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Elucidation of Shimura's Reduction Parameter for the First Ligand Field Band Components of Cobalt(III) and Chromium(III) Mixed Ligand Complexes

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Elucidation was made for Shimura's recently proposed reduction parameter, which enables us to improve the prediction of the first absorption band components from Yamatera's rule, in terms of the angular overlap model(AOM) parameterization for cobalt(III) and chromium(III) mixed ligand complexes. From the configuration interaction between the degenerate components and in view of the empirical relation for the $e_{\sigma a}$ and $e_{\sigma b}$ AOM parameters as revealed recently in the nondegenerate component of *trans*-[Cra_4b_2] type complexes, Shimura's empirical reduction parameter α was elucidated semiquantitatively in relation with the difference between the e_σ parameter values for the a and b ligands, $\Delta'_{\sigma b}=3(e_{\sigma b}-e_{\sigma a})$; the larger the $\Delta'_{\sigma b}$, the smaller the reduction parameter α, and vice versa.

Shimura has recently introduced the empirical reduction parameter to improve the prediction of the first ligand field absorption band components of the low-spin d^6 metal complexes by Yamatera's rule.[1] Neverthless, there has been no elucidation for this reduction parameter to predict the band components of various types of mixed ligand complexes other than quantitative approaches to the shifts of the degenerate component(^1E_a) of the first $^1T_{1g}\leftarrow{}^1A_{1g}(Oh)$ transition in holohedrized tetragonal fields of Co(III) complexes;[2,3] however, these approaches can not predict which ligand combination in the mixed ligand complexes may give significant changes of the reduction parameter values. Moreover, the shift of the nondegenerate component has never been anticipated on the ground of the ligand field theory so far.

In this paper, we will elucidate such deviation of both the nondegenerate and degenerate band components on the basis of theoretical and empirical approaches in terms of the angular overlap model (AOM) parameterization.

Results and Discussion

The Interelectron Repulsion Parameter. The introduction of Shimura's empirical reduction parameter makes it feasible to account for the deviation of the first band components of mixed ligand complexes from Yamatera's rule, even though the transition energies of the first d-d band or ligand parameter (Shimura's quantitative scale (d_X)) of octahedral low-spin d^6 metal complexes depend on both the ligand field splitting parameter (Δ or 10Dq) and the Racah interelectron repulsion parameter $C(=4B)$; i.e., σ_X or $d_X=\Delta_X-C_X$ for the ligand X. The Racah parameter should not be neglected, because the variation of this parameter values in mixed ligand complexes from those in octahedral [MX_6] type complexes may be accounted for by the symmetry-restricted or anisotropic nephelauxetism as for the interpretation of the ^{1}H- and ^{14}N NMR spectra of pentaamminecobalt(III) complexes.[4] When the reduction parameter α equals 1.00, however, Shimura's empirical analyses on the basis of a large number of absorption data suggest that the additivity in mixed ligand complexes and transferability from complex to complex hold for the ligand parameters (d_X) as expected for the ligand field splitting parameter (Δ). The contribution from the Racah parameter of the ligands concerned to the transition energy(σ_X) of each splitting component in the first band (Shimura's Eq. 1[1]) may behave in a similar manner to the ligand field parameters as explained by the anisotropic nephelauxetism.[4] In the case of the rule of average environment (Shimura's Eq. 2[1]), the Racah parameter values in mixed ligand complexes are obtained by the weighted average of those of the ligands concerned. In either case, it is plausible that the Shimura's ligand parameter(d_X) behaves quite similarly to the ligand field splitting parameter(Δ) in mixed ligand complexes. Therefore, the reduction parameter is considered to depend on the variations of either the ligand field parameter or the Racah parameter value B with ligand combinations in mixed ligand complexes. Since the reduction parameters are also found for Cr(III) complexes[5] where the transition energy σ or the ligand parameter d of the first absorption band corresponds solely to the ligand field splitting parameter Δ, it is not likely that the reduction parameter is ascribed to the deviation of the Racah parameter in mixed ligand complexes from those in octahedral [MX_6] type complexes, but it may arise mainly from the reduction in the ligand field splitting parameter(Δ) due to the lowering symmetry of complexes.

