Remarkable Effect of *C*-Methyl Substitutions on the Ligand Field Strength of a Cobalt(III) Complex Containing a Cyclic Tetraamine with a Folded *cis*-Type Configuration

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Cobalt(III) complexes containing an optically active 14-membered cyclic tetraamine (*R,R*-Me_6[14]$aneN_4$, 7(*R*), 14(*R*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and a bidentate ligand (glycinato, *S*-alaninato, or oxalato), in which the tetraamine takes the folded *cis*-type configuration, were prepared and characterized by elementary analyses, ^1H and ^{13}C NMR spectroscopy, and circular dichroism spectroscopy. Electronic absorption and ^{59}Co NMR spectroscopies indicate that stereochemical modification of the 14-membered cyclic ligand with *C*-methyl groups causes an unusual decrease in the ligand field strength of the complex. Rapid dissociation of the chelated alaninato ligand from the cobalt(III) complex, which is generally inert, was observed for the [Co(*S*-alaninato)(*R,R*-Me_6[14]$aneN_4$)]$^{2+}$ complex system. The dependence of the dissociation of the alaninato chelate on the ligand field strength is strongly suggested.

Regulation of the reactivity of transition metal complexes is an important subject in particular in designing highly specific catalysts. Because many physical properties of transition metal complexes are related to the ligand field, it is important to elucidate the effect of modification of the ligand on the ligand field strength of a complex.

We previously reported that stereochemical modification of the ligand can affect the ligand field strength of a cobalt(III) complex considerably.[1] *C*- or *N*-methyl substitutions on the tetraamine ligand in the [Co(alaninato)(tetraamine)]$^{2+}$ system, where tetraamine is a linear tetraamine of the 2,3,2- or 3,2,3-tet type,[2] caused a decrease in the ligand field strength due to the formation of a hindered structure. Because the conformation of the cyclic tetraamine is more rigid than that of linear tetraamines, methyl substitutions on the cyclic tetraamine are expected to exert larger stereochemical effects than those on the linear tetraamines. In the present study, we have chosen a cyclic tetraamine with a 14-membered ring, because it involves both the 2,3,2-tet and 3,2,3-tet units.

A great many complexes containing [14]$aneN_4$[2] (cyclam) or its *C*-methyl derivative have been prepared and their properties have been thoroughly studied.[3] However, in most cases, the tetraamines have planar *trans*-type configurations. Although preparations of some *cis*-type complexes involving [14]$aneN_4$[4,5] and its *C*-methyl derivative[6—9] have been reported, their properties and reactivities have not been sufficiently studied.[9,10]

In the present study, cobalt(III) complexes containing an optically active cyclic tetraamine, *R,R*-Me_6[14]-$aneN_4$,[2] and a bidentate ligand (glycinato, *S*-alaninato, or oxalato) were prepared and the stereochemistry of the *cis*-type coordination of *R,R*-Me_6[14]$aneN_4$ was investigated. The effect of *C*-methyl substitutions of the cyclic tetraamine on the ligand field strength and on the dissociation of the chelated alaninato ligand is elucidated.

Experimental

Preparations. [Co(gly)(*R,R*-Me_6[14]$aneN_4$)]$(ClO_4)_2$ (1a and 1b). To an aqueous solution of *trans*-[$CoCl_2$(*R,R*-Me_6[14]$aneN_4$)]ClO_4 (1.03 g, 2.0 mmol) (prepared by the reported procedures[11] except that the tetraamine used was *R,R*-Me_6[14]$aneN_4$[12] instead of *rac*-Me_6[14]$aneN_4$), glycine (0.18 g, 2.4 mmol) was added, and the pH of the solution was adjusted to 6.5 with NaOH. The mixture was stirred at 50 °C for 2 h, then poured onto an SP-Sephadex C-25 column (Na^+ form, 700 mm×40 mm o.d.). Elution with 0.1 M (1 M=1 mol dm^{-3}) $NaClO_4$ produced two violet bands (**1a** and **1b**) eluting in this order. Concentration of each eluate from the main bands gave microcrystals. Found for **1a**: C, 32.78; H, 6.53; N, 10.61%. Calcd for $Co(C_2H_4NO_2)(C_{16}H_{36}N_4)(ClO_4)_2 \cdot 2H_2O$: C, 33.14; H, 6.80; N, 10.73%. Found for **1b**: C, 35.18; H, 6.71; N, 10.80%. Calcd for $Co(C_2H_4NO_2)(C_{16}H_{36}N_4)(ClO_4)_2$: C, 35.08; H, 6.54; N, 11.36%.

