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Mutual Influences of Ligands as Revealed by the ^{2}H NMR Chemical Shifts and the Angular Overlap Model Parameters: *cis*-[CrX$_2$(N)$_4$] and *fac*-[CrX$_3$(N)$_3$]-Type Complexes with Aromatic Amines[‡]

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A mutual influence of ligands through a π donor–acceptor interaction is found by examining how the X co-ligands of the aromatic amine complexes *cis*-[CrX$_2$([D$_4$]bpy)$_2$]$^{n+}$ (bpy = 2,2′-bipyridine) and *fac*-[CrX$_3$([D$_{12}$]tpa)]$^{n+}$ [tpa = tris(2-pyridyl)amine] affect the ^{2}H NMR chemical shifts in connection with the Angular Overlap Model (AOM) parameterization in an analogous manner to our previous study on the solvatochromism and solvent-dependent ^{2}H NMR spectra of *cis*-[CrF$_2$([D$_4$]bpy)$_2$]$^+$ and *fac*-[CrF$_3$([D$_{12}$]tpa)]. The ranking of the AOM parameter for monodentate and/or didentate ligands can be obtained from this co-ligand effect only from the ^{2}H NMR shifts. The postulated relative order in the two-dimensional spectrochemical series is Cl$^-$ > Br$^-$ > O or N donors (mal^{2-} > acac$^-$ or H$_2$O > dmf > NCS$^-$) for the aromatic amine complexes, which contrasts with the order O or N donors > Cl$^-$ > Br$^-$ for the aliphatic amine complexes(see the preceding paper in this issue). This fact suggests that the Cr–Cl and Cr–Br σ bonds are stronger in the soft acidic aromatic amine complexes than those in the hard acidic aliphatic amine complexes. This means they have a higher affinity for soft basic Cl$^-$ and Br$^-$ ligands and can be explained in terms of the hard/soft acid/base (HSAB) concept.

Introduction

In the preceding paper in this issue[1] we found a linear correlation between the Angular Overlap Model (AOM) parameter e_σ(X) for the X co-ligands and the ^{2}H NMR chemical shift differences ($\Delta\delta$) for the aliphatic amine complexes *trans*-[CrX$_2$([D$_4$]3,2,3-tet)]$^{n+}$ {[D$_4$]3,2,3-tet = 1,10-diamino-4,7-diazadecane [NH$_2$(CH$_2$)$_3$NH(CD$_2$)$_2$NH(CH$_2$)$_3$-NH$_2$]}, and *cis*-[CrX$_2$([D$_4$]trien)]$^{n+}$ {[D$_4$]trien = triethylenetetramine [NH$_2$(CH$_2$)$_2$NH(CD$_2$)$_2$NH(CH$_2$)$_2$NH$_2$]}, which demonstrates a mutual influence between the amine and X ligands. This is based on the fact that the e_σ(X) vs. $\Delta\delta$ relation is parallel to the e_σ(F) vs. $\Delta\delta$ relation, with a variation of the solvent acceptor number (A_N), in the *trans*- and *cis*-[CrF$_2$(N)$_4$] complexes. As a result, we devised a more convenient method for estimating the AOM parameter values, even for didentate ligands, which allows them to be positioned in the two-dimensional spectrochemical series. On the other hand, the solvatochromism and solvent-dependent ^{2}H NMR spectra of the aromatic amine complexes *cis*-[CrF$_2$([D$_4$]bpy)$_2$]$^+$ (bpy = 2,2′-bipyridine)[2] and *fac*-[CrF$_3$([D$_{12}$]tpa)$_3$] [tpa = tris(2-pyridyl)amine][3] have revealed more direct and clearer evidence for a mutual F–Cr–N(aromatic amine) influence due to the strong Cr–N π acceptor and Cr–F π donor properties in terms of the AOM parametrization, as has been found for the NC–Cr–F bond in *trans*-[CrF(CN)(3,2,3-tet)]$^+$.[1] In an analogous manner to this solvent-dependent spectroscopic behavior for the fluorido aromatic amine complexes as well as the co-ligand effect for *trans*- and *cis*-[CrX$_2$(N)$_4$] complexes with aliphatic amines (see ref.[1]), the mutual influence between X ligands and the aromatic amine in *cis*-[CrX$_2$([D$_4$]bpy)$_2$]$^{n+}$ and *fac*-[CrX$_3$([D$_{12}$]tpa)$_3$] is expected to be revealed by examining the ^{2}H NMR chemical shifts in terms of the AOM parameterization.

