

## Bis(2,2'-bipyridine)iodo(oxo)tri- $\mu_3$ -sulfido-tricopper(I)tungsten(VI)

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Received 18 January 2006

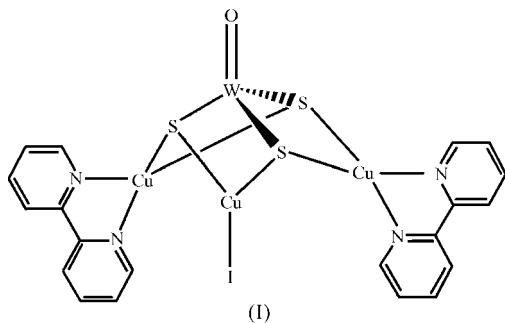
Accepted 1 March 2006

Online 31 March 2006

The title nest-shaped cluster,  $[\text{Cu}_3\text{WIOS}_3(\text{C}_{10}\text{H}_8\text{N}_2)_2]$ , has been synthesized by the reaction of  $(\text{NH}_4)_2[\text{WOS}_3]$ , CuI and 2,2'-bipyridine (bipy) in dimethylformamide under a purified nitrogen atmosphere. The cluster has a neutral skeleton containing the bipy ligands, and the central W atom is tetrahedrally coordinated by three S atoms and one O atom. The three Cu atoms are divided into two different kinds. Two Cu atoms adopt distorted tetrahedral geometry, with each Cu atom coordinated by two S atoms and the two N atoms of a bipy ligand. The other Cu atom adopts a trigonal mode surrounded by two S atoms and one I atom.

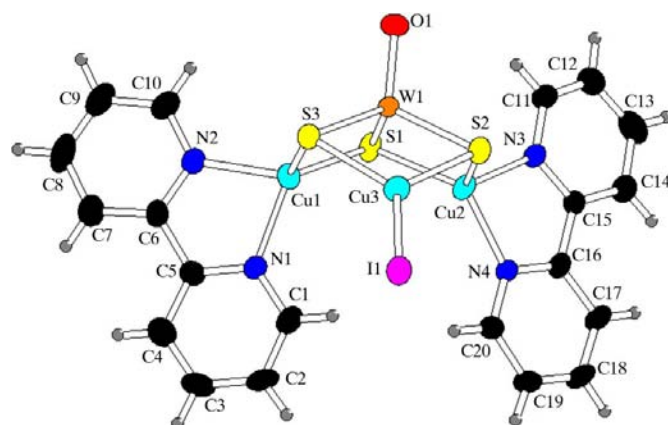
### Comment

Research into chalcogenometallate anions  $[\text{MO}_n\text{S}_{4-n}]^{2-}$  ( $M = \text{Mo}$  and  $\text{W}$ , and  $n = 0-2$ ) and their related cluster compounds has been a comparatively active field in modern chemistry, physics and materials science because of the interesting electronic, biological, optical, structural and catalytic properties of these compounds (Marks *et al.*, 1995; Gray & Lawson, 1999).

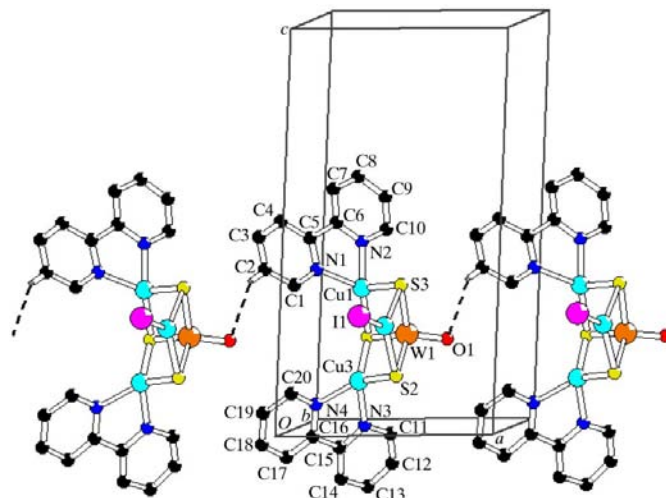


their analogues, which shows the limitation in the structural modification. As far as we know, there are only a few nest-shaped clusters with a 2,2'-bipyridine (bipy) skeleton, and these were reported recently (Hu, Wang *et al.*, 2003; Hu, Zheng *et al.*, 2003; Li *et al.*, 2004). In an attempt to search for better NLO materials, we report here the synthesis and crystal structure of the title compound,  $[\text{Cu}_3\text{WIOS}_3(\text{bipy})_2]$ , (I).

