The First Inorganic “Tennis Ball” Encapsulating an Anion**

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A number of calixarene and glycouril derivatives are known to dimerize and encapsulate reversibly various substrates[1] such as dichloromethane, methane, cyclohexane, adamantane, and ferrocene within their cavities.[2] A notional “tennis ball”[3] coined by Rebek, Jr. came from the roughly spherical dimer of the glycouril derivative which was prepared by condensing two molecules of diphenylglycouril with durene tetrabromide. The tennis ball has the molecular interface which resembles the seam of a real ball. Hydrogen-bond acceptor and donor sites of glycouril units at the ends of the molecule play an important role in the dimerization. The name, “softball”,[4] was used to describe the dimer of bigger glycouril derivatives. Inorganic artificial hosts[5–7] are of great interest because the metal can play a pivotal role in specific functions such as magnetism, catalysis, and molecular recognition. Though the strategy of metal-templated self-assembly is routinely exploited in preparing the inorganic hosts, it is generally difficult to acquire reversible characteristics of the assembly. A metal complex that assembles like the glycourils or calixarenes is desirable since the resulting self-assembled inorganic host molecules may have novel encapsulation or reaction properties. Here we report an anion encapsulating tennis-ball-like dimer which is formed by self-assembly of two metal complexes.

Bis(ethylthio)methylenepropanedioate (BETMP) is a multidentate ligand containing two sulfur atoms and two carboxylate groups. A diamineplatinum(II) moiety, [(dach)Pt^{II}] (dach = *trans*(±)-1,2-diaminocyclohexane) binds to the ligand exclusively through the two sulfur atoms.[8] In our recent crystallographic study of K_2Cu(BETMP), on the other hand, the copper(II) ion was found to be coordinated by carboxylate groups of the ligand.[9] Such different coordination properties of the ligand toward the metal ions prompted us to synthesize a new heteronuclear complex using BETMP, copper(II), and [(dach)Pt^{II}] as building units. We have successfully obtained a crystalline material with the formula $\{(dach)Pt(BETMP)\}_2$-$Cu(BF_4)_2$ ($\mathbf{1}\cdot(BF_4)_2$) from the concentrated aqueous solution of $Cu(BF_4)_2$ and (dach)Pt(BETMP) in a molar ratio of 1:2. The structure of $\mathbf{1}\cdot(BF_4)_2$ was elucidated by the X-ray crystallography (Figure 1).[10] Two molecules of [(dach)Pt(BETMP)] are linked by one copper(II) ion through the carboxylate groups of the BETMP ligand from the opposite sides, and two BF_4 anions weakly interact with the copper ion.

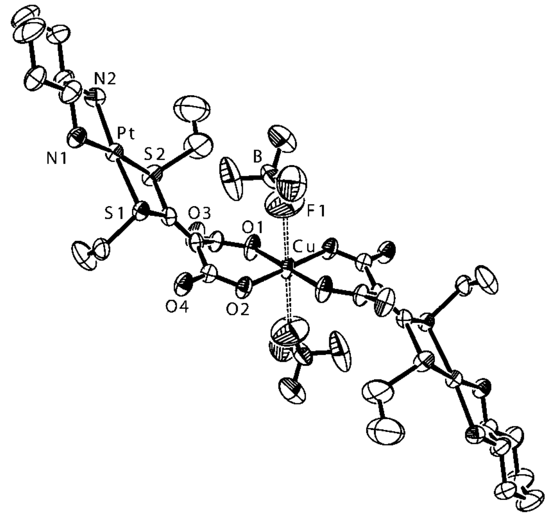

Figure 1. Structure of $\mathbf{1}\cdot(BF_4)_2$ (ORTEP drawing). Hydrogen atoms are omitted for clarity.

Compound **1** is a zwitterionic complex which has an overall +2 charge: +2 charges are located around each platinum atom and −2 charges around the copper atom. If the two Pt complexes in **1** lie in the same direction, then **1** would have concave shape similar to the glycouril compounds that form a tennis ball or softball. Compound **1** contains hydrogen-bonding acceptor (carboxylate) and donor (amine) groups; thus, the dimerization of **1** should be feasible. The tennis-ball-like dimerization of **1** would lead to a maximization of the electrostatic interaction between the opposite local charges, and indeed, **1** has been found to dimerize in methanol to form such a tennis ball.