When the pH of the reaction mixture is higher than 7, a considerable amount of [$Co(CO_3)$(Me_6[14]$aneN_4$)]ClO_4 (**4**) is formed by the facile uptake of dissolved carbon dioxide.[13] Its formation is remarkably suppressed by careful adjustment of the reaction mixture to keep the pH below 7.

[Co(*S*-ala)(*R,R*-Me_6[14]$aneN_4$)]$(ClO_4)_2$ (2a and 2b). These complexes were prepared from *trans*-[$CoCl_2$(*R,R*-Me_6[14]$aneN_4$)]ClO_4 and *S*-alanine by procedures similar to those described above. Development of the column produced two violet bands (**2a** and **2b**) and a minor orange band (**2c**) eluting in this order. Concentration of each eluate from the main bands gave microcrystals. Found for **2a**: C, 34.99; H, 6.55; N, 10.76%. Calcd for

$Co(C_3H_6NO_2)(C_{16}H_{36}N_4)(ClO_4)_2 \cdot H_2O$: C, 35.19; H, 6.78; N, 10.80%. Found for **2b**: C, 35.47; H, 6.35; N, 10.93%. Calcd for $[Co(C_3H_6NO_2)(C_{16}H_{36}N_4)](ClO_4)_2 \cdot 0.5H_2O$: C, 35.69; H, 6.72; N, 10.95%. **2c** is an alaninato–Co(III) complex involving a tetraamine, which is generated from *R,R*-Me_6[14]aneN$_4$ by oxidation; its details will be reported elsewhere.

[Co(C_2O_4)(*R,R*-Me_6[14]aneN$_4$)]ClO_4 (3a and 3b). To an aqueous solution of $K_3[Co(C_2O_4)_3]$,[14] a methanol solution of *R,R*-Me_6[14]aneN$_4$ was added and stirred for 1 h at ca. 40 °C in the presence of activated carbon. The solution was filtered and the filtrate was poured onto an SP-Sephadex C-25 column. Elution with 0.02 M NaCl produced two violet bands (**3a** and **3b**) eluting in this order. The eluate from each band was concentrated, and addition of $NaClO_4$ gave microcrystals, which were collected by filtration, then air dried. Found for **3a**: C, 39.33; H, 6.59; N, 10.23; Cl, 6.41%. Calcd for $Co(C_2O_4)(C_{16}H_{36}N_4)ClO_4 \cdot H_2O$: C, 39.39; H, 6.98; N, 10.21; Cl, 6.46%. Found for **3b**: C, 38.88; H, 7.47; N, 10.02; Cl, 6.52%. Calcd for $Co(C_2O_4)(C_{16}H_{36}N_4)$-$ClO_4 \cdot 1.5H_2O$: C, 38.77; H, 7.05; N, 10.05; Cl, 6.36%.

[Co(CO_3)(*rac*-Me_6[14]aneN$_4$)]Cl (4a and 4b). To an aqueous solution of $K_3[Co(CO_3)_3]$,[15] a methanol solution of *rac*-Me_6[14]aneN$_4$ was added and stirred for 1 h at ca. 40 °C in the presence of activated carbon. The solution was filtered and then poured onto an SP-Sephadex C-25 column. Elution with 0.02 M NaCl produced two violet bands (**4a** and **4b**) eluting in this order. Concentration of the eluate from each band gave microcrystals, which were collected by filtration, then air dried. Found for **4a**: C, 46.47; H, 8.19; N, 12.66%. Calcd for $Co(CO_3)(C_{16}H_{36}N_4)Cl$: C, 46.52; H, 8.27; N, 12.77%. Found for **4b**: C, 45.06; H, 8.05; N, 12.36%. Calcd for $Co(CO_3)(C_{16}H_{36}N_4)Cl \cdot H_2O$: C, 44.69; H, 8.38; N, 12.26%.

