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Nanospheric $[M_{20}(OH)_{12}(maleate)_{12}(Me_2NH)_{12}]^{4+}$ Clusters (M = Co, Ni) with O_h Symmetry

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Supporting Information

ABSTRACT: Nanospheric hydroxo-bridged clusters of $[M_{20}(OH)_{12}(maleate)_{12}(Me_2NH)_{12}](BF_4)_3(OH)\cdot nH_2O$ (M = Co (**1**), Ni (**2**)) with O_h symmetry were afforded under hydrothermal condition with $Co(BF_4)_2\cdot 6H_2O$/$Ni(BF_4)_2\cdot 6H_2O$ and fumaric acid in a DMF/EtOH mixed solvent. They are characterized by elemental analysis, IR, and X-ray diffraction. X-ray single crystal diffraction analyses show that these two complexes are isostructural containing an ideally cubic M_8 core in that each two M atoms are doubly bridged at the edges by one OH^- and one maleate, while these OH^- and maleate groups are coordinated further by exterior identical 12 M atoms which construct a perfect M_{12} icosahedron to encapsulate the cubic core. To our knowledge, such large clusters with O_h symmetry are seldom. The variable-temperature magnetic susceptibility studies reveal that these two isostructures exhibit antiferromagnetic interactions.

The development of nanosized polynuclear coordination clusters is motivated by their aesthetical structures and potential applications in metalloenzyme models, novel catalysts, biosensors, and optoelectronic nanodevices.[1−5] The properties of nanoparticles may exhibit a strong size dependency, different from those of the corresponding bulk materials and the lower nuclearity clusters.[6−9] So people are deviated to the exploration of the molecular structure of nanocluster and its physical−chemical properties as well as the size and shape control of cluster. These investigations can result in precise tuning of electronic, optical, magnetic, and catalytic properties.[10−12] A variety of fascinating nanosized clusters based on alkynyl,[13] carbon monoxide,[14] and chalcogen[15] ligands were reported with aesthetically pleasing molecular structures, for example, fullerene-like clusters with high symmetry. Among the subgroups of nanosized cluster, one is the oxo-bridged transition-metal clusters which would show special electronic or magnetic properties.[16] The oxide/hydroxide are good bridging groups to aggregate metals into nanosized clusters. For the past four decades, these species have been studied as precursors for metal−oxide nanoparticles. The most impressive result is the isolation of giant clusters, consisting of Fe_{64},[17] Co_{36},[18] Ni_{24},[19] Mn_{84},[20] Cu_{44},[21] E_{r60},[22] $Mn_{28}Cu_{17}$,[23] and $Ni_{54}Gd_{54}$.[24] Strategies for their synthesis are usually based on shielded ligands/multidentate ligands which can stabilize large-sized clusters and inhibit the uncontrollable cluster growth and the use of hydrolysis reactions for obtaining both oxo- and hydroxo-containing clusters in the presence of carboxylate groups. Of course, suitable terminal ligand is a primary part to protect high-nuclearity clusters. In addition, the symmetry of cluster would affect the shape of molecule and its lattice packing and possibly further affect the properties of the solid state.[12e] Although some highly symmetric metallosupramolecules have been developed,[25−28] the highly symmetric clusters reported are relatively rare.[29]

