SHORT PAPER

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Synthesis and crystal structure of an 18-Mo girdle-like polyoxomolybdate[†]

Guang Liu, Jian Liu and Shi-Wei Zhang*

*State Key Laboratory for Structural Chemistry of Unstable and Stable Species,
Department of Chemistry, Peking University, Beijing 100871, P. R. China*

Heptamolybdate was reduced in the presence of glycine to yield an 18-Mo girdle-like polyoxomolybdate with a Na^+ cation encapsulated in its centre cavity.

Keywords: 18-Mo girdle-like polyoxomolybdate

Natural complex systems, especially those in biology, are built up in a stepwise manner through a sequence of programmed chemical processes. The chemist is in a position to connect elementary building blocks and their derivatives in different ways, enabling him to synthesise a large variety of important and remarkable substances.[1] Polyoxomolybdates are attractive building blocks because of their various reactivities and potential application in catalysis, electrics, magnetics, nonlinear optics and medicine.[2] A large number of polyoxomolybdates have already been synthesised, and their structural details and physical properties have been widely discussed. On the other hand, molybdenum is one of the important transition metals in biological systems since it is an integral component of the multinuclear M centre of nitrogenases and the active sites of a group of oxotransferases.[3] Therefore, introducing bioactive amino acids into polyoxomolybdates will help the understanding of the bioactivity of molybdenum. But among polyoxomolybdates reported so far, few have a coordinating amino acid in the backbone structure. Through a reduction–oxidation–reconstruction synthetic route,[4,5] several polyoxomolybdates coordinated by amino acids have been synthesised by our group.[6,7] In this paper, we report the synthesis and crystal structure of a new glycine polyoxomolybdate complex (**1**),

$$[Ca_2(H_2O)_8(NH_2CH_2COO^-)_2]^{2+}\cdot\{Na[H_{11}Mo^{I}_{10}Mo_8O_{56}(NH_2CH_2COO^-)_2]^{3-}\}^{2-}\cdot 31H_2O \qquad (\mathbf{1})$$

The single crystal determination of complex (**1**) showed that it had an 18-Mo girdle-like structure (Figs 1 and 2). The structure is constructed of two rings that are related by a symmetry centre. The ring is almost planar and is composed of nine molybdenum centres that are connected by bridging oxygen atoms (see Fig. 3). These nine molybdenum centres are all coordinated by oxygen atoms in the octahedral mode and can be classified into three types. The first type contains Mo1, Mo2, Mo3 and Mo4. Each of these four molybdenum centres has only one oxo-O atom (average Mo=O bond length is 1.680Å) and five μ-O atoms (average Mo–O bond length is 2.063Å). Their valence is 5 according to bond-valence theory.[8] The existence of an Mo–Mo bond between Mo1 and Mo2 (2.6010(13)Å) as well as between Mo3 and Mo4 (2.5956(11)Å) supports this opinion about valence. The second type contains Mo5, Mo6, Mo7 and Mo8, while the third type contains Mo9. Each of these five molybdenum centres has two oxo-O atoms (average Mo=O bond length is 1.707Å) and four μ-O atoms (average Mo–O bond length is 2.095Å). The valence of them is 6 according to bond-valence theory.[8] There is no Mo–Mo bond between them (Mo–Mo distances are all longer than 3.1Å). The nine Mo–O octahedra share vertexes and edges to form a ring (Fig. 4). Every Mo–O octahedron of one ring shares edges with two octahedra of the other ring (Fig. 5). Two rings are connected by 16 μ_3-O atoms with the help of two glycine molecules that bridge the adjacent Mo1 and Mo4 centres in different rings via the oxygen atoms of their carboxyl functions, which each coordinates to an Mo atom. A Na^+ cation (Na1) sits right in the symmetry centre and is coordinated by six oxygen atoms. Two Ca^{2+} cations (Ca2) lie above the ring plane and combine with the ring via bonds to backbone oxygen atoms. Two glycine molecules connect

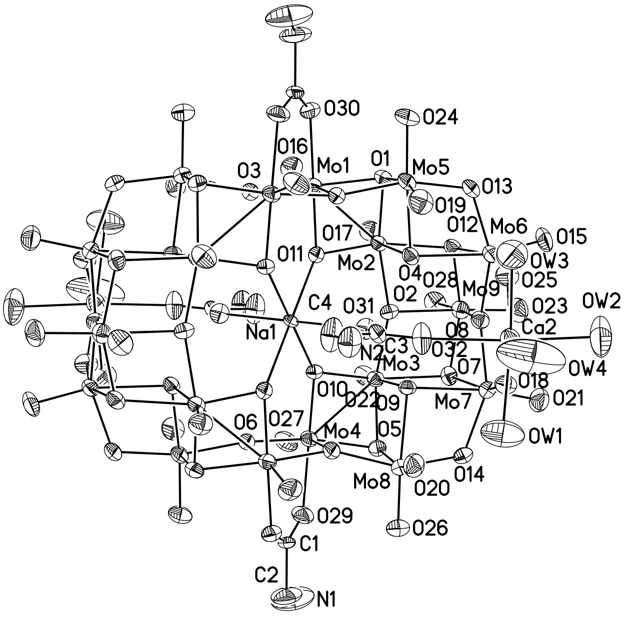

Fig. 1 The structure of complex (**1**) showing 50% probability displacement ellipsoids.

