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The synthesis and crystal structure of a first cubane-like complex of the Mo–Ag–S series: $\{MoAg_3S_3Cl\}(PPh_3)_3S$

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Abstract

A novel Mo–Ag–S cubane-like complex, $\{MoAg_3S_3Cl\}(PPh_3)_3S$, has been synthesized from AgCl, PPh_3 and MoS_4^{2-} in appropriate conditions. Crystallographic data for $C_{54}H_{45}ClP_3Ag_3S_4Mo$: $M_r = 1370.1$, monoclinic, space group $P2_1/c$, $a = 15.78(2)$, $b = 11.239(6)$, $c = 30.38(2)$ Å, $\beta = 93.16(6)°$, $U = 5380(7)$ Å^3; $Z = 4$; $D_{calc} = 1.69$ g cm^{-3}$\mu = 16.11$ cm^{-1}; $T = 296$ K; λ (Mo Kα) = 0.71069 Å, $2\theta_{max} = 50.1°$. Final $R = 0.050$ for 5698 observed reflections with $I > 3\sigma(I)$ and 595 variables. The unit cell contains four discrete neutral molecules. The molecular comprises one cubane-like cluster core $\{MoAg_3S_3Cl\}^{2+}$, three PPh_3 ligands attached to each Ag atoms and one terminal sulfido ligand attached to the Mo atom at 2.103(3) Å. The mean distance between the Mo and Ag atoms is 2.944(2) Å which is too long to effectively bond. The bond lengths of the three Ag–Cl bonds are in the same range and average 2.815(3) Å.

Introduction

Research on the synthetic analogues of the redox sites of iron–sulfur proteins has attracted many scientists to study the homometallic cubane-like $M_4(\mu_3\text{-}S)_4$ core clusters [1]. Meanwhile a number of heterometallic cubane-like clusters $M_2M'_2S_4$ [2] and $M_3M'S_4$ [3] have been obtained by various synthetic methods. It was found that the unit construction method [4] was a more convenient method to obtain clusters with reactive fragments as building blocks. Using the unit construction method, cluster compounds with cores $[M_3CuS_4]$ (M = Mo [5], W [6]), $[M_2M'S_4]$ [7] (M = Mo or W; M′ = Cu or Ag), $[M_2Cu_2S_4]$ [8], and $[MCu_3S_3X]$ [9] (M = Mo, X = Br; M = W, X = Cl) have been synthesized by our group. A thiometallate like MoS_4^{2-} or WS_4^{2-} is one of the best units [10] for the generation of several novel types of polynuclear transition metal compounds.

Several different structural types of polynuclear complexes [10, 11] have been obtained with Cu^+ and thiometallates in the presence of a PPh_3 ligand. The most important one is the cubane-like clusters of $\{MCu_3S_3X\}(PPh_3)_3E$ [11] (M = Mo, or W; X = Cl, or Br; E = S, or O). The soft acid Ag^+ has produced the same [12] as Cu^+, but the cubane-like one has not been reported. The main reason is the very poor solubility of the silver halides in water or organic solvents. We have noticed that the halide anion is absolutely necessary for the formation of the cubane-like clusters. The six cubane-like series of M_3CuS_4 [5, 6], $M_2Cu_2S_4$ [8] and MCu_3S_3X [9, 11] (M = Mo, or W) have been completed. Here, the first example of the Mo–Ag–S cubane-like series, $MoAg_3S_3Cl$, is reported.

Experimental

IR spectra were recorded with a Perkin-Elmer 577 spectrophotometer, using KBr pellets. All reactants and solvents were purchased above the CP grade. $(NH_4)_2MoS_4$ were prepared according to the literature [13].

Synthesis

$\{MoAg_3S_3Cl\}(PPh_3)_3S$

0.69 g $(NH_4)_2MoS_4$ (2.67 mmol) was added to 35 ml CH_2Cl_2 solution of 1.14 g AgCl (8 mmol) and 4.2 g PPh_3 (16 mmol), then stirred for 3 h. After filtration, the filtrate was diffused in a closed container with ether. Four days later, 0.33 g of red crystals was filtered, washed with ether and dried in air. Yield 9.0%. *Anal.* Calc. for $C_{54}H_{45}ClP_3Ag_3S_4Mo$: Mo, 7.00; Ag, 23.62; S, 9.36; P, 6.79; C, 47.34; H, 3.29; Cl, 2.59. Found: Mo, 6.89; Ag, 23.1; S, 9.53; P, 6.59; C, 46.70; H, 3.57; Cl, 2.62%. IR spectra (KBr pellets, cm^{-1}): 3040(w), 1480(s), 1430(s), 1100(s), 746(vs), 710(sh), 694(vs), 516(s), 504(s), 490(s), 430(s).

