



Synthesis and Crystal Structure of a 3-Fold Interpenetrated Supramolecular Cluster Based on The Incomplete Cubane-Like Precursor $[\text{Et}_4\text{N}]_2[\text{WO}(\mu\text{-S})_3(\text{CuNCS})_3]$ and 4,4'-Bipyridine

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A cluster-based 3D polymer $\{[\text{WO}(\mu\text{-S})_3\text{Cu}_3(\text{NCS})(4,4'\text{-bipy})_{2.5}]\cdot 2.5(\text{aniline})\}_n$ (**1**) was isolated by reactions of $[\text{Et}_4\text{N}]_2[\text{WO}(\mu\text{-S})_3(\text{CuNCS})_3]$ with bidentate nitrogen donor ligand 4,4'-bipy in an aniline solution. Compound **1** contains a 3-fold interpenetrated network in which each incomplete cubane-like $[\text{WO}(\mu\text{-S})_3\text{Cu}_3]$ core acts as a tetrahedral four-connecting node to interconnect four other equivalent ones *via* single and double 4,4'-bipy bridges.

Key Words: Crystal structure, 4,4'-Bipyridine, W/Cu/S cluster, Three-fold interpenetration, Supramolecular cluster.

INTRODUCTION

In the past decades, the chemistry of Mo/(W)/Cu/S clusters derived from reactions of metal sulfide synthons (*e.g.*, $[\text{MO}_x\text{S}_{4-x}]^{2-}$ ($\text{M} = \text{Mo}, \text{W}, x = 0-3$); $[\text{Cp}^*\text{MS}_3]^-$ ($\text{Cp}^* =$ pentamethylcyclopentadienyl; $\text{M} = \text{Mo}, \text{W}$) with CuX ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{CN}$) has been extensively investigated because of their novel structures^{1,2}, their potential applications in biological systems^{3,4} and optoelectronic materials^{5,6}. It is worth noting that some of the obtained clusters, especially those with incomplete cubane-like ones, have copper(I) atoms coordinated by terminal halides or pseudohalides, which can be replaced by various inorganic or organic donor ligands to form cluster-based species⁴. For example, the first family of incomplete cubane-like clusters $[\text{Et}_4\text{N}]_2[\text{MO}(\mu_3\text{-S})_3(\text{CuX})_3]$ ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{CN}, \text{NCS}, \text{Br}$) were used to react with 4,4'-bipyridine nitrogen donor ligands to yield polymeric clusters with these ligands coordinated at Cu(I) site⁷⁻¹³. The second family of incomplete cubane-like clusters $[\text{PPh}_4]_2[\text{Cp}^*\text{MO}(\mu_3\text{-S})_3(\text{CuX})_3]$ ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{CN}, \text{NCS}, \text{Br}$) were also chosen to treat with bidentate nitrogen donor ligands and many $[\text{Cp}^*\text{M}(\mu_3\text{-S})_3\text{Cu}_3]$ -based supramolecular compounds with intriguing 1D, 2D and 3D topological structures have been isolated¹⁴⁻¹⁷. In continuation of this work, herein, we reported the synthesis and structure of a three-dimensional 3-fold interpenetrated network $\{[\text{WO}(\mu\text{-S})_3\text{Cu}_3(\text{NCS})(4,4'\text{-bipy})_{2.5}]\cdot 2.5(\text{aniline})\}_n$ (**1**) based on $[\text{Et}_4\text{N}]_2[\text{WO}(\mu\text{-S})_3(\text{CuNCS})_3]$ and 4,4'-bipyridine in aniline solution.

EXPERIMENTAL

The cluster precursor $[\text{Et}_4\text{N}]_2[\text{WO}(\mu\text{-S})_3(\text{CuNCS})_3]$ was prepared according to the literature method¹⁸. 4,4'-Bipyridine was purchased from Aldrich Company. Aniline was freshly distilled under reduced pressure before use.

