A ferromagnetically coupled Fe_{42} cyanide-bridged nanocage

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Self-assembly of artificial nanoscale units into superstructures is a prevalent topic in science. In biomimicry, scientists attempt to develop artificial self-assembled nanoarchitectures. However, despite extensive efforts, the preparation of nanoarchitectures with superior physical properties remains a challenge. For example, one of the major topics in the field of molecular magnetism is the development of high-spin (HS) molecules. Here, we report a cyanide-bridged magnetic nanocage composed of 18 HS iron(III) ions and 24 low-spin iron(II) ions. The magnetic iron(III) centres are ferromagnetically coupled, yielding the highest ground-state spin number ($S = 45$) of any molecule reported to date.
Self-assembled highly symmetric nanostructures are commonplaces in nature: for example, the icosahebra of virus capsids and the cuboctahedra of magnetite nanocrystals in magnetotactic bacteria. Following nature’s lead, attempts to prepare self-assembled discrete molecular architectures constructed through the coordination of metal ions and organic ligands such as metal–organic polyhedra have captivated many scientists’ attention. We used metal–organic complexes as building blocks, which not only act as caps but also contain metal centres and cyano groups that enable the introduction of magnetic interactions. Namely, instead of organic tridentate pyridyl ligands, which can provide a large hollow polyhedral structure, we used monoanionic complex ligand \{Fe(Tp)(CN)3\} as a trinucleating ligand of the metal ions for constructing magnetic nanocages. In addition, the choice of counter metal ions in these structures importantly enables the adjustment of their magnetic properties, facilitating the creation of HS ground states. We employed iron ions in consideration of the magnetic interaction and redox activity of the ferromagnetic metal–cyano compound: Prussian blue FeIII4[FeII(CN)6]3 \(\times\) H2O (refs 16,32). The reaction of Fe(CF3SO3)2, 1,3-di(4-pyridyl)propane (dpp), L-ascorbic acid and Li[Fe(Tp)(CN)3] in H2O led to the isolation of a new \(\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\) spin nanoparticle: \{(Fe(Tp)(CN)3)Fe(HO)2\}Fe(dpp)(H2O)\(\times\)CF3SO3H \(\times\) 18H2O (\(\text{Fe}^{\text{III}}\text{H}^{\text{III}}\) - \(\text{Fe}^{\text{III}}\text{H}^{\text{III}}\)) as green cubic crystals (Supplementary Fig. 1), where \(\text{Fe}^{\text{III}}\) contains 42 iron ions, the largest number of metal centres in any cyano-bridged cluster reported to date.

**Characterization of Fe42 cyanide-bridged nanocage.** Crystallographic analysis of \(\text{Fe}^{\text{III}}\text{H}^{\text{III}}\) \(\times\) 18H2O reveals that each octahedral \(\{\text{Fe(Tp)(CN)3}\}\) unit is connected to three Fe ions by three cyanide anions. The Fe ions are further ligated by water and dpp to give octahedral \{Fe(NC)4(H2O)2\} and \{Fe(NC)4(dpp)(H2O)\} coordination spheres, where the Fe centres are in a weakly distorted octahedral environment with axial water molecules (Fig. 1 and Supplementary Tables 1–3). Thus, \(\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\) spin building units are symmetrically disposed in an O space around a central point providing the cage, with a separation of 1.96 nm between the most distant Fe ions. Six severely disordered, charge-balancing trifluoromethanesulfonate anions are apparent outside the cationic \(\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}\) nanocages, keeping them well separated, and 18 solvent water molecules are located inside the cage.

