Inorganic Chemistry
Communication

Inorg. Chem. **2009**, *48*, 10889–10891 **10889**
DOI: 10.1021/ic901552f

A New Ni_{12} Cluster Based on Polyoxometalate Ligands

Hong-Mei Zhang,[†] Yang-Guang Li,[†] Ying Lu,[*,†] Rodolphe Clérac,[‡,§] Zhi-Ming Zhang,[†] Qiong Wu,[†] Xiao-Jia Feng,[†] and En-Bo Wang[*,†]

[†]*Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, People's Republic of China,* [‡]*CNRS, UPR 8641, Centre de Recherche Paul Pascal (CRPP), Equipe "Matériaux Moléculaires Magnétiques", 115 avenue du Dr. Albert Schweitzer, Pessac F-33600, France, and* [§]*UPR 8641, Université de Bordeaux, Pessac F-33600, France*

Received August 4, 2009

A new Ni_{12} cluster based on polyoxometalate ligands $[Ni_{12}(OH)_9WO_4(W_7O_{26}(OH))(PW_9O_{34})_3]^{25-}$ (**1**) has been assembled in aqueous solution containing $[PW_9O_{34}]^{9-}$, WO_4^{2-}, and $NiCl_2 \cdot 6H_2O$. The Ni_{12} core in **1** shows a unique three-petal flower-shaped structure composed of three Ni_4 cubane units. Magnetic investigation indicates the presence of dominantly ferromagnetic interactions within the Ni_{12} core.

The design and construction of polynuclear 3d transition-metal (TM) clusters have been the focus of recent research interest because of their potential applications in catalysis, magnetism and photochemistry.[1] Commonly, the construction of polynuclear TM clusters demands the participation of O- or N-donor ligands, which not only play the roles of stabilizing and bridging metal ions, but also act as structure-directing agent to induce the formation of aggregates with diverse nuclearities and structural features. Various organic O- or N-containing ligands have been extensively used in building polynuclear TM clusters such as carboxylate, alkoxide and pyridine.[2] Polyoxometalates (POMs), as one kind of significant metal oxide clusters with O-enriched surface, have been considered as one of excellent inorganic multidentate O-donor ligands, which can replace organic ligands to take part in the construction of polynuclear TM clusters.[3] Compared with common organic ligands, POMs with abundant topologies possesses their own structural features in size, shape and symmetry, which lead to different structure-directing roles for the formation of polynuclear TM clusters. To date, some polynuclear 3d TM clusters with unique structure and interesting properties have been synthesized by employing POMs as ligands.[4−7]

Although many different kinds of POMs have been found as ligands presenting in polynuclear TM clusters, we noticed that generally there exists only one kind of POM ligand in the same polynuclear TM clusters. The polynuclear TM clusters containing more than one kind of POM ligand are rarely reported.[8] Especially, up to now, the polynuclear 3d TM cluster with both heteropolyoxometalate and isopolyoxometalate ligands has never been reported. The combined structure-directing roles of different POM ligands might induce the formation of novel polynuclear TM clusters, which would greatly enrich the studies on polynuclear TM clusters. This idea stimulates us to design and synthesize new polynuclear TM clusters by using mixed POM ligands. At the present work, we focus on the reaction system of $[PW_9O_{34}]^{9-}$, WO_4^{2-} with nickel salts based on the following considerations. First, trivacant Keggin anion $[PW_9O_{34}]^{9-}$ is one of the most used POM ligand in the construction of polynuclear TM clusters. The strong coordination ability of this polyanion with TM ions has been well documented in many PW_9-based polynuclear TM clusters.[5,9]

---

*To whom correspondence should be addressed. E-mail: wangeb889@nenu.edu.cn (E-.B.W); luy968@nenu.edu.cn (Y.L.).

(1) (a) Brockman, J. T.; Stamatatos, T. C.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2007**, *46*, 9160. (b) Stamatatos, T. C.; Abboud, K. A.; Wernsdorfer, W.; Christou, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 884. (c) Bell, A.; Aromí, G.; Teat, S. J.; Wernsdorfer, W.; Winpeny, R. E. P. *Chem. Commun.* **2005**, 2808.

