Journal of Organometallic Chemistry 696 (2011) 2654–2659

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Trinuclear copper(I) acetylide complexes bearing carbonyl moiety: Synthesis, characterization, and photophysical properties

Mei Zhang, Bo-Chao Su, Cheng-Luan Li, Yong Shen, Chi-Keung Lam, Xiao-Long Feng, Hsiu-Yi Chao*

MOE Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, PR China

ARTICLE INFO

Article history:
Received 3 March 2011
Received in revised form
6 April 2011
Accepted 13 April 2011

Keywords:
Acetylide
Copper
Luminescence
Synthesis

ABSTRACT

A series of trinuclear copper(I) acetylide complexes with carbonyl moiety, $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC(O)R)_2](ClO_4)$ (R = H (**1**), CH_3 (**2**), OCH_3 (**3**), NH_2 (**4**), NEt_2 (**5**)) (dppm = bis(diphenylphosphino)methane), have been synthesized and characterized. The crystal structures of $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC(O)CH_3)_2](ClO_4)$ (**2**) and $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC(O)NH_2)_2](ClO_4)$ (**4**) were determined by X-ray diffraction. The photophysical properties of complexes **1**–**5** have been studied. Complexes **1**–**5** show luminescence both in the solid state and in acetonitrile solution at 298 K, and their emission energies are in the order: **5** > **4** > **3** > **2** > **1**. Density function theory (DFT) calculations at the hybrid Perdew, Burke, and Ernzerhof functional (PBE1PBE) level were performed on model complex **1** to elucidate the emission origin of complexes **1**–**5**.

1. Introduction

Metal acetylide complexes attract much attention due to their rich structural diversity and potential applications in nonlinear optics, liquid crystals, luminescence, and molecular wires [1–3]. The most common bonding mode for the acetylide group in copper(I) clusters is in a μ_3-η^1 fashion. Gimeno and co-workers reported the synthesis and characterization of the first trinuclear copper(I) complex with two capped μ_3-η^1-acetylides, $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2](BF_4)$ (dppm = bis(diphenylphosphino)methane) [4]. Later, the relationship between the structures and luminescence properties of this class of trinuclear copper(I) acetylide complexes with different diphosphine and acetylide ligands has been extensively studied by Yam and co-workers [5–12]. However, to the best of our knowledge, the synthesis of trinuclear copper(I) acetylide complexes with carbonyl moiety was less explored. Recently, we reported the syntheses as well as luminescence properties of trinuclear copper(I) and silver(I) acetylide complexes with COO^- group, $[M_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{–}COO)Y]$ (M = Cu, Y = OCH_3; M = Ag, Y = Cl) [13]. To extend our work on the trinuclear copper(I) acetylide complexes bearing carbonyl moiety, a series of trinuclear copper(I) acetylide complexes, $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC(O)R)_2](ClO_4)$ (R = H (**1**), CH_3 (**2**), OCH_3 (**3**), NH_2 (**4**), NEt_2 (**5**)), have been synthesized and characterized. We envisaged that if the electron-donating ability of the substituent R could be changed, the energy of the lowest-lying emissive excited state for this kind of trinuclear copper(I) acetylide complexes may be tuned. In addition, by systematic studying the relationship between the nature of the acetylide ligands and emission energies of this class of trinuclear copper(I) acetylide complexes, the lowest-lying emissive excited state of the trinuclear copper(I) acetylide complexes could be easily assigned. In this paper, the syntheses and photophysical properties of a series of trinuclear copper(I) acetylide complexes **1**–**5** will be reported. The X-ray crystal structures of $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC(O)CH_3)_2](ClO_4)$ (**2**) and $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC(O)NH_2)_2](ClO_4)$ (**4**) have also been determined. DFT calculations about the MOs (molecular orbitals) of the trinuclear copper(I) acetylide complex **1** have been utilized for investigating the lowest-lying excited state of complexes **1**–**5**.

