



## Synthesis and structural characterization of a flexible tetradentate ligand and its copper(I) coordination polymers

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### ABSTRACT

A tetradentate Schiff-base ligand, *N,N'*-bis-(4-chlorobenzylidene)-1,2-bis(2-aminophenylthio)ethane, L, and its copper(I) coordination polymers, [Cu<sub>2</sub>(μ-I)<sub>2</sub>-μ-L]<sub>n</sub>·2n(CH<sub>3</sub>CN), LCuI, and [Cu<sub>2</sub>(μ-Cl)<sub>2</sub>-μ-L]<sub>n</sub>, were prepared. The products were characterized via their analytical and spectral properties. The crystal structures of the ligand molecule, L, and the complex, LCuI, were determined by single-crystal X-ray diffraction methods. In both the free molecule and the complex, L adopts an anti, staggered, extended conformation. In LCuI, prepared from L and CuI in acetonitrile, each Cu atom has a distorted tetrahedral coordination sphere composed of a nitrogen atom and a sulfur atom from L and two iodine ligands. LCuI is a sheet polymer, formed from coordination polymer chains containing the dimetal clusters Cu<sub>2</sub>(μ-I)<sub>2</sub>; the chains are cross-linked through π ··· π interactions of phenyl rings.

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### 1. Introduction

The design and construction of metal–organic coordination polymers are of current interest in the fields of supramolecular chemistry and crystal engineering [1–3]. This interest arises from their intriguing variety of architectures and topologies [3–6]. Furthermore, research on the synthesis and characterization of metal–organic coordination polymers is greatly motivated by their potential applications ranging from catalysis [3–10], gas storage [3,5,6,8–10], magnetism [3–7,9,10], molecular sensing [3,6,9,10], non-linear optics [4,5,7,10], ion-exchange [3,4,6], electric conductivity [4,7,9], molecular separation [8,9], host–guest chemistry [4,9], and medicine [5]. Therefore, rational design and synthesis of materials with specific networks has become an important research concern [3].

A large number of coordination polymers with a wide variety of structural motifs has been prepared through the variation of reagents and reaction conditions [6,10]. The structure and the properties of such materials depend on several factors, such as the oxidation state and coordination geometry of central metals, structural chemistry of organic spacers, nature of solvents, pH value, temperature, the counter-anion and molar ratio of central metal to organic ligand [3,4,6,8–12]. In addition to these factors,

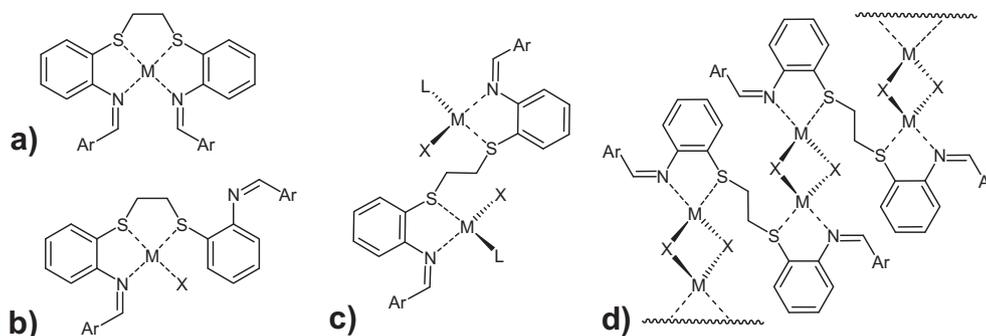
weak interactions (H-bonding, π–π stacking, van der Waals) may also play a major role in ultimately controlling the network [11,13].

Among these factors, the selection of appropriate organic spacers has the greatest influence on determining the structural outcome of target polymers [4,12,14]. The organic spacers serve to link metal sites and to propagate structural information throughout the extended structure. Properties of the organic spacers, such as solubility, coordination preference, length, geometry and relative orientation of the donor groups, play a very important role in dictating polymer framework topology [12,15]. With conformationally flexible spacers, the competition between bridging and chelating coordination modes is an important factor in controlling the self-assembly process [16,17]. So, structural control of metal–organic reactions involving flexible ligands is a great challenge and unexpected topologies often result [6].

