

A new nano-scale ferrocene assembly supported by a supercubane framework

Mitsuru Kondo,^{*,a} Reiko Shinagawa,^a Makoto Miyazawa,^a Md. Khayrul Kabir,^a Yasuhiko Irie,^a Tomonori Horiba,^a Tetsuyoshi Naito,^b Kenji Maeda,^b Shunji Utsuno^b and Fumio Uchida^b

^a Department of Chemistry, Faculty of Science, Shizuoka University, 836 Ohya, Shizuoka 422-8529, Japan. E-mail: scmkond@ipc.shizuoka.ac.jp

^b Hautform Division, Fuji Chemical Co. Ltd., 1683-1880, Nakagaito, Nasubigawa, Nakatsugawa, Gifu 509-9132, Japan

Received 23rd October 2002, Accepted 15th January 2003

First published as an Advance Article on the web 24th January 2003

Six ferrocenedicarboxylate units were supported by a supercubane framework to create a new nano-scale ferrocene assembly with a spherical motif, whose structure and redox properties were characterized.

The synthesis of nano-scale molecules with many ferrocene moieties has received intense attention for the development of nano-scale organometallics.¹⁻³ For the assembly of the ferrocene units, much effort has been devoted to preparing core frameworks that support the multi-ferrocene units. Aromatic,⁴ dendrimeric,³ and inorganic frameworks have been used as the cores to date. Among these frameworks, inorganic ones^{1,5-8} might be useful for the construction of crystalline nano-scale organometallics that are suitable not only for preparation of nano-scale organometallics with homogeneous molecular sizes, but also for regular arrangement of the nano-scale molecules in the solid state. In spite of this intense interest, the synthetic examples are still limited to a few compounds.^{1,6,7}

We have focussed on multi-nuclear manganese oxide as a useful inorganic framework to support the ferrocene units. We have succeeded in the synthesis and structural characterization of a new nano-scale ferrocene assembled molecule, $[\text{Mn}_{13}\text{O}_8(\text{OCH}_3)_6(\text{fcdc})_6] \cdot 8\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH} \cdot 2(\text{CH}_3)_2\text{CO}$ (**1**) (fcdc = 1,1'-ferrocenedicarboxylate).

Compound **1** was obtained as deep brown crystals by diffusion of an acetone solution of H_2fcdc into a methanol solution of $\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ under air.[†] The crystals are slightly soluble in general organic solvents or water. The single crystal X-ray analysis[‡] clearly demonstrates that the compound has six fcdc units supported by the large distorted cationic cubane, $[\text{Mn}_{13}\text{O}_8(\text{OCH}_3)_6]^{12+}$, which is called a supercubane.⁹ Fig. 1 illustrates the overall structure and the supercubane framework with numbering scheme. The supercubane is made up of thirteen manganese ions, six methoxide groups, and eight oxide atoms. It has crystallographic inversion symmetry, in which the Mn(7) atom is located at the inversion centre. The eight vertices of the supercubane are occupied by the six methoxide oxygen atoms and two oxide atoms, in which the two oxide atoms [O(1 and 1*)] are in inverse sites of the cubane. The other six oxide atoms are placed near the centre of each face. Twelve of the manganese ions are located near the centre of each edge, and the other one is at the body centre.

The thirteen manganese ions of the supercubane show mixed valence states, which were assigned by a bond valence sum analysis according to the literature.^{9,10} The results show that Mn(7) at the body centre of the supercubane is Mn(IV), and that six of the manganese ions, Mn(1 and 1*), Mn(2 and 2*), Mn(5 and 5*), are Mn(III). Each Mn(III) ion forms one longer Mn–O bond by Jahn–Teller distortion. The other six manganese ions are Mn(II). As illustrated in Fig. 1b, the Mn(IV) ion, *i.e.*, Mn(7), is surrounded by six O^{2-} anions, while the six Mn(III) ions are bound by the three O^{2-} anions and one

