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In situ assembly of a host-guest linked, mixed valence copper(II)-copper(I) coordination polymer $[\text{Cu}(1,2\text{-en})_2(\mu_3\text{-I})_2\text{Cu}_2(\mu_2\text{-I})_2]_n$ via partial reduction of copper(II) under ambient conditions

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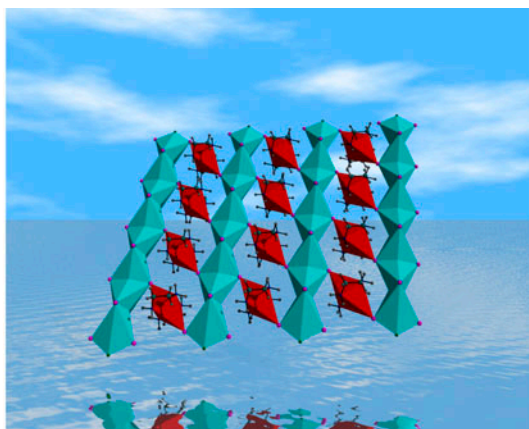
***In situ* assembly of a host–guest linked, mixed valence copper (II)–copper(I) coordination polymer [Cu(1,2-en)₂(μ₃-I)₂Cu₂(μ₂-I)₂]_n via partial reduction of copper(II) under ambient conditions**

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A 2-D coordination polymer, [Cu(1,2-en)₂(μ₃-I)₂Cu₂(μ₂-I)₂]_n (**1**), was formed at room temperature by *in situ* insertion of [Cu(1,2-en)₂]²⁺ guests into 1-D chains of a [Cu₂I₄]²⁻ host [1,2-en = 1,2-diaminoethane]. The structure of the complex was confirmed by single-crystal X-ray diffraction study. The shortest copper(I)–copper(I) distance within the complex is 2.89 Å.

Keywords: Copper(II); Copper(I); μ₃-I; Crystal structure; Coordination polymer

Introduction

Copper(I)–halide-based coordination polymers have attracted considerable attention due to their structural diversity and possible applications in solar energy conversion, luminescence-based sensors, display devices, and probes of biological systems [1].

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Abundance, low cost, and non-toxicity are some of the advantages of copper(I) complexes over second- or third- row transition metal complexes [2]. On the other hand, encouragement for the synthesis of mixed valence copper(I)–copper(II) complexes is provided by their biological modeling applications, for example, to mimic the activities of various multi-copper blue oxidase enzymes such as laccase and ascorbate oxidase [3]. In addition, they find applications in catalysis [4] and molecular magnetism [5]. Mixed valence copper complexes are of special interest because copper(II) and copper(I) prefer different geometries and stereochemistries. Thus, d^9 Cu(II) normally has (distorted) octahedral coordination [6] whereas d^{10} Cu(I) adopts tetrahedral or trigonal planar geometries [7].

The study of coordination polymers of copper(I) with halide bridges is interesting for their intrinsic architectural beauty and their esthetically pleasant structures [8]. Compared with chlorides and bromides, iodides exhibit more versatile bridging modes, ranging from μ_1 - to μ_7 -I [9], showing rhomboid dimers [10], zig-zag chains [11], double-stranded ladders [12], cubane-like and stepped Cu_4I_4 tetramers [13], hexagonal grid chains [14], and Cu_6I_6 hexamers including banded ribbons [14]. The iodide usually acts as reducing agent and may cause a partial reduction of Cu(II) to Cu(I), affording mixed valence Cu(I)–Cu(II) species [15, 16]. In the present work, I^- partially reduces Cu(II) to form 1-D chains of $\text{Cu}_2\text{I}_4^{2-}$. The remaining Cu(II) ions are coordinated by 1,2-diaminoethane (1,2-en) to form $[\text{Cu}(1,2\text{-en})_2]^{2+}$ dications, which are inserted as guests between adjacent chains of $\text{Cu}_2\text{I}_4^{2-}$ to form a 2-D network. Herein, we report the synthesis and characterization of a mixed valence 2-D Cu(I)–Cu(II) coordination polymer, $[\text{Cu}(1,2\text{-en})_2(\mu_3\text{-I})_2\text{Cu}_2(\mu_2\text{-I})_2]_n$ (**1**).

Experimental

Materials

All starting materials were commercially available, reagent grade, and used as purchased.

Preparation

Preparation of $[\text{Cu}(1,2\text{-en})_2](\text{ClO}_4)_2$. A methanol solution (20 mL) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 mM, 0.370 g) was added to a methanol solution (10 mL) of 1,2-diaminoethane (2 mM, 0.148 mL) to provide a deep blue solution. It was kept in an open atmosphere to grow suitable single crystals (0.26 g, 68% yield), which were collected by filtration. Anal. Calcd for $\text{C}_4\text{H}_{16}\text{Cl}_2\text{CuN}_4\text{O}_8$ (382.64) (%): C, 12.56; H, 4.21; N, 14.64. Found (%): C, 12.60; H, 4.20; N, 14.70. IR (KBr, cm^{-1}): 1084, 1113 (ν_{ClO_4}), 3110, 3197 ($\nu_{\text{N-H}}$). Magnetic moment: 1.72 BM.

