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Pentadecadentate Chelating Ligands as Building Blocks for a {Fe_6} Cage with 12 Exo-Coordinated Sodium Cations

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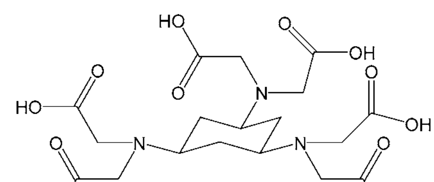
Complexation of the highly branched, pentadecadentate chelating ligand *cis*,*cis*-1,3,5-cyclohexanetriamine-*N*,*N*,*N*′,*N*′,*N*″,*N*″-hexaacetic acid (H_6**L**) with iron(III) and sodium cations in the presence of carbonate anions leads to the formation of an {Fe_6L_2} cluster comprising an {Fe_6} 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 clusters[4] 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 {Fe_{12}} of Lippard,[6] the {Fe_{19}} of Powell,[7] and the elegant series of clusters from {Fe_2} to {Fe_5} of Güdel.[8] In particular, the class of ligands based on carboxymethylamino motifs is extremely versatile, with two classical examples being ethylenediamine tetraacetic acid[9] (EDTA) and the more rigid macrocyclic 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*“,*N*‴-tetraacetic acid[10] (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]



H_6**L**

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*″,*N*″-hexaacetic acid (H_6**L**) with transition metal ions.[13] It is notable that H_6**L** 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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(1) Conn, M. M.; Rebek, J., Jr. *Chem. Rev.* **1997**, *97*, 1647.
(2) Gorden, A. E. V.; Xu, J.; Raymond, K. N.; Durbin, P. *Chem. Rev.* **2003**, *103*, 4207.
(3) Tsukube, H.; Shinoda, S.; Tamiaki, H. *Coord. Chem. Rev.* **2002**, *226*, 227.
(4) Soler, M.; Wernsdorfer, W.; Folting, K.; Pink, M.: Christou, G. *J. Am. Chem. Soc.*, **2004**, *126*, 2156. Winpenny, R. E. P. *Adv. Inorg. Chem.* **2001**, *52*, 1.
(5) Hill, C. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 402. Langley, S.; Helliwell, M.; Raftery, J.; Tolis, E. L.; Winpenny, R. E. P. *Chem. Commun*. **2004**, 142. Lassahn, P. G.; Lozan, V.; Timco, G. A.; Christian, P.; Janiak, C.; Winpenny, R. E. P. *J. Catal.* **2004**, *222*, 260.
(6) Lee, D.; Krebs, C.; Hanh, B. H.; Hendrich, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* **2000**, *122*, 5000.
(7) Goodwin, J. C.; Sessoli, R.; Gatteschi, D.; Wernsdorfer, W.; Powell, A. K.; Heath, S. L., *J. Chem. Soc., Dalton Trans.* **2000**, *12*, 1835.
(8) Boskovic, C.; Sieber, A.; Chaboussant, G.; Güdel, H. U.; Ensling, J.; Wernsdorfer, W.; Neels, A.; Labat, G.; Stoeckli-Evans, H.; Janssen, S. *Inorg. Chem.* **2004**, *43*, 5053.
(9) Smith, R.; Bullock, J. L.; Bersworth, F. C.; Martell, A. E. *J. Org. Chem.* **1949**, *14*, 358.
(10) Stetter, H.; Frank, W. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 760. For related ligands, see: Frost, M. *Nature* **1956**, *178*, 322. Vos, D. E. D.; Bein, T. *J. Organomet. Chem.* **1996**, *520(1)*, 195.
(11) Murugesu, M.; King, P.; Clerac, R.; Anson, C. E.; Powell, A. K. *Chem. Commun.* **2004**, 741. Murugesu, M.; Anson, C. E.; Powell, A. K. *Chem. Commun.* **2002**, 1054. Schmitt, W.; Jordan, P. A.; Henderson, R. K.; Moore, G. R.; Anson, C. E.; Powell, A. K. *Coord Chem Rev.* **2002**, *228*, 115.
(12) Rivals, F.; Steiner, A. *Chem. Commun.* **2001**, 1426.
(13) Grimes, J. H.; Huggard, A. J.; Wilford, S. P. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1225.

10.1021/ic049068w CCC: $27.50

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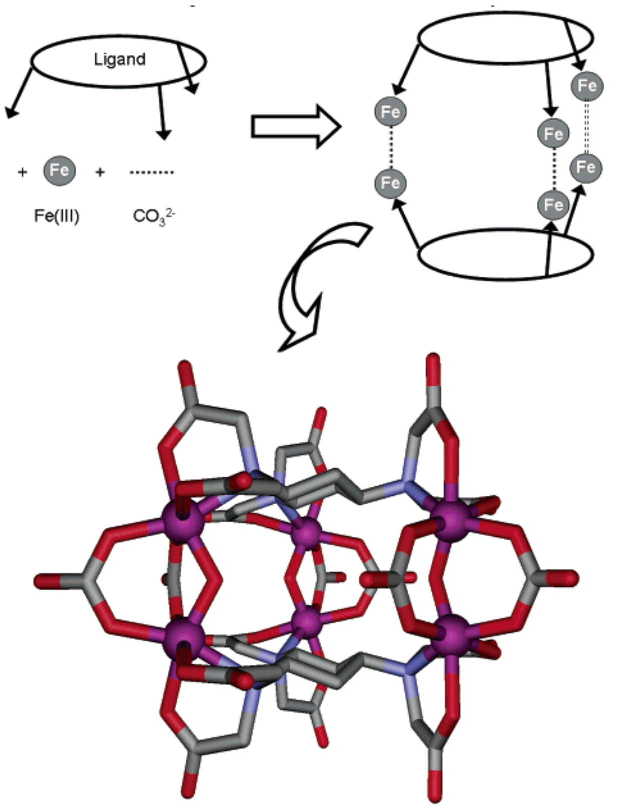

Figure 1. Schematic representation of the cluster assembly and side view of **1a**. C = gray, O = red, N = light blue sticks, Fe(III) = purple spheres. Hydrogen atoms are excluded for clarity.

