Yunfeng Ye, Guodong Tang and Jun Qian*

Synthesis and crystal structure of oktakis(dimethylsulphoxide- $\kappa^1 O$)gadolinium(III) [tetrabromido- μ_2 -bromido- μ_2 -sulfido-di- μ_3 - sulfido- μ_4 -sulfido-tetracopper(I)-tungsten(VI)], $C_{16}H_{48}O_8S_{12}Br_5Cu_4GdW$

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.22 × 0.20 × 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	9.87 mm ⁻¹
Diffractometer, scan mode:	Rigaku Saturn 724 ⁺ , φ and ω
$\theta_{\max}$, completeness:	25.3°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11490, 6878, 0.039
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5277
$N(\text{param})_{\text{refined}}$:	441
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4], PLATON [5]

Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Abstract

$C_{16}H_{48}O_8S_{12}Br_5Cu_4GdW$, monoclinic, $P2_1$ (no. 4), $a = 11.576(2)$ Å, $b = 12.407(3)$ Å, $c = 17.582(3)$ Å, $\beta = 100.76(3)^\circ$, $V = 2480.8(9)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0446$, $wR_{\text{ref}}(F^2) = 0.1169$, $T = 293$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and

Source of material

A mixture of 0.0570 g CuBr (0.4 mmol), 0.0474 g KBr (0.4 mmol) and 0.0350 g $(NH_4)_2WS_4$ (0.1 mmol) were added to 3 mL DMSO with strong stirring to obtain an orange solution. After that, 0.0343 g $Gd(NO_3)_3$ (0.1 mmol) was quickly added in this mixed solution and stirred for 30 min to get a deep red solution. After filtration, 1 mL DMSO was successively added on the top of the above filtrate as buffer solution. Subsequently, 5 mL of isopropyl alcohol was layered carefully on the buffer DMSO solution. Orange crystals were obtained after 10 days at room temperature in dark with a yield of 0.104 g (60% based W).

Experimental details

The structure was solved by direct methods and refined using the SHELX software [3]. All of the hydrogen atoms were placed in the calculated positions (see Table 2).

*Corresponding author: Jun Qian, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, Jiangsu, 212013, P. R. China, E-mail: junqian8203@ujs.edu.cn. <https://orcid.org/0000-0003-1538-6068>

Yunfeng Ye, Jiangsu Nursing Vocational College, Huai'an, Jiangsu, 223300, P. R. China

