Supporting Information

2D-Homometallic- to a 3D-Heterometallic Coordination Polymer: A Metalloligand Approach

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Experimental Section

Solvents were distilled and dried prior to use according to standard procedures. Me_3SnCl and pyridine-2,5-dicarboxylic acid were purchased from Aldrich and $Cu(NO_3)_2 \cdot 3H_2O$ was obtained from sd-Fine chemical company, Mumbai, India. Melting points were measured using a JSGW melting point apparatus and are uncorrected. Elemental analyses were carried out using a Thermoquest CE instruments model EA/110 CHNS-O elemental analyzer. Infrared spectra were recorded as KBr pellets on a FT-IR Bruker-Vector Model. Thermogravimetric Analysis was carried out on a Perkin Elmer Pyris 6 Thermogravimetric analyzer.

Synthesis

$[Cu(\mu\text{-}LH)_2]_n$ (1)

To a solution of pyridine-2,5-dicarboxylic acid (0.081g, 0.50 mmol) and Et_3N (0.21 mL, 1.50 mmol) in a 50 mL mixture of $EtOH/H_2O$ (9:1), $Cu(NO_3)_2 \cdot 3H_2O$ (0.12 g, 0.5 mmol) was added. The mixture was stirred for 3 hours at room temperature to afford a clear blue solution (Solution **A**). The mixture was filtered and kept for slow-evaporation to get single crystals of **1**. Yield: 0.15 g (76%). Mp: >200 °C. Anal. Calcd for $CuC_{14}H_8N_2O_8$ (394.95 g) (%): C, 42.49, H, 2.04, N, 7.08; Found: C 42.43, H 1.98, N, 6.89. IR (KBr, cm^{-1}): 3417.01 (b), 3083.02 (m), 2975.03 (m), 2938.04 (s), 2878.16 (s), 2738.90 (s), 2677.58 (s), 2491.16 (s), 1903.42 (m), 1714.53 (s), 1612.72 (s), 1595.58 (s), 1568.87 (s), 1475.94 (s), 1433.53 (s), 1395.94 (s), 1380.45 (s), 1260.01 (s), 1171.92 (s), 1130.76 (s), 1046.94 (s), 1036.35 (s), 1012.03 (s), 990.19 (s), 895.84 (m), 864.45 (m), 848.57 (m), 771.22 (m), 702.68 (m), 686.80 (s), 573.67 (w), 455.45 (m), 425.00 (w), 403.10 (s). ESI-MS: m/z (%) 393.9496 $[M\text{-}H]^-$ (100).

$[Cu(Me_3Sn)_2(\mu\text{-}L)_2]_n$ (2)

Instead of isolating **1** as described above, to the solution **A,** Me_3SnCl (0.099g, 0.50 mmol) was added. The mixture was refluxed for 4 hours to afford a semi-clear blue solution (Solution **B**). The mixture was filtered and kept for slow-evaporation to get block type single crystals of **2**. Yield: 0.12 g (33%). Mp: >200 °C. Anal. Calcd for $CuSn_2C_{20}H_{24}N_2O_8$ (722.88 g) (%): C, 33.30, H, 3.35, N, 3.88; Found: C 33.27, H 3.21, N, 3.93. IR (KBr, cm^{-1}): 3423.56 (b), 3068.58 (m), 2973.93 (m), 2935.26 (m), 2739.17 (m), 2677.78 (m), 2491.53 (m), 1619.07 (s), 1575.59 (s), 1480.96 (m), 1399.18 (s), 1351.99 (s), 1282.80 (s), 1145.05 (m), 1107.63 (w), 1046.71 (m), 961.50 (w), 878.97 (w), 839.12 (s), 787.20 (s), 764.68 (s), 690.12 (m), 679.71 (m), 549.86 (s), 424.11 (w). ESI-MS: m/z (%) 393.9467 $[Cu(LH)(L)]^-$ (100); 557.9125 $[(Cu)(Me_3Sn)(L)_2]^-$ (18).

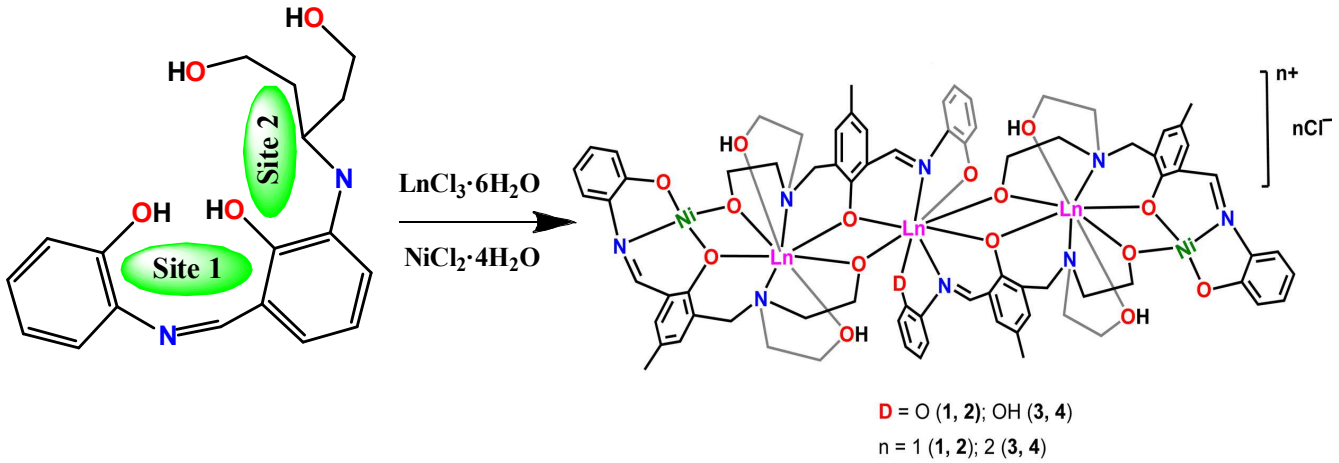
X-ray Crystallographic Study

The crystal data for compounds **1**−**2** were collected on a Bruker SMART APEX CCD Diffractometer. SMART software package (version 5.628) was used for collecting data frames, SAINT software package (version 6.45) for integration of the intensity and scaling and SADABS was used for absorption correction. The structures were solved and refined by full-matrix least-squares on F^2 using SHELXTL software package.[1] Non-hydrogen atoms were refined with anisotropic displacement parameters. In cases of compound **1**, since one of carboxylate O-atom is disordered we have divided it into O4A (53%) and O4 (47%). Figures 2, 4, 5 and S1-S5 and their bonding parameters were obtained from the DIAMOND 3.1f software package.[2]