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The linear complex [11], $MoS_4Ag_2(PPh_3)_3$, is a major by-product which was identified by IR spectra and elemental analysis.

Crystal data and structure determination

A crystal was mounted in random orientation on a glass fibre. Some experimental conditions are reported in Table 1. Data were collected using a RIGAKU AFC5R diffractometer using Mo Kα radiation at *c.* 296 K. Cell constants were obtained by least-squares analysis on 20 diffraction maxima (the search limits of 2θ: 12.0–55.0°). Scan speed varies on the basis of SEARCH intensity, and a total of 10412 (include 10025 unique) reflections was collected. $R_{int} = 4.60\%$. Three standard reflections were measured periodically, no random deviations indicating crystal and electronic stability. Intensity was defined as $C - \frac{1}{2}(t_c/t_b)(b_1 + b_2)$, where C = total number of counts, t_c = time spent counting peak intensity, t_b = time spent counting one side of the background, b_1 = high-angle background counts and b_2 = low-angle background counts; the intensity error $\sigma(F^2) = (C + \frac{1}{4}(t_c/t_b)^2(b_1 + b_2) + (pI)^2)^{1/2}$, where I is the intensity and p is the factor that downweights strong reflections, taken to be 0.05. The data was corrected for Lorentz and polarization factors and for absorption using empirical scan data and DIFABS. Linear decay correction was applied. A total of 5698 reflections with $I > 3\sigma(I)$ was considered observed, and all were used in the refinement.

The structure was solved by direct methods using MITHRIL [14]; the Mo and Ag atoms were located in the E map. The most non-hydrogen atoms were located in the succeeding DIRDIF [15] program and some non-hydrogen atoms were located in the succeeding difference Fourier syntheses. The structure was refined by full-matrix least-squares technique with anisotropic thermal parameters for all Mo, Ag,Cl, S, P and C atoms (595 variables in all). Final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.050$, $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.063$ and $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N)]^{1/2} = 1.43$, $w = 1/\sigma^2(F_o)$. $(\Delta/\sigma)_{max} = 0.44$; in the final difference electron density synthesis the largest and smallest heights were 1.41 and −0.66 e Å^{-3} which were in the vicinity of the Ag and Mo atoms. All calculations were performed on a VAX 785 computer using the TEXSAN [16] program package.

The atomic coordinates and thermal parameters are listed in Table 2; the important bond lengths and bond angles are given in Tables 3 and 4, respectively.

TABLE 1. Crystallographic data for $\{MoAg_3S_3Cl\}(PPh_3)_3S$

Chemical formula	$C_{54}H_{45}ClP_3Ag_3S_4Mo$
Formula weight	1370.1
Crystal colour	orange-red
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell parameters	
a (Å)	15.78(2)
b (Å)	11.239(6)
c (Å)	30.38(2)
β (°)	93.16(6)
V (Å^3)	5380(7)
Z	4
μ	16.11
$F(000)$	2712
$2\theta_{max}$ (°)	50.1
D_{calc} (g cm^{-1})	1.69
Temperature (K)	296
Diffractometer	Rigaku AFC5R
Radiation	Mo Kα (λ = 0.71069 Å)
Solution method	direct methods
Correction	Lp, ψ, DIFABS
No. variables	595
Residuals: R, R_w	0.050, 0.063
Goodness of fit: S	1.43
No. unique data	10025
No. observations with $I > 3(\sigma(I))$	5698
Max. shift $(\Delta/\sigma)_{max}$ in final cycle	0.44
Largest/smallest peaks in final difference map (e Å^{-3})	1.41/−0.66
Scan type	ω
Max. scan speed (° min^{-1})	16
Scan width	1.89° + 0.35° tan Cθ

