Electronic Supplementary Information for Dalton Transactions

Supramolecular copper(I) halide complexes of O_2S_2X (X=S, O and NH) macrocycles exhibiting dinuclear, 1D- and 2D-coordination polymeric structures

Minhye Jo,[a] Joobeom Seo,[a] Leonard F. Lindoy*[b] and Shim Sung Lee*[a]

[a]Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, S. Korea
[b]School of Chemistry, The University of Sydney, NSW 2006, Australia

Experimental Section

Reagents and Instrumentation

All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. Mass spectra were obtained on a JEOL JMS-700 spectrometer. The FT-IR spectra were measured with a Shimadzu FT-IR 8100 spectrometer. The elemental analysis was carried out on a LECO CHNS-932 elemental analyzer.

Crystallographic Structure Determinations

All data were collected on a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo K_α radiation (λ = 0.71073 Å). The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 45 collected frames) using the SMART program. The intensity data were processed using the Saint Plus program. All of the calculations for the structure determination were carried out using the SHELXTL package (version 6.22).[S1] Absorption corrections were applied by using XPREP and SADABS.[S2] In most cases, hydrogen positions were input and refined in a riding manner along with the attached carbons. Relevant crystal data collection and refinement data for the crystal structures of **1**, **2** and **3** are summarised in Table S1.

The structural refinement of **3** was further performed after modification of the data for the noncoordinated lattice solvent molecules using the *SQUEEZE* routine in the PLATON software package,[S3] which led to a better refinement and data convergence. Refinement of the structure converged at a final value of R_1 = 0.0577 and wR_2 = 0.1522 for 7112 reflections with $I > 2\sigma(I)$, and R_1 = 0.0802 and wR_2 = 0.2213 for all 19699 reflections. The largest difference between a peak and a hole was 1.844 and -1.696 e·Å^{-3}, respectively, which can be attributed to ghosts of the heavy Cu atom because these peaks are located at short distances from Cu (1.59 and 0.17 Å, respectively).

References

S1. Bruker, SMART and SAINT: *Area Detector Control and Integration Software Ver. 6.22*; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 2001.

S2. Bruker, SHELXTL: *Structure Determination Programs Ver. 5.16*; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 2000.

S3. A. L. Spek, PLATON program. *Acta Crystallogr. Sect. A*, 1990, **46**, 194.

Table S1. Crystal and experimental data

	1	**2**	**3**
Formula	$C_{40}H_{48}Cu_2I_2O_4S_6$	$C_{44}H_{54}Cl_2Cu_2N_2O_6S_4$	$C_{40}H_{50}Cu_4I_4N_2O_4S_4$
Formula weight	1166.02	1033.11	1512.82
Temperature (K)	173(2)	298(2)	298(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	*C*2/*c*
Z	1	1	4
a (Å)	8.9156(8)	9.7044(11)	14.1994(13)
b (Å)	9.5412(9)	10.1375(11)	19.6855(17)
c (Å)	13.4975(13)	12.7131(14)	24.487(2)
α (º)	81.535(2)	104.412(2)	90
β (º)	80.153(2)	99.681(2)	106.85
γ (º)	77.857(2)	94.493(2)	90
V (Å^3)	1098.55(18)	1184.6(2)	6550.8(10)
D_x (g/cm^3)	1.763	1.448	1.534
$2\theta_{max}$	52	52	54
R	0.0351	0.0378	0.0577
wR	0.0622	0.1109	0.1522
GOF	1.053	1.141	0.970
Data / restraints / parameters	4224 / 0 / 244	4504 / 0 / 271	7112 / 0 / 262
Absorption Correction	Empirical SADABS	Empirical SADABS	Empirical SADABS
Diffractometer	Bruker SMART CCD system	Bruker SMART CCD system	Bruker SMART CCD system
Structure determination	SHELXTL	SHELXTL	SHELXTL
Refinement	full-matrix	full-matrix	full-matrix

