

The self-assembly of small molecular "building blocks" into ordered polyhedral structures, inspired by biological systems, is a highly attractive prospect [1]. In particular, metal-organic polyhedra, discrete molecular architectures constructed through the coordination of metal ions and organic ligands, have recently attracted attention owing to their potential for a variety of applications, such as gas storage, guest recognition, delivery, and catalysis [2]. Here, we introduce our recent study of a synthetic metal-organic spin polyhedron with a nanosized discrete molecular architecture and a cyanide-bridged magnetic Fe₄₂ nanocage comprising 18 high-spin Fell ions and 24 low-spin Fell ions [3]. An important characteristic of the polyhedron is that it is a mixed-valent Fe^{III}₁₈Fe^{II}₂₄ compound and contains 18 ferromagnetically coupled Fe^{III}(S = 5/2) ions as vertices, yielding the highest ground state spin number (S = 45) of any molecule ever prepared.

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Green single crystals of [{Fe^{III-LS}(Tp)(CN)₃}₂₄{Fe^{III-HS}(dpp)(H₂O)}₁₂(CF₃SO₃)₆]·18H₂O (H₂O)₂}₆{Fe^{III-HS}(dpp)(H₂O)}₁₂(CF₃SO₃)₆]·18H₂O (**1**·18H₂O; LS = low-spin, HS = high-spin, Tp = hydrotris(pyrazolyl)borate, dpp = 1,3-di(4-pyridyl) propane) were obtained by the reaction of Fe(CF₃SO₃)₂, dpp, L-ascorbic acid, and Li[Fe(Tp)(CN)₃] in H₂O. The crystal structure revealed by synchrotron radiation at beamline **BL02B1** in collaboration with Dr. Kunihisa Sugimoto (JASRI) is shown in Fig. 1. Each octahedral {Fe(Tp)(CN)₃} unit is connected

to three Fe ions by three cyanide anions. The Fe ions are further ligated with water and dpp to obtain octahedral {Fe(NC)₄(H₂O)₂} and {Fe(NC)₄(dpp)(H₂O)} coordination spheres, where the Fe centers are in a weakly distorted octahedral environment with axial water molecules. Thus, 24 {Fe(Tp)(CN)₃}, 12 {Fe(NC)₄(dpp)(H₂O)}, and 6 {Fe(NC)₄(H₂O)₂} building units are symmetrically formed in an octahedral (cubic) symmetry space around a central point, providing the cube cage with a separation of 1.96 nm between the most distant Fe ions.

Moreover, the 18 Fe^{III-HS} ions in compound 1 can be identified as the vertices of a highly symmetric entity known as a stellated cuboctahedron (Fig. 2). Namely, 12 Fe^{III} centers in {Fe(NC)₄(dpp)(H₂O)} units are defined as the vertices of the cuboctahedron, all sides of which are 7.85 Å long. Six square windows of the cuboctahedron are stellated with 24 isosceles triangles, each having side lengths of 6.83, 6.83, and 7.85 Å, whose six vertices are defined by Fe^{III} ions in the $\{Fe(NC)_4(H_2O)_2\}$ units. To date, only one stellated metal-organic polyhedron with metal ion vertices, i.e., diamagnetic Pd₁₈L₂₄ stellated cuboctahedron, has been reported [4]. On the other hand, the $[Fe^{III}_{18}Fe^{II}_{24}]$ stellated cuboctahedron consists of Fe^{III} metal spin centers as vertices with tridentate cyanide complex ligands, [Fe(Tp)(CN)₃], as opposed to organic tripyridyl ligands; thus, compound 1 is the first example of a



Fig. 1. (a) Photo of cubic crystals consisting of Fe_{42} metal-organic polyhedra. (b) Asymmetric unit of Fe_{42} metal-organic polyhedra with thermal ellipsoids at 30% probability. Hydrogen atoms, counterions, and solvent molecules are omitted for clarity. (c) Molecular structure of an Fe_{42} nanocluster molecule clarified at beamline BL02B1 by single-crystal structure analysis. Fe^{II} and Fe^{III} atoms are shown as green and orange spheres, respectively.



Fig. 2. Schematic view of the stellated cuboctahedron formed by eighteen trivalent iron atoms (Fe^{III-HS} : orange spheres) bearing magnetism. All face-center positions of square faces in the yellow cuboctahedron are capped to have blue stellation, showing beautiful and high symmetry of molecular shape.

stellated metal-organic spin polyhedron.

The magnetic properties of compound **1** indicate the existence of predominantly ferromagnetic interactions. The magnetization data in the range of 300–30 K can be fitted to the Curie–Weiss law, yielding *C* = 83.2 cm³mol⁻¹K and θ = 6.7 K. The magnetization (*M*) at 2 K immediately increases at low fields, and then steadily increases with *H* > 15 kOe to reach a near saturation value of 88.4 $\mu_{\rm B}$ at 50 kOe (Fig. 3), which is in good agreement with the expected value of 90 $\mu_{\rm B}$ (with *g* = 2.0) for a ground state of *S*_T = 90/2. This magnetization behavior is significantly higher than the

Brillouin curve corresponding to 18 non-interacting S_{Fe} spins (S = 5/2), but fits with the Brillouin curve for one S = 45 center (with g = 2.0). These data support the maximum spin state possible, S = 45, which is the largest spin ground state number of any molecule ever prepared. Nowadays, competitive research studies are conducted in the field of molecular magnetism, with the aim to artificially generate magnetic molecules with huge spins as nanoscale permanent magnets. Our findings will provide a deeper understanding of the magnetic behavior on the intermediate scale between molecular and bulk objects.



Fig. 3. Magnetic characteristics of the Fe_{42} metal-organic spin polyhedron and schematic arrangement of atomic magnets. Upward arrows indicate atomic magnets. Red circles are experimental values and the black curve is a theoretical prediction, which show a good agreement.

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References

[1] P.F. Damascene et al.: Science 337 (2012) 453.

[2] D.J. Tranchemontagne *et al.*: Angew. Chem. Int. Ed. **47** (2008) 5136.

[3] S. Kang, H. Zheng, T. Liu, K. Hamachi, S. Kanegawa, K. Sugimoto, Y. Shiota, S. Hayami, M. Mito, T. Nakamura, M. Nakano, M.L. Baker, H. Nojiri, K. Yoshizawa, C. Duan and O. Sato: Nat. Commun. 6 (2015) 5955.

[4] Q.-F. Sun et al.: Nat. Chem. 4 (2012) 330.