Steric Trans Influence of Aminomethane Ligand in *trans*-Aminomethanechlorobis(1,2-diaminoethane)cobalt(III)

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The trans isomer of aminomethanechlorobis(1, 2- diaminoethane)cobalt(III), *trans*- $[CoCl(NH_2Me)(en)_2]^{2+}$, was prepared from *trans*-$[CoCl(NO_2)(en)_2]^+$ by a two-step reaction in which Cl^- was replaced with an NH_2Me and then the remaining NO_2^- was replaced with a Cl^-. The configuration was confirmed by X-ray crystal analysis, and structural comparison was made with its cis isomer. The crystals have the formulae, *trans*-$[CoCl(NH_2Me)(en)_2]Cl(ClO_4)$ and *cis*-$[CoCl(NH_2Me)(en)_2]Cl_2$. The crystallographic data are as follows; Monoclinic, $P2_1/c$, $a=11.515(1)$, $b=7.421(2)$, $c=17.257(1)$ Å, $\beta=99.220(8)^\circ$, $V=1455.6(5)$ Å^3, $Z=4$, and $R=0.043$ for the former, and Orthorhombic, $Fdd2$, $a=26.64(1)$, $b=27.26(1)$, $c=7.570(2)$ Å, $V=5497(3)$ Å^3, $Z=16$, and $R=0.057$ for the latter. The Co–Cl bond of the trans complex is longer than that of the cis complex. It was found that the bulkiness of the Me group effects the trans Co–Cl bond through one of the two flexible equatorial en chelate rings. The kinetic data of an aquation reaction of the trans and the cis complexes show that the Cl^- of the trans complex is substituted more readily than that of the cis is.

Although alkylamine, R-NH_2, complexes of bis(1,2-diaminoethane)cobalt(III) with a cis configuration are well known and their properties and kinetics have been examined extensively,[1—6] those with a trans configuration have not been reported except for ammine complexes in which an alkyl group of the R-NH_2 is a hydrogen atom.[7—9] We report here preparation and characterization of the title complex, *trans*-$[CoCl(NH_2Me)(en)_2]^{2+}$, en=1,2-diaminoethane.

Since the donating ability of an N atom in an aminomethane ligand is almost comparable with that of N atoms in an en ligand, the stabilities of *cis*- and *trans*-$[CoCl(N)_5]^{2+}$ complexes are expected to be comparable from an electronic view point. Nevertheless, the trans complex has not been prepared yet. This suggests that there is a steric factor that destabilizes the trans isomer compared with the cis isomer. In this report, the steric effect of the aminomethane ligand on the stability of the trans complex, especially on the Co–Cl bond at the trans position, is discussed based on the X-ray crystal structures and the kinetics of the *trans*- and *cis*-$[CoCl(NH_2Me)(en)_2]^{2+}$.

Experimental

General Remarks. *cis*-$[CoCl(NH_2Me)(en)_2]Cl_2$[1] and *trans*-$[CoCl(NO_2)(en)_2](NO_3)$[10] were prepared according to procedures in the literature. JEOL GSX-270 and EX-400 instruments were used to obtain ^{1}H and ^{13}C NMR spectra. ^{1}H and ^{13}C NMR data were referred to a methyl signal of sodium 3-(trimethylsilyl)propanesulfonate (DSS). UV spectra were recorded on a Shimadzu UV-160 spectrometer.

Caution! Although we have experienced no difficulties with the perchlorate salts of the complexes mentioned here, these complexes should be treated as potentially explosive and handled with care.

***trans*-$[Co(NO_2)(NH_2Me)(en)_2]Cl(NO_3)$ (2).** Fifteen g (45.0 mmol) of *trans*-$[CoCl(NO_2)(en)_2](NO_3)$ was put in a three-necked vessel with a gas inlet on a side neck and a dry ice-acetone condenser on the middle neck. The bottom of the vessel was cooled in a dry ice–acetone bath. NH_2Me gas was generated by adding dropwise 210 ml of 40% aqueous NH_2Me to 225 g of NaOH pellets, and was introduced into the vessel through a column packed with CaO to dry the gas. When the generation of the gas ceased, the dry ice–acetone bath was removed. After the suspension was stirred for 12 h from the introduction of the gas, the initial red-orange material changed to a yellow suspension of the product. Then, the liquid NH_2Me was left vaporizing spontaneously, and the residue was dried in a vacuum. Because the product was almost pure, it was used for the next step without further purification. Yield 15.3 g (43.3 mmol, 96%; ^{1}H NMR (D_2O) δ=2.85—2.60 (m, 8H, CH_2), 2.19 (s, 3H, CH_3); ^{13}C NMR (D_2O) δ=47.3 (CH_2), 30.9 (CH_3); UV 454.4, 324.5 nm.

