High-Nuclearity Metal−Organic Nanospheres: A Cd$_{66}$ Ball

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S *Supporting Information*

ABSTRACT: Reaction of H$_3$L with Cd(NO$_3$)$_2$·4H$_2$O in DMF at 150 °C for 3 days affords the metal−organic nanosphere [Cd$_{66}$(μ^3-OH)$_{28}$(μ^3-O)$_{16}$(μ^5-NO$_3$-O,O,O',O',-O'',O'')$_{12}$(L)$_{20}$(μ^2-DMF)$_{12}$⊂(DMF)$_9$]. The cluster is composed of a spherical shell of 66 Cd(II) cations bridged by 28 μ^3-hydroxide, 16 μ^3-oxo, and five μ^5-NO$_3^-$ anions surrounded by a shell of 20 tripodal capping ligands (L) and 12 DMF ligands. The 66 Cd(II) cations and 12 NO$_3^-$ anions form a polydeltahedron that has 78 vertices [Cd(II) or NO$_3^-$] (V), 228 edges (E), and 152 triangular faces (F), giving it an Euler characteristic (χ) of 2 (χ = V + F − E). Reaction of H$_3$L with Cd(NO$_3$)$_2$·4H$_2$O at lower temperatures or with CdCl$_2$ affords coordination polymer frameworks instead of nanospheres.

The synthesis of high-nuclearity transition-metal coordination clusters has been the focus of much research over recent years because of interest in tailoring the properties of nanoscale objects. Notable targets are the assembly of clusters and cages incorporating cavities that can act as hosts for guest species[1] as well as clusters, such as polyoxometalates, that have unusual electronic properties.[2] Thus, depending on their shape and composition, large clusters have found relevance in the areas of single-molecule magnets,[3] molecular electronics,[4] and host−guest chemistry[1,5] and are a target for bottom-up nanoscale fabrication techniques.[6] Despite all of their potential applications, large clusters are often most admired for their attractive architectures and topologies.[7] Large clusters described in the literature have exhibited structural motifs reminiscent of zeolites,[8] fullerenes,[9] Platonic and Archimedean solids,[10] and viruses.[11]

One strategy employed to prepare high-nuclearity clusters is to incorporate ligands that act as caps while also encouraging the bridging of metal centers via co-ligands or anions. In this regard, comparisons can be made to the widely studied field of metal−organic framework materials,[12] where ligand design is paramount in encouraging the assembly of arrays of metal centers and/or cluster building blocks. The use of polydentate ligands has been a frequently employed strategy in the synthesis of large d- and f-block clusters. Typically, small ligands such as triethanolamine,[13] iminocarboxylates,[14] epoxysuccinic acid,[15] and threonine are employed,[16] as they have a high degree of freedom and can rearrange their donor atoms to suit the stereoelectronic requirements and preferences of the metal ions. More heavily designed ligands incorporating binding units via pendant linkers impart

structural information to the ligand shape *via* preorganization, which in turn influences directed cluster formation.[17] Reducing the degree of rigidity in these linkers increases the entropic price paid upon complexation but enhances flexibility and serendipity, which are crucial factors in the discovery of energetically favorable structures.[1]
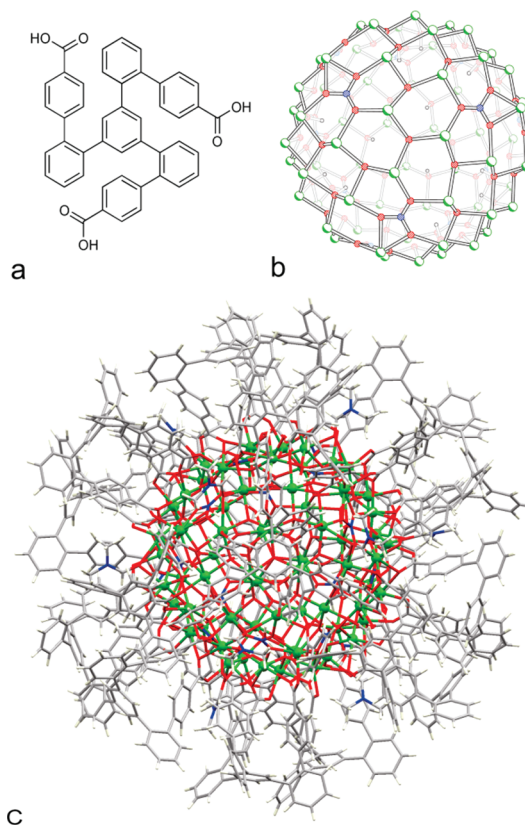

