Syntheses and Structures of a Novel Trinaphthylene Hexaimino Cryptand: Three Different Conformations of a Macrobicyclic Ligand

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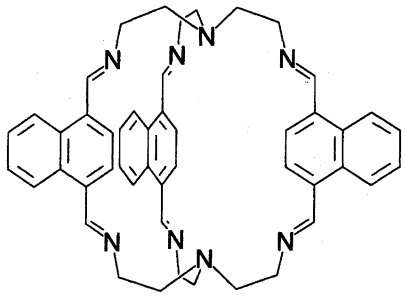
A synthesis in good yield of a new hexaimino cryptand containing two tris(2-aminoethyl)amine moieties bridged by three naphthylene groups is reported. Ag^+ and Cu^+ cryptates of the ligand have also been prepared and characterized. The cryptand and cryptates have been structurally analyzed by X-ray diffraction, unveiling three different conformations. The macrobicyclic ligand has an *anti* conformation in the cryptand, but has a *sym* form in each cryptate. Although the Ag^+ cryptates have a symmetric structure on the three arms, one of the three arms in the Cu^+ complex shows remarkable bending. The bent conformation is intrinsic of the Cu^+ complex, as indicated by X-ray analyses and MM2 calculations. The temperature dependence of the ^1H NMR spectra has also been investigated, revealing fluxional behaviors of the ligand in each compound.

Many attempts to add various functions to cryptands have been made.[1] Lehn has proposed a cryptate having a function as a 'cascade complex',[2] in which the cryptate has a reaction field between two metal ions within the cavity. The cascade complex can also be regarded as being one of the targets in supramolecular chemistry.[3] Although cryptands possessing a large cavity have recently been reported,[4] most of them are suitable for taking hold of organic molecules, rather than metal ions. So far, only a few cryptates that fit the model proposed by Lehn have been prepared.[5] In this context, a new cryptand containing two metal ions was designed in this study.

We have already studied a hexaimino cryptand, pytren,[6] which has a large cavity.[7] It forms a stable complex with large metal ions, such as Ba^{2+} and Ca^{2+}, but does not do so with small-size transition-metal ions. Various hexaimino cryptands have been prepared by [2+3] condensations, owing to the ease of their synthetic methods.[8,9] Since many applications, such as catalysis, can be expected for transition-metal cryptates, we have attempted to prepare the cryptand called nptren (Scheme 1),[10] which can include two transition metals. Although nptren seems to have one large cavity, it is divided into two small ones by sticking naphthylene protons. Here, we report on the structures of Cu^I and Ag^I complexes of nptren and the ligand, itself.

Although conformational differences between the cryptands and cryptates have been known in many macrobicyclic compounds,[8—11] the conformations of the cryptands do not depend on metal species for the dinuclear cryptates reported so far.[8,9] The conformation of the nptren ligand in the Cu^I complex is found to be different from that in the Ag^I complex. Here, we discuss the conformation of the ligand in a crystal and in a solution.



nptren

Scheme 1.

Experimental

All of the solvents were dried over molecular sieves 4A.

1,4-Naphthalenedicarbaldehyde. 1,4-Naphthalenedicarbaldehyde (1,4-NDA) was prepared from 1,4-naphthalenedicarboxylic acid by a similar method to that reported for 2,3-naphthalenedicarbaldehyde,[12] and recrystallized from cyclohexane. The formation of the dicarboxaldehyde was confirmed by ^1H NMR. ^1H NMR ($CDCl_3$) δ = 10.55 (s, 2H), 9.24 (m, 2H), 8.16 (s, 2H), 7.79 (m, 2H).

Free nptren Ligand. To a solution of 1,4-NDA (0.5 mmol) in acetonitrile (AN) (25 mL) was added dropwise an acetonitrile solution (50 mL) of tris(2-aminoethyl)amine (tren) (0.33 mmol). The mixture was stirred for 1 h at room temperature. The resulting colorless needles were separated by filtration, and then recrystallized from tetrahydrofuran (THF)/AN (1 : 1) mixture (72% yield). The crystal contains a solvated H_2O and a CH_3CN molecule. Found: C, 75.64; H, 6.53; N, 15.61%. Calcd for $C_{50}H_{53}N_9O$: C, 75.44; H,

6.71; N, 15.84%. ^{1}H NMR ($CDCl_3$) at 23 °C δ = 9.04 (m, 1H), 8.48 (s, 1H), 7.55 (m, 1H), 5.95 (s, 1H), 3.83 (br t, 2H), 2.91 (br t, 2H), at −60 °C δ = 9.13 (br, 1H), 8.44 (br s, 1H), 7.65 (m, 1H), 5.67 (br s, 1H), 4.02 (br d, 1H), 3.65 (br t, 1H), 3.44 (br t, 2H), 2.35 (br d, 1H).

[Ag_2(nptren)](NO_3)$_2$·5CH_3OH·2H_2O. A solution of tren (0.67 mmol) in methanol (25 mL) was added dropwise to a solution of $AgNO_3$ (0.67 mmol) and 1,4-NDA (1.0 mmol) in methanol (25 mL). The pale-yellow solution was stirred at 50 °C for 2 h in the dark. The yellow powders were obtained by evaporating the solvent. The product was purified by recrystallization from methanol and dried under vacuum (40% yield). Four of the five CH_3OH molecules of the lattice solvents are lost in air immediately. Found: C, 51.27; H, 4.68; N, 12.36%. Calcd for $Ag_2C_{49}H_{56}N_{10}O_9$: C, 51.41; H, 4.93; N, 12.24%. ^{1}H NMR (CD_3CN) at 23 °C δ = 9.35 (br s, 1H), 8.34 (m, 1H), 7.71 (m, 1H), 7.60 (br s, 1H), 3.99 (br t, 2H), 3.15 (t, 2H), at −40 °C δ = 9.39 (d, 1H), 8.34 (m, 1H), 7.73 (m, 1H), 7.67 (s, 1H), 3.96 (br, 2H), 3.13 (br, 2H), in CD_3OD at 23 °C δ = 9.50 (br d, 1H), 8.38 (br m, 1H), 7.73 (m, 1H), 7.71 (br s, 1H), 4.09 (br, 2H), 3.24 (br, 2H), at −40 °C δ = 9.57 (d, 1H), 8.48 (m, 1H), 7.81 (s, 1H), 7.79 (m, 1H), 4.10 (br, 2H), 3.26 (br, 2H).

