

**Figure 6.** Branching ratios of the upper valence orbital ionizations of  $\text{Me}_2\text{Pt}(\text{COD})$  from the experimental measurements (asterisks) and  $X\alpha$ -SW (solid lines) and Gelius model (dashed lines) calculations. (See text.)

obtained with He I and He II radiations.<sup>2a</sup> At high energies ( $h\nu > 55$  eV), however, band A shows a relative intensity reduction. The experimental branching ratios are presented in Figure 6 along with the theoretical values from the  $X\alpha$ -SW and Gelius model calculations. The calculated ratios are based on the previous spectral assignment in which bands A and B were assigned to the

ionizations from MO's with mostly C 2p character, while bands C-F were due to MO's with mostly Pt 5d character.<sup>2a,c</sup> Considering the observed similarity with  $\text{CpPtMe}_3$ , especially above 50 eV, and the computing cost, the  $X\alpha$ -SW ratios were calculated up to 61 eV only. There is a very good agreement between the experimental and  $X\alpha$ -SW ratios. The agreement between the experimental and Gelius model values is also satisfactory except for band B. Therefore, the comparison of the branching ratios supports the previous spectral assignment of this molecule.

### Conclusions

Experimental and theoretical branching ratios strongly support the spectral assignment of the molecule  $\text{CpPtMe}_3$  based on the  $X\alpha$ -SW calculations. The comparison of the observed branching ratios with those calculated with the Gelius model indicates that the intensity changes of the  $\text{CpPtMe}_3$  valence ionization bands as a function of photon energy are largely associated with the Pt 5d and C 2p atomic cross sections. The  $X\alpha$ -SW assignment suggests that the eight upper filled valence MO's of  $\text{CpPtMe}_3$  are composed of the three Pt 5d-based MO's being unevenly sandwiched between the Pt-ligand orbitals. Experimental and theoretical branching ratios also confirm our previous  $X\alpha$ -SW assignment for the  $\text{Me}_2\text{Pt}(\text{COD})$  valence ionizations and lend more confidence to the  $X\alpha$ -SW cross section calculations and molecular orbital assignments in organometallic Pt molecules.

Our new description of the electronic structure of  $\text{CpPtMe}_3$  is clearly quite different from what has been generally accepted for  $\text{CpML}_3$  molecules in general. Clearly, more molecular orbital calculations and photoelectron cross section studies are now needed on  $\text{CpML}_3$  molecules.

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## Solvent-Dependent Deuteron NMR Spectra and Solvatochromism in Ligand Field Absorption Bands for $\text{trans}-[\text{CrX}_2(3,2,3\text{-tet})]^+$ : Correlation with the Angular Overlap Model Parametrization

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The solvent-dependent deuteron nuclear magnetic resonance ( $^2\text{H}$  NMR) and ligand field absorption spectra of  $\text{trans}-[\text{CrX}_2(3,2,3\text{-tet})]^+$ , where 3,2,3-tet denotes 1,10-diamino-4,7-diazadecane ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCD}_2\text{CD}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ) and where axial ligands X are  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NCS}^-$ ,  $\text{CN}^-$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$ , were studied. These solvent dependencies were correlated with Gutmann's acceptor numbers for solvents. The ligand field bands were analyzed by using the angular overlap model, and it was found that the solvatochromism could be ascribed to variations of the metal-ligand  $\sigma$ -bond interactions (expressed by the  $e_\sigma(\text{X})$  and  $e_\sigma(\text{N})$  AOM parameter values) due to the selective solvation toward the axial ligands. A linear relation between the  $^2\text{H}$  NMR shifts and the AOM  $e_\sigma$  parameters provides a direct probe to estimate the AOM  $e_\sigma$  parameter values. A notable ligand field variability was found and substantiated the interligand cooperative effect or cis electronic effect. This fact does not necessarily result either in rigorous parameter transferability from complex to complex or in additivity for mixed-ligand complexes.

### Introduction

It is known that in general there is little solvent dependence of the ligand field d-d transitions in contrast to the noticeable solvatochromism in the charge-transfer transitions of metal complexes.<sup>1</sup> Recently, a solvatochromism was found for  $\text{Co}(\text{III})$  and  $\text{Cr}(\text{III})$  complexes with ethylenediamine- $N,N,N',N'$ -tetraacetate (edta) type ligands,<sup>2,3</sup> which exhibited a fair correlation between the first d-d absorption band maxima and an acceptor

number. This number was defined as a quantitative empirical electron-pair acceptor number for a solvent by Mayer, Gutmann, and Gerger<sup>4</sup> on the basis of the  $^{31}\text{P}$  NMR chemical shift of tri-

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ethylphosphine oxide dissolved in various kinds of solvents. However, the elucidation of the solvatochromism for this type of complex in terms of the ligand field or angular overlap model parametrization was found to be rather phenomenological and complicated, mainly because there exist multiple (at most triple) splitting d-d transition components due to a symmetry much lower than octahedral. This may be caused by anisotropic attack of the solvents.<sup>3</sup> On the other hand, for the higher symmetry complexes of the present type, the simple ligand field splitting formulation makes it feasible to analyze the solvatochromic behavior of the absorption bands in terms of the AOM parametrization.