Figure 1. Views of (a) ligand H$_3$L, (b) the Cd−NO$_3$ core of **1** (carboxylate and DMF ligands omitted), and (c) **1**. Atom colors (all figures): C, gray; H, white; N, blue; O, red; Cd, green.

H$_3$L (Figure 1a) was conceived and designed as an ambivalent nonplanar tecton that can twist to reduce potential phenyl−phenyl C−H interactions. It can thus potentially bind to metal centers either in an *endo* fashion via three carboxylates

on the same trigonal face (to stabilize high-nuclearity clusters) or in an *exo* manner (to generate coordination polymers). We report herein the reproducible and designed synthesis and full characterization of a highly unusual Cd_{66} cluster, **1**, a high-nuclearity system incorporating a unique dual-shell structure (Figure 1) comprising a central inorganic Cd−oxo−hydroxy−nitrate cluster core surrounded by an organic shell of ligands. **1** contains ca. 1238 non-hydrogen atoms and has a molecular weight of ca. 23 800 Da. The pseudospherical ball has an external diameter of 3.18 nm[18] and an internal diameter of 1.22 nm[19] and thus can be considered a metal−organic nanosphere.[20] Interestingly, reaction of H_3L with Cd(II) salts under less vigorous conditions affords coordination polymers, whose syntheses can be controlled to form 1D, 2D, or 3D frameworks.

A solution of H_3L and $Cd(NO_3)_2 \cdot 4H_2O$ in *N,N*-dimethylformamide (DMF) was heated solvothermally at 150 °C for 3 days to give **1** as colorless parallelepipeds. Single-crystal X-ray analysis revealed **1** to be a cluster with the formula $[Cd_{66}(\mu^3\text{-}OH)_{28}(\mu^3\text{-}O)_{16}(\mu^5\text{-}NO_3\text{-}O,O,O',O',O'',O'')_{12}(L)_{20}(\mu^2\text{-}DMF)_{12} \subset (DMF)_9]$. **1** is composed of a spherical shell of 66 Cd(II) cations bridged by 28 μ^3-hydroxide, 16 μ^3-oxo, and 5 μ^5-NO_3^- anions (Figure 1b) surrounded by a shell of 20 tripodal capping ligands (L^{3-}) and 12 DMF ligands. **1** crystallizes in the trigonal space group $R\bar{3}$, and the cluster has C_3 crystallographic symmetry and idealized chiral tetrahedral T symmetry. However, each crystal is a racemate, with chiral molecules of **1** of both hands found in the unit cell.

A dual-shell structure for cluster **1** in which a central inorganic core is covered by an organic layer of L^{3-} ligands can readily be observed (Figure 1c). The 66 Cd(II) cations can be divided into six groups of centers with identical idealized symmetry: groups (i)−(v) each contain 12 centers showing a distorted octahedral coordination geometry, and group (vi) contains six centers having a biscapped square-pyramidal geometry [see the Supporting Information (SI)]. The six groups of Cd(II) cations differ in the make-up of their coordination spheres, which consist of varying combinations of carboxylate, hydroxide, oxo, nitrate, and DMF ligands. Within the groups of Cd(II) cations with identical idealized symmetry are centers with different crystallographic symmetry and hence differing coordinate bond lengths, though for the most part correlations between the geometries in these groups can be seen (Table S3 in the SI). The octahedrally coordinated centers are all bound by either two or three carboxylate ligands and by two or three oxo/hydroxide ligands, with the remaining sites occupied by nitrate or DMF ligands. The biscapped square-pyramidally coordinated Cd(II) cations are all bound by two carboxylate ligands and two chelating nitrate anions resulting in centers with approximate C_{2v} symmetry.