Preparation of $[\text{Cu}(1,2\text{-en})_2(\mu_3\text{-I})_2\text{Cu}_2(\mu_2\text{-I})_2]_n$ (1**).** An acetonitrile solution (10 mL) of 1,2-diaminoethane (1 mM, 0.074 mL) was added to an acetonitrile solution (10 mL) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 mM, 0.370 g) and the solution was stirred for 10 min. A 1 : 1 water–methanol solution (2 mL) of KI (2 mM, 0.332 g) was added, and the reaction was stirred for an additional 1 h. Diffraction-quality single crystals (0.33 g, 40% yield) were obtained after a few days by the slow diffusion of diethyl ether into the mother liquor.

Alternatively, **1** was also prepared by the addition of a methanol solution (20 mL) of $[\text{Cu}(1,2\text{-en})_2](\text{ClO}_4)_2$ (1 mM, 0.382 g) to a methanol (10 mL) solution of KI (4 mM, 0.664 g), followed by the addition of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2 mM, 0.740 g) with constant stirring. Anal. Calcd for $\text{C}_4\text{H}_{16}\text{Cu}_3\text{I}_4\text{N}_4$ (818.43) (%): C, 5.87; H, 1.97; N, 6.85. Found (%): C, 5.70; H, 2.10; N, 7.00. IR (KBr, cm^{-1}): 3232, 3284($\nu_{\text{N-H}}$). Magnetic moment: 1.72 BM.

Physical measurements

C, H, N elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. IR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded as KBr pellets using a Perkin-Elmer Spectrum Two FTIR spectrophotometer. The powder XRD (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.548\text{ \AA}$) generated at 40 kV and 40 mA, in the $2\text{--}50^\circ 2\theta$ range using a 1-D Lynxeye detector at ambient conditions. The simulated PXRD pattern was calculated from the single-crystal structural data (cif file) using the CCDC Mercury software. The UV-vis diffuse reflectance spectrum was recorded on a Shimadzu UV 2401PC with an integrating sphere attachment. BaSO_4 was used as background standard. The Raman spectrum was obtained using a Renishaw InVia Reflex micro-Raman spectrometer with excitation of argon ion (514 nm) lasers. The laser power was kept sufficiently low to avoid heating of the samples, and spectra were collected with a resolution of 1 cm^{-1} . The magnetic susceptibility measurements were done with an EG&PAR vibrating sample magnetometer, Model 155, at room temperature, and diamagnetic corrections were made using Pascal's constants. The thermal behavior was studied in a dynamic nitrogen atmosphere (150 mL min^{-1}) at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ using thermogravimetric (TG) techniques with a NETZSCH TG 209F3 instrument.

X-ray crystallography

A single crystal having suitable dimensions was used for data collection using a "Bruker D8 QUEST area detector" diffractometer equipped with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at 100 K. The molecular structure was solved by direct methods and refined by full matrix least squares calculations on F^2 using the SHELX-97 package [17]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were placed in their geometrically idealized positions and constrained to ride on their parent atoms. A multi-scan empirical absorption correction was applied to the data using SADABS [18], specifically SADABS-2012/1 (Bruker, 2012). $R(\text{int})$ was 0.1211 before and 0.049 after the correction. The ratio of minimum to maximum transmission was 0.40. The $\lambda/2$ correction factor was 0.0015. A summary of the crystal, data collection, and refinement parameters is given in table 1.

Conductivity

The dc-conductivity was measured by the two-probe method at $30\text{ }^\circ\text{C}$ with an electrometer (Keithley, model 617). For electrical conductivity measurements, **1** was pressed to make pellets. The thickness (l) of the pellets was measured at four different positions using a screw gage, and the results were averaged. The conductivities of the pressed samples were determined using the equation:

Table 1. Crystal, data collection, and refinement parameters for **1**.

Formula	C ₄ H ₁₆ Cu ₃ I ₄ N ₄
Formula weight	818.43
Crystal system	Monoclinic
Space group	C _{2/m}
<i>a</i> (Å)	10.3425(11)
<i>b</i> (Å)	13.2442(12)
<i>c</i> (Å)	6.4782(7)
β (°)	117.235(4)
<i>Z</i>	2
<i>d</i> _{calcd} (g cm ⁻³)	3.445
μ (mm ⁻¹)	11.811
<i>F</i> (0 0 0)	734
Total reflections	3768
Unique reflections	951
Observed data [<i>I</i> > 2 σ (<i>I</i>)]	887
No. of parameters	40
<i>R</i> (int)	0.049
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0305, 0.0719
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0278, 0.0705

$$\sigma = \frac{1}{R} \times \frac{l}{a}$$

where *a* is the area and *R* is the resistance. The *I*–*V* characteristic curves were studied at 30 °C by applying voltage from –5 to +5 V, and the current was measured at each applied voltage.

