Is Pyridine a π Acceptor in *trans*-Dihalogenotetrakis(pyridine)chromium(III) Ions?

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Previous workers have concluded that pyridine is a π acceptor in $[\text{Cr(py)}_4\text{AB}]^+$ (py = pyridine; A, B = F, Cl, Br), on the grounds that the angular overlap parameter $\Delta_{\pi\text{py}}$ is negative. This seems to be inconsistent with the behavior of pyridine in other systems. This paper presents a critical evaluation of the approximations and assumptions involved in the determination of $\Delta_{\pi\text{py}}$. It is shown that the angular overlap parameters found for the axial ligands in $[\text{Cr(NH}_3)_4\text{AB}]^+$ are not necessarily transferable to $[\text{Cr(py)}_4\text{AB}]^+$, as proposed by previous workers. A semiempirical relationship is derived between the parameters $\Delta_{\sigma\text{AB}}$ and $\Delta_{\pi\text{AB}}$, so that, for any assumed value of ψ, the pitch angle between the plane of the pyridine molecule and the MN_4 equatorial plane, all the angular overlap parameters can be found. For $\psi = 45°$, a value supported by crystallographic data on related systems, $\Delta_{\pi\text{py}}$ is found to be positive for all the ions except perhaps $[\text{Cr(py)}_4\text{Br}_2]^+$. The effects of varying ψ and the ratio $(\Delta_{\pi\text{AB}}/\Delta_{\sigma\text{AB}})$ are examined; if ψ lies between 35 and 40°, the equations become ill conditioned, but if ψ is greater than 40°, it can be concluded that $\Delta_{\pi\text{py}}$ is probably positive for $[\text{Cr(py)}_4\text{F}_2]^+$ and negative for $[\text{Cr(py)}_4\text{Br}_2]^+$. A more accurate determination of $\Delta_{\pi\text{py}}$ will require further spectroscopic and crystallographic measurements.

Introduction

The extraction of ligand angular overlap parameters from the d–d spectra of tetragonal chromium(III) systems has been an area of continuing interest for several years.[1-14] A particularly thorough analysis of the electronic spectra of $\text{Cr}^{\text{III}}\text{N}_4\text{AB}$ chromophores (A, B = F, Cl, Br) by Glerup et al.[13] led to the conclusion that pyridine (py) is a π acceptor in $[\text{Cr(py)}_4\text{AB}]^+$ ions, since the angular overlap parameter $\Delta_{\pi\text{py}}$ was found to be consistently negative. This seems to be inconsistent with the apparent behavior of pyridine in $[\text{M}^{\text{II}}-(\text{py})_4\text{A}_2]$ (M = Fe, Co, Ni; A = Cl, Br, I, NCS). The d–d spectra of $[\text{Ni(py)}_4\text{A}_2]$ suggest that $\Delta_{\pi\text{py}}$ is positive,[3,15-18] while magnetic studies on $[\text{M(py)}_4\text{A}_2]$ (M = Fe, Co) arrive at a similar conclusion.[19,20] Pyridine is also apparently a π donor in the adduct with N,N'-ethylenebis(salicylaldiminato)cobalt(II).[21] While it is perfectly possible that pyridine might function as a π acceptor in other systems, it seems most unlikely that it should do so in $[\text{Cr(py)}_4\text{AB}]^+$ while at the same time behaving as a π donor in $[\text{M(py)}_4\text{A}_2]$ (M = Fe, Co, Ni). Thus the conclusions of Glerup et al.[13] deserve closer scrutiny. The purpose of this paper is to examine the validity of the assumptions which were necessary to reach these conclusions and to see whether alternative (and possibly more valid) assumptions would lead to a different result.

