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Mutual Influences of Ligands as Revealed by ^{2}H NMR Shifts and the Angular Overlap Model Parameters: *trans*- and *cis*-$[CrX_2(N)_4]$-Type Complexes with Aliphatic Amine Ligands[‡]

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Keywords: Chromium complexes / Ligand effects / N ligands / NMR spectroscopy / Angular overlap model parameters

We have previously reported the relationship between ^{2}H NMR chemical shift differences ($\Delta\delta$) and the angular overlap model (AOM) parameter e_σ(F), which represents the σ antibonding interaction energy obtained from the solvatochromism, for *trans*-$[CrF_2([D_4]$-3,2,3-tet$)]^{n+}$ {$[D_4]$3,2,3-tet = 1,10-diamino-4,7-diazadecane $[NH_2(CH_2)_3NH(CD_2)_2NH(CH_2)_3NH_2]$} and *cis*-α-$[CrF_2([D_4]$trien$)]^{n+}$ {$[D_4]$trien = triethylenetetraamine $[NH_2(CH_2)_2NH(CD_2)_2NH(CH_2)_2NH_2]$}. In analogy to these relations, the co-ligand effect on the $\Delta\delta$ values for *cis*-α-$[CrX_2([D_4]$trien$)]^{n+}$ and *trans*-$[CrX_2([D_4]$3,2,3-tet$)]^{n+}$ is found to be well correlated with the reported e_σ(X) values for the co-ligands X. This is the first example of the co-ligand effect, or a mutual influence of ligands, associated with variation of the Cr–N and Cr–X bonds in *cis*- and *trans*-$[CrX_2N_4]$-type complexes. This $\Delta\delta$ vs. e_σ(X) correlation offers an indirect method for estimating the e_σ(X) values for didentate X_2 as well as monodentate X ligands from the ^{2}H NMR chemical shifts and ranking them in the two-dimensional spectrochemical series. Plots of $\Delta\delta$ vs. e_σ(FX) for *trans*-$[CrF(X)([D_4]$3,2,3-tet$)]^{n+}$ do not necessarily lie on the $\Delta\delta$ vs. e_σ(X) correlation line for the F(X) complexes with averaged $e_\sigma(FX) = 1/2[e_\sigma(X) + e_\sigma(F)]$ values − e_σ[F(CN)] is close to e_σ(F), for example − thereby demonstrating a mutual influence between the CN^- and F^- ligands in the *trans* positions through a push-pull action or π donor–acceptor interaction.

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Introduction

The mutual influence between ligands is one of the fundamental subjects in coordination chemistry since it governs the relative changes in properties upon replacement of one ligand by another.[1] General regularities in mutual influences for SP-4 platinum(II) complexes have been established, such as the *trans* influence, but for OC-6 mixed-ligand complexes they are limited to some *trans*-$[MX_2N_4]$-type complexes where negative correlations have been found between the axial M–X and the basal M–N bond lengths both theoretically and experimentally by X-ray analysis and UV/Vis spectroscopy.[1–5] For example, Bertini et al.[2] and Lever et al.[3] have established negative linear correlations between Ni–N bond lengths and 10 Dq(N) or angular overlap model (AOM) parameter e_σ(N) values, which represent the σ antibonding energy parameter, for some *trans*-$[NiX_2N_4]$ complexes, while Busch et al. have shown that the axial ligand field parameter $[10\,Dq^z(X)]$ decreases as the basal (in-plane) ligand field parameter $[10\,Dq^{xy}(N)]$ increases, which they termed the "electronic *cis* effect".[4] Ito et al. have studied this phenomenon extensively using the X-ray structural parameters of a series of Co^{III}, Ni^{II}, and Zn^{II} macrocyclic tetraamine complexes[5] and a theoretical examination of the relationship between the softness of metal ions in terms of ab initio MO calculations.[6] They found that the lengthening of the average basal M–N bonds on going from smaller to larger macrocyclic tetraamine rings is associated systematically with a shortening of the axial M–NCS or M–Cl bonds and an increase of the overlap population of M–NCS or M–Cl.[6] We have also demonstrated an analogous bond-length variation from solvatochromism and solvent-dependent NMR spectroscopy for the aliphatic amine difluoridochromium(III) complexes *trans*-$[CrF_2([D_4]$3,2,3-tet$)]$ {$[D_4]$3,2,3-tet = 1,10-diamino-4,7-diazadecane $[NH_2(CH_2)_3NH(CD_2)_2NH(CH_2)_3NH_2]$} and *cis*-α-$[CrF_2([D_4]$trien$)]^+$ {$[D_4]$trien = triethylenetetraamine $[NH_2(CH_2)_2NH(CD_2)_2NH(CH_2)_2NH_2]$}, or their aromatic amine analogs, as well as the amino polycarboxylato Cr^{III} or Co^{III} complexes in terms of the AOM parametrization.[7–11] We also found a negative correlation between the ^{2}H NMR shift differences, $\Delta\delta$, and the σ donor AOM parameters e_σ(X) and e_σ(N) of the ligands X and N, which manifests itself as an electronic *cis* effect, or a mutual influ-