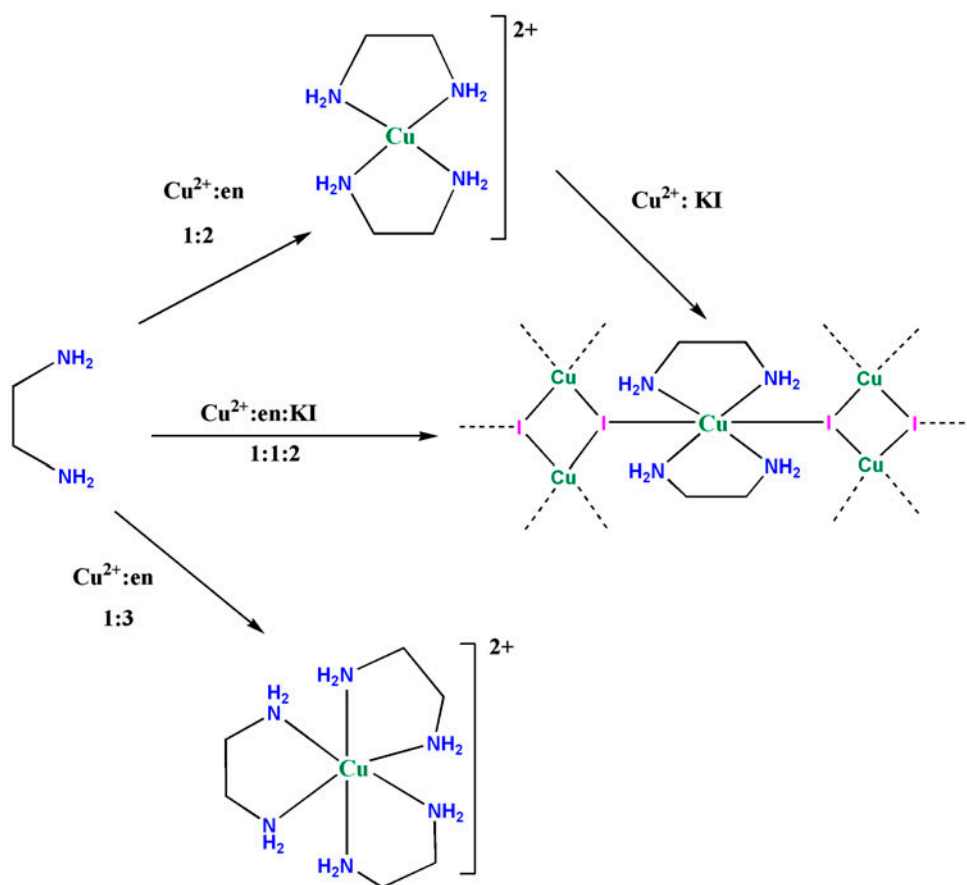
Results and discussion

Synthesis

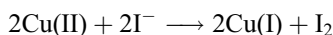
Synthesis of **1** is described in scheme 1. Cu(ClO₄)₂ reacts with excess KI to form [Cu₂I₄]²⁻, in which Cu(II) is reduced to Cu(I). The [Cu₂I₄]²⁻ anion forms an infinite layer structure via two μ_2 -I⁻ anions. The remaining Cu(ClO₄)₂ reacts with 1,2-en to form [Cu(1,2-en)₂]²⁺. This cation is inserted between the [Cu₂I₄]²⁻ anionic layers via weak interaction between the Cu(II) centers through μ_3 -I⁻ anions. The Cu(II) centers thus attain a distorted octahedral geometry with two very long, weak axial bonds.

Complex **1** was characterized by analytical, spectroscopic, and single-crystal X-ray diffraction (XRD) techniques. The reaction of Cu(II) salts with 1,2-en to form [Cu(1,2-en)₂]²⁺ is one of the oldest reactions in coordination chemistry [19]. The formation of [Cu(1,2-en)₃]²⁺ is also possible, if the required stoichiometry is maintained (scheme 1) [20]. Several polyoxometalates have been used under hydrothermal conditions as connecting building blocks with [Cu(1,2-en)₂]²⁺ [21]. The reduction of Cu(II) with I⁻ anions is also a well-known reaction. However, coupling of the complexation reaction with the redox reaction under ambient conditions, to assemble *in situ* a host–guest linked, mixed valence Cu(I)–Cu(II) coordination polymer, is unique in the literature.

