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## Nonadditive and Additive Ligand Fields and Spectrochemical Series Arising from Ligand Field Parameterization Schemes. Pyridine as a Nonlinearly Ligating $\pi$ -Back-Bonding Ligand toward Chromium(III)

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In connection with the parameterization of the ligand field of a series of the *trans*-tetraammine- and *trans*-tetrakis(pyridine)chromium(III) complexes the nonadditive ligand field and the additive ligand field have been characterized. The operator of the former has the symmetry of the whole complex, while that of the latter consists of terms where each term has the symmetry of part of the complex. Within both the nonadditive and the additive ligand fields there are two types of parameterization, which are linearly related to each other. One has been called the crystal field parameterization; the other, the ligand field parameterization. The additive field of a linearly ligating ligand J is characterized by the parameters  $h'_{\sigma J}$  and  $h'_{\pi J}$ , which in the angular overlap model are interpreted as expressing the  $\sigma$ -antibonding and  $\pi$ -antibonding (or bonding) effects upon the d orbitals caused by the interaction with the orbitals of J and consequently are renamed  $e'_{\sigma J}$  and  $e'_{\pi J}$ . Using the angular overlap model, as opposed to the electrostatic model, it is possible to treat nonlinearly ligating ligands such as pyridine in a quite analogous way to that used for systems of linearly ligating ligands. In this way the ligand field of pyridine has been handled. On the basis of solution absorption spectra of the complexes using the angular overlap model and a transferability assumption for common single-ligand parameters, the two-dimensional spectrochemical series of ligands, corresponding to the above-mentioned ligand field parameterization, has been established for chromium(III). The  $\pi$  parameter associated with the chromium(III) to pyridine bond has been found to be negative corresponding to net  $\pi$ -back-bonding, and the angle between the pyridine planes and the plane defined by the four nitrogen ligands has been found to be  $38^\circ$ . A linear relationship between the enthalpies of activation for the hydrolysis of the ions  $[\text{Cr}(\text{H}_2\text{O})_5\text{J}]^{n+}$  and  $\Delta_J$  has been established.

### 1. Introduction

For years this laboratory has studied absorption spectra, circular dichroism spectra, and magnetic, kinetic, and thermodynamic properties of chromium(III) complexes. The present paper is concerned with the ligand field spectra of a particular class of compounds called<sup>1</sup> orthoaxial complexes.

We want to outline briefly the model approach. The word "field", contained in the concept of the ligand field model, would seem to imply that the effect of the ligands is represented by a field, i.e., that we have a perturbation model. We take this to mean a first-order perturbation model with a basis set consisting of five d functions. We refer to a previous paper<sup>2</sup> about details and further references, recapitulating here only that a distinction between a nonadditive<sup>3</sup> and an additive<sup>4</sup> ligand field is useful.

In the semiempirical nonadditive field the effect of all of the ligands in a complex is represented by a perturbation operator which has the symmetry properties of the complex but which cannot be divided into terms representing the individual ligands. The number of independent empirical parameters required to parameterize the field is determined exclusively by the symmetry of the system. In the additive field, on the other hand, the perturbation operator, or rather the nonspherical part of it, is written as a sum of terms representing the individual ligands. This implies the concept of ligand field parameters referring to the individual central ion to ligand bonds and opens up the possibility of transferability of such single-ligand parameters from one complex to another. It is one of the purposes of the present paper to discuss how such a transferability can be investigated experimentally.

In order to compare the theory with experimental results for a  $d^9$  system a model is required also for parameterizing the interelectronic repulsion. Here the usual first-order perturbation treatment is used with the same basis set, i.e., the usual Slater-Condon-Shortley treatment. The combination of the semiempirical ligand field model and the semiempirical repulsion model in this way has been called the expanded radial function model.<sup>5</sup> In the present paper a

barycentered<sup>2</sup> interelectronic repulsion parameter  $b$  will be used. Expressed in this parameter the energies  $\bar{h}[^4F]$  and  $\bar{h}[^4P]$  of the highest spin-multiplicity terms of the  $d^3$  configuration are  $-3b$  and  $7b$ , respectively.

We then define the concept of orthoaxiality. This concept has been discussed previously in the additive ligand field when the orthoaxiality derives its name from the fact that the angles between neighboring central ion to ligand bonds are  $90^\circ$ . The characteristic property of the orthoaxial complexes is that the matrix elements between  $e_g(O_h)$  and  $t_{2g}(O_h)$  orbitals are vanishing and this property may be used as the basis for a redefinition of orthoaxiality in the nonadditive ligand field.

The model basis for theoretical consideration of the spectra of such complexes was developed years ago in a series of papers which were hardly linked together by their own authors and which we therefore want to outline.

It started with a thesis by Ilse,<sup>6</sup> who used the additive fields, known as the point-charge and point-dipole models. This point-dipole model was later used to discuss explicitly orthoaxial complexes,<sup>7,8</sup> but the nonadditive field appeared shortly in a ligand field<sup>9</sup> and in a crystal field<sup>10,11</sup> parameterization<sup>2</sup> and the additive field appeared in a ligand field parameterization.<sup>12,13</sup>

A relationship between the parameters of the nonadditive and the additive field was given<sup>14</sup> first in the crystal field parameterization and later<sup>15,16</sup> in the ligand field parameterization. Relationships between the two kinds of parameterization in the nonadditive field<sup>3,17</sup> and in the additive field<sup>1,4</sup> also exist in the literature. However, the firm distinction between the nonadditive and the additive field is rather recent<sup>2</sup> and so are proposals for standardizing the choice of empirical parameters.<sup>3,4,18-20</sup>

As a consequence of the historical development indicated, a variety of parameters exists in the chemical and physical literature and it is often difficult to compare papers even on closely related subjects.

It was soon realized that the energy of the lowest energy spin-allowed transition  $A_{2g}(O_h) \rightarrow T_{2g}(O_h)$  in octahedral  $d^3$  and  $d^8$  complexes within the expanded radial function model

was equal to the one-electron energy difference  $\Delta$  between the  $e_g(O_h)$  and  $t_{2g}(O_h)$  orbitals. However, it was not until much later that it was found that the energies of the split components of this transition due to an orthoaxial additive ligand field in the pure cubic subconfiguration approximation depend on the  $\Delta$  values for the individual ligands of the complex.<sup>1,22</sup> This rule has been extremely important because it has made assignments of these split components completely unambiguous.

We refer to the truly orthoaxial complexes that have appeared in the literature<sup>23-30</sup> and to the studies concerning almost orthoaxial complexes<sup>31-38</sup> of chromium(III). Since 1968 it has fortunately become customary<sup>25,26,47</sup> to use the full energy matrices of the expanded radial function model in order to derive empirical parameters from experimental energy differences.

In the study of chiral metal ion chromophores<sup>39</sup> it was realized that they can be described as having a major orthoaxial ligand field, mainly but not solely responsible for the position of their energy levels, with a superimposed nonorthoaxial field, responsible for the rotational strengths. We were interested in information about the major orthoaxial field and with this purpose we prepared<sup>40,41</sup> members of the achiral *trans*-tetraamminechromium(III) series to compare this with, for example, the chiral *trans*-bis(*trans*-1(*R*),2(*R*)-cyclohexanediamine)chromium(III) series.<sup>42</sup>

Later we became interested in the *trans*-tetrakis(pyridine)chromium(III) series<sup>43</sup> which in addition to being orthoaxial has three properties of particular interest to ligand field studies. They are potentially chiral and the pyridine molecule is a simple case of a nonlinearly ligating ligand<sup>16</sup> (section 2C), which further has the possibility of  $\pi$ -back-bonding.

In the present paper the spectra of the tetraammine and the tetrakis(pyridine) series have been analyzed simultaneously by introducing the transferability assumption together with the angular overlap model,<sup>15</sup> both of which associate with each metal to ligand bond a  $\sigma$  and a  $\pi$  contribution. Resolution of the pyridine complexes into antipodes has not been accomplished but the nonlinear ligation and the  $\pi$ -back-bonding toward the aromatic ligand pyridine have been illuminated and various spectrochemical series have been established.

## 2. The Ligand Field

**A. The Chemical Approach to Spectroscopy.** The usual experimental spectroscopic approach to transition metal complexes seeks to accumulate as much information as possible about an individual chemical system. Similarly molecular orbital calculations are always concerned with individual systems. In the present paper the gain in generality which arises from the restrictive assumptions of the expanded radial function model is used to treat a series of complexes simultaneously.