Cyanacure (1,2-bis(2-aminophenylthio)ethane) is a flexible dithio-arylether with two *ortho*-amino substituents, enabling it to form various Schiff-base ligands. Cyanacure itself is capable of forming metal complexes via chelation to metal ions from both nitrogen and sulfur atoms [1,18–21]. Cyanacure-derived Schiff-bases can adopt various binding modes such as tetradentate [1,17] or hexadentate [22,23] chelation to one metal center, tridentate chelation to one metal center [24], bridging in bis-bidentate [17,21] or bis-tridentate [23] mode between two metal centers to form bimetallic species, and bridging in bis-bidentate mode

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**Scheme 1.** Usual binding modes of cyanacure-derived Schiff-bases; (a) tetradentate chelating mode; (b) tridentate chelating mode; (c) monomeric bis-bidentate chelating mode; (d) polymeric bis-bidentate chelating mode.

between two metal halide clusters to form polymeric networks [2] (Scheme 1).

The formation of metal complexes by combination of Cu(I) halides and bidentate bridging ligands has been studied extensively and shown to result in 1D chain or 2D sheet networks through the linking of  $\text{Cu}_2\text{X}_2$  moieties by bidentate bridging ligands [25]. A 1D coordination polymer composed of CuI and a cyanacure-derived Schiff-base, *N,N'*-bis-(2-thenylidene)-1,2-bis(2-aminophenylthio)ethane [2] has been reported previously. We report herein the preparation and structural characterization of *N,N'*-bis-(4-chlorobenzylidene)-1,2-bis(2-aminophenylthio)ethane, L, and its copper(I) halide coordination polymers.

## 2. Experimental

### 2.1. Material and physical measurements

1,2-Bis(2-aminophenylthio)ethane (Cyanacure) was prepared using a reported procedure [26]. Other reagents were commercially available and used as received. Elemental analyses (CHN) were performed using a Perkin-Elmer 2400 series (II) CHN elemental analyzer.  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance-300 MHz spectrometer employing tetramethylsilane as an internal reference. FTIR spectra were measured on a Perkin-Elmer 843 spectrometer. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 25 instrument. Molar conductance measurements were carried out on a Metrohm Herisau E 382 conductometer.

### 2.2. Synthesis of the ligand, *N,N'*-bis-(4-chlorobenzylidene)-1,2-bis(2-aminophenylthio)ethane, L

4-Chlorobenzaldehyde (0.53 g, 2 mmol) was added to a solution of 1,2-bis(2-aminophenylthio)ethane (0.276 g, 1 mmol) in EtOH (25  $\text{cm}^3$ ). The mixture was stirred for 45 min to form a yellow precipitate which was then filtered, washed with cold ethanol and dried *in vacuo*. Yield: 0.41 g (78%), mp 147 °C. *Anal. Calc.* for  $\text{C}_{28}\text{H}_{22}\text{Cl}_2\text{N}_2\text{S}_2$ : C, 64.48; H, 4.25; N, 5.37. Found: C, 64.59; H, 4.07; N, 5.36%. IR (KBr pellet,  $\text{v}/\text{cm}^{-1}$ ): 1621 (C=N). UV-Vis:  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $\text{L mol}^{-1}\text{cm}^{-1}$ ) in  $\text{CH}_3\text{CN}$ : 351(10775), 267(65915).  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm):  $\delta$  3.17 (s, 4H), 7.13–7.29 (m, 8H), 7.58 (d,  $J = 8.4$ , 4H), 7.93 (d,  $J = 8.4$ , 4H), 8.53 (s, 2H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , ppm):  $\delta$  30.1, 118.2, 126.3, 126.7, 126.8, 129.0, 130.4, 131.1, 134.8, 136.3, 149.1, 159.3. Pale yellow crystals suitable for X-ray diffraction were obtained from slow diffusion of n-hexane in a solution of L in ethylacetate.

