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Photochemistry of Dihalogenobis(diamine)chromium(III) Complexes in Methanol

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The photochemical reactions of *trans*- and *cis*-$[CrX_2(AA)_2]X$ in methanol were investigated under the ligand-field band irradiation, where X is Cl^- or Br^- ion and AA is en, pn or tn. In the earlier step of irradiation, only trans-to-cis photoisomerization was observed irrespective of diamines. The process of the photoisomerization was reasonably explained in terms of the bond indices calculated on the basis of VC theory. The quantum yields for dichloro complexes were larger than those for dibromo complexes, and the yields increased in the order of pn<en<tn complexes. The photochemistry of *cis*-$[CrCl_2(pn)_2]Cl$ was also studied and the difference of the photochemical reactions from the thermochemical reactions was discussed.

We have systematically studied the thermal cis-trans isomerization of $[CrX_2(AA)_2]X$ type complexes in a solid phase since ten years ago, where X is Cl^- or Br^- ion and AA is a diamine selected from ethylenediamine (en), *dl*-1,2-propanediamine (pn) and 1,3-propanediamine (tn).[1—4] In these studies, cis-to-trans isomerization was detected in the complexes containing tn which forms six-membered chelate ring with chromium(III) ion, whereas trans-to-cis isomerization was recognized in the complexes containing en or pn which forms five-membered chelate ring. The mechanism of the thermal isomerization was verified to be bond rupture.[1c,4]

The isomerization takes place not only in thermal environment, but also under sunlight. We have actually noticed that the exposure of *trans*-$[CrCl_2(pn)_2]Cl$ to sunlight readily causes trans-to-cis isomerization in a solid state. However, the photochemical reaction is difficult to be traced quantitatively in the solid because the reaction takes place just on the surface of the compound. Therefore, few studies have been devoted to the photochemistry in a solid state.[5]

In recent years, on the other hand, the photochemistries of transition metal complexes have extensively been investigated in solution.[6] Whether photochemical reactions are allowed or forbidden have reasonably been discussed on the basis of the orbital symmetries of reactants, products and intermediates.[7]

In the present study, the isomerization and subsequent reactions of $[CrX_2(AA)_2]X$ type complexes in methanol were investigated under the ligand-field band irradiation, where X is Cl^- or Br^- ion and AA is en, pn, or tn.

Experimental

Preparation of Complexes. *trans*-$[CrCl_2(en)_2]Cl$,[8] *cis*-$[CrCl_2(en)_2]Cl$,[9] *trans*-$[CrCl_2(pn)_2]Cl\cdot1.5H_2O$,[10] *cis*-$[CrCl_2(pn)_2]Cl$,[11] *cis*- and *trans*-$[CrCl_2(tn)_2]Cl$,[12] *trans*-$[CrBr_2(en)_2]Br$,[13] *cis*-$[CrBr_2(en)_2]Br$,[14] *cis*- and *trans*-$[CrBr_2(pn)_2]Br$,[1b] and *cis*- and *trans*-$[CrBr_2(tn)_2]Br$[2b] were prepared by the known methods partially modified. The crude products were purified by the recrystallization from dry methanol and ether several times.

Isolation of Products during Photochemical Reactions. *fac-*$[CrCl_2(CH_3OH)(pn)_2]Cl\cdot H_2O$ *and cis-*$[CrBr(CH_3OH)(pn)_2]Br_2$: They were isolated during photochemical reaction of *cis*-$[CrCl_2(pn)_2]Cl$ and *cis*-$[CrBr_2(pn)_2]Br$, respectively. The light of 400 nm was irradiated for more than 600 min on the solution (methanol) containing appropriate amounts of *cis*-$[CrCl_2(pn)_2]Cl$ or *cis*-$[CrBr_2(pn)_2]Br$. The resulting solutions were evaporated to about a half of its volume, and thereto an appropriate amount of ether was added to precipitate the desired materials. The precipitates thus obtained were recrystallized from dry methanol–ether (1:1). The products were identified by means of elemental analyses, TLC, UV- and far-IR spectrophotometry, and molar conductivity measurements. Details will be mentioned in the later section.

