

Stepwise addition of CuBr at $[(\text{dtc})_2\text{Mo}_2(\text{S})_2(\mu\text{-S})_2]$ (dtc = diethyldithiocarbamate): syntheses and crystal structures of two Mo/Cu/S clusters $[(\text{dtc})_2\text{Mo}_2(\mu_3\text{-S})(\mu\text{-S})_3(\text{CuBr})]$ and $[(\text{dtc})_2\text{Mo}_2(\mu_3\text{-S})_4(\text{CuBr})_2]$

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Abstract

Reactions of $[(\text{dtc})_2\text{Mo}_2(\text{S})_2(\mu\text{-S})_2]$ with one or two equivalents of CuBr in CH_2Cl_2 afforded two new heterobimetallic sulfide clusters, $[(\text{dtc})_2\text{Mo}_2(\mu_3\text{-S})(\mu\text{-S})_3(\text{CuBr})]$ (**1**) and $[(\text{dtc})_2\text{Mo}_2(\mu_3\text{-S})_4(\text{CuBr})_2]$ (**2**). Both compounds were characterized by elemental analysis, IR, UV–vis and X-ray analysis. Compound **1** contains a butterfly-shaped $\text{Mo}_2\text{S}_4\text{Cu}$ core in which one CuBr unit is coordinated by one bridging S and two terminal S atoms of the $[(\text{dtc})_2\text{Mo}_2(\text{S})_2(\mu\text{-S})_2]$ moiety. In the structure of **2**, one $[(\text{dtc})_2\text{Mo}_2(\text{S})_2(\mu\text{-S})_2]$ moiety and two CuBr units are held together by six Cu– $\mu_3\text{-S}$ bonds, forming a cubane-like $\text{Mo}_2\text{S}_4\text{Cu}_2$ core.
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1. Introduction

In the past decades, chemistry of the sulfido-bridged dinuclear complexes with a M_2S_4 core (M = Mo, W) with various transition metals has attracted much attention mainly due to their rich chemistry [1–35] and their potential applications in industrial catalytical systems [36–41]. For example, one dinuclear molybdenum–sulfur complex $[\text{Cp}_2\text{Mo}_2(\mu\text{-S})_2(\mu\text{-SH})_2]$ reacts with $[\text{Fe}_2(\text{CO})_6]$, $[\text{Co}_2(\text{CO})_8]$ or $[\text{Ni}(\text{CO})_4]$ to give the tetranuclear bimetallic clusters $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_6(\mu_3\text{-S})_2(\mu\text{-S})_2]$, $[\text{Cp}_2\text{Mo}_2\text{Co}_2(\text{CO})_4(\mu_3\text{-S})_2(\mu_4\text{-S})]$, and $[\text{Cp}_2\text{Mo}_2\text{Ni}_2(\text{CO})_2(\mu_3\text{-S})_4]$ [2]. Another interesting precursor $[(\text{dtc})_2\text{Mo}_2(\text{S})_2(\mu\text{-S})_2]$ [42] has been adopted to react with noble metal complexes to yield a

set of the incomplete $\text{Mo}_2\text{M}'\text{S}_4$ cubane-like clusters and the complete $\text{Mo}_2\text{M}'_2\text{S}_4$ cubane-like clusters (M' = Pt, Pd, Ir) [4,25,29]. However, reactions of these sulfido-bridged dinuclear complexes with Cu(I) are less explored [10,11]. Recently, we are interested in the reactions of the mononuclear metal sulfide complexes such as $[\text{MS}_4]^{2-}$ and $[\text{Cp}^*\text{MS}_3]^-$ (M = Mo, W) [43,44] with Cu(I) and Ag(I). A number of Mo(W)/Cu/(Ag)/S clusters with interesting structures have been isolated [45–57], some of which exhibited good third-order non-linear optical properties [45–47,57]. As our continuing effort to make new Mo(W)/Cu(Ag)/S clusters, we chose $[(\text{dtc})_2\text{Mo}_2(\text{S})_2(\mu\text{-S})_2]$ as starting material to react with CuBr, and found that addition of CuBr to $[(\text{dtc})_2\text{Mo}_2(\text{S})_2(\mu\text{-S})_2]$ could be controlled by their molar ratios. A trinuclear cluster $[(\text{dtc})_2\text{Mo}_2(\mu_3\text{-S})(\mu\text{-S})_3(\text{CuBr})]$ (**1**) and a tetranuclear cluster $[(\text{dtc})_2\text{Mo}_2(\mu_3\text{-S})_4(\text{CuBr})_2]$ (**2**) were isolated therefrom. Herein, we report the synthesis and structural characterization of **1** and **2**.

