Stable Cu^+, Ag^+ complexes of aza-bridged macrocyclic molecules: structure and chemical properties

**Hiroyuki Takemura,*[a] Noriyoshi Kon,[b] Keita Tani,[c] Kô Takehara,[a]
Junko Kimoto,[b] Teruo Shinmyozu[d] and Takahiko Inazu*[b]**

[a] *Department of Chemistry, Faculty of Science, Kyushu University,
Ropponmatsu 4-2-1, Chuo-ku, Fukuoka, 810 Japan*
[b] *Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki 6-10-1,
Higashi-ku, Fukuoka, 812 Japan*
[c] *Division of Natural Science, Osaka Kyoiku University, Kashiwara, Osaka, 582 Japan*
[d] *Institute for Fundamental Research of Organic Chemistry, Kyushu University,
Hakozaki 6-10-1, Higashi-ku, Fukuoka, 812 Japan*

The cage type compounds 1 and 2 form stable Cu^+ or Ag^+ complexes, which have been employed for the preparation of cation-free host molecules.

A reaction between the potassium complex $K^+\subset\mathbf{1}$ and a Cu^{II} salt generates a Cu^I complex. The Cu^{II}/Cu^I redox potential is observed at +0.43 V (*vs.* SCE) in the cyclic voltammetry, which shows that the Cu^+ state is stabilized by its rigid molecular skeleton and spatially fixed coordination sites. A reaction between Ag^+ and $K^+\subset\mathbf{2}$ yields the dinuclear complex $2Ag^+\subset\mathbf{2}$, which has a short $Ag^+ \cdots Ag^+$ distance (2.78 Å). The halide anions (Cl^-, Br^-, I^-) remove one Ag^+ from $2Ag^+\subset\mathbf{2}$ to give $Ag^+\subset\mathbf{2}$, but further demetallation does not occur. CV measurements show that these silver complexes are electrochemically stable. Both silver complexes are stable to sunlight. The first preparations of guest-free hosts have been achieved by treating $Cu^+\subset\mathbf{1}$ or $2Ag^+\subset\mathbf{2}$ with CN^-. Inclusions of neutral guests (NH_3, BH_3) have been attempted using these guest-free hosts.

Introduction

In earlier reports, we showed that the host molecules **1** and **2** formed stable cation complexes with alkali metal cations and a proton. For example, log K_a of K^+, $NH_4^+\subset\mathbf{1}$ were estimated to be 5.2 and 6.3 in [$^2H_6$]-DMSO, respectively. In $CDCl_3$, the stability of $K^+\subset\mathbf{1}$ is very high (log $K_a = 15.1$).[1] These cation-bound hosts are very stable and the cations could not be removed in spite of many attempts. These compounds have electron-rich cavities because of the convergence of the nitrogen lone pairs. The driving forces for the cation inclusions are ion-dipole interactions. Also, the nitrogen lone pair is a good binding site for hydrogen bonds and coordinate bonds. Some neutral chemical species which form hydrogen bonds or coordinate bonds are considered to be possible guests. For example, NH_3 forms hydrogen bonds with itself or with amines,[2] while BH_3 (B_2H_6) forms stable complexes with a wide variety of electron donors. We expected that these hosts **1** and **2** would form inclusion complexes with such neutral chemical species. However, many attempts to prepare the inclusion complexes starting from their cation complexes were unfruitful. Thus, it was concluded that guest-free hosts were necessary to investigate the interactions with these guest molecules. In order to prepare the guest-free **1** and **2**, we employed the reactions between heavy metal complexes of the hosts and CN^-. Furthermore, stabilization of heavy metal complexes is expected because of their structural features: they have spatially fixed tetrahedral or octahedral coordination sites and the cavities are surrounded by the six aromatic rings. We report here aerially and photo- and electrochemically stable Cu^+ or Ag^+ complexes and their reactions with halides and cyanide ions.

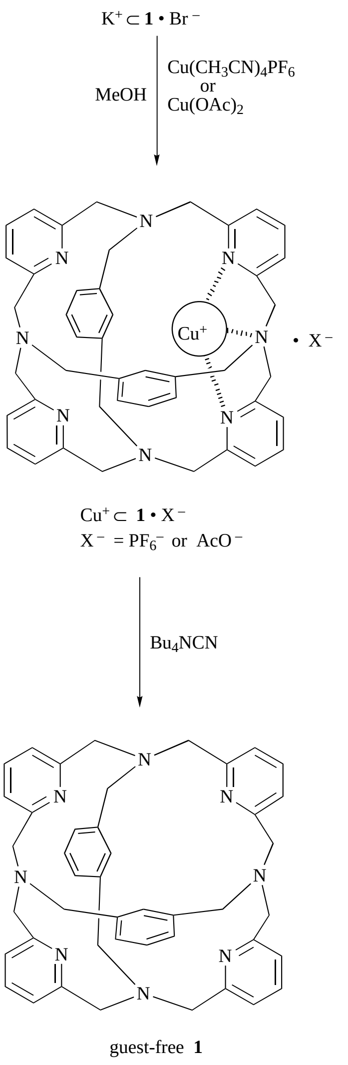
Results and discussion

(i) Cu^+ complex of 1

The preparation of the Cu^+ complex of **1** could be achieved in two ways. A reaction between $K^+\subset\mathbf{1}$ and $Cu(MeCN)_4PF_6$ afforded $Cu^+\subset\mathbf{1}\cdot PF_6^-$ as yellow crystals in 51% yield (Scheme 1). Alternatively, a reaction with the Cu^{II} salt also generated $Cu^+\subset\mathbf{1}$ in 52% yield: refluxing the methanol solution containing equal amounts of $Cu(MeCO_2)_2$ and $K^+\subset\mathbf{1}\cdot Br^-$ for 12 h afforded a mixture of $Cu^{2+}\subset\mathbf{1}$ and $Cu^+\subset\mathbf{1}$ as green and yellow materials, respectively. $Cu^+\subset\mathbf{1}$ was easily isolated from the reaction mixture by column chromatography on silica gel. Excess of $Cu(MeCO_2)_2$ decreased the yield of $Cu^+\subset\mathbf{1}$. The geometry of donor sites (tetrahedral and quasi-planar) of **1** allows both Cu^+ and Cu^{2+} coordinations, thus, planar Cu^{2+} can be converted into tetrahedral coordination and simultaneously reduced to Cu^+.[3] Unfortunately, the crystallographic analysis of $Cu^+\subset\mathbf{1}\cdot PF_6^-$ did not produce good results. However, it appeared that a bridgehead nitrogen and two pyridine rings coordinate to the Cu^+ in a distorted tetrahedral manner and that the position of the Cu^+ ion is not at the centre of the cavity but near the coordinating nitrogen atoms. Further attempts to obtain satisfactory results from crystallographic analysis are being made. The octahedral coordination type host **2** also formed a Cu^+ complex, but less stable than $Cu^+\subset\mathbf{1}$. Therefore, the ligand **1** was employed for investigations of the Cu^+ complex.[4]

In the electronic spectrum of the complex, the characteristic MLCT (metal-to-ligand charge-transfer) transition bands were observed (Fig. 1). The relatively strong band at 259 nm (log $\varepsilon = 4.22$) is assigned to the π–π^* transition and the bands at 364 nm (log $\varepsilon = 3.52$) and 440 nm (log $\varepsilon = 2.50$) are assigned to the MLCT bands.[5]

