Zinc(II) and Copper(I)–Ferrocenedicarboxylate Polyhedron and Polygon

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(Received October 2, 2006; CL-061149; E-mail: hkchae1@snu.ac.kr)

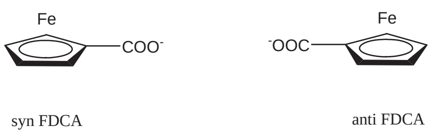
Metal organometallic carboxylates with unusual polyhedral and rectangular shapes have been prepared by the reaction of 1,1′-ferrocenedicarboxylic acid (H_2FDCA) with Zn^{II} and Cu^{II} to give $[Zn_6O_2(FDCA)_5(H_2O)(DMF)]\cdot(DMF)_4$ (**1**), $[Zn_8O_4(FDCA)_6(H_2O)_3]\cdot(DMA)_4\cdot(H_2O)_2$ (**2**), and $[Cu_4(FDCA)_2]$ (**3**), respectively (DMF = *N*,*N*′-dimethylformamide; DMA = *N*,*N*′-dimethylacetoamide). SQUID data of zinc compounds show that iron ions of the ferrocene moieties in the compounds exhibit antiferromagnetic coupling.

A number of studies have been reported to the synthesis and characterization of nanosized metal–organic polyhedra from tetrahedron to sphere (MOPs).[1] Confined 3-D molecular structures have been constructed from joining metal ions with organic linkers such as carboxylates and amines. Success of such design is heavily subject to identifying organic moieties with specific geometry that would assemble into a target shape.[2] Some of MOPs have voids within their structures where guest solvent molecules reside, and thus the potential applications of MOPs to catalysis, gas sorption, separation, and molecular recognition depend upon their ability to remain open in the absence of guests. Furthermore, 3-D discrete MOPs show novel and aesthetic structures which allow them to be interesting subjects for study in solid-state, inorganic or materials chemistry.

Organometallic ligands also provide various types of metal–organic frameworks with a lot of assembled motifs as well as discrete inorganic polyhedra from different kinds of chelating modes.[3] Especially, ferrocene-1,1′-dicarboxylate (FDCA) ligand is of great interest because of characteristic redox activity and conformational freedom as shown in Scheme 1. From the viewpoint of constructing coordination complexes, syn-form FDCA lagands may lead to the formation of polyhedral metal–carboxylate molecular complexes if there are no any other bridging auxiliary ligands around metal centers, while anti-form FDCAs generate coordination polymers.[4] In spite of the intense interest of discrete inorganic cluster molecules through bridging ferrocene carboxylates, the synthetic polyhedral or polygon examples are still limited to a few compounds including a double-wheel of $[Pb_4Na_4]^{12+}$, squares of M_2^{4+} (M = Mo and Rh) and a supercubane of $[Mn_{13}O_8]^{18+}$.[4a,5]

Here, we have tried to get different types of polyhedra and polygons by syn-FDCA-bridging, and finally succeeded in the preparation and characterization of a new series of zinc–ferrocene assembled polyhedra, $[Zn_6O_2(FDCA)_5(H_2O)(DMF)]\cdot(DMF)_4$ (**1**) and $[Zn_8O_4(FDCA)_6(H_2O)_3]\cdot(DMA)_4\cdot(H_2O)_2$ (**2**) as well as cuprous square $[Cu_4(FDCA)_2]$ (**3**) (FDCA = 1,1′-ferrocenedicarboxylate; DMF = *N*,*N*′-dimethylformamide; DMA = *N*,*N*′-dimethylacetoamide) by solvothermal reactions or diffusion reaction.[6] It is worth noting that mixed solvent system plays a key role to facilitate the formation of seed crystals of **2**. In addition, solvothermal reactions in sequence are needed to grow X-ray mountable crystals. These crystals are insoluble in general organic solvents or water but soluble in *N*,*N*′-dimethylsulfoxide very slightly. The infrared spectrum of the clusters clearly showed that the carboxylic acid units have been deprotonated as the $\nu_{C=O}$ stretch shift from 1678 cm^{-1} in the free carboxylic acid to 1576 cm^{-1} in **1**, 1571 cm^{-1} in **2**, and 1545 cm^{-1} in **3**, respectively.[7]

X-ray single-crystal structure analysis revealed that two zinc compounds have polyhedral shape (Figure 1) and a copper cluster shows rectangle (Figure 2). The crystal structure of **1** reveals that the compound is made of two $[Zn_3O]^{4+}$ clusters, five ferrocene-1,1′-dicarboxylates (FDCA) and two solvents (DMF and water), and the linkage of a $[Zn_3O]^{4+}$ cluster by FDCA forms



Scheme 1. Conformers of ferrocenedicarboxylate (FDCA).

