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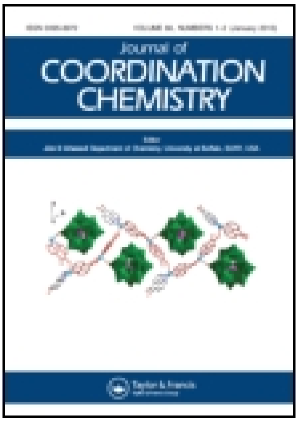

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Synthesis, crystal structure, and electrochemical properties of Cu(I) coordination polymers with two new $(NS)_2$ Schiff-base ligands containing long flexible spacers

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Synthesis, crystal structure, and electrochemical properties of Cu(I) coordination polymers with two new $(NS)_2$ Schiff-base ligands containing long flexible spacers

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Two new $(NS)_2$ Schiff bases, $(4\text{-}NO_2Ph)_2$dapte (*N,N′*-di-(4-nitrobenzaldimine)-1,2-di(o-aminophenylthio)ethane) (**1**) and $(thio)_2$daptx (*N,N′*-di-(thiophenedimine)-1,4-di(o-aminophenylthio)xylene) (**2**), and their 1-D copper(I) coordination polymers $[Cu_2(\mu\text{-}Br)_2(\mu\text{-}(4\text{-}NO_2Ph)_2\text{dapte})]_n$ (**3**), $[Cu_2(\mu\text{-}I)_2(\mu\text{-}(4\text{-}NO_2Ph)_2\text{dapte})]_n$ (**4**), and $[Cu_2(\mu\text{-}I)_2(\mu\text{-}(thio)_2\text{daptx})]_n$ (**5**) have been synthesized and characterized by elemental analyses and IR, UV–Vis, and ^1H NMR spectroscopy. The structures of **4** and **5** have been determined by X-ray crystallography and were shown to consist of $Cu_2(\mu\text{-}I)_2$ secondary building units (SBUs) bridged by $(4\text{-}NO_2Ph)_2$dapte or $(thio)_2$daptx ligands. The $CuNSI_2$ coordination sphere is a distorted tetrahedral in both cases. Both $(4\text{-}NO_2Ph)_2$dapte and $(thio)_2$daptx are N_2S_2-bis-bidentate chelating ligands with the two imine nitrogens and two thioether sulfurs in a *trans* configuration generating dinuclear $[Cu_2(\mu\text{-}(4\text{-}NO_2Ph)_2\text{dapte})]$ and $[Cu_2(\mu\text{-}(thio)_2\text{daptx})]$. These units are connected by two bridging iodides to form 1-D copper(I) coordination polymers. The electrochemical properties of **3**–**5** are also reported and discussed.

Keywords: Bis-bidentate Schiff base; Copper(I) halide aggregate; One-dimensional coordination polymer; X-ray diffraction; Cyclic voltammetry

1. Introduction

The synthesis and characterization of metal–organic coordination polymers is a subject of interest due to their intriguing structures as well as potential applications in materials science as catalysts, molecular-based magnets, zeolite-like porous materials, and luminescent materials [1–3]. The main issue in this area is the development of strategies for a more directed construction of novel coordination architectures with interesting physical properties [4–11].

Due to the numerous advantages that copper(I) offers, such as availability, low price, and strong emissive properties similar to Au(I) complexes, coordination polymers of this metal ion are receiving increasing attention [12]. There has been a vast number of reports on the luminescence and structural features of Cu(I) complexes with rigid, N-donor ligands, mainly pyridine-containing ligands, such as pyridine, 2,2′-bipyridyl, 4,4′-bipyridyl,