The crystalline material $\mathbf{1}\cdot(BF_4)_2$ was dissolved in methanol, and octahedron-shaped crystals were grown from the concentrated solution. The X-ray crystallographic study[10] of the crystal revealed that it has a molecular composition of $[[\{(dach)Pt(BETMP)\}_2Cu]_2(BF_4)](BF_4)_3$ ($\mathbf{2}\cdot(BF_4)_3$). The molecular structure of **2** is shown in Figure 2a, and the core of the structure is shown as a space-filling diagram in Figure 2b. The core of the structure has a nearly spherical shape whose surface is incorporated with six metal centers. The hydrogen-bonding interaction between NH of one monomer and O2 of the other (the N⋯O2 distance is 2.87 Å) is clearly evident in Figure 2b. This interaction is expected to be a driving force for the formation of the dimer as in the case of the tennis ball formation with the glycouril derivatives. The electrostatic interaction between ionic parts of the molecule, and the close contact (3.65 Å) of two sulfur atoms of different monomers seem to also contribute to the gathering of the two monomers. The line of contact between the two monomers resembles the seam of a tennis ball, and hydrogen bonds and sulfur close contacts could be regarded as stitches along the seam. A BF_4 anion is centered in the cavity resulting from the dimerization.

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[**] This work was financially supported by a Korean Research Foundation grant (No. 1997-011-D 00013).

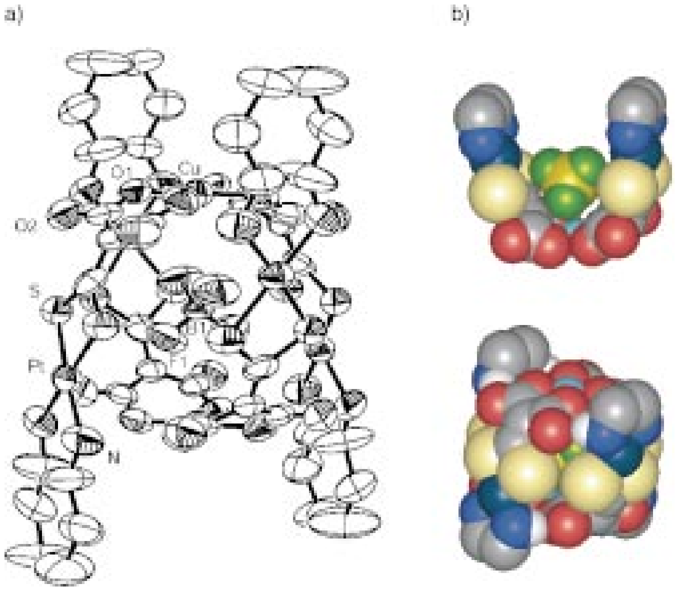


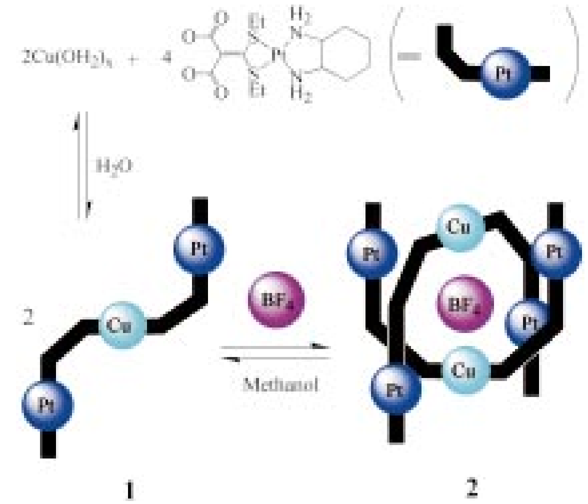
Figure 2. a) Structure of **2** (ORTEP drawing). Hydrogen atoms, three BF_4 anions outside the cavity, and ethyl groups attached to sulfur atoms are omitted for clarity. b) Space-filling diagram of the core of **2** and its interior structure; color code: C: gray; H: white; N: blue; O: red; S: yellow; F: green; B: dark yellow; Cu: sky blue; Pt: dark blue.