The Degenerate Components. As have been claimed previously,[2,3] it is most probable that the transition energy shift of the degenerate component arises from the configuration interaction between two tetragonal splitting components, the ${}^1E_a({}^1T_{1g})$ state in the first band and the ${}^1E_b({}^1T_{2g})$ one in the second band for *trans*-$[Co^{III}a_4b_2]$ type complexes. For the purpose to assess the extent of the transition energy shift (the value of the reduction parameter) in a given mixed ligand complex, the following first order perturbation energy(E') for the ${}^1E_a$ component is taken into consideration.

$$E({}^1E_a) = E_0({}^1E_a) - \frac{\langle {}^1E_a | V(D_4) | {}^1E_b \rangle^2}{E_0({}^1E_b) - E_0({}^1E_a)} \tag{1}$$

As a result, the perturbed transition energy is lowered by the second term(E') of Eq. 1 in comparison with the zeroth-order energy $E_0({}^1E_a)$. The second term(E') is expressed using the AOM parameters $\Delta'_{\sigma b}=3(e_{\sigma b}-e_{\sigma a})$ and the averaged Racah parameter $B=1/2(B_a+B_b)$ for the ${}^1E_a$ component as follows.

$$E'({}^1E_a) = \frac{(\Delta'_{\sigma b})^2}{12(16B - 1/3\Delta'_{\sigma b})} \tag{2}$$

For the other types of mixed ligand complexes, the first order perturbation terms are given by the AOM parameter expression as in the following Eqs. 3—5. Since the reduction parameter α becomes equal to $1-E'/E_0$, $\beta(=1-\alpha)$ is E'/E_0. Therefore, this reduction parameter is approximated by a function of the AOM parameter $\Delta'_{\sigma b}=3(e_{\sigma b}-e_{\sigma a})$, the ligand parameters $d_a=\Delta_a-4B_a$ and $d_b=\Delta_b-4B_b$ $(C=4B)$ as well as the weighted average of the Racah parameter for the degenerate component of $[Coa_nb_{6-n}]$ type complexes. Finally, the following relations are obtained.

$$\beta = \frac{(\Delta'_{\sigma b})^2}{3(16B \pm 1/3\Delta'_{\sigma b})(2d_a + 2d_b)} \qquad \begin{matrix}(3a)\\(3b)\end{matrix}$$

$$\beta = \frac{(\Delta'_{\sigma b})^2}{12(16B \pm 1/6\Delta'_{\sigma b})(3d_a + d_b)} \qquad \begin{matrix}(4a)\\(4b)\end{matrix}$$

$$\beta = \frac{(\Delta'_{\sigma b})^2}{12(16B \pm 1/6\Delta'_{\sigma b})(d_a + 3d_b)} \qquad \begin{matrix}(5a)\\(5b)\end{matrix}$$

where the positive (Eqs. 3a, 4a, 5a) and negative (Eqs. 3b, 4b, 5b) signs of $\Delta'_{\sigma b}$ in the first parenthesized term of the denominators are for *trans*-$[Coa_2b_4]$(3a), *cis*-$[Coa_4b_2]$(4a), $[Coab_5]$(5a), and for *trans*-$[Coa_4b_2]$(3b), $[Coa_5b]$(4b), *cis*-$[Coa_2b_4]$(5b), respectively. In the case of chromium(III) complexes, the ligand field bands can be treated analogously to those of cobalt(III) complexes except for the difference in the spin-multiplicity and the ligand field parameterization between the first ${}^1T_1 \leftarrow {}^1A_1$ of cobalt(III) complexes and the corresponding ${}^4T_2 \leftarrow {}^4A_2$ transition of chromium(III) complexes. This is plausible because the ligand parameters d_X of Co(III) complexes behave in a similar manner to the ligand field parameter Δ in spite of the inclusion of the Racah parameter in the d_X as mentioned before and also because the e_σ values for Cl^-, H_2O, NCS^-, NH_3, ethylenediamine, and OH^- ligands for Cr(III) complexes are well correlated with

Table 1. Calculated and Observed Transition Energies for the Degenerate Component and Reduction Parameters for Some Co(III) Complexes

