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A $[\text{Mo}_2\text{O}_2\text{S}_2]$ -based ring system incorporating tartrate as the bridging ligand: synthesis, structure and catalytic activity of $\text{Cs}_4[\text{Mo}_2\text{O}_2(\mu\text{-S})_2]_2(\mu_4\text{-tart})_2$ ($\text{tart} = [\text{C}_4\text{H}_2\text{O}_6]^{4-}$)

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Abstract: Treatment of $[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6]^{2+}$ with racemic tartaric acid (tartH_4) in the presence of sodium hydroxide and cesium chloride in aqueous solution led to the isolation of a new tetra-molybdenum ring cluster $\text{Cs}_4[\text{Mo}_2\text{O}_2(\mu\text{-S})_2]_2(\mu_4\text{-tart})_2$. The cyclic cluster polyanion consists of two dinuclear $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2]^{2+}$ moieties and two bridging tart^{4-} ligands. The cyclic polyoxothiomolybdate cluster, supported on the mesoporous silica SBA-15, was tested for heterogeneous catalysis in thiophene hydrodesulfurization.

Keywords: catalytic activity; crystal structure; hydrodesulfurization (HDS); oxothiomolybdenum cluster; tartaric acid.

1 Introduction

In the past decade, polyoxothiometalates have emerged as a fascinating class of novel compounds which appear as ring-like clusters based upon the self-condensation of $[\text{M}_2\text{O}_2(\mu\text{-S})_2]^{2+}$ ($\text{M} = \text{Mo}^{\text{V}}, \text{W}^{\text{V}}$) oxothio cations around anionic templates such as phosphate, metalate or polycarboxylate ions. Their $[\text{M}_2\text{O}_2(\mu\text{-S})_2]^{2+}$ building units are connected through double hydroxo bridges [1–3]. To date, a large family of cyclic polyoxothiomolybdates built by connecting the $[\text{M}_2\text{O}_2(\mu\text{-S})_2]^{2+}$ cations by oxygen-containing organic ligands have been isolated and structurally

characterized, leading to a series of cyclic molecular materials with electrocatalytic properties in the hydrogen evolution reaction process [4, 5]. Since Sécheresse and co-workers first reported a neutral cyclic oxothio cluster $[\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{12}(\text{H}_2\text{O})_6]$, a series of anionic oxothiomolybdenum wheels of flexible and fluxional host–guest assemblies with nuclearity varying in the Mo_8 – Mo_{18} range have been synthesized [1, 6, 7]. As well known, tartaric acid and metal-tartrato complexes are important tools for the resolution of racemic compounds [8]. Interesting structures involving bridging tart^{4-} ligands were found in dinuclear vanadium, tungsten and molybdenum complexes [8–12]. In the course of our research on the synthesis of polynuclear metaloxysulfide clusters [13], we tried the reaction of $[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6]^{2+}$ with racemic tartaric acid (tartH_4) in the presence of alkali halide. A new $[\text{Mo}_2\text{O}_2\text{S}_2]$ -based ring cluster $\text{Cs}_4[\text{Mo}_2\text{O}_2(\mu\text{-S})_2]_2(\mu_4\text{-tart})_2$ (**1**) incorporating tart^{4-} as a bridging ligand has been isolated. In this paper, the synthesis, structural characterization and catalytic activity of the title cluster are reported.

2 Experimental section

2.1 General

Tartaric acid was used as a racemic mixture purchased from Energy Chemical. The mesoporous silica SBA-15 was synthesized according to the reported method [14]. Tetraethyl orthosilicate (98.0%), Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$), sublimed sulfur and thiophene were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All other reagents were of analytical grade and used without further purification.

