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Steric Effects of Axial Methyl Substituents on Axial Coordination of Macrocyclic Nickel(II) and Cobalt(III) Complexes

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The nickel(II) complex with L^1 (5,5,7-trimethylcyclam: 5,5,7-trimethyl-1,4,8,11-tetrazacyclotetradecane), *trans*-$[NiL^1(H_2O)_2]Cl_2\cdot H_2O$, was isolated. An X-ray structural analysis gave strong evidence for the presence of steric interaction between the axial methyl substituent at the 5-position and the water molecule coordinating to the nickel(II) ion. The bimacrocyclic cobalt(III) complex with L^3 (6,6′-bi[5*R*(*S*),7*S*(*R*)-dimethyl-1,4,8,11-tetraazacyclotetradecane], *trans*-$[Co_2L^3Cl_4]Cl_2$, was synthesized and its structure was analyzed by X-ray crystallography, as well as the monomacrocyclic *trans*- and *cis*- dichlorocobalt(III) complexes with L^2 (5*R*(*S*),7*S*(*R*)-dimethyl-1,4,8,11-tetraazacyclotetradecane). The structure of *trans*-$[Co_2L^3Cl_4]^{2+}$ was quite different from that of $[Ni_2L^3]^{4+}$. In *trans*-$[Co_2L^3Cl_4]^{2+}$, the bridged six-membered chelate rings adopted an approximately twist-boat conformation. The steric interaction between the coordinated chloride anions on the cobalt(III) ion and the methyl substituents introduced at the 5- and 7-positions in the six-membered chelate ring was discussed.

Recently, we reported the synthesis and the structure of the dinickel(II) complex with a bimacrocyclic ligand, $[Ni_2L^3]^{4+}$, where two 5,7-dimethylcyclam units are linked by a C–C bond.[1)] The close linkage of these two macrocycles results in the formation of unexpected 1,3-diaxial methyl substituents on the bridged six-membered chelate ring, which affords some new properties to the bimacrocyclic complex different from those of the corresponding monomacrocyclic nickel(II) complex with 5,7-dimethylcyclam, $[NiL^2]^{2+}$,[2)] which has two equatorial methyl groups with respect to the six-membered chelate ring.[1)] One significant difference between these complexes is based on the solution behavior in aqueous solutions. Actually, $[Ni_2L^3]^{4+}$ [1)] exists as a four-coordinate square-planar species in an aqueous solution, but $[NiL^2]^{2+}$ [2)] is in equilibrium between four-coordinate species and water-molecule coordinated six-coordinate species in an aqueous solution. This lower capability of water coordination for $[Ni_2L^3]^{4+}$ is assumed to be due to the fact that the axial methyl substituents on the bimacrocyclic skeleton interfere with the water molecule coordination to the axial sites of the macrocyclic nickel(II) complex. Similar effects of the axial methyl substituents at the 5- and/or 7-positions of the 14-membered tetraaza-macrocyclic nickel(II) complexes have been reported by Hay et al.[3)] and McAuley et al.,[4)] but direct evidence for steric interaction between the axial methyl substituents and the coordinated water molecules have not been shown. In this study, we isolated the nickel(II) complex with L^1 (5,5,7-trimethylcyclam), which has both an axial methyl substituent and coordinated water molecules, and found the steric interaction between them by X-ray structural analysis. The bimacrocyclic cobalt(III) complex with L^3, *trans*-$[Co_2L^3Cl_4]Cl_2$, was then synthesized and its structure was identified (Chart 1), as well as the monomacrocyclic cobalt(III) complexes with L^2, to investigate the steric interaction and/or effect between the tightly coordinated chloride anion on the cobalt(III) ion and the methyl substituents introduced at the 5- and 7-positions in the six-membered chelate ring, then comparing its structure with that of $[Ni_2L^3]^{4+}$.

Experimental

Syntheses: *trans*-$[NiL^1(H_2O)_2]Cl_2\cdot H_2O$: $[NiL^1](ClO_4)_2$ was synthesized by the reported method.[5)] The chloride of the Ni(II) complex was obtained by passing the perchlorate through a Cl-form anion-exchange resin column. The slow evaporation of an aqueous solution of the chloride gave crystals suitable for X-ray analysis. Fab-mass (*m*-NBA, *m*/*z*): 399 ($[M-ClO_4]^+$).

***trans*-$[CoL^2Cl_2]Cl$:** The free ligand L^2 (C^*-*meso*: 5*R*(*S*), 7*S*(*R*)) was synthesized by our reported method.[2)] The monomacrocyclic Co(III) complex was prepared by a method similar to that of the bimacrocyclic Co(III) complex. After the aerobic oxida-

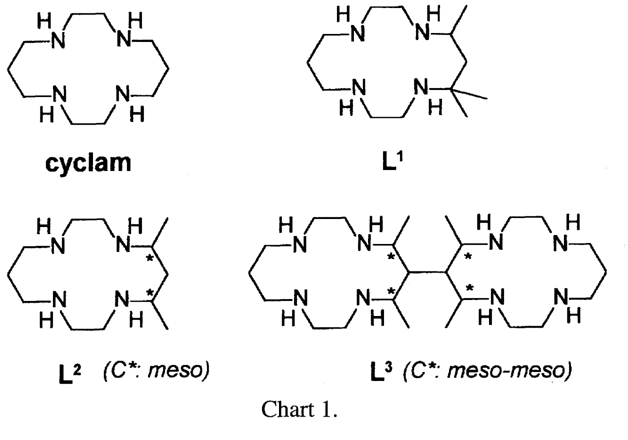

Chart 1.

