DALTON
COMMUNICATION

Synthesis and crystal structure of novel ring-like polyoxomolybdate and its 2-D self-assembly

Guang Liu, Yong-Ge Wei, Jian Liu, Qun Liu, Shi-Wei Zhang* and You-Qi Tang

State Key Laboratory for Structural Chemistry of Unstable and Stable Species,
Peking University, Beijing 100871, P. R. China. E-mail: zsw@ipc.pku.edu.cn

Received 18th February 2000, Accepted 21st February 2000

Heptamolybdate was reduced to yield novel ring-like clusters inside which Ca^{2+} cations are encapsulated and are assumed to be templates; a 2-D compound has also been obtained by a similar method and proved to be constructed of the same cluster rings connected by Ca^{2+} and glycine.

In polyoxomolybdate chemistry a wide variety of compounds, clusters and solid-state structures have been reported, but understanding the driving force for the formation of these high-nuclearity species is still a formidable challenge. Based on the self-assembly point of view, assumptions such as reduction-oxidation-reconstitution[1] and polymerization-reduction-polymerization[2] have been presented, suggesting a two-step process: first, raw materials react with each other to give various building blocks; second, these building blocks assemble automatically under suitable conditions to form products. According to these assumptions, a few types of building blocks can be identified from a large number of polyoxomolybdates and the same building block will prove to have various assembly types and produce various products, just as the $\{Mo^{V}/Mo^{VI}_5\}$ building block does in several compounds prepared by Müller and co-workers and ourselves.[1,3–5] Thus, the search for new building blocks and assembly types is an exciting and challenging task for most scientists working in this field. It will reveal cognate phenomena and present cogent proof of the various mechanisms of formation, leading to a range of new polyoxomolybdates.

We noticed that, although carboxylic acids have already been used in the synthesis of polyoxomolybdates, only a few clusters containing coordinating carboxyl have been isolated, including $[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$ reported by Müller *et al.*,[5] and none of these contains an amino acid. As our experience has proved, it is preferable to carry out reactions in the presence of a high concentration of amino acid in order to introduce it into the product. This may lead to new building blocks or linking types and may also shed light on the biochemical activity of molybdenum. In order to minimize the effect of the organic group on crystallization, we first chose the simplest amino acid, glycine, for the initial trial. In addition, our successful synthesis of a 1-D inorganic polymer[3d] by linking polyoxomolybdate using La^{3+} motivated us to use other metal elements, especially alkali and alkaline-earth metal elements, as linkage centers to form new compounds. The combination of these two ideas led to compounds **1** and **2**;† both contain novel ring-like polyoxomolybdates with Ca^{2+} cations in the ring center.

$$[Ca^{2+}{}_4(H_2O)_{22}(NH_2CH_2COO^-)_2]^{6+}\cdot\{Ca^{2+}@[Mo^{VI}{}_{10}Mo^{V}{}_8O_{52}(OH)_4(NH_3{}^+CH_2COO^-)_2]^{8-}\}^{6-}\cdot 20H_2O \quad \mathbf{1}$$

$$\{[Ca^{2+}{}_3(H_2O)_{13}(NH_3{}^+CH_2COO^-)_3]^{6+}\cdot\{Ca^{2+}@[Mo^{VI}{}_{10}Mo^{V}{}_8O_{52}(OH)_4(NH_3{}^+CH_2COO^-)_2]^{8-}\}^{6-}\cdot 19H_2O\}_n \quad \mathbf{2}$$

