Cu(I) Wires: Structural Polymorphism and Photoluminescence

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Cu(I) Wires: Structural Polymorphism and Photoluminescence

by

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An Honors Thesis Submitted to the
Department of Chemistry
University at Albany, State University of New York
In partial Fulfillment of the Requirements for
An Honors Bachelor of Science Degree in Chemistry
May 2011
I would like to express my sincerest thanks and gratitude to my advisor Dr. Marina A. Petrukhina for not only being a great mentor, but also for providing me with multidisciplinary and collaborative environments to conduct research. I appreciate the time and effort that Prof. Petrukhina spent in revising my work. I would like to take this opportunity to thank the Chemistry Department Chair Prof. Paul J. Toscano for his valuable instructions and advice during my study. A special thank you to the Ph.D. student Oleksandr Hietsoi and to Dr. Alexander S. Filatov for crystal structures determination and characterization. I would also like to thank the graduate students from professor Petrukhina’s lab at University at Albany for their help during the time spent in the lab working on this project.
1. ABSTRACT

Metal wires are a linear arrangement of metal centers that conduct electrical current. Linear polynuclear metal clusters are of great importance for the design of metal-rich nanomaterials and the development of theories describing metal-metal bonds. Theoretical work on metal strings is valuable in understanding their properties and discovering their potential applications as molecular wires.

Linear metal atom chains can be ligand supported or unsupported. The anions of polypyridylamines have been used extensively to support linear metal chains. However, due to challenges involving the synthesis of these ligands, the longest metal chain reported contains nine metal atoms.

Examples of unsupported extended copper chains emphasize the crucial role of cuprophilic interactions in supporting these strings. Also based on Cu···Cu contacts are the infinite helical arrangements of carboxylate bridged copper(I) ions in Cu(I) pivalate and Cu(I) 3,5-bis(trifluoromethyl)benzoate.

Among carboxylates, the 2,4,6-triisopropylbenzoate ligand is known to be sufficiently bulky to prevent self-association of dinuclear paddlewheel units. Therefore, it was selected in this work to bridge copper(I) centers and favor Cu···Cu over Cu···O interactions. The result was the copper(I) 2,4,6-triisopropylbenzoate compound with a remarkable structure which was not known before for this class of compounds: an infinite linear arrangement of copper(I) ions bridged by the carboxylate ligand.

We were successful in isolating two polymorphs of this new extended chain of copper atoms: a “linear” wire and a “zigzag” chain held together by cuprophilic interactions. This allowed us for the first time to study the structure-photoluminescence correlations for two polymorphs of the same chain of metal atoms. Solution crystallization from o-dichlorobenzene resulted in the fragmentation of the infinite string to a nonluminescent dicopper(I) complex.

This study has revealed remarkable structural variations that can be found for carboxylate complexes having the same bridging ligand and the same empirical formula. The consideration of photoluminescent behavior for the structurally diverse copper(I) 2,4,6-triisopropylbenzoate products revealed that emission wavelengths and intensities depend not only on the overall structural type, but show great sensitivity to the subtle differences in spatial distribution of Cu(I) atoms.
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Please note that the crystal structures herein presented adhere by the following color scheme:

- Hydrogen – light grey
- Carbon – dark grey
- Copper – sky blue
- Rhodium – blue
- Nitrogen – dark blue (smaller radius)
- Cobalt – dark blue (larger radius)
- Oxygen – red
- Sulfur – yellow
- Nickel – light green (larger radius)
- Fluorine – light green (smaller radius)
- Chlorine – dark green
- Chromium – purple
- Boron – orange
3. INTRODUCTION

Linear metal complexes are highly valuable in the fundamental study of metal-metal interactions\(^1\) and molecular magnetism. Currently, molecular magnetism is a topic of great interest\(^2\) due to potential applications in nanotechnology\(^3,4\) and use in quantum storage devices.\(^5,6\)

The major draw toward the study of one dimensional metal atom chains is their ability to conduct electrical current, thus making them useful for applications in nanoelectronics\(^7\) as molecular switches and molecular wires.\(^8,9\) Conductivity in an infinite metal atom chain with evenly spaced metal atoms bonded to adjacent metal atoms arises due to electronic delocalization about the metal-based orbitals.\(^10\) This type of conductivity is similar to the way the \(\pi\) orbitals of polyacetylene are conducting.\(^11\) As a result, metal string complexes acting as molecular wires can be considered the building blocks for molecular electronic devices\(^2\) due to their electrical conductivity.

I. Metal wires supported by polypyridylamido ligands

The smallest molecular wire is the extended metal atom chain (EMAC), which is a molecule that consists of a linear chain of directly bonded transition metal atoms surrounded by organic ligands.\(^12\) The term EMAC was coined by F. Albert Cotton from Texas A&M in the 1990’s thus sparking the rebirth of EMACs, but the beginning of linear metal strings pertains to the late nineteen sixties.