### 2.3. Syntheses of the complexes

To a boiling suspension of L (0.61 g, 1 mmol) in  $\text{CH}_3\text{CN}$  (15  $\text{cm}^3$ ), a solution of  $\text{CuX}$  ( $\text{X} = \text{I}$  or  $\text{Cl}$ ) (2 mmol) in  $\text{CH}_3\text{CN}$  (15  $\text{cm}^3$ ) was

added and the mixture was refluxed for 30 min. An orange precipitate was formed on cooling, which was filtered, washed with hot ethyl acetate and dried *in vacuo*.

#### 2.3.1. $[\text{Cu}_2(\mu\text{-Cl})_2-\mu\text{-L}]_n$

Yield: 82%, mp 233 °C. *Anal. Calc.* for  $\text{C}_{28}\text{H}_{22}\text{Cl}_4\text{Cu}_2\text{N}_2\text{S}_2$ : C, 46.74; H, 3.08; N, 3.89. Found: C, 46.60; H, 2.80; N, 3.93%. FTIR (KBr pellet,  $\text{v}/\text{cm}^{-1}$ ): 1621 (C=N). UV-Vis:  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $\text{L mol}^{-1}\text{cm}^{-1}$ ) in  $\text{CH}_3\text{CN}$ : 350(9020), 268(51870).  $A_M/\Omega^{-1}\text{cm}^2\text{mol}^{-1}$  ( $10^{-3}\text{mol dm}^{-3}$  in acetonitrile, 25 °C) 102.7.  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm):  $\delta$  3.10 (s, 4H), 7.31–7.44 (m, 6H), 7.46 (d,  $J = 8.3$ , 4H), 7.67 (br s, 2H), 8.01 (d,  $J = 8.3$ , 4H), 8.85 (s, 2H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , ppm):  $\delta$  32.4, 120.0, 127.9, 128.2, 128.7, 130.5, 132.1, 133.6, 137.0, 138.8, 150.1, 161.9.

#### 2.3.2. $[\text{Cu}_2(\mu\text{-I})_2-\mu\text{-L}]_n$ and $[\text{Cu}_2(\mu\text{-I})_2-\mu\text{-L}]_n \cdot 2n(\text{CH}_3\text{CN})$ , LCuIS

Yield: 76%, mp 230–231 °C. *Anal. Calc.* for  $\text{C}_{28}\text{H}_{22}\text{Cl}_2\text{Cu}_2\text{I}_2\text{N}_2\text{S}_2$ : C, 37.27; H, 2.46; N, 3.10. Found: C, 36.98; H, 2.21; N, 3.10%. IR (KBr pellet,  $\text{v}/\text{cm}^{-1}$ ): 1623 (C=N). UV-Vis:  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $\text{L mol}^{-1}\text{cm}^{-1}$ ) in  $\text{CH}_3\text{CN}$ : 360 (9750), 266 (71065), 252 (70895).  $A_M/\Omega^{-1}\text{cm}^2\text{mol}^{-1}$  ( $10^{-3}\text{mol dm}^{-3}$  in acetonitrile, 25 °C) 106.2.  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm):  $\delta$  3.13 (s, 4H), 7.26–7.38 (m, 6H), 7.47 (d,  $J = 8.5$ , 4H), 7.51 (d,  $J = 7.6$ , 2H), 8.01 (d,  $J = 8.5$ , 4H), 8.69 (s, 2H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , ppm):  $\delta$  31.8, 119.3, 127.5, 128.0, 128.8, 130.7, 131.7, 134.1, 136.1, 136.7, 149.8, 161.4.

Salmon-pink crystals of  $[\text{Cu}_2(\mu\text{-I})_2-\mu\text{-L}]_n \cdot 2n(\text{CH}_3\text{CN})$ , LCuIS, suitable for X-ray diffraction were obtained by slow evaporation of solvent from a solution of  $[\text{Cu}_2(\mu\text{-I})_2-\mu\text{-L}]_n$  in acetonitrile.