To have a better understanding of the reaction pathway, Cu(ClO₄)₂ and 1,2-en were mixed in 1 : 2 M ratio to form [Cu(1,2-en)₂](ClO₄)₂. This complex was collected by filtration and characterized by single-crystal XRD. The structure of the complex has already

Scheme 1. Synthetic pathways for **1**.

been reported [19]. We dissolved 1 mM of the complex in acetonitrile, and a methanol solution of 4 mM KI was added to it. Addition of 2 mM of Cu(ClO₄)₂ to the solution with constant stirring produced **1**. In presence of KI, free Cu(II) is reduced to Cu(I) [16] with the concomitant oxidation of I⁻ anions into I₂ according to the following equation:



Formation of Cu₂I₄²⁻ has also been observed previously [22].

Description of the structure

The single-crystal XRD analysis of **1** revealed that it crystallized in the monoclinic space group *C*_{2/m}. The structure is a quasi-2-D infinite network, in which adjacent 1-D chains of the host [Cu₂I₄]²⁻ are linked up by the guest [Cu(1,2-en)₂]²⁺. The ORTEP of **1** is shown in figure 1. Selected bond lengths and angles are given in table 2. Discrimination between the Cu(I) and Cu(II) centers is based on bond length considerations. The Cu(I)–I bond lengths

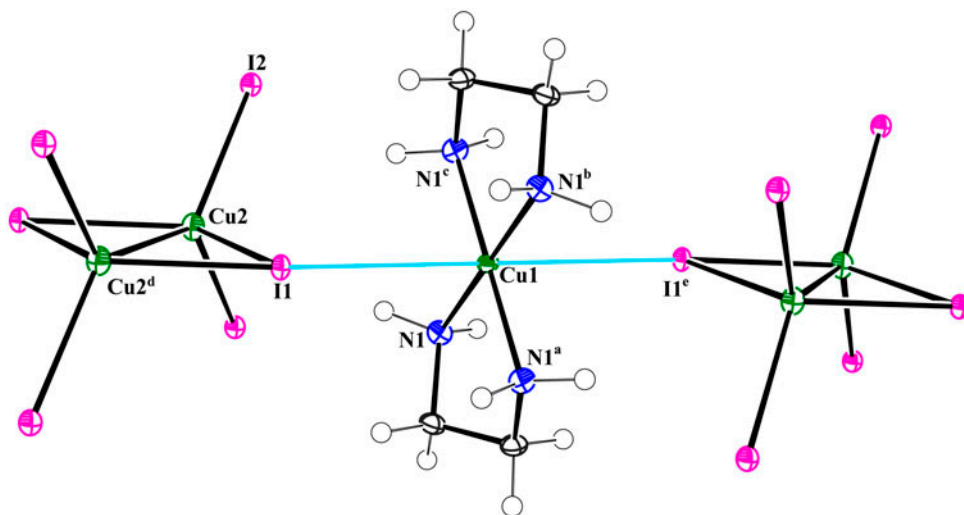


Figure 1. ORTEP view of the mixed valence coordination polymer $[\text{Cu}(1,2\text{-en})_2(\mu_3\text{-I})_2\text{Cu}_2(\mu_2\text{-I})_2]_n$ **1**, with selective atom labeling scheme and 50% probability thermal ellipsoids for all non-hydrogen atoms.

within the $(\text{Cu}_2\text{I}_4)^{2-}$ unit are 2.6406–2.771 Å, as also observed in other copper(I)–iodide complexes [23]. Table 3 contains the Cu(I)–I distances in some complexes. These bond lengths, therefore, support the presence of Cu(I) in **1**. The Cu(II)–N bond distance within the $[\text{Cu}(1,2\text{-en})_2]^{2+}$ unit is 2.003(3) Å, similar to those observed in related complexes [19, 20, 22]. The Cu–N bond distance, therefore, supports the presence of Cu(II) in the complex. The Cu(II)–N bond distances in selected complexes are gathered in table 4.

The Cu(I) center, Cu(2), is coordinated by two Γ^- anions, I(1) and I(2). Two symmetry-related Γ^- anions, I(1)^e and I(2)^d (^d $-x, y, -z$, ^e $-x, y, 1-z$) also coordinate to Cu(2) to complete its tetrahedral geometry. Each Γ^- bridges two Cu(I) centers to form the infinite chain

Table 2. Selected bond lengths (Å) and angles (°) in **1**.

I(1)–Cu(2)	2.6406(9)
I(1)–Cu(2) ^c	2.6660(11)
I(2)–Cu(2)	2.6935(6)
Cu(1)–N(1)	2.003(3)
Cu(1)–I(1)	3.360(6)
Cu(2)–I(1)–Cu(2) ^d	66.01(3)
Cu(2)–I(2)–Cu(2) ^e	83.53(2)
I(1)–Cu(2)–I(2)	112.00(2)
N(1)–Cu(1)–N(1) ^a	85.00(13)
I(1)–Cu(2)–I(2) ^b	112.00(2)
I(1)–Cu(2)–I(1) ^d	113.99(3)
I(1) ^d –Cu(2)–I(2)	110.54(2)
I(2)–Cu(2)–I(2) ^b	96.47(3)

^a $x, -y, z$.