Results and discussion

The crystal structure of the compound consists of four neutral molecules. The ORTEP drawing of one molecular is shown in Fig. 1. The structure is similar to the $\{MoCu_3S_3Cl\}(PPh_3)_3S$ [11] cluster, except for the long distances of the Mo and Ag atoms. The core $\{MoAg_3S_3Cl\}$ is a cubane-like one, which is completed by three Ag atoms, one Cl atom and the terdentate MoS_4^{2-} ligand. Three PPh_3 ligands attach to the three Ag atoms, respectively. The coordination geometry of the Mo atom is a distorted tetrahedron. The bond length of Mo to the terminal sulfido atom S is *c.* 0.14 Å shorter than those to the bridging sulfido atoms. However, the angle between the terminal S and the bridging S atoms (i.e. S–Mo–S(1), S–Mo–S(2) and S–Mo–S(3)) is *c.* 5° shorter than the angles between the bridging S atoms themselves (i.e. S(1)–Mo–S(2) etc.). The three Ag–Cl bond distances are in the range 2.770–2.840 Å. Although the coordination geometry of each Ag atom is distorted, the three Ag atoms are approximately equivalent. Müller *et al.* reported [11] that the $\{MoCu_3S_3Cl\}(PPh_3)_3S$ cluster which crystallized in the orthorhombic $P2_12_12_1$ space group had one short Cu–Cl bond (2.471(4) Å) and two long Cu–Cl bonds (av. 2.744(4) Å). However, in our compounds, such as $\{MoCu_3S_3Br\}(PPh_3)_3E$ (E = O or SCH_2CH_2S) and

TABLE 2. Positional parameters and B_{eq} for {$MoAg_3S_3Cl$}(S)($(PPh_3)_3$)[a]

Atom	x	y	z	B_{eq}[b]
Ag(1)	0.12544(4)	0.23092(8)	0.87326(3)	4.46(4)
Ag(2)	0.30990(5)	0.41538(7)	0.86355(3)	4.23(4)
Ag(3)	0.26791(6)	0.2493(1)	0.96188(3)	5.77(5)
Mo	0.30561(5)	0.15776(7)	0.87369(2)	2.65(3)
Cl	0.1770(2)	0.4352(2)	0.92246(8)	4.3(1)
S	0.3814(2)	0.0233(2)	0.8481(1)	4.6(1)
S(1)	0.2404(1)	0.2555(2)	0.81645(7)	3.4(1)
S(2)	0.2106(2)	0.0704(2)	0.91538(9)	4.0(1)
S(3)	0.3950(1)	0.2741(2)	0.91449(8)	3.4(1)
P(1)	−0.0249(1)	0.2595(2)	0.86234(8)	2.9(1)
P(2)	0.3531(2)	0.6156(2)	0.85261(8)	3.2(1)
P(3)	0.2564(2)	0.2434(2)	1.03976(8)	3.5(1)
C(111)	−0.0805(5)	0.1412(8)	0.8322(3)	3.0(4)
C(112)	−0.1493(6)	0.161(1)	0.8021(3)	4.1(5)
C(113)	−0.1919(7)	0.065(1)	0.7802(3)	4.8(5)
C(114)	−0.1653(7)	−0.050(1)	0.7903(3)	4.3(5)
C(115)	−0.0974(7)	−0.071(1)	0.8197(3)	4.3(5)
C(116)	−0.0537(6)	0.024(1)	0.8404(3)	3.8(5)
C(121)	−0.0798(5)	0.2728(8)	0.9132(3)	3.1(4)
C(122)	−0.0530(6)	0.364(1)	0.9425(3)	4.2(5)
C(123)	−0.0958(7)	0.380(1)	0.9809(4)	5.3(6)
C(124)	−0.1596(8)	0.304(1)	0.9920(4)	5.3(6)
C(125)	−0.1828(7)	0.213(1)	0.9633(4)	5.5(6)
C(126)	−0.1448(6)	0.195(1)	0.9231(3)	4.3(5)
C(131)	−0.0511(6)	0.3961(8)	0.8325(3)	3.3(4)
C(132)	0.0103(6)	0.4433(9)	0.8058(3)	3.9(5)
C(133)	−0.0089(8)	0.548(1)	0.7808(4)	5.1(6)
C(134)	−0.0876(8)	0.605(1)	0.7836(4)	5.2(6)
C(135)	−0.1465(7)	0.556(1)	0.8113(3)	4.5(5)
C(136)	−0.1284(6)	0.4546(9)	0.8361(3)	4.0(5)
C(211)	0.3857(6)	0.6814(8)	0.9057(3)	3.3(4)
C(212)	0.3472(6)	0.7868(9)	0.9207(3)	3.8(4)
C(213)	0.3735(6)	0.828(1)	0.9632(3)	4.1(5)
C(214)	0.4347(7)	0.765(1)	0.9893(3)	4.7(5)
C(215)	0.4733(7)	0.663(1)	0.9734(4)	5.2(6)
C(216)	0.4479(6)	0.620(1)	0.9315(3)	4.0(5)
C(221)	0.2694(6)	0.7128(8)	0.8289(3)	3.6(4)
C(222)	0.1881(6)	0.697(1)	0.8429(3)	4.8(5)
C(223)	0.1219(8)	0.774(1)	0.8270(4)	6.3(7)
C(224)	0.1401(8)	0.863(1)	0.7966(4)	5.9(7)
C(225)	0.2201(8)	0.878(1)	0.7817(4)	5.3(6)
C(226)	0.2873(7)	0.802(1)	0.7977(3)	4.6(5)
C(231)	0.4421(6)	0.641(1)	0.8179(3)	4.2(5)
C(232)	0.4480(8)	0.562(1)	0.7819(4)	6.7(7)
C(233)	0.513(1)	0.582(2)	0.7530(5)	9(1)
C(234)	0.5668(9)	0.680(1)	0.7590(4)	7.2(8)
C(235)	0.5587(8)	0.757(1)	0.7935(4)	6.0(7)
C(236)	0.4957(6)	0.741(1)	0.8243(3)	4.5(5)
C(311)	0.1469(6)	0.2280(9)	1.0547(3)	3.4(4)
C(312)	0.1044(7)	0.122(1)	1.0405(3)	4.8(5)
C(313)	0.0177(7)	0.105(1)	1.0502(4)	5.2(6)
C(314)	−0.0230(7)	0.193(1)	1.0728(4)	5.3(6)
C(315)	0.0179(7)	0.298(1)	1.0853(4)	5.2(6)
C(316)	0.1059(6)	0.315(1)	1.0771(3)	4.3(5)
C(321)	0.2971(6)	0.3736(9)	1.0691(3)	3.7(4)
C(322)	0.3191(7)	0.368(1)	1.1148(3)	4.5(5)
C(323)	0.3521(8)	0.472(1)	1.1367(4)	5.7(6)
C(324)	0.3605(8)	0.578(1)	1.1139(5)	6.2(7)
C(325)	0.3399(9)	0.581(1)	1.0687(5)	7.1(8)
C(326)	0.3079(7)	0.482(1)	1.0459(4)	5.7(6)
C(331)	0.3121(6)	0.1207(8)	1.0675(3)	3.6(4)
C(332)	0.2843(6)	0.064(1)	1.1038(4)	4.3(5)
C(333)	0.3333(7)	−0.028(1)	1.1253(4)	5.6(6)
C(334)	0.4114(7)	−0.058(1)	1.1086(5)	5.8(6)
C(335)	0.4399(7)	−0.003(1)	1.0720(5)	5.8(6)
C(336)	0.3899(6)	0.087(1)	1.0501(4)	4.7(5)