The crystal structures ‡ of **1** and **2** show that they both have the same cluster rings as structure units. The cluster ring contains two oval octagons, each composed of eight Mo centers bridged by oxygen and arranged almost in one plane (Fig. 1). These two octagons, which are related by a symmetry center, overlap together through sixteen μ_3-O atoms and are slightly staggered to form a ramped ring. According to bond-valence theory,[6] the valence of the eight Mo centers in the inner side of the ring (Mo1, Mo2, Mo3, Mo4 and their symmetry equivalents) is 5 and that of the other Mo centers is 6. Four μ_3-O atoms (O4, O9 and their symmetry equivalents) are protonated due to the low pH of the reaction mixture (pH 5). There are Mo–Mo bonds between Mo1 and Mo2, and Mo3 and Mo4, with bond lengths of 2.6 Å. A Ca^{2+} cation (Ca1) sits right in the symmetric center of the polyoxomolybdate ring and is connected with the eight Mo(V) ions by four μ_3-O atoms. Two Mo centers (Mo9 and its symmetric equivalent), both combine with four other Mo atoms, situated on the outer edge along the long axis of the ring. A glycine molecule connects the adjacent Mo1 and Mo4 centers in different asymmetric units *via* the oxygen atoms of its carboxyl function, which both coordinate to a Mo atom. Ca2 lies above the ring plane and combines with the cluster *via* bonds to two backbone oxygen atoms. A glycine molecule connects Ca1 and Ca2 through the two oxygen atoms of its carboxyl group, in the μ-bridging mode. Another Ca^{2+} cation, Ca3, is encapsulated by backbone oxygens and lies on the ring plane but outside the ring. In compound **2**, a glycine molecule connects Ca2 and the Ca3 center of another cluster. The occupancy of this glycine and Ca3 is 0.5 because the distance between two adjacent Ca3 ions from different clusters is only 2.710 Å, too short for their coexistence. The Ca3 center of compound **2** connects with Mo6 and Mo9 through two μ-O atoms and also with the Mo6 ion of another cluster *via* a further μ-O atom to link the cluster rings into chains. Furthermore, these chains are assembled into a 2-D network by the glycine molecule which bridges between the Ca2 and Ca3 atoms

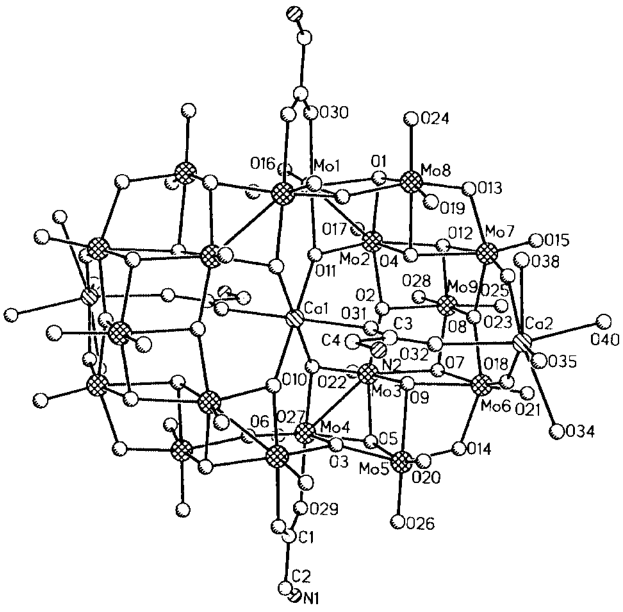

Fig. 1 The structure of the cluster ring.

DOI: 10.1039/b001361g

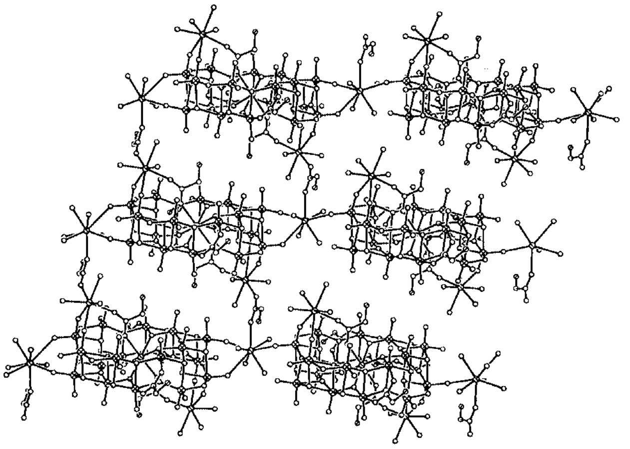

Fig. 2 The 2-D structure of compound **2**.

of different chains (Fig. 2). The amino groups of some glycine molecules in **1** and all the glycine molecules in **2** are protonated to balance the charge (these hydrogen atoms can be seen in the difference Fourier map).

