

# 1D Copper(I) Coordination Polymer [Cu(Clba<sub>2</sub>-1,2-pn)(NCS)]<sub>n</sub>: Synthesis of Microparticles and Single Crystals, Crystal Structure, and Thermal Study

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**ABSTRACT:** *In this research, 1D four-coordinate copper(I) coordination Polymer [Cu(Clba<sub>2</sub>-1,2-pn)(NCS)]<sub>n</sub> (**1**) with thiocyanate anion as bridging ligand, where Clba<sub>2</sub>-1,2-pn = N,N'-bis(2,4-chlorobenzylidene)propane-1,2-diamine), was synthesized by slow evaporation of solvent at room temperature and characterized by elemental analysis (CHN) and single-crystal X-ray diffraction. Microparticles of **1** were prepared by an ultrasonic bath assisted synthesis and characterized by Scanning Electron Microscopy (SEM) and elemental analysis. Thermal stability of **1** was studied by ThermoGravimetry (TG) and Differential Thermal Analysis (DTA). The structure of **1** consists of 1D polymeric chain in which copper(I) ions are bridged by two thiocyanate groups in an end-to-end fashion, with Cu...Cu separation 5.686(4) Å.*

**KEYWORDS:** *Single-crystal X-ray diffraction; four-coordinate; 1D copper(I) coordination Polymer; Microparticles.*

## INTRODUCTION

Schiff bases {R<sub>1</sub>R<sub>2</sub>-C=N-(CH<sub>2</sub>)<sub>n</sub>-C=N-R<sub>1</sub>R<sub>2</sub>} are important ligands because they offer variable bonding modes (chelating and bridging modes) and structural diversity when coordinated, e.g., to copper(I) halides and pseudohalides [1-11]. Recently, preparation of coordination polymers of copper(I) has attracted considerable interest [6-11] due to their application as precursors for the preparation of CuO micro- and

nanoparticles [8]. Different flexible Schiff base ligands [6-9], and thiocyanate ions [10,11] have been widely used for the preparation of copper(I) coordination polymers. The pseudohalide NCS<sup>-</sup> is known to coordinate to copper(I) ion in an end-to-end bridging mode to form 1D copper(I) coordination polymers [10,11].

In continuation of our research of copper(I) coordination compounds, in this paper, we report reaction

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of Clba<sub>2</sub>-1,2-pn with CuNSC and characterize the resulting complex (Scheme 1).

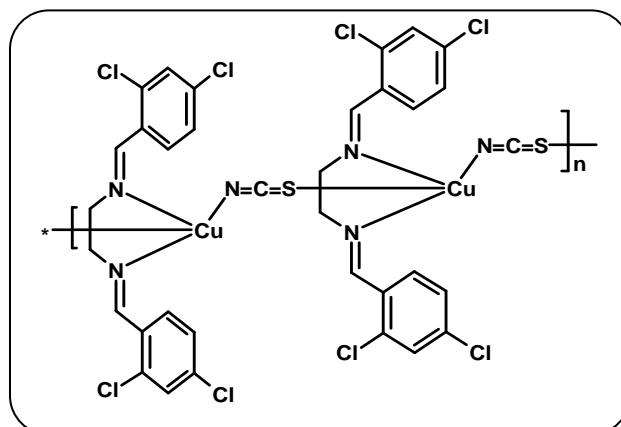
## EXPERIMENTAL SECTION

### Materials and methods

All materials were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer, and results agreed with calculated values. The TG/DTA was performed on a Perkin Elmer TG/DTA lab system 1 (Technology by SII) in an argon atmosphere with a heating rate of 20 °C/min in the temperature span of 25–700 °C. The Scanning Electron Microscopy (SEM) images of complexes were obtained from a Philips XL-30ESEM.

### X-ray structure determination

Single crystal of the dimensions 0.42 mm × 0.05 mm × 0.02 mm of **1** was chosen for X-ray diffraction study. The experiment was done at 95K on a four-circle diffractometer SuperNova of Rigaku Oxford Diffraction using Cu-K $\alpha$  ( $\lambda = 1.54184 \text{ \AA}$ ) microfocus mirror-collimated source and a CCD detector Atlas S2. The data reduction, scaling and absorption correction (numerical absorption correction based on gaussian integration over a multifaceted crystal model) was done using CrysAlis PRO software [12]. The crystal structure was easily solved by charge flipping with program SUPERFLIP [13] and refined with the Jana2006 program package [14] by full-matrix least-squares technique on  $F^2$ . Disorder of the chain connecting N1 and N2 was described using the bond restraints keeping the distances in the minor occupied configuration the same as distances in the major occupied part. We also found a disorder for one of the chlorine atoms, Cl13, and this was described by splitting of the chlorine position. The molecular structure plots were prepared by Diamond 4.0 [15]. All hydrogen atoms were discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice H atoms bonded to C were kept in ideal positions with C–H = 0.96 Å and with  $U_{\text{iso}}(\text{H})$  set to  $1.2U_{\text{eq}}(\text{C})$ . No hydrogen atoms were found on nitrogen. All non-hydrogen atoms were refined using harmonic refinement. Crystallographic data and details of the data collection and structures solution and refinements are listed in Table 1.



