Synthesis, X-ray Structures and Spectroscopic Characterization of Five New Polynuclear Paddle-wheel Cu (II) Complexes Containing Carboxylate as a bridging ligand

การสังเคราะห์ โครงสร้างผลึกและสมบัติทางสเปกโทรสโกปี ของสารเชิงซ้อนพอลินิวเคลียร์คอปเปอร์ (II) ที่มีคาร์บอกซิเลตเป็นลิแกนด์สะพาน

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ABSTRACT

The synthesis, spectroscopic and structural characterization of five new polynuclear paddle-wheel copper(II) complexes $[Cu_4(dpyam)_2(OCOC_2H_5)_2(\mu\text{-}O_2CC_2H_5)_6(H_2O)_2][Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2]\cdot(DMF)_2$ **1**, $[Cu_6(phen)_2(H_2O)_2(\mu\text{-}O_2CC_2H_5)_{12}]_n[Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2]_{2n}\cdot(H_2O)_{0.5n}$ **2**, $\{[Cu_4(phen)_2(\mu\text{-}O_2CC_2H_5)_8]\cdot(H_2O)\}_n$ **3** (dpyam = di-2-pyridylamine, phen = 1,10-phenanthroline), $[Cu_2(\mu\text{-}O_2CC_6H_4OH)4(C_7H_7NO)_2]\cdot6H_2O$ **4** and $[Cu_2(\mu\text{-}O_2CCH_3)4(C_7H_7NO)_2]$ **5** are described. All compounds consist of dinuclear unit, in which the two Cu(II) ions are bridged by four *syn,syn*-η^1:η^1:μ carboxylates ($C_2H_5CO_2^-$ **1-3**, $C_6H_4OHCO_2^-$ **4** and $CH_3CO_2^-$ **5**), showing the paddle-wheel cage type. The Cu(II) chromophores have a square pyramidal geometry. Both terminal position of paddle-wheel unit in **1** is linked with mononuclear $Cu(dpyam)(OCOC_2H_5)(H_2O)$ units by propionate bridges showing *syn,anti*-η^1:η^1:μ coordination mode. The 1D structures of compounds **2** and **3** consist of polymer chains of mononuclear $Cu(\mu\text{-}O_2CC_2H_5)_2(H_2O)(phen)$ and dinuclear $Cu_2(phen)_2(\mu\text{-}O_2CC_2H_5)_4$ repeating units (for **2** and **3**, respectively), connecting with $Cu_2(\mu\text{-}O_2CC_2H_5)_4$ paddle-wheel dinuclear units. Within mononuclear and dinuclear units, the Cu(II) ions have a square pyramidal geometry. However, the outer sphere of compounds **1** and **2** consists of the $Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2$ paddle-wheel molecule in which Cu(II) ions involve a square pyramidal geometry. Compounds **4** and **5** are the dinuclear paddle-wheel molecule and they have 4-acetylpyridine ligand occupies the axial position of each Cu(II) ion.