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2. Results and discussion

2.1. Preparations of **1** and **2**

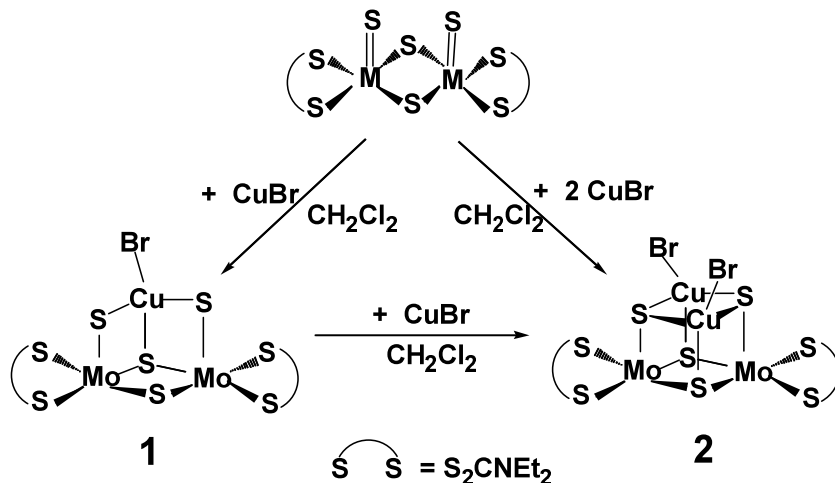
When a suspension of $[(\text{dtc})_2\text{Mo}_2(\text{S})_2(\mu\text{-S})_2]$ in CH_2Cl_2 was treated with equimolar CuBr , the mixture gradually turned a homogenous dark red solution. Diffusion of Et_2O into the solution afforded a trinuclear cluster $[(\text{dtc})_2\text{Mo}_2(\mu_3\text{-S})(\mu\text{-S})_3(\text{CuBr})]$ (**1**) as dark red crystals in 90% yield. An analogous reaction of 1:2 $[(\text{dtc})_2\text{Mo}_2\text{S}_2(\mu\text{-S})_2]\text{-CuBr}$ in CH_2Cl_2 produced a tetranuclear cluster $[(\text{dtc})_2\text{Mo}_2(\mu_3\text{-S})_4(\text{CuBr})_2]$ (**2**) as black crystals in 85% yield. As shown in Scheme 1, compound **2** could be easily formed in ca. 90% yield subject to accurate addition of equimolar CuBr into the solution of **1** in CH_2Cl_2 . In the chemistry of thiometallates, some reactions could be controlled by molar ratios of the reactants. One successful example is the reactions of $[(\text{dtc})_2\text{Mo}_2\text{S}_2(\mu\text{-S})_2]$ with one or two equivalents of $[\text{Pd}(\text{PPh}_3)_4]$, from which the trinuclear cluster $[(\text{dtc})_2\text{Mo}_2(\mu_3\text{-S})(\mu\text{-S})_3\text{Pd}(\text{PPh}_3)]$ and the tetranuclear cluster $[(\text{dtc})_2\text{Mo}_2(\mu_3\text{-S})_4\text{Pd}_2(\text{PPh}_3)_2]$ are isolated [25].

