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SYNTHESES AND CRYSTAL STRUCTURES OF HEPTANUCLEAR CLUSTERS $[VS_4(CuPPh_3)_5Br_2CuX]$ AND $[VS_4(CuPPh_3)_5Br_2CuX] \cdot CH_2Cl_2$ $(X = 0.5Br+0.5Cl)$

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Abstract—The preparation of the title compounds of heptanuclear heterometallic clusters by heating a mixture of $(NH_4)_3VS_4$, CuCl, PPh_3 and Et_4NBr in a solid state reaction at low temperature has been investigated. The compounds $[VS_4(CuPPh_3)_5Br_2CuX]$ (**1**) and $[VS_4(CuPPh_3)_5Br_2CuX] \cdot CH_2Cl_2$ (**2**) have been characterized by single-crystal X-ray diffraction. The clusters consist of a tetrahedral VS_4 core bound to an octahedral array of six copper atoms which have two different coordinations, trigonal planar and tetrahedral. Each copper atom is bound to a terminal ligand: five of these are PPh_3 molecules and one a halogen atom. The geometries of the two additional bridging bromine atoms are different in the title clusters. For cluster **1** both bromine atoms are μ_2 atoms, while for cluster **2** one is μ_2-Br and the other μ_3-Br.

The use of tetrathiometallates $[MS_4]^{n-}$ as ligands coordinating to a wide variety of metal ions for preparation of heterometallic cluster compounds has been studied. The complex chemistry of $[MoS_4]^{2-}$ and $[WS_4]^{2-}$ has been highly developed because of the potential utility of the anion MoS_4^{2-} in imitation of biological systems. The others are VS_4^{3-} and ReS_4^-. Although VS_4^{3-} was first prepared in 1890,[1] the chemistry of this species had not been extensively investigated until vanadium nitrogenase was discovered. The linear trinuclear complex $[VS_4Fe_2Cl_4]^{3-}$ and cubane-like cluster $[VS_4Fe_3Cl_3(DMF)_3]^-$ were first obtained by Holm in 1983[2] and 1986,[3] respectively, and subsequently the tetra-, penta- and hepta nuclear V—Cu—S heterometallic clusters have been reported.[4–7] Herein we report a new method (solid state reaction at low temperature) to prepare V—Cu—S clusters, and the crystal structures of $[VS_4(CuPPh_3)_5Br_2CuX]$ (**1**) and $[VS_4(CuPPh_3)_5Br_2CuX] \cdot CH_2Cl_2$ (**2**) $(X = 0.5Br+0.5Cl)$ are investigated.

EXPERIMENTAL

Materials

Commercially available reagents were used for the syntheses of complexes. $(NH_4)_3VS_4$ was prepared by a reported method.[1]

Synthesis of $[VS_4(CuPPh_3)_5Br_2CuX]$ $(X = 0.5Br+0.5Cl)$ (1)

A mixture of $(NH_4)_3VS_4$ (0.47 g, 2 mmol), CuCl (0.40 g, 4 mmol), PPh_3 (1.57 g, 6 mmol) and Et_4NBr (0.64 g, 2 mmol) was mixed and ground thoroughly in an agate mortar. The solid mixture was transferred to a reaction bottle and heated in an oil bath at 150°C for 22 h. The dark product was extracted

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with 40 cm^3 of CH_2Cl_2 and filtered. Pr^{i}OH–MeCN(25 : 15 cm^3) was added slowly on the surface of the deep red filtrate and left undisturbed at ambient temperature. All operations were performed under dinitrogen. After 3 days, black–red prismatic crystals were obtained from the filtrate. IR: ν(V—S) 441.7/451.3 cm^{-1}. Found: C, 53.2; H, 3.6; P, 7.5; S, 6.1; V, 2.4; Cu, 18.0%; halogen, 1.44 mmol g^{-1}. Calc. for $C_{90}H_{75}P_5S_4Cl_{0.5}Br_{2.5}VCu_6$: C, 51.7; H, 3.6; P, 7.4; S, 6.1; V, 2.4; Cu, 18.3%; halogen, 1.40 mmol g^{-1}.