In this paper, the ^{2}H NMR chemical shifts of *cis*-[CrX$_2$([D$_4$]bpy)$_2$]$^{n+}$ and *fac*-[CrX$_3$([D$_{12}$]tpa)]$^{n+}$ will be explored in terms of the AOM parameterization of the X co-ligands. This could provide a qualitative ranking of the two-dimensional spectrochemical series[4] for the AOM parameters of the co-ligand X in the aromatic amine complexes, which would shed light on how the coordination bond properties differ from each upon replacing the co-ligands and also how they differ from those in the aliphatic amine complexes.

[‡] Mutual Influences of Ligands as Revealed by ^{2}H NMR Shifts and the Angular Overlap Model Parameters, 2. Part 1: Ref.[1]

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Results and Discussion

2,2′-Bipyridine(bpy) Complexes {*cis*-[Cr(F_2 or X_2)(bpy)$_2$]$^+$}

Of the four ^{2}H NMR signals of *cis*-$[CrF_2([D_4]bpy)_2]^+$ shown in Figure 1, the signal at around δ = –25 ppm for the deuteron at the 4 (*para*)-position and that at around δ = 30 ppm for the deuteron at the 5 (*meta*)-position of the pyridyl ring of bpy *trans* to F increase and decrease in absolute shift values, respectively, upon increasing the solvent acceptor number (A_N), as reported previously.[2] This change is also correlated to the AOM parameter $e_\sigma(N_t)$ (N_t denotes the nitrogen of the pyridyl ring *trans* to F) in terms of the ligand-field band analysis on the basis of a fairly large A_N-dependence of the first ligand-field ($^4A_{2g}$-$^4T_{2g}$) band.[2] In other words, the $e_\sigma(N_t)$ and $e_\pi(N_t)$ values change with variation of A_N, as shown by the right ordinate and upper abscissa, respectively, in Figure 2,[2] which suggests that the solvent-dependent behavior of the chemical shifts of $\delta(4)$ and $\delta(5)$ reflects the variation of the Cr–N σ- and π-bond properties, respectively, in the bpy complex: the larger the acceptor number A_N, the smaller the $e_\sigma(F)$ and $e_\pi(F)$ values or the weaker the Cr–F σ and π bonds, and also the larger the $e_\sigma(N_t)$ value or the stronger the Cr–N_t σ bond, the smaller the $|e_\pi(N_t)|$ value or the stronger the Cr–N_t π acceptor bond. This relationship demonstrates the mutual compensation between Cr–N and Cr–F σ and π bonds. The mutual compensation of $e_\pi(N_t)$ and $e_\pi(F)$ in *cis*-$[CrF_2(bpy)_2]^+$ is confirmed by the solvatochromic shift behavior from the $^2E(^2E_g)$ to $^2E(^2T_{1g})$ emitter in a mixture of dmf and water in solvents with smaller A_N with increasing dmf fraction,[5] as also observed for *trans*-$[CrF_2(py)_4]^+$.[2] The $^2E(^2T_{1g})$ emitter, or the lowest excited $^2E(^2T_{1g})$ state, results from a lowering, by $\Delta(t_{2g})^2/[E(^2t_{2g}) - E(^2T_{1g})]$, of the large configurational interaction between the $^2E(^2T_{1g})$ and $^2E(^2T_{2g})$ states due to an increase in $[\Delta(t_{2g}) = e_\pi(F) + |e_\pi(N_t)|]$ caused by the push-pull action between the Cr–F and Cr–N bonds in solvents with smaller A_N. This mutual influence is also supported by the Cr–F and Cr–N bond lengths in *cis*-$[CrF_2(bpy)_2]ClO_4$, where our recent X-ray analysis revealed that the Cr–N bonds *trans* to F [Cr–N2 2.0680(13), Cr–N3 2.0842(14) Å] are significantly longer than those *trans* to another bpy nitrogen atom [Cr–N1 2.0480(14), Cr–N4 2.0511(14) Å].[6]

The four ^{2}H NMR signals observed for the 4-,5- and 4′-,5′-deuterons in the *cis*-$[CrX_2([D_4]bpy)_2]^{n+}$ complexes are assigned to two inequivalent deuterons of the pyridyl rings *trans* [$\delta(4)$ and $\delta(5)$] and *cis* [$\delta(4')$ and $\delta(5')$] to the X ligand in analogy to those for the corresponding difluorido complex [$\delta(4) > \delta(4')$ and $\delta(5) > \delta(5')$], as shown in Figure 1. The NMR spectroscopic data are summarized in Table 1.