***trans*-$[CoCl(NH_2Me)(en)_2]Cl(ClO_4)$ (4).** 25 g of *trans*-$[Co(NO_2)(NH_2Me)(en)_2]Cl(NO_3)$ was added to 100 ml of concd HCl. The solution was heated on a steam bath with addition of 40 ml of concd HCl every half hour to prevent it from drying. After an hour and half, the solution was immediately cooled, and an organic solvent (1 : 1 mixture of ethanol and acetone) was added to precipitate the products. After washing with the above organic solvent and ether, crude *trans*-$[\mathrm{CoCl(NH_2Me)(en)_2]Cl_2}$ (**3**), 16.4 g, was obtained, which contained about 15% of the cis isomer.

Six g of the crude products were dissolved in 24 ml of water. To the solution was added sodium perchlorate by small portions until no further precipitation occured. Because the *trans*-$[\mathrm{CoCl(NH_2Me)(en)_2]Cl(ClO_4)}$ obtained contains a smaller amount of *trans*-$[\mathrm{CoCl_2(en)_2](ClO_4)}$, the products were dissolved in water acidified with $\mathrm{HClO_4}$ to pH 2. After filtration, the solution was concentrated by a vacuum technique at low temperature. The 1.5 g of crystals thus obtained had a good purity that was checked by ^{1}H NMR. ^{1}H NMR ($\mathrm{D_2O}$) $\delta=3.1$—2.8 (m, 8H, $\mathrm{C}H_2$), 1.89 (s, 3H, $\mathrm{C}H_3$); ^{13}C NMR ($\mathrm{D_2O}$) $\delta=47.3$ ($C\mathrm{H_2}$), 30.4 ($C\mathrm{H_3}$); UV 532.5, 470 (sh), 359.0 nm. Anal. Calcd for $\mathrm{C_5H_{21}Cl_3CoN_5O_4}$: C, 15.78; H, 5.56; N, 18.40%. Found: C, 15.85, H, 5.57. N, 18.60%.

X-Ray Structure Determination. Single crystals of *trans*-$[\mathrm{CoCl(NH_2Me)(en)_2]Cl(ClO_4)}$ (**4**) and *cis*-$[\mathrm{CoCl(NH_2Me)(en)_2]Cl_2}$ (**5**) were mounted on Rigaku AFC6 and MAC Science MXC3 diffractometers, respectively, and were irradiated with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ Å). The unit cell dimensions were obtained by least-squares from the angular settings of accurately centered 25 reflections with $20^\circ<2\theta<25^\circ$ and 20 reflections with $30^\circ<2\theta<35^\circ$ for the trans and the cis, respectively. The reflection intensities were recorded in the usual manner at 25 °C, and three check reflections measured after every 200 reflections showed no decrease in the intensity. $P2_1/c$ and $Fdd2$ were selected as space groups for the trans and the cis, respectively, which led to successful refinements.

The structures were solved by a direct method with the program Monte-Carlo Multan.[11] The positions of all hydrogen atoms for the trans could be located in the difference Fourier map and refined isotropically, but those for the cis were calculated by assuming idealized geometries and fixed in the refinements. Absorption and extinction corrections were then applied,[12,13] and several cycles of a full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms led to final R values of 0.043 and 0.057 for the trans and the cis respectively. All calculations were done on a Titan 750 computer using the program system CRYSTAN-GM.[14]

Kinetics of Aquation of *trans*-$[\mathrm{CoCl(NH_2Me)(en)_2]^{2+}}$. The process of the reaction was followed by measuring the increase in concentration of the free chloride ion.[2] A 0.05 M aqueous solution (1 M=1 mol dm^{-3}) was prepared by dissolving 1.25 mmol of *trans*-$[\mathrm{CoCl(NH_2Me)(en)_2]Cl(ClO_4)}$ into 0.1 M $\mathrm{HClO_4}$. The temperature was thermostatted at 20, 30, and 40±0.1 °C. The samples were withdrawn by a pipette at regular intervals and passed through a cooled column packed with a Dowex 50W $\mathrm{H^+}$ form by the immediate elution with cold water. After addition of the 5 ml of 0.05 M $\mathrm{AgNO_3}$ and Fe(III) indicator which was an acidic aqueous solution of potassium iron alum, the effluent and washings, which contained all the ionic chloride in the sample, were titrated with 0.02 M potassium thiocyanate. The data thus obtained were treated by a standard method. Because of the reverse reaction, that is, the anation reaction of the produced aqua complex with the free chloride anion, the plot of $\ln(V_\infty-V_t)$ vs. time, (V_∞=titration volume when the aquation would completely proceed), lost linearity after an initial period. Thus, the initial points, from 6 to 8 points, were used for the calculation of the rate constant.

