CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200501626

Flexibility of Inorganic Tennis Ball Structures Inducing Anion Selectivity

Ki-Hyun Kim,[a] Jung Su Park,[b] Tae Yi Kang,[b] Kyungeun Oh,[a] Mi-Sook Seo,[a] Youn Soo Sohn,[a] Moo-Jin Jun,[b] Wonwoo Nam,*[a] and Kwan Mook Kim*[a]

Abstract: Inorganic tennis balls (ITBs), $[[\{Pt(betmp)(dach)\}_2Cu]_2(X)][X]_3$ (in which X = ClO_4^- (**3**), NO_3^- (**4**), Cl^- (**5**) and Br^- (**6**); dach = *trans*-1,2-diaminocyclohexane and betmp = bisethylthiomethylidenepropanedioate) and $[[\{Pt(dteym)(dach)\}_2Cu]_2(PF_6)][PF_6]_3$ (**7**; dteym = 1,3-dithiepane-2-ylidenemalonate), were prepared as crystals. Investigation of their X-ray crystal structures revealed that shapes of the cavities in ITBs show significant distortions that depend on the properties of the encapsulated anions. The Cu···Cu* distance was observed to be longest in **7** and shortest in **5**, the difference between them being 2.05 Å. The flexibility of cavity structures of ITBs makes it possible to encapsulate various anions inside the cavity, while their distortions may be a reason for the difference in the encapsulating ability for anions, that is, anion selectivity. Especially, the distortions observed in **7** are so severe that the encapsulating ability of the cavity for PF_6^- is very low compared to other anions. The shapes of ITBs with ClO_4^- and BF_4^- ions inside their cavities are very similar; however, ClO_4^- is encapsulated by the cavity better than BF_4^-, which is explicable by the difference of metal–anion interactions. This structural study on ITBs gives a clue to the origin of the anion selectivity of the cavity in ITBs previously investigated by ^{19}F NMR spectroscopy of the ITBs in methanol.

Keywords: anions · host–guest systems · inorganic tennis balls · self-assembly

Introduction

Cavities in coordination boxes, cages, and capsules are attracting interest due to their encapsulation, catalytic, and stereoselective transformation properties.[1,2] "Tennis balls", a name coined by Rebek, Jr., have a roughly spherical cavity formed by the dimerization of two homoglycouril derivatives.[3] Hydrogen-bond acceptor and donor sites in the glycouril units at the ends of the molecule play an important role in this dimerization. Moreover, the cavity produced shows versatile encapsulation and reaction properties.[4–7] Specifically, metal complexes that assemble like glycourils are interesting, since the resulting inorganic host acquires reversible characteristics and is likely to have novel encapsulation or reaction properties due to specific metal functions, such as, magnetism, catalysis, and molecular recognition. We previously reported an "inorganic tennis ball" (ITB) that was obtained by the self-assembly of $Cu(BF_4)_2$ and $[Pt^{II}(betmp)(dach)]$ (in which dach = *trans*-1,2-diaminocyclohexane and betmp = bisethylthiomethylidenepropanedioate).[8] Hydrogen bonding and electrostatic interactions were found to be important for the formation of this tennis ball structure. The cavities in the ITBs show anion selectivity that depends on anion shapes and sizes;[9] this selectivity is essential in the field of anion recognition research.[10] To elucidate the origin of the selectivity, we further investigated how the structural properties of ITBs are dependent on the natures of anions within the cavity, and we report here its results along with the solution properties.

Results and Discussion

Synthesis of ITBs: The self-assembly of $Cu(BF_4)_2$ with $[Pt^{II}(betmp)(dach)]$ yield different products depending on the solvent systems used (Scheme 1).[8] A crystal grown from an aqueous reaction mixture of copper(II) tetrafluoroborate

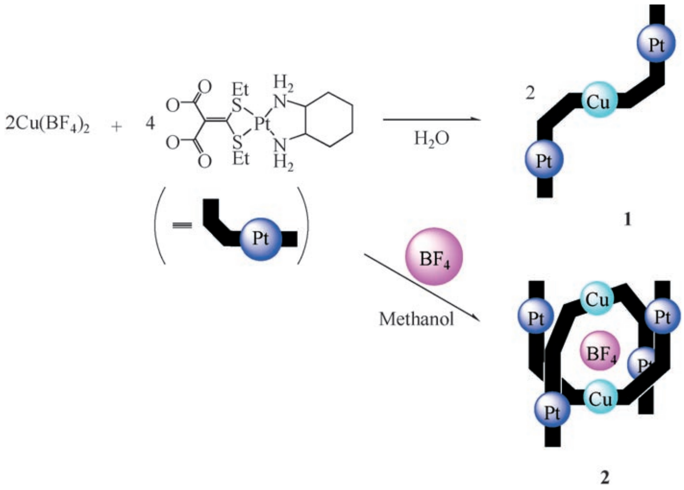
---

[a] K.-H. Kim, K. Oh, Dr. M.-S. Seo, Prof. Y. S. Sohn, Prof. W. Nam, Prof. K. M. Kim
Department of Chemistry
Division of Nano Sciences and Center for Biomimetic Systems
Ewha Womans University, Seoul 120–750 (Korea)
Fax: (+82) 2-3277-3419
E-mail: wwnam@ewha.ac.kr
kkmook@ewha.ac.kr

[b] J. S. Park, T. Y. Kang, Prof. M.-J. Jun
Department of Chemistry, Yonsei University
Seoul 120–749 (South Korea)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

Please note: Minor changes have been made to this manuscript since its publication in Chemistry - A European Journal Early View. The Editor.