The \(57\text{Fe}\) Mössbauer spectrum measured for \(\text{Fe}^{\text{III}}\text{H}^{\text{III}}\) \(\times\) 18H2O at 298 K can be deconvoluted into two doublets exhibiting quadrupole splitting (LS-FeII: \(\delta = 0.065\) mm s\(^{-1}\); \(\Delta\) (quadrupole splitting) = 0.47 mm s\(^{-1}\); HS-FeIII: \(\delta = 0.43\) mm s\(^{-1}\) and \(\Delta = 0.71\) mm s\(^{-1}\)) in a relative intensity ratio of FeII:FeIII = 0.55/0.45 (Supplementary Fig. 2 and Supplementary Table 4). Charge considerations and Mössbauer spectroscopic measurements suggest that \(\text{Fe}^{\text{III}}\text{H}^{\text{III}}\) has 24 FeII\text{HS} ions, to which the cyanide carbon atoms coordinate, and 18 FeIII\text{HS} ions at room temperature. Note that \(\text{Fe}^{\text{III}}\text{H}^{\text{III}}\) was prepared using \(\{\text{Fe}^{\text{III}}\text{H}^{\text{III}}\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{H}^{\text{III}}\text{Fe}^{\text{II}}\}\) as a starting material, where the cyanide carbon atoms are coordinated to FeIII ions. Electron transfer from FeII ions to the FeII\text{LS} \(\langle\text{CN}\rangle\text{Fe}^{\text{III}}\text{H}^{\text{III}}\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{H}^{\text{III}}\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{H}^{\text{III}}\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{H}^{\text{III}}\) units is, therefore, suggested to occur during the reaction, leading to an FeII\text{LS}–CN–FeIII\text{HS} linkage. Further evidence of this linkage was observed through synchrotron X-ray absorption spectroscopy (XAS) at the Fe L-edge. Comparison of XAS for \(\text{Fe}^{\text{III}}\text{H}^{\text{III}}\) with variants of the starting material compound, Li[FeII-LS(Tp)(CN)3] and K2[FeII-LS(Tp)(CN)3], infers that the valence composition of the \(\text{Fe}^{\text{III}}\text{H}^{\text{III}}\) \(\times\) 18H2O is \(\{\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\}\) \(\times\) 18H2O.

One of the challenges in the field of molecular magnetism is to synthetically prepare new nanocriatures with high-ground state spin numbers. To date, numerous high-spin (HS) molecules have been reported. Here, we report a giant spin nanocage that contains 18 HS ferromagnetically coupled FeII \(\langle S = 5/2\rangle\) ions resulting in a molecular ground state spin of \(S = 45\), the largest value known to date. This nanoncage is a mixed valent HS and low-spin (LS) cyano-bridged FeIII\text{HS} \(\{\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\}\times\) 24 compound, structured as a supramolecular cage with a nanometre-sized inner cavity space.

**Results**

**Preparation of Fe42 cyanide-bridged nanocage.** The strategy used to construct the magnetic nanocage is based on the preparation of metal–organic polyhedra. We used metal–organic complexes as building blocks, which not only act as caps but also contain metal centres and cyano groups that enable the introduction of magnetic interactions. Namely, instead of organic tridentate pyridyl ligands, which can provide a large hollow polyhedral structure, we used monoanionic complex ligand \{Fe(Tp)(CN)3\} as a trinucleating ligand of the metal ions for constructing magnetic nanocages. In addition, the choice of counter metal ions in these structures importantly enables the adjustment of their magnetic properties, facilitating the creation of HS ground states. We employed iron ions in consideration of the magnetic interaction and redox activity of the ferromagnetic metal–cyano compound: Prussian blue FeIII4[FeII(CN)6]3 \(\times\) H2O (refs 16,32). The reaction of Fe(CF3SO3)2, 1,3-di(4-pyridyl)propane (dpp), L-ascorbic acid and Li[Fe(Tp)(CN)3] in H2O led to the isolation of a new \(\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\) spin nanomaterial: \{(Fe(Tp)(CN)3)Fe(HO)2\}Fe(dpp)(H2O)\(\times\)CF3SO3H \(\times\) 18H2O (\(\text{Fe}^{\text{III}}\text{H}^{\text{III}}\) - \(\text{Fe}^{\text{III}}\text{H}^{\text{III}}\)) as green cubic crystals (Supplementary Fig. 1), where \(\text{Fe}^{\text{III}}\) contains 42 iron ions, the largest number of metal centres in any cyano-bridged cluster reported to date.

