Supporting Information

A Multi-Metal-Cluster MOF with Cu_4I_4 and Cu_6S_6 as Functional Groups Exhibiting Dual Emission with both Thermochromic and Near-infrared Characters

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Contents

Materials and measurements

All chemicals were used as received without further purification. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr pellets in the range of 4000–400cm^{-1}. Fluorescent spectra were measured on an Edinburgh Instruments analyzer model FLS920 with 450W xenon light. Elemental analyses were carried out on Elementar Vario EL III microanalyzer. Thermogravimetric (TG) analysis was carried out on preweighted samples in a nitrogen stream using a Netzsch STA449C-QMS403C apparatus. Powder X-ray diffraction (PXRD) data were collected on a Rigaku DMAX2500 diffractometer using Cu Kα radiation (λ = 0.154 nm) at a scanning rate of 5° min^{-1} for 2θ ranging from 5 to 50°.

Synthesis

CuI (57 mg, 0.3 mmol) was dissolved in 3 ml MeCN (acetonitrile), and 5-(pyridin-3-yl)-1H-1,2,4-triazole-3-thiol (3-Hptt) (53 mg, 0.3 mmol) was added to 20 mL MeOH. Then, those two solutions were put together and stirred for 5 h. The blown precipitation was obtained and stirred in 20 mL DEF for another 5 h. After filtration, the filtrate was permitted to evaporate at 4°C, and colorless prism crystals were obtained after about 10 days. Yield: 71.89% (93.1 mg) based on CuI. IR data (KBr, cm^{-1}): 2974m, 2759w, 1644vs, 1441s, 1397s, 1309s, 1118m, 985m, 819m, 699m. Using a combination of elemental analysis, TG analysis and single-crystal X-ray diffraction analysis, the compound was formulated as $[(Cu^{I}_{4}I_4)_3(Cu^{I}_{6})_2(3\text{-ptt})_{12}]_n\cdot 24nDEF\cdot 12nH_2O$. Elemental analyses calcd (%) for $[(Cu_4I_4)_3(Cu_6)_2(3\text{-ptt})_{12}]_n\cdot 24nDEF\cdot 12nH_2O$: C 31.34, H 4.49, N 12.90, S 4.92; found: C 31.76, H 4.54, N 12.88, S 4.88. Furthermore, elemental analysis was used after removing all the solvents by soaking in CH_2Cl_2 for 24h three times. All the solvents were removed according to TG analysis. Elemental analyses calcd (%) for $[(Cu_4I_4)_3(Cu_6)_2(3\text{-ptt})_{12}]_n$: C 19.49, H 1.17, N 12.99, S 7.43; found: C 19.77, H 1.23, N 12.13, S 7.43.

X-ray data collection and structure determination

Intensity data for compound **1** was measured on Rigaku Saturn 70 CCD, with graphite-monochromated Mo Kα radiation (λ=0.71073 Å) at 113K. The structures were solved by direct methods and all calculations were performed through using the SHELXL-97[1] program. The coordinate of metal atoms was obtained from the E-map. The successive Difference Fourier syntheses gave all the coordinates of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were located at geometrically calculated positions and refined by riding. As the solvent molecules in **1** were severely disordered and unsuccessfully located and refined them, so they were removed using the SQUEEZE routine of PLATON.[2] Free DEF, water molecules in the asymmetry unit of **1** were determined by TG analyses and element analyses as well. Crystallographic data and structure refinement parameters for compound **1** are summarized in Table S1. Selected bond lengths and bond angles are listed in Supporting Information Table S2. More details on the crystallographic studies as well as atomic displacement parameters are given in Supporting Information as CIF file. Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers of 867097.

Topological Analysis

The point symbol and vertex symbol are computed using TOPOS.[3] The embedding of the tiling representation is performed by Systre[4] and 3dt[5].

