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Synthesis and Characterization of New Trinuclear Copper Complexes

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Abstract

This report describes our approach towards modelling the copper cluster active sites of nitrous oxide reductase and the multicopper oxidases/oxygenases. We have synthesized two mesitylene-based trinucleating ligands, MesPY1 and MesPY2, which employ bis(2-picoly)amine (PY1) and bis(2-pyridylethyl)amine (PY2) tridentate copper chelates, respectively. Addition of cuprous salts to these ligands leads to the isolation of tricopper(I) complexes [(Mes-PY1)Cu^I₃(CH₃CN)₃](ClO₄)₃·0.25Et₂O (**1**) and [(Mes-PY2)Cu^I₃](PF₆)₃ (**3**). Each of the three copper centers in **1** is most likely four-coordinate, with ligated acetonitrile as the fourth ligand; by contrast, the copper centers in **3** are three-coordinate, as determined by X-ray crystallography. The synthesis of [(Mes-PY1)Cu^{II}₃(CH₃CN)₂(CH₃OH)₂](ClO₄)₆·(CH₃OH) (**2**) was accomplished by addition of three equivalents of the copper(II) salt, Cu(ClO₄)₂·6H₂O, to the ligand. The structure of **2** shows that two of the copper centers are tetracoordinate (with MeCN solvent ligation), but have additional weak axial (fifth ligand) interactions with the perchlorate anions; the third copper is unique in that it is coordinated by two MeOH solvent molecules, making it overall five-coordinate. For complexes **2** and **3**, one copper ion center is located on the opposite side of the mesitylene plane as the other two. These observations, although in the solid state, must be taken into account for future studies where intramolecular tricopper(I)/O₂ (or other small molecules of interest) interactions in solution are desirable.

Keywords

trinuclear copper; copper(I) and copper(II); copper clusters; trinucleating ligands; Cu clusters in biology

1. Introduction

Nature has exploited the versatility of metal ion clusters (three or more metal ions held in close proximity) to perform numerous functions in a variety of systems [1]. Iron-sulfur clusters participate in electron storage and transfer (ferredoxins) [1a, 2], as a cofactor

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Dedicated to Professor Jon Zubieta on the occasion of his 65th birthday. All the best to a special guy and wonderful colleague who without hesitation or reservation significantly influenced and aided the launching of KDK's research career. One could not be more grateful

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(FeMoCo) or P-cluster in nitrogenase [1a, 3], and in catalytic/regulatory/structural functions of the hydrolyase family (e.g., aconitase, fumarase A & B, endonuclease III) [4]. A trinuclear zinc cluster comprises the active site of phospholipase C (*Bacillus cereus*) which catalyzes the hydrolysis of phosphodiester bonds in phospholipids [5]. However, perhaps nowhere in nature is the use of metal ion clusters more prevalent than with copper [1, 6]. The multicopper-oxidases, ascorbate oxidase (AO), ceruloplasmin, and laccase, are known to have active sites comprised of a trinuclear cluster whose function is to couple the four-electron reduction of dioxygen to water with the one-electron oxidation of four equivalents of ascorbate, ferrous ion, and phenolic substrate, respectively [7]. X-ray crystallographic insights [8] have confirmed the previous spectroscopic and biochemical studies which showed that this catalytic triad is comprised of one type 2 (mononuclear) and one type 3 (couple binuclear) copper center, both of which represent the minimum structural unit required to retain enzymatic function [7a].

The active site of ascorbate oxidase [8a], which is representative of all three multi-copper oxidases, is shown in Figure 1. The type 2 'normal' copper is ligated by two histidine residues and a hydroxide/water, and is approximately 3.9 – 4.0 Å distant from each copper in the type 3 'coupled binuclear' center, both of which possess three histidine ligands in addition to a bridging hydroxide ligand (giving rise to strong antiferromagnetic coupling between the two copper ions of the type 3 center). These studies also confirmed the presence of a type 1 'blue' copper nearly 12 Å removed from the catalytic triad which serves as an electron-transfer site, mediating uptake of electrons (one-at-a-time) from a substrate donor (which becomes oxidized) and transfer of these reducing equivalents to the trinuclear center, the site of O₂-binding and reduction to water [7a].