$Cu^+\subset\mathbf{1}$ is stable under aerobic conditions both in solution and in the solid state. The cyclic voltammogram of $Cu^+\subset\mathbf{1}\cdot PF_6^-$ in acetonitrile is shown in Fig. 2. A reversible wave was observed and an oxidation potential peak appeared at +0.16 V (*vs.* Ag/AgCl, 100 mV s^{-1}; +0.43 V *vs.* SCE). It is noteworthy that even at a low cathode potential (~ −1.8 V), precipitation of metal copper did not occur. Stable Cu^+ states are reported in an oligo-pyridine-Cu^+ complex (+0.42 V *vs.* SCE) and Cu^+ caten-



Scheme 1 Preparations of Cu$^+$⊂**1** and guest-free **1**

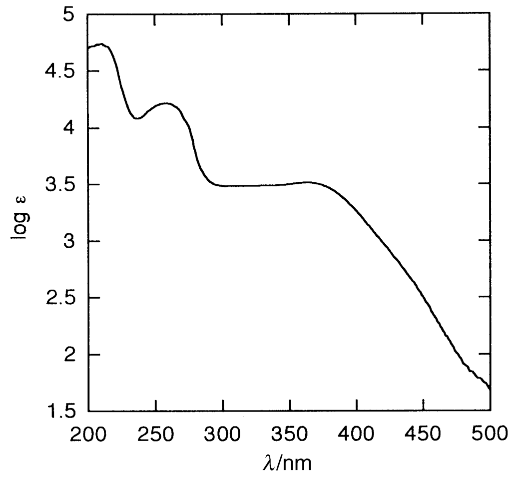


Fig. 1 Electronic spectrum of Cu$^+$⊂**1**·PF$_6^-$ in MeCN

ate (+0.565 V *vs.* SCE).[5a,c] Although tris(2-pyridyl)methylamine is equivalent to the coordination site of **1**, its Cu$^+$ complex is reported to be unstable.[6] In the case of Cu$^+$⊂**1**, the Cu$^+$ state is stabilized by its bulky molecular skeleton and spatially fixed coordination geometry.

Table 1 Selected bond lengths and angles

Bond lengths (Å)		Bond angles (°)	
Ag(1)–Ag(2)	2.780(6)	Ag(1)–Ag(2)–N(3)	148.46(6)
Ag(1)–N(1)	2.441(2)	Ag(1)–Ag(2)–N(4)	96.95(6)
Ag(1)–N(2)	2.258(2)	Ag(1)–Ag(2)–N(9)	141.38(6)
Ag(1)–N(10)	2.348(2)	N(1)–Ag(1)–N(2)	117.97(8)
Ag(2)–N(3)	2.379(2)	N(1)–Ag(1)–N(10)	71.40(8)
Ag(2)–N(4)	2.428(2)	N(2)–Ag(1)–N(10)	156.62(8)
Ag(2)–N(9)	2.448(2)	Ag(2)–Ag(1)–N(1)	124.78(6)
		Ag(2)–Ag(1)–N(2)	84.31(6)
		Ag(2)–Ag(1)–N(10)	108.46(6)
		N(3)–Ag(2)–N(4)	104.15(8)
		N(3)–Ag(2)–N(9)	69.07(8)
		N(4)–Ag(2)–N(9)	70.35(8)

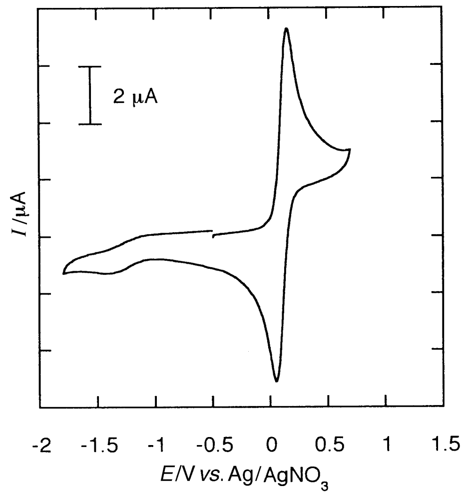


Fig. 2 Cyclic voltammogram of Cu$^+$⊂**1**·PF$_6^-$ in MeCN. Support electrolyte = 0.1 M Et$_4$NClO$_4$, working electrode = Pt disk, reference electrode = Ag/0.01 M AgNO$_3$, counter electrode; Pt wire, scan rate; 100 mV s^{-1}.

(ii) Structure and reactions of the Ag$^+$ complex of 2

The results of elemental analyses of the complexes obtained from reactions between K$^+$⊂**2** and AgNO$_3$ or AgBF$_4$ showed that two Ag$^+$ ions are contained in the complexes. The cavity size of **2** is not large enough to accommodate two silver ions (Ag$^+$: 1.31 Å in radius, cavity size: *ca.* 1.9 Å in radius).

Since, in earlier experiments, 1 : 1 complexes with alkali metal ions (Li$^+$–Cs$^+$) were obtained[1d] this complex in the early stage of the study, was thought to have the formula Ag$^+$⊂**2**·BF$_4^-$· AgBF$_4$. However, cyclic voltammetry showed no ligand-free Ag$^+$ in the solution. Therefore, in order to clarify the structure, an X-ray crystallographic analysis was carried out, revealing that, although the size of Ag$^+$ (1.31 Å in radius) is similar to that of the K$^+$ ion (1.33 Å in radius), two silver ions are actually incorporated into the cavity of **2**. The ligand structure of **2** is considerably distorted and produces enough space for the two silver ions: each of the two silver ions is coordinated to a bridgehead nitrogen and two pyridine nitrogens in pyramidal geometries (Fig. 3). Representative bond lengths and dihedral angles are listed in Table 1 and the coordination geometries around silver ions are illustrated in Fig. 4.

The Ag$^+$–Ag$^+$ distance is 2.78 Å, which is short, compared to some of the reported dinuclear silver complexes or metallic silver (2.889 Å).[7]

By using molecular orbital calculations, Cotton *et al.* concluded that there is no Ag$^+$–Ag$^+$ bond even in the dinuclear complex, which has a short Ag$^+$–Ag$^+$ distance (2.705 Å).[8] Jennische and Hesse pointed out that the Ag$^+$–Ag$^+$ distance is determined not by the bond but by the ligand structures.[9] However, in our experiments, the complex Ag$^+$⊂**2**·BF$_4^-$ was not produced by a reaction between K$^+$⊂**2**·Br$^-$ and equimolar amounts of AgBF$_4$: the product was instead a mixture of 2Ag$^+$⊂**2**·(BF$_4^-$)$_2$ and the K$^+$ complex. Furthermore, the host incorporates one Cu$^+$, although Cu$^+$ (0.96 Å) is smaller than Ag$^+$ (1.31 Å) and both ions have tetrahedral coordination structures.