As discussed later in this paper, both **1** and **2** contain terminal bromides around their cluster framework, which may be replaced by strong donor ligands such as PPh_3 , and 4,4'-bipyridine, forming new substituted products. However, when the solution of **1** or **2** was treated with PPh_3 , or 4,4'-bipyridine, even under the presence of larger anions such as PF_6^- or ClO_4^- , no expected substituted products but the precursor complex $[(\text{dtc})_2\text{Mo}_2\text{S}_2(\mu\text{-S})_2]$ and copper complexes such as $[\text{CuBrPPh}_3]_4$ [58] and $[\text{CuBr}(4,4\text{-bipy})]_n$ [59] were always isolated. The results implied that coordination of CuBr at $[(\text{dtc})_2\text{Mo}_2\text{S}_2(\mu\text{-S})_2]$ may not be strong. In fact, when the solution of **1** or **2** in CH_2Cl_2 was exposed to air for days, it gradually decomposed and formed some insoluble black materials.

Solids **1** and **2** are relatively stable towards oxygen and moisture. They are soluble in CH_2Cl_2 and DMF but insoluble in CH_3CN . The elemental analysis of **1** or **2** is consistent with their chemical formula. In the IR spectra of **1** and **2**, characteristic bands due to $\text{Mo}=\text{S}$ (540 cm^{-1}) and $\text{Mo}_2(\mu\text{-S})_2$ (450 cm^{-1}) vibrations of the precursor $[(\text{dtc})_2\text{Mo}_2\text{S}_2(\mu\text{-S})_2]$ [42] are replaced by a medium strength band at 517 cm^{-1} (**1**) or 518 cm^{-1} (**2**) and a weaker band at 465 cm^{-1} (**1**) or 480 cm^{-1} (**2**). The $^1\text{H-NMR}$ spectrum of **1** in CDCl_3 at room temperature showed a doublet of doublet for methyl groups at 0.98 ppm and a multiplet for methylene groups at 2.83–2.96 ppm, while that of **2** exhibited a quadruplet and triplet related to CH_2 and CH_3 protons at 2.96 and 0.90 ppm. The methyl protons in the dtc ligands of **1** appeared as one signal, suggesting the equivalence of all methyl groups. Both compounds were further confirmed by X-ray crystallography.

2.2. Crystal structure of $[(\text{dtc})_2\text{Mo}_2(\mu_3\text{-S})(\mu\text{-S})_3(\text{CuBr})]$ (**1**)

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ and the asymmetric unit contains one discrete $[(\text{dtc})_2\text{Mo}_2(\mu_3\text{-S})(\mu\text{-S})_3(\text{CuBr})]$ molecule. Fig. 1 shows the molecular structure of **1** and Table 1 lists the selected bond distances and angles. Compound **1** consists of one CuBr unit and one $[(\text{dtc})_2\text{Mo}_2\text{S}_2(\mu\text{-S})_2]$ moiety which are held together by three Cu-S bonds, forming a butterfly-shaped $\text{Mo}_2\text{S}_4\text{Cu}$ core framework. The formal oxidation states for one Cu and two Mo atoms are assumed to be +5 and +1, respectively. Each Mo center is coordinated by one $\mu_3\text{-S}$, two $\mu\text{-S}$ atoms and the two S atoms of a dtc group, forming a distorted square pyramidal geometry. The Mo atom is displaced from the basal plane of its square-pyramid toward $\text{S}(1)$ or $\text{S}(2)$ by 0.70 and 0.73 Å, respectively. The $\text{Cu}(1)$ atom adopts a distorted tetrahedron geometry (bond angles



Scheme 1.