[Cu_2(nptren)]($B(Ph)_4$)$_2$·2CH_3CN. A solution of CuCl (0.08 mmol) in AN (20 mL) was added to a solution of the free ligand (0.04 mmol) in AN (20 mL). The solution was stirred for 30 min at room temperature. After removing the volatiles under reduced pressure to dryness, the resulting red crystals were recrystallized from methanol. The $(B(Ph)_4)^-$ salt of the Cu^+ complex was given by an anion exchange as follows. $NaB(Ph)_4$ was added to a solution of the chloride in methanol. Red crystals of the $B(Ph)_4^-$ salt immediately precipitated, and were recrystallized from AN. The total yield, based on the ligand, was 50%. Small amounts of orange needles were obtained simultaneously in the recrystallization, which gave the same lattice parameters as that for the red crystal. Found: C, 75.98; H, 6.03; N, 9.05%. Calcd for $Cu_2C_{100}H_{94}N_{10}B_2$: C, 75.80; H, 5.98; N, 8.84%.

[Cu_2(nptren)]I_2·H_2O. A solution of CuI (0.08 mmol) in AN (20 mL) was added to a solution of the free ligand (0.04 mmol) in AN (20 mL). The solution was stirred for 30 min at room temperature. Upon removing the volatiles under reduced pressure to dryness, the resulting red crystals were recrystallized from methanol/AN (1 : 1) mixture. The yield was 50%. Found: C, 50.91; H, 4.70; N, 9.89%. Calcd for $Cu_2C_{48}H_{50}N_8I_2O$: C, 50.76; H, 4.44; N, 9.86%. ^{1}H NMR (CD_3CN) at 23 °C δ = 9.12 (s, 1H), 8.11 (m, 1H), 7.60 (m, 1H), 7.46 (s, 1H), 3.95 (t, 2H), 3.23 (t, 2H), at −40 °C δ = 9.15 (s, 1H), 8.17 (m, 1H), 7.61 (m, 1H), 7.50 (s, 1H), 3.93 (br t, 2H), 3.20 (br t, 2H).

Structure Determination.[26] A Rigaku AFC5S diffractometer with a graphite-monochrometor was used for the collecting all of the diffraction data. All of the calculations were performed using the teXsan[13] software. The structures were solved by direct methods,[14] and then expanded using Fourier techniques.[15] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms located at the calculated positions (CH = 0.95 Å) were included, but not refined.

Although the colorless prismatic crystals of the free nptren ligand obtained from a THF/AN solution show intimate twinning, the quality of the crystal was found to be much better than those obtained from methanol or ethanol, which was judged from the peak profiles.

Since the quality of the yellow prismatic crystals of [Ag_2(nptren)](NO_3)$_2$·5CH_3OH·2H_2O given from methanol immediately become worse in air, the data collection was carried out with the crystal sealed in a glass capillary. However the average intensity of the standard reflections was decreased by 15.0% during the data collection. The solvated CH_3OH molecules seemed to be taken away from the crystal. A linear correction factor was applied to the data to account for this decay phenomenon.

A red prismatic crystal for [Cu_2(nptren)]($B(Ph)_4$)$_2$·2CH_3CN of good quality obtained from AN was used in the data collection.

Spectroscopic Measurements. ^{1}H NMR measurements were carried out on a JEOL JNM-GX270 spectrometer. Each spectrum was referenced to the solvent itself at room temperature. A Hitachi 340 spectrophotometer was used in measurements of the UV-vis spectra.

Molecular Mechanics Calculations. The calculations were performed with a Silicon Graphics version of the MM2(87) program,[16] which was modified by us to perform calculations for molecules including up to 50 π-atoms. An SCF-MO calculation option was used to obtain reasonable results for the π-systems. Lone pairs (No. 20 atom in the MM2 program) were placed on all the imino nitrogen atoms (No. 37) of the free ligand. The force-field parameters used for the C, N, and H atoms in the macrobicycle, except for the C(methylene)–N(imine)–C(naphthylene) bending parameter, were taken from the values in the program. For the C–N–C angle, the ideal angle (θ_b) and bending force constants (k_b) were set to 120° and 0.55 mdyn Å rad^{-2}, respectively. The parameters around the metal atoms are listed in Table 3. A tetrahedral geometry around the metal atoms was at first adopted as the ideal structure. However, for that condition we could not reproduce the bond lengths around the metal ions determined by X-ray study, and thus a trigonal pyramidal structure was assumed as the ideal metal coordination geometry. The results show that the steric energy is more stable by 80—125 kJ mol^{-1} than when using the parameters of the tetrahedral structure. As is usual in force-field calculations involving metal atoms, the torsional barriers around the coordinate bonds were assumed to be negligible, and were thus set to zero. The parameters for the M–N stretching term (k_r and r^0) and the non-bonded interaction parameters of the metal atoms (ε) were initially set to 2.5 dyn Å^{-1}, 2.0 Å (Cu) or 2.3 Å (Ag), and 0.165, respectively.[17] The parameters were then gradually changed until the M–N distances observed in the X-ray analyses were reproduced. For each calculation, the initial coordinates were obtained from the crystallographically determined structures.

Results and Discussion

It is well-known that hexaimino cryptands are generally prepared in good yield (60—70%) from a direct condensation between tripod amines and dialdehydes without any template. Although some hexaimino cryptands are obtained in low yield (only 30—40%), the yield can be improved up to 60—90% by using an alkaline-earth metal ion or Ag^+ as a template.[8d,8e,9g] The condensation of 1,4-NDA with tren also gives a hexaimino cryptand, nptren, in high yield without a template, though the yield of the cryptate decreases upon using the Ag^+ ion. The Ag^+ ion would inhibit the formation of a ligand, because the formation of the $[Ag(tren)]^+$ complex was observed.[18] The lack of the ability of the Ag^+ ion for the template may be closely associated with the loose fit of the Ag^+ ion in the cavity, which will be described in a later section.

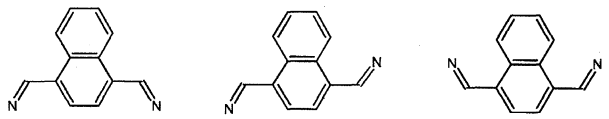
It has been reported that when the Cu ion is encapsulated in a tetrahedral-like coordination site in cryptand, the +1 oxidation state of Cu is stable.[5a] The $[Cu_2(nptren)]^{2+}$ cryptate

was found to be stable in air, and did not show any color change for more than half a year, even in an acetonitrile solution in air.

