Solvent-dependent ^2H Nuclear Magnetic Resonance Spectra and Solvatochromism in Ligand-field Absorption Bands of *cis*-$[CrF_2N_4]$-type Complexes with Triethylenetetramine, Pyridine or 2,2′-Bipyridine

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The solvent-dependent ^2H NMR spectra and solvatochromism in ligand-field absorption bands of *cis*-$[CrF_2N_4]$-type complexes with deuteriated triethylenetetramine (trien), pyridine (py) and 2,2′-bipyridine (bipy) have been used to demonstrate the sensitivity of the angular overlap model parameters to the solvent co-ordination sphere, as has also been observed for *trans*-$[CrF_2([^2H_4]dadad)]^+$ (dadad = 1,10-diamino-4,7-diazadecane). The *cis* effect was found to account reasonably well for the solvent dependence of the spectra for both the *cis* and *trans* complexes. The inverse correlation of the ^2H NMR chemical shifts for the β- and γ-deuterons in the py complexes and 4- and 5-deuterons in the bipy complexes with the solvent electron acceptor number gave direct evidence for the π-acceptor bond properties of aromatic heterocyclic ligands in the complexes.

Previously we have demonstrated the dependence of the ligand-field or angular overlap model (AOM) parameters on the solvent co-ordination sphere by measuring the ligand-field absorption spectra and/or NMR spectra for *trans*-$[CrX_2([^2H_4]dadad)]$ (dadad = 1,10-diamino-4,7-diazadecane) and *cis*- or *trans*-$[MN_2O_4]$-type complexes in various solvents.[1,2] As expected, the *cis* effect was found to be operative for these complexes, and the *trans*-difluoro complex, in particular, exhibited a significant variation for the $e_\sigma(F)$ and $e_\sigma(N)$ AOM parameter values which denote the Cr–F and Cr–N(amine) σ-antibonding interaction energies, respectively; the increase in Cr–F bond length is accompanied by a decrease in $e_\sigma(F)$ and an increase in $e_\sigma(N)$ for the stronger electron-acceptor solvents, and *vice versa* for weaker electron-acceptor solvents. Although a similar variation in bond length is anticipated for *cis* complexes, apart from some spectroscopic (UV/VIS and NMR) studies on *cis*-$[MN_2O_4]$-type complexes, no spectroscopic evidence for a *cis* effect has been reported. The *cis* complexes are of interest as they include aromatic nitrogen containing heterocycles, the π-acceptor properties of which have been the subject of some controversy.[3-10] A number of spectroscopic studies on aromatic heterocyclic complexes have indicated π-back bonding between metal and ligating nitrogens;[3-10] however, there are only a few quantitative or semiquantitative studies on such π-acceptor properties.[3-10]

In this paper we consider the solvent dependence of the ligand-field absorption bands and ^2H NMR spectra for *mer*-$[CrF_3N_3]$ or *cis*-$[CrF_2N_4]^+$-type complexes containing aromatic heterocycles and/or aliphatic amines. By comparison with the spectroscopic data, the *cis* effect, the *trans* influence in the *cis* complexes and the π-acceptor bond properties of the aromatic heterocycles are examined in a semiquantitative manner in terms of the AOM parametrization.

Experimental

Preparation of Deuteriated Ligands.—Deuteriated pyridine ($[^2H_5]$py) (99 atom % ^2H, Sigma) was commercially available. $[4,5,4',5'\text{-}^2H_4]$-2,2′-Bipyridine ($[^2H_4]$bipy) was prepared by the method described by Fisher and Puza.[11] 2,2′-Bipyridine (0.50 g) and platinum asbestos (0.72 g) were placed in a pressure-stable glass reactor containing 10 cm^3 of deuterium oxide. The reactor was purged with nitrogen, sealed tightly and heated at 240 °C for 3 d. After cooling, the reactor was opened and the reaction mixture was extracted with diethyl ether and the desired product purified from diethyl ether–water. The deuteriation was confirmed by ^1H and ^2H NMR spectra. Since the extent of the deuteriation at the 4,4′- and 5,5′-positions was much greater than that at the 3,3′- and 6,6′-positions according to the integrated area of the ^1H NMR signals, the deuteriated bipy is represented as $[^2H_4]$bipy. Yield *ca.* 88%. $[5,5'\text{-}^2H_2]$-4,4′-Dimethyl-2,2′-bipyridine ($[^2H_2]$dmbipy) was obtained from 4,4′-dimethyl-2,2′-bipyridine (dmbipy) using a similar method to that for bipyridine. Yield *ca.* 70%. The deuteriated amine $NH_2CH_2CH_2NHCD_2CD_2NHCH_2CH_2NH_2$ ($[^2H_4]$-trien) was prepared in a similar manner to 1,10-diamino-4,7-diazadecane (dadad)[1] using deuteriated dibromoethane (Aldrich, 99%) instead of $BrCH_2CH_2Br$.

