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Site-Specific Metal Chelation Facilitates the Unveiling of Hidden Coordination Sites in an \(Fe^{II}/Fe^{III}\)-seamed Pyrogallol[4]arene Nanocapsule

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Supporting Information Placeholder

ABSTRACT: Under suitable conditions, C-alkylpyrogallol[4]arenes (PgCs) arrange into spherical metal-organic nanocapsules (MONCs) upon coordination to appropriate metal ions. Herein we present the synthesis and structural characterization of a novel \(Fe^{II}/Fe^{III}\)-seamed MONC, as well as studies related to its electrochemical and magnetic behaviors. Unlike other MONCs which are assembled through 24 metal ions, this nanocapsule comprises 32 Fe ions, uncovering 8 additional coordination sites situated between the constituent PgC sub-units. The \(Fe^{II}\) ions are likely formed by the reducing ability of DMF used in the synthesis, representing a novel synthetic route towards polynuclear mixed-valence MONCs.

The design of metal-organic supramolecular structures with well-defined shapes and dimensions continues to attract intense interest, a primary reason being their ability to mimic biologically active sites.1–8 These inorganic-organic hybrids are typically formed by the metal-directed assembly of suitably functionalized organic ligands,9–17 and recent years have witnessed the synthesis of such species with paramagnetic metal ions; this is a popular strategy due to the inherent potential for one to control or influence the resulting magnetic properties of a system.9,18–24 Our efforts to synthesize such supramolecular hybrids primarily utilize C-alkylpyrogallol[4]arenes (PgCn, where \(n\) is the number of carbon atoms in pendant alkyl chains) as organic ligands. Having upper-rim phenolic groups and an associated bowl conformation, coordination to appropriate metal ions can, under appropriate conditions, drive PgCn8 to form a diverse range of metal-PgCn assembly types.10,25–32 We are specifically interested in MONCs that typically exist in two general forms, termed hexamers (Figure 1a) and dimers hereafter.10,25–31 These hexamers and dimers are nanoscale capsules containing either 6 or 2 PgCn units, and are formed through coordination to 24 or 8 divalent metal ions, respectively. To date we have reported the synthesis and structural characterization of MONCs formed through coordination to different metal ions. Recently, we discovered a novel route to synthesize mixed-valence MONCs through \textit{in-situ} redox chemistry.13,14 This prompted us to investigate different reaction conditions that may promote the formation of other mixed-valence MONCs. Here we present the synthesis and characterization of an iron-based mixed-valence MONC of formula [\(Fe^{II}_{16}Fe^{III}_{16}(PgC_6)(Cl)_16+(DMF)_2(H_2O)_{20-a}\) \((n = 0 – 8)\) \((1)\) (Figure 1b), and, notably, this MONC assembled with 32 metal centers, unveiling 8 additional coordination sites that are located between framework PgC sub-units. This spectacular new capsule is also formed through \textit{in-situ} redox reactions, but, most importantly, displays new structural characteristics that are previously unseen for this assembly type; specific chelating sites tend to coordinate with Fe ions with specific oxidation states and the constituent Fe ions exhibit clearly defined coordination patterns that are unique to each oxidation state.

Figure 1. (a) Side view of \(Cu^{II}\)-seamed MONC, which represents the metal-ligand arrangement of a typical hexameric MONC, showing 24 coordination sites between constituent PgC sub-units. The \(Cu^{II}\) ions coordinate with PgC units in such a way to form 8 \([Cu_2O_2]\) units that cover facets of the MONC. (b) Symmetry expanded single crystal X-ray structure of \(1\) which is assembled through 32 Fe ions. The additional 8 Fe centers are coordinated such that to bridge / connect neighboring \([Fe_3O_2]\) units. PgC alkyl chains and H atoms omitted for clarity. Color code: \(Cu^{II}\) – azure, \(Fe^{II}\) – orange, \(Fe^{III}\) – green, Cl – yellow, O – red, C – gray.

Nanocapsule \(1\) was synthesized by reacting PgC6, FeCl3, and sodium methoxide in a DMF/methanol mixture (Experimental S1 – S3). Slow evaporation of the mother liquor afforded dark blue single crystals that were suitable for diffraction studies over a period of \(\sim 10\) weeks. Compound \(1\) crystallized in the monoclinic space group \(P2_1/n\). As can be seen in Figures 1 – 3, the overall structure
Most hexameric MONCs reported to date have been constructed through the assembly of 24 metal ions and, with 32 metal centers, compound 1 displays the highest metal ion content in a PgC₆-based MONC. The use of 8 additional coordination sites within the MONC framework suggests that bridging FeII ions are large enough to fit in between adjacent PgC₆ units without hindering the self-assembly process, albeit that they sit slightly out of the polyphenolic plane. Interestingly, the reaction conditions used here are similar to those of the previously reported [CoII2₄(PgC₅OH)₆] MONC (Figure S3). However, different structural features exhibited by these two MONCs suggest not only that small changes in reaction conditions may yield MONCs with remarkable features, but also that much remains to be discovered in this burgeoning area of research.

Figure 2. Arrangement of FeII and FeIII ions on the framework of 1. (a) Two [FeO₃] units connected through a bridging FeII ion (Fe7), and (b) arrangement of FeII ions along the metal-organic hemispheres. PgC₆ alkyl chains and H atoms omitted for clarity. Color code: FeII – orange, FeIII – green, Cl – yellow, N – blue, O – red, C – gray.

Figure 3. (a) Side view of 1 showing hydrogen bonding interactions between two hemispheres. (b) Side, and (c) top-down views of hydrogen bonding interactions formed between interior axial ligands in opposing hemispheres. PgC₆ alkyl chains and H atoms omitted for clarity. Color code: FeII – orange, FeIII – green, Cl – yellow, N – blue, O – red, C – gray.

