

## Assembly and Autochirogenesis of a Chiral Inorganic Polythioanion Möbius Strip via Symmetry Breaking

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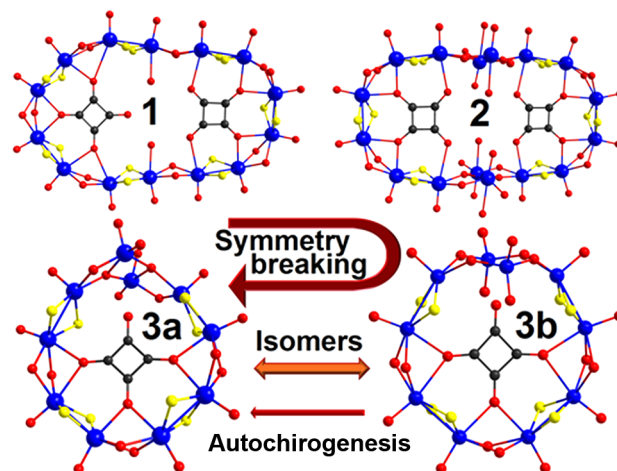
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## Supporting Information

**ABSTRACT:** Using  $[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6]^{2+}$  and squarate dianion, we synthesized the thiometalate ring compounds  $[(\text{Mo}_2\text{S}_2\text{O}_2)_x(\text{OH})_y(\text{C}_4\text{O}_4)_z(\text{Mo}_2\text{O}_8)_o(\text{H}_2\text{O})_p]^{n-}$ , where  $[x,y,z,o,p,n] = [7,14,2,0,2,4]$  for **1**,  $[6,8,2,2,4,8]$  for **2**, and  $[4,6,1,1,0,4]$  for both **3a** and **3b**, which are chiral and nonchiral isomers, respectively. Not only do the four thiometalate clusters show decreasing symmetry at the molecular level across the series, but the incorporation of the “addendum”  $\{\text{Mo}_2\text{O}_8\}_o$  unit also allows the thiometalate ring to twist. The reaction initially yields the chiral molecule **3a** with a twisted ring, which undergoes spontaneous resolution upon crystallization; the reaction mixture later yields the intrinsically nonchiral isomer **3b** with a nontwisted ring. In addition, the compounds are able to promote the electrocatalytic evolution of hydrogen.

Pasteur’s famous experiment demonstrating the handedness of tartaric acid has fascinated generations of scientists.<sup>1</sup> This is because shedding light on how chirality arises in nature is of great interest for both scientific and technological reasons. Chirality in molecules can result from using chiral building blocks or guests,<sup>2</sup> asymmetric arrangements of achiral building blocks,<sup>3</sup> or an intrinsically asymmetric molecular structure,<sup>4</sup> and the design of intrinsically chiral molecules coupled with spontaneous resolution is important.<sup>1</sup> Statistically, only 5–10% of racemates form conglomerate crystals,<sup>5</sup> by means of an autocatalytic mechanism, but these systems show strong stochastic behavior.<sup>6</sup> Thus, the assembly of chiral compounds from achiral starting materials that will also spontaneously resolve is extremely challenging.<sup>7,8</sup>

In this respect, we reasoned that one route to engineer chiral molecules could be possible if one could twist a molecular ring. For instance, the well-known Möbius strip, first described in 1858, is chiral, and it is the bend–twist coupling that results in a symmetry-breaking event to give the overall chiral strip.<sup>9</sup> Inspired by this, we set about attempting to select suitable building units that could “bend” and “twist” to induce a symmetry-breaking process at the molecular level. Among the large number of building blocks we considered, the  $[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6]^{2+}$  unit, first discovered and developed by Müller<sup>10a</sup> and Cadot<sup>10b</sup> in the formation of a fascinating emerging class of thiopolyoxometalates (TPOMs), appears to be an ideal “bend” unit precursor (Figure 1), but the investigation of TPOMs is still in its infancy. Recent work on cyclic oxothiometalates formed by hydrolytic condensation<sup>11</sup> demonstrated the preparation of a novel class of cyclic host–



**Figure 1.** Ball-and-stick representation of the four clusters (Mo, blue; O, red; S, yellow; C, black). Interestingly, compounds **1**, **2**, **3a**, and **3b** approximately have point groups  $C_{2v}$ ,  $C_s$ ,  $C_2$ , and  $C_{2v}$  and crystallize in the space groups  $P\bar{1}$ ,  $P2_1/n$ ,  $P6_322$ , and  $Pc$ , respectively, showing symmetry breaking across the series.