The electronic spectrum of the free ligand is similar to that of the Ag^+ cryptate. A band located at 321 nm ($\varepsilon = 4.7 \times 10^3$) is observed for the free ligand, which should be ascribed to the π–π^* transition. A slight red shift (4 nm) is found in the spectrum of the Ag^+ cryptate. However a quite different spectrum is observed for the Cu^+ cryptate. Particularly, a unique band ($\varepsilon = 7.8 \times 10^2$) is observed at around 400 nm, which is not observed for either the Ag cryptate or the free ligand. This band is assigned to a metal to ligand charge-transfer band, which was deduced from the reported assignments for the Cu(I)–diimine complexes.[19] This absorption must contribute the red color in the crystal containing $[Cu_2(nptren)]^{2+}$.

Crystal Structure. Many conformational isomers are possible for the nptren ligand, due to rotation around the C(naphthylene)–C(imino) bonds. One conjugated moiety of nptren can take three different conformers (Fig. 1). In the present study the *sym* conformation is found in the metal complexes and the *anti* conformation in the free ligand. The formation of the *revs* conformer appears to be unfavorable due to the steric repulsion between the three naphthylene groups, and has not actually been identified.

A summary of the crystal data is given in Table 1. The



sym *anti* *revs*

Fig. 1. Three different arrangements of the conjugated moieties of nptren.

geometries around the metal ions are listed in Table 2, and the averaged bond lengths and angles are given in Fig. 2.

(a) Free Ligand. The structure of the free ligand is shown in Fig. 3. The molecule has a pseudo C_3 axis lying through the bridgehead nitrogen atoms. Each diimino naphthylene group is parallel to the pseudo C_3 axis, and has an unsymmetric *anti* structure similar to that of the diiminophenyl moiety in the cryptand reported by Nelson et al.[8e] Therefore, there are no C_2-axis and mirror planes in the free nptren ligand. One water molecule and one acetonitrile molecule are involved in the unit cell. No interactions have been found between the solvent molecules and the nptren ligand, although some hydrogen bonds have been found in the Nelson's ligand.[8e] Each conjugated plane comprising iminomethyl–naphthylene–iminomethyl is distorted at both edges. The torsion angles, N(imino)–C(imino)–C(1 or 4 of naphthalene ring)–C(4a or 8a of naphthalene ring), are in

Table 1. The Summary of Crystal Data, Details of Intensity Data Collection, and Least-Squares Refinement Prameters[a]

	Free ligand ·H_2O·CH_3CN	$[Ag_2(nptren)](NO_3)_2$ ·$2H_2O$·$5CH_3OH$	$[Cu_2(nptren)]$ $(B(Ph)_4)_2$·$2CH_3CN$	$[Cu_2(nptren)]$ I_2·H_2O
Empirical formula	$C_{50}H_{53}N_9O$	$Ag_2C_{53}H_{72}N_{10}O_{13}$	$Cu_2C_{100}H_{94}N_{10}B_2$	$Cu_2C_{48}H_{50}N_8I_2O$
Formula weight	796.03	1272.95	1584.62	1153.88
Space group	$R\bar{3}$ (No. 148)	$P\bar{1}$ (No. 2)	$P2_1/a$ (No. 14)	$P2_1/a$ (No. 14)
a/Å	43.42(1)	15.56(2)	16.277(1)	14.268(2)
b/Å		15.68(1)	30.888(1)	23.084(3)
c/Å	11.94(1)	15.48(1)	18.093(1)	14.825(2)
α/deg		104.34(5)		
β/deg		119.28(6)	115.178(5)	114.106(9)
γ/deg		65.63(7)		
vol/Å^3	19515(18)	2999(6)	8232.4(9)	4456(1)
d(calcd)/g cm^{-3}	1.22	1.41	1.28	1.69
Z	18	2	4	4
Radiation	Cu $K\alpha$ (λ = 1.54178)	Mo $K\alpha$ (λ = 0.7107)	Cu $K\alpha$ (λ = 1.54178)	Mo $K\alpha$ (λ = 0.7107)
μ/cm^{-1}	5.90	7.18	10.59	23.87
Scan speed/deg min^{-1}	8.0	4.0	8.0	8.0
No. of data	6986	6435	13034	12394
No. unique reflcns	6471	6083	12538	11788
Abs corr	DIFABS[b]	DIFABS[b]	psi	DIFABS[b]
No. of obsd with $I > 3.0\sigma(I)$	2137	2122	6128	2588
No. of variable params	508	713	1027	311
p-factor	0.005	0.005	0.006	0.00
R	0.061	0.064	0.037	0.065
R_w	0.056	0.039	0.027	0.049
Goodness of fit	3.04	1.88	1.81	1.53

a) Least-squares: Function minimized: $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = (S^2(C+R^2B)+(pF_o^2)^2)/Lp^2$, S = Scan rate, C = Total integrated peak count, R = Ratio of scan time to background counting time, B = Total background count, L_p = Lorentz-polarization factor, p = p-factor. b) DIFABS: An empirical absorption correction program. See Ref. 25.

Table 2. Geometries around the Metals

	$[Ag_2(nptren)](NO_3)_2$	$[Cu_2(nptren)](B(Ph)_4)_2$	$[Cu_2(nptren)]I_2$
(a) Distances			
$M–N_{br}$[a)]	2.42(2), 2.51(2)	2.213(3), 2.207(3)	2.25(1), 2.23(1)
$M–N_{im}$[b)]	2.30(1), 2.25(2)	2.029(3), 2.030(3)	2.04(1), 2.06(1)
	2.24(2), 2.28(2)	1.989(3), 2.003(3)	1.98(1), 2.00(2)
	2.29(2), 2.29(2)	1.997(3), 1.997(3)	1.98(1), 1.98(1)
(b) Angles			
$N_{br}–M–N_{im}$	78.7(5), 75.6(6)	83.6(1), 82.6(1)	82.3(5), 85.2(5)
	74.1(6), 75.9(6)	85.0(1), 86.2(1)	84.7(5), 83.6(6)
	77.0(6), 74.6(6)	84.9(1), 85.4(1)	84.9(6), 87.5(6)
$M_{im}–M–N_{im}$	116.8(6), 113.0(7)	115.8(1), 112.9(1)	105.1(6), 111.6(6)
	113.8(6), 115.7(6)	113.8(1), 121.9(1)	117.6(6), 119.7(6)
	113.7(6), 112.8(6)	127.7(1), 122.8(1)	134.1(6), 126.9(6)

a) N_{br} = bridgehead nitrogen atom. b) N_{im} = imino nitrogen atoms.

