

Bis(acetonitrile- κN)bis[hydrido-tris(3,5-dimethylpyrazol-1-yl)- κN^2]-borato]di- μ_3 -sulfido-tetra- μ_2 -sulfido-di- μ_2 -thiocyanato- $\kappa^2 N:S$; $\kappa^2 S:N$ -tetra-copper(I)ditungsten(VI)

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Received 6 May 2011

Accepted 9 June 2011

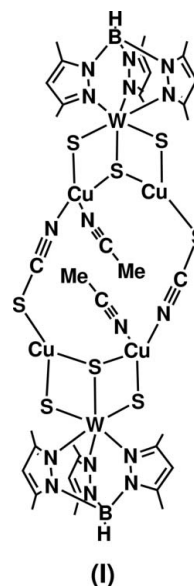
Online 23 June 2011

Reactions of $(Et_4N)[Tp^*WS_3]$ [Tp^* is hydridotris(3,5-dimethylpyrazol-1-yl)borate] with $CuSCN$ in MeCN in the presence of melamine afforded the title neutral dimeric cluster $[Cu_4W_2(C_{15}H_{22}BN_6)_2(NCS)_2S_6(C_2H_3N)_2]$ or $[Tp^*W(\mu_2-S)_2(\mu_3-S)Cu(\mu_2-SCN)(CuMeCN)]_2$, which has two butterfly-shaped $[Tp^*WS_3Cu_2]$ cores bridged across a centre of inversion by two $(CuSCN)^-$ anions. The S atoms of the bridging thiocyanate ligands interact with the H atoms of the methyl groups of the Tp^* units of a neighbouring dimer to form a $C-H \cdots S$ hydrogen-bonded chain. The N atoms of the thiocyanate anions interact with the H atoms of the methyl groups of the Tp^* units of neighbouring chains, affording a two-dimensional hydrogen-bonded network.

Comment

In recent years, the chemistry of the Mo/W/Cu/S clusters derived from reactions of metal sulfide synthons [e.g. $[MS_4]^{2-}$ ($M = Mo, W$) (Müller *et al.*, 1981, 1989; Howard *et al.*, 1986; Holm *et al.*, 1995; Ansari *et al.*, 1990; Hou *et al.*, 1996; Wu *et al.*, 2004; Niu *et al.*, 2004; Zhang, Song & Wang, 2007); $[Cp^*MS_3]^-$ (Cp^* is pentamethylcyclopentadienyl; $M = Mo, W$) (Kawaguchi *et al.*, 1995, 1997; Lang, Kawaguchi, Ohnishi *et al.*, 1997; Lang, Kawaguchi & Tatsumi, 1997; Lang *et al.*, 1998, 1999, 2003; Xu *et al.*, 2006; Zhang, Song, Ren *et al.*, 2007); $[Tp^*MS_3]^-$ [Tp^* is hydridotris(3,5-dimethylpyrazol-1-yl)borate; $M = Mo, W$] (Seino *et al.*, 2001, 2003; Wang *et al.*, 2007; Wei *et al.*, 2009)] with CuX ($X = Cl, Br, I, SCN, CN$) has been extensively investigated because of their structural variety, their potential applications in biological systems (Chan *et al.*, 1995; Che *et al.*, 2001; Eldredge *et al.*, 1990; Stiefel *et al.*, 1993, 1996; George *et al.*, 2000, 2003; Dobbek *et al.*, 2002; Ginda *et al.*, 2003)

and as opto-electronic materials (Shi *et al.*, 1994, 1998; Zheng *et al.*, 1997; Zhang *et al.*, 2000; Che *et al.*, 2001; Coe *et al.*, 2004). Currently we are interested in using $(Et_4N)[Tp^*WS_3]$ (Seino *et al.*, 2001, 2003) for the construction of new W/Cu/S clusters because this synthon can generate more soluble W/Cu/S cluster precursors and some resulting clusters were found to be topologically unique in the chemistry of the tetrathiometalates and showed relatively good third-order nonlinear optical performances in solution. In our previous studies, stepwise addition reactions between $(Et_4N)[Tp^*WS_3]$ and $CuSCN$ have been completed in systems with different molar ratios, which led to the formation of the [1 + 1], [1 + 2], [1 + 3] and [1 + 4] addition products (Wei *et al.*, 2009). As an extension of this study, we carried out reactions of $(Et_4N)[Tp^*WS_3]$ with $CuSCN$ in the presence of melamine (MA), from which a hexanuclear W/Cu/S cluster, $[Tp^*W(\mu_2-S)_2(\mu_3-S)Cu(\mu_2-SCN)(CuMeCN)]_2$, (I), was isolated and whose crystal structure is reported here.