As outlined above, the structure of 1 reveals the presence of two metal-seamed hemispheres that stitch together through 12 hydrogen bonding interactions (Figure 3a). Interestingly, four of these interactions are located within the cavity and are formed between internal water ligands at the edges of opposing hemispheres (O⋯O distances in the range of 2.920-2.990 Å, Figures 3b & 3c). These are unique non-covalent interactions for this system type, as a MONC is typically held together by 24 inter- and intramolecular hydrogen bonding interactions between upper-rim phenolic groups (Figure S4). The internal volume of 1, calculated by using MSroll with a sphere radius of 1.25 Å, was found to be ~1470 Å³. It is clear that the larger void space in 1 (relative to typical MONCs: [CuII2₄(PgC₅OH)₆] = ~1250 Å³, [MnII2₄(PgC₅)₆] = ~1300 Å³, [CoII2₄(PgC₅)₆] = ~1400 Å³) is due to expansion of the entire framework that has been invoked by the additional bridging FeII ions,30,33,39

Considering that the framework of 1 consists of both FeII and FeIII ions, and as only FeIII ions have been used as the starting material, an apparent reduction has taken place during the self-sorting process. This FeIII to FeII reduction has likely been promoted by the reducing ability of DMF upon hydrolysis (Eq. 1).45-47 According to the proposed electron transfer reaction, DMF serves as both the reaction medium and reducing agent in the synthesis of 1.

\[
\text{HCON(CH}_3)_2 + 2 \text{FeIII} + 3 \text{H}_2 \text{O} \rightarrow 2 \text{FeII} + (\text{CH}_3)_2\text{NCOOH} + 2 \text{H}_3\text{O}^+ \quad (1)
\]

The electrochemical activity of FeII/FeIII mixed-valence centers in complex 1 was analyzed by cyclic voltammetry in acetonitrile with tetraethylammonium perchlorate (TEAP) as the supporting
electrolyte in the potential range -1.5 to +1.2 V vs SCE. Two overlapping quasi-reversible reduction waves are seen in this potential range as cathodic peaks (Figure 4). The peak at -0.333 V is consistent with the reduction of Fe^{III} to Fe^{II} and that at the -0.703 V was assigned to the reduction of Fe^{III} to Fe^{I}. The observed irreversibility may be due to structural changes in the complex accompanying the redox processes.

![Figure 4. Cyclic voltammogram of 1 in CH3CN (0.1M TEAP supporting electrolyte, platinum disk working electrode, platinum wire auxiliary electrode) under argon at 100 mV/s, with three successive scans.](image)

Figure 4. Cyclic voltammogram of 1 in CH3CN (0.1M TEAP supporting electrolyte, platinum disk working electrode, platinum wire auxiliary electrode) under argon at 100 mV/s, with three successive scans.

DC magnetic susceptibility measurements were carried out on a powdered polycrystalline sample of compound 1 in an applied magnetic field of $H = 0.1$ T over the temperature range $T = 2 – 300$ K. Figure 5 shows the experimental data plotted as the $\chi M$ product versus $T$, where $\chi M$ is the molar magnetic susceptibility. The value of $\chi M$ at $T = 300$ K is approximately $83$ cm$^3$ K mol$^{-1}$, somewhat lower than that expected for the sum of the Curie constants for 16 non-interacting (high-spin octahedral) Fe$^{II}$ ($s = 2$) ions and 16 non-interacting (high-spin square pyramidal) Fe$^{III}$ ($s = 5/2$) ions, with $g = 2.00$ ($118$ cm$^3$ K mol$^{-1}$). As the temperature decreases, the magnitude of $\chi M T$ decreases steadily, reaching a value of $22.30$ cm$^3$ K mol$^{-1}$ at $T = 2$ K. This behavior indicates the presence of antiferromagnetic (AF) exchange interactions between the constituent metal ions, as would be expected for a large cluster containing multiple O-bridged Fe$^{II}$ and Fe$^{III}$ ions. The large nuclearity of the cage and the number of unique exchange interactions prohibits any detailed quantitative analysis of the data, however a fit of the linear section of the $\chi M$ versus $T$ data (Figure 5 inset, 300 – 120 K) affords Curie and Weiss constants of $C = 114.94$ cm$^3$ K mol$^{-1}$ and $\theta = -119.92$ K, respectively. Magnetization data collected for 1 in the $H = 0 – 7$ T field range at temperatures between $T = 2 – 7$ K are consistent with the presence of AF exchange, the value of $M$ increasing in a near linear-like fashion with increasing $H$, without reaching saturation (Figure S5).

In conclusion, we have presented the synthesis and structural characterization of the first Fe-seamed PgC$_n$-based MONC. The framework of this nanocapsule consists of 32 metal centers, uncovering 8 additional coordination sites between the PgC$_n$ sub-units in previously reported MONCs. The Fe ions coordinating the framework are in two different oxidation states, suggesting an occurrence of a reductive process during self-assembly. This reduction of Fe$^{III}$ to Fe$^{II}$ has apparently been facilitated by the reducing ability of DMF upon hydrolysis and, overall, the formation of this polynuclear cage compound has opened a new pathway to the synthesis of polynuclear mixed-valence complexes. Future studies in this area will be focused on investigating different reaction conditions that aid the formation of such types of mixed-valence complexes and synthesizing analogous MONCs with disparate metal ions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. X-ray crystallography data for nanocapsules 1 (CCDC 1817707) (CIF). Experimental S1-S3, Table S1, Figures S1-S5 (PDF).

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The manuscript was written through contribution of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

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