A copper cluster can also be found at the active site of nitrous oxide reductase (N₂OR) [6, 9], the terminal enzyme of denitrification, whose function is to catalyze the two electron reduction of N₂O to N₂. This environmentally significant reaction is being increasingly scrutinized given the emergence of nitrous oxide as a greenhouse gas produced from biomass, burning of fossil fuels, and also from agriculturally or industrially-related activities [10]. X-ray crystal structures of N₂OR have been reported, and one is depicted in Figure 2 [11].

This so-called CuZ active-site contains four copper ions in close proximity, ligated by a surprisingly low number (seven) of histidine side chain residues. The high-resolution X-ray structures along with resonance Raman spectroscopy [12] and biochemical analyses [13] confirm the presence of a bridging (μ₄) inorganic sulphur. Such an unusual active site has no doubt evolved to overcome the challenges presented by nitrous oxide, namely it being kinetically inert to reduction, as well as being a poor transition metal ligand [14]. To add to the complicated nature of the active site and issues of the mechanism of N₂O activation/reduction, a very recent report [11d] finds this cluster can support two sulfur atoms per four copper ions, and future investigations will require inclusion of this Cu₄S₂(His)₇ center in any discussions.

Particulate methane monooxygenase (pMMO) (found in methanotrophic eubacteria) and ammonia monooxygenase (AMO) (ammonia-oxidizing eubacteria) have been suggested to possess copper clusters, bi- or trinuclear, based upon biochemical, spectroscopic, X-ray crystallographic investigations or computational chemistry [7c, 15]. These multicopper oxygenases catalyze a number of industrially important transformations, including the conversion of methane to methanol, ethane hydroxylation, and the oxidation of a variety of hydrocarbons, halogenated organics, and carbon monoxide [7a, 16]. The uncertainty makes it more difficult to design model complexes for structural, spectroscopic or reactivity studies, however it also makes this approach very valuable.

Although a number of model complexes for trinuclear copper clusters exist [17], including instances involving (ligand) $\text{Cu}^{\text{I}}_3/\text{O}_2$ reactivity [17b,d,m,s], one of the most interesting is that reported by Stack and co-workers [18], whose $[(\text{L})\text{Cu}^{\text{I}}(\text{MeCN})]^+ \{ \text{L} = N\text{-permethylated}(1R, 2R)\text{-cyclohexanediamine} \}$ complex reacts with dioxygen in a 3:1 stoichiometry yielding a crystallographically characterized $[(\text{L})_3\text{Cu}^{\text{II}}_2\text{Cu}^{\text{III}}-(\mu_3\text{-O})_2]^{3+}$ mixed-valence self-assembled product. Here, the O–O bond has been cleaved in a four-electron reduction; two electrons originate from a $\text{Cu}^{\text{I}} \rightarrow \text{Cu}^{\text{II}}$ oxidation, and two electrons from a $\text{Cu}^{\text{I}} \rightarrow \text{Cu}^{\text{III}}$ process. While this work represents a significant advance in modelling the four-electron reduction of O_2 to water by a trinuclear copper complex (actually, in this case, as three initially separate mononuclear copper complexes), additional studies are needed to increase our breadth of knowledge concerning substrate oxidations or four-electron O_2 -reductions mediated by copper ion clusters.

In this report, we present our continuing [17a–e] efforts towards modelling the active sites of the multicopper enzymes. Synthetic procedures are presented here for the functionalization of a mesitylene scaffolding with either bis(2-picolyl)amine (PY1) or bis(2-pyridylethyl)amine (PY2), yielding the trinucleating tridentate ligands Mes-PY1 and Mes-PY2, respectively (Figure 3). In fact, Kimoon Kim and coworkers [17h] previously synthesized a very close analogue of Mes-PY1 however based on the 2,4,6-triethylbenzene framework, and reported on several copper(I) complexes they generated along with their X-ray crystal structures (also see below). Mao and coworkers [17k] used a tricopper(II) complex with ligand analogue of Mes-PY1 (but without the 2-, 4- and 6-methyl substituents) for studies in DNA cleavage chemistry. We have employed PY2 containing similar mesitylene-based ligands [17b,d,h] including studies of copper(I)-dioxygen reactivity [17b,d]. Furthermore, investigations of dioxygen reactivity with mono- and binuclear copper(I) complexes employing similar tridentate pyridyl-alkylamine containing copper chelates have also been previously examined [19], thereby establishing patterns for copper-dioxygen adduct formation.

