

Full Paper

Electrochemical Synthesis and Structural Characterization of a Novel Mixed-valence Copper (I)-copper (II) Complex: {[Bis(ethylenediamine) Copper (II)] Bis[diiodocuprate (I)]}

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Abstract: A novel, mixed-valent copper(I)-copper(II) complex, {[bis(ethylenediamine)copper(II)] bis[diiodocuprate(I)]} (**1**), has been prepared by electrochemical dissolution of a sacrificial copper anode in a solution of ethylenediamine (en), I₂ and tetraethylammoniumperchlorate (TEAP) as supporting electrolyte in acetonitrile (AcN) and characterized by single-crystal X-ray structure determination. The crystal structure of the complex **1** shows that it consists of a CuI₂ polymer formed from I⁻ ligands bridging Cu(I) ions, with a nearly square planar geometry of bivalente Cu(II) atoms chelated by two ethylenediamine ligands. The results also show that direct electrosynthesis of the complex had high current efficiency, purity and electrolysis yield.

Keywords: Copper (I/II); complex; electrosynthesis; ethylenediamine; diiodocuprate(I).

Introduction

The design of complex molecular architectures based on transition metal atoms and organic ligands is an important goal for synthetic chemistry as it provides the opportunity to control or encode the properties of a material at the molecular level [1]. Suitable organic ligands favoring structure-specific self-assembly are the bases for the construction of coordination architectures. On the other hand, copper halides have been successfully used for the synthesis of uncharged coordination polymer arrays [2-4]. Various factors, such as the stoichiometric metal-to-ligand ratio, the halide and the nature and substitution of the ligand have been shown to influence the form of the copper-halide motifs and the structures of the resulting coordination polymer [2,3]. Recently, increasing attention has been paid to the use of flexible bridging units in the construction of supramolecular architectures [5,6] and this approach is attractive because the flexibility and conformation freedoms of such ligands offer the possibility for the construction of unprecedented frameworks with tailored properties and functions [7].

Although to date remarkable Cu(I) complexes [8-11] and examples of Cu(I) complexes with halocuprate anion [12-14] have been reported, there is no report on diiodocuprate (I) anion polymeric complex with ethylenediamine. Thus, we report herein the electrosynthesis and crystal structure of a novel Cu(I) polymeric complex with potentiostatic dissolution of copper anode in a solution of ethylenediamine and iodine in AcN.

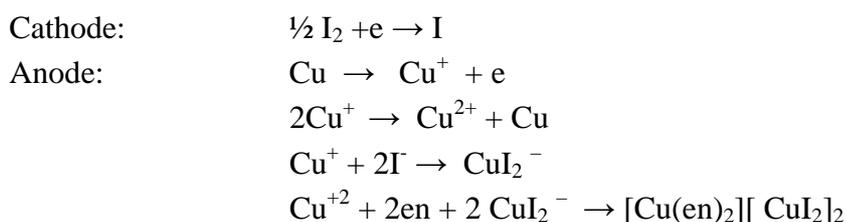
Results and Discussion

Electrosynthesis

Direct anodic dissolution of copper metal and cathodic reduction of iodine in AcN proved to be a simple and efficient one-step route to new copper(I) iodide ligand polymeric complex, $\{[\text{Cu}(\text{en})_2][\text{CuI}_2]_2\}_n$ (**1**) in an undivided cell. The dark brown air-stable crystalline complex is obtained by dissolving in DMF. The complex is insoluble in water and most common organic solvents except DMF. The electrochemical cell for this system could be presented as follows:



The electron transfer reaction mechanism involves the anodic oxidation of copper to Cu^+ , which in the presence of I^- (resulting from the reduction of I_2 at the cathode) forms the CuI_2^- complex. However, since en is a stronger ligand than I^- , some of Cu^+ participates in a disproportionation reaction to form Cu^{+2} as $\text{Cu}(\text{en})_2$.