Found for the former complex: C, 23.57; H, 7.61; N, 15.25%. Calcd for *fac*-$[CrCl_2(CH_3OH)(pn)_2]Cl\cdot H_2O$: C, 23.87; H, 7.34; N, 15.71%. Found for the latter complex: C, 17.61; H, 4.95; N, 11.36; Cr^{3+}, 11.03%. Calcd for *cis*-$[CrBr(CH_3OH)(pn)_2]Br_2$: C, 17.81; H, 5.12; N,11.87;Cr^{3+}, 11.02%.

Preparation of Materials Used as Actinometer. Potassium tris(oxalato)ferrate(III), $K_3[Fe(C_2O_4)_3]$ was prepared by the literature method,[15] and Reinecke's salt, $K[Cr(NCS)_4(NH_3)_2]$ was derived from the corresponding ammonium salt[16] by metathesis.

Measurements. The apparatus used for the photochemical reactions was the lamp house (Model UI-501C) by Ushio Denki Co., Ltd. The light source was a 500 W Ushio short arc xenon lamp (Model UXL-500D-O). The monochromatized beams of 400, 530, and 580 nm were obtained with Toshiba interference filters, KL-40, KL-53 and KL-58, respectively.

The sample solution for photochemical reactions was prepared by dissolving either one of the complexes in absolute methanol. The solution was irradiated in a thermostated spectrophotometric cell of 10 cm length with a continuous mechanical stirring. A part of the beam for irradiation to the sample was simultaneously reflected by quartz plate and introduced into the cell setting the actinometer. The wavelengths used for irradiation were 400 and 580 nm for trans-complexes and 400 and 530 nm for cis-complexes. As the actinometer potassium tris(oxalato)ferrate(III)[17] was used for 400 nm, and Reinecke's salt, for 530 and 580 nm.[18] The temperature applied were 22 and 32 °C. The change in absorbances of the sample solution was measured at each relevant wavelength and the extents of photoconversion were determined. They were corrected by measuring the dark reaction under the same conditions as those for the sample solution.

The photochemical products were identified by measuring electronic spectra, far-IR spectra and molar conductivities, and by means of TLC and thermal analyses. The instruments used for the measurement of spectra were a JASCO UVIDEC-505 UV/VIS recording digital spectrophotometer and a JASCO Model IR-F far infrared spectrophotometer. The measurement of molar conductivities was carried out with a Yokogawa Universal Bridge BV-Z-12A. The plates used for TLC were those of silica gel G 250 made by Merck Ltd. Thermal analyses were performed with a MOM Typ-OD-102 Derivatograph and with a Chyo

Thermobalance.

Results

First, it should be noted for clarification of the following discussion that only trans-to-cis isomerization was detected for all the trans complexes, and no isomerization was found for the cis complexes, but instead the coordination of solvent was recognized.

Photochemical Reactions. *trans-[CrCl$_2$(pn)$_2$]Cl·1.5H$_2$O*: The photochemical behavior of the complex was basically the same irrespective of the irradiation wavelengths (580 and 400 nm) used for excitation. Figure 1 shows the electronic spectral changes with time on 580 nm irradiation in methanol at 22 °C. As seen from the figure, the absorption peaks of the complex shift with time toward those of the corresponding cis complex. Any isosbestic point is not detectable in the spectra. However, the application of TLC to the sample solution after irradiation for about thirty minutes evidenced the presence of *trans*- and *cis*-[CrCl$_2$(pn)$_2$]Cl. Table 1 summarized the R_f values. The R_f's (0.54 and 0.33) for the sample solution are quite close to those of the reference trans-form (0.54) and cis-form (0.34). Thus, the first photochemical reaction within thirty minutes is trans-to-cis photoisomerization.