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ence of ligands, for *trans*-[CrX_2([D_4]3,2,3-tet)].[7] Such a $\Delta\delta$ vs. e_σ(X) correlation should also be present in *cis*-α-[CrX_2([D_4]trien)]$^+$ in view of the solvatochromism and solvent-dependent NMR behavior of the corresponding fluorido complex, although no mutual influence has ever been found for *cis*-[CrX_2N_4]-type complexes on the basis of X-ray structural data or spectroscopic methods. This could provide a convenient and indirect means of estimating the AOM parameter values for didentate as well as monodentate ligands or for ranking them in the two-dimensional spectrochemical series.[12,13] Furthermore, it may offer the possibility of clarifying numerical ambiguities[14,15] in the AOM parameter values and allow the elucidation of chemical properties in the ground or excited states relevant to the thermodynamics or kinetics of thermal or photochemical reactions.[15] Another mutual influence or compensation due to the π donor–acceptor interaction of X–M–Y systems in a *trans* disposition has been theoretically claimed by Burdett,[16] although no such example has been reported so far. Such a mutual influence is expected to be found by examining the solvent-dependent ^{2}H NMR spectra of *trans*-[CrF(CN)([D_4]3,2,3-tet)]$^+$.

Herein we will explore the mutual influence of ligands by studying the correlation of the ^{2}H NMR shifts and AOM parameters of the X co-ligands in *cis*-α-[CrX_2([D_4]trien)]$^{n+}$ and *trans*-[CrF(X)([D_4]3,2,3-tet)]$^{n+}$ and redefining the solvatochromism and ^{2}H NMR spectra of *trans*-[Cr(F or X)$_2$-([D_4]3,2,3-tet)]$^{n+}$.

Results and Discussion

^{2}H NMR Chemical Shifts and AOM Parametrization for *trans*-[CrX_2([D_4]3,2,3-tet)]$^{n+}$

One of the main aims of this paper concerns the *cis* effect, or the mutual influence of ligands in low symmetry, of *cis*-α-[CrX_2([D_4]trien)]$^+$ complexes by examining their ^{2}H NMR chemical shifts and AOM parametrization. Prior to this, however, the ^{2}H NMR spectra of high-symmetry *trans*-[CrF_2(3,2,3-tet)]$^+$ and *trans*-[CrX_2(3,2,3-tet)]$^+$ will be reviewed and re-examined.

As shown in Figure 1, two well-separated ^{2}H NMR signals are observed due to paramagnetic isotropic contact shifts for inequivalent (axial and equatorial) deuterons in the ethylene backbone of *trans*-[CrF_2(3,2,3-tet)]$^+$ (inset of Figure 1) in water. The ^{2}H NMR chemical shift differences ($\Delta\delta$) are well correlated with each of the $^4B_2$ and $^4A_2$ tetragonal splitting components in the ligand-field d–d transition region as well as the solvent acceptor number (A_N) according to the equation $\Delta\delta = 0.409\,A_N + 66.3$ [correlation coefficient (r) = 0.99]. This correlation of $\Delta\delta$ with A_N has been interpreted by a Karplus-like or $\cos^2\theta$ relation for the paramagnetic contact shifts of Cr^{III} complexes according to the following equation:[7] $\Delta\delta = -(3^{1/2}/2)(C\cdot A)\sin 2\phi$, where C is a constant that varies reciprocally with absolute temperature, A is the hyperfine constant for the spin density of deuterons, and ϕ is the torsion angle of the Cr–N–C–C chain of the ethylene backbone in 3,2,3-tet. Since a plot of $\Delta\delta$ vs. inverse temperature ($1/T$) gives a constant value, $\Delta\delta$ is proportional to the spin density of the deuterons concerned, although, in view of the temperature-independent nature of $\sin 2\phi$, there is no conformational change in 3,2,3-tet. In other words the increase of $\Delta\delta$ reflects the increase of the deuteron spin density of C–D or the Cr–N σ-bond interaction energy [e_σ(N)], which is followed by a decrease in the Cr–F σ-bond interaction energy [e_σ(F)], associated with an attack of the stronger electron-acceptor solvents on the fluorido ligands.[7] Evaluation of e_σ(N) and e_σ(F) values obtained from the tetragonal components of the UV/Vis ligand-field bands was revised by using the appropriate Racah parameter B and involving the configurational interaction between the $^4A_2$ ($^4T_1{}^a$) and $^4A_2$ ($^4T_1{}^b$) states.[7] The revised correlations between the AOM parameters and the NMR shift difference $\Delta\delta$ are $e_\sigma(N_c) = 0.013\,\Delta\delta + 6.02$, where N_c is the amine nitrogen *cis* to the fluorido ligands, and $e_\sigma(F) = -0.048\,\Delta\delta + 11.0$.[17]

