

Synthesis and characterization of the first dodecanuclear M–Ag–S cage cluster: $[\text{NET}_4]_2[\{\text{M}_2\text{Ag}_2\text{S}_2\text{O}_2(\text{S}_2\text{C}_2\text{H}_4)_2\}_3(\mu_6\text{-S})]\cdot\text{CH}_2\text{Cl}_2\cdot\text{MeCN}$ ($\text{M} = \text{Mo}, \text{W}$)

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The first dodecanuclear heterobimetallic cage cluster with a central $\mu_6\text{-S}$ ligand, containing the core $[\{\text{M}_2\text{Ag}_2\text{S}_2\text{O}_2(\text{edt})_2\}_3(\mu_6\text{-S})]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{H}_2\text{edt} = \text{ethane-1,2-dithiol}$), is synthesized and characterized; the average $\text{Ag}-\mu_6\text{-S}$ bond length of the core $[\{\text{Mo}(\text{W})_2\text{Ag}_2\text{S}_2\text{O}_2(\text{edt})_2\}_3(\mu_6\text{-S})]^{2-}$ is 2.528 (2.531) Å.

The chemistry of heterometallic cluster compounds has attracted considerable attention for their uses as models for the active sites in a variety of metalloenzymes and their potential applications as functional materials in several fields.¹ Heterometallic cluster compounds containing $[\text{MS}_4]^{2-}/\text{M}^+$ ($\text{M} = \text{Mo}, \text{W}$; $\text{M}^+ = \text{Cu}, \text{Ag}$) have been extensively studied.² At present, some polynuclear $\text{M}^{\text{VI}}\text{-Ag-S}$ ($\text{M} = \text{Mo}, \text{W}$) cluster compounds such as $\text{NET}_4[\{\text{PPh}_3\}_2\text{Ag}(\mu\text{-S})_2\text{Mo}(\mu\text{-S})\text{OCu}(\text{CN})]$ (butterfly),³ $[\{\text{Ag}(\text{PPh}_3)\}_3\text{MoS}_4\text{Cl}]$ (cubane-like),⁴ $[\text{Ag}_6\text{M}_2\text{S}_6\text{O}_2(\text{Me}_3\text{CS})_2(\text{PPh}_3)_4]$ (double-cubane-like),⁵ $[\text{M}_2\text{S}_8\text{Ag}_4(\text{PPh}_3)_4]$ (cage),⁶ $[\text{W}_4\text{Ag}_5\text{S}_{16}\text{Nd}(\text{dmf})_8]_n$ (one-dimensional chain)⁷ and $[\text{WS}_4\text{Ag}\cdot\text{NH}_3\text{C}(\text{CH}_2\text{OH})_3\cdot\text{H}_2\text{O}]_n$ (double chain)⁸ have been characterized. A few $\text{M}^{\text{V}}\text{-Ag-S}$ complexes such as $[\text{M}_2\text{Ag-S}_4(\text{edt})_2(\text{PPh}_3)]^-$ (incomplete cubane-like)⁹ and $[\{\text{PPh}_3\}\text{Ag}\}_2\text{Mo}_2\text{S}_4(\text{tdt})_2]$ (cubane-like)¹⁰ have been reported. However, no non-polymeric M-Ag-S ($\text{M} = \text{Mo}, \text{W}$) complexes with more than nine metal centers have, as yet, been synthesized.

Herein the syntheses and characterization of novel dodecanuclear heterobimetallic clusters $[\text{NET}_4]_2[\{\text{M}_2\text{Ag}_2\text{S}_2\text{O}_2(\text{S}_2\text{C}_2\text{H}_4)_2\}_3(\mu_6\text{-S})]\cdot\text{CH}_2\text{Cl}_2\cdot\text{MeCN}$ ($\text{M} = \text{Mo}, \text{W}$) with cage cores $[\{\text{M}_2\text{Ag}_2\text{S}_2\text{O}_2(\text{S}_2\text{C}_2\text{H}_4)_2\}_3(\mu_6\text{-S})]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$) are described, the first molybdenum(v) or tungsten(v)-silver clusters containing a $\mu_6\text{-S}$ ligand. To our knowledge, this type of cluster containing $\mu_6\text{-S}$ is rare in molybdenum or tungsten(v)-copper(silver) clusters, the only example being $[\text{NET}_4]_2[\text{Mo}_6\text{Cu}_6\text{S}_6(\mu_6\text{-S})\text{O}_6(\text{S}_2)_6]$ synthesized by our group;¹¹ reaction of AgNO_3 with $[\text{NET}_4]_2[\text{Mo}_2\text{S}_2\text{O}_2(\text{S}_2)_2]$ did not lead to an analogous Mo-Ag complex.