The asymmetric unit of (I) contains half of a $[Tp^*W(\mu_2-S)_2(\mu_3-S)Cu(\mu_2-SCN)(CuMeCN)]_2$ molecule, with the molecule containing two $[Tp^*W(\mu_2-S)_2(\mu_3-S)Cu(CuMeCN)]^+$ fragments linked *via* a pair of NCS bridges (Fig. 1). A crystallographic centre of inversion is located at the middle of the $W1 \cdots W1^i$ line [symmetry code: (i) $-x, -y, -z$]. The double butterfly-shaped hexanuclear structure of (I) is unprecedented in Mo(W)/Cu/S cluster chemistry. Each fragment may be viewed as a butterfly-shaped $[Tp^*WS_3Cu_2]$ core, which is similar to those found in $[Tp^*W(\mu_3-S)(\mu-S)_2Cu_2(MeCN)(\mu-CN)]_\infty$ (Wang *et al.*, 2007) and $(Et_4N)[Tp^*W(\mu-S)_3(CuNCS)_2] \cdot ClCH_2CH_2Cl$. The two Cu atoms in each fragment are not equivalent. Cu1 is coordinated by one N atom of the terminal MeCN molecule, two sulfide S atoms and one N atom of the thiocyanate anion, forming a tetrahedral coordination geometry. Cu2 is coordinated by two sulfide S atoms and one S atom of the thiocyanate anion, forming an approximately trigonal-planar geometry. Because of the different coordination geometries of the Cu atoms, the $W \cdots Cu$ separations are

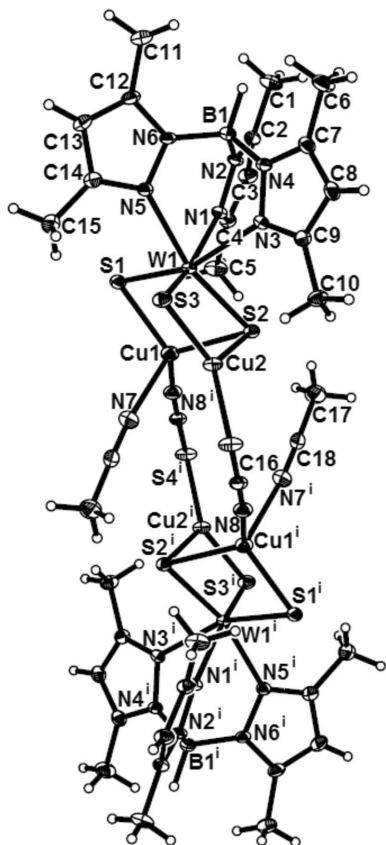


Figure 1
View of the molecular structure of the title cluster, (I), with ellipsoids drawn at the 30% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry code: (i) $-x + 1, -y, -z + 1$.]