Synthesis of $[VS_4(CuPPh_3)_5Br_2CuX]\cdot CH_2Cl_2$(X = 0.5Br+0.5Cl) (**2**)

A mixture of $(NH_4)_3VS_4$ (0.94 g, 4 mmol), CuCl (1.2 g, 12 mmol), PPh_3 (3.14 g, 12 mmol) and Et_4NBr (1.29 g, 4 mmol) was treated using the same method as for **1** and heated at 150°C for 8 h. The dark product was dissolved in 100 cm^3 of CH_2Cl_2 and filtered. Pr^{i}OH–MeCN (60 : 10 cm^3) was added slowly to the filtrate. After 3 days, black–red prismatic crystals were obtained. IR: ν(V—S) 439.7/451.3 cm^{-1}.

X-ray data collection and refinement

A suitable crystal of each of the title clusters was mounted on glass fibres in a random orientation. Diffraction studies were performed on an MSC/Rigaku four-circle diffractometer with Mo-K_α radiation ($\lambda = 0.71069$ Å) equipped with a graphite monochromator. The data were collected at a temperature of 23 ± 1°C. The systematic absences $h0l$ $h+l = 2n+1$ and $0k0$ $k = 2n+1$ define the unique space group $P2_1/n$ (No. 14) for cluster **1**. The intensity data were corrected for Lorentz and polarization, linear decay, empirical absorption and DIFABS[8] for crystal **1**, and the same for crystal **2** except DIFABS. Cell parameters and other relevant details are given in Table 1.

All calculations were performed on a VAX com-

Table 1. Crystallographic data, collection and refinement parameters for **1** and **2**

	1	**2**
Crystal data		
Formula	$C_{90}H_{75}Br_{2.5}Cl_{0.5}P_5S_4Cu_6V$	$C_{91}H_{77}Br_{2.5}Cl_{2.5}P_5S_4Cu_6V$
Formula weight	2089.41	2174.41
Crystal size (mm)	$0.3 \times 0.3 \times 0.4$	$0.3 \times 0.4 \times 0.3$
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	13.616(1)	15.133(3)
b (Å)	30.063(9)	22.888(4)
c (Å)	21.603(2)	13.928(4)
α (°)		97.90(2)
β (°)	94.16(1)	107.64(2)
γ (°)		93.01(2)
V (Å^3)	8819.3	4530.8
Z	4	2
D_c (g cm^{-3})	1.57	1.59
$F(0\,0\,0)$	4188	2178
Collection and refinement parameters		
μ(Mo-K_α) (cm^{-1})	28.8	26.3
Scan mode	ω–2θ	ω–2θ
2θ limits (°)	46.1	52.1
Octants recorded	$+h, +k, \pm l$	$+h, \pm k, \pm l$
Data collected	13,203	18,654
Unique data	11,433	17,944
Data with $I > 3\sigma(I)$	8212	8820
No. of variables	982	994
Goodness-of-fit	0.86	2.32
$R = \Sigma\|\|F_0\| - \|F_c\|\|/\Sigma\|F_0\|$	0.055	0.075
$R_\omega = [\Sigma w(\|F_0\| - \|F_c\|)^2/\Sigma w\|F_0\|^2]^{1/2}$	0.078	0.085
$\Delta\rho_{max}$ (e Å^{-3})	0.76	1.05
$\Delta\rho_{min}$ (e Å^{-3})	−0.67	−2.15

puter using SDP/VAX program. The positions of the atoms, i.e. bromine, copper, vanadium, sulphur, phosphorus and X atoms were revealed by direct methods and the remaining carbon atoms were located in successive difference Fourier maps. X was derived from the process of structure refinement. During the initial refinement, X was considered as chlorine. However, the temperature factor of this atom was too small. Then the multiplicity of the chlorine atom was used in structure refinement. The final multiplicity of chlorine is 1.54 for clusters **1** and **2**. This is consistent with a statistical occupancy (0.5Br+0.5Cl) where the multiplicity is $(35+17)/2 \times 17 = 1.53$. Hydrogen atoms were located theoretically and added to the structure factor calculations, but their positions were not refined.