[Co(gly)([14]aneN$_4$)](ClO_4)$_2$ (5). To an aqueous solution of *cis*-$[CoCl_2$([14]aneN$_4$)]Cl[5] (0.73 g, 2.0 mmol), glycine (0.18 g, 2.4 mmol) was added and the pH of the solution was adjusted to 8.0. The mixture was stirred at 50 °C for 2 h, then poured onto an SP-Sephadex C-25 column (Na^+ form, 700 mm×40 mm o.d.). Elution with 0.1 M $NaClO_4$ produced a red band (**5**) and a violet band (**6**). Concentration of each eluate gave microcrystals, which were collected by filtration. Found for **5**: C, 34.83; H, 6.88; N, 17.16%. Calcd for $Co(C_2H_4NO_2)(C_{10}H_{24}N_4)Cl_2 \cdot 0.5H_2O$: C, 34.88; H, 7.07; N, 16.95%. Electronic absorption spectrum: $\nu/10^3$ cm^{-1} (H_2O) 19.6 (log (ε/mol^{-1} dm^3 cm^{-1}) 1.22), 27.8 (1.22), and 42.0 (4.37).

6 is a *trans*-type complex (*trans*-$[Co(glyH)_2$([14]aneN$_4$)]$(ClO_4)_3$[16]) in which two glycinato ligands coordinate with carboxyl oxygens in the apical positions. Electronic absorption spectrum: $\nu/10^3$ cm^{-1} (H_2O) 18.0 (log (ε/mol^{-1} dm^3 cm^{-1}) 1.67), 22.7 (1.64), 27.2 (1.97), and 42.7 (4.38).

The complex [Co(*S*-ala) ([14]aneN$_4$)]$(ClO_4)_2$ **7**[4] was prepared by similar procedures as above by using *S*-alanine instead of glycine.

Measurements. Electronic absorption (AB) spectra were recorded on a Shimadzu UV-160 spectrophotometer. Circular dichroism (CD) spectra were obtained on a JASCO J-500A spectropolarimeter. These measurements were made on aqueous solutions at concentrations near 2×10^{-3} mol dm^{-3}.

^{1}H NMR (400 MHz) spectra were obtained on a JEOL GX-400 in D_2O. Sodium 3-(trimethylsilyl)propanesulfonate was used as an internal standard. ^{13}C NMR (67.9 MHz) spectra were obtained on a JEOL EX-270 in D_2O. 1,4-Dioxane was used as an internal standard (67.4 ppm). ^{59}Co NMR (95 MHz) spectra were obtained on a JEOL GX-400 at a concentration of 0.2 mol dm^{-3} in D_2O at 22 °C. The observations were performed using 10 mm o.d. sample tubes. A saturated D_2O solution of $K_3[Co(CN)_6]$ was used as an external standard.

The reactions of the alaninato complexes (**2a**, **2b**, or **7**) in 0.1 mol dm^{-3} Na_2CO_3 (pH 11.0) aqueous solutions were followed by measuring the absorbance at the absorption maxima about 550 nm, which showed pseudo first-order kinetics.

Results and Discussion

Preparations and Structural Assignments. Cobalt(III) complexes involving an optically active 14-membered cyclic tetraamine, *R,R*-Me_6[14]aneN$_4$, and a bidentate ligand could be prepared by procedures similar to those for analogous complexes involving a linear tetraamine[1,17,18] rather than *R,R*-Me_6[14]aneN$_4$. The complexes involving glycinato or *S*-alaninato as a bidentate ligand ([Co(gly)(*R,R*-Me_6[14]aneN$_4$)]$^{2+}$ **1** or [Co(*S*-ala)(*R,R*-Me_6[14]aneN$_4$)]$^{2+}$ **2**) were prepared by treating *trans*-$[CoCl_2$(*R,R*-Me_6[14]aneN$_4$)]$^+$ with amino acids in aqueous solutions at pH 6.5. For the preparation of [Co(C_2O_4)(*R,R*-Me_6[14]aneN$_4$)]$^+$ **3** or [Co(CO_3)(Me_6[14]aneN$_4$)]$^+$ **4**, [Co(C_2O_4)$_3$]$^{3-}$ or [Co-(CO_3)$_3$]$^{3-}$ was used as a starting material, respectively, and the cyclic tetraamine was introduced to the complex by treatment in aqueous–methanol solutions.