Schäffer et al. and Kirk et al. have already reported a relatively notable solvent dependence of the absorption spectra for trans-[CrF<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup> and the related complexes in protic and aprotic solvents. They outlined an explanation of these phenomena by referring to hydrogen bonding between the axial fluoro ligands and the solvent and associated them with this angular overlap parametrization.<sup>5,6</sup> However, there has been no elaborate elucidation of the general problem of the solvatochromic behavior of the absorption spectra, and in particular, no connection with the solvent acceptor and/or donor properties was explored as it was done for the edta-like complexes.<sup>3</sup> Such a treatment would be important for understanding the solvatochromism of the ligand field d-d band of transition-metal complexes. Moreover, no correlation has been reported between the <sup>2</sup>H NMR shifts and the ligand field bands.

In this article, we will examine the solvent dependence of the <sup>2</sup>H NMR and the ligand field absorption spectra of trans-[CrX<sub>2</sub>(3,2,3-tet)]<sup>+</sup> complexes (3,2,3-tet (1,10-diamino-4,7-diazadecane) = NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) and analyze it on the basis of AOM parametrization and solvent acceptor numbers. Ligand field variation with solvation or with cooperative effect of the metal-ligand σ-bond interaction between the basal amine and axial (X) ligands will be demonstrated. Finally, a new direct method of estimating the AOM parameters on the basis of <sup>2</sup>H NMR shifts will be presented.

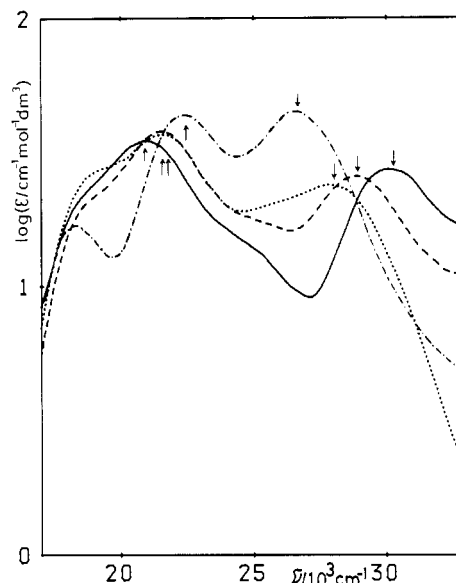
### Experimental Section

**Preparation of the Ligands.** 3,2,3-tet (1,10-diamino-4,7-diazadecane = NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) was prepared by the method of Bosnich et al.<sup>7</sup> The 3,2,3-tet with the deuterated ethylene (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCD<sub>2</sub>CD<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) was obtained by the same method as that for the all-protic 3,2,3-tet with use of deuterated ethylene dibromide instead of the all-protic one.

**Preparation of the Complexes.** trans-[CrX<sub>2</sub>(3,2,3-tet)]ClO<sub>4</sub> (X = F<sup>-</sup>, Cl<sup>-</sup>, NCS<sup>-</sup>) was prepared by the literature method.<sup>7-9</sup> The aqueous solutions of trans-[Cr(H<sub>2</sub>O)<sub>2</sub>(3,2,3-tet)]<sup>3+</sup> and the corresponding dihydroxo complexes were made according to the method of House et al.<sup>9</sup> and confirmed by the absorption spectra.

trans-[CrBr<sub>2</sub>(3,2,3-tet)]ClO<sub>4</sub> was prepared as follows. The corresponding dichloro complex perchlorate was heated to dryness with an appropriate amount of concentrated (48%) hydrobromic acid in a watch glass on a hot plate. This treatment was repeated until the absorption band was shifted to 612 from 585 nm. During the reaction, a small amount of red-brown contaminant was formed. This was removed by washing out with ethanol, and the remaining green precipitate was collected on a glass filter. Anal. Calcd for trans-[CrBr<sub>2</sub>(3,2,3-tet)]ClO<sub>4</sub>·0.5H<sub>2</sub>O: C, 19.43; H, 4.69; N, 11.33. Found: C, 19.48; H, 4.68; N, 11.02.

trans-[Cr(CN)<sub>2</sub>(3,2,3-tet)]ClO<sub>4</sub> was prepared from the dichloro 3,2,3-tet complex and NaCN in dimethyl sulfoxide at 60 °C by the analogous method for the corresponding cyclam complex.<sup>10</sup> Anal. Calcd for trans-[Cr(CN)<sub>2</sub>(3,2,3-tet)]ClO<sub>4</sub>: C, 31.79; H, 5.87; N, 22.25. Found: C, 31.73; H, 5.93; N, 22.18.



**Figure 1.** Solvent-dependent ligand field absorption spectra of trans-[CrF<sub>2</sub>(3,2,3-tet)]<sup>+</sup> in dmf (—), fa (---), H<sub>2</sub>O (···), and ms (-·-·). The arrows ↑ and ↓ denote the <sup>4</sup>B<sub>2</sub> and <sup>4</sup>A<sub>2</sub> components, respectively.

trans-[Cr(NH<sub>3</sub>)<sub>2</sub>(3,2,3-tet)]ClO<sub>4</sub> was obtained by dissolving trans-[CrCl<sub>2</sub>(3,2,3-tet)]ClO<sub>4</sub> in liquid ammonia at 0 °C in a pressure glass tube. Anal. Calcd for [Cr(NH<sub>3</sub>)<sub>2</sub>(3,2,3-tet)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O: C, 17.14; H, 5.39; N, 14.99. Found: C, 17.36; H, 5.29; N, 14.56.

