Bowl–shaped Cu(I) metallamacrocyclic ethylene and carbonyl adducts as structural analogues of organic calixarenes†

Masahiko Maekawa,*[a] Hisashi Konaka,[b] Toshie Minematsu,[c] Takayoshi Kuroda-Sowa,[b] Megumu Munakata[b] and Susumu Kitagawa*[d]

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Three novel Cu(I) metallacalixarenes with C_2H_4 and CO legs, in which an anion is accommodated in the inside cavity, were self-assembled by anion templation and have been structurally characterized.

The rational design of inorganic artificial receptors for host–guest chemistry is one of the most attractive areas in contemporary supramolecular chemistry.[1] In particular, metal-assembled bowl-shaped molecules that are structural analogues of calixarenes and cyclotriveratrylenes, such as metallacalix[3]arenes[2] and metallacalix[4]arenes,[2l,3] have attracted considerable attention. A successful strategy for forming metallamacrocycles closely related to calixarenes is mostly the combination of a *cis*-protected d^8 metal fragment such as Pd(II) and Pt(II) complexes and an appropriate N-heterocyclic ligand such as multidentate pyridine-based ligands, pyrimidine and 4,7-phenanthroline derivatives. The relatively few examples of anion host–guest chemistry have encouraged us to develop the advanced self-assembly of metallacalixarenes, contrary to their versatile behaviors as hosts for inclusion complexation, and efficient ligands for metal ions in classical calixarenes.[4] Very recently, a new approach utilizing anion templation to construct metallamacrocycles and cages has been employed with several successes.[5] However, in contrast to the well-studied templating properties of cationic and neutral species, the use of anionic components to direct self-assembly processes is an area of supramolecular chemistry which is still in its infancy.

The 4-(2-pyridyl)pyrimidine (pprd) ligand is an attractive nitrogen ligand with a bidentate site for chelation and an *exo* N-donor site for bridging. Two coordination sites with *ca.* 90° bond angles are expected to produce both finite metallamacrocyclic compounds and infinite polymeric compounds. Several Ag(I)–pprd complexes have been synthesized, ranging from a square tetranuclear, a rectangular tetranuclear, to a 1D helical infinite polymer.[6] Recently we have reported a series of sandwich-shaped Ag(I)–pprd metallamacrocycles encapsulating XF_6^{2-} (X = Si, Ge and Sn) anions.[7] The roles of the divalent anions have been proved in their formation processes. As a further investigation, we herein attempted to self-assemble novel Cu(I)–pprd metallamacrocycles under C_2H_4 and CO toward structurally and functionally new inorganic anion receptors.

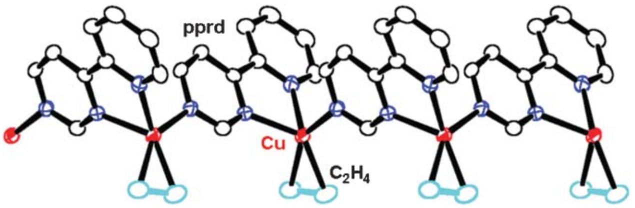

Fig. 1 The infinite 1D zigzag chain structure of $\{[Cu(pprd)(C_2H_4)]PF_6\}_n$ (**1**) extending along the *c*-axis. The PF_6^- anions are omitted for clarity.