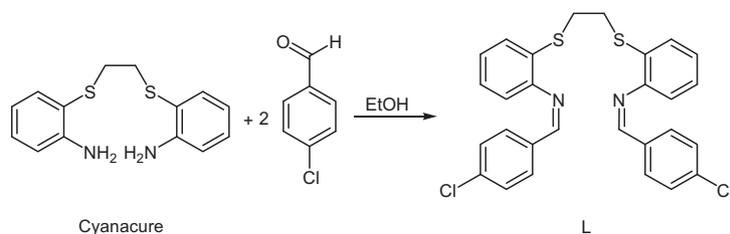
### 2.4. X-ray crystallography

Crystals of L and LCuIS were mounted in oil on glass fibers and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and graphite monochromator. Intensity data were measured at 140 K by thin-slice  $\omega$ - and  $\phi$ -scans. Data were processed using the CrysAlisPro-CCD and -RED [27] programs. The structures were determined by the direct methods routines in the SHELXS program [28] and refined by full-matrix least-squares methods, on  $F^2$ 's, in SHELXL [28]. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions and their  $U_{\text{iso}}$  values were set to ride on the  $U_{\text{eq}}$  values of the parent carbon atoms. Scattering factors for neutral atoms were taken from reference [29]. Computer programs used in this analysis have been noted above, and were run through WinGX [30] on a Dell Precision 370 PC at the University of East Anglia. A summary of crystal and refinement data for L and LCuIS is given in Table 1.

**Table 1**

Crystal and structure refinement data for L and LCuS.

Compound	L	LCuS
Elemental formula	C <sub>28</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>2</sub> S <sub>2</sub>	C <sub>28</sub> H <sub>22</sub> Cl <sub>2</sub> Cu <sub>2</sub> I <sub>2</sub> N <sub>2</sub> S <sub>2</sub> , 2(C <sub>2</sub> H <sub>3</sub> N)
Formula weight	521.5	984.5
Crystal system	monoclinic	monoclinic
Space group	P2 <sub>1</sub> /c (no. 14)	P2 <sub>1</sub> /c (no. 14)
Crystal color and shape	pale yellow prism	salmon-pink plate
Crystal size (mm)	0.39 × 0.26 × 0.25	0.30 × 0.24 × 0.12
a (Å)	8.2795(2)	9.85515(11)
b (Å)	12.6140(2)	15.64116(16)
c (Å)	12.2250(2)	11.22348(12)
β (°)	107.667(2)	96.5560(10)
V (Å <sup>3</sup> )	1216.53(4)	1718.74(6)
Z	2	2
D <sub>calc</sub> (mg m <sup>-3</sup> )	1.424	1.902
F(0 0 0)	540	956
μ (mm <sup>-1</sup> )	0.459	3.340
θ range (°)	3.5–30.0	3.7–30.0
Limiting indices	−11 ≤ h ≤ 11, −17 ≤ k ≤ 17, −17 ≤ l ≤ 17	−13 ≤ h ≤ 13, −22 ≤ k ≤ 22, −15 ≤ l ≤ 15
Completeness to θ = 30.0 (%)	99.8	99.8
Maximum and minimum transmission	1.090 and 0.884	1.243 and 0.765
Reflections collected	23 277	28 141
Unique reflections (R <sub>int</sub> )	3547 (0.030)	4990 (0.033)
Reflections with I > 2σ(I)	2856	4292
Data/restraints/parameters	3547/0/154	4990/0/200
Goodness-of-fit (GOF) on F <sup>2</sup>	1.089	0.993
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.028, wR <sub>2</sub> = 0.076	R <sub>1</sub> = 0.018, wR <sub>2</sub> = 0.040
R indices (all data)	R <sub>1</sub> = 0.039, wR <sub>2</sub> = 0.078	R <sub>1</sub> = 0.024, wR <sub>2</sub> = 0.041
Largest difference peak and hole (e Å <sup>-3</sup> )	0.36 and −0.22	0.39 and −0.56