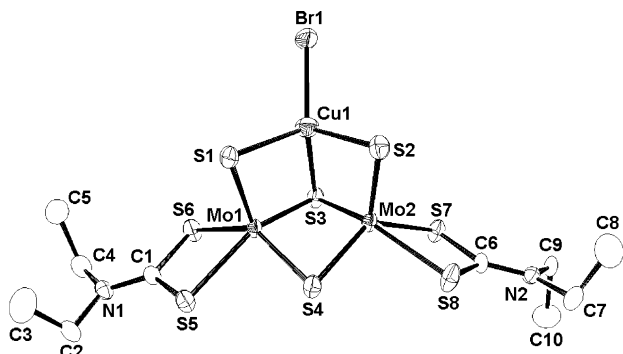


Fig. 1. Molecular structure of $[(dtc)_2Mo_2(\mu_3-S)(\mu-S)_3(CuBr)]$ (**1**) with labeling scheme and 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths			
Mo(1)···Mo(2)	2.7982(9)	Mo(1)···Cu(1)	2.7653(12)
Mo(1)–S(1)	2.143(2)	Mo(1)–S(3)	2.350(2)
Mo(1)–S(4)	2.323(2)	Mo(1)–S(5)	2.440(2)
Mo(1)–S(6)	2.434(2)	Mo(2)···Cu(1)	2.7726(10)
Mo(2)–S(2)	2.142(3)	Mo(2)–S(3)	2.367(2)
Mo(2)–S(4)	2.292(2)	Mo(2)–S(7)	2.436(2)
Mo(2)–S(8)	2.483(2)	Br(1)–Cu(1)	2.3105(12)
Cu(1)–S(1)	2.410(2)	Cu(1)–S(2)	2.409(2)
Cu(1)–S(3)	2.263(3)		
Bond angles			
S(1)–Mo(1)–S(3)	107.77(8)	S(1)–Mo(1)–S(4)	108.80(9)
S(1)–Mo(1)–S(5)	106.08(8)	S(1)–Mo(1)–S(6)	105.71(8)
S(3)–Mo(1)–S(4)	100.61(7)	S(3)–Mo(1)–S(5)	142.59(9)
S(3)–Mo(1)–S(6)	83.86(7)	S(4)–Mo(1)–S(5)	82.97(7)
S(4)–Mo(1)–S(6)	141.75(8)	S(5)–Mo(1)–S(6)	72.00(7)
S(2)–Mo(2)–S(3)	107.17(8)	S(2)–Mo(2)–S(4)	110.35(9)
S(2)–Mo(2)–S(7)	114.25(8)	S(2)–Mo(2)–S(8)	98.55(8)
S(3)–Mo(2)–S(4)	101.05(7)	S(3)–Mo(2)–S(7)	81.35(7)
S(3)–Mo(2)–S(8)	148.40(8)	S(4)–Mo(2)–S(7)	132.34(8)
S(4)–Mo(2)–S(8)	86.47(7)	S(7)–Mo(2)–S(8)	71.38(7)
S(1)–Cu(1)–S(2)	95.08(8)	S(1)–Cu(1)–S(3)	101.99(8)
S(1)–Cu(1)–Br(1)	117.76(6)	S(2)–Cu(1)–S(3)	101.97(8)
S(2)–Cu(1)–Br(1)	114.81(7)	S(3)–Cu(1)–Br(1)	121.07(7)

ranging from 95.08(8) to 121.07(7)°) with one μ₃-S atom, two μ-S atoms, and a terminal bromide. The parent $[(dtc)_2Mo_2S_2(\mu-S)_2]$ moiety appears as an essentially intact unit in the cluster, with the Mo···Mo bond length decreased from 2.814(1) to 2.7982(9) Å. The mean Mo–μ-S(1,2) and Mo–μ₃-S(3) bond lengths, 2.143 and 2.359 Å, are elongated by 0.05 Å compared with those of the corresponding ones of the precursor complex $[(dtc)_2Mo_2S_2(\mu-S)_2]$ [42] as a consequence of the coordination to Cu atom. Other bond lengths and angles of the $[(dtc)_2Mo_2S_2(\mu-S)_2]$ moiety of **1** are comparable to those reported in $[(dtc)_2Mo_2S_2(\mu-S)_2]$. The average Mo···Cu distance of 2.769 Å is close to that of $[MoS_4-Cu_4(dppm)_4](PF_6)_2$ (av. 2.742 Å) [50], but longer than those found in $[Me_4N]_4[MoS_4Cu_5Cl_7]$ (av. 2.652 Å) [60]