Most polyoxomolybdates which have ten to twenty Mo atoms show sphere-shaped or cage-like structures, such as the famous Keggin structure ion, the Dawson structure ion, and many others. But unlike these, **1** and **2** have unusual ring-like structures. The central cavity of the ring is occupied by a Ca^{2+} ion with bonds to the oxygen atoms in the backbone and shows a good fit in terms of size. This experiment is highly repeatable, but under our experimental conditions, no product was obtained when Ca^{2+} was excluded from the reaction mixture. Thus, Ca^{2+} must play an important role in the reaction, which suggests that the Ca^{2+} ion very probably acts as a template during the synthesis. There are a large class of compounds which adopt basket, bowl, belt, barrel and spherical structures and can encapsulate neutral, anionic, and cationic species, and even cation–anion aggregates are of interest with regard to inorganic host–guest chemistry.[7] But for polyoxomolybdates, most guest species are anions, such as Po_4^{3-} and Cl^-, and cationic guests are relatively rare, with the notable exception[8] of $[Na(H_2O)_3Mo_{42}H_{15}O_{109}\{(OCH_2)_3CCH_2OH\}_7]^{7-}$. The cluster in **1** and **2** is another important example in this area. Considering size effects, if Ca^{2+} is replaced by other ions or species, the dimensions of the cluster will change to give new ring-like or other shaped compounds. Another important feature of **1** and **2** is the high ratio of Mo(V) to Mo(VI), 4:5, much higher than most other large polyoxomolybdates. Because of this, these two compounds are red in color, just like the series of polyoxomolybdates based on $[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]^{12-}$ reported previously.[1,3a,3d,4a]

In addition, although Na^+ cations are not present in compound **1**, NaCl is necessary for the preparation of this product. The role that NaCl plays during the synthesis is still under investigation.

In conclusion, that Ca^{2+} acts as template and glycine as ligand to form novel ring-like clusters is an interesting discovery. These clusters not only constitute an independent compound, but may also be assembled as building blocks to give 2-D structures. This discovery motivates us to consider whether other cations and acids can play similar roles under suitable condition. New types of polyoxomolybdate clusters and inorganic polymers are very likely to be found using this idea.

Acknowledgements

This work was supported by NNSF of China (no. 29871003 and no. 29733080).

Notes and references

† Synthesis and selected data for **1** and **2**. **1** was synthesized from the reaction of 0.7 g, 0.6 mmol $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 3.04 g, 40.5 mmol NH_2CH_2COOH, 0.50 g, 4.5 mmol $CaCl_2$, 0.50 g, 8.5 mmol NaCl, and 0.20 g, 1.5 mmol $N_2H_4\cdot H_2SO_4$ in 60 ml water. The mixture was stirred for 10 min at room temperature while a color change occurred from yellow to green. The solution was left to stand without disturbance for one day and the color changed to red. Red triclinic flimsy block crystals of **1** were obtained after half a month with the coexistence of a red precipitate. The crystals were carefully selected out and washed with water. The synthesis of **2** was similar to that of **1**, but no NaCl was added to the reaction mixture. The crystals of **2** are also red triclinic, but much thicker than those of **1**.

Elemental analysis: calc. for **1**: C, 2.47; H, 2.75; Ca, 5.15; Mo, 44.5; N, 1.44; found: C, 2.65; H, 2.34; Ca, 5.37; Mo, 45.0; N, 1.56; calc. for **2**: C, 3.21; H, 2.49; Ca, 4.28; Mo, 46.2; N, 1.87; found: C, 3.29; H, 2.31; Ca, 4.62; Mo, 46.3; N, 1.96%. IR(ν_{max}/cm^{-1}): **1**: 3431m, 3141m, 1621s, 1492s, 1417s, 939s, 735m, 644m; **2**: 3426s, 3232s, 1628s, 968s, 941s, 904s, 730s. TGA: **1**: total loss of mass below 420 °C is 19.64%, corresponding to 42 water molecules; **2**: total loss of mass below 460 °C is 15.21%, corresponding to 32 water molecules.