When we reacted $[Cu(MeCN)_4]PF_6$ with pprd in Me_2CO under C_2H_4, yellowish brown crystals of $\{[Cu(pprd)(C_2H_4)]PF_6\}_n$ (**1**) were formed (see ESI†). The crystal structure of complex **1** is shown in Fig. 1.‡ Each Cu atom is coordinated by three N atoms of pprd and the C=C bond of C_2H_4 in a distorted tetrahedral geometry. The Cu atom is joined by the neighboring pprd ligand in a head-to-tail fashion to form an infinite 1D zigzag chain structure. Cu(I)–C_2H_4 complexes are rather poorly characterized due to the extremely labile nature of the Cu(I)–C_2H_4 interaction.[8] In particular, preparative and structural reports of polynuclear and polymeric Cu(I)–C_2H_4 complexes are still sparse.[8e,f] More recently, C_2H_4 adducts to $CuMCl_4$ (M = Al and Ga) have been characterized by powder X-ray diffraction analysis.[9] In contrast to only two examples of polymeric Cu(I)–C_2H_4 complexes in distorted trigonal-planar geometry,[8e,f] complex **1** is the first instance in distorted tetrahedral geometry. In the coordinated C_2H_4, the C=C distance of 1.314(9) Å is similar to that [1.313 (exptl.) and 1.333 (calc.) Å] of metal-free C_2H_4[10] and those (1.30(1)–1.329(9) Å) in tetrahedral Cu(I)–C_2H_4 complexes.[8a,b]

The reaction of $[Cu(MeCN)_4]PF_6$ with pprd in MeOH under C_2H_4 afforded pale yellow crystals of $[Cu_4(pprd)_4(C_2H_4)_4](PF_6)_4$ (**2**) (see ESI†). The formation of complexes **1** and **2** shows a remarkable solvent effect.[5e] The crystal structure of complex **2** is shown in Fig. 2.‡ The Cu atom is bonded to three N atoms of pprd and the C=C bond of C_2H_4 in distorted tetrahedral geometry. It is to be noted that four Cu atoms are bridged by four pprd ligands in a head-to-tail fashion to form the Cu(I) metallacalix[4]arene with four C_2H_4 legs. Furthermore one PF_6^- anion is functionally accommodated in the inside cavity. Although there are a few reports of the encapsulation of PF_6^- anion into macrocycles and cages,[2a,b,11] this bowl-shaped Cu(I)

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[a] *Research Institute for Science and Technology, Kinki University, Kowakae, Higashi–Osaka, Osaka, 577–8502, Japan. E-mail: maekawa@rist.kindai.ac.jp*
[b] *Department of Chemistry, Kinki University, Kowakae, Higashi–Osaka, Osaka, 577–8502, Japan*
[c] *School of Pharmaceutical Science, Kinki University, Kowakae, Higashi–Osaka, Osaka, 577–8502, Japan*
[d] *Department of Synthetic Chemistry and Biological Chemistry, Kyoto University, Katsura Campus, Sakyo–ku, Kyoto, 615–8510, Japan. E-mail: kitagawa@sbchem.kyoto–u.ac.jp*

† Electronic supplementary information (ESI) available: Crystallographic data of complexes **1–4** and detailed experimental preparations. See DOI: 10.1039/b713618h

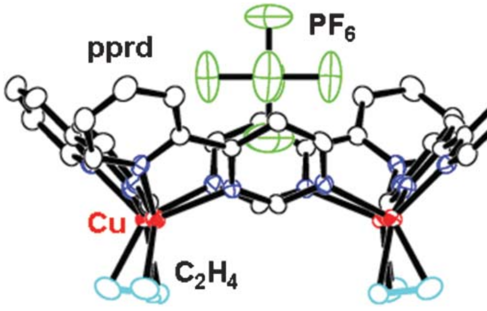

Fig. 2 The crystal structure of $[Cu_4(pprd)_4(C_2H_4)_4](PF_6)_4$ (**2**). The cation moiety lies about a twofold axis and there are thus two independent Cu atoms in the asymmetric unit. Only the encapsulated PF_6^- anion is shown.

metallamacrocycle is of significance as a new anion receptor because they are capable of behaving as structural analogues of organic calixarenes. It would be interesting to elucidate the formation process of the Cu(I) metallamacrocyclic C_2H_4 adduct. Presumably, a chopped Cu(I)–pprd–C_2H_4 complex could be induced from a polymeric Cu(I)–pprd complex by the addition of C_2H_4 since the dark brown suspension gradually changed to a clear yellowish brown solution by the bubbling of C_2H_4 (see ESI†). Subsequently, the PF_6^- anion could act as an anion template to produce metallacalixarene **2**. In the coordinated C_2H_4, two C=C distances of 1.320(7) and 1.366(6) Å are slightly longer than that (1.314(9) Å) for polymeric Cu(I)–C_2H_4 complex **1**.

