Synthesis, characterization and properties of a copper complex with dicyano acetic acid methyl ester ligand derived from tetracyanoethylene

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Abstract

The reaction of CuCl with tetracyanoethylene (TCNE) affords a copper(II) complex, [(DCAE)₂Cu(H₂O)₂] **1** (DCAE: dicyano-acetic acid methyl ester, derived from TCNE). Its structure has been characterized by physics-chemical and spectroscopic methods. Magnetic studies exhibit that no magnetic coupling between two Cu²⁺ via DCAE⁻ unit in the temperature range 300-9 K. Electrochemical studies show that this copper complex can act as an electrocatalyst for hydrogen generation both from acetic acid, with a turnover frequency (TOF) of 74 moles of H₂ per mole of catalyst per hour an potential (OP) of 941.6 (in CH₃CN), and from aqueous buffer (pH 7.0) with a TOF of 285 moles of H₂ per mole of catalyst per hour at an OP of 787.6 mV.

Keywords: TCNE; copper complex; molecular catalyst; proton or water reduction; H₂ evolution

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1. Introduction

We are interested in the chemistry of tetracyanoethylene (TCNE), because of its versatile reactions in different directions [1-5]. Additionally, TCNE can be employed as linkers to bridge metal centers, giving rise to oligonuclear complexes and coordination polymers. Typically, the strong electron-acceptor capacity of TCNE, coupled with its ability to serve as a ligand through two or more of its CN groups, can allow the preparation of polymeric materials [6-9]. So far, several molecular magnetic materials have been provided by reactions of TCNE with paramagnetic metal ions [10-14]. Despite these advances, few materials based on copper complexes supported by TCNE are known. With the goal of giving new organic-based magnets, and molecular-based materials, that stand a good chance of displaying interesting electronic properties, we tried the reaction of CuCl and TCNE with a molar ratio set of 1:2. Surprisingly, an unexpected copper complex, [(DCAE)₂Cu(H₂O)₂] **1** was obtained. In this paper, we describe the synthesis, structure and properties of this complex, as well as its electrocatalytic hydrogen generation both from acetic acid and aqueous buffer.

2. Experimental section

2.1 Physical measurements

Sodium dicyano-acetic acid methyl ester, NaDCAE was prepared following the literature procedures [15]. Elemental analyses for C, H, and N were obtained on a Perkin-Elmer analyzer model 240 instrument. UV-Vis spectra were measured on a

Hitachi U-3010 spectrometer. ESI-MS experiment was performed on a Bruker Daltonics Esquire 3000 spectrometer by introducing samples directly into the ESI source using a syringe pump. Magnetic susceptibility data for powder sample were collected in the temperature range 2-300 K with a Quantum Design SQUID Magnetometer MPMS XL-7. Effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_{\text{M}}T)^{1/2}$, where χ_{M} is the molar magnetic susceptibility. Cyclic voltammograms (CVs) were measured on a CHI-660E electrochemical analyzer under N_2 using a three-electrode cell in which a glassy carbon electrode (1 mm in diameter) was the working electrode, a saturated Ag/AgNO₃ (1.0 M) or Ag/AgCl electrode was the reference electrode, and a platinum wire was the auxiliary electrode. In organic media, the ferrocenium/ferrocene couple was used as an internal standard, and 0.10 M [(n-Bu)₄N]ClO₄ was used as the supporting electrolyte. Controlled-potential electrolysis (CPE) in aqueous media was conducted using an air-tight glass double compartment cell separated by a glass frit. The working compartment was fitted with a glassy carbon plate and an Ag/AgCl reference electrode. The auxiliary compartment was fitted with a Pt gauze electrode. The working compartment contained a 50 mL of 0.25 M phosphate buffer solution, while the auxiliary compartment was filled with 35 mL phosphate buffer solution. After addition of complex **1**, CVs were recorded. After electrolysis, a 0.50 mL aliquot of the headspace was removed and replaced with 0.50 mL of CH₄. The headspace sample was injected into the gas chromatograph (GC).

