Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 5953–5956
DOI: 10.1021/ic1004006

A Doughnut-Like $(\mathrm{Mn}^{\mathrm{III}})_{12}$ Metallocycle Formed by a Rigid Angular Bis-Catecholate with a Nanometer-Sized Central Hole

Brendan F. Abrahams,* Nicholas J. FitzGerald, and Richard Robson*

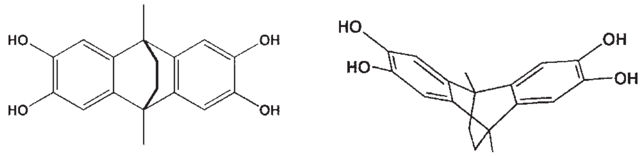
School of Chemistry, University of Melbourne, Victoria 3010, Australia

Received February 27, 2010

Reaction of the rigid angular ligand tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene, hereafter LH_4, with $Mn(CH_3CO_2)_2 \cdot 2H_2O$ in a basic aqueous medium, in air, affords a crystalline product of composition $Na_{12}\{[Mn(H_2O)]_{12}L_{12}\} \cdot xH_2O$. Single-crystal X-ray diffraction reveals the presence of large $[\mathrm{Mn^{III}}_{12}L_{12}]^{12-}$ metallocycles of roughly hexagonal appearance, somewhat resembling a doughnut in which the central hole (van der Waals surface to surface) is roughly a nanometer across. This is the first example of a metal derivative of the fully deprotonated form, L^{4-}. Associations with aquated Na^+ counterions lead to a pleasingly symmetrical packing arrangement resembling honeycomb, with the central holes of individual metallocycles lined up one above the other. The ligand L^{4-}, on account of its rigid angularity and its strong metal binding properties, promises to provide a rich source of unusual metal-containing structures, in particular cages, in future studies.

Introduction

Catechol-based ligands have long been employed as strong metal binding agents for the construction of interesting and potentially useful supramolecular assemblies,[1−4] such as large polyhedra,[2] square and triangular macrocycles,[3] and helicates.[4] Some of these materials have potential applications in gas sorption, as single molecule magnets and as nanoreaction vessels. We report here some of our work with the easily synthesized but previously little studied bis-catecholate tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene, **I** (hereafter LH_4). Surprisingly, only one metal derivative of this interestingly rigid ligand has previously been structurally characterized (to the best of our knowledge), viz., an octauranate cage complex in which the ligand is present in the only partially deprotonated form, LH_2^{2-}.[5] Reported herein is the crystal structure of a novel $\mathrm{Mn^{III}}$ derivative of LH_4, which contains large $[\mathrm{Mn^{III}}_{12}L_{12}]^{12-}$ metallocycles of roughly hexagonal appearance. Associations with aquated Na^+ counterions lead to an interesting, pleasingly symmetrical packing arrangement in the solid state. To the best of our knowledge, this is the first example of a metal derivative of the fully deprotonated form, L^{4-}.



LH₄

---

*To whom correspondence should be addressed. Email: r.robson@unimelb.edu.au (R.R.); bfa@unimelb.edu.au (B.F.A.).

(1) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45–87. (b) Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331–442.

(2) (a) Johnson, D. W.; Raymond, K. N. *Inorg. Chem.* **2001**, *40*, 5157–5161. (b) Terpin, A. J.; Ziegler, M.; Johnson, D. W.; Raymond, K. N. *Angew. Chem., Int. Ed.* **2001**, *40*, 157–160. (c) Davis, A. V.; Fiedler, D.; Ziegler, M.; Terpin, A.; Raymond, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 15354–15363. (d) Bruckner, C.; Powers, R. E.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1998**, *37*, 1837–1839. (e) Yeh, R. M.; Xu, J.; Seeber, G.; Raymond, K. N. *Inorg. Chem.* **2005**, *44*, 6228–6239. (f) Albrecht, M; Janser, I.; Meyer, S.; Weis, P.; Frohlich, R. *Chem Commun.* **2003**, 2854–2855. (g) Caulder, D. L.; Powers, R. E.; Parac, T. N.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1998**, *37*, 1840–1843.

