Pentadecadentate Chelating Ligands as Building Blocks for a \{Fe₆\} Cage with 12 Exo-Coordinated Sodium Cations

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Received July 14, 2004

Complexation of the highly branched, pentadecadentate chelating ligand cis,cis,1,3,5-cyclohexanetriamine-\(N,N',N'',N''',N''''\)-hexaacetic acid (H₆L) with iron(III) and sodium cations in the presence of carbonate anions leads to the formation of an \{Fe₁₂L₆\} cluster comprising an \{Fe₆\} cage linked by 12 exo-coordinated sodium cations to form an extended 3D array.

The design and synthesis of highly branched ligand systems with high denticity for the complexation of metal ions is of great interest because of their possible applications in nanochemistry for producing capsules,¹ in medicine for chelation therapy,² and as sensors,³ as well as the possibility of developing building blocks for the formation of clusters⁴ and arrays with functional properties (e.g., catalytic, porosity or magnetism).⁵ Acetate-based ligand systems are especially suitable building blocks in the synthesis of high-nuclearity iron(III) complexes as demonstrated by the \{Fe₁₂\} of Lippard,⁶ the \{Fe₁₀\} of Powell,⁷ and the elegant series of clusters from \{Fe₄\} to \{Fe₃\} of Güdel.⁸ In particular, the class of ligands based on carboxymethylamino motifs is extremely versatile, with two classical examples being ethylenediaminetetraacetic acid⁹ (EDTA) and the more rigid macrocyclic 1,4,7,10-tetraazaacyclododecane-\(N,N',N'',N''',N''''\)-tetraacetic acid¹⁰ (DOTA). These examples encapsulate one metal ion, but the development of iminodiacetic acid-based and related ligands has provided access to a vast plethora of clusters by the manipulation of subtle control parameters.¹¹ This is because many of these ligands have been predisposed to bridge several metal centers, rather than complex to a single center, and this has been achieved with a lower number of chelating arms than in EDTA or DOTA. However, the construction of high-nuclearity clusters of 3d transition metals with highly branched chelating ligands could also be a viable route, but the design of ligands that can coordinate to a large number of metal ions (e.g., nine) has scarcely been investigated.¹²

In this context, we present the first investigation of the complexation of the ligand cis,cis,1,3,5-cyclohexanetriamine-\(N,N',N'',N''',N''''\)-hexaacetic acid (H₆L) with transition metal ions.¹³ It is notable that H₆L is related to the carboxymethylamino- and iminodiacetic acid-based ligands, but it provides a much larger number of possible donor atoms, fixed to a central core. In this case, the ligand is potentially penta-

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sodium ions in aqueous solution. Cluster 1 solution of H5 by the addition of sodium hydrogencarbonate to an aqueous Hydrogen atoms are excluded for clarity.

iron cage (Figure 1) that is decorated by 12 bridging sodium yields green crystals of the hexameric cluster Na12 \{Fe 6 (O) 3 -

diffusion of ethanol into the reaction mixture over 10 days of 1 equivalent of solid iron(III) chloride (54 mg, 0.199 mmol) and sonication to give a clear orange solution. Slow of 1 equivalent of solid iron(III) chloride (54 mg, 0.199 mmol) until pH 7.5 was reached, followed by the addition (CO 3 ) 6 (\textsuperscript{15}) Crystal data for

Furthermore, the cyclohexane backbone gives conformational modes.\textsuperscript{14} allowing for a large variety of both inter- and intramolecular coordination modes.

These possibilities were realized when L, in the form H3LNa, was complexed to iron(III) salts in the presence of sodium ions in aqueous solution. Cluster 1 was synthesized by the addition of sodium hydrogencarbonate to an aqueous solution of H3LNa (100 mg, 0.199 mmol in 5 mL of methanol) until pH 7.5 was reached, followed by the addition of 1 equivalent of solid iron(III) chloride (54 mg, 0.199 mmol) and sonication to give a clear orange solution. Slow diffusion of ethanol into the reaction mixture over 10 days yields green crystals of the hexameric cluster Na12\{Fe_{6}(O)_{3}-

Coordination modes.

Figure 1. Schematic representation of the cluster assembly and side view of 1a. C = gray, O = red, N = light blue sticks, Fe(III) = purple spheres. Hydrogen atoms are excluded for clarity.

decadentate, with three tertiary amines and six acetate groups. Furthermore, the cyclohexane backbone gives conformational rigidity,\textsuperscript{14} whereas the acetate groups are more flexible, allowing for a large variety of both inter- and intramolecular coordination modes.

The anion [Fe\textsubscript{6}(O)\textsubscript{3}(CO\textsubscript{3})\textsubscript{6}(L)\textsubscript{2}\textsuperscript{12-} (1a) can be described as a cage-like, hexanuclear diligand cluster with overall C\textsubscript{36} symmetry (Figure 1). Each ligand unit, in which all six carboxylic acid groups are deprotonated, coordinates to three iron(III) centers through its amino donors [Fe-N distance = 2.276(4) Å] and corresponding carboxymethyl groups [Fe-O distances between 2.079(3) and 2.134(3) Å]. Two such units are linked together to form a symmetrical dimer in which each of the iron(III) centers from one half is linked to its counterpart via two carbonate bridges and one \(\mu_2\)-oxo bridge [Fe-O distances = 1.999(3) and 2.024(3) Å (carbonate) and 1.794(2) Å (O\textsuperscript{2-})]. Each iron(III) center displays a pseudo-octahedral coordination geometry [bond angles between 74.1(2) and 108.7(2)°, average 90.1(2)°] and is separated from its counterpart by ca. 3.06 Å.