Synthesis of $\{[\text{WO}(\mu\text{-S})_3\text{Cu}_3(\text{NCS})(4,4'\text{-bipy})_{2.5}]\cdot 2.5(\text{ani})\}_n$ (1**):** $[\text{Et}_4\text{N}]_2[\text{WO}(\mu\text{-S})_3(\text{CuSCN})_3]$ (0.403 g, 0.5 mmol), 4,4'-bipy (0.167 g, 1.0 mmol) were added into 15 mL of aniline and stirred in a reaction tube for 1 h at room temperature. The solution was filtered and a dark red filtration solution was obtained. The dropwise addition of ether (20 mL) to the top of the solution led to some dark red block crystals several weeks later, which were collected by filtration and washed with ether and dried *in vacuo*. Yield: 0.412 g (35 % based on W). Elemental analysis confirmed the organic content (found (%): C, 41.59; H, 2.84; N, 9.82. calcd. (%) for $\text{C}_{82}\text{H}_{75}\text{N}_{17}\text{O}_2\text{S}_8\text{Cu}_6\text{W}_2$ (%): C, 42.16; H, 3.24; N, 10.19). IR (KBr, ν_{max} , cm^{-1} , disk): 2095 (s), 1610 (m), 1419 (m), 1261 (m), 1088 (s), 802 (m), 624 (m), 420 (m).

Detection method: The elemental analyses for C, H and N were performed on a Carlo-Erba CHNO-S microanalyzer. IR spectra were recorded on a Varian 1000 FT-IR spectrometer as KBr disks ($4000\text{-}400\text{ cm}^{-1}$). X-Ray quality single crystal of **1** was obtained directly from the above preparations. All measurements were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated $\text{MoK}\alpha$ ($\lambda = 0.71070\text{ nm}$). Cell parameters were refined by using the program CrystalClear (Rigaku and MSc, version 1.3, 2001)

on all observed reflections. The collected data were reduced by using the program Crystal Clear. The reflection data were also corrected for Lorentz and polarization effects. The crystal structure of **1** was solved by direct methods and refined on F^2 by full-matrix least-squares techniques with SHELXTL-97 program¹⁹. Due to the disorder of the phenyl ring on one solvate aniline and it was refined as a rigid group. In addition, this aniline solvent molecule was refined with an occupancy factor of 0.5 to give reasonable temperature factors. All non-hydrogen atoms, except for C37-C42 atoms on the disordered aniline solvent molecule, were refined anisotropically. The C37-C42 atoms on aniline were refined isotropically. All H atoms including N-H were placed in geometrically idealized positions (C-H = 0.95 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic rings, N-H = 0.86 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$) and constrained to ride on their parent atoms. The parameters of the crystal, data collection and refinement are given in Table-1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) (E-mail: deposit@ccdc.cam.ac.uk) as supplementary materials and the CCDC number is 752851.

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR COMPOUND **1**

Complex	1
Empirical formula	$\text{C}_{82}\text{H}_{75}\text{Cu}_6\text{N}_{17}\text{O}_2\text{S}_8\text{W}_2$
Formula weight (g mol^{-1})	2336.13
Wavelength (Å)	0.71070
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.007(2)
b (Å)	27.298(6)
c (Å)	17.677(4)
β (°)	100.46(3)
Volume (Å ³)	4748.6(18)
Z	2
D (g cm^{-3})	1.634
F(000)	2304.0
Absorption coefficient (m m^{-1})	3.96
θ range for data collection (°)	3.05?27.5
Limiting indices	$-12 \leq h \leq 12, -22 \leq k \leq 35,$ $-22 \leq l \leq 14$
Independent reflections	10845 [(R(int) = 0.055)]
Goodness-of-fit on F^2	1.10
Final R^1 and wR^2 [$I > 2\sigma(I)$]	0.062, 0.155
R^1 and wR^2 indices (all data)	0.082, 0.168
Largest diff. peak and hole (e Å^{-3})	1.54 and ?1.87

RESULTS AND DISCUSSION

Crystal structure of 1: The asymmetric unit of **1** contains one $[\text{WO}(\mu\text{-S})_3\text{Cu}_3(\text{NCS})(4,4'\text{-bipy})_{2.5}]$ molecule and two and half an aniline solvent molecules. The incomplete cubane-like $[\text{WOS}_3\text{Cu}_3]$ core in the repeating unit $[\text{WO}(\mu\text{-S})_3\text{Cu}_3(\text{NCS})(4,4'\text{-bipy})_{2.5}]$ also keeps the core structure of the dianion $[\text{WO}(\mu\text{-S})_3(\text{CuSCN})_3]^{2-}$. In each $[\text{WO}(\mu\text{-S})_3\text{Cu}_3]$ unit, the coordination geometry of the W atom is a distorted tetrahedron with the average W-O and W-S bonds being at 1.722(5) and 2.257(8) Å, respectively (Table-2). All the Cu atoms also adopt a distorted tetrahedral coordination geometry. Apart from