Scheme 1. Self-assembly between $CuBF_4$ and [Pt(betmp)(dach)] producing **1** and **2**.

and two equivalents of $[Pt^{II}(betmp)(dach)]$ was found to be a monomeric complex of formula of $[\{Pt(betmp)(dach)\}_2Cu][BF_4]_2$ (**1**), in which two [Pt(betmp)(dach)] complexes bind one copper(II) ion through carboxylate groups. However, from the same self-assembly in methanol, the dimeric supramolecule "ITB" $[[\{Pt(betmp)(dach)\}_2Cu]_2(BF_4)][BF_4]_3$ (**2**) was obtained, in which one BF_4^- ion is encapsulated in the cavity formed between two molecules of $[\{Pt(betmp)(dach)\}_2Cu]$. The shape of the blue crystal of **1** is a monoclinic rectangle, whereas that of greenish-blue **2** is an octahedron.

ITBs with various other anions, $[[\{Pt(betmp)(dach)\}_2Cu]_2(X)][X]_3$ (in which $X=ClO_4^-$ (**3**), NO_3^-(**4**), Cl^- (**5**) and Br^- (**6**)) were prepared as crystals using the same procedures as those used to obtain **2** with appropriate recrystallizations. With $X=PF_6^-$, replacing betmp with 1,3-dithiepane-2-ylidenemalonate (dteym) led to the production of crystalline $[[\{Pt(dteym)(dach)\}_2Cu]_2(PF_6)][PF_6]_3$ (**7**). The procedure depicted in Scheme 2 was used to obtain **7**, because $Cu(PF_6)_2$ was not commercially available. The same procedure was also effectively used to obtain **2**–**4**. The $[Cu(dteym)_2]^{2-}$ complex shown in Scheme 2 was prepared by using a previously described method.[11]

$$[Pt(dach)]I_2 + 2AgPF_6 \xrightarrow{water} [Pt(dach)][PF_6]_2 + 2AgI$$

$$2[Pt(dach)][PF_6]_2 + K_2[Cu(dteym)_2] \xrightarrow{water} [\{Pt(dteym)(dach)\}_2Cu][PF_6]_2 + 4KPF_6$$

$$\xrightarrow{\text{recrystallization in ethanol}} \mathbf{7}$$

Scheme 2. The reaction scheme used to prepare **7**.

When $X=OTf^-$, an inorganic tennis ball with an empty cavity is obtained. We previously reported the crystal structure of $[[\{Pt(dteym)(dach)\}_2Cu]_2][OTf]_4$ (**8**), which was obtained by following the procedure depicted in Scheme 1 by using $Cu(OTf)_2$ and [Pt(dteym)(dach)].[9]

UV/Vis spectroscopy and ESI-MS: Table 1 lists the λ_{max} of UV/Vis spectra for **1**–**8** measured in methanol, water, and in the solid state. The UV/Vis spectra in both methanol and solid state exhibited λ_{max} in similar range 680–730 nm, which means that the structural properties of these compounds in methanol are similar to the solid-state structures. However, the UV/Vis spectra recorded in water at 5 mM showed maximum absorption λ_{max} in the range 780–800 nm. It is known that the hydrated copper(II) ion shows λ_{max} at around 800 nm[12] and copper carboxylate complexes have maxima at 680–720 nm;[13] therefore, it is likely that all the tennis balls are dissociated to $Cu^{II}(OH_2)_x$ + 2[Pt(betmp)(dach)] at low concentrations in water. The complex $K_2[Cu(betmp)_2]$ shows λ_{max} values at 712, 722, and 689 nm in methanol, water, and in the solid state. It should be noted that all are similar; this fact suggests that copper–carboxylate coordination is robust in both methanol and water in contrast to those of the tennis balls. The coordination of sulfur atoms to platinum seems to delocalize the carboxylate electrons throughout the ligand and hence weaken copper–carboxylate bonds in the case of tennis balls.

Table 1. UV/Vis λ_{max} [nm] values of ITBs in methanol, water, and in the solid state.

Compounds	In methanol	In water	Solid
$K_2[Cu(betmp)_2]$	712	722	689
1	685	790–800	712
2	685	790–800	692
3	691	790–800	691
4	706	790–800	708
5	720	790–800	718
6	725	790–800	720
7	725	790–800	723
8	729	790–800	736

It is remarkable that $[[\{Pt(dteym)(dach)\}_2Cu]_2][OTf]_4$ (**8**) has a λ_{max} at 729 nm in methanol, which is quite different from those of **2**–**4**. In view of the fact that **8** has an empty cavity, a significant coordination interaction between Cu^{II} and the anion in the cavities of **2**–**6** should be presumed in methanol.