(2) (a) Stamatatos, T. C.; Abboud, K. A.; Wernsdorfer, W.; Christou, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 6694. (b) Xu, J. Y.; Qiao, X.; Song, H. B.; Yan, S. P.; Liao, D. Z.; Gao, S.; Journaux, Y.; Cano, J. *Chem. Commun.* **2008**, 6414. (c) Fang, X. K.; Kögerler, P. *Chem. Commun.* **2008**, 3396.

(3) (a) Mal, S. S.; Kortz, U. *Angew. Chem., Int. Ed.* **2005**, *44*, 3777. (b) Bassil, B. S.; Dickman, M. H.; Römer, I.; Kammer, B. V. D.; Kortz, U. *Angew. Chem., Int. Ed.* **2007**, *46*, 6192.

(4) (a) Wang, J. P.; Ma, P. T.; Shen, Y.; Niu, J. Y. *Cryst. Growth Des.* **2007**, *7*, 603. (b) Pradeep, C. P.; Long, D. L.; Kögerler, P.; Cronin, L. *Chem. Commun.* **2007**, 4254. (c) Mialane, P.; Dolbecq, A.; Marrot, J.; Rivière, E.; Sécheresse, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 3523. (d) Zhao, J. W.; Zhang, J.; Zheng, S. T.; Yang, G. Y. *Chem. Commun.* **2008**, 570.

(5) (a) Zhao, J. W.; Zhang, J.; Zheng, S. T.; Yang, G. Y. *Inorg. Chem.* **2007**, *46*, 10944. (b) Wu, Q.; Li, Y. G.; Wang, Y. H.; Wang, E. B.; Zhang, Z. M.; Clérac, R. *Inorg. Chem.* **2009**, *48*, 1606.

(6) Zhang, Z. M.; Qi, Y. F.; Qin, C.; Li, Y. G.; Wang, E. B.; Wang, X. L.; Su, Z. M.; Xu, L. *Inorg. Chem.* **2007**, *46*, 8162.

(7) Godin, B.; Chen, Y. G.; Vaissermann, J.; Ruhlmann, L.; Verdaguer, M.; Gouzerh, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 3072.

(8) (a) Zhang, Z. M.; Li, Y. G.; Wang, E. B.; Wang, X. L; Qin, C.; An, H. Y. *Inorg. Chem.* **2006**, *45*, 4313. (b) Juan, J. M. C.; Coronado, E.; Aliaga, A. F.; Mascarós, J. R. G.; Saiz, C. G.; García, C. J. G. *Inorg. Chem.* **2004**, *43*, 2689. (c) Ritorto, M. D.; Anderson, T. M.; Neiwert, W. A.; Hill, C. L. *Inorg. Chem.* **2004**, *43*, 44.

(9) (a) Kadamany, G. A. A.; Hussain, F.; Mal, S. S.; Dickman, M. H.; Laronze, N. L.; Marrot, J.; Cadot, E.; Kortz, U. *Inorg. Chem.* **2008**, *47*, 8574. (b) Kortz, U.; Mbomekalle, I. M.; Keita, B.; Nadjo, L.; Berthet, P. *Inorg. Chem.* **2002**, *41*, 6412.

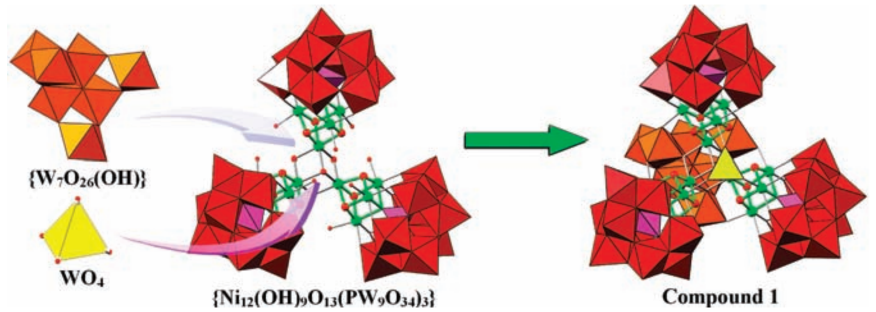

Figure 1. View of the construction of polyanion **1**.