Similar to C_2H_4 adduct **2**, the reaction of $[Cu(MeCN)_4]PF_6$ with pprd under CO gave pale yellow crystals of $[Cu_4(pprd)_4(CO)_4](PF_6)_4$ (**3**) (see ESI†). The crystal packing structure of complex **3** is shown in Fig. 3.‡ The structure of metallacalix[4]arene with four CO legs essentially resembles that of C_2H_4 adduct **2**, in which the PF_6^- anion is accommodated in the inside cavity. The square Cu_4 core with two adjacent Cu···Cu distances of 5.914 Å is slightly smaller than those (6.055 and 6.083 Å) of C_2H_4 adduct **2**. The striking feature is that one PF_6^- anion is encapsulated in the inside cavity surrounded by four CO legs, enhancing the stabilization of the metallacalixarene. The cation moieties of $[Cu_4(pprd)_4(CO)_4]^{4+}$ capturing two PF_6^- anions arrange in alignment along the *c*-axis. In the coordinated CO, the Cu–C–O angle of 175.6(3)° is slightly bent. The C≡O distance of 1.121(4) Å is close to that (1.13 Å) of metal-free CO and those (1.113(5)–1.128(5) Å) in tetrahedral Cu(I)–CO complexes with three N-donor atoms.[12]

Further attempts to react $[Cu(C_2H_4)_n]ClO_4$ with pprd in Me_2CO under C_2H_4 afforded pale yellowish brown crystals of $\{[Cu_3(pprd)_3(C_2H_4)_3](ClO_4)_3\}_3$ (**4**) (see ESI†). A crystallographic study showed that there are three independent $[Cu_3(pprd)_3(C_2H_4)_3](ClO_4)_3$ complexes in the unit cell,‡ which have the same conformation. The crystal structure of $[Cu_3(pprd)_3(C_2H_4)_3](ClO_4)_3$ (motif 1) including Cu(1), Cu(2) and Cu(3) atoms is shown in Fig. 4. Similar to metallacalix[4]arenes **2** and **3**, three Cu atoms are bridged by three pprd ligands in a head-to-tail arrangement to provide the metallacalix[3]arene with three C_2H_4 legs. In the Cu_3 core, the neighboring Cu···Cu distances are 5.90, 5.99 and 6.13 Å, respectively. One ClO_4^- anion is encapsulated in the inside cavity. Although there have been several reports of the encapsulation of NO_3^-,[2a,b,13] BF_4^-,[2a,b,14] PF_6^-,[2a,b,11] Cl_2[15] and I_2^{2-} [16] anions into macrocycles and cages, less is known about the encapsulation of a ClO_4^- anion.[2a,13g,17] On the basis of these results, it is proved that the conformation of Cu(I)–pprd metallamacrocyclic C_2H_4 and CO adducts can be controlled by the choice of anion: the smaller tetrahedral ClO_4^- anion preferentially can induce the metallacalix[3]arene (complex **4**) and the larger octahedral PF_6^- anion can produce the metallacalix[4]arene (complexes **2** and **3**). These findings are expected to contribute a scaffold for the design and architecture of structurally and functionally new inorganic anion receptors. In the coordinated C_2H_4, three C=C distances of 1.30(1), 1.31(1) and 1.32(1) Å are slightly shorter than those (1.366(6) and 1.320(7) Å) of the C_2H_4 adduct **2**.