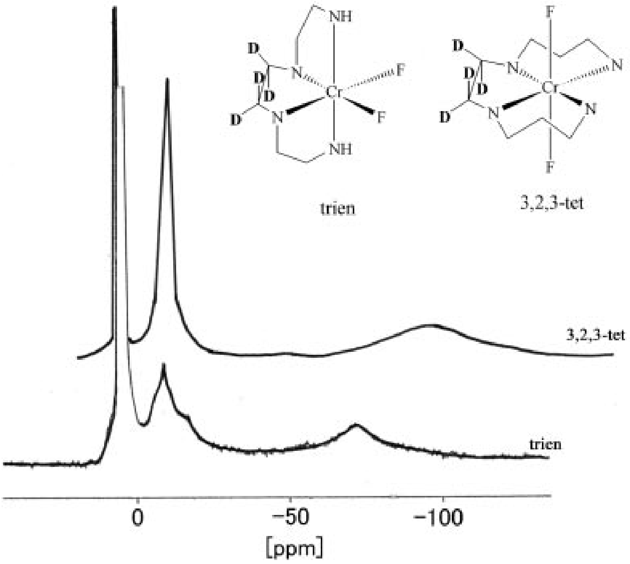

Figure 1. ^{2}H NMR spectra of *trans*-[CrF_2([D_4]3,2,3-tet)]$^+$ and *cis*-α-[CrF_2([D_4]trien)]$^+$ in dmf at 26 °C. The inset shows the structures of the 3,2,3-tet and trien complexes.

In an analogous manner to the difluorido complex, we also examined whether there is a linear correlation between $\Delta\delta$ and e_σ(N) or e_σ(X) for *trans*-[CrX_2([D_4]3,2,3-tet)]$^{n+}$ complexes. The ^{2}H NMR spectrum of *trans*-[CrF_2([D_4]-3,2,3-tet)]$^+$ in dmf at 26 °C is shown in Figure 1 and Table 1 gives the shift differences ($\Delta\delta$) together with the AOM parameter values for the X_2 complexes. We re-examined the previously reported relationship between ^{2}H NMR $\Delta\delta$ and e_σ(X) values by replacing the appropriate e_σ(X) values for F$^-$, H_2O, NH_3, and Br$^-$ (Table 1). This gave a slightly better correlation (r = 0.97) for plots of $\Delta\delta$ vs. e_σ(X) values (Table 1) than obtained previously (r = 0.95),[7] as summarized in Table 1 and shown in Figure 2. However, this should not be over-estimated in view of the ranges of estimated e_σ(X) values for some ligands, which depend on the complexes used or the estimation methods.[15] Furthermore, $\Delta\delta$ is also correlated with the e_σ(N) values obtained from the ${}^4B_2({}^4T_1)$ component [$E = 3e_\sigma(N)$] observed for some $[CrX_2(3,2,3\text{-tet})]^{n+}$ complexes, as reported previously,[7] where the least-squares calculation for the correlation was incorrectly made. In fact, the $e_\sigma(X)$ values decrease and the $e_\sigma(N)$ ones increase with increasing $\Delta\delta$, as shown in Figure 2, which leads to Equations (1) and (2) (in units of 10^3 cm^{-1}).

Table 1. AOM parameter values and ^2H NMR chemical shift differences for *trans*-$[CrX_2(3,2,3\text{-tet})]^{n+}$ in H_2O.

X_2	$\Delta\delta$ [ppm]	$e_\sigma(N)$[a]	$e_\sigma(X)$[a]	Ref.
OH^-	73.3	6.80	8.63	[19]
F^-	87.9	7.23	7.80	[18]
CN^-	89.7		7.50	[21]
NH_3	101.9		6.97	[19]
NCS^-	103.7		6.41	[20]
H_2O	97.5	7.52	6.76	[13]
Cl^-	109.0	7.40	5.56	[19]
Br^-	113.7	7.68	5.34	[19]

[a] Calculated from Equations (1–3), see text.