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

These possibilities were realized when **L**, in the form H_5**L**·Na, 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 H_5**L**·Na (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 $Na_{12}[Fe_6(O)_3(CO_3)_6(\mathbf{L})_2]\cdot 36H_2O$ (**1**)[15] in a yield of 35%, whereby the hexa-deprotonated ligand **L** is utilizing all 15 donor atoms in coordinative interactions, forming a $\{Fe_6L_2\}$ hexanuclear iron cage (Figure 1) that is decorated by 12 bridging sodium ions (Figure 2).

(14) Seeber, G.; Pickering, A. L.; Long, D.-L.; Cronin, L. *Chem. Commun.* **2003**, 2002.

(15) Crystal data for **1**: ($C_{42}H_{114}Fe_6N_6Na_{12}O_{81}$), M = 2610.3, hexagonal, space group $P6_3/m$, a = 17.8474(4) Å, c = 18.0638(4) Å, V = 4983.0(2) Å^3, Z = 2, μ(Mo-K_α) = 1.012 mm^{-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 equipped with a molybdenum rotating anode source (λ = 0.7107 Å). Structure solution with SHELXS97 and refinement with SHELXL97 using WinGX.[16] Hydrogen atom positions calculated and subsequently riding.

(16) Farrugia; L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

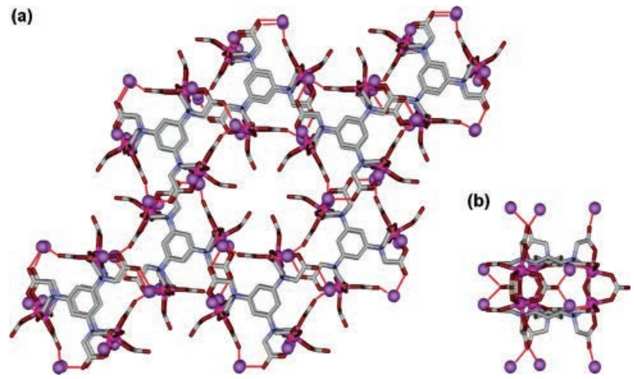

Figure 2. (a) Top view (c axis) of cluster array and (b) side view of single cluster unit with sodium−oxygen contacts highlighted in bright red. C = gray, O = dark red, N = light blue sticks, Fe = purple spheres, Na = light purple spheres. Hydrogen atoms and water molecules are not shown.

The anion $[Fe_6(O)_3(CO_3)_6(\mathbf{L})_2]^{12-}$ (**1a**) can be described as a cage-like, hexanuclear diligand cluster with overall C_{3h} 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 μ_2-oxo bridge [Fe−O distances = 1.999(3) and 2.024(3) Å (carbonate) and 1.794(2) Å (O^{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

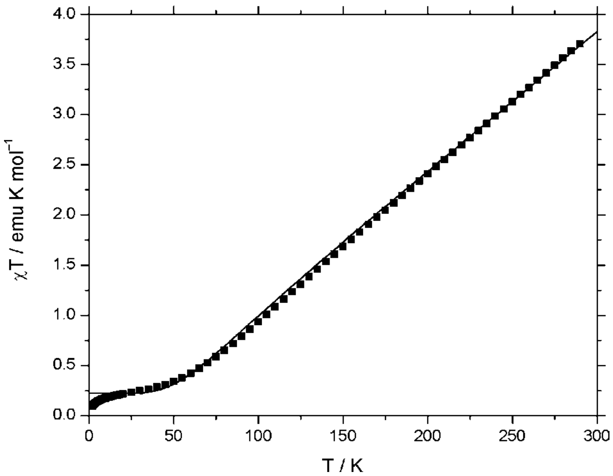

Figure 3. Temperature dependency of χT for **1** at 0.1 Tesla. Experimental values are represented by squares; the fit to an Fe^{III}_2 Heisenberg model is shown by a gray line.

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 ($s = {}^5/_2$) of the three $Fe(\mu\text{-}CO_3)_2(\mu\text{-}O)Fe$ dimers in **1a**, a structural motif that is rare in coordination chemistry.[17] The experimental susceptibility data (Figure 3) can be fitted to a corresponding isotropic spin dimer model yielding an exchange constant of $J = -79$ 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.

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_6**L** ligand can be directly compared with the less highly branched ligand *cis*,*cis*-1,3,5-cyclohexanetriamine-*N*,*N′*,*N″*-triacetic acid,[18] which is restricted to chelate a single metal ion as a result of the axial, rather than equatorial (as in **L**), orientation of the coordinating 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 capsules (with cavities capable of small molecule encapsulation), and the development of novel magnetic materials.

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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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(17) Drüke, S.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem*. **1989**, *28*, 1414.

(18) Luo, H.; Eberly, N.; Rogers, R. D.; Brechbiel, M. W. *Inorg. Chem.* **2001**, *40*, 493.