Addition of cuprous or cupric salts to the Mes-PY1 and Mes-PY2 ligands yield tricopper complexes which have been structurally characterized. However, the results of our X-ray diffraction studies show that the mesitylene-based ligands employed here may be unable to provide the desired geometry of three copper ions held within close proximity to each other to potentially facilitate intramolecular copper dioxygen chemical reactivity, where the stoichiometry of reaction taking place is $\text{Cu}^{\text{I}}/\text{O}_2 = 3:1$.

2. Experimental

2.1. Materials and Methods

Reagents and solvents used were of commercially available reagent quality unless otherwise stated. Under argon, methanol, dichloromethane, and acetonitrile (CH_3CN) were distilled from CaH_2 , while diethyl ether was distilled from Na/benzophenone. Deionized water (18.3 $\text{M}\Omega\cdot\text{cm}$) was provided for by a Sybron/Barnstead PCS water deionizer. Preparative thin-layer chromatography was performed on a Harrison Research Chromatotron Model 8924 equipped with a 4mm Adsorbosil-Plus P (silica gel, Alltech Associates) plate. Thin-layer chromatography was performed on ‘Baker-Flex’ aluminum oxide (IB–F) and silica gel (IB2–F) plates (J. T. Baker). Alumina (EM-Science, AX-0612, 80–200 mesh) and silica gel 60 (EM-Science, 7734, 70–230 mesh) were also purchased from commercial sources. All ligands were synthesized and characterized in air unless otherwise stated. Preparation and handling of air-sensitive materials were carried out under an argon atmosphere using standard Schlenk techniques. Solvents and solutions were deoxygenated by either repeated freeze-pump-thaw cycles (5 $\times$), or by bubbling of argon (> 25 min.) directly through the solution. Solid samples were stored and transferred, and samples for spectroscopic

characterization were prepared, in an MBraun LabMaster 130 inert atmosphere (<1 ppm O₂, <1 ppm H₂O) glovebox under nitrogen atmosphere. NMR spectra were measured on a Varian NMR instrument at 400 MHz (¹H). All spectra were recorded in 5-mm-o.d. NMR tubes, and chemical shifts were reported as δ values downfield from an internal standard of Me₄Si (¹H). Low-temperature UV-visible spectral studies were carried out with a Hewlett-Packard 8453A diode array spectrometer using the Agilent Chemstation software. The spectrometer was equipped with a variable-temperature dewar and cuvette assembly as described elsewhere [20].

2.2 Ligands and copper complex syntheses

2.2.1. Mesitylene-PY1—To a three-neck 250 mL round bottom flask equipped with a stir bar and a rubber septum was added in the following order under argon: 2,4,6-tris(bromomethyl)mesitylene (1.0 g, 2.51 mmol; Aldrich), 125 mL ethyl acetate, bis(2-picolyl)amine (2.1 g, 10.5 mmol; Richmond Chemicals), 200 mg KI, and diisopropylethylamine (2.0 mL, 11.5 mmol). After several minutes of stirring under argon, the pale yellow solution slowly turned orange, and a white precipitate was formed on the sides of the flask. The reaction mixture was stirred for five days, after which 10 g phthalic anhydride was added (primary/secondary amine scavenger). After stirring for a further 24 hours, the reaction mixture was filtered, an additional 250 mL ethyl acetate was added, and the organic layer was extracted with 1 M NaOH (2 × 500 mL) and water (1 × 500 mL). After drying over Na₂SO₄ and filtration, the solution was concentrated *in vacuo* to give a dark red/brown solid. The crude material was applied to an alumina column (unactivated, 80–200 mesh, 4.0 cm. o.d. × 18 cm.) and eluted with 2% methanol in ethyl acetate. Removal of solvent gave mesitylene-PY1 (1.51 g, 2.01 mmol) as an off-white solid in 80% yield. TLC (alumina, 3% CH₃OH in EtOAc) R_f: 0.35. ¹H NMR (CDCl₃): δ 2.22 (s, 9 H, CH₃), 3.62–3.67 (m, 18H, NCH₂), 6.99–7.03 (m, 6H, py-5H), 7.21–7.24 (m, 6H, py-3H), 7.41–7.46 (m, 6H, py-4H), 8.38–8.40 (m, 6H, py-6H). CI+ MS: (m + H⁺): *m/z* 754.

