Note

Synthesis and Crystal Structure of a Novel Mixed Nido-like and Half-open Cubane-like Cluster $[(n\text{-Bu})_4N]_3[MoS_4Cu_5Br_6]$

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Reaction of $(NH_4)_2MoS_4$ with $[Cu(MeCN)_4](BF_4)$ and $(n\text{-}Bu)_4NBr$ in CH_2Cl_2 afforded a new hexanuclear cluster $[(n\text{-}Bu)_4N]_3[MoS_4Cu_5Br_6]$ (1). 1 crystallizes in the monoclinic system, space group $P2_1/c$, with lattice parameters $a = 1.17383(4)$ nm, $b = 2.40136(4)$ nm, $c = 2.64112(5)$ nm, $\beta = 94.2020(5)°$, $V = 7.4247(5)$ nm^3 and $Z = 4$. The structure of the $[MoS_4Cu_5Br_6]^{3-}$ trianion of 1 is composed of one nido-like $[MoS_3Cu_3]$ core and one half-open cubane-like $[MoS_3Cu_3Br]$ core, which are interconnected by sharing the same MoSCuS plane. The Mo···Cu distances vary in the range of $0.2622(6)$—$0.2692(5)$ nm.

Keywords   molybdenum cluster, copper cluster, sulfide cluster, crystal structure

Introduction

The chemistry of the thiometallate anions is currently a subject of intense interest due to their rich structural diversity,[1-8] their relevance to industrial catalytic process[9,10] and metalloenzymes,[11,12] and their potential utility as non-linear optical materials.[13-16] We have reported the synthesis of a nido-like tetranuclear anionic cluster $[(n\text{-}Bu)_4N]_2[MoOS_3Cu_3(NCS)_3]$ obtained from the reaction of $(NH_4)_2MoOS_3$ with CuNCS and $(n\text{-}Bu)_4NBr$ in the solid state at 90 °C.[17] On the other hand, Chen *et al.* reported a half-open cubane-like tetranuclear anionic cluster $[NEt_4]_3[WOS_3Cu_3Br_4]$, generated from the reaction of $(NH_4)_2WO_2S_2$ with CuBr and Et$_4$NBr in the solid state at 70 °C.[18] Another example of pentamethylcy-

clopentadienyl trithiotungstate anion $(Cp^*WS_3^-)$,[19,20] neutral tetranuclear cluster $[Cp^*WS_3Cu_3Br_2(PPh_3)_2]$, was also reported to have a similar structure.[21] In this paper we present the crystal structure of an intriguing hexanuclear anionic cluster $[(n\text{-}Bu)_4N]_3[MoS_4Cu_5Br_6]$ (1), in which it contains both nido and half-open cubane frameworks.

Experimental

Materials

All manipulations were carried out in air. $(NH_4)_2MoS_4$ and $[Cu(MeCN)_4](BF_4)$ were prepared according to the reported methods.[22,23] All reagents and solvents were of analytical grade and used without further purification. IR spectra (KBr disc) were recorded on a Nicolet MagNa-IR 550 spectrophotometer.

Preparation

To an Erlenmeyer flask containing 50 mL of CH_2Cl_2 was added $(NH_4)_2MoS_4$ (0.26 g, 1 mmol), $[Cu(CH_3CN)_4](BF_4)$ (0.18 g, 0.5 mmol) and $(n\text{-}Bu)_4NBr$ (0.96 g, 3 mmol). The resulting mixture was allowed to stir at room temperature for 0.5 h to give rise to a dark red suspension. After filtering off some black powder [mainly the unreacted $(NH_4)_2MoS_4$], the CH_2Cl_2

filtrate was layered with ca. 50 mL of i-PrOH and then allowed to stand at ambient temperature for one month. During that period, a large amount of black insoluble powder and a small portion of the X-ray quality dark red crystals of $[(n\text{-Bu})_4N]_3[MoS_4Cu_5Br_6]$ (**1**) were observed. The mixture products were filtered and the crystals of **1** were mechanically separated from the black powder. Yield 0.01 g (5.72 % based on Cu); IR (KBr) ν ($Mo\text{-}S_{br}$): 459 (w), 439 (w) cm^{-1}. The identity of **1** was finally confirmed by single-crystal X-ray crystallography analysis.