2.2 Synthesis of $\text{Cs}_4[\text{Mo}_2\text{O}_2(\mu\text{-S})_2]_2(\mu_4\text{-tart})_2$ (**1**)

TartH_4 (0.75 g, 5 mmol) was dissolved in 50 mL water. Ten milliliters of the oxothio dimer $[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6]^{2+}$ solution

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[1] was dropped into the above solution. The solution was adjusted with 1.0 M aqueous KOH to $\text{pH} \approx 3.5$ and heated to 60°C for 45 min with continuous stirring. After cooling to room temperature, the fine powder was eliminated by centrifugation before the addition of solid CsCl (3.4 g, 20 mmol). The solution was allowed to stir for additional 1 h. A red microcrystalline solid was collected by filtration, washed with cold ethanol and dried with diethyl ether (yield: 1.0 g, 71%). – ^1H NMR [400 MHz, $[\text{D}_6]$ dimethyl sulphoxide (DMSO), 25°C , tetramethylsilane (TMS)]: $\delta = 3.12$ (s, $[\text{O}_2\text{CCH}(\text{O})\text{CH}(\text{O})\text{CO}_2]^{4-}$) ppm. – $\text{C}_8\text{H}_4\text{Cs}_4\text{Mo}_4\text{O}_{16}\text{S}_4$ (1399.2): calcd. C 6.86, Mo 27.42 (26.47), S 9.15; Cs 37.99; found C 6.45, Mo 26.47, S 8.69, Cs 36.48. Red crystals suitable for X-ray diffraction analysis were obtained by dissolving 0.1 g of red microcrystalline powder in 10 mL of distilled water and standing for 3 days at room temperature.

2.3 Compound 1 on SBA-15 support

SBA-15 (100 mg) was degassed at 120°C under vacuum for 6 h. Fifteen milligrams of **1** was dissolved in deionized water which was degassed with N_2 bubbling for 15 min. The activated SBA-15 (1.5 g) was suspended in the above solution, and the mixture was stirred at 60°C for 20 h. The excess water was removed using a rotary evaporator, and the resulting yellow solid was dried at 80°C overnight. The product was washed with deionized water and MeOH until the filtrate became colorless. Finally, the solid product was dried in an oven at 120°C for 8 h and stored for further applications.

2.4 X-ray crystallography

A suitable single crystal of **1** was selected and mounted on a Bruker SMART Apex CCD area-detecting diffractometer using graphite-monochromated MoK_α ($\lambda = 0.71073$ Å) radiation at room temperature. Data were measured using ω scans with 0.5° per frame, such that a hemisphere was collected. Cell parameters were retrieved using the SMART software and refined on all observed reflections using SAINT [15]. Data reduction was performed with SAINT software with corrections for Lorentz polarization and decay. Absorption corrections were applied using SADABS [16]. The structure was solved by Direct Methods using SHELXS-97 and refined by least squares on F^2 (SHELXL-97) [17, 18]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined employing a riding model with displacement parameters $1.5\times$ or $1.2\times$ those of the bound carbon atoms. Refinement

was accomplished by full-matrix least squares based on F^2 , and produced a final $wR2$ value of 0.0724. A conventional $R1 = 0.0333$ was calculated using 3120 observed [$I > 2.0\sigma(I)$] data, 163 parameters and 0 restraints. The largest peak in the final difference map had a height of $2.840 \text{ e } \text{\AA}^{-3}$ and is in the vicinity of the cesium atom.

CCDC 1495650 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3 Results and discussion

The reaction involved complete deprotonation to produce the tart^{4-} anion as a ligand, and no self-condensation of the $[\text{M}_2\text{S}_2\text{O}_2]^{2+}$ units occurred. Each molybdenum atom is chelated by a pair of oxygen atoms from carboxyl and hydroxyl groups and the ring cluster **1** is formed. The title cluster has been characterized by ^1H NMR, infrared spectroscopy and microanalyses (Figs. S1 and S2). One singlet at around 3.12 ppm was observed in the ^1H NMR spectrum; the other two peaks are attributed to solvent DMSO (2.51 ppm) and water (3.37 ppm). The $\text{Mo}=\text{O}$ bonds give two strong bands at 946 and 921 cm^{-1} . A medium-intensity vibration at 549 cm^{-1} is attributable to the $\text{Mo}-\text{O}$

Table 1: Crystallographic data and experimental details for **1**.