Fig. 1 shows the molecular structure of (I) and the atomic labelling scheme. Selected bond lengths and angles are listed in Table 1. Atom W1 is tetrahedrally coordinated by atom O1 and the three  $\mu_3$ -S atoms. The  $\text{W}=\text{O}$  bond length of 1.717 (4) Å is characteristic of a double bond, while the  $\text{W}-\text{S}$  bond distances [2.2531 (18)–2.2649 (17) Å] indicate single bonds. The three Cu atoms are divided into two different kinds. Atom Cu3 adopts a trigonal mode, surrounded by two  $\mu_3$ -S atoms and one I atom, forming the  $[\text{CuS}_2\text{I}]$  unit. Atoms Cu1 and Cu2 adopt a distorted tetrahedral geometry, with each Cu atom coordinated by two  $\mu_3$ -S atoms and the two N atoms of a 2,2'-bipy ligand, forming a  $[\text{CuS}_2(\text{bipy})]$  unit. Owing to their different coordination modes, atom Cu3 has a slightly



**Figure 1**  
The molecular structure of (I), shown with 30% probability displacement ellipsoids.



**Figure 2**  
The packing of (I), projected down the  $b$  axis. Broken lines indicate  $\text{C}-\text{H}\cdots\text{O}$  interactions. H atoms have been omitted.

Current research activity concerning the Mo(W)/Cu(Ag)/S clusters is aimed at investigating properties such as catalysis, conductivity and strong non-linear optical (NLO) characteristics (Fujita *et al.*, 1994; Aumuller *et al.*, 1986; Hou *et al.*, 1996). The literature on this subject is exhaustive, but mainly focuses on a narrow range of structure types in which the ligands attached to the Cu (Ag) atoms are a halogen, pyridine,  $\text{PPh}_3$  or

shorter Cu—W distance than atoms Cu1 and Cu2. The bipy act as bidentate ligands to atoms Cu1 and Cu2. As shown in Fig. 2, the complexes are linked *via* C—H...O interactions (Table 2), forming a chain structure along the *a* axis.

## Experimental

All reactions and manipulations were performed in oven-dried glassware under a purified nitrogen atmosphere using standard Schlenk techniques. The solvents and other chemicals were commercially available and were used without further purification. The starting material (NH<sub>4</sub>)<sub>2</sub>[WOS<sub>3</sub>] was prepared according to a literature method (McDonald *et al.*, 1983). A well ground mixture of CuI (0.191 g, 1.0 mmol), (NH<sub>4</sub>)<sub>2</sub>WOS<sub>3</sub> (0.174 g, 0.5 mmol), bipy (0.156 g, 1.0 mmol) and (*n*-Bu)<sub>4</sub>NI (0.369 g, 1.0 mmol) was added to CH<sub>2</sub>Cl<sub>2</sub> (15 ml) and stirred for 12 h under pure nitrogen. The red solution was filtered and *i*-PrOH (40 ml) was added to the filtrate. The filtrate was left to stand for several days whereupon red-brown crystals were produced (yield 0.25 g, 27%). Analysis calculated for C<sub>20</sub>H<sub>16</sub>Cu<sub>3</sub>IN<sub>4</sub>OS<sub>3</sub>W: C 25.94, H 1.74, N 6.05%; found: C 25.98, H 1.78, N 6.01%.