^b $-x, -y, -z$.

^c $-x, y, -z$.

^d $-x, y, 1-z$.

Table 3. Cu(I)–I distances (Å) of selected literature complexes.

Complexes	Cu(I)–I bond distance (Å)		References
[Cu(1,2-en) ₂ (μ ₃ -I) ₂ Cu ₂ (μ ₂ -I) ₂] _n (1)	2.6406(9)	2.6660(11)	This work
{[Cu(1,2-pn) ₂ (μ ₃ -I)Cu ₂ (μ ₂ -I) ₃ (CH ₃ CN)]·CH ₃ CN} _n (2) (1,2-pn = 1,2-diamino-1-propene)	2.671(1)	2.734(1)	[22]
{[MC] ₂ [Cu ₄ (μ ₃ -I) ₄ (μ ₂ -I) ₂] _n (MC ⁺ = N-methyl-4-cyanopyridium)	2.709(1)	2.771(1)	
	2.639(3)	2.659(3)	[23]
	2.679(3)	2.719(3)	
	2.636(3)	2.632(3)	
	2.654(3)	2.664(3)	
	2.675(3)	2.689(3)	
	2.725(3)	2.634(3)	
	2.712(3)	2.695(3)	
	2.633(3)	2.712(3)	
{[PC][(Cu ₂ I ₄) _{1/4} (Cu ₂ I ₄) _{1/4}]} _n (PC ⁺ = N-propyl-4-cyanopyridinium)	2.6649(12)	2.6663(12)	[23]
	2.6730(12)	2.6761(12)	
{[iPC][(Cu ₂ I ₄) _{1/4} ((Cu _{1/2}) ₄ I ₄) _{1/4}]} _n (iPC ⁺ = N-isopropyl-4-cyanopyridium)	2.6746(18)	2.6667(18)	[23]
	2.6608(9)	2.6608(8)	
	2.6619(8)	2.6619(8)	
{[EV] _{1/4} [(Cu _{1/2}) ₄ I ₄]} _n (EV ²⁺ = N,N'-diethyl-4,4'-bipyridinium)	2.6696(5)	2.6696(5)	[23]
{[PV] _{1/2} [(Cu ₂ I ₄) _{1/4} ((Cu _{1/2}) ₄ I ₄) _{1/4}]} _n (PV ²⁺ = N,N'-dipropyl-4,4'-bipyridinium)	2.6580(8)	2.6580(8)	[23]
	2.6822(8)	2.6822(8)	
	2.6755(15)	2.6686(15)	

of [Cu₂I₄]²⁻ dianions. The shortest Cu(I)–Cu(I) distance within the [Cu₂I₄]²⁻ unit is 2.891 (1) Å, which is slightly greater than the sum of their van der Waals radii (2.80 Å). On the other hand, the Cu(II) center, Cu(1), is coordinated by four nitrogens, N(1), N(1)^a, N(1)^b, and N(1)^c (^ax, -y, z, ^b1 - x, y, 1 - z, ^c-x, -y, -z), from two 1,2-en moieties in the equatorial plane. The five-member chelate ring, Cu(2)–N(1)–C(1)–C(1)^a–N(1)^a, assumes a half-chair configuration with puckering parameters *Q*(2) = 0.478(5) Å and *φ*(2) = 90.0(4)° [24]. The N(1)–Cu(1)–N(1)^a angle is 85.00(13)°, as also observed in similar complexes [19, 20, 22]. Two I⁻ anions, I(1) and I(1)^c, from two adjacent 1-D chains of [Cu₂I₄]²⁻ coordinate in the axial positions of Cu(1) with a relatively long Cu(II)–I distance (3.360 Å) to complete the distorted octahedral geometry of Cu(1). This forms a quasi-2-D infinite coordination network with the repeating unit [Cu(1,2-en)₂(μ₃-I)₂Cu₂(μ₂-I)₂]. The relatively long Cu(1)–I distance is a direct consequence of the Jahn Teller effect, as expected for a d⁹ Cu(II) system. The Cu(1)–I bond distances are a little long compared to distances in other complexes [25]; however, similar and longer Cu(II)–I bond distances are found in the literature [26] (table 5).

Table 4. Cu(II)–N distances (Å) of selected literature complexes.

Complexes	Cu(II)–N bond distance (Å)		References
[Cu(1,2-en) ₂ (μ ₃ -I) ₂ Cu ₂ (μ ₂ -I) ₂] _n (1)	2.003(3)		This work
{[Cu(1,2-pn) ₂ (μ ₃ -I)Cu ₂ (μ ₂ -I) ₃ (CH ₃ CN)]·CH ₃ CN} _n (2) (1,2-pn = 1,2-diamino-1-propene)	2.001(5)	2.007(5)	[22]
	2.016(4)		
[Cu(ClO ₄) ₂ (C ₂ H ₈ N ₂) ₂]	2.012(2)	2.019(2)	[19]
[Cu(C ₂ H ₈ N ₂) ₃]SO ₄	2.063(3)	2.048(3)	[20]
	2.055(3)	2.045(3)	
	2.052(3)	2.049(3)	

Table 5. Cu(II)–I distances (Å) of selected literature complexes.