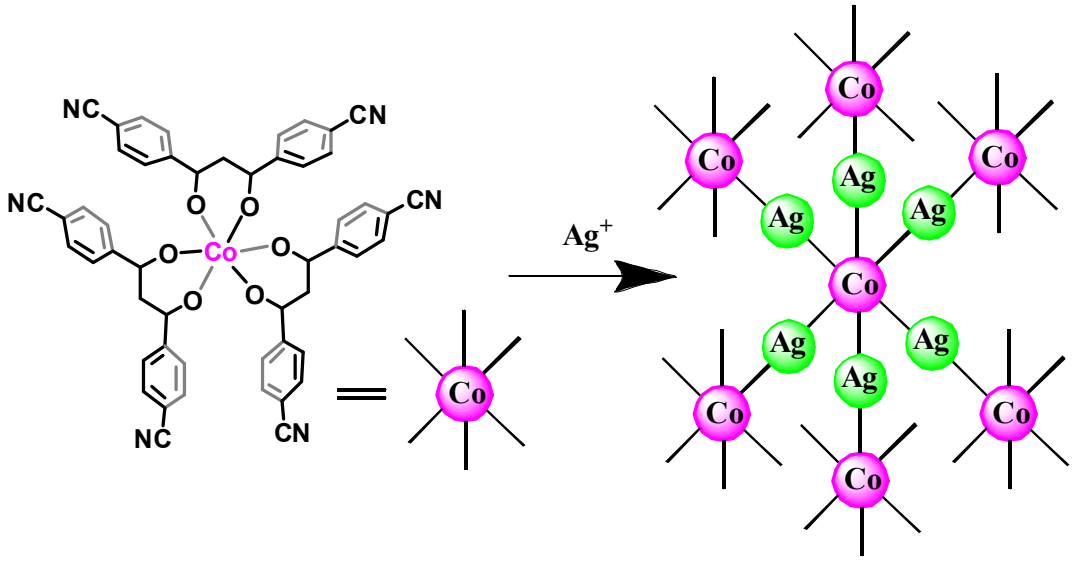
(1) Sheldrick, G. M. SHELXTL version 6.14; Bruker AXS Inc.: Madison, WI, **2003**.

(2) DIAMOND version 3.1f; Crystal Impact GbR: Bonn, Germany, **2004**.

(a)


HO
HO
Site 2
N
OH
HO
Site 1
N
LnCl3·6H2O
NiCl2·4H2O
HO
Ni
Ln
Ln
Ln
Ni
OH
OH
D
n+
nCl⁻
D = O (1, 2); OH (3, 4)
n = 1 (1, 2); 2 (3, 4)

(b)


NC
CN
NC
CN
Co
NC
CN
Co
Ag+
Co
Co
Co
Ag
Ag
Ag
Co
Ag
Ag
Ag
Co
Co
Co

(c)

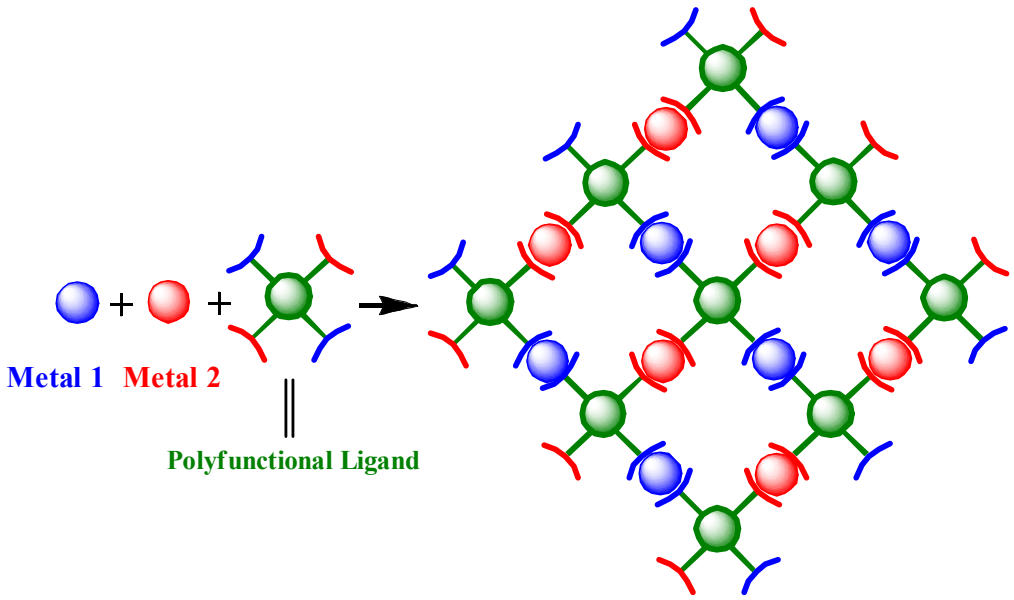
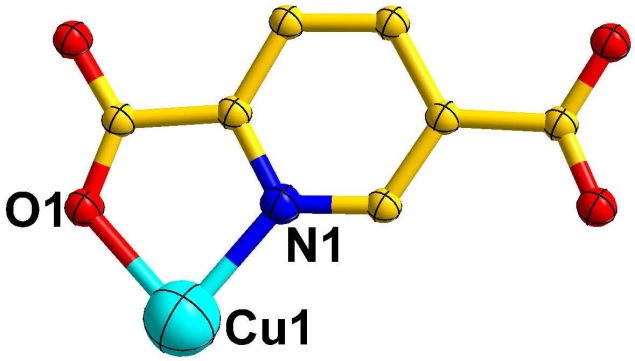