Preparation of Complexes.—The complexes *cis*-$[CrF_2([^2H_4]trien)]Cl$,[12] *trans*-$[CrF_2([^2H_5]py)_4]Cl$,[12] *mer*-$[CrF_3([^2H_5]py)_3]$,[13] *cis*-$[CrF_2([^2H_4]bipy)_2]ClO_4$[14] were prepared by modified literature methods using the deuteriated ligands, and *cis*-$[CrF_2([^2H_2]dmbipy)_2]ClO_4$ from $[5,5'\text{-}^2H_2]$-4,4′-dimethyl-2,2′-bipyridine by a similar method to that for *cis*-$[CrF_2([^2H_4]bipy)_2]ClO_4$.

Measurements.—Solution absorption spectra were measured by a Shimadzu UV-2100 and/or a Hitachi UV-330 spectrophotometer. Luminescence spectra were obtained using a JASCO R-800 laser Raman spectrophotometer at room temperature equipped with a NEC GLS 3200 argon-gas laser, ^2H NMR spectra using a JEOL JMN GX-400 and/or GSX-270 spectrometer at 26 °C on solutions ranging from 40 to 20 mg per 2.5 cm^3. In order to increase the solubility in aprotic solvents, the corresponding tetraphenylborate salts were obtained by adding an appropriate amount of sodium tetraphenylborate to the aqueous solutions of the complex perchlorates. External standards of $CDCl_3$ and $Me_3SiCD_2CD_2COONa$ were assigned chemical shifts of δ 7.24 and 0.589, 1.972, respectively. The following solvents used for the measurements were of spectrograde or reagent grade; their acceptor numbers[15] are given in parentheses: *N,N*-dimethylacetamide (dma) (13.6), *N,N*-dimethylformamide (dmf) (16.0), MeCN (18.9), dimethyl sulfoxide (dmso) (19.3), chloroform (23.1), *N*-methylformamide (nmf) (31.0), formamide (fa) (39.8), methanol (41.3), H_2O (54.8).

Results and Discussion

Assignment of ^{2}H *NMR Signals*.—Two well separated ^{2}H NMR signals due to paramagnetic isotropic contact shifts for two inequivalent deuterons (equatorial and axial) in the ethylene backbone were observed for *cis*-$[CrF_2([^2H_4]trien)]^+$.[1] The lower field signal near δ 0 and the higher field signal near δ −70 are assigned to the axial and equatorial deuterons, respectively, in accordance with the previous assignment for *trans*-$[CrF_2([^2H_4]dadad)]^+$.[1]

Three well separated signals were observed for *trans*-$[CrF_2([^2H_5]py)_4]^+$ and one signal at lower field together with two pairs of signals at higher field for *mer*-$[CrF_3([^2H_5]py)_3]$ as previously reported,[13] assigned to α-, γ- and β-deuterons of pyridine on the basis of the intensity ratio and by comparison with spectra of α-deuteriated pyridine complexes.[13] These values of contact shifts correlate well with the theoretical spin densities obtained for the pyridine radical anion.[16] The ^{2}H NMR spectrum of *cis*-$[CrF_2([^2H_4]bipy)_2]^+$ showed two lower field signals (δ 15 and 30) and two higher field signals (δ −20 and −35) as shown in Fig. 1. In the ^{2}H NMR spectrum of Cr^{III} $[6,6'-^2H_2]$-2-2'-bipyridine complexes the highest field signal near δ −100 was assigned to the 6,6'-deuterons;[17] accordingly the lower and higher field signals are assigned to the 5,5'- and 4,4'-deuterons, respectively. The NMR assignments for the bipyridine complex are confirmed by the fact that the ^{2}H NMR spectrum for *cis*-$[CrF_2([^2H_2]dmbipy)_2]^+$ exhibits only two peaks in the lower field (δ 15 and 30) but no peak in the higher field region (*δ* −20 to −30). The pair of chemical shifts observed in each region results from the *cis* complex having a C_2 symmetry axis which distinguishes the two sets of inequivalent deuterons at the 4,4'- and 5,5'-positions in the bipyridine as indicated in the inset of Fig. 1.