Crystal structure analysis

A dark red single crystal was placed on a glass fiber and mounted on a Rigaku Mercury CCD X-ray diffractometer (3 kV, sealed tube). Diffraction data were collected at -80 ℃ using graphite monochromated Mo Kα ($\lambda = 0.071070$ nm) with a detector distance of 3.50 cm to the crystal and swing angle of 9.94°. Indexing was performed from 4 images each of which was exposed for 20 s. A total of 720 oscillation images were collected. A sweep of data was done using ω scans from $-80.0°$ to 100° in 0.5° step, at $\chi = 45.0°$ and $\phi = 0.0°$. A second sweep was performed using ω scans from $-80.0°$ to 100.0° in 0.5° step, at $\chi = 45.0°$ and $\phi = 90.0°$. The collected data were reduced by using the program Crystal-Clear (Rigaku and MSC, 1999) and an empirical absorp-

tion correction was applied which resulted in transmission factors ranging from 0.77 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 43.89). Reflections with $2\theta \leqslant 55.0°$ were used for structure solution and refinement.

The structure was solved by heavy-atom Patterson methods[24] and expanded using Fourier techniques.[25] Mo, Br, Cu and S atoms were refined anisotropically, while C and N atoms were refined isotropically. All the hydrogen atoms were put on the calculated positions (C—H, 0.095 nm) and were allowed to ride on their respective parent atoms. The final least-square cycle gave $R = 0.068$, $R_w = 0.071$ for 2923 reflection with $I > 3.00\sigma(I)$. The weighting scheme is $w = 1/\sigma^2(F_o)$. Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in F_{calcd}.[26,27] All calculations were performed on a Dell workstation using the Crystal Structure crystallographic software package (Rigaku and MSC, 2001). A summary of the key crystallographic information is given in Table 1.

Results and discussion

X-Ray analysis revealed that **1** consists of one independent $[MoS_4Cu_5Br_6]^{3-}$ trianion and three $(n\text{-Bu})_4N^+$ cations in an asymmetric unit. Fig. 1 shows a perspective view of the trianion with atomic scheme. Table 2 lists

Table 1 Summary of crystallographic results for $[(n\text{-Bu})_4N]_3[MoS_4Cu_5Br_6]$ (**1**)

Empirical formula	$C_{48}H_{108}Br_6Cu_5MoN_3S_4$	$F(000)$	3512
Formula weight	1748.74	Crystal dimensions (mm)	$0.30 \times 0.20 \times 0.10$
Wave length	0.07107 nm	θ range for data collection (°)	0.995—25.00
Crystal system, space group	monoclinic, $P2_1/c$	Limiting indices	$-15 \leqslant h \leqslant 15$, $-30 \leqslant k \leqslant 31$, $-28 \leqslant l \leqslant 34$
Lattice parameters		Reflections measured/unique	82457/29258
a (nm)	1.17383(4)	Absorption	Empirical
b (nm)	2.40136(4)	Max. and min. transmission	1.000 and 0.7653
c (nm)	2.64112(5)	Refinement method	Full-matrix least-squares on F
β (°)	94.2020(5)	Observations $[I > 3.00\sigma(I)]$/parameters	2923/350
V (nm^3)	7.4247(5)	Goodness of fit on F	1.64
Z	4	Final R and R_w	0.068, 0.071
Calculated density (Mg/m^3)	1.564	Max shift/error in final cycle	0.00
Absorption coefficient (mm^{-1})	4.95	Largest diff. peak and hole (e/nm^3)	800 and -830

atomic coordinates and equivalent temperature factors for non-hydrogen atoms. Selected bond lengths and angles are presented in Table 3.