Metal 1
Metal 2
Polyfunctional Ligand

Chart S1. (a) Schematic presentation of synthesis of a heterometallic Ln^{III}/Ni^{II} complex by ligand which have distinct binding sites[3] (b) Schematic presentation of assembly of a 3D polymer utilizing metalloligand as starting material[4] (c) Schematic presentation of one-pot synthesis of a heterometallic coordination polymer using a mixture of metal salts along with a polyfunctional ligand.

(3) Chandrasekhar, V.; Bag, P.; Kroener, W.; Gieb, K.; Müller, P. *Inorg. Chem.* **2013** (**DOI:** 10.1021/ic4019025)

(4) Carlucci, L.; Ciani, G.; Maggini, S.; Proserpio, D. M.; Visconti, M. *Chem. Eur. J.* **2010**, *16*, 12328.

(a)



(b)

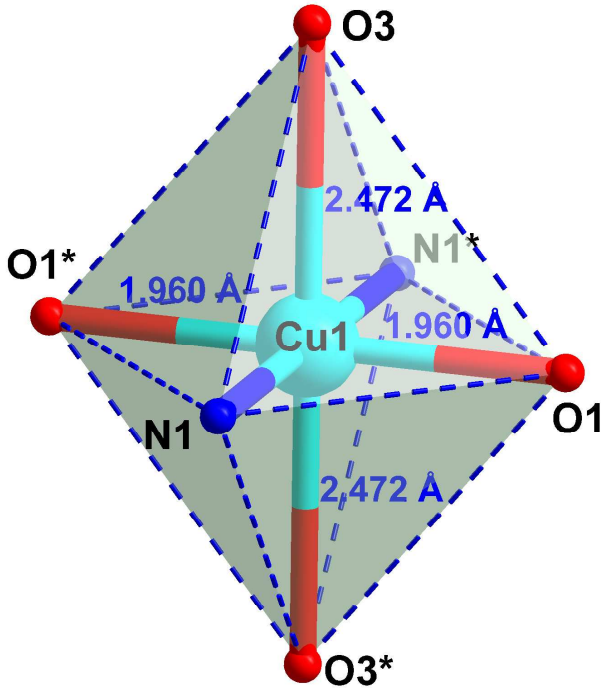


Figure S1. (a) Asymmetric unit of **1** (b) Distorted octahedral geometry around Cu(II) in **1.**