2. Results and discussion

2.1. Syntheses and characterization of complexes 1–5

Trinuclear bi-capped copper(I) acetylide complexes, $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC(O)R)_2](ClO_4)$ [R = H (**1**), CH_3 (**2**), OCH_3 (**3**), NH_2 (**4**), NEt_2 (**5**)], were synthesized from the reaction of $[Cu_2(dppm)_2(CH_3CN)_4](ClO_4)_2$ with corresponding $HC{\equiv}CC(O)R$ or $Me_3Si\text{–}C{\equiv}CC(O)R$ in a molar ratio of 3:4 in the presence of aqueous ammonium or an excess of KF in acetonitrile/water or acetonitrile/methanol mixture under anaerobic condition. All these trinuclear copper(I) acetylide complexes gave satisfactory elemental analyses

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* Corresponding author. Tel.: +86 020 84110062; fax: +86 020 84112245.
E-mail address: zhaoxy@mail.sysu.edu.cn (H.-Y. Chao).

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doi:10.1016/j.jorganchem.2011.04.015

and were characterized by positive ESI-MS, IR, ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. They are air-stable in the solid state at 298 K.

The IR spectra of the trinuclear copper(I) acetylide complexes **1**–**5** reveal two bands at 1989–2015 cm^{-1} and 1589–1678 cm^{-1}, characteristic of the ν(C≡C) and ν(C=O) stretches of acetylide ligands, respectively. The ^{1}H NMR spectra of complexes **1**–**5** in acetone-d$_6$ show three resonances at *ca.* δ 7.24, 7.16, and 7.00 ppm, which are doublet, triplet, and triplet, respectively. These peaks are assigned as the resonances of the protons on the phenyl groups of dppm ligands. The chemical shift at *ca.* 3.5 ppm is ascribed as the resonance of the protons of CH$_2$ moieties on dppm ligands. The ^{31}P {^{1}H} NMR spectra of the trinuclear copper(I) acetylide complexes **1**–**5** in acetone-d$_6$ exhibit a singlet at δ −2.71 to −4.10 ppm, suggesting that the six phosphorus atoms are chemically shift equivalent. The upfield ^{31}P{^{1}H} NMR chemical shift from δ −2.71 to −4.10 ppm upon going from **1** to **5** is in line with the increasing electron-donating ability of the acetylide ($^-$C≡CC(O)R) ligand: R = H < CH$_3$ < OCH$_3$ < NH$_2$ < NEt$_2$.

2.2. X-ray crystal structures of complexes 2 and 4

The perspective drawings of complex cations of [Cu$_3$(μ-dppm)$_3$(μ$_3$-η^1-C≡CC(O)CH$_3$)$_2$](ClO$_4$) (**2**) and [Cu$_3$(μ-dppm)$_3$(μ$_3$-η^1-C≡CC(O)NH$_2$)$_2$](ClO$_4$) (**4**) are shown in Figs. 1 and 2, respectively. The crystallographic data of **2** and **4** as well as selected bond distances and angles are listed in Tables 1 and 2, respectively. In complexes **2** and **4**, three copper atoms are bridged by three dppm ligands to form a roughly planar [Cu$_3$P$_6$] core. The Cu–P distances are in the range of 2.2455(14)–2.2895(13) Å, which are similar to those found in other trinuclear copper(I) acetylide complexes [4–13]. The Cu$_2$P$_2$C rings form envelope-like conformations with the methylene carbon atoms on the flap, one of them folded toward one of the faces of the Cu$_3$ triangles and the other two folded away from it. Each acetylide ligand is C-bonded to the three copper atoms in an asymmetric μ$_3$-η^1 bridging mode with different Cu–C distances. The Cu–C bond distances in **2** and **4** are in the range of 2.060(3)–2.352(3) and 2.071(5)–2.349(5) Å, respectively. The bond angles between the acetylide ligands and copper atoms in **2** and **4** are in the range of 113.8(3)–149.7(3)° and 116.1(4)–144.4(4)°, respectively. The C(76)–C(77) and C(80)–C(81) bond distances for complex **2** as well as C(76)–C(77) and C(79)–C(80) bond distances for **4** are in the range of 1.188(5)–1.219(5) Å, indicating the triple bond character and metal–acetylide σ-bonding [14]. The copper⋯copper distances in **2** and **4** are in the range of 2.5485(6)–2.7085(6) Å and 2.5201(9)–2.7025(9) Å, respectively, which are shorter than the sum of van der Waals radii for copper (2.8 Å) [15]. This observation suggests the presence of weak metal–metal interactions between copper atoms. In **4**, there are intramolecular N–H⋯O hydrogen bonding interactions between the hydrogen atoms of the NH$_2$ groups of acetylide