Guodong Tang, School of Chemistry and Chemical Engineering, Huaiyin Normal University, Huai'an, Jiangsu, 223300, P. R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
W1	0.13443 (8)	0.68772 (7)	0.22458 (5)	0.0190 (2)
Gd1	0.70752 (8)	0.11726 (8)	0.25551 (5)	0.0101 (2)
Br1	0.2800 (2)	0.40576 (19)	0.19271 (14)	0.0314 (6)
Br2	−0.0621 (2)	0.4782 (2)	−0.00076 (12)	0.0313 (6)
Br3	0.1677 (2)	0.3866 (2)	0.40569 (13)	0.0346 (6)
Br4	0.3093 (2)	0.9085 (2)	0.44834 (13)	0.0331 (6)
Br5	0.5191 (2)	0.6317 (2)	0.15024 (16)	0.0419 (7)
Cu1	0.0359 (3)	0.5647 (2)	0.10787 (16)	0.0277 (7)
Cu2	0.2326 (3)	0.8057 (2)	0.34381 (15)	0.0254 (7)
Cu3	0.1726 (3)	0.4957 (2)	0.29721 (16)	0.0301 (7)
Cu4	0.3324 (2)	0.6116 (3)	0.18259 (14)	0.0296 (7)
S1	−0.0014 (5)	0.5616 (5)	0.2278 (3)	0.0273 (14)
S2	0.1739 (5)	0.6942 (5)	0.1051 (3)	0.0230 (12)
S3	0.0713 (6)	0.8458 (5)	0.2569 (3)	0.0333 (16)
S4	0.3005 (5)	0.6438 (4)	0.3107 (3)	0.0239 (14)
S5	0.9700 (5)	0.2369 (5)	0.2094 (3)	0.0257 (13)
S6	0.5886 (7)	0.3314 (7)	0.1352 (4)	0.051 (2)
S7	0.7256 (5)	0.3572 (4)	0.3575 (3)	0.0219 (13)
S8	0.5144 (5)	0.0969 (5)	0.3867 (3)	0.0252 (13)
S9	0.4426 (5)	0.0275 (5)	0.1384 (3)	0.0273 (14)
S10	0.6509 (5)	−0.1509 (5)	0.2963 (4)	0.0290 (14)
S11	0.8701 (5)	0.0728 (5)	0.4390 (3)	0.0259 (14)
S12	0.8253 (5)	−0.0393 (5)	0.1190 (3)	0.0273 (14)
O1	0.5167 (12)	0.0431 (12)	0.2195 (8)	0.023 (3)
O2	0.6066 (14)	0.1624 (12)	0.3527 (8)	0.028 (4)
O3	0.7315 (14)	0.3021 (12)	0.2804 (8)	0.025 (4)
O4	0.8647 (12)	0.1598 (12)	0.1975 (8)	0.025 (4)
O5	0.6180 (13)	0.2084 (12)	0.1425 (8)	0.028 (4)
O6	0.8637 (12)	0.1245 (13)	0.3617 (8)	0.025 (3)
O7	0.7073 (12)	−0.0475 (11)	0.3282 (8)	0.022 (3)
O8	0.7409 (13)	−0.0267 (12)	0.1788 (8)	0.027 (4)
C1	1.018 (2)	0.227 (2)	0.1202 (12)	0.038 (7)
H1A	1.0177	0.1527	0.1048	0.057*
H1B	1.0958	0.2557	0.1255	0.057*
H1C	0.9655	0.2671	0.0815	0.057*
C2	0.5945 (18)	0.4310 (19)	0.3366 (12)	0.026 (5)
H2A	0.5890	0.4657	0.2873	0.039*
H2B	0.5939	0.4845	0.3760	0.039*
H2C	0.5289	0.3832	0.3352	0.039*
C3	0.717 (2)	0.392 (2)	0.1086 (16)	0.052 (8)
H3A	0.6966	0.4615	0.0858	0.078*
H3B	0.7456	0.3468	0.0720	0.078*
H3C	0.7770	0.4005	0.1540	0.078*
C4	0.496 (3)	0.340 (3)	0.0408 (18)	0.080 (11)
H4A	0.4987	0.4118	0.0211	0.120*
H4B	0.4166	0.3223	0.0448	0.120*
H4C	0.5234	0.2901	0.0064	0.120*
C5	0.367 (3)	−0.090 (3)	0.1463 (18)	0.069 (9)
H5A	0.2901	−0.0735	0.1558	0.103*
H5B	0.4089	−0.1323	0.1884	0.103*
H5C	0.3602	−0.1305	0.0990	0.103*
C6	0.324 (3)	0.115 (3)	0.1360 (19)	0.080 (10)
H6A	0.2979	0.1127	0.1848	0.120*
H6B	0.2603	0.0935	0.0955	0.120*
H6C	0.3473	0.1872	0.1263	0.120*

