Two W/Cu/S clusters: tetraethyl-ammonium bromidodi-μ_2-sulfido-sulfido[tris(3,5-dimethylpyrazol-1-yl)-borato]copper(I)tungsten(VI) and tetraethylammonium dibromido-μ_3-sulfido-di-μ_2-sulfido-[tris(3,5-di-methylpyrazol-1-yl)borato]dicopper(I)-tungsten(VI)

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The reaction of $(Et_4N)[Tp*WS_3]$ [Tp* = hydrogen tris(3,5-dimethylpyrazol-1-yl)borate] with one or two equivalents of CuBr afforded the [1 + 1] and [1 + 2] addition products $(Et_4N)[Tp*WS(\mu\text{-}S)_2(CuBr)]$ {or $(C_8H_{20}N)[CuWBr(C_{15}H_{22}BN_6)S_3]$, (I)} and $(Et_4N)[Tp*W(\mu_3\text{-}S)(\mu\text{-}S)_2(CuBr)_2]$ {or $(C_8H_{20}N)[Cu_2WBr_2(C_{15}H_{22}BN_6)S_3]$, (II)}. The anion of (I) contains a $[W(\mu\text{-}S)_2Cu]$ core formed by the addition of one CuBr unit to the $[Tp*WS_3]$ species. The anion of (II) has a butterfly-shaped $[W(\mu_3\text{-}S)(\mu\text{-}S)_2Cu_2]$ core formed by the addition of two CuBr units to the $[Tp*WS_3]$ species. The $[Tp*WS_3]$ sections of each complex exhibit approximate C_{3v} point symmetry and have closely comparable geometry. In (II), both the anion and cation lie on a crystallographic mirror plane. The structure of (I) is noncentrosymmetric and polar.
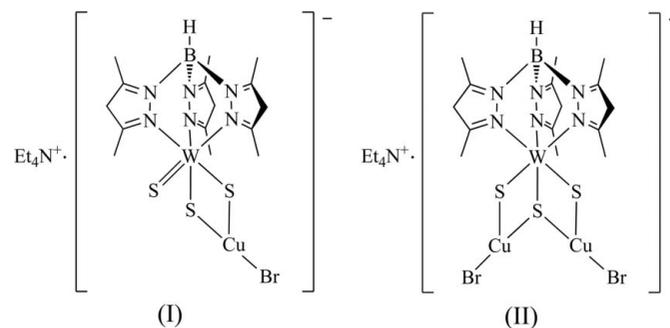
Comment

In the past decades, the chemistry of Mo(W)/Cu/S clusters derived from reactions of metal sulfide synthons such as $[MO_xS_{4-x}]^{2-}$ or $[Cp*MS_3]^-$ (M = Mo or W, x = 0–3, Cp* = pentamethylcyclopentadienyl) with CuX (X = Cl, Br, I, NCS, CN) has been investigated extensively because of their novel structures (Chisholm et al., 2002; Parkin, 2004; Zulys et al., 2005) and their potential applications in biological systems (Lewinski et al., 2006) and opto-electronic materials (Vahrenkamp, 1999). Among these Mo(W)/Cu/S clusters, a complete series of products obtained by the stepwise addition of CuX has not previously been realized in a system involving the same components CuX and $[MS_4]^{2-}$ or $[EMS_3]^{n-}$ (E = O, n = 2 or E = Cp*, n = 1) in different molar ratios (Bunge et al.,

2007; Boomishankar et al., 2006; Malik et al., 1997; Kaupp et al., 1991). Recently, we have investigated the preparation of Mo(W)/Cu/S clusters from the precursor $(Et_4N)[Tp*WS_3]$, where Tp* = hydrogen tris(3,5-dimethylpyrazol-1-yl)borate (Seino et al., 2001), and this compound has been found to undergo stepwise addition reactions with one to four equivalents of CuNCS to yield the products $[Tp*WS_3(CuNCS)_n]^-$ (n = 1 or 2), $[Tp*WS_3(CuNCS)_3Br]^{2-}$ and the polymeric $\{Tp*WS_3(CuNCS)_4\}^-$ (Wei, Li, Ren et al., 2009). In a continuation of our work in this area, we treated the precursor $(Et_4N)[Tp*WS_3]$ with one to three equivalents of CuBr in a stepwise manner (Scheme 1 shows the stepwise addition of Cu^+ to the WS_3 core to construct a cubane-like unit) and