The corresponding deuterated complexes for the <sup>2</sup>H NMR measurements were obtained by the same methods as those for the all-protic complexes. They were confirmed by the absorption spectra.

The optical resolution of the difluoro complex was carried out by the method of House et al.<sup>11</sup> with use of dihydrogen benzoyl (+)-tartrate. The optical purity (Δε<sub>520</sub> = +0.28) of the (+)-<sub>585</sub>-isomer was found to be almost the same as that reported in the literature.<sup>11</sup>

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.

### Measurements

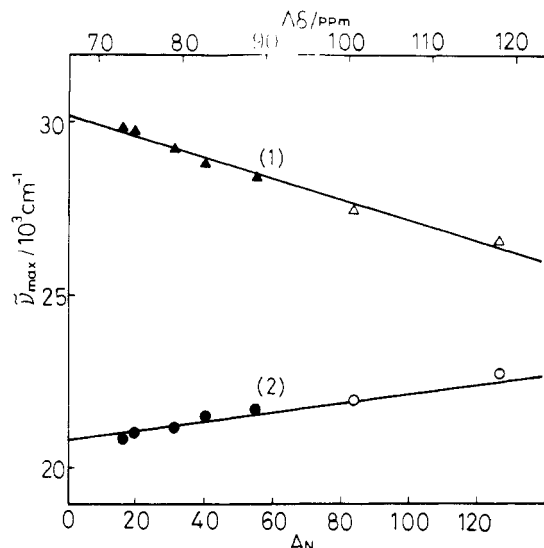
Absorption spectra in solutions were measured by a Shimadzu UV-240 spectrophotometer. Diffuse-reflectance spectra were obtained by a Hitachi 330 spectrophotometer with a reflectometer. Circular dichroism (CD) spectra were obtained by a Jasco J-500C spectropolarimeter at ambient temperature. The solid-state CD spectrum was measured in the multiple scattering system by the Nujol mull method<sup>12</sup> with the above spectropolarimeter. <sup>2</sup>H NMR spectra were measured by a JEOL GX-270 and/or GSX-400 spectrometer at 20 °C on solutions ranging in concentration from 80 to 20 mM (1 mM = 10<sup>-3</sup> mol dm<sup>-3</sup>). There was negligible concentration dependence of the chemical shifts. An external standard of C<sup>2</sup>HCl<sub>3</sub> was assigned a chemical shift of 7.24 ppm. Note that "downfield" shifts are defined as positive. The solvents used for the measurements were of spectrograde or reagent grade. The abbreviations for the solvents in parentheses and their acceptor numbers in square brackets as found in the literature<sup>4</sup> are as follows: *N,N*-dimethylacetamide (dma) [13.6], *N,N*-dimethylformamide (dmf) [16], acetonitrile (an) [18.9], dimethyl sulfoxide (dmsO) [19.3], *N*-methylformamide (nmf) [31], formamide (fa) [39.8], H<sub>2</sub>O [54.8], formic acid (fm) [83.6], methanesulfonic acid (ms) [126.3].

### Results and Discussion

**Ligand Field Spectra.** In the region of the first (<sup>4</sup>T<sub>2g</sub> ← <sup>4</sup>A<sub>2g</sub>) and the second (<sup>4</sup>T<sub>1g</sub> ← <sup>4</sup>A<sub>2g</sub>) ligand field absorption bands for trans-[CrF<sub>2</sub>(3,2,3-tet)]<sup>+</sup>, two split components due to low symmetry are observed, as in Figure 1. Each such component was assigned to the tetragonal split component by the single-crystal polarized spectrum of trans-[CrF<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub>.<sup>13</sup> As shown in Figure 1, the higher frequency band maxima due to the nondegenerate <sup>4</sup>B<sub>2</sub> and <sup>4</sup>A<sub>2</sub> components of the first and the second band region (denoted by the arrows ↑ and ↓, respectively, in Figure 1)

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**Figure 2.** Plot of the absorption band maxima ( $\nu_{\max}/10^3 \text{ cm}^{-1}$ ) vs the acceptor numbers ( $A_N$ ) (bottom abscissa) and the  $^2\text{H}$  NMR shift differences  $\Delta\delta$  (top abscissa) for  $\text{trans-}[\text{CrF}_2(3,2,3\text{-tet})]^+$ : (1) ( $\blacktriangle$  and  $\triangle$ )  $^4\text{A}_2$  component; (2) ( $\bullet$  and  $\circ$ )  $^4\text{B}_2$  component. (Lines shown are least-squares-fit.) Only absorption data are given; no adequate  $^2\text{H}$  NMR data exist for fm and ms solutions corresponding to the  $\circ$  and  $\triangle$  points.

are shifted to the higher and lower frequency sides, respectively, as the acceptor numbers of the solvents increase from dmf over water to ms. Figure 2 shows that there is a fair linear relationship of both the  $^4\text{B}_2$  and  $^4\text{A}_2$  components with the acceptor numbers of the solvents. The transition energies of the former and the latter components for the pure cubic subconfiguration approximation are given in terms of the AOM parameters as follows:<sup>14</sup>

