

Formation of unsymmetrical trinuclear metallamacrocycles based on two different cone calix[4]arene macrocyclic rings

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Abstract

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. A combination of tetrasulfonylcalix[4]arene (3-4H) together with a calix[4]arene dicarboxylate derivative 2-4H led, in the presence of $MII(NO_3)_2$ ($M = Co, Ni, Zn$), to the formation of three novel isostructural metallomacrocycles of formula $[M_3(DMF)_2(\mu_3-H_2O)-(2-2H)-3]$. The structure of the prepared coordination compounds was studied in the solid state using single crystal/powder X-ray diffraction studies. The X-ray diffraction on single crystal revealed that the structure of the obtained supramolecular complexes is composed of a trinuclear metallic cluster $[M_3]^+6$ held between one di-deprotonated molecule of $(2-2H)_2^-$ offering two carboxylate groups for binding metal cations and one tetra-deprotonated compound 34^- , where four oxygen atoms, belonging to four deprotonated phenolic moieties and three oxygen atoms coming from three SO_2 groups, are coordinated with the cluster core. Thus, an example of an easily reproducible molecular recognition pattern involving two different types of calix[4]arene based ligands, displaying different coordination moieties, and trinuclear metallic clusters, is reported here. In addition, it has been shown that the cone moieties of the calixarene also encapsulate solvent molecules.

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Keywords

Carboxylic derivatives of calix[4]arene, Coordination compounds, Metallomacrocycle, Tetrasulfonylcalix[4]arene, Trinuclear clusters

References

- [1] Yang, H.-B. Monograph in Supramolecular Chemistry: Metallomacrocycles: From Structures to Applications; The Royal Society of Chemistry: Cambridge, UK, 2017.
- [2] Saalfrank, R.W.; Stark, A.; Peters, K.; von Schnering, H.-G. The First "Adamantoid" Alkaline Earth Metal Chelate Complex: Synthesis, Structure, and Reactivity. *Angew. Chem. Int. Ed.* 1988, 27, 851-853.
- [3] Guerriero, P.; Tamburini, S.; Vigato, P.A. From mononuclear to polynuclear macrocyclic or macroacyclic complexes. *Coord. Chem. Rev.* 1995, 139, 17-243.
- [4] Leininger, S.; Olenyuk, B.; Stang, P.J. Self-Assembly of Discrete Cyclic Nanostructures Mediated by Transition Metals. *Chem. Rev.* 2000, 100, 853-907.
- [5] Fujita, M. Self-Assembly of [2]Catenanes Containing Metals in Their Backbones. *Acc. Chem. Res.* 1999, 32, 53-61.

