

[Mo₈S₄O₁₂(OH)₈(C₂O₄)]: a novel polyoxothiomolybdate ring synthesized *via* a hydrothermal method

Xiao-Ping Zhan, Can-Zhong Lu,* Wen-Bin Yang, Hong-Wei Ma, Chuan-De Wu and Quan-Zheng Zhang

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.
E-mail: czlu@ms.fjirsm.ac.cn

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A hydrothermally synthesized new octameric ring, [Mo₈S₄O₁₂(OH)₈(C₂O₄)], formed by edge-sharing Mo₂(S)O₃ building blocks, is presented.

The chemistry of sulfur-containing polyoxometalates (polyoxothiomolybdates) is interesting because of their diverse applications in many modern fields¹ such as the hydrodesulfurization process,² hydrogenation catalysis,³ inorganic and bio-inorganic fields,⁴ and microporous and mesoporous materials.⁵ Compared with extensively studied high-nuclearity polyoxomolybdates, only a few low-nuclearity polyoxothiomolybdates have been obtained by sulfurization of oxo precursors so far.⁶ Therefore, the synthesis of high-nuclearity sulfur-containing species by combining polyoxometalate and thiomolybdate chemistry represents a stimulating challenge. Some methods for introducing sulfur into polyoxometalates have been reported, for example: (i) A Keggin-type α -[PW₁₁NbSO₃₉]⁴⁻ polyoxothioanion was obtained from α -[PW₁₁NbO₄₀]⁴⁻, of which the terminal oxygen atom of a Nb=O group was selectively replaced by a sulfur atom;⁷ (ii) γ -[SiW₁₀M₂S₂O₃₈]⁶⁻ was obtained through stereospecific addition of a [Mo₂S₂O₂]²⁺ fragment to the γ -[SiW₁₀O₃₆]⁸⁻ anion;⁸ (iii) The self-condensation method based on [Mo₂S₂O₂]²⁺ building blocks to synthesize many new structures or frameworks with higher sulfur contents has been widely used. A series of ring-shaped clusters have been reported so far, such as, [Mo₁₂S₁₂O₁₂(OH)₁₂(H₂O)₆]⁹, [Mo₉S₈O₁₂(OH)₈(H₂O)₂]²⁻,¹⁰ [Mo₁₀S₁₀O₁₀(OH)₁₀(H₂O)₃]¹¹, [Mo₈S₈O₈(OH)₈(C₂O₄)]²⁻,¹² [Mo₁₀S₁₀O₁₀(OH)₁₀(H₃C₅O₄)]²⁻,¹² [Mo₁₂S₁₂O₁₂(OH)₁₂(H₁₀C₇O₄)]²⁻,¹² and [W₈S₈O₈(OH)₈(H₃WO₆)]³⁻.¹³ These kinds of compound have in common a neutral cyclic backbone {Mo_{2n}S_{2n}O_{2n}(OH)_{2n}}, which presents interesting properties: (i) The characterization of the cyclic backbone permits the encapsulation of various substrates such as dicarboxylate, phosphate, or metalate; (ii) In most cases, the architectural cyclic sizes and shapes more or less depend on the substrates, illustrating the template effects of the substrates. For instance, the reported Mo₈-, Mo₁₀-, and Mo₁₂-clusters were synthesized by addition of suitable linear dicarboxylate, *i.e.*, oxalate, glutarate, or pimelate, respectively.

Herein, we describe a ring-shaped polyoxothiomolybdate [H₂N(CH₃)₂](H₃O)[Mo₈S₄O₁₂(OH)₈(C₂O₄)]·5.5H₂O **1** in detail, which is obtained from a mixture of Na₂MoO₄·H₂O, La(NO₃)₃, NH₂NH₂·H₂SO₄, Na₂(C₂O₄), DMSO, and H₂O by a hydrothermal reaction.† The ring shape of the anion [Mo₈S₄O₁₂(OH)₈(C₂O₄)]²⁻ **1a** is built up by novel [Mo₂S₂O₂]²⁺ building blocks *via* edge-sharing connections. The significance of this investigation is that it presents another method to obtain new polyoxothiomolybdates and, more novel ring-shaped compounds can be obtained by addition of suitable carboxylates as templates.