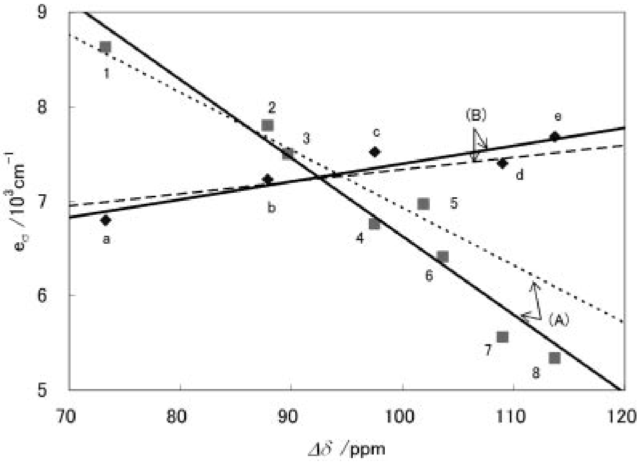

Figure 2. Plots of the AOM parameter values $e_\sigma(X)$ vs. the ^2H NMR shift difference ($\Delta\delta$) in H_2O for *trans*-$[Cr(X)_2(3,2,3\text{-tet})]^{n+}$ (——). (A): 1–8: $e_\sigma(X)$ values taken from the literature (see text and Table 1); (B) a–d: $e_\sigma(N)$ values obtained from the aqueous absorption data (${}^4B_2$ component). 1/a: $(OH)_2$; 2/b: F_2; 3: $(CN)_2$; 4: $(NH_3)_2$; 5: $(H_2O)_2$; 6: $(NCS)_2$; 7/c: Cl_2; 8/d: Br_2. The solid lines are least-squares fits. The dotted lines in (A) and (B) are calculated from $e_\sigma(N_c) = 0.013\Delta\delta + 6.02$ (6) and the solid lines from $e_\sigma(F) = -0.048\Delta\delta + 11.0$ (7) for the difluorido complex [see Equations (f) and (g) in ref.[17]].

$$e_\sigma(X) = -0.083\,\Delta\delta + 14.9\ (r = 0.97) \tag{1}$$

$$e_\sigma(N) = 0.019\,\Delta\delta + 5.50\ (r = 0.92) \tag{2}$$

Combining these two equations leads to Equation (3).

$$e_\sigma(X) = -4.37\,e_\sigma(N) + 38.9 \tag{3}$$

The slope and intercept of Equation (3) are similar to those of the revised equation $e_\sigma(F) = -3.67\,e_\sigma(N) + 33.1$ (8) [see also caption of Figure 2 and Equation (h) in ref.[17]] for the difluorido complex discussed in ref.[17] It is possible that the change of $e_\sigma(F)$ or $e_\sigma(X)$ can vary 3–4 times as much as $e_\sigma(N)$ since the Cr–F or Cr–X bond is influenced by four *cis*(basal N) ligands, in analogy to the ligand effect reported by Burdett et al.[16] and Timney.[23] The $e_\sigma(X)$ vs. $e_\sigma(N)$ correlation for the X_2 complexes is parallel to the $e_\sigma(F)$ vs. $e_\sigma(N)$ correlation for the difluorido complex.[7] This means that a mutual influence between the axial X ligands and the basal amine ligands occurs through the σ-bond interactions in a compensatory way according to the electronic *cis* effect as a result of a cooperative charge redistribution due to the electroneutrality principle through the σ bonds. This σ bond pathway gives more definite and clearer physical meaning to the negative correlation between the axial-basal bond length than the ligand-field parameter 10 Dq (Δ) values consisting of e_σ and e_π [$10\,Dq\ (\Delta) = 3e_\sigma - 4e_\pi$] for which correlations between the axial and basal ligands have been claimed for several tetragonal $[MX_2Y_4]$-type complexes.[2–6] The change of $e_\sigma(N)$ associated with the variation of $e_\sigma(X)$ indicates the invalidity of transferring the AOM parameters from one complex to another.

The $e_\sigma[F(X)]$ values for the heteroligand complexes *trans*-$[CrF(X)(3,2,3\text{-tet})]^{n+}$ ($X = NH_3, CN^-, Cl^-, Br^-$) were estimated from the observed ^2H NMR shift difference ($\Delta\delta$) according to Equation (3). These $e_\sigma(FX)$ values were compared with the average $e_\sigma(FX)$ value $[e_\sigma(F) + e_\sigma(X)]/2$ obtained by assuming holohedralized symmetry, as shown in Table 2. The estimated $e_\sigma(FX)$ values calculated from the $\Delta\delta$ values deviate from the average values by 1.6–9.7%, although the increasing order is not necessarily in line with the predicted one given in Table 2.