Compound	$\text{Cs}_4[\text{Mo}_2\text{O}_2(\mu\text{-S})_2](\mu_4\text{-tart})_2$
Empirical formula	$\text{C}_8\text{H}_4\text{Cs}_4\text{Mo}_4\text{O}_{16}\text{S}_4$
Formula weight	1399.2
Crystal system	Orthorhombic
Space group	$Pbca$
a , Å	11.012(3)
b , Å	15.496(4)
c , Å	15.840(4)
V , Å ³	2702.9(13)
Z	4
D_{calcd} , g cm ⁻³	3.440
Temperature, K	296(2)
$F(000)$, e	2528
$\mu(\text{MoK}_\alpha)$, mm ⁻¹	7.497
Refl. total	15 488
Refl. unique/ R_{int}	3120/0.0332
Ref. parameters	163
$R1^a/wR2^b$ [$I > 2\sigma(I)$]	0.0333/0.0720
$R1^a/wR2^b$ (all data)	0.0363/0.0724
GoF ^c	2.590
$\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³	+2.84/−1.80

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2)]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^c $\text{GoF} = S = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

stretching. The peaks at 1632 and 1375 cm^{-1} for the typical $\nu(\text{CO}_2^-)$ in the infrared spectrum indicates the carboxylate groups of the tart^{4-} ligand in the title cluster. The less

intense absorptions at 462 and 419 cm^{-1} for the Mo–S–Mo stretching modes appear as weak and sharp bands in the wavenumber region below 500 cm^{-1} , which is in good

Fig. 1: Molecular structure of the $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2](\mu_4\text{-tart})_2\}^{4-}$ anion in **1**. Selected distances (Å) and angles (deg): Mo(1)–O(4) 1.684(3), Mo(1)–O(2) 1.996(4), Mo(1)–S(1) 2.3243(14), Mo(1)–S(2) 2.3102(15), Mo(1)–Mo(2) 2.8650(8), C(1)–O(1) 1.219(6), C(1)–O(3) 1.316(6), Mo(2)–O(5) 1.678(4), Mo(2)–O(6) 2.099(4), Mo(2)–O(7) 2.003(4), Mo(2)–S(1) 2.3171(15), Mo(2)–S(2) 2.3301(15), C(4)–O(6) 1.301(6), C(4)–O(8) 1.232(6); O(2)–Mo(1)–O(3) 76.77(14), O(4)–Mo(1)–O(2) 108.37(17), O(4)–Mo(1)–O(3) 102.88(17), O(4)–Mo(1)–S(1) 104.73(13), O(4)–Mo(1)–S(2) 105.58(15), S(2)–Mo(1)–S(1) 101.07(5), S(1)–Mo(2)–S(2) 100.69(5), O(7)–Mo(2)–O(6) 77.24(14).

Fig. 2: Molecular structure of **1**; hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Cs(1)–O(4) 3.128(4), Cs(1)–O(5) 3.304(4), Cs(1)–S(1) 3.7148(16), Cs(2)–O(7) 3.057(4), Cs(2)–S(2) 3.4483(16), Cs(2)–S(1A) 3.6988(16), Cs(2)–O(1A) 3.325(4), Cs(2)–O(3A) 3.202(4); O(4)–Cs(1)–O(5) 65.22(10), O(4)–Cs(1)–S(1) 54.92(7), O(5)–Cs(1)–S(1) 53.36(7), O(3A)–Cs(2)–O(1A) 39.63(9).

agreement with the values previously reported in the literature [11, 13].