The structure of the trianion of **1** may be viewed as a combination of a nido-like [MoS_3Cu_3] core and a half-open cubane-like [MoS_3Cu_3Br] core, sharing the same Mo(1)S(2)Cu(5)S(4) plane. Occurrence of such mixed structural cores in the same cluster framework is rare in

the chemistry of thiometallates. The structure of the nido core of **1** is close to those observed in several nido-like clusters such as [(n-Bu)$_4$N]$_2$[MoOS$_3$Cu$_3$(NCS)$_3$],[17] [NEt$_4$]$_4$[MoOS$_3$Cu$_3$BrI^2]$_2$[28] and [PPh$_4$]$_2$[Cp*MS$_3$Cu$_3$X$_3$]$_2$ (M = W, X = Cl,[21] Br;[29] M = Mo, X = Br[21]). It is noted that all the three Cu atoms in [(n-Bu)$_4$N]$_2$[MoOS$_3$Cu$_3$-(NCS)$_3$] adopt a trigonal-planar coordination. However, like those found in [NEt$_4$]$_4$[MoOS$_3$Cu$_3$BrI$_2$]$_2$ and

Table 2   Atomic coordinates and thermal parameters (10^2 nm^2) for **1**

Atom	x	y	z	$B_{eq}{}^a$	Atom	x	y	z	$B_{eq}{}^a$
Mo(1)	0.1496(3)	0.1982(1)	0.76866(13)	2.71(9)	C(16)	0.416(4)	0.440(2)	0.221(2)	7.4(13)
Br(1)	0.4026(3)	0.2681(2)	0.9105(2)	4.57(13)	C(17)	1.061(3)	0.559(1)	0.253(1)	3.3(9)
Br(2)	−0.0016(4)	0.0691(2)	0.8902(2)	5.0(1)	C(18)	1.147(3)	0.521(2)	0.283(2)	4.7(11)
Br(3)	−0.1367(4)	0.1387(2)	0.6352(2)	4.40(13)	C(19)	1.234(3)	0.562(2)	0.309(1)	3.6(9)
Br(4)	0.2896(4)	0.3393(2)	0.6545(2)	5.0(1)	C(20)	1.328(4)	0.526(2)	0.343(2)	5.7(11)
Br(5)	−0.0401(3)	0.2989(2)	0.6891(2)	3.51(11)	C(21)	1.039(3)	0.481(2)	0.182(2)	5.1(11)
Br(6)	−0.1211(4)	0.3225(2)	0.8416(2)	4.30(13)	C(22)	1.121(3)	0.513(1)	0.150(1)	3.3(9)
Cu(1)	0.2856(4)	0.2341(2)	0.8460(2)	3.6(1)	C(23)	1.167(4)	0.469(2)	0.113(2)	6.9(13)
Cu(2)	0.0743(4)	0.1288(2)	0.8351(2)	3.5(1)	C(24)	1.231(6)	0.495(3)	0.082(3)	17.9(29)
Cu(3)	−0.0085(4)	0.1803(2)	0.6928(2)	4.0(2)	C(25)	0.898(3)	0.484(1)	0.2445(13)	3.0(9)
Cu(4)	0.1869(4)	0.2791(2)	0.7016(2)	4.0(2)	C(26)	0.831(3)	0.515(2)	0.286(1)	4.1(10)