Table 2. AOM parameter values and ^2H NMR chemical shift differences for *trans*-$[CrF(X)(3,2,3\text{-tet})]^{n+}$ in H_2O.

X	$\Delta\delta$ [ppm]	$e_\sigma(FX)$ (est.) [10^3 cm^{-1}]	$e_\sigma(FX)$ (av.) [10^3 cm^{-1}]	Error [$e_\sigma(\text{est.}) - e_\sigma(\text{av.})]/e_\sigma(\text{av.})$
CN	86.2	7.78	7.65	0.016
Cl	93.2	7.19	6.68	0.077
Br	93.0	7.20	6.57	0.097
NH_3	98.2	6.77	7.39	–0.083
OH	72.7	8.89	8.22	0.082
H_2O	95.7	6.98	7.70	–0.092

The solvent-dependent ^2H NMR shift behavior for the FX complexes demonstrates a fairly linear correlation of the $\Delta\delta$ values with A_N, as shown in Figure 3. Moreover, the least-squares lines for the plots of $\Delta\delta$ vs. A_N lie roughly between those of the F_2 and X_2 complexes, except for the F(CN) complex (see below). This fact indicates the additivity of the σ interaction as well as the selective solvation, which affects the energies of the d orbitals that point towards the axial ligands in the FX complexes in the same way as in the F_2 complex.

For the F(CN) complex, the solvent-dependent NMR shift differences ($\Delta\delta$) tend to deviate from the average values with decreasing solvent acceptor number (A_N) and lie closer to those for the F_2 complex than the average of the F_2 and $(CN)_2$ complexes, as shown in Figure 3. This may be due to a mutual influence through the push-pull action[24] or an additional *trans* influence between the π-donor F^- and π-acceptor CN^- ligands similar to that found for the aromatic amine complexes.[8,25] The larger the σ donor or $e_\sigma(F)$ and

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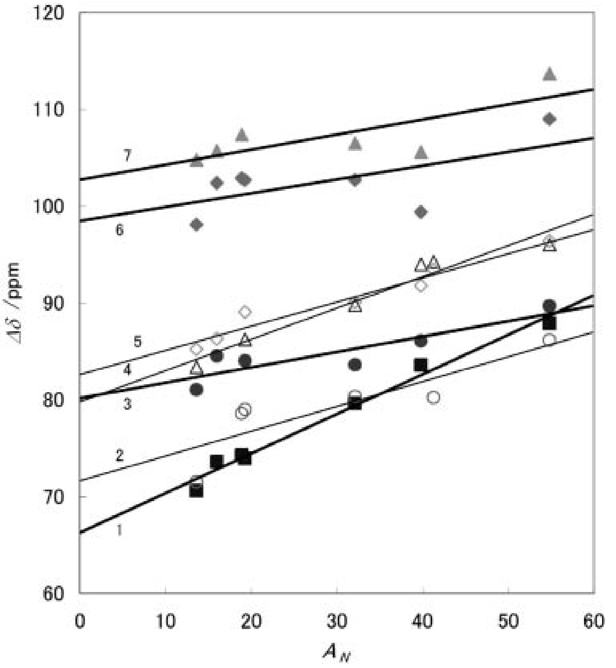

Figure 3. Plots of the ^{2}H NMR shift differences ($\Delta\delta$) vs. the acceptor numbers A_N for *trans*-[CrX_2(3,2,3-tet)]$^+$. 1: F_2; 2: F(CN); 3: $(CN)_2$; 4: F(Cl); 5: F(Br); 6: Cl_2; 7: Br_2.