Here two isostructural nanospheric icosanuclear clusters of $[M_{20}(OH)_{12}(maleate)_{12}(Me_2NH)_{12}](BF_4)_3(OH)\cdot nH_2O$ (M = Co (**1**), Ni (**2**)), supported by the simple ligand of maleate, are reported. They were obtained by hydrothermal reaction of $Co(BF_4)_2\cdot 6H_2O$/$Ni(BF_4)_2\cdot 6H_2O$ and fumaric acid in a 1:5 (v:v) DMF/EtOH mixed solvent (total of 12 mL) at 160 °C for 72 h. In the reactive system, the fumarate transfers into the maleate configuration to participate in coordination. Normally this transferration temperature is higher (250−300 °C). The hydrolysis of *N*,*N*′-dimethylformamide (DMF) results in the formation of dimethylamine, which performs as a terminal ligand to stabilize the cluster. The hydrolysis of DMF is usually observed with drastic heating and/or with the presence of metal ions.[30] These two complexes are characterized by elemental analysis, IR, and X-ray diffraction (XRD) (seeing Supporting Information). XRD analyses show that they are isostructural, crystallized in the cubic symmetry with space group *Pm*-3*n*, and consist of a tetracationic spherical cluster $[M_{20}(OH)_{12}(maleate)_{12}{-}(Me_2NH)_{12}]^{4+}$ with three BF_4^- and one OH^- groups serving as counterions (Figure 1). As an example, only the structure of **1** is discussed in detail. There are two crystallographically independent Co^{2+} centers in **1**. Co1 and its symmetry-related atoms are doubly bridged by 12 OH^- and 12 maleate groups, respectively, to form a cubic Co_8 core, while these OH^- and maleate groups are further bridged by exterior 12 symmetry-related Co2 atoms, resulting in the cation sphere of $[Co_{20}(OH)_{12}(maleate)_{12}(Me_2NH)_{12}]^{4+}$ in which a cubic Co_8 core is encapsulated by an ideally icosahedral Co_{12} sphere. Hydroxo group performs as a μ_3-bridge to link two Co1 atoms and one Co2 atom, while maleate ligand performs as a μ_5-$\kappa^2O{:}\kappa^2O'{:}\kappa^1O''{:}\kappa^1O'''$ coordination mode to bridge two Co1 and three Co2 atoms (Figure S1, Supporting Information). The 20 Co^{2+} centers are all six-coordinated and in distorted octahedral coordination. Co1 is coordinated by three μ_3-OH groups and three carboxylate oxygen atoms from a different

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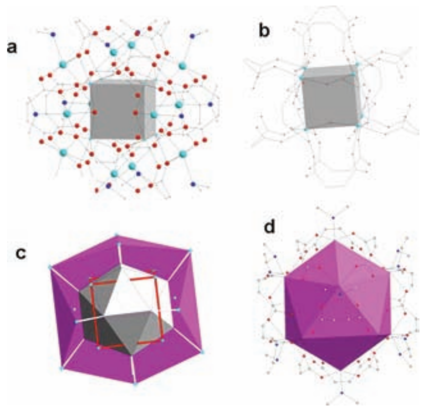

Figure 1. (a) Spherical $[M_{20}(OH)_{12}(maleate)_{12}(Me_2NH)_{12}]^{4+}$ cation highlighting the cubic M_8 core: cyan, Co; red, O; light gray, C; blue, N. (b) M_8 cube constructed by bridging hydroxide and maleate groups. (c) Three concentric polyhedra: purple, outer M_{12} icosahedron; light gray, O_{12} icosahedron; red, M_8 cube. (d) Perfect icosahedron of outer M_{12}.

maleate, while Co2 is coordinated by one μ_3-OH, four carboxylate oxygen atoms from different maleate groups, and one nitrogen atom from terminal dimethylamine. The Co1−O (μ_3-OH, 2.09 Å; carboxylate κ^2O, 2.123 Å), Co2−O (μ_3-OH, 2.189 Å; carboxylate κ^2O, 2.109 Å; carboxylate κ^1O, 2.072 Å) and Co2−N (termial dimethylamine, 2.155 Å) distances are within the ranges expected for such coordination.