tion followed by the addition of concd. hydrochloric acid, a small amount of blue crystal, which was assigned to *cis*-[CoL^{2}Cl$_2$]Cl by X-ray analysis (see later) and the following synthesis, was formed. The blue crystal was filtered off and the green filtrate was evaporated to dryness to yield the crude product of *trans*-[CoL^{2}Cl$_2$]Cl, which was recrystallized from hot concd. hydrochloric acid. The obtained crystal was washed with acetone and dried in vacuo at 80 °C (yield about 50%). Anal. Found: C, 36.40; H, 7.04; N, 14.13%. Calcd for $C_{12}H_{28}N_4CoCl_3$: C, 36.61; H, 7.18; N, 14.23%. Fab-mass (*m*-NBA, *m*/*z*): 357 ([M − Cl]$^+$). ^{13}C NMR (DMSO-d_6, TMS) δ = 18.4 (*q*), 27.2 (*t*), 44.7 (*t*), 48.2 (*t*), 49.8 (*t*), 53.1 (*t*), 54.3 (*d*). VIS (1 mol dm^{-3} HCl, 25 °C): 635 (31). CV (1 mol dm^{-3} HCl): $E_{1/2} = -0.10$ V (reversible, ΔE_p = 90 mV).

A crystal of *trans*-[CoL^{2}Cl$_2$]Cl·HCl·5H$_2$O suitable for X-ray analysis was isolated from concd hydrochloric acid. The crystal contained five moles of water, which were also confirmed by the Karl Fischer method.[6]

***cis*-[CoL^{2}Cl$_2$]Cl:** The aqueous suspension (20 ml) of Na$_3$[Co(CO$_3$)$_3$]·3H$_2$O[7] (1.9 g) and the hydrochloride of L^2 (1.5 g) was heated at about 80 °C for 15 min to give a reddish purple solution, which was filtered and dried. The residue was dissolved in 40 ml methanol and filtered. To the filtrate was added concd. hydrochloric acid (4 ml) that gave a dark green solution, from which blue crystals formed upon cooling with an ice bath. The crystals were filtered and dried in vacuo at 80 °C (yield 1.1 g). Fab-mass (*m*-NBA, *m*/*z*): 357 ([M−Cl]$^+$). VIS (H$_2$O, 25 °C): 525 (101), 384 (104). CV (1 mol dm^{-3} HCl): $E_{1/2}$ = 0.04 V (reversible, ΔE_p = 80 mV). The blue crystal of *cis*-[CoL^{2}Cl$_2$]Cl is not very stable; it changes to *trans*-[CoL^{2}Cl$_2$]Cl during the recrystallization from dilute hydrochloric acid.

***trans*-[Co$_2$L^{3}Cl$_4$]Cl$_2$:** The bimacrocyclic free ligand L^3 (C*-*meso-meso*: 5*R*(*S*), 7*S*(*R*), 5′*S*(*R*), 7′*R*(*S*)) was synthesized by our reported method.[1] To a methanol solution (5 ml) of L^3 (0.2 g), was added a methanol solution (7.5 ml) of CoCl$_2$·6H$_2$O (0.25 g). After this was bubbled with air for 1 h, concd hydrochloric acid (3 ml) was added to the brown-red mixture, which was further bubbled with air for 1 h. The resulting green solution was evaporated to dryness to yield the crude product, which was recrystallized from hot 0.1 mol dm^{-3} hydrochloric acid. The obtained crystal was washed with acetone and dried in vacuo at 80 °C (yield 0.1 g, 24%). Anal. Found: C, 36.58; H, 6.84; N, 14.08%. Calcd for $C_{24}H_{54}N_8Co_2Cl_6$: C, 36.71; H, 6.93; N, 14.27%. Fab-mass (*m*-NBA, *m*/*z*): 713 ([M−2Cl−H]$^+$). ^{13}C NMR (DMSO-d_6, TMS) δ = 17.0 (*q*), 27.6 (*t*), 40.0 (*d*), 40.1 (*t*), 52.4 (*t*), 54.4 (*t*), 55.7 (*d*). VIS (H$_2$O, 25 °C): 637 (81), 438 (108). CV (1 mol dm^{-3} KCl): $E_{1/2}$ = 0.11 V (reversible, E_{pc} = 0.05 V, E_{pa} = 0.16 V, ΔE_p = 110 mV).

The crystal of *trans*-[Co$_2$L^{3}Cl$_4$]Cl$_2$·10H$_2$O suitable for X-ray analysis was obtained by recrystallization from water. The amount of water in the crystal was also checked by the Karl Fischer method.[6]

Physical Measurements: The vis-absorption spectra were obtained using a Hitachi 340 spectrophotometer. Fab-mass and ^{13}C NMR spectra were recorded with a JEOL JMS-DX303 spectrophotometer and JEOL JNM-FX90Q and JNM-EX270 spectrophotometers, respectively. Cyclic voltammograms (CV) were recorded with a Yanagimoto Polarographic Analyzer P1100 (reference electrode: Ag/AgCl (3.33 mol dm^{-3} KCl); working electrode: Pt-disk; counter electrode: Pt-spiral).