The purpose of this approach is to try, particularly by invoking the transferability assumption, to extract from a large amount of ligand field spectral material the chemically interesting information it might contain. One might say it is a chemical approach to spectroscopy rather than a physical one.

We have been concerned with the visible absorption spectra of solutions mainly of tetragonal chromium(III) complexes and have used a Gaussian analysis data reduction to represent our experimental spectra. This is from a theoretical point of view a most doubtful procedure, and from a statistical point of view it is rarely justified. However, a broad shoulder on a broad absorption band of a chromium(III) complex has always been taken as evidence for the existence of at least two electronic transitions and this interpretation has to our knowledge always been borne out by the internal consistency found for series of solution spectra. Furthermore, polarized

spectra of crystals containing the same chromophoric complexes have often revealed shoulders as separate bands and thereby confirmed their interpretation. Approximate positions of the individual components of overlapping absorption bands have often simply been estimated from inspection of absorption curves. We believe that a curve analysis procedure is a more satisfactory way of obtaining these positions and this is the reason for our choice.

So we consider our work, based upon a mass of undetailed information and a generally applicable theoretical model, as complementary to work concerned with detailed information and detailed calculations on individual systems.

**B. The Nonadditive Field.** From electron spin resonance studies in this laboratory<sup>44</sup> it could be concluded that all *trans*-tetraammine- and -tetrakis(pyridine)chromium(III) complexes, dissolved in glasses, have essentially tetragonal symmetry. The zero-field splittings could largely be explained on the basis of the one-electron energy differences which in agreement with the present work previously were found by us<sup>25</sup> on the basis of the absorption spectra of the *trans*-tetraammine complexes. It was further shown in one instance by comparison of the ESR spectra of  $[\text{Cr}(\text{py})_4\text{Br}_2]^+$  in a glass and diluted in a crystal matrix of known structure<sup>45</sup> that the magnetic tetragonal axis coincides with the molecular tetragonal axis, as opposed to the case of a similar ethylenediamine complex.<sup>48</sup> This means that the holohedrized symmetry<sup>45</sup> is in all cases  $D_{4h}$  so that the energy levels within the expanded radial function model can be characterized by irreducible representations of this group.

In general one may think about the ligand field operator  $V$  as consisting of an unobservable part of spherical<sup>3</sup> symmetry  $V(R_{3i})$ , which has no influence upon energy differences within a  $d^q$  configuration, and a remaining part  $\bar{V}$ .  $\bar{V}$  may be expressed as a sum of terms whose number is determined by symmetry.<sup>3</sup> We shall speak about a ligand field parameterization<sup>3</sup> when one uses the one-electron energies to define the parameters. This may be done either in terms of a set of independent energy differences or in terms of the energies measured relative to their average energy.<sup>3</sup> Generally one has in both cases to supplement the energy parameters with parameters representing the symmetry-required non-diagonal elements of  $\bar{V}$ .

Such nondiagonal elements do not occur in orthoaxial complexes except when the lowest possible holohedrized symmetry  $D_{2h}$  is attained. Even in this case it is possible to define the  $e_g(O_h)$  and  $t_{2g}(O_h)$  orbitals out of the  $d$  set in a way which for practical purposes is unique. This is because the three perpendicular symmetry axes of  $D_{2h}$  may also be taken to define an octahedron. This is the basis for the strong-field quantization used in the  $d^3$  energy matrix (Table I) of the expanded radial function model.

In tetragonal symmetry the two ligand field parameterizations may be expressed by the defining equations<sup>49</sup>

$$\bar{h}[\epsilon] \equiv (3/5)\Delta(d) + (1/2)\Delta(e) \quad (1a)$$

$$\bar{h}[\theta] \equiv (3/5)\Delta(d) - (1/2)\Delta(e) \quad (1b)$$

$$\bar{h}[\xi] \equiv -(2/5)\Delta(d) + (2/3)\Delta(t_2) \quad (1c)$$

$$\bar{h}[\eta] = \bar{h}[\xi] \equiv -(2/5)\Delta(d) - (1/3)\Delta(t_2) \quad (1d)$$

where  $\bar{h}[\epsilon]$ , for example, is the diagonal element  $\langle \epsilon | \bar{V} | \epsilon \rangle$  of the ligand field operator. When this operator is written as a sum<sup>25</sup> of a cubic term  $\bar{V}(O_h)$  and two tetragonal terms  $\bar{V}(D_{4h}^e)$  and  $\bar{V}(D_{4h}^{t_2})$ , then the three terms are associated with the symmetry parameters  $\Delta(d)$ ,  $\Delta(e)$ , and  $\Delta(t_2)$ , respectively. Equation 1 contains the definitions of these parameters in terms of the one-electron energies.  $\Delta(e)$  and  $\Delta(t_2)$  are seen to be the tetragonal splitting parameters within the subshells  $e_g$  and  $t_{2g}$  and  $\Delta(d)$  is the energy difference between the

Table I. Energy Matrices in the Expanded Radial Function Model for a Complex of Symmetry  $D_{2h}$  (or Higher Symmetry) of a  $d^3$  or  $d^8$  Configuration of Maximum Spin Multiplicity<sup>a</sup>

$e^2 t_2$	$T_1$	$B_1$	$-b + \bar{h} \theta\rangle + \bar{h} \epsilon\rangle + \bar{h} \xi\rangle$	$4b$	$0$
$et_2^2$	$T_1$	$B_1$	$4b$	$5b + \bar{h} \theta\rangle + \bar{h} \epsilon\rangle + \bar{h} \eta\rangle$	$s$
$et_2^2$	$T_2$	$B_1$	$0$	$0$	$-3b + \bar{h} \epsilon\rangle + \bar{h} \xi\rangle + \bar{h} \eta\rangle$
$e^2 t_2$	$T_1$	$B_2$	$-b + \bar{h} \theta\rangle + \bar{h} \epsilon\rangle + \bar{h} \eta\rangle$	$4b$	$0$
$et_2^2$	$T_1$	$B_2$	$4b$	$5b + (1/4)\bar{h} \theta\rangle + (3/4)\bar{h} \epsilon\rangle + \bar{h} \xi\rangle + \bar{h} \eta\rangle + (3^{1/2}/2)s$	$-(3^{1/2}/4)\bar{h} \theta\rangle - \bar{h} \epsilon\rangle - (1/2)s$
$et_2^2$	$T_2$	$B_2$	$0$	$-(3^{1/2}/4)\bar{h} \theta\rangle - \bar{h} \epsilon\rangle - (1/2)s$	$-3b + (3/4)\bar{h} \theta\rangle + (1/4)\bar{h} \epsilon\rangle + \bar{h} \xi\rangle + \bar{h} \eta\rangle - (3^{1/2}/2)s$
$e^2 t_2$	$T_1$	$B_3$	$-b + \bar{h} \theta\rangle + \bar{h} \epsilon\rangle + \bar{h} \xi\rangle$	$4b$	$0$
$et_2^2$	$T_1$	$B_3$	$4b$	$5b + (1/4)\bar{h} \theta\rangle + (3/4)\bar{h} \epsilon\rangle + \bar{h} \eta\rangle + \bar{h} \xi\rangle - (3^{1/2}/2)s$	$(3^{1/2}/4)\bar{h} \theta\rangle - \bar{h} \epsilon\rangle - (1/2)s$
$et_2^2$	$T_2$	$B_3$	$0$	$(3^{1/2}/4)\bar{h} \theta\rangle - \bar{h} \epsilon\rangle - (1/2)s$	$-3b + (3/4)\bar{h} \theta\rangle + (1/4)\bar{h} \epsilon\rangle + \bar{h} \eta\rangle + \bar{h} \xi\rangle + (3^{1/2}/2)s$
$t_2$	$A_2$	$A$	$-3b + \bar{h} \xi\rangle + \bar{h} \eta\rangle + \bar{h} \xi\rangle$	$0$	$0$

<sup>a</sup> The matrices are given in the cubic strong-field description which means that the functions referring to the diagonal belong to pure cubic subconfigurations as indicated in the first column. These functions are further characterized by spanning irreducible representations of the octahedral group  $O_h$  as indicated in the second column. They also span irreducible representations of the group  $D_{2h}$  as indicated in the third column. Throughout, the designation of the gerade parity has been omitted. The matrix elements are given in terms of the barycentered one-electron energies  $\bar{h}$  (eq 1) and the barycentered interelectronic repulsion parameter  $b$  giving the F and P multiplet terms the energies  $-3b$  and  $7b$ , respectively.  $b$  is equal to 1.5 times the Racah parameter  $B$ .  $s$  is quite generally given by  $s = \langle \theta | V | \epsilon \rangle$ . In the nonadditive ligand field the energy matrix represents the most general orthoaxial complex. In the additive field of a meridional  $N_3A_3$  complex (A and N linearly ligating) with two A's on the z axis and two N's on the y axis  $s$  is given by  $s = (3^{1/2}/12)(\Delta_{ON} - \Delta_{\sigma A})$ .

average energies<sup>25</sup> of these two subshells. The signs are of course important. It is further seen that the barycenter rule applies to the whole d shell. This is a way of expressing that the operator  $\bar{V}$  contains no spherically symmetrical part. Analogously the validity of the barycenter rule for the  $e_g$  and  $t_{2g}$  subshells expresses that neither the operator  $\bar{V}(D_{4h}^g)$  nor the operator  $\bar{V}(D_{4h}^{h^2})$  contains a cubically symmetrical part.