guest oxothiomolybdates, allowing the shape and size of the rings to be defined by the coordinated guest.<sup>12</sup>

To explore this idea, we chose the squarate dianion to template the self-condensation with  $[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6]^{2+}$ , because squarate is both rigid and planar, allowing the cyclic bend part to be obtained easily. Additionally, the small size of the squarate anion could lead to defects or a distortion in the ring structure. On the basis of the above idea, we introduced the  $\{\text{Mo}_2\text{O}_8\}$  unit to act as a “symmetry breaker” that would break the planarity of the ring as well as engineer a distortion.

Using this “symmetry-breaking” strategy with the combination of the correct ring building block and small template, we show herein how this symmetry breaking is manifested in a stepwise manner in the planar molecule  $(\text{NMe}_4)_4[(\text{Mo}_2\text{S}_2\text{O}_2)_7(\text{OH})_{14}(\text{C}_4\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 13\text{H}_2\text{O}$  (**1**,  $\{\text{Mo}_{14}\}$ ), the nonplanar molecule  $\text{K}_8[(\text{Mo}_2\text{S}_2\text{O}_2)_6(\text{OH})_8(\text{C}_4\text{O}_4)_2(\text{Mo}_2\text{O}_8)_2(\text{H}_2\text{O})_4] \cdot 15\text{H}_2\text{O}$  (**2**,  $\{\text{Mo}_{16}\}$ ) formed by the addition of  $\{\text{Mo}_2\text{O}_8\}$  units into the system, and the chiral ringlike structure  $\text{KH}[\text{NMe}_4]_2[(\text{Mo}_2\text{S}_2\text{O}_2)_4(\text{OH})_6(\text{Mo}_2\text{O}_8)(\text{C}_4\text{O}_4)] \cdot 10\text{H}_2\text{O}$  (**3a**,  $\{\text{Mo}_{10}\}$ ), which were obtained under different reaction conditions. Furthermore, it was possible to isolate the nonchiral version of the ring, **3b**, which has a mirror plane within the ring (Figure 1).

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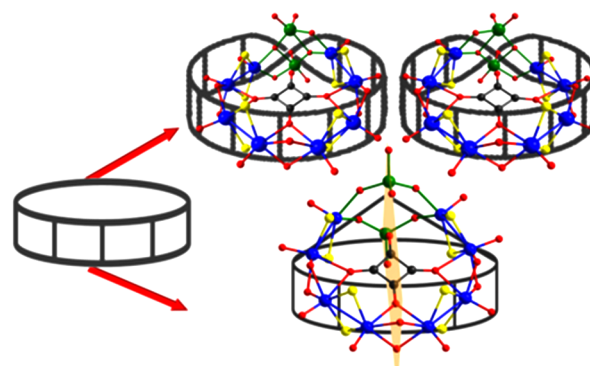
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The third reaction system, yielding **3a**, can be regarded as an autochirogenic system, in which we found the chiral cluster to be predominant over the nonchiral isomer  $K_4[(Mo_2S_2O_2)_4(OH)_6(Mo_2O_8)(C_4O_4)] \cdot 13H_2O$  (**3b**,  $\{Mo_{10}\}$ ) (Figure 1). The chiral cluster **3a** was *always* produced first and in highest yield from the reaction mixture (ca. 35 vs <1% for **3a** vs **3b**, respectively). This phenomenon is comparable to sensitized photochirogenesis. For example, Kanamata and co-workers reported an example of photochirogenesis wherein planar, nonchiral (*Z*)-cyclooctene was transformed into the corresponding planar, chiral *E* isomer,<sup>13</sup> while in our system, there is no need for either a sensitizer or UV light. Here, by the controlled addition of hydroxide ions,<sup>14</sup> we found that the self-condensation process of the freshly prepared  $[Mo_2S_2O_2(H_2O)_6]^{2+}$  proceeds directly and that the squarate anion has a direct bearing on the  $[Mo_2S_2O_2(H_2O)_6]^{2+}$  self-condensation in the formation of compound **1**. Next, sodium molybdate dihydrate was introduced into the system, giving rise to the nonplanar compound **2** and the chiral cluster **3a**. The isomeric nonchiral cluster **3b** was obtained from the mother liquor of **3a**. It is worth mentioning that even when we tried adding more KCl to the solution to induce precipitation of **3b**, the chiral compound **3a** crystallized first. Furthermore, **3a** could be also synthesized using continuous flow with an increased crystallization rate compared with the “one-pot” system [see the Supporting Information (SI)].