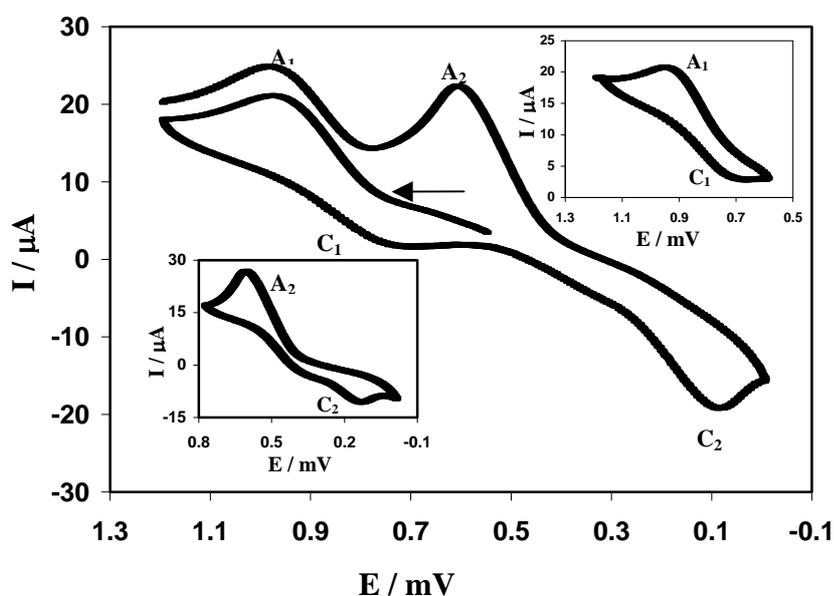


Electrochemistry

A sweep for complex from +0.4 to +1.2 V shows only one quasi-reversible anodic peak ($E_{A1} = 0.98$ V) and the backwards cathodic sweep (+1.2 to 0.0 V) shows two cathodic peaks at $E_{C1} = 0.74$ V and $E_{C2} = 0.09$ V (Figure 1). In a second reversing anodic sweep another anodic peak ($E_{A2} = 0.61$ V) corresponding to the reoxidation of the product of cathodic peak at $E_{C2} = 0.09$ V appeared. If the studied range is limited from +1.2 to +0.6 V (Figure 1, inset, right) a quasi-reversible wave at $E_{C1} = 0.74$ V and $E_{A1} = 0.98$ V was observed and assigned to the Cu(II)/Cu(I) redox couple, while a potential sweep in the limited range of +0.8 to 0.0 V shows the second redox couple ($E_{C2} = 0.09$ V, $E_{A2} = 0.61$ V) corresponding to Cu(I)/Cu(0). The latter redox assignment is further supported by recording the cyclic voltammogram of CuI under the same experimental conditions. As it can be seen from Figure 1 (inset, left) the Cu(I) in CuI cyclic voltammogram is reduced to Cu(0) at $E_{C2} = 0.09$ V and its anodic compartment wave is observed at $E_{A2} = 0.61$ V, which is a good indication of the presence of a Cu(I)/Cu(0) redox couple in the complex.

Since the cyclic voltammogram of ethylenediamine didn't show any wave in the potential range of 0.0 to 1.2 V (data not shown), thus the redox couples in the complex have been assigned to the metal center in the complex. Therefore, the observed cyclic voltammogram was consistent and characteristic of two Cu (II)/Cu (I) and Cu (I)/Cu (0) redox couples in the structure of the complex.

Figure 1. Cyclic voltammogram of **1** at the glassy carbon electrode in DMF. Initial anodic scan from 0.6 V to 1.2 V and reversing scan up to 0.0 V. Inset right: cyclic voltammogram of **1** in the 1.2 V to 0.6 V range. Inset left: cyclic voltammogram of CuI in the 0.8 V to 0.0 V range. Scan rate 50 mVs^{-1} .