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บทคัดย่อ

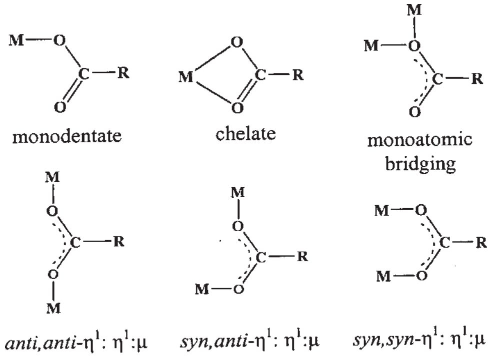
งานวิจัยนี้ได้สังเคราะห์ ศึกษาสมบัติทางสเปกโทรสโกปีและโครงสร้างผลึกของสารเชิงซ้อนพอลินิวเคลียร์คอปเปอร์(II) ที่มีคาร์บอกซิเลตเป็นลิแกนด์สะพาน โครงสร้างของสาร $[\mathrm{Cu_4(dpyam)_2(OCOC_2H_5)_2(\mu\text{-}O_2CC_2H_5)_6(H_2O)_2}]$ $[\mathrm{Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2}]\cdot\mathrm{(DMF)_2}$ **1**, $[\mathrm{Cu_6(phen)_2(H_2O)_2(\mu\text{-}O_2CC_2H_5)_{12}}]_n\cdot[\mathrm{Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2}]_{2n}\cdot\mathrm{(H_2O)_{0.5n}}$ **2**, $\{[\mathrm{Cu_4(phen)_2(\mu\text{-}O_2CC_2H_5)_8}]\cdot\mathrm{(H_2O)}\}_n$ **3**, $[\mathrm{Cu_2(\mu\text{-}O_2CC_6H_4OH)_4(C_7H_7NO)_2}]\cdot\mathrm{6H_2O}$ **4** และ $[\mathrm{Cu_2(\mu\text{-}O_2CCH_3)_4(C_7H_7NO)_2}]$ **5** ประกอบด้วยหน่วยไดนิวเคลียร์ที่มีโครงสร้างแบบ paddle-wheel และมีคาร์บอกซิเลต ($\mathrm{C_2H_5CO_2^-}$ **1-3**, $\mathrm{C_6H_4OHCO_2^-}$ **4** และ $\mathrm{CH_3CO_2^-}$ **5**) สี่หมู่เป็นลิแกนด์สะพานแบบ *syn,syn*-η^1:η^1:μ เชื่อมระหว่างไอออนคอปเปอร์(II)ทั้งสอง โดยแต่ละไอออนคอปเปอร์(II) มีโครงสร้างแบบ square pyramid สำหรับสาร **1** ที่ปลายทั้งสองข้างของหน่วยไดนิวเคลียร์ paddle-wheel นี้จะเชื่อมต่อกับหน่วยมอนอนิวเคลียร์ $\mathrm{Cu(dpyam)(OCOC_2H_5)(H_2O)}$ ด้วยลิแกนด์สะพานโพรพิโอเนตแบบ *syn,anti*-η^1:η^1:μ สาร **2** และ **3** มีโครงสร้างเป็นสายโซ่ที่มีหน่วย paddle-wheel เชื่อมต่อกันด้วยสะพานมอนอนิวเคลียร์ $\mathrm{Cu(phen)(\mu\text{-}O_2CC_2H_5)_2(H_2O)}$ สำหรับสาร **2** และสะพานไดนิวเคลียร์ $\mathrm{Cu_2(phen)_2(\mu\text{-}O_2CC_2H_5)_4}$ สำหรับสาร **3** แต่ละไอออนคอปเปอร์(II) ในหน่วยมอนอนิวเคลียร์และไดนิวเคลียร์ มีโครงสร้างแบบ square pyramid นอกจากนี้นอกเขตโคออร์ดิเนชันของสาร **1** และ 2 ยังมีโมเลกุล paddle-wheel $\mathrm{Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2}$ ด้วย สาร **4** และ **5** มีโครงสร้างเป็นไดนิวเคลียร์ paddle-wheel ที่มี 3-ไฮดรอกซีเบนโซเอต และอะซิเตตเป็นเป็นลิแกนด์สะพานเชื่อมระหว่างไอออนคอปเปอร์(II)ทั้งสอง และมี 4-อะซิทิลพิลิดีนเป็นลิแกนด์ในตำแหน่งปลายทั้งสองข้างของแต่ละไอออนคอปเปอร์(II)

Key Words : Copper(II), Crystal structure, Carboxylato bridge

คำสำคัญ : คอปเปอร์(II) โครงสร้างผลึก สะพานคาร์บอกซิเลต

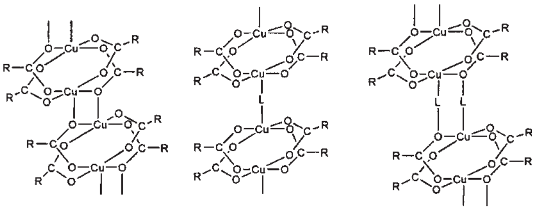
Introduction

The coordination chemistry of the copper(II) complexes with various carboxylates has been investigated for a long time. Dinuclear and polynuclear copper(II) carboxylates have received great attention in the studies of exchange-coupling interactions between adjacent metal centers, as well as for their special bioactive and biocatalytic functions (Marinho, M.V. *et al.* 2004). In addition carboxylate anions exhibit a versatile coordination behavior displaying distinct bonding modes toward metal cations, such as monodentate and chelate, as well as η^1:η^1:μ bridging ligands in *syn,syn*, *syn,anti*, *anti,anti* conformations. Another type of coordination modes is the mono atomic bridge in which two metal ions are connected by a single oxygen atom of carboxylate group. This diversity of coordination modes assumed by carboxylate ligands is shown in Scheme 1.



Scheme 1

A large number of paddle-wheel type dimeric copper(II) carboxylate adducts, $[\mathrm{Cu_2(RCO_2)_4L_2}]$, where L is an apical ligand with an oxygen or a nitrogen atom, have been reported in an effect to clarify the factors influencing the magnitude of the intramolecular magnetic exchange interaction which occurs between two Cu(II) ions of a paddle-wheel moiety in these compounds (Kozlevcar, B. *et al.* 2004). The polynuclear copper(II) carboxylates were found to exhibit three classes of local paddle-wheel structure: (A) stepped polymeric structure with the second lone pair is donated to a metal ion of another paddle-wheel unit; (B) stepped without additional ligands with polymeric structures can also be obtained by means of ligands which are able to bridge between dinuclear units; (C) the bridging ligand coordinates axially to a Cu ion and at the same time interacts with a carboxylate oxygen atom of another paddle-wheel unit (Rao, V.M. *et al.* 1983). An example of each class is presented in Scheme 2.



class A class B class C

Scheme 2

The influence of the different chelate and different coordination modes of carboxylate ligands on the structure of five new polynuclear paddle-wheel copper(II) complexes are investigated in the present work.

