Edinburgh Research Explorer

Encapsulation of a Magnesium Hydroxide Cubane by a Bowl-Shaped Polypyrrolic Schiff Base Macrocycle

OPEN ACCESS

Encapsulation of a magnesium-hydroxide cubane by a bowl-shaped polypyrrolic Schiff-base macrocycle**

James W. Leeland,[1] Fraser J. White[1] and Jason B. Love[1]

[1]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

[*]Corresponding author; e-mail: jason.love@ed.ac.uk

Supporting information:
Full experimental details and crystallographic data for 1·THF and 2 (CIF). This material is available free of charge via the Internet at http://pubs.acs.org

Graphical abstract:
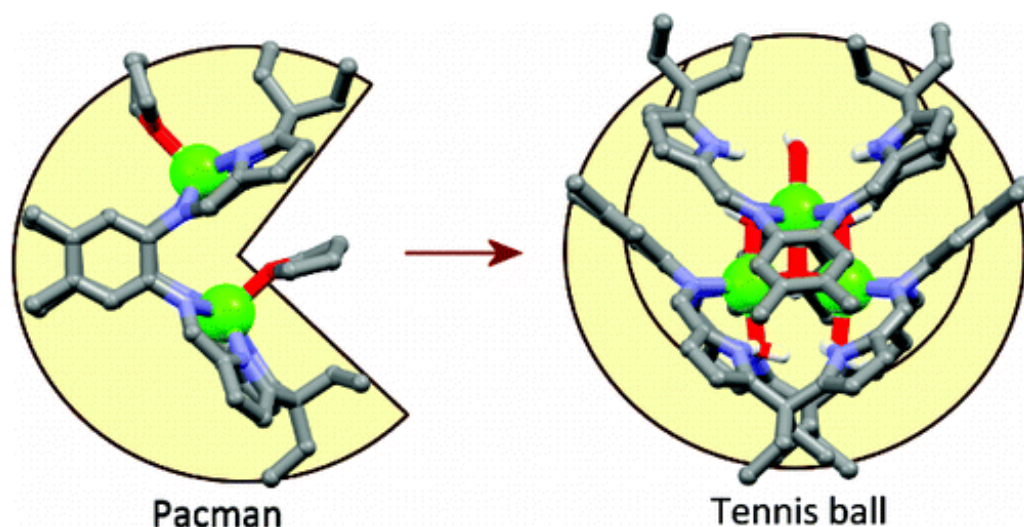

Pacman   →   Tennis ball

Abstract

Hydrolysis of a Pacman-shaped binuclear magnesium complex of a polypyrrolic Schiff base macrocycle results in the formation of a new magnesium hydroxide cubane that is encapsulated by the macrocyclic framework through both coordinative and hydrogen-bonding interactions.

Introduction

Molecular capsules present unique microenvironments for guest molecules and can be formed through spontaneous assembly processes.[1] For example, naturally-curved building blocks such as glycourils, resorcinarenes, or cyclotriveratrylenes that incorporate complementary recognition groups engender capsule formation through supramolecular interactions.[2] Alternatively, metallo-tectons allied with organic ligand spacers allow the construction, through metal-ligand bond formation, of well-defined nanoscale cavities based on Platonic and Archimedian polyhedra.[3] These enzyme-like environments facilitate a myriad of unusual chemical transformations and catalysis,[4] and, significantly, can be used to pacify normally-reactive materials such as white phosphorus or stabilize reactive intermediates and unstable species through cavity confinement.[5] As such, the design of new frameworks that promote the formation of encapsulating environments is a burgeoning area of research.

