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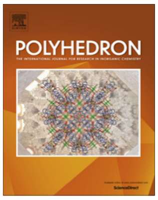

Dicopper moieties stabilized by Fréchet-type dendrons: Syntheses and structural characterizations ☆

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ABSTRACT

Five paddlewheel-shaped dicopper molecules, **1**, **2a**, **2b**, **3** and **4**, were synthesized from the reaction of copper acetate and different generations of Fréchet-type dendrons (H**G1**–H**G4**). All compounds showed diagnostic bands in their FTIR spectra for the coordinated carboxylate groups with separations of CO_{asym} and CO_{sym} lower than 200 cm^{-1} suggesting the formation of dimers. A broad absorbance band centered at 700, 695, 695 and 693 nm was observed for compounds **1**–**4** respectively, which is ascribed to the d–d charge-transfer in Cu(II) complexes. A LMCT absorption was observed near 304, 290, 298 and 294 nm for compounds **1**–**4** respectively. Magnetic susceptibility measurements for **1**, **2a** and **3** at 1.53, 1.53 and 1.7 respectively in the solid state at 293 K are also suggestive of a dimeric arrangement. The structures of H**G2**, **1**, **2a**, and **2b** were characterized unambiguously with single crystal X-ray diffraction. Three molecules constituted the asymmetric unit of H**G2** in the monoclinic space group $P2_1/n$ and resulted in dimers formed via intermolecular carboxylic acid-type hydrogen bonds. Compounds **1**, **2a**, and **2b** contain centrosymmetric paddlewheel-shaped dinuclear copper molecules bridged by four carboxylate groups in *syn*, *syn* arrangements. The copper centers in compounds **1**, **2a**, and **2b** are all coordinated by four carboxylate O atoms in a square pyramidal geometry and the ligands on the apical positions are disordered and occupied by either water, THF, pyridine or methanol molecules. In **1**, all the hydroxyl O atoms are involved in hydrogen bonding, which results in the formation of a 3D network. π–π stacking interactions involving phenyl rings were observed in the crystal structures of H**G2**, **2a** and **2b**.

1. Introduction

Metallodendrimers, i.e., dendrimers that are functionalized with transition metal atoms, have attracted widespread interest for the property of luminescence and for various applications such as catalysts, sensors, nanomedicines, and molecular electronics [1–3]. The integration of metal centers into dendrimers can be accomplished by the use of metallo-branching centers, or by interior metal coordination and encapsulation at precise chelating sites [2]. There are numerous reports focused on the incorporation of mononuclear species, high nuclearity clusters or polyoxometallates as the centers or branching points into dendrimers [4,3,5–8]. In contrast, the incorporation of bimetallic species with a paddlewheel structure into dendrimers has been limited, especially considering their unique topologies and high stabilities [9–11].

There is strong interest in the study of structural aspects of dendrimers since it allows us to understand the conformation, topology and self-assembly process of these dendrimers [12]. Interestingly, due to the difficulties in obtaining single crystals, there are few reports of crystallographic studies [12–15]. We have reported on a series of quadruply bonded dimolybdenum compounds bridged by four Fréchet-type dendritic polyesters [9]. We now extend our investigation to the related paddlewheel Cu_2^{4+} cores supported by four dendritic polyesters with active carboxylate groups [16]. Dimeric paddlewheel copper carboxylates generally formulated as $Cu_2(OOCR)_2L_2$ (L = axial ligand), where the R represents a variety of small and bulky organic groups, have been extensively studied during the previous decades [17–26]. However, paddlewheel copper dimers supported by dendrons have not so far been detailed and given the known instability of copper dimers in solution [27], it was not clear if a dimeric arrangement would be maintained with increasing dendron size in the solid state.