The first EMAC was synthesized back in 1968 by Hurley and Robinson\(^13\) who correctly determined the formula of the Ni complex of di-2-pyridylamido ligand based on elemental analysis data. Its crystal structure, on the other hand, became known more than two decades later thanks to amazing work done by Adulchecha and Hathaway.\(^14\) The influential discovery that the dpa\(^-\) anion can “arrange” three Ni atoms in a linear chain sparked a vivid interest in the study of additional EMACs. As a result numerous EMACs have been synthesized with various metals (Cu, Rh, Co, Ru, Ni, Cr) and their magnetic and electronic properties have been extensively studied.\(^15\)

The chemistry of EMACs is of great interest in the field of molecular wire development. EMACs are known to be valuable for their interesting photophysical\(^16\) and magnetic properties, and for their superconductivity.\(^17\) Studies of electronic exchange interactions in these linear
chains are useful for understanding magnetic behavior in more complex species. Structural analysis and magnetic measurements revealed that the strength of metal-metal interactions of these multinuclear metal string complexes is in the order of Cr>Co>Ni; and the stronger the metal-metal interaction is, the better the conductivity of molecular metal wires. Linear metal atom chains such as EMACs are synthesized using expanded bridging ligands that contain numerous pyridine and amino groups, like the deprotonated forms of polypyridylamines (Fig. 1). Polypyridylamido ligands, also known as oligo-α-pyridylamido ligands, have been shown to stabilize linear chains of three, five, seven, and nine metal atoms in complexes of the type $M_{3+2n}L_4X_2$ (M is the metal atom, L is the polypyridylamido ligand with nitrogen donor atoms, and $X^-$ is the anion occupying the axial positions).

Polypyridylamido ligands favor the formation of chains by bringing metal atoms together and aligning them in a linear string. The number of metal atoms in a chain depends on the number of nitrogen atoms in the ligand. Hence EMACs are unique metal atom chains because their length can be predetermined exactly. Moreover, the fact that their ends are capped by anions ensures individual EMAC molecules with no aggregation, thus enabling control over the exact length of the wire.

![Figure 1](image)

**Figure 1.** The general structure of polypyridylamine ligands.

- $n = 0$  Hdpa (dipyridylamine, $N_3$)
- $n = 1$  H$_2$tpda (tripyridyltriamine, $N_5$)
- $n = 2$  H$_3$eptta (tetrapyridyltriamine, $N_7$)
- $n = 3$  H$_4$pepta (pentapyridyltetraamine, $N_9$)
- $n = 4$  H$_5$heppa (hexapyridylpentaamine, $N_{11}$)
- $n = 5$  H$_6$hphe (heptapyridyhexaamine, $N_{13}$)

The typical crystal structures of metal string complexes ranging from trinuclear to nonanuclear metal chains are similar (Fig. 2). The structural motif consists of four all-syn type polypyridylamido anions wrapped around the co-linear metal chain. The M–M–M angle deviates only slightly from 180°. The inner metal atoms are six-coordinate, bonded to other two metal...
atoms along the axis of the molecule and to four nitrogen atoms perpendicular to the axis of the molecule. The charge is balanced by anionic ligands (such as Cl\(^-\), CN\(^-\), N\(_3^-\), NCS\(^-\)). Neutral ligands (water, acetonitrile) can also occupy the axial positions.

![Figure 2](image)

**Figure 2.** The typical structure of a metal string complex.

### 1.1 Trinuclear metal wires

The compounds of type M\(_3\)(dpa\(_4\))\(_2\)Cl\(_2\) were the first examples of complexes in which three metal atoms are arranged in a linear chain. The ligand used to stabilize linear trinuclear chains is the anion of the shortest polypyridylamine, di-2-pyridylamine (dpa\(^-\)).

![Figure 3](image)

**Figure 3.** A side view of the complex Ni\(_3\)(dpa\(_4\))\(_2\)Cl\(_2\) complex. Hydrogen atoms are omitted for clarity.

The structure of the first EMAC Ni\(_3\)(dpa\(_4\))\(_2\)Cl\(_2\) (shown in Fig. 3) consists of a linear string of three nickel atoms wrapped by four dpa\(^-\) ligands and capped by two Cl\(^-\) anions. A view looking down the Ni\(_3\) axis in Fig. 4 reveals that the polypyridylamido ligands are not planar, but
are wrapped helically around the metal chain due to steric repulsions between adjacent hydrogen atoms (Fig. 5). There is a total end-to-end twist of about 40° in each Ni₃(dpa)₄X₂ molecule.

![Image](image_url)

**Figure 4.** A view of the Ni₃(dpa)₄Cl₂ complex looking down the Ni₃ axis showing the helical arrangement of ligands. Chlorines and hydrogen atoms are omitted for clarity.

![Image](image_url)

**Figure 5.** The dpa⁻ ligand with H···H repulsions between the two pyridine rings.

Similar structures of dpa⁻ were obtained with Rh, Ru, Co, and Cr. Although the Ni₃(dpa)₄Cl₂ complex does not have any bond between the Ni²⁺ ions (both Ni···Ni distances are 2.443(1) Å), the trichromium,²¹ trirhodium,²⁵ triruthenium,²⁵ and tricobalt,³⁴ complexes of dpa⁻ all have metal-metal bonds. Later on, the Cl⁻ axial ligands were substituted for acetonitrile,²⁶ cyanide, dicyanamide, and thiocyanate²⁷ to yield the same trinuclear structural motif. Substituting both Cl⁻ ligands with BF₄⁻ gives Co₃(dpa)₄(BF₄)₂ which is known to have the shortest Co–Co distance in this class of compounds (2.25 Å).

