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Conformation of 18-Membered Tetraimino Macrocyclic Complex; Structure of Two Metal Complexes and Molecular Mechanics Study

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The conformations of metal complexes of 18-membered tetraimino macrocycles have been studied. A correlation between the bond length of the metal–nitrogen bond and the conformation of the macrocycle has been found in the published X-ray data. Molecular mechanics (MM) calculations based on the Points-On-a-Sphere (POS) method reproduce the correlation. The effect of the MM force constants on the conformation of the ligand has been extensively studied. The MM study clarified that the conformation of the macrocycle is principally determined by the length of the coordination bond and that the methyl groups substituted at the imine carbon plays an important role in the conformation of the macrocycles. Two X-ray crystal structure analyses of macrocycle L^H complexes, $[Ba(L^H)(ClO_4)_2Ba(L^H)(H_2O)(ClO_4)(\mu\text{-}ClO_4)]$ and $[Sr(L^H)(ClO_4)_2]$, were included in the study to complement the structural data.

The syntheses and structures of the metal complexes containing macrocyclic ligands[1] L and L^H have been investigated over the past two decades.[2] Potential applications for catalysis and NMR imaging have been reported.[3] Benetollo, Bombieri and Vallarino have extensively contributed to the work. We also have been studying the structures and properties of the complexes and the related macrocycles.[4] These macrocyclic complexes are mainly prepared by metal-templated, Schiff-base condensation of 2,6-dicarbonylated pyridine and ethylenediamine. The framework of the macrocycle (Chart 1) is so flexible that the complexes can adopt a variety of conformations. Most complexes of the ligands adopt a folded-butterfly conformation, but some has a skew conformation in which a C_2 axis runs just through the two pyridine rings. Many complexes of the ligands contain rare earth metals or alkaline earth metals, which have a coordination number of 8–12; this means there are additional ligands besides the macrocycles.

Some papers pointed out that there is a correlation between the size of the metal ion encapsulated and the conformation of the ligand.[5,6,7,8] Generally, the complexes containing large metal ions have a tendency to show planar conformation; on the other hand, the ones containing small metal ions show folded conformation. In this paper, two new crystal structures of the metal complexes of L^H are presented. The results includes structural data of the complexes of long metal to nitrogen (M–N) distances (> 2.8 Å), which have been missing in the reported works.

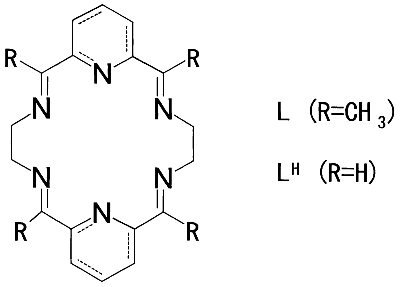

Chart 1.

Molecular mechanics models have been developed for coordination compounds.[9,10] MM calculations of coordination compounds can be made easily by using commercially available software. However, it is a serious problem that there are no standard MM parameters for metal atoms. We could reproduce almost any structure if we would adjust the MM parameters. However, critical evaluation of the methodology is also insufficient.[11] In this study, POS (points-on-a-sphere) method is used to predict the conformation of the macrocyclic compound and a methodology to obtain reasonable MM parameters is proposed. The effect of the methyl groups on the ring has also been described.

Experimental

Preparation of Macrocyclic Complexes. *Warning*! Perchlorate salts of metal complexes are potentially explosive. Only a small amount of the material should be prepared, and it should be handled with great care.

Methanol was dried over 3 A molecular sieves before use.

$[Ba(L^H)(ClO_4)_2Ba(L^H)(H_2O)(ClO_4)(\mu\text{-}ClO_4)]$. 2,6-pyridinedicarboxaldehyde (2.0×10^{-3} mol) and ethylenediamine (2.0×10^{-3} mol) were added to a solution of barium perchlorate (1.0×10^{-3} mol) in 30 mL of methanol. The solution was refluxed for 3 h and concentrated in vacuo to a small amount of volume. The pale yellow precipitates which deposited were collected by filtration and recrystallized from hot methanol. Yield: 0.14 g (25%). Anal. Calcd for $Ba_2(C_{18}H_{18}N_6)_2(ClO_4)_2(H_2O)$: C, 32.58; H, 2.89; N, 12.66%. Found: C, 32.18; H, 3.16; N, 12.30%.

$[Sr(L^H)](CF_3SO_3)_2\cdot(H_2O)$. The strontium complex was prepared in a similar manner to that described above, using strontium trifluoromethanesulfonate instead of the barium salt. Recrystallization from ethanol/methanol mixture (3 : 1) gave the strontium complex (0.27 g, 45%) as a white powder. Anal. Calcd for $SrC_{18}H_{18}N_6(CF_3SO_3)_2\cdot(H_2O)$ (722.2): C, 33.26; H, 2.79; N, 11.64%. Found: C, 33.48; H, 2.75; N, 11.59%. The perchlorate salt, $[Sr(L)](ClO_4)_2$, was prepared by a similar method using strontium perchlorate as a starting material, and was obtained as yellow crystals.

X-ray Crystal Structure Determination. X-ray measurements were performed on a Rigaku AFC5S diffractometer. The ω–2θ scan method was employed with a scanning rate of 8°/min. Three standard reflections were monitored during the data collection; these showed no significant variance. Calculations were carried out using the program package teXsan.[12] The position of the metal atom was determined by the heavy-atom method, and the remaining structures were solved by Fourier syntheses. Absorption correction by means of the Ψ scan method was applied. The positional and anisotropic thermal parameters of non-hydrogen atoms were determined by full-matrix least-squares refinements on F^2. The positional parameters of hydrogen atoms were determined by geometrical calculations. The parameters of the hydrogen atoms were included as fixed contributions in the refinements. For the crystal of the barium complex, the maximum and minimum peaks on the final difference Fourier map corresponds to 1.4 and -1.2 e/Å^3, respectively. These residual densities were found only near the barium atom. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 17335 and 17336. The data are also deposited as Document No. 75045 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Crystal Data for $[Ba(L^H)(ClO_4)_2Ba(L^H)(H_2O)(ClO_4)(\mu\text{-}ClO_4)]$. $Ba_2Cl_4O_{17}N_{12}C_{36}H_{38}$, M = 1327.24, triclinic, $a = 15.958(5)$, $b = 16.134(5)$, $c = 11.114(4)$ Å, $\alpha = 96.54(3)$, $\beta = 108.93(3)$, $\gamma = 62.82(2)$ °, $U = 2405(1)$ Å^3, $T = 295$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, μ(Mo-$K\alpha$) = 1.9 mm^{-1}, 14505 reflections measured, 14037 unique ($R_{\text{int}} = 0.029$) , 9658 used ($I > 1.0\ \sigma(I)$). The final $R(F^2)$ and $wR(F^2)$ was 0.069 and 0.108, respectively.