(3) (a) Abrahams, B. F.; Price, D. J.; Robson, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 806–810. (b) Abrahams, B. F.; Boughton, B. A.; Choy, H.; Clarke, O.; Grannas, M. J.; Price, D. J.; Robson, R. *Inorg. Chem.* **2008**, *47*, 9797–9803. (c) Duhme, A.-K.; Davies, S. C.; Hughes, D. L. *Inorg. Chem.* **1998**, *37*, 5380–5382. (d) McCord, D. J.; Small, J. H.; Greaves, J.; Van, Q. N.; Shaka, J.; Fleishier, E. B.; Shea, K. J. *J. Am. Chem. Soc.* **1998**, *120*, 9763–9770. (e) Abrahams, B. F; FitzGerald, N. J; Robson, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 8640–8643.

(4) (a) Albrecht, M. *Chem. Soc. Rev.* **1998**, *27*, 281–287. (b) Albrecht, M.; Janser, I.; Frohlich, R. *Chem. Commun.* **2005**, 157–165. (c) Albrecht, M.; Kamptmann, S.; Frohlich, R. *Polyhedron* **2003**, *22*, 643–645. (d) Albrecht, M.; Janser, I.; Kamptmann, S.; Weis, P.; Wibbeling, B.; Frohlich, R. *Dalton Trans.* **2004**, 37–43. (e) Albrecht, M.; Janser, I.; Houjou, H.; Frohlich, R. *Chem.—Eur. J.* **2004**, *10*, 2839–2850. (f) Albrecht, M.; Kotila, S. *Angew. Chem., Int. Ed.* **1995**, *34*, 2134–2137. (g) Albrecht, M.; Kotila, S. *Angew. Chem., Int. Ed.* **1996**, *35*, 1208–1210. (h) Albrecht, M.; Kotila, S. *Chem. Commun.* **1996**, 2309–2310. (h) Kersting, B.; Meyer, M.; Powers, R. E.; Raymond, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 7221–7222. (i) Caulder, D.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1997**, *36*, 1440–1442. (j) Meyer, M.; Kersting, B.; Powers, R. E.; Raymond, K. N. *Inorg. Chem.* **1997**, *36*, 5179–5191. (k) Enemark, E. J.; Stack, T. D. P. *Angew. Chem., Int. Ed.* **1995**, *34*, 996–998. (l) Enemark, E. J.; Stack, T. D. P. *Inorg. Chem.* **1996**, *35*, 2719–2720. (m) Duhme, A.-K.; Dauter, Z.; Hider, R. C.; Pohl, S. *Inorg. Chem.* **1996**, *35*, 3059–3061.

(5) Masci, B.; Thuery, P. *Supramol. Chem.* **2003**, *15*, 95–99.

Experimental Section

Synthesis. Preparation of LH_4. Concentrated hydrochloric acid (6 mL) was added to a molten mixture of catechol (24 g, 0.22 mol), mercaptobenzoic acid (100 mg, 0.6 mol), and acetonylacetone (3 mL, 0.026 mol). The reaction mixture was refluxed for 6 h, after which time the hot solution was added to 400 mL of boiling water. A gummy byproduct was removed by filtration, and the hot solution was allowed to cool overnight. The crystalline product was further recrystallized from anisole and was dried at the pump to give brownish plates. Yield: 4.5 g (59.1%). Elemental analysis (%) found: C, 72.5; H, 6.0. Calcd for $C_{18}H_{18}O_4$: C, 72.5; H, 6.1.

Solvated $Na_{12}\{[Mn(H_2O)]_{12}L_{12}\}$. A solution containing LH_4 (19.4 mg, 0.065 mmol) in dioxane (3 mL) was added to a solution of $Mn(CH_3COO)_2 \cdot 2H_2O$ (9.74 mg, 0.065 mmol) in water (1 mL). This mixture was then treated with excess NaOH (41.6 mg, 1.04 mmol) in water (2 mL). Dark brown crystals began to separate from solution after several days. The crystals were filtered off, washed with water, and dried in the air. Yield: 6 mg (21%). Elemental analysis (%) found: C, 49.3; H, 4.7. Calcd for $Na_{12}\{[Mn(H_2O)]_{12}L_{12}\} \cdot 32H_2O$: C, 49.3; H, 4.9.