Structural studies

The crystallographic data are summarized in Table 1 and selected bond distances and angles are given in Table 2. Views of the $[\text{Cu}(\text{en})_2][\text{CuI}_2]_2$ complex **1** shown in Figures 2 and 3 reveal that it crystallized in the monoclinic crystal system with space group $C2/m$. Complex **1** is mixed-valence. The asymmetric unit of **1** contains two crystallographically independent metal centers in the crystal structure. The bivalent Cu (1) atom has a nearly square planar geometry and was chelated by two ethylenediamine ligands. The two inter and intraligand N–Cu–N angles differ only slightly from 90° ($85.51(27)^\circ$ – $94.49(27)^\circ$), and the two N–Cu–N angles are close to 180° . The Cu–N distance $2.003(10)\text{\AA}$ is similar to those found in other Cu(II) complexes [15–17]. The structure of **1** consisted of a chain of alternatively perpendicular planes Cu_4I_4 running along the *c* axis of CuI_2^- formed from I^- ligands bridging Cu (I) ions. The monovalent Cu(2) atom ion in this complex is distorted tetrahedral. The $\text{I1}^i\text{—Cu2—I1}$ angle is much less than 109.5° , being only $96.72(0)^\circ$. On the contrary, the I2—Cu2—I1 angle ($112.25(0)^\circ$), is much larger than those of a tetrahedral complex. The average Cu–I bond distance (2.6752 \AA) is similar to that found in other Cu (I) (diimine) pseudotetrahedral complexes [18–20]. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters are reported in Table 3.

Figure 2. ORTEP view of the crystal structure of $[\text{Cu}(\text{C})_2]^+$, showing the atom labeling scheme. The thermal ellipsoids enclose 50% of the electronic density.

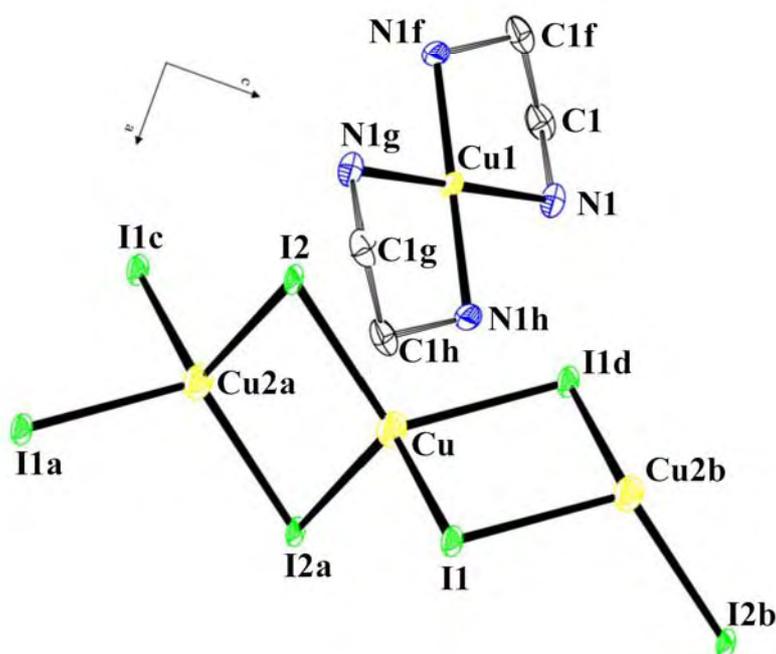
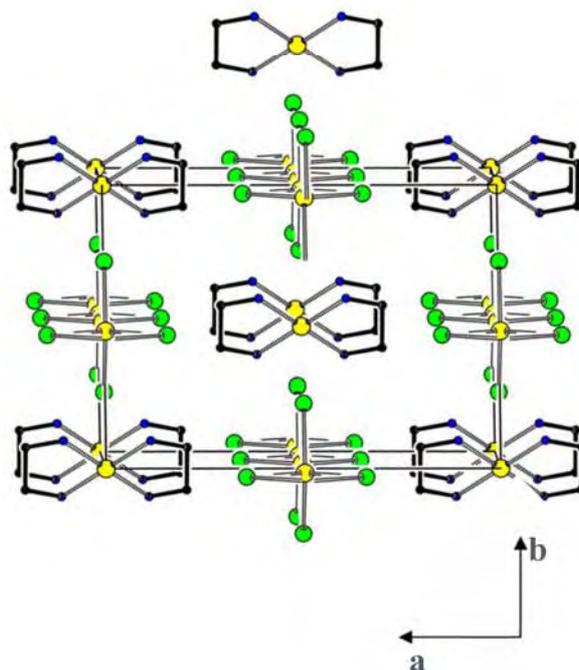