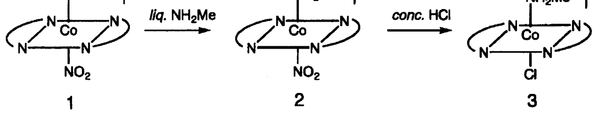
Results and Discussion

Preparation of *trans*-$[\mathrm{CoCl(NH_2Me)(en)_2]Cl(ClO_4)}$. A trans isomer of the corresponding ammine complex, *trans*-$[\mathrm{CoCl(NH_3)(en)_2]^{2+}}$ can be prepared from its aqua complex, *trans*-$[\mathrm{Co(OH_2)(NH_3)(en)_2]^{3+}}$ by an anation with a $\mathrm{Cl^-}$ anion.[8] The starting trans aqua complex is isolated by fractional crystallization from a mixture of *trans*- and *cis*-$[\mathrm{Co(OH_2)(NH_3)(en)_2]^{3+}}$, which are equilibrated in an alkaline solution prepared by an aquation of *cis*-$[\mathrm{CoCl(NH_3)(en)_2]^{2+}}$.[9] This route was first used to isolate the *trans*-$[\mathrm{Co(OH_2)(NH_2Me)(en)_2]^{3+}}$ with a *cis*-$[\mathrm{CoCl(NH_2Me)(en)_2]Cl_2}$ as a starting complex. The complex obtained, however, was only the cis isomer, *cis*-$[\mathrm{Co(OH_2)(NH_2Me)(en)_2]^{3+}}$. The reason for the result is considered to be a lower trans/cis ratio in the $[\mathrm{Co(OH_2)(NH_2Me)(en)_2]^{3+}}$ solution than that in the $[\mathrm{Co(OH_2)(NH_3)(en)_2]^{3+}}$ solution.

The *cis*-$[\mathrm{CoCl(NH_2Me)(en)_2]Cl_2}$ can be prepared readily by the route in Eq. 1, where *trans*-$[\mathrm{CoCl_2(en)_2]Cl}$ reacts with an aqueous aminomethane to produce the cis complex.[1—4)]

$$trans\text{-}[\mathrm{CoCl_2(en)_2]Cl} \xrightarrow{\mathrm{NH_2Me_{aq}}} cis\text{-}[\mathrm{CoCl(NH_2Me)(en)_2]Cl_2} \tag{1}$$

In this route, a trans configuration of the starting complex is changed to a cis configuration in the alkaline condition by the aminomethane. Thus, the key step is how to substitute a ligand with the aminomethane with the steric configuration retained. W. G. Jackson and A. M. Sargeson reported that stereomobility in the aquation reaction of *trans*-$[\mathrm{CoX(A)(en)_2]^{n+}}$ depends on the donation ability of the ligand A.[15] When the A is $\mathrm{CN^-}$, $\mathrm{NO_2^-}$, or $\mathrm{NH_3}$, the trans configuration is retained. L. G. Vanquickenborne and K. Pierloot interpreted these results theoretically by considering the activation energy of the steric change in a five-coordinate transition state.[16] Considering these reports, we finally succeeded in synthesizing the *trans*-$[\mathrm{CoCl(NH_2Me)(en)_2]^{2+}}$ by a route shown in Scheme 1. The ligands of the five coordinate intermediates in this route are composed of all strongly donating atoms to retain the configuration. At the first step, *trans*-$[\mathrm{CoCl(NO_2)(en)_2]^+}$ is refluxed with liquid $\mathrm{NH_2Me}$ at a low temperature. The red-orange suspension of the starting complex gradually changes to a yellow suspension of a product, *trans*-$[\mathrm{Co(NO_2)(NH_2Me)(en)_2]^{2+}}$. Chloride anion of **1** is substituted with a $\mathrm{NH_2Me}$ through $[\mathrm{Co(NO_2)(en)_2]^{2+}}$ intermediate with the configuration retained. At the second step,



Scheme 1.

the NO_2^- of **2** is removed under strongly acidic conditions, and is substituted with Cl^- anion through $[Co(NH_2Me)(en)_2]^{3+}$ intermediate. The trans configurations of **2** and **3** were confirmed with ^{13}C NMR. D. A. House and J. W. Blunt used ^{13}C NMR as a technic for distinguishing between *cis*- and *trans*-dianionobis(1,2-diaminoethane)cobalt(III) complexes.[17] They reported that the trans complex has a single signal for the four methylene carbons of the en ligands, whereas the cis has two or more signals. Since both **2** and **3** have a single signal at almost the same area, 47.3 ppm, trans configurations for both complexes were thus confirmed. **3** can be recrystallized as a chloride perchlorate salt, *trans*-$[CoCl(NH_2Me)(en)_2]Cl(ClO_4)$, which has a suitable size for X-ray crystal analysis.