and $[MoS_4Cu_6Br_4(Py)_4]_n$ (av. 2.657 Å) [61]. Noticeably, the mean Cu(1)–μ-S(1,2) bond length of 2.410 Å is 0.147 Å longer than that of the Cu(1)–μ₃-S(3) bond (2.263 Å). The terminal Cu–Br bond length of 2.3105(12) Å is similar to those in $[Et_4N]_2[Cu_2Br_4]$ (av. 2.319 Å) [62] and $[PPh_4]_2[Cp^*MoS_3Cu_3Br_3]_2$ (av. 2.312 Å) [53]. It is worth noting that the μ-S(4) atom moves 0.95 Å out of the triangular face of Mo(1), S(3) and Mo(2). In this regard, the Mo₂S₄Cu core structure is closely related to that found in $[Cp^*WS_3M'_2Br(PPh_3)_2]$ (M' = Cu [55], Ag [49]), in which two M' atom are bound to Cp*WS₃ moiety across two S–S edges and a bromide further bridges the two M' atoms to form WS₃M'₂Br butterfly-shaped structure. In the latter two structures, the bridging bromide also moves out of the triangular face of M'(1), S(1) and M'(2) by 0.83 Å (M' = Cu) and 0.89 Å (M' = Ag).

2.3. Crystal structure of $[(dtc)_2Mo_2(\mu_3-S)_4(CuBr)_2]$ (**2**)

Compound **2** crystallizes in the monoclinic space group $P2_1/m$ and the asymmetric unit contains one-half of the discrete $[(dtc)_2Mo_2(\mu_3-S)_4(CuBr)_2]$ molecule. Fig. 2 shows the molecular structure of **2** and Table 2 lists the selected bond distances and angles. The molecule contains one $[(dtc)_2Mo_2S_2(\mu-S)_2]$ moiety and two CuBr units which are assembled into a distorted Mo₂S₄Cu₂ cubane-like core. Alternatively, the structure of **2** can be viewed as being constructed from addition of one more CuBr unit onto the framework of **1**. The formal oxidation states for each Mo and Cu of **2** remain +5 and +1. A crystallographic mirror plane runs through Cu(1), Cu(2), Br(1), Br(2), S(1) and S(2) atoms. The Mo₂S₄Cu₂ cubane-like core is closely related to those found in $[(edt)_2Mo_2(\mu_3-S)_4(CuPPh_3)_2]$ (edtH₂ = 1,2-ethanedithiol) [10] and $[Et_4N]_2[(OC_4H_8edt)_2V_2(\mu_3-S)_4(M'SPH)_2]$ (M' = Cu, Ag) [63]. Each Mo center in **2** adopts the same coordination geometry to that observed

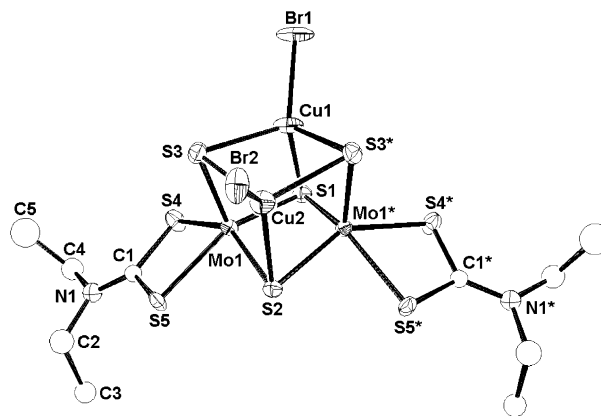


Fig. 2. Molecular structure of $[(dtc)_2Mo_2(\mu_3-S)_4(CuBr)_2]$ (**2**) with labeling scheme and 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and bond angles (°) for **2**