The ESI-MS spectrum of compound **2** exhibits m/z peaks at 795.9 and 1236.7. The peak at 795.9 corresponds to $[[\{Pt(betmp)(dach)\}_2Cu]_2(BF_4)]^{3+}$, which strongly suggests the existence of a tennis ball structure in the solution state. ESI-MS data for **3**–**6** shows such ion peaks are given in the Experimental Section.

Crystallographic structures: The crystallographic data for **3**–**7** are given in Table 2. Selected bond lengths for compound **3**–**5** and **7** are listed in Table 3. The structural data of an ITB usually shows severe disordering of anions outside the cavity. However, the data is considered to be reasonable to describe the structural properties of tennis ball core regions.

Table 2. Crystallographic data for **3–7**.

	3	**4**	**5**	**6**	**7**
formula	$C_{57}H_{100}Cu_2N_8O_{32}Pt_4S_8Cl_4$	$C_{56}H_{104}Cu_2N_{12}O_{32}Pt_4S_8$	$C_{56}H_{96}Cu_2N_8O_{16}Pt_4S_8Cl_4$	$C_{56}H_{96}Cu_2N_8O_{16}Pt_4S_8Br_4$	$C_{56}H_{92}Cu_2N_8O_{18}Pt_4S_8P_4F_{24}$
M_r	2731.15	2657.41	2443.11	2620.92	2909.1
crystal system	tetragonal	orthorhombic	tetragonal	tetragonal	orthorhombic
space group	$I4_1$ (No.142)	$P22_12_1$ (No.18)	$I4_1/amd$ (No.141)	$\mathrm{I}4_1/amd$ (No.141)	$P22_12_1$ (No. 18)
a [Å]	22.435(4)	12.665(3)	23.085(6)	23.102(6)	29.570(11)
b [Å]	22.449(5)	15.719(4)	23.085(6)	23.102(6)	17.221(5)
c [Å]	23.20(4)	22.666(10)	22.69(6)	22.74(6)	12.542(6)
V [Å^3]	116987(20)	4513(3)	12091(32)	12138(32)	6387(4)
Z	4	2	4	4	2
ρ_{calcd} [g cm^{-3}]	1.552	1.956	1.342	1.434	1.513
μ [mm^{-1}]	5.424	6.908	5.224	6.433	4.952
$F(000)$	5312	2596	4728	5016	2804
crystal size	0.37×0.43×0.45	0.35×0.40×0.45	0.15×0.15×0.25	0.17×0.20×0.20	0.30×0.45×0.48
θ range	1.26–25.20	1.58–24.95	1.26–23.99	1.76–25.44	1.76–28.40
unique reflections	955	2238	1099	886	14811
restraints/parameters	42/161	180/532	18/139	96/121	48/568
GOF on F^2	1.232	1.087	1.262	1.287	0.995
$R1$ [$I>2\sigma(I)$]	0.0857	0.0599	0.0972	0.1596	0.0582
$wR2$	0.1932	0.1465	0.2445	0.3071	0.1435
largest diff. peak/hole [e Å^{-3}]	0.942/−0.718	1.961/−1.113	1.055/−0.705	1.079/−0.978	1.830/−1.216

Table 3. Selected bond lengths [Å] for **3–7**.

3		**4**		**5**		**6**		**7**	
Pt−N	2.01(3)	Pt1−N1	2.05(4)	Pt−N	2.07(3)	Pt−N1	2.06(5)	Pt1−N1	2.092(9)
Pt−S	2.264(10)	Pt1−N2	2.07(5)	Pt−S	2.270(10)	Pt−S1	2.271(18)	Pt1−N2	2.100(10)
Cu−O1	1.93(2)	Pt1−S1	2.26(2)	Cu−O1	1.94(2)	Cu−O1	1.96(4)	Pt1−S1	2.2803
Cl1−O3	1.30(3)	Pt1−S1	2.257(15)	Cu−Cl1	2.793(13)	Cu−Br1	2.858(18)	Pt1−S2	2.298(3)
		Cu1−O1	1.96(3)					Cu1−O1	1.915(9)
		Cu1−O3	1.90(3)					Cu1−O3	1.965(8)
								Cu1−F4	2.319(11)
								Cu2−F2	2.318(12)