Crystal Data for Solvated $Na_{12}\{[Mn(H_2O)]_{12}L_{12}\}$. M_r = 9583.21, monoclinic, $C2/c$, a = 30.624(4) Å, b = 51.439(6) Å, c = 32.370(4) Å, β = 110.290(2)°, V = 47827(10) Å^3, Z = 4, $2\theta_{max}$ = 50.1°, Mo Kα radiation, λ = 0.71073 Å, T = 130K, μ(MoKα) = 0.430 mm^{-1}, 125 102 reflections measured, 42 164 unique, which were used in all calculations, 737 parameters, wR_2 = 0.2793 (all data) and R_1 = 0.0927 ($I > 2\sigma(I)$). The structure was solved by direct methods and refined using a full-matrix least-squares procedure based on F^2 (SHELX97).[6] Crystallographic analysis was performed using the WinGX system of programs.[7]

Results and Discussion

Reaction of LH_4 with $Mn(CH_3COO)_2 \cdot 2H_2O$ in a basic aqueous medium in air affords hydrated crystals of composition $Na_{12}\{[Mn(H_2O)]_{12}L_{12}\}$ suitable for single-crystal X-ray diffraction experiments. The crystals have monoclinic symmetry and space group $C2/c$. Metallocycles of composition $\{[Mn(H_2O)]_{12}L_{12}\}^{12-}$ are present, details of which are considered below. There are equal numbers of two distinct types of ligand, L_a^{4-} and L_b^{4-}, and six crystallographically distinct types of Mn^{III} center, all with very similar coordination environments. For descriptive purposes, all 12 of the Mn centers may be considered equivalent. Six L_a^{4-} ligands and six pairs of Mn centers assemble into a metallocycle shown in Figure 1a and b. As is apparent in the figure, each L_a^{4-} ligand is directly associated with four Mn cations—it chelates a Mn cation at each end, but also one catechol oxygen center at each end bridges to a second Mn center. Four-membered Mn−O−Mn−O rings are thus formed. Although the $[Mn_{12}(L_a)_6]^{12+}$ metallocycle, as viewed in Figure 1a, might appear on first inspection to possess pseudo 6-fold symmetry, it is clear in Figure 1b that there are “upper” and “lower” L^{4-} anions, which lead to only a pseudo 3-fold axis passing through the center of the metallocycle . Likewise, there are “upper” and “lower” Mn centers. The six “upper” metal centers are essentially coplanar and close to the corners of a regular hexagon; the six lower ones similarly form an equivalent pseudo hexagon.

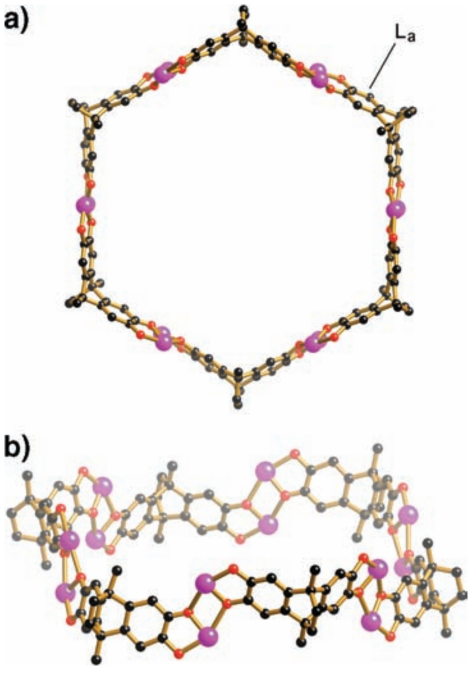


Figure 1. (a) $Mn_{12}(L_a)_6$ metallocyclic component of $Na_{12}\{[Mn(H_2O)]_{12}L_{12}\} \cdot xH_2O$ viewed down the pseudo-3-fold axis and (b) a side-on view.

The complete $\{[Mn(H_2O)]_{12}L_{12}\}^{12-}$ system is shown in Figure 2a. The six-coordinate Mn environment, consisting of one chelated L_a^{4-}, one chelated L_b^{4-}, a coordinated water molecule directed away from the metallocycle center, and a “bridge bond” to an oxygen donor of an L_a^{4-} ligand chelated to a neighboring Mn center, is shown in Figure 2b. As can be seen, the two aqua ligands per Mn pair are on the same side of the four-membered Mn−O−Mn−O ring. In contrast to L_a^{4-}, the L_b^{4-} ligands are directly associated with only two metal centers that are chelated at opposite ends. As is consistent with the oxidation state of +3 for the Mn center, significant tetragonal elongation of the coordination environment is clearly apparent, the elongated bonds being the “bridge bonds” (average, *ca.* 2.41 Å) as indicated in Figure 2b, and those *trans* to them (average Mn−O, *ca.* 2.16 Å); by contrast, the average $Mn-OH_2$ bond is *ca.* 1.90 Å in length. Bond valence sum calculation indicates an “average oxidation state” for M_n of *ca.* 2.9. As can be seen in Figure 2a (and Figure S1, Supporting Information), the L_b^{4-} ligands act as capping units, partially blocking the otherwise open top and bottom faces of the $[Mn_{12}(L_a)_6]^{12+}$ metallocyclic hexagon (as it is seen in Figure 1a). Three L_b^{4-} ligands are located above the average plane of the macrocycle, and three are located below, as can be seen in Figure 2. When viewed side on (Figure S1), the $\{[Mn(H_2O)]_{12}L_{12}\}^{12-}$ metallocycle has a doughnut-like appearance with a central cavity of significant size, the separation between directly opposed Mn^{III} centers being *ca.* 2.25 nm. Although the $\{[Mn(H_2O)]_{12}L_{12}\}^{12-}$ metallocycle lies only on a crystallographic center of inversion, it does possess approximate D_{3d} point group symmetry.