Crystal Data for $[Sr(L^H)(ClO_4)_2]$. $SrC_{18}\ H_{18}N_6Cl_2O_8$, M = 604.90, triclinic, $a = 8.465(2)$, $b = 15.317(2)$, $c = 9.063(1)$ Å, $b = 99.89(2)$ °, $U = 1157.7(4)$ Å^3, $T = 295$ K, space group $P2_1/c$ (no. 14), $Z = 2$, μ(Mo-$K\alpha$) = 5.8 mm^{-1}, 1939 reflections measured, 1725 unique ($R_{\text{int}} = 0.027$), 1720 used ($I > 0$). The final $R(F^2)$ and $wR(F^2)$ was 0.076 and 0.124, respectively.

MM Calculations. MM calculations were carried out on a MS-Windows based personal computer using the Tinker program package, which was explored by Prof. Ponder.[13] MM3(96)[14] Force field was applied in all calculations. All metal-dependent parameters for MM calculation are discussed in a later section and are listed in Table 6. Default values of the parameters of the MM3 force field were used for all the metal-independent parameters including out-of-bending, bond dipole, and cross energy terms such as stretch-bend terms. Atom type 37 was used for all nitrogen atoms. Modified Pariser–Parr–Pople type SCF–MO calculations were included in order to modify the parameters of the π-conjugated groups.[15] Hay's method[16] for defining the structure of a metal complex was employed in order to calculate the MM energy on the POS method using a normal MM program, as follows. Six separate lanthanum atoms (atom type 128 in the MM3 force field) are attached to each donor nitrogen atom of the ligand rather than attaching of all the donor atoms to a single metal center. The initial coordinates of the lanthanum atoms were set very near the origin (computation error occurs if the metal atoms are set just on the origin) and the coordinates of the six atoms were restrained to the origin with 99999 kcal/Å^2 harmonic potential. The connectivity list is edited such that the metal atoms are attached to one another in a ring formation. Thus, each metal atom is connected to one nitrogen atom and two adjacent metal atoms. The results showed that the offsets of each metal atom from the origin were within 0.00005 Å in all x, y, and z coordinates. N–M–N bending interactions, N–M–N–X torsional strains, and van der Waals interactions that involve the metal ion were all neglected. Other metal-dependent parameters were set as described later. The generation of the initial structures were performed by the FREEWHEEL software.[17] The calculations of best planes and the dihedral angles of between them were done by a software coded by Ito.[18]

Results and Discussion

Conformation of the Macrocyclic Ligands. A General View. Table 1 shows the structural data of the complexes containing the ligand L or an analogous ligand found in the Cambridge database.[19] The macrocyclic ligands have a common structure where two π-conjugated planar groups (N=C–C_5H_3N–C=N) are linked by two aliphatic diamine units. The two planar groups are not coplanar, and the dihedral angle between the two planar groups has been used as a measure of the coplanarity.[6,20] Here the dihedral angle was defined as follows. First, best-plane calculations using ten carbon and nitrogen atoms of the diiminopyridyl groups determine each of the conjugated planes. Then the dihedral angle between the two planes, which was defined as 180° when the macrocycle has a planar conformation, was calculated. The non-coplanarity would expect to correlate with the cavity-size of the macrocycle. As pointed out by Vallarino et al.,[8] the dihedral angle could be decomposed into two components: 1) twisting of the macrocycle about an axis through the pyridine N atoms and 2) bending at the ethylenediamine hinges. As Bombieri pointed out, we could not found any clear correlation between the M–N bond length and either the twist angle or the bending angles. However, we want to focus on a simple trend in the structural parameters, as shown in Fig. 1. First, a clear correlation between the dihedral angles and the average M–N bond lengths was observed. Second, the dihedral angles are generally closer to 180° for the complexes of L^H than that of L. Of course, other

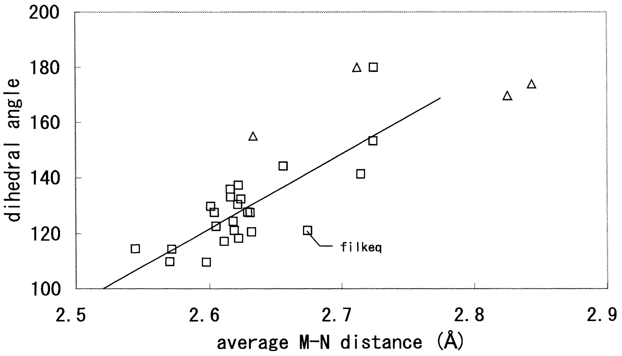

Fig. 1. The dihedral angles between the two π-conjugated groups of the macrocyclic ligands in the reported crystals found in the CCDC database. Square denotes the metal complex of the ligand L, and triangle that of L^H. The solid line shows the best-fit line calculated from the data of the L complex.

Table 1. Crystallographic Data Reported for the Macrocyclic Complexes Reported in the CCDC Database