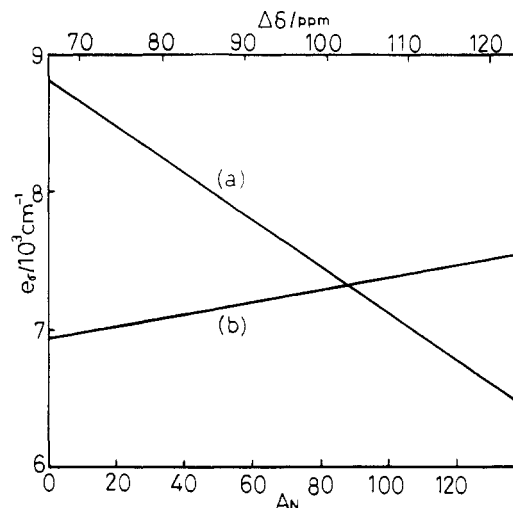
$$E(^4\text{B}_2) = 3e_\sigma(\text{N}) \quad (1)$$

$$E(^4\text{A}_2) = 2e_\sigma(\text{F}) + e_\sigma(\text{N}) + 12B \quad (2)$$

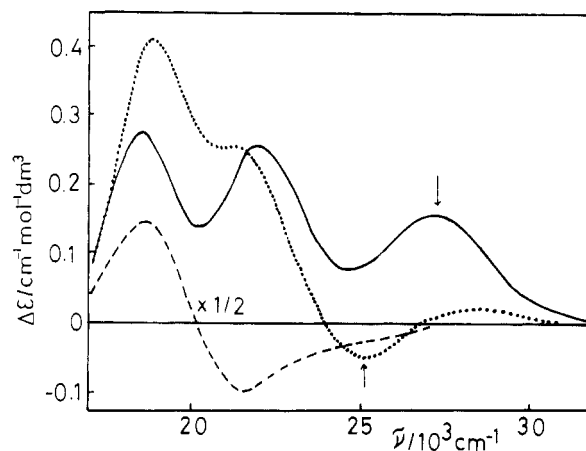
where  $e_\sigma(\text{N})$  and  $e_\sigma(\text{F})$  denote the Cr-amine and Cr-F AOM  $\sigma$ -antibonding interaction energy parameters, respectively. The  $^4\text{A}_2$  transition energy is susceptible to the change of the Racah parameter  $B$  owing not only to the first-order term ( $12B$  in eq 2) but also to the second-order perturbation arising from the mixing with the upper  $^4\text{A}_2(^4\text{T}_{1g}(t_{2g}e_g^2))$  state. It is evident that the Racah parameter ( $B$ ) is hardly affected by the solvents in view of the fact that the CD peaks assignable to the  $^2\text{E}_g$  split components of  $(+)\text{_{589-trans-}CrF}_2(3,2,3\text{-tet})^+$  near  $15000 \text{ cm}^{-1}$  are shifted to the higher frequency side only by ca.  $300 \text{ cm}^{-1}$  on going from dmf to ms. This shows little decrease in the symmetry-restricted covalency.<sup>15</sup> Thus, the solvatochromic shifts in the spin-allowed transitions should be ascribed to the changes of the AOM  $e_\sigma$  parameters of the ligands. As shown in Figure 2, the slope for the  $^4\text{B}_2$  component is positive, whereas that of the  $^4\text{A}_2$  one is negative; i.e.,  $E(^4\text{B}_2) = 0.013A_N + 20.8$  (the correlation coefficient  $r = 0.99$ ) and  $E(^4\text{A}_2) = -0.03A_N + 30.12$  ( $r = 0.99$ ). These facts together with the relations of eqs 1 and 2 indicate that the  $e_\sigma(\text{N})$  and  $e_\sigma(\text{F})$  values increase and decrease, respectively, with increasing acceptor numbers of the solvents. On the basis of this and the assumption that the Racah parameter  $B$  is  $460 \text{ cm}^{-1}$ , the  $e_\sigma(\text{N})$  and  $e_\sigma(\text{F})$  values are obtained as the following linear functions of the acceptor numbers of the solvents:  $e_\sigma(\text{N}) = 0.0043A_N + 6.94$  and  $e_\sigma(\text{F}) = -0.017A_N + 8.83$  in units of  $10^3 \text{ cm}^{-1}$ . And they lead to the following equation:

$$e_\sigma(\text{F}) = -4e_\sigma(\text{N}) + 36.6 \quad (3)$$

Figure 3 shows that the signs for  $e_\sigma(\text{N}) - e_\sigma(\text{F})$  invert on going from aqueous over formic acid solutions to ms solution. This sign inversion may be associated with the following CD behavior. The



**Figure 3.** Correlation of the AOM parameter values with the acceptor numbers ( $A_N$ ), assuming the Racah parameter  $B = 460 \text{ cm}^{-1}$ ; (a)  $e_\sigma(\text{F})$ ; (b)  $e_\sigma(\text{N})$ .