Interestingly, while for Ni, Ru, and Rh neutral complexes of dpa⁻ only symmetric forms have been reported, the analogous Cr and Co complexes can have two structural forms: symmetrical and unsymmetrical.²⁶,²⁸ A symmetrical linear array forms when all valence electrons are symmetrically distributed and delocalized over all three metal atoms. In the unsymmetrical
form two of the metal atoms are bonded to each other, while the third one is separated. The existence of these polymorphs is attributed to bond-stretch isomerism,\textsuperscript{29} which is “the unusual phenomenon whereby molecules differ only in the length of one or more bonds”.\textsuperscript{30,31}

Linear tricobalt and trichromium chains exhibit polymorphism of the M\textsubscript{3}\textsuperscript{6+} string\textsuperscript{32,35} depending on the crystallization environment, the nature of the metal ions, the oxidation states of the complexes, and the nature of the axial ligands.\textsuperscript{33} The symmetrical structure has a D\textsubscript{4} symmetry and two equivalent M–M bonds. The unsymmetrical structure has a C\textsubscript{4} symmetry with two unequal M–M distances.

![Figure 6. Two polymorphs of Co\textsubscript{3}(dpa)\textsubscript{4}Cl\textsubscript{2}: symmetrical (left) and unsymmetrical (right).](image)

The complex Co\textsubscript{3}(dpa)\textsubscript{4}Cl\textsubscript{2} is a very well studied example of bond-stretch isomerism.\textsuperscript{34,35} It has temperature dependent symmetrical and unsymmetrical structural arrangements (Fig. 6). The temperature dependence of the Co–Co distances in Co\textsubscript{3}(dpa)\textsubscript{4}Cl\textsubscript{2} is correlated to the temperature dependence of their magnetic moments.\textsuperscript{26} This thermally induced spin transition of the Co\textsubscript{3}(dpa)\textsubscript{4}Cl\textsubscript{2} complex gives rise to special magnetic properties which can be used in developing molecular electronic devices.\textsuperscript{2} Density functional calculations\textsuperscript{36} on the Co\textsubscript{3}(dpa)\textsubscript{4}Cl\textsubscript{2} complex confirmed the view of a three-centered-three-electron bond in its symmetrical form\textsuperscript{35} where both Co–Co distances equal 2.3178(9) Å.

Synthesis of other trinuclear complexes with ligands such as DPhIP (2,6-di(phenylimino) piperidinate),\textsuperscript{37} BPAP (2,6-bisphenylaminopyridinate),\textsuperscript{38} DPyF (dipyridylformamidinate)\textsuperscript{39} (Fig. 7) also yields linear metal strings.

![Figure 7. Schematic representation of the DPhIP, BPAP, and DPyF ligands.](image)
The structure of [Cr₃(DPhIP)₄Cl]Cl reveals a linear, unsymmetrical Cr₃⁶⁺ chain supported by a set of four di(phenylimino)piperidine anions (Fig. 8). The axial ligand arrangement is different from that of the symmetrical Cr₃(dpa)₄Cl₂ complex, where each terminal Cr atom is axially bound to a Cl⁻ anion. The compound [Cr₃(DPhIP)₄Cl]Cl has only one axial Cl⁻ anion, while the other chloride lies between the cations surrounded by six H atoms. There are two different Cr–Cr distances: Cr₁–Cr₂ is 2.659(2) Å and Cr₂–Cr₃ is much shorter, only 1.932(2) Å. The short Cr–Cr distance is comparable to those found in dichromium complexes bridged by formamidinate ligands.

![Figure 8](image)

**Figure 8.** A view of the [Cr₃(DPhIP)₄Cl]Cl complex. The isolated chlorine ion and the hydrogen atoms are omitted for clarity.

The trichromium complexes of BPAP and DPyF are unsymmetrical, and similarly to the chromium complex with DPhIP, they all have a very short Cr–Cr quadruple bond (less than 2.0 Å) and a long distance to the isolated Cr²⁺ ion (2.59 to 2.74 Å).

### 1.2 Pentanuclear metal wires

Transition metal complexes of the tripyridyldiamido dianion (tpda²⁻) are pentanuclear with five-centered metal–metal bonds. The structure of the Ru complex of tpda²⁻ [Ru₅(μ₅-tpda)₄(NCS)₂] (Fig. 9) shows a collinear chain of five metal atoms helically coordinated by four tpda²⁻ ligands, the same as the other members of the pentanuclear family of EMACs.
In contrast to the linear tricobalt polypyridylamido complexes, the Co$_5$(tpda)$_4^{2+/3+}$ complexes have only symmetrical chains, with Co–Co distances ranging from 2.20 to 3.32 Å.\textsuperscript{42} The inner Co–Co distances are 0.05 Å longer than the outer ones, due to the interaction between the axial ligands and the outer cobalt atoms. Chromium complexes of tpda$^2-$ have also been synthesized\textsuperscript{43} and their structure is consistent with the structural motif set forth by Ru$_5(\mu_5$-tpda)$_4$(NCS)$_2$.

Interesting are the examples of unsymmetrical pentanuclear Ni complexes such as [Ni$_5$(tpda)$_4$(H$_2$O)(BF$_4$)](BF$_4$)$_2$ and [Ni$_5$(tpda)$_4$(CF$_3$SO$_3$)$_2$](CF$_3$SO$_3$)$_2$.\textsuperscript{44} The unsymmetrical Ni–Ni distances in [Ni$_5$(tpda)$_4$(H$_2$O)(BF$_4$)]$^{2+}$ (Fig. 10) are 2.337, 2.261, 2.245, and 2.300 Å (from Ni1 to Ni5).

Figure 9. The structure of [Ru$_5(\mu_5$-tpda)$_4$(NCS)$_2$]. Hydrogen atoms are omitted for clarity.