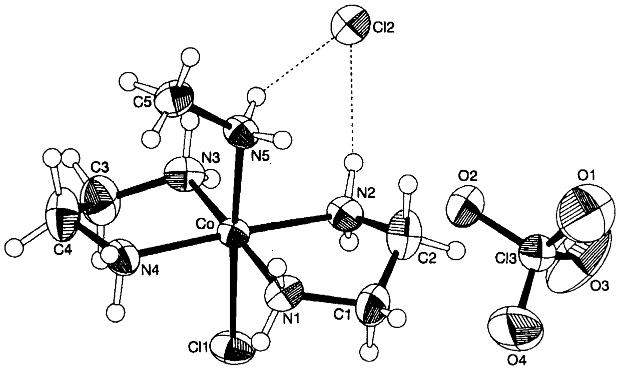


Fig. 1. ORTEP drawing of *trans*-$[CoCl(NH_2Me)(en)_2]Cl(ClO_4)$ (**4**) showing the atom labeling scheme and 50% probability thermal ellipsoids.

X-Ray Structure Analysis. Besides *trans*-$[CoCl(NH_2Me)(en)_2]Cl(ClO_4)$ (**4**), a chloride salt of the corresponding cis complex, *cis*-$[CoCl(NH_2Me)(en)_2]Cl_2$ (**5**), was also analyzed. Crystallographic data and refinement conditions are summarized in Table 1. Final atomic coordinates for both salts are given in Tables 2 and 3. Figures 1 and 2 show the respective molecular structures with atomic numbering schemes. A listing of selected bond distances and angles are given in Table 4.[18]

Descriptions of the Crystal Structures. In Fig. 1 it is shown that aminomethane and chloride anion are at the axial positions of the complex, as we expected. Both en ligands at the equatorial position

Table 1. Crystal Data, Experimental Conditions, and Refinement Details

Compound	**4**	**5**
Chemical formula	$C_5\ H_{21}\ Cl_3\ Co\ N_5\ O_4$	$C_5\ H_{21}\ Cl_3\ Co\ N_5$
Formula weight	383.50	316.50
Crystal size/mm^3	0.56×0.21×0.10	0.50×0.40×0.30
Unit-cell dimensions:		
a/Å	11.515 (1)	26.64 (1)
b/Å	7.421 (2)	27.26 (1)
c/Å	17.257 (1)	7.570 (2)
$\beta/^\circ$	99.220 (8)	
Volume of unit cell/$Å^3$	1455.5 (5)	5499 (3)
Crystal system	Monoclinic	Orthorhombic
Space group	$P\ 2_1/c$ (# 14)	$Fdd2$ (# 43)
Z value	4	16
Densities: D_{obsd}; D_{calcd}/g cm^{-3}	1.70; 1.75	1.50; 1.53
$F(000)$	784	2623
Linear absorption coefficient/cm^{-1}	16.48 (Mo $K\alpha$)	17.17 (Mo $K\alpha$)
Diffractometer used	Rigaku AFC-6	MAC Science MXC3
Radiation	Mo $K\alpha$	Mo $K\alpha$
λ/Å	0.71073	0.71073
Maximum $\sin\theta/\lambda$	0.650	0.651
Total reflections measured	3845	1811
Unique reflections	3351	1756
Internal consistency : R_{int}	0.02	0.00
Function minimized was	$\Sigma[w(\lvert F_o\rvert^2-\lvert F_c\rvert^2)^2]$ which $w=1.0/(\sigma\lvert F_o\rvert)^2$	$\Sigma[w(\lvert F_o\rvert^2-\lvert F_c\rvert^2)^2]$ which $w=1.0/(\sigma\lvert F_o\rvert)^2$
Reflections used ($F > 3.00(\sigma(F))$)	2744	1628
No. of variables	232	132
Residuals:	R; R_w 0.043; 0.035	R; R_w 0.057; 0.078
Goodness of fit: S	2.45	2.60
Maximum shift/ esd in final cycle	0.40	0.92
Maximum negative peak in final diff. map/e$Å^{-3}$	−0.55 (0.219 0.291 0.234)	−0.63 (0.138 0.178 0.332)
Maximum positive peak in final diff. map/e$Å^{-3}$	0.77 (−0.160 −0.254 −0.293)	1.39 (0.250 −0.250 0.026)