**Figure 4.** Circular dichroism curves for  $(+)\text{_{589-trans-}CrF}_2(3,2,3\text{-tet})^+$  in ms (—),  $\text{H}_2\text{O}$  (⋯), and Nujol mull (---). The arrows indicate the  $^4\text{E}_b$  components, of which the CD signs are inverted with variations of solvents from  $\text{H}_2\text{O}$  to ms.

sign inversion of the  $^4\text{E}_b$  CD component around  $25000\text{--}27000 \text{ cm}^{-1}$  in the second band region of  $(+)\text{_{589-trans-}CrF}_2(3,2,3\text{-tet})^+$  occurs on going from aqueous over formic acid solutions to ms solution, as shown in Figure 4. This is interpreted in relation to the signs for  $e_\sigma(\text{N}) - e_\sigma(\text{F})$  on the basis of the following borrowing mechanism, as claimed previously for  $\text{trans-}[\text{CrX}_2(\text{N})_4]$  type complexes.<sup>16</sup> That is, the magnetic dipole forbidden  $^4\text{E}_b(^4\text{T}_{1g}) \leftarrow ^4\text{B}_1(^4\text{A}_{2g})$  transition attains the rotational strength by acquiring a small part,  $(3^{1/2}/2)(e_\sigma(\text{N}) - e_\sigma(\text{F})) / (E(^4\text{E}_b) - E(^4\text{E}_a))$ , of the rotational strength for the magnetic dipole allowed  $^4\text{E}_a(^4\text{T}_{2g}) \leftarrow ^4\text{B}_1(^4\text{A}_{2g})$  transition near  $18800 \text{ cm}^{-1}$  via the configurational interaction  $\langle \psi(^4\text{E}_a) | V(D4) | \psi(^4\text{E}_b) \rangle = (3^{1/2}/2)(e_\sigma(\text{N}) - e_\sigma(\text{F}))$ ; hence the CD signs are governed by the signs of  $e_\sigma(\text{N}) - e_\sigma(\text{F})$ , as revealed previously for  $\text{trans-dihalo bis(diamine)}$  complexes with three kinds of chiral diamines.<sup>16</sup> Accordingly, it appears that the present value of the Racah parameter or the linear correlation of  $e_\sigma(\text{F})$  with  $A_N$  in Figure 3 is valid.

Equation 3 substantiates the interligand cooperative effect or cis electronic effect as found for the spectroscopic and structural behavior for the  $\text{trans-}[\text{MX}_2(\text{N})_4]$  type of  $\text{Co(III)}$  and  $\text{Ni(II)}$  complexes with various kinds of amines;<sup>18-21</sup> the longer the Cr-F

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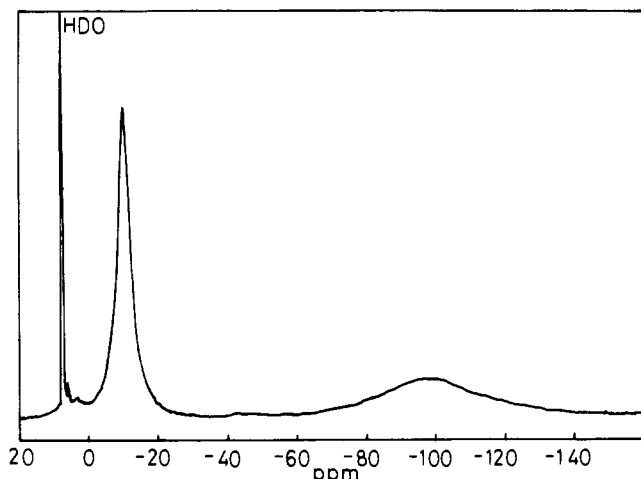


Figure 5. <sup>2</sup>H NMR spectrum of *trans*-[CrF<sub>2</sub>(3,2,3-tet-d<sub>4</sub>)]<sup>+</sup> in H<sub>2</sub>O at 20 °C. Shifts are relative to C<sup>2</sup>HCl<sub>3</sub> (7.24 ppm).

bonds, the shorter the Cr–N bonds become, and vice versa. As far as the  $e_{\sigma}$  parameters are concerned, the ligand field changes so much with the variations in the solvents' acceptor numbers that inversion of the tetragonal distortion occurs on going from *dma* to *ms*. It should be noted that the ligand field parameters must be estimated and compared for complexes in similar environments. It is interesting to test how the *trans*-difluoro complex in the solid state is surrounded by the second coordination sphere with use of this relation. The diffuse-reflectance spectrum of *trans*-[CrF<sub>2</sub>(3,2,3-tet)]ClO<sub>4</sub> shows that the environment around the complex ion in the solid state corresponds to the acceptor number 35 or resembles that in *N*-methylformamide (*nmf*) solution, as in Figures 2 and 3. This is also supported by the CD sign behavior of the <sup>4</sup>E<sub>g</sub> component in the solid state, as in Figure 4.