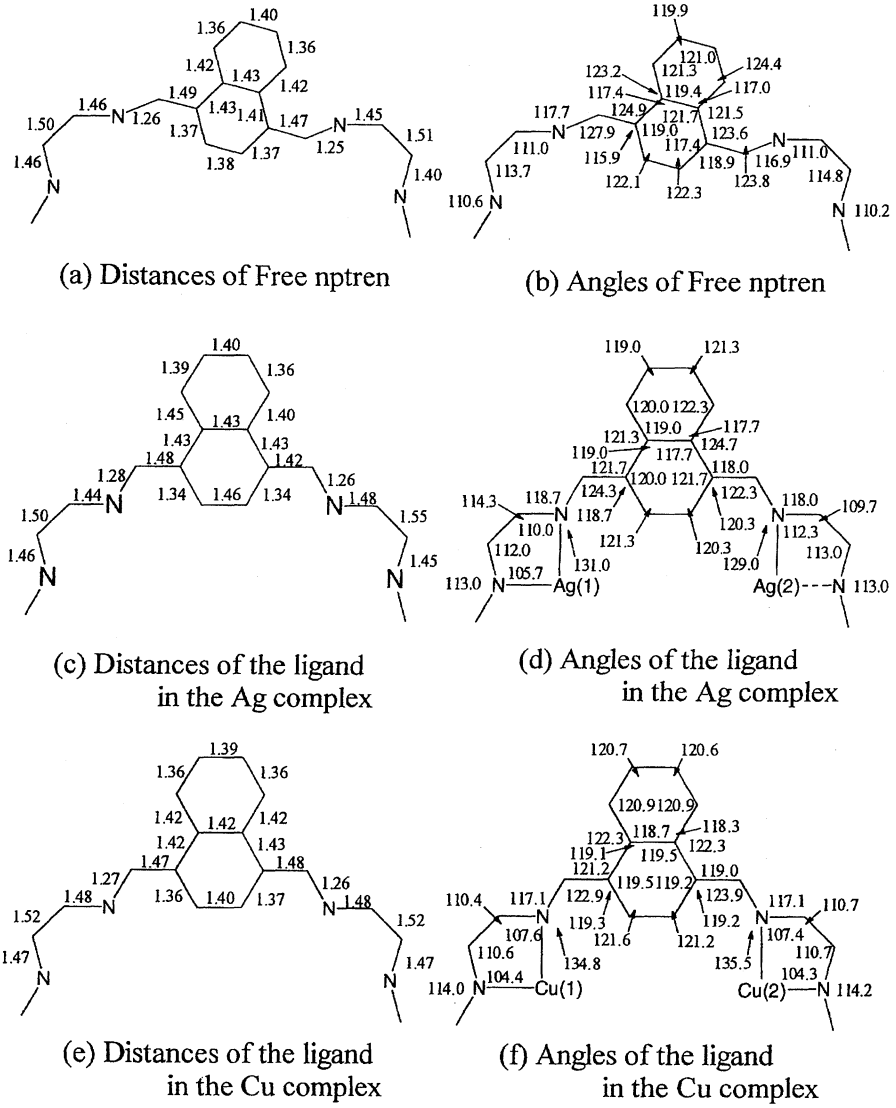


Fig. 2. Averaged distances and angles of nptren compounds. The data are averaged over the three arms of nptren.

the 173°—159° or −1°—7° range. The average distance of the C(imino)–C(naphthylene ring) bonds is 1.48 Å, which is closer to the single bond rather than the conjugated bond. The rotational barrier around these bonds would not be high due

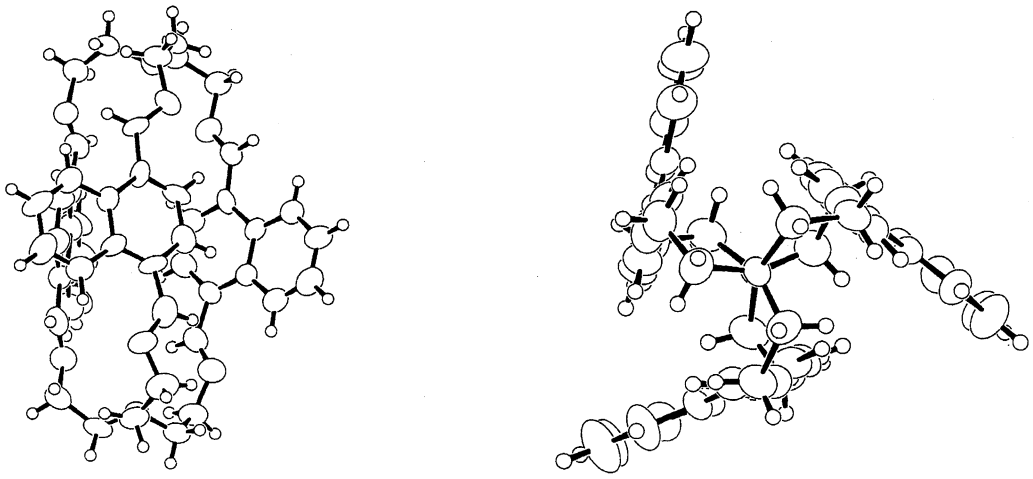


Fig. 3. ORTEP drawings of free nptren ligand. (a) A side view, (b) A view down the N(bridgehead)···N(bridgehead) axis.

Table 3. Force-Field Parameters for Metals

	Cu^+		Ag^+	
(a) Bond stretching				
	k_r	r_0	k_r	r_0
$M–N_{br}$	2.50	2.10	2.50	2.50
$M–N_{im}$	2.50	2.00	2.50	2.30
(b) Non-bonded parameters				
	ε	Radius	ε	Radius
	0.122	1.40	0.122	1.72
(c) Angle bending	k_θ	θ_0	k_θ	θ_0
$C_{tr}–N_{br}–M$	0.45	109.2	0.45	109.2
$C_{tr}–N_{im}–M$	0.45	120.0	0.45	120.0
$C_{np}–N_{im}–M$	0.45	120.0	0.45	120.0
$N_{br}–M–N_{im}$	0.30	90.0	0.30	90.0
$N_{im}–M–N_{im}$	0.30	120.0	0.30	120.0
(d) Out of plane				
$M–N_{im}$	0.05		0.05	
(e) Torsional parameters				
angle	V1	V2	V3	
$N_{br}–C_{tren}–C_{tren}–N_{im}$	0.00	0.00	0.10	
$C_{tren}–C_{tren}–N_{im}–C_{im}$	0.34	0.00	−0.90	
$C_{naph}–C_{im}–N_{im}–C_{tren}$	0.00	10.00	0.00	

to the considerable single–bond character. The 2-H atoms of each naphthalene ring is located just above the center of the neighboring 6-membered aromatic ring (outward ring of each naphthalene). The distances between the hydrogen atoms and the center of the aromatic rings are 2.61, 2.68, and 2.71 Å, respectively, suggesting that there are intramolecular edge-to-face interactions.[20] Further, intermolecular face-to-face interactions have been observed.[20,21] One of the naphthalene planes is parallel to a naphthalene plane of the neighboring molecule, and a quarter part of the fused ring is overlapped, where the distance between the rings is 3.54 Å.