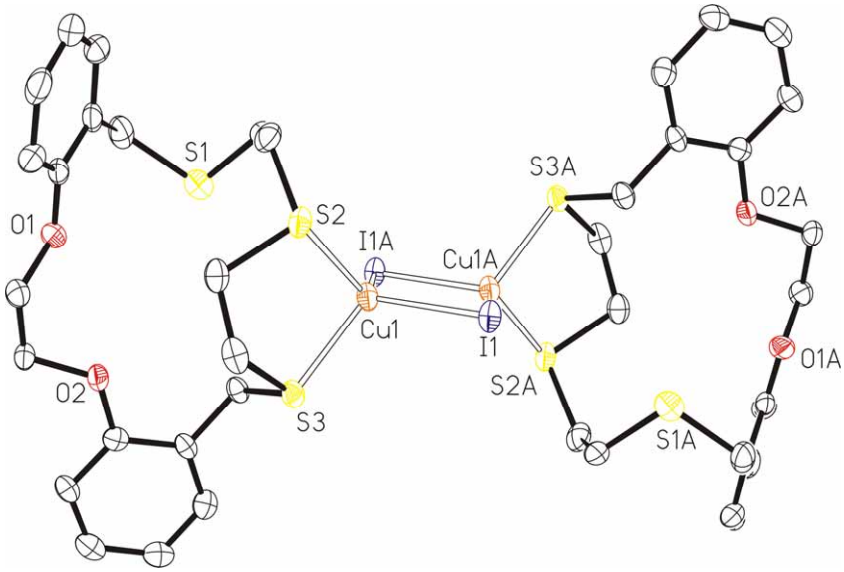


Fig. S1 Crystal structure of **1**, $[(Cu_2I_2)(\mathbf{L}^1)_2]$. Hydrogen atoms are omitted. Selected bond distances (Å) and bond angles (°): Cu1-S2 2.330(1), Cu1-S3 2.363(1), Cu1-I1A 2.589(7), Cu1-I1 2.663(7), Cu1A-I1 2.589(7), Cu1···Cu1A 2.683(1), S2-Cu1-S3 91.06(5), S2-Cu1-I1 102.78(4), S2-Cu1-I1A 120.62(4), S2-Cu1-Cu1A 135.31(5), S3-Cu1-I1 106.94(4), S3-Cu1-I1A 112.91(4), I1-Cu1-I1A 118.57(2), S3-Cu1-Cu1A 131.66(5), I1A-Cu1-Cu1A 160.65(2), I1-Cu1-Cu1A 57.92(2), Cu1A-I1-Cu1 61.43(2). [Symmetry code A: $-x+1, -y+2, -z+1$].

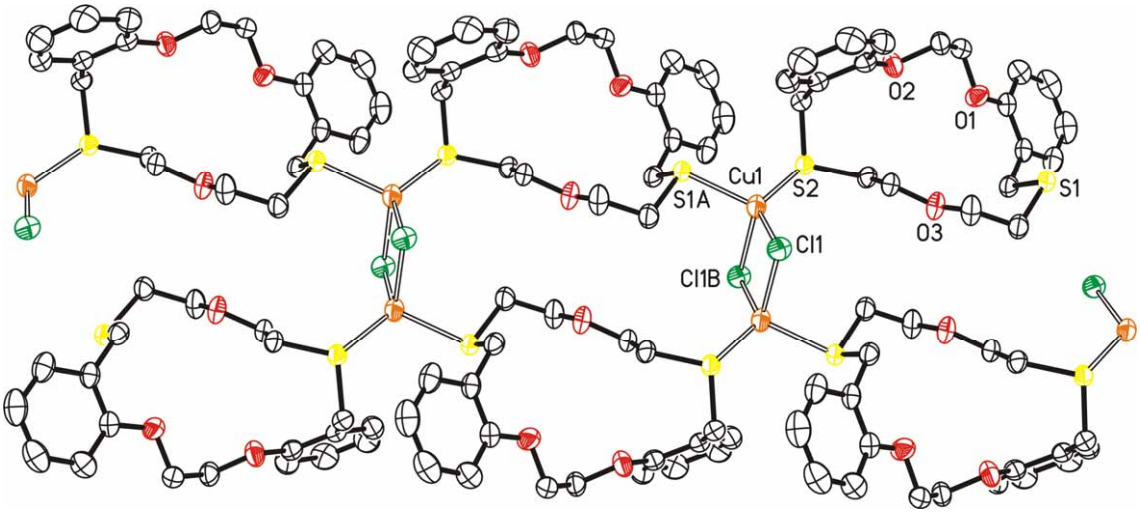


Fig. S2 Crystal structure of **2**, $[(Cu_2Cl_2)(\mathbf{L}^2)_2]_n$. Hydrogen atoms and solvent molecules are omitted. Selected bond distances (Å) and bond angles (°): Cu1-S2 2.260(9), Cu1-Cl1 2.313(9), Cu1-S1A 2.314(9), Cu1-Cl1B 2.516(9), S2-Cu1-Cl1 126.52(3), S2-Cu1-S1A 113.29(3), S2-Cu1-Cl1B 100.93(3), Cl1-Cu1-S1A 109.32(3). [Symmetry codes A: $x, y-2, z$; B: $-x+1, -y+1, -z+1$].