Cu(5)	−0.0088(4)	0.2744(2)	0.7886(2)	3.9(1)	C(27)	0.737(3)	0.474(2)	0.302(2)	5.0(11)
S(1)	0.2579(9)	0.1437(4)	0.8230(4)	4.2(3)	C(28)	0.668(4)	0.501(2)	0.346(2)	7.7(14)
S(2)	−0.0362(9)	0.1798(4)	0.7792(4)	3.2(3)	C(29)	0.904(3)	0.567(2)	0.186(2)	4.3(10)
S(3)	0.1849(8)	0.1848(4)	0.6886(4)	3.6(3)	C(30)	0.816(4)	0.538(2)	0.148(2)	6.0(12)
S(4)	0.1843(8)	0.2886(4)	0.7896(4)	2.9(3)	C(31)	0.761(4)	0.586(2)	0.114(2)	8.3(15)
N(1)	0.588(2)	0.2725(10)	0.2358(10)	2.1(6)	C(32)	0.670(6)	0.565(3)	0.078(3)	14.7(23)
N(2)	0.978(3)	0.522(1)	0.2164(13)	5.2(9)	C(33)	0.149(3)	0.181(2)	−0.023(1)	4.3(10)
N(3)	0.075(3)	0.213(2)	0.014(2)	6.9(10)	C(34)	0.244(4)	0.144(2)	0.004(2)	6.8(13)
C(1)	0.508(3)	0.224(1)	0.2570(12)	2.5(8)	C(35)	0.317(4)	0.113(2)	−0.033(2)	8.3(15)
C(2)	0.575(3)	0.177(2)	0.280(2)	5.0(11)	C(36)	0.395(4)	0.075(2)	−0.010(2)	6.0(12)
C(3)	0.483(4)	0.131(2)	0.291(2)	6.4(12)	C(37)	0.017(3)	0.173(2)	0.053(1)	4.2(10)
C(4)	0.538(5)	0.081(2)	0.320(2)	10.3(17)	C(38)	−0.051(4)	0.127(2)	0.022(2)	5.8(11)
C(5)	0.663(3)	0.249(2)	0.196(1)	4.1(10)	C(39)	−0.088(4)	0.086(2)	0.060(2)	5.8(12)
C(6)	0.594(3)	0.230(2)	0.1493(13)	3.4(8)	C(40)	−0.177(4)	0.041(2)	0.031(2)	6.9(13)
C(7)	0.675(3)	0.205(2)	0.112(1)	4.4(10)	C(41)	−0.016(5)	0.238(2)	−0.018(2)	9.0(15)
C(8)	0.603(3)	0.185(2)	0.063(1)	4.9(10)	C(42)	−0.107(4)	0.279(2)	0.010(2)	6.7(13)
C(9)	0.670(3)	0.2931(13)	0.2798(12)	2.3(8)	C(43)	−0.198(5)	0.301(2)	−0.024(2)	11.2(18)
C(10)	0.611(3)	0.316(1)	0.3283(13)	3.3(9)	C(44)	−0.293(5)	0.335(2)	−0.002(2)	12.2(20)
C(11)	0.709(3)	0.327(2)	0.3689(13)	3.5(9)	C(45)	0.142(3)	0.254(2)	0.051(2)	5.4(11)
C(12)	0.660(3)	0.353(2)	0.416(2)	5.3(11)	C(46)	0.196(5)	0.300(2)	0.018(2)	9.4(16)
C(13)	0.499(3)	0.317(1)	0.2164(13)	2.9(8)	C(47)	0.285(7)	0.336(3)	0.052(3)	17.4(31)
C(14)	0.560(4)	0.362(2)	0.192(2)	6.3(12)	C(48)	0.363(5)	0.312(3)	0.064(2)	10.6(19)
C(15)	0.474(3)	0.413(2)	0.175(2)	4.7(10)					