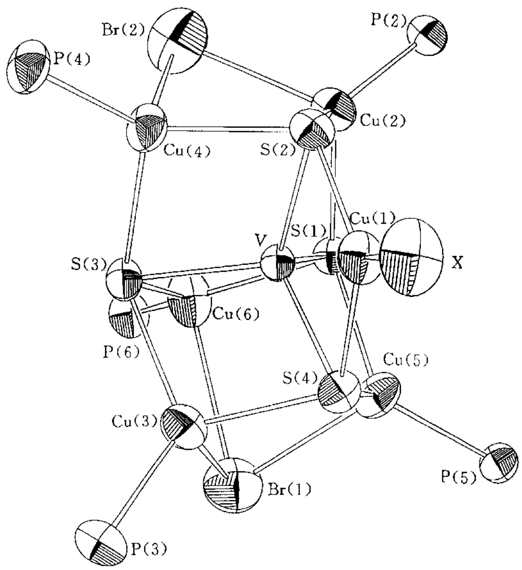

Fig. 2. The molecular structure for **2** with aryl groups omitted, along with the atomic numbering scheme.

RESULTS AND DISCUSSION

Selected bond lengths and angles for **1** and **2** are given in Table 2. The molecular structures for **1** and **2** with aryl groups omitted are presented in Figs 1 and 2, respectively.

The structures of **1** and **2** possess a central VS$_4$ moiety in a tetrahedral geometry with S—V—S angles ranging from 108.46(7) to 110.49(7)° for **1** and 108.32(9) to 110.2(1)° for **2**. This is the same as that of free VS$_4^{3-}$, but the mean V—S distance (2.205 Å for **1** and 2.216 Å for **2**) is a little longer than that of free VS$_4^{3-}$ (2.154 Å).[1] Six copper atoms encapsulate the VS$_4$ core, resulting in an octahedral array as shown in Fig. 3, exemplified by **1**. In clusters **1** and **2** each copper atom has a terminal ligand. Cu(1) is bound to a halogen (0.5Br+0.5Cl) atom and the others are bound to PPh$_3$ molecules. Four μ_4-S atoms are connected with the vanadium and three copper atoms. The Cu—S—V angles, in the range of 71.09(5)–73.27(5)° for **1** and 71.45(8)–73.12(8)° for **2**, result from the rigidity of the central VS$_4$ tetrahedron geometry. Six copper atoms are present in the structure of clusters **1** and **2** with two different coordinations, trigonal planar and tetrahedral. In cluster **1**, Cu(1) and Cu(6) are planar tricoordinated with the sum of Cu(1) and Cu(6) angles, 359.75° and 359.58°, while in cluster **2** only

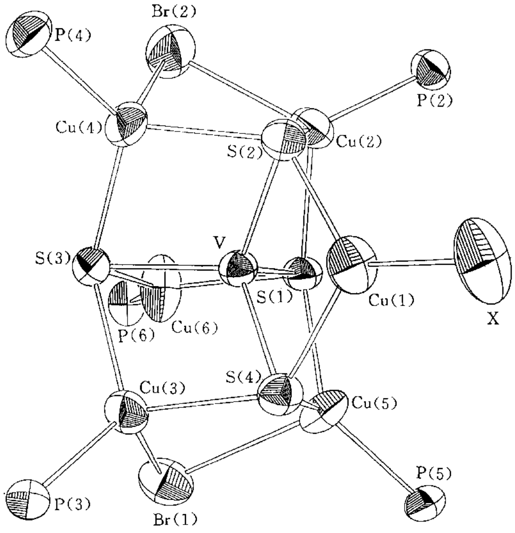

Fig. 1. The molecular structure for **1** with aryl groups omitted, along with the atomic numbering scheme.