the larger the π donor or $|e_\pi(F)|$, then the larger the π acceptor or $e_\pi(CN)$ becomes by the push-pull action, which leads to a smaller $e_\sigma(CN)$ due to the relationship $\Delta = 3e_\sigma(CN) - 4e_\pi(CN)$. The $e_\sigma(F)$ and $e_\sigma(CN)$ values in the F(CN) complex are larger and smaller by $\delta e_\sigma(F)$ and $\delta e_\sigma(CN)$, respectively, than those in the F_2 and $(CN)_2$ complexes. The additional parts $\delta e_\sigma(F)$ and $\delta e_\sigma(CN)$ may also be elucidated on the basis of the AOM approach including the quartic terms of Burdett et al.,[16] which gives $\delta e_\sigma(F) \propto e_\sigma(F)[e_\sigma(F) - e_\sigma(CN)]$ and $\delta e_\sigma(CN) \propto e_\sigma(CN)[e_\sigma(CN) - e_\sigma(F)]$. As $e_\sigma(F)$ is larger than $e_\sigma(CN)$, and since the difference $e_\sigma(F) - e_\sigma(CN)$ increases for the F_2 and $(CN)_2$ complexes with decreasing A_N, $e_\sigma[F(CN)]$ is predicted to become closer to that of $e_\sigma(F)$,[26] as found for the solvent-dependent ^{2}H NMR spectra (Figure 3). This mutual influence between F^- and CN^- is in accordance with the interpretation for the unusual photochemical reactivity of *trans*-[CrF(CN)(NH_3)$_4$]$^+$.[27] It follows, however, that the additive ligand-field or holohedralized symmetry assumption[13] may not always be confirmed for the F(CN) complex.

^{2}H NMR Chemical Shifts and AOM Parametrization for *cis*-α-[CrX_2([D_4]trien)]$^{n+}$

Two well-separated ^{2}H NMR signals are observed for *cis*-α-[CrX_2([D_4]trien)]$^{n+}$, similarly to the *trans*-3,2,3-tet complexes (Figure 1). The chemical shift difference ($\Delta\delta$) values are summarized in Table 3. A plot of $\Delta\delta$ vs. $e_\sigma(X)$ gives a fairly linear correlation for the reported $e_\sigma(X)$ values of the monodentate ligands together with that of the didentate dianionic oxalato ligand (Table 3 and Figure 4). This correlation gives Equation (4).

Table 3. AOM parameter values and ^{2}H NMR chemical shift differences for *cis*-α-[CrX_2([D_4]trien)]$^{n+}$.

X_2	$\Delta\delta$ [ppm]	$e_\sigma(X)$ [10^3 cm^{-1}][a]
F_2	62.9	7.80[18]
Cl_2	85.6	5.56[19]
$(NCS)_2$	80.6	6.41[20]
$(OH)_2$	57.3	8.63[19]
$(H_2O)_2$	70.3	6.76[13]
ox	78.3	6.75[28]

[a] Calculated from Equation (4).

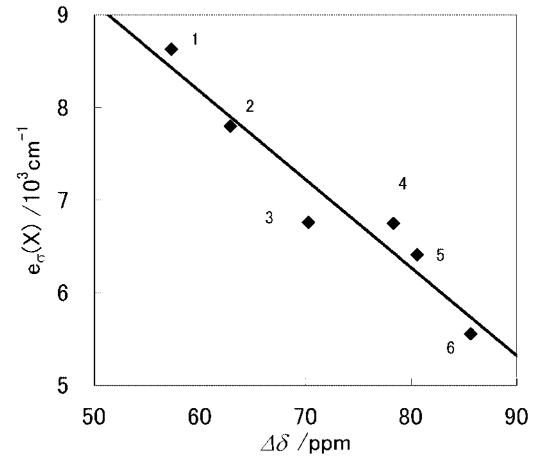

Figure 4. Plots of the AOM parameter values vs. the ^{2}H NMR shift difference ($\Delta\delta$) for *cis*-α-[CrX_2(trien)]$^{n+}$ in water. 1: OH^-; 2: F^-; 3: H_2O, 4: oxalato^{2-}; 5: NCS^-; 6: Cl^-.

$$e_\sigma(X) = -0.095\Delta\delta + 13.90 \quad (r = 0.96) \tag{4}$$

The slope and intercept of this equation are not very different from those of Equation (1) for the *trans*-[CrX_2(3,2,3-tet)]$^+$ complexes, which suggests that the variation of $\Delta\delta$ with $e_\sigma(X)$ for the *cis* complexes has the same cause as for the *trans* complexes.

Equation (4) could therefore be used to provide $e_\sigma(X)$ values for didentate and monodentate ligands from the ^{2}H NMR shift difference for the deuterated trien complexes. The e_σ value for the acac complex [e_σ(acac)], for example, was estimated from its $\Delta\delta$ value to be 6770 cm^{-1} which is smaller than that (7400–7700 cm^{-1}) obtained spectroscopically and by AOM calculations for [Cr(acac)$_3$].[28a] This may be due to the different number of acac ligands in the tris(acac) and mono(acac) complexes as the spin-forbidden transition energy of [Cr(acac)(en)$_2$]$^{2+}$[29] is larger than that of [Cr(acac)$_2$(en)]$^+$[29] and [Cr(acac)$_3$][30] – the mono(acac) complex is less covalent than the tris- and bis(acac) complexes.