Further irradiation brought about subsequent spectral changes, suggesting that a secondary photochemical reaction occurs besides the trans-to-cis isomerization. The secondary photochemical reaction was found to be parallel to the reaction of *cis*-[CrCl$_2$(pn)$_2$]Cl as described later.

trans-[CrCl$_2$(en)$_2$]Cl, trans-[CrBr$_2$(en)$_2$]Br, trans-[CrBr$_2$(pn)$_2$]Br, trans-[CrCl$_2$(tn)$_2$]Cl and trans-[CrBr$_2$(tn)$_2$]Br: The photochemical behaviors of the complexes were monitored on 580 and 400 nm irradiations in methanol at 22 and 32 °C. In all cases, the absorption spectra of the trans complexes shifted to those of the corresponding cis complexes. After the irradiation for about thirty minutes, the sample solutions were checked by TLC. Inspection of the R_f values in Table 1 reveals that all the sample solutions contain both trans and cis complexes. Thus, the photochemical reaction within 30 min is trans-to-cis isomerization. Interesting is that the direction of photo-isomerization (trans-to-cis) of the tn complexes is contrast to that of the thermal isomerization (cis-to-trans).

Further irradiation on the solution of *trans*-[CrBr$_2$(pn)$_2$]Br causes an additional reaction other than iso-

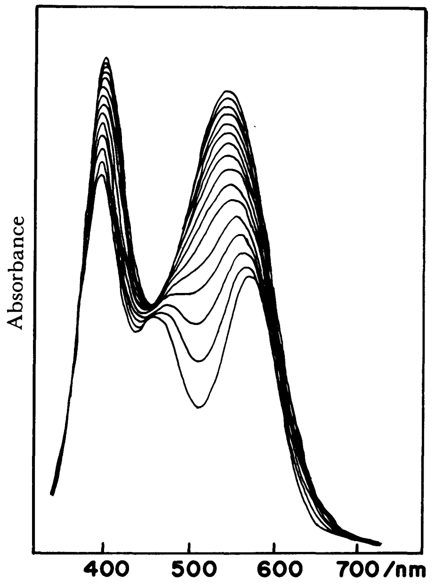


Fig. 1. Electronic spectral changes with time of *trans*-[CrCl$_2$(pn)$_2$]Cl·1.5H$_2$O in methanol on 580 nm irradiation at 22 °C. The spectra were monitored every ten minutes.

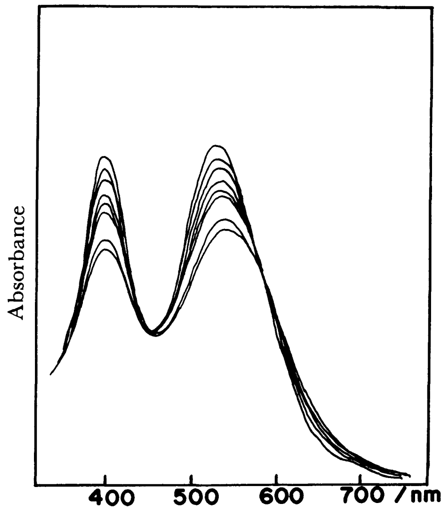


Fig. 2. Electronic spectral changes with time of *cis*-[CrCl$_2$(pn)$_2$]Cl in methanol on 530 nm irradiation at 22 °C. The spectra were monitored every twenty minutes.

Table 1. R_f Values by thin layer chromatography(TLC)[a]

Starting complex	Sample solution[b]		Reference complex *trans*-form	*cis*-form
trans-[CrCl$_2$(pn)$_2$]Cl·1.5H$_2$O	0.54	0.33	0.54	0.34
trans-[CrCl$_2$(en)$_2$]Cl	0.60	0.41	0.60	0.40
trans-[CrCl$_2$(tn)$_2$]Cl	0.47	0.17	0.47	0.18
trans-[CrBr$_2$(pn)$_2$]Br	0.63	0.43	0.63	0.43
trans-[CrBr$_2$(en)$_2$]Br	0.70	0.34	0.70	0.33
trans-[CrBr$_2$(tn)$_2$]Br	0.55	0.22	0.55	0.22
cis-[CrCl$_2$(pn)$_2$]Cl	0.32	0.09[c]		0.34
cis-[CrBr$_2$(pn)$_2$]Br		0.13[c]		0.32

a) The mixture of l-butanol, methanol, and acetic acid (7:2:1) was used as the developer. b) The sample solutions were irradiated for about 30 min and checked by TLC. c) The value is that for the secondary photochemical product.