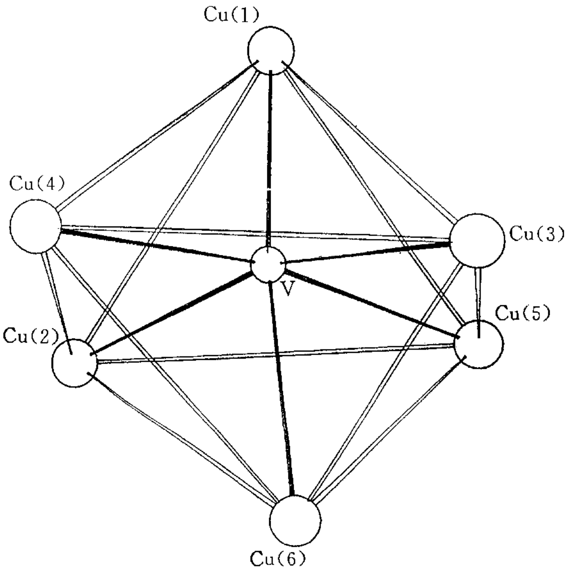

Fig. 3. Six copper atoms around vanadium in an octahedral array for **1**.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**[a]

	1	**2**		**1**	**2**
Br(1)—Cu(3)	2.499(2)	2.597(2)	Cu(4)—S(2)	2.328(2)	2.326(2)
Br(1)—Cu(5)	2.761(1)	2.666(2)	Cu(4)—S(3)	2.293(2)	2.342(2)
Br(1)—Cu(6)	3.053(2)[b]	2.858(2)	Cu(4)—P(4)	2.228(2)	2.225(3)
Br(2)—Cu(2)	2.508(1)	2.524(2)	Cu(5)—S(1)	2.308(2)	2.310(2)
Br(2)—Cu(4)	2.651(1)	2.573(2)	Cu(5)—S(4)	2.296(2)	2.301(2)
Cu(1)—X	2.228(1)	2.225(2)	Cu(5)—P(5)	2.225(2)	2.216(3)
Cu(1)—S(2)	2.240(2)	2.257(2)	Cu(6)—S(1)	2.243(2)	2.277(2)
Cu(1)—S(4)	2.250(2)	2.248(2)	Cu(6)—S(3)	2.257(2)	2.268(2)
Cu(2)—S(1)	2.340(2)	2.334(2)	Cu(6)—P(6)	2.202(2)	2.227(2)
Cu(2)—S(2)	2.315(2)	2.328(2)	V—S(1)	2.202(2)	2.196(2)
Cu(2)—P(2)	2.201(2)	2.209(3)	V—S(2)	2.200(2)	2.213(2)
Cu(3)—S(3)	2.306(2)	2.302(2)	V—S(3)	2.220(2)	2.214(3)
Cu(3)—S(4)	2.355(2)	2.318(2)	V—S(4)	2.199(2)	2.223(3)
Cu(3)—P(3)	2.201(2)	2.206(3)			
Cu(3)—Br(1)—Cu(5)	76.07(4)	76.54(5)	S(1)—Cu(6)—S(3)	105.76(7)	103.75(8)
Cu(3)—Br(1)—Cu(6)		72.48(4)	S(1)—Cu(6)—P(6)	117.26(7)	124.3(1)
Cu(5)—Br(1)—Cu(6)		73.99(4)	S(3)—Cu(6)—P(6)	136.56(7)	130.0(2)
Cu(2)—Br(2)—Cu(4)	78.01(3)	79.65(5)	S(1)—V—S(2)	108.61(7)	110.0(1)
X—Cu(1)—S(2)	126.12(6)	126.90(8)	S(1)—V—S(3)	108.46(7)	108.32(9)
X—Cu(1)—S(4)	127.24(6)	125.88(9)	S(1)—V—S(4)	109.20(6)	109.8(1)
S(2)—Cu(1)—S(4)	106.39(6)	106.88(8)	S(2)—V—S(3)	110.45(6)	110.2(1)
Br(2)—Cu(2)—S(1)	109.52(6)	109.37(8)	S(2)—V—S(4)	109.60(7)	109.32(9)
Br(2)—Cu(2)—S(2)	94.81(5)	91.95(7)	S(3)—V—S(4)	110.49(7)	109.3(1)
Br(2)—Cu(2)—P(2)	119.19(6)	109.40(8)	Cu(2)—S(1)—Cu(5)	134.33(7)	131.9(1)
S(1)—Cu(2)—S(2)	100.36(6)	101.56(8)	Cu(2)—S(1)—Cu(6)	101.99(7)	107.5(1)