Figure 3. A view of the overall network slightly offset from directly down the c axis.**Table 1.** Crystal data and structure refinement for **1**.

	1
T/K	293(2)
Crystal System	Monoclinic
Space group	C 2/m
$a/\text{\AA}$	10.3632(11)
$b/\text{\AA}$	13.2843(13)
$c/\text{\AA}$	6.5115(7)
β°	117.339(11)
$V/\text{\AA}^3$	796.30(16)
$Z, D_{\text{calc}}/\text{Mg.m}^{-3}$	2, 3.346
μ/mm^{-1}	11.700
$F(000)$	702.0
Crystal size/ mm^3	
θ°	2.69 to 28.050
$h/k/l$	-12,13/-17,17/-8, 8
Refl. unique	996
Refl. Observed [$I > 2\sigma(I)$]	915
$R(\text{int})$	0.040
Data /restraints/parameters	996/ 0 /40
Goodness-of-fit on F^2	1.280
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0614, wR_2 = 0.1632$
R indices for all data	$R_1 = 0.0649, wR_2 = 0.1661$
Largest difference Peak and hole ($e. \text{\AA}^{-3}$)	0.799 and -0.740

$$[*] R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right\}^{1/2}$$

Table 2. Selected geometric parameters (Å, °) for **1**.

I1—Cu2 ⁱ	2.696(1)	Cu1—N1 ^{iv}	2.003(10)
I1—Cu2	2.696(1)	Cu1—N1	2.003(10)
I2—Cu2	2.642(24)	Cu1—N1 ⁱⁱⁱ	2.003(10)
I2—Cu2 ⁱⁱ	2.671(3)	Cu1—N1 ^v	2.003(10)
Cu2—I2 ⁱⁱ	2.671(3)	N1—C1	1.477(11)
Cu2—Cu2 ⁱⁱ	2.930(2)	C1—C1 ^v	1.506(16)
Cu2 ⁱ —I1—Cu2	83.28(0)	N1 ⁱⁱⁱ —Cu1—N1	179.99(27)
Cu2—I2—Cu2 ⁱⁱ	66.93(5)	N1 ⁱⁱⁱ —Cu1—N1 ^{iv}	85.51(27)
I2—Cu2—I1	112.25(0)	N1—Cu1—N1 ^{iv}	94.49(27)
I2 ⁱⁱ —Cu2—I1	110.73(0)	N1 ⁱⁱⁱ —Cu1—N1 ^v	94.49(27)
I1 ⁱ —Cu2—I1	96.72(0)	N1—Cu1—N1 ^v	85.51(27)
I2—Cu2—Cu2 ⁱⁱ	57.01(4)	N1 ^{iv} —Cu1—N1 ^v	179.99(27)
I2 ⁱⁱ —Cu2—Cu2 ⁱⁱ	56.06(4)	C1—N1—Cu1	107.34(49)
I1 ⁱ —Cu2—Cu2 ⁱⁱ	131.61(0)	N1—C1—C1 ^v	107.20(69)
I2—Cu2—I2 ⁱⁱ	113.07(6)		

Symmetry codes:

- (i) -x, 1-y, 1-z; (ii) -x, 1-y, -z; (iii) -1-x, 1-y, -z; (iv) x, 1-y, z;
(v) -1-x, y, -z.