Figure 10. The structure of the [Ni$_5$(tpda)$_4$(H$_2$O)(BF$_4$)]$^{2+}$ in [Ni$_5$(tpda)$_4$(H$_2$O)(BF$_4$)](BF$_4$)$_2$. Hydrogen atoms of the pyridine rings are omitted for clarity.
From the practical application point of view, among the pentanickel linear chains the complex \([\text{Ni}_5(\mu_5\text{-tpda})_4(\text{NCS})_2]\) is the most valuable one because it has been shown to bind to a Ag or Au surface to form a monolayer, thus acting as a molecular metal wire.\(^{45}\)

1.3 Heptanuclear metal wires

Complexes of tetrapyrydyltriadimido trianion (teptra\(^{3-}\))\(^{23}\) ligands are heptanuclear with delocalized multiple bonds. A representative member of the heptanuclear class of complexes is \([\text{Cr}_7(\mu_7\text{-teptra})_4\text{Cl}_2]\).\(^{23}\) Its structure (Fig. 11) is essentially identical to those of \([\text{Ni}_7(\mu_7\text{-teptra})_4\text{X}_2]\) \((\text{X} = \text{Cl}, \text{NCS})\),\(^{46}\) exhibiting a heptanuclear chain helically wrapped by four all-syn type teptra\(^{3-}\) ligands.

![Figure 11. The structure of \([\text{Cr}_7(\mu_7\text{-teptra})_4\text{Cl}_2]\). Hydrogens atoms are omitted for clarity.](image)

1.4 Nonanuclear metal wires

Polypyridylamido complexes with nickel are known to form the most extended discrete metal chains. Although the longest linear metal string reported to date is the nonanuclear Ni complex with the peptea\(^{4-}\) ligand, Pantazis and McGrady estimated that 4-5 nm chains of up to 17 metal atoms can be accessed.\(^{47}\)
The longest metal chain supported by polypyridylamido ligands is \([\text{Ni}_9(\mu_9\text{-peptea})_4\text{Cl}_2]\).\(^{24}\) It incorporates nine Ni atoms and has a length of 2 nm. The crystal structure of \([\text{Ni}_9(\mu_9\text{-peptea})_4\text{Cl}_2]\) shown in Fig. 12 displays the unique geometric conformation of these metal chain complexes. The steric crowding of the \(\beta\)-C hydrogen atoms on the pyridyl rings forces the oligo-\(\alpha\)-pyridylamido ligand to bind helically with the Ni ion. The peptea\(^4\) ligands are non-planar, with a 45° dihedral angle among the planes of the pyridine rings. An end view of the molecule looking down the Ni\(_9\) axis gives a clear view of its helical structure (Fig. 13).
Comparisons of Ni–N and Ni–Ni distances among tri-, tetra-, penta-, and nona-nickel(II) linear chains (Fig. 14) reveals that the inner Ni–Ni and Ni–N distances are shorter than the outer Ni–Ni and Ni–N distances, respectively, due to the interaction between the axial ligands and the outer nickel atoms.\textsuperscript{24}

![Diagram of Ni–N and Ni–Ni distances for tri-nickel(II) to nona-nickel(II) complexes of polypyridylamido ligands.]

**Figure 14.** Ni–N and Ni–Ni distances for tri-nickel(II) to nona-nickel(II) complexes of polypyridylamido ligands.

### 1.5 Redox properties of metal chains supported by polypyridylamido ligands

The redox properties of polynuclear polypyridylamido complexes vary from one metal to another. Some of the transition metal EMACs exhibit significant structural changes upon oxidation, which makes them suitable as an on/off molecular switch.

Upon oxidation, the nickel and chromium EMACs show significant changes, while the cobalt analog exhibits only slight differences.\textsuperscript{33} For example, the one-electron oxidized form [Co$_3$(dpa)$_4$Cl$_2$]BF$_4$ has Co–Co distances (2.32 Å) similar to those in the neutral species Co$_3$(dpa)$_4$Cl$_2$ and as a result the Co complexes do not have potential to be used as molecular switches. In contrast, the oxidized trichromium complex of dpa$^-$ is unsymmetrical with a Cr–Cr quadruple bond and one isolated chromium atom, while the neutral trichromium complex is symmetrical with a bond order of 1.5 between adjacent metal atoms.
EMACs of nickel are also important for their redox properties, because oxidation of Ni\(_{\text{II}}\)\(_{2n+}^+\) complexes to Ni\(_{\text{II}}\)\(_{(2n+1)}^+\) leads to the delocalization of Ni–Ni bonds\(^{48}\). Reaction of Ni\(_3\)(dpa)\(_4\)Cl\(_2\) with AgPF\(_6\) gives the cation Ni\(_3\)(dpa)\(_4\)\(_{3+}\), which displays major structural changes, with Ni–Ni distances shortened by 0.14 Å. Furthermore, the distance between the terminal metal atom and the anion is lengthened, which suggests that PF\(_6^-\) coordinates to Ni weaker than Cl\(^-\). All these structural changes are explained by the formation of a three-centered Ni–Ni bond in the symmetric Ni\(_3\)(dpa)\(_4\)\(_{3+}\) cation\(^{12}\).

On the other hand, when the complex Cu\(_3\)(dpa)\(_4\)Cl\(_2\) is oxidized, the copper-copper distances see a modest increase from 2.47 to 2.51 Å. This increase is attributed to electrostatic repulsions between the more highly charged Cu ions\(^{50}\). And the fact that the inner Cu–N distance (1.89 Å) is shorter than the outer two Cu–N distances of 2.06 Å suggests that the middle copper atom is Cu\(^{III}\), while the outer two coppers are Cu\(^{II}\). Thus, oxidation of Cu\(_3\)(dpa)\(_4\)Cl\(_2\) contrasts remarkably to the oxidation of Ni\(_3\)(dpa)\(_4\)Cl\(_2\) since the oxidized Cu complex lacks the delocalization of bonding interaction\(^{49}\).