A plot of $\delta(4)$ vs. $\delta(5)$ gives the following well-defined linear correlation for the X complexes in water: $-\delta(4) = -1.91\delta(5) + 83.7$ (r = 0.98).

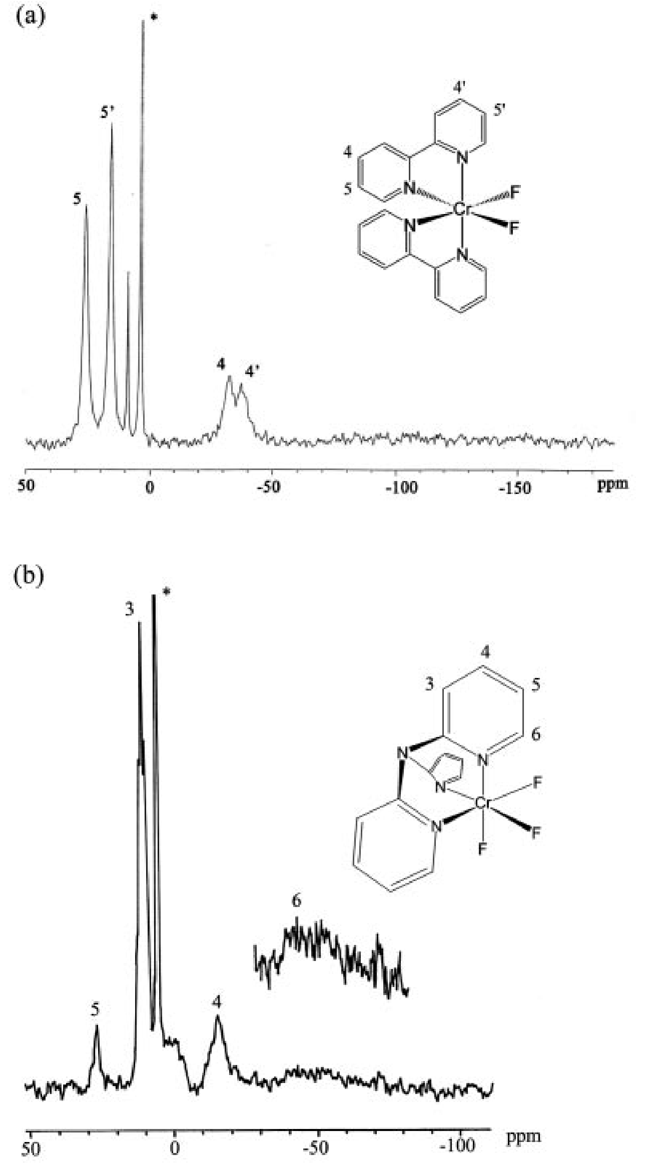

Figure 1. ^{2}H NMR spectra of $[CrF_2([D_4]bpy)_2]^+$ in formamide (a) and $[CrF_3([D_{12}]tpa)]$ in dmf (b). The insets show the structures with the positions of the deuterons used for assignment of the NMR signals labeled. The asterisks indicate solvent signals.

This correlation is similar to that for *cis*-$[CrF_2([D_4]bpy)_2]^+$ [$-\delta(4) = -1.45\delta(5) + 68.65$ (r = 0.99)], as shown in Figure 2. Since there is no direct method for correlating the ligand-field band with the ^{2}H NMR chemical shift for *cis*-$[CrX_2(bpy)_2]^{n+}$ complexes, however, the scales for the $e_\sigma(N_t)$ and $e_\pi(N_t)$ values in Figure 2 are not necessarily useful for estimating the AOM parameters. Assuming that the variation of $e_\sigma(X)$ results in change in the $e_\sigma(N)$ values similar to that found for the aliphatic amine complexes,[1] the increase in $\delta(4)$ and the decrease in $\delta(5)$ should be associated with the increase in $e_\sigma(N_t)$ and the decrease in $e_\pi(N_t)$, respectively, as a result of the decrease in $e_\sigma(X)$ in a manner analogous to that for *cis*-$[CrF_2([D_4]bpy)_2]^+$. The co-ligand dependence of the ^{2}H NMR chemical shifts for the bpy complexes shows that $\delta(4)$ or $e_\sigma(N_t)$ increase in the order $F^- < Cl^- < Br^- < mal^{2-} < acac^- <$ dmf in dmf and $Cl^- < Br^- < F^- < mal^{2-} < acac^- <$ dmf in H_2O, thereby reflecting the increasing order of the Cr–N σ-bond interaction energy or $e_\sigma(N_t)$. Likewise, the decreasing order of $\delta(4)$ corre-