Bond lengths			
Mo(1)···Cu(1)	2.783(2)	Mo(1)···Cu(2)	2.792(3)
Mo(1)···Mo(1*)	2.766(2)	Mo(1)–S(1)	2.342(3)
Mo(1)–S(2)	2.346(3)	Mo(1)–S(3)	2.175(4)
Mo(1)–S(4)	2.459(4)	Mo(1)–S(5)	2.425(3)
Br(1)–Cu(1)	2.279(3)	Br(2)–Cu(2)	2.292(4)
Cu(1)–S(1)	2.235(6)	Cu(1)–S(3)	2.403(4)
Cu(2)–S(2)	2.235(6)	Cu(2)–S(3)	2.399(3)
Cu(1)···Cu(1*)	3.090(3)		
Bond angles			
S(1)–Mo(1)–S(2)	105.00(10)	S(1)–Mo(1)–S(3)	105.6(2)
S(1)–Mo(1)–S(4)	85.43(11)	S(1)–Mo(1)–S(5)	141.7(2)
S(2)–Mo(1)–S(3)	105.1(2)	S(2)–Mo(1)–S(4)	146.9(2)
S(2)–Mo(1)–S(5)	81.57(10)	S(3)–Mo(1)–S(4)	101.98(13)
S(3)–Mo(1)–S(5)	108.95(13)	S(4)–Mo(1)–S(5)	71.80(11)
S(1)–Cu(1)–S(3)	101.72(13)	S(1)–Cu(1)–Br(1)	119.0(2)
S(3)–Cu(1)–Br(1)	116.43(12)	S(1)–Cu(1)–S(3*)	101.72(10)
S(3)–Cu(1)–S(3*)	98.36(11)	S(3*)–Cu(1)–Br(1)	116.43(8)
S(2)–Cu(2)–S(3)	101.5(1)	S(2)–Cu(2)–Br(2)	126.8(2)
S(3)–Cu(2)–Br(2)	112.18(13)	S(2)–Cu(2)–S(3*)	101.52(11)
S(3)–Cu(2)–S(3*)	98.56(11)	S(3*)–Cu(2)–Br(2)	112.18(9)

in **1**, while each Cu atom is tetrahedrally coordinated by three μ_3 -S atoms and a terminal bromide. Like that of **1**, the parent $[(dte)_2Mo_2S_2(\mu-S)_2]$ moiety of **2** remains intact in the cluster. The change from terminal sulfur to bridging μ_3 -sulfido increases the Mo–S bond length slightly from an average of 2.092 to 2.175 Å. The bonds of the Cu atoms to the terminal sulfur atoms (av. 2.356 Å) are longer than the other Cu–S bonds (av. 2.235 Å). The average Mo–Cu and Cu–Br bond lengths, 2.788 and 2.285 Å, are somewhat longer than those of the corresponding ones in **1**. The Mo···Mo distance of 2.766(2) Å is shorter than those in **1** and other $Mo_2S_4M_2$ cubane-like clusters ($M' = Cu$, 2.858 Å [10]; $M' = Fe$, 2.822 Å [21]; $M' = Co$, 2.838 Å [23]; $M' = Ni$, 2.829 Å [64]). The long Cu···Cu separation (3.090(3) Å) indicates that their bonding interactions, if any, should be very weak.