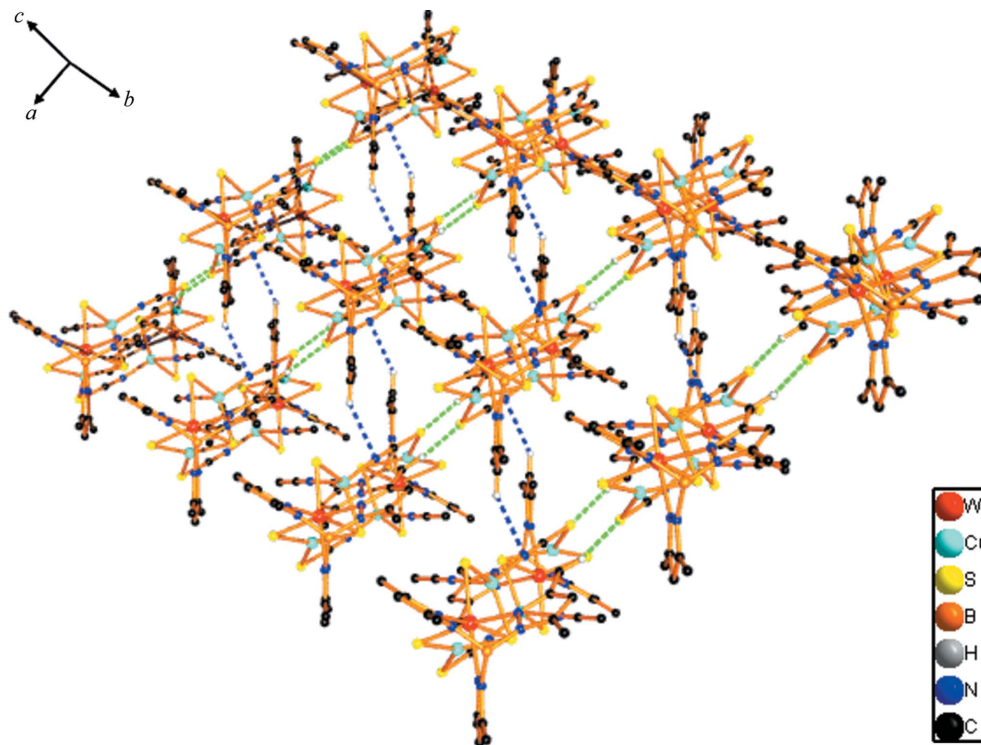


Figure 2
View of the two-dimensional network of title clusters. Dashed lines indicate $C5-H5B \cdots S4(x - 1, y, z)$ and $C8-H8 \cdots N8(-x + 2, -y + 1, -z + 1)$ interactions (green and blue, respectively, in the electronic version of the paper) and their symmetry-related counterparts.

different. The $W1 \cdots Cu1$ distance involving the tetrahedrally coordinated Cu atom [2.6354 (9) Å; Table 1] is shorter than the corresponding distances in $[Tp^*W(\mu_3-S)(\mu-S)_2Cu_2(MeCN)(\mu-CN)]_\infty$ [2.6560 (9) Å] and $(Et_4N)[Tp^*W(\mu-S)_3(CuNCS)_2] \cdot ClCH_2CH_2Cl$ [2.6404 (11) Å] (Wei *et al.*, 2009). The tetrahedrally coordinated $W1 \cdots Cu1$ [2.6737 (14) Å] contact is longer than the corresponding contacts in $[Tp^*W(\mu_3-S)(\mu-S)_2Cu_2(MeCN)(\mu-CN)]_\infty$ [2.6694 (10) Å]. The Cu—S bond lengths also reflect the different coordination modes of the Cu atoms [an average of 2.2086 (14) Å for a trigonal geometry and an average of 2.2475 (14) Å for a tetrahedral environment]. The Cu—N(NCS) bond length [1.931 (4) Å] is almost the same as those of the copper(I) complexes containing bridging thiocyanates and coordinated MeCN in $[Tp^*W(\mu_3-S)(\mu-S)_2Cu_2(MeCN)(\mu-CN)]_\infty$ [1.930 (7) Å]. The Cu—N(MeCN) bond length [2.213 (5) Å] is shorter than those of $[Tp^*W(\mu_3-S)(\mu-S)_2Cu_2(MeCN)(\mu-CN)]_\infty$ [2.425 (7) Å]. It should be noted that the $Cu1-\mu_3-S2-Cu2$ angle [78.26 (5)°] is 17.7° smaller than that in the cationic cluster $(PPh_4)[Cp^*WS_3(CuCN)_2]$ (Lang *et al.*, 2004) and slightly smaller than that in $[Tp^*W(\mu_3-S)(\mu-S)_2Cu_2(MeCN)(\mu-CN)]_\infty$ [79.68 (6)°].

The S atoms of each cluster core in (I) interact with the H atoms of the methyl groups of the Tp^* units to form four intramolecular C—H \cdots S contacts ($C5 \cdots S2$, $C5 \cdots S1$, $C10 \cdots S2$ and $C15 \cdots S1$; Table 2). The S atoms of the bridging thiocyanate anion interact with the H atoms of the methyl groups of the Tp^* units of a neighbouring dimer to form one intermolecular hydrogen bond [$C5 \cdots S4(x - 1, y, z)$], forming a C—H \cdots S hydrogen-bonded chain. The N atoms of the thiocyanate anion interact with the H atoms of the methyl groups

of the Tp^* units of neighbouring chains to form one intermolecular contact $[\text{C}8 \cdots \text{N}8(-x + 2, -y + 1, -z + 1)]$. Together these interactions afford a two-dimensional hydrogen-bonded network extended along the ab plane (Fig. 2).

Experimental

To a red solution containing $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}_3]$ (19 mg, 0.025 mmol) in MeCN (5 ml) was added CuNCS (6 mg, 0.050 mmol) and excess melamine. The resulting mixture was stirred for 5 min to form a dark-red solution and filtered. Diethyl ether (20 ml) was carefully layered onto the filtrate to form black block-shaped crystals, which were collected by filtration, washed with Et_2O and dried *in vacuo* (yield: 15 mg, 75% based on W). Analysis calculated for $\text{C}_{36}\text{H}_{50}\text{B}_2\text{Cu}_4\text{N}_{16}\text{S}_8\text{W}_2$: C 26.91, H 3.14, N 13.95%; found: C 23.78, H 3.25, N 13.82%. IR (KBr disc): 2564 (*w*), 2122 (*s*), 2062 (*m*), 2090 (*s*), 1631 (*w*), 1546 (*m*), 1451 (*m*), 1439 (*m*), 1414 (*m*), 1347 (*m*), 1221 (*m*), 1072 (*w*), 1034 (*w*), 860 (*w*), 822 (*w*), 798 (*w*), 691 (*w*), 650 (*w*), 479 (*w*), 418 (*w*) cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ 2.04 (*s*, 6H, CH_3CN), 2.33 (*s*, 18H, CH_3 in Tp^*), 2.72 (*s*, 18H, CH_3 in Tp^*), 6.08 (*s*, 6H, CH in Tp^*). The B–H proton was not located.