2.2.2. [(Mes-PY1)Cu^I₃(CH₃CN)₃](ClO₄)₃·0.25(Et₂O) (1)—To a 100 mL Schlenk tube equipped with a stir bar was added Mes-PY1 (0.250 g, 0.332 mmol) and [Cu(CH₃CN)₄](ClO₄)⁷³ (0.326 g, 0.996 mmol). The tube was evacuated and filled with argon four times. De-oxygenated acetonitrile was added (20 mL), and the yellow solution was allowed to stir for thirty minutes before layering (without stirring) with de-oxygenated diethyl ether (70 mL). After four days, large yellow crystals had formed on the sides of the Schlenk tube, and were sent for crystal structure determination without further manipulation. Isolation of a solid was accomplished by decantation of the mother liquor from the crystalline material, followed by washing with de-oxygenated diethyl ether. Drying *in vacuo* for 24 hours yielded **1** as a bright yellow, free-flowing microcrystalline solid (380 mg) in 84% yield. ¹H-NMR (CD₃NO₂): δ 1.11 (t, 1.5H, Et₂O: CH₃), 2.05 (s, 9 H, MeCN), 2.36 (s, 9 H, CH₃), 3.41 (q, 1H, Et₂O: CH₂), 3.73 (s, 12H, NCH₂), 3.91 (s, 6H, Mes-CH₂), 7.25–7.36 (m, 12H, py-5H, py-3H), 7.72–7.81 (m, 6H, py-4H), 8.43–8.47 (m, 6H, py-6H). Anal. Calcd for C₅₄H₆₀Cl₃Cu₃N₁₂O₁₂·0.25(CH₃CH₂)₂O: C, 47.61; H, 4.55; N, 12.14. Found: C, 47.28; H, 4.47; N, 11.80.

2.2.3. [(Mes-PY1)Cu^{II}₃(CH₃CN)₂(CH₃OH)₂](ClO₄)₆·(CH₃OH) (2)—To a 100 mL reaction tube equipped with a stir bar was added Mes-PY1 (0.250 g, 0.332 mmol), Cu^{II}(ClO₄)₂·6H₂O (0.370 g, 0.996 mmol), 10 mL MeCN and 15 mL MeOH. After 30 minutes of stirring, the medium blue solution was layered (without further stirring) with diethyl ether (75 mL). After two days, blue plate-like crystals formed on the sides of the flask, and were sent for crystal structure determination without further manipulation. Isolation of a solid was accomplished by decantation of the mother liquor from the crystalline material, followed by drying *in vacuo* for 12 hours, thereby yielding **2** as a blue,

free-flowing microcrystalline solid (348 mg) in 68% yield. Anal. Calcd for $C_{55}H_{69}Cl_6Cu_3N_{11}O_{27}$: C, 38.42; H, 4.04; N, 8.96. Found: C, 38.07; H, 3.97; N, 8.67.

2.2.4. KCN Reduction of [(Mes-PY1)Cu^{II}₃(CH₃CN)₂(CH₃OH)₂](ClO₄)₆·(CH₃OH)

(2)—To a 10 mL Schlenk flask equipped with a stir bar was added 30 mg **2** (1.75×10^{-5} mol), 34 mg KCN (30 fold excess), and 2 mL CD₃NO₂ under argon. The medium blue solution turned pale yellow over one hour, during which a small amount of precipitate formed. The solution was filtered through a cotton plug, transferred to an NMR tube, and its spectrum recorded. Integration against the ligand peaks revealed two molecules of acetonitrile and three of methanol per ligand/complex **2**. This finding was consistent with the results of the elemental analysis (above).