Complexes	Cu(II)–I bond distance (Å)		References
[Cu(1,2-en) ₂ (μ ₃ -I) ₂ Cu ₂ (μ ₂ -I) ₂] _n (1)	3.360(6)		This work
{[Cu(1,2-pn) ₂ (μ ₃ -I)Cu ₂ (μ ₂ -I) ₃ (CH ₃ CN)]·CH ₃ CN} _n (2) (1,2-pn = 1,2-diamino-1-propene)	3.231(4)		[22]
[Cu ₂ ^{II} I ₂ (η ³ -N ¹ ,N ² -S-bpytsc) ₂ ·2CH ₃ CN (Hbpytsc = 2-benzoylpyridine thiosemicarbazone)	3.221(4)		[26(b)]
CuL ₄ I ₂ (L = imidazole)	3.423	3.866	[26(a)]

Two types of I[−] are present in the Cu₂I₄^{2−} unit; one bridges two Cu(2) centers in a μ₂-fashion, while the other bridges two Cu(2) and one Cu(1) in a μ₃-fashion. Several Cu(I) complexes and Cu(I)–Cu(II) mixed valence complexes are reported [22, 27]. However, there is only one report of a Cu(I)–Cu(II) mixed valence coordination polymer, {[Cu(1,2-pn)₂(μ₃-I)Cu₂(μ₂-I)₃(CH₃CN)]·CH₃CN}_n (1,2-pn = 1,2-diamino-1-propene) (**2**), where the Cu(I) and Cu(II) centers are bridged by I[−] [22]. The shortest Cu(I)–Cu(II) and Cu(I)–Cu(I) distances in **1** are 5.990(1) and 2.891(1) Å, which may be compared with 4.407(9) and 2.414(1) Å, respectively, in **2** [22]. Complex **1** formed a nice 2-D sheet, whereas **2** formed a 1-D chain [22].

The hydrogen, H(1-D), attached to the amine N(1) forms an intramolecular hydrogen bond with I(2) (figure 2). The N(1)–H(1-D)···I(2) angle is 153° and the N(1)–I(2) donor–acceptor distance is 3.610(4) Å. The I(2)–H(1-D) acceptor–hydrogen distance is 2.70 Å. Another weak hydrogen bonding interaction is between H(1A), attached to C(1), and a symmetry-related (1/2 − x, 1/2 − y, −z) I(2). The C(1)–H(1A)···I(2) angle is 133° and the C(1)–I(2) donor–acceptor distance is 3.700(5) Å. The I(2)–H(1A) acceptor–hydrogen (H1A) distance is 2.95 Å.

IR, Raman, and electronic spectra and PXRD data

The infrared spectrum of **1** shows absorption bands at 3232 and 3284 cm^{−1} assigned to NH₂ stretching vibrations. The band corresponding to the C–H stretch occurs at 2924 cm^{−1}. The Raman spectrum shows a band at 2974 cm^{−1} due to the NH₂ stretch. The bands corresponding to C–H stretching and bending vibrations occur at 2940 and 1560 cm^{−1}, respectively. The electronic spectrum was recorded in diffuse reflectance mode [28]. The spectrum exhibits three broad spectral bands at 322, 474, and 635 nm (figure 3), which may be assigned as the B_{1g} → E_g, B_{1g} → B_{2g}, and B_{1g} → A_{1g} transitions, respectively [29]. The experimental powder XRD pattern of the bulk product of **1** is in agreement with the XRD pattern simulated from the single-crystal XRD data (figure 4), indicating phase purity of the bulk sample.

Conductivity

Complex **1** showed a dc conductivity of 0.15 × 10^{−8} s cm^{−1}. In figure 5, the *I*–*V* characteristic curve is shown, which clearly indicates the semiconducting nature of **1** with rectification behavior [30]. The calculated rectification ratio (RR) (the ratio of current at selected forward bias voltage to current at the same reverse bias voltage) for **1** is ≈6.6, which is considerable [31]. The RR values of some selected complexes are gathered in table 6, which clearly