**Scheme 2.** Preparation of L.

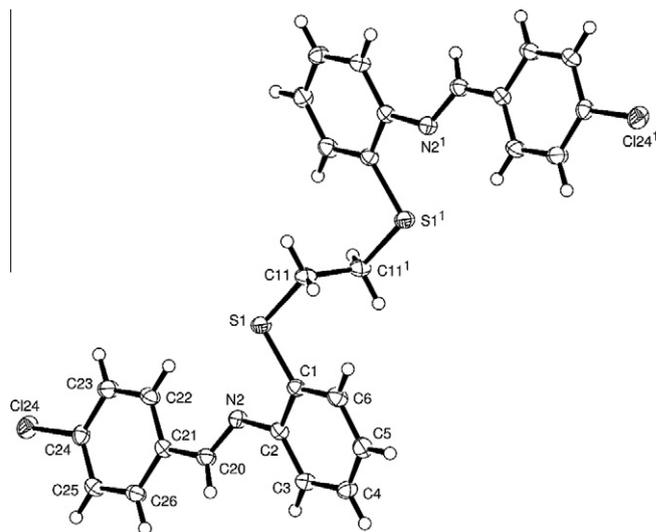
### 3. Results and discussion

#### 3.1. Synthesis

*N,N'*-Bis-(4-chlorobenzylidene)-1,2-bis(2-aminophenylthio)ethane, L, was prepared from a 1:2 mixture of 1,2-bis(2-aminophenylthio)ethane (cyanacure) and 4-chlorobenzaldehyde in ethanol (Scheme 2).

L is a N<sub>2</sub>S<sub>2</sub>-donor ligand with two rigid N,S-donor moieties connected through a flexible –CH<sub>2</sub>–CH<sub>2</sub>– spacer. While L can act as a simple tetradentate ligand chelating to a single metal ion, it can also act as a bis-bidentate ligand, bridging between two metal ions. These different coordination modes are usual for cyanacure-derived Schiff-bases. For instance, in treatment of *N,N'*-bis-(3-phenylprop-2-en-1-ylidene)-1,2-bis(2-aminophenylthio)ethane with Cu(I) perchlorate, the metal ion releases its labile ligand, and the flexible Schiff-base chelates it in tetradentate mode [17]. On the other hand, in treatment with Cu(I) halides which do not have labile ligands, the flexible Schiff-base ligand coordinates to each Cu(I) halide center in bidentate mode, which allows it to bridge between two metal centers. In the latter case, if a suitable monodentate ligand (such as PPh<sub>3</sub>) is present, the tetragonal coordination sphere of Cu(I) is saturated with the additional ligand and a bimetallic complex will result [17]. Otherwise, halide ions may bridge between tri-coordinated Cu(I) ions to form a 1D coordination polymer [2]. Therefore, we per-

formed the reaction of L with Cu(I) halides in acetonitrile, in order to obtain and examine the coordination polymers produced.

**Fig. 1.** View of a molecule of L, indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

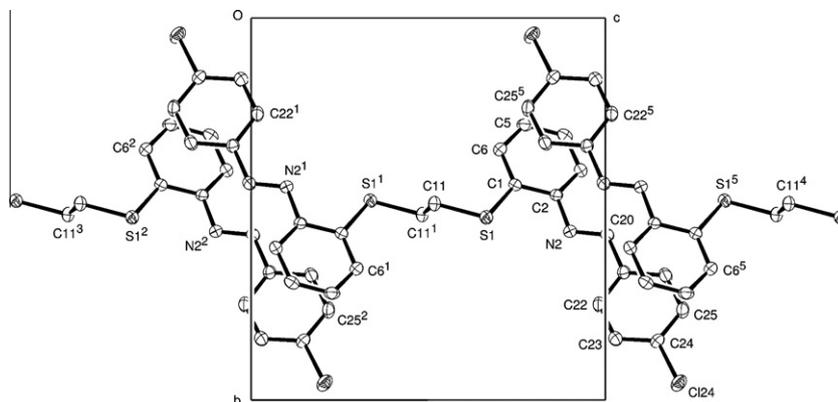


Fig. 2. Chains of L molecules linked through  $\pi \cdots \pi$  interactions between the C(1–6) and C(21<sup>5</sup>–26<sup>5</sup>) rings and the C(21–26) and C(1<sup>5</sup>–6<sup>5</sup>) rings.