Determination of Angular Overlap Parameters in Tetragonal $\text{Cr}^{\text{III}}\text{N}_4\text{AB}$ Chromophores

Here we shall sketch briefly the arguments whereby Glerup et al.[13] deduced that pyridine is a π acceptor in $[\text{Cr(py)}_4\text{AB}]^+$. Four spin-allowed transitions can be observed (with the aid of Gaussian analysis) in the solution spectra of $\text{Cr}^{\text{III}}\text{N}_4\text{AB}$ chromophores. From these, the nonadditive ligand-field parameters $\Delta(\text{d})$, $\Delta(\text{e})$, and $\Delta(\text{t}_2)$, together with the Racah parameter B, can be obtained by solving the energy matrices. The nonadditive parameters describe the one-electron splitting in D_{4h} symmetry; $\Delta(\text{d})$ is the splitting under the cubic component of the ligand-field operator of the d orbitals, while $\Delta(\text{e})$ and $\Delta(\text{t}_2)$ are the baricentered splittings of the cubic e_g and t_{2g} levels, respectively, under the tetragonal perturbation. Thus $\Delta(\text{e})$ and $\Delta(\text{t}_2)$ are equal respectively to $E(\text{d}_{x^2-y^2}) - E(\text{d}_{z^2})$ and $E(\text{d}_{xy}) - E(\text{d}_{xz,yz})$, while $\Delta(\text{d})$ is the difference between the average energies of these subshells. These nonadditive parameters are related to the additive angular overlap parameters $\Delta_{\sigma\text{N}}$, $\Delta_{\pi\text{N}}$, $\Delta_{\sigma\text{AB}}$, and $\Delta_{\pi\text{AB}}$ by (1)–(3), assuming that the equatorial ligands are linearly ligating.

$$\Delta(\text{d}) = \tfrac{2}{3}(\Delta_{\sigma\text{N}} - \Delta_{\pi\text{N}}) + \tfrac{1}{3}(\Delta_{\sigma\text{AB}} - \Delta_{\pi\text{AB}}) \qquad (1)$$

$$\Delta(\text{e}) = \tfrac{2}{3}(\Delta_{\sigma\text{N}} - \Delta_{\sigma\text{AB}}) \qquad (2)$$

$$\Delta(\text{t}_2) = \tfrac{1}{2}(\Delta_{\pi\text{N}} - \Delta_{\pi\text{AB}}) \qquad (3)$$

The problem of finding the four additive parameters, given the three nonadditive ones, can be solved for $[\text{Cr(NH}_3)_4\text{AB}]^+$ by setting $\Delta_{\pi\text{N}}$ equal to zero; this can be justified on the grounds that the ammonia molecule has no suitable orbitals for π overlap. Thus $\Delta_{\sigma\text{N}}$, $\Delta_{\sigma\text{AB}}$, and $\Delta_{\pi\text{AB}}$ can be found. In $[\text{Cr(py)}_4\text{AB}]^+$, $\Delta_{\pi\text{py}}$ may well be nonzero, since pyridine has accessible π-bonding and π-antibonding MO's with nodal surfaces in the molecular plane. Five unknowns now appear in eq 1–3 since we can no longer neglect $\Delta_{\pi\text{py}}$ and moreover $\tfrac{3}{2}\cos 2\psi$ has to be subtracted from the right-hand side of (3); ψ is the angle between the plane of the pyridine molecule and the MN_4 equatorial plane. The equations relating the nonadditive and additive ligand-field parameters can be solved if it is assumed that $\Delta_{\lambda\text{AB}}$ ($\lambda = \sigma, \pi$) parameters take the same values in $[\text{Cr(py)}_4\text{AB}]^+$ as in $[\text{Cr(NH}_3)_4\text{AB}]^+$. Then $\Delta_{\sigma\text{py}}$, $\Delta_{\pi\text{py}}$, and $(\cos 2\psi)\Delta_{\pi\text{py}}$ can be found. Such calculations, after a careful statistical analysis, led to $\Delta_{\pi\text{py}} = (-2.0 \pm 0.2) \times 10^3$ cm^{-1} and $\psi = (37.8 \pm 1.1)°$. Thus the conclusion that pyridine is a π acceptor in these systems depends on the assumption of the transferability of the $\Delta_{\lambda\text{AB}}$ parameters, but without assuming any restrictions on the value of ψ, except that it is the same for all the $[\text{Cr(py)}_4\text{AB}]^+$ ions. These two points must therefore be examined in detail.