(b) $[Ag_2(nptren)]^{2+}$ Complex. The structure of $[Ag_2(nptren)]^{2+}$ is shown in Fig. 4. Each bis(iminomethyl)naphthalene has a symmetric *sym* structure. The two Ag^+ ions are encapsulated into two tren moieties of the ligand, respectively. Each Ag^+ ion has a distorted trigonal pyramidal geometry, in which the two Ag^+ ions are displaced by 0.53 and 0.58 Å out of the trigonal coordination planes. Although the Ag–N(imino) bond length is comparable for the two Ag^+ coordination spheres, the Ag–N(br) distances (N(br) = bridgehead nitrogen atom) are considerably different between them: Ag(1)–N(br) = 2.42(2) Å and Ag(2)–N(br) = 2.51(2) Å. The Ag(2)–N(br) distance seems to be too long for a normal coordination bond. These results indicate the weak coordination of the Ag(2) ion. The distances between the Ag^+ ions and H atoms in the 2,3-positions of the naphthalene ring are considerably short: 2.38, 2.48, and 2.42 Å for the Ag(1) site and 2.85, 2.84, and 2.68 Å for the Ag(2) site.

The Ag^+ cryptate has a pseudo C_3-axis which runs through the two bridgehead nitrogen atoms. Although many cryptands show a reduction of the distance between the bridgehead nitrogen atoms upon complexation, the distance of 10.85 Å is not clearly different from that of the free ligand (10.80 Å). As is distinct from the free nptren, the three naphthalene rings are located radially, and the angles between the naphthalene ring planes are 69°, 54°, and 64°. The distortions in the conjugated groups are more obvious than that in the free ligand. The distortions around the Ag(2) site are larger than that on Ag(1) site. (The torsion angles of N(imino)–C(imino)–C(1 or 4 of naphthalene ring)–C(4a or 8a of naphthalene ring) are 148—159° for the Ag(1) site and 145—146° for the Ag(2) site). The H atoms in the 2,3-positions of each of the three naphthalene rings are directed to the center of the inward ring of the neighboring naphthalene rings. The distances between the H atoms and the center of the rings are 2.96, 3.02, and 3.11 Å for the Ag(1) site and 3.32, 3.27,

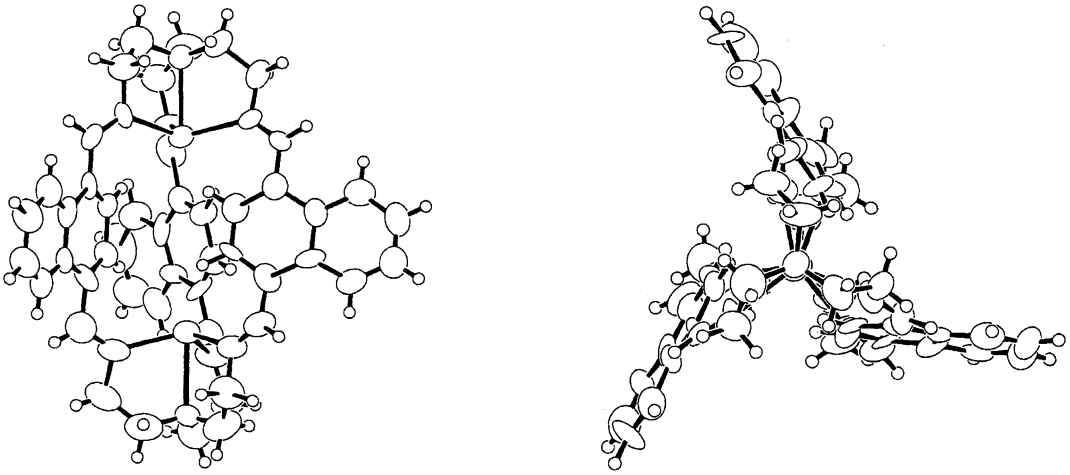


Fig. 4. ORTEP drawings of $[Ag_2(nptren)]^{2+}$. (a) A side view, (b) A view down the N(bridgehead)···N(bridgehead) axis.

and 3.36 Å for the Ag(2) site. Therefore, some edge-to-face aromatic–aromatic interactions should be working, and the interaction is strong on the Ag(1) site.[20d] The distances between the naphthalene rings are clearly longer than that of the free ligand, which would be caused by an expansion of the cavity with the metals and a conformational change in the ligand. An intermolecular overlapping of the naphthalene rings is also observed, as in the case of the free nptren, where the shortest distance between the two naphthalene planes is 3.47 Å, which is similar to the case of the free nptren ligand.

(c) $[Cu_2(nptren)]^{2+}$ Complex. The structure of $[Cu_2(nptren)]^{2+}$ is shown in Fig. 5. The coordination geometries around the Cu^+ ions are similar to those in the Ag^+ cryptate. However, the extent of distortion from an ideal trigonal pyramid is relatively small in the Cu^+ complex. The Cu^+ ions exist 0.19 and 0.18 Å apart from the base planes comprising the three imino nitrogen atoms, respectively. The Cu–N bond lengths are similar at the two Cu^+ sites. The most remarkable structural difference between the Cu^+ and Ag^+ cryptates is found in the orientation of the naphthalene rings (Fig. 5b). Since one of the naphthalene rings has been found to be bent to a high degree, C_3 symmetry is completely lost in the Cu^+ cryptates. The fact that the Cu–N(imine) distances are significantly shorter than those of the Ag^+ cryptate may be the main origin of the reduction of symmetry; the short distance should cause a steric repulsion between the naphthalene rings. The bent conjugated group has a particularly large distortion from a plane. The torsion angles of N(imino)–C(imino)–C(1-naphthalene)–C(4a-naphthalene) for this group are 133.0° and 96.0°. The distances between the Cu^+ ions and the 2 or 3-H atom are very short: 2.50, 2.33, and 4.32 Å for the Cu(1) site and 2.33, 2.92, and 3.22 Å for the Cu(2) site. Some of them are closer than the sum of the van der Waals radii.