Metal and macrocycle	REFcode[a]	Average M–N/Å	σ(M–N)/Å	Dihedral angle/°	Staggered angle/°	M–O distance[b]/Å	Coordination number	Axial ligands[c]	Reference
Ba $\mathrm{L^H}$ (1)		2.844	0.015	174	0.5	2.90	10	$\mathrm{ClO_4^-}$[D], $\mathrm{ClO_4^-}$, $\mathrm{H_2O}$	this work
Ba $\mathrm{L^H}$ (2)		2.825	0.014	169.7	73.2	2.90	10	2($\mathrm{ClO_4^-}$)[D], $\mathrm{ClO_4^-}$	this work
Sr $\mathrm{L^H}$		2.712	0.010	180	0	2.62	10	2($\mathrm{ClO_4^-}$)[D]	this work
Sr L	eiapsr	2.725 [f]	0.017	180	—[d]	2.62	8	2Cl	32
Pb L	eiappb	—[d]	—[d]	—[d]	—[d]	—	8	$\mathrm{SCN^-}$, $\mathrm{NCS^-}$	32
La L	epaila10	2.724	0.032	153.3	31.9	2.53	12	3($\mathrm{NO_3^-}$)[D]	5
La $\mathrm{L^2}$ [e]	zuwfom	2.715	0.031	141.4	28.2	2.53	9	$\mathrm{3NCS^-}$	33
Ce L	filkeq	2.674	0.053	121.1	0.13	2.55	11	2($\mathrm{NO_3^-}$)[D], $\mathrm{H_2O}$	5
Eu L	ninxen	2.656	0.027	144.2[f]	—[d]	2.45	10	$\mathrm{CH_3COO^-}$[D], dbm[g][D]	34
Sm $\mathrm{L^H}$	celrug	2.633	0.024	155.1	25.9	2.45	10	$\mathrm{H_2O}$, $\mathrm{OH^-}$, $\mathrm{NO_3^-}$[D]	35
Eu L	kihsez	2.632	0.033	120.6	21.8	2.45	10	$\mathrm{2CH_3COO^-}$[D]	36
Sm L	zawwoj	2.631	0.041	127.4	12.2	2.45	9	$\mathrm{CrO_4^-}$[D], $\mathrm{CrO_4^-}$	39
Eu L	zawwid	2.629	0.048	127.6	13.1	2.45	9	$\mathrm{CrO_4^-}$[D], $\mathrm{CrO_4^-}$	39
Nd L	kihsav	2.624	0.013	132.4	20.6	2.46	10	$\mathrm{2CH_3COO^-}$[D]	36
Nd L	filkiu (1)	2.622	0.051	118.3	18.5	2.46	10	$\mathrm{NO_3^-}$[D], 2($\mathrm{H_2O}$)	5
Gd L	vedsec	2.622	0.033	130.4	22.4	2.39	10	2($\mathrm{CH_3COO^-}$)[D]	7
Gd $\mathrm{L^3}$ [e]	juvzij	2.622	0.043	137.4	26.8	2.39	9	$\mathrm{3H_2O}$	37
Eu L	kifkoz01	2.619	0.040	121.1	32.6	2.45	9	$\mathrm{3NCS^-}$	38
Eu L	zawwez	2.618	0.037	124.3	20.8	2.45	9	$\mathrm{CrO_4^-}$[D], $\mathrm{CrO_4^-}$	39
Eu L	jitfat	2.616	0.046	136.0	16.4	2.45	10	μ-$\mathrm{CO_3^{2-}}$[D], 2($\mathrm{CH_3COO^-}$)[D]	40
Nd L	filkiu (2)	2.611	0.112	117.2	14.7	2.46	10	$\mathrm{NO_3^-}$[D], 2($\mathrm{H_2O}$)	5
Eu L	lapjan	2.605	0.033	122.6	18.5	2.45	10	2($\mathrm{CH_3COO^-}$)[D]	41
Tb L	zokyut	2.604	0.047	127.5	14.1	2.40	9	$\mathrm{CrO_4^-}$[D], $\mathrm{H_2O}$	8
Gd L	vujpev	2.601	0.043	129.7	18.2	2.39	10	2($\mathrm{CH_3COO^-}$)[D]	42
Eu L	kifkoz02	2.598	0.047	109.6	22.6	2.45	9	$\mathrm{3NCS^-}$	43
Y L	kidzay	2.572	0.043	114.3	24.3	2.37	9	$\mathrm{CH_3COO^-}$[D], ($\mathrm{CH_3COO^-}$ or $\mathrm{H_2O}$)[h]	44
Y L	kifkit01	2.570	0.059	109.7	26.2	2.37	9	$\mathrm{3NCS^-}$	43
Lu L	dowcib	2.544	0.051	114.5	25.7	2.34	9	($\mathrm{CH_3COO^-}$)[D], ($\mathrm{CH_3COO^-}$ or $\mathrm{H_2O}$)[h]	45

a) If an asymmetric unit of the crystals has two discrete complex molecules, the numbers in parentheses are labeled to distinguish them.

b) Metal–Water distances taken from Ref. 30. If several values have been reported for a metal ion, averaged values are listed.

c) [D] denotes didentate ligand.

d) The values cannot be calculated because the crystal parameters have not been deposited in the CCDC database.

e) $\mathrm{L^2}$ is 4(S), 16(S)-dimethyl derivative of L. $\mathrm{L^3}$ has two 1,2-diaminocyclohexyl groups instead of the two 1,2-diaminoethane moieties of $\mathrm{L^H}$.

f) The reported value in the reference is used because the coordinates have not been submitted in the CCDC database.

g) dbm = 1,3-diphenylpropane-1,3-dione

h) Disordered two acetato and aqua ligands were found.

factors besides the size of the metal ions should contribute to the conformation of the complexes. The factors are 1) the effect of the axial ligands, 2) the effect of the alkyl groups substituted on the ring, and 3) the crystal packing requirements. However, in many of the reported crystal structures, which are accumulated in Table 1, one of the most important factor to determine the conformation of the ligand is the size of the metal ions. We want to see how the metal-nitrogen bond length affects the overall conformation of the macrocycles in this paper.

Furthermore, one common feature was found for the conformation of the ligand L (not for L^H). The two chelates of the ethylenediamine residue in the opposite positions across the metal ion show the STAGGERED conformation in almost all the structures of ligand L. Table 1 contains the data of the staggered angles. An exception in the complexes of L was found in the complex,[5] "filkeq", which is the Reference Code in the CSD database. In this complex, the two diamine chelates are parallel with each other. The complex shows an abnormal dihedral angle as shown in Fig. 1, which should be ascribed to the exceptional conformation.

Preparation of the Barium and Strontium Complexes. Although there are a lot of reported macrocyclic complexes containing rare earth metals, only one structure of the complex containing an alkaline earth metal has been known. Cabral et al. briefly reported[21] the preparation and the structure of strontium(II) and lead(II) complexes of the ligand L. However, the detailed structural data have not been published. The complexes were prepared by template condensation of dialdehyde and diamines in the presence of the metal ions. The reported strontium complex has two axial chlorine atoms.

In this work, template condensation of 2,6-pyridinedicarboxaldehyde and ethylenediamine in the presence of the appropriate alkaline earth metal perchlorates afforded the macrocyclic complexes in moderate yield. Trifluoromethanesulfonate salt was also obtained for the strontium complex. Crystals suitable for X-ray crystallography were obtained from methanol solution of the perchlorate salts.