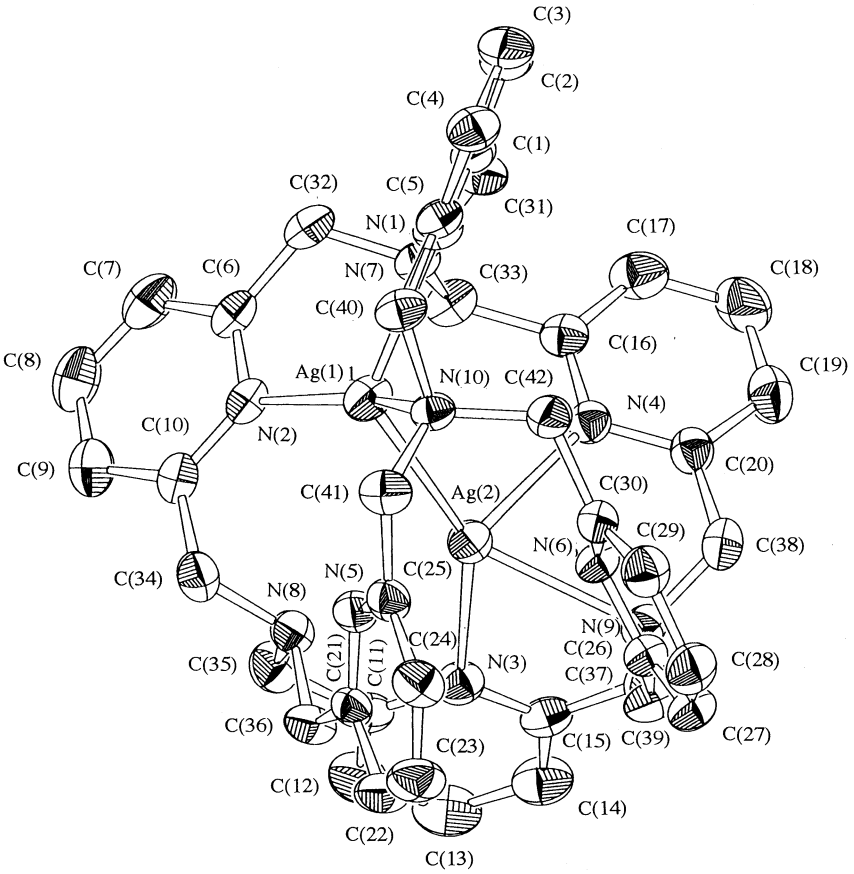


Fig. 3 X-Ray structure of $2Ag^{+}\subset\mathbf{2}\cdot(BF_4^{-})_2$. Hydrogen atoms are omitted for clarity. The numbering of the atoms is different from that of the standard nomenclature. The bond between two Ag atoms shown here is not an actual bond.

Table 2 Crystallographic data for $2Ag^{+}\subset\mathbf{2}\cdot(BF_4^{-})_2$

Formula	$C_{42}H_{42}N_{10}Ag_2B_2F_8$
F_w	1076.20
Crystal shape	Column
Crystal dimensions, mm	0.30 × 0.10 × 0.25
Crystal system	Triclinic
Lattice parameters	
a/Å	13.357(3)
b/Å	14.787(3)
c/Å	12.726(3)
Space group	$P\bar{1}$
Z	2
V/Å^3	2069.2(9)
D_c/g cm^{-3}	1.727
T/K	288
Radiation (λ, Å)	Mo-Kα (0.710 69)
μ/cm^{-1}	10.27
R (R_w) (%)	0.032 (0.034)

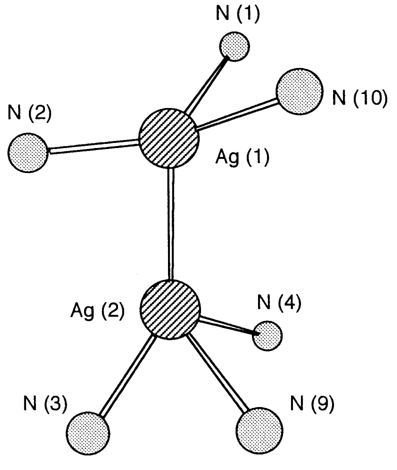


Fig. 4 Bond lengths and angles for Ag^{+} ions and coordinated nitrogen atoms. The structure was produced by the Chem 3D software on the basis of the crystallographic data.

It is unclear why the host incorporates two Ag^{+} ions simultaneously in its cavity by consuming the free energy which distorts the host structure. So far, we do not know whether these results point to the existence of Ag^{+}–Ag^{+} interactions or not.

In the ^{1}H NMR spectrum, the appearance of signals is very similar to that of $K^{+}\subset\mathbf{2}$ and each signal is sharp at room temperature: the molecular movement of the host and the intracavity Ag^{+} exchange are rapid in the solution, while distortion of the structure could not be observed. However, at the low temperatures, both the movements of the host and the Ag^{+} exchanges are frozen and the signals split into complex patterns (Fig. 5).

The silver complex $Ag^{+}\subset\mathbf{2}$ was obtained by treating $2Ag^{+}\subset\mathbf{2}$ with halide ions. However, $Ag^{+}\subset\mathbf{2}$ was unexpectedly stable toward halide ions. The reactions between $2Ag^{+}\subset\mathbf{2}\cdot(NO_3^{-})_2$ and excess of Bu_4NX ($X = Cl^{-}, Br^{-}, I^{-}$) were monitored by means of ^{1}H NMR spectroscopy (Fig. 6). One of the silver ions of $2Ag^{+}\subset\mathbf{2}$ was removed by halide ions and a small amount of $H^{+}\subset\mathbf{2}$ was generated as a by-product. However, further demetallation did not occur, even when the solution was heated. After the addition of Bu_4NI into a solution of $2Ag^{+}\subset\mathbf{2}\cdot(NO_3^{-})_2$ in CD_3OD, the aromatic protons shifted to a higher field (~ 0.2 ppm) and the benzyl protons slightly shifted to higher field (0.02 ppm). Since further information was not obtained by the spectra, we attempted to isolate the products. Treatment of $2Ag^{+}\subset\mathbf{2}\cdot(BF_4^{-})_2$ with Me_4NBr in methanol at room temperature gave $Ag^{+}\subset\mathbf{2}\cdot Br^{-}$ as stable colourless crystals. This complex was then isolated and fully characterized on the basis of its ^{1}H NMR and FAB mass spectra and elemental analysis (Scheme 2). According to the results of the X-ray analysis described

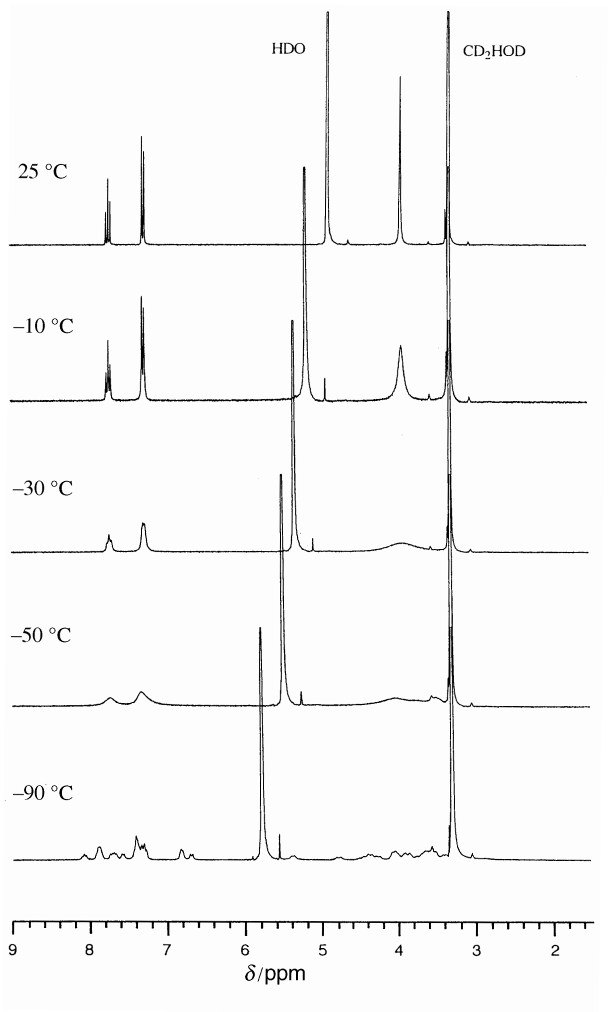


Fig. 5 VT NMR of $2\mathrm{Ag}^+\subset\mathbf{2}\cdot(\mathrm{BF}_4^-)_2$ in [^{2}H$_4$]methanol

above, the structure of $2\mathrm{Ag}^+\subset\mathbf{2}$ is distorted and one of the two silver ions can interact with a bromide ion. The strain may be a driving force for the removal of one silver ion. After the removal of Ag^+, the host's structure changes so as to accommodate one silver ion with six pyridine rings and so it is protected from further attacks of the halide anions. The $\mathrm{Ag}^+\cdots\mathrm{Br}^-$ distance in this system could not be estimated because $\mathrm{Ag}^+\subset\mathbf{2}\cdot\mathrm{Br}^-$ crystals suitable for X-ray crystallographic analysis were not obtained.