Conclusions

The mutual influence of ligands for both *trans*- and *cis*-[CrX_2(N)$_4$] complexes of aliphatic amines behaves in a fundamentally similar manner to the solvent-dependence of the

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AOM parameter e_σ(F) and the ^{2}H NMR chemical-shift difference $\Delta\delta$ in *trans*- and *cis*-[CrF$_2$(N)$_4$]-type complexes. In view of this significant correlation, the $\Delta\delta$ values are an indicator of the relative strength of the Cr–N and Cr–X σ-bonds: the smaller the e_σ(N), the larger the e_σ(X). This suggests that the transferability assumption from one complex to another[13] is invalid for both e_σ(X) and e_σ(N).

In general, the AOM parameters have been evaluated by a conventional procedure that involves fitting the absorption bands in the spin-allowed ligand-field d–d transitions to the calculated energy levels by varying the AOM parameter values,[13,18–22] which requires the correct assignment of the well-resolved ligand-field band components. However, the spin-allowed ligand-field bands of most *trans*- and *cis*-[CrX$_2$N$_4$]-type complexes exhibit poorly defined or no splitting into degenerate or nondegenerate components, except for a limited number of complexes such as *trans*-difluorido tetraamine complexes. Thus, the positions of the absorption bands have to be resolved into their Gaussian components by curve deconvolution techniques for most complexes. This often produces uncertainties in the AOM parameter estimations. The present procedure for estimating the AOM parameters overcomes this major disadvantage of the conventional direct method even though preparation of the deuterated ligands is a tedious process. In addition, this method can be applied to complexes whose ligand-field bands cannot be observed due to overlapping with intraligand transitions of spectroscopically nontransparent ligands or with MLCT bands in the ligand-field band region, as found for complexes of the nitroxide radical.[31]

Once the e_σ(X) values have been obtained from Equations (1) or (4), the Cr–X π-bond interaction or e_π(X) parameter values can be estimated from the relation of the available ligand-field parameter $\Delta(X) = 10\,Dq(X) = 3e_\sigma(X) - 4e_\pi(X)$ by substituting the appropriate e_σ(X) values. Both e_σ(X) and e_π(X) for the ligands can then be positioned in the two-dimensional spectrochemical series, which is distinguished from the traditional spectrochemical series by the straightforward reflection of the ground-state electronic properties. Thus, the present complexes *trans*-[CrX$_2$([D$_4$]3,2,3-tet)]$^{n+}$ and *cis*-α-[CrX$_2$([D$_4$]trien)]$^{n+}$ can be used as reference complexes for ranking the two-dimensional spectrochemical series.

The additive nature of the ligand field for *trans*-[CrF(X)(3,2,3-tet)]$^{n+}$, is mostly validated for the FCl and FBr complexes but not for the F(CN) complex, which demonstrates a mutual influence between F and CN through a push-pull action or a donor–acceptor π mutual compensation.

Experimental Section

Preparation of the 3,2,3-tet Complexes

***trans*-[CrF(H$_2$O)(3,2,3-tet)](ClO$_4$)$_2$:** *trans*-[CrF$_2$(3,2,3-tet)](ClO$_4$)[7] (1.0 g) was stirred with 5 mL of perchloric acid (70%) at 30 °C overnight.[32] The resultant orange crystals were filtered, then washed with acetone and diethyl ether and dried in air. Yield: 52.7%. C$_8$H$_{24}$Cl$_2$CrFN$_4$O$_9$ (462.20): calcd. C 20.79, H 5.23, N 12.12; found C 20.85, H 5.30, N 12.06.

***trans*-[CrF(X)(3,2,3-tet)]ClO$_4$ (X = Cl, Br):** A mixture of *trans*-[CrF(H$_2$O)(3,2,3-tet)](ClO$_4$)$_2$ (0.5 g) and an excess of NH$_4$X (X = Cl, Br; 0.5 g) was refluxed in methanol at 70 °C for 45 min. The color of the solution turned from orange to red and powdery complexes were obtained after filtration and drying. Yields for the Cl and Br complexes were about 70%. C$_8$H$_{22}$Cl$_2$CrFN$_4$O$_4$ (380.18): calcd. C 25.27, H 5.83, N 14.74; found C 25.39, H 5.94, N 14.64. C$_8$H$_{22}$BrClCrFN$_4$O$_4$ (424.64): calcd. C 22.63, H 5.22, N 13.19; found. C 22.71, H 5.30, N 13.13.