Scheme 1

obtained the [1 + 1], [1 + 2] and [1 + 3] products, (Et_4N)-$[Tp*WS(\mu\text{-}S)_2(CuBr)]$, $(Et_4N)[Tp*W(\mu_3\text{-}S)(\mu\text{-}S)_2(CuBr)_2]$ and $(Et_4N)[Tp*W(\mu_3\text{-}S)_3(CuBr)_3]$. We have reported the crystal structure of the [1 + 3] product previously (Wei, Li, Cheng et al., 2009). We report herein he crystal structures of the [1 + 1] and [1 + 2] complexes, (I) and (II).

Scheme 2

The anion of complex (I) comprises a $[Tp*WS_3]^-$ unit and one CuBr group, with a pair of μ-S atoms forming a WS_2Cu ring (Fig. 1). One terminal S atom is retained. The structure closely resembles that of the anion in the related compound $(Et_4N)[Tp*WS(\mu\text{-}S)_2(CuNCS)]$ (Wei, Li, Ren et al., 2009). It is noteworthy that the comparable [1 + 1] addition complex is not known among the M/Cu/S clusters based on the related precursor $[PPh_3][Cp*MS_3]$, while for the $(Et_4N)[OMS_3]$

metal-organic compounds

Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary size.
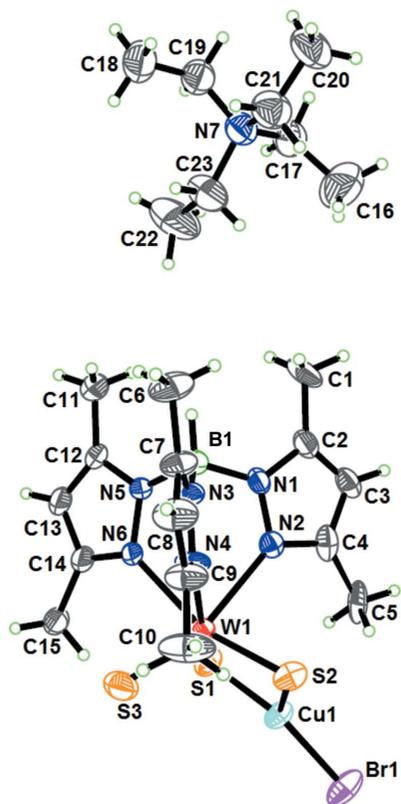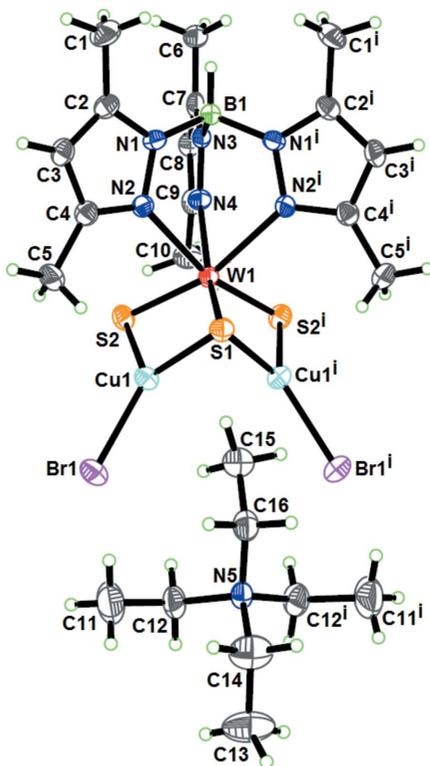