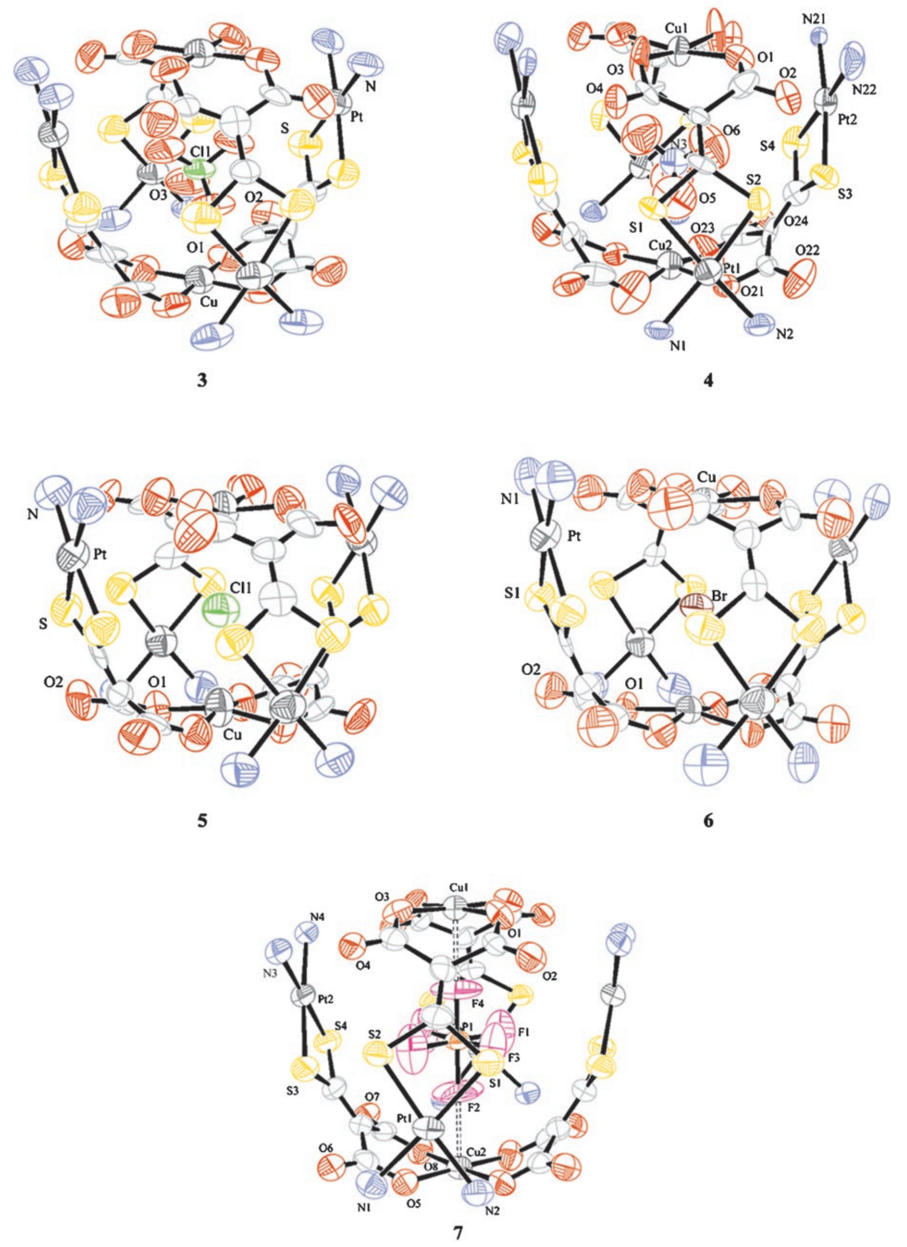
Figure 1 shows crystal structures of ITBs **3–7**. All ITBs shown are composed of two identical molecules. Dimeric interactions between two molecules, for example, through S···S* and N···O* interactions (in which * denotes an atom in the other molecule constituting the tennis ball) make a cavity in which an anion is encapsulated. The anion in the cavity connects two copper atoms; this is also an important force to stabilize the tennis ball structure. We can find significant differences among the cavity shapes of the tennis balls investigated. The interatomic distances Cu···Cu*, S···S*, and N···O* observed in the structural data of **2–8** are given in Table 4.

The crystallographic structure of **3** shows features similar to those of **2**, reported previously.[8] The ClO_4^- ion is very similar to BF_4^- in its size and shape. The NO_3^- ion in **4** looks like ClO_4^- because of severe disordering. The distances S···S* and N···O* are similar between **3** and **4**, but the distance Cu···Cu* of **4** is shorter than that in **3** by 0.6 Å. This shift of copper atom towards the inside of the cavity observed in **4** (with respect to **3**) reflects the difference of the ionic size between ClO_4^- and NO_3^-.

In the crystal structures of **5** and **6**, Cl^- and Br^- are placed at the center of the cavity. The Cu−Br distance of 2.86 Å in **6** is slightly longer than the Cu−Cl distance of 2.79 Å in **5**. Considering the ionic radii of Br^- and Cl^- (1.82 Å and 1.67 Å, respectively), **5** and **6** accommodate significant coordination interactions between copper(II) and anions. The Cu···Cu* distances of **5** and **6** are less than those found in **2–4** by 1.5–0.8 Å. The copper ions in **5** and **6** are directed toward to the center of the cavity, but the S···S* distance is slightly longer than that of **3**. It may be surmised that sizes of the cavities in **5** and **6** represent the minimum that can be achieved by this system. Deviation of the copper ion from the plane of coordinated oxygen atoms is a result of the optimization of copper–anion interaction and a minimization of molecular distortions of the cavity shape.

Severe distortions of the shapes are evident in **7** relative to others. The Cu···Cu* distance in **7** is 7.64 Å, which 0.69 Å larger than that of **2**, and 2.05 Å larger than that of **5**. The PF_6^- ion, with octahedral symmetry, interacts with copper ions through two fluorides; the Cu−F distance is 2.34 Å. The S···S* distances in **7** are 3.87–4.00 Å, which are also longer than those of other tennis balls. The distortions in the cavity shape in **7** suggest that the PF_6^- ion is probably the largest anion that this cavity can encapsulate. This type of PF_6^- encapsulation between two copper(II) centers is comparable with that between two Pd^{II} centers in a previously reported quadruply stranded helicate supramolecule.[14]

Even though the crystal structure of **7** indicates that PF_6^- ion is encapsulated in the cavity, it is likely that the PF_6^- ion leaves the cavity in methanol; this is strongly supported by ^{19}F NMR spectroscopic data. Integration of the peaks corresponding to PF_6^- ion in the ^{19}F NMR spectrum in



3 **4** **5** **6** **7**

Figure 1. ORTEP drawings of **3–7**. Only core structures are shown for clarity.