Both the solids and the solutions of $2\mathrm{Ag}^+\subset\mathbf{2}$ and $\mathrm{Ag}^+\subset\mathbf{2}\cdot\mathrm{Br}^-$ are stable toward sunlight: precipitation of silver by exposure to direct sunlight for at least 6 h could not be observed. Methanol solutions containing $2\mathrm{Ag}^+\subset\mathbf{2}\cdot(\mathrm{NO}_3^-)_2$ and excess amounts of I^- or Cl^- ions were also stable. Irradiation of the solution with a high-pressure Hg lamp (100 W) for 1 h gave radical-mediated products: the NMR spectra showed that some parts of the complex decomposed, but characterization of the products could not be achieved (Fig. 6).

Unlike those of $2\mathrm{Ag}^+\subset\mathbf{2}$, the ^{1}H NMR spectra of $\mathrm{Ag}^+\subset\mathbf{2}$ at low temperatures (~−90 °C) showed that the ligand structure is not distorted. The spectrum is quite similar to that of $\mathrm{K}^+\subset\mathbf{2}$ at low temperatures. Hence, the Ag^+ ion of $\mathrm{Ag}^+\subset\mathbf{2}$ is located at the centre of the cavity and the whole structure is the same as that of $\mathrm{K}^+\subset\mathbf{2}$.

Cyclic voltammetry of $2\mathrm{Ag}^+\subset\mathbf{2}\cdot(\mathrm{NO}_3^-)_2$ was carried out in acetonitrile (Fig. 7). No redox waves appeared in the range of −0.75–+0.5 V, but irreversible waves were observed in the range of −1.5 V–+0.5 V (Ag/0.01 M AgNO_3 as a reference electrode). The peak that corresponds to the reaction (1) appeared at −1.20 V (P3). A peak at −1.01 V (P2) corresponds to the absorption of the complex on the electrode. A redox couple, $\mathrm{Ag}^+/\mathrm{Ag}^0$ was observed at −0.44 V (P1) and +0.00 V (P4) after the reaction (1) took place at −1.20 V. The couple $\mathrm{Ag}^+/\mathrm{Ag}^0$ grows as the cycle is repeated. This is ascribed to the silver metal precipitation, resulting from the reaction (1), on the electrode. On the other hand, the reaction (2) does not take place even at the low cathode potential (~−1.5 V). This is clearly shown by the CV measurement of $\mathrm{Ag}^+\subset\mathbf{2}\cdot\mathrm{BF}_4^-$ under the same conditions [Fig. (7b)]. Also in this case, the peak corresponding to the reaction (2) was not observed.

$$2\mathrm{Ag}^+\subset\mathbf{2} \longrightarrow \mathrm{Ag}^0 + \mathrm{Ag}^+\subset\mathbf{2} \qquad (1)$$

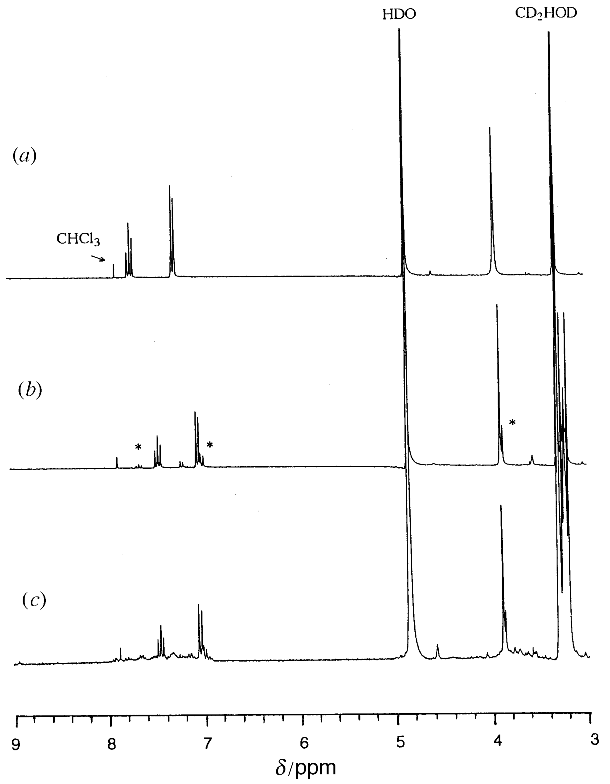


Fig. 6 ^{1}H NMR (270 MHz) spectral changes of $2\mathrm{Ag}^+\subset\mathbf{2}\cdot(\mathrm{NO}_3^-)_2$ in $\mathrm{CD}_3\mathrm{OD}$ by addition of $\mathrm{Bu}_4\mathrm{NI}$ and irradiation of light; (*a*) $2\mathrm{Ag}^+\subset\mathbf{2}\cdot(\mathrm{NO}_3^-)_2$ in $\mathrm{CD}_3\mathrm{OD}$; (*b*) after addition of $\mathrm{Bu}_4\mathrm{NI}$ into (*a*); (*c*) after irradiation of high pressure-Hg lamp to (*b*) for 1 h. * Shows the signal of $\mathrm{H}^+\subset\mathbf{2}$.

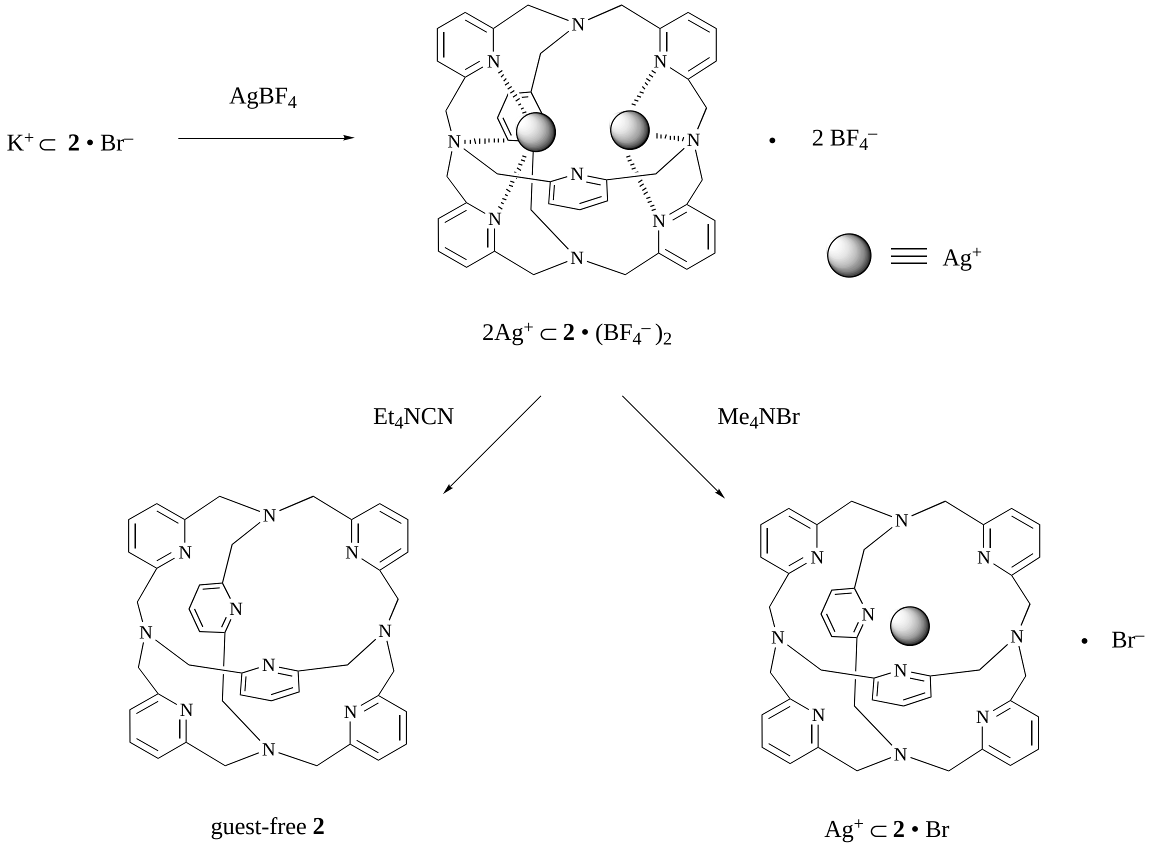
$$\mathrm{Ag}^+\subset\mathbf{2} \longrightarrow \mathrm{Ag}^0 + \mathbf{2} \qquad (2)$$