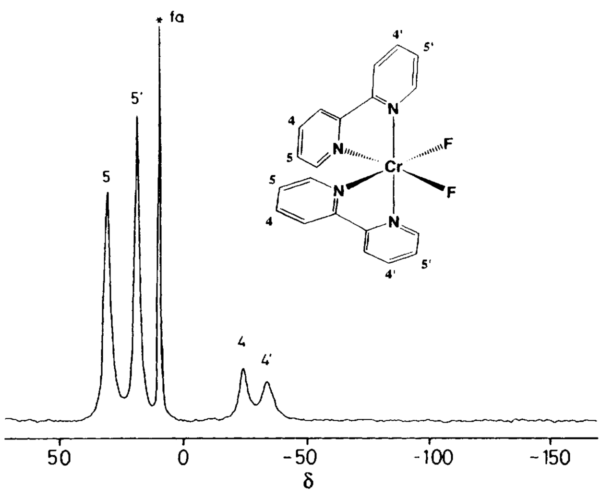

Fig. 1 The ^{2}H NMR spectrum of *cis*-$[CrF_2([^2H_4]bipy)_2]^+$ in formamide. Numbering scheme shown in inset

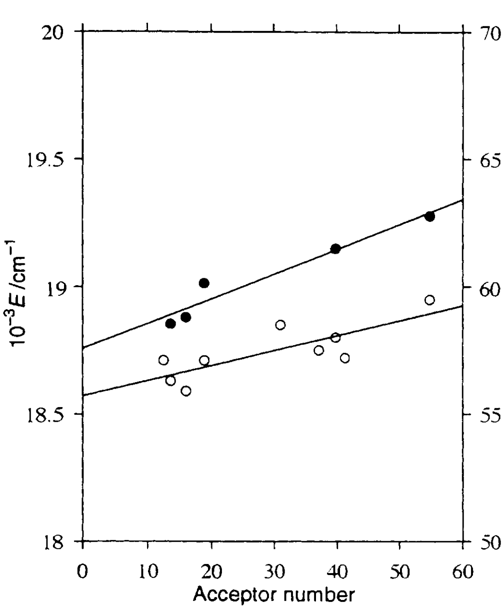

Fig. 2 Plots of the absorption band maxima (10^{-3} E_{max}/cm^{-1}) (○) (left ordinate) and the ^{2}H NMR shift difference (Δδ) (●) (right ordinate) *vs.* acceptor number for *cis*-$[CrF_2([^2H_4]trien)]^+$. The lines shown are the least-squares

Solvent Dependence of ^{2}H *NMR Shifts and Ligand-field Band*.—*cis*-$[CrF_2([^2H_4]trien)]^+$. As shown in Fig. 2 and Table 1, *cis*-$[CrF_2([^2H_4]trien)]^+$ gives fairly good correlations between the solvents acceptor number (A_N) and the first ligand-field $^4T_2 \longleftarrow {}^4A_2$ transition energy (*E*) and also with the ^{2}H NMR chemical shift difference (Δδ): $E = 0.0059\ A_N + 18.57 \times 10^3\ cm^{-1}$ (the correlation coefficient $r = 0.804$); $\Delta\delta = 0.0973\ A_N + 57.57$ ($r = 0.969$). The magnitudes of the slopes for these relations are less than those found for *trans*-$[CrF_2([^2H_4]dadad)]^+$, but the slopes have the same sign in both complexes. The dependence of the AOM $e_\sigma(N)$ parameter on the solvent acceptor number is obtained as follows. The band maxima are approximated by the average cubic ligand field, $E = e_\sigma(N_c) + e_\sigma(N_t) + \frac{1}{3}\ \{3e_\sigma(F) - 4e_\pi(F)\}$ where N_c and N_t are the nitrogens in the *cis* and *trans* positions to the fluoro ligand. We assume that $\Delta(F)$ $[= 3e_\sigma(F) - 4e_\pi(F)]$ is solvent independent[1] and that the solvent dependence of the Cr–N_c bond *cis* to F is the same as that in *trans*-$[CrF_2([^2H_4]dadad)]^+$, *i.e.*, $e_\sigma(N_c) = 0.0043A_N + 6.94 \times 10^3$ cm^{-1}, from which the relation $e_\sigma(N_t) = 0.0016A_N + 6.46 \times 10^3\ cm^{-1}$ is then derived. The variation of $e_\sigma(N_c)$ and $e_\sigma(N_t)$ with A_N clearly indicates that the Cr–N_t bond *trans* to the F ligand is almost one third as susceptible to the solvent acceptor properties as the Cr–N_c bond *cis* to F. Similarly, the correlation between the ^{2}H NMR chemical shift difference (Δδ) and A_N follows the equation $\Delta\delta = 0.0973A_N + 57.57$ ($r = 0.969$) (Fig. 2) giving a slope which is four times smaller than that for the dadad complex ($\Delta\delta = 0.41A_N + 66.3$) as shown in Table 1. Since the ^{2}H NMR shifts or the spin density on the deuterons of the ethylene backbone should be affected almost exclusively by the spin transfer through the closer Cr–N_t bond but not the remote Cr–N_c bond, this parallel behaviour between the AOM parameter and NMR shifts indicates that the Cr–N_t bond in the trien complex is more inert to solvent co-ordination than the Cr–N_c bond in the dadad complex.[1] This result may arise from the difference in the conformation of the ethylene backbone or Cr–N–C–C torsion angles and/or the geometry around the secondary amine nitrogen between the *cis*-trien and *trans*-dadad configurations. No *trans* influence is expected for the Cr–N_t bond in the trien complex, which is in accordance with no noticeable difference between Cr–N_t and Cr–N_c bond lengths in *cis*-$[CrF_2N_4]$-type complexes.[18]