The NO_3^- anions lie parallel to the surface of the spherical inorganic core, and each bridges five Cd(II) centers (Figure 2c). Identification of the 28 HO$^-$ and 16 O^{2-} anions in the structure was determined by charge-balancing considerations to give an overall neutral species. Over the 16 crystallographically unique oxygen sites, the locations of HO$^-$ groups were found by considering the observed Cd−O bond lengths and peaks in the crystallographic electron density map. Six of the O atoms (five full and one one-third occupancy) have average Cd−O bond lengths longer than the global mean value and have electron density peaks suggesting their assignment as HO$^-$ groups. Four more HO$^-$ sites are expected but could not be clearly distinguished from the spread of mean Cd−O bond lengths at the remaining sites. Thus, the HO$^-$ sites are
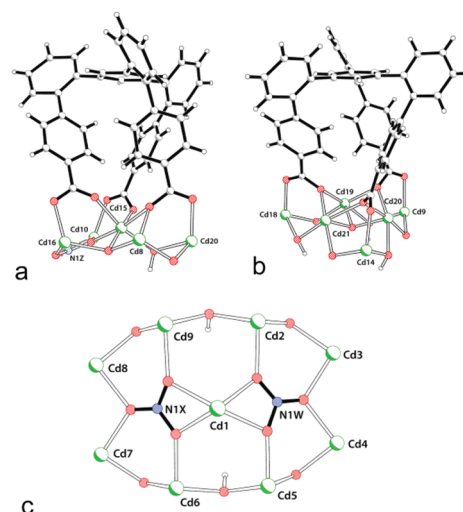

Figure 2. Views of the coordination environments of (a) ligand A at a threefold-symmetric site, (b) ligand D at a nonsymmetric site, and (c) nitrate anions W and X (carboxylate and DMF ligands omitted).

disordered among the remaining O^{2-} atoms. All HO$^-$ and O^{2-} groups act as μ^3-ligands bridging three Cd(II) cations and project into the center of the sphere (Figure S2 in the SI). Within the inorganic shell, peaks were observed in the electron density map but could not be successfully modeled. SQUEEZE[21] was applied to the data to confirm that this 861 Å^3 void contains 383 electrons, suggesting the presence of approximately nine small solvent molecules assigned as DMF. In the organic shell, the ligands and DMF molecules sterically block the entire surface of the metallo core except for small clefts through which NO_3^- anions are visible.

In the idealized T symmetry of the cluster, there are two ligand environments (Figure 2): eight ligands (A, B, G, H; Figure 2a) sit at the corners of a cubic array at positions of threefold symmetry bridging a triangle of three symmetry-related Cd(II) cations, and 12 ligands (C, D, E, F; Figure 2b) sit on the edges of the cubic array and bind to one central Cd(II) via their three carboxylate groups. The two types of ligand have opposing twist: clockwise for the eight threefold-symmetric ligands and anticlockwise for the remaining 12 ligands.

The 66 Cd(II) atoms and 12 NO_3^- anions can be viewed as the vertices of a polydeltahedron (Figure 3). The Cd vertices
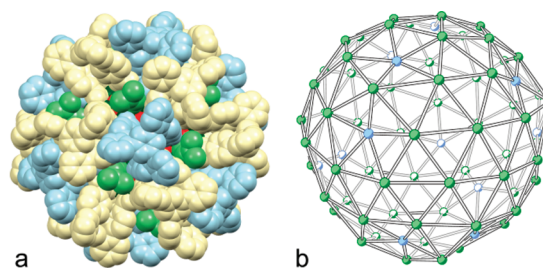

Figure 3. (a) Space-filling view of **1**. Colors: Ligand, blue and yellow; DMF, green. (b) Polydeltahedron formed by **1** based upon 66 Cd(II) centers (green) and 12 NO_3^- anions (blue) as vertices.

are all six-connected with Cd···Cd separations ranging from 3.49 to 3.99 Å, with the NO_3^- anions five-connected to Cd(II) centers (Cd···N separations ranging from 2.74 to 3.33 Å). Importantly, the 12 NO_3^- vertices are the precise number of

five-coordinate defects necessary to allow the 66 six-coordinate vertices to enclose a sphere, as stated by Euler's theorem.[22] Thus, the convex polyhedron has 78 vertices [Cd(II) and NO_3^-] (V), 228 edges (E), and 152 triangular faces (F), giving it a closed-shell Euler characteristic (χ) of 2 ($\chi = V + F - E$).