### II. Copper wires supported by polypyridylamido ligands

Copper is known to be the only one of the coinage metals group that forms linear arrays of metal atoms supported by N-donor ligands. The first copper polypyridylamido complex to be structurally characterized was the nitrogen bridged copper complex of dpa\(^-\), Cu\(_3\)(dpa)\(_4\)Cl\(_2\).\(^{50}\) Up to that date, all the linear tricopper complexes contained either oxygen\(^{51}\) or chloride\(^{52}\) bridges and had Cu···Cu distances greater than 3 Å.

Cu\(_3\)(dpa)\(_4\)Cl\(_2\) has the same structural motif as its analogs, Co\(_3\)(dpa)\(_4\)Cl\(_2\) and Cr\(_3\)(dpa)\(_4\)Cl\(_2\): a linear chain of three metal atoms with four dpa\(^-\) ligands wrapped helically around the collinear metal core with Cu···Cu distances of 2.4712(4) Å. Each copper has an octahedral environment with the two end copper atoms slightly displaced from the plane of the nitrogen atoms.

The first linear tetranuclear copper chain to be reported was the copper complex of DPhIP (Fig. 15).\(^{53}\) The [Cu\(_4\)(DPhIP)\(_4\)]\(_{2+}\) cation in [Cu\(_4\)(DPhIP)\(_4\)][CuCl\(_2\)]\(_2\)·3CH\(_2\)Cl\(_2\)·H\(_2\)O has an approximate D\(_{2d}\) symmetry. The four copper atoms are aligned along an S\(_4\) axis of an idealized D\(_{2d}\) ligand arrangement. The two outer copper atoms Cu\(_4\) and Cu\(_3\) are monovalent and in a linear arrangement, while the two inner copper atoms Cu\(_1\) and Cu\(_2\) are divalent and have square
planar coordination environments. The Cu1⋯Cu2 distance between the divalent metal ions is 2.479(2) Å. The Cu1⋯Cu4 and Cu2⋯Cu3 distances are somewhat longer, 2.525(2) and 2.518(2) Å.

**Figure 15.** The structure of the [Cu₄(DPhIP)₄]²⁺ cation in [Cu₄(DPhIP)₄][CuCl₂]₂·3CH₂Cl₂·H₂O. Solvent molecules and hydrogen atoms are omitted for clarity.

A view down the copper axis (Fig. 16) reveals an almost complete overlapping of the ligands surrounding the copper chain, lacking the helical arrangement encountered in the tricopper linear complex with dpa⁻.⁵⁰

**Figure 16.** A view down the axis of the [Cu₄(DPhIP)₄]²⁺ cation in [Cu₄(DPhIP)₄][CuCl₂]₂·3CH₂Cl₂·H₂O. Solvent molecules and hydrogen atoms are omitted for clarity.

Polypyridylamidom ligands limit the length of EMACs because of the limited number of nitrogen atoms that can be incorporated in the ligand’s structure. In order to extend the number
of metal atoms in the chain, new ligands have been developed by replacing the pyridine rings in the supporting ligands with pyrazine or pyrimidine rings.\textsuperscript{54} Noteworthy are the Cu\textsuperscript{I} complexes with the N-donor pentaazadienide ligands\textsuperscript{55} (schematically shown in Fig. 17) such as Cu\textsubscript{3}(tolN\textsubscript{5}tol)\textsubscript{3} and Cu\textsubscript{3}(p-EtOPhN\textsubscript{5}PhOEt)\textsubscript{3}.

![Figure 17](image)

**Figure 17.** Pentaazadienide ligands (the other two resonance structures are not shown). For R = CH\textsubscript{3} the ligand is tolN\textsubscript{5}tol.

The trinuclear chain Cu\textsubscript{3}(tolN\textsubscript{5}tol)\textsubscript{3} (shorthand for Cu\textsubscript{3}(1,5-ditolyl-1,4-pentaazadien-3-ido)\textsubscript{3}) was synthesized back in 1985 by Beck and Strahle.\textsuperscript{55} The crystal structure reveals a linear tricopper chain in which three N\textsubscript{5} zigzag chains coordinate the Cu\textsuperscript{+} ions with the outer and the middle N atoms such that each metal atom is in a trigonal planar environment (Fig. 18). This linear Cu\textsubscript{3}\textsuperscript{3+} chain has two slightly different Cu⋯Cu distances: 2.348(2) and 2.358(2) Å, which are some of the shortest known Cu⋯Cu distances. Another example of a trigonal chain complex with very short Cu⋯Cu distances (2.35 Å) is Cu\textsubscript{3}(p-EtOPhN\textsubscript{5}PhOEt)\textsubscript{3}.

![Figure 18](image)

**Figure 18.** The structure of Cu\textsubscript{3}(tolN\textsubscript{5}tol)\textsubscript{3}. Hydrogen atoms are omitted for clarity.