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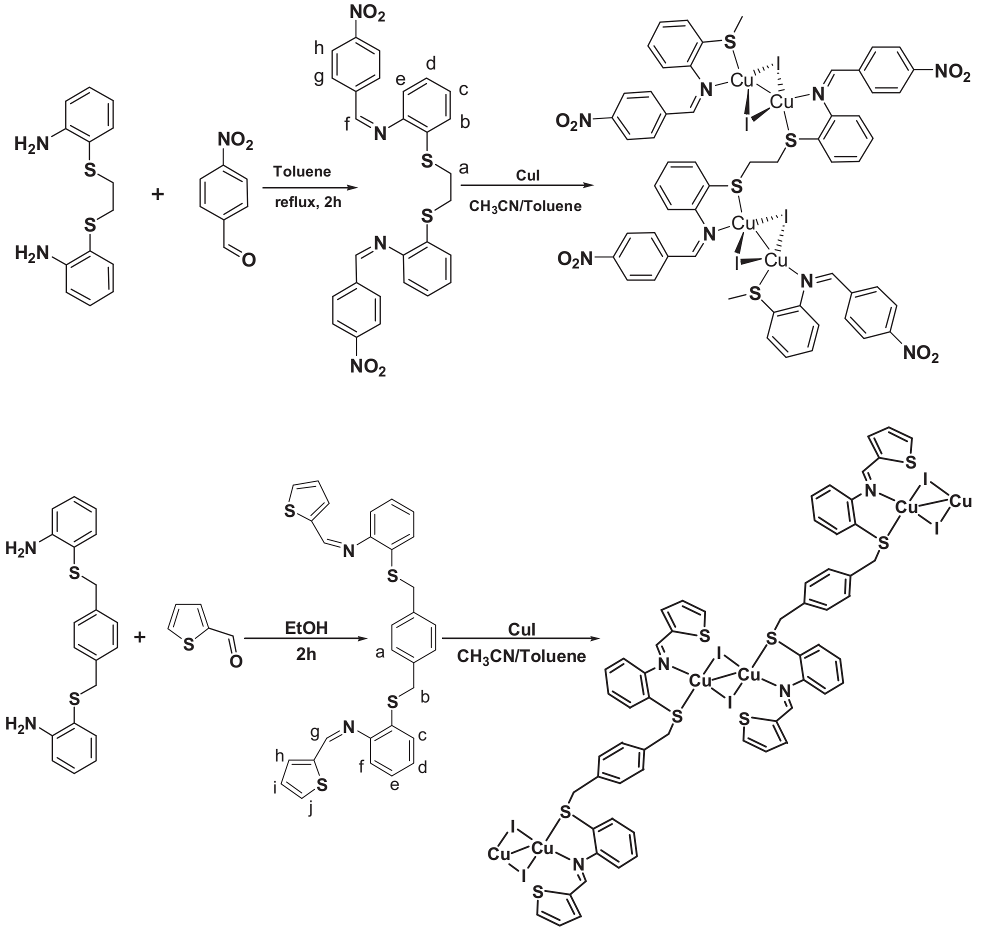
*Corresponding authors. Email: amirnasr@cc.iut.ac.ir and phenanthroline and other auxiliary ligands, such as phosphines and halides [13]. Recently, there have been some reports on polymeric copper(I) halide complexes containing thioether-donating groups. However, the data on this type of ligand and its coordination habits are still sparse [14–16]. Bridging bis-bidentate ligands gives rise to more interesting copper(I) halide architectures than monodentate- or bidentate-chelating ligands [17]. The redox properties of copper(I) are also controlled by the ligand environment and the geometry imposed on the metal center.

As part of our ongoing investigation on the coordination habits of the flexible Schiff-base ligands derived from dapte and daptx with copper(I) metal centers [14–18], we herein report the synthesis of two new $(NS)_2$ ligands and their polymeric copper(I) complexes, $[Cu_2(\mu\text{-}X)_2(\mu\text{-}(4\text{-}NO_2Ph)_2dapte)]_n$ (X = Br, I) and $[Cu_2(\mu\text{-}I)_2(\mu\text{-}(thio)_2daptx)]_n$, in which the tetradentate Schiff bases act as *bis*-bidentate bridging ligands between two copper(I) centers (scheme 1).



Scheme 1. Synthesis of $[Cu_2(\mu\text{-}I)_2(\mu\text{-}(4\text{-}NO_2Ph)_2dapte)]_n$ (**4**) and $[Cu_2(\mu\text{-}I)_2(\mu\text{-}(thio)_2daptx)]_n$ (**5**).

2. Experimental

2.1. *Material and physical measurements*

All solvents and chemicals were commercial-reagent grade and used as-received from Aldrich and Merck. 1,2-Bis(o-aminophenylthio)ethane (dapte) and 1,4-bis(o-aminophenylthio)xylene (daptx) were prepared as reported in [19] and [20], respectively. Elemental analyses were performed with a Perkin–Elmer 2400II CHNS-O elemental analyzer. Infrared spectra as KBr pellets were obtained on a FT-IR JASCO 680 PLUS spectrophotometer in the range 4000–400 cm^{-1} and UV–vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. ^1H NMR spectra were obtained on a BRUKER AVANCE DR X500 (500 MHz) and Bruker AVANCE III 400 MHz spectrometer. Proton chemical shifts are reported in parts per million (ppm) relative to an internal standard of Me_4Si. Cyclic voltammograms were recorded using a SAMA Research Analyzer M-500. Three electrodes were utilized in this system, a glassy carbon working electrode, a platinum disk auxiliary electrode, and Ag wire as reference electrode. The glassy carbon-working electrode (Metrohm 6.1204.110) with 2.0 ± 0.1 mm diameter was manually cleaned with 1 µm alumina polish prior to each scan. The cyclic voltammograms of the complexes were obtained at 25 °C under argon atmosphere in DMSO solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte and complex concentrations of about 4×10^{-3} M. Ferrocene (Fc) was used as the internal standard and all redox potentials are referenced to the $Fc^{+/0}$ ($E^0 = 0.40$ V vs. SCE) couple under the same conditions [21].