Two stereoisomers were obtained for each complex system, which could be separated by using cation exchange column chromatography. The AB and CD spectra of **1a**, **1b**, **2a**, **2b**, **3a**, and **3b** are shown in Fig. 1. The two isomers of each complex system show nearly inverted CD patterns, and can be classified into two groups. The first isomers eluting faster from the cation exchange column (group **a**; **1a**, **2a**, and **3a**) show negative and positive Cotton effects from lower energy in the first d–d absorption region. The second isomers (group **b**; **1b**, **2b**, and **3b**), however, show positive and negative Cotton effects from lower energy in the same region.

^{13}C NMR chemical shifts, which are listed in Table 1, also show similarities for the members in each group. The ^{13}C chemical shifts of the tetraamine part in the group **a** complexes are very close to each other; the maximum deviation of the signals for corresponding carbons is 1.7 ppm. Similarly, the ^{13}C chemical shifts of the tetraamine part in the group **b** complexes are very similar to each other. However, the shifts between the two groups are apparently different from each other. Simple ^{13}C NMR spectra for **3a**, **3b**, **4a**, and **4b** indicate that the tetraamine ligands coordinate with C_2 symmetries in these complexes. In contrast, the corresponding signals for the cyclic tetraamine moiety split slightly into

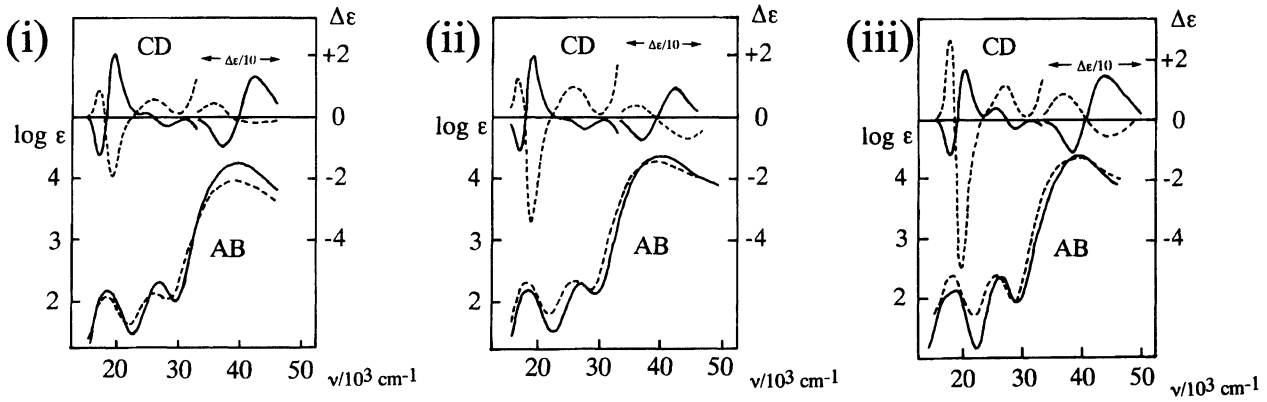

Fig. 1. Electronic absorption (AB) and circular dichroism (CD) spectra of (i) **1a** (—) and **1b** (---), (ii) **2a** (—) and **2b** (---), (iii) **3a** (—) and **3b** (---).

Table 1. ^{13}C NMR Spectral Data

	Tetraamine								Bidentate ligand			
No.	>C<	>CH–	–CH_2–			–CH_3			>C=O	>CH–	–CH_2–	–CH_3
1a	59.8 58.8	48.8 48.2	47.8 47.7	44.2 42.8	42.8 42.5	30.0 29.2	24.0 22.9	19.7 19.5	185.3		45.6	
2a	59.9 58.7	48.5 48.3	47.5 47.4	44.1 43.0	42.8 42.6	30.2 29.0	24.1 22.5	19.8 19.4	185.2	53.6		18.5
3a	58.2	48.7	47.3	43.8	43.1	29.1	22.6	19.4	169.1			
4a	58.8	48.0	47.6	43.4	43.1	29.2	23.5	19.2	169.1			
1b	57.1 56.5	53.4 52.7	52.0 51.5	49.1 47.4	42.8 42.0	29.8 29.7	26.2 25.5	20.4 20.1	185.1		46.0	
2b	57.1 56.9	53.4 52.6	52.1 51.6	49.4 47.3	43.0 42.2	30.0 29.4	26.0 26.0	20.6 20.3	186.0	54.7		18.6
3b	56.4	53.4	51.6	48.0	43.3	29.1	25.6	19.9	167.6			
4b	56.7	52.5	51.5	48.2	42.9	29.3	26.3	19.9	169.5			

Chemical shifts (ppm) are given in reference to internal 1,4-dioxane (67.4 ppm).

two signals in **1a**, **1b**, **2a**, and **2b**, because of the loss of the C_2 symmetries due to the chelation of the amino acidato ligands.