Pyridine complexes. The first ligand-field absorption band of *trans*-$[CrF_2([^2H_5]py)_4]^+$ is assigned to the $^4B_2$ tetragonal component by comparison with the solution and single-crystal absorption spectrum.[3,6] The transition energy of the $^4B_2$ component increased with increasing acceptor number of the solvent. The variation in the transition energy $E(^4B_2)$

Table 1 Dependence of spectroscopic (Δδ in ppm) and AOM parameters (in 10^3 cm^{-1}) on solvent acceptor number

	Observed		Derived	
Complex	Parameter	Fit	Parameter	Fit
trans-$[CrF_2([^2H_4]dadad)]^+$ [1]	$^4B_2 \longleftarrow {}^4B_1$ transition energy	$E = 0.013A_N + 20.8$	$e_\sigma(N_c)$	$e_\sigma(N_c) = 0.0043A_N + 6.94$
	$^4A_2 \longleftarrow {}^4B_1$ band	$E = -0.03A_N + 30.12$	$e_\sigma(F)$	$e_\sigma(F) = -0.017A_N + 8.83$
	^2H chemical shift difference	$\Delta\delta = 0.41A_N + 66.3$		
cis-$[CrF_2([^2H_4]trien)]^+$	$^4T_2 \longleftarrow {}^4A_2$ transition energy*	$E = 0.0059A_N + 18.57$	$e_\sigma(N_t)$	$e_\sigma(N_t) = 0.0016A_N + 6.46$
	^2H chemical shift difference	$\Delta\delta = 0.0973A_N + 57.57$		
trans-$[CrF_2([^2H_5]py)_4]^+$	$^4B_2 \longleftarrow {}^4B_1$ transition energy	$E = 0.0077A_N + 18.57$		
	^2H chemical shift	$\delta(D^\beta) = -0.066A_N + 15.54$		
mer-$[CrF_3([^2H_5]py)_3]$	^2H chemical shift	$\delta(D^\beta) = -0.057A_N + 15.58$		
		$\delta(D^\beta) = -0.051A_N + 13.37$		
cis-$[CrF_2([^2H_4]bipy)_2]^+$	$^4E \longleftarrow {}^4B_1$ transition energy	$E = 0.0216A_N + 18.1$	$e_\sigma(N_t)$	$e_\sigma(N_t) = 0.029A_N + 4.67$
			$e_\pi(N_t)$	$e_\pi(N_t) = 0.044A_N - 3.72$
	^2H chemical shift	$\delta(D^4) = -0.164A_N - 18.0$	$e_\sigma(N_t)$	$e_\sigma(N_t) = -0.177\delta(D^4) + 1.46$
		$\delta(D^5) = -0.113A_N + 34.8$	$e_\pi(N_t)$	$e_\pi(N_t) = -0.384\delta(D^5) + 9.56$
		$\delta(D^{4'}) = -0.034A_N - 32.7$		
		$\delta(D^{5'}) = -0.022A_N + 19.3$		
		$\lvert\delta(D^4)\rvert = 1.43\delta(D^5) + 67.86$		

* Average cubic field.