Figure 2
The molecular structure of (II), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary size. Methyl H atoms on C6, C10, C13 and C15 are disordered over the mirror plane. [Symmetry code: (i) $x, -y + \frac{3}{2}, z$.]
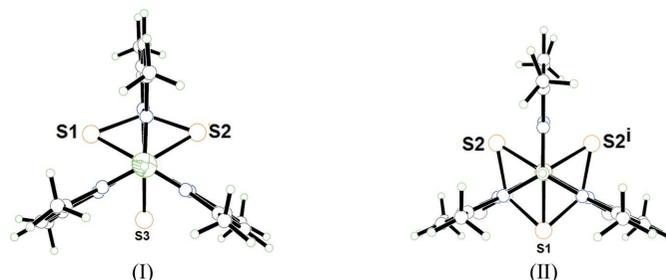

Figure 3
A view of the anions in (I) and (II) along the approximate threefold axis of the Tp* group. [Symmetry code: (i) $x, -y + \frac{3}{2}, z$.]

precursor, reactions with one equivalent of CuCl and CuCN have been reported to yield the products [Me$_4$N][WOS(μ-S)$_2$(CuCl)] (Shamsur Rahman et al., 2000) and (Et$_4$N)-[MoOS(μ-S)$_2$(CuCN)] (Zhang et al., 2008), respectively. In (I), atom Cu1 adopts a trigonal planar geometry, coordinated by one terminal Br atom and two μ-S atoms. The W1···Cu1 distance of 2.5893 (11) Å is slightly shorter than those in other butterfly-shaped or incomplete cubane core clusters. The terminal W1—S3 bond length of 2.141 (3) Å is similar to that in [WS$_4$Cu$_2$(dppm)$_3$] [2.146 (4) Å; dppm = bis(diphenylphosphino)methane; Lang & Tatsumi, 1998], but slightly shorter than those in the corresponding precursor (Et$_4$N)[Tp*WS$_3$] (mean 2.193 Å; Seino et al., 2001) and in the cluster (Et$_4$N)[Tp*WS(μ-S)$_2$(CuNCS)] [2.154 (3) Å; Wei, Li, Ren et al., 2009]. The mean W—μ-S (2.268 Å), Cu—μ-S (2.193 Å) and Cu—Br [2.2831 (14) Å] bond lengths are slightly longer than the corresponding values in the complex (Et$_4$N)[Tp*WS(μ_3-S)$_3$(CuBr)$_3$] (Wei, Li, Cheng et al., 2009).

The anion of complex (II) has a butterfly-shaped [WS$_3$Cu$_2$] structure in which one [Tp*WS$_3$] unit and two CuBr groups are linked via one μ_3-S and two μ-S atoms (Fig. 2). Atoms W1, S1, B1, N3, N4 and C6—C10 lie on a crystallographic mirror plane. Similar butterfly-shaped [WS$_3$Cu$_2$] cores have been observed in (Et$_4$N)[Tp*WS$_3$(CuNCS)$_2$] (Wei, Li, Ren et al., 2009), (PPh$_4$)[(Cp*WS$_3$(CuCN)$_2$] (Lang et al., 2004) and [MOS$_3$M'$_2$(PPh$_3$)$_3$] (M = W, Mo; M' = Cu, Ag) (Müller et al., 1983). Each Cu atom in (II) adopts a trigonal planar geometry, coordinated by one μ-S atom, one μ_3-S atom and one terminal Br atom. The W···Cu distance of 2.6239 (10) Å is longer than that in complex (I), but similar to those found in other complexes containing three-coordinated Cu, such as (Et$_4$N)[Tp*WS(μ_3-S)$_3$(CuBr)$_3$] [2.6404 (2) Å; Wei, Li, Cheng et al., 2009] and (PPh$_4$)[Cp*WS$_3$(CuCN)$_2$] [2.666 (3) Å; Lang et al., 2004]. Because of the coordination of the S atoms to the Cu atoms, the W1—S1 bond length of 2.331 (2) Å is longer than the W1—S2 bond length of 2.2293 (18) Å, and both bonds are elongated relative to the mean W—S bond length (2.193 Å) in the precursor (Et$_4$N)[Tp*WS$_3$] (Seino et al., 2001).