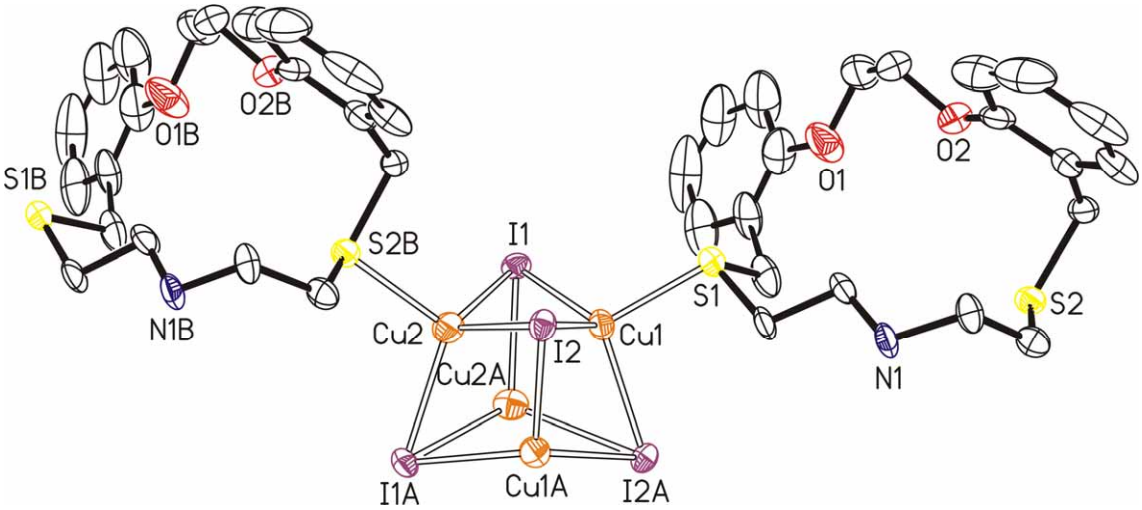
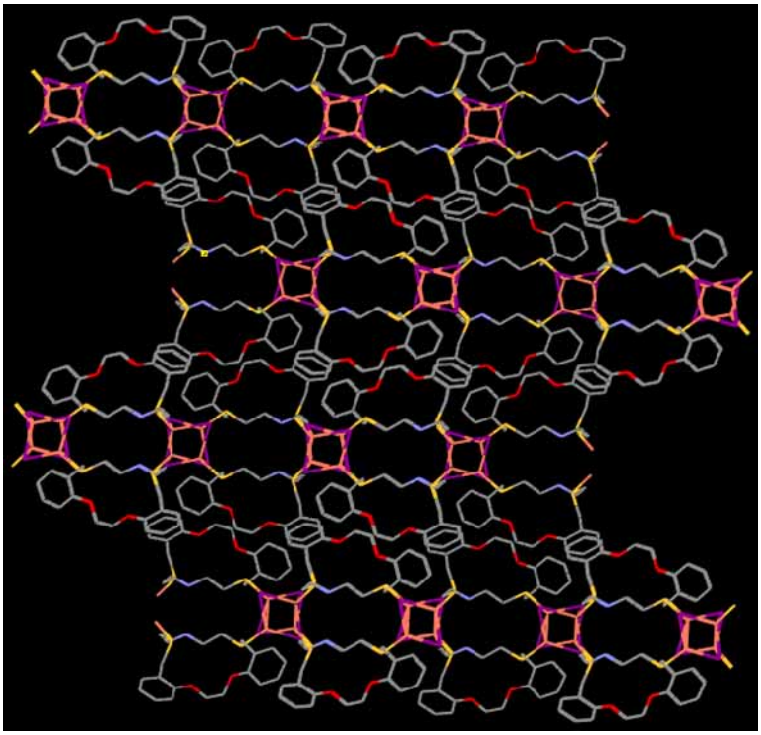
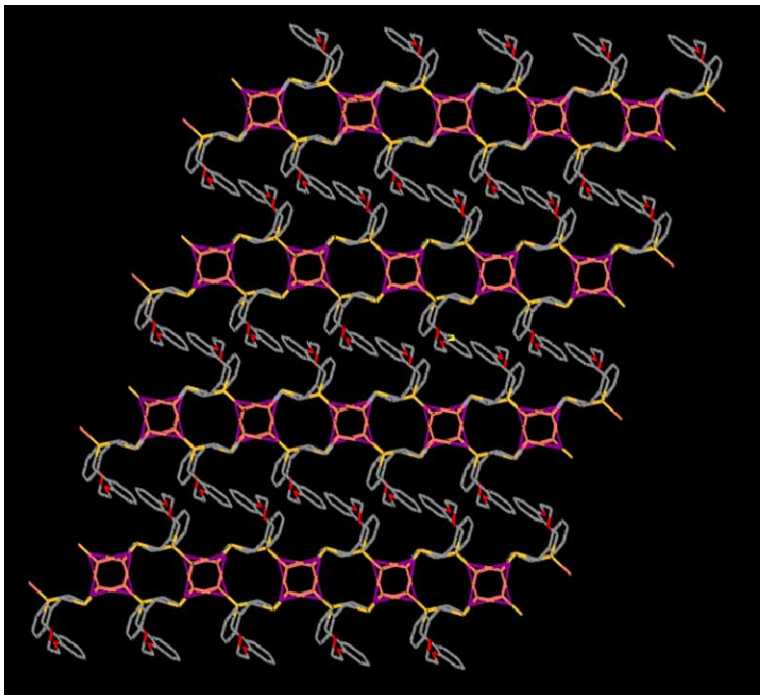