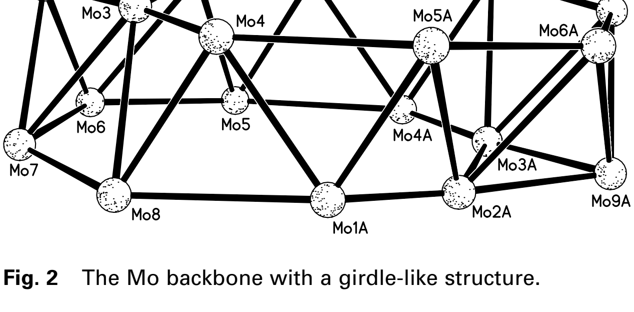

Fig. 2 The Mo backbone with a girdle-like structure.

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* To receive any correspondence. E-mail: zsw@ipc.pku.edu.cn

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

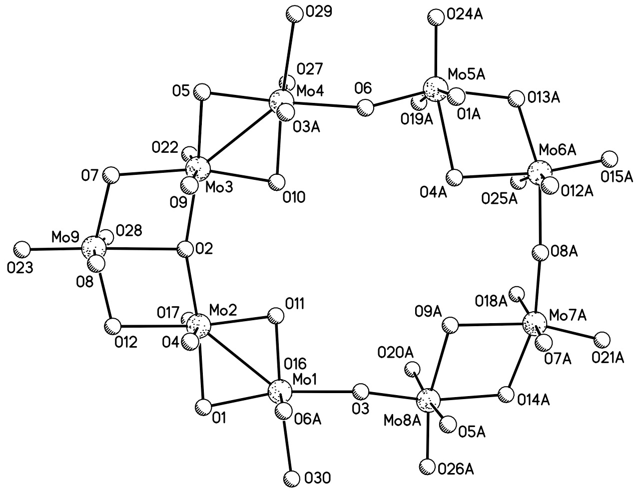

Fig. 3 The structure of one ring.

Na^+ and Ca^{2+} cations through the oxygen atoms of their carboxyl functions, in the μ_2-bridging mode.

The structure of the girdle backbone of complex (**1**) is similar to those of the two complexes (**2**) and (**3**) reported by us before,[7] but there is some difference between them. The centre cation of complexes (**2**) and (**3**) is Ca^{2+} while that of complex (**1**) is Na^+. Many other metal cations were tried in the reaction mixture, but no product has been obtained so far. This indicates that the girdle structure is rigid and the dimension of the central cavity is just suitable for Na^+ and Ca^{2+} (these two cations have almost the same radius). Another difference is that the Ca3 cations of complexes (**2**) and (**3**) are absent in case of complex (**1**). This pair of Ca^{2+} cations (Ca3) is important for complexes (**2**) and (**3**), because it is the reactive site of their condensation parallel to the girdle plane. The pair of glycine molecules of complexes (**2**) and (**3**) that coordinates to Ca2 and Ca3 and is important to the condensation perpendicular to the girdle plane, is also lacking in complex (**1**). Thus the molecules of complex (**1**) have no way to condense and can only interact through hydrogen bonds.

There are some types of polyoxomolybdates, such as Keggin and Dawson structural complexes, which can be modified by cations and ligands while keeping the main structure steady. These three complexes (**1**), (**2**) and (**3**) indicate a possible new structural type with a formula of $[Mo_{18}O_{56}]^{x-}$. Investigation of new complexes belonging to this type is still being undertaken in our group.

Experimental

Preparation of complex (**1**): Complex (**1**) was synthesised from the reaction of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (0.7 g, 0.6 mmol), NH_2CH_2COOH (3.04 g, 40.5 mmol), $CaCl_2$ (0.50 g, 4.5 mmol), NaCl (1.50 g, 25.6 mmol), and $N_2H_4\cdot H_2SO_4$ (0.20g, 1.5 mmol) in water (60 ml, 3.3 mol). The mixture was stirred for 10 min at room temperature, then left to stand without disturbance for two weeks. Red rod-like crystals were obtained concurrently with a red precipitate. The crystals were carefully selected out and washed with water.

Elemental analysis: calc. for complex (**1**) $C_8H_{105}Ca_2Mo_{18}N_4NaO_{103}$: C, 2.57; H, 2.81; Ca, 2.14; Mo, 46.3; N, 1.50; Na, 0.62; found: C, 2.69; H, 2.50; Ca, 2.41; Mo, 46.4; N, 1.55; Na, 0.62%.

IR(ν_{max}/cm^{-1}) (KBr disc.): 3425s, 3173m, 1588s, 1492s, 1454s, 1417s, 939s, 896s, 740m, 638m.

TGA: total loss of mass of complex (1) below 376°C is 18.71%, corresponding to 39 water molecules.