Transferability of Angular Overlap Parameters in Tetragonal Cr^{III} Systems

The idea that Δ_λ for a particular ligand bound to Cr^{III} is roughly independent of the other ligands present and is therefore transferable from one complex to another is attractive but difficult to justify theoretically. We therefore have to rely on experimental evidence to judge the validity of this assumption. In $[\text{Cr(NH}_3)_4\text{AB}]^+$, $[\text{Cr(NH}_3)_5\text{A}]^{2+}$, and $[\text{Cr-}(\text{NH}_3)_6]^{3+}$, Δ_N ($=\Delta_{\sigma\text{N}} - \Delta_{\pi\text{N}}$) varies only between 20.8 and 21.6×10^3 cm^{-1}.[10,13] It might be expected that the angular overlap parameters for halide ligands could be more sensitive to the charge of the complex and to the other ligands present; but Δ_A ($=\Delta_{\sigma\text{A}} - \Delta_{\pi\text{A}}$) (A = F, Cl, Br) does not vary much in Cr^{III} systems. For example, Δ_F is roughly constant in CrF_3, CrF_6^{3-}, and $[\text{Cr(NH}_3)_4\text{F}_2]^+$.[13,22,23] However, it is possible that small variations in Δ_A over a series of compounds may conceal much larger variations in $\Delta_{\sigma\text{A}}$ and $\Delta_{\pi\text{A}}$. In Table I are collected angular overlap parameters for halide ligands in tetragonal $\text{Cr}^{\text{III}}\text{N}_4\text{A}_2$ chromophores. (Most of the information given here is tabulated in a somewhat different form in ref 12.)

The data in Table I would seem to confirm our suspicion that $\Delta_{\sigma\text{A}}$ and $\Delta_{\pi\text{A}}$ can vary individually much more than their difference, Δ_A, even over a range of complexes with saturated amine ligands where the in-plane bonding is unlikely to vary significantly. Clearly, we must reject the assumption that halide angular overlap parameters are transferable from one

Table I. Angular Overlap Parameters (cm^{-1} × 10^3) for Axial Ligands in Tetragonal Cr^{III}N$_4$A$_2$ Chromophores, with $\Delta_{\pi N}$ Assumed To Be Zero

ion	$\Delta_{\sigma A}$	$\Delta_{\pi A}$	Δ_A	ref
[Cr(NH$_3$)$_4$F$_2$]$^+$	22.3	7.0	15.3	13
[Cr(CH$_3$NH$_2$)$_4$F$_2$]$^+$	22.4	6.5	15.9	7, 12
[Cr(C$_2$H$_5$NH$_2$)$_4$F$_2$]$^+$	22.4	6.5	15.9	7, 12
[Cr(C$_3$H$_7$NH$_2$)$_4$F$_2$]$^+$	22.8	6.5	16.3	7, 12
[Cr(en)$_2$F$_2$]$^{+\ a}$	24.1	8.0	16.1	6, 8
[Cr(pd)$_2$F$_2$]$^{+\ b}$	27.3	9.8	17.5	12
[Cr(pnd)$_2$F$_2$]$^{+\ c}$	25.2	7.7	17.5	12
[Cr(chd)$_2$F$_2$]$^{+\ d}$	24.5	8.1	16.4	12
[Cr(daud)F$_2$]$^{+\ e}$	25.1	7.9	17.2	12
[Cr(dadd)F$_2$]$^{+\ f}$	25.4	8.2	17.2	12
[Cr(datd)F$_2$]$^{+\ g}$	25.4	8.1	17.3	12
[Cr(NH$_3$)$_4$Cl$_2$]$^+$	16.0	2.9	13.1	13
[Cr(en)$_2$Cl$_2$]$^{+\ a}$	17.6	4.2	13.4	8, 9
[Cr(pd)$_2$Cl$_2$]$^{+\ b}$	17.5	4.2	13.3	12
[Cr(NH$_3$)$_4$Br$_2$]$^+$	15.1	3.6	11.5	13
[Cr(en)$_2$Br$_2$]$^{+\ a}$	15.4	3.0	12.4	8, 9
[Cr(pd)$_2$Br$_2$]$^{+\ b}$	16.3	3.6	12.7	12

^{a} en = 1,2-diaminoethane. ^{b} pd = 1,3-diaminopropane. ^{c} pnd = 1,2-diaminopropane. ^{d} chd = 1,2-diaminocyclohexane. ^{e} daud = 1,11-diamino-4,8-diazaundecane. ^{f} dadd = 1,12-diamino-5,8-diazadodecane. ^{g} datd = 1,13-diamino-5,9-diazatridecane.