2.2 Synthesis of complex **1**

A solution of TCNE (0.261 g, 2 mmol) in methanol (10 mL) was treated with a solution of CuCl (0.100 g, 1 mmol) in CH₃CN/methanol (5 mL). The mixture was stirred at room temperature for 1 h, no reaction was observed. After the addition of one drop of water, the solution color turned from yellow to green. Green crystals were obtained from the filtrate which was allowed to stand at room temperature for several days, collected by filtration, and dried in *vacuo*. Yield: 0.193 g (56.0%). Calcd for C₁₀H₁₄CuN₄O₈: C 31.46, H 2.64, N 14.68. Found: C 31.62, H 2.68, N 14.6. IR bands (KBr pellets, cm⁻¹): ν = 2251 (m), 2182 (s) ($\nu(\text{C}\equiv\text{N})$); ν = 1641 (s) ($\nu(-\text{CO}_2^-)$).

2.3 Crystal structure determination

X-ray data measurement for complex **1** was conducted on a Bruker Smart Apex II DUO area detector using graphite monochromated Mo-K α radiation (λ = 0.71073 Å). All empirical absorption corrections were applied by using the SADABS program [16]. The structure was solved using direct methods and the corresponding non-hydrogen atoms are refined anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL-97 computer program [17]. Crystallographic data for complex **1** are given in Table S1 and selected bond lengths and angles are listed in Table S2. CCDC 671102 contains the supplementary crystallographic data for this paper. This data can be obtained free

of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

3. Results and discussion

3.1 General characterization

In order to prepare metal-organic frame linked by TCNE, we tried the reaction of CuCl and TCNE at a molar ratio set of 1:2. However, this reaction affords a water soluble copper(II) complex **1** supported by two dicyano- acetic acid methyl ester (DCAE⁻) ligands (Scheme 1). Based on the literature precedent [2,15,18], a possible mechanism for the formation of DCAE⁻ from TCNE was illustrated by Scheme 2. First, the addition of CuCl leads to the formation of [TCNE]⁻, then provides an intermediate [C₂(CN)₃]⁻ by losing one CN⁻. In the presence of O₂, further reaction provides one dicyano species [(CN)₂C=C-O]⁻ by losing one CN⁻. Finally, the reaction of [(CN)₂C=C-O]⁻ with methanol (solvent) provides DCAE⁻ anion. This result shows that TCNE undergoes numerous reactions [19]. From Fig. S1 (infrared spectrum of **1**), complex **1** shows two $\nu(\text{C}\equiv\text{N})$ stretches at 2251 and 2182 cm⁻¹ at lower energy than that of the free tetracyanoethylene (2258 and 2215 cm⁻¹) (Fig. S2), assigning to the cyanide mode of **1**. As shown in Fig. S3, complex **1** exhibits an absorption band at about 228 nm, which can be assigned to metal-ligand charge transitions. From Fig. S4, in the pH range 2.5 to 11.0, no new peak appeared, suggesting this complex is stable under these conditions.

Scheme 1 Synthesis of complex **1**.

Scheme 2 The procedure for the formation of dicyano- acetic acid methyl ester anion (DCAE⁻).

Complex **1** crystallizes in space group P2(1)/n, with two formula units present per unit cell. As shown in Fig. 1, **1** consists of one Cu²⁺, two H₂O and two dicyano-acetic acid ester anions. The coordination geometry of copper in **1** is tetragonal, and is coordinated by two O atoms from H₂O, two N atoms from dicyano-acetic acid ester anion. Cu–N distances are 1.9617(15), and 1.9618(15) Å, respectively, and the Cu–O lengths are 1.9631(13), and 1.9632(13) Å, respectively. Interestingly, the introduction of methanol into complex **1** led to the dissociation of a DCAE⁻ ion from copper atom. This was in agreement with result from ESI-MS measurement which exhibited one ion at a mass-to-charge ratio (*m/z*) of 286.0946, with the mass and isotope distribution pattern corresponding to that of [(DCAE)Cu(H₂O)₂(CH₃OH)₂]⁺ (Fig. S5).