merization, which is a reaction similar to that of *cis*-$[CrBr_2(pn)_2]Br$ as mentioned later.

cis-$[CrCl_2(pn)_2]Cl$: When the cis complex is irradiated, an isosbestic point appears at 587 nm in the spectra irrespective of the irradiation wavelengths (530 and 400 nm). Figure 2 shows the spectral changes with time on 530 nm irradiation at 22 °C. After appropriate irradiation times, aliquot of the sample solution was taken out to be analyzed by TLC. Two R_f values were obtained: one (0.32) is due to the cis complex and the other (0.09) may come from another product. We then tried to isolate the product as mentioned in Experimental section.

The molar conductivity of the product was 80.78 $\Omega^{-1}cm^{-1}$ in methanol at 25 °C, suggesting that the compound is 1-1 valence type. Far-IR spectra of the product showed the absorption peaks due to Cr–O (530 and 395 cm^{-1}), Cr–N (575 cm^{-1}) and Cr–Cl (490 and 290 cm^{-1}) stretching vibrations. The weight loss (13.9%) observed upon heating the compound at 180 °C corresponds to the evolution of one mole of H_2O (5.1%) plus one mole of CH_3OH (8.9%). These results support that the photoproduct has the formula of $[CrCl_2(CH_3OH)(pn)_2]Cl$. Two isomers are feasible for the configuration of the product: one is facial and the other, meridional with respect to the position of two chloride ions and methanol. The electronic spectrum of the product is illustrated in Fig. 3 together with those of *fac*- and *mer*-$[CrCl_2(H_2O)(dien)]^+$ (dien: diethylenetriamine). Comparison of these spectra readily reveals that the products has *fac*-configuration.

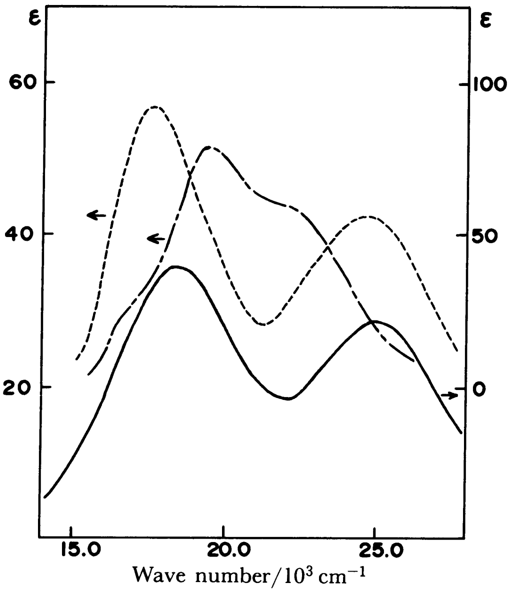


Fig. 3. Electronic spectra of *fac*-$[CrCl_2(CH_3OH)(pn)_2]$-Cl in methanol (——), *fac*-$[CrCl_2(H_2O)(dien)]^+$ in 0.6 M $HClO_4$ (1 M=1 mol dm^{-3}) (----), and *mer*-$[CrCl_2(H_2O)(dien)]^+$ in 1 M $HClO_4$ (— — —).