Table II. Ligand-Field Parameters Δ_{py} and Δ_{AB} (cm^{-1} × 10^3) for [Cr(py)$_4$AB]$^+$, Assuming Pyridine To Be Effectively a Linear Ligator^a

AB	Δ_{py}	Δ_{AB}
FF	19.5	16.9 (15.3)
ClCl	19.4	14.2 (13.1)
BrBr	19.5	12.8 (11.5)
FCl	19.4	16.1 (14.3)
FBr	19.7	15.0 (13.6)

^{a} Data for [Cr(NH$_3$)$_4$AB]$^+$ are given in parentheses.

that some correlation of this kind does exist in Cr^{III}N$_4$A$_2$ chromophores. We now explore a possible method of establishing a relationship between $\Delta_{\sigma AB}$ and $\Delta_{\pi AB}$.

A Semiempirical Relationship between $\Delta_{\sigma AB}$ and $\Delta_{\pi AB}$

If we now take pyridine to be effectively a linear ligator, we can readily determine Δ_{AB} (=$\Delta_{\sigma AB} - \Delta_{\pi AB}$) and Δ_{py} (=$\Delta_{\sigma py} - \Delta_{\pi py}$) for the [Cr(py)$_{4AB}$]$^+$ ions from eq 4 and 5. The

$$\Delta_{py} = \Delta(d) + \tfrac{1}{2}\Delta(e) - \tfrac{2}{3}\Delta(t_2) \qquad (4)$$

$$\Delta_{AB} = \Delta(d) - \Delta(e) + \tfrac{4}{3}\Delta(t_2) \qquad (5)$$

nonadditive ligand-field parameters $\Delta(d)$, $\Delta(e)$, and $\Delta(t_2)$ can be obtained from the data in Table II of ref 13. Our values of Δ_{AB} and Δ_{py} are given in Table II, together with the corresponding values for [Cr(NH$_3$)$_4$AB]$^+$. It is seen that Δ_{AB} is always greater for [Cr(py)$_4$AB]$^+$ than for [Cr(NH$_3$)$_4$AB]$^+$, suggesting (on the basis of the trends exhibited in Table I) that $\Delta_{\sigma AB}$ and $\Delta_{\pi AB}$ may be larger in the pyridine derivatives. This would, of course, affect any conclusions concerning the sign and magnitude of $\Delta_{\pi py}$.

A possible origin of the variations in the parameters listed in Table I lies in changes in the metal–halogen bond lengths in the series of species with different equatorial ligands. Such variations in bond length could arise from electronic and/or steric factors. There are, of course, other possible reasons for the observed variation in the halide angular overlap parameters. No doubt they are sensitive to the formal charge on the metal, which in turn will be dependent on the equatorial ligands. However, the metal–halogen bond length will be sensitive to the electronic requirements of the metal, and it could be argued that significant changes in the equatorial metal–ligand bonding should be reflected in changes in the axial bond lengths. The effects of varying the internuclear distance on angular overlap parameters are well documented;[14,27,28] other factors which may affect the parameters independently are not so well understood. Thus the dependence of the angular overlap parameters on the metal–halogen distance deserves close analysis. The angular overlap model suggests[28] that Δ_λ is proportional to the square of the diatomic overlap integral S_λ, so that the dependence of Δ_λ on the internuclear distance can be gauged from (6) and (7). If we

$$\Delta_\sigma = K_\sigma S_\sigma^2 \qquad (6)$$

$$\Delta_\pi = K_\pi S_\pi^2 \qquad (7)$$

assume that only ligand np orbitals are involved in the bonding, K_π should be equal to $^4/_3 K_\sigma$. In practice, however, K_π/K_σ is usually less than $^4/_3$.[14] This could be taken to indicate some contribution to Δ_σ from interactions involving the ligand ns orbitals, but other explanations are possible; in particular, it must be noted that the ratio S_π/S_σ is strongly dependent on the wave functions used in the calculation and hence on the assumed charges on the atoms, and it may be best to regard K_π and K_σ in (6) and (7) as independent parameters which can only be found by appeal to experimental data. If $\Delta_{\sigma A}$ and $\Delta_{\pi A}$ are known for any Cr^{III}N$_4$A$_2$ chromophore, and the Cr–A distance is known (or can be estimated), we can find the