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (B_{eq}) of *trans*-$[CoCl(NH_2Me)(en)_2]Cl(ClO_4)$

Atom	x	y	z	B_{eq}[a) ($Å^2$)
Co	−2221.0 (4)	2270.5 (5)	89.4 (2)	2.12 (4)
Cl1	−633.7 (7)	2636 (1)	−543.7 (5)	3.54 (5)
Cl2	−3757.8 (7)	−2674 (1)	352.0 (5)	3.25 (5)
Cl3	−2628.4 (8)	−2875 (1)	−2400.6 (5)	3.32 (5)
O1	−3848 (3)	−3006 (6)	−2570 (2)	8.8 (2)
O2	−2258 (2)	−3012 (4)	−1569 (1)	4.36 (9)
O3	−2145 (4)	−4312 (5)	−2753 (2)	9.3 (2)
O4	−2258 (4)	−1224 (5)	−2659 (2)	8.3 (1)
N1	−3114 (3)	3940 (4)	−659 (2)	3.0 (1)
N2	−2793 (3)	395 (4)	−678 (2)	2.85 (9)
N3	−1306 (3)	592 (4)	818 (2)	3.0 (1)
N4	−1567 (3)	4168 (4)	828 (2)	2.9 (1)
N5	−3622 (2)	1834 (4)	591 (2)	2.59 (9)
C1	−3522 (4)	2993 (6)	−1422 (2)	4.0 (1)
C2	−3771 (4)	1083 (6)	−1267 (3)	4.2 (1)
C3	−380 (4)	1581 (6)	1334 (3)	4.5 (1)
C4	−859 (4)	3360 (7)	1542 (3)	4.5 (1)
C5	−3848 (4)	2769 (6)	1307 (2)	3.6 (1)

a) $B_{eq}=4/3\Sigma\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (B_{eq}) of *cis*-$[CoCl(NH_2Me)(en)_2]Cl_2$

Atom	x	y	z	B_{eq}[a) ($Å^2$)
Co	829.8 (4)	−1469.0 (3)	−4039.6	2.46 (5)
Cl1	1474.5 (9)	−1764.0 (9)	−5652 (5)	4.78 (8)
Cl2	−686 (3)	752 (1)	916 (5)	10.4 (2)
Cl3	−427.0 (8)	−2070.2 (7)	−1154 (4)	4.25 (8)
N1	1286 (3)	−1350 (3)	−2076 (13)	4.4 (2)
N2	702 (3)	−2099 (2)	−2958 (12)	3.6 (2)
N3	971 (3)	−820 (3)	−5018 (12)	3.7 (2)
N4	285 (2)	−1146 (2)	−2800 (11)	2.8 (2)
N5	415 (3)	−1652 (3)	−6112 (10)	3.4 (2)
C1	1329 (10)	−1800 (5)	−963 (32)	14 (1)
C2	971 (5)	−2115 (6)	−1240 (28)	8.7 (6)
C3	686 (5)	−451 (3)	−4067 (20)	6.1 (4)
C4	205 (4)	−642 (3)	−3544 (18)	4.7 (3)
C5	−164 (4)	−1665 (4)	−5988 (16)	4.8 (3)

a) $B_{eq}=4/3\Sigma\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

have normal bond distances and angles. On the other hand, a bond angle of Co–N5–C5 in the aminomethane moiety, 123.7(2) °, is significantly larger than the ideal tetrahedral angle 109.5 °. This distortion was usually observed for an aminoethane ligand coordinating to a metal in an octahedral complex. For example, 122.7 ° was reported for $[CoCl(NH_2Me)_5](NO_3)_2$.[19] This is explained by steric repulsion between the Me group and one of its cis ligands. Actually, in some less crowded complexes, for example *trans*-$[PtCl_2(NH_2Me)_2]$, the angle is 113.2 °, which is close to the regular value.[20] Since the Me group in Fig. 1 is above one of the en chelates, it makes steric repulsion with the chelate. The interatomic distances between the Me and the en are 2.01 and 2.07 Å for H5B(C5)···H4B(C4) and H5C(C5)···H44B(N4), respectively,[21] both of which are less than the sum of van der Waals radii, 2.40 Å.[22]

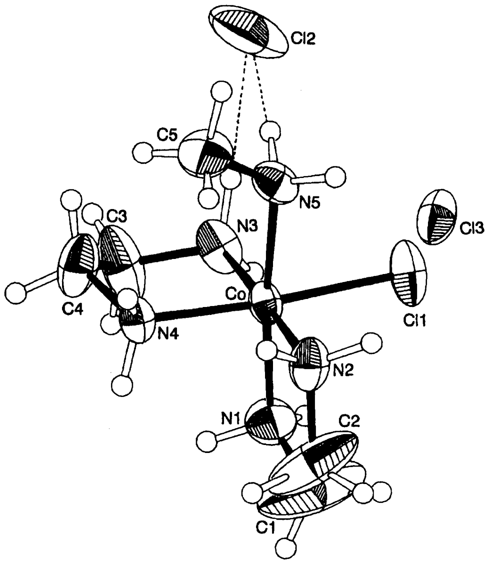


Fig. 2. ORTEP drawing of *cis*-$[CoCl(NH_2Me)(en)_2]Cl_2$ (**5**) showing the atom labeling scheme and 50% probability thermal ellipsoids.