cis-$[CrBr_2(pn)_2]Br$: The spectral changes with time under 530 and 400 nm irradiations gave isosbestic points at 593, 483, and 442 nm for about 200 min. The first photoproduct giving these isosbestic points is assumed to be *fac*-$[CrBr_2(CH_3OH)(pn)_2]^+$, but the complex were unable to be isolated. After the irradiation for more than 600 min, the isosbestic points disappeared because of the formation of the secondary photoproduct. Details of the product are still unkown. We tentatively speculate from the electronic spectrum that the product is *fac*-$[CrBr(CH_3OH)_2(pn)_2]^{2+}$. Attempt to isolate the product was carried out as mentioned in Experimental section. However, the material isolated was always identified to be *cis*-$[CrBr(CH_3OH)(pn)_2]Br_2$ by TLC, elemental analysis, molar conductivity, far-IR spectra and thermal analysis. This is probably because upon crystallization, a unidentate pn contained in *fac*-$[CrBr(CH_3OH)_2(pn)_2]^{2+}$ functions as bidentate accompanied by the expulsion of one mole of CH_3OH from coordination sphere.

Quantum Yields. The photochemical product of each trans complex was the corresponding cis complex in the earlier step of irradiation. The ratios of the starting trans- to the cis-isomers produced were calculated from the absorbances of the resulting solution and those of the reference trans- and cis-isomers as reported previously.[1] The quantum yields were estimated by the use of those of the actinometers. Table 2 summarizes the quantum yields.

Discussion

Photochemistry of trans Complexes. *(1) Labilization Mode*: Gaussian analyses of the electronic spectra of the trans complexes gave four resolved curves. Figure 4 shows four Gaussian curves obtained for *trans*-$[CrCl_2$-

TABLE 2. QUANTUM YIELDS (ϕ) FOR trans-to-cis ISOMERIZATION OF *trans*-$[CrX_2(AA)_2]X$

Starting complex AA	Irradiation wavelength (nm)	Temp. /°C	Quantum yield (ϕ)	
			X=Cl	X=Br
pn	580	22	0.229±0.006	0.0453±0.0007
		32	0.194±0.005	0.0394±0.0003
	400	22	0.200±0.002	0.0182±0.0003
		32	0.149±0.002	0.0140±0.0006
en	580	22	0.302±0.003	0.0581±0.0004
		32	0.351±0.003	0.0671±0.0007
	400	22	0.276±0.004	0.0213±0.0003
		32	0.313±0.003	0.0254±0.0005
tn	580	22	0.346±0.005	0.135±0.002
		32	0.403±0.002	0.169±0.002
	400	22	0.308±0.008	0.0565±0.0004
		32	0.390±0.008	0.0721±0.0003

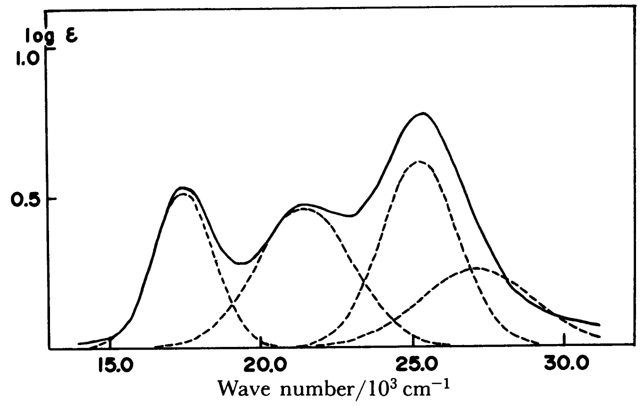


Fig. 4. Electronic spectrum of *trans*-$[CrCl_2(pn)_2]Cl\cdot 1.5H_2O$ with four Gaussian curves.