2.2.5. Mesitylene-PY2—To a three-neck 250 mL round bottom flask equipped with a stir bar and a rubber septum was added in the following order under argon: 2,4,6-tris(bromomethyl)mesitylene (1.0 g, 2.51 mmol), 125 mL ethyl acetate, bis((2-pyridyl)ethyl)amine [21] (2.3 g, 10.1 mmol), 200 mg KI, and di-isopropylethylamine (2.0 mL, 11.5 mmol). After several minutes of stirring under argon, a white precipitate was formed. The reaction mixture was stirred for five days, after which 10 g phthalic anhydride was added (primary/secondary amine scavenger). After stirring for a further 24 hours, the reaction mixture was filtered, an additional 250 mL ethyl acetate was added, and the organic layer was extracted with 1 M NaOH (2 × 500 mL) and water (1 × 500 mL). Drying over Na₂SO₄, filtration, and concentration via rotary evaporation yielded a dark brown oil. The crude material was applied to an alumina column (unactivated, 80–200 mesh, 4.0 cm. o.d. × 18 cm.) and eluted with 2 – 3% ethanol/dichloromethane. Removal of the solvent gave mesitylene-PY2 (1.25 g, 1.49 mmol) as a light yellow oil in 59% yield. TLC (alumina, 2% t-Butyl alcohol in EtOAc) R_f: 0.30. ¹H-NMR (CDCl₃): δ 2.16 (m, 9H, CH₃), 2.89 (m, 24H, NCH₂CH₂), 3.70 (s, 6H, Mes-CH₂), 6.87 – 7.01 (m, 6H, py-5H), 7.02–7.04 (m, 6H, py-3H), 7.38 – 7.42 (m, 6H, py-4H), 8.41 – 8.43 (m, 6H, py-6H). CI+ MS: (m + H⁺): m/z 838.5.

2.2.6 [(Mes-PY2)Cu^I₃](PF₆)₃ (3)—To a 100 mL Schlenk tube equipped with a stir bar was added Mes-PY2 (0.300 g, 0.356 mmol) and [Cu(CH₃CN)₄](PF₆) [22] (0.400 g, 1.07 mmol). The tube was evacuated and filled with argon four times. De-oxygenated dichloromethane was added (20 mL), and the yellow solution was allowed to stir for thirty minutes before layering (without stirring) with de-oxygenated diethyl ether (80 mL). After several days, large yellow crystals had formed on the sides of the Schlenk tube, and were sent for crystal structure determination without further manipulation. Isolation of a solid was accomplished by decantation of the mother liquor from the crystalline material, followed by washing with de-oxygenated diethyl ether. Drying *in vacuo* for 24 hours yielded **3** as a dark yellow, free-flowing powder (402 mg) in 77% yield. ¹H-NMR (CD₃NO₂): δ 2.16 (m, 9H, CH₃), 3.02 (m, 24H, NCH₂CH₂), 3.78 (s, 6H, Mes-CH₂), 7.18 – 7.21 (m, 12H, py-5H, py-3H), 7.46 – 7.59 (m, 6H, py-4H), 8.52 – 8.56 (m, 6H, py-6H).

3. Results and Discussion

3.1 Synthesis

Both mesitylene-based trinucleating ligands are synthesized from the commercially available precursor 2,4,6-tris(bromomethyl)mesitylene. Functionalization of the alkyl-halide groups with bis(2-picolyl)amine (PY1) or bis(2-(pyridylethyl))amine (PY2) affords the desired Mes-PY1 or Mes-PY2 ligands, respectively, in good yield and in gram-scale quantities. Utilization of a catalytic amount of potassium iodide, in addition to a large excess of the secondary amine, resulted in the exclusive formation of the tri-substituted ligand over the mono- and di-substituted ones. This was corroborated by mass spectrometry on the

ligands, where the parent molecular ion was observed, and further supported by NMR spectral analysis, which showed proper integration when comparing the three methyl groups of the mesitylene unit and the six methylene or ethylene arms of the respective PY1 or PY2 moieties.

3.2. [(Mes-PY1)Cu^I₃(CH₃CN)₃](ClO₄)₃·Et₂O (1)

Addition of three equivalents [Cu^I(CH₃CN)](ClO₄) to the Mes-PY1 ligand in acetonitrile solvent, followed by layering with diethyl ether, led to the formation of large yellow crystals of complex **1**. The presence of acetonitrile ligands in the isolated solid was confirmed by NMR spectroscopy on this diamagnetic tricopper(I) (*d*¹⁰) complex. While crystals were isolated, a full X-ray crystal structure analysis with fully refined structure could not be obtained. On the basis of chemical expectations derived from study of a large number of other copper(I) complexes with these pyridylalkylamine tridentate ligands, there is little doubt that the complex possesses three nearly identical copper(I) ions in a pseudotetrahedral environment. Ligation of three N-atoms from the PY2 chelated along with the acetonitrile nitrogen atom is expected [17h,20,23–25], see diagram below.

As mentioned, Kim and coworkers [17h] also reported on copper complexes with a 2,4,6-triethylbenzene analogue of Mes-PY1, and the tricopper(I) complex [(L)Cu^I₃(CH₃CN)₃]³⁺, essentially the same complex as formulated here. They used a different counter-anion, PF₆[−], and obtained crystals from a different solvent. It is interesting to note that in the Kim structure, all three copper ion centers reside on the same side of the mesitylene plane; all three pairwise Cu...Cu distances are similar but greater than 7 Ångstroms.