The negative charge on $\{[Mn(H_2O)]_{12}L_{12}\}^{12-}$ is balanced by 12 Na^+ cations, six of which are located inside the metallocycle in the manner indicated in Figure 3a. Each of the “internal” Na^+ cations carries two molecules of water and is bound to three catechol oxygen centers. The “external” Na^+ cations appear in linear trios, as shown in Figure 3b.

---

(6) Sheldrick, G. M. *SHELX97 - Programs for Crystal Structure Analysis*, release 97−2; Institüt für Anorganische Chemie der Universität Göttingen: Göttingen, Germany, 1998.

(7) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

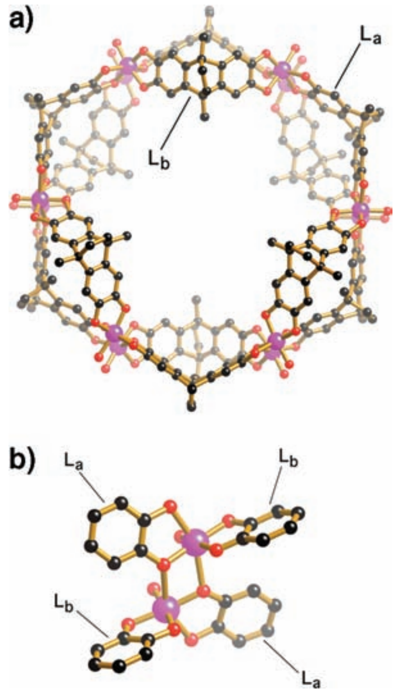


Figure 2. (a) Complete $\{[Mn(H_2O)]_{12}L_{12}\}^{12-}$ metallocycle looking down the pseudo-3-fold axis. (b) A pair of Mn^{III} centers in the metallocycle.

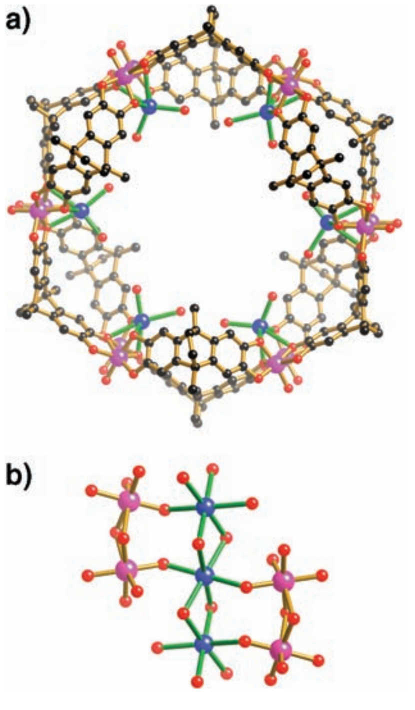


Figure 3. The role of sodium. (a) A view of the metallocycle showing the "internal" aquated Na^+ cations (represented as blue spheres). For clarity, Na–O are represented with green bonds. (b) The binding of one metallocycle to another via "external" aquated Na_3 clusters.

Some of the water molecules bound to Mn^{III} (discussed earlier and shown in Figure 2) act as bridges to two of the Na^+ cations within the linear Na_3 cluster, as shown in Figure 3b. A second metallocycle interacts in the same way with the Na_3 cluster, which acts as glue to cement the two metallocycles together, as can be seen in Figure 3b. The central Na^+ cation of the trio interacts simultaneously with coordinated water molecules from separate metallocycles, while the terminal Na^+ cations each interact with a particular metallocycle.