S(1)—Cu(2)—P(2)	111.51(6)	107.8(1)	Cu(2)—S(1)—V	72.67(6)	72.36(8)
S(2)—Cu(2)—P(2)	118.97(7)	134.57(9)	Cu(5)—S(1)—Cu(6)	95.58(6)	93.0(1)
Br(1)—Cu(3)—S(3)	102.31(5)	100.79(8)	Cu(5)—S(1)—V	72.96(5)	72.90(8)
Br(1)—Cu(3)—S(4)	97.79(5)	94.99(7)	Cu(6)—S(1)—V	72.80(5)	73.12(8)
Br(1)—Cu(3)—P(3)	112.14(5)	110.68(8)	Cu(1)—S(2)—Cu(2)	117.25(7)	129.2(2)
S(3)—Cu(3)—S(4)	102.34(6)	103.03(9)	Cu(1)—S(2)—Cu(4)	125.44(7)	112.5(2)
S(3)—Cu(3)—P(3)	122.08(6)	124.0(2)	Cu(1)—S(2)—V	71.28(5)	71.45(8)
S(4)—Cu(3)—P(3)	116.65(6)	118.3(1)	Cu(2)—S(2)—Cu(4)	88.80(7)	89.11(8)
Br(2)—Cu(4)—S(2)	90.82(6)	90.77(7)	Cu(2)—S(2)—V	73.21(5)	72.17(7)
Br(2)—Cu(4)—S(3)	99.07(5)	101.62(7)	Cu(4)—S(2)—V	72.52(5)	73.37(8)
Br(2)—Cu(4)—P(4)	115.24(6)	117.99(9)	Cu(3)—S(3)—Cu(4)	128.59(8)	129.4(1)
S(2)—Cu(4)—S(3)	103.56(6)	102.18(8)	Cu(3)—S(3)—Cu(6)	92.90(6)	90.01(9)
S(2)—Cu(4)—P(4)	118.29(7)	123.7(1)	Cu(3)—S(3)—V	72.49(5)	72.74(8)
S(3)—Cu(4)—P(4)	123.65(7)	115.9(2)	Cu(4)—S(3)—Cu(6)	111.00(7)	113.9(2)
Br(1)—Cu(5)—S(1)	99.00(5)	97.16(7)	Cu(4)—S(3)—V	72.85(5)	73.03(8)
Br(1)—Cu(5)—S(4)	92.23(5)	93.57(7)	Cu(6)—S(3)—V	72.19(5)	72.97(8)
Br(1)—Cu(5)—P(5)	107.20(6)	110.83(8)	Cu(1)—S(4)—Cu(3)	129.76(8)	116.2(2)
S(1)—Cu(5)—S(4)	102.41(6)	103.22(8)	Cu(1)—S(4)—Cu(5)	111.54(8)	125.2(2)
S(1)—Cu(5)—P(5)	126.07(7)	121.5(1)	Cu(1)—S(4)—V	71.09(5)	71.49(8)
S(4)—Cu(5)—P(5)	122.20(7)	124.0(1)	Cu(3)—S(4)—Cu(5)	88.56(6)	89.80(8)
Br(1)—Cu(6)—S(1)		92.8(2)	Cu(3)—S(4)—V	71.91(5)	72.28(8)
Br(1)—Cu(6)—S(3)		94.4(2)	Cu(5)—S(4)—V	73.27(5)	72.61(8)
Br(1)—Cu(6)—P(6)		96.2(1)			

[a] Estimated standard deviations are given in parentheses.

[b] This value indicates that non-bonding exists between Br(1) and Cu(6) for **1**.