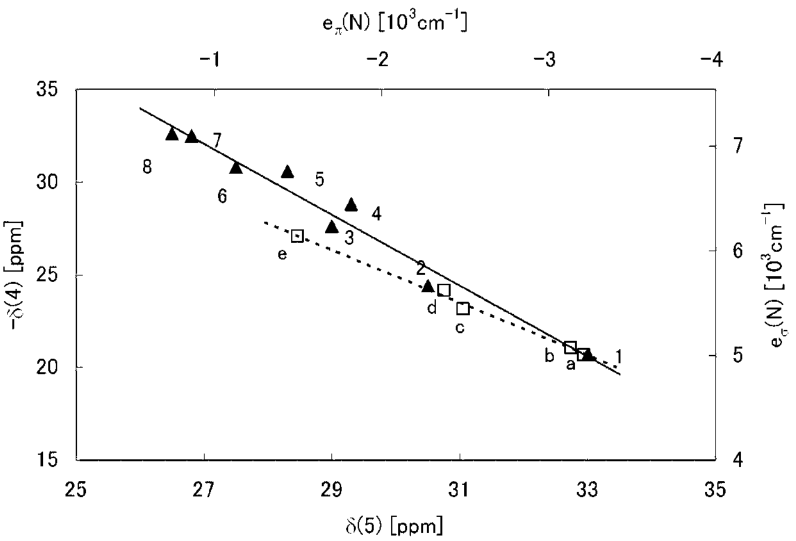

Figure 2. Plots of the ^{2}H NMR chemical shifts of the deuterons in the 4- and 5-positions of *cis*-$[CrF_2([D_4]bpy)_2]^+$ (□) in dmf (a), dmso (b), nmf (c), fa (d), and water (e) and for *cis*-$[CrX_2([D_4]bpy)_2]^{n+}$ (▲) [X = F (1), Cl (2), Br (3), mal (4), acac (5), acaCl (6), acaBr (7), and dmf (8)]. The lines shown are the least-squares fit. The right ordinate and upper abscissa show the $e_\sigma(N_t)$ and $e_\pi(N_t)$ values, respectively, for *cis*-$[CrF_2(bpy)_2]^+$.

Table 1. ^{2}H NMR chemical shifts (δ values, ppm) of *cis*-$[CrX_2([D_4]bpy)_2]^{n+}$.

X_2	Chemical shift[a]	
	$-\delta(4)$	$\delta(5)$
F_2	20.7	33.0
Cl_2	24.4	30.5
Br_2	27.6	29.0
acac	30.6	28.3
$(dmf)_2$	32.6	26.5
mal	28.8	29.3
acaCl	30.8	27.5
acaBr	32.5	26.8

[a] $-\delta(4) = -1.91\delta(5) + 83.7$ (r = 0.98).

sponds to that of e_σ(X), namely $F^- > Cl^- > Br^- > mal^{2-} > acac^- >$ dmf in dmf and $Cl^- > Br^- > F^- > mal^{2-} > acac^- >$ dmf in water. This order is similar to the rank of the two-dimensional spectrochemical series for e_σ(X),[1,4,9–11] excluding Cl^- and Br^-, rather than the rank for e_π(X), in other words the Cr–X σ-bond properties or e_σ(X) are correlated directly with the variation of $e_\sigma(N_t)$ and $e_\pi(N_t)$. Thus, the ^{2}H NMR chemical shifts provide a method for evaluating the rank of the AOM parameter e_σ(X) in the two-dimensional spectrochemical series.