Equation 1 may be inserted into the  $10 \times 10$  energy matrix of Table I. Thereby this matrix is converted into a matrix which falls into blocks of  $1 \times 1$  [ $B_1(D_{4h})$ ],  $1 \times 1$  [ $B_2(D_{4h})$ ],  $2 \times 2$  [ $A_2(D_{4h})$ ], and  $3 \times 3$  [ $E(D_{4h})$ ].

It is readily verified that the barycenter rule for  $\Delta(e)$  and  $\Delta(t_2)$  applies to the cubic parentage functions of  $T_1$  and  $T_2$  type and for  $\Delta(d)$  and  $b$  it applies to the whole  $d^3$  or  $d^8$  configuration.

The symmetry parameters  $\Delta(d)$ ,  $\Delta(e)$ , and  $\Delta(t_2)$  of the ligand field parameterization are linearly related<sup>2</sup> to any other internally linearly independent set of three symmetry parameters. The circumstance that a function set, in this case a d set, adapted to spherical symmetry is used as the zero-order functions suggests an expansion of the perturbation Hamiltonian in terms whose electronic factors transform irreducibly under the three-dimensional rotation-inversion group  $R_{3i}$ . Such a procedure, which today rationally can be followed using 3/ symbols<sup>2,18,51</sup> and the Wigner-Eckart theorem, has in fact been applied from the childhood of the crystal field model and we shall therefore call parameterizations of this type crystal field parameterizations.<sup>3</sup> We wish to stress that this naming does not imply that the parameters should be interpreted electrostatically.

**C. The Additive Ligand Field.** When the ligand field operator is assumed to consist of a sum of terms, where each term represents the perturbation from one particular ligand we speak about the additive ligand field.

In this case we write the operator as A and it has the form

$$A = \sum_{(jJ)} A^{(jJ)}$$

where j within a chosen frame for the particular central ion to ligand system represents the position and rotational orientation of the ligand J so that (jJ) is a set of variables which are bound together during the summation. The additive field has been discussed in earlier papers<sup>4,15,16</sup> and will not be treated further here. However, one important property of A must be stressed. This operator can, like the nonadditive field operator V, be thought of as consisting of a spherical part  $A(R_{3i})$  and a remaining part  $\bar{A}$ .  $A(R_{3i})$  has no consequences for the application of the model and may therefore equally well be written  $V(R_{3i})$  to stress the fact that the assumption of additivity need not be made<sup>4</sup> for the spherically symmetrical field term.

In representing the additive field we shall use here the assumptions of the angular overlap model. This means that we use the single-ligand parameters  $\Delta_{\sigma}$  and  $\Delta_{\pi}$  to which we may add an extra subindex J to refer to the ligand J while we remember that in this work all parameters refer to chromium(III).

For linearly ligating ligands, i.e., ligands for which the central ion to ligand system has the symmetry  $C_{\infty v}$ , their formal expressions are<sup>4</sup>

$$\Delta_{\sigma J} = 3(e_{\sigma J} - e_{\delta J}) \quad (2a)$$

$$\Delta_{\pi J} = 4(e_{\pi J} - e_{\delta J}) \quad (2b)$$

where  $e_{\lambda J}$  ( $\lambda = \sigma, \pi, \delta$ ) are the one-electron energies of the ligand field model in the system consisting of the central ion M and a single ligand of type J. The expressions of eq 2 require only the assumptions of additivity and linear ligation in order to be valid within a d basis set. However, in the angular overlap model the parameters are interpreted as

associated with the involvement of the d electrons in the M–J bonding. So when  $\delta$  bonding is unimportant relative to  $\sigma$  and  $\pi$  bonding,  $e_{\sigma J} - e_{\delta J}$  is the  $\sigma$ -antibonding energy of that d orbital which in the M–J system is  $d\sigma$ , i.e., has rotational symmetry about the M–J bond.  $e_{\pi J} - e_{\delta J}$  may be written as

$$e_{\pi J} - e_{\delta J} = (e_{\pi J} - e_{\delta J})^a + (e_{\pi J} - e_{\delta J})^b \quad (3)$$

where the superindices a and b refer to antibonding and bonding. In eq 3 the a term is positive and the b term is negative, so that the net energetic consequence, which is the experimentally accessible quantity, may become negative if  $\pi$  back-bonding gives the dominating contribution to the  $d\pi$ -electron energy.

Assuming the ligand ammonia to be effectively linearly ligating, the parameters of the nonadditive field for the system *trans*-[Cr(NH<sub>3</sub>)<sub>4</sub>AB]<sup>n+</sup> may be expressed in terms of  $\Delta_\sigma$  and  $\Delta_\pi$  parameters for the individual chromium(III) to ligand bonds. Abbreviating  $\Delta_{\sigma\text{NH}_3}$  and  $\Delta_{\pi\text{NH}_3}$  as  $\Delta_{\sigma\text{N}}$  and  $\Delta_{\pi\text{N}}$ , the parameters of the nonadditive field may be expressed in terms of those of the additive field as

$$\Delta(d) = 1/6(\Delta_{\sigma\text{A}} - \Delta_{\pi\text{A}}) + 1/6(\Delta_{\sigma\text{B}} - \Delta_{\pi\text{B}}) + 2/3(\Delta_{\sigma\text{N}} - \Delta_{\pi\text{N}}) \quad (4a)$$

$$\Delta(e) = -1/3(\Delta_{\sigma\text{A}} - \Delta_{\sigma\text{N}}) - 1/3(\Delta_{\sigma\text{B}} - \Delta_{\sigma\text{N}}) \quad (4b)$$

$$\Delta(t_2) = -1/4(\Delta_{\pi\text{A}} - \Delta_{\pi\text{N}}) - 1/4(\Delta_{\pi\text{B}} - \Delta_{\pi\text{N}}) \quad (4c)$$

It is seen that when N = A = B = J, then  $\Delta(e) = \Delta(t_2) = 0$  and

$$\Delta(d) = \Delta_{\sigma\text{J}} - \Delta_{\pi\text{J}} = \Delta_{\text{J}}$$

which is the general expression for the cubic field parameter for the complex [MJ<sub>6</sub>]<sup>n+</sup> in the additive field model. It is also seen that the parameter  $\Delta(d)$  for the cubic part of the nonadditive field in the additive field is equal to the average  $\Delta_{\text{J}}$  for all the ligands<sup>52</sup> of the complex [Cr(NH<sub>3</sub>)<sub>4</sub>AB]<sup>n+</sup>.

