

Hydrothermal Assembly of a Novel Three-Dimensional Framework Formed by $[\text{GdMo}_{12}\text{O}_{42}]^{9-}$ Anions and Nine Coordinated Gd^{III} Cations

Chuan-De Wu, Can-Zhong Lu,* Hong-Hui Zhuang, and Jin-Shun Huang

The State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China

Received December 17, 2001

There has been extensive interest in heteropolyoxometalates, owing to their fascinating properties and great potential applications in many fields (such as, catalysis, material science, medicine, and magnetochemistry) as well as their unusual topological properties.^{1–4} Although various preparation methods have been proposed to obtain such polynuclear complexes, a “rational” synthetic method is still one of the major challenges in heteropolyoxometalatic chemistry.

One of the challenging tasks in polyoxometalatic chemistry is to find some novel units and then to link them up into larger clusters, or to one-, two-, even three-dimensional extended solid frameworks in appropriate ways. Lanthanide ions and their complexes exhibit unique spectroscopic and magnetic properties, which have wide potential applications.^{5–10} It has been well-known that the rare earth elements are highly oxophilic, and many polymolybdates have oxygen-rich compositions, suggesting that the combination of them may generate some interesting novel complexes. However, the heteropolymolybdates containing lanthanide elements remain largely unexplored. These results do not mean the polymolybdate and the lanthanide ions cannot coexist together. Contrarily, as the oxygen atoms on the surface of the polymolybdates are rather reactive, some lanthanide ions can readily incorporate into polymolybdates, which in most cases only precipitate instead of crystallize. One of the effective methods is by reacting rare earth metal salts with traditional polymolybdate or by using protecting methods using appropriate ligands.^{11–17} However, the synthesis of higher-dimensional extended solids based on lanthanides and polymolybdates is still one of the great challenges facing chemists. Recent elaboration has proven that hydrothermal reaction, which causes a reaction shifting from kinetic to thermodynamic domain compared to traditional aqueous reactions, provides a powerful tool for the synthesis of higher-dimensional oxide frameworks.¹⁸ Thus, one-pot hydrothermal synthesis provides an alternative way to the above-mentioned step-by-step aggregation process for the design of heteropolymolybdate frameworks containing lanthanide. In this communication we report the synthesis and characterization of the first three-dimensional framework, $[\text{Gd}(\text{H}_2\text{O})_3]_3[\text{GdMo}_{12}\text{O}_{42}] \cdot 3\text{H}_2\text{O}$ **1**, containing Silverton-type anions linked by gadolinium(III) cations.

A mixture of gadolinium(III) chloride (0.55 mmol, prepared from Gd_2O_3 dissolved in 35% HCl) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (0.18 g, 0.146 mmol) in 18 mL of water at low pH (0.80) was heated at 170 °C for 5 days, and the colorless crystals of complex **1** were obtained. The structural analysis¹⁹ suggests that the structure of complex **1** is a three-dimensional framework of Silverton-type anions linked by nine coordinated gadolinium(III) atoms. Two strong bands at 966 and 931 cm^{-1} in the infrared spectrum of **1** are ascribed to $\nu(\text{Mo}=\text{O})$. Multiple bands attributed to the bridging $(\text{Mo}-\text{O}-\text{Mo}(\text{Gd}))$ -group absorptions are found in the 908–409 cm^{-1} region.

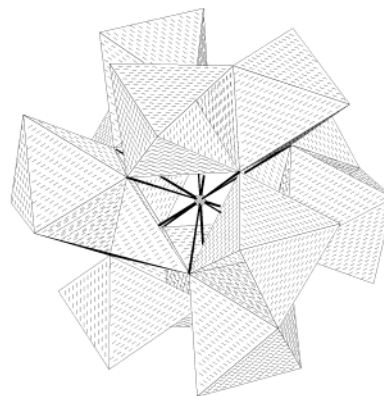


Figure 1. Structure of the $[\text{GdMo}_{12}\text{O}_{42}]^{9-}$ anion: $\{\text{Mo}_{12}\}$ fragment is in polyhedral representation and central 12-coordinated Gd^{III} cation in ball-and-stick representation.

X-ray structural analysis suggests that the central anion has D_{3d} symmetry. The anion consists of six Mo_2O_9 units and a 12-coordinate Gd^{III} atom at the center, which is a Silverton-type anion, such as $[\text{Ce}^{4+}\text{Mo}_{12}\text{O}_{42}]$.^{8–20} To the best of our knowledge, it is the first example that a paramagnetic lanthanide(III) cation is introduced into the Silverton-type anionic center in the heteropolymolybdate chemistry. As shown in Figure 1, each Mo_2O_9 is formed by two octahedra by sharing a face, and then six such Mo_2O_9 units are linked to each other through corner-sharing to build up the anion. Two corners are on the shared face, while the other two are the innermost ones opposite to the shared face. The Mo–O bond lengths can be divided into three different classes according to the manner of their coordination. The octahedral geometry around each molybdenum in the $\{\text{GdMo}_{12}\text{O}_{42}\}$ unit is defined by two terminal oxygen atoms with Mo–O distances within 1.70(1)–1.72(1) Å, three inner shared-face oxygen atoms involved in corner-sharing (1.88(1)–2.30(1) Å), and only one oxygen atom in the shared face, not involved in corner-sharing with the Mo–O distance of about 1.94(1)–1.95(1) Å. The 12 molybdenum atoms form a slightly distorted icosahedron around the central Gd^{III} atom. In other words, the Gd atom is 12-coordinate, and the coordination polyhedron is an icosahedron, in which the 12 oxygen atoms are from six Mo_2O_9 units. The two independent Gd–O distances are 2.50(1) and 2.53(1) Å.