Crystallographic Study: The X-ray crystallography of single crystals of *trans*-[NiL^1(H$_2$O)$_2$]Cl$_2$·H$_2$O (0.45×0.45 ×0.25 mm, purple, rhombic), *trans*-[Co$_2$L^{3}Cl$_4$]Cl$_2$·10H$_2$O (0.65 ×0.20×0.10 mm, green, plate), *trans*-[CoL^{2}Cl$_2$]Cl·HCl·5H$_2$O (0.60×0.15×0.10 mm, green, plate), *cis*-[CoL^{2}Cl$_2$]Cl (0.35×0.20 ×0.15 mm, blue, prismatic), was done on a MAC Science MXC3k four-circle diffractometer with graphite-monochromatized Mo *Kα* radiation (λ = 0.71073 Å) and the ω–2θ scan technique. Details of the crystallographic data are listed in Table 1. The structures were solved by the direct method (SIR 92 and DIRDIF) and refined by the full-matrix least-squares method. All the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their calculated positions (C–H: 0.96 Å) with isotropic thermal parameters fixed at 1.1 times those of the non-hydrogen atoms to which they are covalently bonded. All of the calculations were carried out using a SUN SPARK 10 work station

Table 1. Crystallographic Data

	trans-[NiL^1(H$_2$O)$_2$]Cl$_2$·H$_2$O	*cis*-[CoL^{2}Cl$_2$]Cl	*trans*-[CoL^{2}Cl$_2$]Cl·HCl·5H$_2$O	*trans*-[Co$_2$L^{3}Cl$_4$]Cl$_2$·10H$_2$O
Chem. formula	$C_{13}H_{36}N_4O_2Cl_2Ni$	$C_{12}H_{28}N_4Cl_3Co$	$C_{12}H_{39}N_4O_5Cl_4Co$	$C_{24}H_{74}N_8O_{10}Cl_6Co_2$
Formula weight	426.05	393.57	520.21	965.48
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	Aa	$P2_1/n$	$P2_1/a$
a/Å	8.678(1)	15.976(4)	22.899(3)	20.608(4)
b/Å	32.300(5)	11.843(3)	8.056(1)	6.635(3)
c/Å	7.515(1)	9.092(2)	13.418(2)	16.116(3)
β/deg	104.06(1)	94.15(2)	106.17(1)	105.54(1)
V/Å^3	2043.4(4)	1715.7(7)	2377.3(6)	2123.1(8)
Z	4	4	4	2
ρ_{calcd}/g cm^{-3}	1.400	1.524	1.453	1.510
ρ_{measd}/g cm^{-3}	1.385	1.527	1.443	1.484
λ/Å	0.71073 (Mo *Kα*)	0.71073 (Mo *Kα*)	0.71073 (Mo *Kα*)	0.71073 (Mo *Kα*)
T/°C	25	25	25	25
μ/cm^{-1}	12.334	14.662	11.746	12.117
Unique reflections	4677	1975	4792	4298
Used reflections[a]	3546 ($> 2\sigma(I)$)	1575 ($> 2\sigma(I)$)	3743 ($> 2\sigma(I)$)	3282 ($> 2\sigma(I)$)
R[a]	0.054	0.063	0.050	0.064
R_w[b]	0.064	0.073	0.060	0.072

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $R_w = \{\Sigma w(|F_o| - |F_c|)^2|/\Sigma w|F_o|^2\}$; $w = \exp(10.0\sin^2(\theta)/\lambda^2)/(\sigma^2(F_o)+0.001F_o^2)$.

(Crystan-GM program system provided by MAC Science). The atomic coordinates, thermal parameters, bond distances and angles, and $F_o - F_c$ tables were deposited as Document No. 71056 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The two water-molecule coordinated nickel(II) complex, in spite of the presence of axial methyl substituents on its six-membered chelate rings, should provide direct evidence for interactions between the axial methyl substituents and the coordinated water molecules. We tried to obtain such a complex by changing the number and position of the methyl substituents and a variety of counter anions for the 14-membered tetraazamacrocyclic nickel(II) complexes. At last, we found that the use of $[NiL^1]^{2+}$, which has only one axial methyl group at the 5-position of the six-membered chelate ring, enables the isolation of a very rare complex with both an axial methyl group and two coordinated water-molecules. Recrystallization of the chloride salt of $[NiL^1]^{2+}$ from water gave a crystal of *trans*-$[NiL^1(H_2O)_2]Cl_2 \cdot H_2O$ of which the cation's structure is shown in Fig. 1 and Table 2. The macrocyclic skeleton of the nickel(II) complex has the *trans*-III[8] N_4 configuration (1(*R*), 4(*R*), 8(*S*), 11(*S*)), having two chair six-membered and two gauche five-membered chelate rings. The central nickel(II) ion is indeed in a high-spin six-coordinate geometry accompanied by two water molecules; the average value of the Ni–N bond lengths is 2.077 Å, which is typical of six-coordinate tetraazamacrocyclic nickel(II) complexes.[9] The most remarkable feature of the nickel(II) complex is the distorted coordination of the oxygen atom, O(19), which is on the same side of the N_4 plane as the axial methyl substituent. The coordinated water molecule, O(19), is bent toward the N(11) atom being directed away from the axial methyl substituent; the angle of the O(19)–Ni(1) bond to the best N_4 plane is 85.8°. On the other hand, the coordinated water molecule, O(18), on the other side of the N_4 plane against O(19) is not in a distorted coordination; the angle of the O(18)–Ni(1) bond to the best N_4 plane is 89.2°. The Ni(1)–N(4) bond length (2.105(2) Å) is slightly longer than those of the other Ni–N bond lengths (2.060(2), 2.070(2), and 2.073(2) Å). The value of the Ni–O bond length is slightly longer on the side where the axial methyl substituent orients itself (2.236(2) Å) than on the other side (2.187(2) Å). Such a distorted coordination of the water molecule has not been observed for some other water coordinated nickel(II) complexes without axial methyl substituents: ex) $[NiL^2(H_2O)_2]^{2+}$ [2] and $[Ni(cyclam)(H_2O)_2]^{2+}$.[10] Thus, these results obviously show that the axial methyl substituent on the 5-position strongly affects the water-molecule coordination to the nickel(II) ion; it is direct evidence for the steric interaction between them. A fairly large steric repulsion should operate between the axial methyl substituent and the water molecule judging from the close distance of O(19)···C(15) (3.358(3) Å) due to the 1,3-diaxial relation ship on the six-membered chelate ring. The reason why unfavorable water coordination is retained in this crystal is probably due to the stabilization by hydrogen-bonding networks among the coordinated water molecules, chloride ions, and crystal water molecules (Fig. 2).[11]