[a] All atoms were refined anisotropically. [b] $B_{eq}=4/3\Sigma_i\Sigma_j B_{ij}a_ia_j$.

TABLE 3. Selected bond lengths

Atoms	Distance	Atoms	Distance
Ag(1)–Mo	2.959(3)	Ag(3)–Cl	2.770(3)
Ag(2)–Mo	2.913(2)	Mo–S	2.103(3)
Ag(3)–Mo	2.961(3)	Mo–S(1)	2.257(3)
Ag(1)–S(1)	2.587(3)	Mo–S(2)	2.242(3)
Ag(1)–S(2)	2.551(3)	Mo–S(3)	2.246(3)
Ag(2)–S(1)	2.512(3)	P(1)–C(111)	1.81(1)
Ag(2)–S(3)	2.548(3)	P(1)–C(121)	1.819(9)
Ag(3)–S(2)	2.592(3)	P(1)–C(131)	1.82(1)
Ag(3)–S(3)	2.548(3)	P(2)–C(211)	1.823(9)
Ag(1)–P(1)	2.400(3)	P(2)–C(221)	1.83(1)
Ag(2)–P(2)	2.380(3)	P(2)–C(231)	1.82(1)
Ag(3)–P(3)	2.384(3)	P(3)–C(311)	1.819(9)
Ag(1)–Cl	2.835(3)	P(3)–C(321)	1.81(1)
Ag(2)–Cl	2.840(3)	P(3)–C(331)	1.82(1)