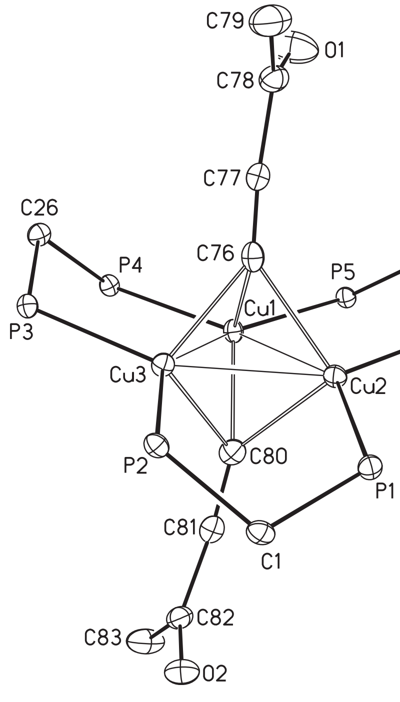

Fig. 1. Perspective view of the cation in **2** with the atomic numbering scheme. All hydrogen atoms and the phenyl rings in dppm ligands are omitted for clarity.

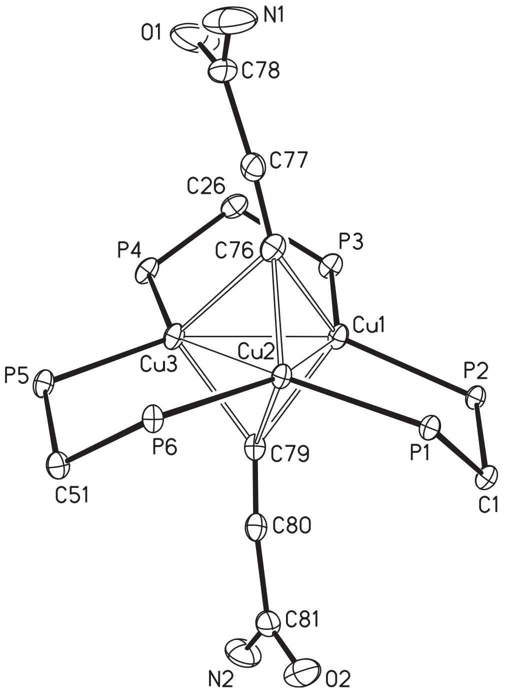

Fig. 2. Perspective view of the cation in **4** with the atomic numbering scheme. All hydrogen atoms and the phenyl rings in dppm ligands are omitted for clarity.

Table 1
Crystallographic data for **2** and **4**.

	2	4
Formula	$C_{86}H_{78}ClCu_3O_7P_6$	$C_{81}H_{70}ClCu_3N_2O_6P_6$
M (g/mol)	1635.37	1579.28
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*
a (Å)	19.718(3)	19.917(3)
b (Å)	15.699(2)	15.540(2)
c (Å)	24.885(4)	24.382(3)
α (°)	90	90
β (°)	93.821(2)	94.226(3)
γ (°)	90	90
V (Å^3)	7686.4(19)	7525.8(18)
Z	4	4
D_c (g cm^{-3})	1.413	1.394
Temp (K)	110(2)	110(2)
Reflection collected	14991	35227
Independent reflections	11334	14724
R_{int}	0.0313	0.0345
R,[a] R_w[b] [$I > 2\sigma(I)$]	0.0417, 0.1089	0.0590, 0.1879
Goodness-of-fit	1.059	1.073

[a] $R = \Sigma(|F_0|-|F_c|)/\Sigma|F_0|$

[b] $R_w = [\Sigma w(|F_0|-|F_c|)^2/\Sigma w|F_0|^2]^{1/2}$