We have described extensively the metallation chemistry of the Schiff-base polypyrrolic macrocycle H_4L.[6;7] In most cases, wedged-shaped complexes with 'Pacman'-like structures are formed (Chart 1) providing unique molecular cleft environments for chemical reactions including oxygen-reduction catalysis and uranyl reduction.[8] If the pyrrole nitrogens remain protonated however, a different class of bowl-shaped binuclear complex is formed in which the pyrrole hydrogens participate in hydrogen-bonding to the ancillary ligands.[9;10] In this work, we describe a Pacman-to-bowl geometry transformation due to hydrolysis that results in the formation of a new magnesium hydroxide cubane that is encapsulated by two bowl-shaped macrocyclic ligands through both supramolecular interactions and metal-ligand bond formation.
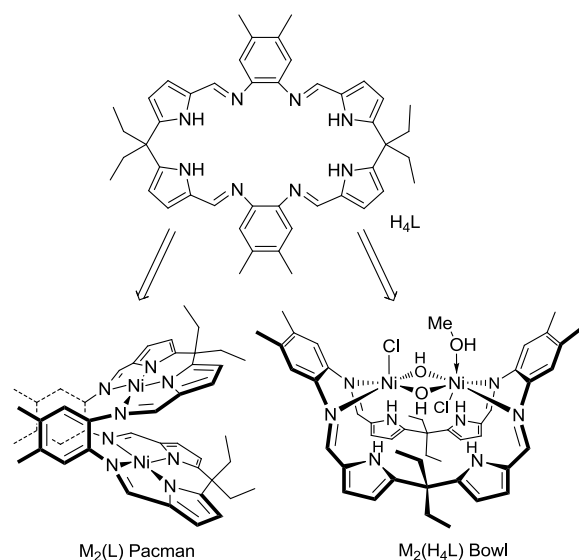
← *Chart 1.* Metallation (e.g. by Ni) of the Schiff-base pyrrole macrocycle H_4L leading to either Pacman or bowl-shaped bimetallic complexes.

The reaction between Bu$_2$Mg and H$_4$L in THF resulted in the clean formation of the binuclear, THF-solvated magnesium complex [Mg$_2$(THF)$_2$(L)] **1.THF** in excellent yield. The EI mass spectrum of **1.THF** displayed a peak at m/z 760 for the molecular ion, and the ^{1}H NMR spectrum (Fig. S1, supporting information) showed the disappearance of the NH resonance of H$_4$L and a shift of the imine resonance from 8.30 ppm in H$_4$L to 7.71 ppm in **1.THF**. Two sets of resonances are present at 2.15/2.06 and 1.13/1.05 ppm for the CH$_2$ and CH$_3$ protons of the *meso*-ethyl substituents were seen, showing that a wedged, Pacman structure with dissimilar endo- and exo-ethyl substituents is present in solution. A similar reaction between Bu$_2$Mg and H$_4$L carried out in Et$_2$O results in the Et$_2$O-solvate [Mg$_2$(OEt$_2$)$_2$(L)], **1.OEt$_2$** while dissolution of this material in pyridine forms the pyridine solvate **1.py** quantitatively.

The X-ray crystal structure of **1.THF** using crystals grown from a toluene/hexane mixture was determined and confirms the overall wedged-shaped structure (Fig. 1).
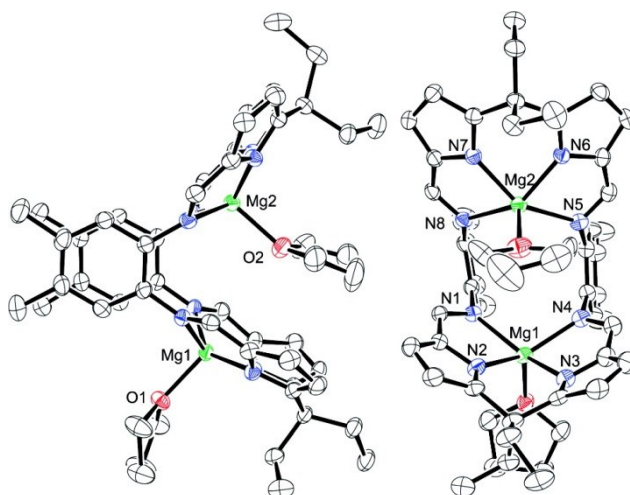
Figure 1. Side-on and face-on views of the solid state structure of [Mg$_2$(THF)$_2$(L)].PhMe **1THF**. For clarity, the toluene molecule of crystallization, a disorder component in the endo-THF molecule and all hydrogen atoms are omitted (displacement ellipsoids are drawn at 50% probability). Selected bond lengths (Å) and angles (°): Mg1-N1 2.165(2), Mg1-N2 2.039(2), Mg1-N3 2.067(2), Mg1-N4 2.131(2), Mg1-O1 2.043(2), Mg…Mg 4.6504(9), ∑ angles Mg1 343.1, bite angle 70.0, twist angle 7.0.