The distance from the boron atom to the van der Waals surface of each atom surrounding the anion lies in the range of 2.1–2.4 Å. The volume of the cavity calculated from the minimum distance is 39 Å^3, which is comparable to that of the tennis ball described by Rebek, Jr. et al.[3]

The existence of the tennis ball structure of $\mathbf{2}\cdot(BF_4)_3$ in methanol is supported by ^{19}F NMR data. The spectra recorded both in D_2O and [D$_1$]methanol with 2,3-tetrafluorobutane-1,4-diol as an internal standard exhibit the same signals for the free BF_4 anion and the internal standard. The ratio of the integral of the BF_4 signal of $\mathbf{2}\cdot(BF_4)_3$ to the signal of the internal standard, however, drops by approximately 25% in [D$_1$]methanol compared with that in D_2O. The same result was obtained when $\mathbf{1}\cdot(BF_4)_2$ was used instead of $\mathbf{2}\cdot(BF_4)_3$. Such a reduction of the BF_4 signal in [D$_1$]methanol implies that one BF_4 ion is encapsulated by the tennis ball in methanol; the paramagnetic copper ions make the NMR signal of this BF_4 ion undetectable.

UV/Vis spectra of $\mathbf{2}\cdot(BF_4)_3$ and $\mathbf{1}\cdot(BF_4)_2$ recorded in water and methanol at a concentration of 5 mM show a maximum absorption λ_{max} at 795 and 695 nm, respectively. It is known that the hydrated copper(II) ion shows a λ_{max} at around 800 nm[11] and copper carboxylate complexes at 680–720 nm;[12] therefore, it is likely that **1** (or **2**) is partly dissociated to $Cu^{II}(OH_2)_x + 2$[(dach)Pt(BETMP)] at low concentration in water.

Based on the results of ^{19}F NMR, UV/Vis, and crystallographic studies, it can be concluded that $Cu(BF_4)_2$ and two equivalents of [(dach)Pt(BETMP)] assemble to form the heterotrinuclear complex $\mathbf{1}\cdot(BF_4)_2$, and two copies of **1** assemble to form the inorganic tennis ball **2**, which encapsulates one BF_4 anion (Scheme 1). The formation of **1** can be described as copper-templated self-assembly and that of **2** as noncovalent-bond-directed self-assembly. In water, **1** begins to crystallize at concentrations of about ~0.1 M, and significant amounts of the dissociated form exist at the lower concentration. In methanol, however, **2** is predominantly observed. The occurrence of different assembling processes observed in water and methanol can be explained by the different coordination capability and hydrogen-bonding ability of the solvents. We have also obtained very similar crystallographic and UV/Vis spectroscopic results in case of different anions such as NO_3 and ClO_4.



Scheme 1. The self-assembly processes leading to **1** and **2**.

The tennis ball or softball structures known to date are composed of organic moieties and are formed in aprotic solvents. Compound **2** is the first example of a metal-containing tennis ball that is formed in methanol. The platinum atoms in the shell of **2** constitute an important part of the structure, whereas the copper atoms play a key role in directing the assembly of **1** in water and in the encapsulation of the anion through their interaction in methanol.

Experimental Section

Crystallization of $\mathbf{1}\cdot(BF_4)_2$: An aqueous solution (5 mL) of $Cu(BF_4)_2\cdot xH_2O$ (0.54 g, 2.3 mmol) was added to the aqueous slurry (5 mL) of [(dach)Pt(BETMP)] (2.4 g, 4.4 mmol) which was prepared by the literature method.[8] After the addition, a clear solution was obtained, from which blue, block crystals of $\mathbf{1}\cdot(BF_4)_2$ (2.45 g, 85%) were obtained in a few days.

Crystallization of $\mathbf{2}\cdot(BF_4)_3$: Compound $\mathbf{1}\cdot(BF_4)_2$ was dissolved in a minimum volume of methanol, from which blue-green octagonal crystals of $\mathbf{2}\cdot(BF_4)_3$ were isolated in 90% yield. Compound $\mathbf{2}\cdot(BF_4)_3$ could be also obtained by the addition of $Cu(BF_4)_2\cdot xH_2O$ to [(dach)Pt(BETMP)] in methanol.

Received: February 19, 2001 [Z16638]

