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, $[\text{Cu}_3^{\text{I}}(\text{dppm})_3(\mu_3\text{-Cl})_2] \cdot [\text{TCMA}]$ **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 Cu_3P_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 moles of H_2 per mole of catalyst per hour at an overpotential of 941.6 mV.

Keywords: Copper(I) complex; crystal structure; photoluminescence; proton reduction; hydrogen generation

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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 $[\text{Cu}^{\text{I}}_3(\text{dppm})_3(\mu_3\text{-Cl})_2] \cdot [\text{TCMA}]$ **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, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and dppm provides an unexpected trinuclear copper(I) complex **1** (Scheme 1), which can't be obtained by the reaction of TCNE, 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, TCMA^- . Based on the literature precedent [3,11,12], a possible mechanism for the formation of 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 O_2 provides an active species,

A. Furthermore, **A** reacts with CH_3OH to give 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 cm^{-1} at lower energy than that of the free tetracyanoethylene (2215 and 2258 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.

Scheme 1 Synthesis of complex **1**.

Scheme 2 The procedure for the formation of TCMA^- anion.

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 TCMA^- anion. As shown in Fig. 1, three copper atoms are connected by dppm ligands

to form a Cu_3P_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 μ_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 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].

Fig. 2. Emission spectra of complex **1** and blank in DMF.

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 [(n-Bu)₄N]ClO₄ 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 Ag/AgNO₃, which can be assigned to that of Cu^I/Cu⁰.

Fig. 3. Cyclic voltammogram of 1.78 μM complex **1** in DMF. Conditions: room temperature, 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. Ferrocene internal standard (*).

From Fig. 4 it can be seen that the catalytic currents near -0.86 V versus Ag/AgNO₃ 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 Cu(I) to Cu(0) and protonation. Interestingly, with the acetic acid concentration increases from 0.0 to 2.68 mM (Fig. 4), the potential of Cu^I/Cu⁰ 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**.

Fig. 4. CVs of a 1.78 μM solution of complex **1**, with varying concentration of acetic acid in DMF. 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 (*).

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 Ag/AgNO₃, the maximum charge reached 45 mC during 2 min of electrolysis, with accompanying evolution of a gas, which was confirmed as H₂ by gas chromatography. According to Fig. S5, ~0.73 μ L of H₂ was produced over an electrolysis period of 2 h under -1.45 V versus Ag/AgNO₃. 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 complex does indeed serve as effective hydrogen producer under such conditions. From Equations (1) [19] and (2) [20], the TOF was estimated to be 99.9 moles of hydrogen per mole of catalyst per hour (Eq. S1 and Fig. S6), which is higher than a dinuclear copper(I) supported by 1-[(2-methoxy) benzene]-3-[2-(chloro)benzene] triazene ion that shows a TOF of 65 moles of H₂ per mole of catalyst per hour at an overpotential of 941.6 mV [21], yet smaller than a trinuclear copper(I) with triazenido ligands that exhibits a TOF of 136 moles of H₂ per mole of catalyst per hour at an overpotential of 688 mV [22].

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

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

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

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.

Fig. 5. (a) Charge buildup versus time from electrolysis of a 0.071 μM complex **1** in DMF (0.10 M $[n-Bu_4N]ClO_4$) under various applied potentials. All data have been deducted blank. (b) Charge buildup versus time from electrolysis of a 0.10 M $[n-Bu_4N]ClO_4$ solution in DMF under -1.45 V versus $Ag/AgNO_3$.

We used UV-vis spectra to examine the stability of complex **1** by employing an optically semi-transparent thin layer electrode. As shown in Fig. S7, the intensity of the absorption band at 267 nm slightly increases during 3 h electrolysis, but the peak position does not change, indicating **1** is stable under these conditions.

Summary

$CuCl_2 \cdot 2H_2O$ reacts with dppm, and TCNE to produce one unexpected trinuclear copper(I) complex $[Cu^I_3(dppm)_3(\mu_3-Cl)_2] \cdot [TCMA]$ **1**, which can't be obtained by the reaction of $CuCl$, dppm, and TCNE. Complex **1** exhibits photoluminescence behavior at room temperature. And **1** also can electrocatalyze hydrogen generation from acetic acid.

Acknowledgements

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To a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.171 g, 1 mmol) in methanol (10 mL) was added dppm (0.385 g, 1 mmol) in 30 mL CH_2Cl_2 , which leads to the formation of colorless solution after stirring for a period of 2 h. To this solution was added TCNE (0.102 g, 1 mmol) in 10 mL CH_2Cl_2 , and the mixture was stirred for another 60 min. Single crystals were obtained from the filtrate which was allowed to stand at room temperature for several days, collected by filtration, and dried in *vacuo* (0.31 g, 59% yield). Calcd for $\text{C}_{82}\text{H}_{69}\text{Cu}_3\text{Cl}_2\text{N}_3\text{O}_2\text{P}_6$: C, 62.49; H, 4.36; N, 2.67. Found: C, 62.32; H, 4.33; N, 2.67. IR band (KBr pellet, cm^{-1}): $\nu = 2199, 2169 \nu(\text{C}\equiv\text{N})$. Fluorescence spectrum: $\lambda_{\text{ex}} = 355 \text{ nm}$, $\lambda_{\text{em}} = 447 \text{ nm}$.

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

Fig. 2. Emission spectra of complex **1** and blank in DMF.

Fig. 3. Cyclic voltammogram (CV) of 1.78 μM complex **1** in DMF. Conditions: 0.10 M $[\text{n-Bu}_4\text{N}]\text{ClO}_4$ as supporting electrolyte, scan rate: 100 mV/s, glassy carbon working electrode (1 mm diameter), Pt counter electrode, Ag/AgNO_3 reference electrode. Ferrocene internal standard (*).

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