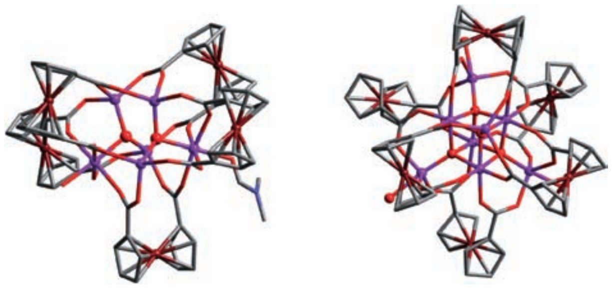


Figure 1. Molecular structures of polyhedral diagrams of zinc clusters **1** (left) and **2** (right).[8]

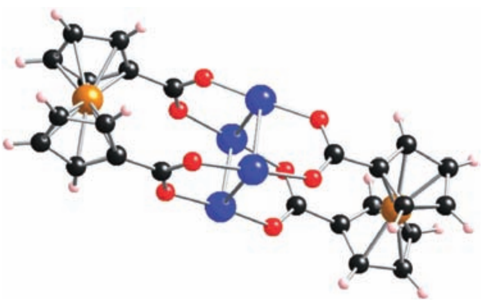


Figure 2. Molecular structure of copper cluster $[Cu_4(FDCA)_2]$ (**3**).

a $[Zn_6O_2]^{8+}$ core. An overall schematic polyhedron of metals is a trigonal prism of six zinc ions in the trigonal bipyramid of five iron ions. An interesting feature of the structure is that three zinc atoms of the $[Zn_3O]^{4+}$ cluster are coordinated by an oxo [μ_3-O] ligand, whereas most of oxygens of zinc oxo clusters are typically bridging two zinc atoms in a linear [μ_2-O] manner or four zinc atoms in a tetrahedral [μ_4-O] manner. The $[Zn_4(\mu_4\text{-}O)]$ core is wellknown for zinc aggregates because the structure of zinc oxide itself has a $[Zn_4(\mu_4\text{-}O)]$ core, with tetrahedral coordination of both zinc and oxygen atoms on the extended array. The crystal structure analysis demonstrates that compound **2** is consisted of a $[Zn_4O_4]^{4+}$ core supported by peripherally tetrahedral coordination of four other zinc atoms, which are bridged by six FDCA ligands and a solvate molecule (H_2O or DMA). It is noteworthy that six periperal iron atoms form an octahedron, whose similar structure is also observed in $[Mn_{13}O_8]^{18+}$.[5b] A zinc center of a $[Zn_4O_4]^{4+}$ cube core coordinates three carboxylates of different FDCA ligands and three oxo [μ_3-O] ligands, while a peripheral zinc atom of tetrahedral shape shows five coordination with three different FDCA ligands, one oxo [μ_3-O] ligand and a solvate molecule. Cyclopentadienyl rings of FDCA in **2** have a staggered conformation while those of FDCA in **1** show an eclipsed conformation. FDCA bridges four different zinc centers. An overall schematic polyhedron of metals is a triakistetrahedron, the dual of truncated tetrahedron of eight zinc ions. The molecular structure of cuprous cluster is shown in Figure 2. The structure is characterized by a square-planar tetranuclear cuprous cluster that is bridged by ferrocene moieties. The Cu–Cu distances within the Cu_4 cluster are in the range 2.6575(14)–2.7437(13) Å, while the shortest Cu···Cu internuclear distance is 2.975 Å, slightly longer than the sum of the van der Waals radii, which leads the cluster to be packed efficiently in the cell and cuprous ions to be stable. The cyclopentadienyl rings of FDCA ligands bear two carboxylate groups in a syn arrangement coordinated to four Cu^{I} ions whose shape is a distorted square. The almost parallel Cp rings adopt an almost eclipsed conformation which is similar to those of zinc complex **1**.

Chemical formulae of $[Zn_6O_2(FDCA)_5(H_2O)(DMF)]\cdot(DMF)_4$ (**1**) and $[Zn_8O_4(FDCA)_6(H_2O)_3]\cdot(DMA)_4\cdot(H_2O)_2$ (**2**) can be speculated from X-ray analysis and elemental analysis. From these formulations, iron centers of FDCA in $[Zn_6O_2]^{8+}[(FDCA)_5]^{8-}$ (**1**) and $[Zn_8O_4]^{8+}[(FDCA)_6]^{8-}$ (**2**) are expected to be mixed-valenced, which is supported from magnetic measurements under 1 T in the temperature range of 30–300 K. Magnetic moments (effective magnetic moment = 1.90 BM/Fe for **1** and 1.84 BM/Fe for **2** from the slopes in the plot of $1/\chi_M$ vs. T) decrease with the decreasing temperature implying the existence of an antiferromagnetic coupling between the paramagnetic Fe^{III} centers.

In conclusion, this report demonstrates that a syn-form ferrocene moiety can be linked to zinc oxide and copper(I) clusters, each of which is fully characterized by single crystal X-ray diffractions. The resulting zinc polyhedra have unique structures with mixed-valence iron(II)/(III) that show antiferromagnetic couplings, while a copper(I) cluster shows an effective packing shape.

HKC thanks Seoul National University for a new faculty member in 2005 and Korea Science and Engineering Foundation (R01-2006-000-10956-0 from the Basic Research Program). We also thank to Dr. H. Li for initial work of **1** and Prof. M. Yaghi of UCLA for helpful discussions and X-ray investigation.