Two dendrons used in this study are those derived by the di-esterification of 3,5-dihydroxybenzoic acid (H**G1**, MW = 154.12

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g/mol) with two equivalents of benzoic acid (H**G2**, MW = 362.34 g/mol). A bigger dendron used had two 3,5-dihydroxybenzoate linkages between H**G1** and then four capping benzoic acid groups, H**G3**, MW = 842.77 g/mol, and the last had six interstitial benzoate molecules esterified with eight benzoic acid groups, H**G4**, MW = 1803.63 g/mol [16]. The synthesis and characterization of these desired copper dendrimers are presented here, as well as the crystal structures of dendron H**G2** and the copper dendrimers, $Cu_2(\mathbf{G1})_4(THF)_2$, $Cu_2(\mathbf{G1})_4(THF)(py)$ and $Cu_2(\mathbf{G2})_4(py)_2$ which contained extensive disorder, and, $Cu_2(\mathbf{G2})_4(CH_3OH)_2$. This report is of importance in that it details crystal structures of dendrimers which are acknowledged as being “difficult to crystallize” [12].

2. Experimental

2.1. General method

Infrared spectra were obtained on a PerkinElmer Spectrum one FT-IR spectrometer. A PerkinElmer Lambda 35 UV/Vis Spectrometer was used for the UV/Vis spectra. A Fisher-Johns melting point apparatus (Fisher Scientific Company) was used for the melting point determinations. A Johnson Matthey Auto MSB instrument was used for magnetic susceptibility measurements. DSC analyses were conducted on a Shimadzu DSC-50 analyzer under a slow nitrogen stream. Solvents were used as received from commercial suppliers. Most chemicals were purchased from Aldrich, and all chemicals were used as received. The Fréchet-type dendrons were prepared according to literature methods [9,16]. Crystals of dendron H**G2** were obtained by allowing the evaporation of a dichloromethane solution at room temperature. The elemental analyses were conducted by Galbraith Lab.

2.2. Synthesis and characterization of $Cu_2(G1)_4(py)_2$, (**1**)

Excess pyridine (0.19 g, 2.4 mmol) was added slowly to a methanol solution (10 mL) of 3,5-dihydroxybenzoic acid, H**G1**, (0.308 g, 2.00 mmol) under constant stirring. This mixture was then added to a methanol solution (15 mL) of copper acetate hydrate (0.200 g, 1.00 mmol). The reaction mixture was stirred for one hour at ambient temperature resulting in a blue solution. A blue precipitate formed after the blue solution was concentrated using a rotary evaporator. The crude product was recrystallized from a THF solution resulting in 0.29 g of **1**. Yield: 73.0%. Blue crystals suitable for X-ray diffraction were obtained by allowing the slow diffusion of dichloromethane into a THF solution of **1**. This afforded mostly $Cu_2(\mathbf{G1})_4(THF)(py)$, **1a**. IR (neat, cm^{-1}): 3511(w), 2973(w), 1608(w), 1578(w), 1545(s), 1487(m), 1449(m), 1369(s), 1358(s), 1299(s), 1248(w), 1220(w), 1155(s), 1071(w), 1045(w), 1003(s), 877(m), 787(s), 753(s), 694(s). UV (THF) 700 nm (br), 304 nm (sh).

2.3. Synthesis and characterization of $Cu_2(G2)_4(Py)_2$, (**2a**)

Excess pyridine (0.4 g, 5 mmol) was added to a THF solution (10 mL) of dendron H**G2** (0.362 g, 1.00 mmol) with constant stirring. The solution was then added to a methanol solution (10 mL) of copper acetate hydrate (0.100 g, 0.50 mmol) and stirred for one hour at room temperature resulting in a blue solution. A blue residue was afforded after solvents were removed by rotary evaporation. The blue residue was redissolved in dichloromethane. Bluish green crystals were obtained after adding hexane to the dichloromethane solution and cooling in a freezer for a few hours. The bluish green crystals were isolated by filtration and dried under vacuum overnight. Crystals of **2a** suitable for single X-ray diffraction were obtained by slow diffusion of hexane into a solution of **2a** in dichloromethane. Yield: 0.31 g, 72%. *Anal.* Calc. for $Cu_2C_{94}H_{62}O_{24}N_2$: C, 65.24; H, 3.61; N, 1.62. Found: C, 64.73; H, 3.85; N, 1.54%. IR (neat, cm^{-1}): 3077(w), 1731(s), 1625(w), 1585(m), 1449(w), 1394(m), 1316(w), 1243(s), 1181(w), 1127(s), 1059(s), 1026(m), 899(w), 771(m), 695(s). UV (THF) 695 nm (br), 290 nm (sh).