Although the right-hand sides of eq 4 contain six parameters, only three linear combinations of these parameters may be determined from the experiment. If, however, the angular overlap model interpretation of parameters is valid,  $\Delta_{\pi\text{N}}$  should vanish. We therefore define new parameters measured relative to  $\Delta_{\pi\text{N}}$

$$\Delta'_{\lambda\text{J}} = \Delta_{\lambda\text{J}} - \Delta_{\pi\text{N}} \quad (\lambda = \sigma, \pi)$$

We want to estimate the linear combinations defined through

$$\Delta'_{\sigma\text{AB}} \equiv 1/2(\Delta'_{\sigma\text{A}} + \Delta'_{\sigma\text{B}}) \quad (5a)$$

$$\Delta'_{\pi\text{AB}} \equiv 1/2(\Delta'_{\pi\text{A}} + \Delta'_{\pi\text{B}}) \quad (5b)$$

$$\Delta'_{\sigma\text{N}} \equiv \Delta_{\text{N}} \quad (5c)$$

and rewrite eq 4 as

$$\Delta(d) = 1/3\Delta'_{\sigma\text{AB}} - 1/3\Delta'_{\pi\text{AB}} + 2/3\Delta'_{\sigma\text{N}} \quad (6a)$$

$$\Delta(e) = -2/3\Delta'_{\sigma\text{AB}} + 2/3\Delta'_{\sigma\text{N}} \quad (6b)$$

$$\Delta(t_2) = -1/2\Delta'_{\pi\text{AB}} \quad (6c)$$

We consider next the [Cr(py)<sub>4</sub>AB]<sup>n+</sup> system of symmetry C<sub>4</sub> and with A and B linearly ligating. The pyridine molecules form a four-bladed propeller around the A–Cr–B axis (z axis) with the nitrogen ligators in the xy plane. The pyridine molecular plane forms an angle  $\psi$  with the xy plane. Using the angular overlap model we assume that only two one-electron single-ligand parameters are nonvanishing,  $e_{\sigma\text{py}}$  and  $e_{\pi\text{py}}$ . The latter parameter is associated with the  $\pi$  orbitals whose node planes coincide with the pyridine molecular plane.

We then define

$$\Delta_{\text{py}} = \Delta_{\sigma\text{py}} - \Delta_{\pi\text{py}} = 3e_{\sigma\text{py}} - 2e_{\pi\text{py}}$$

where the coefficient 2 arises from the above-mentioned restriction upon the  $\pi$  orbitals which participate in the metal–pyridine bonding, and express the symmetry parameters  $\Delta(d)$ ,  $\Delta(e)$ , and  $\Delta(t_2)$  in terms of the additive field for [Cr(py)<sub>4</sub>AB]<sup>n+</sup>

$$\Delta(d) = 1/3\Delta'_{\sigma\text{AB}} - 1/3\Delta'_{\pi\text{AB}} + 2/3\Delta'_{\sigma\text{py}} - 2/3\Delta'_{\pi\text{py}} \quad (7a)$$

$$\Delta(e) = -2/3\Delta'_{\sigma\text{AB}} + 2/3\Delta'_{\sigma\text{py}} \quad (7b)$$

$$\Delta(t_2) = -1/2\Delta'_{\pi\text{AB}} + 1/2\Delta'_{\pi\text{py}} - 3/2(\cos 2\psi)\Delta_{\pi\text{py}} \quad (7c)$$

corresponding to eq 6 for the [Cr(NH<sub>3</sub>)<sub>4</sub>AB]<sup>n+</sup> system. To obtain these equations of which only the last equation differs from that of the ammonia case, eq 45 of ref 16 has been used. Again it must be emphasized that, except for the  $\Delta_{\pi\text{py}}$  parameter,  $\Delta_{\pi\text{N}}$  has been used as the zero point for all the parameters of eq 7.

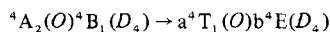
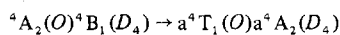
Therefore the situation is as follows. First, the symmetry parameters  $\Delta(d)$ ,  $\Delta(e)$ , and  $\Delta(t_2)$  for each tetraammine or tetrakis(pyridine) complex can be determined from the experimental transition energies. Second, the three parameters  $\Delta'_{\sigma\text{N}}$ ,  $\Delta'_{\sigma\text{AB}}$ , and  $\Delta'_{\pi\text{AB}}$  can be calculated from eq 6 on the basis of  $\Delta(d)$ ,  $\Delta(e)$ , and  $\Delta(t_2)$  for the [Cr(NH<sub>3</sub>)<sub>4</sub>AB]<sup>n+</sup> complex. Third, on the assumption that  $\Delta'_{\sigma\text{AB}}$  and  $\Delta'_{\pi\text{AB}}$ , determined from the [Cr(NH<sub>3</sub>)<sub>4</sub>AB]<sup>n+</sup> spectra, take on the same values for [Cr(py)<sub>4</sub>AB]<sup>n+</sup>,  $\Delta'_{\sigma\text{py}}$ ,  $\Delta'_{\pi\text{py}}$ , and  $\Delta_{\pi\text{py}}(\cos 2\psi)$  can be calculated from eq 7 on the basis of  $\Delta(d)$ ,  $\Delta(e)$ , and  $\Delta(t_2)$  for the [Cr(py)<sub>4</sub>AB]<sup>n+</sup> complex (Table II). [The angle  $\psi$  can only be determined if an additional assumption is made about the value of  $\Delta_{\pi\text{N}}$  (Table IV).]

Until now, all considerations have been concerned with [Cr(NH<sub>3</sub>)<sub>4</sub>AB]<sup>n+</sup>–[Cr(py)<sub>4</sub>AB]<sup>n+</sup> pairs, and the parameters  $\Delta'_{\sigma\text{AB}}$  and  $\Delta'_{\pi\text{AB}}$  averaging over A and B have been involved.

An extension of the transferability assumption to bridge between different [Cr(NH<sub>3</sub>)<sub>4</sub>AB]<sup>n+</sup>–[Cr(py)<sub>4</sub>AB]<sup>n+</sup> pairs using eq 5 and assuming  $\Delta'_{\sigma\text{N}}$ ,  $\Delta'_{\lambda\text{py}}$ ,  $\Delta'_{\lambda\text{A}}$ , and  $\Delta'_{\lambda\text{B}}$  ( $\lambda = \sigma, \pi$ ) to be transferable leads to the data reduction (Table III). Finally, the assumption of transferability of  $\Delta_{\pi\text{py}}(\cos 2\psi)$  gives the final data reduction (Table IV).

**D. Assignment of Absorption Bands.** A few examples will show how certain assignments of the d–d transitions can be made on the basis of comparative spectral studies using chemical arguments about the variation in the angular overlap model parameters on going from one complex to another.

The assignment of the split components of the first cubic parentage absorption band is a simple matter since their positions depend only on the  $\Delta$  values<sup>1,22</sup> of the individual ligands of the complex in question. Let us therefore focus attention upon the split components of the second cubic parentage band. The transitions are



Let us characterize them by their excited states and call them the A<sub>2</sub> and E transitions.

Let us consider first the series (Figure 1) of *trans*-tetraammine complexes of (OH)<sub>2</sub>, (H<sub>2</sub>O)(OH), and (H<sub>2</sub>O)<sub>2</sub>. There is clearly a gradual decrease of the magnitude of the splitting as one goes from (OH)<sub>2</sub> to (H<sub>2</sub>O)<sub>2</sub>. Therefore if we look at the (OH)<sub>2</sub> and (OH)(H<sub>2</sub>O) complexes alone, we can conclude in the first place that the A<sub>2</sub> transitions correspond for both systems either to the high-energy component or to the low-energy component, since it is impossible, if an additive field is assumed, that A<sub>2</sub> is the high-energy component in one of the complexes and the low-energy component in the other one as this would have required a larger splitting in the (H<sub>2</sub>O)<sub>2</sub> complex than in the (OH)(H<sub>2</sub>O) complex. Then it is only possible that A<sub>2</sub> is the high-energy component in both the (OH)<sub>2</sub> and the (OH)(H<sub>2</sub>O) systems since the opposite as-

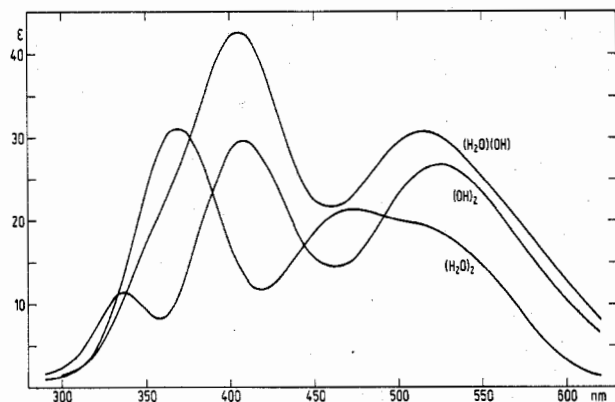


Figure 1. Solution absorption spectra of the dihydroxo, the aquahydroxo, and the diaqua complexes of the *trans*-tetraamminechromium(III) series.

