

# Association of two incomplete cubane $\text{WS}_3\text{Cu}_3$ clusters in the crystal structures of $[\text{PPh}_4]_2\{[(\text{C}_5\text{Me}_5)\text{WS}_3]_2\text{Cu}_6(\text{NCS})_6\}$ and $[\text{PPh}_4]_2\{[(\text{C}_5\text{Me}_5)\text{WS}_3]_2\text{Cu}_6\text{Br}_6\}$

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**Two double cubane-like clusters,  $[\text{PPh}_4]_2\{[(\text{C}_5\text{Me}_5)\text{WS}_3]_2\text{Cu}_6(\text{NCS})_6\}$  **1** and  $[\text{PPh}_4]_2\{[(\text{C}_5\text{Me}_5)\text{WS}_3]_2\text{Cu}_6\text{Br}_6\}$  **2**, are self-assembled by the reactions of  $[\text{PPh}_4][(\text{C}_5\text{Me}_5)\text{WS}_3]$  with  $\text{CuNCS}$  and  $\text{CuBr}$  in acetonitrile, respectively, the crystal structures of which consist of two  $\text{WS}_3\text{Cu}_3$  incomplete cubes linked by NCS and Br bridges.**

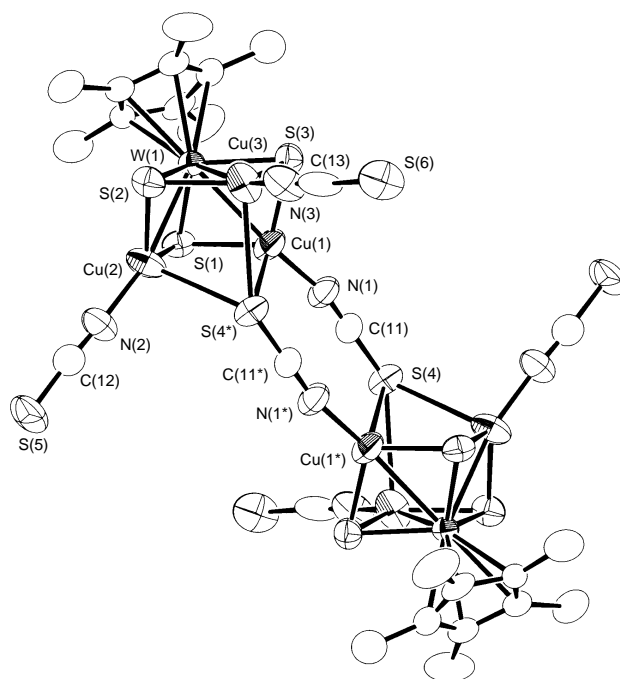
The linkage of transition-metal clusters has been the subject of recent interest.<sup>1–4</sup> It has been shown that cubane clusters of homo- and hetero-metallic sulfides can be assembled in various ways. An example is the thiolate-bridged double-cubane cluster  $[\text{Mo}_2\text{Fe}_7\text{S}_8(\text{SPh})_9]^{3-}$ , which was obtained from the reaction of  $\text{FeCl}_3$  with  $[\text{NH}_4]_2[\text{MoS}_4]$  and  $\text{NaSPh}$ .<sup>5</sup> The similar self-assembly of  $\text{FeCl}_3$ ,  $[\text{NBu}^n_4]_2[\text{MoS}_4]$  and  $\text{NaSEt}$  gave rise to  $[\text{Mo}_2\text{Fe}_7\text{S}_8(\text{SEt})_{12}]^{3-}$ .<sup>6</sup> Two molecules of the cubane cluster  $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$  were linked upon treatment with  $\text{Li}_2\text{S}$  to generate  $[(\text{Fe}_4\text{S}_4\text{Cl}_3)_2\text{S}]^{4-}$ ,<sup>7</sup> while the incomplete cubane-like cluster  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  also served as a starting material for the synthesis of double-cubane complexes such as  $[(\text{H}_2\text{O})_9\text{Mo}_3\text{S}_4\text{CuCuS}_4\text{Mo}_3(\text{H}_2\text{O})_9]^{8-}$ .<sup>8</sup> More recently, the preformed mixed-metal cubane clusters  $[\text{MoFe}_3\text{S}_4\text{Cl}_3(\text{Cl}_4\text{cat})(\text{L})]^{2-}$  (cat = catechol; L = coordinating solvent molecule) have been assembled into various double-cubane clusters in the presence of the appropriate polycarboxylic acid.<sup>9</sup>