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR **1**

W1...Cu3	2.6862(12)	W1...Cu2	2.7085(11)
W1...Cu1	2.7203(10)	W1-O1	1.722(5)
W1-S1	2.2547(18)	W1-S2	2.2645(19)
W1-S3	2.254(2)	Cu1-S1	2.335(2)
Cu1-S2	2.308(2)	Cu2-S3	2.295(2)
Cu2-S2	2.298(2)	Cu3-S1	2.295(3)
Cu3-S3	2.283(2)	Cu1-N1	1.948(6)
Cu1-N5	2.116(7)	Cu2-N2	2.035(6)
Cu2-N6	2.042(5)	Cu3-N4 ^b	2.059(6)
Cu3-N3 ^b	2.091(6)	—	—
O1-W1-S1	110.8(2)	O1-W1-S2	110.0(2)
O1-W1-S3	109.8(2)	S1-W1-S2	109.20(7)
S1-W1-S3	108.69(7)	S3-W1-S2	108.32(7)
N5-Cu1-S2	104.95(17)	N2-Cu2-N6	114.5(2)
N1-Cu1-S1	118.9(2)	N2-Cu2-S3	110.1(2)
N5-Cu1-S1	100.28(18)	N6-Cu2-S3	106.71(19)
N1-Cu1-N5	106.5(3)	N2-Cu2-S2	110.4(2)
N1-Cu1-S2	118.8(2)	N6-Cu2-S2	108.9(2)
S2-Cu1-S1	105.01(7)	N4 ^b -Cu3-S1	120.3(2)
N4 ^b -Cu3-N3 ^a	99.8(3)	N3 ^a -Cu3-S1	107.7(2)
N4 ^b -Cu3-S3	106.04(17)	S3-Cu3-S1	106.33(8)

a: $-x, -y + 1, -z + 1$. b: $x - 1, -y + 1/2, z - 1/2$.

the coordination of two $\mu_3\text{-S}$ atoms, Cu1 is coordinated by one N atom from 4,4'-bipy and one N atom from a terminal NCS^- , while Cu2 and Cu3 by two N atoms from two 4,4'-bipy. The mean $\text{W}\cdots\text{Cu}$ contact (2.705(1) Å) and the terminal W-O, $\text{W}\cdots\mu_3\text{-S}$, $\text{Cu}\cdots\mu_3\text{-S}$ and $\text{Cu}\cdots\text{N}(4,4'\text{-bipy})$ bond lengths are quite similar to those of the corresponding ones in $\{[\text{W}_4\text{O}_4\text{S}_{12}\text{Cu}_{12}\text{Cl}_2(4,4'\text{-bipy})_{12}]\text{Cl}\cdot 4\text{H}_2\text{O}\}_n$ ⁹, $\{[\text{WOS}_3\text{Cu}_3(4,4'\text{-bipy})_3][\text{I}]\}_n$ ¹⁰ and $\{[\text{NH}_4][\text{W}_2\text{O}_2\text{S}_6\text{Cu}_6\text{I}_3(4,4'\text{-bipy})_4]\cdot 5\text{H}_2\text{O}\}_n$ ¹³. In **1**, each cluster core serves as a tetrahedral four-connecting node and is coordinated by five bridging 4,4'-bipy ligands, which link four equivalent cluster cores that lie at the corners of a slightly distorted tetrahedron as indicated in Fig. 1, forming a single adamantane type unit. This unit is further interconnected by 4,4'-bipy bridges to form a unique 3D diamonded

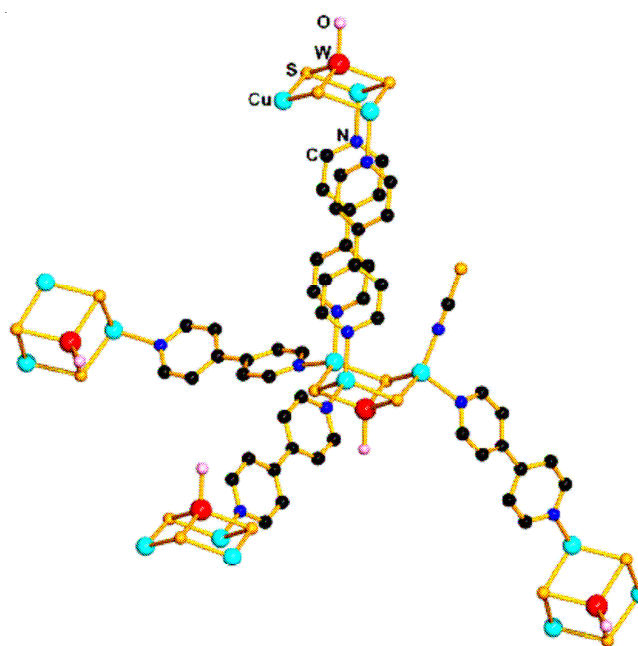


Fig. 1. View of the interactions of a $[\text{WO}(\mu\text{-S})_3\text{Cu}_3(\text{NCS})]$ core via a double 4,4'-bipy bridge and three single 4,4'-bipy bridges in **1**