2.2. *Synthesis*

2.2.1. Schiff base $(4\text{-}NO_2Ph)_2$dapte (1). 4-Nitrobenzaldehyde (302 mg, 2 mM) was added to a solution of dapte (276 mg, 1 mM) in toluene (5 mL) with continuous stirring. The mixture was refluxed for about 2 h after which the solution was cooled to room temperature resulting in the formation of yellow microcrystals (342 mg, 63% yield) which were isolated by filtration and washed with cold ethanol. Anal. Calcd for $C_{28}H_{22}N_4O_4S_2$ (%): C, 61.98; H, 4.09; N, 10.33. Found (%): C, 61.92; H, 4.14; N, 10.06. IR (KBr pellet, cm^{-1}): 1598 m (υ C=N), 1513 m, 1341 s (υ NO_2), 851 m (υ C–N). UV–Vis: λ_{max} (nm) (ε, mol^{-1} L cm^{-1}) (chloroform): 390 (7800), 292(26,450). ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 3.18$ (s, 4H, H_a), 6.97 (d, $J = 7.5$ Hz, 2H, H_e), 7.11–7.19 (m, 4H, $H_{d,c}$), 7.26 (d, $J = 7.4$ Hz, 2H, H_b) 8.31 (d, $J = 8.7$ Hz, 4H, H_g), 8.45 (s, 2H, H_f), 8.71 (d, $J = 8.8$ Hz, 4H, H_h).

2.2.2. Schiff base $(thio)_2$daptx (2). This compound was synthesized similar to **1**, except that 2-thiophenecarbaldehyde (224 mg, 2 mM) was used instead of 4-nitrobenzaldehyde. A yellow precipitate (422 mg, 78% yield) was isolated. Anal. Calcd for $C_{30}H_{24}N_2S_4$: C, 66.63; H, 4.47; N, 5.18. Found: C, 64.82; H, 4.38; N, 5.26. IR (KBr pellet, cm^{-1}) 1617 s (υ C=N). UV–vis: λ_{max} (nm) (ε, mol^{-1} L cm^{-1}) (chloroform): 357 (2230), 297 (14,500). ^1H NMR ($CDCl_3$, 500 MHz), δ (ppm) = 4.12(s, $4H_b$), 6.96 (dd, $J = 7.8$, 1.3 Hz, $2H_f$), 7.1–7.22 (m, $6H_{d,e,i}$), 7.25 (s, $4H_a$), 7.26 (dd, $J = 7.5$, 1.3 Hz, $2H_c$), 7.49 (dd, $J = 3.6$, 1.0 Hz, $2H_h$), 7.52 (d, $J = 5.6$ Hz, $2H_j$), 8.42 (s, $2H_g$).

2.2.3. $[Cu_2(\mu\text{-}Br)_2(\mu\text{-}(4\text{-}NO_2Ph)_2dapte)]_n$ (3). A 5 ml toluene solution of **1** (54 mg, 0.1 mM) was added to a solution of CuBr (15 mg, 0.1 mM) in CH_3CN (5 mL) with continuous stirring. The mixture was stirred at room temperature for about 10 min to give a clear red solution. Red-brown crystals (63 mg, 75% yield) were obtained after two days by slow evaporation from the filtrate. Yield 63 mg (75%). Anal. Calcd for $C_{28}H_{22}Br_2Cu_2N_4O_4S_2$ (%): C, 40.54; H, 2.67; N, 6.75. Found (%): C, 40.51; H, 2.60; N, 6.81. IR (KBr pellet, cm^{-1}): 1587 m (υ C=N), 1516 m, 1342 s (υ NO_2), 849 m (υ C–N). UV–vis: λ_{max} (nm) (ε, mol^{-1} L cm^{-1}) (DMSO): 388 (13,800), 291 (42,300). ^1H NMR (DMSO, 400 MHz), δ (ppm) = 3.20 (s, $4H_a$), 7.27 (m, $6H_{c,d,e}$), 7.38 (d, $J = 8.0$ Hz, $2H_b$), 8.20 (d, $J = 8.0$ Hz, $4H_g$), 8.33 (d, $J = 12.0$ Hz, $4H_h$), 8.73 (s, $2H_f$).