Equation 3 may make it feasible to examine whether the sum rule properties of the AOM parameters [ $\sum e_{\lambda}(i) = \sum(e_{\sigma}(i) + e_{\pi}(i))$ ] based on the cellular ligand field model<sup>22</sup> or the constancy of the nonadditive ligand field parameter ( $\Delta$  or  $10Dq = 3e_{\sigma}(F) - 4e_{\pi}(F)$ ) for the fluoro ligand holds with variations of the solvents. The Cr–F  $\pi$ -bond interaction (expressed by the  $e_{\pi}(F)$  parameter value) should decrease for the sum rule or increase for the constancy of the  $\Delta$  value with increasing  $e_{\sigma}(N)$ . There are two different experimental results for the solvent dependence of the  $e_{\pi}(F)$  parameter value for the difluoro complexes. On one hand, the lowest frequency <sup>2</sup>E<sub>a</sub>(<sup>2</sup>T<sub>1g</sub>) CD components for (+)<sub>589</sub>-*trans*-[CrF<sub>2</sub>(3,2,3-tet)]<sup>+</sup> and *trans*-[CrF<sub>2</sub>((*S,S*)-*chxn*)<sub>2</sub>]<sup>+</sup> ((*S,S*)-*chxn* = (1*S*,2*S*)-1,2-*trans*-cyclohexanediamine) on going from *dma* to *ms* give negligible solvatochromic shifts and/or fail to be detected; this fact leads to little change in  $e_{\pi}(F)$ .<sup>16,17</sup> On the other hand, the phosphorescence spectrum due to the lowest frequency <sup>2</sup>E<sub>a</sub>(<sup>2</sup>T<sub>1g</sub>) ← <sup>4</sup>B<sub>1</sub>(<sup>4</sup>A<sub>2g</sub>) transition of *trans*-[CrF<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup> in tetrahydrofuran ( $A_N = 8.0$ ) is found to shift to the lower frequency by ca. 800 cm<sup>-1</sup> as compared to the case in water at room temperature.<sup>23</sup> This fact indicates that the  $e_{\pi}(F)$  value increases with increasing  $e_{\sigma}(F)$  value as a result of the large configurational interaction between the <sup>2</sup>E<sub>a</sub>(<sup>2</sup>T<sub>1g</sub>) and <sup>2</sup>E<sub>b</sub>(<sup>2</sup>T<sub>2g</sub>) states,<sup>16,17</sup> since the lower energy shift of the <sup>2</sup>E<sub>a</sub>(<sup>2</sup>T<sub>1g</sub>) state is estimated to be  $4e_{\pi}(F)/(6B + 2C)$ . This phosphorescence result is different from the former CD behavior. The latter case is more plausible than the former because the phosphorescence spectra for the lowest doublet excited states are more sensitive and more accurate than the CD spectra. Therefore, it is likely that the solvatochromism does not lend support to the sum rule properties, but there seems

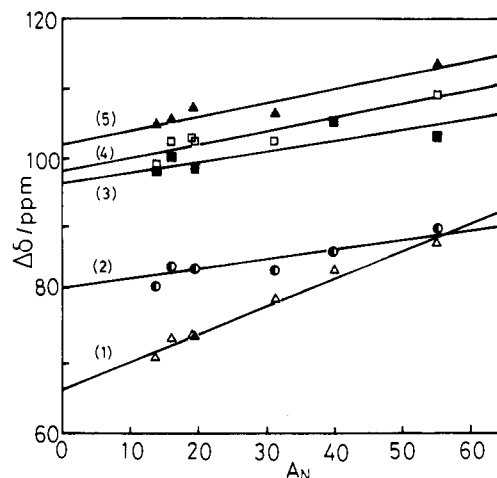


Figure 6. Plot of the <sup>2</sup>H NMR shift differences  $\Delta\delta$  vs the acceptor numbers  $A_N$  for *trans*-[CrX<sub>2</sub>(3,2,3-tet)]<sup>+</sup>: (1) F<sup>-</sup> (Δ); (2) CN<sup>-</sup> (○); (3) NCS<sup>-</sup> (■); (4) Cl<sup>-</sup> (□); (5) Br<sup>-</sup> (▲). Lines shown are least-squares-fit with 0.41, 66.4, and 0.99 for (1), 0.16, 80.2, and 0.89 for (2), 0.155, 96.7, and 0.82 for (3), 0.20, 97.8, and 0.89 for (4), and 0.195, 102.4, and 0.94 for (5) as the slopes, the intercepts (ppm), and the correlation coefficients, respectively. The least-squares analyses were made for the numbers of the solvents corresponding to the points plotted. The points corresponding to the  $\Delta\delta$  values in *fm* and *ms* solutions are omitted for the reason described in the text.

to be a tendency for the  $\Delta$  parameter to keep constant with variations of the solvents.