$(pn)_2]Cl\cdot 1.5H_2O$. These four peaks are assigned to the transition to excited states, $^4E_g{}^a$, $^4B_{2g}$, $^4A_{2g}$ and $^4E_g{}^b$ from the ground state $^4B_{1g}$ in D_{4h} symmetry of the trans complexes; the irradiation at 580 nm populates $^4E_g{}^a$ state, while the irradiation at 400 nm populates $^4A_{2g}$ state.[19]

Adamson *et al.* reported that the quartet excited state is inherently short-lived, but the state is labile enough for reaction to take place because it is in nearly pentagonal pyramid with a lengthened metal-ligand bond.[20]

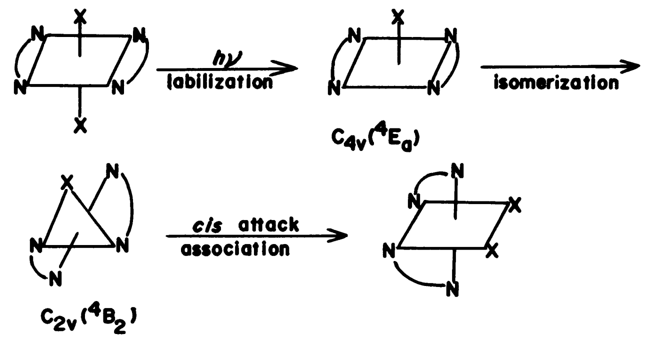
The ratios of quantum yields at 580 and 400 nm are approximately constant for chlorides (*ca.* 1.1) and the bromides (2.4—2.8). This suggests that the photochemical reactions are related to either one of two excited states, $^4E_g{}^a$ and $^4B_{2g}$.

Table 3. Bond indices I* (Cr–L)(μm^{-1}) in the excited state for *trans*-$[CrX_2(AA)_2]X$

State	I*	X=Cl	X=Br
$^4E_g{}^a$	Cr–X	0.90	0.81
	Cr–N	1.21	1.22
$^4B_{2g}$	Cr–X	1.39	1.27
	Cr–N	0.90	0.90

The bond indices I* in the excited $^4E_g{}^a$ and $^4B_{2g}$ states were estimated according to VC theory[21], which are listed in Table 3. It may be deduced from the table that the bond Cr–X is ruptured in $^4E_g{}^a$ state and the bond Cr–N is ruptured in $^4B_{2g}$ state. MO theory gives the same results for the trans complexes.[22] In $^4E_g{}^a$ state, the axial π bond is strengthened and the σ bond is weakened; so the bond Cr–X is relatively activated. On the other hand, in $^4B_{2g}$ state, the equatorial π bond is weakened and σ bond, strengthened, the bond Cr–N being activated. It may therefore be concluded that the bond labilized in the trans complexes is Cr–X rather than Cr–N and the photoactive state which can undergo photoisomerization is $^4E_g{}^a$. The energies of 580 and 400 nm (206 and 299 kJ mol^{-1}) are enough to rupture the coordination bond.

(2) *Photochemical Processes*: Assuming that the photoactive state is ^4E_a and the reaction proceeds *via* five-coordinated intermediate, the allowed processes can be expressed as follows:



Scheme 1.

The first process is photolabilization expelling a halogeno ligand to form a five-coordinated intermediate of tetragonal pyramid (TP) with C_{4v} symmetry in ^4E_a state. The second process involves isomerization from TP to trigonal bipyramid (TBP) with X^- in equatorial position (C_{2v}) which is more energetically favored than with X^- in axial position (C_{3v}) d_{yz} is empty in the $^4B_2$ state of TBP, making cis attack easy. Therefore, exclusive production of the cis complexes from the corresponding trans complexes is reasonably explained by VC theory using five-coordinated intermediate.[22,23]

(3) *Comparison of Quantum Yields*: The quantum yields of the trans-dichloro complexes are larger than those of the trans-dibromo complexes as seen in Table 2. This may depend upon the small ionic radius of Cl^- (1.81 Å) compared with that of Br^- (1.96 Å). The yields increase in the following order of the diamines contained, pn<en<tn. The difference may depend upon the isomerization step in Scheme 1. Above all, the intermediate in the tn complexes is more stereomobile than those in the en or pn complexes, since the six-membered chelate ring in the tn complexes can be more easily elongated in the intermediates than the five-membered chelate ring in the en and pn complexes.