Experimental

1. Reagents and physical measurements

All reagents are commercial grade materials and were used without further purification. Elemental analyses (C, H, N) were determined on a Perkin-Elmer PE 2400 CHNS/O Analyzer.

IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer as KBr disc in the 4000-450 cm^{-1} spectral range. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin-Elmer Lambda2S spectrophotometer. The X-band powder EPR spectra were obtained on polycrystalline samples at room temperature and 77 K with a JEOL RE2X electron spin resonance spectrometer.

2. Syntheses

2.1 $[Cu_4(dpyam)_2(OCOC_2H_5)_2(\mu\text{-}O_2CC_2H_5)_6(H_2O)_2][Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2]\bullet(DMF)_2$ (1)

A mixing solution of dpyam (1.0 mmol) in DMF : ethanol (20:10 ml) was added to a warm aqueous solution (10 ml) of $Cu(CO_3)\bullet Cu(OH)_2\bullet nH_2O$ (1.5 mmol). Then an aqueous solution (10 ml) of $NaO_2CCH_2CH_3$ (1.5 mmol) was added to the mixture yielding a blue solution and the blue precipitate formed in a few minutes. Its color became light blue by slow addition of the concentrate propionic acid (5 ml) yielding a clear, light blue solution. After a month, blue polygon-shaped crystals were obtained which were filtered off, washed with the mother liquid and air-dried. Yield ca. 65%. $C_{62}H_{102}Cu_6N_8O_{30}$: Anal. Calc. C 40.90; H 5.65; N, 6.15 Found: C 40.50; H 5.61; N, 6.04 %.

2.2 $[Cu_6(phen)_2(H_2O)_2(\mu\text{-}O_2CC_2H_5)_{12}]_n[Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2]_{2n}\bullet(H_2O)_{0.5n}$ (2)

A mixing solution of phen (1.0 mmol) in acetonitrile : ethanol (20:10 ml) was added to a warm aqueous solution (10 ml) of $Cu(CO_3)\bullet Cu(OH)_2\bullet nH_2O$ (1.5 mmol). Then an aqueous solution (10 ml) of $NaO_2CCH_2CH_3$ (1.5

mmol) was added to the mixture yielding a blue solution and the blue precipitate formed in a few minutes. The resulting solution became clear and light blue in color by slow addition of the concentrate propionic acid (7 ml). After a month, blue polygon-shaped crystals of compound **2** were obtained. Yield ca. 50%. $C_{168}H_{254}Cu_{20}N_8O_{93}$: Anal. Calc. C 39.22; H 4.98; N, 2.17 Found: C 39.05; H 4.41; N, 2.01 %.

2.3 $\{[Cu_4(phen)_2(\mu\text{-}O_2CC_2H_5)_8]\cdot(H_2O)\}_n$ (3)

This complex was prepared by following an analogous procedure to that of **2** but using Cu(CO3)•Cu(OH)2•nH2O 1 mmol, phen 1.0 mmol, $NaO_2CCH_2CH_3$ 1 mmol and propionic acid 2 ml. After a month, blue polygon-shaped crystals of compound **3** were obtained. Yield ca. 70%. $C_{48}H_{56}Cu_4N_4O_{17}$: Anal. Calc. C, 47.44; H, 4.65; N, 4.61 Found: C,47.33; H, 4.87; N, 4.73 %.

2.4 $[Cu_2(\mu\text{-}_2CC_6H_4OH)_4(C_7H_7NO)_2]\cdot 6H_2O$ (4)

A warm solution of 3-Hydroxybenzoic acid (1.0 mmol) in methanol (20 ml) was added to a hot aqueous solution (10 ml) of $Cu(BF_4)_2$ (1 mmol). An aqueous solution (10 ml) of 4-Acethylpyridine (1 mmol) was then added. The resulting green solution was allowed to evaporate at room temperature until green needle-like crystals of **4** separated. Yield: ca. 80%. Anal. Calc. for $C_{42}H_{46}Cu_2N_2O_{20}$: C, 51.91 ; H, 4.15; N, 2.88 Found: C, 51.91; H, 4.20; N, 2.85 %.

2.5 $[Cu_2(\mu\text{-}O_2CCH_3)_4(C_7H_7NO)_2]$ (5)

The ligand 4-Acethylpyridine (1 mmol), dissolved in acetonitrile (10 ml) and a warm solution of $Cu(CH_3COO)_2$ (1 mmol) were mixed together. The blue solution was slowly evaporated at room temperature until dark blue crystals of 5 separated. Yield ca. 70%. *Anal.* Calc. for $C_{22}H_{26}Cu_2N_2O_{10}$: C, 43.64 ; H, 4.33; N, 4.63 Found: C, 43.69 ; H, 4.25; N, 4.58 %.