As shown in Figure 2, the crystallization-independent Gd^{III} cation, in a slightly disordered tricapped trigonal prism, is situated at the outer sphere of the $[\text{Mo}_{12}\text{GdO}_{42}]^{9-}$ anion. The coordination oxygen atoms around the Gd^{III} cation can be divided into two classes according to different sources: the first one contains the three aqua ligands with Gd–O distances within 2.39(2)–2.48(1) Å; the other contains the six terminal oxygen atoms of molybdenum (2.36(1)–2.48(1) Å). These coordination patterns cause the Mo–O distances

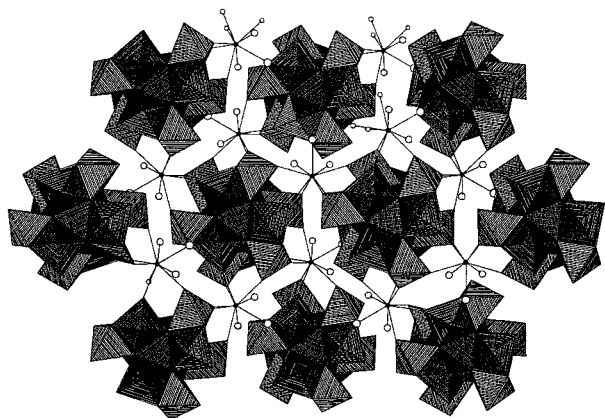


Figure 2. Polyhedral representation of the $[\text{GdMo}_{12}\text{O}_{42}]^{9-}$ anion and ball-and-stick representation of the nine-coordinated Gd^{III} cations down along the c axis.

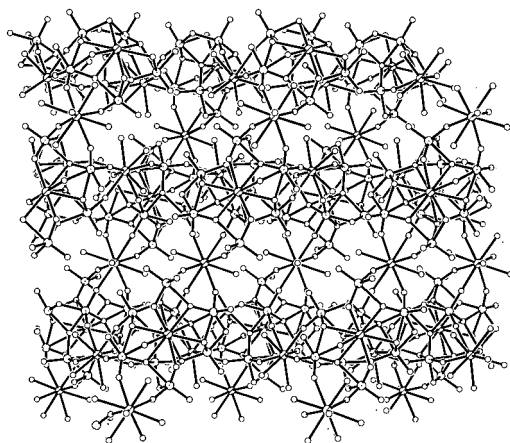


Figure 3. Packing diagram of **1** viewed down the a axis.

(1.71(1)–1.72(1) Å) to be slightly longer than the unshared average Mo–O bond (1.70(1) Å). It is very interesting that each polyanion $[\text{Mo}_{12}\text{GdO}_{42}]^{9-}$ acts as an 18-dentate ligand to link up six Gd^{III} atoms in a staggered manner to generate a remarkable three-dimensional framework (Figure 3).

The extended structure of **1** contains small voids, which are occupied by lattice water molecules. By neglecting all lattice water molecules, a calculation²¹ shows that the effective volume of these void regions is about 1368 Å³ per unit cell, comprising 24.4% of the crystal volume. The lattice water molecules in the voids are bonded to the terminal oxygen atoms of molybdenum and to the aqua ligands of Gd^{III} cations through relative weak hydrogen bonding with $\text{O}\cdots\text{O}$ distances of 2.99(2)–3.04(2) Å.

The temperature dependence of the magnetic susceptibility was measured from 300.0 to 5.0 K. At room temperature, the $\chi_{\text{M}}T$ value is 15.82 emu K mol⁻¹, which slightly exceeds the spin-only value for two uncorrelated $S = 7/2$ Gd^{III} centers (15.75 emu K mol⁻¹). The product $\chi_{\text{M}}T$ magnitude decreases slightly to 14.51 emu K mol⁻¹ while the temperature was lowered to 5.0 K. All data closely follow the Curie–Weiss law with $C = 15.77(1)$ emu K mol⁻¹, and $\theta = -1.82(1)$ K, indicating a weak antiferromagnetic interactions between the Gd^{III} cations. The magnetic data are well consistent with the expected values for $S = 7/2$ ground state, and the small θ value indicates that the interaction coupling transferred by diamag-

netic molybdenum(VI) is very weak. The EPR spectra of polycrystalline **1** give broad signals with $g = 1.9915$, $\Delta H = 1541$ G at room temperature, and $g = 1.9958$, $\Delta H = 1458$ G at 77 K. These results are almost consistent with the magnetic susceptibility measurements, which reveal that the overall interactions between the paramagnetic Gd^{III} centers are transferred by O–Mo–O units.