Second, in a wider pH value range, WO_4^{2-} can aggregate into isopolyanion with diverse nuclearity depending on different pH value, which will provide isopolyanion ligand for the build of polynuclear TM clusters.[10] Moreover, the use of changeable isopolyanion by adjusting reaction pH value may increase the flexibility of the combined PW$_9$-isopolytungstate ligand system. Third, polynuclear Ni(II) clusters have attracted much attention among the family of polynuclear TM clusters due to their interesting magnetic properties. The synthesis of polynuclear Ni(II) cluster with organic ligands has blossomed in the past two decades.[11] However, the studies about the polynuclear especially high nuclear nickel clusters based on POM ligands are very limited.[8a,12] Hence, the design and synthesis of high nuclear nickel cluster based on POM ligand remains a challenge. From this reaction system, we successfully obtained a new dodecanuclear nickel cluster based on mixed heteropolyanion $[PW_9O_{34}]^{9-}$ and isopolyanion $[W_7O_{26}(OH)]^{11-}$ ligands, $[Ni_{12}(OH)_9WO_4(W_7O_{26}(OH))(PW_9O_{34})_3]^{25-}$ (**1**).[13] To the best of our knowledge, **1** represents the highest nuclearity nickel cluster based on POM ligands from a magnetic point of view.

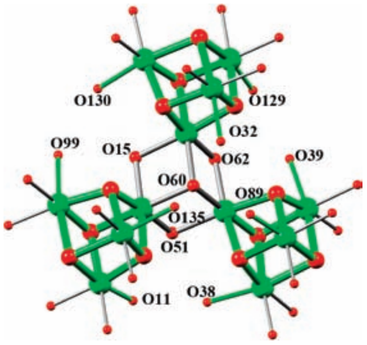

Figure 2. Ball-and-stick representation of the $[Ni_{12}(OH)_9O_{13}]^{11-}$ core in **1**. Green balls represent Ni atoms and red balls represent oxygen atoms.

The Ni$_{12}$ core in **1** shows a unique three-petal, flower-shaped structure composed of three Ni$_4$ cubane units.

The molecular structure of **1**[14] is composed of a large $[Ni_{12}(OH)_9O_{13}(PW_9O_{34})_3]^{38-}$ moiety sandwiched between a single WO$_4$ tetrahedron and a $[W_7O_{26}(OH)]^{11-}$ fragment (Figure 1). In the $[Ni_{12}(OH)_9O_{13}(PW_9O_{34})_3]^{38-}$ moiety, the central dodecanuclear nickel core $[Ni_{12}(OH)_9O_{13}]^{11-}$ is surrounded by three $[PW_9O_{34}]^{9-}$ ligands. The central Ni$_{12}$ core is formed by the condensation of three distorted [Ni$_4$O(OH)$_3$] cubane units (Figure 2). The three [Ni$_4$O(OH)$_3$] cubane units are connected by a central μ_4-O (O60) and three μ_3-O (O15, O51, O62) between adjacent [Ni$_4$O(OH)$_3$] units. In each cubane unit, the four nickel atoms are linked together by one μ_4-O atom derived from [PO$_4$] group and three μ_3-OH bridges. These OH groups are identified by the BVS calculations.[15] All the nickel atoms possess distorted octahedral coordination geometry, and the Ni−O bond lengths and O−Ni−O bond angles are in the ranges of 1.956(19)−2.229(18) Å and 80.1(7)−176.7(7)° respectively. Although some dodecanuclear nickel clusters have been reported,[16] the Ni$_{12}$ core in **1** represents the second Ni$_{12}$ cluster formed by three [Ni$_4$O$_4$] cubane units. The first example of Ni$_{12}$ clusters built by three [Ni$_4$O$_4$] cubane units is the complex

---

(10) (a) Tytko, K. H.; Glemser, O. *Adv. Inorg. Chem. Radiochem.* **1976**, *19*, 239. (b) Pope, M. T. *Heteropoly and Isopoly Oxometallates*; Springer-Verlag: Berlin, 1983.