To find why the Me–N bond takes such a crowded orientation, the hydrogen-bond network between the complex and the counter ions were examined, Table 5. One of the amino hydrogen atoms of the aminomethane makes a strong hydrogen bond with the chloride anion, N5–H55B····Cl2, which is shown by the broken line in Fig. 1. This chloride anion makes another hydrogen bond with an amino hydrogen atom of the equatorial en ligand in the same molecule, N2–H22B····Cl2. As the result, the chloride anion bridges the two amino groups with strong hydrogen bonds, and forces the methyl group of the aminomethane above the en chelates.

A molecular structure of *cis*-$[CoCl(NH_2Me)(en)_2]^{2+}$ is shown in Fig. 2. To our surprise, the aminomethane, one of the en ligands, and one of the two chloride counterions take a situation similar to that in Fig. 1. The chloride bridges the two amino groups by the strong hydrogen bonds, N5–H55B····Cl2 and N3–H33A···Cl2. The C5–N5 bond is forced to orient above the en chelate. Co–N5–C5 angle is opened considerably, 120.9(6) °, and the interatomic distances between the Me group and the en chelate are 2.01 and 2.16 Å for H5C(C5)···H4B(C4) and H5C(C5)···H44B(N4), respectively.[21] Other structural parameters are almost normal except for those around C1 and C2. These two methylene groups of the en ligand have extremely large thermal parameters because of a disorder in two puckering conformations of the en chelate ring. As the result, the C1–C2 bond length and N1–C1–C2 bond angle take artificial values, 1.30(3) Å and 118(2) °, respectively.

Steric Trans Influence in *trans*-$[CoCl(NH_2Me)(en)_2]^{2+}$. The Co–Cl bond length of the trans com-

Table 4. Selected Bond Distances and Angles of *trans*-$[CoCl(NH_2Me)(en)_2]Cl(ClO_4)$ and *cis*-$[CoCl(NH_2Me)(en)_2]Cl_2$

trans–$[CoCl(NH_2Me)(en)_2]Cl(ClO_4)$		*cis*–$[CoCl(NH_2Me)(en)_2]Cl_2$	
Bond distances (Å)			
Co–N1	1.958 (3)	Co–N1	1.948 (9)
Co–N2	1.961 (3)	Co–N2	1.933 (7)
Co–N3	1.953 (3)	Co–N3	1.955 (8)
Co–N4	1.967 (3)	Co–N4	1.940 (7)
Co–N5	1.977 (3)	Co–N5	1.984 (8)
Co–Cl1	2.291 (1)	Co–Cl1	2.255 (3)
Bond angles (°)			
N1–Co–N2	85.4 (1)	N1–Co–N2	86.2 (4)
N1–Co–N3	178.7 (2)	N1–Co–N3	91.1 (4)
N1–Co–N4	94.6 (1)	N1–Co–N4	91.3 (3)
N1–Co–N5	90.8 (1)	N1–Co–N5	173.6 (3)
N1–Co–Cl1	89.1 (1)	N1–Co–Cl1	89.8 (3)
N2–Co–N3	94.0 (1)	N2–Co–N3	177.1 (4)
N2–Co–N4	176.6 (1)	N2–Co–N4	93.8 (3)
N2–Co–N5	88.2 (1)	N2–Co–N5	90.8 (3)
N2–Co–Cl1	88.3 (1)	N2–Co–Cl1	92.6 (2)
N3–Co–N4	85.9 (1)	N3–Co–N4	85.2 (3)
N3–Co–N5	90.4 (1)	N3–Co–N5	92.0 (3)
N3–Co–Cl1	89.7 (1)	N3–Co–Cl1	88.4 (2)
N4–Co–N5	95.1 (1)	N4–Co–N5	94.5 (3)
N4–Co–Cl1	88.4 (1)	N4–Co–Cl1	173.5 (2)
N5–Co–Cl1	176.52 (9)	N5–Co–Cl1	84.7 (2)
Co–N1–C1	109.9 (2)	Co–N1–C1	110 (1)
Co–N2–C2	110.8 (2)	Co–N2–C2	108.1 (7)
Co–N3–C3	109.5 (2)	Co–N3–C3	109.8 (7)
Co–N4–C4	110.5 (2)	Co–N4–C4	109.9 (6)
Co–N5–C5	123.7 (2)	Co–N5–C5	120.9 (6)