	E_{calcd}	σ_{obsd}	Δ[a)]	α_{calcd}[b)]	α[c)]	Δ'_σ	Eq.[d)]
	$10^3\ cm^{-1}$	$10^3\ cm^{-1}$	%			$10^3\ cm^{-1}$	
trans-$[CoCl_2(en)_2]^+$	16.76	16.3	2.8	0.989	0.96	−4.26	3a
cis-$[CoCl_2(en)_2]^+$	19.12	18.69	2.3	0.997	0.98	−4.26	4a
trans-$[CoBr_2(en)_2]^+$	16.25	15.21	6.8	0.980	0.93	−6.0	3a
cis-$[CoBr_2(en)_2]^+$	18.88	18.10	4.3	0.994	0.965	−6.0	4a
trans-$[Co(CN)_2(NH_3)_4]^+$	23.3	23.9	−2.5	0.876	0.91	13.02	3a
	23.8[e)]	23.9	−0.4	0.898	0.91	12.6	3a
cis-$[Co(CN)_2(en)_2]^+$	23.78	22.99	3.8	0.988	0.955	12.64	4a
	23.16[e)]	22.99	2.8	0.982	0.955	12.2	4a
trans-$[Co(CN)_4(NH_3)_2]^-$	25.46	24.2	5.2	0.958	0.91	13.02	3b
cis-$[Co(CN)_4(NH_3)_2]^-$	28.69	28.0	2.5	0.979	0.955	13.02	5a
$[CoCl(CN)_5]^{3-}$	26.57	25.63	3.7	0.977	0.935	17.58	4b
	26.27[e)]	25.63	3.4	0.965	0.935	22.33	4b
$[CoBr(CN)_5]^{3-}$	26.30	25.2	4.3	0.974	0.93	18.66	4b

a) $\Delta=100\ (E_{calcd}-\sigma_{obsd})/\sigma_{obsd}$. b) Calculated from the relation $\alpha=1-\beta$ and Eqs. 3—5 by using the following parameter values. The ligand parameter:[1)] d(en)=21.4, $d(NH_3)=21.0$, $d(Cl^-)=12.5$, $d(Br^-)=11.7$, $d(CN^-)=32.1$; the AOM parameter values:[7)] $e_\sigma(Cl^-)=6.29$, $e_\sigma(Br^-)=5.93$(estimated from the relation $e_\sigma(Co^{III})=1.11e_\sigma(Cr^{III})$), $e_\sigma(CN^-)=12.15$, $e_\sigma(en)=7.91$, $e_\sigma(NH_3)=7.81$ in units of $10^3\ cm^{-1}$ and the weighted average of the Racah parameter values for each ligand which contributes to the degenerate component are obtained from the following Racah parameter values: $B/cm^{-1}=616(N)$, $469(CN^-)$, $456(Cl^-)$, $386(Br^-)$; these values are taken from R. Bramley, M. Brorson, A. M. Sargeson, and C. E. Schäffer, *J. Am. Chem. Soc.*, **107**, 2780 (1985). c) From Ref. 1. d) Equations used for the calculations of E_{calcd}, α_{calcd}, and α. e) By using the $e_\sigma(CN^-)=12.00$ calculated on the basis of the absorption data of Ohkawa et al. (K. Ohkawa, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **39**, 1715 (1966)).

Table 2. Calculated and Observed Transition Energies for the Degenerate and/or Nondegenerate Component and Reduction Parameters for Some *trans*-$[Cr^{III}X_2(N)_4]$ Type Complexes