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{eq} = (8/3 \, \pi^2)[U_{11} \cdot (aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^* \, bb^*)\cos \gamma + 2U_{13}(aa^* \, cc^*)\cos \beta + 2U_{23}(bb^* \, cc^*)\cos \alpha]$.

Table 3 Selected bond lengths (nm) and angles (°) for **1**

|			
Mo(1)···Cu(1)	0.2641(6)	Mo(1)···Cu(2)	0.2622(6)
Mo(1)···Cu(3)	0.2663(6)	Mo(1)···Cu(4)	0.2687(6)
Mo(1)···Cu(5)	0.2692(5)	Mo(1)—S(1)	2.268(11)
Mo(1)—S(2)	0.2261(10)	Mo(1)—S(3)	0.2208(10)
Mo(1)—S(4)	0.2268(10)	Br(1)—Cu(1)	0.2258(6)
Br(2)—Cu(2)	0.2270(6)	Br(3)—Cu(3)	0.2287(7)
Br(4)—Cu(4)	0.2303(6)	Br(5)···Cu(3)	0.2873(6)
Br(5)—Cu(4)	0.2705(6)	Br(5)—Cu(5)	0.2694(6)
Br(6)—Cu(5)	0.2302(6)	Cu(1)—S(1)	0.2271(12)
Cu(1)—S(4)	0.2259(11)	Cu(2)—S(1)	0.2229(11)
Cu(2)—S(2)	0.2259(11)	Cu(3)—Cu(4)	0.3291(7)
Cu(3)—Cu(5)	0.3391(7)	Cu(3)—S(2)	0.2327(10)
Cu(3)—S(3)	0.2283(11)	Cu(4)—Cu(5)	0.3369(6)
Cu(4)—S(3)	0.2289(11)	Cu(4)—S(4)	0.2339(11)
Cu(5)—S(2)	0.2305(11)	Cu(5)—S(4)	0.2289(10)
S(1)-Mo(1)-S(2)	108.1(4)	S(1)-Mo(1)-S(3)	112.8(4)
S(2)-Mo(1)-S(3)	109.9(4)	S(1)-Mo(1)-S(4)	108.6(4)
S(2)-Mo(1)-S(4)	108.2(4)	S(3)-Mo(1)-S(4)	109.3(4)
Cu(4)-Br(5)-Cu(5)	77.2(2)	Br(1)-Cu(1)-S(1)	127.7(4)
Br(1)-Cu(1)-S(4)	123.4(4)	S(1)-Cu(1)-S(4)	108.8(4)
Br(2)-Cu(2)-S(1)	128.4(4)	Br(2)-Cu(2)-S(2)	122.0(4)
S(1)-Cu(2)-S(2)	109.5(4)	Br(3)-Cu(3)-S(2)	121.1(4)
Br(3)-Cu(3)-S(3)	126.5(4)	S(2)-Cu(3)-S(3)	105.0(4)
Br(4)-Cu(4)-Br(5)	111.8(2)	Br(4)-Cu(4)-S(3)	122.6(4)
Br(5)-Cu(4)-S(3)	99.2(3)	Br(4)-Cu(4)-S(4)	121.5(3)
Br(5)-Cu(4)-S(4)	91.1(3)	S(3)-Cu(4)-S(4)	104.1(4)
Br(5)-Cu(5)-Br(6)	116.0(2)	Br(5)-Cu(5)-S(2)	95.9(3)
Br(6)-Cu(5)-S(2)	118.6(3)	Br(5)-Cu(5)-S(4)	92.5(3)
Br(6)-Cu(5)-S(4)	122.1(3)	S(2)-Cu(5)-S(4)	106.0(4)
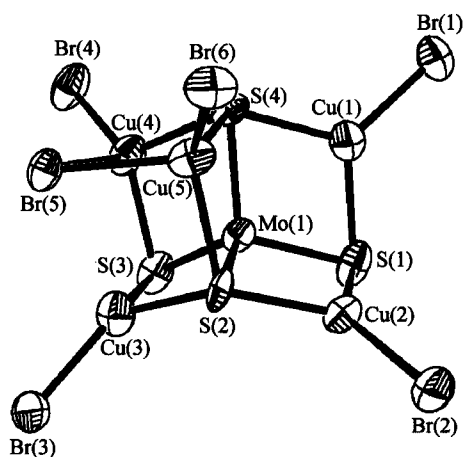
Fig. 1 Perspective view of the trianion [MoS$_4$Cu$_5$Br$_6$]$^{3-}$ of **1** with labeling scheme and 50% thermal ellipsoids.