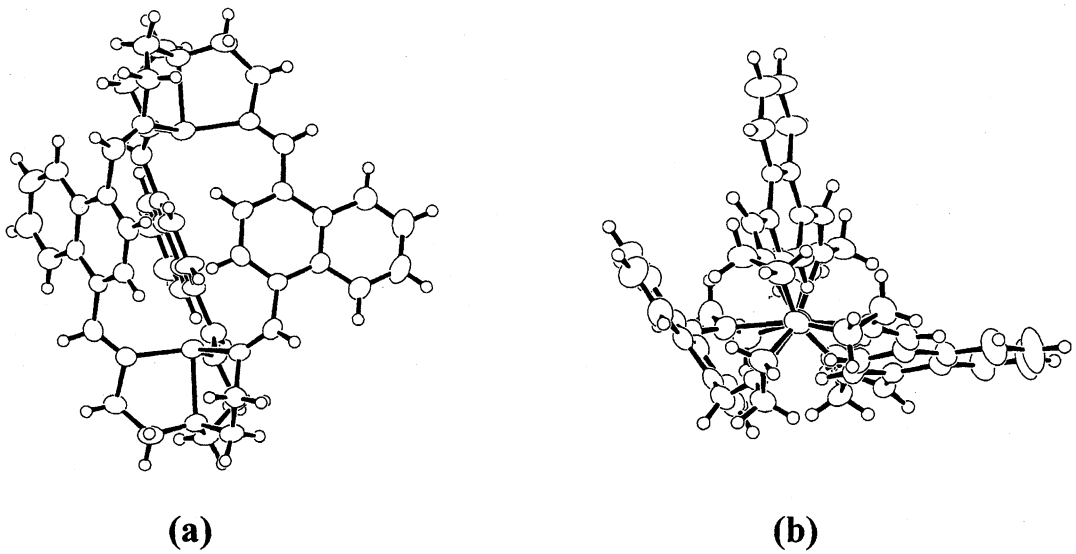


Fig. 5. ORTEP drawings of $[Cu_2(nptren)]^{2+}$. (a) A side view, (b) A view down the N(bridgehead)···N(bridgehead) axis.

Because of the large counter anions ($B(Ph)_4^-$) present in the lattice, no intercationic interaction is achieved in the crystal. However, some cation-anion interactions are found: A strong edge-to-face interaction is formed between the 8-H atom of a naphthalene group and the center of a phenyl group of $B(Ph)_4^-$ (the distance between them is 2.44 Å).

In order to investigate the conformation of the complex having no interaction between the complex cation and the counter anion, the structure of the I^- salt of the Cu^+ complex is also determined. Although an H_2O molecule also exists in a unit cell, there are no interactions with the complex cation. A comparison between the structure in the $B(Ph)_4^-$ salt and that in the I^- salt is shown in Figs. 6a and 6b. The geometries around the Cu^+ ions are given in Table 2. The bond lengths between the Cu^+ ion and the bridgehead nitrogen atom are 2.25(1) and 2.23(1) Å, and are slightly longer than that in the $B(Ph)_4^-$ salt. Although both structures of the nptren ligand show unsymmetrical conformations, the two naphthalene groups, which are not largely bent, are turned to different directions from the ligand in the $B(Ph)_4^-$ salt. The difference is brought about a cation-cation interaction, which occurs by using the small I^- anion. The largely bent naphthalene group is parallel to the adjacent naphthyl group in the same ligand. The distances between the naphthalene plane and the C atoms of the adjacent naphthalene are 3.36—3.86 Å. The latter naphthalene group is also located parallel to the bent naphthalene group of the neighboring molecule, and the intermolecular aromatic–aromatic distance is estimated to be 3.40—71 Å.

The Unsymmetrical Structure of the Cu^+ Complex. Both crystal analyses of the Cu^+ complexes revealed that they have unsymmetrical structures, which are distinct from the C_3-symmetric structure of the Ag^+ complex. Therefore, the unsymmetrical structure, which has one largely bending naphthalene group, seems to be intrinsically stable for the Cu^+ complex. In order to confirm the hypothesis, molecular-mechanics calculations were performed. For the initial coordinates, the X-ray results of the unsymmetrical Cu^+ complex and that of the symmetrical Ag^+ complex were used for a comparison. The energy-minimized structures maintained the starting ones, i.e. the calculation gave on unsymmetrical structure when starting with the unsymmetrical one, and vice versa (Figs. 6c and 6d). However, the steric energy of the calculated unsymmetrical structure is 84.27 kJ mol^{-1}, which is significantly lower than the symmetrical structure of 105.39 kJ mol^{-1}. The result would support that an unsymmetric structure showing that a bending of one arm in the ligand is an intrinsicably stable structure of the dinuclear Cu^+ complex.

Molecular-mechanics calculations were also performed for a dinuclear Ag^+ complex. When symmetrical and unsymmetrical structures are adopted as the starting structure of the ligand, the energy-minimized structure also holds the initial geometries as well as the Cu^+ complex. The steric energy of the symmetric and unsymmetric structures are 83.72 and 106.65 kJ mol^{-1}, respectively. For the Ag^+ complex, the symmetric structure, which is found in an X-ray diffraction study, was shown to be more stable than the unsymmetric structure.

For the free nptren ligand, the steric energy of *anti* and *sym* structure was calculated to be 3.56 and 31.84 kJ mol^{-1}, respectively. Obviously, the *anti*-conformation of the free ligand found in the X-ray diffraction study is intrinsically more stable than the *sym*-conformation.

Behaviors in Solution. All of the compounds show two multiplets and two singlets for the conjugated moieties, and two triplets or broad peaks for the tren moieties in the ^1H NMR spectra. As shown in Figs. 7 and 8, the order of the peaks for the conjugated systems of the free ligand is different from that of the Ag^+ cryptate. The Ag^+ cryptate and Cu^+ cryptate give similar spectra. The characteristic two multiplets, which were also observed in the spectrum of 1,4-NDA, were assigned to the protons in the 5, 6, 7, and 8 positions of 1,4-naphthalene. The two singlets can be assigned to the protons of the iminomethyl and 2 (and 3)-positions of the 1,4-naphthalene ring. The ratio of the integrated intensities of these four peaks is 1 : 1 : 1 : 1. They were assigned, as shown in the Figs. 7 and 8, using the ^1H-