The two Mg cations adopt square-based pyramidal geometries in which the iminopyrrolide N$_4$-donor sets occupy the basal planes (Mg1/Mg2 0.56 Å out of the N$_4$ plane) and a molecule of THF at each apical site. Interestingly, one molecule of THF is found within the cleft while the other is outside. This causes the two metallated compartments to diverge significantly in order to accommodate the guest molecule resulting in a Mg-Mg bite angle of 70.0° compared to the more usual 53-62° range seen for bimetallic complexes of L, and a

small lateral twist angle of 7.0° (*cf.* 11-29° in M$_2$(L) complexes with no endogenous ligand).[7] Similar geometric features were seen by us in the structurally-related complex [Cu$_2$(*exo*-py)(*endo*-py)(L)].[10]

While **1.THF** appears indefinitely stable under anhydrous conditions, an alternative attempt to crystallize **1** from a benzene/hexane mixture resulted in the formation of the new cluster complex [{Mg$_4$(μ_3-OH)$_4$(OH)$_4$}(H$_2$L)$_2$] **2**, presumably by hydrolysis by adventitious water and which has been characterized by X-ray crystallography (Fig. 2). The solid-state structure of **2** comprises a new, magnesium hydroxide cubane Mg$_4$(μ-OH)$_4$(OH)$_4$ that is encapsulated by two orthogonally-oriented H$_4$L macrocycles through both coordinative and hydrogen bonding interactions. In the asymmetric unit, the bonding of Mg1 is representative of each magnesium cation and is bound to the macrocycle through the two imine nitrogens N1 and N8 of H$_4$L, two bridging hydroxides O1 and O2, and a terminal hydroxide O4. This results in a binuclear arrangement of the metals in the asymmetric unit with the bowl-shape arising from the hinging of the two H$_2$N$_4$ compartments at the meso-carbons in a manner similar to that seen in Ni and Cd complexes of H$_4$L. [9;10]
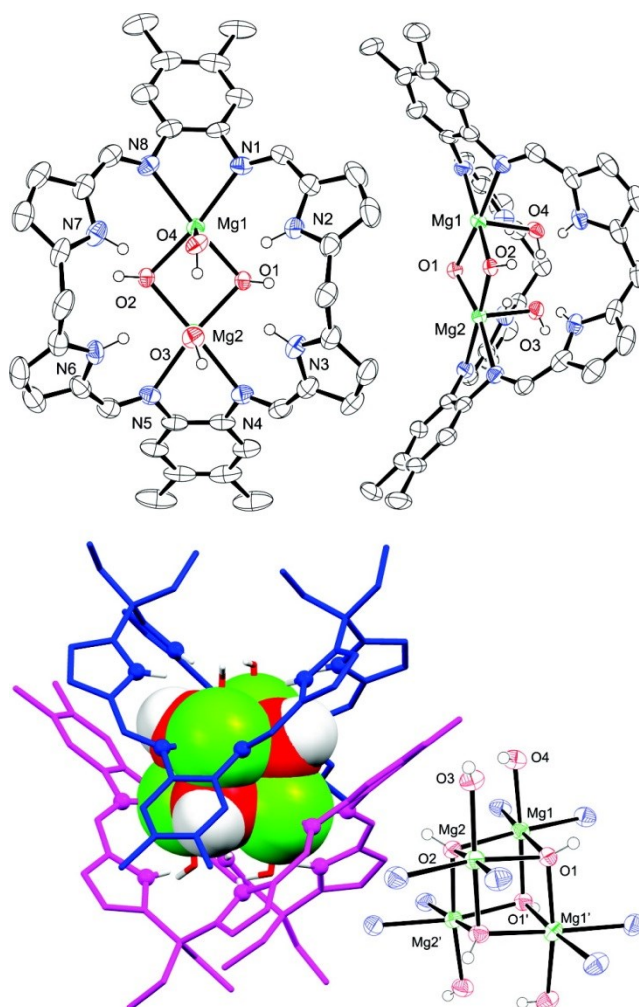