Magnetic properties of Fe42 cyanide-bridged nanocage. Figure 3a shows the magnetic properties of a polycrystalline sample of \(\text{Fe}^{\text{III}}\text{H}^{\text{III}}\) \(\times\) 18H2O under a direct current field of 10 kOe from 300 to 30 K and 100 Oe from 30 to 2 K. It indicates the existence of predominantly ferromagnetic interactions and a resulting giant ground-state spin for \(\text{Fe}^{\text{III}}\text{H}^{\text{III}}\) \(\times\) 18H2O. At 300 K, the \(\chi_{\text{m}}\) \(T\) product is 85.5 cm\(^3\) mol\(^{-1}\) K, and the data in the range 300–30 K can be fitted to the Curie–Weiss law, yielding \(C = 83.2\) cm\(^3\) mol\(^{-1}\) K and \(\theta = +6.7\) K. This \(C\) value is consistent with the expectations (78.8 cm\(^3\) mol\(^{-1}\) K with \(g = 2.0\)) for 18 uncoupled FeII centres (\(S = 5/2\)). On cooling, the \(\chi_{\text{m}}\) \(T\) product becomes slightly larger with temperature, abruptly increasing to 863 cm\(^3\) mol\(^{-1}\) K at 2 K (Supplementary Fig. 4). This magnetic behaviour and the positive Weiss constant suggest the existence of dominant ferromagnetic exchange interactions in \(\text{Fe}^{\text{III}}\text{H}^{\text{III}}\). Figure 3b shows \(\chi_{\text{m}}^{-1}\) versus the T-plot for various applied fields, which displays an inflection in \(\chi_{\text{m}}^{-1}\) between 10 and 5 K as excited states depopulate, on further cooling below 5 K the slope starts to become linear again, suggesting that it is just the ground state that is mainly populated.
A scale bar indicates 10 kOe to reach a near saturation value of 88.4 increases at low fields, and then steadily increases with 1-18H2O with thermal ellipsoids at 30% probability. Hydrogen atoms, counterions and solvent molecules have been omitted for clarity. (d) View of the crystal packing for cyano-bridged [Fe42] framework. (e) Scanning electron microscope image of crystals of compound 1-18H2O, illustrating the cubic faces.

Discussion

DFT calculations were carried out to estimate changes in the electronic structures of 1-18H2O. Calculations were simplified to a cyano-bridged molecular square formulated as [FeII-CN-FeIII]2 with a Tp ligand on the FeII ion, a pyridine ligand, and H2O on the FeIII ion (Fig. 4, and Supplementary Tables 5–7). Figure 4 shows HS ferromagnetic (HSFM) state was the ground state, and LS ferromagnetic (LSFM) and antiferromagnetic (LSAF) states were above 5.5 kcal mol-1 and 1.5 kcal mol-1, respectively. DFT calculations indicate the ferromagnetic character of a magnetic coupling between the two diagonal FeIII-HS ions in the square framework. The calculated J value (35.5 cm-1 at the B3LYP* level) for the tetranuclear cyanobridge square complex overestimates the magnitude of the exchange coupling parameters. The overestimation of coupling constants by a factor of 2–4 is not unusual in DFT calculations. The calculation predicts the correct sign for J corresponding to the ferromagnetic nature of the ground state in the Fe42 nanocage.

We have presented a Fe42 cyanide-bridged nanocage with a HS framework. Many metal–cyanide clusters have been synthesized since the discovery of Prussian blue. Our metal–cyanide polyhedron is the largest cyanide-bridged polymeric cluster and exhibits a rare hollow structure. Among the various morphologies of nanoarchitectures, hollow spheres are of great interest because of their high surface to volume ratio and large pore volume, which could be exploited for promising applications in the controlled encapsulation and release of molecules.

In summary, we report a new high-nuclearity iron complex with a HS framework. In the Fe42 cyanide-bridged nanocage,
Magnetic metal centres are ferromagnetically coupled, yielding the highest ground state spin number \((S = 45)\) of any prepared molecule.