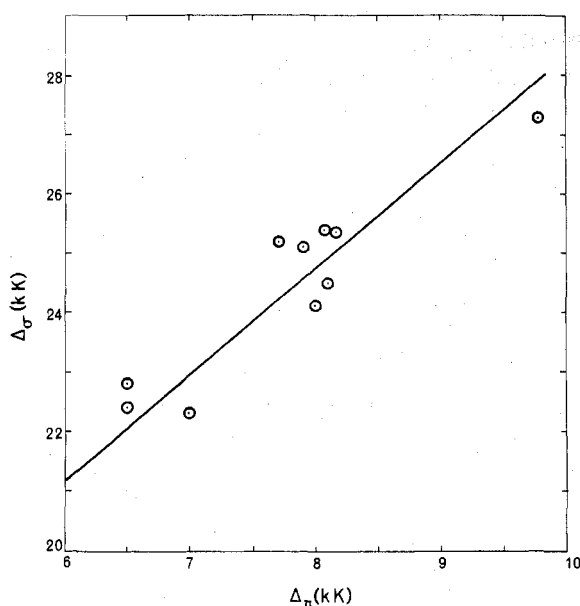Cr^{III}N$_4$AB chromophore to another. For example, if the $\Delta_{\lambda F}$ parameters appropriate to [Cr(en)$_2$F$_2$]$^+$ were used directly in the analysis of the spectrum of [Cr(pd)$_2$F$_2$]$^+$, it would be inferred that pd is a π acceptor, which is chemically absurd.

If we cannot deduce the $\Delta_{\lambda AB}$ parameters in [Cr(py)$_4$AB]$^+$ from the results for [Cr(NH$_3$)$_4$AB]$^+$, we are faced with the apparently hopeless task of finding five additive ligand-field parameters from only three nonadditive ones. The problem is less formidable if it can be assumed that pyridine is effectively a linear ligator in [Cr(py)$_4$AB]$^+$, so that $\psi = 45°$ and the term containing ψ vanishes. The validity of such an assumption will now be examined.

Orientation of Pyridine Molecules in *trans*-Tetrakis(pyridine) Complexes

Glerup et al.[13] assumed that the pyridine molecules in [Cr(py)$_4$AB]$^+$ form a propeller-like arrangement, with a single constant value of ψ, the angle between the plane of a pyridine molecule and the MN$_4$ equatorial plane; each M–N vector is assumed to be collinear with the twofold axis of the pyridine molecule. Thus the symmetry is assumed to be D_4 for [Cr(py)$_4$A$_2$]$^+$ and C_4 for [Cr(py)$_4$AB]$^+$, but it is argued[13] that the holohedrized symmetry D_{4h} is valid in both cases. The angle ψ was found to be about 38° from the analysis described above. This can ultimately be confirmed only by X-ray analysis, but the available crystallographic data for related systems suggest that $\psi = 45°$ would be a fair approximation. Studies of [Co(py)$_4$A$_2$] (A = Cl, Br)[24] found ψ to be 45°, although only a limited amount of X-ray data was taken. The magnetic properties of these compounds[20] were successfully interpreted in terms of the angular overlap model, with pyridine taken to be effectively linearly ligating: no evidence for π-bonding anisotropy was found. A more accurate X-ray analysis has been peformed on [Ni(py)$_4$I$_2$],[25] where two values of ψ were found, viz., 37 and 55°, with a mean of 46°. In [Rh(py)$_4$Br$_2$]Br·6H$_2$O, with which [Cr(py)$_4$Br$_2$]Br·6H$_2$O is isomorphous,[26] the mean value of ψ is found to be about 45°.