Like the aliphatic amine complex *cis*-α-$[CrX_2([D_4]trien)]^{n+}$, the bpy complexes are able to provide some information about the as-yet unknown ranking of the AOM parameters even for the didentate ligands. Thus, the ^{2}H NMR spectroscopic data of *cis*-$[Cr([D_4]bpy)_2(acaX)]^{2+}$ complexes (X = Cl, Br) containing didentate ligands were examined by plotting δ(4) vs. δ(5). As compared with the −δ(4) or e_σ(N) values for the acetylacetonate analogues, the Cr–O(acaX) σ bond is a little weaker than the Cr–O(acac) σ bond, although the covalency in Cr–O(acaX) is estimated to be larger than that in Cr–O(acac), as inferred from the nephelauxetic effect estimated from the lowest ligand-field doublet (^2E_g) position by the emission for $[Cr(acaX)_3]$[7] and circular dichroism for (+)-$[Cr(acaX)_2(en)]^+$.[8] This may result from a difference in co-ligands between bpy and acac or en (ethylenediamine) and/or in the number of acac ligands as found in the aliphatic amine (acac) complexes.[1]

It should be noted that the rank of e_σ(X) in the two-dimensional spectrochemical series for the bpy complexes is $F^- > Cl^- > Br^- >$ oxygen donors ($mal^{2-} > acac^- >$ dmf) in dmf and $Cl^- > Br^- >$ oxygen donors ($mal^{2-} > acac^- >$ dmf) $> F^-$ in water, as suggested from the order of −δ(4). This is contrast to the order of the AOM parameters ($OH^- > F^- > CN^- > NH_3 > NCS^- > H_2O > Cl^- > Br^-$) of 3,2,3-tet and trien complexes.[1,4,9–11] This difference will be discussed in connection with the case of the tpa complexes.

Tris(2-pyridyl)amine (tpa) Complexes

As shown in Figure 1, *fac*-$[CrF_3([D_{12}]tpa)]$ exhibits four ^{2}H NMR signals. A pair of signals at the 4 (*para*)- and 3 (*meta*)-positions is found to demonstrate a linear correlation with variation of A_N, as shown in Figure 3 and represented by $-\delta(4) = -4.00\delta(3) + 63.6$ (r = 0.90). Such a solvent-dependent NMR behavior is related to the significant solvatochromism observed: the AOM parameters e_σ(N) and e_π(N) associated with variation of the Cr–F σ-donor interaction, or e_σ(F), are evaluated by considering a large trigonal splitting due to the unusual anisotropic π interaction in the ligand-field ($^4T_2$–$^4A_2$) transition.[3]

In analogy to this correlation, *fac*-$[CrX_3([D_{12}]tpa)]$ complexes exhibit a linear relation between the ^{2}H NMR chemical shifts of the deuterons at positions 4 ($\delta \approx -20$ ppm) and 5 ($\delta \approx 20$ ppm) with change of X, as shown in Figure 3; the NMR spectroscopic data are summarized in Table 2. In the case of the X_3 complexes, δ(4) is linearly correlated with δ(5) but not with δ(3), which gives $-\delta(4) = -2.05\delta(5) + 66.1$

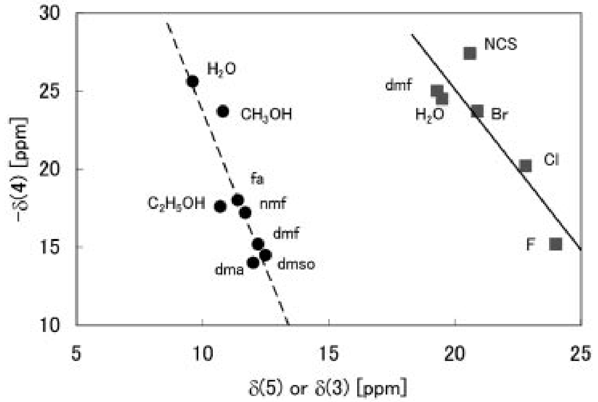

Figure 3. Plots of the ^{2}H NMR chemical shifts for the deuterons in the 4- and 3-positions of *fac*-[$CrF_3([D_{12}]tpa)$] (●) and the deuterons in the 4- and 5-positions of *fac*-[$CrX_3([D_{12}]tpa)$]$^{n+}$ (■). The lines shown are the least-squares fit.