Crystal data for 1: $C_7H_5N_4S_1Cu_2I_1$, M_r = 431.19, Cubic, space group *Ia*-3*d*, *a* = 41.856 (3) Å, *V* = 73329 (9) Å^3, *Z* = 96, ρ_{calcd} = 0.937 g cm^{-3}. After using SQUEEZE/PLATON, R_1 = 0.086 and wR_2 = 0.28 for 201503 reflections collected, 4703 observed reflections ($I > 2\sigma(I)$) of 5369 (Rint = 0.0331) unique reflections and 106 parameters, GooF = 1.14.

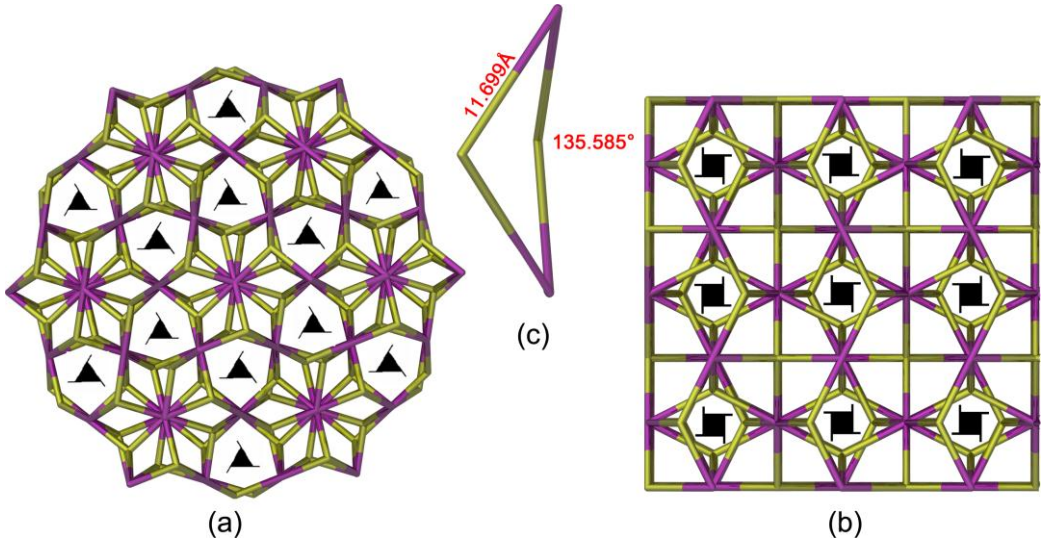

Figure S1. The topology of compound **1** from (a) [1 1 1] and (b) [1 0 0], [0 1 0], [0 0 1]; (c) the rhombus-shape window along helical chains. Solvent molecules are omitted for clarity.

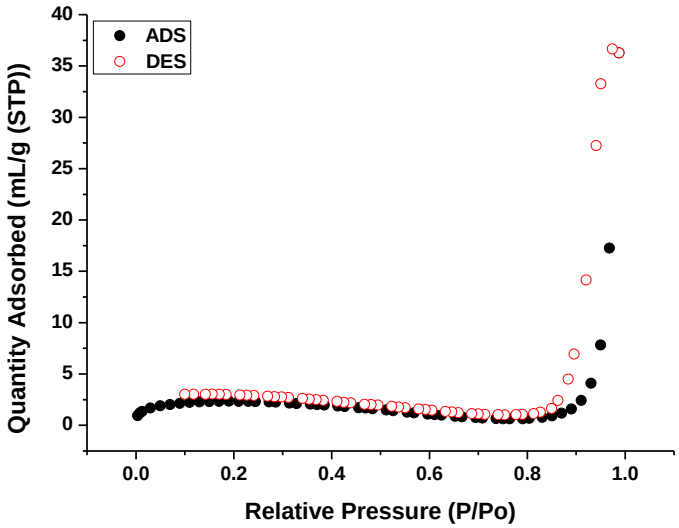

Figure S2. N_2 sorption isotherms for heat-activated sample of compound **1** at 77 K.