The starting material $[\text{NET}_4]_2[\text{Mo}_2\text{O}_2\text{S}_2\text{edt}_2]$ **3** was prepared according to ref. 12 and $[\text{NET}_4]_2[\text{W}_2\text{S}_4(\text{edt})_2]$ **4** was obtained by published procedure;¹³ all other chemicals were purchased. Both compounds **1** and **2** were synthesized in the air by the ‘spontaneous self-assembly’ method. To the solution of $[\text{NET}_4]_2[\text{Mo}_2\text{S}_2\text{O}_2(\text{edt})_2]$ **3** (0.356 g, 0.5 mmol in 20 ml MeCN –20 ml CH_2Cl_2) was added AgNO_3 (0.17 g, 1.0 mmol in 20 ml MeCN –20 ml CH_2Cl_2), and the mixture was stirred for 0.5 min. Then two drops of an $(\text{NH}_4)_2\text{S}$ solution (containing 8% S) were added, the reaction mixture was stirred for 5 min, and the resulting brown precipitate was filtered off. The orange filtrate was allowed to stand at room temp. in the air for 5 days after which 0.06 g of red crystals of **1** were obtained.† Similarly, to a solution of $[\text{NET}_4]_2[\text{W}_2\text{S}_4(\text{edt})_2]$ **4** (0.470 g, 0.5 mmol in 20 ml MeCN –20 ml CH_2Cl_2) was added four drops of aqueous H_2O_2 (30% H_2O_2) under stirring for 2 h, AgNO_3 (0.17 g, 1.0 mmol in 20 ml MeCN –20 ml CH_2Cl_2) was then added and the mixture was stirred for 0.5 min. Two drops of $(\text{NH}_4)_2\text{S}$ solution were added and the reaction mixture stirred for 5 min, and the resulting brown precipitate was filtered off. The yellow filtrate was allowed to stand at room temp. in the air for 5 days after which 0.07 g of orange crystals of **2** were obtained.†

X-Ray structure analysis‡ revealed the existence of the cage core of $[\{\text{M}_2\text{Ag}_2\text{S}_2\text{O}_2(\text{edt})_2\}_3(\mu_6\text{-S})]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$), a tripolymer consisting of three $[\text{M}_2\text{S}_2\text{O}_2(\text{edt})_2]^{2-}$ and two Ag^+ fragments, with an S atom in the center binding to six Ag atoms. Cluster **1** is isomorphous with the corresponding tungsten cluster **2** and only the structure of **1** is thus described. An ORTEP drawing of the anion of **1** is shown in Fig. 1. From the configuration of the twelve metal atoms and all the S atoms, the core can be described as a cage with an S^{2-} at its center. The cage has two windows each composed of a puckered $\text{Ag}_3\text{S}_6\text{C}_6$ 15-membered ring which is composed of three Ag atoms combining three $-\text{SC}_2\text{H}_4\text{S}^-$ units; the S^{2-} ion can enter the cage through the window and is coordinated to six Ag atoms, forming $\mu_6\text{-S}$. The $\text{Ag}-\mu_6\text{-S}$ distances range from 2.504 to 2.556 Å, av. 2.528 Å (in **2** the av. $\text{Ag}-\mu_6\text{-S}$ length is 2.531 Å). There are three weak Ag-Ag metal-metal bonds with $\text{Ag}(1)\text{-Ag}(2)$, $\text{Ag}(3)\text{-Ag}(4)$, $\text{Ag}(5)\text{-Ag}(6)$ 3.0652, 3.0354, 3.0799 Å, respectively; angles $\text{Ag}(1)\text{-}\mu_6\text{-S}\text{-Ag}(2)$, $\text{Ag}(3)\text{-}\mu_6\text{-S}\text{-Ag}(4)$, $\text{Ag}(5)\text{-}\mu_6\text{-S}\text{-Ag}(6)$ are 74.24, 74.13, 75.18°, respectively.