TABLE 4. Selected bond angles

Atoms	Angle	Atoms	Angle
P(1)–Ag(1)–S(2)	130.79(9)	Ag(2)–Mo–Ag(1)	75.59(4)
P(1)–Ag(1)–S(1)	128.2(1)	Ag(2)–Mo–Ag(3)	75.96(4)
P(1)–Ag(1)–Cl	102.55(9)	Ag(1)–Mo–Ag(3)	70.53(6)
S(2)–Ag(1)–S(1)	92.3(1)	Ag(3)–Cl–Ag(1)	75.15(9)
S(2)–Ag(1)–Cl	100.4(1)	Ag(3)–Cl–Ag(2)	80.23(8)
S(1)–Ag(1)–Cl	94.25(8)	Ag(1)–Cl–Ag(2)	78.72(8)
P(2)–Ag(2)–S(1)	135.8(1)	Mo–S(1)–Ag(2)	75.10(9)
P(2)–Ag(2)–S(3)	121.9(1)	Mo–S(1)–Ag(1)	74.96(9)
P(2)–Ag(2)–Cl	103.93(9)	Ag(2)–S(1)–Ag(1)	89.79(9)
S(1)–Ag(2)–S(3)	95.7(1)	Mo–S(2)–Ag(1)	75.9(1)
S(1)–Ag(2)–Cl	95.8(1)	Mo–S(2)–Ag(3)	75.15(9)
S(3)–Ag(2)–Cl	92.8(1)	Ag(1)–S(2)–Ag(3)	83.3(1)
P(3)–Ag(3)–S(3)	132.0(1)	Mo–S(3)–Ag(2)	74.54(9)
P(3)–Ag(3)–S(2)	118.4(1)	Mo–S(3)–Ag(3)	76.00(9)
P(3)–Ag(3)–Cl	112.6(1)	Ag(2)–S(3)–Ag(3)	90.4(1)
S(3)–Ag(3)–S(2)	92.24(9)	C(111)–P(1)–C(131)	106.1(4)
S(3)–Ag(3)–Cl	94.5(1)	C(111)–P(1)–C(121)	104.5(4)
S(2)–Ag(3)–Cl	101.1(1)	C(131)–P(1)–C(121)	104.4(4)
S–Mo–S(2)	107.8(1)	C(211)–P(2)–C(231)	105.0(5)
S–Mo–S(3)	105.7(1)	C(211)–P(2)–C(221)	105.6(4)
S–Mo–S(1)	108.0(1)	C(231)–P(2)–C(221)	104.0(5)
S(2)–Mo–S(3)	111.3(1)	C(321)–P(3)–C(331)	103.7(5)
S(2)–Mo–S(1)	111.0(1)	C(321)–P(3)–C(311)	105.6(4)
S(3)–Mo–S(1)	112.8(1)	C(331)–P(3)–C(311)	104.7(4)

{WCu_3S_3Cl}($(PPh_3)_3S\cdot 0.5(CH_3)_2CHOH$) which each has the triclinic $P\bar{1}$ space group, there exist three long Cu–X bonds. The title compound also has three long Ag–Cl bonds.

As mentioned above the halide anion is necessary for the formation of the cubane-like clusters, the weak interaction between Cl and the three Ag atoms stabilizes it. The linear complex, $MoS_4Ag_2(PPh_3)_3$ [11], is easily formed and always present in the synthesis of the cubane-like clusters.

The designed synthesis of the first cubane-like complex of {$MoAg_3S_3Cl$}($(PPh_3)_3S$) shows the similarity be-

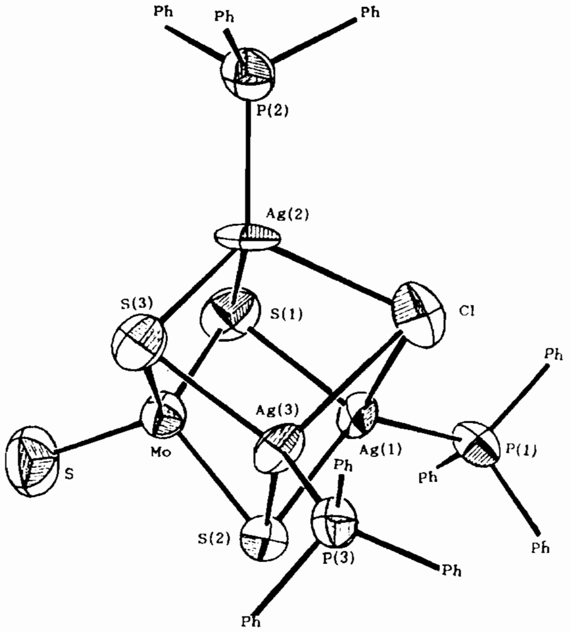

Fig. 1. The configuration of the cubane-like molecule $\{MoAg_3S_3Cl\}(S)(PPh_3)_3$.

tween the M/Ag chemistry and M/Cu chemistry (M = Mo, W) in the transition metal sulfido-bridging cluster chemistry. Other compounds of the cubane-like series of Mo(W)–Ag–S clusters will be obtained in the near future.

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