Recently we found a facile route to the organometallic trithiotungsten(vi) complex  $[\text{PPh}_4][(\text{C}_5\text{Me}_5)\text{WS}_3]$  *via* C–S bond cleavage of ethanedithiolate.<sup>10</sup> The terminal sulfides in  $[(\text{C}_5\text{Me}_5)\text{WS}_3]^-$  appear to be more reactive than those of  $[\text{PPh}_4]_2[\text{WS}_4]$ , and they react readily with alkyl halides and even with non-activated alkynes such as  $\text{PhC}\equiv\text{CPh}$  and  $\text{PhC}\equiv\text{CH}$ . Having noted that  $[(\text{C}_5\text{Me}_5)\text{WS}_3]^-$  may be a potential building block for heterometallic sulfide clusters, we examined its reactions with  $\text{CuNCS}$  and  $\text{CuBr}$ . In this paper we report two double cubane-like clusters,  $[\text{PPh}_4]_2\{[(\text{C}_5\text{Me}_5)\text{WS}_3]_2\text{Cu}_6(\text{NCS})_6\}$  **1** and  $[\text{PPh}_4]_2\{[(\text{C}_5\text{Me}_5)\text{WS}_3]_2\text{Cu}_6\text{Br}_6\}$  **2**, obtained from these reactions.

Compound **1** was prepared by the following procedure.  $\text{CuNCS}$  (0.05 g, 0.42 mmol) was added to  $[\text{PPh}_4][(\text{C}_5\text{Me}_5)\text{WS}_3]$  (0.11 g, 0.14 mmol) in MeCN (20 ml) and the mixture was stirred for 24 h at room temperature. After filtering off insoluble materials, the resultant solution was concentrated to *ca.* 5 ml under reduced pressure, and  $\text{Et}_2\text{O}$  (5 ml) was added. On standing for two days, dark red needles of **1**·MeCN were obtained in 75% yield. Compound **2** was prepared as dark red crystals in 84% yield by a procedure similar to that above, starting from  $\text{CuBr}$ . **1** and **2** are stable to oxygen and moisture and soluble in MeCN and  $\text{Me}_2\text{SO}$ .†

The X-ray analysis of **1**† revealed that the asymmetric unit consists of two crystallographically independent halves of  $[(\text{C}_5\text{Me}_5)\text{WS}_3]_2\text{Cu}_6(\text{NCS})_6]^{2-}$  dianions, two  $[\text{PPh}_4]^+$  cations, and one MeCN solvent molecule. The structure of one of the two cluster dianions of **1** is presented in Fig. 1, where an inversion centre resides at the centre of the molecule. The structure of the other cluster dianion is nearly the same as that shown in Fig. 1. Three  $\text{CuNCS}$  molecules are bound to a  $(\text{C}_5\text{Me}_5)\text{WS}_3$  fragment, forming a  $\text{WS}_3\text{Cu}_3$  incomplete cubane structure. Two such incomplete cubes are linked *via* interactions between the sulfur end of one NCS ligand in each cluster and

three coppers of the other cluster. Thus the NCS sulfur fills a void of the  $\text{WS}_3\text{Cu}_3$  incomplete cubane. The occurrence of triple bridging of the NCS sulfur is unprecedented, although double bridging was observed in the polymeric structures of  $[\text{Hpy}][\text{Cu}_2(\text{NCS})_3]$ <sup>11</sup> and  $[\text{NEt}_4]_3[\text{WS}_4\text{Cu}_4(\text{NCS})_5]$ .<sup>12</sup> The eight-membered  $\text{Cu}(1)\text{N}(1)\text{C}(11)\text{S}(4)\text{Cu}(1^*)\text{N}(1^*)\text{C}(11^*)\text{S}(4^*)$  ring is nearly planar. The  $(\text{C}_5\text{Me}_5)\text{WS}_3$  unit has a slightly distorted three-legged piano-stool structure, and the  $\text{S}_3$  plane is parallel (179°) to the  $\text{C}_5\text{Me}_5$  ring. The W–S bond lengths of 2.267(3)–2.290(3) Å fall between the W–S (thiolate) single bonds and W=S double bonds in  $[(\text{C}_5\text{Me}_5)\text{W}(\text{S})_2(\text{SCH}_2\text{Ph})]$  [2.328(4) *vs.* 2.149(3) Å] and  $[(\text{C}_5\text{Me}_5)\text{W}(\text{S})\{\text{SC}(\text{Ph})=\text{C}(\text{Ph})\text{S}\}]^-$  [2.326(2) Å *vs.* 2.186(2) Å].<sup>10</sup> The short W–Cu distances of 2.638(2)–2.682(2) Å suggest a dative interaction between  $d^0 \text{W}^{\text{VI}}$  and  $d^{10} \text{Cu}^{\text{I}}$ , which are comparable to those observed in  $[\text{NEt}_4]_3[\text{WS}_4\text{Cu}_4(\text{NCS})_5]$  [2.624(2)–2.708(2) Å]<sup>12</sup> and  $[\text{NEt}_4]_3[\text{WOS}_3(\text{CuBr})_3(\mu\text{-Br})]$  [2.665(3)–2.681(2) Å].<sup>13</sup> The coordination geometry at each copper atom is approximately trigonal planar, to which an NCS sulfur is weakly bound from the direction perpendicular to the plane. Thus the Cu–S(NCS) bond lengths of 2.742(4)–3.060(3) Å are significantly longer than the Cu–S(sulfide) distances of 2.214(4)–2.249(4) Å in the trigonal plane, and the Cu–S(NCS)–