Although the available data are limited, there is some justification for treating pyridine in [Cr(py)$_4$AB]$^+$ as a linear ligator, with $\psi = 45°$. Thus the number of unknowns in eq 1–3 is reduced to four, still one too many. The problem can be solved if we can find some theoretical or empirical relationship between $\Delta_{\sigma AB}$ and $\Delta_{\pi AB}$ which will reduce the number of unknowns in (1)–(3) to three. The data in Table I suggest

Figure 1. Theoretical plot of $\Delta_{\sigma F}$ vs. $\Delta_{\pi F}$ for Cr^{III}N$_4$F$_2$ chromophores. The circles are experimental points from the data in Table I.

constants K_σ and K_π from the diatomic overlap integrals (σ and π) between chromium 3d orbitals and ligand np orbitals. Hence, by calculating the overlap integrals over a range of internuclear distances, we can determine the radial variation of $\Delta_{\sigma A}$ and $\Delta_{\pi A}$. These are then no longer independent parameters, and we can now find all the required angular overlap parameters from $\Delta(d)$, $\Delta(e)$, and $\Delta(t_2)$.

Determination of Angular Overlap Parameters for [Cr(py)$_4$AB]$^+$

In the Cr^{III}N$_4$F$_2$ chromophores listed in Table I, the mean values of $\Delta_{\pi F}$ and $\Delta_{\sigma F}$ are 7.7 and 24.4 × 10^3 cm^{-1}, respectively. If we associate these with a Cr–F distance of 1.95 Å, we can determine the constants K_π and K_σ in (6) and (7) and plot a graph of $\Delta_{\pi F}$ vs. $\Delta_{\sigma F}$ as the Cr–F distance is varied on either side of the assumed mean value of 1.95 Å, as discussed above. The overlap integrals were calculated from the atomic wave functions of Clementi[29] for the 3d orbitals of Cr$^+$ and the 2p orbitals of F. The resulting plot is shown in Figure 1 together with the experimental points from the data in Table I. The theoretical curve clearly reflects the correlation between $\Delta_{\sigma F}$ and $\Delta_{\pi F}$ suggested by Table I, although there is a considerable scatter of points about the curve; this is not surprising, since the experimental data are not strictly comparable, some of the spectra having been obtained from low-temperature single-crystal or diffuse-reflectance measurements and others from solution measurements. Moreover, most of the species concerned may not be truly orthoaxial and there are doubtless numerous other sources of uncertainty. From the data in Table II, we might expect $\Delta_{\sigma F}$ and $\Delta_{\pi F}$ to be somewhat greater in [Cr(py)$_4$F$_2$]$^+$ than in [Cr(NH$_3$)$_4$F$_2$]$^+$. In the range $\Delta_{\pi F}$ = (7–9) × 10^3 cm^{-1}, the theoretical curve in Figure 1 can be fitted rather well to the linear eq 8. This provides a simple

$$\Delta_{\sigma F} = (1.75\Delta_{\pi F} + 10.80) \times 10^3 \text{ cm}^{-1} \qquad (8)$$

relationship between $\Delta_{\sigma F}$ and $\Delta_{\pi F}$ which will assist us in solving the equations which relate the additive and nonadditive lig-and-field parameters. Equation 8 is close to the empirical "best straight line" correlation between the points in Figure 1 and so may be regarded as essentially an empirical correlation with some theoretical basis. The Cr–F bond lengths which are consistent, using (6) and (7), with the range of angular overlap parameters shown in Figure 1, lie between 1.9 and 2.0 Å, which seems reasonable.

Table III. Angular Overlap Parameters (cm^{-1} × 10^3) for [Cr(py)$_4$AB]$^+$, Calculated As Described in the Text

AB	FF	ClCl	BrBr	FCl	FBr
$\Delta_{\pi py}$	1.6	0.9	−0.5	2.1	0.7
$\Delta_{\sigma py}$	21.1	20.3	19.0	21.5	20.4
$\Delta_{\pi F}$	8.2			8.9	7.9
$\Delta_{\sigma F}$	25.1			26.4	24.7
$\Delta_{\pi Cl}$		4.9		5.4	
$\Delta_{\sigma Cl}$		19.1		20.1	
$\Delta_{\pi Br}$			4.1		4.4
$\Delta_{\sigma Br}$			16.8		17.6