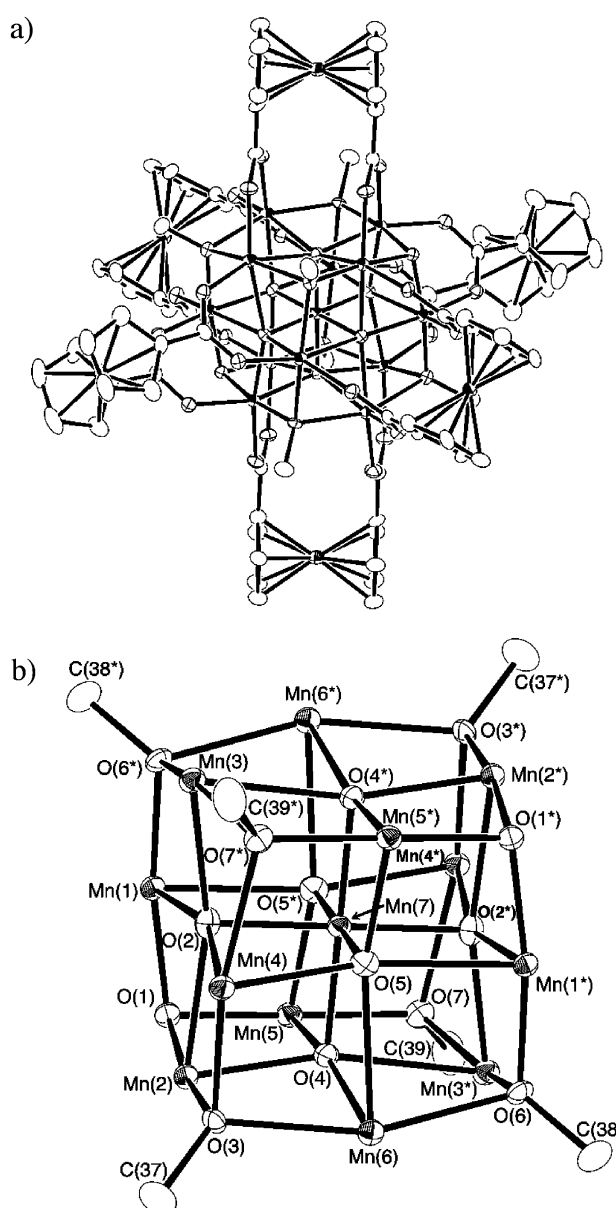


Fig. 1 Views of the crystal structure of **1** (a) and part of the supercubane framework (b) (30% probability level, hydrogen atoms are omitted for clarity). Symmetry equivalent positions: * = $-x, -y, -z$.

methoxide oxygen atom. On the other hand, Mn(II) ions are bound by two O^{2-} anions and two methoxide oxygen atoms. That is, manganese ions with the higher oxidation state are surrounded by more negative anionic oxygen donors.

The cationic supercubane supports six fcdc units. Every face of the supercubane contains four manganese ions at the four edges. The four oxygen donors of the two carboxylate ligands of the fcdc bind to the four manganese ions. As a result, each manganese ion is based on a distorted octahedral geometry (Fig. 1a). A similar supercubane is found in the basic framework of the reported compound, $[\text{Mn}_{13}\text{O}_8(\text{OCH}_3)_6(\text{benzoate})_{12}]$,⁹ which contains twelve benzoate anions instead of the six fcdc units of **1**. The edge length of the supercubane is about 6 Å. Connections of six fcdc units to this cubane create a nano-scale molecule about 21 Å across the molecule; the distance between the terminal hydrogen atoms of the cyclopentadienyl rings at the inverse sides of the molecule is about 19 Å. Although various nano-scale ferrocene assemblies have been prepared by using inorganic frameworks, only two ferrocene assembled motifs are known, *i.e.*, linear⁷ and disk-like (drum,⁶ square⁸ and wheel¹). The homogeneous arrangement of the ferrocene units in all directions found in **1** is unprecedented. That is, compound **1** is a new nano-scale ferrocene assembly that has a spherical motif with a homogeneous molecular size.

Each nano-scale unit of **1** is well associated *via* intermolecular CH- π interactions between cyclopentadienyl rings to produce a well-ordered three-dimensional arrangement. The cavities created among the spherical molecules are filled with crystalline solvent, water, acetone, and methanol molecules.

One of the unique features of ferrocene and its derivatives is their high redox ability. We characterized the electrochemical behaviour of the new ferrocene assembled compound **1** by measurement of its CV in the solid state.^{1,5,11,12} Fig. 2 shows

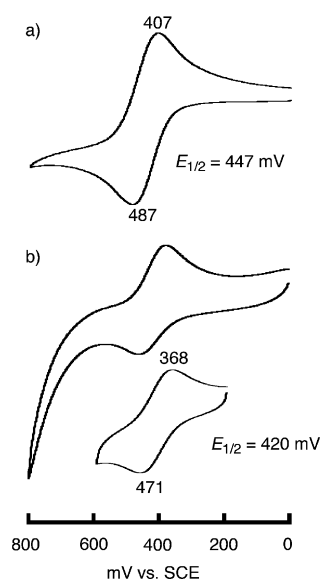


Fig. 2 Solid state cyclic voltammograms of H₂fcdc (a) and **1** (b).

