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The non-templated empty cavity and its selective anion binding despite having similar shapes

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An inorganic tennis ball with an empty cavity was formed without any assistance of guest molecules, and found to bind various anions selectively depending on their size and copper–anion interaction strengths without much change of the shapes.

Interest has been increasing in the development of receptors able to bind selectively anionic guest species[1] due to the biological,[2] environmental[3] and catalytic[4] importance of anions. A strategy for incorporating transition metal centers into receptors is usually employed in order to enhance the receptor's binding affinity for anions.[5] Even though many receptors have been developed for anion binding, receptors that can bind anionic guests, with different affinities depending on their sizes and shapes, are limited.

We have previously reported[6] that the self-assembly of CuX$_2$ (where X = BF$_4^-$, NO$_3^-$, and ClO$_4^-$) and (dach)Pt(betmp) [dach = *trans*-(±)-1,2-diaminocyclohexane and betmp = bis(ethylthio)methylenepropanedioate] produces a supra-molecule [[{(dach)Pt(betmp)}$_2$Cu]$_2$(X)][X]$_3$ (**1**(X)·[X]$_3$, where (X) denotes the anion inside the cavity) *via* non-covalent interactions in methanol solution. The supra-molecule **1**(X) resembles the notional tennis ball[7] formed by two glycoluril units in its molecular shape, so we called it an "Inorganic Tennis Ball". It was uncertain whether such a ball could be established without the help of an anion inside, and whether the cavity could bind anions with selectivity.

In our subsequent work, efforts to obtain an inorganic tennis ball with an empty cavity were made using a relatively large anion, triflate (OTf$^-$). Our attempts to isolate or characterize it, from a methanol solution containing Cu(OTf$^-$)$_2$ and (dach)Pt(betmp), failed due to its unstable properties. However, it could have been successfully obtained using the ligand 1,3-dithiepan-2-ylidenemalonate (dteym) instead of the betmp *via* the same self-assembly process.† It has a chemical formula of [[{(dach)Pt(dteym)}$_2$Cu]$_2$][OTf$^-$]$_4$ (**2**·[OTf$^-$]$_4$).

The crystal structure‡ of **2** is shown in Fig. 1 as a ball and stick representation, and is composed of two identical U-shaped units of {(dach)Pt(dteym)}$_2$Cu, which are cross-linked with each other. There are two close interactions between the two units which may assist in the dimerization. One is an NH···O hydrogen bonding interaction and the other is an S···S interaction. An electrostatic interaction is also expected to play an additional significant role in the dimerization. The coordination geometry around the Cu(II) is a square pyramid with an ethanol oxygen at the distance of 2.252(12) Å at its axial position. The dimer **2** has a nearly spherical empty cavity with a distance of 6.73 Å for the Cu···Cu, which is comparable to the previously reported 6.95 Å of **1**(BF$_4^-$)·[BF$_4^-$]$_3$.[6] Careful examination of the residual peaks in the crystallographic data of **2** did not indicate the existence of any solvents or molecules in the cavity.

The empty cavity of the inorganic tennis ball **2** can be filled by BF$_4^-$ if it is present. Once BF$_4^-$ has been included into the cavity, its ^{19}F NMR signal will be strongly influenced by the two paramagnetic copper ions in the cavity shell. Indeed, the signal intensity of the BF$_4^-$ appearing at −4 ppm in the ^{19}F NMR spectrum of **2**·[OTf$^-$]$_4$ (4.6 mM) and BF$_4^-$ (5.0 mM) in the deuterated methanol solution corresponded to less than 13% of the total amount of BF$_4^-$ added, while the signal intensity of the OTf$^-$ at −78 ppm fully reflected the total amount of OTf$^-$ existing in the solution (Fig. 2a–b). The lost intensity of the BF$_4^-$ signal should correspond to the amount within the