In 2005, Chan \textit{et al}\textsuperscript{56} synthesized and structurally characterized two linear chains of copper(I) atoms [(\textit{n}-Bu)\textsubscript{4}N][Cu\textsubscript{4}(pmf)\textsubscript{3}(SCN)\textsubscript{2}] (Fig. 19) and K[Cu\textsubscript{4}(pmf)\textsubscript{3}(SCN)\textsubscript{2}] that display a
slightly different structural motif. In both complexes, the four copper(I) atoms are bridged by three tetradeutate pmf\(^{-}\) ligands (pmf\(^{-}\) is the anion of \(N,N'\)-bis(pyrimidyl-2-yl)formamidine) and axially capped by two SCN\(^{-}\) ions. The two outer copper atoms are in a tetrahedral coordination environment, while the inner ones are trigonal planar. In \([\text{(n-Bu)}_4\text{N}][\text{Cu}_4(\text{pmf})_3(\text{SCN})_2]\), the Cu\(^{I}\)–Cu\(^{I}\) distance between the inner copper(I) atoms is 2.5214(5) Å, and the outer copper-copper distances are somewhat longer, 2.5342(5) and 2.5292(5) Å.

![Figure 19. Structure of the \([\text{Cu}_4(\text{pmf})_3(\text{SCN})_2]\)\(^{-}\) anion in \([\text{(n-Bu)}_4\text{N}][\text{Cu}_4(\text{pmf})_3(\text{SCN})_2]\). Hydrogen atoms are omitted for clarity.](image)

The above mentioned polynuclear complexes of copper with polypyridylamido and pentaaedienide ligands have no Cu–Cu bonds. All of the linear strings of Cu\(^{I}\) ions are held together by ligand supported cuprophilic interactions, which are due to strong attractive forces between closed d\(^{10}\) electronic shells. It is noteworthy that for the last two decades cuprophilicity has been discussed and studied thoroughly\(^{57}\) because of its large effect on the stability, chemical and photophysical behavior of copper clusters.

### III. Unsupported copper chains

The trinuclear copper complex \(\text{Cu}_3(\text{tolN}_5\text{tol})_3\) is one of the many examples of copper complexes exhibiting ligand supported cuprophilicity, with some very short Cu–Cu distances (2.348 and 2.358 Å).\(^{55}\) It has been determined that ligand architecture is the main factor that causes ligand supported cuprophilic interactions to be shorter than the unsupported ones.\(^{58}\) And although examples of unsupported Cu–Cu interactions are scarce, recent investigations have
lead to reports of unsupported Cu\textsuperscript{I}···Cu\textsuperscript{I} contacts between negatively charged cuprate molecules\textsuperscript{59} and uncharged trinuclear copper complexes.\textsuperscript{60}

The trinuclear species [CuL]\textsubscript{3} (where L is the deprotonated form of 2-[3(5)-pyrazolyl]pyridine) reported by Singh \textit{et al}\textsuperscript{60} was the first example of Cu···Cu interactions in the absence of any bridging ligands. [CuL]\textsubscript{3} crystallizes as a dimer of two trinuclear units with two short Cu···Cu contacts of 2.905(3) Å.

Interesting and unique are examples of infinite arrays of Cu\textsuperscript{I} atoms held by cuprophilic interactions in the absence of any bridging ligation, like the ones formed by the [Cu(NH\textsubscript{3})\textsubscript{2}]\textsuperscript{+} cation\textsuperscript{61} or C\textsubscript{6}F\textsubscript{5}Cu(py)\textsuperscript{62} ("py" stands for pyridine).

In the solid state of [Cu(NH\textsubscript{3})\textsubscript{2}]Br, the [Cu(NH\textsubscript{3})\textsubscript{2}]\textsuperscript{+} moieties form infinite linear polymeric Cu\textsuperscript{I} chains spanning the crystal lattice.\textsuperscript{61} The Cu\textsuperscript{I}···Cu\textsuperscript{I} distances are relatively short, 2.931(1) Å. Each Cu\textsuperscript{I} ion is surrounded by two nitrogen atoms and two other Cu\textsuperscript{I} centers in a planar fashion (Fig. 20). The bromide acts as a counter ion and does not coordinate copper centers, but it uses hydrogen bonds to connect to six different ammonia units. Adjacent [Cu(NH\textsubscript{3})\textsubscript{2}]\textsuperscript{+} cations adopt a staggered conformation with respect to each other.

![Figure 20](image.png)

\textit{Figure 20.} A schematic representation of the structure of [Cu(NH\textsubscript{3})\textsubscript{2}]Br. Hydrogen bonds between the bromines and the NH\textsubscript{3} moieties are not shown.

A similar structural motif was found in the ligand unsupported organocopper pyridine complex C\textsubscript{6}F\textsubscript{5}Cu(py),\textsuperscript{62} which also forms one-dimensional chains of copper atoms with ligands in adjacent units arranged in a staggered conformation. The blue-luminescent complex has Cu\textsuperscript{I}···Cu\textsuperscript{I} distances of 2.8924(3) Å associated with cuprophilic interactions. The Cu\textsuperscript{I}···Cu\textsuperscript{I}
contacts are similar to those reported by Wagner\textsuperscript{61} in [Cu(NH\textsubscript{3})\textsubscript{2}]\textsuperscript{+}. But in contrast to the cationic complex, the individual moieties in C\textsubscript{6}F\textsubscript{5}Cu(py) are neutral. As it can be seen in Fig. 21, the copper centers adopt a nearly linear coordination geometry with a 178.54(6)\textdegree angle. Moreover, aggregation of individual C\textsubscript{6}F\textsubscript{5}Cu(py) units forms an unprecedented linear supramolecular stack (Fig. 22).