2.2.4. $[Cu_2(\mu\text{-}I)_2(\mu\text{-}(4\text{-}NO_2Ph)_2dapte)]_n$ (4). This compound was made analogously to **3** except that CuI (19 mg, 0.1 mM) was used instead of CuBr. Dark-red single crystals (66 mg, 72% yield) suitable for X-ray diffraction were obtained after three days by slow evaporation from the filtrate. Anal. Calcd for $C_{28}H_{22}Cu_2I_2N_4O_4S_2$ (%): C, 36.41; H, 2.4; N, 6.07. Found (%): C, 35.82; H, 2.52; N, 6.24. IR (KBr pellet, cm^{-1}): 1589 m (υ C=N), 1521 m, 1345 s (υ NO_2), 851 m (υ CN). UV–vis: λ_{max} (nm) (ε, mol^{-1} L cm^{-1}) (DMSO): 337 (30,200), 291 (52,000). ^1H NMR (DMSO, 400 MHz), δ (ppm) = 3.21 (s, $4H_a$), 7.31 (m, $6H_{c,d,e}$), 7.45 (bd, $2H_b$), 8.23 (d, $J = 8.0$ Hz, $4H_g$), 8.32 (d, $J = 8.0$ Hz, $4H_h$), 8.77 (s, $2H_f$).

2.2.5. $[Cu_2(\mu\text{-}I)_2(\mu\text{-}(thio)_2daptx)]_n$ (5). A 5 ml CH_3CN solution of CuI (19 mg, 0.1 mM) was added carefully to a cold solution of $thio_2daptx$ (54 mg, 0.1 mM) in toluene (25 mL) and the mixture was placed in a refrigerator. Dark-red single crystals (55 mg, 60% yield) suitable for X-ray diffraction were obtained after 3 d. Anal. Calcd for $C_{15}H_{12}CuINS_2$: C, 39.09; H, 2.62; N, 3.04. Found: C, 39.51; H, 2.41; N, 3.15%. IR (KBr pellet, cm^{-1}): 1590 s (υ C=N). UV–vis: λ_{max} (nm) (ε, mol^{-1} L cm^{-1}) (DMSO): 356 (8600), 293 (25,300). ^1H NMR (DMSO, 400 MHz), δ (ppm) = 4.16 (s, $4H_b$), 7.14–7.23 (m, $8H_{d,e,f,i}$), 7.29 (s, $4H_a$), 7.34 (d, $J = 7.2$ Hz, $2H_c$), 7.74 (d, $J = 3.1$ Hz, $2H_h$), 7.85 (d, $J = 4.6$ Hz, $2H_j$), 8.67 (s, $2H_g$).

2.3. *X-ray crystallography for 4 and 5*

Data for **4** and **5** were collected using the St Andrews Robotic diffractometer (Saturn724 CCD) at 125 K with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71075$ Å) [22]. All data were corrected for Lorentz, polarization, and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections. The structures were solved by direct methods and refined by full-matrix least squares against F^2 (SHELXL) [23]. Non-hydrogen atoms were refined anisotropically. All hydrogens were assigned riding isotropic displacement parameters and constrained to idealized geometries. Crystal data and structure refinement parameters are listed in table 1.

2.4. *Antibacterial activity*

The antibacterial activity of **4** and **5** (at 100 $\mu g\,mL^{-1}$) was tested against three gram-positive bacteria in DMSO solution by the well-known diffusion method using Sabouraud dextrose agar and Müller Hinton agar [24], but none of the two complexes showed any activity. Details are provided in the Supplementary material.

Table 1. Crystal data and structure refinement parameters for **4** and **5**.

Compound	**4**	**5**
Empirical formula	$C_{14}H_{11}CuIN_2O_2S$	$C_{15}H_{12}CuINS_2$
Formula weight	461.75	460.85
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.825(5)	7.352(2)
b (Å)	9.108(4)	9.090(2)
c (Å)	10.321(5)	11.621(3)
α (°)	65.73(2)	77.036(14)
β (°)	88.97(5)	87.232(16)
γ (°)	84.81(4)	89.291(16)
V (Å^3)	753.0(6)	756.0(3)
Z	2	2
D_{calc} (Mg m^{-3})	2.037	2.025
μ (mm^{-1})	3.64	3.75
F(000)	446	446
θ ranges (°)	2.32–26.34	1.8–26.36
Index ranges	$-10 \leqslant h \leqslant 10$, $-11 \leqslant k \leqslant 11$, $-12 \leqslant l \leqslant 12$	$-15 \leqslant h \leqslant 18$, $-17 \leqslant k \leqslant 18$, $-21 \leqslant l \leqslant 21$
Reflections collected	8429	9427
Independent reflections (R_{int})	2983 (0.051)	3029 (0.088)
Min. and max. transmission	0.669, 0.899	0.806, 0.929
Data/restraints/parameters	2983/0/190	3029/0/181
Goodness-of-fit on F^2	1.226	1.161
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0471$, $wR_2 = 0.1590$	$R_1 = 0.0718$, $wR_2 = 0.1323$
R indices (all data)	$R_1 = 0.0588$, $wR_2 = 0.2058$	$R_1 = 0.0882$, $wR_2 = 0.1394$
Largest diff. peak and hole (e Å^{-3})	1.628 and −1.525	0.992 and −1.162