Table 2. Selected Bond Distances for $[Ba(L^H)(ClO_4)_2\text{-}Ba(L^H)(H_2O)(ClO_4)(\mu\text{-}ClO_4)]$

Atom	Atom	Distance/Å	Atom	Atom	Distance/Å
Ba1	O1	2.813(8)	Ba2	O9	2.800(6)
Ba1	O5	2.903(6)	Ba2	O10	2.855(6)
Ba1	O12	2.981(5)	Ba2	O14	2.913(5)
Ba1	O13	2.972(5)	Ba2	O15	3.008(6)
Ba1	N1	2.845(5)	Ba2	N7	2.832(5)
Ba1	N2	2.817(5)	Ba2	N8	2.828(5)
Ba1	N3	2.827(5)	Ba2	N9	2.867(6)
Ba1	N4	2.832(6)	Ba2	N10	2.851(6)
Ba1	N5	2.832(6)	Ba2	N11	2.850(6)
Ba1	N6	2.807(5)	Ba2	N12	2.840(6)

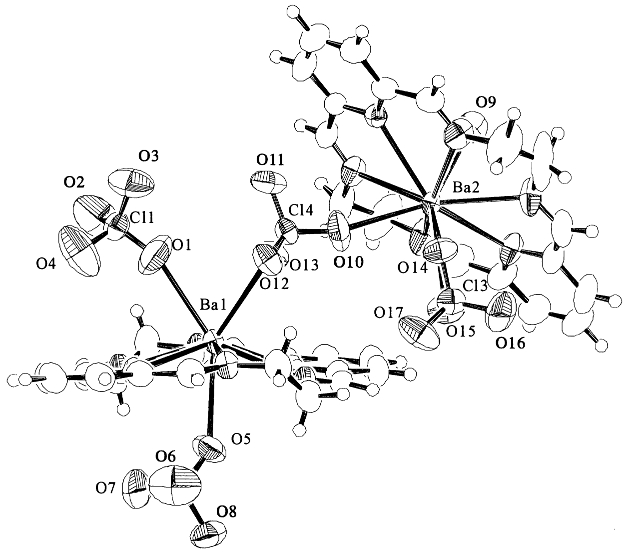

Fig. 2. An ORTEP drawing of the barium(II) complex.

Crystal Structure of the Barium Complex. The bond lengths and angles around the barium ions were listed in Tables 2 and 3, respectively. The structure of the barium complex is described as a perchlorato-bridged dimers as shown in Fig. 2. There are two ten-coordinate barium ions that are bridged by a perchlorato ligand. Each barium ion is coordinated to the six nitrogen atoms of the macrocycle L^H. The coordination geometries around the two barium ions are similar as shown in Fig. 3. One of the two barium ions (Fig. 3, left) has a didentate perchlorato, a monodentate perchlorato and a bridging perchlorato ligand besides the macrocycle. The other barium ion is coordinated by a water molecule, a didentate perchlorato chelate, and a monodentate perchlorato ligand. The

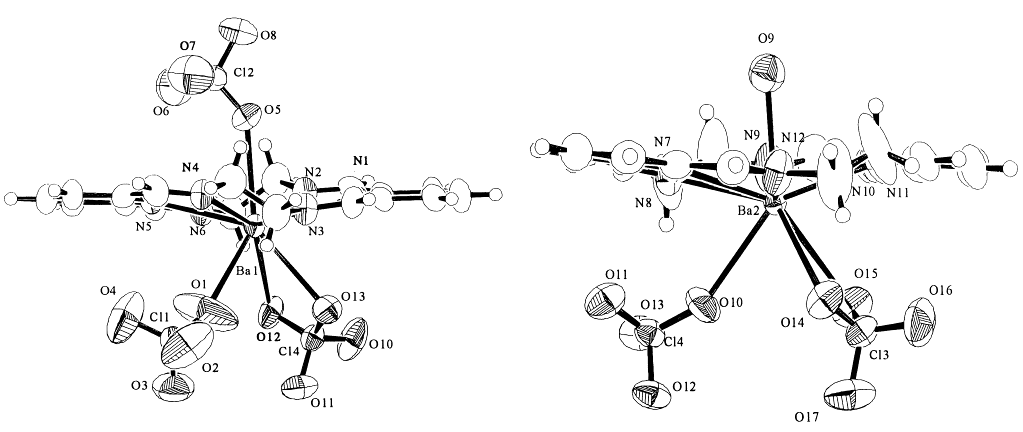

Fig. 3. The coordination-structure around the two barium ions.

Table 3. Selected Bond Angles for [$Ba(L^H)(ClO_4)_2Ba(L^H)(H_2O)(ClO_4)(\mu\text{-}ClO_4)$]