[represented by the AOM parameters as $\Delta(N) = 3e_\sigma(N) - 2e_\pi(N)$ where pyridine (N) is a non-linear ligand with $\psi = \pi/4$][3] with the acceptor number [$E = 0.0077A_N + 18.57 \times 10^3$ cm^{-1} ($r = 0.83$)]] was much smaller than that for the *trans*-dadad complex as in Table 1. This fact alone does not determine the solvent dependence of the $e_\sigma(N)$ and $e_\pi(N)$ or the $e_\sigma(F)$ and $e_\pi(F)$ parameter values. The position of the lowest ^2E_g ($^2T_{1g}$) state as measured by the luminescence spectra shifts to lower energy with decreasing solvent acceptor number, giving a linear relation with a similar slope to that found for the dadad complex ($E = 0.0126A_N + 11.95 \times 10^3$ for the py complex and $E = 0.0165A_N + 12.55 \times 10^3$ cm^{-1} for the dadad complex). Since the lowering of the ^2E_g ($^2T_{1g}$) state results from the increase in the tetragonal splitting of the t_{2g} orbital [$\Delta(t_{2g}) = e_\pi(N) - 2e_\pi(F)$ assuming $\psi = \pi/4$],[6,19] this solvent variation of the ^2E_g ($^2T_{1g}$) component indicates that $|\Delta(t_{2g})|$ increases with decreasing acceptor number. The parameters $e_\sigma(F)$ and $e_\pi(F)$ should decrease by the selective solvation of two axial F ligands in the py complex. On the other hand, the Cr–py bond is π-accepting, or has a negative value for $e_\pi(N)$, as revealed from a ligand-field band analysis[3] and luminescence study.[6] In this case, the Cr–py σ-donor interaction decreases to offset the increase in $e_\sigma(F)$ and $e_\pi(F)$ value, whereas $e_\pi(N)$ should increase to maintain a constant $\Delta(N)$ [$= 3e_\sigma(N) - 2e_\pi(N)$], as revealed from the small solvent dependence of the $^4B_2$ component (see above). The increment of both $e_\pi(F)$ and $|e_\pi(N)|$ with decreasing acceptor number results in the increase in $\Delta(t_{2g})$ and hence a lowering of the luminescence peak. The π-acceptor interaction of the Cr–py bond is confirmed by the ^2H NMR chemical shift behaviour. The dependence of the γ- and β-deuteron NMR chemical shifts on solvation is the same as that for the AOM parameters. Fig. 3 shows the ^2H NMR chemical shifts of *mer*-$[CrF_3([^2H_5]py)_3]$ and *trans*-$[CrF_2([^2H_5]py)_4]^+$ for a range of solvents. The chemical shifts or the spin densities of the β- and γ-deuterons decrease and increase, respectively, with increasing acceptor number of the solvent, giving a good linear relationship (except for the γ-deuteron signals of *trans*-$[CrF_2([^2H_5]py)_4]^+$ which exhibit scattered plots). Although only four solvents afforded sufficient solubility to measure the NMR spectra of the tris(pyridine) complex, the NMR behaviour seems to be reliable in view of the fact that the slopes for two β-deuterons (−0.057 and −0.051) of the tris(pyridine) complex are similar to that (−0.066) for *trans*-$[CrF_2([^2H_5]py)_4]^+$ as shown in Table 1. The NMR chemical shift for the β-signal in the pyridine complexes is associated with the decreasing value of $|e_\pi(N)|$ as the solvent acceptor number increases, whereas the γ-deuteron signal assigned to the mutually *trans* pyridines in the tris(pyridine) complex seems to represent the change in $e_\sigma(N)$ as is more clearly evident for the bipy complexes (see below). In other words, the spin densities of the γ- and β-deuterons in the pyridine complexes are more populated in the σ- and π*-orbitals of pyridine, respectively, as predicted from Hückel molecular-orbital calculations.[16] The NMR evidence for the π-acceptor bond was also proposed from a previous study[20] on low-spin d^6 metal pyridine complexes. Unlike the present case, the ^{13}C NMR chemical shifts at the γ-as well as the β-positions appeared to be a sensitive and reliable probe of π-back bonding.[20] This discrepancy may be due to the difference in the origins of the chemical shift.