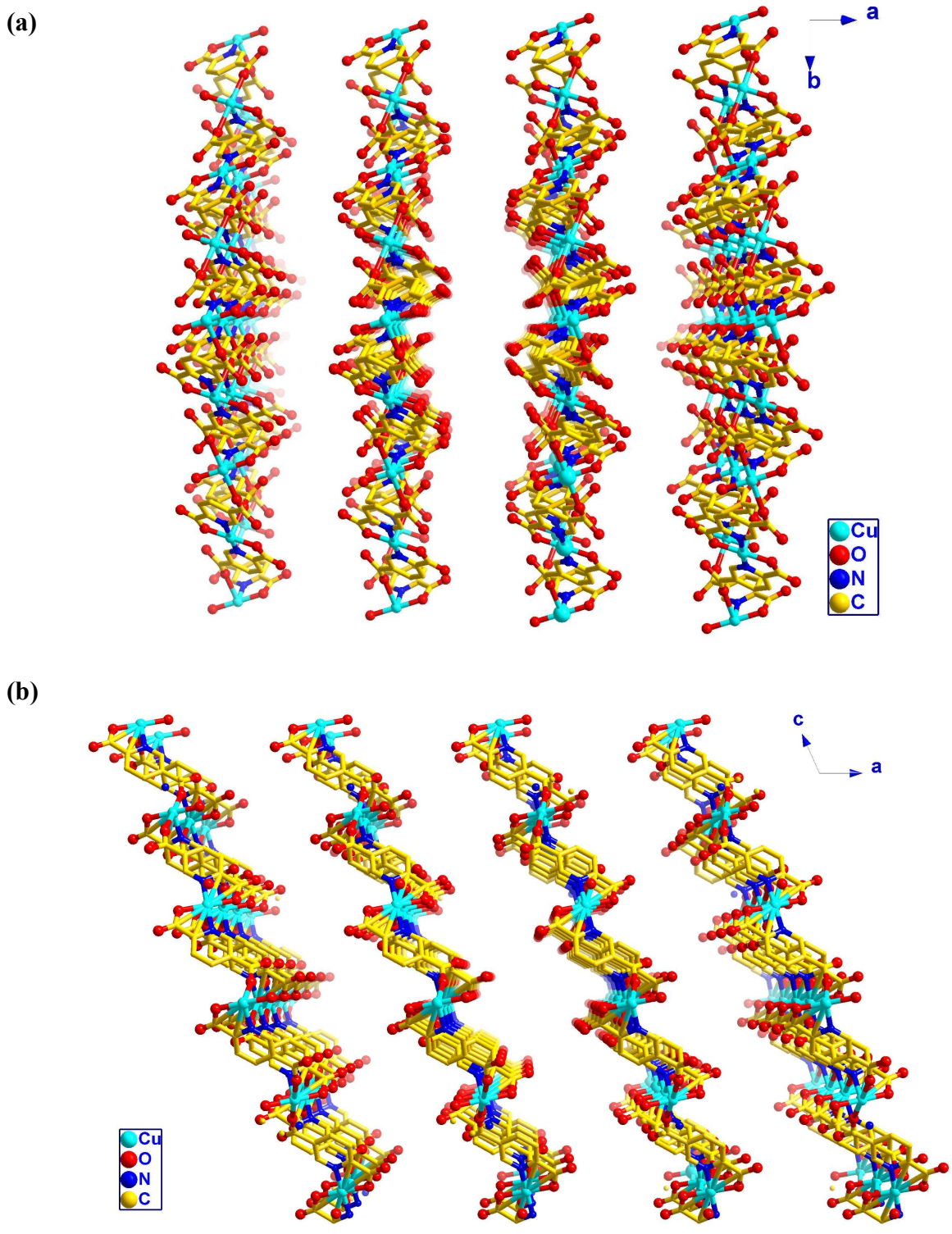


Figure S2. (a) Arrangement of 2D polymers of **1** along c-axis (b) Arrangement of 2D polymers of **1** along b-axis.

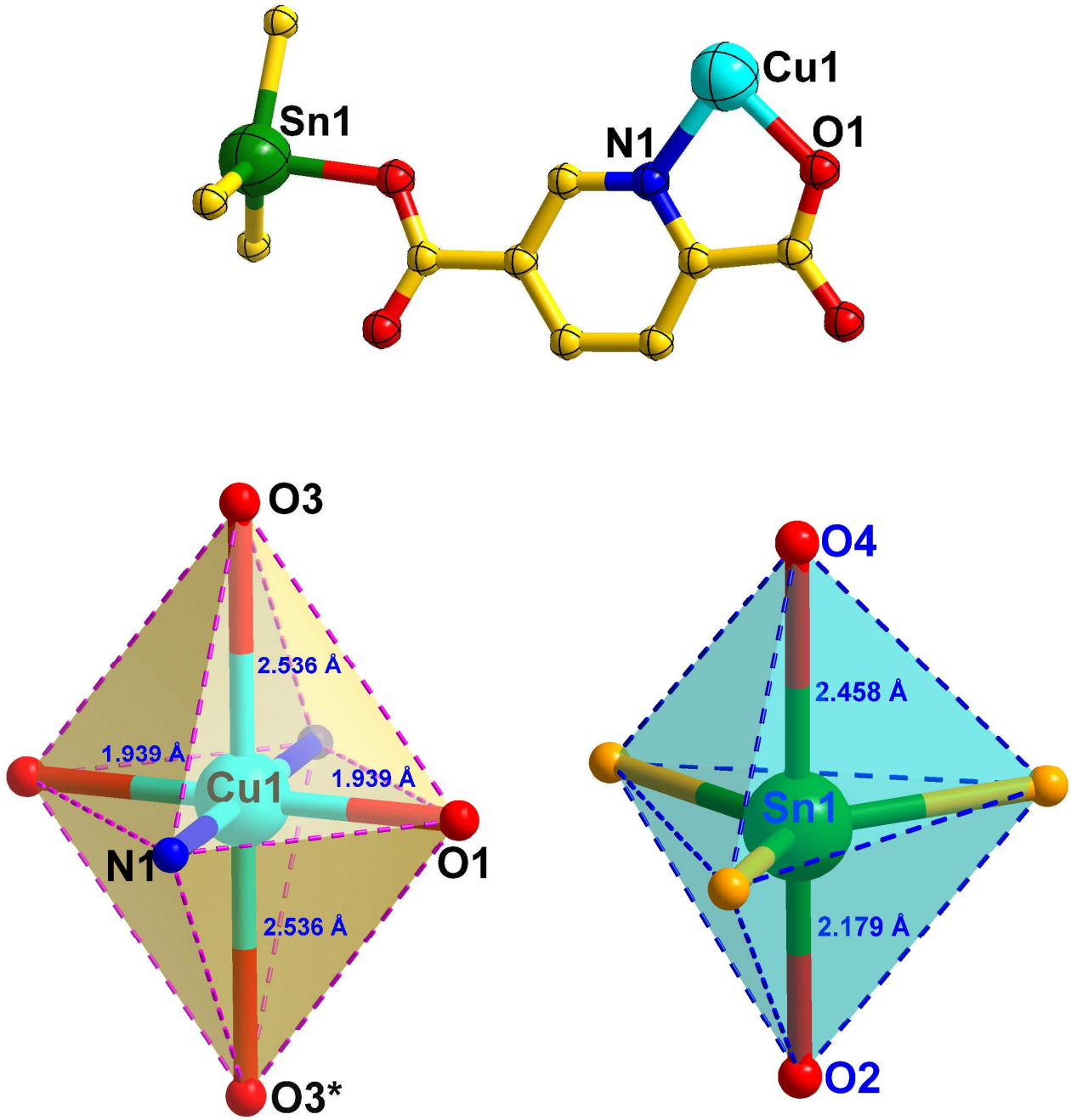


Figure S3. (a) Asymmetric unit of **2** (b) Geometry around Cu(II) in **2** (c) Geometry around tin centre in **2**.