3. Crystallography

The X-ray single-crystal data were collected at 273 K for complexes 3 and at 293 K for **1**, **2**, **4** and **5**, respectively, on a 1 K Bruker SMART CCD area-detector diffractometer using graphite monochromated MoK_α radiation (λ = 0.71073 Å) at a detector distance of 4.5 cm and swing angle of -30°. A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ angle (0, 88, 180°) and each exposure of 40 s covered 0.3° in ω. Data reduction and cell refinements were performed using the program SAINT (Bruker, 1997b). An empirical absorption correction by using the SADABS (Sheldrick, 1996) program was applied, which resulted in transmission coefficients ranging from 0.741 to 1.000 for **1**, 0.608 to 1.000 for **2**, 0.818 to 1.000 for **3** and 0.311 to 1.000 for **4**. The structures were solved by direct on $(F_{obs})^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 software package (Sheldrick, 2000b). The molecular graphics were created by using SHELXTL-PC (Sheldrick, 2000a) package.

Results and Discussion

1. Crystal structure of $[Cu_4(dpyam)_2(OCO\ C_2H_5)_2(\mu\text{-}O_2CC_2H_5)_6\ (H_2O)_2][Cu_2(\mu\text{-}O_2CC_2H_5)_4\ (H_2O)_2]\cdot(DMF)_2$ (1)

The crystal structure of **1** consists of a centrosymmetric tetranuclear $[Cu_4(dpyam)_2(OCO\ C_2H_5)_2(\mu\text{-}O_2CC_2H_5)_6(H_2O)_2]$, noncoordinating $[Cu_2(\mu\text{-}O_2CC_2H_5)_4\ (H_2O)_2]$ and DMF molecules.

The “outer” Cu ions (Cu(1), Cu(1)A), with a CuN2O2O’ chromophore, have an intermediate geometry. The Cu(II) atom is five-coordinated with a basal plane consisting of two N atoms (Cu(1)-N(1), 1.983(3), Cu(1)-N(2), 2.033(3) Å) of dpyam and two O atoms (Cu(1)-O(2), 1.942(2), Cu(1)-O(4), 1.963(2) Å) of two different propionate ligands. The coordinated water molecule O(1) occupies the apical position at a distance of 2.259(2) Å. The CuN$_2$O$_2$ chromophore is non-planar with tetrahedral twist of 31.2(1)°. The copper line above this plane, 0.252(1) Å toward O(1). The copper chromophore can be described as having an intermediate geometry. The distortion of intermediate geometry can be best described by the structural parameter τ (τ = 0 for square pyramid and τ = 1 for trigonal bipyramid (Addison, A.W. *et al.* 1984), with in this case is 0.483.

The “inner” Cu ions (Cu(2), Cu(2)A), involves a five coordinate CuO4O’ chromophore, four oxygens of four different carboxylate groups coordinate to Cu(2) in equatorial positions, at mean distance of 1.967(3) Å. An another propionate O atom coordinate at the apical position, at 2.100(2) Å, completing the square pyramidal coordination geometry with τ value of 0.003. Four propionate anions bridge two copper ions in a *syn,syn*-η^1:η^1:μ showing the paddle-wheel unit with Cu···Cu distance of 2.632(1) Å. The basal plane is non-planar with a slight tetrahedral twist of 16.5(1)° at Cu(2). The Cu metal atom lies 0.202(1) Å above the basal plane toward the axial site. The “outer” and “inner” units are linked by propionate bridges showing *syn,anti*-η^1:η^1:μ coordination mode from an axial position of one chromophore to an equatorial position of the other one.

An uncoordinate molecule of [Cu$_2$(μ-O$_2$CC$_2$H$_5$)$_4$(H$_2$O)$_2$] similar to the “inner”, involves a centrosymmetric dinuclear paddle-wheel unit in which four propionato groups are bridging the two Cu atoms, in a *syn,syn*-η^1:η^1:μ disposition. An O atom of water molecule occupies the axial position of each Cu atom at a distance of 2.156(2) Å, completing the square pyramidal coordination geometry with τ value of 0.001. The Cu(3)···Cu(3)A distance is 2.647(1) Å. The basal plane is non-planar with a slight tetrahedral twist of 17.2(1)° at Cu(3). The Cu metal atoms lies 0.210(1) Å above the basal plane toward the axial site.