	E_{calcd}	σ_{obsd}	Δ[a)]	α_{calcd}[b)]	α[c)]	Δ'_σ	Eq.[d)]	Ref.[e)]
	10^3 cm^{-1}	10^3 cm^{-1}	%			10^3 cm^{-1}		
$[CrF_2(3.2.3\text{-tet})]^+$	21.1*1)	22.5	−6.2	0.99		1.0	7	8
$[CrF_2(en)_2]^+$	18.5*3)	18.8 (sh)#)	−1.6		1.00		1	f)
	18.5*2)		−1.6	1.00		1.0	3b	
	21.7*3)	21.4	+2.3		1.00		1	f)
$[Cr(OH)_2(3.2.3\text{-tet})]^+$	20.8*1)	20.4	+2.0	0.95		4.0	7	8
$[Cr(OH)_2(en)_2]^+$	17.1†)	18.25#)	−5.9		0.94		1	g)
	18.0*2)		−1.3	0.985		4.0	3b	
	20.6†)	19.92	+3.4		0.94		1	g)
$[Cr(CN)_2(3.2.3\text{-tet})]^+$	20.14			0.94		4.5	7	8
$[Cr(CN)_2(en)_2]^+$	22.96*3)	23.15	−0.8		0.98		2	h)
	23.89*2)			0.99		4.5	3b	
$[CrBr_2(3.2.3\text{-tet})]^+$	23.0*1)	21.9	+5.0	1.08		−6.0	7	8
$[CrBr_2(en)_2]^+$	16.51*3)	16.5#)	+0.1		0.98		1	i)
	16.5*2)		0.0	0.98		−6.0	3b	
	21.46*3)	21.7(sh)	−0.1		0.98		1	i)
$[CrCl_2(3.2.3\text{-tet})]^+$	22.85*2)	22.3	+2.5	1.07		−5.2	7	8
$[CrCl_2(en)_2]^+$	17.20*3)	17.29#)	−0.5		0.98		1	j)
	17.29*2)		0.0	0.985		−5.2	3b	
$[Cr(H_2O)_2(3.2.3\text{-tet})]^{3+}$	22.5*1)	23.1	−2.5	1.05		−4.0	7	8
$[Cr(H_2O)_2(en)_2]^{3+}$	19.65*3)	19.68#)	−0.2		1.00		1	g)
	19.49*2)		−0.1	0.99		−4.0	3b	
	21.9*3)	22.47	+2.1		1.00		1	g)

a) $\Delta=100\,(E_{calcd}-\sigma_{obsd})/\sigma_{obsd}$. b) Calculated from the relation $\alpha=1-\beta$ and Eq. 3b by using the following parameter values. The ligand parameter:[5)] $d(en)=21.9$, $d(F^-)=15.1$, $d(OH^-)=14.65$, $d(CN^-)=26.5$, $d(Br^-)=11.7$, $d(Cl^-)=12.5$, $d(H_2O)=17.4$; the AOM parameter values:[7)] $e_\sigma(en)=7.3$; $e_\sigma(OH^-)=8.66$; $e_\sigma(CN^-)=8.48$; $e_\sigma(F^-)=7.63$; $e_\sigma(Br^-)=5.34$; $e_\sigma(Cl^-)=5.56$; $e_\sigma(H_2O)=5.94$; in units of 10^3 cm^{-1} and the weighted average of the Racah parameter values for each ligand which contributes to the degenerate component are obtained from the following Racah parameter values ; B/cm^{-1}=620 (en), 820 (F^-), 460 (OH^-), 530 (CN^-), 370 (Br^-), 560 (Cl^-), 725 (H_2O). c) From Ref. 5. d) Equations used for the calculations of E_{calcd}, α_{calcd}, and α; Eqs. 1 and 2 from Ref. 1. e) References for the observed absorption band positions. f) J. M. Dejorine, W. R. Moison, and J. W. Vaughn, *Inorg. Chem.*, **13**, 66 (1974). g) W. A. Baker, Jr. and M. G. Phillips, *Inorg. Chem.*, **5**, 1042 (1966). h) S. Kaizaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **48**, 902 (1975). i) L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964). j) M. Linhard and M. Weigel, *Z. Phys. Chem. (Frankfurt am Main)*, **5**, 20 (1955). (sh): shoulder. #): The observed degenerate component. *1), *2): Obtained by the present approach for the nondegenerate and degenerate component, respectively. *3): Shimura's unpublished results from Ref. 5. †): Obtained from Shimura's treatment.