Table 2. Selected Bond Lengths (Å) and Angles (deg) of *trans*-$[NiL^1(H_2O)_2]Cl_2 \cdot H_2O$

Ni(1)–N(1)	2.070(2)	Ni(1)–N(8)	2.060(2)
Ni(1)–N(4)	2.105(2)	Ni(1)–N(11)	2.073(2)
Ni(1)–O(18)	2.187(2)	Ni(1)–O(19)	2.236(2)
N(4)–Ni(1)–N(1)	84.5(1)	N(4)–Ni(1)–N(11)	178.8(1)
N(8)–Ni(1)–N(1)	179.0(1)	N(8)–Ni(1)–N(4)	95.2(1)
N(8)–Ni(1)–N(11)	85.7(1)	N(8)–Ni(1)–O(19)	90.8(1)
N(11)–Ni(1)–N(1)	94.5(1)	O(18)–Ni(1)–N(1)	89.8(1)
O(18)–Ni(1)–N(4)	90.0(1)	O(18)–Ni(1)–N(8)	89.2(1)
O(18)–Ni(1)–N(11)	89.2(1)	O(18)–Ni(1)–O(19)	175.6(1)
O(19)–Ni(1)–N(1)	90.1(1)	O(19)–Ni(1)–N(4)	94.4(1)
O(19)–Ni(1)–N(11)	86.4(1)		

The equilibrium between the four-coordinate and water coordinated six-coordinate species as described in Eq. 1 was spectrophotometrically investigated using an aqueous solution of $[NiL^1]^{2+}$.

$$[NiL]^{2+} + 2H_2O \rightleftharpoons [NiL(H_2O)_2]^{2+} \qquad (1)$$

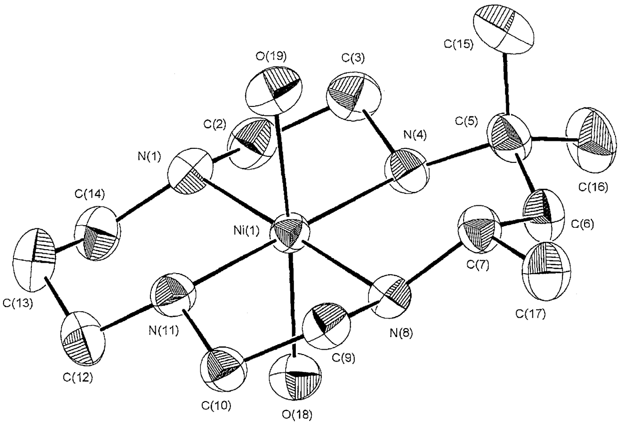

Fig. 1. ORTEP drawing of *trans*-$[NiL^1(H_2O)_2]^{2+}$ with probability level of 50%.

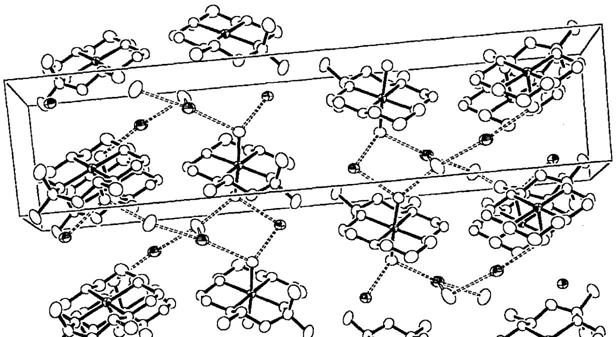

Fig. 2. Scheme of intermolecular hydrogen-bondings found in *trans*-$[NiL^1(H_2O)_2]Cl_2 \cdot H_2O$. Shadowed and open ellipsoids around the macrocycles denote chloride ions and water molecules, respectively. Dotted sticks indicate hydrogen bonds.