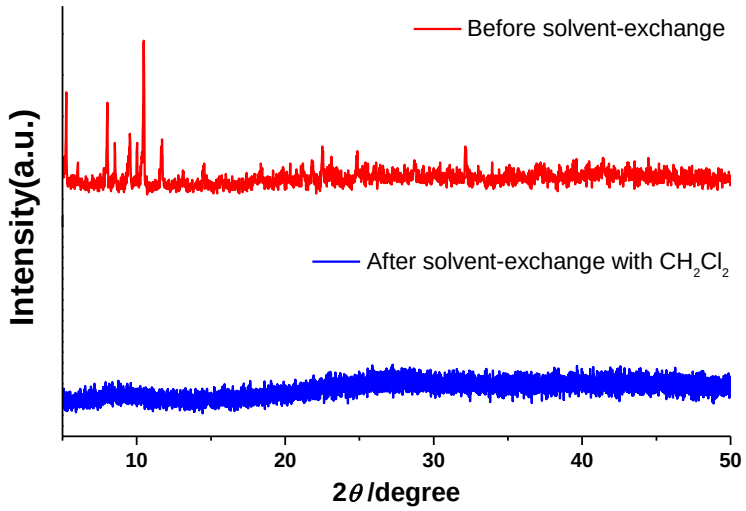

Figure S3. The PXRD pattern of compound **1** before and after solvent exchange with CH_2Cl_2, respectively.

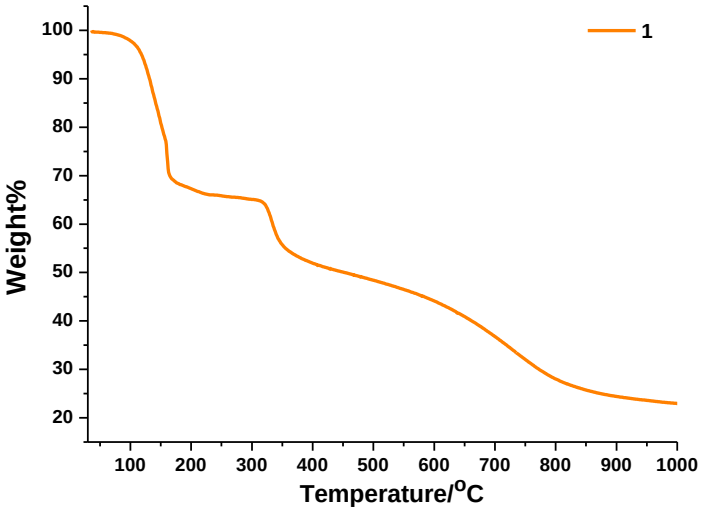

Figure S4. The TG analysis of compound **1**. The TG curve of **1** has a weight loss in the temperature ranges of 85–225 °C (33.84%), corresponding to the loss of free solvent molecules: a water and two DEF (*calcd.* 33.78%). After then, the structure begins to decompose.

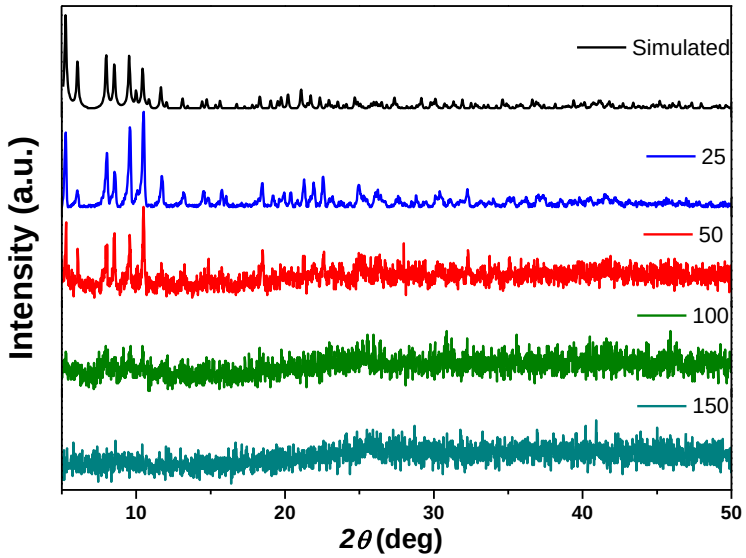

Figure S5. The temperature-dependent PXRD pattern of compound **1** at 25 °C, 50 °C, 100 °C and 150 °C, respectively.

