Inorg. Chem. **2006**, *45*, 7986–7987

Inorganic Chemistry
Communication

Extended Calix[4]arene Analogues by Two P–Cu^{I}–P Bridges and Anion Encapsulation

Xiang-Tai Meng,[†] Qing-Shan Li,*[,†] Feng-Bo Xu,*[,†] Hai-Bin Song,[†] Christopher E. Anson,[‡] and Zheng-Zhi Zhang*[,†]

State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China, and Institute of Inorganic Chemistry, Karlsruhe University (TH), Karlsruhe 76131, Germany

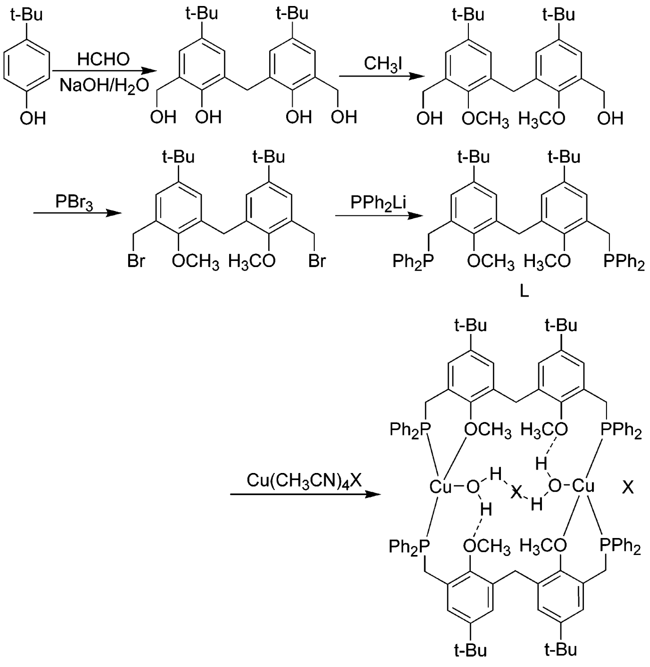
Received May 22, 2006

Two novel extended calix[4]arene analogues by two P–Cu^{I}–P bridges have been synthesized. The molecular structures and anion encapsulation ability for ClO_4^- and BF_4^- have been studied by X-ray analysis.

Calixarenes and their analogues have been widely regarded as important macrocyclic host molecules in host−guest chemistry.[1−7] In the solid state, the cone shapes of the calixarenes give bowl cavities that can encapsulate some small molecules, both charged and neutral by weak interactions including H-bonding, H−aromatic, and aromatic−aromatic $\pi-\pi$-stacking interactions. With the cyclic much larger, the conformations become more complex. So, it is very difficult to enlarge the calixarene's cavity and at the same time to hold the cone conformation.[7]

Phenol-based macrocyclic compounds show apparent similarities to the extensive family of calixarenes.[8] Related pseudocalixarenes by two diimine bridges have also been reported by McKee and co-workers.[9] In an attempt to combine some properties of the phosphine and calixarene systems, we design and synthesize new extended calix[4]arene analogues by two P−Cu^{I}−P bridges, which endow themselves with large cavities, adopt flattened cone conformations, and possess additional recognition sites by metal units. The experimental results exhibit that the new extended calix[4]arene analogues can encapsulate ClO_4^- and BF_4^- anions.

Scheme 1



1 X=ClO_4^-
2 X=BF_4^-

We first synthesize a new analogue containing the half-calix[4]arene fragment diphosphine ligand **L**, and then ligand **L** reacts with Cu^{I} complexes to obtain the corresponding new extended calix[4]arene analogues $[Cu_2\mathbf{L}_2(H_2O)_2ClO_4]ClO_4$ (**1**) and $[Cu_2\mathbf{L}_2(H_2O)_2BF_4]BF_4$ (**2**) (Scheme 1). As shown in Scheme 1, the synthesis of **L** was carried out by four steps, using commercial 4-*tert*-butylphenol as the starting material.[10] The crude ligand was recrystallized from dichloromethane and methanol. In ^{31}P NMR, ligand **L** displays a single resonance at δ −10.704 in $CDCl_3$. **1** and **2** were obtained by reacting **L** with wet $Cu(CH_3CN)_4ClO_4$ and wet $Cu(CH_3CN)_4BF_4$ at room temperature in dichloromethane, respectively, and the corresponding ^{31}P NMR resonances are

---

* To whom correspondence should be addressed. E-mail: qli@nankai.edu.cn (Q.-S.L.), xufb@nankai.edu.cn (F.-B.X), zzzhang@nankai.edu.cn (Z.-Z.Z.).