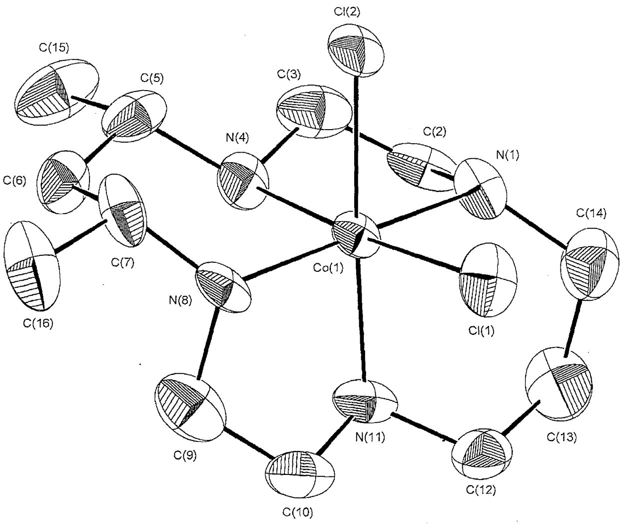

Fig. 3. ORTEP drawing of *cis*-$[CoL^2Cl_2]^+$ with probability level of 50%.

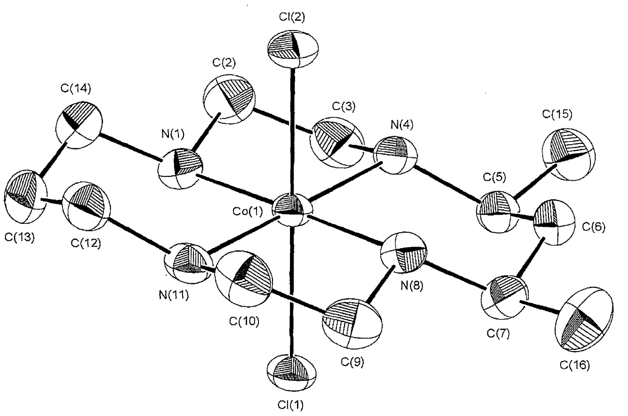

Fig. 4. ORTEP drawing of *trans*-$[CoL^2Cl_2]^+$ with probability level of 50%.

As suggested above, the presence of the axial methyl group on the 5-position of the six-membered chelate ring is anticipated to be unfavorable for the water molecule coordination to the central nickel(II) ion. Actually, the equilibrium for $[NiL^1]^{2+}$ shifts to the four-coordinate side compared to that observed for $[NiL^2]^{2+}$, which has only equatorial methyl substituents. The vis-absorption spectrum of $[NiL^1]^{2+}$ in an aqueous solution shows only one absorption band around 457 nm ($\varepsilon = 74$ mol^{-1} dm^3 cm^{-1}), which is ascribable to the band due to the four-coordinate species, and its molar absorption coefficient is very similar to that found for a nitromethane solution, non-coordinating solvent (463 nm ($\varepsilon = 76$)). This similarity in the molar absorption coefficient suggests that over 90% of the complex cation in the aqueous solution exists as a four-coordinate species. On the other hand, the aqueous solution of $[NiL^2]^{2+}$ is known to show bands due to both four-coordinate and six-coordinate species (λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) at 25 °C: 673 (2), 460 (22), 337 (7.3) in H_2O; 466 (70) in nitromethane); the estimated value of the ratio of [four-coordinate species] : [six-coordinate species] at 25 °C from vis-absorption spectra is about 25 : 75.[2)]

Thus, the structural and solution studies on $[NiL^1(H_2O)_2]^{2+}$ clearly showed that steric interaction does operate between the coordinated water molecule and the axial methyl substituent. We then anticipate that stronger steric interaction might be observed in the nickel(II) complex having two axial methyl substituents on both 5- and 7-positions than in the nickel(II) complex with one axial methyl substituent on the 5-position. Therefore, the isolation of the water molecule (or chloride ion) coordinated bimacrocyclic nickel(II) complex with L^3 was tried for the clarification of the steric interaction, though, no such complex has been yet isolated. A similar recrystallization of the chloride salt of $[Ni_2L^3]^{4+}$ from water gave not the water molecule (or chloride ion) coordinated complex but the yellow square-planar complex,[12)] which has a very similar structure to the previously reported $[Ni_2L^3](CF_3SO_3)_4$.[1)] If the nickel(II) complex with L^3 forms a six-coordinate species by axial ligand coordination, retaining the original configuration of $[Ni_2L^3]^{4+}$, the 1,3,5-triaxial relationship would hold between the methyl substituents and the coordinated ligand, this should be an unfavorable situation that causes large steric repulsion. It is likely that $[Ni_2L^3]^{4+}$ does not take the unusual 1,3,5-triaxial form, because the nickel(II) complex has such flexibility that it can adopt four coordinate or six coordinate geometry alternatively depending on its coordination environments. We then tried to force the formation of a six-coordinate metal complex with L^3 using the cobalt(III) complex, because it is well known that cobalt(III) complexes commonly have a