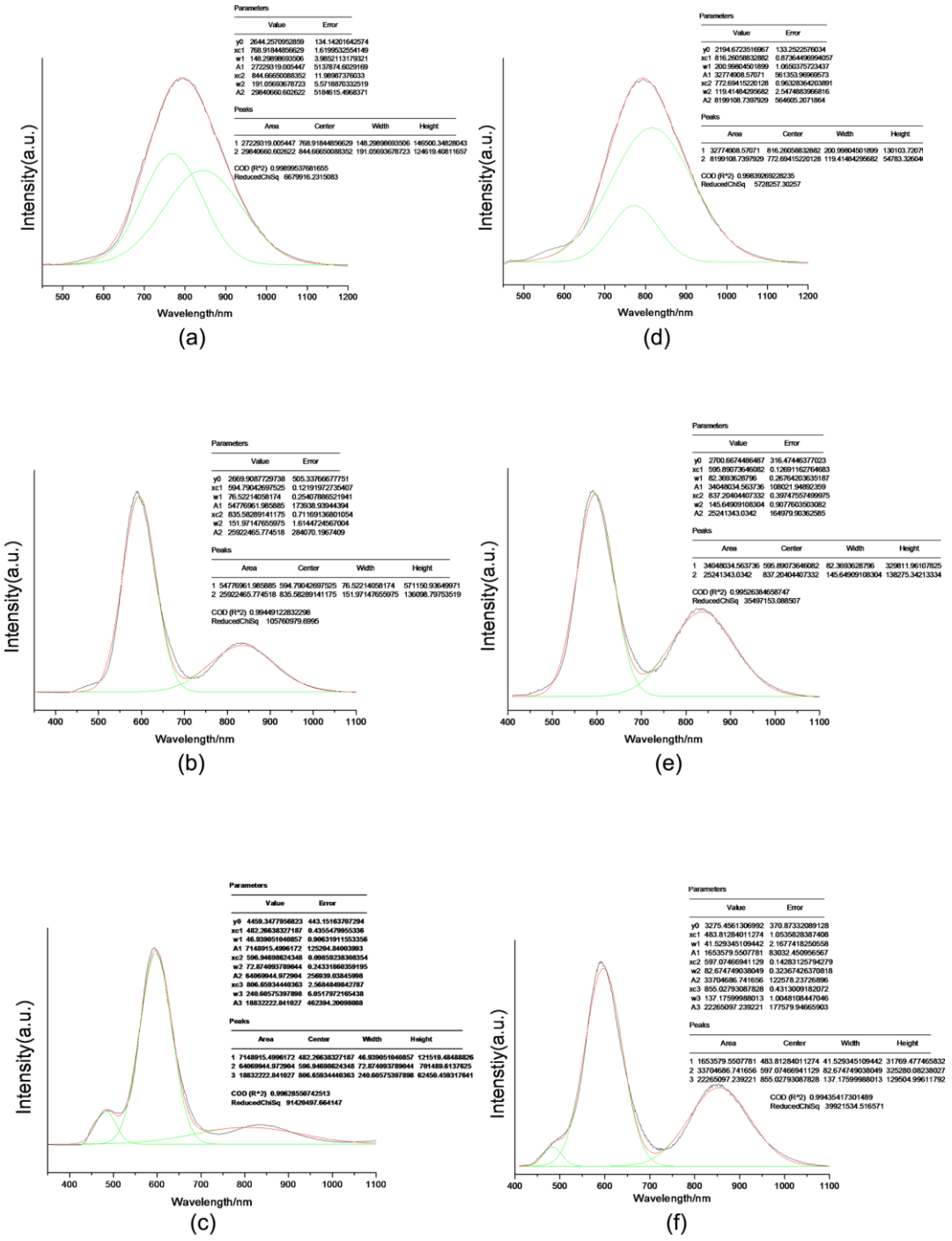

Figure S6. Emission spectra of compound **1** and the fitted Gaussian profile excited by 323 nm at room temperature (a), 77 K(b) and 10 K(c); and 365 nm at room temperature (d), 77 K(e) and 10 K(f). (Black: measured spectra, Red: Gauss fitting result, Green: Gauss fitting peak 1–3)