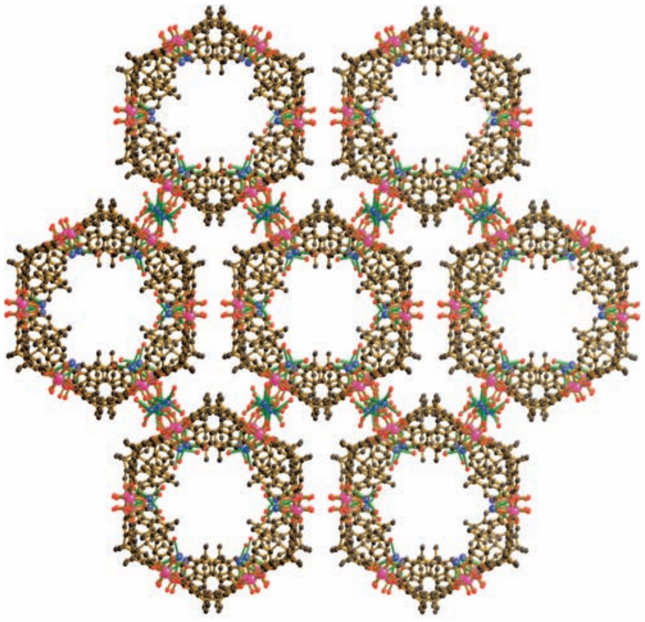


Figure 4. A central column of metallocycles and six near-neighbor columns. Only four of the six contacts between the central column and its neighbors involve the Na_3 "glue".

In the extended structure, $\{[Mn(H_2O)]_{12}L_{12}\}^{12-}$ metallocycles stack one on top of another (see Figure S2, Supporting Information), to form infinite columns running parallel to the *c* axis. This arrangement generates large channels of roughly nanometer size, with the cross-section passing through the centers of the metallocycles; these channels are occupied by disordered water molecules.

All columns are parallel, each being surrounded by six neighbors in a honeycomb fashion (Figure 4). As can be seen, the exterior Na_3 clusters link each column to four of the six neighboring columns in the manner discussed above and as was shown in Figure 3b.

Crystals of $Na_{12}\{[Mn(H_2O)]_{12}L_{12}\}\cdot xH_2O$ contain vast regions of space occupied by disordered water. A calculation of the solvent accessible volume reveals that the metallocyclic anions and their associated aquated Na^+ cations account for only 44% of the total crystal volume. An estimation of residual electron density indicated that there are on the order of 970 water molecules present in the unit cell.[8,9] This approximation is in excellent agreement with the volume available to accommodate these solvent molecules (assuming a single water molecule has a volume of ~ 30 Å^3).

Crystals of $Na_{12}\{[Mn(H_2O)]_{12}L_{12}\}\cdot xH_2O$ display a very low solubility in a variety of solvents, including water,

---

(8) Sluis, P. v.d.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194–201.

(9) Unsurprisingly, given these enormous solvent-filled regions, crystals of $Na_{12}\{[Mn(H_2O)]_{12}L_{12}\}\cdot xH_2O$ are extremely weakly diffracting. The crystals in addition are exceptionally fragile and require very careful handling. Upon exposure to air, the crystals begin to lose crystallinity almost immediately and degrade even when coated in protective oil. This fragility along with the weakly diffracting nature of the crystals made the data collection, refinement of the structure, and the modeling of solvent molecules particularly challenging. Repeated attempts were made to obtain high quality crystallographic data including the use of synchrotron radiation. However, in each case, the weakly diffracting nature of the crystals did not allow for the unambiguous assignment of water molecules.

acetonitrile, acetone, and tetrahydrofuran. Despite repeated attempts in a range of solvents, electrospray mass spectrometric studies failed to provide any indication of the metallocycle in solution. This was not surprising given the very poor solubility of the crystals.

The compound described here represents only the second example of a coordination compound derived from LH_4 and the first example involving its fully deprotonated form. The generation of the doughnut-like metallocyclic complex $\{[Mn(H_2O)]_{12}L_{12}\}^{12-}$ represents an interesting and unusual example of self-assembly. In addition to the interesting internal structural features of the metallocycle, an aesthetically appealing packing arrangement, which leaves vast regions of water-filled space, is observed. In light of the results presented here, the ligand L^{4-}, on account of its rigid angularity and its strong metal binding properties, promises to provide a rich source of unusual metal-containing structures, in particular cages, in future studies.

Acknowledgment. We gratefully acknowledge the financial support of the Australian Research Council. NJF is grateful to the Albert Shimmins Fund (University of Melbourne) for a writing-up award. We thank Dr Berin Boughton for his efforts in attempting to obtain ESMS data on the sample.

Supporting Information Available: Crystallographic data in CIF format and special crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.