Table 3. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U _{iso} */U _{eq}
I1	0.0000	0.34835 (5)	0.5000	0.0159 (3)
I2	-0.24076 (7)	0.5000	-0.17764 (10)	0.0145 (3)
Cu1	-0.5000	0.5000	0.0000	0.0127 (4)
Cu2	-0.00269 (16)	0.5000	0.2230 (2)	0.0227 (4)
N1	-0.3879 (8)	0.6107 (5)	0.2179 (11)	0.0174 (13)
C1	-0.4199 (10)	0.7046 (6)	0.0819 (15)	0.0208 (16)

Conclusions

The utility of direct and uncomplicated electrosynthesis to obtain this type of copper complex of ethylenediamine with high yield and high purity has been demonstrated. Comparing with the usual chemically copper complexes of ethylenediamine prepared over the years [21], the resulting complex is a new and unusual member of an interesting class of mixed-valence one-dimensional supramolecular copper complexes.

Experimental

Apparatus

Electrochemical experiments were performed using a Metrohm model 746 VA trace analyzer connected a 747 VA stand. A glassy carbon electrode (0.2 mm diameter) was used as the working electrode. A platinum wire and a commercial KCl saturated Ag/AgCl electrode from Metrohm were used as the auxiliary and reference electrodes, respectively. The solutions were purged with 99.999% argon for 10 min before the start of the experiments. Electrosynthesis was performed using a Zahner elektrik PP200 potentiostat/galvanostat. The electrochemical cell consists of a tall-form beaker (100 mL) with three cross sectional openings. The potential of copper anode was held 0.5 V with respect to an Ag/AgCl reference electrode and a platinum sheet was used as a cathode counter electrode. A magnet stirring system was also used.

Reagents

Acetonitrile (AcN, Merck), ethylenediamine (en, Merck), iodine (Merck), dimethylformamide (DMF, Merck) and tetrabutylammonium perchlorate (TBAP, Fluka) as supporting electrolyte were used as received.

Characterization of the Complex [22]

Diffraction data for **1** were collected on a STOE-IPDSII diffractometer using graphite-monochromated Mo-K α radiation (λ 0.71073Å). Data were collected and integrated using the stoe X-AREA software package [23]. A numerical absorption correction was applied using X-RED and X-SHAPE software [24]. The structure was 100 solved by direct methods (SHELXS-97 [25]). The structure refinement was performed by a full-matrix least-squares method against F² (SHELXL-97 [25]). All non-H-atoms were refined anisotropically, all H-atoms were inserted in the calculated positions.

Electrosynthesis

Electrosynthesis was carried out in an undivided cell. The copper anode and platinum cathode were inserted in a solution of ethylenediamine (0.030 g, 0.5 mmol), iodine (0.126 g, 0.5 mmol) and 0.10 M TBAP as supporting electrolyte in can (50 mL). Potentiostatic oxidation of the copper anode at 0.5 V resulting in colorless solution initially. Electrolysis was stopped after 30 minutes and brown product was filtered off, washed with AcN and dried. The final brown precipitate was dissolved in DMF and allowed to stand over several days to deposit the complex as dark brown prisms suitable for X-ray crystallography. The IR spectra of both, brown precipitate and its crystalline complex showed the same bands, indicating that DMF did not engaged in the resulted crystalline complex.

Microanalysis

Found: C, 5.86; H, 1.95; N, 6.84. C₄H₁₆Cu₃I₄N₄ required C, 5.87; H, 1.97; N, 6.85 %; Crystal data: C₄H₁₆Cu₃I₄N₄, 802.30, monoclinic, space group C2/m, a=10.3632(11), b=13.2843(13), c=6.5115(7) Å, β=117.339(11), U = 2713 Å³, Z = 2, μ(Mo-Kα) = 3.346 cm⁻¹, T = 293(2) K, N = 996, N_o [[I>2σ(I)]] = 915; R = 0.0614, R_w = 0.1632.

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