Each Mo atom displays tetragonal-pyramid (*TPY*) coordination geometry, with two S atoms of $-\text{SC}_2\text{H}_4\text{S}^-$ (S_{edt}), two bridging S atoms of binuclear molybdenum (S_{br}) and one terminal oxygen atom. The oxygen atom occupies the axial position of each *TPY* and the four remaining sulfido atoms are

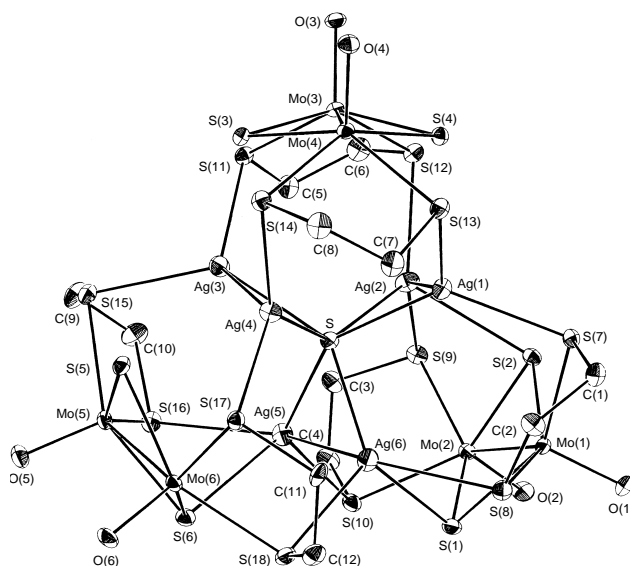


Fig. 1 ORTEP diagram of $[\{\text{Mo}_2\text{Ag}_2\text{S}_2\text{O}_2(\text{edt})_2\}_3(\mu_6\text{-S})]^{2-}$ (10% displacement ellipsoids). Selected distances (Å) and angles (°): $\text{Mo}(1)\text{-Mo}(2)$ 2.8861(14), $\text{Mo}(3)\text{-Mo}(4)$ 2.8859(13), $\text{Mo}(5)\text{-Mo}(6)$ 2.8802(14), Mo-S_{edt} (av) 2.438(3), $\text{Ag}(1)\text{-Ag}(2)$ 3.0652(14), $\text{Ag}(3)\text{-Ag}(4)$ 3.0354(14), $\text{Ag}(5)\text{-Ag}(6)$ 3.0799(15), $\text{Ag}(1)\text{-S}$ 2.556(3), $\text{Ag}(2)\text{-S}$ 2.523(3), $\text{Ag}(3)\text{-S}$ 2.533(3), $\text{Ag}(4)\text{-S}$ 2.504(3), $\text{Ag}(5)\text{-S}$ 2.539(3), $\text{Ag}(6)\text{-S}$ 2.510(3), $\text{Ag}(5)\text{-S}(16)$ 2.694(3), Ag-S_{edt} (av) 2.584(3), $\text{S}(1)\text{-Ag}(6)$ 2.794(3), $\text{S}(2)\text{-Ag}(2)$ 2.721(3), $\text{S}(3)\text{-Ag}(3)$ 2.863(3), $\text{S}(4)\text{-Ag}(1)$ 2.853(3), $\text{S}(5)\text{-Ag}(4)$ 2.889(3), $\text{S}(6)\text{-Ag}(5)$ 2.758(3); $\text{Ag}(1)\text{-S-Ag}(2)$ 74.24(8), $\text{Ag}(3)\text{-S-Ag}(4)$ 74.13(9), $\text{Ag}(5)\text{-S-Ag}(6)$ 75.18(9), $\text{S}_{\text{br}}\text{-Mo-S}_{\text{br}}$ (av) 101.73(11), $\text{S}_{\text{edt}}\text{-Mo-S}_{\text{edt}}$ (av) 81.27(11).

equatorial. The average $S_{br}-Mo-S_{br}$ angle is 101.73° . Each Mo atom is chelated by one $-SC_2H_4S-$ forming a five-membered ring, and the average $Mo-S_{edt}$ and average $S_{edt}-Mo-S_{edt}$ angle are 2.438 \AA and 81.27° , respectively. The average $Mo-Mo$ distance of 2.8841 \AA is almost the same as in $[M_2Ag-S_4(edt)_2(PPH_3)]^{-9}$ (2.881 \AA) and slightly longer than in $[NEt_4]_2[Mo_2S_4(edt)_2]^{17}$ (2.863 \AA).

Each $-SC_2H_4S-$ is coordinated by two Ag atoms through its two S atoms with $Ag-S_{edt}$ ranging from 2.496 to 2.694 \AA , and the average $Ag-S_{edt}$ distance is 2.584 \AA .