3.2 Magnetic properties

The magnetic behavior of complex **1** was investigated in the temperature range 2-300 K for molar susceptibility. As shown in Fig. 2a, the value of $\chi_M T$ at room temperature, $0.499 \text{ cm}^3 \text{Kmol}^{-1}$, is close to the value of $0.50 \text{ cm}^3 \text{Kmol}^{-1}$ of one copper(II) ions ($S = 1/2$). This value remain almost constant with cooling down up to 9.0 K, then they decrease sharply at low temperature reaching a value of $0.25 \text{ cm}^3 \text{Kmol}^{-1}$ at 2.0 K. The decrease of $\chi_M T$ values in the low temperature region may be due to very weak antiferromagnetic coupling between metal ions. This weak antiferromagnetic interaction can be understood taking into account the large separation (about $5.5 \text{ \AA}$) between the paramagnetic copper centres in complex **1**. This result is in agreement with the magnetic analysis by Curie-Weiss law ($\chi_M = C/(T-\theta)$, $\theta = -0.95^\circ$) (Fig. 2b). Based on above analysis, the oxidation state of copper in complex **1** is +2.

3.3 Linear scan voltammetry

It has been shown that copper complexes can act as electro-catalysts for hydrogen production via an unstable hydride intermediate [20,21]. To study its function as one new material, e. g. electrocatalyst in liquid, first we investigated the electrochemical behavior via using linear scan voltammetry (LSV).

As shown in Fig. 3, the potentials for reduction of **1** are the same as that of the back-ground (ca. -1.70 V versus Ag/AgCl), indicating that no proton is lost during the initial reduction. According to Fig. 3, the peak current increases continually with increasing concentrations of complex **1** from 0.0 to 0.156 mM, and no turning point is found, demonstrating that **1** undergoes redox cycling during the electrochemical

experiments. From Fig. S6, the catalytic current increases significantly with decrease of pH from 8.0 to 4.3, suggesting that there is a protonation step in the catalytic reaction.

3.4 Cyclic voltammetry

We then explored its electrochemical properties via cyclic voltammetry, which was conducted in CH₃CN with 0.10 M [(n-Bu)₄N]ClO₄ as the supporting electrolyte. As shown in Fig. 4a, the cyclic voltammogram of 2.67 mM complex **1** shows a quasireversible couple at 0.69 V and a reversible redox couple at 1.11 V versus Ag/AgNO₃, respectively. For comparison, NaDCAE displays a quasireversible redox peak at 0.67 V and a reversible redox couple at 1.12 V versus Ag/AgNO₃ (Fig. S7). These two oxidation waves of **1**, being close to the oxidations of NaDCAE, are assigned to NaDCAE. Scanning to cathodic potential reveals two quasireversible couples at -0.82 V and -1.50 V versus Ag/AgNO₃, which are assigned to the Cu^{II/I} and Cu^{I/0} couples, respectively. Scan rate analyses of voltammograms exhibit linear dependences in plots of current versus $v^{1/2}$ (Fig. S8), as expected for diffusional species at all observed redox events.

3.5 Electrocatalytic hydrogen generation from acetic acid in CH₃CN

To determine catalytic activity of this copper complex, acetic acid was chosen as proton resource. From Fig. 4b it can be seen that the catalytic current near -1.55 and -0.94 V versus Ag/AgNO₃ increased markedly with the sequential increments of acetic acid concentration (from 0.00 to 5.964 mM). This rise in current can be