The structure of the title cluster was confirmed by an X-ray diffraction study. Crystallographic data and experimental details are shown in Table 1. The new tetranuclear tartrato cluster of molybdenum(V) **1** shows two $\{\text{Mo}_2\text{S}_2\text{O}_2\}$ units linked by two bridging tart^{4-} ligands, as shown in Figs. 1 and 2. Each Mo^{V} atom is pentacoordinate. The geometry of the coordination polyhedron can be described in terms of a square pyramid distorted toward a trigonal bipyramid. Three of the coordination sites on the Mo^{V} atom are occupied by a terminal oxygen atom and two sulfur atoms, and the other two by two oxygen atoms from a tart ligand (one from hydroxylate and the other one from carboxylate). The bond lengths of $\text{Mo}^{\text{V}}\text{--Mo}^{\text{V}}$ [2.8650(8) Å], $\text{Mo}=\text{O}$ [1.684(3) Å] and Mo--S [2.3102(15), 2.3243(14) Å] are comparable to the related clusters containing $\{\text{Mo}_2\text{S}_2\text{O}_2\}$ units [7]. The Mo1--O2 bond length is 1.996(4) Å, near to that of Mo1--O3 [2.086(4) Å]. The bond angle of O2--Mo1--O3 is $76.77(14)^\circ$, similar to that in the peroxo complex $\text{K}_4[\text{Mo}_2\text{O}_2(\text{O}_2)_4(\text{C}_4\text{H}_2\text{O}_6)] \cdot 4\text{H}_2\text{O}$ ($75.83(5)^\circ$) with a tetradentately bridging tartrate [10]. The Cs1 and Cs2 atoms adopt ten and nine coordination modes, respectively, with Cs–O and Cs–S bond lengths in the ranges of 3.005(4)–3.572(4) Å and 3.654(2)–3.715(2) Å, respectively.

Cluster **1** was loaded on the mesoporous silica SBA-15 by the immersion method, and the supported catalyst of **1**/SBA-15 was characterized by IR spectroscopy, low-angle X-ray diffraction (LAXRD), transmission electron microscopy (TEM) and low-pressure N_2 sorption measurement. The LAXRD patterns (Fig. S3) and TEM images (Fig. S4) of SBA-15 and **1**/SBA-15 indicated that the supported catalyst maintained the pore structure of SBA-15. The energy dispersive X-ray spectrum (Fig. S5) showed the peaks of C, O, Mo, S and Cs, which indicated that the molybdenum sulfide cluster has been loaded on SBA-15. Figure 3a shows the N_2 sorption isotherms and pore distribution of SBA-15 and **1**/SBA-15. The Brunauer-Emmett-Teller surface area and pore volume of **1**/SBA-15 are lower than those of SBA-15 (Table S1), because the cluster occupies part of the inner surface area and the micropore volume [13]. The reducibility of the **1**/SBA-15 catalyst was studied by the temperature-programmed reduction (TPR) method in the temperature range 20–600°C. The TPR curve of **1**/SBA-15 (Fig. 3b) indicated hydrogen absorption from 330°C to 362°C and reached a peak at 347°C.

The catalytic activity of **1**/SBA-15 was evaluated in the thiophene-ethanol system. In a stainless autoclave reactor, the catalytic reaction was carried out at 280°C and for different times. From 2 h to 16 h, the conversion rate of

Fig. 3: (a) N_2 sorption isotherms of SBA-15 (■) and **1**/SBA-15 (●); (b) TPR curve of **1**/SBA-15. The insets are the corresponding pore size distribution curves.

thiophene increased with the reaction time. After 16 h, the hydrodesulfurization (HDS) effect was no longer increased (Fig. S6). Subsequently, the thiophene-ethanol system was studied by gas chromatography (GC) and GC-mass spectrometry (GC-MS). The GC result showed that 85.8% of thiophene was desulfurized after 16 h at 280°C. The GC-MS result indicated that the HDS product of thiophene was 1-butanol (Fig. S7). This product was also reported by other oxothiomolybdenum catalytic system containing $\{\text{Mo}_2\text{O}_2\text{S}_2\}$ building unit [13], while molybdenum hydride complexes could catalyze the cleavage of the C–S bonds of thiophene to liberate but-1-ene [19]. Compared to (Co)MoS₂ catalysts [20], **1**/SBA-15 showed relatively higher catalytic activity for the HDS of thiophene.

In summary, a new $[\text{Mo}_2\text{O}_2\text{S}_2]$ -based ring cluster **1** incorporating tart^{4-} as a bridging ligand was synthesized and characterized by single-crystal X-ray diffraction along with spectroscopic methods. The cyclic cluster polyanion consists of two dinuclear $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2]^{2+}$ moieties and two

bridging tart^{4-} ligands. The cyclic polyoxo-thiomolybdate cluster was effectively supported on SBA-15. Catalytic activity of the supported catalyst was tested for the thiophene HDS reaction.

4 Supplementary information

NMR and IR spectra and other supporting data associated with this article can be found in the online version (DOI: 10.1515/znb-2017-0002).

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