



## Short communication

## Synthesis and properties of an unexpected trinuclear copper(I) complex supported by diphenylphosphinomethane

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## ABSTRACT

The reaction of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , diphenylphosphinomethane (dppm), and tetracyanoethylene (TCNE) affords one unexpected trinuclear copper(I) complex,  $[\text{Cu}_3(\text{dppm})_3(\mu_3\text{-Cl})_2] \cdot [\text{TCMA}]$  **1** (TCMA: tricyanoacrylmethylate, a new compound deriving from TCNE). Structural study shows that three copper atoms are connected by dppm ligands bridging each edge to form a  $\text{Cu}_3\text{P}_6$  unit. At room temperature, **1** appears photoluminescence at 447 nm. And **1** also can electrocatalyze hydrogen generation from acetic acid with a turnover frequency (TOF) of 99.9 mol of  $\text{H}_2$  per mole of catalyst per hour at an overpotential of 941.6 mV.

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## 1. Introduction

Researchers often focus their interests on tetracyanoethylene (TCNE) chemistry, because TCNE is one of the most versatile organic compounds as it is used in many different reactions [1–4]. It has been shown that TCNE has the ability to accept one or two electrons to form anions and to bond with metal ions. And several molecular magnetic materials have been provided by reactions of TCNE with paramagnetic metal ions [5–9]. Despite these advances, few materials based on copper complexes supported by TCNE are known. To meet this need, we have tried the reaction of TCNE,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and dppm with a molar ratio set of 1:1:1, surprisingly, an unexpected product  $[\text{Cu}_3(\text{dppm})_3(\mu_3\text{-Cl})_2] \cdot [\text{TCMA}]$  **1** was obtained. In this paper, we describe synthesis, structure and properties of complex **1**, as well as its electrocatalytic hydrogen generation from acetic acid.

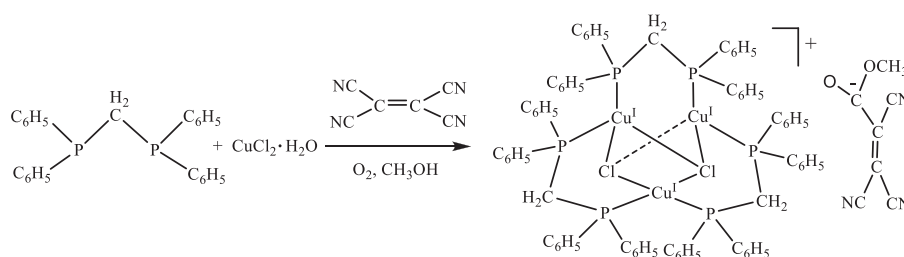
Generally, the reactions of TCNE (linker) with transition metal compounds afford polymers bridged by TCNE. However, the reaction of TCNE,  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$  and dppm provides an unexpected trinuclear copper(I) complex **1** (Scheme 1), which can't be obtained by the reaction of TCNE,  $\text{CuCl}$  and dppm [10]. It is noteworthy that the copper oxidation state of **1** is +1. During the course of the synthesis of complex **1** outlined above, probably, TCNE facilitates the reduction of the copper(II) to copper(I). The more detailed mechanistic studies are under investigation. Meanwhile, the above reaction also affords a tricyanoacrylmethylate ion,  $\text{TCMA}^-$ . Based on the literature precedent

[3,11,12], a possible mechanism for the formation of  $\text{TCMA}^-$  is illustrated by Scheme 2. TCNE reacts with water in basic condition to form pentacyanopropenide,  $[\text{C}_3(\text{CN})_5]^-$ . Then, the addition of  $\text{O}_2$  provides an active species, **A**. Furthermore, **A** reacts with  $\text{CH}_3\text{OH}$  to give  $\text{TCMA}^-$ . This is consistent with that TCNE undergoes numerous reactions [13]. From Fig. S1, the infrared spectrum of **1** shows two  $\nu(\text{C}\equiv\text{N})$  stretches at 2199 and 2169  $\text{cm}^{-1}$  at lower energy than that of the free tetracyanoethylene (2215 and 2258  $\text{cm}^{-1}$ ) (Fig. S2), assigning to two different cyanide modes of **1**. From Fig. S3, complex **1** exhibits a high-energy absorption band at about 267 nm, which is assigned to intraligand transitions.