3. Results and discussion

3.1. *Synthesis*

The synthesis of $[Cu_2(\mu\text{-}I)_2(\mu\text{-}(4\text{-}NO_2Ph)_2\text{dapte})]_n$ (**4**) and $[Cu_2(\mu\text{-}I)_2(\mu\text{-}(\text{thio})_2\text{daptx})]_n$ (**5**) are summarized in scheme 1. Complex **4** was synthesized by the reaction of CuI and $(4\text{-}NO_2Ph)_2$dapte in 1:1 CH_3CN/toluene solution, and the crystals suitable for X-ray crystallography were obtained by slow evaporation of the reaction solution at room temperature. A similar procedure was used for the synthesis of **3** from CuBr and **1**. Complex **5** was synthesized by the reaction of CuI and (thio)$_2$daptx in 1:5 CH_3CN/toluene solution and the crystals suitable for X-ray crystallography were obtained by slow evaporation of the reaction solution in the refrigerator.

3.2. *Spectral characterization*

The main features of the IR spectra of **1** and **2** are the bands at 1598 cm^{-1} and 1617 cm^{-1}, respectively, characteristic of the azomethine group. The ν(C=N) is generally shifted to lower frequencies in the copper complexes relative to the free ligand indicating a decrease in the C=N bond order due to the coordination of the imine nitrogen to the metal and back-bonding from Cu(I) to the π^* orbital of azomethine group. The corresponding bands appear at 1587, 1589, 1590 cm^{-1} in the spectra of **3**, **4**, and **5**, respectively, and are in agreement with those observed in the related Schiff-base complexes [16]. The NO_2 vibrations (1513–1521 and 1341–1345 cm^{-1}) and the band due to the C–N (nitroaromatic) stretch (849–851 cm^{-1}) appear at the appropriate positions in the IR spectra of **1**, **3**, and **4** [25].

Three main features are observed in the ^{1}H NMR spectra of **1**–**5**. First, the signal due to the imine protons appears as a singlet at 8.45 ppm (H_f) in the spectrum of **1** and at 8.73 and 8.77 ppm in the spectra of the Cu(I) complexes **3** and **4**, respectively. This signal appears at 8.52 ppm (H_g) in the spectrum of **2** and at 8.67 ppm in the spectrum of **5**. The shift of this signal to lower field in the spectra of the Cu(I) complexes is in accordance with expectations. Second, the aromatic protons appear in the expected region between 6.96 and 8.33 ppm for **1**–**5**. Protons *ortho* to a nitro group are ususally shifted to lower fields. Overall, the aromatic protons in these systems cannot be assigned with very high level of certainty due to the conformational flexibility of the ligands. The assignment of H_e (6.97 ppm) and H_b (7.26 ppm) in **1**, for example, was made only after the inspection of a ball-and-stick model which showed that the H_e atom is located in the shielding zone of the neighboring nitrobenzene ring. Third, the signals due to the aliphatic protons appear as singlets at 3.18 ppm (H_a) in the spectrum of **1** and at 3.20 and 3.21 ppm in the spectra of **3** and **4**, respectively. This signal appears at 4.12 ppm (H_b) and 4.16 ppm in the spectra of **2** and **5**, respectively. The observed ^{1}H NMR spectral data of **1**–**5** correlate well with those reported for related compounds [14]. Moreover, based on the similarity between the spectral properties of **3** and **4**, a structure similar to that of **4** can be inferred for **3**.

3.3. *Cyclic voltammetry*

Figure 1 shows the cyclic voltammograms of **3**, **4**, and **5**. All three complexes exhibit two irreversible oxidation processes between −0.20 and +0.80 V. The anodic peak potentials are $E_{Pa1} = +0.38$ and $E_{Pa2} = +0.79$ V for **3**, $E_{Pa1} = +0.26$ and $E_{Pa2} = +0.62$ V for **4**, and $E_{Pa1} = +0.27$ and $E_{Pa2} = +0.42$ V for **5**.