Fig. 3 illustrates how the S and Cu^I centres of (I) and (II) build up sequentially towards the corners of a cubane-like unit. Firstly, one Cu^I centre is added to the Tp*WS$_3$ unit to construct the [Tp*WS(μ-S)$_2$Cu] core with one terminal S atom remaining. Secondly, the two Cu^I centres in (II) form the
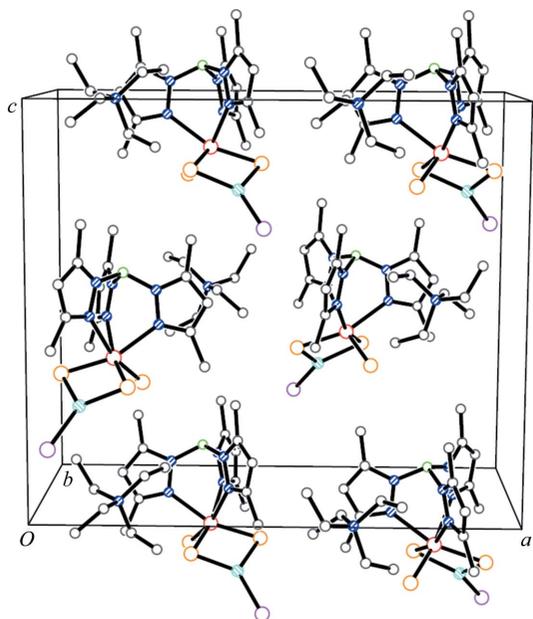
Figure 4
A packing diagram of (I), viewed along the *b* axis, showing the noncentrosymmetric and polar arrangement. H atoms have been omitted.

butterfly core [Tp*W(μ-S)$_2$(μ_3-S)Cu$_2$]. A third Cu^I centre can then be added to the butterfly core of (II) to produce an incomplete cubane-like unit, [Tp*W(μ_3-S)$_3$Cu$_3$], as in the previously published structure (Et$_4$N)[Tp*W(μ_3-S)$_3$(CuBr)$_3$] (Wei, Li, Cheng *et al.*, 2009). Throughout this sequence, the geometry of the [Tp*WS$_3$] unit remains essentially unchanged: the r.m.s. deviations for overlay of the 26 non-H atoms in the core onto the precursor [Tp*WS$_3$] are 0.14, 0.10 and 0.30 Å for (I), (II) and (Et$_4$N)[Tp*W(μ_3-S)$_3$(CuBr)$_3$], respectively. The [Tp*WS$_3$] unit exhibits approximate C_{3v} point symmetry and one of the mirror planes is retained as a crystallographic symmetry element in (II).

Packing diagrams are shown for (I) and (II) in Figs. 4 and 5, respectively. The structures contain comparable stacks of alternating complexes and Et$_4$N$^+$ cations running along the *b* axes. In (I), these stacks are arranged so that the Cu—Br bonds point towards the same direction along the *c* axis, forming a noncentrosymmetric and polar structure. In (II), the stacks are arranged in a centrosymmetric manner.
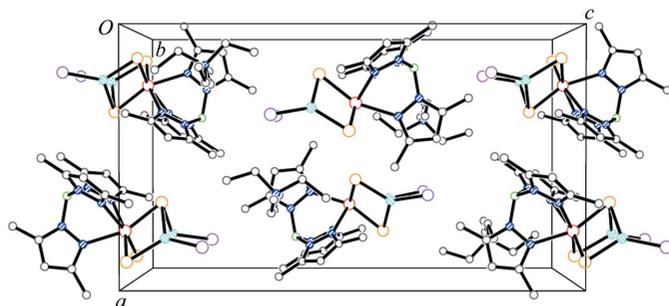
Experimental

All manipulations were performed under an argon atmosphere using standard Schlenk-line techniques. The precursor (Et$_4$N)[Tp*WS$_3$] was prepared as reported previously (Seino *et al.*, 2001). For these reactions, CHCl$_3$ is a better solvent than MeCN because CuBr is poorly soluble in CHCl$_3$ and it can facilitate the stepwise introduction of CuBr into [Tp*WS$_3$]$^-$. Compound (I) is air sensitive and easily oxidized in solution to form (Et$_4$N)[Tp*WO(μ-S)$_2$(CuBr)]. Complex (II) is relatively air and moisture stable in the solid state.