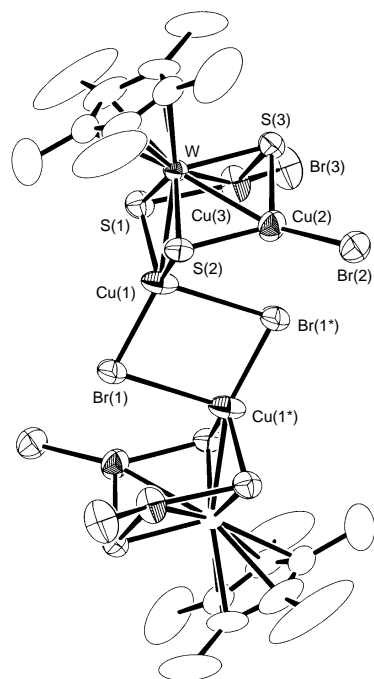


**Fig. 1** ORTEP drawing of one of the two cluster dianions of **1**, with labelling scheme and 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): W–Cu(1) 2.644(2), W–Cu(2) 2.668(2), W–Cu(3) 2.644(2), W–S(av.) 2.281(2), Cu–S(av.) 2.230(2), Cu–S(4\*) (av.) 2.952(4), Cu–N(av.) 1.88(3), S–W–S(av.) 105.8(1), S–Cu–S(av.) 109.3(1), S–Cu–S(4\*) (av.) 97.4(1), W–S–Cu(av.) 72.0(1), Cu–S(4\*)–Cu(av.) 65.7(1), S(4\*)–Cu(1)–N(1) 98.4(3), Cu(1)–N(1)–C(11) 168(1), N(1)–C(11)–S(4) 179(1).

Cu angles [61.83(1)–70.34(8)°] are acute compared with the other Cu–S–Cu angles [88.0(1)–95.2(1)°].

The crystal of **2**† consists of one discrete [(C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub>]<sub>2</sub>Cu<sub>6</sub>Br<sub>6</sub>]<sup>2-</sup> dianions and two [PPh<sub>4</sub>]<sup>+</sup> cations. The cluster dianion, shown in Fig. 2, is composed of two incomplete WS<sub>3</sub>Cu<sub>3</sub> cubes of [(C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub>Cu<sub>3</sub>Br<sub>3</sub>]<sup>-</sup>, which are interconnected by a four-membered CuBr<sub>2</sub>Cu ring. A crystallographic inversion centre is again located at the centre of the dianion. The main framework of the cluster dianion of **2** is similar to that of [NEt<sub>4</sub>]<sub>4</sub>[(MoOS<sub>3</sub>)<sub>2</sub>Cu<sub>6</sub>I<sub>6</sub>].<sup>14</sup> In the CuBr<sub>2</sub>Cu ring, the Cu(1)–Br(1\*) [or Cu(1\*)–Br(1)] bond distance of 2.876(1) Å is 0.52 Å longer than that of Cu(1)–Br(1) [or Cu(1\*)–Br(1\*)]. Therefore, the interaction between the two incomplete cubes in **2** is weak, as in the case of **1**. A notable difference between the structures of **1** and **2** is that Br(1) [or Br(1\*)] of **2** coordinates to one copper of the other incomplete cube while for **1** the terminal sulfur of NCS is bound to three coppers. As a consequence, there are two different types of copper geometries in the cluster dianion of **2**. Cu(2) and Cu(3) are trigonal planar, while Cu(1) adopts a distorted tetrahedral geometry. Owing to the different coordination environment, the W–Cu(1) distance of 2.676(8) Å is slightly longer than those of W–Cu(2) [2.657(8) Å] and W–Cu(3) [2.649(1) Å]. In each (C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub> unit, the S<sub>3</sub> plane is parallel (178°) to the C<sub>5</sub>Me<sub>5</sub> ring, and the three W–S distances of 2.280(2)–2.284(2) Å are very close to those of **1**.