The dapte and daptx spacers are not capable of facilitating sufficient electronic communication between the two copper centers. It is reasonable to assume that the polymeric complexes undergo partial solvolysis in DMSO prior to the electrochemical processes and are converted to [(X)(DMSO)Cu(μ-L)Cu(DMSO)(X)] (X = Br or I) in equilibrium with their polymeric form. The observation of two oxidation waves for **3**–**5** in a relatively narrow potential range can thus be explained by the presence of the dinuclear solvated species in equilibrium with the polymeric form as shown in scheme 2. The first and the second oxidation waves correspond to Cu^I–Cu^I/Cu^{II}–Cu^{II} and $[Cu^I–Cu^I]_n/[Cu^{II}–Cu^{II}]_n$ electrochemically irreversible processes, respectively. The irreversibility of the oxidation process is presumably due to the chemical reactions that occur after the electron transfer. Similar behavior has been reported for related complexes [26].

The oxidation potentials, E_{Pa2}, become more positive in the following order **5** < **4** < **3**. The observed trend is presumably associated with the decreasing electron-donating character of the ligands coordinated to Cu(I), which make the central metal-ion harder to oxidize.

3.4. *Structural descriptions of 4 and 5*

The X-ray structures of **4** and **5** (figures 2 and 3) reveal that the complexes are neutral compounds consisting of $Cu_2(\mu\text{-}I)_2$ units bridged by $(4\text{-}NO_2Ph)_2$dapte or (thio)$_2$daptx *trans* to each other to construct infinite chain architectures. Selected bond distances and angles are listed in table 2. The 1-D array in these complexes is comparable with similar polymeric copper(I) complexes reported in the literature [27–29] as well as the Ag(I)

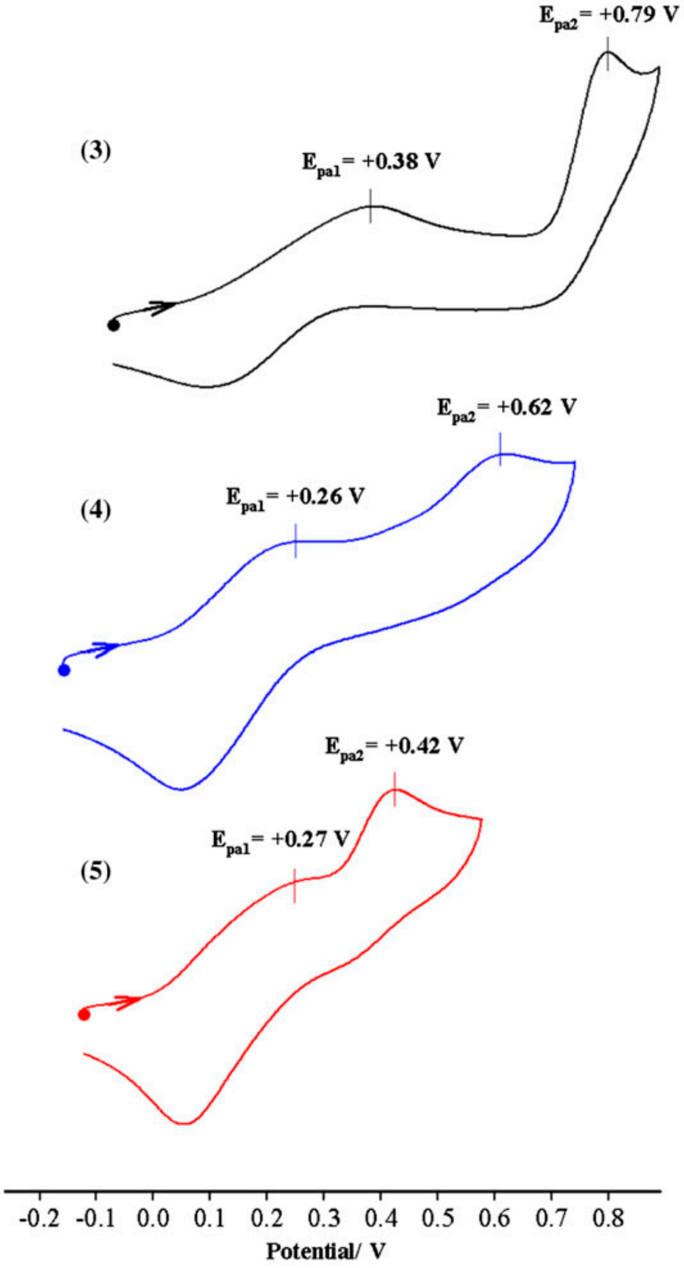
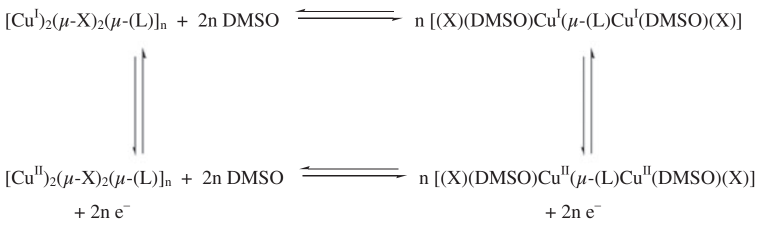