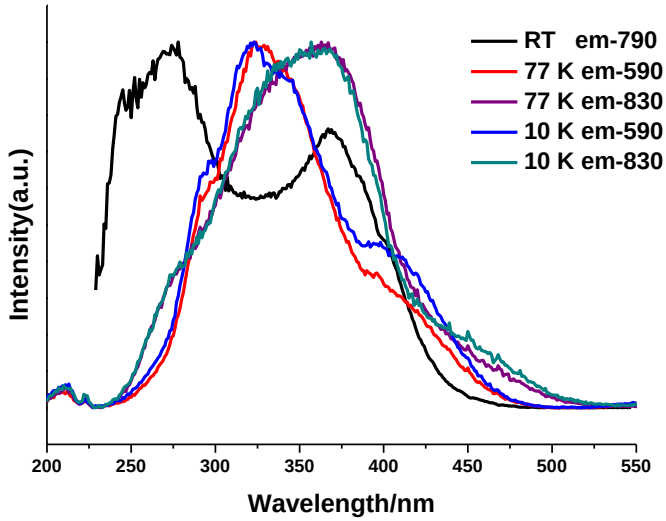

Figure S7. The excitation spetra of compound **1** for λ_{em} = 790, 590 and 830 nm at room temperature, 77 K and 10 K.

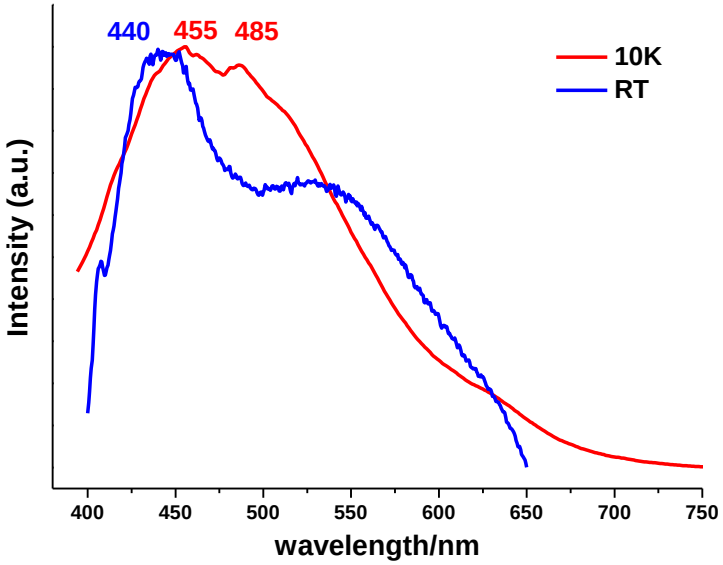

Figure S8. The emission spetra of ligand 3-Hptt for λ_{ex} = 365 nm at room temperature and 10 K.