Scheme 1: Chemical structure of  $[\text{Cu}(\text{Clba}_2\text{-1,2-pn})(\text{NCS})]_n$  (**1**).

Table 1: Crystallographic data and structural refinement details

Chemical formula	$\text{C}_{18}\text{H}_{14}\text{Cl}_4\text{Cu}_1\text{N}_3\text{S}_1$
Formula weight	509.7
Crystal system, space group	Monoclinic, $C2/c$
T, K	120.0 (1)
$a$ , Å	48.008 (2)
$b$ , Å	5.6862 (2)
$c$ , Å	15.2151 (12)
$\alpha$ , deg	90
$\beta$ , deg	106.230 (5)
$\gamma$ , deg	90
$V$ , Å <sup>3</sup>	3987.9 (4)
Z	8
$\mu$ , mm <sup>-1</sup>	7.53
$R_{\text{int}}$	0.082
S	1.61
Measured reflections	12065
Independent reflections	3509
Parameters	255
Reflections with $I > 3\sigma(I)$	2860
$R(F^2 > 3\sigma(F^2))$	0.061
$wR(F^2)$	0.149
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ , e Å <sup>-3</sup>	0.87, -0.57
$T_{\text{min}}, T_{\text{max}}$	0.299, 0.862
Size, mm	0.42 × 0.05 × 0.02

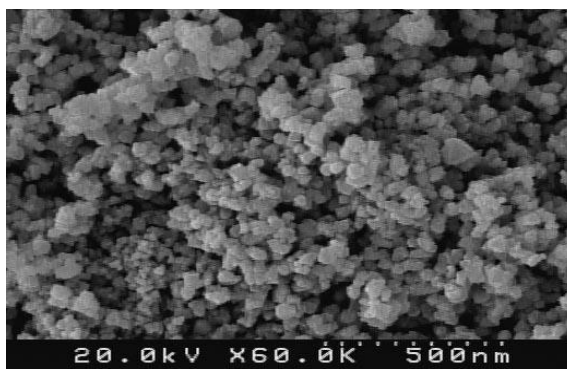


Fig. 1: SEM image of micro-sized of 1.

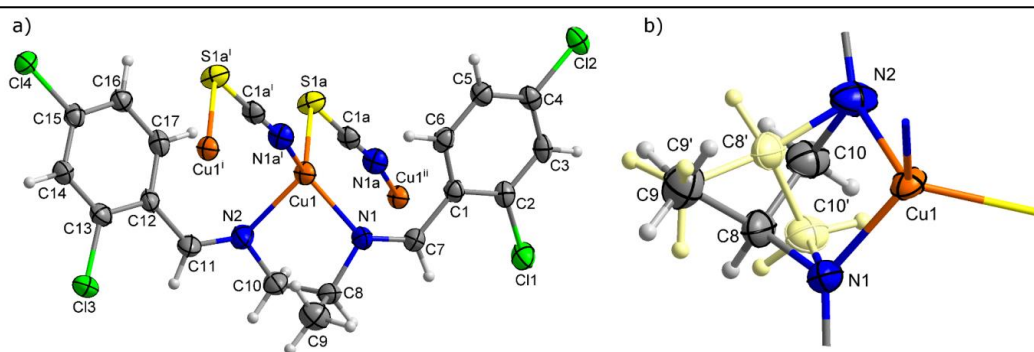


Fig. 2: a) Asymmetric unit of 1 extended with symmetry-related SCN atoms connecting the complex to the neighboring molecules. Symmetry codes: (i)  $x, y+1, z$ ; (ii)  $x, y-1, z$ . b) Details of the disordered chain connecting N1 and N2. The minor occupied chains with refined occupancy 0.117(9) is visualized in light yellow color.