The lattice structure is stabilized by a complicated hydrogen bonding network between the oxygen atom of the non-bridged propionato ligand and nitrogen atom of amine with N···O distance of 2.790(1) Å); between the water oxygen atom of uncoordinated dinuclear paddlewheel unit and the oxygen atom of *syn,syn*-η^1:η^1:μ bridged propionato ligand and non-bridged propionato ligand (O···O distances of 2.861(1) and 2.832(1) Å, respectively); between the water oxygen atom of “outer” molecule and the oxygen atom of *syn,syn*-η^1:η^1:μ, *syn,anti*-η^1:η^1:μ bridged propionato ligands and water oxygen atom of uncoordinated dinuclear paddle-wheel unit (O···O distances of 2.970(1), 3.002(1) and 2.829(1) Å, respectively).

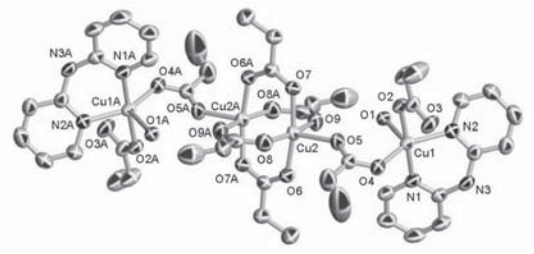


Figure 1 Thermal ellipsoid (30% probability) plot of $[Cu_4(dpyam)_2(OCOC_2H_5)_2(\mu\text{-}O_2CC_2H_5)_6(H_2O)_2][Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2]\cdot(DMF)_2$ **1**. Hydrogen atoms in dpyam and propionato ligands are omitted for clarity.

2. Crystal structure $[Cu_6(phen)_2(H_2O)_2(\mu\text{-}O_2C\ C_2H_5)_{12}]_n[Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2]_{2n}\cdot(H_2O)_{0.5n}$ (2)

The asymmetric unit of **2** consists of a hexanuclear $[Cu_6(phen)_2(H_2O)_2(\mu\text{-}O_2CC_2H_5)_{12}]$, a dinuclear $[Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2]$, two halves of two independent dinuclear $[Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2]$ units, and a half of water molecule. Compound **2** involves one dimensional structure arised from the hexanuclear unit and consists of zig-zag chains of mononuclear $Cu(\mu\text{-}O_2CC_2H_5)_2(H_2O)(phen)$ repeating units running along the *b* axis, which are connected along the unit cell diagonal via $Cu_2(\mu\text{-}O_2CC_2H_5)_4$ paddle-wheel dinuclear units. Both mononuclear and dinuclear units are linked by the syn,anti-triatomic propionato bridge in an axial-equatorial configuration which are consistent with the class B (Scheme 2). There are four outer distinct Cu···Cu separations along the *b* axis which alternate according to the sequence ABCD where (using the viewpoint of Fig. 3) A = Cu(1)···Cu(2) = 5.074(1) Å; B = Cu(3)···Cu(4) = 4.287(1) Å; C = Cu(4)···Cu(5) = 5.077(1) Å; D = Cu(6)···Cu(1)' = 4.293(1) Å. The inner distinct Cu(2)···Cu(3) = 2.621(1) Å; Cu(5)···Cu(6) = 2.621(1) Å.

The paddle-wheel dinuclear $Cu_2(\mu\text{-}O_2CC_2H_5)_4$ units in the chain contain four bridging propionates in the *syn,syn*-η^1:η^1:μ coordination mode, as found in $[Cu_2(O_2CC_2H_5)_4(H_2O)_2]$ (Battaglia, L.P. *et al.* 1986) and complex **1**. Square pyramidal coordination at Cu(2), Cu(3), Cu(5) and Cu(6) are completed by oxygen atoms of another propionate bridging molecules at distances of 2.132(2), 2.129(2), 2.127(3) and 2.126(3) Å, with the τ values of 0.045, 0.053, 0.046 and 0.048, respectively. The basal planes have a slight tetrahedral twist of 17.1(1), 15.9(1), 16.8(1) and 15.9(1)° at Cu(2), Cu(3), Cu(5) and Cu(6), respectively. The Cu atoms are displaced from the basal planes at distances of 0.204(1), 0.190(1), 0.202(1) and 0.191(1) Å for Cu(2), Cu(3) Cu(5) and Cu(6), respectively. The Cu(2)···Cu(3) and Cu(5)···Cu(6) separations [2.621(1) and 2.621(1) Å] are slightly longer than the 2.611(2) Å separation in $[Cu_2(O_2CC_2H_5)_4(H_2O)_2]$ and almost identical to that in **1**.