The X-ray structural study ‡ of **1** (Fig. 1) reveals that its ring-shaped backbone is built up by four novel [Mo₂S₂O₂]²⁺ building blocks. The [Mo₂S₂O₂]²⁺ unit is composed of two Mo centres, two terminal oxygens, one bridging μ -O and one bridging μ -S. Four such [Mo₂S₂O₂]²⁺ units are connected *via* edge-sharing

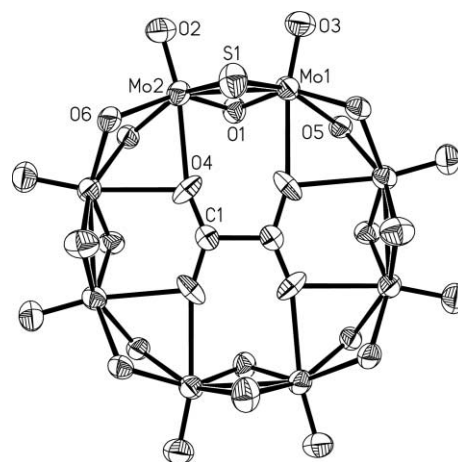


Fig. 1 ORTEP¹⁵ drawing of the anion of **1** (50% thermal ellipsoid probability), showing the eight-membered ring (each of the central carbon atoms is found to be distributed at two positions with an occupancy of 0.5, and only one orientation of the central carbon atoms is shown). Selected bond lengths (Å): Mo(1)–O(1) 1.929(3), Mo(1)–O(3) 1.668(4), Mo(1)–O(5) 2.075(3), Mo(1)–S(1) 2.3174(14), Mo(2)–O(1) 1.951(3), Mo(2)–O(2) 1.660(4), Mo(2)–O(6) 2.102(3), Mo(2)–S(1) 2.3313(15). Selected bond angles (°): O(3)–Mo(1)–O(1) 105.05(17), O(3)–Mo(1)–O(5) 100.47(16), O(1)–Mo(1)–O(5) 86.49(13), O(3)–Mo(1)–S(1) 103.48(13), O(1)–Mo(1)–S(1) 100.70(10), O(5)–Mo(1)–S(1) 152.14(10), Mo(1)–S(1)–Mo(2) 70.43(4), Mo(1)–O(1)–Mo(2) 87.39(13).

into a ring-shaped backbone {Mo₈}. Compared to the above-mentioned ring-shaped compounds of the type {Mo_{2n}S_{2n}O_{2n}(OH)_{2n}}, half of the bridging sulfur atoms of the ring are replaced by oxygen atoms, giving a ring which can be formulated as {Mo_{2n}S_nO_{3n}(OH)_{2n}}. The Mo– μ -S bond distances (2.317–2.331 Å), Mo– μ -O bond distances (1.929–1.951 Å) and Mo–terminal-O bond distances (1.660–1.668 Å) in a [Mo₂SO₃]²⁻ building block are all within expected limits. The μ -O bond distances (1.929–1.951 Å) between two [Mo₂SO₃]²⁻ building blocks indicate these oxygen atoms are hydrogenated. In the {Mo₈} ring of **1a**, two types of Mo–Mo distances are observed: short Mo–Mo distances (2.680 Å) within a [Mo₂SO₃]²⁻ building block, and long Mo–Mo distances (3.245 Å) between two blocks. The long Mo–Mo distances are comparable to those reported for related polyoxothiomolybdates, while the short Mo–Mo bond distances are about 0.12 Å shorter,^{9–12} suggesting the existence of stronger Mo^V–Mo^V metallic interactions. Obviously this is contributed to by one S atom being replaced by an O atom in a [Mo₂S₂O₂]²⁺ unit, giving a [Mo₂SO₃]²⁻ unit that builds up the backbone of **1**. The inner-diameter of the neutral cyclic [Mo₈S₄O₁₂(OH)₈] is about 7.76 Å, which is encapsulated by an oxalic acid molecule connected *via* bridged oxygen atoms. It should be pointed out that two carbon atoms of oxalic acid are equally dispersed at four positions with an occupancy of 0.5.

It is well known that DMSO decomposes readily above 130 °C, especially under acidic conditions, therefore we conclude

that the bridging sulfur atoms are due to DMSO fragmentation under hydrothermal conditions. On the other hand, as there is no lanthanum incorporated in compound **1**, a blank experiment without addition of $\text{La}(\text{NO}_3)_3$ was also carried out, but no **1** could be isolated. This fact indicates that $\text{La}(\text{NO}_3)_3$ should play an important role in the reactive system for the formation of **1**, however, its exact role is still to be investigated further.