[†] Nankai University.

[‡] Karlsruhe University (TH).

(1) Gutsche, C. D. In *Calixarenes; Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, U.K., 1989.

(2) *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Vicens, J., Böhmer, V., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1990.

(3) Masci, B.; Mortera, S. L.; Persiani, D.; Thuéry, P. *J. Org. Chem.* **2006**, *71*, 504−511.

(4) Turner, B.; Shterenberg, A.; Kapon, M.; Suwinska, K.; Eichen, Y. *Chem. Commun.* **2001**, 13−14.

(5) Rebek, J., Jr. *Chem. Commun.* **2000**, 637−643.

(6) Saha, A.; Nayak, S. K.; Chottopadhyay, S.; Mukherjee, A. K. *J. Phys. Chem. B* **2004**, *108*, 7688−7693.

(7) (a) Hiratani, K.; Kasuga, K.; Goto, M.; Uzawa, H. *J. Am. Chem. Soc.* **1997**, *119*, 12677−12678. (b) Qin, D. B.; Xu, F. B.; Li, Q. S.; Song, H. B.; Zhang, Z. Z. *Synlet* **2005**, *19*, 2987−2989.

(8) Gutsche, D. C. *Calixarenes revisited*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, U.K., 1998.

(9) (a) Fontecha, J. B.; Goetz, S.; McKee, V. *Angew. Chem., Int. Ed.* **2002**, *41*, 4553−4556. (b) Fontecha, J. B.; Goetz, S.; McKee, V. *Dalton Trans.* **2005**, 923−929.

10.1021/ic060892p CCC: $33.50

© 2006 American Chemical Society
Published on Web 08/26/2006

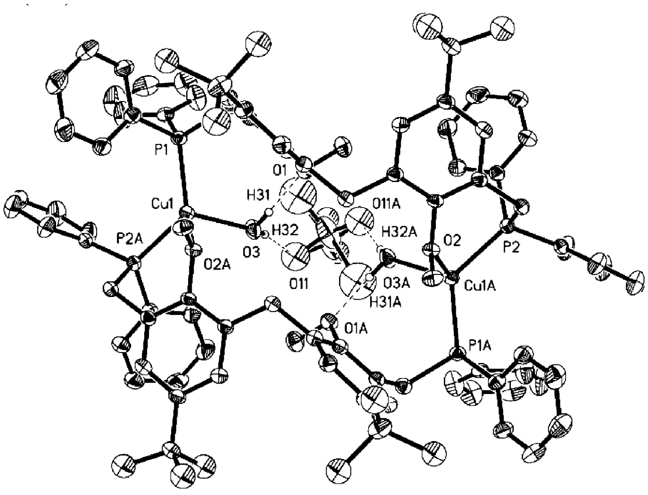


Figure 1. ORTEP drawing (20% probability ellipsoids) of the molecular structure of **1**. H atoms not involved in the H bondings are omitted for clarity. The perchlorate anion is disordered.

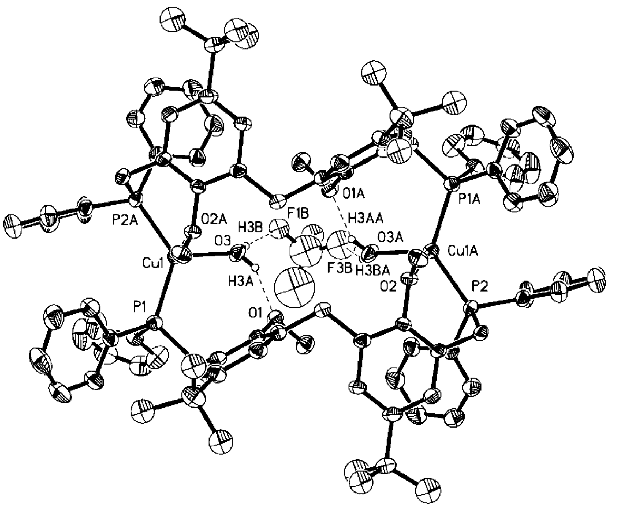


Figure 2. ORTEP drawing (20% probability ellipsoids) of the molecular structure of **2**. H atoms not involved in the H bondings are omitted for clarity. The tetrafluoroborate anion is disordered.

at δ 0.395 and 0.280. A single crystal of **1** was grown by slow diffusion of *n*-hexane into a dichloromethane solution, and that of **2** was obtained by slow diffusion of *n*-pentane into a mixed solution of 1,2-dichloroethane and ethanol.