Crystal data

$[\text{Cu}_4\text{W}_2(\text{C}_{15}\text{H}_{22}\text{BN}_6)_2(\text{NCS})_2\text{S}_6 \cdot (\text{C}_2\text{H}_3\text{N})_2]$	$\beta = 93.73$ (3°)
$M_r = 1606.88$	$\gamma = 112.33$ (3°)
Triclinic, $P\bar{1}$	$V = 1330.3$ (5) \AA^3
$a = 9.3349$ (19) \AA	$Z = 1$
$b = 9.954$ (2) \AA	Mo $K\alpha$ radiation
$c = 15.547$ (3) \AA	$\mu = 6.24$ mm^{-1}
$\alpha = 92.21$ (3°)	$T = 223$ K
	$0.17 \times 0.15 \times 0.12$ mm

Data collection

Rigaku Mercury diffractometer	5976 independent reflections
Absorption correction: multi-scan (<i>REQAB</i> ; Jacobson, 1998)	5024 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.417$, $T_{\max} = 0.522$	$R_{\text{int}} = 0.035$
12835 measured reflections	Standard reflections: 0

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.072$	
$S = 1.02$	
5976 reflections	$\Delta\rho_{\max} = 0.96$ e \AA^{-3}
318 parameters	$\Delta\rho_{\min} = -1.14$ e \AA^{-3}

All H atoms were placed in geometrically idealized positions (C–H = 0.98 \AA for methyl groups, C–H = 0.99 \AA for methylene groups and C–H = 0.95 \AA for phenyl groups) and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for phenyl groups and $1.5U_{\text{eq}}(\text{C})$ for methyl groups. The H atom of the BH group was located in a difference Fourier map and its positional and isotropic displacement parameters were refined freely.

Data collection: *CrystalClear* (Rigaku/MS, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors thank the NNSF of China (grant Nos. 20871088, 20901054 and 90922018), the Nature Science Key Basic

Table 1

Selected geometric parameters (\AA , $^\circ$).

W1–S1	2.2250 (15)	Cu1–S1	2.2356 (13)
W1–S3	2.2414 (13)	Cu1–S2	2.2594 (16)
W1–S2	2.3274 (12)	Cu2–S3	2.1870 (14)
W1–Cu2	2.6354 (9)	Cu2–S2	2.2185 (14)
W1–Cu1	2.6737 (14)	Cu2–S4	2.2202 (14)
Cu1–N7	2.213 (5)	N8–Cu1 ⁱ	1.931 (4)
S1–W1–S3	103.79 (5)	N7–Cu1–S1	105.52 (13)
S1–W1–S2	104.38 (6)	N8 ⁱ –Cu1–S2	113.49 (13)
S3–W1–S2	104.49 (5)	N7–Cu1–S2	115.02 (14)
N8 ⁱ –Cu1–N7	92.82 (19)	S1–Cu1–S2	106.31 (6)
N8 ⁱ –Cu1–S1	123.14 (14)		

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
C5–H5B \cdots S4 ⁱⁱ	0.97	2.85	3.518 (5)	127
C8–H8 \cdots N8 ⁱⁱⁱ	0.94	2.60	3.456 (7)	152
C5–H5A \cdots S2	0.97	2.84	3.491 (6)	125
C5–H5C \cdots S1	0.97	2.80	3.510 (6)	131
C10–H10C \cdots S2	0.97	2.86	3.415 (6)	117
C15–H15A \cdots S1	0.97	2.63	3.415 (6)	138

Symmetry codes: (ii) $x - 1, y, z$; (iii) $-x + 2, -y + 1, -z + 1$.

Research of Jiangsu Province for Higher Education (grant No. 09 K J A150002), the Specialized Research Fund for the Doctoral Program of Higher Education of the Ministry of Education (grant No. 20093201110017), the Qin-Lan and the ‘333’ Projects of Jiangsu Province, and the ‘Soochow Scholar’ Program and the Program for Innovative Research Team of Soochow University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: YF3004). Services for accessing these data are described at the back of the journal.

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