Table 2 lists the ^{1}H NMR spectral data for the methylene protons of the glycinato ligand in **1a** and **1b**, along with the data for the glycinato-[14]aneN$_4$–cobalt(III) complex system, *cis*-[Co(gly)([14]aneN$_4$)]$^{2+}$ (**5**) and *trans*-[Co(glyH)$_2$([14]aneN$_4$)]$^{3+}$ (**6**). The methylene protons of the unidentate glycinato in **6** are observed as a singlet and those of the bidentate one in **5** give the AB pattern. The methylene protons of the glycinato in **1a** and **1b** are observed as AB patterns. Therefore, the glycinato ligand undoubtedly coordinates bidentedly both in **1a** and **1b**. The larger $\Delta\delta$ values ($\Delta\delta = |\delta_{H_A} - \delta_{H_B}|$) for **1a** and **1b** than that for **5** represent the effect of *C*-methyl substitutions in the tetraamine part, which provide different environments around two sides of the glycinato chelate plane. On the basis of these observations, it can be concluded that all complexes (**1a**—**4a** and **1b**—**4b**) involve chelated bidentate ligands, and thus the tetraamine takes two *cis*-type configurations.

Table 2. ^{1}H NMR (400 MHz) Spectral Data for the CH_2 Signals of the Glycinato Ligand in *cis*-[Co(glycinato)(tetraamine)]$^{2+}$

Tetraamine		Pattern	δ/ppm[a]	$\Delta\delta$/Hz[b]	J/Hz
R,*R*-Me$_6$[14]aneN$_4$	(**1a**)	AB	3.48	52.3	17.9
R,*R*-Me$_6$[14]aneN$_4$	(**1b**)	AB	3.63	61.4	18.1
[14]aneN$_4$	(**5**)	AB	3.59	17.2	17.5
[14]aneN$_4$[c]	(**6**)	Singlet	3.55		

a) The mean value of δ_{H_A} and δ_{H_B} for the AB pattern signals. b) $\Delta\delta = |\delta_{H_A} - \delta_{H_B}|$. c) *trans*-[Co(glyH)$_2$([14]aneN$_4$)]$^{3+}$.[16]

For the *cis*-type coordination of *R*,*R*-Me$_6$[14]aneN$_4$, two stereoisomers have been predicted (Fig. 2).[7a] However, only one of these geometries ((i) in Fig. 2) have been found for Ni(II),[7,12] Co(II),[8] and Cr(III)[9] complexes. The two stereoisomers obtained in the present study can be assigned to (i) and (ii) in Fig. 2. This is strongly supported by the CD spectra, which indicate that the two isomers are nearly mirror images of each other. The absolute configurations are tentatively assigned in analogy to the analogous complexes involving the unsubstituted cyclic tetraamine.[4] The complexes in group **a** are expected to take Δ_5 configurations, whereas those in group **b** are expected to take Λ_5 configurations. Δ_5 and Λ_5 represent absolute configurations around the cobalt center defined by the two five-membered chelate rings of the cyclic tetraamine part. These assignments should be confirmed by the X-ray crystallographic study. The proposed structures for the complexes are shown in Fig. 3.