For the synthesis of (I), CuBr (14.4 mg, 0.1 mmol) was added to a solution of (Et$_4$N)[Tp*WS$_3$] (75 mg, 0.1 mmol) in CHCl$_3$ (15 ml). After being stirred for half an hour, the resulting red solution was filtered and Et$_2$O (30 ml) was carefully layered onto the surface of the filtrate. After 4 d, red prisms of (I) were collected by filtration, washed with Et$_2$O and dried *in vacuo* {yield 72.3 mg, 80% based on (Et$_4$N)[Tp*WS$_3$]}. Analysis calculated: C 32.46, H 4.98, N 11.52%; found C 32.32, H 4.55, N 11.95%. IR (KBr disc, cm^{-1}): 2978 (*m*), 2920 (*m*), 2554 (*w*), 1628 (*w*), 1546 (*s*), 1440 (*s*), 1435 (*s*), 1418 (*s*), 1035 (*m*), 860 (*w*), 806 (*w*), 691 (*w*), 651 (*w*), 459 (*m*), 416 (*w*). UV–visible {MeCN, λ_{max} [nm (ε M^{-1} cm^{-1})]}: 333 (14300), 445 (6400), 524 (3000). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.36–1.40 (*t*, 12H, CH$_2$CH$_3$), 2.37 (*s*, 9H, CH$_3$ in Tp*), 2.95 (*s*, 9H, CH$_3$ in Tp*), 3.33–3.39 (*q*, 8H, CH$_2$CH$_3$), 5.94 (*s*, 3H, CH in Tp*), the B—H proton was not identified.

For the synthesis of (II), CuBr (28.8 mg, 0.2 mmol) was added to a solution of (Et$_4$N)[Tp*WS$_3$] (75 mg, 0.1 mmol) in CHCl$_3$ (15 ml). A procedure identical to that used for (I) afforded dark red blocks of (II) {yield 93 mg, 85% based on (Et$_4$N)[Tp*WS$_3$]}. Analysis calculated: C 27.78, H 4.26, N 9.86%; found: C 27.32; H 4.55; N 9.95%. IR (KBr disc, cm^{-1}): 2979 (*m*), 2921 (*m*), 2554 (*w*), 1628 (*w*), 1546 (*s*), 1440 (*s*), 1435 (*s*), 1418 (*s*), 1035 (*m*), 860 (*w*), 806 (*w*), 693 (*w*), 651 (*w*), 469 (*w*), 420 (*w*). UV–visible {MeCN, λ_{max} [nm (ε M^{-1} cm^{-1})]}: 323 (16300), 420 (8890), 544 (5800). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.36–1.40 (*t*, 12H, CH$_2$CH$_3$), 2.37 (*s*, 9H, CH$_3$ in Tp*), 2.96 (*s*, 9H, CH$_3$ in Tp*), 3.31–3.38 (*q*, 8H, CH$_2$CH$_3$), 5.92 (*s*, 3H, CH in Tp*), the B—H proton was not identified.

Compound (I)

Crystal data

(C$_8$H$_{20}$N)[CuWBr(C$_{15}$H$_{22}$BN$_6$)S$_3$]	$V = 3196.6$ (11) Å^3
$M_r = 850.95$	$Z = 4$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 19.058$ (4) Å	$\mu = 5.73$ mm^{-1}
$b = 10.276$ (2) Å	$T = 293$ K
$c = 16.323$ (3) Å	$0.35 \times 0.30 \times 0.25$ mm