It is interesting that the distances of six S_{br} atoms of the three $[Mo_2S_2O_2(edt)_2]$ moieties of cluster **1** to the corresponding Ag atoms are different, and all are longer than the longest $Ag-S_{edt}$ [$Ag(5)-S(16)$ $2.694(3) \text{ \AA}$] or the longest $Ag-\mu_6-S$ distance [$Ag(1)-S$, $2.556(3) \text{ \AA}$]. Two S_{br} atoms of one $[Mo_2S_2O_2(edt)_2]$ are also weakly bonded to the corresponding Ag atoms [$S(1)-Ag(6)$ $2.794(3)$, $S(1)-Ag(2)$ $2.721(3) \text{ \AA}$] while only one S_{br} atom of a second $[Mo_2S_2O_2(edt)_2]$ is bonded [$S(6)-Ag(5)$ $2.758(3) \text{ \AA}$], the other S_{br} atom of this $[Mo_2S_2O_2(edt)_2]$ shows a longer $Ag\cdots S_{br}$ non-bonding distance [$S(5)-Ag(4)$ $2.889(3) \text{ \AA}$]; for the third $[Mo_2S_2O_2(edt)_2]$, none of S_{br} atom bonds to Ag [$S(4)\cdots Ag(1)$ $2.853(3)$, $S(3)\cdots Ag(3)$ $2.863(3) \text{ \AA}$]. The three longer $Ag\cdots S_{br}$ non-bonding distances suggest that there is only weak interaction between $Ag(1)$ and $S(4)$, $Ag(3)$ and $S(3)$, $Ag(4)$ and $S(5)$. Therefore, there are three four-coordinate Ag atoms in compound **1** [$Ag(2)$, $Ag(5)$, $Ag(6)$]; (two S_{edt} , one S_{br} and μ_6-S atom) to give a distorted tetrahedral geometry [angles $S-Ag-S$ are in the wide range $68.00(10)$ – $128.11(10)^\circ$]. The other Ag atoms [$Ag(1)$, $Ag(3)$, $Ag(4)$] are three-coordinate, each being coordinated by three S atoms (μ_6-S and two S_{edt}).

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Footnotes

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† Spectroscopic data for **1**: IR (KBr pellet): ν/cm^{-1} : $\nu(Mo-\mu-S)$ and $\nu(Mo-\mu_3-S)$ 468.6 m, 439.7 m; $\nu(Mo-O)$ 954.6 s. UV (dmf solution): λ/nm ($\epsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 266 (3.7×10^4), 302 (3.8×10^4).

For **2**: IR (KBr pellet): ν/cm^{-1} : $\nu(W-\mu-S)$ and $\nu(W-\mu_3-S)$ 464.8 m, 424.3 m; $\nu(W-O)$ 962.3 s. UV (dmf solution): λ/nm ($\epsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 280 (3.17×10^4), 340 (1.45×10^4).

‡ For all structural analyses, all calculations were performed on a Indyworkstation of a silicon Graphics instrument with SHELXTL program.¹⁴ The structure was solved by direct methods, and the positions of Mo/W and Ag atoms were obtained from E maps. The remaining non-hydrogen atoms were located from successive difference Fourier maps. The refinement of structures was performed by full least-squares techniques on F^2 using SHELXL-93.¹⁵ Data were corrected with program SADABS.¹⁶

Crystal data: **1**: $C_{31}H_{69}Ag_6Cl_2Mo_6N_3O_6S_{19}$, $M_r = 2482.29$, tetragonal, space group $I4_1/a$, $a = b = 42.013(4)$, $c = 16.034(2) \text{ \AA}$, $U = 28301.4 \text{ \AA}^3$, $Z = 16$, $D_c = 2.331 \text{ g cm}^{-3}$, $T = 293(2) \text{ K}$; $\lambda(Mo-K\alpha) = 0.71073 \text{ \AA}$, θ

range 1.93 – 23.26° . Siemens Smart CCD diffractometer, ω scan. 10 141 unique reflections were used in the refinement and 7231 reflections with $I > 2\sigma(I)$ used to calculate R and R_w . The last successful full-matrix least-squares refinement with anisotropic thermal parameters for Mo, Ag, S, O, C atoms of the cluster core, isotropic thermal parameters for all N, C, Cl atoms of the cations and the solution molecule (538 variables) converged to $R = 0.0499$, $R_w = 0.1062$, $GOF = 1.079$ (no attempt was made to locate hydrogen atoms).

2: $C_{31}H_{69}Ag_6Cl_2N_3O_6S_{19}W_6$, $M_r = 3010.26$. $a = b = 42.0176(6)$, $c = 16.0098(3) \text{ \AA}$, $U = 28265.0 \text{ \AA}^3$, $D_c = 2.830 \text{ g cm}^{-3}$, $T = 293(2) \text{ K}$, θ range 1.37 – 23.24° . 10 126 unique reflections were used in the refinement and 7609 reflections with $I > 2\sigma(I)$ used to calculate R and R_w . Anisotropic thermal parameters for W with other details as above. $R = 0.0586$, $R_w = 0.1440$, $GOF = 1.020$. CCDC 182/517.

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