Figure 2. The X-ray crystal structure of [{Mg$_4$(μ_3-OH)$_4$(OH)$_4$}(H$_2$L)$_2$] **2**. For clarity, benzene solvent of crystallization, ethyl carbon meso-substituents, and hydrogen atoms except those involved in hydrogen-

bonding are omitted (where shown, displacement ellipsoids are drawn at 50% probability). Top: back and side-on views of the asymmetric unit that highlight the hydrogen-bonding interactions and curvature of the ligand framework; bottom left: encapsulation of the cubane core by the organic framework; bottom right: Mg cubane core showing all donor atoms. Selected bond lengths (Å) and angles (°): Mg1–O1, 2.091(2); Mg1–O1′, 2.049(2); Mg1–O2, 2.059(2); Mg1–O4, 2.065(2); Mg1–N1, 2.195(2); Mg1–N8, 2.240(3); Mg2–O3, 2.020(2); Mg2–O2′, 2.058(2); Mg2–N4, 2.264(3); Mg2–N5, 2.216(3); Mg1···Mg2, 3.040(1); Mg1–O1–Mg2, 94.00(8); Mg1–O2–Mg2, 94.06(8); O1–Mg1–O4, 170.06(9); O2–Mg2–O3, 170.25(9); O1–Mg1–O2, 84.60(8); O1–Mg2–O2, 84.34(8).

This bimetallic structure is stabilized through a variety of reinforcing hydrogen-bonding interactions between the pyrrole hydrogens and both bridging and terminal hydroxides (N…O 2.734(3) to 3.270(3) Å) and an internal hydrogen bond between the two terminal hydroxides (O3···O4 2.605(3) Å); all of these hydrogens were located in the difference Fourier map and refined with appropriate restraints. The octahedral coordination sphere of Mg1 is completed by a symmetry-related oxygen donor from a μ^3-OH group so forming the Mg cubane through the orthogonal assembly of two binuclear $Mg_2(OH)_4(H_4L)$ structural motifs. The encapsulation of the Mg hydroxide core by the organic framework results in an overall 'tennis ball' topology, similar to those seen by Rebek and co-workers in spontaneously-assembled C-shaped glycouril capsules,[11] although the cavity prescribed by the framework in **2** is clearly much smaller as a consequence of encapsulation.

The tennis-ball structure of **2** seen in the solid state appears to be retained in solution. The ^{1}H NMR spectrum of **2** (Fig. S2) displays a broad resonance at 10.6 ppm that is attributable to hydrogen-bonded NH/OH protons, and is a feature that is absent in the ^{1}H NMR spectrum of **1.THF**. Furthermore, the imine resonance at 7.98 ppm in **2** has shifted from 7.71 ppm in **1.THF**. Significantly, two environments are seen for the *meso*-ethyl groups at 2.40 and 2.18 ppm (CH_2) and 1.03 and 0.56 ppm (CH_3) and which are reflected in the ^{13}C NMR spectrum with resonances at 26.36 and 25.38 ppm (CH_2) and 8.49 and 7.92 ppm (CH_3). This dissimilarity of the ethyl groups implies a rigid bowl-shaped structure is adopted in which the ethyl groups are oriented endo- and exo- to the encapsulated cubane. Significantly, the NOESY spectrum of **2** displays NOE between the pyrrole protons (6.58 and 6.08) and the aryl methyl protons (2.08 ppm, Fig. S3). Both of these interactions indicate that the macrocyclic environment in solution is similar to that seen in the solid state.

The IR spectrum also supports the presence of OH and NH groups with absorptions seen at 3440 and 3280 cm^{-1} and the ESI mass spectrum displays a molecular ion at *m/z* 1665 (9%).

The bulk formation of **2** by intentional hydrolysis of **1.THF** was investigated and it was found that the addition of 4.7 equivalents of water to **1.THF** in benzene resulted in the precipitation of pure **2** as a bright yellow solid in a 45 % yield. Furthermore, the ^{1}H NMR spectrum of the filtrate showed the presence of **2** and free macrocycle H_4L only, in a 1.0:1.5 ratio, and indicates that upon hydrolysis **1.THF** undergoes

predominantly sole conversion to **2**. On standing in solution under aerobic conditions, **2** decomposes slowly to H_4L (25% after 48 h, Fig. S4), but is stable indefinitely in the solid state.