The mononuclear $Cu(\mu\text{-}O_2CC_2H_5)_2(H_2O)(phen)$ units (Cu(1), Cu(4)), with a CuN_2O_2O' chromophore, have a square pyramidal geometry with the small τ values of 0.017 and 0.015 for Cu(1) and Cu(4), respectively, in contrast to those of compound **1** (τ = 0.483). The basal plane of a square pyramidal chromophore consists of two N atoms of phen and two O atoms of two different propionato bridges. The coordinated water molecules (O(1), O(15)) occupy the apical positions at distances of 2.342(3) and 2.346(3) Å for Cu(1) and Cu(4), respectively. The CuN_2O_2 chromophores are non-planar with a slight tetrahedral twist of 10.8(1)° and 10.9(1)°, for Cu(1) and Cu(4), respectively. The Cu(1) and Cu(4) line above the basal planes, 0.135 and 0.136 Å toward O(1) and O(15), respectively.

Three discrete independent $[Cu_2(\mu-O_2CC_2H_5)_4(H_2O)_2]$ units also involve the dinuclear paddle-wheel unit with comparable structural data to those of another paddle-wheel units of compounds **1** and **2**. The square pyramidal coordinations are completed by oxygen atoms of water molecules at the axial distances of 2.164(3) and 2.159(3) Å at Cu(7) and Cu(8), 2.156(3) Å at Cu(9) and 2.141(3) Å at Cu(10), with the τ values of 0.077, 0.076, 0.001 and 0.061, respectively. The basal planes are non-planar with a slight tetrahedral twist of 17.2(1) and 17.3(1)° at Cu(7) and Cu(8), 16.6(1)° at Cu(9) and 16.9(1)° at Cu(10). The Cu atoms are lifted above the basal planes at distances of 0.206(1), 0.207(1), 0.202(1) and 0.202(1) Å for Cu(7), Cu(8), Cu(9) and Cu(10), respectively. The Cu···Cu distances are 2.636(1) Å for Cu(7)···Cu(8), 2.632(1) Å for Cu(9)···Cu(9A) and 2.627(1) Å for Cu(10)···Cu(10A).

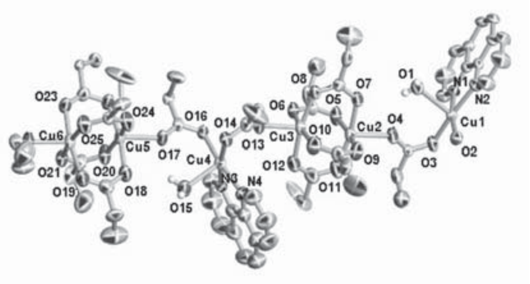


Figure 2 Thermal ellipsoid (30% probability) plot of $[Cu_6(phen)_2(H_2O)_2(\mu-O_2CC_2H_5)_{12}]_n$ $[Cu_2(\mu-O_2CC_2H_5)_4(H_2O)_2]_{2n}\bullet(H_2O)_{0.5n}$ 2. Hydrogen atoms in phen, propionato ligands and H_2O are omitted for clarity.

The lattice structure is stabilized by a complicated hydrogen bonding network between the water oxygen atoms of independent, uncoordinated dinuclear paddle-wheel units and the oxygen atoms of *syn,syn*-η^1:η^1:μ bridged propionato ligands (O···O distances vary from 2.793(1) to 2.990(1) Å); between the coordinated water oxygen atoms and the oxygen atoms of *syn,syn*-η^1:η^1:μ, *syn,anti*-η^1:η^1:μ bridged propionato ligands and water oxygen atoms of discrete dinuclear paddle-wheel units (O···O distances vary from 2.844(1) to 3.0112(1) Å).

3. Crystal structure of $\{[Cu_4(phen)_2(\mu-O_2C\ C_2H_5)_8]\bullet(H_2O)\}n$ (3)

The structure of compound 3 involves one dimensional structure arised from the tetranuclear units and consists of chains of dinuclear $Cu_2(\mu-OCOC_2H_5)_2(\mu-O_2CC_2H_5)_2(phen)_2$ repeating units which are connected to each other along the unit cell diagonal via $Cu_2(\mu-O_2CC_2H_5)_4$ paddle-wheel dinuclear units. This structure is depicted in Fig. 3 together with the numbering scheme. Both dinuclear units are linked by the syn,anti-triatomic propionato bridge in an axial-equatorial configuration. The polynuclear copper(II) carboxylates were found to exhibit three classes of local paddle-wheel structure. Compuond 3 has a structure derived from class B, with a dimer molecule bridging two dinuclear units.

The paddle-wheel dinuclear $Cu_2(\mu-O_2CC_2H_5)_4$ units in the chain contain four bridging propionates in the *syn,syn*-η^1:η^1:μ coordination mode. The geometry around the Cu(2) and Cu(2)A atoms can be considered as a square pyramidal environment (τ = 0.005) with five oxygen atoms of five different propionate groups. The corresponding

Cu-O distances in the basal plane are in the range 1.952(3) to 1.962(3)(2) Å. An O atom of bridging propionates occupies the axial position at a distance of 2.120(2) Å. The basal planes have a slight tetrahedral twist of 16.72(1)°. The Cu atoms are displaced from the basal planes at distances of 0.003 Å. The Cu(2)···Cu(2)A separations [2.623(1) Å] are slightly longer than the 2.611(2) Å separation in $[Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2]$.