Table 3. V—Cu and selected Cu···Cu distances (Å) for **1** and **2**[a]

	1	**2**		**1**	**2**
V—Cu(1)	2.586(1)	2.611(2)	Cu(1)···Cu(5)	3.758(2)	4.038(2)
V—Cu(2)	2.693(1)	2.676(2)	Cu(2)···Cu(4)	3.249(2)	3.265(2)
V—Cu(3)	2.677(1)	2.679(2)	Cu(2)···Cu(5)	4.283(2)	4.240(2)
V—Cu(4)	2.681(1)	2.713(2)	Cu(2)···Cu(6)	3.561(1)	3.718(2)
V—Cu(5)	2.683(1)	2.679(2)	Cu(3)···Cu(4)	4.143(2)	4.190(2)
V—Cu(6)	2.638(1)	2.665(1)	Cu(3)···Cu(5)	3.247(1)	3.260(2)
Cu(1)···Cu(2)	3.888(1)	4.143(2)	Cu(3)···Cu(6)	3.718(2)	3.307(1)
Cu(1)···Cu(3)	4.169(1)	3.876(2)	Cu(4)···Cu(6)	3.749(1)	3.863(2)
Cu(1)···Cu(4)	4.060(1)	3.812(2)	Cu(5)···Cu(6)	3.371(1)	3.327(2)

[a] Estimated standard deviations are given in parentheses.

Cu(1) is planar tricoordinated with the sum of Cu(1) angles, 359.66°. The geometry of the other tetrahedrally coordinated copper atoms is distorted from the ideal tetrahedron, with angles at copper atoms in the range of 90.82(6)–126.07(7)° for **1** and 90.77(7)–130.0(2)° for **2**. The mean Cu—S distance for tetracoordinated copper atoms [2.318(2) Å for **1** and 2.311(2) Å for **2**] is longer than that for the tricoordinated copper atoms [2.248(2) Å for **1** and 2.253(2) Å for **2**]. This reflects that the greater the coordination number of the copper atom, the longer the Cu—S bond.

Two additional bridging bromine atoms in cluster **1** are μ_2 atoms, where Br(1) links Cu(3) and Cu(5), and Br(2) links Cu(2) and Cu(4) to form two six-membered CuBrCuSCuS rings with the boat conformation, and the core of cluster **1** has approximate mirrior symmetry across the middle plane [VS(1)S(3)Cu(6)P(6)Cu(1)X], while in cluster **2** the geometry of two additional bridging bromine atoms is the same as the bridging chlorine atoms in the cluster $[VS_4(CuPPh_3)_5Cl_2CuCl]\cdot CH_2Cl_2$ (**3**),[7] where Br(1) is a μ_3 atom which leads to the formation of a distorted cubane-like VS_3Cu_3Br framework, and Br(2) is a μ_2 atom linking Cu(2) and Cu(4) to form a six-membered CuBrCuSCuS ring with the boat conformation. Although clusters **2** and **3** are allomers, their chemical stabilities are quite different. Clusters **1** and **2** are stable in air, while cluster **3** can be stable only in the mother liquor under solvent atmosphere.[7] This indicates that the presence of a solvent CH_2Cl_2 molecule does not affect the chemical stability of the heptanuclear $[VS_4Cu_6]$ clusters; however, the instability of cluster **3** results from the difference of bridging halogen atoms. Nevertheless, the geometry of bridging halogen atoms can be affected by the presence of the solvent molecule CH_2Cl_2, which probably results in different close packed lattices. The Cu—Br distances, in the range of 2.499(2)–2.651(1) Å for **1** and 2.524(2)–2.858(2) Å for **2**, are longer than the covalent bond length of 2.31 Å,[9] and shorter than the ionic bond length of 2.92 Å.[9] This shows that the Cu—Br bonds are strongly polarized ionic bonds derived from the transition metal Cu^+ ions having 10 *d* electrons which shield the nuclei poorly, polarizing the large size of the anion Br^-.

The Cu···Cu distances of 3.247(2)–4.283(2) Å for **1** and 3.307(1)–4.240(2) Å for **2** (see Table 3) indicate that there is no metal–metal bond between copper atoms. The V—Cu distances are 2.586(1)–2.693(1) Å for **1** and 2.611(2)–2.713(2) Å for **2**, compared with the metal–metal bond length of 2.59 Å for V—Cu,[9] and according to the ROP (~0.09) of Cu—V bonds calculated from EHMO,[10] which shows that a weak copper–vanadium interaction probably exists.

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