Similar relationships can be derived between the halide angular overlap parameters for Cr^{III}N$_4$Cl$_2$ and Cr^{III}N$_4$Br$_2$ chromophores, although in these cases the experimental data in Table I are more limited and we have to rely more heavily on the theoretical expressions. Assuming the mean Cr–Cl and Cr–Br distances to be 2.35 and 2.50 Å, respectively, we obtain (9) and (10) using the functions of Clementi[29] for chlorine 3p

$$\Delta_{\sigma Cl} = (1.91\Delta_{\pi Cl} + 9.75) \times 10^3 \text{ cm}^{-1} \qquad (9)$$

$$\Delta_{\sigma Br} = (2.03\Delta_{\pi Br} + 8.63) \times 10^3 \text{ cm}^{-1} \qquad (10)$$

and bromine 4p orbitals. Thus we can find all the Δ_λ parameters for [Cr(py)$_4$A$_2$]$^+$. In the mixed-halide species [Cr(py)$_4$AB]$^+$, there are still four independent parameters to be determined from the three nonadditive parameters, using (8)–(10) and assuming that $\Delta_{\lambda AB}$ is the arithmetic mean of $\Delta_{\lambda A}$ and $\Delta_{\lambda B}$. However, if we calculate $\Delta_{\lambda A}$ and $\Delta_{\lambda B}$ over a range of assumed values for $\Delta_{\pi py}$, we find that the halide parameters vary quite sharply as $\Delta_{\pi py}$ is varied. If we insist that $\Delta_{\pi F}$ lies between 6 and 10 × 10^3 cm^{-1}, and that $\Delta_{\pi Cl}$ and $\Delta_{\pi Br}$ both lie between 2 and 6 × 10^3 cm^{-1}, we are restricted to only rather small ranges of acceptable $\Delta_{\pi py}$ values, within about 0.3 × 10^3 cm^{-1}. The most probable set of parameters is taken to be that which is most consistent with the results for [Cr(py)$_4$A$_2$]$^+$ species.

Results and Discussion

The results of the calculations described in the previous section are summarized in Table III. It is seen that $\Delta_{\pi py}$ is positive for all the species except [Cr(py)$_4$Br$_2$]$^+$. The variation of $\Delta_{\pi py}$ with the axial ligands makes good sense; pyridine is probably functioning simultaneously as both a π donor and a π acceptor, and the sign of $\Delta_{\pi py}$ indicates which of these functions is dominant. If the axial ligands are poor donors (e.g., F$^-$) we might expect that pyridine will donate more strongly than with better donors (e.g., Br$^-$) in the axial positions, in which case the π-acceptor function of pyridine may dominate. This kind of behavior is well-known in "nonclassical" complexes with ligands like CO and PR$_3$.

It is difficult to estimate the errors inherent in the results of Table III; they depend upon our assumptions concerning the relative magnitudes of $\Delta_{\sigma AB}$ and $\Delta_{\pi AB}$, as well as on our assumption that ψ = 45°. It is now necessary to find out how sensitive the sign and magnitude of $\Delta_{\pi py}$ are to these assumptions. Equations 1–3 may be rewritten as (11)–(13), with

$$2\Delta_{\sigma py} - 2\Delta_{\pi py} + (1 - x)\Delta_{\sigma AB} = 3\Delta(d) \qquad (11)$$

$$2\Delta_{\sigma py} - 2\Delta_{\pi AB} = 3\Delta(e) \qquad (12)$$

$$(1 - 3\cos 2\psi)\Delta_{\pi py} - x\Delta_{\sigma AB} = 2\Delta(t_2) \qquad (13)$$

$\Delta_{\pi AB}/\Delta_{\sigma AB} = x$. Eliminating $\Delta_{\sigma py}$ and $\Delta_{\sigma AB}$ from these, we obtain (14). Thus the sign and magnitude of $\Delta_{\pi py}$ are de-

$$\Delta_{\pi py} = \frac{3\Delta(d) - 3\Delta(e) + 2x^{-1}(3 - x)\Delta(t_2)}{3x^{-1}[(1 - x) - (3 - x)\cos 2\psi]} \qquad (14)$$