Exactly, the inner Co_8 cube can be formulated as $[Co_8(OH)_{12}]$ if the bridging μ_3-OH groups at the edges are taken into consideration. Each μ_3-OH group in the cubic $[Co_8(OH)_{12}]$ structure is attached to one exterior Co atom of an icosahedral Co_{12}. So, the inner $[Co_8(OH)_{12}]$ cube can be treated as a subpolyhedral template to direct the formation of outer 12 nuclear icosahedron. Surely, the bridging maleate groups are also in a cubic arrangement around the $[Co_8(OH)_{12}]$ cube. The Co−Co distance in the edge (linked by μ_3-OH) is about 3.78 Å, and the Co−$O_{hydroxo}$−Co angle is 129.6°. This angle value is much larger than the normal values of Co−$O_{hydroxo}$−Co (90−110°). The cube-like Co_8 core is also observed in the larger nanosphere $\{Co_{32}\}$[31] cluster in which the Co_8 cube is encapsulated by Co_{24} sodalite cage, but these Co atoms in the Co_8 cube are not bridged to each other by any type of bridging ligand, and the Co−Co distance in the edge (4.62 Å) is larger than the corresponding value in **1**. The smaller Co−Co distance in inner $[Co_8(OH)_{12}]$ cube of **1** would match the size of outer 12 Co icosahedron.

To further understand the overall structure, a geometric anatomy of **1** is necessary. Two sets of Co atoms, Co_8 and Co_{12}, construct a perfect cubic and an icosahedral polyhedron, respectively, which are concentric. Moreover, paying attention on the 12 bridging μ_3-OH groups, these protonated O atoms construct a regular icosahedron, which is also concentric with the above-mentioned two sets of Co polyhedra. So there are three concentric polyhedra, the inner cubic Co_8, the middle icosahedral O_{12}, and the outer icosahedral Co_{12} polyhedra, each of which retains the highest degree of symmetry.

These two complexes are keplerate-type clusters with high symmetry. The cis-conformation of maleate would fit into the formation of such a nanospherical structure. The diameter of the spherical unit ($C_{methyl}\cdots C_{methyl}$) is ∼15.7 Å, which is the same order of magnitude as those of the smallest nanoparticles. In the solid states of **1** and **2**, molecules present a close packing with body centered cubic lattices in which each molecule is surrounded by eight nearest neighbors placed at the vertices of a cube. These also support the conclusion that the highest symmetries would result in nearly spherical nature of molecule, while the cubic lattice would result from the spherical nature of these molecules.[32] As we know, these two clusters are the first examples of Co and Ni complexes with the highest symmetry.

The temperature-dependent magnetic susceptibility of **1** and **2** were investigated in 2−300 K with a 1000 Oe applied field (Figure 2). The $\chi_M T$ value of complex **1** at 300 K is 55.77 cm^3 mol^{-1} K corresponding to 20 noninteracting S_i = 3/2 centers with g = 2.45, which is much larger than the spin-only values of 20 isolated high-spin d^7 ions (37.50 cm^3 mol^{-1} K), due to the strong orbital contributions of the distorted octahedral Co^{2+} ions. As the temperature is lowered, the $\chi_M T$ value decreases gradually to a minimum of 12.54 cm^3 mol^{-1} K at 2 K. The temperature dependence of molar susceptibility in 30−300 K is well described by a Curie−Weiss law of $1/\chi_M = (T - \theta)/C$, with Curie constant C = 61.73 cm^3 mol^{-1} K (approximating to 20 S_i = 3/2 centers with g = 2.45) and Weiss constant θ = −30.16 K, which indicates an antiferromagnetic interaction between the metal centers in Co_{20} clusters. For **2**, at 300 K the value of the product $\chi_M T$ is ca. 24.42 cm^3 mol^{-1} K. We assume that this value corresponds to that for 20 noninteracting S_i = *1* centers with g = 2.21. $\chi_M T$ decreases steadily to 20.39 cm^3 mol^{-1} K at 22K, and then it increases sharply to a maximum value of 25.44 cm^3 mol^{-1} K at 3.5K. Below this temperature it falls again to 23.98 cm^3 mol^{-1} K at 2K, possibly due to intercluster antiferromagetic interactions. In the range of 25 − 300 K, the temperature dependence of molar susceptibility is well described by a Curie−Weiss Law of $1/\chi_M = (T - \theta)/C$ with Curie constant C = 25.10 cm^3 mol^{-1} K (approximating to 20 S_i = 1 centers with g = 2.25) and Weiss constant θ = −6.69 K, which indicates an antiferromagnetic interaction between the metal centers in Ni_{20} clusters. Below 10 K, there is a split-up between a zero-field-cooled−field-cooled (ZFC−FC) plot, while the alternating current (ac) susceptibility signals are slightly frequency dependent in this temperature range (Figures S5 and S6, Supporting Information). These magnetic phenomena could indicate the presence of spin canting behavior. More in-depth magnetic studies are still underway.