3.3. X-ray structure of [(Mes-PY1)Cu^{II}₃(CH₃CN)₂(CH₃OH)₂(H₂O)](ClO₄)₆·(CH₃OH) (2)

Addition of three equivalents CuII(ClO₄)₂·6H₂O to the Mes-PY1 ligand in a methanol-acetonitrile solvent mixture, followed by layering with diethyl ether, afforded after several days complex **2** as medium-blue plate-like crystals suitable for X-ray diffraction. A single crystal was harvested directly from the mother liquor, coated with epoxy, and mounted on the diffractometer in a glass capillary.

As can be seen from the ORTEP diagram in Figure 4, Cu1 is in a unique ligand environment, and is overall pentacoordinate. In addition to the two pyridyl {Cu-N_{pyridine} =

1.965 Å (ave)} and one amine ($\text{Cu-N}_{\text{amine}} = 2.039 \text{ Å}$) nitrogen donors, the Cu1 center is also ligated by two methanol solvent molecules ($\text{Cu-O}_{\text{MeOH}} = 2.026, 2.268 \text{ Å}$). By contrast, the Cu2 and Cu3 cupric ions are bound by one acetonitrile ligand each ($\text{Cu-N}_{\text{MeCN}} = 1.966, 1.989 \text{ Å}$) as well as by the tridentate PY1 copper chelate ($\text{Cu-N}_{\text{pyridine}} = 1.97 - 1.98 \text{ Å}$; $\text{Cu-N}_{\text{amine}} = 2.039 \text{ Å}$). Furthermore, additional weak axial interactions exist between the oxygen atoms of the perchlorate anions and the Cu2 & Cu3 centers, as shown..

The unsymmetrical nature of **2** is reminiscent of another structurally characterized trinuclear copper(II) complex, $[(\text{L}')\text{Cu}^{\text{II}}_3(\text{NO}_3)_2(\text{H}_2\text{O})_3](\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, where L' represents the trinucleating ligand tris(N,N-bis(2-picoly)aminoethyl)amine. In that structure, all three cupric ions were in different ligand environments, one of which was coordinated in a square pyramidal geometry to two water molecules $\{\text{Cu-OH}_2 = 2.008(7) \text{ \AA} \text{ \& } 2.226(7) \text{ \AA}\}$ and the three nitrogen donors of the PY1 chelate $\{\text{Cu-N}_{\text{pyridine}} = 1.97 - 1.98 \text{ Å}$; $\text{Cu-N}_{\text{amine}} = 2.055 \text{ Å}\}$ [17c, 26]; a tricopper(I) complex analogue is also known [17a].

Complex **2** possesses one copper center on the opposite face of the mesityl plane as the other two, again casting doubt on whether simultaneous and intramolecular interactions between all three copper centers are possible. Furthermore, the crystal structure of **2** also shows additional methanol solvent molecules in the unit cell. In order to confirm the presence or absence of these in the isolated solid, and to overcome the problems associated with NMR spectroscopy on a paramagnetic copper(II) sample, a reduction of **2** was performed in CD_3NO_2 using potassium cyanide (see Experimental Section). This resulted in the formation of copper(I) cyanide as a precipitate, leaving behind (in solution) the Mes-PY1 ligand and any solvent molecules. By employing this approach, NMR spectral analysis and integration revealed two molecules each of MeCN and MeOH present in the isolated solid of **2**, as was corroborated by the elemental analysis using this formulation. This contrasts with the five (total) molecules of MeOH in the crystal structure, and the discrepancy is most likely due to loss of solvent upon drying of the isolated solid.

3.4. X-ray structure of $[(\text{Mes-PY2})\text{Cu}^{\text{I}}_3](\text{PF}_6)_3$ (**3**)

Crystallization of $[(\text{MesPY2})\text{Cu}^{\text{I}}_3](\text{PF}_6)_3 \cdot (\text{CH}_2\text{Cl}_2)_2$ (**3**) was accomplished from the addition of three equivalents $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})](\text{PF}_6)$ to the Mes-PY2 ligand in dichloromethane solvent, followed by layering with diethyl ether. This procedure yielded large dark-yellow crystals suitable for x-ray diffraction after several days.