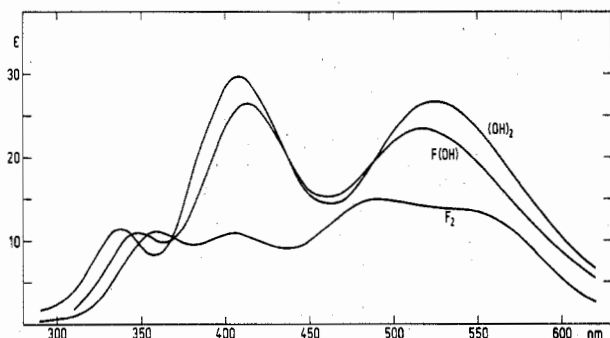


Figure 2. Solution absorption spectra of the dihydroxo, the fluorohydroxo, and the difluoro complexes of the *trans*-tetraamminechromium(III) series.

signment of the split bands would have led to negative values for both  $\Delta_{\sigma\text{OH}} - \Delta_{\pi\text{OH}_2}$  and  $\Delta_{\pi\text{OH}} - \Delta_{\pi\text{OH}_2}$ , a chemically unacceptable situation if the angular overlap model interpretation of the parameters shall be reasonable. Once the assignments have been made in this way for the  $(\text{OH})_2$  complexes, it is obvious from Figure 2 that the  $A_2$ -split components also have to be the high-energy ones for the  $(\text{OH})\text{F}$  and  $\text{F}_2$  complexes. In a similar way one can, by comparative studies like the examples given, arrive at assignments in other cases.

For difluoro-<sup>33</sup> and dibromobis(ethylenediamine)chromium(III)<sup>35</sup> complexes unambiguous assignments have been made on the basis of polarized crystal spectra. So, having illustrated above how one can go about making assignments partially on the basis of chemical arguments, we are now able to go the other way around: from the spectroscopically assigned bands of the  $\text{F}_2$  complex ( $A_2$  at higher energy) we may now conclude from the additivity assumption applied to the spectra of Figure 2 that  $A_2$  also is the higher energy component of a  $^4T_1$  for the  $(\text{OH})\text{F}$  and  $(\text{OH})_2$  complexes. In this way one obtains large values for the  $\Delta'_{\sigma\text{OH}}$  and  $\Delta'_{\pi\text{OH}}$  parameters discussed above, and these values lend support to the angular overlap model interpretation of the empirical parameters.<sup>4</sup>

### 3. Method of Calculation

All calculations of parameters dealt with in this paper were performed within the framework of regression analysis. This technique is excellently described in a number of textbooks and will consequently not be covered here.

The calculations to obtain the final parameters from the initial visible absorption spectra were carried out in three distinct steps.

In the first step the observed visible absorption spectra, measured at 5-nm intervals, were expressed as a sum of four  $\lambda$  Gaussian curves,<sup>53</sup> e.g.

$$\epsilon(\lambda) = \sum_{i=1}^4 D_i \exp[-((\lambda - \lambda_i)/\sigma_i)^2]$$

For almost symmetrical spectral bands without indications of band splittings attempts at resolving these into more than one Gaussian component frequently resulted in difficulties as expected. Either the normal equations of the regression analysis procedure became singular or the results were such that one Gaussian component described the major part of the spectral band and the remaining Gaussian components described minor deviations from the true Gaussian shape of the spectral band. Such behavior is obviously unwanted and was overcome simply by adding extra information about acceptable Gaussian component heights to the normal equations. For an unresolved spectral band of height  $D$ , which is required by the model to represent two bands and thus to be expressed as a sum of two Gaussian curves, extra pseudoexperiments have been added. These state that the individual component heights have been measured with a mean value  $D/2$  and variance  $(D/20)^2$ . This approach produced acceptable parameter vectors for all of the spectra treated in this paper, and as a test of the independence of this final parameter vector upon the extra pseudoexperiments the following conditions were used. Let  $\mathbf{a}^*$  be the minimum parameter vector calculated from all of the experiments and  $\bar{\mathbf{a}}$  the linear approximation to the minimum parameter vector calculated only from the genuine experiments. Let further  $\mathbf{A}$  be the variance matrix calculated from  $\mathbf{a}^*$  but without the extra height experiments; then sufficiently small values of  $P\{\chi^2 < (\mathbf{a}^* - \bar{\mathbf{a}})^T \mathbf{A}^{-1} (\mathbf{a}^* - \bar{\mathbf{a}})\}$  for rank  $\mathbf{A}$  degrees of freedom were taken as an indication of independence between the calculated minimum parameter vector,  $\mathbf{a}^*$ , and the extra pseudoexperiments. For further calculations the desired parameter vector was assumed to be estimated with mean value  $\mathbf{a}^*$  and variance matrix  $\mathbf{A}$ . The Gaussian type of data reduction is essential for the following calculations but unsatisfactory for at least two major reasons. First, none of the measured absorption spectra could be approximated to any degree of satisfaction with a function of this form when compared to the measuring accuracy. Second, even if this initial data reduction was acceptable from a statistical point of view, the following data reduction step, i.e., the exclusion of spectral band heights and spectral bandwidths from the total experimental material, necessitated by the unfortunate limitations of the ligand field model, places attempts upon a quantitative discussion of visible absorption spectra at a most undesirable level. With these obvious model deficiencies in mind, we have accepted the Gaussian shape data reduction and taken the Gaussian component positions to represent the vertical transition energies of the ligand field model.<sup>39</sup>

It was found convenient not to carry the Gaussian component positions as explicit parameters. Instead they were calculated from the three ligand field parameters  $\Delta(d)$ ,  $\Delta(e)$ , and  $\Delta(t_2)$  and the single barycentered interelectronic repulsion parameter  $b$  by diagonalization of the appropriate energy matrix. Consequently the regression analysis procedure<sup>54</sup> yielded directly the four above parameters<sup>55</sup> together with Gaussian component heights and bandwidths.

In the second step the three ligand field parameters were transformed into the parameters of the angular overlap model, either by eq 6 and 7 for the *trans*-tetraammine-*trans*-tetrakis(pyridine) pairs or by eq 6 alone for the *trans*-tetraamminebromochlorochromium(III) ion as in this case the corresponding pyridine complex was not prepared. The results of these calculations are given in Table II.

In the final calculational step average single-ligand parameters were calculated from those of the individual species or pairs of species investigated. As a quantitative description of the measured absorption spectra was not possible with the

Table II. Angular Overlap Model Parameters (in kK) (Eq 6 and 7), Derived from the Solution Absorption Spectra of *trans*-Tetraammine and *trans*-Tetrakis(pyridine) Complexes<sup>a</sup>

	$\Delta'_{\sigma N}$	$\Delta'_{\sigma AB}$	$\Delta'_{\pi AB}$	$\Delta'_{\sigma py}$	$\Delta'_{\pi py}$	$\Delta_{\pi py}(\cos 2\psi)$
<i>trans</i> -[Cr(NH <sub>3</sub> ) <sub>4</sub> F <sub>2</sub> ] <sup>+</sup>	20.84	22.3	7.0	18.3	-2.0	-0.79
<i>trans</i> -[Cr(py) <sub>4</sub> F <sub>2</sub> ] <sup>+</sup>						
<i>trans</i> -[Cr(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup>	21.10	16.0	2.9	17.1	-2.9	-0.57
<i>trans</i> -[Cr(py) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup>						
<i>trans</i> -[Cr(NH <sub>3</sub> ) <sub>4</sub> Br <sub>2</sub> ] <sup>+</sup>	21.66	15.1	3.6	17.3	-2.8	-0.65
<i>trans</i> -[Cr(py) <sub>4</sub> Br <sub>2</sub> ] <sup>+</sup>						
<i>trans</i> -[Cr(NH <sub>3</sub> ) <sub>4</sub> FCl] <sup>+</sup>	21.03	18.8	4.5	16.9	-3.4	-0.74
<i>trans</i> -[Cr(py) <sub>4</sub> FCl] <sup>+</sup>						
<i>trans</i> -[Cr(NH <sub>3</sub> ) <sub>4</sub> FBr] <sup>+</sup>	21.37	19.0	5.4	18.2	-2.2	-0.71
<i>trans</i> -[Cr(py) <sub>4</sub> FBr] <sup>+</sup>						
<i>trans</i> -[Cr(NH <sub>3</sub> ) <sub>4</sub> BrCl] <sup>+</sup>	21.14	15.7	2.8			

<sup>a</sup> See also discussions at the ends of sections 2C and 3.