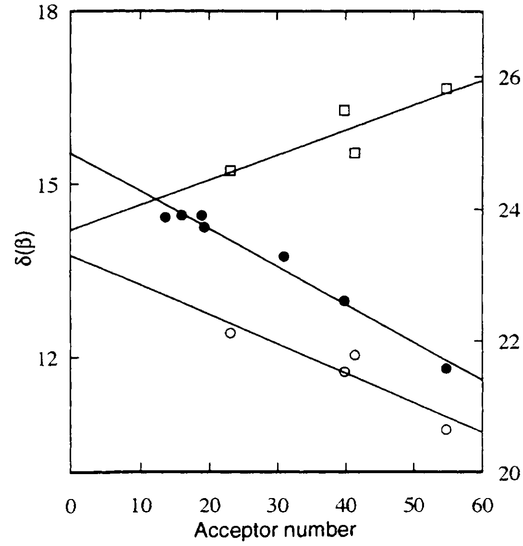

Fig. 3 Plots of the ^2H NMR shifts of the pyridine complexes *vs.* acceptor number: ○ and ●, β-deuterons of *mer*-$[CrF_3([^2H_5]py)_3]$ and *trans*-$[CrF_2([^2H_5]py)_4]^+$, respectively, and □, γ deuterons of *mer*-$[CrF_3([^2H_5]py)_3]$. Lines shown are the least-squared-fits

The two slopes for the β-deuterons are slightly different in the py complexes. According to the intensity ratio, the lower field signal at δ 10–15 is assigned to the β-deuterons in the pyridine *trans* to the fluoro and the higher field one to the β-deuteron *trans* to the pyridine. The slope for the former is *ca.* 10% greater for than for the latter deuterons, suggesting a negligible additional *trans* influence (as well as the *cis* effect) as seen for *cis*-$[CrF_2([^2H_4]trien)]^+$ (see below), but in contrast to the large difference in the ^{2}H NMR behaviour of inequivalent 4- and 5-deuterons observed for *cis*-$[CrF_2([^2H_4]bipy)_2]^+$ (see below).

While the π-acceptor interaction of Cr–N(py) bond has been assumed only indirectly from the ligand-field spectra, the ^{2}H NMR chemical shift data provide direct evidence.

cis-$[CrF_2([^2H_4]bipy)_2]^+$. The ^{2}H NMR spectrum of *cis*-$[CrF_2([^2H_4]bipy)_2]^+$ resembles that of the pyridine complexes. The lower and higher field signals decrease and increase, respectively, with increasing solvent acceptor number, as shown in Fig. 4. Consequently, the ^{2}H NMR behaviour of the 4,4′- and the 5,5′-deuterons reflect the σ- and π-bond properties in the bipy complex, respectively, substantiating the π-acceptor ability $[e_\pi(N) < 0]$ as observed for the py complexes. This experimental result agrees with the previous theoretical study based on the extended-Hückel molecular orbital (MO) method.[21] According to theoretical calculations, the 4,4′- and 5,5′-carbons have greater spin density populations in the highest occupied (σ) and the lowest unoccupied (π*) MOs respectively. The slopes for the plots of the NMR shifts for the 4-, 4′- and the 5-, 5′- deuterons *vs.* acceptor number are different as shown in Fig. 4 and Table 1. For the 5-,5′-deuteron pair, the slopes (−0.113 and −0.022) of the lower and higher field signals are nearly twice and half, respectively, as large as that (−0.051) of the β-deuteron for the pyridine *cis* to the fluoro ligand in *mer*-$[CrF_3([^2H_5]py)_3]$ and *trans*-$[CrF_2([^2H_5]py)_4]^+$. The slope (0.034) for the higher field signal of the 4,4′-pair is close to that (0.038) of the γ-deuteron for the mutually *trans* pyridine in *mer*-$[CrF_3(py)_3]$, whereas the lower field signal gives a five-fold larger slope (0.164). Thus, the lower and higher field signals are assigned to the 4-, 5- and 4′-, 5′-deuterons of the bipy ligand, respectively, as depicted in the inset of Fig. 1. The difference between the slopes for the 4-, 5- and 4′-, 5′-deuterons results from the significant difference in the σ-donor and π-acceptor ability between the Cr^{III} ion and the inequivalent nitrogens in the bipy complex, which may arise from the additional *trans* influence (as well as the *cis* effect). It is apparent from Fig. 5 and Table 1 that a plot of $\delta(D^4)$ *versus* $\delta(D^5)$ gives a straight line in contrast to that of $\delta(D^{4'})$ *versus* $\delta(D^{5'})$ which is confined to a small region. The difference between the Cr–N(bipy) bonds of the bipy complex is supported by the ligand-field band analysis in terms of the AOM parametrization as described below.