The solid-state packing in **1** is defined by hexagonal sheets of balls (centroid−centroid separations ranging from 3.55 to 4.09 nm) running parallel to the (110) plane to give sheets stacking in an ABAB pattern (plane separation of 2.89 nm). The stacking does not give a hexagonal close-packed structure because the spheres do not lie above and below the triangular pockets of the layers; instead, each sphere lies approximately halfway between two spheres from the layer above and layer below (separations of 3.52 and 3.55 nm) with a longer distance to the two next closest spheres (both 4.09 nm) (see the SI).

The synthesis of **1** is entirely reproducible: multiple batches of the Cd_{66} nanosphere complex were prepared from separate batches of H_3L, resulting in the exclusive formation of uniform crops of parallelepipeds of **1** as confirmed by elemental analysis, NMR spectroscopy, mass spectrometry, and X-ray diffraction, which gave the correct unit cell dimensions for **1**. Crystals of a different solvate of the Cd_{66} sphere, **1a**, were prepared under identical conditions but using 1,4-dioxane as a cosolvent along with DMF. The structure of **1a** was refined in the space group *Pnnn* with the asymmetric unit containing only a quarter of the molecule (see the SI for further discussion).

1 is only sparingly soluble in several organic solvents, including $CHCl_3$, C_6H_5Me, and C_6H_6. The ${}^1H$ NMR spectrum recorded in CD_2Cl_2 features broad overlapping peaks in the 9.25−5.75 ppm region. Nine peaks of varying intensity can be discerned, and these are spread over a larger range than for the free ligand H_3L (7.95−6.62 ppm). Identical ${}^1H$ NMR spectra were observed for samples of **1** prepared from four different batches of H_3L. The broad nature of these peaks is consistent with the ligands being part of a large species with restricted tumbling in solution. ${}^1H$ NMR spectra of **1** in toluene-d_8 collected at temperatures ranging from 298 to 363 K showed few changes: one broad feature disappeared and minor changes occur in the chemical shifts of others, indicating little chemical change over the temperature range studied. The MALDI mass spectrum of a sample of **1** deposited from a CH_2Cl_2 solution featured a very broad peak spread over the range m/z 21800−23800. The minimum expected spread of mass spectral peaks for intact, **1** given the isotope pattern for 66 cadmium atoms, would be ca. m/z 100 (see the SI). The X-ray structure gives an average electron count for the encapsulated contents of the inorganic core. Although assigned to nine molecules of DMF, variations in content from cluster to cluster are likely. Additionally, even the mild conditions of MALDI could readily displace any number of the 12 surface-bound DMF ligands. Thus, a peak spread of m/z 1533, equivalent to 21 DMF molecules, combined with the resolution limitations of the technique, explains the broadness of the observed mass spectral peak. Further evidence for the persistence of **1** in solution was provided by dynamic light scattering (DLS) measurements in $CHCl_3$, which indicated the presence of a species with a diameter of 2.9 ± 1.1 nm.

The large size of **1** allowed its characterization and direct visualization using high-resolution transmission electron microscopy (TEM). A sample of **1** was deposited from $CHCl_3$ solution onto a copper-grid-mounted lacy carbon film. TEM images confirmed the presence of particles of a range of sizes encompassing that expected for the intact complex (see the SI).

The distribution of sizes suggests that the molecules were damaged by the electron beam, so a sample of **1** was subsequently deposited from chloroform solution into multi-walled carbon nanotubes (MWNTs) prior to imaging. MWNTs have previously been used as transparent test tubes for visualizing molecular clusters using TEM, acting as an electromagnetic shield and a heat and charge sink to minimize the detrimental effects of the electron beam on the sample.[23] Molecules of **1** imaged inside MWNTs showed consistently good agreement with the size expected for intact clusters (Figure 4).
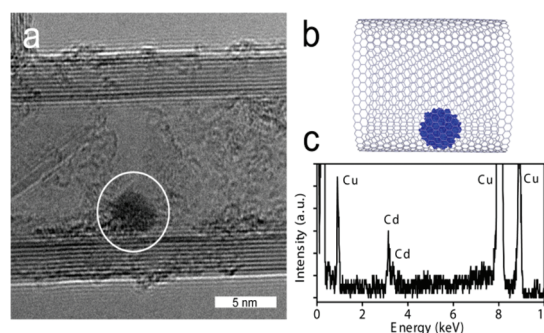