### Crystal data

[Cu <sub>3</sub> WIOS <sub>3</sub> (C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> ]	<i>Z</i> = 2
<i>M<sub>r</sub></i> = 925.97	<i>D<sub>x</sub></i> = 2.372 Mg m <sup>-3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> $\alpha$ radiation
<i>a</i> = 8.895 (1) Å	Cell parameters from 3064 reflections
<i>b</i> = 9.828 (1) Å	$\theta$ = 2.4–26.8°
<i>c</i> = 16.331 (2) Å	$\mu$ = 8.30 mm <sup>-1</sup>
$\alpha$ = 79.66 (1)°	<i>T</i> = 293 (2) K
$\beta$ = 85.90 (1)°	Block, red-brown
$\gamma$ = 67.38 (1)°	0.30 × 0.20 × 0.20 mm
<i>V</i> = 1296.4 (3) Å <sup>3</sup>	

### Data collection

Bruker SMART APEX CCD area-detector diffractometer	4503 independent reflections
$\varphi$ and $\omega$ scans	3824 reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )
Absorption correction: empirical (using intensity measurements) (SADABS; Bruker, 2000)	<i>R</i> <sub>int</sub> = 0.026
<i>T</i> <sub>min</sub> = 0.148, <i>T</i> <sub>max</sub> = 0.191	$\theta_{\max}$ = 25.0°
6494 measured reflections	<i>h</i> = -10 → 6
	<i>k</i> = -11 → 11
	<i>l</i> = -19 → 19

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$
$wR(F^2) = 0.079$	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 1.05	( $\Delta/\sigma$ ) <sub>max</sub> = 0.002
4503 reflections	$\Delta\rho_{\max} = 1.33 \text{ e \AA}^{-3}$
298 parameters	$\Delta\rho_{\min} = -1.35 \text{ e \AA}^{-3}$

All H atoms were positioned geometrically, with C—H distances of 0.93 Å and *U*<sub>iso</sub>(H) values of 1.2*U*<sub>eq</sub>(C).

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

**Table 1**

Selected geometric parameters (Å, °).

W1—O1	1.717 (4)	Cu1—S1	2.2517 (17)
W1—S1	2.2531 (18)	Cu1—S3	2.2810 (19)
W1—S3	2.2556 (15)	Cu2—N4	2.037 (5)
W1—S2	2.2649 (17)	Cu2—N3	2.099 (5)
W1—Cu3	2.6551 (8)	Cu2—S1	2.2741 (18)
W1—Cu2	2.6662 (8)	Cu2—S2	2.2818 (19)
W1—Cu1	2.6680 (9)	Cu3—S2	2.2650 (17)
Cu1—N1	2.057 (5)	Cu3—S3	2.2658 (18)
Cu1—N2	2.076 (5)	Cu3—I1	2.4435 (9)
O1—W1—S1	110.80 (18)	N2—Cu1—S3	108.65 (14)
O1—W1—S3	110.76 (16)	S1—Cu1—S3	107.24 (7)
S1—W1—S3	108.07 (6)	N4—Cu2—S1	129.03 (16)
O1—W1—S2	110.50 (18)	N3—Cu2—S1	107.22 (14)
S1—W1—S2	108.58 (6)	N4—Cu2—S2	116.21 (16)
S3—W1—S2	108.03 (6)	N3—Cu2—S2	113.02 (15)
N1—Cu1—N2	79.5 (2)	S1—Cu2—S2	107.27 (6)
N1—Cu1—S1	121.81 (15)	S2—Cu3—S3	107.67 (6)
N2—Cu1—S1	124.53 (15)	S2—Cu3—I1	127.99 (5)
N1—Cu1—S3	112.81 (16)	S3—Cu3—I1	124.34 (5)

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C2—H2...O1 <sup>i</sup>	0.93	2.57	3.202 (9)	126

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

This work was supported by the National Natural Science Foundation of China (grant Nos. 20571039 and 20171020) and the Ministry of Education of China (grant No. 20050284031). The authors thank Mr Yong-Jiang Liu for the data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1248). Services for accessing these data are described at the back of the journal.

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