Atom	Atom	Atom	Angles/°	Atom	Atom	Atom	Angles/°
O1	Ba1	O5	143.5(2)	O9	Ba2	O10	140.0(2)
O1	Ba1	O12	67.7(2)	O9	Ba2	O14	141.2(2)
O1	Ba1	O13	71.4(3)	O9	Ba2	O15	143.8(2)
O1	Ba1	N1	131.2(3)	O9	Ba2	N7	72.3(2)
O1	Ba1	N2	139.3(2)	O9	Ba2	N8	75.5(2)
O1	Ba1	N3	94.4(3)	O9	Ba2	N9	74.4(2)
O1	Ba1	N4	75.7(2)	O9	Ba2	N10	75.2(2)
O1	Ba1	N5	75.7(3)	O9	Ba2	N11	75.6(2)
O1	Ba1	N6	99.2(3)	O9	Ba2	N12	78.3(2)
O5	Ba1	O12	140.3(2)	O10	Ba2	O14	66.0(2)
O5	Ba1	O13	142.9(2)	O10	Ba2	O15	75.2(2)
O5	Ba1	N1	78.0(2)	O10	Ba2	N7	71.8(2)
O5	Ba1	N2	71.2(2)	O10	Ba2	N8	70.7(2)
O5	Ba1	N3	84.2(2)	O10	Ba2	N9	104.5(2)
O5	Ba1	N4	72.4(2)	O10	Ba2	N10	138.8(2)
O5	Ba1	N5	72.6(2)	O10	Ba2	N11	135.5(2)
O5	Ba1	N6	78.9(2)	O10	Ba2	N12	96.7(2)
O12	Ba1	O13	45.7(1)	O14	Ba2	O15	45.7(1)
O12	Ba1	N1	95.2(1)	O14	Ba2	N7	104.3(1)
O12	Ba1	N2	72.1(2)	O14	Ba2	N8	136.6(2)
O12	Ba1	N3	125.2(2)	O14	Ba2	N9	136.1(2)
O12	Ba1	N4	143.3(2)	O14	Ba2	N10	100.4(2)
O12	Ba1	N5	108.4(1)	O14	Ba2	N11	70.2(2)
O12	Ba1	N6	69.9(1)	O14	Ba2	N12	68.6(2)
O13	Ba1	N1	65.2(1)	O15	Ba2	N7	143.1(1)
O13	Ba1	N2	85.4(2)	O15	Ba2	N8	124.7(2)
O13	Ba1	N3	79.7(2)	O15	Ba2	N9	90.6(2)
O13	Ba1	N4	124.0(2)	O15	Ba2	N10	69.0(2)
O13	Ba1	N5	144.3(2)	O15	Ba2	N11	80.4(2)
O13	Ba1	N6	114.2(1)	O15	Ba2	N12	111.6(2)
N1	Ba1	N2	58.0(2)	N7	Ba2	N8	57.6(2)
N1	Ba1	N3	57.6(2)	N7	Ba2	N9	113.2(2)
N1	Ba1	N4	111.4(2)	N7	Ba2	N10	147.5(2)
N1	Ba1	N5	150.5(2)	N7	Ba2	N11	112.6(2)
N1	Ba1	N6	117.9(2)	N7	Ba2	N12	57.5(2)
N2	Ba1	N3	114.3(2)	N8	Ba2	N9	58.9(2)
N2	Ba1	N4	143.6(2)	N8	Ba2	N10	114.4(2)
N2	Ba1	N5	112.1(2)	N8	Ba2	N11	151.1(2)
N2	Ba1	N6	60.0(2)	N8	Ba2	N12	114.5(2)
N3	Ba1	N4	59.0(2)	N9	Ba2	N10	57.1(2)
N3	Ba1	N5	116.7(2)	N9	Ba2	N11	112.6(2)
N3	Ba1	N6	163.1(2)	N9	Ba2	N12	152.7(2)
N4	Ba1	N5	58.0(2)	N10	Ba2	N11	57.4(2)
N4	Ba1	N6	114.9(2)	N10	Ba2	N12	115.0(2)
N5	Ba1	N6	58.0(2)	N11	Ba2	N12	58.9(2)

last perchlorato serves as a bridging ligand. The Ba–O distances range from 2.80 Å to 3.01 Å in the two coordination moieties. All the Ba–O bond lengths in perchlorato chelates (2.91–3.01 Å) are longer than any Ba–O bonds from the Ba atom to the monodentate perchlorato ligand. The Ba–O bond of the coordinated water molecule was the shortest (2.799(6) Å) among the Ba–O bonds. On the other hand, the Ba–N bond lengths are in the narrow range 2.81–2.87 Å. Each macrocyclic ligand L^H contains two π-conjugated $N{=}CH\text{–}C_5H_3N\text{–}CH{=}N$ groups. The deviation from planarity is little in all the four π-conjugated groups, such that the average deviation of the non hydrogen atoms from the best planes is smaller than 0.05 Å. Both the conformations of the two macrocyclic ligands are nearly planar. The average deviations of the 6 nitrogen atoms from the best plane defined by the 6 atoms are 0.17 Å and 0.06 Å, respectively, for the ligands containing Ba1 and Ba2. Both the barium atoms are lifted from the best planes by ca. 0.7 Å. The dihedral angles between the two planes defined as described before are 174° and 169° in the two macrocycles. Although there are some differences in the relative conformation of the two chelates of the ethylenediamine moieties in the two macrocycles, the planarity of the macrocycles is notable as compared with the other complexes listed in Table 1. Clearly, the barium atom is too large to be encapsulated in the hole of the ligand L^H. The barium atoms seem to force the macrocycle to be planar.

Crystal Structure of the Strontium Complex. The important bond lengths and angles are listed in Tables 4 and 5 respectively. The structure of the strontium complex is simpler than that of the barium complex. The Sr atom is encapsulated in a macrocyclic ligand, L^H, and two perchlorato ligands attach didentately as shown in Fig. 4. The strontium atom is located at the origin of the unit cell, which corresponds to an inversion center. The dihedral angle of the two bis(diiminomethyl)pyridyl group is just 180° because of the requirements from symmetry. Two Sr–O distances are 2.858(8) and 2.828(8) Å, respectively, while the Sr-N distances are in the range 2.696(6)–2.719(5) Å.

MM Calculations. A lot of papers have been published for MM calculation of macrocyclic complexes.[22,23,24] In these studies, the POS method[25] have been demonstrated to be useful in predicting the geometries of many metal complexes, which contain especially large metal ions, such as alkali metal, alkaline earth metal and lanthanide complexes.[26,27]

Table 4. Selected Bond Distances for $[Sr(L^H)(ClO_4)_2]$

Atom	Atom	Distance/Å	Atom	Atom	Distance/Å
Sr1	O1	2.858(8)	Sr1	N1	2.696(6)
Sr1	O3	2.828(8)	Sr1	N2	2.719(5)
			Sr1	N3	2.718(6)

Many attempts have been made to obtain the MM parameters, but generally they are still obtained by manual fitting to experimentally observed structures.[9] One can generally obtain ranges of parameters that yielded similar levels of agreement with experiment.[27] To identify a narrower range of transferable parameters, structural data of several complexes for a given metal ion type are necessary. For coordination compounds, wide variations of the parameters have been reported. For example, the stretching force constant of 0.55 mdyn $Å^{-1}$ was used for Gd–O (C=O) bond in the Hay's paper, whilst 0.1 mdyn $Å^{-1}$ was adopted for similar Gd–O bond by Cundari et al.[28] In this paper, we propose a strategy to estimate reasonable metal-dependent MM parameters by a different approach.