3. Experimental

3.1. General

All manipulations were carried out under argon using standard Schlenk-line techniques. $[(dte)_2Mo_2S_2(\mu-S)_2]$ was prepared according to the literature method [42]. Other chemicals were obtained from commercial sources and used as received. All solvents were predried over activated molecular sieves and refluxed over the appropriate drying agents under argon. Other reagents were used as received. The IR spectra were recorded on a Nicolet MagNa-IR 550 spectrophotometer as KBr disk (4000–400 cm^{-1}). UV–vis spectra were measured on UV-240 spectrophotometer. Elemental analyses for C,

H, and N were performed on an EA1110CHNS elemental analyzer. 1H -NMR spectra were recorded at ambient temperature on a Varian UNITYplus-400 spectrometer. 1H -NMR chemical shifts were referenced to the $CDCl_3$ signal.

3.2. Syntheses

3.2.1. Preparation of $[(dte)_2Mo_2(\mu_3-S)(\mu-S)_3(CuBr)]$ (**1**)

CuBr (14.4 mg, 0.1 mmol) was added to a suspension of $[(dte)_2Mo_2S_2(\mu-S)_2]$ (61.6 mg, 0.1 mmol) in CH_2Cl_2 (30 ml). The mixture was stirred at room temperature (r.t.) for 0.5 h, and the dark-red suspension gradually turned into dark red solution and then filtered. The filtrate was layered with Et_2O (30 ml) to produce dark red crystals of **1** in 2 days, which were collected by filtration, washed with Et_2O and dried in air. Yield: 68.4 mg (90%). Anal. Calc. for $C_{10}H_{20}BrCuMo_2N_2S_8$: C, 15.80; H, 2.66; N, 3.69. Found: C, 15.13; H, 2.58; N, 3.42%. 1H -NMR ($CDCl_3$, 400 MHz): δ 0.98 (dd, 12H, NCH_2CH_3), 2.83–2.96 (m, 8H, NCH_2CH_3). UV–vis (CH_2Cl_2) (λ_{max}/nm ($\epsilon/M^{-1} cm^{-1}$)): 238 (64300), 260 (62200), 405 (10500), 495 (4200). IR (KBr disc, cm^{-1}): 2974 (w), 2932 (w), 1539 (vs), 1439 (m), 1385 (s), 1350 (m), 1281 (m), 1196 (m), 1153 (w), 1072 (m), 845 (w), 779 (w), 517 (m), 465 (w).

3.2.2. Preparation of $[(dte)_2Mo_2(\mu_3-S)_4(CuBr)_2]$ (**2**)

Method 1: CuBr (28.8 mg 0.2 mmol) was added to a suspension of $[(dte)_2Mo_2S_2(\mu-S)_2]$ (61.6 mg 0.1 mmol) in CH_2Cl_2 (30 ml). Work-up similar to that used in the isolation of **1** gave rise to black crystals of **2**, which were collected by filtration, washed with Et_2O , and dried in air. Yield: 76.8 mg (85%). Anal. Calc. for $C_{10}H_{20}Br_2Cu_2Mo_2N_2S_8$: C, 13.29; H, 2.24; N, 3.10. Found: C, 13.23; H, 2.24; N, 2.99%. 1H -NMR ($CDCl_3$, 400 MHz): δ 0.96 (t, 12H, NCH_2CH_3), 2.90 (q, 8H, NCH_2CH_3). UV–vis (CH_2Cl_2) (λ_{max}/nm ($\epsilon/M^{-1} cm^{-1}$)): 236 (67700), 275 (58100), 420 (4840). IR (KBr disc, cm^{-1}): 2967 (w), 2924 (w), 1539 (vs), 1454 (s), 1385 (s), 1277 (s), 1154 (m), 1073 (m), 841 (m), 779 (w), 518 (m), 480 (w).

Method 2: CuBr (9.4 mg, 0.066 mmol) was added to a solution of **1** (50 mg, 0.066 mmol) in CH_2Cl_2 (20 ml). Work-up similar to that used in the isolation of **1** afforded black crystals of **2**, which were collected by filtration, washed with Et_2O , and dried in air. Yield: 53.7 mg (90%).