Compound **1** crystallizes in the  $P\bar{1}$  space group, and the  $[(Mo_2O_2S_2)_7(OH)_{14}(C_4O_4)_2(H_2O)_2]^{4-}$  polythioanion structure is a tetradecanuclear wheel with an oval-shaped cavity that encapsulates two squarate anions with approximate  $C_{2v}$  symmetry. The coordination geometries of the two anions differ by a  $45^\circ$  rotation (Figure 1), and the  $Mo^V$ – $Mo^V$  moieties can be clearly identified, with bond distances ranging between 2.84(8) and 2.85(7) Å. The molybdenum atoms of the tetradecanuclear wheel are each bound to a terminal oxo group [ $Mo^V=O_t = 1.66(5)$ – $1.69(4)$  Å] and are alternatively bridged by two hydroxo ligands [2.06(7)–2.13(2) Å], two sulfido bridges [2.31(2)–2.32(9) Å], and two coordinated water molecules [2.27(9)–2.34(3) Å]. To break the symmetry and coplanarity, the molybdate unit  $\{Mo_2O_8\}$  was introduced into the system, and a nonplanar molecule **2** with  $C_s$  symmetry was successfully obtained. In the  $[(Mo_2S_2O_2)_6(OH)_8(C_4O_4)_2(Mo^VI_2O_8)_2(H_2O)_2]^{8-}$  structure, two units corresponding to the right half of **1**,  $\{(Mo_2S_2O_2)_3(OH)_4(C_4O_4)\}$ , are linked by two  $[Mo^VI_2O_8(H_2O)_2]^{4-}$   $\{Mo_2\}$  units to construct the skeleton of the hexadecanuclear elliptical ring. Two squarate anions are located in the central cavity, and each is bonded to six adjacent  $Mo^V$  atoms through  $Mo^V$ – $\mu_4$ -O interactions. Thanks to the introduction of the  $\{Mo_2\}$  units, a spectacular ring expansion via the  $Mo^V$ – $\mu_2/\mu_3$ -O– $Mo^VI$  linkages occurs, forming the unprecedented hexadecanuclear nonplanar paralleled macrocycle **2** with  $C_s$  point-group symmetry. This represents a drop in symmetry from  $C_{2v}$  as a result of the addition of the  $\{Mo_2\}$  units. Therefore, we hypothesized that if we were to retain only half of the nonplanar ring, we could access a ring system with even lower symmetry by reducing the amount of the squaric acid and also by changing the ratio of  $[Mo_2S_2O_2(H_2O)_6]^{2+}$  to sodium molybdate. As a result, we observed spontaneous resolution, and the conglomerate crystallized separately. Here, compound **3a** crystallized in the chiral space group  $P6_322$ , and the formula of the chiral cyclic cluster is  $[(Mo^V_2S_2O_2)_4(OH)_6(Mo^VI_2O_8)(C_4O_4)]^{4-}$ ; the two chiral forms of the crystals could be separated manually under a polarizing microscope (Figures

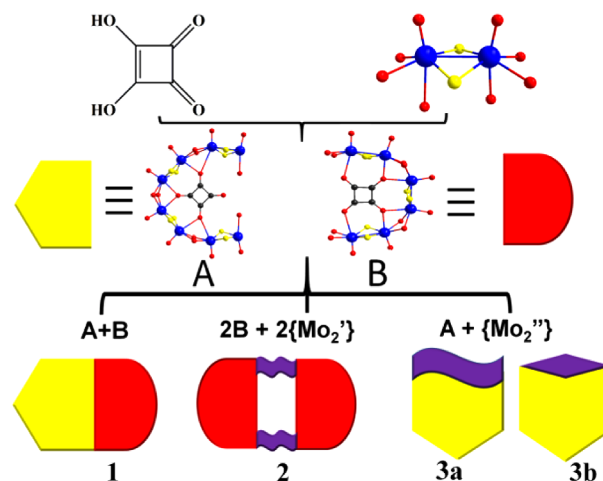
S2 and S21 in the SI). A noteworthy feature is that four  $\{Mo^V_2O_2S_2\}$  units are connected to each other by hydroxo double bridges, building up the “bend” part of the molecule, and the ring is completed by the incorporation of a  $\{Mo^VI_2O_8\}$  unit, which also contributes to the asymmetry of the circular ring, realizing the “twist” and the chirality of the molecule (Figure 1). The key difference between **3a** and **3b** is that the  $[Mo^VI_2O_8]^{4-}$  unit adopts two distinct configurations (Figure 2