The asymmetric unit cell of **3** contains two molecules of dichloromethane in addition to three PF_6^- anions, none of which interact with the copper ions. All three copper centers are three-coordinate (Figure 5), with ligation provided for by the two pyridyl and one amine nitrogen-donors of each PY2 arm; bond angles and distances are typical for three-coordinate copper(I) complexes [20a, 23a, 25]. In contrast to the trigonal planar geometry expected for three coordinate $\text{L}_3\text{Cu}^{\text{I}}$ (L = unidentate N-donor) complexes [25c], the coordination geometry of the cuprous ions in **3** are T-shaped, being typical of the many three-coordinate copper(I) complexes employing the tridentate N-donor PY2 chelate (Table 1).

The T-shaped geometry is comprised of two shorter Cu-N_{py} bonds ($1.89 - 1.95 \text{ Å}$), and a longer $\text{Cu-N}_{\text{amine}}$ bond ($2.20 - 2.41 \text{ Å}$), resulting in acute angles for $\text{N}_{\text{py}}\text{-Cu-N}_{\text{amine}}$ ($96 - 105^\circ$), and much larger angles for $\text{N}_{\text{py}}\text{-Cu-N}_{\text{py}}$ ($151 - 163^\circ$) (Figure 5). In fact, this angle for Cu2 in $[(\text{Mes-PY2})\text{Cu}^{\text{I}}_3](\text{PF}_6)_3 \cdot 2\text{CH}_2\text{Cl}_2$ (**3**) is greater (162.9°) than for either Cu1 (151.5°) or Cu3 (156.6°), leading to slightly shorter Cu-N_{py} (by $0.01 - 0.05 \text{ Å}$) bond distances than those found for Cu1 or Cu3, and a corresponding lengthening of the $\text{Cu-N}_{\text{amine}}$ ($96 - 105^\circ$) bond by $\sim 0.2 \text{ Å}$. Thus, Cu2 may also be described as a copper environment possessing a pseudo two-coordinate copper(I) complex which is distorted from linearity [23d, 27] with Cu-N bond lengths falling in the range expected for linear two coordinate copper complexes

[28]. Overall, the bond lengths in 3-coordinate copper complexes such as **3** are shorter than those found in the tetracoordinate copper(I) complexes (Cu-N = 1.95 – 2.07 Å) employing the same PY2 chelate (fourth ligand = CO [25a], PPh₃ [20b], CH₃CN [20a], pyridyl [23b], phenoxo [20c]), with somewhat more tetrahedral angles ∠L-Cu-L (L = pyridyl-N, amine-N, or exogenous ligand) of ~95 – 125°, also found in the four-coordinate system.

The structure of **3** again shows that only two of the copper centers are found on the same side of the mesitylene plane, as for **1** and **2**, this despite the use of the longer-armed (i.e., larger chelate ring size) PY2 copper-chelate. NMR spectroscopy on the isolated solid of **3** did not reveal the presence of dichloromethane solvate, most likely attributed to its removal during the isolation of the bulk material.

4.0 Conclusions

Our efforts into modelling the active sites of copper-cluster containing enzymes have led us to synthesize mesitylene-based trinucleating ligands which employ tridentate copper-chelates as their copper binding site. A few close analogues of Mes-PY1 and their tricopper(I) or tricopper(II) derivatives have been previously also described in the literature. Here, structural characterization of the resulting tricopper complexes revealed that the trimethyl-mesitylene motif may not provide the cluster-like geometry required for Cu^I₃/O₂ intramolecular reactivity, since we observe that structures **2** and **3** possess two copper centers located on one side of the mesityl place, with the third on the other 'opposite' side. While this separation of copper centers in the solid-state does not preclude the desired multicopper-dioxygen reactivity in solution, it may promote complicated intermolecular reactions/products seen previously for an analogous system [17d]. Pairwise copper(I) dioxygen chemistry, i.e., with two copper ions involved, can and has been described by us previously. The results presented here do reveal the diverse nature of compounds which can be synthesized with the mesitylene based platform, both tricopper(I) and tricopper(II) complexes. Further reactivity studies should expand our knowledge of cooperative interactions of multicopper containing chemical systems, also providing a fundamental basis for further understanding the properties of biological copper ion clusters.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Appendix A. Supplementary material

CCDC xxxxxx contains supplementary crystallographic data for complex [(Mes-PY1)Cu^{II}₃(CH₃CN)₂(CH₃OH)₂](ClO₄)₆·(CH₃OH) (**2**) and [(Mes-PY2)Cu^I₃](PF₆)₃ (**3**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Highlights

- Mesitylene can be derivatized to give trinucleating ligands for copper ion complexes.
- Trinuclear copper(I) and copper(II) complexes have been synthesized.
- X-ray structures of two tricopper complexes are reported.