Fig. S3 Crystal structure of **3**, $[(Cu_4I_4)(\mathbf{L}^3)_2]_n$. Hydrogen atoms are omitted. Selected bond distances (Å) and bond angles (°): Cu1-S1 2.317(2), Cu1-I1 2.616(1), Cu1-I2 2.677(1), Cu1-I2A 2.707(1), Cu2-S2B 2.340(2), Cu2-I1 2.638(1), Cu2-I1A 2.611(1), Cu2-I2 2.780(1), Cu2-Cu1A 2.791(2), Cu1···Cu1A 2.7321(19), Cu1···Cu2 2.7701(14), Cu1···Cu2A 2.7914(15), Cu2···Cu2A 2.650(2), Cu1A-I2 2.707(1), Cu2A-I1 2.611(1), S1-Cu1-I1 115.34(6), S1-Cu1-I2 100.07(6), I1-Cu1-I2 113.20(4), S1-Cu1-I2A 103.87(6), I1-Cu1-I2A 110.93(4), I2-Cu1-I2A 112.73(4), I1-Cu2-S2B 109.71(6), I1-Cu2- I1A 115.66(4), I1A-Cu2-S2B 109.97(6), I2-Cu2-S2B 102.61(7), I2-Cu2-I1A 108.81(4), I1-Cu2-I2 109.27(4), Cu1-I1-Cu2A 64.55(3), Cu2-I1-Cu2A 60.64(4), Cu1-I1-Cu2 63.64(3), Cu1-I2-Cu1A 60.99(4), Cu1-I2-Cu2 60.98(3). [Symmetry codes A: $-x+1, y, -z+1/2$; B: $x-1/2, y-1/2, z$].



(a)



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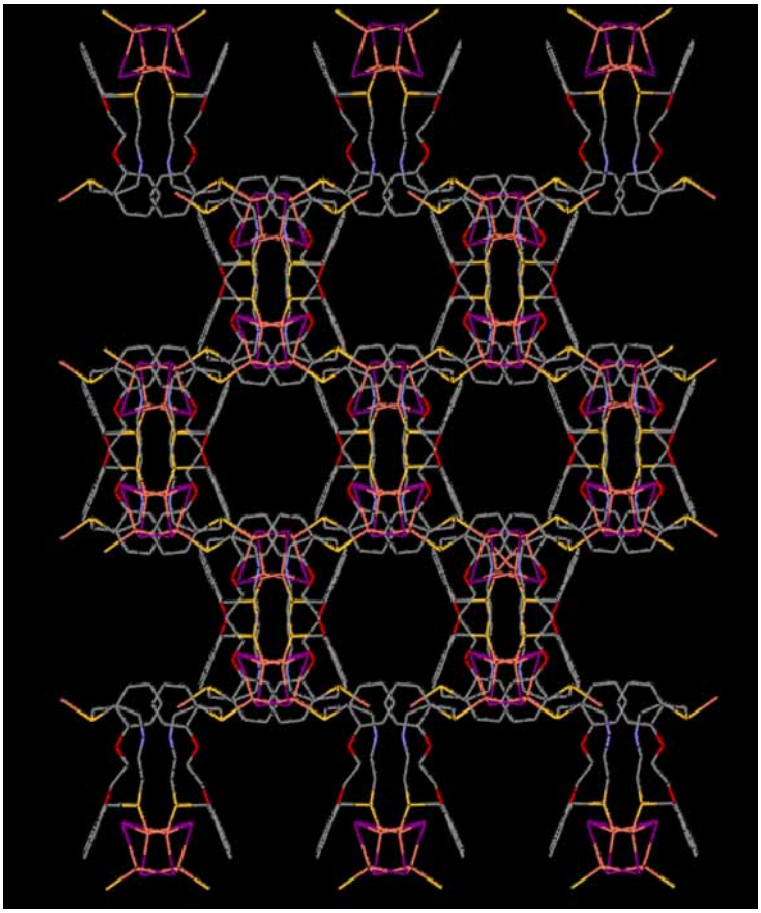

(c)

Fig. S4 Packing structures of **3**; (a) *a*-axis projection, (b) *b*-axis projection, and (c) *c*-axis projection.