(4) *Activation Energies*: The quantum yields exhibit temperature dependence at two wavelengths at 22 and 32 °C. The apparent activation energies (E_a) were estimated from the plots of log ϕ *vs.* $1/T$, which are listed in Table 4. The values for each complex are roughly the same for both wavelengths. Thus, the photochemical reactions may occur from the same excited state, *i. e.*, the thermally equilibrated excited state (thexi state) $^4E_g{}^0$.[20]

Table 4. Apparent activation energies (*E*a) for photoisomerization of *trans*-$[CrX_2(AA)_2]X$

AA	Irradiation wavelength(nm)	*E*a (kJ mol^{-1})	
		X=Cl	X=Br
pn	580	−12.6±3.8	−10.4±1.7
	400	−22.5±1.7	−19.6±4.4
en	580	11.2±1.4	10.8±1.3
	400	11.9±1.8	13.2±2.5
tn	580	11.3±1.7	16.8±2.0
	400	17.6±3.3	18.2±0.8

The negative activation energies in the pn complexes are explainable by assuming that the electrons excited under irradiation relax to the $^4E_g{}^0$ state, but a part of the electrons are excited to the $^4E_g{}^a$ state by thermal energy to be deactivated instantly. Thus, the energy difference between $^4E_g{}^a$ and $^4E_g{}^0$ states may be small in the

Table 5. Quantum yields (ϕ) for the photochemical reaction of *cis*-$[CrCl_2(pn)_2]Cl$

Irradiation wavelength (nm)	Temp./°C	Quantum yield (ϕ)
530	22	0.049 ± 0.001
	32	0.052 ± 0.001
400	22	0.051 ± 0.001
	32	0.050 ± 0.001

Table 6. Bond indices I* (Cr–L)(μm^{-1}) in the excited state for *cis*-$[CrX_2(AA)_2]X$

State	I*	X=Cl	X=Br
$^4B_2$	$Cr-N_{ax}$	1.44	1.44
	$Cr-N_{eq}$	0.90	0.90
	Cr–X	0.97	0.89
^4E_a	$Cr-N_{ax}$	0.95	0.97
	$Cr-N_{eq}$	1.14	1.13
	Cr–X	1.11	1.01

case of the pn complexes. On the other hand, the activation energies in the en and tn complexes are positive because of the energy difference between $^4E_g{}^a$ and $^4E_g{}^o$ states being large, and so the energy enough for reaction to occur is thermally supplied.

Photochemistry of cis Complexes. The excited energy levels become higher in the following order: $^4B_2 < {}^4E_a < {}^4E_b < {}^4A_2$ in C_{2v} symmetry for the cis complexes. Since the quantum yields under 530 and 400 nm irradiations are nearly the same as seen in Table 5, the reaction is considered to take place from either one of $^4B_2$ and ^4E_a states.[24] On the basis of VC theory, the bond indices were estimated as listed in Table 6. Comparison of the bond indices reveals that the bond $Cr-N_{eq}$ may be ruptured in the $^4B_2$ state and the bond $Cr-N_{ax}$, in the ^4E_a state. However, it is not so easy to determine from which excited state the photochemical reaction of *cis*-$[CrX_2(AA)_2]X$ takes place.

Comparison of Photochemical Reaction with Thermochemical Reaction. The mechanisms in the photochemical and thermochemical reactions can not be discussed on the same basis because the photochemical reaction occurs at the excited state, whereas the thermochemical reaction occurs at the ground state. However, the apparent difference was found in the direction of the isomerization. In thermal environment, the complexes containing five-membered chelate diamines such as en and pn undergo trans-to-cis isomerization and the complexes containing six-membered chelate diamine tn undergo cis-to-trans isomerization.[1c] In the ligand-field photochemistry, on the other hand, only trans-to-cis isomerization was observed irrespective of the diamines contained. Accordingly, in the case of $[CrX_2(tn)_2]X$, the direction of the isomerization is mutually reverse between photochemical and thermochemical reactions as follows:

$$\textit{trans}\text{-}[CrX_2(tn)_2]X \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} \textit{cis}\text{-}[CrX_2(tn)_2]X$$

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