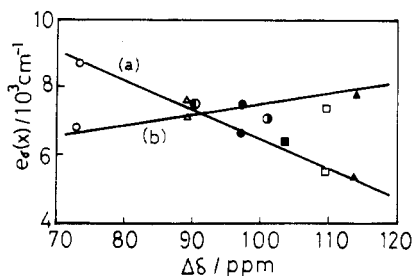
**<sup>2</sup>H NMR Spectral Behavior.** The present solvatochromism observed for the ligand field bands is also substantiated by the <sup>2</sup>H NMR spectra of the 3,2,3-tet complexes with the deuterated ethylene backbone. Two well-separated <sup>2</sup>H NMR signals due to paramagnetic isotropic contact shifts for inequivalent (axial and equatorial) deuterons in the ethylene backbone were observed for *trans*-[CrF<sub>2</sub>(3,2,3-tet)]<sup>+</sup> in H<sub>2</sub>O, as shown in Figure 5. The lower field (0 to -20 ppm) and higher field (-90 to -120 ppm) signals are assigned to the axial and equatorial deuterons, respectively, according to the Karplus-like or cos<sup>2</sup>  $\theta$  relation by taking into consideration the torsion angles for the Cr–N–C–D chains in the ethylene backbone. The <sup>2</sup>H NMR chemical shift differences ( $\Delta\delta$ ) for the difluoro complex are well correlated with the acceptor numbers of the solvents, as shown in Figure 6, as well as with each of the highest frequency nondegenerate (<sup>4</sup>B<sub>2</sub> and <sup>4</sup>A<sub>2</sub>) absorption band maxima in both the first and the second band region, as shown in the top abscissa of Figure 2. In this case, the points for  $\Delta\delta$  vs  $\nu_{\max}$  ( $\Delta\delta$  vs  $A_N$ ) in *fm* and *ms* are omitted for least-squares analyses owing to the large irregular  $\Delta\delta$  values (86.7 ppm for *fm* and 96.7 ppm for *ms*). Though within a limited range of acceptor numbers, the <sup>2</sup>H NMR shift differences are considered to be equivalent to the extent of the bond interaction between the electron acceptor and triethylphosphine oxide or the acceptor numbers:  $A_N = 2.44\Delta\delta - 161.8$  (the correlation coefficient  $r = 0.99$ ). This correlation of  $\Delta\delta$  with  $A_N$  is interpreted by the Karplus-like or cos<sup>2</sup>  $\theta$  relation for the paramagnetic contact shifts of Cr(III) complexes as in the following equation:<sup>24</sup>

$$\Delta\delta = \delta_{ax} - \delta_{eq} = -(3^{1/2}/2)(CA_n) \sin 2\phi \quad (4)$$

where  $C$  is the constant varying reciprocally with absolute temperature and  $A_n$  is the hyperfine constant including the spin density of deuterons.  $\Delta\delta$  is proportional to the spin density of the deuterons concerned as well as to  $\sin 2\phi$  where  $\phi$  is a torsion angle in the Cr–N–C–C chain of the ethylene backbone. The fact that the variable-temperature <sup>2</sup>H NMR spectra obey the Curie law suggests a negligible change of the torsion angle  $\phi$  or a rigid conformation of the ethylene backbone chelate rings with variations of solvents. Otherwise, the change of the angle  $\phi$  with temperature due to conformational lability brings about the large deviation from the Curie behavior of the  $\Delta\delta$  value as found in Ni(II)

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**Figure 7.** Plot of the AOM parameter values vs the  $^2\text{H}$  NMR shift differences  $\Delta\delta$  for  $\text{trans-}[\text{CrX}_2(3,2,3\text{-tet})]^{n+}$  in aqueous solution: (b)  $e_\sigma(\text{N})$  from the aqueous absorption data (nondegenerate  $^4\text{B}_2$  component) of the 3,2,3-tet complexes; (a)  $e_\sigma(\text{X})$  from ref 26 and 28 for  $\text{X} = \text{OH}^-$  (O),  $\text{F}^-$  ( $\Delta$ ),  $\text{CN}^-$  ( $\bullet$ ),  $\text{H}_2\text{O}$  ( $\circ$ ),  $\text{NH}_3$  ( $\oplus$ ),  $\text{NCS}^-$  ( $\blacksquare$ ),  $\text{Cl}^-$  ( $\square$ ),  $\text{Br}^-$  ( $\blacktriangle$ ). Lines shown are least-squares-fit.

complexes.<sup>25</sup> Thus, it is evident that the solvent-dependent NMR shift differences are mainly dependent on the spin density of the deuterons. This deuteron spin density increases with increasing  $\sigma$ -bond interaction for the Cr–N bonds (in other words the  $e_\sigma(\text{N})$  value) or shortening of the Cr–N bonds, followed by the decrease in the Cr–F  $\sigma$ -bond interaction ( $e_\sigma(\text{F})$ ) or the lengthening of the Cr–F bonds as a result of the attack on the fluoro ligands by the stronger electron acceptor solvents. This is the finding, as evidently shown in Figure 3, where the  $\Delta\delta$  values (given in the top abscissa) indicate a fair linear relation with the  $e_\sigma$  parameters for  $\text{trans-}[\text{CrF}_2(3,2,3\text{-tet})]^+$  in various solvents. Thus, the NMR shift differences are found to be a measure of the Cr–N and Cr–F  $\sigma$ -bond interaction. Such bond length variation with the  $e_\sigma$  values in tetragonal mixed-ligand complexes were observed for Co(III), Ni(II), and Cu(II) complexes.<sup>18–21</sup>

For the dichloro and dibromo complexes, the solvatochromic shifts for the nondegenerate ligand field components could be observed only in the first band region but not in the second band because of there being no discernible splitting in the latter region. However, the  $^2\text{H}$  NMR shift differences for these complexes along with the dicyano and diisothiocyanato complexes give fair correlations with the acceptor numbers of the solvents, as shown in Figure 6. Therefore, the selective solvation affecting the d-orbital energies takes place toward the axial ligands even in this type of complex, not specifically only toward the fluoro ligands as noted by Kirk et al.<sup>6</sup> For the dichloro complex, it has been claimed that the amine proton solvation by the donor solvents gives rise to the additional chirality arising from asymmetric nitrogen atoms and hence the remarkable CD changes occur.<sup>7</sup> In the present case, however, there seems to be a negligible effect of the solvents' donor properties on the d-orbital energies.