assigned to the catalytic generation of H₂ from acetic acid [22]. The result indicates that H₂ production electrocatalyzed by complex **1** requires the reduction potentials of Cu(II) to Cu(I) and Cu(I) to Cu(0). Note, with the acetic acid concentration increased from 0.0 to 1.36 mM (Fig. 4b), the reduction potentials near -1.55 and -0.94 V versus Ag/AgNO₃ moved to more anodic value for 460 mV from -1.55 to -1.09 V versus Ag/AgNO₃ and for 110 mV from -0.94 to 0.83 V versus Ag/AgNO₃, respectively. Upon the addition of 5.964 mM acetic acid, the onset of catalytic current moved positive for about 300 mV from -0.74 to 0.44 V versus Ag/AgNO₃. On the basis of literature precedents [23] and above analyses, the catalytic cycle depicted in Scheme 3 for the generation of hydrogen from acetic acid mediated by **1** was proposed. One-electron reduction of [(DCAE)Cu^{II}(H₂O)₂]⁺ gives a putative [(DCAE)Cu^{II}(H₂O)₂] species. Addition of H⁺ to [(DCAE)Cu^{II}(H₂O)₂] affords the Cu^{III}-H species. Further one-electron reduction of the Cu^{III}-H species affords dihydrogen, and regenerates the starting complex **1**. Further mechanistic studies are under investigation.

Scheme 3 The possible catalytic mechanism for proton reduction by complex **1**.

To verify that complex **1** is responsible for the catalysis indeed, several control experiments were carried out. Under the same conditions, CVs of NaDCAE, acetic acid, CuCl, and the mixture of NaDCAE and CuCl were each measured. As can be seen in Fig. S7 and Figs. S9-S11, the catalytic performance achieved by **1** is not matched by just NaDCAE, acetic acid and CuCl, as might arise from dissociation of NaDCAE, nor can it be accomplished with DCAE^- bound to copper center. Therefore, a coordination of the copper ion and DCAE^- is essential for catalytic activity.

The system was further characterized by bulk electrolysis from 0.13 μM complex **1** in CH_3CN with acetic acid at variable applied potential. From Fig. S12a (the total charges of bulk electrolysis from complex **1** in the presence of acetic acid), the charge significantly increased at lower potential. When the applied potential was -1.45 V versus Ag/AgNO_3 , the maximum charge reached 154 mC used 2 min. Whilst a controlled-potential electrolysis (CPE) experiment under the same potential but without complex **1** gave a charge of only 16 mC (Fig. S12b), indicating that this complex does indeed serve as effective hydrogen producer under such conditions. According to Equations (1) [24] and (2) [25], the TOF was estimated to be 74 moles of hydrogen per mole of catalyst per hour at an overpotential of 941.6 mV (Fig. S13).

$$\text{TOF} = \Delta C / (F \cdot n_1 \cdot n_2 \cdot t) \quad (1)$$

$$\text{Overpotential} = \text{Applied potential} - E_{\text{HA}}^{\ominus}$$

$$= \text{Applied potential} - (E_{\text{H}}^{\ominus} - (2.303RT/F)\text{p}K_{\text{aHA}}) \quad (2)$$

Where, ΔC is the charge from the catalyst solution during CPE minus the charge from solution without catalyst during CPE; F is Faraday's constant, n_1 is the number of moles of electrons required to generate one mole of H_2 , n_2 is the number of moles of catalyst in solution, and t is the duration of electrolysis.

3.6 Electrocatalytic hydrogen evolution from aqueous buffer

We then explored the electrocatalytic behavior in aqueous media. As shown in Fig. S14, the current strength increased with increasing concentrations of complex **1** from 0.00 to 30.43 mM. To further probe the nature of this reduction process, we

investigated the pH dependence of the cathodic peak potential. From Fig. S15, the current strength increased significantly under lower pH values, which is consistent with a catalytic process [26], indicating **1** also can catalyze water reduction to H₂.