The dinuclear $[Cu_2(\mu\text{-}OCOC_2H_5)_2(\mu\text{-}O_2CC_2H_5)_2(phen)_2]$ units, Cu(1) and Cu(1)A, with a CuN_2O_2O' chromophore, have a distorted square pyramidal geometry with the small τ values of 0.290. The basal plane of CuN_2O_2O' chromophore consists of two N atoms of phen and two O atoms of two different propionato bridges and it is non-planar with a slight tetrahedral twist of 24.05(1)°. An O atom of propionato bridges occupies the axial position at a distance of 2.354(2) Å. The Cu atoms lie above the basal planes, 0.215 Å toward the axial sites. Both Cu(1) and Cu(1)A are linked by the doubly bridged monoatomic propionato groups in an axial-equatorial configuration with Cu···Cu distance of 3.408(1) Å.

The interplanar distances between the phen rings of two adjacent chains are 3.488-3.494 Å, indicating definite π-stacking interaction. The 2D layer resulting form stacks in the crystal structure.

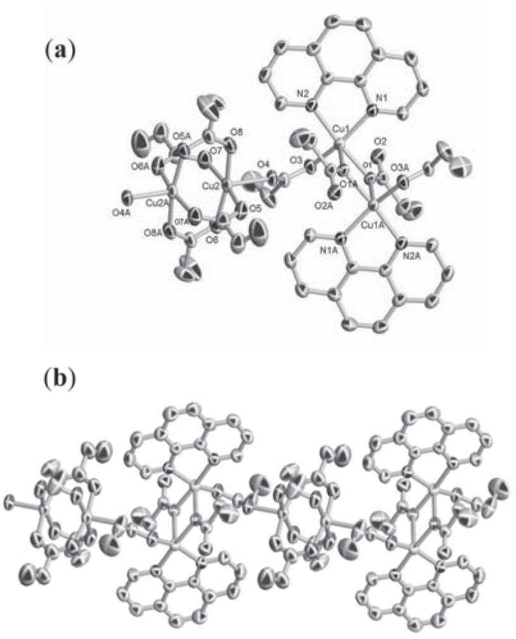


Figure 3 (a) Thermal ellipsoid (30% probability) plot of $\{[Cu_4(phen)_2(?\text{-}O_2CC_2H_5)_8]\bullet(H_2O)\}_n$ 3. Hydrogen atoms and uncoordinating H_2O are omitted for clarity. (b) View of the 1-D polymeric chain.

4. Crystal structure of $[Cu_2(\mu\text{-}O_2CC_6H_4OH)_4(C_7H_7NO)_2]\bullet6H_2O$ (4)

The structure of compound 4 consists of centrosymmetric dinuclear paddle-wheel unit. Both Cu(II) ions are linked by four carboxylato groups of 3-hydroxybenzoate ligand in a *syn,syn*-η^1:η^1:μ disposition. The pyridyl nitrogen atom of 4-acetylpyridine dispositions at the apex, completing the square pyramidal coordination geometry with a τ value of 0.002. The Cu-O distances are ranging from 1.958 to 1.970 Å with the Cu-N distance of 2.181(2) Å. A view of the dinuclear species is given in Fig. 4. The Cu···Cu distance is 2.654(1) Å. The basal plane is non-planar with a slight tetrahedral twist of 17.2(1)° and Cu atoms lie 0.001 Å above the basal plane toward the axial sites.

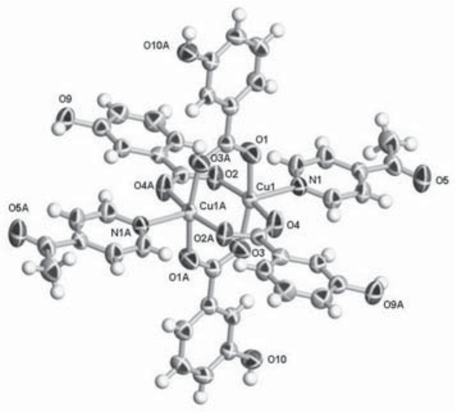


Figure 4 Thermal ellipsoid (50% probability) plot of $[Cu_2(\mu\text{-}O_2CC_6H_4OH)_4(C_7H_7NO)_2]\cdot 6H_2O$ 4. Uncoordinating H_2O are omitted for clarity.