By comparison with other ring-shaped $\{\text{Mo}_{2n}\text{S}_{2n}\text{O}_{2n}(\text{OH})_{2n}\}$ -type compounds, **1** has some interesting features. First, its basic building block $[\text{Mo}_2\text{SO}_3]$, building up a $\{\text{Mo}_{2n}\text{S}_n\text{O}_{3n}(\text{OH})_{2n}\}$ -type compound, is different from the reported $[\text{Mo}_2\text{S}_2\text{O}_2]$ one which built up $\{\text{Mo}_{2n}\text{S}_{2n}\text{O}_{2n}(\text{OH})_{2n}\}$ -type compounds. The second feature is that **1a** is obtained by a one-pot hydrothermal synthesis, which might explain why its building block is different from those of the reported compounds and provide some clues for the synthesis of new compounds in this field. Finally, it should be pointed out that the sulfur atoms of **1a** should come from thermally-decomposed fragments of DMSO under violent hydrothermal reaction conditions, whereas, the sulfur atoms in the $\{\text{Mo}_{2n}\text{S}_{2n}\text{O}_{2n}(\text{OH})_{2n}\}$ -type compounds come from the precursor $[\text{Mo}_2\text{S}_2\text{O}_2]$ under mild aqueous solution conditions. The successful isolation of compound **1** not only offers a novel cyclic polyoxothiomolybdate with a new building block, but also provides some useful information for new attempts on new polyoxothiomolybdates in the field. As reported in the literature, different templates decide the rings' size and shape; new series of $\{\text{Mo}_{2n}\text{S}_n\text{O}_{3n}(\text{OH})_{2n}\}$ -type compounds might be synthesized with inner oxalic acid being replaced by other organic acids or metals. This is currently under investigation in our laboratory.

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Notes and references

† Synthetic details: A mixture of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3$, $\text{NH}_2\text{-NH}_2 \cdot \text{H}_2\text{SO}_4$, $\text{Na}_2(\text{C}_2\text{O}_4)$, DMSO, and H_2O in the mole ratio 4.1 : 1.0 : 1.5 : 4.0 : 6.4 : 277 was sealed in a 20 ml Teflon-lined autoclave, then heated at 160 °C for 72 h. After cooling to room temperature at 5 °C h⁻¹, yellow block crystals were isolated, which were washed with ethanol and dried (yield: 30% based on Mo). Elemental analysis: calc. for $\text{C}_4\text{H}_{30}\text{NO}_{30.5}\text{S}_4\text{Mo}_8$: C, 3.25; H, 2.03; N, 0.95; O, 33.06; S, 8.69; Mo, 52.00. Found: C, 3.17; H, 2.12; N, 1.05; O, 33.01; S, 8.64; Mo, 52.04%.
‡ Crystal data: compound **1** ($\text{C}_4\text{H}_{30}\text{NO}_{30.5}\text{S}_4\text{Mo}_8$, $M_r = 1476.05$), tetragonal, space group $P4/mnc$, $a = 14.8640(7)$, $b = 14.8640(7)$, $c = 21.4507(14)$ Å, $V = 4739.3(4)$ Å³, $Z = 4$, $D_c = 2.069$ g cm⁻³, $\mu(\text{Mo-K}\alpha) =$

2.296 mm⁻¹, $T = 293(2)$ K, final $R = 0.0659$ and $wR = 0.2534$ for 1490 observed reflections with $I > 2\sigma(I)$ from 2105 independent reflections. The data set was collected on a Siemens Smart CCD diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at room temperature. The structure was solved by direct methods and succeeding difference Fourier syntheses, and then refined anisotropically by a full-matrix least-squares method for all metal atoms and partial oxygen atoms. Hydrogen atoms were refined in calculated positions for the protonated $\text{NH}_2(\text{CH}_3)_2$ cations but were unable to be located for the OH, water or protonated water species. All calculations were performed using the SHELXTL-97 program package.¹⁴ CCDC reference number 201691. See <http://www.rsc.org/suppdata/dt/b3/b300828b/> for crystallographic data in CIF or other electronic format.

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