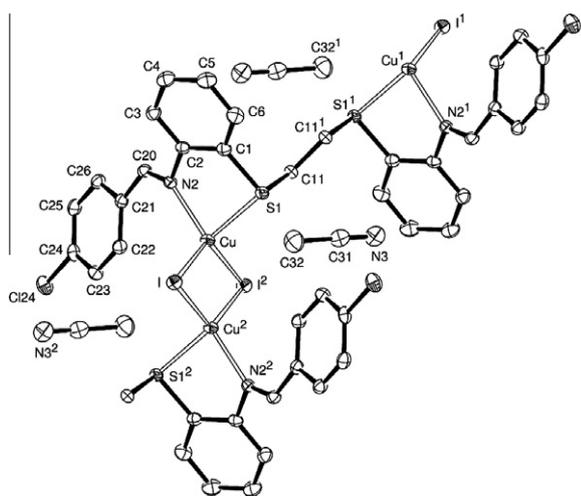


Fig. 3. View of a portion of the polymer chain of LCuIS, indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

The Cu(I) complexes,  $[\text{Cu}_2(\mu\text{-Cl})_2\text{-}\mu\text{-L}]_n$  and  $[\text{Cu}_2(\mu\text{-I})_2\text{-}\mu\text{-L}]_n$ , were prepared from a 1:2 mixture of L and CuX (X = Cl or I) in acetonitrile. We obtained suitable single crystals for X-ray crystallography from solutions of L and its CuI complex,  $[\text{Cu}_2(\mu\text{-I})_2\text{-}\mu\text{-L}]_n$ , in ethyl acetate and acetonitrile solutions, respectively. The latter crystallized with solvent molecules to form crystals of  $[\text{Cu}_2(\mu\text{-I})_2\text{-}\mu\text{-L}]_n \cdot 2n(\text{CH}_3\text{CN})$ , LCuIS. However, our efforts to obtain single crystals from  $[\text{Cu}_2(\mu\text{-Cl})_2\text{-}\mu\text{-L}]_n$  were unsuccessful.

### 3.2. Analytical and spectral characterization

The elemental analysis data are in good agreement with the calculated values for the proposed formulae of the ligand and its complexes. Both the chloride and iodide complexes are non-electrolyte species, according to molar conductance measurements [31]. The IR spectrum of the free ligand, L, shows a relatively strong C=N stretching band at  $1621\text{ cm}^{-1}$ , which is also present as a medium band in the IR spectra of both complexes, at approximately the same wave number. The  $^1\text{H}$  NMR spectrum of L presents a singlet at  $\delta$  3.17 for the central ethylene moiety, a multiplet at  $\delta$  7.13–7.29 for protons of the electron-rich aminothiophenyl rings, a doublet of doublets centered at  $\delta$  7.75 for the protons of the electron-poor 4-chlorophenyl rings, and a singlet at  $\delta$  8.53 for the imine protons. A similar pattern may be observed in the  $^1\text{H}$  NMR spectra of  $[\text{Cu}_2(\mu\text{-I})_2\text{-}\mu\text{-L}]_n$  and  $[\text{Cu}_2(\mu\text{-Cl})_2\text{-}\mu\text{-L}]_n$  complexes; nevertheless, there

Table 2  
Selected bond lengths (Å) and angles (°) for L and LCuIS.