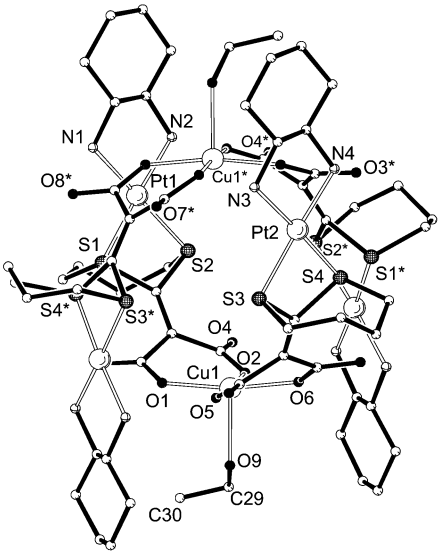

Fig. 1 Ball and stick representation of **2**. A solvent ethanol is coordinated to Cu1. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Cu(1)–O(1) 1.941(9), Cu(1)–O(2) 1.926(8), Cu(1)–O(5) 1.924(8), Cu(1)–O(6) 1.952(9), Cu(1)–O(9) 2.252(11), Pt(1)–N(1) 2.058(11), Pt(1)–N(2) 2.034(11), Pt(1)–S(1) 2.273(3), Pt(1)–S(2) 2.274(4). Close distances [Å]: S(2)···S(2)* 3.64, S(3)···S(3)* 3.80, S(1)···S(4)* 3.88, O(8)*···N(1) 3.18, O(4)*···N(2) 2.91, O(7)*···N(3) 2.99, O(3)*···N(4) 3.13. Symmetry transformation: * = 1 − *x*, *y*, 0.5 − *z*.

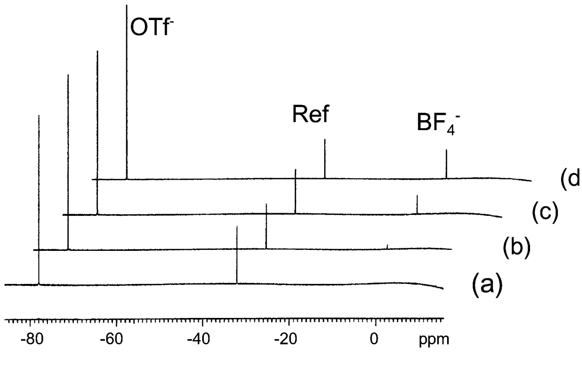

Fig. 2 ^{19}F NMR spectra in CD$_3$OD showing the different binding affinities of anions within the cavity of **2**·[OTf$^-$]$_4$. The compound 2,2,3,3-tetrafluoro-1,4-butanediol was added as a reference (ref). (a) **2**·[OTf$^-$]$_4$ + 1.1 ref. (b) **2**·[OTf$^-$]$_4$ + 1.1 ref + 1.1 [Et$_4$N][BF$_4^-$]. (c) **2**·[OTf$^-$]$_4$ + 1.1 ref + 1.1 [Et$_4$N][BF$_4^-$] + 1.1 [Et$_4$N][Cl$^-$]. (d) **2**·[OTf$^-$]$_4$ + 1.1 ref + 1.1 [Et$_4$N][BF$_4^-$] + 1.1 [Et$_4$N][ClO$_4^-$].

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inorganic tennis ball. The equilibrium reaction (1) was supposed, and the binding constant of the cavity for the BF_4^- ($K_{\mathrm{bind,tfb}}$) was estimated to be larger than 2.7×10^4 M^{-1} based on these facts.

$$\mathbf{2}\cdot[OTf^-]_4 + BF_4^- \rightleftarrows \mathbf{2}(BF_4^-)\cdot[OTf^-]_4 \qquad (1)$$

A series of ^{19}F NMR studies were carried out to compare the affinity of the cavity for various anions with that for BF_4^- (Fig. 2c–d). The hidden intensity of the BF_4^- signal reappeared when Cl^- was added to the deuterated methanol solution of $\mathbf{2}\cdot[OTf^-]_4$ and BF_4^-, due to the competition of the Cl^- and BF_4^- for inclusion into the cavity. When ClO_4^- was added, the BF_4^- signal was larger than when Cl^- was added. The amount of Cl^- or ClO_4^- included in the cavity can be calculated from the BF_4^- signal intensity. The relative binding affinity of the cavity ($K_{\mathrm{bind,X}}/K_{\mathrm{bind,tfb}}$) for various Xs can be calculated from the expression $[\mathbf{2}(X)][BF_4^-]/[\mathbf{2}(BF_4^-)][X]$, and the results are tabulated in Table 1.

Table 1 Relative binding constants of **2** for various anions, $K_{\mathrm{bind,X}}/K_{\mathrm{bind,tfb}}$.[a]

Anions, X	$K_{\mathrm{bind,X}}/K_{\mathrm{bind,tfb}} \pm 3\sigma$
BF_4^-	1
$CF_3SO_3^-$	No binding
Cl^-	0.6 ± 0.2
Br^-	10.3 ± 4.2
I^-	9.7
NO_3^-	8.3 ± 1.3
ClO_4^-	9.8 ± 4.0

[a] The binding constants were averaged with data sets obtained at three different concentrations of each anion. In the case of anion I^-, only one datum at low concentration was obtained due to a solubility problem. Tfb = BF_4^-.