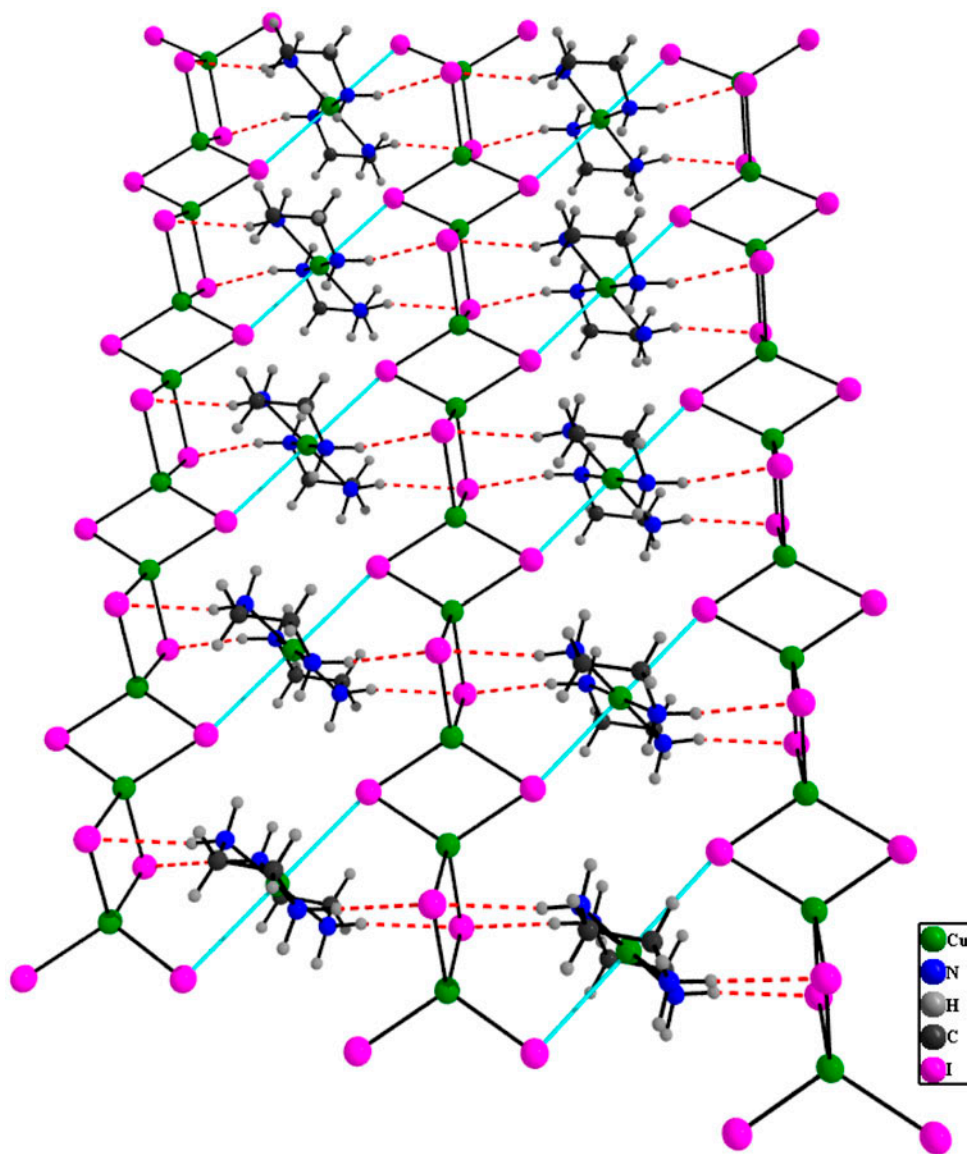


Figure 2. H-bonding network in **1**, to form a 2-D sheet.

indicates that the RR value of **1** is comparable with the reported complexes. Due to its semi-conducting and rectification behavior, **1** may find applications in photoelectric devices, high-frequency oscillators, and logic gate fabrication systems.

TG analysis

The TG curve of **1** is shown in figure 6. There are two zones of weight loss, between 100 and 525 °C and between 525 and 700 °C. The first weight loss step (~30 wt%) converts **1**

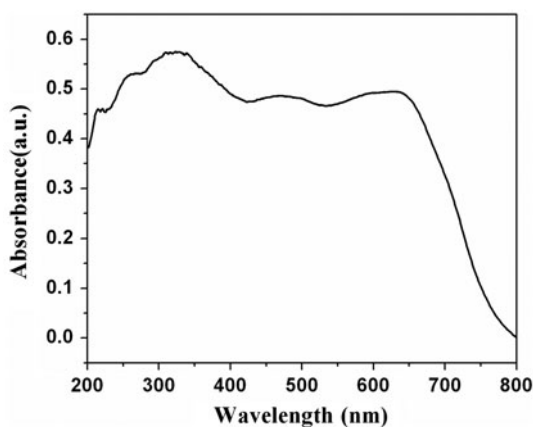


Figure 3. Solid-state UV-vis spectrum of **1**.