Each cluster unit coordinates to 12 crystallographically defined sodium ions, which link the clusters together in a hexagonal array via the carboxymethyl groups of the ligand and the carbonate bridges between the iron(III) pairs (Figure 2). Chemical analysis reveals the presence of an additional six disordered sodium ions for each cluster unit. Each pair of iron(III) ions has an associated pair of sodium ions (Na-Na distance = ca. 3.29 Å), bridged by the free oxygen atom of one carbonate bridge [Na-O distance = 2.421(4) Å] and two water molecules [Na-O distances = 2.533(14) and 2.286(7) Å]. Each sodium ion bridges two cluster units through the carbonyl oxygen atoms of the ligand carboxymethyl groups [Na-O distances = 2.440(4) and 2.484(4) Å]. An additional, nonbridging water molecule [Na-O distance = 2.301(5) Å] completes the pseudo-octahedral coordination geometry around each sodium ion [bond angles between 77.3(2) and 111.6(2)°, average 90.6(2)°].

In addition to the lattice of sodium ions, the structure of 1 contains a complex network of water molecules that connect the ligand carbonyl oxygen atoms of adjacent clusters by hydrogen bonds. Disordered water molecules form hydrogen-bonded interactions with the iron(III)-coordinated oxygen atoms of 1a of the carbonate ligands and also with the non-sodium-coordinating free carbonate oxygen atoms. Furthermore, the overall hexagonal packing of the cluster units leads to the formation of cavities between units that run parallel to the crystallographic c axis and are

Figure 2. (a) Top view (c axis) of cluster array and (b) side view of single cluster unit with sodium—oxygen contacts highlighted in bright red. C = gray, O = dark red, N = light blue sticks, Fe = purple spheres, Na = light purple spheres. Hydrogen atoms and water molecules are not shown.

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\textsuperscript{(15)} Crystal data for I: (C\textsubscript{42}H\textsubscript{114}Fe\textsubscript{6}Na\textsubscript{12}O\textsubscript{81}), M = 2610.3, hexagonal, space group P6\textsubscript{3}m, a = 17.8474(4) Å, c = 18.0638(4) Å, V = 4983.0-

(2) Å\textsuperscript{3}, Z = 2, \mu(Mo-K\textsubscript{α}) = 1.012 mm\textsuperscript{-1}, 19743 reflections measured, 3027 unique that were used in all calculations. Final R1 = 0.063 and wR2 = 0.181 (all data). Data were measured at 150(2) K on a Nonius Kappa-CCD diffractometer with a molybdenum rotating anode source (\(\lambda = 0.7107 \) Å). Structure solution with SHELXS97 and refinement with SHELXL97 using WinGX.\textsuperscript{16} Hydrogen atom positions calculated and subsequently riding.

filled by a combination of disordered water molecules and
sodium cations.

Magnetic susceptibility data of 1 are characterized by
antiferromagnetic coupling between the iron(III) centers
\( s = \frac{3}{2} \) of the three Fe(\( \mu \)-CO\(_3\))(\( \mu \)-O)Fe dimers in 1a, a
structural motif that is rare in coordination chemistry.\(^\text{17}\) The
experimental susceptibility data (Figure 3) can be fitted to a
corresponding isotropic spin dimer model yielding an
exchange constant of \( J = -79 \text{ cm}^{-1} \) \( (g = 2.0) \), while all
other intramolecular magnetic interactions are negligible, as
the aliphatic backbone of L does not mediate magnetic
exchange to a significant extent.

Figure 3. Temperature dependency of \( \chi T \) for 1 at 0.1 Tesla. Experimental
values are represented by squares; the fit to an Fe\(^{III}\) Heisenberg model is
shown by a gray line.

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28, 1414.

This work demonstrates that highly branched ligands with
a rigid core are able to facilitate the construction of a highly
anionic multinuclear cage that itself can coordinate to a large
number of additional cations. The H\(_2\)L ligand can be directly
compared with the less highly branched ligand \( \text{cis,cis-1,3,5-}
\text{cyclohexanetetramine-N,N',N''-triacetic acid} \),\(^\text{18}\) which is re-
stricted to chelate a single metal ion as a result of the axial,
rather than equatorial (as in L), orientation of the coordinat-
ing amino groups attached to the cyclohexane backbone.

In summary, highly chelating, multibranched ligands with
inherent rigidity might allow the design of sophisticated
cluster capsules and other complexes. Further work will
develop the assembly concept based on this ligand and aim
to produce networks with solvent channels so that the highly
anionic nature of the cluster units can be investigated with
respect to acid–base catalysis, the formation of larger
capules (with cavities capable of small molecule encapsula-
tion), and the development of novel magnetic materials.

Acknowledgment. This work was funded by the Uni-
versity of Glasgow, the Leverhulme Trust, the EPSRC, and
the Royal Society. Ames Laboratory is operated for the U.S.
Department of Energy by Iowa State University under
Contract W-7405-Eng-82.

Supporting Information Available: X-ray crystal data in CIF
format, full synthetic method, magnetochemical and analytical
details. This material is available free of charge via the Internet at
http://pubs.acs.org.

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