‡ Crystal data for **1**: $M = 3882$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.453(2)$, $b = 14.510(3)$, $c = 17.654(4)$ Å, $\alpha = 114.07(3)$, $\beta = 93.80(3)$, $\gamma = 90.24(3)°$, $U = 2671.2(1.2)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.41$ g cm^{-3}, $\rho_{obsd} = 2.43$ g cm^{-3}, μ(Mo-Kα) = 2.67 mm^{-1}, $T = 293$ K, 9386 independent reflections collected, 7875 observed for $F_0 > 4\sigma(F_0)$ ($R_{int} = 0.0674$), $R_1 = 0.0568$ (observed data) and $wR_2 = 0.1663$ (all data) for 663 parameters. **2**: $M = 3739$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.921(2)$, $b = 14.689(3)$, $c = 15.169(3)$ Å, $\alpha = 74.73(3)$, $\beta = 87.91(3)$, $\gamma = 66.73(3)°$, $U = 2347.1(8)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.65$ g cm^{-3}, $\rho_{obsd} = 2.63$ g cm^{-3}, μ(Mo-Kα) = 2.67 mm^{-1}, $T = 293$ K, 8618 reflections measured, 8265 unique ($R_{int} = 0.045$), 7839 observed for $F_0 > 4\sigma(F_0)$, $R_1 = 0.0306$ (observed data) and $wR_2 = 0.0847$ (all data) for 653 parameters. CCDC reference number 186/1869. See http://www.rsc.org/suppdata/dt/b0/b001361g/ for crystallographic files in .cif format.

1 S. W. Zhang, Y. G. Wei, Q. Yu, M. C. Shao and Y. Q. Tang, *J. Am. Chem. Soc.*, 1997, **119**, 6440.

2 K. Wassermann, M. H. Dickman and M. T. Pope, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1445.

3 (*a*) S. W. Zhang, D. Q. Liao, M. C. Shao and Y. Q. Tang, *J. Chem. Soc., Chem. Commun.*, 1986, 835; (*b*) S. W. Zhang, G. Q. Huang, M. C. Shao and Y. Q. Tang, *J. Chem. Soc., Chem. Commun.*, 1993, 37; (*c*) C. C. Jiang, Y. G. Wei, Q. Liu, S. W. Zhang, M. C. Shao and Y. Q. Tang, *Chem. Commun.*, 1998, 1937; (*d*) G. Liu, Y. G. Wei, Q. Yu, Q. Liu and S. W. Zhang, *Inorg. Chem. Commun.*, 1999, **2**, 434.

4 (*a*) A. Müller, E. Krickemeyer, S. Dillinger, H. Bögge, W. Plass, A. Proust, L. Dloczik, C. Menke, J. Meyer and R. Rohlting, *Z. Anorg. Allg. Chem.*, 1994, **620**, 599; (*b*) A. Müller, E. Krickemeyer, J. Meyer, H. Bögge, F. Peters, W. Plass, E. Diemann, S. Dillinger, F. Nonnenbruch, M. Randerath and C. Menke, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2122; (*c*) A. Müller, E, Krickemeyer, H. Bögge, M. Schmidtmann, F. Peters, C. Menke and J. Meyer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 484; (*d*) A. Müller, J. Meyer, E. Krickemeyer, C. Beugholt, H. Bögge, F. Peters, M. Schmidtmann, P. Kögerler and M. J. Koop, *Chem. Eur. J.*, 1998, **4**, 1000; (*e*) A. Müller, M. Koop, H. Bögge, M. Schmidtmann and C. Beugholt, *Chem. Commun.*, 1998, 1501; (*f*) A. Müller, F. Peters, M. T. Pope and D. Gatteschi, *Chem. Rev.*, 1998, **98**, 239; (*g*) A. Müller, S. Q. N. Shah, H. Bögge and M. Schmidtmann, *Nature*, 1999, **397**, 48; (*h*) A. Müller, S. K. Das, H. Bögge, C. Beugholt and M. Schmidtmann, *Chem. Commun.*, 1999, 1035; (*i*) A. Müller, M. Koop, H. Bögge, M. Schmidtmann, F. Peters and P. Kögerler, *Chem. Commun.*, 1999, 1885.

5 A. Müller, E, Krickemeyer, H. Bögge, M. Schmidtmann and F. Peters, *Angew. Chem., Int. Ed.*, 1998, **37**, 3360.

6 I. D. Brown, *Structure and Bonding in Crystals*, Academic Press, New York, 1981, vol. 2, pp. 1–30.

7 P. C. H. Mitchell, *Nature*, 1990, **348**, 15.

8 M. I. Khan and J. Zubieta, *J. Am. Chem. Soc.*, 1992, **114**, 10058.

Communication b001361g