Cubanes are an important class of cluster compound, with Fe_4S_4 cubanes playing central electron transport and storage roles in biology and forming the basis of many FeS enzymes such as in nitrogenases.[12] Furthermore, transition metal and mixed-metal cubanes are current synthetic targets due to the identification of a Ca-Mn oxo cubane core at the oxygen evolving center of Photosystem II (Fig. 3),[13] as well as being of interest as single molecule magnets.[14] Magnesium cubanes usually comprise four magnesium centers occupying opposing corners of a cube that are bridged by μ_3-N-imido or μ_3-O-alkoxy substituents (Fig. 3); the magnesium cations are octahedral or tetrahedral depending on the ligands used.[15] Of the sixteen known structures of discrete Mg_4O_4 cubanes,[16] none employ nitrogen donor ligands to complete the coordination sphere of the metal in the $[M_4O_4]$ cubane core (M = Group 2), in contrast to that seen in transition metal analogues. The composition of the cubane core in **2** is also unique in that it contains only bridging and terminal OH groups (Mg-O 2.020(2) – 2.065(2) Å). To our knowledge, structurally-characterized cubanes in which the vertices are solely hydroxides are unknown, as are those with terminal hydroxides.[16] Furthermore, there is only a single structure reported that incorporates a Mg-μ-OH-Mg motif, in this case as part of a face-shared methoxy-magnesium double cubane.[17] The Mg-μ-OH bond distances in **2** (2.049(2)- 2.095(2) Å) are within the ranges reported for μ^3-OH (2.0030(16)-2.1208(15) Å) and μ^2-OH (1.951(6) – 2.093(2) Å) bond distances such as those found in closely-related magnesium alkoxycubanes.
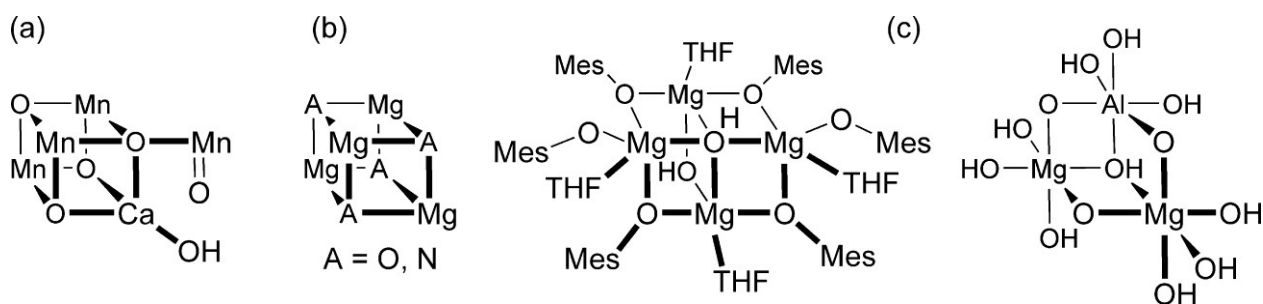

Figure 3. Representative examples of metal cubanes: (a) oxygen evolving center of Photosystem II; (b) Mg alkoxide or amide cubane; (c) theoretical models for brucite and layered double-hydroxide minerals

The Mg(OH) cubane in **2** has potential relevance to the mineralization of $Mg(OH)_2$ to form materials such as brucite, which contains infinite $[Mg(OH)_4]$ sheets, or layered double hydroxides (LDHs) such as hydrotalcite $Mg_6Al_2(CO_3)(OH)_{16} \cdot 4(H_2O)$. Furthermore, metal oxide nanoparticles, LDHs, and thin metal oxide films have potential as functional and optical materials, and in catalysis, and can be synthesized using a 'bottom-up' approach by the controlled hydrolysis of Mg alkyls or alkoxide clusters.[18] The formation and stability of various Mg hydroxide clusters related to Al-Mg LDHs and brucite minerals has been evaluated by DFT and

compared to experimental findings (Fig 3c), and contain structural motifs similar to those in **2**.[19] As such, the formation of the cubane in **2** represents a possible structural motif on the pathway to magnesium hydroxide materials that has been stabilized through encapsulation by the macrocyclic framework.

We have shown that hydrolysis of the bimetallic magnesium Pacman complex **1.THF** results in the formation of a new magnesium hydroxide cubane **2** in which two, orthogonally-oriented macrocycles encapsulate the unusual core in a tennis-ball motif. It is hoped that the macrocycle and its variants have the potential to envelop and stabilize other metal clusters through a combination of dative and hydrogen-bonding interactions and that this may lead to the generation of new encapsulated materials and reagents.