**Methods**

Synthesis of \(\text{Fe}_{42}\) cyanide-bridged nanocage. \([\text{Fe(Tp})(\text{CN})_{32}^{\cdot} \text{Fe(H}_{2}\text{O})_{26}^{\cdot} \text{Fe(dpp)}(\text{H}_{2}\text{O})_{12}^{\cdot} \text{CF}_{3}\text{SO}_{3})_{6}]^{\cdot} \cdot \text{C}_{18}\text{H}_{2}\text{O}\).
A 1 mL aqueous solution of 17 μmol of Li[Fe(Tp)(CN)3] and 8.3 μmol of 1,3-dif(4-pyridyl)propane was slowly layered over a 2 mL aqueous solution of 8.3 μmol of Fe(CF3SO3)2 and 1.7 μmol of l-aspartic acid with H2O (1 mL) as a middle buffer layer under an aerobic condition. Crystallization required several weeks and gave crystals in 30% yield based on Li[Fe(Tp)(CN)3]. The crystals were washed with H2O and dried under reduced pressure for 12 h. As prepared, the crystals were vacuum dried, having approximately 50H2O molecules inside the cage (compound 1 - ca 50H2O), which become partially desolvated when exposed to air at room temperature. Therefore, the physical measurements performed on compound 1 - 18H2O were prepared carefully to prevent desolvation. The reported structures have been characterized by the single-crystal X-ray crystallography (Supplementary Tables 1-3 and Supplementary Data 1 and 2).

Elemental analysis. Elemental analysis for Ca6Fe2(F2O3)2Fe(CF3SO3)2N20O3H2O (1 - 18H2O) is as follows: calculated (found) C, 40.45 (40.65); H, 3.71 (3.54) and N, 25.16 (25.30). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was performed to measure the Fe content in the solid sample of 1 - 18H2O. ICP-AES analysis shows that the Fe contents in 1 - 18H2O is 16 wt%, which is in good agreement with the calculated value of 16.8 wt%. In addition, analysis of the sulfur content of 1 - 18H2O with total sulfur analyser (TOX-100) reveals the sulfur content is 1.6 wt% (calcd. 1.4 wt%).

X-ray structure determination. Single-crystal synchrotron radiation X-ray diffraction experiments were performed at 295 K for 1 - 18H2O, and 100 K for 1 - ca 50H2O using a Rigaku Mercury 2 CCD detector at BL26B1/SPring-8 (Hyogo, Japan). The wavelength was selected by monochromating the incident X-ray. Measurements were performed on a Quantum Design SQUID (MPMS XL-5 and MPMS XL-7) magnetometer. To prevent the loss of uncoordinated water molecules, the sample was wrapped tightly with plastic film and placed in a sapphire sample holder. X-ray absorption spectra were measured by the total electron yield method with a 57Co/Rh source in the transmission mode. All isomer shifts are given as relative to the Fe56 atom in Fe3O4 at room temperature.

XAS measurements. X-ray absorption spectra were measured on the soft X-ray undulator beam-line BL25SU at Spring 8, Japan. Soft X-rays circularly polarized from a twin helical undulator were monochromated and focused onto a thin polycrystalline layer of 1 - 18H2O. The measured sample was fixed with carbon tape to a sapphire sample holder. X-ray absorption spectra were measured by the total electron yield method in which the sample current is directly measured while scanning the photon energy. Measurements were performed at zero applied magnetic field and hence both positive and negative X-ray helices resulted in equivalent absorption spectra. The sample chamber for the soft XAS keeps a high vacuum of 10-10 Pa or better. The measurements of 1 - 18H2O were repeated incrementally over several days and were found not to exhibit changes in spectral line shape with respect to the time spent under vacuum. Care was taken during XAS measurements to control the effect of photoelectrons. The incident beam intensity was incrementally reduced until consistent multiple measurements at the same sample spot were obtained after an intensity reduction to 7%. To ensure damage was not encountered in short time periods, rapid measurements over defined features of the L3 edge were measured repeatedly and ensured to be coincident.

DFT calculation. Full details of computational method are given in the Supporting Methods.

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Author contributions

T.L. and C.D. in Dalian and O.S. in Fukuoka conceived and supervised the project. S. Kang, K.H., S. Kanegawa and H.Z. planned, implemented materials synthesis and characterization and analysed the magnetic measurements data. K.S. finalized the synchrotron X-ray data. Y.S. and K.Y. contributed to the DFT calculation. S.H. performed the Mössbauer measurement. M.N. and M.M. contributed to analyses of the magnetic susceptibility. M.L.B. and H.N. were responsible for experiments performed in large magnetic fields and XAS measurements. T.N. contributed to the XAS experiments. S. Kang, Y.S., L.T. and O.S. wrote the manuscript. All authors discussed the results and commented on the manuscript. S. Kang, and H.Z. contributed to this work equally.

Additional information

Accession codes: The X-ray crystallographic coordinates for structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 932131 and 932133. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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