Table 4. Long distances [Å] between two atoms belonging to the two different molecules that make up an ITB.

	Cu···Cu*	S···S*	N···O*
2[8]	6.95	3.65	3.00
3	7.06	3.66	2.98
4	6.40	3.64, 3.65	2.92, 3.10
5	5.59	3.73	2.99
6	5.73	3.77	2.99
7	7.64	3.87, 4.00, 3.04, 3.08	2.90, 2.97
8[9]	6.73	3.64, 3.88, 3.80	3.10, 2.92, 2.99, 3.01

[D$_1$]methanol containing [[{Pt(dteym)(dach)}$_2$Cu]$_2$][OTf]$_3$ (**8**) and one equivalent of PF_6^- indicates that almost all of the PF_6^- is not encapsulated. It appears that **7** can be only obtained under special recrystallization conditions as described in the Experimental Section. Water may play an important role in the formation of the crystal structure of **7**. The crystal packing structure of **7** is shown briefly in Figure 2, depicting only copper, PF_6^-, water and oxygen atoms coordinated to copper. The units of [[{Pt(dteym)(dach)}$_2$Cu]$_2$(PF$_6$)] are connected by water molecules with distances from the two bridged coppers of 2.35 and 2.55 Å. Close contact between these two units is hindered by the dach groups of each unit. When PF_6^- fills the cavity, the Cu···Cu distance is increased and this may help to minimize steric hindrance between the dach groups when a water molecule bridges two units of **7**.

Closer inspection of structure of **7** indicates that linear anions such as N_3^- and SCN^- would also increase Cu···Cu distances and distort the cavity. The triflate anion which is larger than PF_6^- was found not to be included in the cavity of **7**.

Anion selectivity studied by ^{19}F NMR spectroscopy: The crystal structure of **8** indicates that it has a tennis ball structure without an internal anion.[9] Therefore, the empty cavity of inorganic tennis ball **8** is a receptor for various anions.[9] The relative selectivities for anions versus BF_4^- can be determined by ^{19}F NMR (Figure 3). Table 5 lists this selectivity for various anions.

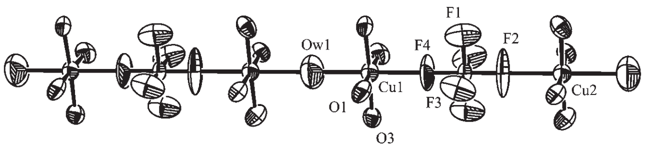


Figure 2. A packing structure of **7** shown by atoms of PF_6^-, Cu1, Cu2, Ow1, O1, and O3.

The anions BF_4^- and ClO_4^- have similar sizes, shapes, charges and hydrophilicities,[15] and the hexanuclear cation [{(en)Pt(bpz)Pd(en)}$_3$]$^{12+}$ (en = ethylenediamine) has been

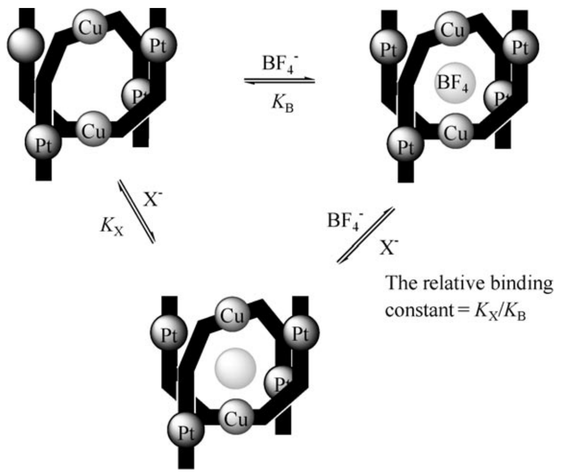


Figure 3. The empty cavity of an ITB as a receptor for anions. The relative binding constant for an X^- ion is defined as the ratio of K_X to K_B.

Table 5. Relative binding constants (K_X/K_B) of an ITB's cavity for various anions.[a]

Anion	K_X/K_B	Anion	K_X/K_B
BF_4^-	1	$CF_3SO_3^-$	0.0
Cl^-	0.6	Br^-	10.
NO_3^-	8.3	ClO_4^-	9.8
SCN^-	0.7	PF_6^-	≪0.1

[a] These data were reported in reference [9]. In addition, the data for the SCN^- and PF_6^- ions are given.

reported to have similar binding affinities for both BF_4^- and ClO_4^-.[16] As is shown by the crystal structures of **2** and **3**, they have almost identical structural features. It is remarkable that the cavity of ITB distinguishes them with significantly different binding affinities. This discrimination is believed to be due to the different coordination ability of the two anions to the copper(II) ion.