![Figure 21. The C\textsubscript{6}F\textsubscript{5}Cu(py) unit.](image)

IV. Carboxylate supported copper chains

In addition to N-donor polydentate ligands, O-donor carboxylate groups are also known to function as such bridges. Our lab has extensive experience in working with carboxylates, which are valuable ligands in field of copper coordination compounds.\textsuperscript{63,64,65,76} Copper(I) carboxylates have rich photoluminescence properties and a remarkable structural diversity. Amongst many structural motifs, there are only two copper carboxylates that exhibit an infinite chain of copper atoms, namely Cu(I) pivalate\textsuperscript{66} and Cu(I) 3,5-bis(trifluoromethyl)benzoate.\textsuperscript{68}
These two copper clusters both have extended double helical Cu(I) polymeric structures held by cuprophilicity.

Figure 23. A fragment of the molecular structure of Cu(I) pivalate (top) and a schematic representation of the structure of Cu(I) pivalate (bottom).

The unique crystal structure of Cu(I) pivalate\textsuperscript{66} contains both right-handed and left-handed helices in the same unit cell. The resulting infinite cylindrical helical chain is formed by the alternation of carboxylate groups and Cu\textsuperscript{I} ions (Fig. 23). The cuprophilic interactions fall in the category of ligand supported Cu\textsuperscript{I}···Cu\textsuperscript{I} contacts. The unit of [Cu\textsubscript{5}(O\textsubscript{2}CC(CH\textsubscript{3})\textsubscript{3})\textsubscript{5}]\textsubscript{∞} (Fig. 24) is asymmetric and it consists of a pentagon with five Cu\textsuperscript{I} ions and five pivalate ligands. Awaga \textit{et al.}\textsuperscript{66} concluded that the conformation of Cu\textsuperscript{I} atoms is determined by cuprophilicity. The presence of cuprophilic interactions can be deduced from the short Cu\textsuperscript{I}···Cu\textsuperscript{I} distances (2.871(2) to 2.962(2) Å) which are shorter than the sum of van der Waals radii of Cu\textsuperscript{I} centers (1.92 Å).\textsuperscript{67}
Similarly to Cu(I) pivalate, copper(I) 3,5-bis(trifluoromethyl)benzoate\textsuperscript{68} has both left- and right-handed helices in the same unit cell. In the solid state, \([\text{Cu(O}_2\text{C}(3,5-\text{CF}_3)_2\text{C}_6\text{H}_3)]_\infty\) has a infinite double-helical structure (Fig. 25) with Cu\textsuperscript{I}⋯Cu\textsuperscript{I} contacts ranging from 2.69 to 3.14 Å. In contrast to Cu(I) pivalate, the compound \([\text{Cu(O}_2\text{C}(3,5-\text{CF}_3)_2\text{C}_6\text{H}_3)]_\infty\) is strongly luminescent in the solid state at room temperature (\(\lambda_{\text{max}}=594\) nm). Each copper center has a see-saw coordination environment. Its unit cell is also asymmetric, containing seven unique copper atoms bridged by carboxylates in a symmetrical fashion.\textsuperscript{68}

Interestingly, what these two infinite copper(I) chains have in common is their ligands’ bulkiness. The pivalate and 3,5-bis(trifluoromethyl)benzoate ligands are both large enough to interfere with potential intermolecular Cu⋯O contacts. In general, 1D and 2D polymeric structures of copper(I) carboxylates are formed based on additional Cu⋯O interactions due to the fact that the intermolecular axial coordination through copper-oxygen interactions imparts stability to copper clusters. Preventing these highly stabilizing Cu⋯O contacts in Cu(I) pivalate and Cu(I) 3,5-bis(trifluoromethyl)benzoate results in the enhancement of cuprophilic interactions.
thus giving rise to extended copper chains. With this in mind, for this project we chose 2,4,6-triisopropylbenzoate in an attempt to synthesize an infinite copper wire.

The 2,4,6-triisopropylbenzoate ligand (TiPB) (Fig. 26) is the anion of 2,4,6-triisopropylbenzoic acid. TiPB is bulky enough to block the oxygen atoms of carboxylates and the axial positions entirely, thus preventing interaction between the oxygen atom and the metal atom of the neighboring molecule.

![Figure 26. The 2,4,6-triisopropylbenzoate ligand.](image)

V. Rh(II), Cr(II), and Mo(II) complexes with the 2,4,6-triisopropylbenzoate ligand

TiPB was found to introduce enough steric hindrance to render impossible axial ligation and self-association between the dimeric units of Cr, Mo, and Rh clusters. The axial sites are blocked by the sterically large TiPB ligands, thus making difficult to approach the metal from the axial direction by other ligands. Complexes of Rh(II), Cr(II), and Mo(II) with TiPB ligands were all shown to form discrete paddlewheel structures without axial ligation.

Paddlewheel complexes without exogenous axial ligands are of great interest because they offer a clear view at the ‘real’ metal-metal bond, since axial ligands affect the strength of the metal-metal bond by weakening it. For example, Cr₂(TiPB)₄ (Fig. 27) has a “supershort” quadruple Cr–Cr bond (1.9662(5) Å) which is 0.4 Å shorter than that in Cr₂(TiPB)₄·2OC(CH₃)₂. In the latter complex, the Cr–Cr bonds are weakened due to destabilization of the Cr–Cr σ and σ* orbitals by strong electron donor ability of acetone.