The slopes for the plot of the NMR shift differences vs the acceptor numbers in Figure 7 provide a measure of the relative sensitivity toward solvent change of the two experiments, the spin density of the deuterons in the basal 3,2,3-tet ligand, and the degree of the solvents' electron pair acceptor interaction with the donor axial ligands. These slopes are similar to each other for the dichloro, dibromo, dicyano, and diisothiocyanato complexes but are the largest for the difluoro complex, as in Figure 6. This may be ascribed to the largest electronegativity of the fluoro ligand or the strongest donor properties, as suggested by Schäffer et al.<sup>5</sup> On the other hand, the diaqua and diammine complexes may give no correlation of the NMR shift differences with the acceptor numbers of the solvents, because they have protons acting as acceptors available for hydrogen bonding induced by the solvents' donor properties. In fact, the diammine complex gives no linear correlation between the acceptor numbers and the NMR shift differences: 100.9 (dmf), 101.9 (an), 96.5 (nmf), 97.7 (fa), 102 ppm ( $\text{H}_2\text{O}$ ).

The relation analogous to that in Figure 3 is found for the case of several complexes with different axial ligands. The NMR shift differences in aqueous solution are correlated not only with the  $e_\sigma(\text{X})$  parameter values estimated from the aqueous solution absorption spectra and/or single-crystal spectra<sup>13,26,28</sup> but also with

the  $e_\sigma(\text{N})$  ones obtained from the  $^4\text{B}_2$  absorption component for some 3,2,3-tet complexes. The obtained results show fair correlations of  $e_\sigma(\text{X})$  and  $e_\sigma(\text{N})$  with  $\Delta\delta$ , as in Figure 7. That is, the  $e_\sigma(\text{X})$  values decrease, but the  $e_\sigma(\text{N})$  ones increase with decreasing  $\Delta\delta$ , resulting in the relations  $e_\sigma(\text{X}) = -0.09\Delta\delta + 15.3$  (the correlation coefficient  $r = 0.95$ ) and  $e_\sigma(\text{N}) = 0.037\Delta\delta + 3.75$  ( $r = 0.90$ ) in units of  $10^3 \text{ cm}^{-1}$ . These relations lead to the following equation:

$$e_\sigma(\text{X}) = -2.43e_\sigma(\text{N}) + 24.4 \quad (5)$$

The correlation of Figure 7 cannot be obtained by using the intercepts of the lines in Figure 6, of which the  $\Delta\delta$  values correspond to the case in hypothetically noninteractive hexane solvent with  $A_N = 0$ . This means that the solvation or the second coordination sphere plays an important and significant role in evaluating the AOM parameters, as discussed above for the difluoro complex. It is seen that there exists a significant correlation between the  $^2\text{H}$  NMR shift differences in aqueous solutions and the AOM values estimated from the absorption spectra in aqueous solutions or in the solid state. Hence, the  $\Delta\delta$  value is an indicator of the relative extent of the metal–ligand  $\sigma$ -bond interaction between the basal and axial ligands, as noted similarly above for the difluoro complexes. The relation  $e_\sigma$  and  $\Delta\delta$  in Figure 7 is more convenient for estimating the AOM parameter values of certain ligands for this type of complex in aqueous solution directly from the  $^2\text{H}$  NMR shift differences, and also more advantageous for further developing two-dimensional spectrochemical series,<sup>26</sup> than the conventional indirect fitting procedures on the basis of the absorption data and theoretical calculations with diagonalization of the energy matrix.<sup>13,26</sup>

Figure 7 and eq 5 reveal that the  $\sigma$ -bond interaction energy parameter ( $e_\sigma$ ) of the axial ligands influences that of the basal ones in such a way that there exists a reverse correlation between these  $e_\sigma$  parameter values even with variations of axial ligands in mixed-ligand complexes. This shows the manifestation of the cis electronic effect, arising from the cooperative charge redistribution due to the electroneutrality principle in a complex as a whole, reported for Ni(II) complexes with various kinds of macrocyclic tetramines.<sup>18–21</sup> For these Ni(II) complexes, the spectral variations are related apparently to the nonadditive ligand field parameter ( $\Delta$  or  $10Dq$ ), actually to the  $\sigma$ -bond interaction ( $e_\sigma$ ), for axial ligands.<sup>18</sup> Thus, the ligand field in mixed-ligand complexes is also found to be so variable for the AOM  $e_\sigma$  parameter with variations of axial ligands that there is an inverse tetragonal distortion with respect to the  $e_\sigma$  parameters on going from hydroxo over fluoro ligands to halo ligands, as discussed above for the difluoro complex. The present fact does not necessarily corroborate rigorous parameter transferability from complex to complex or additivity in mixed-ligand complexes though these properties have been assumed for the AOM parameterization<sup>26</sup> and still have remained controversial.<sup>27</sup> Moreover, the changeable behavior of the  $e_\sigma(\text{N})$  parameter associated with  $e_\sigma(\text{X})$  for various kinds of axial ligands in  $\text{trans-}[\text{CrX}_2(3,2,3\text{-tet})]^+$  may provide some clue to elucidate Shimura's new empirical reduction parameter, which has recently been introduced to improve the prediction of the first d–d band components for mixed-ligand octahedral complexes of  $d^3$  and low-spin  $d^6$  metals.<sup>29</sup> This subject will be discussed in detail elsewhere.<sup>30</sup>

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