($r = 0.88$). Although the reason for the discrepancy between $\delta(3)$ and $\delta(5)$ on going from the F complex to the X complexes is not clear so far, the same situation is encountered, in an electronic sense, for *fac*-[$CrX_3([D_{12}]tpa)$]$^{n+}$ as for the fluorido complex, since both 3- and 5-^{2}H of the pyridyl groups in tpa are located at the *meta* position, which makes it likely that the relation between $\delta(3)$ and $\delta(5)$ in Figure 3 reflects a similar co-ligand dependence on the $e_\sigma(N)$ and $e_\pi(N)$ values to that found for the bpy complexes (vide supra). This parallel correlation between the F and X complexes means that the variation of $e_\sigma(X)$ must be associated with a change of $e_\sigma(N)$ and $e_\pi(N)$ values. Thus, the variation of $\delta(4)$ with change of X ligands corresponds to the changes of the Cr–N σ-bond properties, or $e_\sigma(N)$, for *fac*-[$CrX_3(tpa)$]$^{n+}$; the $e_\sigma(N)$ values increase in the order $F^- < Cl^- < Br^- < H_2O <$ dmf $< NCS^-$ in dmf. On the other hand, the Cr–X σ-bond properties, or $e_\sigma(X)$, decrease in the reverse order ($F^- > Cl^- > Br^- > H_2O >$ dmf $> NCS^-$ in dmf). This order is similar to that for the aliphatic amine complexes except that the $e_\sigma(Cl)$ and $e_\sigma(Br)$ values are larger than those of the NCS^- and O-donor ligands as well as those for the bpy complexes (see above), thereby corresponding to the ranking in the two-dimensional spectrochemical series.

Table 2. ^{2}H NMR chemical shifts (δ values, ppm) for *fac*-[$CrX_3([D_{12}]tpa)$]$^{n+}$ in dmf.

X	Chemical shifts[a]	
	$\delta(4)$	$\delta(5)$
F	–15.2	24.0
Cl	–20.2	22.8
Br	–23.7	20.9
dmf	–25.0	19.3
H_2O	–24.5	19.5
NCS	–27.4	20.6

[a] $-\delta(4) = -2.05\delta(5) + 66.1$ ($r = 0.88$).

The difference in ranking of $e_\sigma(Cl)$ and $e_\sigma(Br)$ in the two-dimensional spectrochemical series between the aliphatic and aromatic amine complexes can be explained as follows. This difference in Cr–X σ bond is related to the symbiosis[12] in terms of the hard/soft acid/base (HSAB) principle.[13] Since the coordination site at {$Cr(bpy)_2$} or {Cr(tpa)} becomes a softer acid due to the π donor–accepter cooperative interaction through the dπ orbital,[13c] the Cl^- and Br^- ligands, which are soft bases, are more favored in the aromatic amine complexes than in the aliphatic amine complexes. The present result may provide a clue to explaining the confusing experimental results whereby the much greater robustness of the Cr–Cl bond towards acid hydrolysis for aromatic amine complexes than for the corresponding aliphatic amine complexes is not necessarily accompanied by an increased thermodynamic stability of [$CrCl_2(bpy)_2$]$^+$, which is not very different from that of the corresponding ethylenediamine complex.[14–16]

Conclusions

We have demonstrated that there are significant correlations between the ^{2}H NMR chemical shifts $\delta(4)$ and $\delta(5)$ of the pyridyl deuterons of *cis*-[$CrX_2([D_4]bpy)_2$]$^{n+}$ and *fac*-[$CrX_3([D_{12}]tpa)$]$^{n+}$. These correlations reflect the variation of the AOM parameters with change of the X co-ligands in an analogous manner to the solvent-dependency of the ^{2}H NMR chemical shifts of the fluorido complexes *cis*-[$CrF_2([D_4]bpy)_2$]$^+$ and *fac*-[$CrF_3([D_{12}]tpa)$], and is an indicator of the relative strength of $e_\sigma(X)$ for certain didentate as well as monodentate X ligands. The ranking of $e_\sigma(X)$ of both the bpy and tpa complexes in the two-dimensional spectrochemical series is different from that for complexes of the aliphatic amines 3,2,3-tet and trien, and this difference has been explained on the basis of the bond nature or a symbiosis in terms of the HSAB principle, which may provide a clue to explaining the robustness of the chlorido and bromido aromatic amine complexes.

Experimental Section

Preparation: *cis*-[$CrF_2(bpy)_2$]ClO_4,[17] *cis*-[$CrCl_2(bpy)_2$]ClO_4,[16] and *cis*-[$CrBr_2(bpy)_2$]ClO_4[16] were prepared by literature methods.