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6 a) Typical procedure: $[Zn_6O_2(FDCA)_5(H_2O)(DMF)]\cdot4DMF$ (**1**). DMF solution (10 mL) containing 1,1′-ferrocenedicarboxylic acid (H_2FDCA) (55 mg, 0.20 mmol) and $Zn(NO_3)_2\cdot6H_2O$ (60 mg, 0.20 mmol) was diffused by triethylamine (0.2 mL) in DMF (2 mL) for 2 weeks. The black block crystals were isolated to give 21 mg (25%). Anal. Calcd for $C_{75}H_{77}O_{28}N_5Fe_5Zn_6$: C, 41.54; H, 3.59; N, 3.23%. Found: C, 41.88; H, 3.63; N, 3.48%. FT-IR (KBr, cm^{-1}): 1637(m), 1571(s), 1490(vs), 1403(s), 1368(m). b) $[Zn_8O_4(FDCA)_6(H_2O)_3]\cdot4DMA\cdot2H_2O$ (**2**). Solution (1.8 mL) of an equal amount of DMA and ethanol containing H_2FDCA (18 mg, 0.07 mmol) and $Zn(NO_3)_2\cdot6H_2O$ (21 mg, 0.07 mmol) was heated at 83 °C for 10 h and then cooled to room temperature. The resulting mixture was again heated to 93 °C for 12 h. The dark red cubic crystals were obtained (9 mg, 32%). Anal. Calcd for $C_{88}H_{94}O_{37}N_3Fe_6Zn_8$: C, 39.76; H, 3.57; N, 2.11%. Found: C, 39.84; H, 3.48; N, 2.15%. FT-IR (KBr, cm^{-1}): 1663(s), 1576(s), 1490(vs), 1388(vs), 1357(m). c) $[Cu_4(FDCA)_2]$ (**3**). DMA solution (1.4 mL) of H_2FDCA (5.5 mg, 0.02 mmol) and $Cu(NO_3)_2\cdot3H_2O$ (4.8 mg, 0.02 mol) was placed in a Pyrex tube and heated at 80 °C for 12 h. The pale yellow plate crystals were obtained (9 mg, 56%). Anal. Calcd for $C_{24}H_{16}O_8Cu_4Fe_2$: C, 36.11; H, 2.02%; Found C, 36.06; H, 2.03%. FT-IR (KBr, cm^{-1}): 1658(w), 1576(sh), 1545 (vs), 1495(vs), 1403(vs), 1367(s).

7 Crystal Data. All measurements were made on a SMART CCD area detector with graphite-monochromated Mo Kα radiation: $[Zn_6O_2(FDCA)_5(H_2O)(DMF)]\cdot4DMF$ (**1**): monoclinic, space group $P2_1/n$, $a = 15.0363(13)$, $b = 22.620(2)$, $c = 23.0084(17)$ Å, $\alpha = 90°$, $\beta = 98.511(3)°$, $\gamma = 90°$, $V = 7739.6(11)$ Å^3, $Z = 4$, $D_{calcd} = 0.766$ Mg/m^3, $\mu = 0.907$ mm^{-1}, $1.43° \leq \theta \leq 27.44°$, $-25 \leq h \leq 25$, $-24 \leq k \leq 26$, $-25 \leq l \leq 24$. Total of 53100 reflections, unique 3029. $R_1 = 0.0962$ with $I > 2\sigma(I)$, $wR2 = 0.2729$, GOF = 0.862. CCDC-622019. $[Zn_8O_4(FDCA)_6(H_2O)_3]\cdot4DMA\cdot2H_2O$ (**2**): cubic, space group $Pa(3)$, $a = 26.1553(5)$ Å, $\alpha = 90°$, $V = 17892.8(6)$ Å^3, $Z = 8$, $D_{calcd} = 1.813$ Mg/m^3, $\mu = 2.815$ mm^{-1}, $1.64° \leq \theta \leq 27.53°$, $-19 \leq h \leq 19$, $-29 \leq k \leq 20$, $-23 \leq l \leq 29$. Total 48228 reflections, unique 17474. $R_1 = 0.0459$ with $I > 2\sigma(I)$, $wR2 = 0.1232$, GOF = 0.824. CCDC-622020. $[Cu_4(FDCA)_2]$ (**3**): monoclinic, space group $P2(1)/c$, $a = 9.0078(6)$, $b = 20.4502(13)$, $c = 12.1546(8)$ Å, $\alpha = 90°$, $\beta = 106.0090(10)°$, $\gamma = 90°$, $V = 2152.2(2)$ Å^3, $Z = 4$, $D_{calcd} = 2.464$ Mg/m^3, $\mu = 5.250$ mm^{-1}, $1.99° \leq \theta \leq 27.60°$, $-11 \leq h \leq 11$, $-25 \leq k \leq 26$, $-15 \leq l \leq 15$. Total 18113 reflections, unique 4886. $R_1 = 0.0624$ with $I > 2\sigma(I)$, $wR2 = 0.1067$, GOF = 0.987. CCDC-622018.

8 Better descriptions of polyhedra are shown in Figures S1 and S2.

Published on the web (Advance View) December 16, 2006; doi:10.1246/cl.2007.150