Table III. Spectrochemical Series<sup>a</sup>

	J				
	NH <sub>3</sub>	py	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>
$\Delta'_{\sigma J} = \Delta_{\sigma J} - \Delta_{\pi NH_3}$	21.08 ± 0.07	17.4 ± 0.3	22.2 ± 0.2	16.4 ± 0.5	14.4 ± 0.3
$\Delta'_{\pi J} = \Delta_{\pi J} - \Delta_{\pi NH_3}$	0	-2.3 ± 0.3	6.82 ± 0.11	3.3 ± 0.6	2.0 ± 0.4
$\Delta_J$	21.08 ± 0.07	19.71 ± 0.15	15.39 ± 0.13	13.15 ± 0.10	12.42 ± 0.16

<sup>a</sup> The first two rows are the set consisting of the  $\Delta_{\sigma J}$  and  $\Delta_{\pi J}$  series, also called the two-dimensional spectrochemical series. The third row is the usual spectrochemical series of  $\Delta_J$  for cubic complexes which here has been derived solely on the basis of tetragonal complexes. All parameters in the table are the same (within the standard deviations) as those found previously<sup>2,25,47</sup> for the *trans*-tetraammine series except for  $\Delta_{NH_3}$  which was taken previously from the spectrum of the hexaamminechromium(III) ion as 21.6 kK (cf. also discussions at the ends of sections 2C and 3).

Gaussian component shape model, realistic error estimates of the parameters obtained by these computations were lacking. For further calculations it was however assumed that the correlation coefficients and the relative magnitudes of the estimated standard deviations were well defined. The standard deviations upon the mean values of the parameters in Tables III and IV are based upon this hypothesis and upon a common adjustment of the absolute size of all of the standard deviations upon the mean values of the parameters from the individual experiments to fulfill a  $\chi^2$  test at the 50% confidence level for these latter data reductions.

Computer programs were written in the Algol 6 dialect for the RC4000 computer, and the calculations were carried out at the H. C. Ørsted Institute.

#### 4. Results and Discussion

In Table II are given individual values for angular overlap parameters for five pairs of tetraammine and tetrakis(pyridine) complexes (eq 6 and 7). The parameter  $\Delta'_{\sigma N}$  is through the model given directly as the energy of the transition  ${}^4B_{1g} \rightarrow {}^4B_{2g}(D_{4h})$  in all the tetraammine complexes, and the lack of constancy of this transition energy thereby becomes a direct measure of the deficiency of the additive ligand field. This deficiency can also be read out of Table II where  $\Delta'_{\sigma py}$  appears in the region between 16.9 and 18.3 kK and  $\Delta'_{\pi py}$  between -3.4 and -2.0 kK. The negative value of  $\Delta'_{\pi py}$  is of particular interest, because it corresponds within the conceptional framework of the angular overlap model (eq 3) to a net  $\pi$  back-bonding from chromium(III) to the pyridine ligand. Even though the estimated values of this parameter are not in very good agreement, the parameter is consistently found to be negative. This is to our knowledge the first case of such a direct ligand field parametric piece of evidence for  $\pi$  back-bonding, although the small variation in  $\Delta$  values for d<sup>6</sup> hexacyanometalates [Mn(I), Fe(II), Co(III)] has been taken as evidence for  $\pi$  back-bonding to CN<sup>-</sup> a long time ago.<sup>56</sup>

In the first two rows of numbers of Table III the results shown in Table II have been collected using eq 5 to obtain average single-ligand parameters  $\Delta'_{\sigma J}$  and  $\Delta'_{\pi J}$ . The value zero for  $\Delta'_{\pi N}$  arises from its definition. Variances upon and covariances between the data of Table II, although not tabulated,

are of course essential for this calculation. From the estimated single-ligand parameters  $\Delta'_{\sigma J}$  and  $\Delta'_{\pi J}$ ,  $\Delta_J = \Delta'_{\sigma J} - \Delta'_{\pi J} = \Delta_{\sigma J} - \Delta_{\pi J}$  has been calculated and is given in the third row.

The parameter values for F<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup> are not different from our earlier ones,<sup>25,47</sup> but the results given here have been obtained in a much more objective way than previously and are now based also upon the spectra of the tetrakis(pyridine) series.  $\Delta'_{\sigma N} = \Delta_N$  was previously taken from the transition  ${}^4A_{2g} \rightarrow {}^4T_{2g}(O_h)$  of the hexaamminechromium(III) ion but is in this work derived from the *trans*-tetraammine series only. It is, of course, a deficiency of the additive ligand field that the spectra of the tetraammines give a smaller average value for  $\Delta_{NH_3}$  than does the spectrum of the hexaammine.

In Table IV the information derived from the pyridine complexes through eq 7c has been included by making the additional geometrical assumption that a common value for  $\psi$  may be used for all of the pyridine complexes. This assumption may be tested statistically and it was found to be justified.

From the additional assumption of  $\Delta_{\pi N} = 0$ ,  $\psi$  is estimated to be  $37.8 \pm 1.1^\circ$ , which is in fair agreement with the value of approximately  $45^\circ$  known from a crystal structure.<sup>46</sup> Assuming  $\Delta_{\pi N} \neq 0$  would be the same as allowing for a linear electrostatic field contributing to the perturbation from ammonia on top of the perturbation arising from the bonding. Such a discussion would require also an electrostatic contribution to the perturbation from pyridine and this has been excluded from the beginning by keeping only the  $\pi$  parameter associated with the  $\pi$  orbitals whose node plane coincides with the pyridine's molecular plane.

It may be noted by inspection of eq 7 that pyridine is effectively linearly ligating when  $\psi = 45^\circ$ . We wish to stress, however, that the mean value and standard deviation obtained for  $\psi$  exclude this situation.

We now return to the spectra of *trans*-[Cr(NH<sub>3</sub>)<sub>4</sub>AB]<sup>n+</sup> and *trans*-[Cr(py)<sub>4</sub>AB]<sup>n+</sup> complexes (A, B = Br, Cl, F) on which the parameter values of Table IV are based. For all of these complexes we have calculated (Table V) the transition energies associated with the parameters of Table IV. The interelectronic repulsion parameter *b* was arbitrarily put equal to 1000 cm<sup>-1</sup>, but the partial derivatives of the transition

Table IV.<sup>a</sup> Angular Overlap Model Parameters from Final Data Reduction (cf. Sections 2C and 3)

$\Delta'_\sigma\text{NH}_3$	21.11 ± 0.07									
$\Delta'_\sigma\text{py}$	17.54 ± 0.27	-0.244								
$\Delta'_\pi\text{py}$	-2.00 ± 0.20	-0.450	+0.890							
$\Delta'_\sigma\text{F}$	22.16 ± 0.20	-0.419	+0.702	+0.683						
$\Delta'_\pi\text{F}$	6.77 ± 0.12	-0.410	+0.478	+0.574	+0.757					
$\Delta'_\sigma\text{Cl}$	16.63 ± 0.41	-0.109	+0.538	+0.478	+0.279	+0.069				
$\Delta'_\pi\text{Cl}$	3.48 ± 0.44	+0.018	+0.492	+0.411	+0.231	+0.152	+0.978			
$\Delta'_\sigma\text{Br}$	14.76 ± 0.27	-0.020	+0.559	+0.393	+0.396	+0.405	+0.425	+0.428		
$\Delta'_\pi\text{Br}$	2.50 ± 0.39	+0.132	+0.570	+0.301	+0.379	+0.528	+0.423	+0.443	+0.955	
$\Delta_{\pi\text{py}}(\cos 2\psi)$	-0.50 ± 0.06	+0.460	-0.196	-0.439	-0.135	-0.152	+0.069	+0.152	+0.405	+0.528

<sup>a</sup> This table is based upon the assumption that  $\Delta_{\pi\text{py}}(\cos 2\psi)$  is common to all complexes of the tetrakis(pyridine) series. The first column gives this parameter and the angular overlap model parameters, the second one gives their values (mean values ± their standard deviations), and the rest of the table is the lower left part of the matrix of correlation coefficients. It is seen that only corresponding  $\Delta_{\sigma J}$  and  $\Delta_{\pi J}$  are strongly (and everywhere positively) correlated which means that their difference  $\Delta_J = \Delta_{\sigma J} - \Delta_{\pi J}$  is in most cases better determined than the individual parameters, as also indicated in Table III. It is further seen that the angular overlap model parameter values, standard deviations taken into account, are the same in Tables III and IV. The value -0.50 for the parameter  $\Delta_{\pi\text{py}}(\cos 2\psi)$  corresponds to  $\psi = 37.8 \pm 1.1^\circ$  when  $\Delta_{\pi\text{N}}$  is put equal to zero.