The successful syntheses of **1** and **2** in high yields are interesting examples of how relatively complicated clusters can be formed by the self-assembly of two [PPh<sub>4</sub>][(C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub>] and six CuX (X = NCS, Br) components. As the linkage of two incomplete cubes is weak in either case, they may be cleaved easily in the presence of strong donor ligands such as PPh<sub>3</sub>, dppm and bipyridine. In fact, **2** reacts readily with PPh<sub>3</sub> in



**Fig. 2** ORTEP drawing of the cluster dianion of **2**, with labelling scheme and 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): W–Cu(1) 2.676(8), W–Cu(2) 2.657(1), W–Cu(3) 2.649(1), W–S(av.) 2.282(2), Cu–S(av.) 2.234(2), Cu–Br(av.) 2.308(1), Cu(1)–Br(1\*) 2.876(1); S–W–S(av.) 105.8(1), S–Cu–S(av.) 109.2(2), W–S–Cu(av.) 71.2(2), Cu(1)–Br(1)–Cu(1\*) 83.00(4), Br(1)–Cu(1)–Br(1\*) 97.00(4).

acetonitrile to give [(C<sub>5</sub>Me<sub>5</sub>)WS<sub>3</sub>Cu<sub>3</sub>Br<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>].<sup>15</sup> Details of their reactivity will be described elsewhere.

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## Footnotes

† Synthetic manipulations were carried out under an argon atmosphere. *Spectroscopic data for 1*: <sup>1</sup>H NMR (Me<sub>2</sub>SO, 500 MHz, 25 °C), δ 7.72–7.97 (PPh<sub>4</sub><sup>+</sup>, m, 40 H), 2.14 (C<sub>5</sub>Me<sub>5</sub>, s, 30 H). Anal. Calc. for C<sub>74</sub>H<sub>70</sub>Cu<sub>6</sub>N<sub>6</sub>P<sub>2</sub>S<sub>12</sub>W<sub>2</sub>: C, 39.69; H, 3.16; N, 3.75; S, 16.84. Found: C, 39.63; H, 3.11; N, 3.87; S, 16.51%. IR (Nujol mull, CsI): ν(W–S<sub>br</sub>) 470w, 455m, 410m cm<sup>-1</sup>. UV–VIS (MeCN) λ<sub>max</sub>/nm (10<sup>-3</sup> ε<sub>max</sub>/m<sup>-1</sup> cm<sup>-1</sup>): 472 (0.297), 445 (0.334), 329 (0.891). *For 2*: <sup>1</sup>H NMR (Me<sub>2</sub>SO, 500 MHz, 25 °C), δ 7.72–7.99 (PPh<sub>4</sub><sup>+</sup>, m, 40 H), 2.10 (C<sub>5</sub>Me<sub>5</sub>, s, 30 H). Anal. Calc. for C<sub>68</sub>H<sub>70</sub>Br<sub>6</sub>Cu<sub>6</sub>P<sub>2</sub>S<sub>6</sub>W<sub>2</sub>: C, 34.46; H, 2.98; S, 8.12. Found: C, 34.21; H, 2.95; S, 7.86%. IR (KBr pellet): ν(W–S<sub>br</sub>) 453m, 409m cm<sup>-1</sup>. UV–VIS (MeCN) λ<sub>max</sub>/nm (10<sup>-3</sup> ε<sub>max</sub>/m<sup>-1</sup> cm<sup>-1</sup>): 486 (0.156), 445 (0.152), 329 (0.621).