Detailed Description on the Current MM Method. The default MM3(96) parameters were applied to all metal-independent terms, as described in the experimental section. The SCF–MO calculations were included in the MM calculations in order to modify the stretching and torsional parameters within the π-conjugated groups, $N=CR–C_5H_3N–CR=N$ ($R=CH_3$ or H). The calculation showed that the π-bond order of the C=N imine bond is 0.95 and that of the $CR–C_5H_3N$ bond is only 0.23. The calculated bond lengths are 1.29 and 1.48 Å respectively. The calculated values reproduce the X-ray results very well. X-ray studies of this work showed that the C=N bond lengths are very short (1.25–1.29 Å) in the complexes, and that the bonds are comparatively long (1.46–1.50 Å) for the bonds between the imine carbon and the aromatic carbon.

In the POS method applied here, the parameters that must be determined are M–N stretching, M–N–X bending and M–N–X–X torsional parameters. After many trial and error calculations, the standard parameters for this MM study were set as

Table 5. Selected Bond Angles for $[Sr(L^H)(ClO_4)_2]$

Atom	Atom	Atom[a)]	Angles/°	Atom	Atom	Atom[a)]	Angles/°
O1	Sr1	O3	45.6(2)	O3	Sr1	N2	71.6(2)
O1	Sr1	O3*	134.4(2)	O3	Sr1	N2*	108.4(2)
O1	Sr1	N1	83.4(2)	O3	Sr1	N3	69.9(2)
O1	Sr1	N1*	96.6(2)	O3	Sr1	N3*	110.1(2)
O1	Sr1	N2	110.6(2)	N1	Sr1	N2	60.1(2)
O1	Sr1	N2*	69.4(2)	N1	Sr1	N2*	119.9(2)
O1	Sr1	N3	109.4(2)	N1	Sr1	N3	118.9(2)
O1	Sr1	N3*	70.6(2)	N1	Sr1	N3*	61.1(2)
O3	Sr1	N1	83.4(2)	N2	Sr1	N3	59.6(2)
O3	Sr1	N1*	96.6(2)	N2	Sr1	N3*	120.4(2)

a) An asterisk denotes the atom symmetrically moved along the twofold axis.

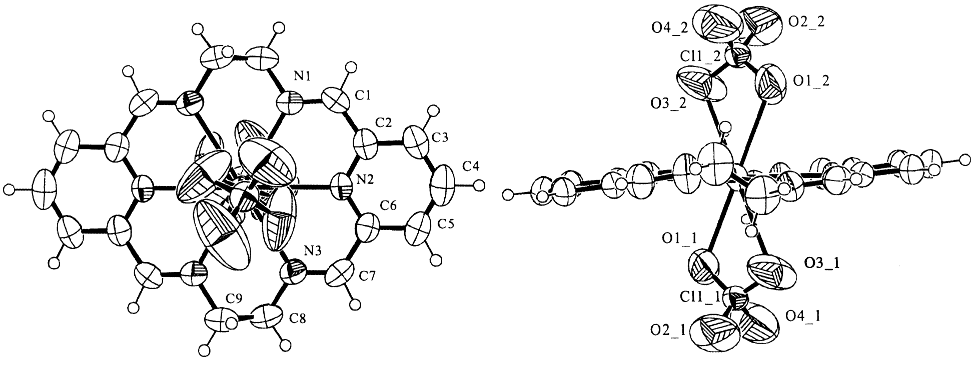

Fig. 4. A top view (left) and a side view (right) of the strontium complex.

shown in Table 6. The effect of varying each parameter was studied in detail.

Some papers pointed out that the stretching force constants should decrease with increase of the ionic radius of the central metals; the force constants vary within 25% over all the lanthanide series.[27] However, in this paper, we assume that the stretching force constants are invariable regardless of the kind of metals. A wide variation in the MM force constants has been used even for the same M–N bond (vide supra), so that the assumption could be applied to make a rough estimate of the "true" value of MM force constants.

Initial Structures and Local Minimums. In order to find the conformations of local minimum energy, MM calculations started from different initial structures were examined. A notable result clarified was the importance of the relative conformation of the two ethylenediamine chelates. Both the staggered and parallel conformation for the two ethylenediamine chelates were tested as the initial structures. If the initial structure has the parallel conformation of the two chelates, the optimized structure has also the parallel conformation; and vice versa. If r_0 was greater than 2.5 Å, the MM energy of the optimized parallel structure was larger than that of the optimized staggered structure. On the other hand, if r_0 was shorter than 2.5 Å, the MM energy of the optimized parallel structure was slightly smaller than that of the optimized staggered structure, but the optimized parallel structure showed an unnaturally folded conformation in which the dihedral angle of the two conjugated groups is near 90°. The complexes with parallel conformation are rarely found in X-ray data, as stated above. From these results, we concluded that the staggered conformation is normally preferred for the ligand. Thus, we only describe MM calculations on the staggered conformations in detail.

The Influence of the M–N Stretching Parameters on the Conformation of the Complex. We have been interested in studying whether the overall conformation of the macrocycle, especially the trend shown in Fig. 1, can been reproduced or not by varying only the ideal bond length (r_0). In order to study this, the optimized conformations of the macrocycle complexes were calculated with increase of r_0 of the M–N bond (for every 0.05 Å).

In the staggered conformation, different initial structures do not generally converge into one optimized structure for each set of the MM parameters. At first, the result for the ligand L with $k_s = 0.5$ mdyn Å^{-1} is described. When the r_0 value is in the range 2.5–2.95 Å, there are two structures of local-minimum-energy. One conformer (skew) adopts D_2 symmetry and the other conformer (folded skew) has only one two-fold axis. These are shown in Fig. 6 (b and c). The skew conformer shows lower MM energy than the folded skew conformation in the range $r_0 = 2.5$–2.75 Å, but the opposite results were obtained in the range $r_0 = 2.8$–2.95 Å. The largest difference in the MM energy between the two conformers is 0.93 kcal/mol with $r_0 = 2.95$ Å.