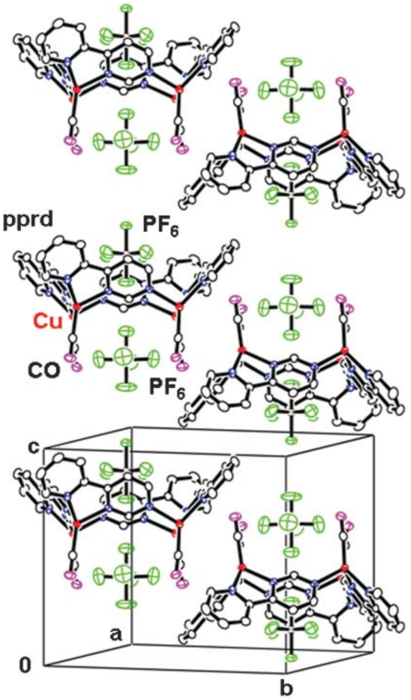

Fig. 3 The crystal packing structure of $[Cu_4(pprd)_4(CO)_4](PF_6)_4$ (**3**) along the *c*-axis. There are four independent PF_6^- anion: two have crystallographically imposed fourfold symmetry and the other two have crystallographically imposed $\bar{4}$ symmetry. Only one of two PF_6^- anions with fourfold symmetry is encapsulated.

We investigated the structures of C_2H_4 and CO adducts **1–4** in solution by ^1H NMR, with resonances being assigned by ^1H–^1H COSY NMR techniques. Complexes **1–4** redissolved in $(CD_3)_2CO$ showed relatively well-resolved ^1H NMR signals at 23 °C without any dissociation species. In metallacalixarenes **2–4**, all of the ^1H

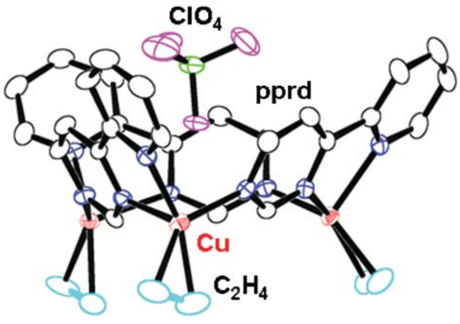

Fig. 4 The crystal structure of motif 1 (including Cu(1), Cu(2) and Cu(3)) atoms in $\{[Cu_3(pprd)_3(C_2H_4)_3](ClO_4)_3\}_3$ (**4**). Only one of the three cations in the asymmetric unit with its encapsulated ClO_4^- anion is shown.

NMR resonances in the coordinated pprd ligand shifted downfield relative to the metal-free pprd ligand, with coordination shifts ($\Delta\delta = \delta_{\text{complex}} - \delta_{\text{metal-free}}$) of 0.26–0.53. In contrast, the coordinated C_2H_4 gave one sharp ^1H NMR resonance at δ 4.88, 4.87 and 4.96 for complexes **1**, **2** and **4**, shifted upfield relative to metal-free C_2H_4 (δ 5.37). These chemical shift values are within the range of those (δ 4.41–5.20) in tetrahedral Cu(I)–C_2H_4 complexes.[8a,b] The ^1H NMR studies indicate that the structures of Cu(I) metallamacrocyclic C_2H_4 and CO adducts are maintained in solution.

The $\nu_{C=C}$ bands of C_2H_4 adducts **1**, **2** and **4** are observed at 1542, 1541 and 1537 cm^{-1} (metal-free C_2H_4, 1623 cm^{-1}), respectively. In contrast, the $\nu_{C\equiv O}$ band of CO adduct **3** appears at 2124 cm^{-1} (metal-free CO, 2143 cm^{-1}), higher than those (2063–2119 cm^{-1}) in cationic and neutral tetrahedral Cu(I)–CO complexes with three N-donor atoms,[8k,12a–d] indicative of poor Cu → CO π back–bonding.

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‡ CCDC 659368–659371 for complexes **1–4**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713618h

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