- [6] Rojo, J.; Romero-Salguero, F.J.; Lehn, J.-M.; Baum, G.; Fenske, D. Self-Assembly, Structure, and Physical Properties of Tetranuclear ZnII and Coll Complexes of [2 × 2] Grid-Type. *Eur. J. Inorg. Chem.* 1999, 1999, 1421-1428.
- [7] Song, J.; Moon, D.; Lah, M.S. Manganese Metallamacrocycles with Various Coordination Solvents. *Bull. Korean Chem. Soc.* 2002, 23, 708-714.
- [8] Lee, S.J.; Lin, W.B. Chiral MetalloCycles: Rational Synthesis and Novel Applications. *Acc. Chem. Res.* 2008, 41, 521-537.
- [9] El-Sayed, M.; Yuan, D. Metal-Organic Cages (MOCs): From Discrete to Cage-based Extended Architectures. *Chem. Lett.* 2020, 49, 28-53.
- [10] Deiters, E.; Bulach, V.; Hosseini, M.W. Porphyrin based metallamacrocycles. *New J. Chem.* 2006, 30, 1289-1294.
- [11] Durot, S.; Flamigni, L.; Taesch, J.; Dang, T.T.; Heitz, V.; Ventura, B. Synthesis and Solution Studies of Silver(I)-Assembled Porphyrin Coordination Cages. *Chem. Eur. J.* 2014, 20, 9979-9990.
- [12] Gutsche, C.D. Calixarenes Revised: Monographs in Supramolecular Chemistry; The Royal Society of Chemistry: Cambridge, UK, 1998; Volume 6.
- [13] Ikeda, A.; Shinkai, S. Novel Cavity Design Using Calix[n]arene Skeletons: Toward Molecular Recognition and Metal Binding. *Chem. Rev.* 1997, 97, 1713-1734.
- [14] Kajiwara, T.; Iki, N.; Yamashita, M. Transition metal and lanthanide cluster complexes constructed with thiacalix[n]arene and its derivatives. *Coord. Chem. Rev.* 2007, 251, 1734-1746.
- [15] Ovsyannikov, A.; Solovieva, S.; Antipin, I.; Ferlay, S. Coordination Polymers based on calixarene derivatives: Structures and properties. *Coord. Chem. Rev.* 2017, 352, 151-186.
- [16] Taylor, S.M.; Karotsis, G.; McIntosh, R.D.; Kennedy, S.; Teat, S.J.; Beavers, C.M.; Wernsdorfer, W.; Piligkos, S.; Dalgarno, S.J.; Brechin, E.K. A Family of Calix[4]arene-Supported [MnIII2MnII2] Clusters. *Chem. Eur. J.* 2011, 17, 7521-7530.
- [17] Kajiwara, T.; Kobashi, T.; Shinagawa, R.; Ito, T.; Takaishi, S.; Yamashita, M.; Iki, N. Highly Symmetrical Tetranuclear Cluster Complexes Supported by p-tert-Butylsulfonylcalix[4]arene as a Cluster-Forming Ligand. *Eur. J. Inorg. Chem.* 2006, 2006, 1765-1770.
- [18] Iki, N.; Kumagai, H.; Morohashi, N.; Ejima, K.; Hasegawa, M.; Miyanari, S.; Miyano, S. Selective oxidation of thiacalix[4]arenes to the sulfinyl- and sulfonylcalix[4]arenes and their coordination ability to metal ions. *Tetrahedron Lett.* 1998, 39, 7559-7562.
- [19] Mislin, G.; Graf, E.; Hosseini, M.W.; De Cian, A. Sulfone-calixarenes: A new class of molecular building block. *J. Chem. Soc. Chem. Commun.* 1998, 1345-1346.
- [20] Bi, Y.; Du, S.; Liao, W. Thiacalixarene-based nanoscale polyhedral coordination cages. *Coord. Chem. Rev.* 2014, 276, 61-72.
- [21] Lamouchi, M.; Jeanneau, E.; Novitchi, G.; Luneau, G.; Brioude, A.; Desroches, C. Polynuclear Complex Family of Cobalt(II)/Sulfonylcalixarene: One-Pot Synthesis of Cluster Salt [Co14II]+[Co4II]- and Field-Induced Slow Magnetic Relaxation in a Six-Coordinate Dinuclear Cobalt(II)/Sulfonylcalixarene Complex. *Inorg. Chem.* 2014, 53, 63-72.
- [22] Du, S.; Hu, C.; Xiao, J.-C.; Tana, H.; Liao, W. A giant coordination cage based on sulfonylcalix[4]arenes. *Chem. Commun.* 2012, 48, 9177-9179.
- [23] Xiong, K.; Jiang, F.; Gai, Y.; He, Z.; Yuan, D.; Chen, L.; Su, K.; Hong, M. Self-Assembly of Thiacalix[4]arene-Supported Nickel(II)/Cobalt(II) Complexes Sustained by in Situ Generated 5-Methyltetrazolate Ligand. *Cryst. Growth. Des.* 2012, 12, 3335-3341.
- [24] Geng, D.; Han, X.; Bi, Y.; Qin, Y.; Li, Q.; Huang, L.; Zhou, K.; Song, L.; Zheng, Z. Merohedral icosahedral M48 (M = ¼ Coll, NiII) cage clusters supported by thiacalix[4]arene. *Chem. Sci.* 2018, 9, 8535-8541.
- [25] Shi, C.; Chen, M.; Han, X.; Bi, Y.; Huang, L.; Zhou, K.; Zheng, Z. Thiacalix[4]arene-supported tetradecanuclear cobalt nanocage cluster as precursor to synthesize CoO/Co9S8@CN composite for supercapacitor Application. *Inorg. Chem. Front.* 2018, 5, 1329-1335.
- [26] Bi, Y.; Xu, G.; Liao, W.; Du, S.; Wang, X.; Deng, R.; Zhang, H.; Gao, S. Making a [Co24] metallamacrocycle from the shuttlecock-like tetranuclear cobalt-calixarene building blocks. *Chem. Commun.* 2010, 46, 6362-6364.
- [27] Klein, C.; Graf, E.; Hosseini, M.W.; De Cian, A.; Kyritsakas, N. Design and Structural Analysis of Metallamacrocycles Based on Zinc Halides and a V-Shaped Bimonodentate Ligand of the Cyclophane Type. *Eur. J. Inorg. Chem.* 2003, 7, 1299-1302.
- [28] Ehrhart, J.; Planeix, J.-M.; Kyritsakas-Gruber, N.; Hosseini, M.W. Synthesis and structural studies of metallamacrotricycles based on a metacyclophane in 1,3-alternate conformation bearing four imidazolyl units. *Dalton Trans.* 2009, 14, 2552-2557.
- [29] Ehrhart, J.; Planeix, J.-M.; Kyritsakas-Gruber, N.; Hosseini, M.W. Molecular tectonics: Formation and structural studies on a 2-D directional coordination network based on a non-centric metacyclophane based tecton and zinc cation. *Dalton Trans.* 2010, 39, 2137-2146.