<i>L</i>			
C(11)–C(11 <sup>1</sup> )	1.531(2)	N(2)–C(20)	1.2746(14)
C(11)–S(1)	1.8081(12)	C(20)–C(21)	1.4656(15)
S(1)–C(1)	1.7693(11)	C(2)–N(2)	1.4158(14)
C(11 <sup>1</sup> )–C(11)–S(1)	113.04(11)	C(20)–N(2)–C(2)	119.75(10)
C(1)–S(1)–C(11)	103.10(5)	N(2)–C(20)–C(21)	122.51(10)
C(11 <sup>1</sup> )–C(11)–S(1)–C(1)	67.06(12)	C(2)–N(2)–C(20)–C(21)	–177.75(10)
C(11)–S(1)–C(1)–C(6)	18.95(11)	C(1)–C(2)–N(2)–C(20)	–152.42(11)
<i>LCuIS</i>			
Cu–I	2.6265(2)	Cu–N(2)	2.1020(12)
Cu–I <sup>2</sup>	2.6047(2)	Cu...Cu <sup>2</sup>	2.6416(4)
Cu–S(1)	2.3613(4)		
I–Cu–I <sup>2</sup>	119.343(7)	N(2)–Cu–I <sup>2</sup>	123.29(3)
S(1)–Cu–I	104.441(12)	N(2)–Cu–S(1)	85.98(4)
N(2)–Cu–I	108.56(3)	Cu–I–Cu <sup>2</sup>	60.657(7)
S(1)–Cu–I <sup>2</sup>	108.131(12)		
Cu <sup>2</sup> –I–Cu–N(2)	148.53(4)	I–Cu–N(2)–C(2)	79.79(10)
Cu–S(1)–C(1)–C(2)	–18.39(12)	I <sup>2</sup> –Cu–N(2)–C(2)	–133.20(8)
S(1)–Cu–N(2)–C(2)	–24.11(9)	N(2)–Cu–S(1)–C(1)	20.43(6)
I–Cu–S(1)–C(1)	–87.71(5)	Cu–N(2)–C(2)–C(1)	19.19(17)
I <sup>2</sup> –Cu–S(1)–C(1)	144.21(5)	C(20)–N(2)–C(2)–C(1)	–149.65(14)
Cu <sup>2</sup> –I–Cu–S(1)	–120.891(14)	C(2)–N(2)–C(20)–C(21)	–169.26(14)
C(1)–S(1)–C(11)–C(11 <sup>1</sup> )	78.4(2)	N(2)–C(20)–C(21)–C(22)	8.3(2)
S(1)–C(1)–C(2)–N(2)	2.06(19)		

Symmetry transformations used to generate equivalent atoms: In L: <sup>1</sup>1 – x, 1 – y, 1 – z. In LCuIS: <sup>2</sup>2 – x, 1 – y; <sup>1</sup>1 – z; <sup>2</sup>2<sup>1</sup> – x, 1 – y, 1 – z.

are some downfield shifts especially for the imine protons (from  $\delta$  8.53 to 8.69 and 8.85, respectively), and for the two protons of the aminothiophenyl rings in the *ortho* position to the amino substituent groups; from around  $\delta$  7.29 to 7.51 and 7.67, respectively. These downfield shifts relative to the corresponding signals in the free ligand can be attributed to the deshielding effect resulting from the coordination of the imine nitrogens.  $^{13}\text{C}$  NMR spectra of L show a signal at  $\delta$  30.1 for ethylene moiety, 10 signals from  $\delta$  118.2 to 149.1 for aromatic rings, and a signal at  $\delta$  159.3 for imine carbons. The same pattern is observed in  $^{13}\text{C}$  NMR spectra of both complexes.

### 3.3. Description of crystal structures

In the solid state, the central –S–CH<sub>2</sub>–CH<sub>2</sub>–S– moiety of the molecule L adopts an anti, staggered conformation (Fig. 1). The