According to the results of CV measurements, the Ag^+ ions of these two complexes are stabilized by the ligand structure. An Ag^+ ion of $2\mathrm{Ag}^+\subset\mathbf{2}$ can be removed only at the low cathode potential (−1.20 V), producing $\mathrm{Ag}^+\subset\mathbf{2}$. After the removal of one Ag^+, further demetallation reaction does not occur, at least at the cathode potential of −1.5 V.

As a result, insoluble and photosensitive AgX (X = Cl, Br, I) becomes soluble and stable towards light because of effective shielding of Ag^+ and ion pair separation by the host. Furthermore, accommodation of Ag^+ by the large and rigid host's skeleton greatly stabilizes the redox properties of Ag^+.

(iii) Guest-free 1 and 2

In a previous report, we described the high cation affinities of compounds **1** and **2**. A proton could not be removed from $\mathrm{H}^+\subset\mathbf{1}$ and $\mathrm{H}^+\subset\mathbf{2}$ even using strong bases.[1] Other attempts to obtain guest-free **1** and **2** were unsuccessful. For example, a solution of $\mathrm{K}^+\subset\mathbf{2}$ in water/MeOH = 1:1 (v:v) was heated in a sealed tube at 150 °C for 7 days.[1d,10] In spite of these severe conditions, starting material was recovered unchanged and no metal-free ligand was detected. Therefore, we employed alternative methods in order to obtain guest-free **1** and **2**. Sauvage *et*



Scheme 2 Preparations of $2Ag^+\subset\mathbf{2}\cdot(BF_4^-)_2$, $Ag^+\subset\mathbf{2}\cdot Br^-$ and guest-free **2**

al. succeeded in preparing metal-free catenane from reactions between Cu^+ catenates and KCN or Me_4NCN. Lehn *et al.* synthesized a macrobicyclic cryptand starting from its Ag^+ complex and H_2S.[11] These methods were applied to the preparation of the cation-free compounds **1** and **2**. However, the introduction of H_2S gas into an aqueous solution of $2Ag^+\subset\mathbf{2}\cdot(NO_3^-)_2$ immediately generated $nH^+\subset\mathbf{2}$ ($n = 1$, 2 or 3): protons liberated by the reaction of H_2S and Ag^+ were captured by **2**.[12] Protonation of **2** occurred even in the presence of a base, Me_4NOH. When KCN was employed for the demetallation of $Cu^+\subset\mathbf{1}$ and $Ag^+\subset\mathbf{2}$, the complexes $K^+\subset\mathbf{1}$, **2** were obtained instead of the cation-free **1** and **2**. Similar occurrences were mentioned in connection with the synthesis of cation-free catenane.[11a] Tetraalkylammonium cyanide would be a suitable reagent to achieve the desired goal. A reaction between $Cu^+\subset\mathbf{1}\cdot PF_6^-$ and Bu_4NCN proceeded cleanly and quantitatively: the yellow colour immediately disappeared when a solution of $Cu^+\subset\mathbf{1}$ was treated with Bu_4NCN (Scheme 1). Metal-free **1** was precipitated from the reaction mixture as colourless crystals. The ^1H NMR spectra drastically changed after the addition of CN^-: the benzene inner protons of **1** shifted from 8.73 to 8.16 ppm and the relatively broad AB quartet of the methylene became sharp. As in the case of $Cu^+\subset\mathbf{1}$, the two silver ions of $2Ag^+\subset\mathbf{2}\cdot(BF_4^-)_2$ could be removed simultaneously by Et_4NCN in MeCN (Scheme 2).

Both guest-free **1** and **2** are relatively labile when exposed to air: they absorb moisture and/or CO_2, yielding less soluble materials. The NMR spectra showed that more than three kinds of protonated species are produced. Previously, we reported that the bond isomer of **2** easily absorbed water molecules, producing a hydrated material.[13] However, in the case of compounds **1** and **2**, no hydration occurred, instead, protons were subtracted from water.[14] The reactions of **2** with water in a toluene or a pyridine solution at 100 °C were monitored by ^1H NMR spectroscopy. After a week, compound **2** was completely consumed and the generation of protonated species and a water inclusion complex were observed.

(iv) Attempts to include NH_3 and BH_3 molecules

A water complex $H_2O\subset\mathbf{2}$ was characterized by means of mass and NMR spectroscopy as described in a previous report.[1a] In the next stage of our investigation, we were interested in the inclusion complexes, $NH_3\subset\mathbf{L}$ and $BH_3\subset\mathbf{L}$ ($\mathbf{L} = \mathbf{1}$, **2**). A cryptand–borane complex was reported in which borane molecules coordinate from the outside of the cryptand, but in general, borane inclusion complexes are unknown.[15] Several attempts to prepare inclusion complexes through reactions between $NH_4^+\subset\mathbf{L}$ and OH^- (subtraction of H^+ from NH_4^+), $K^+\subset\mathbf{L}$ and $Bu^tNH_2\cdot BH_3$ (replacement of K^+ by BH_3), $H^+\subset\mathbf{L}$ and BH_4^- (complexation after deprotonation by BH_4^-) were unsuccessful. Therefore, it was concluded that direct reactions between neutral guests and the guest-free hosts should be carried out.

The guest-free **2** was dissolved in dry liquid ammonia and the solution was left for 2 h. After the ammonia had evaporated, a white powder remained, which was shown to be $NH_4^+\subset\mathbf{2}$ from its NMR spectrum. There are two possible ways to produce $NH_4^+\subset\mathbf{2}$. A proton transfer from trace amounts of water to a possible intermediate inclusion complex $NH_3\subset\mathbf{2}$ may produce $NH_4^+\subset\mathbf{2}$. $NH_3\subset\mathbf{2}$ is thought to be a stronger base than **2** itself because of the formation of favourable $N\cdots H^+\cdots N$ bonds.

$$\mathbf{2} + NH_3 \longrightarrow [NH_3\subset\mathbf{2}] \xrightarrow{H_2O} NH_4^+\subset\mathbf{2}\cdot OH^-$$

The counter anion is a hydroxide ion, because the addition of a small amount of water to a $CDCl_3$ solution of the product resulted in the remarkable growth of $CHCl_3$ signal, which is caused by the following reaction.

$$CDCl_3 + H_2O \xrightleftharpoons{NH_4^+\subset\mathbf{2}\cdot OH^-} CHCl_3 + HDO$$

Another possibility is to trap the NH_4^+ ion from the equilibrium mixture:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \ (K = 1.79 \times 10^{-5})$$