As shown in Figure 1, **1** adopts a flattened cone conformation. Each Cu adopts a distorted tetrahedral geometry and is bound to two P atoms and two O atoms (one from coordinated water and another from OCH_3). The Cu−Cu distance is 8.015 Å. The Cu−P distances are essentially equivalent, Cu1−P1 [2.2404(10) Å] and Cu1−P2A [2.2306(11) Å], which are similar to those reported in the literature.[11] Surprisingly, the bond distance of Cu1−O3 [2.062(3) Å] is significantly shorter than that of Cu1−O2A [2.466(2) Å]. The P1−Cu1−P2A angle [128.21(4)°] is larger than the ideal tetrahedral value (109.5°) forcing smaller values for P2A−Cu1−O2A [87.12(6)°] and O2A−Cu1−O3 [89.27(12)°]. The dihedral angle of the skeleton of two benzene rings at the same ligand is 91.2°. The perchlorate anions are disordered. One perchlorate anion is encapsulated in the cavity via the H bonding between the perchlorate and the coordinated water molecule and the other in the lattice. The two H atoms on the aquo O3 were located and refined. One forms a H bond to O1 of the organic ligand with O3−O1 = 2.718 Å, while the other makes a H bond to O11 of the perchlorate with O3−O11 = 2.929 Å.

Like the Cu complex **1**, the molecule structure of **2** adopts a similar flattened cone conformation (Figure 2), and the geometries around the Cu atoms are similar to those of complex **1**. The angles of P1−Cu1−P2 [128.57(10)°] and P3−Cu2−P4 [128.52(10)°] are almost equivalent with the corresponding P−Cu−P angles of complex **1**. One of the anions BF_4^- was encapsulated in the cavity via H bonding between the anion and the coordinated water molecule. At the same time, the ^{19}F NMR spectrum also indicates that there are two kinds of BF_4^- anions and one was encapsulated (Figure 3). Exchange between the coordinated molecule and free BF_4^- anions slowly on the NMR time scale is responsible for the formation of the distinct signals.[12]

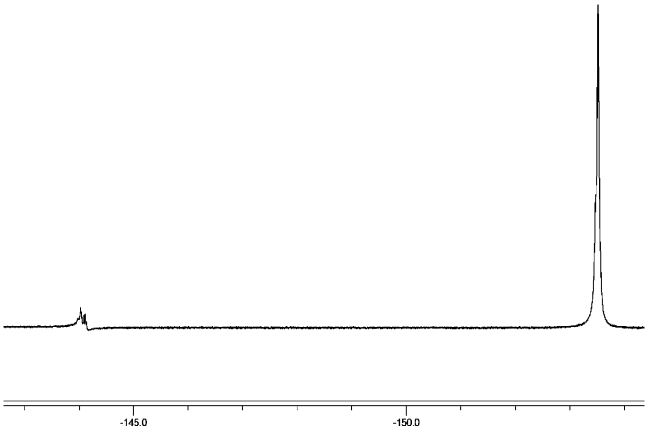


Figure 3. ^{19}F NMR (400-MHz) signals for compound **2**.

In conclusion, we have designed and synthesized a new class of extended calix[4]arene analogues by two $P{-}Cu^{I}{-}P$ bridges. The new compounds exhibit encapsulation behavior for ClO_4^- and BF_4^- anions, owing to much larger cavities and the additional recognition site of the metal units. We predict that the new class of compounds would have novel recognition ability for inorganic and organic molecules by using different metal species and changing their valence states.

Acknowledgment. We gratefully acknowledge the financial assistance provided by the National Natural Science Foundation of China (Project 20472036).

Supporting Information Available: Details of experimental procedures and X-ray crystal structure CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060892P

---

[10] (a) Dhawan, B.; Gutsche, C. D. *J. Org. Chem.* **1983**, *48*, 1536−1539. (b) Masci, B.; Finelli, M.; Varrone, M. *Chem.*−*Eur. J.* **1998**, *4*, 2018−2030. (c) Smith, R. C.; Protasiewicz, J. D. *Organometallics* **2004**, *23*, 4215−4222.

[11] Wada, S.; Maekawa, M.; Munakata, M. *Inorg. Chem.* **1995**, *34*, 1455−1465.

[12] (a) Paul, R. L.; Argent, S. P.; Jeffery, J. C.; Harding, L. P.; Lynam, J. M.; Ward, M. D. *Dalton Trans.* **2004**, 3453−3458. (b) Fleming, J. S.; Mann, K. L. V.; Carraz, C. A.; Psillakis, E.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 1279−1281.