**Figure 2.** Schematic representation of (top) the Möbius strip formed using the ring twist to chirality approach presented here and (bottom) the ability to refill the ring and form a nonchiral version.

and Figure S3). Furthermore, we could obtain **3b** from the mother liquor that initially yielded **3a**. Intriguingly, the chiral cluster **3a** was always produced first in high yield, and **3b** crystallized in a much lower yield after **3a** was separated from the mother liquor.

On the basis of the above structures, we propose a new library of virtual oxothioanion building units A and B templated by the squarate anion, as depicted in Figure 3. Compound **1**



**Figure 3.** Schematic representation of the new building blocks A and B and cartoon representations of the four compounds.

can be regarded as the direct combination of building blocks A and B. When two B building blocks are connected by two  $\{Mo_2\}$  anions (violet strips), molecule **2** is formed. As for **3**, building block A is capped by one  $[Mo_2O_8]^{4-}$   $\{Mo_2\}$  unit (violet strip). To explore our hypothesis on the self-condensation process and investigate the clusters in more detail, we carried out electrospray ionization mass spectrometry (ESI-MS) studies in acetonitrile solution (Figure S22), which

provided unambiguous and direct evidence for the presence of the three polythioanion clusters in the solution, although a multitude of charged states resulting from the variable numbers of protons and potassium or tetramethylammonium ions gave overlapping envelopes.

These ESI-MS studies allowed the identification of the  $\{\text{Mo}_{14}\}$  cluster; for example, peaks at  $m/z$  844.4, 856.8, and 1330.7 could be assigned to molecular clusters with charges of  $-3$ ,  $-3$ , and  $-2$ , respectively (Figure S22 and Table S2). Similarly, in the  $\{\text{Mo}_{16}\}$  cluster, the peaks at  $m/z$  1376.0 and 1395.0 can unambiguously be regarded as species with a charge of  $-2$  having the typical formulas  $\{\text{H}_6[(\text{Mo}_2\text{S}_2\text{O}_2)_6(\text{OH})_8(\text{C}_4\text{O}_4)_2(\text{Mo}_2\text{O}_8)_2](\text{H}_2\text{O})\}^{2-}$  and  $\{\text{K}_1\text{H}_5[(\text{Mo}_2\text{S}_2\text{O}_2)_6(\text{OH})_8(\text{C}_4\text{O}_4)_2(\text{Mo}_2\text{O}_8)_2](\text{H}_2\text{O})\}^{2-}$ , respectively (Figure S22, Table S3), while in the chiral  $\{\text{Mo}_{10}\}$  cluster, the strong peaks clearly observed at  $m/z$  872.4 and  $m/z$  1688.8, 1854.8, and 1908.0 could be ascribed to chiral molecular clusters with charges of  $-2$  and  $-1$ , respectively (Figure S23 and Table S4). We also observed the peaks for the two thiometalate building blocks  $[\text{H}_2(\text{Mo}_2\text{S}_2\text{O}_2)_4(\text{OH})_{10}(\text{C}_4\text{O}_4)]^{2-}$  (A) and  $[(\text{NMe}_4)_2(\text{Mo}_2\text{S}_2\text{O}_2)_3(\text{OH})_8(\text{C}_4\text{O}_4)(\text{H}_2\text{O})_4]^{2-}$  (B) at  $m/z$  718.5 and 666.7 respectively, consistent with our hypothesis. Because of the presence of the  $\{\text{Mo}_2\text{O}_8\}$  unit, we did not observe the peaks of the isolated building blocks A or B or of **3a**, but it was possible to see evidence of aggregation of the molecules (2-mer up to the 8-mer).