### Preparation of [Cu(Clba<sub>2</sub>-1,2-pn)(NCS)]<sub>n</sub> (1)

To a solution of Clba<sub>2</sub>-1,2-pn (0.01 mmol) in CH<sub>3</sub>CN (5 mL) positioned in an ultrasonic bath, a solution of CuNCS (0.1 mmol) in CH<sub>3</sub>CN (5 mL) was added and displayed to ultrasonund for 30 min. The obtained precipitate was filtered off and washed with Et<sub>2</sub>O. Anal. Calcd. for C<sub>18</sub>H<sub>14</sub>Cl<sub>4</sub>Cu<sub>1</sub>N<sub>3</sub>S<sub>1</sub>: C, 42.38.; H, 2.75.; N, 8.24%. Found; C, 42.43.; H, 2.69.; N, 8.31%. Yellow-orange single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature for several days.

### RESULTS AND DISCUSSION

Reaction of Clba<sub>2</sub>-1,2-pn with copper(I) thiocyanate in 1:1 molar ratio in an ultrasonic bath formed insoluble copper(I) coordination polymer [Cu(Clba<sub>2</sub>-1,2-pn)(NCS)]<sub>n</sub> (1). The morphology, structure, and size of the powder of 1 were investigated by SEM. The SEM image (Fig. 1) indicates the formation of partially

agglomerated uniformly sized particles on the border between the micro and nanoscale.

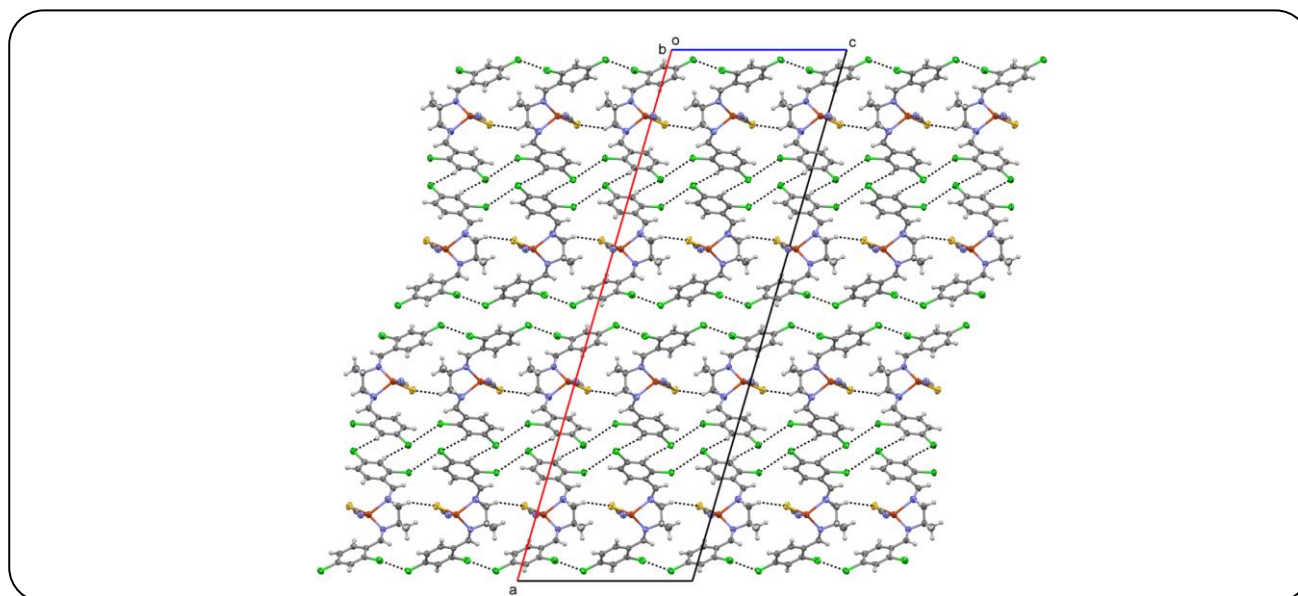
The molecular structure of 1 is shown in Fig. 2. Selected bond distances and angles are shown in Table 2 and Table 3. Single-crystal X-ray reveals that 1 crystallizes in the monoclinic system with *C2/c* space group. The coordination sphere around the copper(I) ion consists of two imine nitrogen atoms from one Schiff base unit, one sulfur atom and one nitrogen atom from two bridging thiocyanate anions. The copper(I) ion adopts a distorted tetrahedral geometry [11,12]. Each Schiff base unit acts as a bidentate ligand using its imine nitrogen's to form Cu(Clba<sub>2</sub>-1,2-pn) unit, then coordination of two bridging NCS<sup>-</sup> leading to the polymeric copper(I) complex [Cu(Clba<sub>2</sub>-1,2-pn)(NCS)]<sub>n</sub> (1) [11,12]. The distances between copper(I) and coordinated atoms are as follows: Cu1-N1=2.037(4) Å, Cu1-N2 = 2.152(3) Å, Cu1-N1a = 1.917(4) Å, and Cu1-S1a= 2.3215(14) Å bond lengths are similar to those found in the copper(I) coordination