References

[1] Conn, M. M.; Rebek Jr, J., *Chem. Rev.* **1997,** 97, 1647; Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek Jr, J., *Angew. Chem. Int. Ed.* **2002,** 41, 1488; Vriezema, D. M.; Comellas Aragones, M.; Elemans, J. A. A. W.; Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M., *Chem. Rev.* **2005,** 105, 1445; Purse, B. W.; Rebek Jr, J., *Proc. Nat. Acad. Sci.* **2005,** 102, 10777; Kleij, A. W.; Reek, J. N. H., *Chem. Eur. J.* **2006,** 12, 4218; Ajami, D.; Rebek Jr, J., *Proc. Nat. Acad. Sci.* **2007,** 104, 16000; Dalgarno, S. J.; Power, N. P.; Atwood, J. L., *Coord. Chem. Rev.* **2008,** 252, 825; Klosterman, J. K.; Yoshizawa, M.; Fujita, M., *Angew. Chem. Int. Ed.* **2009,** 48, 3418; Jin, P.; Dalgarno, S. J.; Atwood, J. L., *Coord. Chem. Rev.* **2010,** 254, 1760.

[2] Branda, N.; Wyler, R.; Rebek Jr, J., *Science* **1994,** 263, 1267; Meissner, R. S.; Rebek Jr, J.; de Mendoza, J., *Science* **1995,** 270, 1485; Kang, J.; Rebek Jr, J., *Nature* **1996,** 382; MacGillivray, L. R.; Atwood, J. L., *Nature* **1997,** 389, 469; Rivera, J. M.; Martín, T.; Rebek Jr, J., **1998,** 279, 1021; Gibb, C. L. D.; Gibb, B. C., *J. Am. Chem. Soc.* **2006,** 128, 16498; Hardie, M. J., *Chem. Soc. Rev.* **2010,** 39, 516.

[3] Fujita, M.; Oguro, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Oguro, K., *Nature* **1995,** 378, 469; Caulder, D. L.; Powers, R. E.; Parac, T. N.; Raymond, K. N., *Angew. Chem. Int. Ed.* **1998,** 37, 1840; Caulder, D. L.; Raymond, K. N., *Acc. Chem. Res* **1999,** 32, 975; Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B., *Acc. Chem. Res* **2005,** 38, 371; Mal, P.; Schultz, D.; Beyeh, H.; Rissanen, K.; Nitschke, J. R., *Angew. Chem. Int. Ed.* **2008,** 47, 8297.

[4] Kang, J.; Rebek Jr, J., *Nature* **1997,** 385, 50; Merlau, M. L.; del Pilar Mejia, M.; Nguyen, S. T.; Hupp, J. T., **2001,** 40, 4239; Leung, D. H.; Fiedler, D.; Bergman, R. G.; Raymond, K. N., *Angew. Chem. Int. Ed.* **2004,** 43, 963; Yoshizawa, M.; Tamura, M.; Fujita, M., *Science* **2006,** 312, 251; Leung, D. H.; Bergman, R. G.; Raymond, K. N., *J. Am. Chem. Soc.* **2007,** 129, 2746; Pluth, M. D.; Bergman, R. G.; Raymond, K. N., *Science* **2007,** 316, 85; Natarajan, A.; Kaanumalle, L. S.; Jockusch, S.; Gibb, C. L. D.; Gibb, B. C.; Turro, N. J.; Ramamurthy, V., *J. Am. Chem. Soc.* **2007,** 129, 4132; Koblenz, T. S.; Wassenaar, J.; Reek, J. N. H., *Chem. Soc. Rev.* **2008,** 37, 247; Podkoscielny, D.; Gadde, S.; Kaifer, A. E., *J. Am. Chem. Soc.* **2009,** 131, 12876; Dube, H.; Ams, M. R.; Rebek Jr, J., *J. Am. Chem. Soc.* **2010,** 132, 9984; Wiester, M. J.; Ulmann, P. A.; Mirkin, C. A., *Angew. Chem. Int. Ed.* **2010,** 49, 2; Meeuwissen, J.; Reek, J. N. H., *Nat. Chem.* **2010,** 2, 615.

[5] Fiedler, D.; Bergman, R. G.; Raymond, K. N., *Angew. Chem. Int. Ed.* **2006,** 45, 745; Dong, V. M.; Fiedler, D.; Carl, B.; Bergman, R. G.; Raymond, K. N., *J. Am. Chem. Soc.* **2006,** 128, 14464; Kawano, M.; Kobayashi, Y.; Ozeki, T.; Fujita, M., *J. Am. Chem. Soc.* **2006,** 128, 6558; Mal, P.; Breiner, B.; Rissanen, K.; Nitschke, J. R., *Science* **2009,** 324, 1697.