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[10] The X-ray data were collected on an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-ray tube at room temperature. Crystal data of **1** $\cdot$ $(BF_4)_2$: triclinic, $P\bar{1}$ (no. 2), $Z = 1$, $a = 10.289(3)$, $b = 11.209(2)$, $c = 11.752(3)$ Å, $\alpha = 96.81(2)$, $\beta = 112.58(2)$, $\gamma = 111.33(2)^\circ$, $V = 1111.9(4)$ Å^3, $\mu = 7.023$ mm^{-1} , $\rho_{calcd} = 2.032$ g cm^{-3}, $R1 = 0.0343$, $wR2 = 0.0912$ for 3636 unique reflections($I > 2\sigma(I)$) and 268 variables. Crystal data of **2** $\cdot$ $(BF_4)_3$: tetragonal, $I4_1/acd$ (no. 142), $Z = 4$, $a = 22.498(4)$, $c = 23.16(4)$ Å, $V = 11724(21)$ Å^3, $\mu = 5.324$ mm^{-1} , $d_{calcd} = 1.501$ g cm^{-3}, $R1 = 0.0733$, $wR2 = 0.1879$ for 1109 unique reflections($I > 2\sigma(I)$) and 147 variables. The structure solution and refinement of the data were handled with the SHELXS-86 and SHELXL-97 programs. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-160943 (**1** $\cdot$ $(BF_4)_2$) and CCDC-160944 (**2** $\cdot$ $(BF_4)_3$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Optically Active Seleninic Acids: Optical Resolution and Stability

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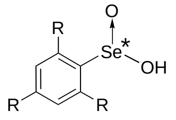
Tricoordinate sulfur compounds are well known to have pyramidal structures, and many chiral tricoordinate sulfur compounds have already been isolated and clearly characterized.[1] Recently, chiral tricoordinate selenium and tellurium compounds, such as oxides,[2] onium salts,[3] ylides,[4] and imides,[5] have also been isolated, and their properties have been studied.[6–8] Chalcogenic acids are also tricoordinate and are considered to have pyramidal structures. However, no studies on optically active chalcogenic acids have been reported. There are at least two possible explanations for this: first, sulfinic acids readily undergo disproportionation[9] to give thiol sulfonates and sulfonic acids. Second, facile racemization of chalcogenic acids may occur via achiral chalcogenate anions with extrusion of a proton and/or by an intra- or intermolecular proton-transfer reaction. Seleninic acids do not disproportionate to the corresponding selenol selenonates and selenonic acids. Therefore, it may be possible to isolate optically active seleninic acids if we could suppress their racemization. We examined the optical resolution of areneseleninic acids by means of liquid chromatography on an optically active column and found that seleninic acid could be optically resolved, although the racemization was fast, especially at high concentrations, and also that bulky alkyl substituents on the benzene ring of areneseleninic acids were effective in retarding racemization. Here we describe the first optical resolution and the stability of seleninic acids.

When the optical resolution of 2,4,6-trimethylbenzeneseleninic acid (**2**) was examined on an analytical scale by liquid chromatography on an optically active column packed with amylose carbamate derivative/silica gel (Daicel Chiralpak AS; 4.6 × 250 mm), two peaks corresponding to he enantiomers were observed on the chromatogram, whereas only one peak was observed in the case of benzeneseleninic acid (**1**), as shown in Figure 1. This result shows that



1: R = H
2: R = Me
3: R = Et
4: R = *i*Pr
5: R = *t*Bu

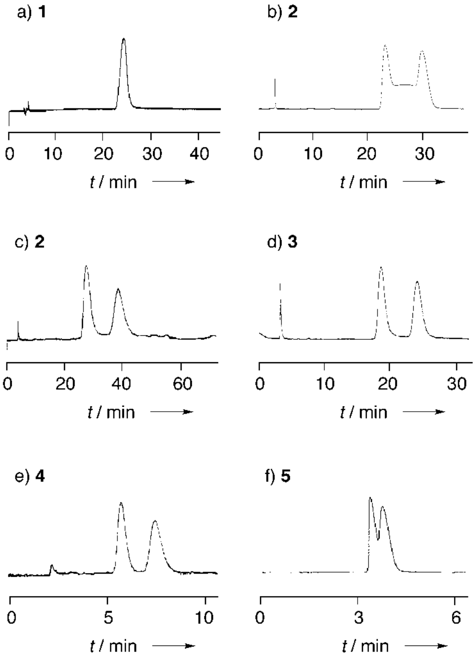


Figure 1. Chromatographic resolution of racemic seleninic acids **1**–**5** on an optically active column packed with amylose carbamate derivative/silica gel (Daicel Chiralpak AS; 4.6 × 250 mm) by HPLC on an analytical scale at 25 °C at a flow rate of 1.0 cm^3 min^{-1}. Eluent: a) hexane/2-propanol (85/15); b) hexane/2-propanol (95/5); c) hexane/2-propanol (90/10) (at 0 °C); d) hexane/2-propanol (98/2); e) hexane/2-propanol (98/2); f) hexane/2-propanol (98/2).

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