(11) (a) Ochsenbein, S. T.; Murrie, M.; Rusanov, E.; Evans, H. S.; Sekine, C.; Güdel, H. U. *Inorg. Chem.* **2002**, *41*, 5133. (b) Khanra, S.; Weyhermüller, T.; Rentschler, E.; Chaudhuri, P. *Inorg. Chem.* **2005**, *44*, 8176. (c) Brown, E. J.; Klair, A. K. D.; Elliott, M. I.; Oates, J. E. T.; Timmins, P. L.; Walton, P. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1392.

(12) (a) Juan, J. M. C.; Coronado, E.; Mascarós, J. R. G.; García, C. J. G. *Inorg. Chem.* **1999**, *38*, 55. (b) Mbomekalle, I. M.; Keita, B.; Nierlich, M.; Kortz, U.; Berthet, P.; Nadjo, L. *Inorg. Chem.* **2003**, *42*, 5143. (c) Zheng, S.-T.; Zhang, J.; Clemente-Juan, J. M.; Yuan, D.-Q.; Yang, G.-Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 7176.

(13) Synthesis of $Na_{25}\{Ni_{12}(OH)_9WO_4[W_7O_{26}(OH)][PW_9O_{34}]_3\}\cdot 86H_2O$ (**1**): $Na_9[A\text{-}PW_9O_{34}]\cdot 7H_2O$ (0.39 mmol) was added with stirring to 30 mL $NiCl_2\cdot 6H_2O$ (2 mmol) solution. After $Na_9[A\text{-}PW_9O_{34}]\cdot 7H_2O$ was completely dissolved, $Na_2WO_4\cdot 2H_2O$ (9.09 mmol) was added. The pH value of the resulting mixture was adjusted to 7.5 with acetic acid. The mixture was refluxed for 2 h and then cooled to room temperature and filtered. The filtrate was kept at room temperature with slow evaporation for two weeks, resulting the green block crystals of **1** (yield 43% based on phosphorus). Anal. Calcd for **1**: Na, 4.94; Ni, 6.05; W, 55.29; P, 0.80. Found: Na, 5.16; Ni, 6.14; W, 55.09; P, 0.71. IR (KBr pellet, ν/cm^{-1}): 3363, 1641, 1044, 952, 899, 804 and 711 (see Figure S1 in the Supporting Information). The TG curve of **1** (Figure S2) shows a total weight loss of 13.77% in the range of 24−420 °C, which agrees with the loss of 86 crystal water molecules and 10 hydroxyls in the structure (calcd 14.07%).

(14) Crystal data of **1**: $H_{182}Na_{25}Ni_{12}O_{228}P_3W_{35}$, M_r = 11638.39, triclinic, space group $P\bar{1}$, a = 21.505(4) Å, b = 22.959(5) Å, c = 26.026(5) Å, α = 66.49(3)°, β = 74.21(3)°, γ = 62.52(3)°, V = 10392(4) Å^3, Z = 2, $R1(wR_2)$ = 0.0703 (0.1472). The data were collected at 150(2) K on a Rigaku RAXIS RAPID IP diffractometer with monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined using full-matrix least-squares on F^2. All calculations were performed using the SHELX97 program package. CSD reference number: 420702.

(15) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244.

(16) (a) Benelli, C.; Blake, A. J.; Brechin, E. K.; Coles, S. J.; Graham, A.; Harris, S. G.; Meier, S.; Parkin, A.; Parsons, S.; Seddon, A. M.; Winpenny, R. E. P. *Chem.—Eur. J.* **2000**, *6*, 883. (b) Andres, H.; Basler, R.; Blake, A. J.; Cadiou, C.; Chaboussant, G.; Grant, C. M.; Güdel, H.-U.; Murrie, M.; Parsons, S.; Paulsen, C.; Semadini, F.; Villar, V.; Wernsdorfer, W.; Winpenny, R. E. P. *Chem.—Eur. J.* **2002**, *8*, 4867.