In aqueous solution, anions accumulate more in the low-density water sites in the order: $ClO_4^- > NO_3^- > I^- > Br^- > Cl^-$, which is known as the Hofmeister series.[9] Although the order of the affinity studied in this work partly coincided with this series, additional factors such as coordination interactions between the metal and anions, and sizes and shapes of the anions should be considered in order to explain precisely the affinity of our molecular system.

One unique feature of the cavity of the present molecule is that it totally excludes the triflate anion. Many of the receptors[5a,5e] so far reported have been known to bind triflate with significant binding affinities. The size of the triflate anion must be the reason why it was not included in the cavity of the ball. Obviously, the cavity has a limited size for the accommodation of a triflate anion.

Another interesting feature of the cavity of **2** is that it distinguishes BF_4^- and ClO_4^- with significantly different binding affinities, even though the anions BF_4^- and ClO_4^- have similar sizes, shapes, charges and hydrophilicities,[10] and the hexanuclear cation, $[\{(en)Pt(bpz)Pd(en)\}_3]^{12+}$, reported[5b] by B. Lippert *et al.* showed a similar binding affinity toward both the BF_4^- and ClO_4^- anions. Crystal structures of the anion-encapsulating inorganic tennis balls $\mathbf{1}(BF_4^-)$[6] and $\mathbf{1}(ClO_4^-)$[11] are very similar to each other. The distances between the two coppers forming the cavity shell in these crystal structures are 6.95 Å for $\mathbf{1}(BF_4^-)$ and 7.05 Å for $\mathbf{1}(ClO_4^-)$. These Cu···Cu distances are slightly increased compared with the distance in $\mathbf{2}\cdot[OTf^-]_4$. It is likely that such slight variation in the Cu···Cu distances just helps the tennis ball keep an appropriate interaction between the metal and the anions. The difference between Cu···O and Cu···F interaction strengths may explain the difference of the binding affinity of **2** for ClO_4^- and BF_4^-.

In conclusion, we have identified the crystal structure of the inorganic tennis ball with an empty cavity which assembles without any guest molecules. The size and shape of the cavity were not changed much, whether empty or filled by anions such as BF_4^-, ClO_4^-. This is a unique feature in contrast to a few other anion-containing metal–ligand capsules[12] which often end up forming different topologies in the presence of different counteranions, rather than empty capsules. **2** is a quite interesting example of a metal-incorporated anion binding receptor, in which the metal acts as a recognition center through metal–anion interactions.

Notes and references

† Preparation of $\mathbf{2}\cdot[OTf^-]_4$: the aqueous solution (5 ml) of $Cu(OTf^-)_2\cdot xH_2O$ (0.54 g, 2.3 mmol) was added to an aqueous slurry (5 ml) of (dach)Pt(dteym) (2.4 g, 4.4 mmol) which was prepared using our previously reported method.[8] The resulting clear solution was totally evaporated, and the residue dissolved in ethanol (5 ml). The sky-blue octagonal crystals, $\mathbf{2}\cdot[OTf^-]_4$, were isolated in 90% yield from the ethanol solution. IR (cm^{-1}): 3209(s), 2839(m), 1638(s), 1371(s), 1282(s), 1170(s), 1031(s), 788(m), 517(m).

‡ All the X-ray data were collected on a Nonius kappa-CCD system equipped with a Mo X-ray tube at the temperature 210 K, in the service crystallography laboratory located in the Department of Chemistry at the University of Toronto, Canada. Crystal data of $\mathbf{2}\cdot[CF_3SO_3^-]_4$: *monoclinic*, *C*2/*c* (No. 15), $Z = 4$, $a = 30.6281(11)$, $b = 19.8478(7)$, and $c = 21.0157(6)$ Å, $\beta = 111.450(2)°$, $V = 11890.6(7)$ Å^3, $\mu = 5.338$ mm^{-1}, $d_{\mathrm{calc}} = 1.743$ g cm^{-3}, $R1 = 8.00$, $wR2 = 20.65\%$ for 12926 unique reflections ($I \geq 2\sigma(I)$), 652 variables and 79 restraints. The structure solution and refinement of the data were handled with the SHELXS-86 and SHELXL-97 programs. CCDC 189845. See http://www.rsc.org/suppdata/cc/b3/b302648e/ for crystallographic data in .cif or other electronic format.

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