Table 3. Selected Bond Lengths (Å) and Angles (deg) of Cobalt(III) Complexes with L^2

	cis-$[CoL^2Cl_2]Cl$		
Co(1)–Cl(1)	2.273(3)	Co(1)–Cl(2)	2.267(3)
Co(1)–N(1)	1.970(9)	Co(1)–N(4)	2.027(9)
Co(1)–N(8)	1.992(10)	Co(1)–N(11)	2.010(8)
Cl(1)–Co(1)–Cl(2)	87.2(1)	Cl(1)–Co(1)–N(1)	92.2(3)
Cl(1)–Co(1)–N(4)	175.4(3)	Cl(1)–Co(1)–N(8)	91.3(3)
Cl(1)–Co(1)–N(11)	88.9(3)	Cl(2)–Co(1)–N(1)	89.4(3)
Cl(2)–Co(1)–N(4)	88.7(3)	Cl(2)–Co(1)–N(8)	93.7(3)
Cl(2)–Co(1)–N(11)	176.1(3)	N(4)–Co(1)–N(1)	85.5(4)
N(4)–Co(1)–N(8)	91.1(4)	N(4)–Co(1)–N(11)	95.1(4)
N(8)–Co(1)–N(1)	175.4(3)	N(8)–Co(1)–N(11)	86.7(4)
N(11)–Co(1)–N(1)	90.5(4)		
	trans-$[CoL^2Cl_2]Cl \cdot HCl \cdot 5H_2O$		
Co(1)–Cl(1)	2.268(1)	Co(1)–Cl(2)	2.239(1)
Co(1)–N(1)	1.985(3)	Co(1)–N(4)	1.993(2)
Co(1)–N(8)	2.004(2)	Co(1)–N(11)	1.972(2)
Cl(1)–Co(1)–Cl(2)	179.7(1)	Cl(1)–Co(1)–N(1)	88.0(1)
Cl(1)–Co(1)–N(4)	92.1(1)	Cl(1)–Co(1)–N(8)	91.9(1)
Cl(1)–Co(1)–N(11)	87.8(1)	Cl(2)–Co(1)–N(1)	91.8(1)
Cl(2)–Co(1)–N(4)	87.8(1)	Cl(2)–Co(1)–N(8)	88.4(1)
Cl(2)–Co(1)–N(11)	92.3(1)	N(1)–Co(1)–N(8)	179.0(1)
N(1)–Co(1)–N(11)	92.8(1)	N(4)–Co(1)–N(1)	86.1(1)
N(4)–Co(1)–N(8)	94.9(1)	N(4)–Co(1)–N(11)	178.9(1)
N(8)–Co(1)–N(11)	86.1(1)		

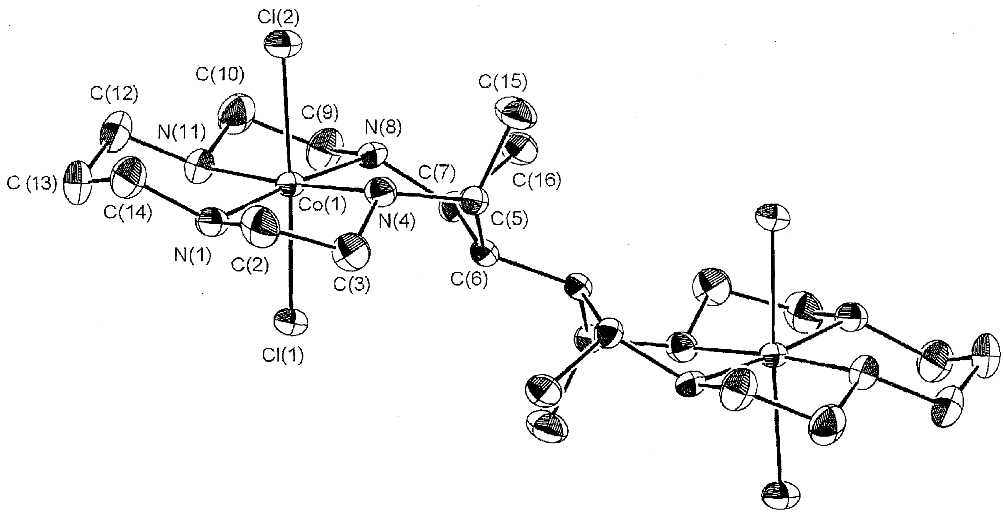

Fig. 5. ORTEP drawing of *trans*-$[Co_2L^3Cl_4]^{2+}$ with probability level of 50%.

low-spin six-coordinate geometry; the axial ligands are expected to be tightly coordinated to the macrocyclic cobalt(III) complex different from the nickel(II) complexes. This property seems to be very suitable for observations of the steric interaction and/or effect between the methyl substituents introduced on the 5- and/or 7-positions and the coordinated ligand to the cobalt(III) ion. The corresponding monomacrocyclic cobalt(III) complexes with L^2 were also synthesized for the comparison to the bimacrocyclic one.