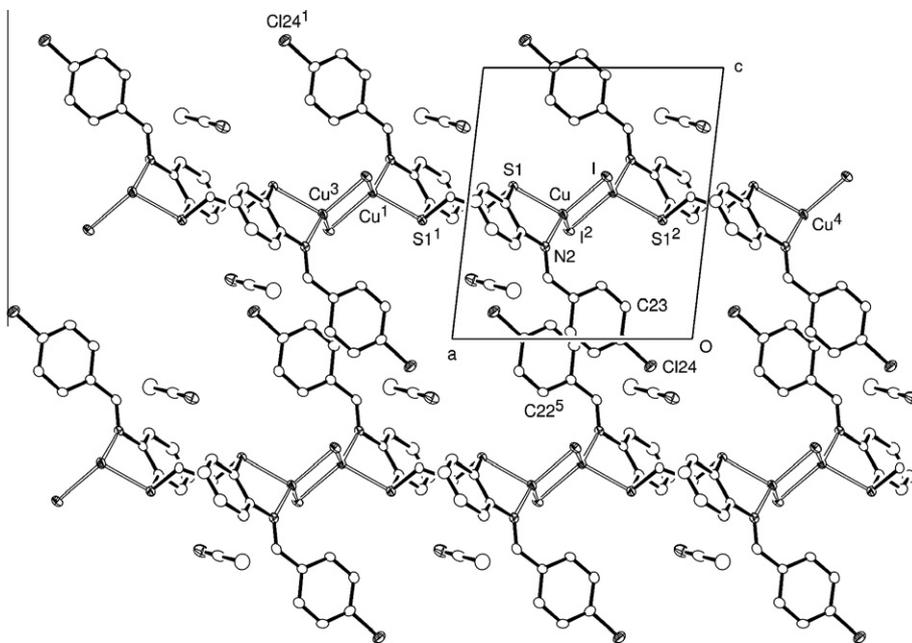


Fig. 4. A sheet of LCuLS, viewed down the crystallographic *b* axis. The  $C_6$  rings of C(21–26) and C(21<sup>5</sup>–26<sup>5</sup>) are overlapping.

molecule lies about a center of symmetry at the mid-point of the C(11)–C(11<sup>1</sup>) bond; this is typical of molecules with this linking group [22,32–34]. There is a rotation about the C(2)–N(2) bond so that the planes of the two six-membered rings are rotated 21.64(5)° apart. Each Cl–C<sub>6</sub>H<sub>4</sub>–CH=N–C<sub>6</sub>H<sub>4</sub> unit of the molecule overlies a symmetry-related unit, with the  $C_6$  rings approximately parallel (Fig. 2) allowing  $\pi \cdots \pi$  interactions and closest interatom contacts of C(6).. $C(25^4)$  3.372(2) and C(1).. $C(26^4)$  3.397(2) Å. Molecules are thus linked in chains parallel to the (1 0 1) vector.

In crystals of the complex LCuLS, the ligand L again shows an extended form and lies about a center of symmetry at the mid-point of the C(11)–C(11<sup>1</sup>) bond. It is therefore able to coordinate, through its two pairs of S,N donor atoms, to two Cu atoms, labeled Cu and Cu<sup>1</sup> (Fig. 3). The Cu atom is part of a Cu<sub>2</sub>( $\mu$ -I)<sub>2</sub> group which also lies about a center of symmetry, and links to the next L ligand (labeled N(2<sup>2</sup>), etc); chains of a coordination polymer are thus formed parallel to the crystallographic *a* axis. A very similar arrangement has been noted in [Cu<sub>2</sub>( $\mu$ -I)<sub>2</sub>( $\mu$ -N,N'-di-(thiophenecarbaldehyde)-1,2-di(*o*-aminophenylthio)ethane)]<sub>n</sub> [2]; the principal difference in the pattern of the polymer chain is in the torsion angles about the C–S–C–C link which for C(1)–S(1)–C(11)–C(11<sup>1</sup>) in our complex is 78.4(2)° (Table 2), compared with –53.8(4)° for the corresponding angle in the previous structure. In our complex, pairs of chlorophenyl groups overlap, ca. 3.220 Å apart, about a further center of symmetry, and form crosslinks of  $\pi \cdots \pi$  interactions between the chains to give a sheet polymer (Fig. 4).

In this structure, the bonding about each Cu is approximately tetrahedral, with an acute N(2)–Cu–S(1) angle of 85.98(4)°. The normals to the two  $C_6$  ring planes within the ligand L deviate by 44.71(6)° by rotation principally about the N(2)–C(2) bond.

#### 4. Conclusions

The flexible ligand L prefers an anti, staggered conformation to avoid the steric repulsion of bulky substituents. In treatment with Cu(I) halides, it retains its extended form to link the Cu<sub>2</sub>X<sub>2</sub> clusters. This coordination mode leads to the formation of 1D coordination polymers, a phenomenon previously observed in treatment of another cyanacure-derived Schiff-base with CuI [2]. Supplementary

data: CCDC 808928 and 808927 contain the supplementary crystallographic data for L and LCuLS, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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