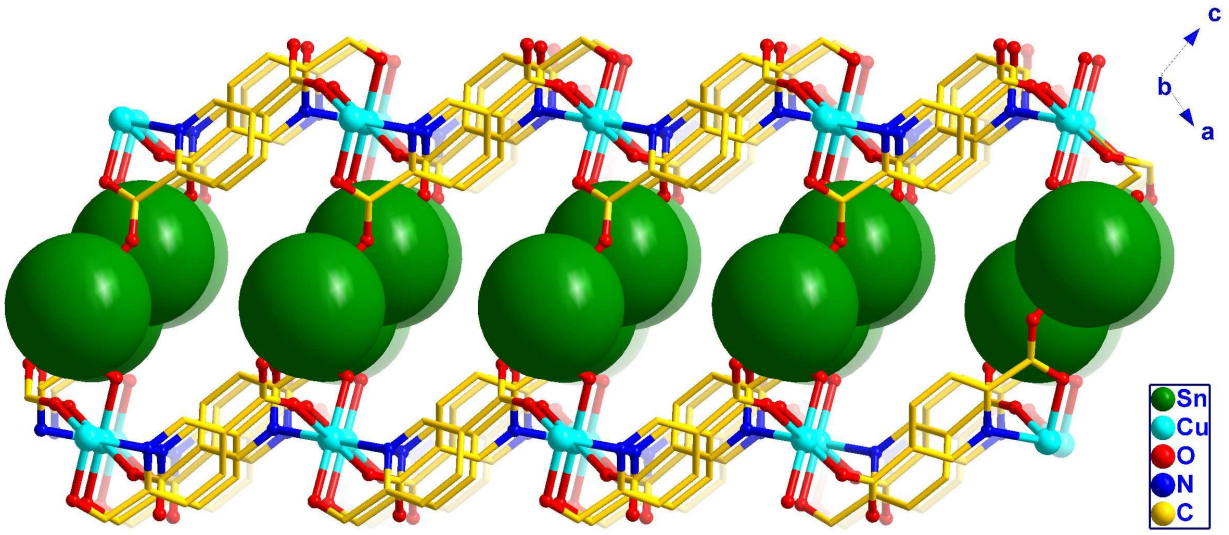
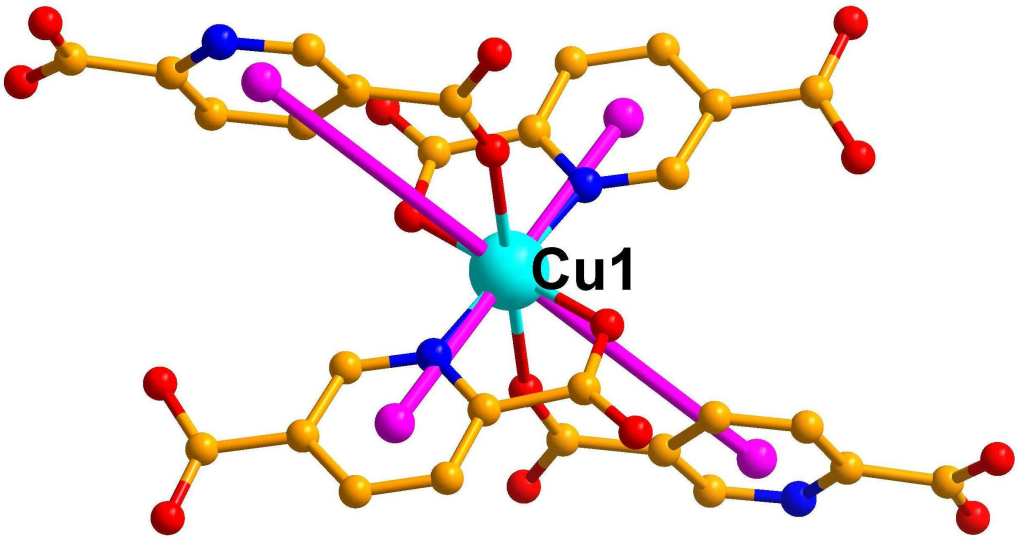


Figure S4. Me_3Sn motifs as a glue between two 2D layers containing copper in **2** (methyl groups are deleted for clarity).

(a)



(b)

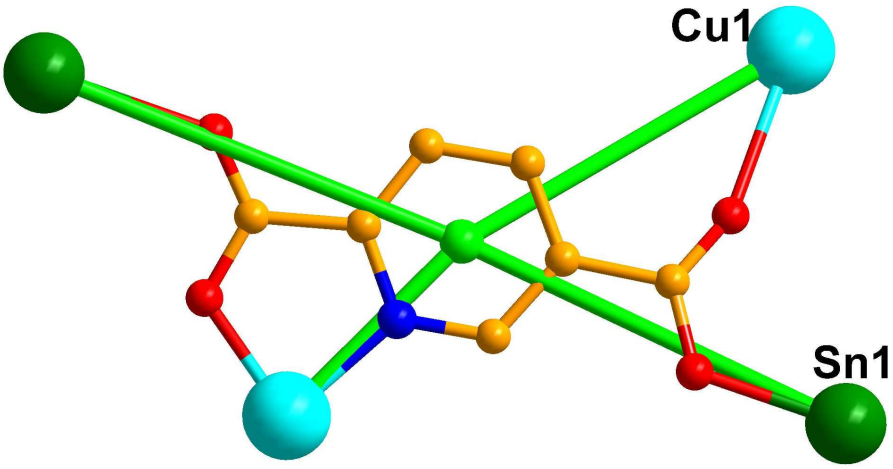


Figure S5. (a) Cu(II) centered 4-connected node (b) Ligand centered 4-connected node for the ***sqc*** topological net of compound **2**.