the CV charts of **1** and H₂fcdc, which was measured for comparison. H₂fcdc shows the H₂fcdc⁺/H₂fcdc couple as a quasi-reversible wave at 447 mV (*vs.* SCE). The corresponding couple is observed at 420 mV for **1**. As shown in Fig. 2b, the quasi-reversible wave of **1** is observed as a single peak, demonstrating that each fcdc unit of **1** is independently oxidized and reduced. This is because each fcdc unit, which is in a similar environment, does not strongly interact with the others. The

slight negative shift of the potential of **1** from that of H₂fcdc seems to be due to the electron withdrawing effect of the supercubane framework. In contrast to the case of H₂fcdc, **1** shows an irreversible oxidation at a higher potential than approximately 600 mV, which could be ascribed to oxidation of the supercubane core.¹³

In summary, an inorganic supercubane framework was exploited for an assembly of six ferrocene units to create a new nano-scale ferrocene assembly that arranges itself three-dimensionally. The obtained material shows a high redox activity based on the ferrocene moieties. This spherical structure of about 2 nm in size is an unprecedented ferrocene assembled motif among the nano-scale ferrocene assemblies reported to date.

This work was supported by the Izumi Science and Technology Foundation. We thank the Center for Instrumental Analysis, Shizuoka University, for assistance in obtaining the X-ray crystal structure. We also thank Prof. Dr. A. Nakamura (OM Research) and Prof. Dr. S. Kitagawa (Kyoto University) for helpful discussions and encouragement.

Notes and references

† Yield: 33%. Anal. calc. for C₈₆H₁₀₂Fe₆Mn₁₃O₅₀: C, 34.60; H, 3.44. Found C, 34.85; H, 3.22%.

‡ Crystallographic data for **1**: C₈₆H₁₀₂Fe₆Mn₁₃O₅₀, *M* = 2985.0, triclinic, space group *P*1 (no. 2), *a* = 13.998(4), *b* = 14.616(4), *c* = 15.45(4) Å, *a* = 63.32(1), *β* = 74.33(1), *γ* = 79.72(1)°, *V* = 2707(1) Å³, *Z* = 1, *D_c* = 1.831 g cm⁻³, *μ*(Mo-Kα) = 2.321 mm⁻¹, *F*(000) = 1499, *T* = 233 K, *λ* = 0.7107 Å, *ω* scans, *R* = 0.059, *wR* = 0.064 for 7877 unique reflections (*R_{int}* = 0.027) with *I* > 2σ(*I*) and 686 parameters. The data collection was performed on a Rigaku CCD Mercury system. The structure was solved by direct methods using SIR-92.¹⁴ All non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included but not refined. CCDC reference number 196077. See <http://www.rsc.org/suppdata/dt/b2/b210475j/> for crystallographic data in CIF or other electronic format.

- V. Chandrasekhar, S. Nagendran, S. Bansal, M. A. Kozee and D. R. Powell, *Angew. Chem., Int. Ed.*, 2000, **39**, 1833.
- H. P. Dijkstra, P. Steenwinkel, D. M. Grove, M. Lutz, A. L. Spek and G. van Koten, *Angew. Chem., Int. Ed.*, 1999, **38**, 2185.
- G. R. Newkome, E. He and C. N. Moorefield, *Chem. Rev.*, 1999, **99**, 1689.
- For example (a) H. Nishihara, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 19; (b) M. Iyoda, T. Kondo, T. Okabe, H. Matsuyama, S. Sasaki and Y. Kuwatani, *Chem. Lett.*, 1997, 35; (c) T. Akiyama, Y. Kawaharada, A. Kondo, M. Kajitani, A. Endo, K. Shimizu and A. Sugimori, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3589; (d) S. Nakashima, S. Nakazaki, H. Sakai, M. Watanabe, I. Motoyama and M. Sato, *Inorg. Chem.*, 1998, **37**, 1959.
- P. Jutzi, N. Lenze, B. Neumann and H.-G. Stammer, *Angew. Chem., Int. Ed.*, 2001, **40**, 1423.
- N. Prokopuk and D. F. Shriver, *Inorg. Chem.*, 1997, **36**, 5609.
- R. Rulkens, A. J. Lough and I. Manners, *J. Am. Chem. Soc.*, 1994, **116**, 797.
- F. A. Cotton, L. M. Daniels, C. Lin and C. A. Murillo, *J. Am. Chem. Soc.*, 1999, **121**, 4538.
- Z. Sun, P. K. Gantzel and D. N. Hendrickson, *Inorg. Chem.*, 1996, **35**, 6640.
- H. H. Thorp, *Inorg. Chem.*, 1992, **31**, 1585.
- D. Astruc, *New J. Chem.*, 1992, **16**, 305.
- J.-L. Fillaut, J. Linares and D. Astruc, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2460.
- C. Philouze, G. Blondin, J.-J. Girerd, J. Guilhem, C. Pascard and D. Lexa, *J. Am. Chem. Soc.*, 1994, **116**, 8557.
- A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.