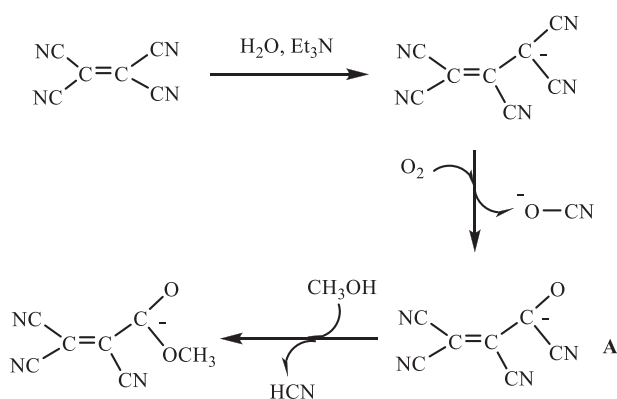
Complex **1** crystallizes in space group  $P-1$ , with two formula units present per unit cell, and consists of one trinuclear copper(I)  $[\text{Cu}_3(\text{dppm})_3(\mu_3\text{-Cl})_2]^+$  unit, and one  $\text{TCMA}^-$  anion. As shown in Fig. 1, three copper atoms are connected by dppm ligands to form a  $\text{Cu}_3\text{P}_6$  unit. Each copper atom is coordinated by two chloride ions and two phosphorus atoms of dppm. Both chloride ions are bonded to the three copper atoms in a  $\mu_3$  fashion from opposite faces of the triangle. The  $\text{Cu}_2\text{P}_2\text{C}$  rings adopt envelope conformations with the methylene carbon atoms on the flap, one of them folded toward one of the faces, and the other two away from it. The two phenyl rings attached to a phosphorus center stay on opposite sides of the plane formed by the three copper centers. The Cu–P bond lengths vary over a small range of 2.2331(3)–2.2649(3) Å. Cl(6) binds the copper atoms with one short (2.4007(3) Å) and two long (2.4855(3) and 2.4925(4) Å) bonds, whereas Cl(11) binds the copper atoms with one short (2.4157(4) Å) and two long (2.5182(4) and 2.5712(3) Å) bonds. Note, in DMF, **1** exhibits the same form as that in solid, which is in agreement with the

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Scheme 1. Synthesis of complex 1.

Scheme 2. The procedure for the formation of TCMA<sup>−</sup> anion.