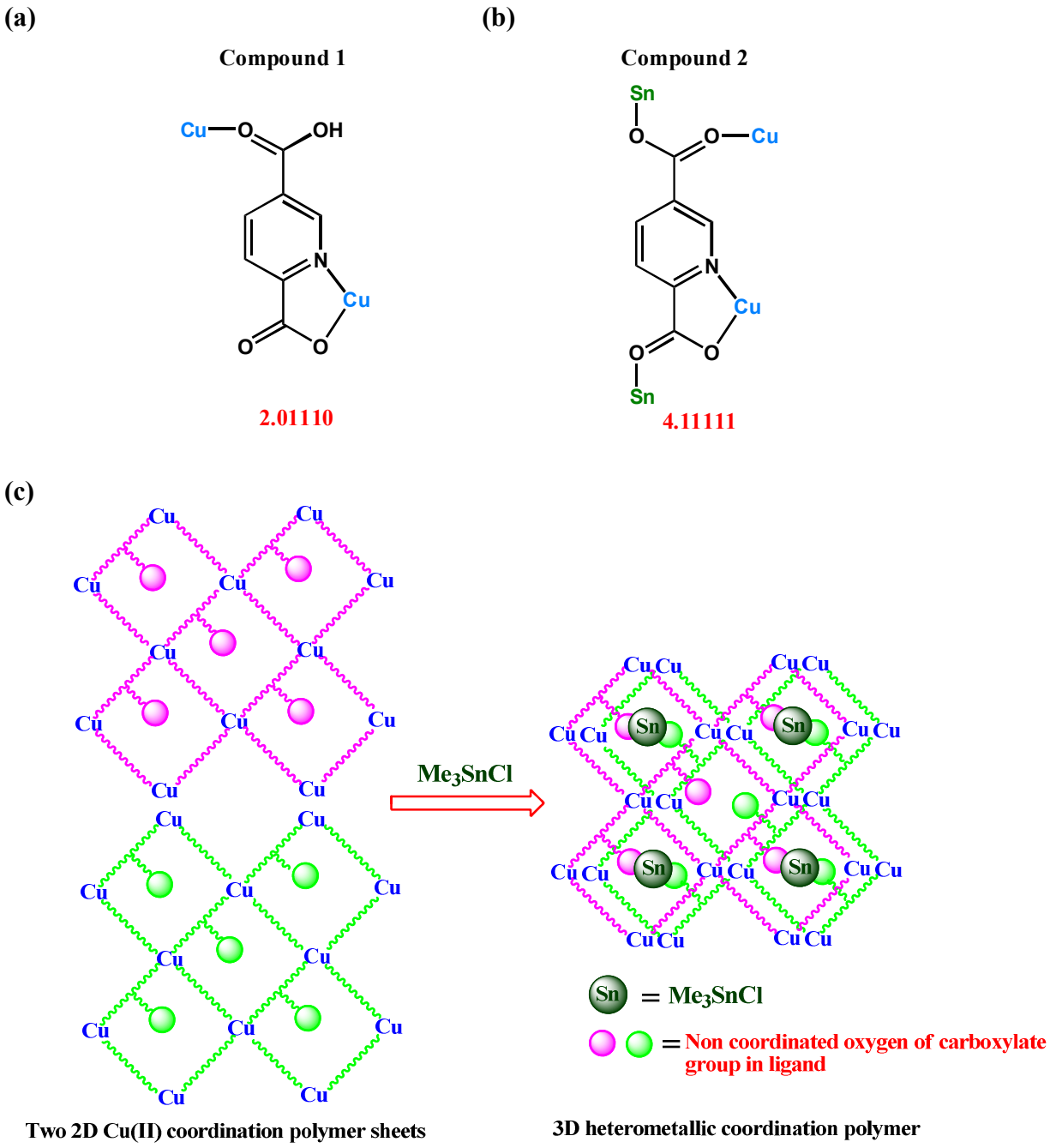


Chart S2. (a) Coordination mode of ligand LH^- in compound **1** (b) Coordination mode of ligand L^{2-} in compound **2** (Harris notation used as per reference 3) (c) Schematic presentation of step-wise synthesis of 3D heterometallic coordination polymer from 2D homometallic coordination polymer.

(5) Coxall, R. A.; Harris, S. G.; Henderson, D. K.; Parsons, S.; Tasker, P. A.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **2000**, 2349.