Figure 1. Cyclic voltammograms of DMSO solutions of **3–5** at a scan rate of $100\,mV\,s^{-1}$, $c \sim 4 \times 10^{-3}$ M.

complex reported by Vittal *et al*. [30]. The separation between the two copper(I) centers making up the base Cu_2I_2 unit is 2.7230(21) Å in **4** and 2.577(2) Å in **5**, and these distances are close to that observed in $[Cu_4I_4(py)_4]$ [31] and smaller than those observed in $Cu_2Br_2(PPh_3)L$ (L = pyrazine) (2.83–2.89 Å) [32] and other dimeric complexes, such as $[(PPh_3)_2Cu_2(\mu\text{-}I)_2(\mu\text{-}4,4'\text{-bpy})]_n$ (3.143 Å) [28] and $[(Phca_2pn)Cu(\mu\text{-}I)_2Cu(Phca_2pn)]$



Scheme 2. Solvolysis and electrochemical processes in DMSO solutions of **3**–**5**.

(3.372 Å) [33]. The shorter Cu–Cu distance and smaller CuICu angle (58.75°) in **5** as compared with **4** (Cu-I-Cu, 62.64°) are in agreement with the direct correlation between the Cu–Cu distance and Cu–I–Cu angle suggested by Slawin *et al*. [34]. Our limited survey of the literature also confirms the existence of such a correlation [35–37]. The stabilizing effect of metal–metal interactions can be significant for Cu–Cu distances below the sum of two copper van der Waals radii (2.80 Å). The rather short Cu–Cu distances in **4** and **5** may thus contribute to the stabilization of these two structures.

The coordination spheres of the four-coordinate Cu(I) centers in **4** and **5** are completed by one S atom and one N atom from the corresponding Schiff-base and two iodine atoms to form distorted tetrahedron geometries, which are non-ideal as a consequence of the restricting bite angle of the chelating ligands. The intra-ligand angle S3–Cu1–N8 (87.9 (2)°) and the three angles S3–Cu1–I1, S3–Cu1–I1b, and N8–Cu1–I1 (104.11(7), 110.30(8), and 127.5(2)°, respectively) in **4** deviate from the ideal value of 109.5° for a regular tetrahedron. Similar values are also observed for **5**. The bond distances Cu1–N8, 2.122(7) Å, and Cu1–S3, 2.299(3) Å for **4** and Cu1–N14, 2.076(8) Å, and Cu1–S6, 2.390(3) Å for **5** along with the Cu–I bond distances (2.6046(19) and 2.6333(14) Å for **4** and 2.6192(15) and 2.6355(15) Å for **5**) are similar to those in related chain [27–30] and dinuclear copper (I) complexes [32–39].

Examination of the crystal packing shows that the adjacent 1-D polymer chains in **4** are held together by (NO…H) and (I…H) hydrogen bonds (table 3) to form a 3-D framework

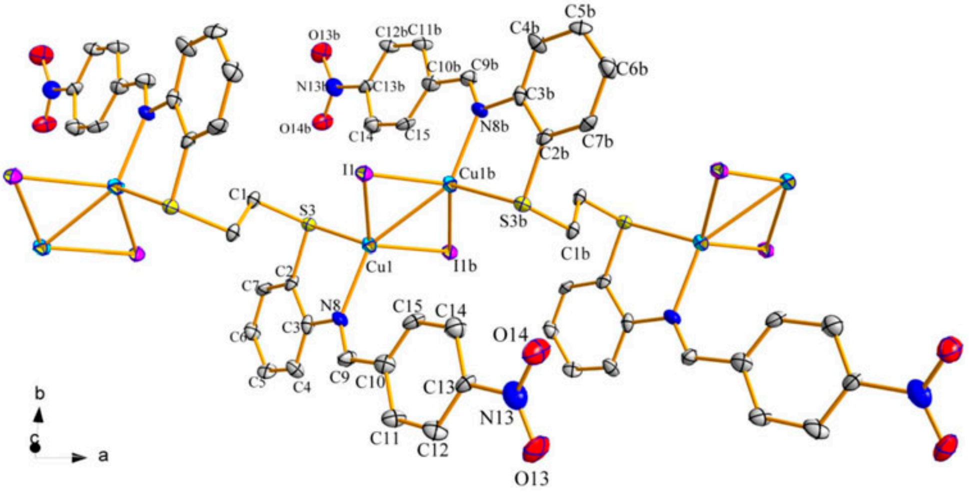


Figure 2. View of the structure of **4** with 50% probability ellipsoids. Hydrogens are omitted for clarity.