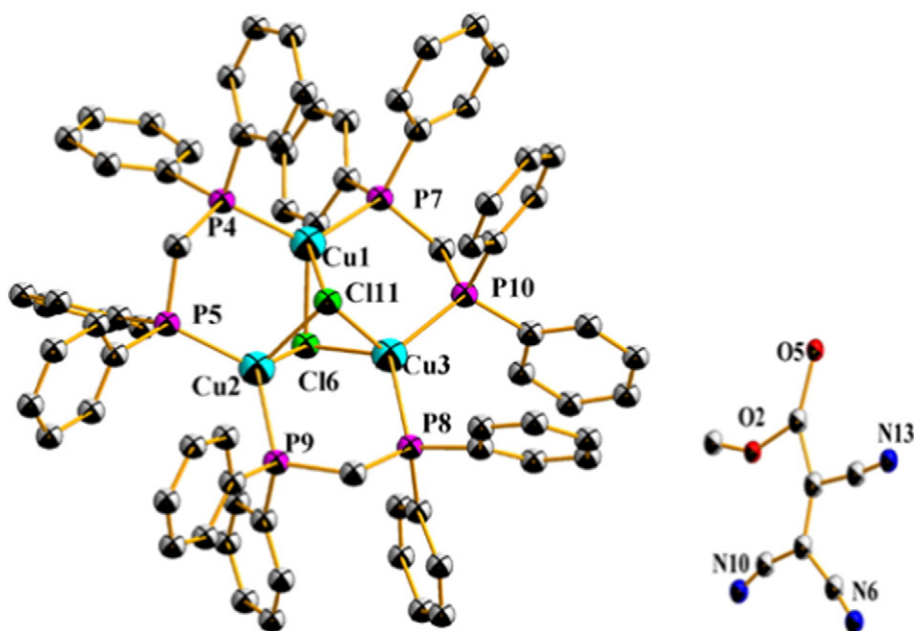
result from ESI-MS measurement which exhibits one ion at a mass-to-charge ratio ( $m/z$ ) of 1413.0886, with the mass and isotope distribution pattern corresponding to that of  $[\text{Cu}_3(\text{dppm})_3(\text{Cl})_2]^+$  (Fig. S4), indicating that this complex is stable in solution.

It has been shown that many  $d^{10}$  metal complexes display fascinating luminescent properties [14], therefore, we measured the emission spectrum of complex **1** in DMF at room temperature. As shown in Fig. 2, irradiation of complex **1** around 355 nm gives a strong emission at 447 nm, which are found in other copper(I) complexes [15–18].

To explore if this copper(I) complex can act as an electrocatalyst, the electrochemical measurements for complex **1** were conducted in DMF solution with 0.10 M  $[(\text{n-Bu})_4\text{N}]\text{ClO}_4$  as the supporting electrolyte. Fig. 3 represents the CV of complex **1** in DMF, and a quasi-reversible redox couple is found in the potential of  $-0.82$  V versus  $\text{Ag}/\text{AgNO}_3$ , which can be assigned to that of  $\text{Cu}^{\text{I}}/\text{Cu}^0$ .

From Fig. 4 it can be seen that the catalytic currents near  $-0.86$  V versus  $\text{Ag}/\text{AgNO}_3$  increase with increasing proton concentration (acetic acid concentration increased from 0.0 to 2.68 mM). This indicates that hydrogen evolution electrocatalyzed by **1** requires the reduction of  $\text{Cu}(\text{I})$  to  $\text{Cu}(\text{0})$  and protonation. Interestingly, with the acetic acid concentration increases from 0.0 to 2.68 mM (Fig. 4), the potential of  $\text{Cu}^{\text{I}}/\text{Cu}^0$  moves positive about 60 mV from  $-0.88$  V to  $-0.82$  V, and the onset of the catalytic wave also moves positive about 430 mV compared to that in the absence of **1**.

To further testify the catalytic activities of this copper(I) complex, bulk electrolysis was conducted in DMF with acetic acid at variable applied potential using a glassy carbon plate electrode in a double-compartment cell. Fig. 5a shows the total charges of bulk electrolysis from complex **1** in the presence of acid, and the charge significantly increased when the applied potential was set to more negative. When the applied potential was  $-1.45$  V versus  $\text{Ag}/\text{AgNO}_3$ , the maximum charge reached 45 mC during 2 min of electrolysis, with accompanying evolution of a gas, which was confirmed as  $\text{H}_2$  by gas chromatography. According to Fig. S5,  $\sim 0.73$   $\mu\text{L}$  of  $\text{H}_2$  was produced over an electrolysis period of 2 h under  $-1.45$  V versus  $\text{Ag}/\text{AgNO}_3$ . And a controlled-potential electrolysis (CPE) experiment under the same potential without **1** gave a charge of only 8 mC (Fig. 5b), showing that this copper

Fig. 1. ORTEP drawing of complex **1** with thermal ellipsoids on the 30% probability level (hydrogen atoms are not shown).

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