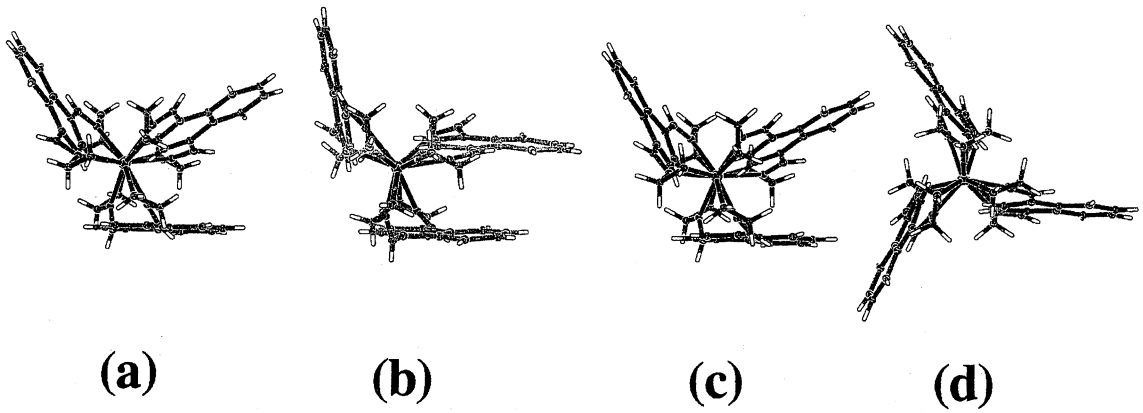


Fig. 6. The structures of Cu^+ complex resulted from X-ray diffractions and MM2 calculations. (A view down the N(bridgehead)···N-(bridgehead) axis.) (a) X-ray result of $B(Ph)_4^-$ salt, (b) X-ray result of I^- salt, (c) energy-minimized strucuture starting from unsymmetrical conformation, (d) energy-minimized strucuture starting from symmetrical conformation.

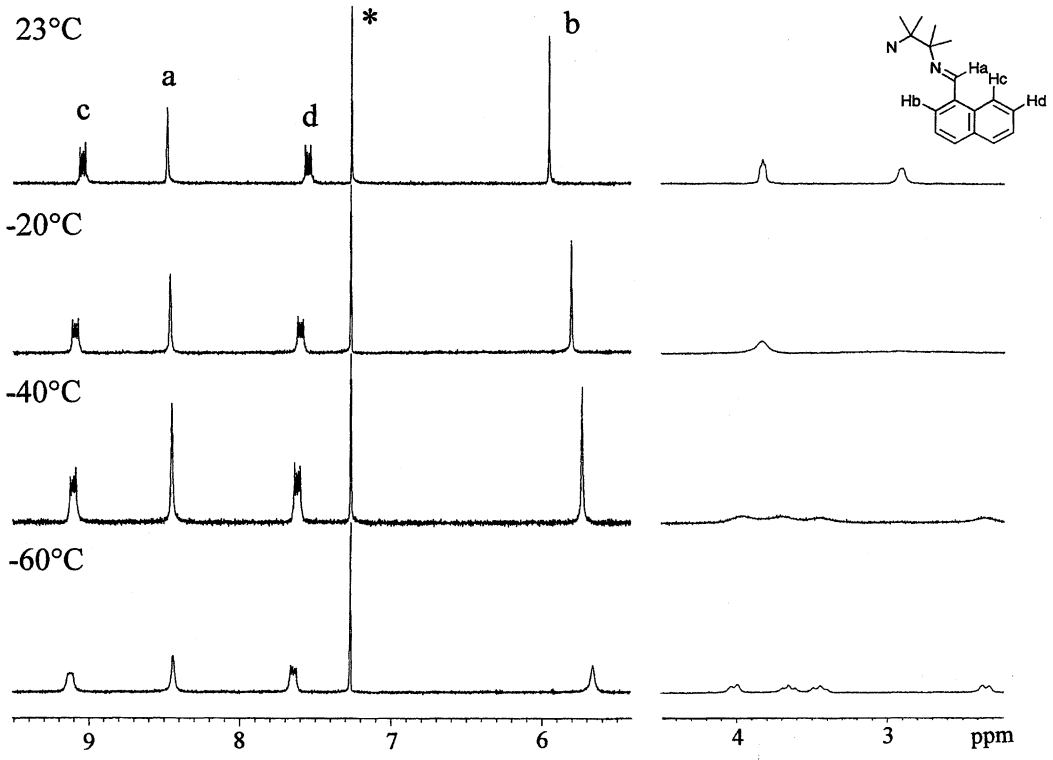


Fig. 7. ^{1}H NMR spectra of the free ligand in $CDCl_3$. Peak * corressponds to $CDCl_3$.

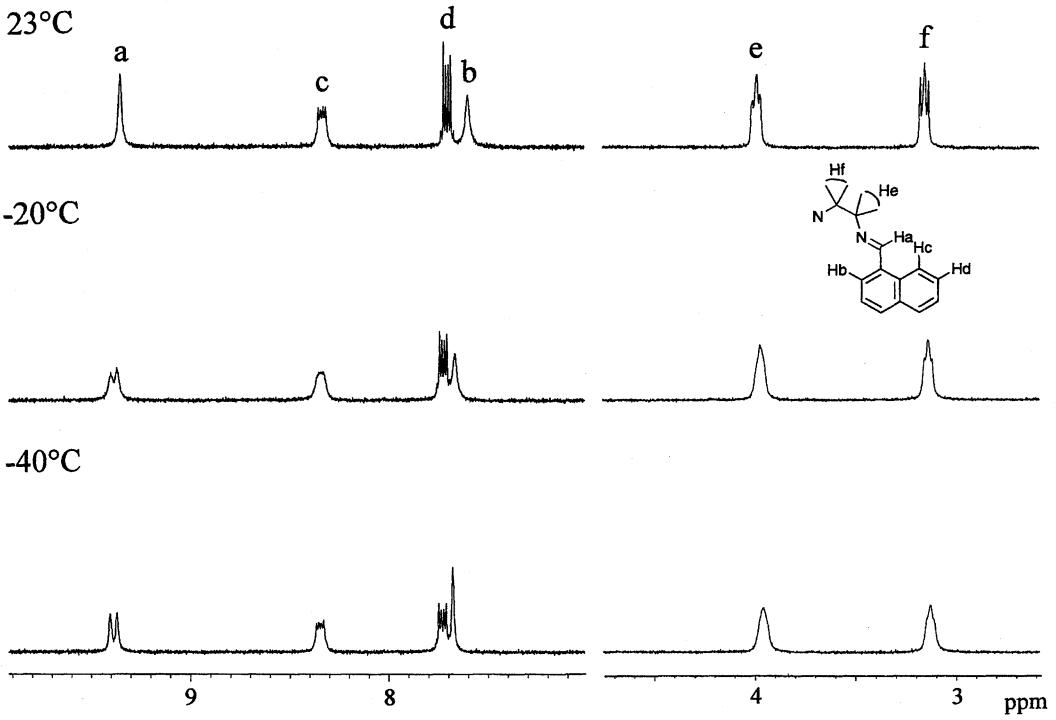


Fig. 8. ^{1}H NMR spectra of $[Ag_2(nptren)]^{2+}$ in CD_3CN.