Data collection

Rigaku Mercury CCD diffractometer	29584 measured reflections
Absorption correction: multi-scan (Jacobson, 1998)	5857 independent reflections
$T_{min} = 0.147$, $T_{max} = 0.239$	5342 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	$\Delta\rho_{max} = 1.05$ e Å^{-3}
$wR(F^2) = 0.084$	$\Delta\rho_{min} = -0.59$ e Å^{-3}
$S = 1.10$	Absolute structure: Flack (1983),
5710 reflections	2678 Friedel pairs
344 parameters	Flack parameter: 0.004 (10)
84 restraints	
H-atom parameters constrained	

Figure 5
A packing diagram of (II), viewed along the *b* axis, showing the centrosymmetric arrangement. H atoms have been omitted.

metal-organic compounds

Compound (II)

Crystal data

Data collection

Refinement

H atoms were placed geometrically and constrained to ride on their parent atoms, with B—H = 0.98 Å and C—H = 0.96 (methyl), 0.97 (methylene) or 0.93 Å (aromatic), and with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms or 1.2U_{eq}(C) otherwise. In (I), extensive rigid-bond and similarity restraints were applied to the displacement parameters of atoms C4, C5, C9, C10, N7 and C16—C23. In (II), the methyl H atoms on C6 and C10 (in the pyrazole ring) and on C13 and C15 (in the Et$_4$N$^+$ cation) are disordered over the mirror plane.

For both compounds, data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

References

Boomishankar, R., Richards, P. I. & Steiner, A. (2006). *Angew. Chem. Int. Ed.* **45**, 4632–4634.

Bunge, S. D., Lance, J. M. & Bertke, J. A. (2007). *Organometallics*, **26**, 6320–6328.

Chisholm, M. H., Gallucci, J. & Phomphrai, K. (2002). *Inorg. Chem.* **41**, 2785–2794.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Jacobson, R. (1998). Private communication to Rigaku Corporation, Tokyo, Japan.

Kaupp, M., Stoll, H., Preuss, H., Kaim, W., Stahl, T., Van Koten, G., Wissing, E., Smeets, W. J. J. & Spek, A. L. (1991). *J. Am. Chem. Soc.* **113**, 5606–5618.

Lang, J. P. & Tatsumi, K. (1998). *Inorg. Chem.* **37**, 6308–6316.

Lang, J. P., Xu, Q. F., Ji, W., Elim, H. I. & Tatsumi, K. (2004). *Eur. J. Inorg. Chem.* pp. 86–91.

Lewinski, J., Sliwinski, W., Dranka, M., Justyyniak, I. & Lipkowski, J. (2006). *Angew. Chem. Int. Ed.* **45**, 4826–4829.

Malik, M. A., O'Brien, P., Motevalli, M. & Jones, A. C. (1997). *Inorg. Chem.* **36**, 5076–5081.

Müller, A., Schimanski, U. & Schimanski, J. (1983). *Inorg. Chim. Acta*, **76**, 245–246.

Parkin, G. (2004). *Chem. Rev.* **104**, 699–767.

Rigaku (2001). *CrystalClear* and *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.

Seino, H., Arai, Y., Iwata, N., Nagao, S., Mizobe, Y. & Hidai, M. (2001). *Inorg. Chem.* **40**, 1677–1682.

Shamsur Rahman, A. B. M., Boller, H. & Klepp, O. K. (2000). *Inorg. Chim. Acta*, **305**, 91–94.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Vahrenkamp, H. (1999). *Acc. Chem. Res.* **32**, 589–596.

Wei, Z. H., Li, H. X., Cheng, M. L., Tang, X. Y., Zhang, Y. & Lang, J. P. (2009). *Inorg. Chem.* **48**, 2808–2817.

Wei, Z. H., Li, H. X., Ren, Z. G., Lang, J. P., Zhang, Y. & Sun, Z. R. (2009). *Dalton Trans.* pp. 3425–3433.

Zhang, W. H., Song, Y. L., Zhang, Y. & Lang, J. P. (2008). *Cryst. Growth Des.* **8**, 253–258.

Zulys, A., Dochnahl, M., Hollmann, D., Lohnwitz, K., Herrmann, J.-S., Roesky, P. W. & Blechert, S. (2005). *Angew. Chem. Int. Ed.* **44**, 7794–7798.