Prior to the electrochemical studies, the stabilities of compounds **1–3a** were assessed by UV–vis spectroscopy in distilled water and 0.1 M  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  (Figures S8–S13). The main absorption peaks for the three compounds come at 271, 273, and 275 nm, respectively, corresponding to  $\text{E} \rightarrow \text{Mo}$  ( $\text{E} = \text{O}, \text{S}$ ) ligand-to-metal charge transfer (LMCT). The spectra were perfectly unchanged after 24 h in 0.1 M  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ . According to the previous literature, thiometalates can be efficient electrocatalysts for hydrogen evolution, mimicking some biologically studied hydrogenases.<sup>15</sup> Consequently, the electrochemical behaviors of compounds **1–3a** were investigated by cyclic voltammetry at the same concentration of 1.6 mM in 0.1 M  $\text{HOAc}/\text{NaOAc}$  buffer solution containing 0.2 M  $\text{Na}_2\text{SO}_4$  as the supporting electrolyte (Figure 4).

Comparison of the three compounds shows that there is only one characteristic reductive peak occurring near  $-0.8$  V for **1**, while **2** and **3a** have one characteristic irreversible reductive peak. The irreversible reductive peak for **2** and **3a**, which is

centered around  $E_{\text{pc}} = -0.7$  V vs  $\text{Ag}/\text{AgCl}$ , contains a contribution arising from the reduction of some  $\text{Mo}^{\text{VI}}$  centers of the ring as well as proton reduction. At the same concentration of **2** and **3a**, the redox current for **2** appeared to be larger than that of **3a**, probably because **2** has more  $\text{Mo}^{\text{VI}}$  units. As for **1**, the well-separated reduction peak corresponds to a proton reduction process. Relative to the blank buffer solution, the reduction current increased dramatically, which indicates that the compounds exhibit some degree of electrocatalytic behavior. Furthermore, the cyclic voltammograms of the three compounds were measured at different potential scan rates (Figures S24–S26). The redox wave peak at  $E_{\text{pc}} = -0.7$  V vs  $\text{Ag}/\text{AgCl}$  remained chemically irreversible regardless of the scan rate. Remarkably, the scan rate did not affect the intrinsic electrochemical behavior of **1–3a**, but the cathodic peak potentials were slightly shifted to negative values as the scan rate increased. Additionally, UV–vis measurements on the solutions used for the electrochemical measurements showed the compounds to be stable under the electrocatalytic reaction conditions (Figures S27–S29).

In conclusion, we have presented a symmetry-breaking strategy for the assembly of a chiral polythioanion ring cluster,  $\{\text{Mo}_{10}\}$ , templated by the squarate anion with the topology of a Möbius strip, giving an autochirogenic system. Introducing the dimeric  $\{\text{Mo}_2\text{O}_8\}$  unit to the system not only breaks the symmetry of the ring molecule but also suggests that it should be possible to produce a range of hybrid clusters containing both polyoxometalate- and polythiometalate-based building blocks. In going from **1** to **2** to **3a**, the symmetry of the molecule is gradually broken, providing evidence of a symmetry-breaking process; the chiral cluster **3a** was synthesized in both the one-pot batch and the linear flow system. We also found that the chiral cluster **3a**, which is predominant over the nonchiral cluster **3b**, appears to constitute the first “inorganic” autochirogenic system, and the ESI-MS studies provided evidence for the building-block principle in solution.

## ■ ASSOCIATED CONTENT

### Supporting Information

Materials, instrumentation, synthesis, crystallographic procedures and data (CIF), UV–vis spectral studies, powder X-ray diffraction (PXRD) patterns, and mass spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

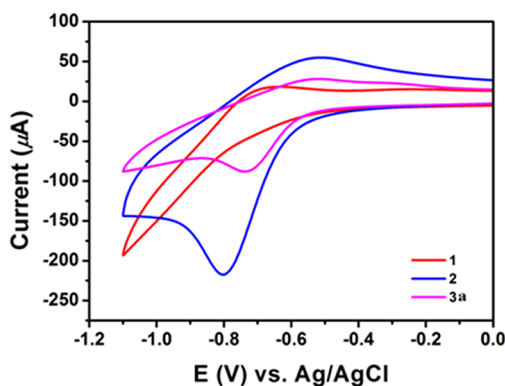
The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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**Figure 4.** Cyclic voltammograms of compounds **1–3a** at a concentration of 1.6 mM in a 0.1 M  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  buffer containing 0.2 M  $\text{Na}_2\text{SO}_4$ . The scan rate was 200 mV/s.

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