(17) Cooper, G. J. T.; Newton, G. N.; Kögerler, P.; Long, D.-L.; Engelhardt, L.; Luban, M.; Cronin, L. *Angew. Chem., Int. Ed.* **2007**, *46*, 1340.

(18) (a) Yang, E. C.; Wernsdorfer, W.; Zakharov, L. N.; Karaki, Y.; Yamaguchi, A.; Isidro, R. M.; Lu, G. D.; Wilson, S. A.; Rheingold, A. L.; Ishimoto, H.; Hendrickson, D. N. *Inorg. Chem.* **2006**, *45*, 529. (b) Cánovas, M. M.; Helliwell, M.; Ricard, L.; Rivière, É.; Wernsdorfer, W.; Brechin, E.; Mallah, T. *Eur. J. Inorg .Chem.* **2004**, 2219.

$[Ni_{12}(trans\text{-}tachH)_6(OMe)_{12}(OAc)_9(CO_3)]^{7+}$, in which three cubane units are connected by a central carbonate anion and six acetate ligands.[17] Because several known nickel clusters formed by single $[Ni_4O_4]$ cubane core exhibit single-molecule magnet behavior,[18] the studies on the magnetic properties of the polynuclear nickel clusters assembled by multiple $[Ni_4O_4]$ cubane units might be interesting. The peripheral $[PW_9O_{34}]$ ligands exhibit the typical trivacant B-α-Keggin-type structure. Each $[PW_9O_{34}]$ moiety acts as a hepta-dentate ligand coordinating with the Ni_{12} core through the seven terminal oxygen atoms on the trivacant face.

In **1**, the WO_4 and $[W_7O_{26}(OH)]^{11-}$ units, locating in the two sides of the large $[Ni_{12}(OH)_9O_{13}(PW_9O_{34})_3]^{38-}$ moiety, are tetra-dentate and nona-dentate ligands, respectively. The tetrahedral WO_4 unit coordinates to the Ni_{12} core by a μ_4-O (O60) and three μ-O (O32, O89, O135). In most TM clusters based on POM ligands, single tetrahedral unit is PO_4 unit.[5a,9a,12a] A single WO_4 tetrahedral unit has never been found in the structure of POM-based TM clusters until now, but it has ever been found in the structure of a 1D coordination polymer $[Re_2(DMBA)_4(\mu\text{-}O,O'\text{-}WO_4)]_\infty$ synthesized from Na_2WO_4 solution.[19] The $[W_7O_{26}(OH)]^{11-}$ unit is a new heptanuclear tungstate cluster, which has been found neither as discrete cluster nor as building unit of large tungstate cluster. The unique $[W_7O_{26}(OH)]^{11-}$ unit is composed of seven WO_6 octahedra through sharing edges and corners (see Figure S3 in the Supporting Information). The $[W_7O_{26}(OH)]^{11-}$ unit coordinates to the Ni_{12} core by three μ_3-O (O15, O51, O62) and six μ-O (O11, O38, O39, O99, O129, O130).

^{31}P NMR spectrum of **1** (see Figure S4 in the Supporting Information) shows only one peak at 1.88 ppm corresponding to the three symmetry-equivalent P atoms in each B-α-$PW_9O_{34}{}^{9-}$ ligand (the $[Ni_{12}(OH)_9O_{13}(PW_9O_{34})_3]^{38-}$ moiety has a approximate C_{3v} symmetry). Because B-α-$PW_9O_{34}{}^{9-}$ itself is not stable in aqueous solution and easily transfers into other polyanions,[20] such ^{31}P NMR data suggest that **1** remains intact in aqueous solution.