***cis*-[$Cr(mal)(bpy)_2$]ClO_4:** This complex was obtained from the reaction of an equimolar mixture of *cis*-[$CrCl_2(bpy)_2$]ClO_4 and sodium malonate in water. The yield was about 50%. $C_{23}H_{18}ClCrN_4O_8$ (565.86): calcd. C 48.82, H 3.21, N 9.90; found C 48.81, H 3.23, N 9.88.

***cis*-[$Cr(acac)(bpy)_2$]$(ClO_4)_2$:** *cis*-[$Cr(OTf)_2(bpy)_2$](OTf) [OTf = trifluoromethanesulfonate ($CF_3SO_3^-$)] was obtained by treating *cis*-[$CrCl_2(bpy)_2$]Cl with HOTf according to the method described for *cis*-[$Cr(OTf)_2(en)_2$]Cl.[18] This OTf complex was dissolved in methanol together with an equimolar amount of acetylacetone and urea and the solution was refluxed for 1.5 h at 70 °C in a water bath. After cooling, the solvent was removed on a rotary evaporator under reduced pressure. The solution was chromatographed on a SP-Sephadex Na^+ column with 0.2 M sodium chloride solution as eluent. The first orange eluate was desalted by concentration. An orange precipitate was obtained by adding sodium perchlorate to the solution. The precipitate was filtered off, washed with ethanol and diethyl ether and air-dried. The precipitate was recrystallized from acetone by adding ethanol. The crystals were washed with ethanol and diethyl ether and air-dried. The yield was about 9%. $C_{25}H_{23}Cl_2CrN_4O_{10}$ (662.37): calcd. C 45.33, H 3.50, N 8.46; found C 44.89, H 3.45, N 8.52.

***cis*-[Cr(acaCl)(bpy)$_2$](ClO$_4$)$_2$·0.75H$_2$O and *cis*-[Cr(acaBr)(bpy)$_2$](ClO$_4$)$_2$·0.75H$_2$O:** These complexes were prepared by treating $[Cr(acac)(bpy)_2](ClO_4)_2$ with an equimolar amount of the corresponding *N*-halosuccinimide according to the method reported for the 3-haloacetylacetonato complexes $[Cr(acaX)(en)_2]Cl_2$.[19] The yields for the acaCl and acaBr complexes were about 15 and 22%, respectively. $C_{25}H_{23.5}Cl_3CrN_4O_{10.75}$ (710.33): calcd. C 42.27, H 3.34, N 7.89; found C 41.50, H 3.44, N 8.10. $C_{25}H_{23.5}BrCl_2CrN_4O_{10.75}$ (754.78): calcd. C 39.78, H 3.14, N 7.42; found C 38.76, H 2.99, N 7.35.

***fac*-[CrF$_3$(tpa)] and *fac*-[Cr(H$_2$O)$_3$(tpa)](OTf)$_3$:** These complexes were synthesized by the previously reported method.[2,20]

***fac*-[Cr(NCS)$_3$(tpa)]:** A 1:3 mixture of $[Cr(H_2O)_3(tpa)](OTf)_3$ and sodium thiocyanate was refluxed in ethanol for 50 min. After cooling, the red precipitate was filtered off and washed with ethanol, water, and diethyl ether. The yield was about 73%. $C_{18}H_{12}CrN_7S_3$ (474.53): calcd. C 45.56, H 2.55, N 20.66; found C 45.60, H 2.61, N 20.41.

***fac*-[Cr(dmf)$_3$(tpa)] (OTf)$_3$:** This complex was obtained by leaving *fac*-[Cr(OTf)$_3$(tpa)] to stand overnight in dmf. The color of the solution changed from violet to pink. Diethyl ether was added to this reaction solution to give an oily residue. The supernatant fluid was then decanted off and the residual oil was treated with diethyl ether to give a pink precipitate, which was filtered off, washed with diethyl ether, and air-dried. The yield was about 88%. $C_{27}H_{33}CrF_9N_7O_{12}S_3$ (966.77): calcd. C 33.54, H 3.44, N 10.14; found. C 33.19, H 3.33, N 10.16.

The deuterated bpy and tpa ligands were obtained by a previously reported method.[2,3] The deuterated bpy and tpa complexes were prepared according to the above methods for the corresponding bpy and tpa complexes.

Measurements: The ^2H NMR spectra were recorded with Jeol JMN GX-400 and/or GSX270 spectrometers at 26 °C for 2 mM solutions. 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.

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