‡ *Crystal data for 1*·CH<sub>3</sub>CN: C<sub>76</sub>H<sub>73</sub>Cu<sub>6</sub>N<sub>7</sub>P<sub>2</sub>S<sub>12</sub>W<sub>2</sub>, *M* = 2280.10, triclinic, space group *P* $\bar{1}$ , *a* = 17.059(5), *b* = 26.508(7), *c* = 9.515(4) Å, α = 90.36, β = 91.98(3), γ = 87.53(2)°, *U* = 4295(2) Å<sup>3</sup>, *Z* = 2. Of 11384 reflections collected (Mo–Kα 2θ = 55.0°, 296 K) on a Rigaku AFC7R diffractometer; 11336 were unique and 6823 [*I* > 3.00σ(*I*)] were observed. The structure was solved by direct methods and expanded using Fourier techniques. All atoms except for the phenyl carbons and MeCN were refined anisotropically. H atoms were included but not refined. The final cycle of full-matrix least-squares refinement was converged with *R* = Σ(|*F*<sub>o</sub>| – |*F*<sub>c</sub>|)/Σ|*F*<sub>o</sub>| = 0.037 and *R*<sub>w</sub> = [Σw(|*F*<sub>o</sub>| – |*F*<sub>c</sub>|)<sup>2</sup>/Σw|*F*<sub>o</sub>|<sup>2</sup>]<sup>1/2</sup> = 0.038. *For 2*: C<sub>68</sub>H<sub>70</sub>Br<sub>6</sub>Cu<sub>6</sub>P<sub>2</sub>S<sub>6</sub>W<sub>2</sub>, *M* = 2370.00, monoclinic, space group *P*2<sub>1</sub>/*a*, *a* = 9.871(1), *b* = 27.789(5), *c* = 14.496(3) Å, β = 100.53(1)°, *U* = 3909(1) Å<sup>3</sup>, *Z* = 4. Of 9701 reflections collected (Mo–Kα 2θ = 55.0°, 296 K) on a Rigaku AFC7R diffractometer, 6134 [*I* > 3.00σ(*I*)] were observed. The structure was solved by direct methods and expanded using Fourier techniques. All the heavy atoms were refined anisotropically. H atoms were included but not refined. The final cycle of full-matrix least-squares refinement was converged with *R* = Σ(|*F*<sub>o</sub>| – |*F*<sub>c</sub>|)/Σ|*F*<sub>o</sub>| = 0.036 and *R*<sub>w</sub> = [Σw(|*F*<sub>o</sub>| – |*F*<sub>c</sub>|)<sup>2</sup>/Σw|*F*<sub>o</sub>|<sup>2</sup>]<sup>1/2</sup> = 0.040.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/349.

## References

- 1 F. A. Cotton, P. A. Kibala and W. J. Roth, *J. Am. Chem. Soc.*, 1988, **110**, 298.
- 2 J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.
- 3 A. Müller and C. Beugholt, *Nature*, 1996, **383**, 296.
- 4 V. A. Grillo, Z. Sun, K. Folting, D. N. Hendrickson and G. Christou, *Chem. Commun.*, 1996, 2233.
- 5 G. Christou, C. D. Garner, F. E. Mabbs and T. J. King, *J. Chem. Soc., Chem. Commun.*, 1978, 740.
- 6 T. E. Wolff, J. M. Berg, P. P. Power, K. O. Hodgson and R. H. Holm, *J. Am. Chem. Soc.*, 1979, **101**, 5454.
- 7 P. R. Challen, S. M. Koo, W. R. Dunham and D. Coucouvanis, *J. Am. Chem. Soc.*, 1990, **112**, 2455.
- 8 T. Shibahara, H. Akashi and H. Kuroya, *J. Am. Chem. Soc.*, 1988, **110**, 3313.
- 9 K. D. Demadis and D. Coucouvanis, *Inorg. Chem.*, 1995, **34**, 436.
- 10 H. Kawaguchi and K. Tatsumi, *J. Am. Chem. Soc.*, 1995, **117**, 3885.
- 11 C. L. Raston, B. Walter and A. H. White, *Aust. J. Chem.*, 1979, **32**, 2757.
- 12 J. M. Manoli, C. Potvin, F. Secheresse and S. Marzak, *Inorg. Chim. Acta*, 1988, **150**, 259.
- 13 Z. R. Chen, H. W. Hou, X. Q. Xin, K. B. Yu and S. Shi, *J. Phys. Chem.*, 1995, **99**, 8717.
- 14 H. W. Hou, D. L. Long, X. Q. Xin, X. X. Houng, B. S. Kang, P. Ge, W. Ji and S. Shi, *Inorg. Chem.*, 1996, **35**, 5363.
- 15 J. P. Lang and K. Tatsumi, to be published.

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