Low binding affinity of the cavity for anions such as N_3^-, SCN^-, and PF_6^- is due to cavity distortions as was shown by the study of the crystal structure of **7**. In aqueous solution, anions accumulate more in low-density water sites in the order $ClO_4^- > NO_3^- > I^- > Br^- > Cl^-$, that is, the Hofmeister series.[17] Although the order of affinity found in the present study is partly in agreement with this series, the interaction between metals and anions, and the sizes and shapes of anions are important factors determining ITBs anion selectivity.

Conclusion

Based on the results of ^{19}F NMR and UV/Vis spectroscopy, ESI-MS, and X-ray crystal structures, we conclude that CuX_2 and the two equivalent complexes, [Pt(betmp)(dach)] or [Pt(dteym)(dach)], assemble to form ITBs with an encapsulated anion or empty cavity in methanol. Investigations of the crystal structures of the ITBs revealed cavity shape distortions that depend on the properties of the encapsulated anions, which is an important determinant of ITBs anion selectivity.

Experimental Section

General methods: [Pt(betmp)(dach)], [Pt(dteym)(dach)], $[Pt(dach)]I_2$ and $K_2[Cu(dteym)_2]$ were synthesized by using previously described methods.[12,18] $Cu(ClO_4)_2$, $Cu(NO_3)_2$, $CuCl_2$, $CuBr_2$, $AgPF_6$ and all solvents were purchased from Aldrich Sigma, and were used without further purification. Melting points were determined on a Büchi melting point apparatus. IR spectra were obtained on a Beckman Acculab 4 unit with KBr pellets. ^{19}F NMR spectra were recorded with a Bruker AM 500 spectrometer. Electrospray ionization mass (ESI-MS) spectra were obtained by using a Thermo Finnigan (San Jose, CA) LCQ^{TM} Advantage MAX quadrupole ion-trap instrument by directly introducing samples in MeOH at 10 μM into the source at 25 μL min^{-1} by using a syringe pump. The spray voltage of the spectrometer was set at 4.7 kV, and the capillary temperature used was 180 °C. X-ray data were collected using Enraf-Nonius CAD4 or SMART APEX CCD systems equipped with a Mo X-ray tube. Crystallographic data manipulations were performed by using SHELXS-86 and SHELXL-97 software.[19,20] CCDC-298996–299000 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Measurement of the relative binding constants of ITB's cavity for various anions, K_X/K_B: In a typical experiment, a solution of **8**, Bu_4NBF_4, and Bu_4NCl in [D$_1$]methanol (20.0 mM, 0.20 mL), were mixed in an NMR tube. The ^{19}F NMR spectrum for this solution exhibited two signals at $\delta = -78$ and -1.8 ppm corresponding to $CF_3SO_3^-$ and BF_4^- ions, respectively. The signal of BF_4^- ion inside the cavity does not appear due to paramagnetic copper(II) ions in **8**. The concentrations of BF_4^-, Cl^-, BF_4^--encapsulated tennis ball (**8**(BF_4^-)) and Cl^--encapsulated tennis ball (**8**-(Cl^-)) in solution were calculated from the integration of the signals of $CF_3SO_3^-$ and BF_4^- ions in the ^{19}F NMR spectrum. We assumed in this calculation that the sum of [**8**(BF_4^-)] and [**8**(Cl^-)] was equal to initial concentration of **8**. Then, $K_{Cl^-} = [\mathbf{8}(Cl^-)]/[Cl^-][\mathbf{8}]$, $K_B = [\mathbf{8}(BF_4^-)]/[BF_4^-][\mathbf{8}]$ and $K_{Cl^-}/K_B = [\mathbf{8}(Cl^-)][BF_4^-]/[\mathbf{8}(BF_4^-)][Cl^-]$. K_{X^-}/K_B for other anions were also measured in the same way.

Preparation of $[[\{Pt(betmp)(dach)\}_2Cu]_2(ClO_4)][ClO_4]_3$ (3): Copper(II) perchlorate (0.13 g, 0.50 mmol) was added to a slurry of [Pt(betmp)-(dach)] (0.53 g, 1.02 mmol) in methanol (100 mL). Solid [Pt(betmp)-(dach)] was dissolved in methanol over 30 min at RT, and remaining solid was filtered off. Crystalline compound **3** was obtained by slow evaporation of the filtrate. Compound **3** lost its crystallinity immediately on exposure to air due to desolvation. Yield: 0.64 g (95 %); m.p. 182 °C (decomp); elemental analysis calcd (%) for $C_{56}H_{96}N_8O_{16}S_8Cu_2Pt_4{\cdot}4\,ClO_4$: C 24.9, H 3.58, N 4.15; found: C 25.2, H 3.55, N 3.87; ESI-MS (4.7 kV): m/z (%): 800.0 (72) $[M-3\,ClO_4]^{3+}$, 1249.7 (100) $[M-3\,ClO_4]^{2+}$; IR (KBr): $\tilde{\nu} = 3407$ (br), 3212 (s), 3116 (s), 3038 (s), 2937 (s), 2885 (s), 1627 (vs), 1450 (m), 1386 (vs), 1119 (vs), 760 (m), 626 cm^{-1} (s).