**Table 2: Selected bond distances of 1.**

X–Y	X–Y (Å)	X–Y	X–Y (Å)
Cu1–S1a	2.3215(14)	Cu1–N1	2.037(4)
Cu1–N1a <sup>i</sup>	1.917(4)	Cu1–N2	2.152(3)
S1a–C1a	1.654(5)	N1a–C1a	1.156(6)
N1–C7	1.272(7)	N1–C8	1.498(8)
N2–C10	1.470(8)	N2–C11	1.264(8)

Symmetry code: (i)  $x, y+1, z$ .**Table 3: Selected bond angles of 1.**

X–Y–Z	X–Y–Z (°)	X–Y–Z	X–Y–Z (°)
S1a–Cu1–N1	110.80(13)	S1a–Cu1–N1a <sup>i</sup>	107.64(13)
N1–Cu1–N1a <sup>i</sup>	131.76(17)	S1a–C1a–N1a	178.9(5)
Cu1–S1a–C1a	100.15(17)	Cu1–N1–C7	134.2(4)
Cu1–N1–C8	108.2(3)	C7–N1–C8	116.6(5)
C10–N2–C11	117.8(6)	Cu1 <sup>ii</sup> –N1a–C1a	162.9(4)
N1–C7–C1	125.3(5)	N1–C8–C9	110.9(5)
N2–C10–C8	109.3(5)	N2–C11–C12	122.9(6)

Symmetry codes: (i)  $x, y+1, z$ ; (ii)  $x, y-1, z$ **Fig. 3: Noncovalent interactions in the structure of complex 1.**

polymer  $[\text{Cu}((3,4,5\text{-MeO-ba})_2\text{en})(\text{SCN})]_n$  [10]. Also, the distance between two copper(I) ions ( $5.686(4)$  Å) is similar to that found in  $[\text{Cu}((3,4,5\text{-MeO-ba})_2\text{en})(\text{SCN})]_n$  [10].

The chains are formed in direction of the  $y$  axis. The chains are further connected via weak hydrogen bonds

and chlorine–chlorine interactions into double layers. The double layers are further held together only by weak Van der Waals forces (see Fig 3). For further information on hydrogen bonds and chlorine–chlorine interactions see Table 4 and Table 5.

Table 4: Hydrogen bonds of **1**.

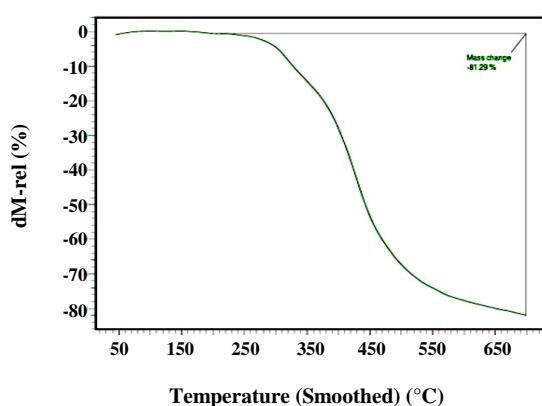
D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
C10–H2c10...S1a <sup>i</sup>	0.96	2.98	3.670 (7)	129
C14–H1c14...Cl4 <sup>ii</sup>	0.96	2.90	3.802 (6)	157

Symmetry codes: (i)  $x, -y, z+1/2$ ; (ii)  $-x+1/2, -y+5/2, -z$ .

Table 5: Chlorine–chlorine interactions of **1**.

Cl–Cl	Cl–Cl (Å)
Cl1–Cl2 <sup>i</sup>	3.5757 (19)
Cl3–Cl4 <sup>ii</sup>	3.354 (4)
Cl3 <sup>1</sup> –Cl4 <sup>ii</sup>	3.79 (4)

Symmetry codes: (i)  $x, -y-1, z+1/2$ ; (ii)  $x, -y+2, z+1/2$ .

Fig. 3: TG curve of **1**.

The results of the thermal gravimetric analysis of **1** under Ar atmosphere are shown in Fig. 3. Complex **1** is stable up to 250°C, indicating there is no water molecule as lattice water or coordinated in the complex. Under further heating the complex decomposes in two stages defined by temperature ranges 250–370 °C, and 370–700 °C, respectively. The overall weight loss 81.29% (calcd. 81.22%) corresponds to losing the C<sub>18</sub>H<sub>14</sub>Cl<sub>4</sub>N<sub>3</sub> group, with the final product CuS (18.71 %, calcd. 18.78 %).

#### SUPPLEMENTARY DATA

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 1488877. Copy of the data can be obtained free of charge on <https://www.ccdc.cam.ac.uk>.

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