Figure 1.

Active site structure of ascorbate oxidase showing the type 2/type 3 catalytic triad, and the type 1 'blue' copper electron-transfer center. Coordinates (1AOZ) were taken from the Protein Data Bank (Brookhaven) and displayed using the program Rasmol..

Figure 2.
The CuZ active site of nitrous oxide reductase. Coordinates (1QN1) were taken from the Protein Data Bank (Brookhaven) and displayed using the program Rasmol.

Figure 3.

Figure 4. Displacement ellipsoid plot (50% probability level) of a $\{[(\text{Mes-PY1})\text{Cu}^{\text{II}}_3(\text{CH}_3\text{CN})_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})(\text{ClO}_4)_2]_2\}^{8+}$ moiety of complex **2**.

Figure 5.

Displacement ellipsoid plot (50% probability level) of the cationic portion of [(Mes-PY2)CuI₃](PF₆)₃ (**3**). Selected bond distances [Å] and angles [°]: Cu(1)-N11 2.204(3), Cu(1)-N12 1.949(3), Cu(1)-N13 1.949(3), Cu(2)-N31 2.408(3), Cu(2)-N32 1.915(4), Cu(2)-N33 1.896(3), Cu(3)-N51 2.237(3), Cu(3)-N52 1.923(4), Cu(3)-N53 1.933(4), N11-Cu(1)-N12 104.8(2), N11-Cu(1)-N13 97.9(2), N12-Cu(1)-N13 151.5(2), N31-Cu(2)-N32 96.8(14), N31-Cu(2)-N33 99.4(2), N32-Cu(2)-N33 162.9(2), N51-Cu(3)-N52 100.6(2), N51-Cu(3)-N53 101.6(2), N52-Cu(3)-N53 156.6(2).

Table 1

Structural Data for Selected Three-Coordinate Copper (I) Complexes.

Complex	Cu-Npy ₁	Cu-Npy ₂	Cu-N _{amine}	∠Npy ₁ -Cu-Npy ₂	∠Npy ₁ -Cu-N _{amine}	∠Npy ₂ -Cu-N _{amine}	Ref.
<i>a</i>							
[(Mes-PY2)CuI ₃] ³⁺ (3)							
Cu1	1.949	1.949	2.204	151.5	104.8	97.9	
Cu2	1.915	1.896	2.408	162.9	96.8	99.4	
Cu3	1.923	1.933	2.237	156.6	100.6	101.6	
[(Bpy2)Cu]PF ₆	1.893	1.873	2.216	158.4	99.6	98.8	[29]
[(PhPY2)Cu]PF ₆	1.922	1.915	2.228	159.6	101.1	99.0	[24]
[(<i>m</i> -XYL)Cu ₂](PF ₆) ₂							[25i]
Cu1	1.937	1.924	2.121	151.4	102.5	104.0	
Cu2	1.904	1.918	2.196	150.8	99.7	104.4	
[(N3OR)Cu ₂](PF ₆) ₂ <i>c</i>							[25g]
Cu1	1.878	1.881	2.214	156.6	102.0	100.2	
Cu2	1.935	1.912	2.212	146.2	100.7	104.9	
[(N3OR) ₁ Cu ₂](PF ₆) ₂ <i>d</i>							[27]
Cu1 <i>b</i>	2.016	2.054	2.242	110.2	99.3	96.1	
Cu2	1.949	1.943	2.166	146.6	101.8	104.6	
[(N4)Cu ₂](ClO ₄) ₂ <i>e,f</i>	1.934	1.944	2.145	139.6	100.5	105.3	[20a]

a this work;

b distorted geometry due to additional copper-ligand interactions (pseudo-five-coordinate);

c R = (C₆H₅)(C₆H₄)CO₂;

d R₁ = C(O)(CH=CH)(C₆H₅);

e the copper ions in this structure are distorted from 3-coordinate by weak bonding interactions with the perchlorate anions.