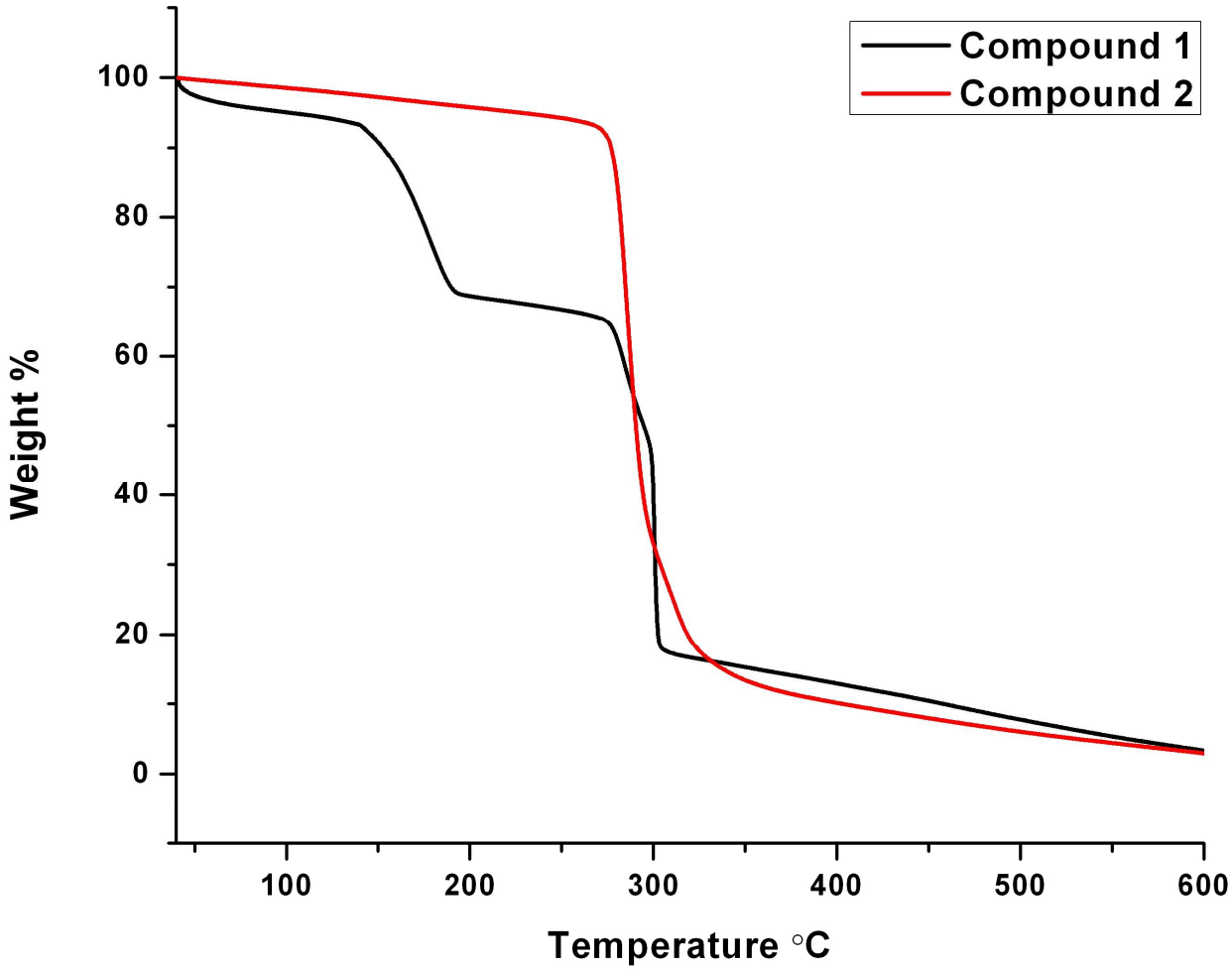


Figure S6. Thermogravimetric curve of compounds **1**-**2**.

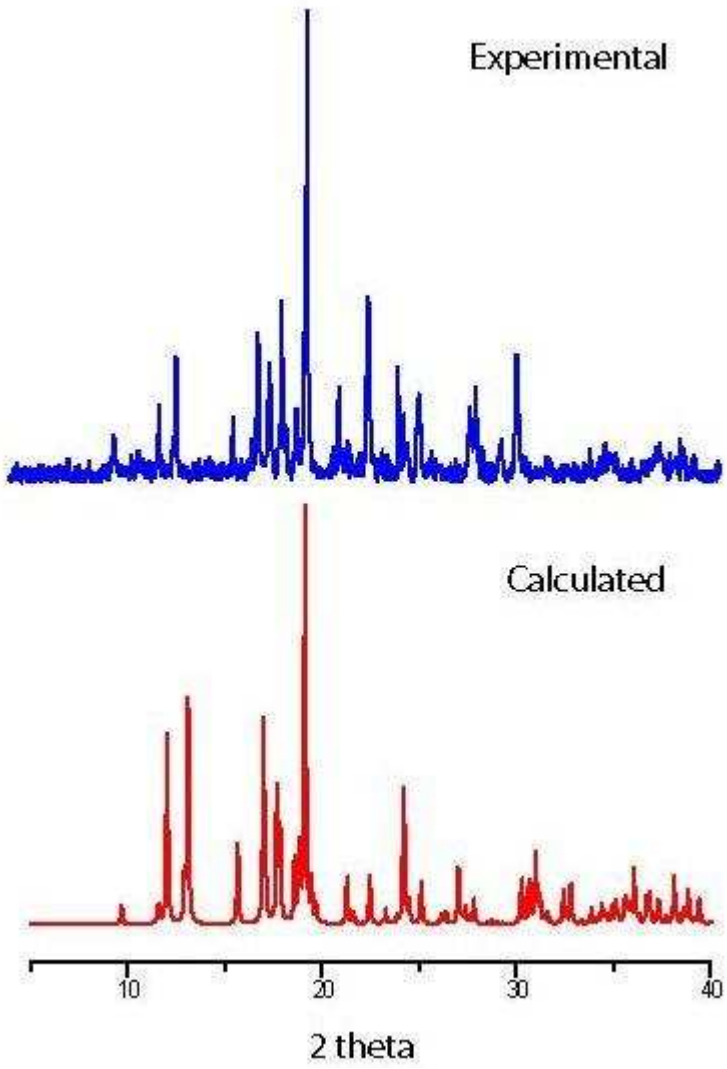


Figure S7. Calculated and experimental PXRD of compound **2**.

Table 1. Crystal data and structure refinement parameters of **1-2**

Parameters	**1**	**2**
Empirical formula	C14 H8 Cu N2 O8	C20 H24 Cu N2 O8 Sn2
Formula weight	395.77	721.33
Temperature	293(2) K	293(2)K
Wavelength	0.71069Å	0.71069 Å
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 12.460(5)Å	a = 10.901(5)Å
	b = 9.968(5)Å	b = 10.346(5) Å
	c = 14.021(5)Å	c = 11.834(5) Å
	α = 90°	α = 90 °
	β = 114.069(5)°	β = 107.066(5)°
	γ = 90°	γ = 90 °
Volume	1590.0(12)Å^3	1275.9(10)Å^3
Z, Calculated density	2, 0.827Mg/m^3	2, 1.878Mg/m^3
Absorption coefficient	0.710mm^{-1}	2.813 mm^{-1}
F(000)	398	702
Crystal size	0.15 x 0.11 x 0.07 mm^3	0.22 x 0.18 x 0.15 mm^3
θ range for data collection	4.09 to 25.02°.	2.23 to 25.50°.
Limiting indices	-14<=h<=10, -11<=k<=11, -14<=l<=16	-13<=h<=12, -12<=k<=9, -11<=l<=14
Reflections collected / unique	7981 / 2758 [R(int) = 0.0503]	6695 / 2358 [R(int) = 0.0275]
Completeness to theta	98.4%	99.2 %
Data / restraints / parameters	2758 / 54 / 109	2358 / 0 / 154
Goodness-of-fit on F^2	1.151	1.094

Final R indices [I >2σ(I)]	R_1 = 0.0722, wR_2 = 0.2320	R_1 = 0.0309, wR_2 = 0.0749
R indices (all data)	R_1 = 0.0853, wR_2 = 0.2445	R_1 = 0.0368, wR_2 = 0.0895
Largest diff. peak and hole	2.109 and -0.630 e.Å^{-3}	1.317 and -0.587 e.Å^{-3}

Table 2. Bond length **(Å)** and bond angles **(°)** of compound **1**.