Preparation of $[[\{Pt(betmp)(dach)\}_2Cu]_2(NO_3)][NO_3]_3$ (4): Compound **4** was obtained by using copper(II) nitrate instead of copper(II) perchlorate in the procedure described for **3**. Single crystals were grown in acetone/water co-solvent. Yield: 0.58 g (87 %); m.p. 141 °C (decomp); elemental analysis calcd (%) for $C_{56}H_{96}N_8O_{16}S_8Cu_2Pt_4{\cdot}6\,H_2O{\cdot}4\,NO_3$: C 25.3, H 4.10, N 5.32; found: C 25.2, H 3.95, N 5.41; ESI-MS (4.7 kV): m/z(%): 787.3 (100) $[M-3\,NO_3]^{3+}$, 1212.1 (98) $[M-2\,NO_3]^{2+}$; IR (KBr): $\tilde{\nu} = 3412$ (br), 3196 (s), 3034 (s), 2935 (s), 2864 (m), 1628 (vs), 1450 (m), 1383 (vs), 1265 (m), 1177 (m), 750 cm^{-1} (m).

Preparation of $[[\{Pt(betmp)(dach)\}_2Cu]_2(Cl)][Cl]_3$ (5): Copper(II) chloride (0.13 g, 1.0 mmol) was added to a slurry of [Pt(betmp)(dach)] (1.06 g, 2.04 mmol) in methanol (300 mL). The solid [Pt(betmp)(dach)] was allowed to dissolve over 30 min at RT, and then the remaining solid was filtered off. Crystals of **5** were grown in ether/methanol layer diffusion of the crude product. Yield: 0.77 g (63 %); m.p. 228 °C (decomp); elemental analysis calcd (%) for $C_{56}H_{96}N_8O_{16}S_8Cu_2Pt_4{\cdot}4\,Cl$: C 27.5, H 3.96, N 4.59; found: C 27.6, H 3.93, N 4.48; ESI-MS (4.7 kV): *m*/*z* (%): 778.9 (100) $[M{-}3\,Cl]^{3+}$, 1184.7 (48) $[M{-}2\,Cl]^{2+}$; IR (KBr): $\tilde{\nu}=3438$ (s), 3175 (s), 3086 (s), 2935 (s), 1629 (vs), 1449 (m), 1364 (vs), 1176 (m), 762 (s), 534 cm^{-1} (m).

Preparation of $[[\{Pt(betmp)(dach)\}_2Cu]_2(Br)][Br]_3$ (6): Compound **6** was obtained by using copper(II) bromide instead of copper(II) chloride in the procedure described for **5**. Yield: 0.72 g (55%); m.p. 216°C (decomp); elemental analysis calcd (%) for $C_{56}H_{96}N_8O_{16}S_8Cu_2Pt_4{\cdot}4\,Br$: C 25.7, H 3.69, N 4.28; found: C 25.5, H 3.66, N 4.36; ESI-MS (4.7 kV): *m*/*z* (%): 793.3 (100) $[M{-}3\,Br]^{3+}$, 1229.6 (50) $[M{-}2\,Br]^{2+}$; IR (KBr): 3421 (br), 3180 (s), 3087 (s), 2930 (s), 2866 (m), 1629 (vs), 1449 (m), 1363 (vs), 1176 (m), 762 (s), 538 cm^{-1} (m).

Preparation of $[[\{Pt(dteym)(dach)\}_2Cu]_2(PF_6)[PF_6]_3$ (7): $[Pt(dach)]I_2$ (0.563 g, 1.00 mmol) was suspended in water (50 mL) containing silver hexafluorophosphate (0.506 g, 2.00 mmol) and stirred for 4 h. The yellow precipitate (AgI) which formed was removed by filtration. $K_2[Cu(dteym)_2]$ (0.30 g, 0.50 mmol) was added to this filtrate and the reaction mixture was stirred for 1 h. The precipitate (KPF_6) was removed by filtration, and the filtrate was evaporated to dryness. Compound **7** was obtained as crystals by recrystallizing the crude product in diethyl ether/ethanol layer. Yield: 0.66 g (91%); m.p. 193°C (decomp); elemental analysis calcd (%) for $C_{56}H_{88}N_8O_{16}S_8Cu_2Pt_4{\cdot}2\,H_2O{\cdot}4\,PF_6$: C 23.1, H 3.19, N 3.85; found: C 23.0, H 3.24, N 3.89; ESI-MS (4.7 kV): *m*/*z* (%): 812.5 (22) $[M{-}3\,PF_6]^{3+}$, 1184.7 (100) $[M{-}2\,PF_6]^{2+}$; IR (KBr): $\tilde{\nu}=3444$ (br), 3192 (vs), 2894 (s), 2882 (s), 1631 (vs), 1370 (vs), 1306 (m), 1173 (m), 840 (vs), 784 (m), 561 cm^{-1} (s).

Acknowledgements

This research was supported by the Ministry of Science and Technology of Korea through NRL and Creative Research Initiative Program (W.N.) and by the SRC program of MOST/KOSEF (grant: R11-2005-008-00000-0) and by the Korea Research Foundation (grant: KRF-2004-005-C00093).