^{1}H NOE[22] technique.

Although the conformation around the naphthalene groups in the free ligand is characterized as *anti* in the crystal, the structure in solution is shown to have D_3 symmetry, according to the ^{1}H NMR results (Fig. 7). Although no change in the spectrum was observed upon cooling down to −40 °C, a broadening of the peaks was found at −60 °C. This result suggests that there is a fast rotating motion around the C(iminomethyl)–C(naphthalene ring) bond at room temperature. A large difference in the proton chemical shifts for the 2, and 3-positions of the 1,4-naphthylene group between the free ligand and the Ag^+ cryptate was observed ($\Delta\delta = 1.65$ ppm). The large higher-field shift for the free ligand probably arises from edge-to-face aromatic interactions. The

lower-field shift by the agostic interaction between the Ag^+ ion and the protons of the 2 (and 3)-position may also contribute the large difference. Further, a higher field shift is observed in the protons of the 2 (and 3)-position of the free ligand upon cooling. When the solution is cooled, the swing motion of the naphthylene group should slow down, and the average distance between the H atoms of the 2,3-position and the neighboring naphthyl rings must be shortened. On the other hand, a lower-field shift upon cooling in Ag^+ cryptate was observed, which would also have originated from the same slowing-down of the swing motion. In this case, since the agostic interaction between H atoms of the 2,3-position and the Ag^+ ions would become stronger upon cooling, the interaction causes the lower-field shift.

The methylene peaks of the tren moieties in the free ligand show a strong temperature dependence in their shapes. The higher-field peak decoalesces at −20 °C and splits into two peaks at 2.34 and 3.41 ppm at −60 °C. Although the lower-field peak also shows a decoalescence, the splitting at low temperature is small. The change in the methylene peaks indicates a non-equivalence of the geminal protons in each methylene group in the tren moiety at low temperature.

The peak of the iminomethyl protons for the Cu^+ and Ag^+ cryptates shows a large lower-field shift compared to that of the free ligand ($\Delta\delta = 0.94$ and 0.97 ppm for the Ag^+ and Cu^+ complex, respectively) (Fig. 8). Not only the lower-field shift caused by the coordination of the metals, but also a higher-field shift induced by the neighboring lone pairs of the imino groups on the free ligand must work on the effect.[9e] Furthermore, a splitting of the iminomethyl peak for the Ag^+ complex has been observed upon cooling in an acetonitrile (AN) solution. This splitting corresponds to a non-equivalence of the iminomethyl-protons. One of the two peaks shows a very small shift compared to that observed at room temperature; the other is located in the lower-field side of the former one. A similar splitting was also observed in methanol, even at room temperature. When an excess amount of Ag^+ was added to an AN solution of the Ag^+ cryptate, no splitting on ^1H NMR was observed at any temperature. The crystallographic results show that the bond around one Ag^+ ion is clearly weaker than the other Ag^+ ion. Therefore, we assume that the non-equivalence in the NMR spectra is due to the release of one Ag^+ ion from the cavity. We tried to measure the concentration of the Ag^+ released ($[Ag^+]$).[23] In AN solution under the same conditions as that for the measurements of ^1H NMR, $[Ag^+]$ was determined to be only 3% of the total metal complex at room temperature. On the other hand, this ratio was 24% in methanol. Further, the extraction of only one Ag^+ ion was observed when the complex was treated with an excess amount of Cl^-.[24] These results may indicate that: 1) the Ag^+ cryptate almost sustains its dinuclear structure in AN at room temperature, but the stability constant of the second complexation appears to be extremely low compared to the first one; 2) upon cooling the equilibrium shifts to the mononuclear $[Ag(nptren)]^+$ complex.

Although the Cu^+ complex has an unsymmetric structure in the crystal, ^1H NMR studies have revealed that the complex takes a D_3 symmetry in any solvent. The spectrum does not change in the 23——40 °C temperature range. There are two possible models for evaluating this observation: Either the swing motion of the three naphthylene groups must occur even at low temperature, or the Cu^+ complex must have an intrinsic D_3 symmetric structure in solution. The stability of the unsymmetric structure, which results from X-ray diffraction and MM calculation, supports the former idea.

Conclusion

We have presented the syntheses, crystal structures, and ^1H NMR spectra of a new cryptand and its dinuclear cryptates of Ag^+ and Cu^+. The *anti*-conformation of the ligand found in the crystal are essentially stable, even though these structures could not be directly detected in solution due to the rapid conformational motions. Two different structures are found between the Ag^+ complex and Cu^+ complex: the Ag^+ complex has a symmetrical structure, while the Cu^+ complex has an unsymmetrical one. The current study appears to be a good example which demonstrates that the conformation of a cryptand can be discretely changed with a choice of the metal ion to be encapsulated in its cavity. We believe that this finding must be useful in designing new functional molecules.

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22) For the Ag^+ complex, irradiation to the singlet peak (9.35 ppm) enhances the peak area of the multiplet at 8.32 ppm to 138%. The irradiation upon the singlet at 7.60 ppm shows no enhancement. The broad triplet at 3.98 ppm was assigned to methylene proton on imino side, and the sharp triplet at 3.15 ppm was assigned to the methylene on the bridge head side since irradiation to the singlet peak (9.35 ppm) also enhances the peak area of the methylene proton (3.98 ppm). For the free ligand, irradiation on the singlet at 8.49 ppm enhanced the multiplet at 9.05 ppm to 115% and the singlet at 5.95 ppm to 115% at the same time. Irradiation upon the singlet at 5.95 ppm enhanced the singlet at 8.49 ppm to 116%.

23) The concentration of the free silver ion was measured with the silver selective electrode (DKK, type 7080), whose potential being measured with a digital multimeter (ADVANTEST, TR 6846). The data were collected at 23 °C. The concentration of the Ag^+complex was 5×10^{-3} M (M = mol dm^{-3}) (same concentration as ^{1}H NMR measured). In all the measurements the ionic strength was kept constant at I=0.1 M with tetrabutylammonium perchlorate and performed under nitrogen.

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26) Tables of coordinates involving hydrogen atoms, anisotropic thermal parameters of the non-hydrogen atoms, bond lengths and angles involving hydrogen atoms, and complete $F_o - F_c$ data are deposited as Document No. 69003 at the Office of the Editor of Bull. Chem. Soc. Jpn.