those of the corresponding Co(III) complexes according to the relation $e_\sigma(Cr^{III})=0.9e_\sigma(Co^{III})$ except for the cyano ligand. Thus, Shimura's reduction parameter is also applied to chromium(III) complexes.[5)] For chromium(III) complexes, in fact, the analogous relations for the perturbed transition energies of the degenerate component are obtained only by replacing $16B$ in the first parenthesized term of the denominators of Eqs. 3—5 by $12B$. According to the above equations, the calculated α values from the relation $\alpha=1-\beta$ are obtained by using the AOM e_σ values in the references[6,7)] as in Tables 1 and 2. It is seen that the α values depend mainly on the coefficient of the denominators of Eqs. 3—5 (3 for Eqs. 3 and 12 for Eqs. 4 and 5) for a given $\Delta'_{\sigma b}$ value and also depend on the $\Delta'_{\sigma b}$ value for the complexes with the same geometrical structure. This tendency of the numerical behavior of the β values is similar to the empirical relations found for Shimura's reduction parameter; the relation $\alpha=1-2\beta$ for trans type complexes (Eq. 3) and the relation $\alpha=1-\beta$ for *cis*-$[Ma_nb_{6-n}]$ (n=2 and 4) and $[Ma_nb_{6-n}]$ (n=1 and 5) type complexes(Eqs. 4 and 5) tend to hold for the β value of a given ligand, and the α values also decrease with increasing the difference between the e_σ values for the ligands concerned ($\Delta'_{\sigma b}$) as shown in Ref. 1 and Tables 1 and 2. That is, the calculated α values for trans complexes are always smaller than those for cis ones. In the case of (N, O) mixed ligand complexes where $\Delta'_{\sigma O}=3(e_{\sigma O}-e_{\sigma N})$ is estimated to be -1.8×10^3 cm^{-1},[6)] the calculated α values become close to 1.00, whereas (CN^-, X) mixed ligand complexes with the large $\Delta'_{\sigma X}=3(e_{\sigma X}-e_{\sigma CN})$ values (-12—-22×10^3 cm^{-1}) for X=amines and halogeno ligands give the large reduction parameter values. These anticipated tendency of the α values are in fairly good accordance with that for the empirical α values for Cr(III) as well as Co(III) complexes as shown in Tables 1 and 2. Taking account of the correlation between the reduction parameters and the AOM parameter difference $\Delta'_{\sigma b}$, the order for the e_σ values is predicted to be $CN^->N>O>Cl^->Br^->I^-$. This is consistent with the proposed order for the

AOM e_σ values; i.e., the two-dimensional spectrochemical series.[2,7] Thus, these plausible tendency of the α values supports that Shimura's reduction parameter of the degenerate component arises from the configuration interaction between the two degenerate components and can be elucidated semiquantitatively in terms of the $\Delta'_{\sigma\mathrm{b}}$ values as shown in Tables 1 and 2. The discrepancy between the empirical and calculated reduction parameter values may be due to the neglect of the configuration interaction between the degenerate ${}^1\mathrm{E_a}({}^1\mathrm{T_{1g}})$(Co(III))(${}^4\mathrm{E_a}({}^4\mathrm{T_{2g}})$(Cr(III))) component and the upper ${}^1\mathrm{E}$(Co(III))(${}^4\mathrm{E}$(Cr(III))) one other than the ${}^1\mathrm{E_b}({}^1\mathrm{T_{2g}})$(Co(III))(${}^4\mathrm{E_b}({}^4\mathrm{T_{1g}})$(Cr(III))) one.

The Nondegenerate Component. No transition energy change is expected for the nondegenerate component(${}^1\mathrm{A_2}({}^1\mathrm{T_{1g}})$), because there is no configuration interaction between the nearby excited states with the same symmetry representation in terms of the ligand field theory. However, Shimura's empirical analyses for a large number of the absorption spectral data indicate that the position of the nondegenerate component is also susceptible to the shift by the same amount as the reduction parameter for the degenerate component. This may be interpreted by our recent ^{2}H NMR study in combination with the ligand field absorption spectra of Cr(III) complexes.[8] The shifts of the nondegenerate component are observed for the absorption spectra of *trans*-[$\mathrm{CrX_2}$(3.2.3-tet)]$^+$ where 3.2.3-tet refers to 4,7-diazadecane-1,10-diamine ($\mathrm{NH_2CH_2\,CH_2\,CH_2\,NHCH_2\,CH_2\,NHCH_2\,CH_2\,CH_2\,NH_2}$). That is, the nondegenerate ${}^4\mathrm{B_2}$ components of the first band of the dihydroxo, difluoro, dichloro, dibromo, and diaqua complexes which exhibit a distinct tetragonal splitting are not always located at the same position, but they are shifted with variation of the axial ligands. The correlation of the AOM e_σ parameter and the ^{2}H NMR shift differences($\Delta\delta$) between the axial and equatorial deuterons of the deuterated ethylene backbone for the *trans*-3.2.3-tet Cr(III) complexes gives the relations $e_{\sigma\mathrm{N}}=0.037\Delta\delta+3.75$ and $e_{\sigma\mathrm{X}}=-0.09\Delta\delta+15.3$ and then leads to the following equation.