[PPh$_4$]$_2$[Cp*MS$_3$Cu$_3$X$_3$]$_2$, two Cu atoms, Cu(1) and Cu(2), in the nido part of **1**, assume a trigonal planar coordination geometry, coordinated by a terminal Br, one μ_3-S and one μ_4-S, while the third one, Cu(5), is tetrahedrally coordinated by a terminal Br, one μ_2-Br and two μ_4-S atoms. Owing to the different coordination environments, the Mo(1)···Cu(5) distance of 0.2692(5) nm is longer than those of Mo(1)···Cu(1) [0.2641(6) nm] and Mo(1)···Cu(2) [0.2622(6) nm]. The mean Mo···Cu distance of 0.2652 nm is very close to those found in [(n-Bu)$_4$N]$_2$[MoOS$_3$Cu$_3$(NCS)$_3$] and [PPh$_4$]$_2$-[Cp*MoS$_3$Cu$_3$Br$_3$]$_2$. The Cu—S distances reflect the mode of coordination of the copper atoms, 0.2254 nm for trigonal geometry and 0.2297 nm for a tetrahedral environment. Although the Cu(5)—Br(6) bonds length is

comparable to those of $Cu(1)$—$Br(1)$ and $Cu(2)$—$Br(2)$, the $Cu(5)$—μ_2-$Br(5)$ bond length of 0.2694 (6) nm is longer by 0.042 nm than the average length (0.2277 nm) of the three terminal Cu—Br bonds, but shorter by 0.023 nm than that of the corresponding ones in $[PPh_4]_2[Cp^*MoS_3Cu_3Br_3]_2$ (av. 0.2919 nm).[21]

On the other hand, the main structural feature of the half-open cubane-like core of **1** resembles those of $[NEt_4]_3[WOS_3Cu_3Br_4]$ and $[Cp^*WS_3Cu_3Br_2(PPh_3)_2]$. The $Cu(3)$ atom assumes a trigonal planar geometry, coordinated by one terminal Br, one μ_3-S and one μ_4-S. The $Cu(4)$ atom has a similar distorted tetrahedral geometry to that of the $Cu(5)$ atom. However, the former is coordinated by one terminal Br, one μ_2-Br, one μ_3-S and one μ_4-S. Again, because of the different coordination geometry, the $Mo(1)\cdots Cu(3)$ distance of $0.2663(6)$ nm is shorter than those of $Mo(1)\cdots Cu(4)$ and $Mo(1)\cdots Cu(5)$. The mean $Mo\cdots Cu$ distance (0.2668 nm) is slightly longer than those found in $[NMt_4]_5[MoS_4Cu_6Cl_9]$ (av. 0.2647 nm).[30] It is worth noting that the $Br(5)$ atom moves out of the plane of $Cu(4)$, $S(4)$ and $Cu(5)$, tilting away from the $Cu(3)$ atom. This results in a long $Cu(3)\cdots Br(5)$ distance of $0.2873(6)$ nm, which is shorter than those of the corresponding bonds found in $[NEt_4]_3[WOS_3Cu_3Br_4]$ (0.3349 nm) and $[Cp^*WS_3Cu_3Br_2(PPh_3)_2]$ (0.315 nm). The $Cu(4)$-$Br(5)$-$Cu(5)$ bond angle of $77.2(2)°$ is larger than those of the corresponding angles of $[NEt_4]_3[WOS_3Cu_3Br_4]$ $[72.4(1)°]$ and $[Cp^*WS_3Cu_3Br_2(PPh_3)_2]$ $[68.03(7)°]$. The mean Cu—$Br(5)$ distance (0.2700 nm) within the $Cu(4)S(4)Cu(5)Br(5)$ linkage is much longer than those of all the terminal Cu—Br bonds. Intriguingly, the three-coordinated $Cu(3)$—S lengths (av. 0.2305 nm) are almost the same as those of the four-coordinated Cu—S bond lengths. The central $Mo(1)$ atom is coordinated by four S atoms, forming an approximate tetrahedral geometry. Because of the bonding interactions between the Cu and S atoms, the average Mo—S bond length (0.2251 nm) in **1** is elongated by 0.007 nm relative to the Mo = S bonds in $(NH_4)_2MoS_4$.[31]

The structure of each of the three $[(n\text{-}Bu)_4N]^+$ cations is close to a normal tetrahedral geometry, and all C—C and C—N bond lengths and C-C-C, C-N-C, N-C-C angles are consistent with those found in $[(n\text{-}Bu)_4N]_2$-$[MoOS_3Cu_3(NCS)_3]$.[17]

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