Table 3. Absorption and ^{59}Co NMR (95 MHz) Spectral Data of the [Co(alaninato)(tetraamine)]$^{2+}$ Complexes and Pseudo First-Order Rate Constants for the Dissociation of the Chelated Alaninato Ligand from the Complex at pH 11.0, 30 °C

Tetraamine		Absorption maxima λ/nm		^{59}Co chemical shift δ/ppm	^{59}Co line width $\Delta\nu$/Hz	Rate constant $k/10^{-4}$ s^{-1}
R,*R*-Me$_6$[14]aneN$_4$	(**2a**)	543	373	9337	4300	90
R,*R*-Me$_6$[14]aneN$_4$	(**2b**)	556	388	9666	4800	90
[14]aneN$_4$	(**7**)	512	360	8337	2300	1.6
1,5*R*,7*R*,11-Me$_4$-2,3,2-tet	(**8**)[1)]	514	367	8615	3000	2

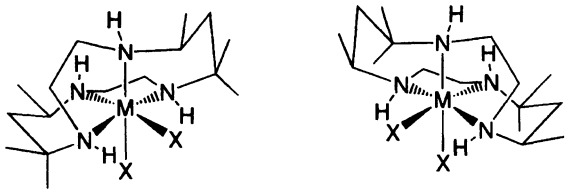

Fig. 2. Two possible stereoisomers of the *R*,*R*-Me$_6$[14]aneN$_4$ ligand with the *cis*-type configuration.[7a)] Δ_5 and Λ_5 represent absolute configurations around the cobalt center defined by the two five-membered chelate rings of the cyclic tetraamine part. *R* and *S* in parentheses represent absolute configurations of the coordinated nitrogen atoms. X_2 is one bidentate or two unidentate ligands.

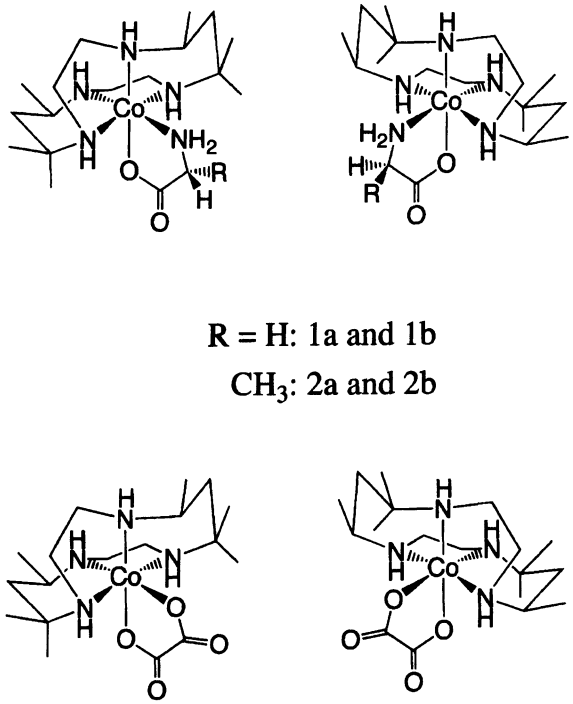

Fig. 3. Proposed stereochemistries of the complexes.

It is worth noting that the electronic absorption spectra of **3a** and **4a** have a very characteristic shape. Numerous studies indicate that cobalt(III) complexes with *trans*-N_4O_2 geometry show splitting of the first d–d absorption peak, whereas those with *cis*-N_4O_2 type geometry show no splitting. Such a difference in the shape of the absorption peak has been regarded as empirical evidence for the assignment of the coordination geometry.[17,19—21)] Although the above results indicate that **3a** and **4a** have *cis*-N_4O_2-type geometries, a shoulder appears in the lower energy region of the first d–d absorption peak in both spectra. However, the shoulders are clearly different from those for complexes with *trans*-N_4O_2 geometry, whose absorption spectra show a shoulder in the higher energy region of the first d–d absorption peak. The shoulders in the AB spectra of **3a** and **4a** indicate that the two components in the first d–d transition have a larger separation than usual, presumably due to the unusual electronic property of the complexes.

Effect of *C*-Methyl Substitutions on the Ligand Field Strength of the Complex. Table 3 lists the electronic absorption and ^{59}Co NMR spectroscopic data for [Co(*S*-ala)(tetraamine)]$^{2+}$. The absorption maxima of **2a** and **2b** are remarkably shifted to lower energy compared with those of **7** due to *C*-methyl substitutions on the cyclic tetraamine ligand. The first absorption maximum is shifted from 512 nm for **7** to 543 and 556 nm for **2a** and **2b**, respectively. The effect of stereochemical modification of the tetraamine ligand is larger than that observed for the analogous complex system involving a linear tetraamine, for which the absorption maximum is shifted from 492 nm to 514 nm.[1)]

The effect of *C*-methyl substitutions is also observed in the ^{59}Co NMR chemical shift. It is known that the ^{59}Co NMR chemical shift is related to the d–d transition energy of the complex.[22,23)] Our previous study indicated that this kind of correlation stands for a series *R*-alaninato–cobalt(III) complexes involving a linear tetraamine, which spans a relatively small range.[1)] The ^{59}Co NMR chemical shifts of **2a** and **2b** are remarkably larger than that of **7**.