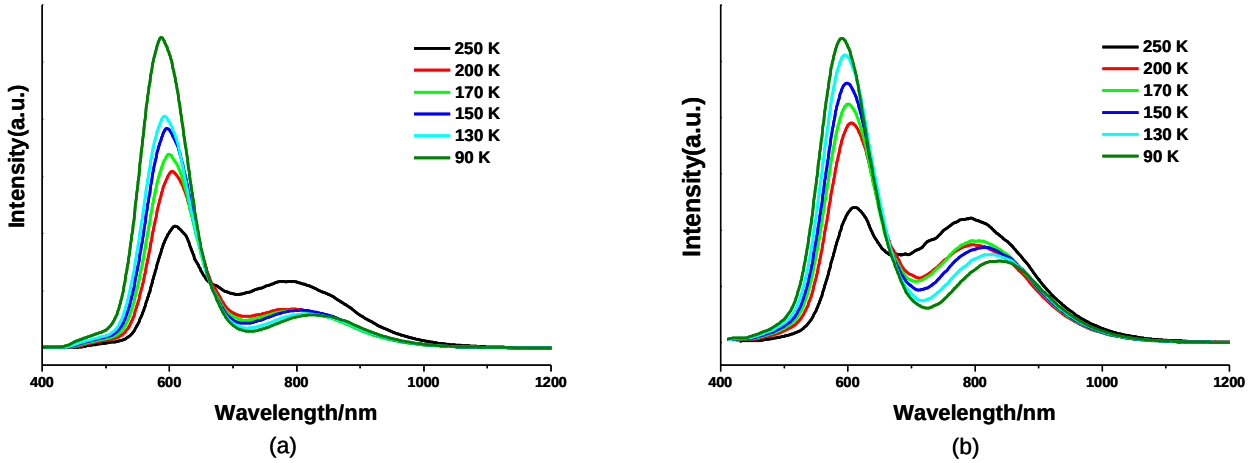

Figure S9. The temperature-dependent luminescent spectra of compound **1** from 250 K to 90 K upon excitation of (a) 323 nm and (b) 365 nm, respectively.

Table S1. Crystallographic data and structure refinement details for **1**

Compound	**1**
Empirical formula	$C_7H_5N_4S_1Cu_2I_1$
Formula weight	431.19
Crystal system	Cubic
Space group	*Ia-3d*
a [Å]	41.856 (3)
V [Å^3]	73329 (9)
Z	96
Dc [g/cm^{-3}]	0.937
μ [mm^{-1}]	2.46
Goodness-of-fit on F^2	1.14
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.086, 0.26
R_1,[a] wR_2[b] (all data)	0.096, 0.28
Reflns. Collected	201503
Reflns. Unique (R_{int})	5369 (0.06.)

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) for **1**[a]