The monomacrocyclic and bimacrocyclic cobalt(III) complexes were easily obtained by the complex formation of Co^{2+} with L^2 and L^3, respectively, followed by the aerobic oxidation to the cobalt(III) complexes. Both of the ligands gave a green complex as a main product, the vis-absorption spectrum of which resembled that of the monomacrocyclic cobalt(III) complex, *trans*-$[Co(cyclam)Cl_2]^+$.[8] In the course of the synthesis of *trans*-$[CoL^2Cl_2]^+$, a small amount of the blue cobalt(III) complex was also obtained and it was confirmed as *cis*-$[CoL^2Cl_2]Cl$ by X-ray structural analysis (Table 3); no *cis*-dichlorocobalt(III) complex was obtained for the bimacrocyclic cobalt(III) complex with L^3. The structure of the cation in the *cis*-complex is shown in Fig. 3. The macrocyclic skeleton is folded along the N(1)···N(8) axis with the nitrogen V configuration.[8] Two chloride ions coordinate to the cobalt(III) ion in the *cis*-position. The five-membered chelate rings and the six-membered chelate rings are in the gauche and chair forms, respectively. The methyl substituents at the 5- and 7-positions adopt an equatorial position with respect to the six-membered chelate ring. This blue cobalt(III) complex was the intermediate which was easily transformed into the green *trans*-complex during the recrystallization from dilute hydrochloric acid. The cation part of *trans*-$[CoL^2Cl_2]Cl{\cdot}HCl{\cdot}5H_2O$ is shown in Fig. 4. The structure is very similar to that of the already reported *trans*-$[NiL^2(H_2O)_2]^{2+}$ except for the axially coordinated ligands. The cobalt(III) ion is coordinated by two chloride ions in the *trans*-position. The methyl substituents at the 5- and 7-positions occupy equatorial position with respect to the six-membered chelate ring. The macrocyclic skeleton takes the

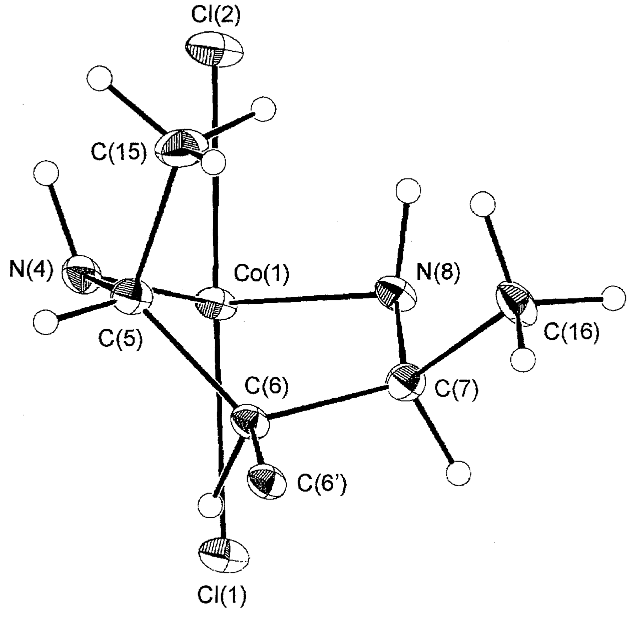

Fig. 6. View of the twist-boat six-membered chelate ring of *trans*-$[Co_2L^3Cl_4]^{2+}$ along the bridged C(6)–C(6′) bond.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of *trans*-$[Co_2L^3Cl_4]Cl_2{\cdot}10H_2O$

Co(1)–Cl(1)	2.259(1)	Co(1)–Cl(2)	2.279(2)
Co(1)–N(1)	1.971(4)	Co(1)–N(4)	1.966(4)
Co(1)–N(8)	1.968(3)	Co(1)–N(11)	1.963(4)
C(6)–C(6′)	1.559(5)		
Cl(1)–Co(1)–Cl(2)	176.8(1)	Cl(1)–Co(1)–N(1)	85.8(1)
Cl(1)–Co(1)–N(4)	97.7(1)	Cl(1)–Co(1)–N(8)	90.3(1)
Cl(1)–Co(1)–N(11)	86.8(2)	Cl(2)–Co(1)–N(1)	93.9(1)
Cl(2)–Co(1)–N(4)	85.5(1)	Cl(2)–Co(1)–N(8)	90.1(1)
Cl(2)–Co(1)–N(11)	90.0(2)	N(1)–Co(1)–N(8)	175.5(2)
N(4)–Co(1)–N(1)	86.2(2)	N(4)–Co(1)–N(8)	92.0(2)
N(11)–Co(1)–N(1)	94.8(2)	N(11)–Co(1)–N(4)	175.4(2)
N(11)–Co(1)–N(8)	87.3(2)		

most stable *trans*-III configuration consisting of two chair six-membered and two gauche five-membered chelate rings. In this case, there is no distortion for the chloride coordination.

On the other hand, the structure of *trans*-$[Co_2L^3Cl_4]^{2+}$, as shown in Fig. 5, is remarkably different from that of the monomacrocyclic complex, *trans*-$[CoL^2Cl_2]^+$, as well as being different from that of the corresponding dinickel(II) complex, $[Ni_2L^3]^{4+}$.