For other k_s values, similar calculations were carried out, and two local minimum structures were found in a certain range of r_0 value. In Fig. 5, the dihedral angles of the two conjugated groups were plotted against the optimized M–N distance. If there are two energy-minimum structures starting

Table 6. The MM Parameters Used in This Study and Some Published Works for Metal Dependent Terms. Strain-Free Values Used Are in Parentheses

Term, [unit of force constants]	Standard organic MM3 parameters		Metal dependent parameters			
				"Standard parameters" in this work	Bell, Drew[23]	Cundari[28]
Stretching, k_s [mdyn/Å]	$C(sp^3)$–N	5.0 (1.43 Å)	M–N	0.5 (2.3–3.0 Å)	99 (2.4–3.3 Å)	0.2 (2.53 Å)
Bending, k_b [mdyn Å/rad^2]	$C(sp^3)$–N=$C(sp^2)$	0.72 (109°)	M–N=$C(sp^2)$	0.5 (109°)	0.30 (120°)	0.5 (120°)
			M–N–$C(sp^3)$	0.5 (109°)		
Torsional, V_2 [kj/mol]	$C(sp^3)$–$C(sp^2)$=N–$C(sp^3)$	6.0 (180°)	$C(sp^3)$–$C(sp^2)$=N–M	2.0 (180°)	M–N–C–X 2.0 (180°)	1–2=N–Gd 0.0 (180°)
	$C(sp^2)$–$C(sp^2)$=N–C(sp3)	10.0 (180°)	$C(sp^2)$–$C(sp^2)$=N–M	2.0 (180°)		2–2=N–Gd 15.0 (180°)
	H–$C(sp^2)$=N–$C(sp^3)$	12.2 (180°)	H–$C(sp^2)$=N–M	2.0 (180°)		
	$C(sp^3)$–$C(sp^3)$–N=C(sp2)	0	$C(sp^3)$–$C(sp^3)$–N–M	0		1–1–N–Gd 0.0 (180°)
	H–$C(sp^3)$–N=$C(sp^2)$	−0.98 (120°)	H–$C(sp^3)$–N–M	0		

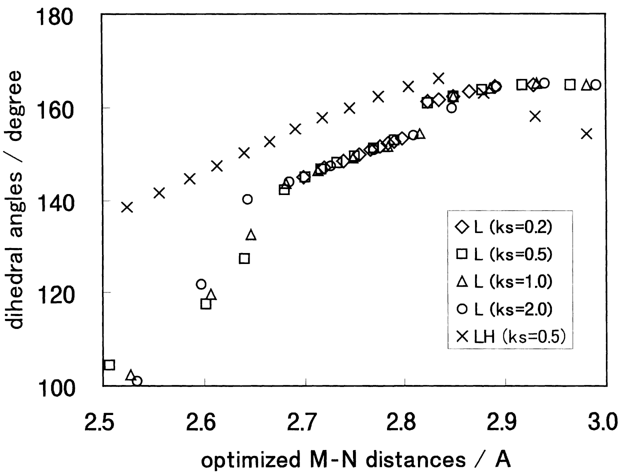

Fig. 5. The dihedral angels calculated by MM method with increase of r_0 using the standard force constants for the complex of L and L^H. Variation of the stretching force constants, k_s, from 0.2 to 2.0 mdyn $Å^{-1}$.

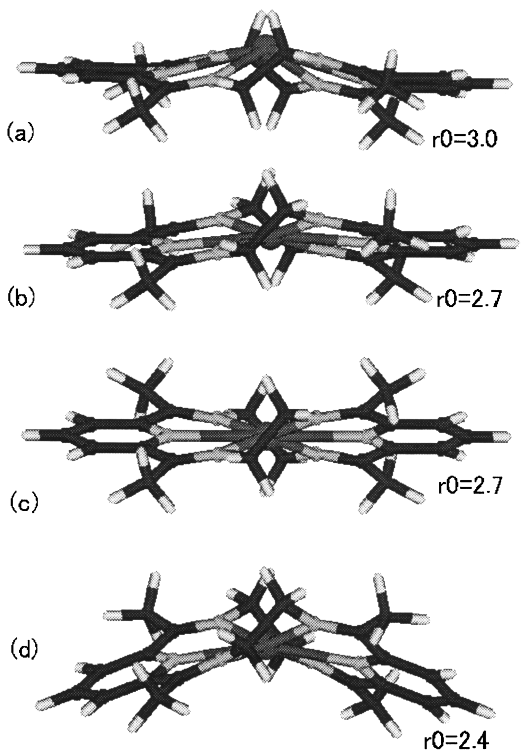

Fig. 6. Conformations of the optimized structure of ML complex with $k_s = 0.5$ mdyn $Å^{-1}$; (a) $r_0 = 3.0$ Å, (b) $r_0 = 2.7$ Å, a folded-skew conformation, (c) $r_0 = 2.7$ Å, a skew conformation, (d) $r_0 = 2.4$ Å, a folded conformation.

from the same r_0, the geometrical parameters of the more stable conformer were plotted. The plot shows a clear correlation: i.e. the longer the M–N length, is the more the dihedral angle. There are two discontinuous points in the plot, at the M–N distances of 2.8 Å and 2.65 Å. The folded-skew conformation is the most stable in the right side of the plot, the skew (D_2) conformer has the minimum energy between the two points, and folded conformation (Fig. 6(d)) shows minimum at the left side. The MM result clearly represents the observed feature depicted in Fig. 1.

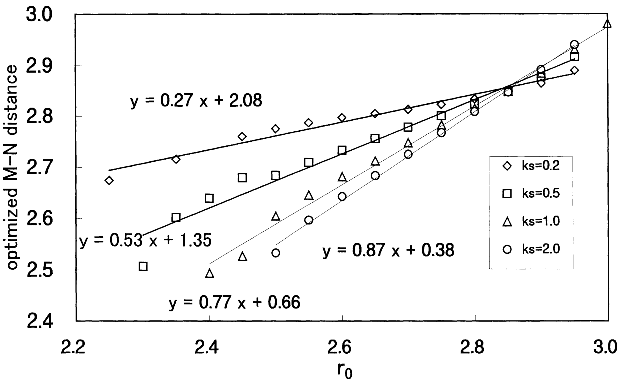

Fig. 7. The optimized M–N length vs r_0 plot calculated by the MM method. The solid lines shown in the figure are the best-fit lines calculated by least-square's method.

The relationship between the optimized M–N length and the dihedral angle of the macrocycle is independent of the stretching force constant k_s, as seen in Fig. 5. Although some disorder is seen around the discontinuous points, all the plots coincide well with each other. The result is interpreted as follows. The stretching energy shows the minimum at the M–N length, 2.86 Å.[29] If r_0 is shorter than this, the optimized structure is such that all the M–N bonds are too short to be fit within the hole of the macrocycle, so that the ligand has more bend conformation and the M–N bond is more stretched from r_0. Thus, if r_0 is shorter than 2.86, the optimization with large k_s parameter gives a structure of shorter M–N length and more bend conformation, on the other hand, that with small k_s parameter gives longer M–N length and more planar conformation.