A relatively large solvent dependence [equation (1)] in the

$$E = 0.0216A_N + 18.1 \qquad (1)$$

first ligand-field band is found ($r = 0.995$). This supports the assignment of the band to the ^{4}E degenerate state in the holohedral tetragonal (D_4) field, because an opposite dependence on the acceptor number is predicted for the assignment to the $^4B_2$ state $[E = \frac{1}{2}\Delta(F) + \frac{1}{2}\Delta(N) - e_\pi(N)]$, or because the average cubic ligand field $[E = \frac{2}{6}\Delta(F) + \frac{4}{6}\Delta(N)]$ should lead to a small solvent dependence of the first band position. Assuming that the anisotropic π interaction is only perpendicular to the bipy chelate ring and that $\Delta(F) = 3e_\sigma(F) - 4e_\pi(F) = 15.39^3 \times 10^3$ and $\Delta(N_{bipy}) = 3e_\sigma(N) - 2e_\pi(N) = 21.44^5 \times 10^3$ cm^{-1} are independent of solvent acceptor number, the energy of the ^{4}E band is given by equation (2) where N_t and N_c are the nitrogens *trans* and *cis* to the fluoro

$$\begin{aligned} E &= \tfrac{3}{4}e_\sigma(F) - e_\pi(F) + \tfrac{3}{4}e_\sigma(N_t) + \tfrac{3}{2}e_\sigma(N_c) - e_\pi(N_c) \\ &= \tfrac{3}{4}e_\sigma(N_t) + \tfrac{1}{4}[\Delta(F) + 2\Delta(N)] \\ &= \tfrac{3}{4}e_\sigma(N_t) + 14.6) \end{aligned} \qquad (2)$$

ligand, respectively. Equations (1) and (2) give relation (3)

$$e_\sigma(N_t) = 0.029A_N + 4.67 \qquad (3)$$

and then from $\Delta(N_{bipy}) = 3e_\sigma(N_t) - 2e_\pi(N_t)$, equation (4) is

$$e_\pi(N_t) = 0.044A_N - 3.72 \qquad (4)$$

obtained. The dependence of $e_\sigma(N)$ on the solvent acceptor number is much greater for the bipy complex than that found for the dadad $[e_\sigma(N_c) = 0.0043A_N + 6.94]$ and trien $[e_\sigma(N_t) = 0.0016A_N + 6.46]$ complexes as compared in Table 1, suggesting that the additional *trans* influence and/or the push–pull action between the Cr–F π-donor and Cr–N π-acceptor bond in the bipy complex is more significant than the *cis* effect in the dadad and trien complexes.

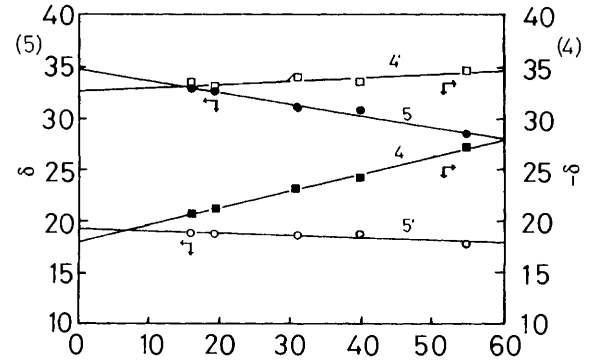

Fig. 4 Plots of the ^{2}H NMR shifts of *cis*-$[CrF_2([^2H_4]bipy)_2]^+$ *vs.* acceptor number: ■ and □, 4- and 4′- deuterons; ● and ○, 5- and 5′-deuterons, respectively. Lines shown are the least-squared-fits