Figure 4. (a) Conventional bright-field TEM image of **1** inserted into a nanotube (scale bar is 5 nm). (b) Schematic representation of (a). (c) EDX spectrum of the selected area in the nanotube (circle), confirming the presence of Cd-containing molecules within the nanotube (Cu peaks are due to the copper TEM support grid).

The presence of cadmium in the species imaged by TEM both on carbon films and inside MWNTs was confirmed by localized energy-dispersive X-ray (EDX) spectroscopy.

To probe the conditions necessary for the formation of **1**, reactions were carried out at lower temperatures under various conditions and with $CdCl_2$ instead of $Cd(NO_3)_2\cdot4H_2O$. These lower-energy experiments afforded the 1D and 2D coordination frameworks **2**, **3**, and **4** (see the SI).

Thus, diffusion of diisopropyl ether into a solution of H_3L and $Cd(NO_3)_2\cdot4H_2O$ in DMF and 1,4-dioxane at room temperature resulted in a crop of colorless crystals whose single-crystal X-ray structure revealed a 1D coordination polymer $[Cd_3(L)_2(DMF)_5(H_2O)_2]_\infty$, **2**. In **2**, pairs of tricarboxylic L^{3-} ligands in tripodal conformations sandwich triangular arrays of three Cd(II) cations (Cd−Cd separations of 7.89−8.14 Å) with each carboxylate group chelating to one Cd(II) cation in a η^2-fashion. Adjacent $[Cd_3(L)_2]$ moieties are bridged in an anti conformation by pairs of chelated carboxylates, resulting in the formation of Cd_2O_2 squares.

Reaction of H_3L with $Cd(NO_3)_2\cdot4H_2O$ in DMF at an intermediate temperature of 80 °C for 2 weeks yielded colorless, thin, platelike crystals. X-ray analysis revealed a 2D coordination framework, $[Cd_3(L)_2(DMF)_4]_\infty$, **3**, composed of linear $[Cd_3(RCO_2)_6(DMF)_4]$ clusters, with each carboxylate ligand bridging three clusters to form 2D sheets. In contrast to the tripodal conformation adopted in **1** and **2**, two of the arms of L^{3-} in **3** project above the plane of the central phenyl ring and one lies below.

To assess the role of the NO_3^- anions, H_3L was treated with $CdCl_2$ in DMF at 150 °C for 3 days. Colorless crystals were obtained, and their structure was revealed by X-ray analysis to be $\{[Cd_3Cl(L)_2(DMF)(Me_2NH)]Me_2NH_2\}_\infty$, **4**. This 2D coordination framework is composed of $[Cd_3Cl(RCO_2)_6]$ clusters bridged via six different ligands, resulting in sheets of

kgd topology, identical to the topology observed for **3**. Within the Cd_3Cl cluster, the Cl^- anion is bound to three Cd(II) cations arranged in a T-shaped geometries.[24]

In conclusion, we have successfully demonstrated the synthesis and characterization of a highly unusual high-nuclearity Cd_{66} metal−organic nanosphere. Our strategy leads to the formation of a dual-shell cluster consisting of an inorganic shell built from Cd(II) cations and O^{2-}, HO^-, and NO_3^- anions capped by an organic shell of tricarboxylate and DMF ligands. The cluster forms a unique polydeltahedron that also encompasses a large void space with a diameter of over 1 nm containing nine DMF molecules. Reactions at lower temperatures suggested the presence of a large thermodynamic barrier that must be overcome to form nanospheres, while reactions in the absence of NO_3^- anions confirmed that the presence of this anion is needed to template the formation of nanospheres. Future work seeks to develop and investigate new methodologies for the synthesis of complex high-nuclearity metal nanoclusters and aggregates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Single-crystal X-ray structures, experimental details, characterization data, and NMR and mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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