These results indicate that the ligand field of **2** is unusually weak, and the ligand field strength of a complex is more effectively regulated by stereochemical modification of a 14-membered cyclic ligand than a linear one.

The line width of the ^{59}Co resonance is also characteristic. The widths at half-height of the ^{59}Co resonance for **2a** and **2b** are 4300 and 4800 Hz, respectively, which are considerably larger than that for **7** (2300 Hz). It is generally accepted that the line width of the ^{59}Co signal mainly depends on quadrupolar relaxation, and the dominant factor which affects the line width is the symmetry of the configuration of the electrons around Co.[23,24] The very large line widths observed for **2a** and **2b** suggest that stereochemical modification with *C*-methyl substitutions causes distortion of the regular octahedral geometry around Co.

Dissociation of the Chelated Alaninato Ligand from the Complex. The coordination of the chelated amino acidato ligand on cobalt(III) is generally so stable that racemization of amino acidato occurs without dissociation under basic conditions.[25] In previous studies, we have reported that the dissociation of the chelated alaninato ligand occurs readily for the alaninato–cobalt(III) complex involving a methyl-substituted linear tetraamine under mild basic conditions.[1,18] In order to elucidate whether such a reaction is observed for the complexes involving the cyclic tetraamine, the following experiment was conducted.

2a was treated in a D_2O solution of 0.1 M carbonate buffer (pD=10) at 30 °C for 30 min. ^1H NMR spectroscopy after separation of the reaction mixture using an SP-Sephadex C-25 column (Na^+ form) indicated that the reaction gives a carbonato complex (**4**) and free alanine. The reaction is almost quantitative. No deuterium replacement of the α-proton of alanine was observed, suggesting that racemization does not occur during the reaction.

The pseudo first-order rate constants at pH=11.0, 30 °C are listed in Table 3. The rate constants for **2a** and **2b** are fairly larger than that for **7**, and larger than that for the analogous complex containing a methyl-substituted linear tetraamine, $[Co(R\text{-ala})(1,5R,7R,11\text{-}Me_4\text{-}2,3,2\text{-tet}^{2)})]^{2+}$ (**8**).[1] It is apparent that the dissociation of the alaninato ligand depends on the ligand field strength of the complex. The dissociation occurs more readily for the complex with the weaker ligand field. This result indicates that the ligand exchange reaction of the generally inert chelate can be controlled by suitable design of the ligand field of the complex. This information will be important in designing catalytic reactions using metal complexes.

Conclusion

Cobalt(III) complexes involving a methyl-substituted 14-membered cyclic tetraamine, *R,R*-Me_6[14]$aneN_4$, and a bidentate ligand, in which the tetraamine takes the *cis*-type configuration, were prepared and found to form two stereoisomers. Their ligand field strengths are unusually weak compared with analogous complexes involving the unsubstituted cyclic tetraamine, [14]$aneN_4$, instead of *R,R*-Me_6[14]$aneN_4$. The very large ^{59}Co NMR line width for $[Co(S\text{-alaninato})(R,R,\text{-}Me_6[14]aneN_4)]^{2+}$ indicates distortion of the electronic structure from the usual octahedral geometry. Thus, stereochemical modification of the cyclic tetraamine ligand is effective for the regulation of the ligand strength and of the reactivities of the transition metal complexes.[9,10]

References

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2) The following abbreviations for the tetraamine ligands are used. 2,3,2-tet: 3,7-diaza-1,9-diaminononane, 3,2,3-tet: 4,7-diaza-1,10-diaminodecane, [14]$aneN_4$: 1,4,8,11-tetraazacyclotetradecane, *R,R*-Me_6[14]$aneN_4$: 7(*R*),14(*R*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, 1,5*R*,7*R*-Me_4-2,3,2-tet: 6(*R*),8(*R*)-6,8-dimethyl-2,5,9,12-tetraazatridecane.

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