Table 5. Hydrogen-Bond Distances of *trans*-$[CoCl(NH_2Me)(en)_2]Cl(ClO_4)$ and *cis*-$[CoCl(NH_2Me)(en)_2]Cl_2$
Hydrogen-Atom's Coordinates Used Were Those for Which an Ideal Bond Length and a Tetrahedral Angle are Assumed.

trans–$[CoCl(NH_2Me)(en)_2]Cl(ClO_4)$			*cis*–$[CoCl(NH_2Me)(en)_2]Cl_2$		
N1–H11A··O2	2.131	i)	N1–H11A··Cl2	2.290	vi)
N2–H22B··Cl2	2.205	ii)	N2–H22B··Cl3	2.372	vii)
N3–H33A··Cl1	2.479	iii)	N3–H33A··Cl2	2.178	viii)
N3–H33B··O3	2.054	iv)	N3–H33B··Cl3	2.342	ix)
N5–H55A··Cl2	2.276	v)	N4–H44A··Cl2	2.259	vi)
N5–H55B··Cl2	2.480	ii)	N5–H55B··Cl2	2.416	viii)

Symmetry operations; i): $x, y+1, z$; ii): x, y, z; iii): $-x, -y, -z$; iv): $x, -y-0.5, z$; v): $-x-1, -y, -z$; vi): $x, y, z+1$; vii) $-x+0.5, -y, z+0.5$; viii): x, y, z; ix): $-x+0.25, y+0.25, z+0.25$.

plex is 2.291(1) Å, which is slightly longer than that of the cis complex, 2.255(3) Å. Here, the reason of this elongation is discussed from the steric view-point.

In the trans complex, the methyl group of the aminomethane makes a steric repulsion with one of the two equatorial en chelates. Because of this repulsion, the C3 and C4 of the en chelates are pushed by the Me group toward the chloride ligand. In Fig. 3 is shown deviations from the least-squares plane, which is defined by the four equatorial donor atoms, N1, N2, N3, and N4 for the trans complex (Fig. 3a), and Cl1, N2, N3, and N4 for the cis complex (Fig. 3b). The right chelate in Fig. 3a does not suffer a steric repulsion; the methylene carbons, C1 and C2 have almost symmetric deviations, −0.280 and 0.298 Å, respectively. At the left chelate, the C4 takes a small positive value 0.080 Å, and the C3 takes a large negative value, −0.466 Å. These values indicate that this ethylene chain goes down from the plane. As a result, the ethylene group approaches the chloride ligand, and makes steric repulsion with it. Actually, the interatomic distance is 2.84 Å for H3B(C3)···Cl1, which is less than the sum of van der Waals

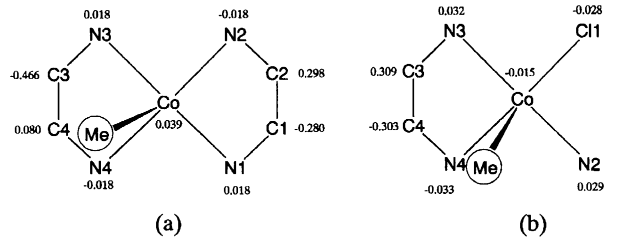


Fig. 3. Deviations from the least-squares plane defined by the four equatorial donor atoms for **4** (a) and **5** (b). Positive value denotes an atom up the paper plane.

radii, 2.95 Å, while the distance from the other chelate is 3.07 Å for H1B(C1)···Cl1.[22] In this manner, the aminomethane has a steric effect on the chloride ligand at the trans position through the flexible equatorial en ligand.

The methyl group in **5** also makes steric repulsion with one of the en rings. The ethylene group of the chelate, however, does not deviate from the regular position, because the methyl group is not on the flexible ethylene group but slightly outside the N4 atom. In any case, such a situation does not have any effect on the geometrically distant Co–Cl bond. Thus, the steric effect exerted by the aminomethane contributes to the observed lengthening in the trans complex. Such effect may be an example called as a steric trans influence. L. G. Marzilli et al. have widely reviewed the structural properties of organocobalt coenzyme B_{12} models, that is, *trans*-$[CoR(DH)_2L]$, R=alkyl, DH=dimethylglyoxime, and L=phosphorus or amino ligand.[23] They reported that a slight but significant increase of the Co–R bond was observed when a phosphorus ligand was changed. They attributed the lengthening to the steric trans influence exerted by L on the trans Co–R bond through the equatorial ligands, although an electronic trans influence may also play a role. A report of such a steric trans influence in the octahedral complexes, however, is very rare compared to many reports of an electronic trans influence, which is frequently observed in cobalt(III) complexes containing SO_3^{2-}, $S_2O_3^{2-}$, NO_2^-,[24,25] and phosphorus ligands.[26]