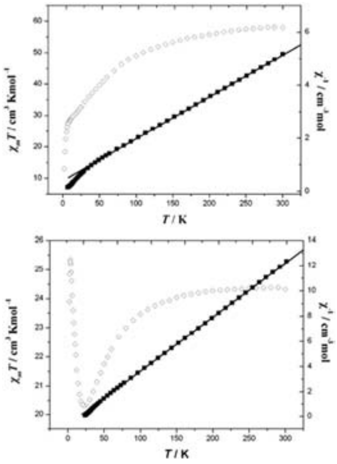

Figure 2. Plots of temperature dependence of $\chi_M T$ and $1/\chi_M$ of **1** (top) and **2** (bottom).

In summary, two isostructural icosanuclear clusters of Co and Ni, supported by the simple maleate groups, are developed through hydrolysis reaction. The hydroxide performs as a good bridging group to aggregate metals into nanosized clusters, while here the Me_2NH from the hydrolysis of DMF is important as a terminally stabilizing reagent. These two clusters are also prepared by the reaction of maleate with metal tetrafluoroborate in DMF/EtOH, whereas they are not afforded by using directly maleate and Me_2NH in the reactive system. So it seems plausible that the hydrolysis process of DMF is indispensable for the formation of such highly symmetrical icosanuclear clusters. We tried to use other cobalt/nickel salts instead of cobalt/nickel tetrafluoroborate to prepare these two complexes but were unsuccessful. Perhaps the BF_4^- anion also plays an extentsive role in the hydrolysis of metal ions for these two nanospheric structures. To our knowledge, such large clusters with O_h symmetry are seldom. Further research on more interesting clusters is proceeding using the hydrolysis reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic method, powder XRD, additional structural figures, magnetic characterization, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268.

(2) Thomas, L.; Lionti, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. *Nature* **1996**, *383*, 145.

(3) Li, G.; Lei, Z.; Wang, Q.-M. *J. Am. Chem. Soc.* **2010**, *132*, 17678.

(4) Kamat, P. V. *J. Phys.Chem. B* **2002**, *106*, 7729.

(5) Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, 251.

(6) Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239.

(7) Gatteschi, D.; Sessoli, R.; Villain, J. *Molecular Nanomagnets*; Oxford University Press: New York, 2007.

(8) Schmid, G. *Clusters and Colloids: From Theory to Applications*; VCH: Weinheim, Germany, 1994.

(9) Timco, G. A.; Carretta, S.; Troiani, F.; Tuna, F.; Pritchard, R. J.; Muryn, C. A.; McInnes, E. J. L.; Ghirri, A.; Candini, A.; Santini, P.; Amoretti, G.; Affronte, M.; Winpenny, R. E. P. *Nat. Nanotechnol.* **2009**, *4*, 173.

(10) Seo, D.; Park, J. C.; Song, H. *J. Am. Chem. Soc.* **2006**, *128*, 14863.

(11) (a) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27. (b) Corrigan, J. F.; Fuhr, O.; Fenske, D. *Adv. Mater.* **2009**, *21*, 1867.