- [30] Chernova, E.F.; Ovsyannikov, A.S.; Ferlay, S.; Solovieva, S.E.; Antipin, I.S.; Konovalov, A.I.; Kyritsakas, N.; Hosseini, M.W. Molecular tectonics: From a binuclear metallamacrocycle to a 1D isostructural coordination network based on tetracyanomethyl[1.1.1.1]metacyclophane and a silver cation. *Mendeleev Commun.* 2017, 27, 260-262.
- [31] Lesińska, U.; Bocheńska, M. Lower-Rim-Substituted tert-Butylcalix[4]arenes; Part IX: One-Pot Synthesis of Calix[4]arene-Hydroxamates and Calix[4]arene-Amides. *Synthesis* 2006, 16, 2671-2676.
- [32] Hallale, O.; Bourne, S.A.; Koch, K.R. Metallamacrocyclic complexes of Ni(II) with 3,3,3',3'-tetraalkyl-1,4'-aroylbis(thioureas): Crystal and molecular structures of a 2:2 metallamacrocycle and a pyridine adduct of the analogous 3:3 complex. *CrystEngComm* 2005, 7, 161-166.
- [33] Ferrer, M.; Gutierrez, A.; Mounir, M.; Rossell, O.; Ruiz, E.; Rang, A.; Engeser, M. Self-Assembly Reactions between the Cis-Protected Metal Corners (N–N)MII (N–N = Ethylenediamine, 4,4'-Substituted 2,2'-Bipyridine; M = Pd, Pt) and the Fluorinated Edge 1,4-Bis(4-pyridyl)tetrafluorobenzene. *Inorg. Chem.* 2007, 46, 3395-3406.
- [34] Burkill, H.A.; Robertson, N.; Vilar, R.; White, A.J.P.; Williams, D.J. Synthesis, Structural Characterization, and Magnetic Studies of Polynuclear Iron Complexes with a New Disubstituted Pyridine Ligand. *Inorg. Chem.* 2005, 44, 3337-3346.
- [35] Granzhan, A.; Schouwey, C.; Riis-Johannessen, T.; Scopelliti, R.; Severin, K. Connection of Metallamacrocycles via Dynamic Covalent Chemistry: A Versatile Method for the Synthesis of Molecular Cages. *J. Am. Chem. Soc.* 2011, 133, 7106-7115.
- [36] Shan, N.; Vickers, S.J.; Adams, H.; Ward, M.D.; Thomas, J.A. Switchable electron-transfer processes in a mixed-valence, kinetically locked, trinuclear Ru(II) metallamacrocycle. *Angew. Chem. Int. Ed.* 2004, 43, 3938-3941.
- [37] Rouge, P.; Silva Pires, V.; Gaboriau, F.; Dassonville-Klimpt, A.; Guillon, J.; Da Nascimento, S.; Leger, J.-M.; Lescoat, G.; Sonnet, P. Antiproliferative effect on HepaRG cell cultures of new calix[4]arenes. *J. Enz. Inhib. Med. Chem.* 2010, 25, 216-227.
- [38] Hosseini, A.; Taylor, S.; Accorsi, G.; Armaroli, N.; Reed, C.A.; Boyd, P.D.W. Calix[4]arene-Linked Bisporphyrin Hosts for Fullerenes: Binding Strength, Solvation Effects, and Porphyrin-Fullerene Charge Transfer Bands. *J. Am. Chem. Soc.* 2006, 128, 15903-15913.
- [39] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H.J. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *Appl. Cryst.* 2009, 42, 339-341.
- [40] Sheldrick, G.M. SHELXT: Integrating space group determination and structure solution. *Acta Crystallogr.* 2015, 71, 3-8.
- [41] Sheldrick, G.M. A Short History of SHELX. *Acta Crystallogr.* 2007, 64, 112-122.
- [42] Macrae, C.F.; Edgington, P.R.; McCabe, P.; Pidcock, E.; Shields, G.P.; Taylor, R.; Towler, M.; Van De Streek, J. Visualization and analysis of crystal structures. *J. Appl. Crystallogr.* 2006, 39, 453-457.
- [43] Guzei, I.A. An idealized molecular geometry library for refinement of poorly behaved molecular fragments with constraints. *J. Appl. Crystallogr.* 2014, 47, 806-809. Available online: <https://www.ccdc.cam.ac.uk/structures/> (accessed on 27 March 2020).
- [44] Wang, S.; Hang, X.; Zhu, X.; Han, H.; Zhang, G.; Liao, W. 1D morning glory-like calixarene-based coordination polymers as a support for Au/Ag nanoparticles. *Polyhedron* 2017, 130, 75-80.
- [45] Katsenis, A.D.; Kessler, V.G.; Papaefstathiou, G.S. High-spin Ni(II) clusters: Triangles and planar tetranuclear complexes. *Dalton Trans.* 2011, 40, 4590-4598.
- [46] Schmitz, S.; van Leusen, J.; Izarova, N.V.; Bourone, S.D.M.; Ellern, A.; Kögerler, P.; Monakhov, K.Y. Triangular {Ni₃} coordination cluster with a ferromagnetically coupled metal-ligand core. *Polyhedron* 2018, 144, 144-151.