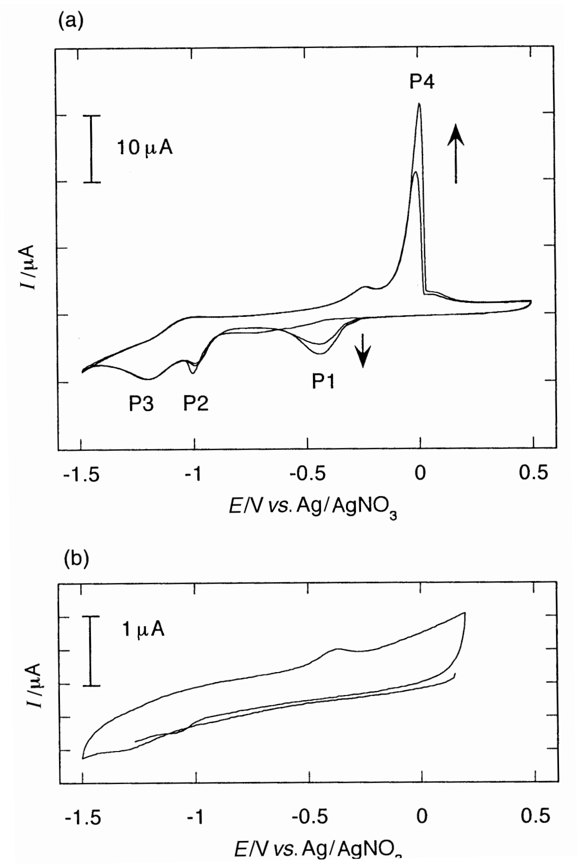


Fig. 7 Cyclic voltammogram of (a) $2Ag^+\subset\mathbf{2}\cdot(NO_3^-)_2$ and (b) $Ag^+\subset\mathbf{2}\cdot BF_4^-$ in 0.1 M Et_4NClO_4–MeCN. Support electrode; Et_4NClO_4, working electrode; Pt disk, reference electrode; Ag/0.01 M $AgNO_3$, counter electrode; Pt wire, scan rate; 100 mV s^{-1}.

In another experiment, dry NH_3 gas was introduced into a $[^2H_8]$toluene solution of **2** and the NMR sample tube was sealed with Ar gas. The NH_3 proton signal appeared at 0.02, −0.14 and −0.30 ppm (*J* = 43 Hz) as a relatively broad triplet in $[^2H_8]$toluene (the methyl proton of toluene served as an internal reference; $PhCHD_2$, 2.1 ppm), but no spectral changes were observed. After 24 h at room temperature, a white powder was precipitated and the signals of **2** disappeared. The material, which was soluble in $CDCl_3$, was revealed to be $NH_4^+\subset\mathbf{2}\cdot OH^-$. Similar results were obtained in the reaction between **1** and NH_3.

In these experiments, the intermediate species ($NH_3\subset\mathbf{2}$) was not found by NMR spectroscopy. Although all of the experiments were carried out under dry conditions, trace amounts of water lead to the formation of NH_4^+ complexes. Lehn *et al.*, also pointed out that the NH_3 cryptate is a short-lived species.[16] According to the results, hydrogen bond interactions between NH_3 and the hosts **L** were too weak to form a stable inclusion complex, but stronger cation-dipole interactions $\mathbf{L}\cdots NH_4^+$ lead to the formation of $NH_4^+\subset\mathbf{2}$ in the presence of trace amounts of water.

Pyridine–borane or amine–borane complexes are well-known as stable substances. The host **2** is expected to be a good and suitable ligand for borane because six pyridine lone pairs are converging into the cavity. A reaction between $Bu^tNH_2\cdot BH_3$ and **2** in $[^2H_8]$toluene at 100 °C for 1 week did not occur since $Bu^tNH_2\cdot BH_3$ is very stable. Instead of the amine complex, an $Me_2S\cdot BH_3$ complex was employed. Addition of **2** to a solution of $Me_2S\cdot BH_3$ in $[^2H_8]$toluene immediately yielded a colourless precipitate. The intensity of the BH_3 quartet signal which appears at 2.65, 2.25, 1.86 and 1.46 ppm (*J* = 106 Hz) decreased. Although the mixture was heated at 100 °C for a week, its NMR spectrum showed no change and signals corresponding to the borane inclusion complex were not detected. The resultant insoluble material thought to be a borane adduct, $\mathbf{2}\cdot n BH_3$ in which borane molecules coordinate from the outside of the host molecule. In order to remove the excess of BH_3 and dissolve the adduct, the precipitates were dispersed in $[^2H_8]$-THF and heated at 50 °C for 2 weeks, but the mixture did not change. Thus, the structural information could not be obtained so far. Quenching the excess of BH_3 of the adduct with methanol produced slow recovery of guest-free **2** with $nH^+\subset\mathbf{2}$ (*n* = 1–3) as by-products.

Experimental

All mps were measured in Ar sealed tubes and were uncorrected. The ^1H NMR spectra were recorded on a JEOL GSX 270 (270 MHz) spectrometer and UV/VIS spectra were recorded on a Shimadzu UV-2200 spectrometer. Cyclic voltammetry was performed using a Fuso Model 311 Polarograph with a Model 321 potential-sweep unit at 25 ± 0.1 °C. A Pt disk was used as the working electrode. An Ag/0.01 M $AgNO_3$ /0.1 M Et_4NClO_4 (MeCN) and a Pt wire were used as the reference electrode and the counter electrode, respectively. Support electrolyte (Et_4NClO_4, Tokyo Kasei, special analysis grade) was dried *in vacuo* at 50 °C for several hours.

X-Ray crystallographic analysis of $2Ag^+\subset\mathbf{2}\cdot(BF_4^-)_2$

Crystal data: $C_{42}H_{42}N_{10}Ag_2B_2F_8$ (formula weight 1076.20), colourless column, triclinic (recrystallized from methanol), crystal dimensions 0.30 × 0.10 × 0.25 mm, D_c 1.727 g cm^{-3}, space group $P\bar{1}$ (#2): $a = 13.357(3)$, $b = 14.787(3)$, $c = 12.726(3)$ Å, $\alpha = 112.51(2)°$, $\beta = 116.53(2)°$, $\gamma = 75.88(2)°$, $V = 2069.2(9)$ $Å^3$, Z = 2, $F_{000} = 1080$. All measurements were performed on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.710\ 69$ Å), $\mu = 10.27\ cm^{-1}$. The data were collected at a temperature of 15 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 55.0°. Of the 9914 reflections which were collected, 9505 were unique ($R_{int} = 0.009$). The data were corrected for Lorentz and polarization effects. The structure was solved following the heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atom coordinates were refined but their isotropic total background counts were held fixed. The final cycle of full-matrix least-squares refinement was based on 8241 observed reflections [$I > 3.00\sigma(I)$] and 704 variable parameters. The final *R* factors were $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.032$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}} = 0.034$. The maximum and minimum peaks on the final difference Fourier map are 1.26 and −0.68 e $Å^{-3}$, respectively. All calculations were performed using the teXscan[17] crystallographic software package from Molecular Structure Corporation. Detailed crystallographic results have been deposited with the Cambridge Crystallographic Data Centre.† Any requests for this material should be accompanied by a full bibliographic citation together with the reference number 207/71.