---

[1] Coordination boxes/cages: a) D. Fiedler, D. H. Leung, R. G. Bergman, K. N. Raymond, *Acc. Chem. Res.* **2005**, *38*, 351; b) M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.* **2005**, *38*, 369; c) T. D. Hamilton, L. R. MacGillivray, *Cryst. Growth Des.* **2004**, *4*, 419; d) W. Saalfrank, B. Demleitner, H. Glaser, H. Maid, S. Reihs, W. Bauer, M. Maluenga, F. Hampel, M. Teichert, H. Krautscheid, *Eur. J. Inorg. Chem.* **2003**, 822; e) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972; f) R. G. F. Swieger, T. J. Malefetse, *Coord. Chem. Rev.* **2002**, *225*, 91; g) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853; h) J. A. R. Navarro, B. Lippert, *Coord. Chem. Rev.* **1999**, *185*, 653.

[2] Molecular capsules: a) D. Zuccaccia, L. Pirondini, R. Pinalli, E. Dalcanale, A Macchioni, *J. Am. Chem. Soc.* **2005**, *127*, 7025; b) F. Hof, S. L. Craig, C. Nuckolls, J. Rebek, Jr., *Angew. Chem.* **2002**, *114*, 1556; *Angew. Chem. Int. Ed.* **2002**, *41*, 1488; c) F. Corbellini, R. Fiammengo, P. Timmerman, M. Crego-Calama, K. Versluis, A. J. R. Heck, I. Luyten, D. N. Reinhoudt, *J. Am. Chem. Soc.* **2002**, *124*, 6569; d) L. R. MacGillivray, J. L. Atwood, *Angew. Chem.* **1999**, *111*, 1080; *Angew. Chem. Int. Ed.* **1999**, *38*, 1018; e) M. M. Conn, J. Rebek, Jr., *Chem. Rev.* **1997**, *97*, 1647.

[3] R. Wyler, J. de Mendoza, J. Rebek, Jr., *Angew. Chem.* **1993**, *105*, 1820; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1699.

[4] N. Branda, J. Wyler, J. Rebek, Jr., *Science* **1994**, *263*, 1267.

[5] R. S. Meissner, J. Rebek, Jr., J. de Mendoza, *Science* **1995**, *270*, 1485.

[6] J. Kang, J. Rebek, Jr., *Nature* **1996**, *382*, 239.

[7] O'Leary, R. M. Grotzfeld, J. Rebek, Jr., *J. Am. Chem. Soc.* **1997**, *119*, 11701.

[8] K. M. Kim, J. S. Park, Y.-S. Kim, Y. J. Jun, T. Y. Kang, Y. S. Sohn, M.-J. Jun, *Angew. Chem.* **2001**, *113*, 2524; *Angew. Chem. Int. Ed.* **2001**, *40*, 2458.

[9] K. M. Kim, K.-H. Kim, T. Y. Kang, J. S. Park, R. Song, M.-J. Jun, *Chem. Commun.* **2003**, 1410.

[10] a) J.-M. Lehn in *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim (Germany), **1995**, pp. 31–35; b) P. A. Gale, *Coord. Chem. Rev.* **2000**, *199*, 18; c) J. J. Bodwin, A. D. Cutland, R. G. Malkani, V. L. Pecoraro, *Coord. Chem. Rev.* **2001**, *216*, 489; d) P. D. Beer, P. A. Gale, *Angew. Chem.* **2001**, *113*, 502; *Angew. Chem. Int. Ed.* **2001**, *40*, 486; e) P. D. Beer, *Acc. Chem. Res.* **1998**, *31*, 71.

[11] J. S. Park, K.-T. Youm, M.-J. Jun, *Polyhedron*, **2002**, *21*, 1273.

[12] J. Bjerrum, C. J. Ballhausen, C. K. Jørgensen, *Acta Chem. Scand.* **1954**, *8*, 1275.

[13] D. P. Graddon, *J. Inorg. Nucl. Chem.* **1958**, *7*, 93.

[14] D. A. McMorran, P. J. Steel, *Angew. Chem.* **1998**, *110*, 3495; *Angew. Chem. Int. Ed.* **1998**, *37*, 3295.

[15] O. S. Jung, Y. J. Kim, Y.-A. Lee, J. K. Park, H. K. Chae, *J. Am. Chem. Soc.* **2000**, *122*, 9921.

[16] R.-D. Schnebeck, E. Freisinger, B. Lippert, *Angew. Chem.* **1999**, *111*, 235; *Angew. Chem. Int. Ed.* **1999**, *38*, 168.

[17] a) F. Hofmeister, *Arch. Exp. Pathol. Pharmakol.* **1888**, *24*, 247; b) A. A. Zavitsas, *J. Phys. Chem. B* **2001**, *105*, 7805.

[18] K. M. Kim, M.-J. Jun, Y. S. Sohn, *Polyhedron* **1997**, *16*, 3705.

[19] G. M. Sheldrick, SHELXS-86: Program for Solution of Crystal Structure, University of Göttingen, (Germany), **1986**.

[20] G. M. Sheldrick, SHELXL-97: Program for Refinement of Crystal Structure, University of Göttingen, (Germany), **1997**.

Received: December 26, 2005
Revised: February 22, 2006