$$e_{\sigma\mathrm{X}} = -2.43e_{\sigma\mathrm{N}} + 24.4, \qquad (6)$$

in units of $10^3\,\mathrm{cm}^{-1}$ as previously described.[8] On the basis of Eq. 6, the transition energy of the nondegenerate ${}^4\mathrm{B_2}$ component($3e_{e\mathrm{N}}$) is expressed with use of the relation $\Delta'_{\sigma\mathrm{X}}=3(e_{\sigma\mathrm{X}}-e_{\sigma\mathrm{N}})$) as follows,

$$E({}^4\mathrm{B_2}) = 3e_{\sigma\mathrm{N}} = 21.4(1 - 0.013\Delta'_{\sigma\mathrm{X}}) \qquad (7)$$

The coefficient 21.4 in Eq. 7 is close to the nondegenerate component positions observed for the case of $\Delta'_{\sigma\mathrm{X}}=0$, or approximates to $3e_{\sigma\mathrm{N}}$(10Dq) for the amine ligand and $0.013\Delta'_{\sigma\mathrm{X}}$ corresponds to Shimura's parameter β. In the case of *trans*-[$\mathrm{Co^{III}X_2(en)_2}$] type complexes, the transition energy of the ${}^1\mathrm{A_2}$ component($3e_{\sigma\mathrm{N}}-C$) or the ligand parameter d is represented by the equation $21.22(1-0.013\Delta'_{\sigma\mathrm{X}})$ according to the relation $e_\sigma(\mathrm{Co^{III}})=1.11e_\sigma(\mathrm{Cr^{III}})$ together with $d=3e_{\sigma\mathrm{N}}-C(C=2.46\times10^3\,\mathrm{cm}^{-1})$ from Eq. 7. The coefficient 21.22 is also close to the band positions for $\Delta'_{\sigma\mathrm{X}}=0$, or almost equals the ligand parameter(d) value for the amine ligand, and $0.013\Delta'_{\sigma\mathrm{X}}(=\beta)$ just accidentally coincides with that for Cr(III) complexes. Since $\Delta'_{\sigma\mathrm{X}}$ is at most $13(\times10^3\,\mathrm{cm}^{-1})$ for *trans*-[$\mathrm{CoX_2(N)_4}$] type complexes as shown in Table 1, the largest value of β is estimated to be around 0.17; i. e., it is of the same order of magnitude as Shimura's empirical parameter values for Co(III) complexes. The reduction parameter α is correlated with the difference between the AOM e_σ parameter values for the basal(N) and axial(X) ligands, $=1/3\Delta'_{\sigma\mathrm{X}}$, as in the case of the degenerate component. Since the $e_{\sigma\mathrm{N}}$ parameter values increase with decreasing the $e_{\sigma\mathrm{X}}$ values as seen from Eq. 6, the e_σ parameter values of two kinds of ligands in mixed ligand complexes tend to vary in an opposite way and to compensate each other as discussed previously.[8] Therefore, the reduction of the transition energy of the nondegenerate component results from the charge redistribution due to the electroneutrality principle through the metal-ligand σ bonds. According to Eq. 7, however, the reduction parameter α becomes less than 1.00 for chromium(III) complexes of trans type with the positive value of the $\Delta'_{\sigma\mathrm{X}}$ where the e_σ parameter values for such $\mathrm{F^-}$, $\mathrm{CN^-}$, and $\mathrm{OH^-}$ ligands are larger than those for the amine ligands as shown in Table 2. For the negative values of $\Delta'_{\sigma\mathrm{X}}$ for the aqua, chloro, and bromo chromium(III) complexes,[5,8] the reduction parameter α becomes larger than 1.00 as in Table 2. The latter case is contrary to Shimura's treatment, which is significant even for the ligands with the weaker σ bond interaction or smaller e_σ parameter values than those for the amine ligands as found for the dichloro, dibromo, and diaqua tetramine Co(III) and Cr(III) complexes as in Tables 1 and 2. This contradiction remains still open to question.

In conclusion, the present theoretical and empirical approaches reveal that Shimura's reduction parameter has a significant implication for the ligand field parameterization and is elucidated semiquantitatively in connection with the $\Delta'_{\sigma\mathrm{b}}$ values for the nondegenerate component as well as the degenerate one, though there is a different behavior in the nondegenerate case between the present approach and Shimura's treatment.

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