Preparation of $Cu^+\subset\mathbf{1}$

$Cu^+\subset\mathbf{1}\cdot PF_6^-$ from the Cu^I salt. The potassium complex $K^+\subset\mathbf{1}\cdot Br^-$ (37 mg, 0.046 mmol) and $Cu(MeCN)_4\cdot PF_6$ (25.8 mg, 0.069 mmol) were dissolved in acetonitrile (5 cm^3) and the solution was stored under an Ar atmosphere for 1 week. After concentration of the solution, precipitated yellow granules were collected and washed with water. The complex was dissolved in a minimum amount of methanol and slowly passed through an anion exchange column (Muromac 1-X_8, PF_6^- form). The solution was evaporated to dryness and column chromatographed on silica gel (CH_2Cl_2–MeOH = 98 : 2, v/v). Recrystallization of

---

† For details of the scheme, see Instructions for Authors (1997), *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1.

the resultant powder from EtOH–CH_2Cl_2 afforded yellow granules (21 mg, 51%), mp >258° C (decomp.) (Found: C, 55.8; H, 5.2; N, 11.6. $C_{44}H_{44}N_8\cdot CuPF_6\cdot 1/2CH_2Cl_2\cdot H_2O$ requires C, 56.03; H, 4.97; N, 11.75%). The quantities of CH_2Cl_2 and H_2O were confirmed by means of the ^{1}H NMR spectrum. λ_{max}(MeCN)/nm 208 (ε 54 900 dm^3 mol^{-1} cm^{-1}), 259 (16 500) and 364 (3300); δ_H(270 MHz; $CDCl_3$; Me_4Si) 8.73 (2 H, s, benzene-H), 7.70, 7.68, 7.65 (4 H, t, *J* 7, Py-H), 7.29, 7.26 (8 H, d, *J* 6, Py-H), 7.17–7.14 (6 H, m, benzene-H), 3.76, 3.54 (16 H, ABq, *J* 13, pyridine-CH_AH_B) and 3.52 (8 H, s, benzene-CH_2); *m/z* (FAB) 747 (M + $^{63}Cu^+$, 99%) and 749 (M + $^{65}Cu^+$, 63%).

$Cu^+\subset\mathbf{1}\cdot Br^-$ from the Cu^{II} salt. The $K^+\subset\mathbf{1}\cdot Br^-$ (12.2 mg, 0.015 mmol) and $Cu(MeCO_2)_2\cdot 6H_2O$ (4.2 mg, 0.021 mmol) were dissolved in methanol (5 cm^3) and the solution was heated under reflux overnight. After the concentration of the solution, precipitated yellow granules were collected and washed with water. The complex was dissolved in a minimum amount of methanol and slowly passed through an anion exchange column (Muromac 1-X_8, Br^- form). The solution was evaporated to dryness and column chromatographed on silica gel (CH_2Cl_2–MeOH = 98 : 2, v/v). Recrystallization of the resultant powder from methanol afforded yellow granules (6.5 mg, 52%). ^{1}H NMR and FAB mass spectra of this material completely coincide with that of $Cu^+\subset\mathbf{1}\cdot PF_6^-$ which is obtained from the Cu^I salt.

Preparation of $2Ag^+\subset\mathbf{2}\cdot(BF_4^-)_2$ and $2Ag^+\subset\mathbf{2}\cdot(NO_3^-)_2\cdot H_2O$

The potassium complex $K^+\subset\mathbf{2}\cdot Br^-$ (25.8 mg, 0.026 mmol) and $AgBF_4$ (22.1 mg, 0.11 mmol) was dissolved in methanol (20 cm^3) and the solution was stirred at room temperature overnight. It was then passed through a Celite column and evaporated. The resultant powder was recrystallized twice from methanol to give colourless needles (27 mg, 78%) mp >284 °C (decomp.) (Found: C, 46.8; H, 4.0; N, 13.0. $C_{42}H_{42}N_{10}\cdot 2AgBF_4$ requires C, 46.87; H, 3.93; N, 13.01%); δ_H(270 MHz; CD_3OD; Me_4Si) 7.76, 7.73, 7.70 (6 H, t, *J* 8, Py-H), 7.29, 7.26 (12 H, d, *J* 8, Py-H) and 3.93 (24 H, s, CH_2); *m/z* (FAB) 991 (M + 2 $^{109}Ag^+$ + BF_4^-, 5%), 989 (M + $^{107}Ag^+$ + $^{109}Ag^+$ + BF_4^-, 10%), 987 (M + 2 $^{107}Ag^+$ + BF_4^-, 6%), 795 (M + $^{109}Ag^+$, 13%) and 793 (M + $^{107}Ag^+$, 16%).

$2Ag^+\subset\mathbf{2}\cdot(NO_3^-)_2\cdot H_2O$ was prepared by the reaction between $K^+\subset\mathbf{2}\cdot Br^-$ and $AgNO_3$. The procedure is the same as that of $2Ag^+\subset\mathbf{2}\cdot(BF_4^-)_2$, mp >274 °C (decomp.) (Found: C, 48.3; H, 4.3; N, 16.0. $C_{42}H_{42}N_{10}\cdot 2AgNO_3\cdot H_2O$ requires C, 48.29; H, 4.25; N, 16.09%).

Preparation of $Ag^+\subset\mathbf{2}\cdot Br^-\cdot H_2O$

The silver complex $2Ag^+\subset\mathbf{2}\cdot(BF_4^-)_2$ (42.1 mg, 0.039 mmol) and Me_4NBr (39.5 mg, 0.26 mmol) were dissolved in methanol (30 cm^3) and the solution was stirred at room temperature overnight. It was then passed through a Celite column and evaporated. The resultant powder was recrystallized twice from MeOH–AcOEt to give colourless needles (25.4 mg, 73%), mp >243 °C (decomp.) (Found: C, 56.6; H, 4.9; N, 15.6. $C_{42}H_{42}N_{10}\cdot AgBr\cdot H_2O$ requires C, 56.51; H, 4.74; N, 15.69%); δ_H(270 MHz; CD_3OD; Me_4Si) 7.48, 7.45, 7.42 (6 H, t, *J* 8, Py-H), 7.05, 7.02 (12 H, d, *J* 8, Py-H) and 3.88 (24 H, s, CH_2); *m/z* (FAB) 793 (M + $^{107}Ag^+$, 100%) and 795 (M + $^{109}Ag^+$, 95%).

Preparation of guest-free 1

A reaction mixture obtained from $K^+\subset\mathbf{1}\cdot Br^-$ (74 mg, 0.092 mmol) and $Cu(MeCN)_4\cdot PF_6$ (53 mg, 0.14 mmol) was column chromatographed on silica gel (CH_2Cl_2–MeOH = 95 : 5, v/v). The $Cu^+\subset\mathbf{1}\cdot PF_6^-$ thus obtained was dissolved in MeCN (10 cm^3) and the solution of Bu_4NCN in MeCN was added to it until the yellow colour of the solution disappeared. After 1 h, the solution was concentrated to 1 cm^3 and precipitated colourless crystals were filtered off and washed with a small amount of MeCN and then with water. Recrystallization of the crystals from MeCN–CH_2Cl_2 gave colourless granules (43.4 mg, 80% from $K^+\subset\mathbf{1}\cdot Br^-$) of **1**, mp 243–243.3 °C (Found: C, 77.1; H, 6.5; N, 16.3. $C_{44}H_{44}N_8$ requires C, 77.16; H, 6.48; N, 16.36%); δ_H(270 MHz; $CDCl_3$; Me_4Si) 8.15 (2 H, s, benzene-H), 7.41, 7.38, 7.35 (4 H, t, *J* 8, Py-H), 7.01, 6.98 (8 H, d, *J* 8, Py-H), 7.25–7.21 (6 H, m, benzene-H), 3.78, 3.61 (16 H, ABq, *J* 12, pyridine CH_AH_B) and 3.65 (8 H, s, benzene-CH_2); *m/z* (FAB) 685 (M + H$^+$, 51%).