[6] Sessler, J. L.; Cho, W.-S.; Dudek, S. P.; Hicks, L.; Lynch, V. M.; Huggins, M. T., *J. Porphyrins Phthalocyanines* **2003,** 7, 97; Givaja, G.; Blake, A. J.; Wilson, C.; Schröder, M.; Love, J. B., *Chem. Commun.* **2003**, 2508.

[7] Love, J. B., *Chem. Commun.* **2009**, 3154.

[8] Givaja, G.; Volpe, M.; Edwards, M. A.; Blake, A. J.; Wilson, C.; Schröder, M.; Love, J. B., *Angew. Chem. Int. Ed.* **2007,** 46, 584; Askarizadeh, E.; Bani Yaghoob, S.; Boghaei, D. M.; Slawin, A. M. Z.; Love, J. B., *Chem. Commun.* **2010,** 46, 710; Arnold, P. L.; Patel, D.; Blake, A. J.; Wilson, C.; Love, J. B., *J. Am. Chem. Soc.* **2006,** 128, 9610; Arnold, P. L.; Patel, D.; Wilson, C.; Love, J. B., *Nature* **2008,** 451, 315; Arnold, P. L.; Pécharman, A.-F.; Hollis, E.; Yahia, A.; Maron, L.; Parsons, S.; Love, J. B., *Nat. Chem.* **2010,** 2, 1056.

[9] Givaja, G.; Blake, A. J.; Wilson, C.; Schroder, M.; Love, J. B., *Chem. Commun.* **2005**, 4423; Veauthier, J. M.; Tomat, E.; Lynch, V. M.; Sessler, J. L.; Mirsaidov, U.; Markert, J. T., *Inorg. Chem.* **2005,** 44, 6736; Tomat, E.; Cuesta, L.; Lynch, V. M.; Sessler, J. L., *Inorg. Chem.* **2007,** 46, 6224; Cuesta, L.; Tomat, E.; Lynch, V. M.; Sessler, J. L., *Chem. Commun.* **2008**, 3744.

[10] Givaja, G.; Volpe, M.; Leeland, J. W.; Edwards, M. A.; Young, T. K.; Darby, S. B.; Reid, S. D.; Blake, A. J.; Wilson, C.; Wolowska, J.; McInnes, E. J. L.; Schröder, M.; Love, J. B., *Chem. Eur. J.* **2007,** 13, 3707.

[11] Wyler, R.; de Mendoza, J.; Rebek Jr, J., *Angew. Chem. Int. Ed.* **1993,** 32, 1699.

[12] Kaim, W.; Schwederski, B., *Bioinorganic chemistry: inorganic elements in the chemistry of life*. John Wiley & Sons Ltd: Chichester, 1999; Rao, P. V.; Holm, R. H., *Chem. Rev.* **2004,** 104, 527.

[13] Barber, J., *Phil. Trans. R. Soc. B* **2008,** 363, 2665.

[14] Inglis, R.; Stoumpos, C. C.; Prescimone, A.; Siczek, M.; Lis, T.; Wernsdorfer, W.; Brechin, E. K.; Milios, C. J., *Dalton Trans.* **2010,** 39, 4777.

[15] Rood, J. A.; Noll, B. C.; Henderson, K. W., *Inorg. Chem.* **2007,** 46, 7259.

[16] Allen, F., *Acta Crystallographica Section B* **2002,** 58, 380.

[17] Sathyamurthy, R.; Brumaghim, J. L.; VanDerveer, D. G., *J. Chem. Crystallogr.* **2006,** 37, 109.

[18] Abrahams, B. F.; Hudson, T. A.; Robson, R., *J. Am. Chem. Soc.* **2004,** 126, 8624; Hudson, T. A.; Berry, K. J.; Moubaraki, B.; Murray, K. S.; Robson, R., *Inorg. Chem.* **2006,** 45, 3549; Heitz, S.; Aksu, Y.; Merschjann, C.; Driess, M., *Chem. Mater.* **2010,** 22, 1376.

[19] Sato, H.; Morita, A.; Ono, K.; Nakano, H.; Wakabayashi, N.; Yamagishi, A., *Langmuir* **2003,** 19, 7120; Yan, H.; Wei, M.; Ma, J.; Li, F.; Evans, D. G.; Duan, X., *J. Phys. Chem. A.* **2009,** 113, 6133.