5. Crystal structure of $[Cu_2(\mu\text{-}O_2CCH_3)_4(C_7H_7NO)_2]$ (5)

The compound **5** consists of centrosymmetric dinuclear units, similar to other copper acetate derivates, in which four acetate groups are bridging the two Cu atoms and a 4-acetylpyridine ligand occupies the axial position of each Cu atom, coordinated to them through the pyridine nitrogen atom giving CuO_4N chromophore. This structure is depicted in Fig. 5 together with the numbering scheme. Each copper atom has a square pyramidal geometry, with four oxygen atoms in a basal plane (Cu-O distances vary from 1.965(1) to 1.972(1) Å); the fifth coordination position is occupied by the nitrogen of a 4-acetylpyridine ligand at 2.198(1) Å. The CuO_4N chromophore is nonplanar with tetrahedral twist of 18.15(1)°. The copper atoms are displaced by 0.001 Å from the basal planes toward the apical positions. The trigonality index $\tau = 0.002$ corresponds clearly to a square pyramidal coordination. Four acetate anions bridge two copper ions in a *syn,syn*-η^1:η^1:μ showing the paddle-wheel unit with Cu···Cu distance of 2.631(4) Å.

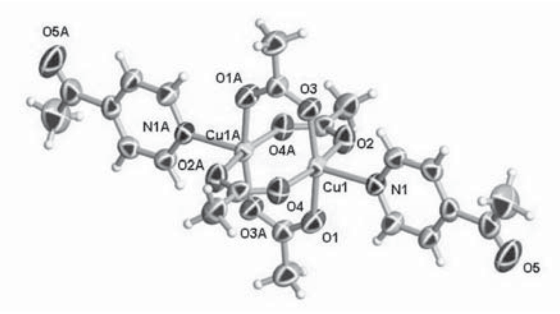


Figure 5 Thermal ellipsoid (50% probability) plot of $[Cu_2(\mu\text{-}O_2CCH_3)_4(C_7H_7NO)_2]$ 5.

6. Spectroscopic properties

6.1 IR spectra

The IR spectra of all complexes exhibit the antisymmetric and symmetric carboxylate stretching vibrations at ca.1578-1625 cm^{-1} and 1400-1468 cm^{-1}, respectively. These bands are assigned to the stretching modes of the triatomic carboxylate bridges (Christou, G. *et al.* 1990). The strong bands at 1558, 1374 cm-1 for 1, 1566, 1373 cm^{-1} for 2 and 1567, 1372 cm^{-1} for 3 are assigned to the antisymmetric and symmetric carboxylate stretching modes of the monoatomic carboxylate group (Chailuecha, C. *et al.* 2006).

6.2 Electronic Diffuse Reflectance Spectra

The electronic reflectance spectrum of compound 1 consists of a single board peak centered at 13 860 cm^{-1}, resulting from the overlap of two nearly equal energy peaks, a higher energy peak of the square pyramidal chromophore and a lower energy peak of intermediate five-coordinate chromophore. The one-electron ground state configuration is $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} \rightarrow d_{yz}$. The transitions may be assigned as the d_{xy}, d_{xz}, d_{yz}, $d_{z^2} \rightarrow d_{x^2-y^2}$ for both distorted geometries. The electronic diffuse reflectance spectra of complexes **2**, **3**, **4** and **5** show a broad band centered at 13 800 cm^{-1} for **2**, 13 510 cm^{-1} for 3, 13 460 cm^{-1} for 4 and 14 170 cm^{-1} for 5, respectively. These features are consistent with the square pyramidal geometry and the d_{xy}, d_{yz}, d_{xz}, d_{z^2} $\rightarrow$ dx2-y2 transition is assigned for a broad band (Hathaway, B.J.).

6.3 EPR spectra

The EPR spectra of complexes **1** and **2** were recorded as a polycrystalline powder at RT and 77 K. The observed EPR spectrum of complexes **1** and **2** are isotropic at room temperature with g_{iso} = 2.09 and 2.12, respectively, giving no information regarding to the electronic ground state, at liquid nitrogen temperature (77 K) these values are just slightly increased.

Conclusions

In this work we have presented the synthesis and spectroscopic study of five new polynuclear tetracarboxylato-bridged copper(II) complexes. Four carboxylate ligands bridge two copper ions in a *syn,syn*-η^1:η^1:μ mode showing the paddle-wheel unit. Compound 1 consists of a centrosymmetric tetranuclear $[Cu_4(dpyam)_2(OCOC_2H_5)_2(\mu\text{-}O_2CC_2H_5)_6(H_2O)_2]$, noncoordinating $[Cu_2(\mu\text{-}O_2CC_2H_5)_4(H_2O)_2]$ and DMF molecules. The terminal chromophores of tetranuclear compound have an intermediate 5-coordinate geometry while both central chromophores have a distorted square pyramidal geometry. Compounds **2** and **3** exhibit an one dimensional chain structure. The adjacent chains of compound **3** are connected to form a 2D structure through the π-π interaction. Compounds **4** and **5** involve a dinuclear paddle-wheel structure which have 4-acetylpyridine ligand at the apical position and the coordination geometry around each Cu(II) ion is distorted square pyramidal.

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