Table 2: (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C7	0.804 (2)	−0.1801 (18)	0.0862 (13)	0.031 (6)
H7A	0.8474	−0.2270	0.1247	0.046*
H7B	0.8320	−0.1887	0.0385	0.046*
H7C	0.7221	−0.1979	0.0784	0.046*
C8	0.741 (2)	0.024 (2)	0.0360 (14)	0.045 (7)
H8A	0.6708	−0.0166	0.0181	0.067*
H8B	0.7866	0.0282	−0.0043	0.067*
H8C	0.7202	0.0959	0.0494	0.067*
C9	0.989 (2)	−0.020 (2)	0.4446 (13)	0.040 (7)
H9A	0.9594	−0.0896	0.4270	0.060*
H9B	1.0301	−0.0253	0.4973	0.060*
H9C	1.0425	0.0049	0.4126	0.060*
C10	0.593 (3)	−0.207 (2)	0.3762 (16)	0.053 (8)
H10A	0.6515	−0.2042	0.4225	0.080*
H10B	0.5705	−0.2811	0.3649	0.080*
H10C	0.5248	−0.1669	0.3835	0.080*
C11	0.945 (2)	0.1663 (19)	0.5045 (12)	0.037 (7)
H11A	1.0037	0.2018	0.4818	0.056*
H11B	0.9812	0.1299	0.5509	0.056*
H11C	0.8899	0.2187	0.5167	0.056*
C12	0.818 (2)	0.4654 (18)	0.3621 (14)	0.030 (6)
H12A	0.8965	0.4406	0.3605	0.044*
H12B	0.8189	0.5040	0.4095	0.044*
H12C	0.7920	0.5123	0.3190	0.044*
C13	1.099 (2)	0.160 (2)	0.2627 (13)	0.051 (8)
H13A	1.1091	0.1752	0.3170	0.077*
H13B	1.1685	0.1803	0.2439	0.077*
H13C	1.0854	0.0839	0.2545	0.077*
C14	0.400 (2)	0.197 (2)	0.3917 (15)	0.052 (7)
H14A	0.4166	0.2334	0.4407	0.078*
H14B	0.3248	0.1616	0.3863	0.078*
H14C	0.3973	0.2485	0.3507	0.078*
C15	0.5746 (19)	0.089 (2)	0.4881 (11)	0.029 (6)
H15A	0.6482	0.0509	0.4955	0.044*
H15B	0.5208	0.0507	0.5140	0.044*
H15C	0.5869	0.1600	0.5092	0.044*
C16	0.769 (2)	−0.238 (2)	0.2994 (18)	0.054 (8)
H16A	0.8319	−0.2016	0.2823	0.081*
H16B	0.7444	−0.2989	0.2661	0.081*
H16C	0.7943	−0.2634	0.3515	0.081*

Comment

Heteroethiometallic Mo(W)/S/Cu(Ag) clusters have attracted much attention because of their intriguing skeletal structures and topologies [6, 7], as well as the potential applications in non-linear optical (NLO) materials [8, 9] NLOs are of great interest due to their multifunctional applications in optical fibers, ultrafast optical communication, optical computing, logic devices, optical switching, and optical limiting [10–12]. As a result, considerable efforts in crystal engineering have been devoted to the

design and syntheses of various kinds of Mo(W)/S/Cu(Ag) clusters with unique NLO properties [13–16]. Until now, many Mo(W)/S/Cu(Ag) clusters have been synthesized to achieve a variety of structures, which origin from the assembly of $(NH_4)_2MS_4$ ($M = Mo, W$) or $(NH_4)_2MOS_3$ ($M = Mo, W$) precursors with different cuprous salts or silver salts [17]. To further study the structure-activity relationship of Mo(W)/S/Cu(Ag) clusters, here we introduced CuBr as the cuprous salt and prepared a semi-open cubic cluster with extra side.

As shown in the figure, the asymmetric unit of the title structure consists of the anion $[WS_4Cu_4Br_5]^{3-}$ and the cation $[Gd(DMSO)_8]^{3+}$. The Gd(III) cation is coordinated by O atoms from eight DMSO molecules. The anion is a cluster, which contains three differently coordinated sulfido ligands (μ_2 -S, μ_3 -S and μ_4 -S), two differently bonded bromido ligands (μ_2 -Br and terminal Br), and three different coordination environments for the Cu(I) centers. Cu1 is coordinated by two μ_3 -S atoms and one terminal Br in a T-shaped mode and connected with two Cu atoms and W through two μ_3 -S bridges. Cu2 is coordinated with one μ_2 -S, one μ_4 -S and a terminal Br in a planar triangular mode. Cu3 and Cu4 have the same coordination environment, in which the Cu center is coordinated with one μ_3 -S, one μ_4 -S, one μ_2 -Br and one terminal Br atom to form a distorted tetrahedral coordination configuration. The W(VI) is 4-coordinated by four S atoms, displaying a distorted tetrahedron. The whole structure of title cluster exhibits a semi-open cubic cluster with an additional face, which is different to the common pentanuclear cluster [18].

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