Table V. Transition Energies (kK) for *trans*-AB(NH<sub>3</sub>)<sub>4</sub> and *trans*-AB(py)<sub>4</sub> Complexes<sup>a</sup>

A B	<sup>a</sup> E	<sup>4</sup> B <sub>2</sub>	b <sup>4</sup> E	<sup>a</sup> A <sub>2</sub>	$\partial[\text{a}^4\text{E}]/\partial b$	$\partial[\text{b}^4\text{B}_2]/\partial b$	$\partial[\text{b}^4\text{E}]/\partial b$	$\partial[\text{a}^4\text{A}_2]/\partial b$
F F	18.23	21.11	24.95	28.20	0.013	0	5.835	4.394
	17.42	19.05	23.49	28.08	0.308	0	5.495	3.508
Cl Cl	16.94	21.11	25.66	24.88	0.135	0	5.289	5.203
	16.58	19.05	23.74	24.92	0.008	0	5.378	4.599
Br F	17.39	21.11	25.34	25.99	0.057	0	5.526	4.955
	16.92	19.05	23.54	25.99	0.010	0	5.532	4.262
Cl F	17.66	21.11	25.24	26.56	0.026	0	5.630	4.839
	17.11	19.05	23.51	26.53	0.042	0	5.572	4.103
Br Br	16.34	21.11	25.92	23.71	0.227	0	5.012	5.390
	16.07	19.05	23.91	23.79	0.062	0	5.142	4.853
Br Cl	16.64	21.11	25.78	24.30	0.180	0	5.154	5.299

<sup>a</sup> Based upon the ligand field parameters of Table IV and using  $b = 1000 \text{ cm}^{-1}$ . In the first column the AB ligands are given. The results for the ammonia complexes are in each upper row with those for the pyridine complexes directly below. The transitions are characterized in the table by the irreducible representations associated with the excited levels in the group  $D_4$ . The ground level is in all cases <sup>4</sup>B<sub>1</sub>( $D_4$ ). The partial derivatives of the transition energies with respect to the repulsion parameters are also given.

energies with respect to  $b$  are also given in the table.

Since the zero point for the repulsion energy is here the <sup>4</sup>F multiplet term and since the <sup>4</sup>P term has the energy  $10b$ , a derivative with respect to  $b$  of a given level, multiplied by 10, is a measure of the percentage of <sup>4</sup>P character in that level. The value  $1000 \text{ cm}^{-1}$  for  $b$  is rather close to the values found for all complexes studied. It should be mentioned that this parameter is rather poorly determined in the present data material and therefore no attempt could be made at using this material to reestablish the nephelauxetic series.<sup>56</sup>

On comparison of the energies of corresponding transitions in tetraammine and tetrakis(pyridine) complexes it is apparent that those whose excited levels are <sup>a</sup>E and <sup>a</sup>A<sub>2</sub> have much the same energies in the two series although certain irregularities exist for <sup>a</sup>E. On the other hand the transitions whose excited levels are <sup>4</sup>B<sub>2</sub> and b<sup>4</sup>E have quite different energies but nearly the same energy difference of about 2 kK both for <sup>4</sup>B<sub>2</sub> and b<sup>4</sup>E.

The ligands water and hydroxide were included in our previous work.<sup>25,47</sup> However, they are not linearly ligating and therefore there is not enough geometrical knowledge available to treat their complexes properly by the angular overlap model. Further their ESR spectra<sup>44</sup> indicate rhombic distortions. We tried to handle the aqua and hydroxo complexes under the assumption that they behaved effectively as linearly ligating and succeeded in part with the aqua complexes.

The values of the parameters for water were  $\Delta'_\sigma\text{H}_2\text{O} = 23.7 \pm 1.8$  and  $\Delta'_\pi\text{H}_2\text{O} = 7.7 \pm 2.0$  giving  $\Delta_{\text{H}_2\text{O}} = 16.0 \pm 0.3$  which is 1.4 kK smaller than the value observed for the hexaaqua-chromium(III) ion. The very high value of  $\Delta_{\pi\text{H}_2\text{O}}$  may indicate that the oxygen is trigonally or planarly ligating,<sup>16</sup> i.e., coordinating in such a way that the chromium(III) ion lies in the plane of the water molecule. We have also analyzed

the spectra<sup>57-59</sup> of all the ten isomers of the ammineaqua-chromium(III) series, again by assuming both ammonia and water to be linearly ligating. In this case we found  $\Delta'_\sigma\text{N} = 21.8 \pm 0.1$ ,  $\Delta'_\sigma\text{H}_2\text{O} = 20.3 \pm 0.9$ ,  $\Delta'_\pi\text{H}_2\text{O} = 3.0 \pm 0.9$ , and  $\Delta_{\text{H}_2\text{O}} = 17.3 \pm 0.1$ . Here the three complexes  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ , and *fac*- $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]^{3+}$  (holohedric symmetry  $O_h$ ), of course, contribute strongly to  $\Delta_{\text{H}_2\text{O}}$  and  $\Delta_{\text{NH}_3}$ . The much lower value of  $\Delta_{\pi\text{H}_2\text{O}}$  found here may indicate that the oxygen in these complexes is partially tetrahedrally ligating.<sup>16</sup> This apparently strange behavior may tentatively be associated with differences in cation-solvent or cation-anion interactions since in the tetraammine and tetrakis(pyridine) cases where  $\Delta'_\pi\text{H}_2\text{O} = 7.7 \text{ kK}$  the major amount of experimental material is based upon dipositive chromium(III) complexes, whereas in the case of the aquaammine series ( $\Delta'_\pi\text{H}_2\text{O} = 3.0$ ) only tripisitive chromium(III) complexes contribute. In this connection it should be emphasized that all of the ions of Tables II-IV have unit positive charge. The value  $\Delta_{\text{NH}_3} = 21.1$  found for these 1+ ions, compared with  $\Delta_{\text{NH}_3} = 21.8$  found for the 3+ ions, may similarly be caused by different interactions with the second sphere.

That fact that the single-ligand parameters for F<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup> were found to be the same in this work as in our previous work,<sup>25,47</sup> even though the hexaammine had previously been used to fix  $\Delta'_\sigma\text{NH}_3$ , is understandable from our present calculations by the fact that this parameter was found to be little correlated with the other single-ligand parameters (Table IV).

The analysis of the hydroxo complexes by the Gaussian procedure failed to such an extent that it would be unreasonable to give parameter values on this basis. When we did obtain parameter values in our previous work, it was because we fixed the energy of the transition <sup>4</sup>B<sub>1g</sub> → <sup>4</sup>B<sub>2g</sub> ( $D_{4h}$ ). This transition never appears separated in the hydroxo complexes but according to the additive field model its energy should



Table VI. Additive Ligand Field Parameters for Linearly Ligating Ligands in Orthoaxial Complexes

	Yamatera parameters			McClure parameters			Perumareddi parameters		
	$\Delta_N$	$\delta_\sigma$	$\delta_\pi$	$\Delta_N$	$4\delta\sigma$	$4\delta\pi$	$10Dq_{N_4AB}$	$(5/2)D^t_{N_4AB}$	$6D_s_{N_4AB}$
$\Delta'_{\sigma N} = \Delta_N$	1	0	0	1	0	0	1	0	0
$\Delta'_{\sigma AB}$	1	1	0	1	1	0	1	3	1
$\Delta'_{\pi AB}$	0	0	-1	0	0	1	0	-4	1

<sup>a</sup> The parameters of the present paper (eq 5) are expressed in terms of parameter sets frequently used in the literature. Each parameter of the set  $\{Dq, Ds, Dt\}$  has been supplemented with the subindex  $N_4AB$  to indicate that it is used as an additive field parameter. With the transferability assumption one then has  $Dq_{N_6} = Dq_{N_4AB}$  which using the table gives  $\Delta_{AB} = \Delta'_{\sigma AB} - \Delta'_{\pi AB} = 10Dq_{N_6} + (35/2)D^t_{N_4AB}$  which is a slight generalization of the expression of Wentworth and Piper.<sup>22</sup>

equal  $\Delta'_{\sigma N}$ . However, in the Gaussian analysis description this transition tends to move several kK toward the red. The spectra of the hydroxo complexes are not easy to understand even if nonlinear ligation of  $\text{OH}^-$  is taken into account. The split components of the second spin-allowed band  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  ( $O_h$ ) often appear well separated and not excessively broad [Figure 1] while the first spin-allowed band  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  ( $O_h$ ) at the same time is poorly split and cannot be represented by two Gaussians. If this behavior of the first band were caused by a superposition of spectra for molecules with hydroxide ions in different rotational orientations with respect to the chromium(III) to oxygen bond, one would have expected similar split behaviors<sup>60</sup> of the two first cubic spin-allowed transitions  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  ( $O_h$ ) and  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  ( $O_h$ ). In spite of these problems we still believe that our previous values<sup>4,25,47</sup>  $\Delta'_{\sigma\text{OH}} = 26$  kK and  $\Delta'_{\pi\text{OH}} = 9$  kK, although not valuable in a quantitative sense, are meaningful in attributing to the ligand  $\text{OH}^-$  the highest values for both parameters.