To further get the evidence for the activity in aqueous media, the bulk electrolysis of a 7.14 μ M complex **1** was conducted in a neutral buffer under variable applied potentials. When the applied potential was -1.45 V versus Ag/AgCl, the maximum charge was 95 mC over 2 min without complex **1** (Fig. 5a). Under the same conditions, the charge reached 748 mC with addition of complex **1** (Fig. 5b), accompanied by the appearance of gas bubbles which was confirmed to be H₂ by GC analysis. From Fig. S16, ~9.24 mL of H₂ was obtained over an electrolysis period of 2 h with a Faradaic efficiency of 95% for dihydrogen (Fig. S17). According to Equations (1) and (3) [27], we also calculated the TOF for the catalyst as reaching a maximum of 285 moles of hydrogen per mole of catalyst per hour at an OP of 787.6 mV (Fig. S18).

$$\text{Overpotential} = \text{Applied potential} - E(\text{pH}) = \text{Applied potential} - (-0.059\text{pH}) \quad (3)$$

It is not easy to compare the catalytic efficiency between different electrocatalytic systems in term of TOF, due to possible differences in the experimental conditions conducted. Based on TOF, the electro-catalytic activity of complex **1** is higher than a copper complex supported by a tetradentate amine phenol ligand that shows a TOF of 104.3 mol of H₂ per mole of catalyst per hour at an OP of 839 mV [28], but lower than Cu(oxpn)Cu(OH)₂ [oxpn = *N,N'*-bis(3-aminopropyl)oxamido] that exhibits a TOF of 1383 mol of hydrogen per mole of catalyst per hour at an OP of 689 mV [29].

3.7 Investigation of the stability and durability of complex 1

In order to determine whether **1** retains activity over longer time periods, a 72 h CPE at -1.45 V versus Ag/AgCl was conducted in a neutral buffer containing 10.56 μM complex **1**. According to Fig. S19, the catalyst affords a charge build-up over time, with no substantial loss in activity used 48 hours, and a total of 739 C is passed during the electrolysis.

4. Conclusion

In this paper, we have described the reactivity of TCNE with CuCl. In the presence of methanol, TCNE affords a dicyano- acetic acid methyl ester ion (DCAE^-). Another hand, as a ligand, DCAE^- coordinates with copper atom to form polymer. No magnetic interactions between copper(II) centres is attributed to too far between two paramagnetic copper ions. In liquid, this copper complex can electrocatalyze H_2 production both from acetic acid and aqueous buffer. Our ongoing efforts are focused on controlling the ligand and reaction conditions to give related polymers with novel physical and chemical properties.

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Fig. 1. ORTEP drawing of complex **1** with thermal ellipsoids on the 50% probability level (hydrogen atoms are not shown) (top) and crystal packing diagram of complex **1** (down).

Fig. 2. (a) Temperature dependence of $\chi_M T$ at an applied field of 1000 Oe. (b) Temperature dependence of χ_M^{-1} at an applied field of 1000 Oe.

Fig. 3. Linear scan voltammetrys of neutral buffer solutions (pH 7.0) without and with complex 1. Conditions: Glassy carbon working electrode, Pt counter electrode, Ag/AgCl reference electrode, scan rate 100 mV/s.

Fig. 4. (a) Cyclic voltammograms (CVs) of 2.67 mM solution of complex 1 in CH₃CN with 0.10 M of [n-Bu₄N]ClO₄ at a glassy carbon electrode and a scan rate of

100 mV/s. Ferrocene internal standard (*). (b) CVs of a 2.67 mM solution of complex **1**, with varying concentrations of acetic acid in CH₃CN. Conditions: 0.10 M [n-Bu₄N]ClO₄ as supporting electrolyte, scan rate: 100 mV/s, glassy carbon working electrode (1 mm diameter), Pt counter electrode, Ag/AgNO₃ reference electrode, Fc internal standard.

Fig. 5. (a) Charge buildup versus time from electrolysis of a 7.14 μM complex **1** in a 0.25 M buffer (pH 7.0). All data have been deducted blank. (b) Charge buildup versus time from electrolysis of a 0.25 M buffer (pH 7.0) under -1.45 V versus Ag/AgCl. Conditions: scan rate: 100 mV/s, glassy carbon working electrode (1 mm

diameter), Pt counter electrode, Ag/AgCl reference electrode.