From the linear correlation between the ^{2}H NMR chemical shifts for the 4,5-deuterons and the acceptor number of the solvents in Fig. 4, equations (5) and (6) are derived with r =

$$\delta(D^4) = -0.164A_N - 18.0 \qquad (5)$$

$$\delta(D^5) = -0.113A_N + 34.8 \qquad (6)$$

0.997 and 0.988, respectively, as shown in Table 1. Since the AOM parameter values for the Cr–N_t bonds have a more dominant effect on the spin densities of the 4,5- than the 4′,5′-deuterons, they can be related to the chemical shifts by equations (7) and (8). A plot of the chemical shifts *vs.* $e_\sigma(N_t)$ and

$$e_\sigma(N_t) = -0.177\delta(4) + 1.46 \qquad (7)$$

$$e_\pi(N_t) = -0.383\delta(5) + 9.56 \qquad (8)$$

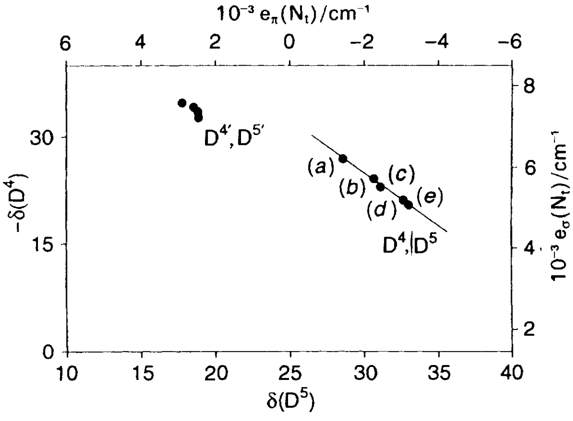

Fig. 5 Plots of the ^{2}H NMR shifts of 4-,5- and 4′-,5′-deuterons for *cis*-$[CrF_2([^2H_4]bipy)_2]^+$ in (*a*) H_2O, (*b*) fa, (*c*) dmso, (*d*) nmf and (*e*) dmf. The line shown is the least-squared-fit. The right ordinate and upper abscissa show the AOM $e_\sigma(N_t)$ and $e_\pi(N_t)$ values, respectively, which are correlated with the chemical shifts by equations (7) and (8)

$e_\pi(N_t)$ is given in Fig. 5. The range in the variation of $e_\sigma(N_t)$ values with solvent (5.10×10^3–6.23×10^3 cm^{-1}) is much greater than that (7.9×10^3–8.5×10^3 cm^{-1}) for the dadad and trien complexes. The estimated $e_\pi(N_t)$ values (-1.34×10^3 to -3.05×10^3 cm^{-1}) lie outside the range reported by Josephsen and Schäffer[5] and Ryu and Endicott,[8] but are close to the value calculated (-2280 cm^{-1}) by Lee and Hoggard[10] for $[Cr(bipy)_3]^{3+}$.

Assuming that the $e_\sigma(F)$ ($= -0.017A_N + 8.83$) value in the dadad complex can be transferred to the trien and bipy complexes, the $e_\sigma(N)$ *vs.* $e_\sigma(F)$ relations are obtained as follows: $e_\sigma(N_c) = -0.250e_\sigma(F) + 9.15$, $e_\sigma(N_t) = -0.094e_\sigma(F) + 7.29$, and $e_\sigma(N_t) = -1.71e_\sigma(F) + 19.73$ for the dadad, trien and bipy complexes respectively. It seems that the $e_\sigma(N_t)$ value for the bipy complex is more susceptible to the variation of the $e_\sigma(F)$ parameter than for the dadad and trien complexes, probably because of the additional *trans* influence. The fact that $e_\sigma(N_t)$ is less dependent on $e_\sigma(F)$ for the trien complex may be the consequence of the Cr–N$_t$ bond rigidity.

Conclusion

As seen in Table 1, the solvent dependence of the ligand-field bands and ^{2}H NMR chemical shifts in *cis*-$[CrF_2N_4]$ or *mer*-$[CrF_3N_3]$-type complexes with aliphatic amines or pyridines is fundamentally the same as that in the corresponding *trans* isomers except for the rigidity of the Cr–N bond in the former. The *trans* influence is found to be negligible (in addition to the *cis* effect) for the *cis* complexes as expected, but not for the *trans* complexes. The relationship between the NMR chemical shifts and ligand-field band and/or the AOM parameters provide more direct evidence for the π-acceptor bond properties in the aromatic nitrogen-containing heterocyclic ligands than the ligand-field band analysis. For the bipy complex, the degree of the π-acceptor interaction is estimated to be similar to that calculated on the basis of the ligand-field analysis.[10] The large additional *trans* influence, acting as well as the *cis* effect, is operative probably resulting from the push–pull action which does not occur in the trien and py complexes.

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