***trans*-[CrF(NH$_3$)(3,2,3-tet)](ClO$_4$)$_2$:** *trans*-[CrBr(F)(3,2,3-tet)]ClO$_4$ was treated with an excess of liquid ammonia in a pressure tube at 0 °C for 2 h. The ammonia was then evaporated at atmospheric pressure at room temperature to give an orange powder. This was recrystallized by adding sodium perchlorate to the aqueous solution. Yield was about 60%. C$_8$H$_{25}$Cl$_2$CrFN$_5$O$_8$ (461.21): calcd. C 20.83, H 5.46, N 15.19; found C 21.21, H 5.56, N 15.29.

***trans*-[CrF(CN)(3,2,3-tet)]BPh$_4$·0.46NaBPh$_4$·3H$_2$O:** *trans*-[CrF(H$_2$O)(3,2,3-tet)](ClO$_4$)$_2$ (0.76 g) was dissolved in 10 mL of DMSO. Sodium cyanide (0.1 g) was added to this solution and the mixture was heated to 140 °C. The solution was then cooled to room temperature and the desired complex was eluted on a column of Sephadex C-25 using 0.1 M sodium bromide solution as the eluent. A small amount of the starting complex remained on the top of the column. The first eluate was collected by filtration and was desalted by condensation a few times. The desired complex precipitated upon addition of sodium tetraphenylborate to the aqueous solution. C$_{44.02}$H$_{57.2}$B$_{1.46}$CrFN$_5$Na$_{0.46}$O$_3$ (801.99): calcd. for C 65.96, H 7.19, N 8.73; found C 65.25, H 7.23, N 8.85.

Preparation of the [D$_4$]3,2,3-tet Complexes

Deuterated [D$_4$]3,2,3-tet was prepared by a previously reported method.[7] The [D$_4$]3,2,3-tet complexes were prepared by the same methods as the corresponding 3,2,3-tet complexes.

Preparation of the trien Complexes

***cis*-α-[CrF$_2$(trien)]ClO$_4$:** This complex was prepared by a literature method.[33]

cis-α-[CrCl$_2$(trien)]Cl, *cis*-α-[Cr(NCS)$_2$(trien)]Cl, and *cis*-α-[Cr(ox)(trien)]ClO$_4$ were also prepared by literature methods.[34]

***cis*-α-[Cr(acac)(trien)](PF$_6$)$_2$:** Acetylacetone (1.0 g) was added to 100 mL of an aqueous solution of *cis*-α-[CrCl$_2$(trien)]Cl (3.3 g). The solution was then neutralized with 1 M NaOH solution, and the mixture was heated in a water bath for 60 min. The color of the solution changed from violet to red. The desired complex was separated by column chromatography on SP-Sephadex Na$^+$ with 0.2 M sodium chloride solution as eluent. The sodium chloride in the eluate was removed by condensation. The PF$_6$ salt was obtained by adding NaPF$_6$ to the aqueous solution. C$_{11}$H$_{25}$CrF$_{12}$N$_4$O$_2$P$_2$ (587.27): calcd. C 22.50, H 4.29, N 9.54; found C 22.48, H 4.31, N 9.52.

Deuteriation of [D$_4$]trien and Its Complexes: Deuteriated triethylenetetraamine ([D$_4$]trien = NH$_2$CH$_2$CH$_2$NHCD$_2$CD$_2$NHCH$_2$CH$_2$NH$_2$) was prepared by a previously reported method.[8] The product was used without purification. The [D$_4$]trien complexes were prepared by the same methods as the trien complexes.

Measurements: UV/Vis spectra in solution were measured with a Shimazu UV-2100 and/or a Hitachi UV-330 spectrophotometer. ^{2}H NMR spectra were measured with a Jeol JMN GX-400 and/or a JEOL JMN GSX-270 spectrometer at 26 °C for products in 2 mM

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dmf solution. External standards of $CDCl_3$ and $(CH_3)_3SiCD_2CD_2CO_2Na$ (TSP) were assigned chemical shifts of $\delta = 7.24$ and 0.589 ppm, respectively. The solvents used for the measurements were of spectro or reagent grade. The abbreviations for the solvents (in parentheses) and their A_N values (in square brackets), as found in ref.[7–11], are as follows: *N*,*N*-dimethylacetamide (dma) [13.6], *N*,*N*-dimethylformamide (dmf) [16.0], acetonitrile (an) [18.9], dimethyl sulfoxide (dmso) [19.3], chloroform [23.1], *N*-methylformamide (nmf) [32.1], formamide (fm) [39.8], methanol [41.3], water [54.8].

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