net (Fig. 2). Each single net interpenetrates two other identical ones, resulting a triply interpenetrated net (Fig. 3). Such 3D nets stack along the *a* axis to give 1D irregular channels in the unit cell of the crystal. Although such 3-fold interpenetration significantly reduces the solvent-accessible void, these channels are filled by aniline solvent molecules (Fig. 4).

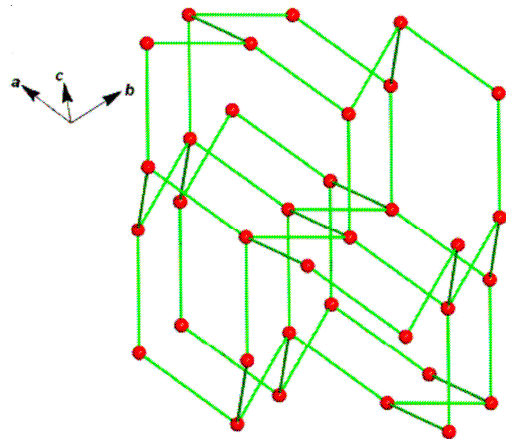


Fig. 2. A ball-stick view of showing the distorted adamantane-shaped unit within the network of **1**. Red balls and green sticks represent $[\text{WO}(\mu\text{-S})_3\text{Cu}_3(\text{NCS})]$ cores and 4,4'-bipy bridges

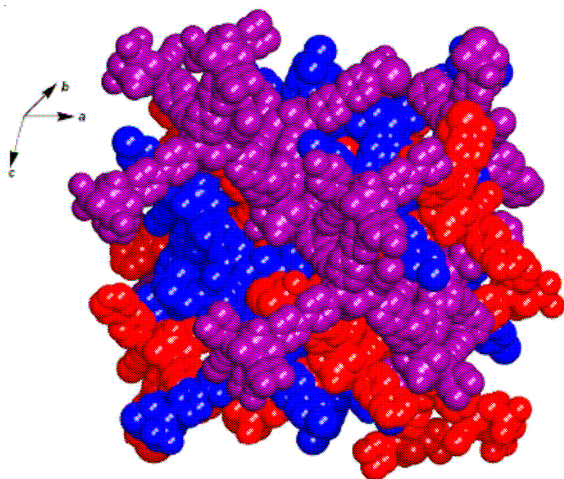


Fig. 3. A space-filling representation of the view of the triply interpenetrating frameworks in red, purple and blue

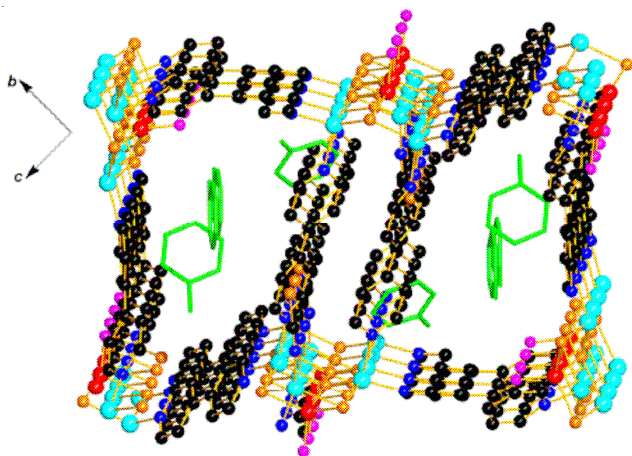


Fig. 4. View of the aniline solvated molecules in the channels formed from the interpenetration of the three diamond networks extending along the *a* axis

Physical properties and IR spectrum: Compound **1** is relatively stable toward air and moisture and is insoluble in organic solvents such as DMF, MeCN and CH_2Cl_2 . In the IR spectrum of **1**, band at 2095 cm^{-1} is assigned to the NCS stretching vibration. Bands at 1610 , 1419 and 1261 cm^{-1} are assumed to be the pyridyl and aniline rings. Bands at $802/420\text{ cm}^{-1}$ are assigned as the terminal W-O and bridging W-S stretching vibrations, respectively.

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