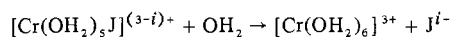
The well-known  $\Delta_J$  spectrochemical series previously based upon spectra of octahedral complexes has here been reestablished on the basis of tetragonal complexes. In addition to this series we have obtained the  $\Delta'_{\sigma J}$  and  $\Delta'_{\pi J}$  series which have previously been called the two-dimensional spectrochemical series,<sup>13</sup> i.e.

$$\Delta_J: \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{H}_2\text{O} < \text{py} < \text{NH}_3$$

$$\Delta'_{\sigma J}: \text{Br}^- < \text{Cl}^- < \text{py} < \text{H}_2\text{O} (?) < \text{NH}_3 < \text{F}^- < \text{OH}^- (?)$$

$$\Delta'_{\pi J}: \text{py} < \text{NH}_3 < \text{Br}^- < \text{Cl}^- < \text{H}_2\text{O} (?) < \text{F}^- < \text{OH}^- (?)$$

It must be emphasized that even with the bonding interpretation of the parameters of the angular overlap model the parameters refer only to the nonspherical part of the Hamiltonian and only to the bonding which is associated with the d orbitals, which means that even if the parameters have a chemical significance, they may not have a chemical importance. Therefore it is interesting to note that the enthalpies of activation for the aquation processes<sup>59,61,63-65</sup>



accurately, except for fluoride for which special circumstances operate,<sup>61,62</sup> follow the  $\Delta_J$  series as depicted in Figure 3. This correlation and similar correlations for other systems<sup>66</sup> do point toward a chemical importance of such parameters, and this will be the subject of a more detailed report later.

## Appendix

Usually complexes parameterized as orthoaxial ones are handled using the additive ligand field. In Table VI the additive field parameter set of eq 5  $\{\Delta'_{\sigma N}, \Delta'_{\sigma AB}, \Delta'_{\pi AB}\}$ , referring to the chromophore  $[\text{MN}_4\text{AB}]$ , is expressed in terms of the parameters most frequently used in the current literature. Common to all of the parameterization schemes is the fact that they are based upon shifts in the d-electron energies on going from the parent chromophore  $[\text{MN}_6]$  to the actual chromophore  $[\text{MN}_4\text{AB}]$ . Yamatera<sup>12</sup> and McClure,<sup>13</sup> who

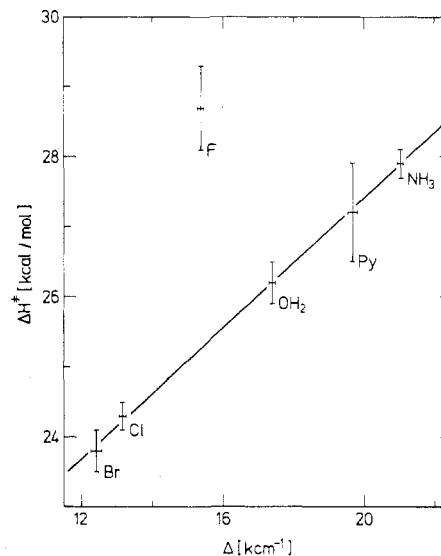


Figure 3. Empirical linear correlation between the enthalpies of activation  $\Delta H^\ddagger$  for the processes  $[\text{Cr}(\text{OH}_2)_5\text{J}]^{(3-i)+} + \text{OH}_2 \rightarrow [\text{Cr}(\text{OH}_2)_6]^{3+} + \text{J}^{i-}$  and  $\Delta_J$ . Error bars are drawn as  $\pm$  the estimated standard deviations.

used ligand field parameterization schemes, only discussed shifts, and their parameters have therefore been supplemented with the parameter  $\Delta_N$  which expresses the energy difference  $h[\epsilon] - h[\zeta]$  in the parent chromophore  $[\text{MN}_6]$ .

The parameter  $Dq$  out of the set<sup>67,68</sup>  $\{Dq, Ds, Dt\}$  also refers to the  $[\text{MN}_6]$  chromophore and the relationship  $\Delta_N = 10Dq_{\text{MN}_6}$  is valid. The consequence is that  $Dq$ , even though its corresponding operator<sup>2,3</sup> has cubic symmetry, does not refer to the average cubic field in the chromophore  $[\text{MN}_4\text{AB}]$  but incorporates a field component of cylindrical symmetry. Similarly the supposedly cylindrical field parameter  $Dt$  contains cubic field components. These unfortunate circumstances result in the breaking down of the barycenter rule for  $Dt$  contributions when the energies of the tetragonal-split components of  $e_g(O_h)$  and  $t_{2g}(O_h)$  are expressed in terms of the set  $\{Dq, Ds, Dt\}$ . Actually this set belongs to the non-additive field. It corresponds to three linearly independent operators and is as such complete even though this has been refuted.<sup>20</sup> The unfortunate property of the set of operators is that those corresponding to  $Dq$  and  $Dt$  are nonorthogonal.<sup>69</sup>

**Registry No.** *trans*- $[\text{Cr}(\text{NH}_3)_4\text{F}_2]^+$ , 31253-66-4; *trans*- $[\text{Cr}(\text{py})_4\text{F}_2]^+$ , 47514-84-1; *trans*- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ , 22452-49-9; *trans*- $[\text{Cr}(\text{py})_4\text{Cl}_2]^+$ , 51266-53-6; *trans*- $[\text{Cr}(\text{NH}_3)_4\text{Br}_2]^+$ , 51266-63-8; *trans*- $[\text{Cr}(\text{py})_4\text{Br}_2]^+$ , 51266-52-5; *trans*- $[\text{Cr}(\text{NH}_3)_4\text{FCl}]^+$ , 44437-04-9; *trans*- $[\text{Cr}(\text{py})_4\text{FCl}]^+$ , 51266-55-8; *trans*- $[\text{Cr}(\text{NH}_3)_4\text{FBr}]^+$ , 51266-64-9; *trans*- $[\text{Cr}(\text{py})_4\text{FBr}]^+$ , 51266-54-7; *trans*- $[\text{Cr}(\text{NH}_3)_4\text{BrCl}]^+$ , 22452-50-2; *trans*- $[\text{Cr}(\text{NH}_3)_4(\text{OH})_2]^{2+}$ , 51266-65-0; *trans*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OH})]^{2+}$ , 31564-04-2; *trans*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ , 36834-73-8; *trans*- $[\text{Cr}(\text{NH}_3)_4\text{F}(\text{OH})]^+$ , 58816-90-3;  $[\text{Cr}(\text{OH}_2)_5\text{Br}]^{2+}$ , 26025-60-5;  $[\text{Cr}(\text{OH}_2)_5\text{Cl}]^{2+}$ , 14404-08-1;  $[\text{Cr}(\text{OH}_2)_5\text{F}]^{2+}$ , 19559-07-0;  $[\text{Cr}(\text{OH}_2)_6]^{3+}$ , 14873-01-9;  $[\text{Cr}(\text{OH}_2)_5(\text{py})]^{3+}$ ,



34714-27-7;  $[\text{Cr}(\text{OH}_2)_5(\text{NH}_3)]^{3+}$ , 42402-03-9.

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- (55) In our earlier work<sup>25</sup> the parameters were obtained in a different way. From the four transition energies, which were obtained either just by inspection of the absorption curves or by Gaussian analysis, the parameters were obtained by the solution of a set of four nonlinear equations. This was accomplished by Newton's method. The present approach has, besides the rigorous fashion in which the transition energies are obtained, the added advantage that the number of spectral transitions may be greater than the number of parameters without altering the scheme of calculation.
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