The above results show that the relationship between the optimized M–N length and the dihedral angle of the macrocycle is reproduced independently of the value of k_s. Then what value of k_s is the most reasonable? We determined k_s "experimentally" as follows. The optimized M–N length is more expanded from r_0 as the k_s value becomes smaller and as r_0 becomes smaller. Thus, if k_s is small, the r_0 vs optimized M–N length plot has a small slope as shown in Fig. 7. If k_s is a very large value, the slope of the plot should be close to unity. It is reasonable that the r_0 value is in correlated with the bond radius of the metal ions. We assume that, if metal ions bond to a certain donor atom, the change in the bond radii of the metal ions coincide with the change in r_0. In this study, we adopt "ionic radii in solution" [30] measured by solution X-ray technique as the bond radius rather than the ordinarily used ionic radii obtained from the data of ionic crystals,[31] because 1) the latter varies with the coordination number and 2) the former, which is a measure of M–O (water) length, may correlate better with coordination bonds than the latter. Actually, the observed M–N length determined by X-rays (Table 1) is in linear correlation with the M–O length reported in Ref. 30, as shown in Fig. 8. However, the slope is about 0.5 which is far smaller than unity. This means the M–N bonds are expanded when a metal of smaller ionic radius is encapsulated in the macrocycle. We can compare the plot with that in Fig. 7. In Fig. 7, the slope is near 0.5 when k_s has the value of 0.5 mdyn/Å; thus we conclude the

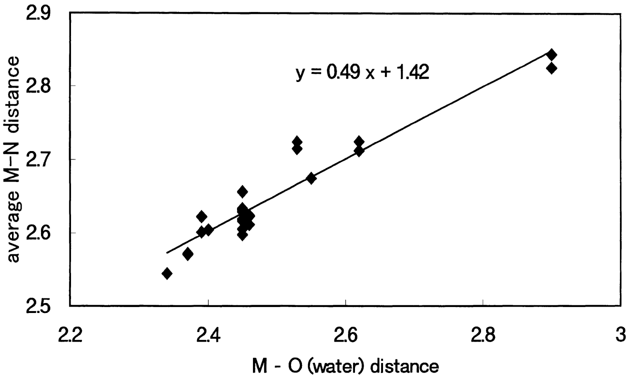

Fig. 8. The plots of the reported average M–N length vs M–O distance of the central metal ions taken from Ref. 30. The data were taken from Table 1. The solid line denotes a linear-relationship calculated by a least-square's method.

k_s (0.5 mdyn/Å) is approximately reasonable.

Figure 5 also includes the MM results for the macrocycle complexes of the L^H ligand. The MM parameters were identical with those in the M–N complexes. The initial structure is made by simply deleting the four methyl groups from the initial structure of the L complex. One notable result is that we only found one local minimum in the MM energy potential for each starting r_0. The optimized structure of the ML^H complex was found to be more planar than that of the ML complex. Further, the dihedral angles of the L^H ligand are less sensitive to the M–N length. This result agrees with the observed trends, although the number of the reported samples of L^H is small (see Fig. 1). For example, [Sm(L^H)] complex, CCDC code cerlug, shows the dihedral angles of 155 degrees and the average M–N length of 2.633(2) Å; such geometry is far from those of the other complexes of the L ligand.

M–N–X Bending and N–M–N–X Torsional Parameters. Figure 9 shows the optimized geometry when r_0 and the bending force constants, k_b, were varied. Although some minor differences are observed, r_0 vs the dihedral angles plots roughly coincide with each other. This result also shows the independence of the MM force constants from the M–N vs dihedral angle relationship.

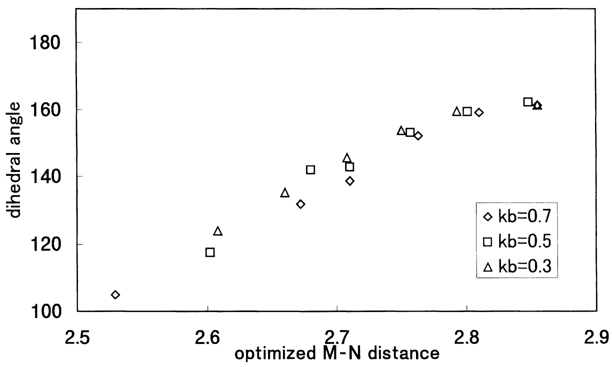

Fig. 9. The dihedral angles calculated by MM method. Variation of the bending force constants, k_b, of M–N–X bending.

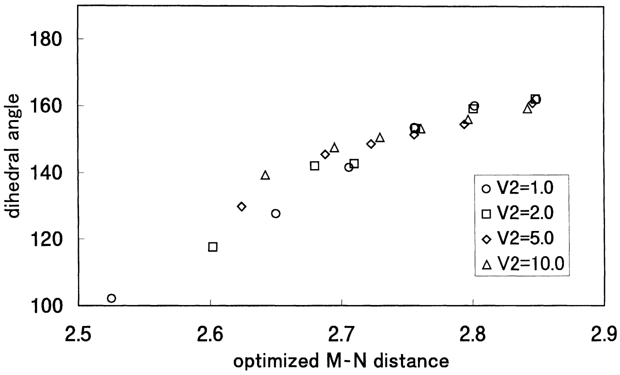

Fig. 10. The dihedral angles calculated by MM method. Variation of the torsional force constants, V_2.

For the torsional parameter, similar results were drawn; see Fig. 10. The variation of the V_2 constant ranging from 1.0 to 10.0 kcal/degree was tested. Although the dispersion of the dihedral angles is larger than in the preceding results, a similar relationship is reproduced from the calculation with any torsional parameters.

Conclusion of the MM Study. In this study, extensive calculations were performed to study the effect of the MM parameters on the optimized conformation of the macrocycle-metal complexes. We focused on the dihedral angle between the two π-conjugated groups and the M–N distance. Our results show that the relationship observed in accumulated X-ray data (Fig. 1) is reproduced by the MM calculations based on the POS method. A reasonable k_s value is determined to 0.5 mdyn/Å, which was obtained from the [r_0] vs [optimized M–N length] plots. The macrocycle L^H is essentially more planar than L, as shown in the MM calculations and the X-ray data. These results show that the M–N bond length and the substituted groups essentially determine the conformation of the macrocyclic complexes, although the other effects (axial coordination and crystal packing effect) may play additional roles in the conformation.

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