Bond length (Å)		**Bond angle (°)**	
Cu(1)- O(1)	1.960(3)	O(1)-Cu(1)-O(1)#1	180.0
Cu(1)- O(1)#1	1.960(3)	O(1)-Cu(1)-N(1)	83.10(14)
Cu(1)- N(1)	1.981(4)	O(1)#1-Cu(1)-N(1)	96.90(14)
Cu(1)- N(1)#1	1.981(4)	O(1)-Cu(1)-N(1)#1	96.90(14)
O(1)- C(1)	1.241(6)	O(1)#1-Cu(1)-N(1)#1	83.10(14)
O(2)- C(1)	1.229(6)	N(1)-Cu(1)-N(1)#1	179.998(2)
O(3)- C(7)	1.231(7)	C(1)-O(1)-Cu(1)	115.4(3)
N(1)- C(2)	1.347(6)	C(2)-N(1)-C(6)	118.5(4)
N(1)- C(6)	1.348(6)	C(2)-N(1)-Cu(1)	111.5(3)
C(1)- C(2)	1.524(7)	C(6)-N(1)-Cu(1)	130.0(3)
C(2)- C(3)	1.374(6)	O(2)-C(1)-O(1)	127.4(4)
C(3)- C(4)	1.373(7)	O(2)-C(1)-C(2)	116.9(4)
C(4)- C(5)	1.405(7)	O(1)-C(1)-C(2)	115.7(4)
C(5)- C(6)	1.384(7)	N(1)-C(2)-C(3)	121.7(4)
C(5)- C(7)	1.521(8)	N(1)-C(2)-C(1)	114.1(4)
C(7)- O(4)	1.210(9)	C(3)-C(2)-C(1)	124.2(4)
C(7)- O(4A)	1.377(8)	C(4)-C(3)-C(2)	120.0(5)
		C(3)-C(4)-C(5)	119.4(4)
		C(6)-C(5)-C(4)	117.2(5)
		C(6)-C(5)-C(7)	121.1(5)
		C(4)-C(5)-C(7)	121.7(4)
		N(1)-C(6)-C(5)	123.3(4)
		O(4)-C(7)-O(3)	122.7(6)
		O(4)-C(7)-O(4A)	31.0(4)

		O(3)-C(7)-O(4A)	124.8(5)
		O(4)-C(7)-C(5)	115.6(6)
		O(3)-C(7)-C(5)	118.8(5)
		O(4A)-C(7)-C(5)	114.3(5)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z+1

Table 3. Bond length **(Å)** and bond angles **(°)** of compound **2**.

Bond length (Å)		**Bond angle (°)**	
Sn(1)-C(10)	2.121(4)	C(10)-Sn(1)-C(9)	117.9(2)
Sn(1)-C(9)	2.126(5)	C(10)-Sn(1)-C(8)	118.83(19)
Sn(1)-C(8)	2.128(5)	C(9)-Sn(1)-C(8)	122.53(18)
Sn(1)-O(2)	2.178(3)	C(10)-Sn(1)-O(2)	89.38(15)
Sn(1)-O(4)	2.459(3)	C(9)-Sn(1)-O(2)	91.98(16)
Cu(1)-O(1)	1.938(3)	C(8)-Sn(1)-O(2)	97.30(16)
Cu(1)-O(1)#1	1.939(3)	C(10)-Sn(1)-O(4)	90.59(15)
Cu(1)-N(1)	1.981(3)	C(9)-Sn(1)-O(4)	87.47(15)
Cu(1)-N(1)#1	1.981(3)	C(8)-Sn(1)-O(4)	83.28(15)
O(1)-C(1)	1.274(5)	O(2)-Sn(1)-O(4)	179.36(11)
O(2)-C(2)	1.293(5)	O(1)-Cu(1)-O(1)#1	179.999(1)
O(3)-C(2)	1.230(5)	O(1)-Cu(1)-N(1)	83.69(13)
O(4)-C(1)#2	1.246(5)	O(1)#1-Cu(1)-N(1)	96.31(13)
N(1)-C(7)	1.320(6)	O(1)-Cu(1)-N(1)#1	96.31(13)
N(1)-C(3)	1.343(6)	O(1)#1-Cu(1)-N(1)#1	83.69(13)
C(1)-O(4)#3	1.246(5)	N(1)-Cu(1)-N(1)#1	180.00(16)
C(1)-C(3)	1.514(6)	C(1)-O(1)-Cu(1)	115.0(3)
		C(2)-O(2)-Sn(1)	119.6(3)
		C(1)#2-O(4)-Sn(1)	133.0(3)
		C(7)-N(1)-C(3)	119.7(4)
		C(7)-N(1)-Cu(1)	128.7(3)
		C(3)-N(1)-Cu(1)	111.5(3)
		O(4)#3-C(1)-O(1)	125.7(4)
		O(4)#3-C(1)-C(3)	118.9(4)

		O(1)-C(1)-C(3)	115.5(4)
		O(3)-C(2)-O(2)	125.9(4)
		O(3)-C(2)-C(6)	119.7(4)
		O(2)-C(2)-C(6)	114.4(4)
		N(1)-C(3)-C(4)	121.8(4)
		N(1)-C(3)-C(1)	114.3(4)
		C(4)-C(3)-C(1)	123.9(4)
		C(3)-C(4)-C(5)	118.9(4)
		C(4)-C(5)-C(6)	119.9(4)
		C(5)-C(6)-C(7)	117.7(4)
		C(5)-C(6)-C(2)	121.7(4)
		C(7)-C(6)-C(2)	120.5(4)
		N(1)-C(7)-C(6)	121.9(4)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z #2 x,y,z+1

#3 x,y,z-1