The EPR spectrum of **1** at 77 K (see Figure S5 in the Supporting Information) shows a Ni(II) signal with the average $g = 2.31$. Magnetic susceptibility of **1** was investigated at 1000 Oe and from 2.0 to 300 K on a polycrystalline sample. As shown in Figure 3, the χT product at room temperature is 12.1 $cm^3\ K\ mol^{-1}$, in good agreement with the expected value for 12 uncoupled Ni(II) centers ($C = 1.00\ cm^3\ K\ mol^{-1}$, $S = 1$, $g = 2.0$ for each Ni(II) ion). When the temperature is lowered, the χT product continuously increases and reaches 23.2 $cm^3\ K\ mol^{-1}$ at 8.0 K, indicating that intramolecular ferromagnetic interactions are dominant between Ni(II) centers in the Ni_{12} core. Below 8.0 K, χT quickly drops to the 19.8 at 2.0 K, probably as a result of the presence of magnetic anisotropy (zero-field splitting of the ground state) or weak antiferromagnetic intra/inter-complex interactions. Because of the low symmetry of the Ni_{12} core (12 crystallographically independent Ni(II) sites), 21 different intracomplex magnetic interactions are present in the complex that make it impossible to model the susceptibility even with a simple Heisenberg model. Moreover, considering that all Ni−O−Ni angles within the Ni_{12} cluster are in the range of 90−105° (see Figure S6 in the Supporting Information), in which the Ni···Ni ferromagnetic exchange pathways are dominant.[12a] Thus, the attempt to model the susceptibility with a single average Ni−Ni magnetic interaction carried out, however, such a model does not work. Nevertheless, the presence of overall ferromagnetic interactions is clearly established by above data but the ground state of the complex should not be $S = 12$ as judged by the χT product observed at low temperatures that is far from the expected $S = 12$ value (78 $cm^3\ K\ mol^{-1}$). Therefore, antiferromagnetic interactions should be in competition with the ferromagnetic ones within the Ni_{12} core.

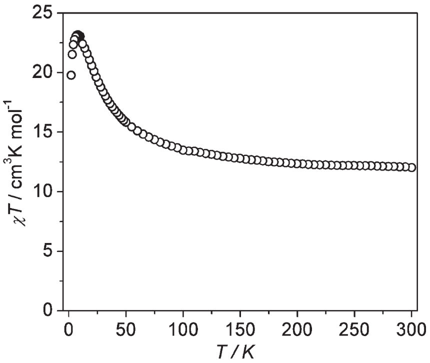

Figure 3. Temperature dependence of χT for **1** at 1000 Oe (with χ defined as M/H per Ni_{12} core).

In conclusion, the new Ni_{12} cluster **1** based on mixed heteropolyanion $[PW_9O_{34}]^{9-}$ and isopolyanion $[W_7O_{26}(OH)]^{11-}$ ligands has been successfully prepared, representing the currently highest nuclearity nickel cluster based on inorganic POM ligands from a magnetic point of view. Magnetic study shows that compound **1** exhibits dominantly ferromagnetic interactions within the Ni_{12} core. This work may suggest a new route to prepare polynuclear TM clusters based on mixed POM ligands.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (20701005 and 20901015), the Science and Technology Development Project Foundation of Jilin Province (20080120) and Science Foundation for Young Teachers of Northeast Normal University (20090406).

Supporting Information Available: X-ray crystallographic file for **1** in CIF format; IR, ^{31}P NMR and ESR spectra, TG curve, cyclic voltammogram, bond lengths and angles, BVS of the monoprotonated oxygen atoms, and structural figures of $[W_7O_{26}(OH)]^{11-}$ unit (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

---

(19) Dequeant, M. Q.; McGuire, R.; McMillin, D. R.; Ren, T. *Inorg. Chem.* **2005**, *44*, 6521.

(20) (a) Hill, C. L.; Weeks, M. S.; Schinazi, F. *J. Med. Chem.* **1990**, *33*, 2767. (b) Howell, R. C.; Perez, F. G.; Jain, S.; Horrocks, W.; Rheingold, A. L.; Francesconi, L. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 4031.