2.4. Synthesis and characterization of $Cu_2(G2)_4(CH_3OH)_2$, (**2b**)

Dendron H**G2** (0.181 g, 0.50 mmol) was dissolved in 20 mL of dichloromethane in a Sigma–Aldrich storage 1” diameter tube (capacity 100 mL). Methanol (30 mL) was then layered on top followed by a methanol solution (10 mL) of copper acetate hydrate (0.050 g, 0.25 mmol). The tube was sealed and allowed to stand undisturbed at room temperature for one week allowing sufficient time for crystal growth. Blue crystals of **2b** were isolated and dried under vacuum. Yield: 0.14 g, 70%. *Anal.* Calc. for $Cu_2C_{86}H_{60}O_{26}\cdot 0.5CH_2Cl_2\cdot 0.5CH_3OH$: C, 61.65; H, 3.72. Found: C, 61.71; H, 3.63%. IR (neat, cm^{-1}): 3559(w), 3069(w), 1733(vs), 1636(w), 1591(m), 1452(w), 1392(s), 1313(w), 1242(s), 1178(w), 1128(s), 1059(s), 1022(m), 906(m), 774(s), 696(s).

2.5. Synthesis and characterization of $Cu_2(G3)_4(Py)_2$, (**3**)

Compound **3** was obtained by following a similar procedure to that for **2a**, but dendron H**G3** was used in place of H**G2**. Yield: 0.32 g, 70%. *Anal.* Calc. for $Cu_2C_{206}H_{126}O_{56}N_2\cdot CH_2Cl_2$: C, 66.53; H, 3.45; N, 0.75. Found: C, 66.79; H, 3.63; N, 0.78%. IR (neat, cm^{-1}): 3064(w), 1736(vs), 1622(w), 1585(m), 1488(w) 1445(m), 1397(w), 1377(m), 1299(m), 1239(s), 1196(m), 1125(s), 1055(s), 1024(s), 897(m), 753(m), 696(s). UV (THF) 695 nm (br), 298 nm (sh).

2.6. Synthesis and characterization of $Cu_2(G4)_4(Py)_2$, (**4**)

Compound **4** was obtained by following a similar procedure to that for **2a**, but dendron H**G4** was used in place of H**G2**. The blue gum-like precipitate was recrystallized from a dichloromethane/diethylether solution yielding a crystalline powder. Yield: 0.26 g, 61%. *Anal.* Calc. for $Cu_2C_{430}H_{254}O_{120}N_2\cdot CH_2Cl_2$: C, 68.29; H, 3.40; N, 0.37. Found: C, 68.36; H, 3.50; N, <0.5%. IR (neat, cm^{-1}): 3093(w), 1735(vs), 1591(m), 1444(m), 1302(w), 1316(w), 1294(m), 1239(s), 1178(s), 1126(s), 1077(w) 1054(s), 1023(m), 900(w), 753(m), 699(s). UV (THF) 693 nm (br), 294 nm (sh).

2.7. X-ray crystallography

All single crystal XRD analyses were performed on a Bruker AXS SMART APEX CCD system using Mo Kα radiation (λ = 0.71073 Å) at 100 (2) K. Single crystals of compounds were mounted on Mitegen micromesh supports using viscous oil flash-cooled to 100 K. Data were collected, unit cells determined, and the data integrated and corrected for absorption and other systematic errors using the APEX2 suite of programs [28]. All structures were solved by direct methods, refined by full matrix least squares against Fo^2 with all reflections using SHELXL-97 [29] and completed using previously published procedures [29–32]. H**G2** was found to be non-merohedrally twinned consisting of two components. One of the benzoate fragments in one of the three molecules in complex H**G2** which constituted the asymmetric unit was disordered over two positions (55.5(3):44.5(3)% occupancies). The crystals for complex **1** consisted of four major non-merohedral twin moieties and also contained disorder. The main molecule was arranged around an inversion center with a Cu–Cu distance of 2.6193(13) Å. The axial ligands in this molecule consisted of THF and pyridine molecules and converged to a 53(1):47(1) occupancy ratio. This would suggest that the crystal consisted of a co-crystallization either of 94%