3.3. X-ray crystallography

X-ray quality crystals of **1** and **2** were obtained directly from the above preparations. All measurements were made on a Rigaku Mercury CCD X-ray diffractometer (3 kV, sealed tube) at 193 K by using graphite

monochromated Mo–K α ($\lambda = 0.71070 \text{ \AA}$). A dark red prism of **1** with dimensions $0.40 \times 0.30 \times 0.10 \text{ mm}^3$ and a black plate of **2** with dimensions $0.15 \times 0.10 \times 0.10 \text{ mm}^3$ were mounted at the top of a glass fiber. Diffraction data were collected at ω mode with a detector distance of 54.8 mm (**1**) or 44.5 mm (**2**) to the crystal. Indexing was performed from six images each of which was exposed for 10 s (**1**) or 15 s (**2**). A total of 1080 (**1**) or 720 (**2**) oscillation images were collected in the range $1.96 < 2\theta < 50.70^\circ$ for **1** and $1.98 < 2\theta < 54.94^\circ$ for **2**. The collected data were reduced by using the program CrystalClear (Rigaku and MSC, Ver.1.3, 2001), and an empirical absorption correction was applied which resulted in transmission factors ranging from 0.229 to 0.649 for **1** and from 0.465 to 0.524 for **2**. The reflection data were also corrected for Lorentz and polarization effects.

The structures of **1** and **2** were solved by direct methods [65] (**1**) or heavy-atom Patterson method [66] (**2**) and refined by full-matrix least-squares on F [67]. All the non-hydrogen atoms except the C and N atoms in **2** were refined anisotropically. All hydrogen atoms were introduced at the calculated positions and included in the structure–factor calculations. Neutral atom scattering factors were taken from Cromer and Waber [68]. All the calculations were performed on a Dell workstation using the CRYSTALSTRUCTURE crystallographic software package (Rigaku and MSC, Ver.3.16, 2003). A summary of the key crystallographic information for **1** and **2** is given in Table 3.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 214943 and 214944 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Table 3
Crystallographic data for **1** and **2**

	C ₁₀ H ₂₀ BrCuMo ₂ N ₂ S ₈	C ₁₀ H ₂₀ Br ₂ Cu ₂ Mo ₂ N ₂ S ₈
Molecular formula	C ₁₀ H ₂₀ BrCuMo ₂ N ₂ S ₈	C ₁₀ H ₂₀ Br ₂ Cu ₂ Mo ₂ N ₂ S ₈
Formula weight	760.17	903.62
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/m$
Unit cell dimensions		
a (Å)	7.092(1)	7.091(5)
b (Å)	31.410(4)	18.392(11)
c (Å)	11.178(2)	10.072(7)
β (°)	108.213(7)	105.883(8)
V (Å ³)	2365.3(6)	1263.4(15)
Z	4	2
T (K)	193	193
D_{calc} (g cm ⁻³)	2.135	2.375
λ (Mo–K α) (Å)	0.71070	0.71070
μ (cm ⁻¹)	43.30	64.56
$2\theta_{\text{max}}$ (°)	50.70	54.94
Total reflections	19865	10061
Unique reflections	4342 ($R_{\text{int}} = 0.064$)	2985 ($R_{\text{int}} = 0.078$)
No. observations	2882	1059
($I > 2.00\sigma(I)$)		
No. parameters	237	107
R^a	0.033	0.032
R_w^b	0.038	0.040
GOF ^c	1.022	1.021
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.77	0.62
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	–0.68	–0.65

$$^a R = \sum ||F_o| - |F_c|/\sum |F_o|.$$

$$^b R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}.$$

$$^c \text{GOF} = \{\sum w(|F_o| - |F_c|)^2/(M - N)\}^{1/2}, \text{ where } M \text{ is the number of reflections and } N \text{ is the number of parameters.}$$

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