $Cr(PDO)_3$, monosubstituted R, and disubstituted R. In all cases, where R = CH_3, *tert*-C_4H_9, and C_6H_5, the effect of adding two R groups is not twice the effect of one. Rather, the second group barely changes β_{35} at all. It is possible that the addition of the second R group increases the effectiveness of the CFC mechanism and this cancels a further decrease in β_{35} due to SRC.

The nephelauxetic series that results from β_{35} variations in the 1,3-diketonates is understandable on the basis of inductive effects. The change in β_{35} for the aliphatically substituted chelates is rather well predicted by the Hammett σ functions for these *R* groups substituted in the meta position.[15] One concludes, therefore, that the phenyl group is very strongly electron withdrawing since $Cr(C_6H_5PDO)_3$ and $Cr(DBM)_3$ exhibit the greatest decrease of β_{35} from the free-ion value. This is reasonable if the chelate ring is considered to be an electron-rich "sink." With respect to other ligands the 1,3-diketones are strong B_{35} reducers. They have an effect as strong as or stronger than that of CN^-. Some are even stronger than sulfur donors such as the diethyldithiophosphinato group, dtp: for $Cr(CN)_6{}^{3-}$, $\beta_{35} = 0.53$ cm^{-1};[2] for $Cr(dtp)_3$, $\beta_{35} = 0.44$ cm^{-1};[2] for $Cr(acac)_3$, $\beta_{35} = 0.55$ cm^{-1}; for $Cr(DBM)_3$, $\beta_{35} = 0.32$ cm^{-1}.

The overall view of the ligand field effects of the 1,3-diketonates is somewhat perplexing at this time. It is difficult to explain Δ values about the same as $Cr(H_2O)_6{}^{3+}$ which are not very dependent upon the R groups, β_{55} values indicating strong back-bonding, and β_{35} values typical of "soft" sulfur-donating ligands. One approximation of the theory is that there is no interaction between the $^4T_1$ state and the charge-transfer states. Such an interaction could account for a lowering of the $^4T_1$ state and a β_{35} which is artificially low. However, inspection of the absorption energies assigned to the $^4T_1$ and the charge-transfer states do not give any strong experimental indication of an interaction of this type.

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