Preparation of guest-free 2

To a solution of the silver complex $2Ag^+\subset\mathbf{2}\cdot(BF_4^-)_2$ (28.0 mg, 0.026 mmol) in MeCN (15 cm^3) was added Et_4NCN (42 mg, 0.27 mmol) and the solution was stirred under an Ar atmosphere at room temperature for 2 h. The precipitate was collected and recrystallized from CH_2Cl_2–MeCN to give colourless needles (10.2 mg, 55%), mp 256 °C (Found: C, 73.3; H, 6.1; N, 20.1. $C_{42}H_{42}N_{10}$ requires C, 73.44; H, 6.16; N, 20.39); δ_H(270 MHz; $CDCl_3$; Me_4Si) 7.45, 7.42, 7.39 (6 H, t, *J* 8, Py-H), 7.04, 7.01 (12 H, d, *J* 8, Py-H) and 3.91 (24 H, s, CH_2); *m/z* (FAB) 687 (M + H$^+$, 100%).

The reaction between 2 and NH_3

Compound **2** (12 mg, 0.017 mmol) was introduced into a flame-dried flask under Ar gas; the flask was then cooled to −80 °C. Dry ammonia gas (distilled from sodium–liquid ammonia mixture) was introduced into the flask. After 1 cm^3 of liquid ammonia had been condensed, the mixture was stirred for 2 h under an Ar atmosphere. Alternatively, compound **2** (5 mg, 7.3 × 10^{-3} mmol) was dissolved in dry [$^2H_8$]toluene and the ammonia gas was allowed to bubble through it for 5 min. The NMR tube was sealed with Ar gas and the spectra were recorded.

Acknowledgements

This research was supported by a Grant-in-Aid for Encouragement of Young Scientists (No. 05740398) provided by the Ministry of Education, Science and Culture, Japan.

References

1 (*a*) H. Takemura, T. Shinmyozu and T. Inazu, *J. Am. Chem. Soc.*, 1991, **113**, 1323; (*b*) H. Takemura, T. Shinmyozu and T. Inazu, *Tetrahedron Lett.*, 1988, **29**, 1789; (*c*) H. Takemura, T. Hirakawa, T. Shinmyozu and T. Inazu, *Tetrahedron Lett.*, 1984, **25**, 5053; (*d*) H. Takemura, T. Shinmyozu and T. Inazu, *Coord. Chem. Rev.*, in press; (*e*) H. Takemura, Ph.D. Thesis, Kyushu University, 1992.

2 (*a*) P. A. Kollman and L. C. Allen, *Chem. Rev.*, 1972, **72**, 283; (*b*) P. A. Kollman and L. C. Allen, *J. Am. Chem. Soc.*, 1971, **93**, 4991; (*c*) H. J. Berthold, W. Preibsch and E. Vonholdt, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1524.

3 In this case, an oxidation reaction takes place, but we did not clarify which materials were oxidized.

4 A benzene analogue of **1** and **2** (compound **3**, Fig. 8) showed no inclusion ability towards alkali metal ions but formed a Cu^+ complex. The cavity has poor ability as a ligand because the cavity size of **3** is 1.8 Å in diameter (half that of **2**) and has only four bridgehead nitrogens as donor atoms. The reaction between **3** and $Cu(MeCN)_4PF_6$ in MeCN–CH_2Cl_2 gave colourless crystals. The complex is unstable and easy to decompose under aerobic conditions. Only FAB mass and NMR spectra supported the formation of the complex. Exposure of the complex to air gradually generates metal-free **3** and an inorganic Cu^{II} salt. A silver complex of **3** was

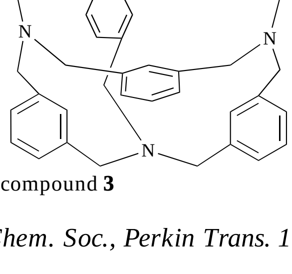


Fig. 8 Structure of compound **3**

also formed by the reaction between **3** and $AgBF_4$, but this complex was less stable than the Cu^+ complex. Further identification or characterization of the $Cu^+\cdot\mathbf{3}$ and $Ag^+\cdot\mathbf{3}$ were not carried out because of their lability.

5 (*a*) C. Dietrich-Buchecker, J.-P. Sauvage and J.-M. Kern, *J. Am. Chem. Soc*., 1989, **111**, 7791; (*b*) K. T. Potts, M. Keshavarz-K, F. S. Tham, H. D. Abruña and C. R. Arana, *Inorg. Chem*., 1993, **32**, 4422; (*c*) K. T. Potts, M. Keshavarz-K, F. S. Tham, H. D. Abruña and C. Arana, *Inorg. Chem*., 1993, **32**, 4436.

6 K. D. Karlin, J. C. Hayes, S. Juen, J. P. Hutchinson and J. Zubieta, *Inorg. Chem*., 1982, **21**, 4106.

7 (*a*) C. E. Housecroft, *Coord. Chem. Rev.*, 1992, **115**, 141; (*b*) M. Munakata, M. Maekawa, S. Kitagawa and M. Adachi, *Inorg. Chim. Acta*, 1990, **167**, 181.

8 F. A. Cotton, X. Feng, M. Matusz and R. Poli, *J. Am. Chem. Soc.*, 1988, **110**, 7077.

9 P. Jennische and R. Hesse, *Acta Chem. Scand*., 1971, **25**, 423.

10 D. J. Cram, T. Kaneda, R. C. Helgeson and G. M. Lein, *J. Am. Chem. Soc*., 1979, **101**, 6752.

11 (*a*) C. O. Dietrich-Bucheker and J.-P. Sauvage, *J. Am. Chem. Soc*., 1984, **106**, 3043; (*b*) C. Dietrich-Bucheker and J.-P. Sauvage, *Tetrahedron*, 1990, **46**, 503; (*c*) J. C. Rodriguez-Ubis, B. Alpha, D. Plancherel and J.-M. Lehn, *Helv. Chim. Acta*, 1984, **67**, 2264.

12 In a separate experiment, compound **2** was titrated with picric acid. Stoichiometry and shift values of the methylene signals of $n\mathrm{H}^+\subset\mathbf{2}$ ($n = 1$, 2 and 3) were observed. The results were used for the determination of the number of protons captured in the cavity of **2**.

13 H. Takemura, S. Osada, T. Shinmyozu and T. Inazu, *J. Chem. Soc.*, *Perkin Trans. 1*, 1996, 277.

14 In order to test the basicity of the ligand, a reaction between guest-free **2** and *p*-$TsNH_2$ in dry DMSO was monitored by ^1H NMR spectroscopy ($pK_a = 15.58$ in DMSO; K. Izutsu, *Acid–Base Dissociation Constants in Dipolar Aprotic Solvents*, Chemical Data Series No. 35, IUPAC, Blackwell Scientific Publications, Oxford, 1990, p. 89). The reaction proceeded very slowly, and broad signals appeared after 16 days. The spectrum at 100 °C showed well-resolved sharp signals which correspond to $3\mathrm{H}^+\subset\mathbf{2}$, $2\mathrm{H}^+\subset\mathbf{2}$, $\mathrm{H}^+\subset\mathbf{2}$ and the starting material **2**. According to the result, the proton cryptate $\mathrm{H}^+\subset\mathbf{2}$ is also a strong base itself and further protonation reactions occur.

15 B. Metz, D. Moras and R. Weiss, *J. Chem. Soc.*, *Perkin Trans. 2*, 1976, 423.

16 E. Graf, J.-P. Kintzinger, J.-M. Lehn and J. LeMoigne, *J. Am. Chem. Soc*., 1982, **104**, 1672.

17 teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 and 1992).

Paper 6/04966D
Received 15*th July* 1996
Accepted 14*th October* 1996