termined by the signs and magnitudes of the numerator and

denominator in (14). It will be immediately noticed that the denominator vanishes when $\cos 2\psi = (1-x)/(3-x)$. Thus there will be a range of values for ψ over which eq 11-13 are ill conditioned, and meaningful angular overlap parameters cannot be obtained. The critical value of ψ (which we denote as ψ_c) at which the denominator vanishes ranges from 35.3° for $x = 0$ to 39.2° for $x = 0.5$. It is somewhat paradoxical that the value of ψ obtained by Glerup et al.[13] falls in this range. It must be remembered, however, that this value was obtained by numerical analysis of the data for the whole series of complexes, finding a single value of each angular overlap parameter which best fitted the data as a whole. Since we wish to avoid any assumption of transferability of angular overlap parameters, we have to find analytic solutions to (11)-(13) or (1)-(3), making reasonable assumptions concerning the magnitude of ψ and the relative magnitudes of $\Delta_{\pi AB}$ and $\Delta_{\sigma AB}$; this procedure clearly fails if ψ is close to ψ_c. The denominator is positive if $\psi > \psi_c$ and negative if $\psi < \psi_c$. The sign of the numerator of (14) depends on the nonadditive ligand-field parameters and on x. For $[Cr(py)_4F_2]^+$, the numerator is positive if $x > 0.28$. All the $Cr^{III}N_4F_2$ chromophores in Table I have greater x values than this, so that it seems reasonable to conclude that the numerator in (14) will be positive for $[Cr(py)_4F_2]^+$; a negative numerator would require, on the basis of (8) and the results summarized in Figure 1, that $\Delta_{\pi F}$ is less than 6×10^3 cm^{-1}. Thus in the case of $[Cr(py)_4F_2]^+$, we can say that $\Delta_{\pi py}$ will be positive if $\psi > 40°$ and negative if $\psi < 35°$: if ψ lies between 35 and 40°, the equations become ill conditioned and we can say little about $\Delta_{\pi py}$. In the case of $[Cr(py)_4Cl_2]^+$, the numerator is positive if $x > 0.22$; this is precisely the mean value of x in the relevant species in Table I, so we cannot be sure of the sign of the numerator here. But for $[Cr(py)_4Br_2]^+$, the numerator is positive for $x > 0.26$. It seems more likely, on the basis of the (admittedly limited) data in Table I, that x will be less than 0.26 in this species, so the numerator is probably negative. For $[Cr(py)_4FCl]^+$ and $[Cr(py)_4FBr]^+$ the situation is uncertain, as for $[Cr(py)_4Cl_2]^+$.

The situation may be summarized as follows: (i) If $\psi > 40°$, $\Delta_{\pi py}$ is probably positive for $[Cr(py)_4F_2]^+$ and negative for $[Cr(py)_4Br_2]^+$ but uncertain for the other species. (ii) If $\psi < 35°$, $\Delta_{\pi py}$ is probably negative for $[Cr(py)_4F_2]^+$ and positive for $[Cr(py)_4Br_2]^+$ but is still of uncertain sign for the other species. (iii) If ψ lies between 35 and 40°, we cannot obtain meaningful angular overlap parameters since ψ is too close to ψ_c.

Possibility (i) seems more likely than (ii), since we have argued that $\Delta_{\pi py}$ is likely to be more positive for $[Cr(py)_4F_2]^+$ than for $[Cr(py)_4Br_2]^+$, and the limited crystallographic data suggest that ψ should be close to 45°. Possibility (iii) cannot be excluded, however.

The results of this work are thus somewhat inconclusive, and the question posed by the title remains open. It is clear that the sign of $\Delta_{\pi py}$ in these species is strongly dependent on the assumptions and approximations invoked. It is also dependent on the accuracy of the nonadditive ligand-field parameters; for example, an uncertainty of 10% (or about 0.3×10^3 cm^{-1}) in the value for $\Delta(t_2)$ would mean an uncertainty of nearly 10% in the critical value of x at which the numerator becomes zero in (14). Moreover, the true symmetry of these ions may well be D_2 or C_2; this should lead to splitting of the E_g states, which has not been observed in the broad, room-temperature solution spectra. Until such splittings have been observed, it seems inappropriate to discuss the possible effects on the calculated angular overlap parameters of the low-symmetry components. Further work is clearly needed in order to determine the sign and magnitude of $\Delta_{\pi py}$ in these complexes. We require low-temperature single-crystal spectra for at least one species of known crystal structure. It is to be hoped that the problems raised in the present paper will stimulate such further investigations.

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