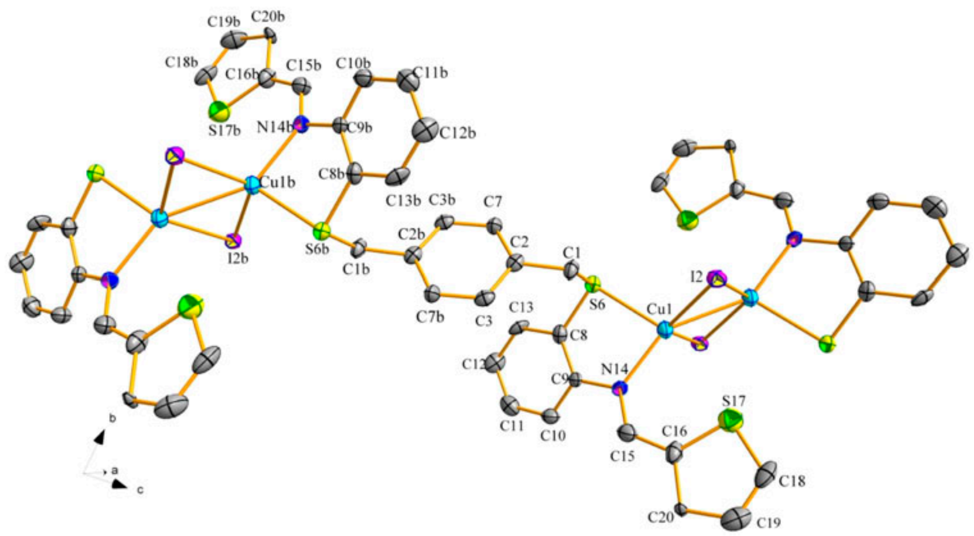


Figure 3. View of the structure of **5** with 50% probability ellipsoids. Hydrogens are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for **4** and **5**.

4		**5**	
I1–Cu1	2.633(2)	I2–Cu1	2.6192(15)
I1–Cu1b	2.6047(19)	I2–Cu1b	2.6355(15)
Cu1–S3	2.299(2)	Cu1–S6	2.390(3)
Cu1–N8	2.122(8)	Cu1–N14	2.076(8)
N8–C9	1.277(12)	N14–C15	1.304(12)
Cu1–Cu1b	2.723(2)	Cu1–Cu1b	2.577(2)
Cu1–I1–Cu1b	62.64(6)	Cu1–I2–Cu1b	58.75(4)
I1–Cu1–S3	104.12(8)	I2–Cu1–S6	102.43(8)
I1–Cu1–N8	127.52(19)	I2–Cu1–N14	128.5(2)
I1–Cu1–I1b	117.36(7)	I2–Cu1–I2b	121.26(5)
S3–Cu1–N8	87.9(2)	S6–Cu1–N14	85.8(2)
I1b–Cu1–S3	110.30(8)	I2b–Cu1–S6	109.49(7)
I1b–Cu1–N8	104.8(2)	I2b–Cu1–N14	102.3(2)
$b = 1 - x, 2 - y, -z$		$b = 1 - x, 1 - y, 2 - z$	

structure. Moreover, there are $\pi \ldots \pi$ stacking interactions between the phenyl rings of the nitrobenzyl and the iminothiophenyl groups coordinated to adjacent Cu(I) centers with the shortest distance 3.3 Å between the C13 and C5 atoms. There are fewer intermolecular interactions in **5**, only (I…H) hydrogen bonds that might hold the chains together (table 3).

4. Conclusion

Two tetradentate flexible Schiff-bases (N_2S_2) were used to synthesize new 1-D copper coordination polymers. The ligands are *bis*-bidentate ligands bridging dinuclear copper(I) halide units. Similar to compounds prepared from CuI and dapte derivatives, these ligands are good candidates for forming 1-D coordination polymers with close Cu…Cu distances.

Table 3. Hydrogen–bonding interactions in **4** and **5**.

4			**5**		
D–H···A	(Å)	∠ (°)	D–H···A	(Å)	∠ (°)
C1–H1B…O13	3.305(11)	135	C10–H10···I2 k	3.98(1)	159
C6–H6…O14	3.181(13)	127			
C7–H7…O13	3.427(13)	154			
C15–H15…I1	3.881(10)	151			

The continuation of this work may open new avenues to making compounds with interesting physical properties.

Supplementary material

^{1}H NMR, IR, and UV spectra for **1**–**5**; data on antibacterial activity studies; and hydrogen bonding schemes for **4** and **5**. X-ray crystallographic data for **4** and **5** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication, CCDC No. 851506 (for **4**) and No. 851511 (for **5**). Copies of the data can be obtained free of charge on request at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223 336033; Email: deposit@ccdc.cam.ac.uk).

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