(12) (a) Bruce, D. W.; O'Hare, D.; Walton., R. I.; *Molecular Materials*; Wiley: Hoboken, NJ, 2010. (b) Müller, A; Sarkar, S.; Shah, S. Q. N.; Bögge, H.; Schmidtmann, M.; Sarkar, S.; Kögerler, P.; Hauptfleisch, B.; Trautwein, A. X.; Schünemann, V. *Angew. Chem., Int. Ed.* **2008**, *38*, 3238. (c) Müller, A.; Todea, A. M.; van Slageren, J.; Dressel, M.; Bögge, H.; Schmidtmann, M.; Luban, M.; Engelhardt, L.; Rusu, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3857. (d) Shaw, R.; Tidmarsh, I. S.; Laye, R. H.; Breeze, B.; Helliwell, M.; Brechin, E. K.; Heath, S. L.; Murrie, M.; Ochsenbein, S.; Güdel, H.-U.; McInnes, E. J. L. *Chem. Commun.* **2004**, 1418. (e) Garlea, V. O.; Nagler, S. E.; Zarestky, J. L.; Stassis, C.; Vaknin, D.; Kögerler, P.; McMorrow, D. F.; Niedermayer, C.; Tennant, D. A.; Lake, B.; Qiu, Y.; Exler, M.; Schnack, J.; Luban, M. *Phys. Rev. B.* **2006**, *73*, 024414.

(13) Rais, D.; Yau, J.; Mingos, D. M. P.; Vilar, R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3464.

(14) Tran, N. T.; Powell, D. R.; Dahl, L. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4121.

(15) Wang, X.-J.; Langetepe, T.; Persau, C.; Kang, B.-S.; Sheldrick, G. M.; Fenske, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3818.

(16) Kong, X.-J.; Ren, Y.-P.; Long, L.-S.; Zheng, Z.; Huang, R.-B.; Zheng, L.-S. *J. Am. Chem. Soc.* **2007**, *129*, 7016.

(17) Liu, T.; Zhang, Y.-J.; Wang, Z.-M.; Gao, S. *J. Am. Chem. Soc.* **2008**, *130*, 10500.

(18) Alborés, P.; Rentschler, E. *Angew. Chem., Int. Ed.* **2009**, *48*, 9366.

(19) Ochsenbein, S. T.; Murrie, M.; Rusanov, E.; Stoeckli-Evans, H.; Sekine, C.; Güdel, H. U. *Inorg. Chem.* **2002**, *41*, 5133.

(20) Tasiopoulos, A. J.; Vinslava, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2117.

(21) Murugesu, M.; Clérac, R.; Anson, C. E.; Powell, A. K. *Inorg. Chem.* **2004**, *43*, 7269.

(22) Kong, X.-J.; Wu, Y.; Long, L.-S.; Zheng, L.-S.; Zheng, Z. *J. Am. Chem. Soc.* **2009**, *131*, 6918.

(23) Wang, W.-G.; Zhou, A.-J.; Zhang, W.-X.; Tong, M.-L.; chen, X.-M.; Nakano, M.; Beedle, C. C.; Hendrickson, D. N. *J. Am. Chem. Soc.* **2007**, *129*, 1014.

(24) Kong, X.-J.; Ren, Y.-P.; Chen, W.-X.; Long, L.-S.; Zheng, Z.; Huang, R.-B.; Zheng, L.-S. *Angew. Chem., Int. Ed.* **2008**, *47*, 2398.

(25) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502.

(26) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972.

(27) Hong, M.; Zhao, Y.; Su, W.; Cao, R.; Fujita, M.; Zhou, Z.; Chan, A. S. C. *J. Am. Chem. Soc.* **2000**, *122*, 4819.

(28) Zheng, S.-T.; Zhang, J.; Li, X.-X.; Fang, W.-H.; Yang, G.-Y. *J. Am. Chem. Soc.* **2010**, *132*, 15102.

(29) Kong, X.-J.; Long, L.-S.; Zheng, Z.; Huang, R.-B.; Zheng, L.-S. *Acc. Chem. Res.* **2010**, *43*, 201 andthe references therein.

(30) Wang, Y.; Cao, R.; Bi, W.; Li, X.; Yuan, D.; Sun, D. *Micro. Meso. Mater.* **2006**, *91*, 215.

(31) Bi, Y.; Wang, X.-T.; Liao, W.; Wang, X.; Wang, X.; Zhang, H.; Gao, S. *J. Am. Chem. Soc.* **2009**, *131*, 11650.

(32) Echeverría, J.; Casanova, D.; Llunell, M.; Alemany, P.; Alvarez, S. *Chem. Commun.* **2008**, 2717.