In *trans*-$[Co_2L^3Cl_4]^{2+}$, two equivalent macrocycles are equatorially linked at the 6-position by the C–C bond, the midpoint of which is an inversion center (Table 4). Although the N_4 configuration of the macrocyclic rings is the *trans*-III, the conformation of the six-membered chelate ring bearing methyl substituents is quite different from that of $[Ni_2L^3]^{4+}$, which has the same ligand. Each macrocycle in the cobalt(III) complex consists of one chair and one approximately "twist-boat" six-membered chelate rings and two gauche five-membered chelate rings, but $[Ni_2L^3]^{4+}$ takes two chair six-membered chelate rings. In the twist-boat six-membered chelate ring, one methyl substituent, C(15), occupies the pseudoaxial position with respect to the chelate ring and the other methyl substituent, C(16), takes the isoclinal position (see Fig. 6).[13] These results mean that there is no 1,3-diaxial relationship between the methyl substituents in *trans*-$[Co_2L^3Cl_4]^{2+}$, unlike the case of $[Ni_2L^3]^{4+}$. Because of this structure, the distance between the methyl substituents (3.302(6) Å) on the 5- and 7-positions in *trans*-$[Co_2L^3Cl_4]^{2+}$ is slightly longer than that (average value: 3.176 Å) found in $[Ni_2L^3]^{4+}$, in which two axial methyl substituents are laid on the chair-form six-membered chelate ring; the twist-boat conformation should be more favorable for the reduction in the steric repulsion between the methyl substituents than the chair-conformation with the 1,3-diaxial methyl substituents. The distances between the coordinated chloride ion and these methyl substituents (Cl(2)···C(15): 3.827(4) Å; Cl(2)···C(16): 4.981(4) Å) are also considerably longer than that (3.358(3) Å) between the coordinated H_2O and the axial methyl substituent found in *trans*-$[NiL^1(H_2O)_2]^{2+}$, indicating that the steric interactions between these moieties may be largely reduced in *trans*-$[Co_2L^3Cl_4]^{2+}$. Contrary to the case of $[NiL^1(OH_2)_2]^{2+}$, the coordination of the chloride ions to the cobalt(III) ion is not distorted but almost perpendicular to the N_4 macrocyclic plane of the cobalt(III) complex. The Co(III)···Co(III) distance (8.062(1) Å) in *trans*-$[Co_2L^3Cl_4]^{2+}$ is shorter than the Ni(II)···Ni(II) distance (8.297 Å) in $[Ni_2L^3]^{4+}$.[14]

As already described, the configuration of L^3 of *trans*-$[Co_2L^3Cl_4]^{2+}$ was different from that of $[Ni_2L^3]^{4+}$ in spite of the use of the ligand, which was liberated from $[Ni_2L^3]^{4+}$. The cobalt(III) complex takes the twist-boat form for the bridged six-membered chelate rings, however, the twist-boat form of the six-membered chelate ring is less stable than the chair one. It is reasonable to interpret the twist-boat form as follows. If the cobalt(III) complex adopts the chair forms for the bridged six-membered chelate rings, the 1,3,5-triaxial relationship, as discussed above, would hold between the methyl substituents and the coordinated chloride ion. Although large steric repulsion should operate between them in this situation, the cobalt(III) complex could not refuse the unusual 1,3,5-triaxal relationship by releasing chloride ions to change to the four-coordinate species, unlike the nickel(II) complex. Accordingly, the bridged six-membered chelate rings in the cobalt(III) complex are considered to adopt the twist-boat form in order to avoid the unfavorable 1,3,5-triaxial relationship and to decrease the steric repulsion as possible.

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6) Although the chemical formula of complexes with the fewer crystal water molecules, *tri-* and *tetra*-hydrates for *trans*-$[CoL^2Cl_2]$-$Cl\cdot HCl\cdot 5H_2O$ and *hexa-* and *octa*-hydrates for *trans*-$[Co_2L^3Cl_4]$-$Cl_2\cdot 10H_2O$, were tried in the X-ray structural analysis, no satisfactory results were obtained.

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11) The hydrogen-bond parameters are as follows:

		*T*a	*T*b	*T*c
Cl(1)–O(18)^i	3.048(1)	0	0	0
Cl(2)–O(19)^i	3.224(2)	0	0	0
Cl(1)–O(19)^i	3.104(2)	0	0	−1
Cl(2)–O(20)^i	3.074(2)	0	0	1
Cl(2)–O(20)^{ii}	3.260(2)	0	1	1
O(18)–O(20)^i	2.805(3)	0	0	0
Cl(1)–N(1)^i	3.277(1)	0	0	−1
Cl(1)–N(4)^i	3.493(1)	0	0	0
Cl(2)–N(8)^i	3.419(1)	0	0	1
N(11)–O(20)^i	3.405(3)	0	0	1

Key to symmetry operations: (i) x, y, z; (ii) $x+1/2, -y+1/2, z$. *T*a, *T*b, and *T*c are unit cell translations (atom(2)).

12) Preliminary X-ray structural analysis: *trans*-$[Ni_2L^3]$-$Cl_4\cdot 6H_2O$: $C_{24}Cl_4H_{66}N_8Ni_2O_6$: Triclinic, space group: $P\bar{1}$, $a = 7.431(3)$ Å, $b = 8.701(2)$ Å, $c = 15.697(2)$ Å, $\alpha = 88.59(1)°$, $\beta = 81.33(2)°$, $\gamma = 73.85(2)°$, $V = 963.4(4)$ Å^3, $Z = 1$, $R = 0.093$, $R_w = 0.107$.

13) ^{13}C NMR spectrum of *trans*-$[Co_2L^3Cl_4]^{2+}$ in DMSO-d_6 was measured at room temperature. It showed only one methyl signal at 17.0 ppm, which is reasonably explained in terms of the rapid thermal flexing of the twist-boat six-membered chelate rings in the solution.

14) Cyclic voltammetry of *trans*-$[Co_2L^3Cl_4]^{2+}$ in an aqueous solution showed only one wave for the $[Co^{III}Co^{III}]/[Co^{II}Co^{II}]$ redox couples, which indicates that there is no strong interaction between these cobalt ions under the present conditions.