Bond lengths (Å)			
I1—Cu2^{i}	2.6376 (12)	C4—C3	1.403 (14)
I1—Cu2^{ii}	2.6971 (14)	C4—H4	0.9500
I1—Cu2	2.7641 (14)	C3—C7	1.363 (15)
Cu1—N1	1.977 (6)	C3—C2	1.500 (13)
Cu1—S1^{iii}	2.244 (2)	C5—N4	1.349 (12)
Cu1—S1^{iv}	2.252 (2)	C5—C6	1.360 (14)
Cu2—N4	2.041 (7)	C5—H5	0.9500
Cu2—I1^{i}	2.6376 (12)	C7—C6	1.366 (14)
Cu2—Cu2^{i}	2.662 (2)	C7—H7	0.9500
Cu2—I1^{v}	2.6971 (14)	C6—H6	0.9500
Cu2—Cu2^{ii}	2.7111 (18)	N1—C2	1.329 (10)
Cu2—Cu2^{v}	2.7111 (18)	N1—C1	1.376 (10)
S1—C1	1.696 (8)	N3—C2	1.355 (12)
S1—Cu1^{iv}	2.244 (2)	N3—N2	1.377 (10)
S1—Cu1^{iii}	2.252 (2)	N3—H3	0.8800
C4—N4	1.297 (12)	N2—C1	1.320 (10)
Angles (°)			
Cu2^{i}—I1—Cu2^{ii}	61.08 (4)	N4—C4—H4	118.3
Cu2^{i}—I1—Cu2	59.00 (4)	C3—C4—H4	118.3
Cu2^{ii}—I1—Cu2	59.51 (4)	C7—C3—C4	118.1 (9)
N1—Cu1—S1^{iii}	122.9 (2)	C7—C3—C2	121.3 (9)
N1—Cu1—S1^{iv}	122.6 (2)	C4—C3—C2	120.6 (9)
S1^{iii}—Cu1—S1^{iv}	113.21 (9)	N4—C5—C6	121.7 (9)
N4—Cu2—I1^{i}	109.9 (2)	N4—C5—H5	119.1
N4—Cu2—Cu2^{i}	143.4 (3)	C6—C5—H5	119.1
I1^{i}—Cu2—Cu2^{i}	62.87 (4)	C3—C7—C6	118.1 (10)
N4—Cu2—I1^{v}	105.1 (2)	C3—C7—H7	121.0
I1^{i}—Cu2—I1^{v}	113.81 (4)	C6—C7—H7	121.0
Cu2^{i}—Cu2—I1^{v}	110.52 (2)	C5—C6—C7	120.2 (10)
N4—Cu2—Cu2^{ii}	139.2 (2)	C5—C6—H6	119.9
I1^{i}—Cu2—Cu2^{ii}	110.85 (4)	C7—C6—H6	119.9
Cu2^{i}—Cu2—Cu2^{ii}	60.59 (3)	C4—N4—C5	117.7 (8)
I1^{v}—Cu2—Cu2^{ii}	58.38 (5)	C4—N4—Cu2	119.5 (6)
N4—Cu2—Cu2^{v}	150.8 (3)	C5—N4—Cu2	122.8 (6)
I1^{i}—Cu2—Cu2^{v}	60.54 (3)	C2—N1—C1	104.9 (6)
Cu2^{i}—Cu2—Cu2^{v}	60.59 (3)	C2—N1—Cu1	136.6 (6)
I1^{v}—Cu2—Cu2^{v}	61.47 (5)	C1—N1—Cu1	118.5 (5)
Cu2^{ii}—Cu2—Cu2^{v}	58.81 (5)	C2—N3—N2	101.0 (7)
N4—Cu2—I1	101.9 (3)	C2—N3—H3	129.5

$I1^{i}$—Cu2—I1	115.17 (4)	N2—N3—H3	129.5
$Cu2^{i}$—Cu2—I1	58.13 (4)	N1—C2—N3	114.0 (8)
$I1^{v}$—Cu2—I1	109.84 (4)	N1—C2—C3	126.8 (8)
$Cu2^{ii}$—Cu2—I1	59.01 (4)	N3—C2—C3	118.9 (8)
$Cu2^{v}$—Cu2—I1	107.10 (4)	C1—N2—N3	112.4 (8)
C1—S1—$Cu1^{iv}$	102.2 (3)	N2—C1—N1	107.2 (7)
C1—S1—$Cu1^{iii}$	103.8 (3)	N2—C1—S1	125.4 (7)
$Cu1^{iv}$—S1—$Cu1^{iii}$	100.17 (8)	N1—C1—S1	127.5 (5)
N4—C4—C3	123.5 (10)		

[a]Symmetry codes: (i) 3/2-x, y, -z; (ii) 1/4+x, 5/4-z, 11/4+y; (iii) 2+x, -y, 3/2-z; (iv) 1+x, 1-y, 1/2-z; (v) 3/4+z, 5/4+y, 5/4-x.

Reference

1. (a) G. M. Sheldrick, *SHELXS97, Program for Crystal Structure Solution* (1997) University of Göttingen, Göttigen, Germany; (b) G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*, (1997) University of Göttingen, Göttigen, Germany.
2. P. van der Sluis and A. L. Spek, *Acta Crystallographica Section A*, 1990, **46**, 194-201.
3. Blatov, V. A. *Multipurpose crystallochemical analysis with the program package TOPOS. IUCr CompComm Newsletter* **2006**, *7*, 4-38. TOPOS is available at http://www.topos.ssu.samara.ru.
4. O. Delgado-Friedrichs and M. O'Keeffe, *Acta Crystallographica Section A*, 2003, **59**, 351-360.
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