Crystal structure determination: The structure of complex (**1**) was determined from single crystal X-ray diffraction data collected on a Rigaku AFC6S diffractometer operating at 50kV and 30mA (graphite monochromatised Mo-Kα radiation; $\lambda = 0.71073$Å). A red rod-like crystal (0.15mm × 0.25mm × 0.50mm) was sealed in glass tube and centred. The unit cell parameters were obtained at 293(2)K based on 25 peaks ($5° \le \theta \le 12°$). A total of 6359 reflections ($1.71° \le \theta \le 22.01°$) were collected and all data were corrected for absorption on the basis of φ-scan profiles. The structure was solved by direct method and difference Fourier map using SHELXS97 program and refined on F^2 by full-matrix least-squares techniques using SHELXL97 program. Monoclinic, space group *C2/c* (no. 15), $a = 37.056(7)$Å, $b = 11.541(2)$Å, $c = 29.292(6)$Å, $\beta = 125.47(3)°$, $V = 10202(3)$Å^3, $Z = 4$, calc. density 2.432g/cm^3, $F(000) = 7248$, $\mu = 2.363$mm^{-1}. The structure was refined against 634 parameters, $R_1 = 0.0361$ for 5119 $I > 2\sigma(I)$ data and $wR_2 = 0.1074$ for 6243 unique data, goodness of fit was 1.033.

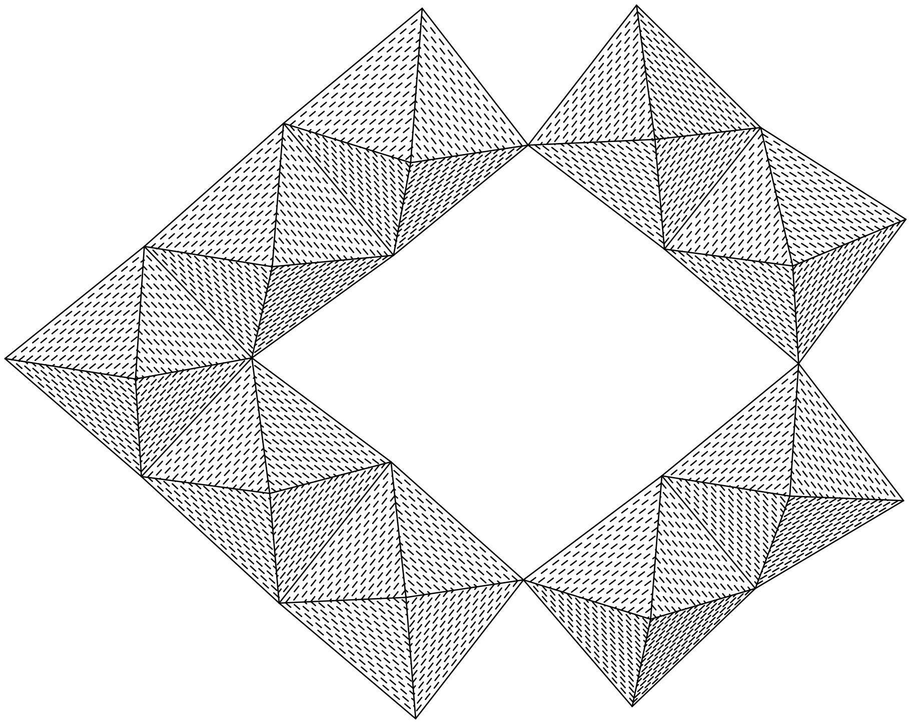

Fig. 4 The conjunction of Mo–O octahedra in one ring.

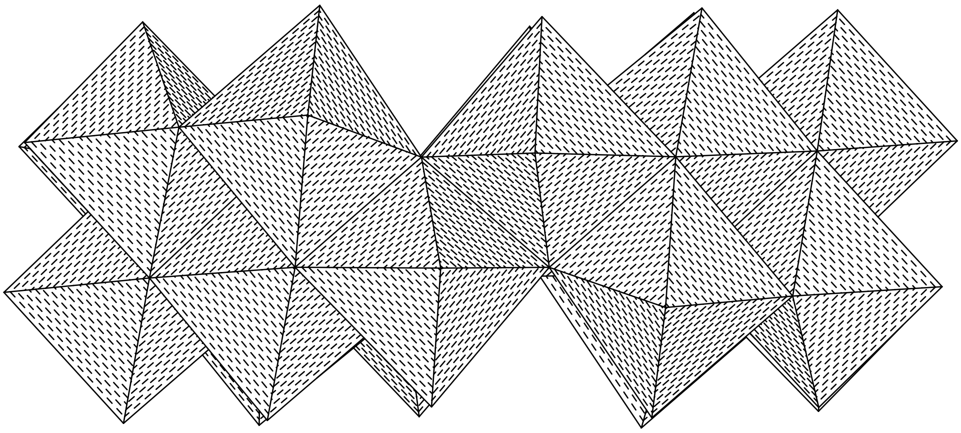

Fig. 5 The conjunction of Mo–O octahedra of different rings.

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