In conclusion, although hydrothermal synthetic methods have been extensively used to prepare polymolybdate-containing inorganic/organic hybrid materials,²² the synthesis of heteropolymolybdate-containing lanthanides by a hydrothermal synthetic method has fallen far behind. The successful synthesis of the novel three-dimensional framework of **1** suggests that the hydrothermal synthesis method is an effective method to construct some higher-dimensional frameworks for novel heteropolymolybdates containing lanthanide elements.

Acknowledgment. This work was supported by 973 Program of the MOST (001CB108906), National Natural Science Foundation of China (20073048), NSF of Fujian, and the Chinese Academy of Sciences.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths, angles, anisotropic thermal parameters, variable-temperature magnetic susceptibilities and supplementary figures for **1** (PDF). X-ray crystallographic file (CIF) This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Hill, C. L. Ed. *Chem. Rev. Polyoxometalates* **1998**, 98.
- Pope, M. T.; Müller, A. *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994.
- Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, 30, 34.
- Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer: New York, 1983.
- Aime, S.; Botta, M.; Fasano, M.; Terreno, E. *Chem. Soc. Rev.* **1998**, 27, 19.
- Oh, S. J.; Choi, Y.-S.; Hwangbo, S.; Bae, S. C.; Ku, J. K.; Park, J. W. *Chem. Commun.* **1998**, 2189.
- Bruice, T. C.; Tsubouchi, A.; Dempcy, R. O.; Olson, L. P. *J. Am. Chem. Soc.* **1996**, 118, 9867.
- Comblin, V.; Gilsoul, D.; Hermann, M.; Humblet, V.; Jacques, V.; Mesbahi, M.; Sauvage, C.; Desreux, J.-F. *Coord. Chem. Rev.* **1999**, 185–186, 451.
- Büzli, J.-C. G. In *Lanthanide Probes in Life, Chemical and Earth Science*; Büzli, J.-C. G., Choppin, G. R., Eds.; Elsevier: Amsterdam, 1989; pp 219–293.
- Elhabiri, M.; Scopelliti, R.; Büzli, J.-C. G.; Piguet, C. *J. Am. Chem. Soc.* **1999**, 121, 10747.
- Molchanov, V. N.; Tatjanina, I. V.; Torchenkova, E. A. *J. Chem. Soc., Chem. Commun.* **1981**, 93.
- Yamase, T.; Naruke, H. *J. Chem. Soc., Dalton Trans.* **1991**, 285.
- Kitamura, A.; Ozeki, T. and Yagasaki, A. *Inorg. Chem.* **1997**, 36, 4275.
- Hashimoto, M.; Takata, M.; Yagasaki, A. *Inorg. Chem.* **2000**, 39, 3712.
- Kessler, Y. G.; Turova, N. Y.; Panov, A. N.; Yanovsky, A. I.; Pisarevsky, A. P.; Struchkov, Y. T. *Polyhedron* **1996**, 15, 335.
- Villanneau, R.; Proust, A.; Robert, F.; Gouzerh, P. *J. Chem. Soc., Dalton Trans.* **1999**, 421.
- Wu, C.-D.; Lu, C.-Z.; Liu, J.-C.; Zhuang, H.-H.; Huang, J.-S. *J. Chem. Soc., Dalton Trans.* **2001**, 3202.
- Gopalakrishnan, J. *Chem. Mater.* **1995**, 7, 1265; Rabenau, A. *Angew. Chem., Int. Ed. Engl.* **1985**, 24, 1026; Ludise, R. A. *Chem. Eng. News* **1987**, 65(40), 30; Lu, J. Y.; Lawandy, M. L.; Li, J.; Yuen, T.; Lin, C. L. *Inorg. Chem.* **1999**, 38, 2695.
- Crystal data for **1**: crystal dimensions 0.20 × 0.16 × 0.12 mm³, Formula $\text{H}_{24}\text{Gd}_2\text{Mo}_{12}\text{O}_{60}$, FW 2764.47, Trigonal, space group $R\bar{3}c$, $a = 17.263(1)$ Å, $c = 25.614(1)$ Å, $U = 6610.3(3)$ Å³, $Z = 6$, $R1(wR2) = 0.0467(0.1124)$ and $S = 1.105$ for 1130 reflections with $F_o > 4\sigma(F_o)$.
- Dexter, D. D.; Silverton, J. V. *J. Am. Chem. Soc.* **1968**, 90, 3589
- "PLATON program". Spek, A. L. *Acta Crystallogr., Sect. A.* **1990**, 46, 194.
- Hagman, P. J.; Hagman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, 38, 2638 and references therein.

JA017782W