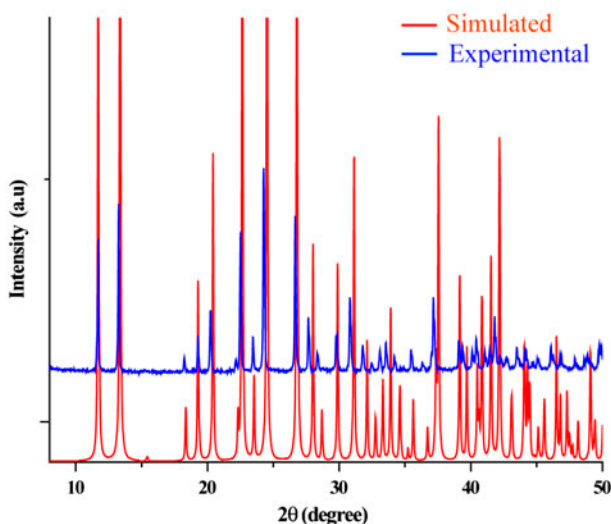


Figure 4. Experimental and simulated PXRD patterns of **1**.

completely into 3CuI (Calcd 30.17 wt%). The second weight loss step (~ 47 wt%) is due to the liberation of iodine from CuI . In this step, the sample completely loses the iodine and is transformed into copper (Calcd 46.5 wt%). The remaining residue (23 wt%) is consistent with the amount of Cu in **1** (23.3 wt%).

Concluding remarks

To summarize, we have constructed a mixed valence quasi-2-D host–guest coordination polymer, $[\text{Cu}(1,2\text{-en})_2(\mu_3\text{-I})_2\text{Cu}_2(\mu_2\text{-I})_2]_n$, containing a 1-D chain of $[\text{Cu}_2\text{I}_4]^{2-}$ dianions as the host, into which $[\text{Cu}(1,2\text{-en})_2]^{2+}$ dicationic species are inserted *in situ*. The Cu(I) centers of the

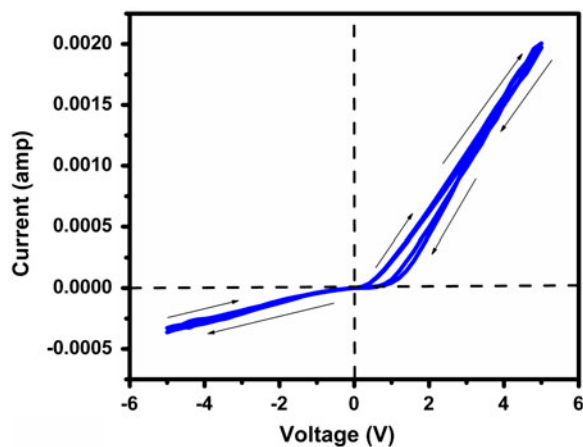


Figure 5. Current–Voltage characteristic curves of **1**.

Table 6. RR of selected literature complexes.

Complexes	RR	References
$\text{FcC}_{11}\text{SSC}_{11}\text{Fc}$ (Fc = ferrocene)	0.85	[32]
$\text{CH}_3\text{OCSC}_{11}\text{Fc}$ (Fc = ferrocene)	1.14	[32]
Poly(o-methoxy aniline)	1.2	[31]
7-(ferrocenyl)-1-undecanethiol	4.5	[33]
9-(ferrocenyl)-1-undecanethiol	5	[33]
$[\text{Cu}(1,2\text{-en})_2(\mu_3\text{-I})_2\text{Cu}_2(\mu_2\text{-I})_2]_n$ (1)	6.6	This work

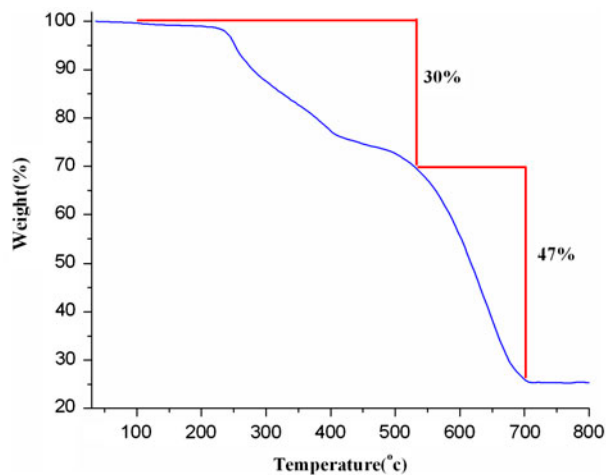


Figure 6. TGA curve of **1**.

$[\text{Cu}_2\text{I}_4]^{2-}$ moieties are the *in situ* reduction product of Cu(II) centers, assisted by I^- anions. There is no example of the incorporation of a Cu(II) complex guest in a $[\text{Cu}_2\text{I}_4]^{2-}$ host to form a mixed valence Cu(I)–Cu(II) coordination polymer. We expect that this new approach for generating a mixed valence coordination polymer will frequently be used to prepare a variety of host–guest complexes. We are currently trying to prepare more of these types of mixed valence complexes.

Supplementary material

Crystallographic data for $[\text{Cu}(1,2\text{-en})_2(\mu_3\text{-I})_2\text{Cu}_2(\mu_2\text{-I})_2]_n$ (**1**) have been deposited at the Cambridge Crystallographic Data Center, CCDC 953054. This information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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