Since the observed elongation of the Co–Cl bond in the crystal is only 0.036 Å, a question has been raised whether this bond is actually weakened in solution or not. The methyl group of the trans complex takes the sterically crowded position by the counter anion in the crystal. In aqueous solution, however, it is considered that the Co–NH_2Me bond rotates freely because the counter anion dissociates from the complex. Therefore, the methyl group may take the less crowded position like that is shown in Fig. 3b. In such a case, the two methylene groups of each en ligand in the trans complex symmetrically deviate up and down from the equatorial plane. The steric trans influence is not expected in such a situation. So, we have measured the aquation rate of the trans complex to make this point clear by the comparison with those of the relevant complexes.[5] The rates are given in Table 6. The rate of the trans complex is seven times faster than that of the cis complex. This suggests that the steric effect of the methyl group is not lost in the solution. In addition, the rate of *trans*-$[CoCl(NH_3)(en)_2]^{2+}$ is similar to that of the cis complex.[5] This is reasonable because the *trans*-$[CoCl(NH_3)(en)_2]^{2+}$ can be regarded as the analog of the *trans*-$[CoCl(NH_2Me)(en)_2]^{2+}$ without the methyl group. Therefore it is considered that when the Co–NH_2Me bond rotates, the methyl group passes above the en chelates to make the steric trans influence. This is why the Co–Cl bond of the trans complex cleaves more readily.

Finally, relative stability between *trans*- and *cis*-$[CoCl(NH_2Me)(en)_2]^{2+}$ is discussed. When the trans isomer was heated by 60 °C in 6 M HCl solution for 25 h, the UV spectra of the solution became almost similar to that of the solution containing the cis isomer only. In addition to this result, an isomerization reaction was examined using corresponding aqua complexes, *trans*- and *cis*-$[Co(OH_2)(NH_2Me)(en)_2]^{3+}$. The chloride ligand of the trans or the cis complex could be removed immediately by $Hg(NO_3)_2$ to produce the corresponding aqua complexes with the configuration retained.[15,27] The isomerization of the trans aqua complex to the cis was monitored by the ^1H NMR signal of the methyl group. Thirty-eight % of *trans*-$[Co(OH_2)(NH_2Me)(en)_2]^{3+}$ changes to the cis isomer at pH 1 and 50 °C after 17 h. When the experiment was done under the same conditions using *cis*-$[Co(OH_2)(NH_2Me)(en)_2]^{3+}$, the isomerized amount was less than 5%. These results indicate the instability of the trans configuration compared to the cis configuration. In general, these kinds of isomerization occur in the five coor-

Table 6. Kinetic Parameters for the Aquation of Some $[CoCl(NH_2R)(en)_2]^{2+}$ Complexes

Complex	$k_{298.2}/s^{-1}$	$\Delta H^{\#}_{298.2}$	$\Delta S^{\#}_{298.2}$	Ref.
		$kJ\,mol^{-1}$	$J\,mol^{-1}\,K^{-1}$	
trans−$[CoCl(NH_2Me)(en)_2]^{2+}$	24×10^{-7}	92	−44	This work
cis−$[CoCl(NH_2Me)(en)_2]^{2+}$	2.9×10^{-7}	94	−47	5
trans−$[CoCl(NH_3)(en)_2]^{2+}$	3.5×10^{-7}	100	−33	5
cis−$[CoCl(NH_3)(en)_2]^{2+}$	4.2×10^{-7}	98	−39	5

dinate intermediate, [15,16] $[Co(NH_2Me)(en)_2]^{3+}$, which is generated by the dissociation of the chloride ligand or the aqua ligand. In the five coordinate species, the above-mentioned steric repulsion between the aminomethane and the en operates as a major factor that governs the stability. When the aminomethane ligand rotates around the Co–NH_2Me bond, the methyl group suffers steric repulsion from the en ligands in the trans configuration. On the other hand, in the cis configuration, only one en chelate can possibly cause such steric repulsion. Thus, the cis configuration is more stable than the trans configuration. In addition, because the Co–Cl bond of the *trans*-$[CoCl(NH_2Me)(en)_2]^{2+}$ cleaves more readily, the trans complex is prone to be the five coordinate species compared to the cis isomer. This kinetic effect also contributes to the isomerization from the trans to the cis.

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