![Figure 27. A schematic representation of the Cr₂(TiPB)₄ cluster. The R groups represent phenyl rings with three isopropyl groups at carbons 2, 4, and 6.](image)
Complex Mo$_2$(TiPB)$_4$\textsuperscript{70} has the same paddlewheel arrangement as Cr$_2$(TiPB)$_4$, featuring four carboxylato groups that bridge the quadruply bonded Mo$^{4+}$ unit (Fig. 28). The Mo–Mo bond of 2.076(1) Å is shorter than those in other quadruply bonded Mo$_2$(O$_2$CR)$_4$ compounds.

Figure 28. The structure of Mo$_2$(TiPB)$_4$. Isopropyl groups and hydrogen atoms are omitted for clarity.

Rh$_2$(TiPB)$_4$\textsuperscript{71} was the first discrete dinuclear rhodium carboxylate. The structure of Rh$_2$(TiPB)$_4$ is similar but not identical to the Cr and Mo analogues. A major difference is that the dirhodium tetracarboxylate exhibits an internal twist angle of 13.15°, which is not present in the Cr and Mo compounds. Moreover, the Rh(II)TiPB complex has a single Rh–Rh bond, while the Cr and Mo analogues have quadruple Cr–Cr and Mo–Mo bonds, respectively.

The complex of copper(II) with TiPB was expected to be a discrete paddlewheel complex, similarly to the Rh, Cr, and Mo analogues. Surprisingly, Cu(II)TiPB is an excellent example of spin frustration (Fig. 29) and was found to have a trinuclear Cu$_3^{6+}$ unit with a threefold symmetry.\textsuperscript{72} The Cu$_3$(O$_2$C$_{16}$H$_{23}$)$_6$ molecules have an equilateral triangular arrangement. Each Cu(II) center is in a square planar coordination environment of four O atoms.
Based on the ability of the TiPB ligand to interfere with axial M···O interactions, as seen from the above literature examples, it has potential for the isolation of the first infinite linear array of Cu(I) atoms. The latter can function as a molecular wire and thus is of interest for prospective applications in nanoelectronics. Therefore, in this work we set up to target its preparation using the 2,4,6-triisopropylbenzoate ligand. The aim is to use the bulky triisopropyl groups to sterically hinder the formation of Cu···O interactions and to enhance copper-copper contacts. The prediction is that Cu(I)TiPB will attain a structural arrangement of copper atoms without precedence both in the family of copper(I) carboxylates and in the family of transition metal complexes with the TiPB ligand.
4. RESULTS AND DISCUSSION

I. Synthesis

The preparation of the title carboxylate, copper(I) 2,4,6-triisopropylbenzoate (Cu(I)TiPB), was accomplished by a ligand exchange reaction based on refluxing copper(I) acetate, metallic copper and excess 2,4,6-triisopropylbenzoic acid in m-xylene. A slow stream of dry nitrogen was blown over the refluxing reaction mixture and a Dean and Stark trap was used to remove the acetic acid byproduct. The product is insoluble in hexanes, thus making possible removal of the excess carboxylic acid by several hexane washings, followed by drying the resulting solid under dynamic vacuum with mild heating at 65 °C.

A high boiling point solvent such as m-xylene was used due to the fact that the ligand precursor, 2,4,6-triisopropylbenzoic acid, has a high melting point of 185 °C. Furthermore, because copper(I) acetate is not a discrete molecule and has a polymeric structure based on Cu---O interactions between the Cu(I) acetate dimers, m-xylene can not act as an axial coordinating solvent and as a result it is insoluble in m-xylene at low temperatures. However, at high temperatures the carboxylic acid molecules begin to slowly degrade the Cu(I) acetate polymer by coordinating to the copper centers. As a result, Cu(I) acetate becomes soluble in m-xylene, therefore making possible ligand exchange at copper centers.

The elemental analysis of starting bulk copper(I) 2,4,6-triisopropylbenzoate (1) confirmed a 1:1 [Cu]:(O$_2$C$_{16}$H$_{23}$) stoichiometry, suggesting the [Cu(O$_2$C$_{16}$H$_{23}$)] composition. Several solution crystallization techniques usually employed to access crystalline copper(I) clusters were used to attempt crystallization of 1 from solution, but without success. Complex 1 is a well-defined chemical compound and cannot be represented as a random mixture of species, such as oligomeric parts of Cu wires, because significant variations in crystallization conditions do not result in any changes in X-ray powder diffraction (XRPD) spectrum and infra-red spectroscopy (IR) fingerprints (Fig. 42 in Supporting Information (SI)). Thus, layering the solutions of 1 in aromatic solvents (benzene, toluene, or m-xylene) with hexanes at room temperature, using low temperature-induced crystallization or heating of the m-xylene solution in a sealed ampule at 215 °C all led to the recovery of unchanged 1 (no solvents are co-crystallized within the crystals).
A common requisite for crystallization of a compound is solubility or volatility. Luckily, Cu(I)TiPB is volatile and the sublimation-deposition approach can be used for crystal growth. This solvent-free crystallization technique is highly useful for the isolation of crystalline products without exogenous ligands. Thus, crystals of Cu(I)TiPB (2) in the form of colorless thin needles are accessible in nine weeks by gas-phase sublimation of 1 at 186 °C in a sealed evacuated Pyrex tube.

Interestingly, controlled variation of experimental conditions has allowed us to isolate the second structural polymorph of Cu(I)TiPB (3), which sublimes at 215 °C in 4 days. The crystals of 3 are deposited in the form of colorless blocks. It is worth mentioning that the sublimation of bulk Cu(I)TiPB at higher temperatures, i.e. 230-250 °C, leads to the decomposition to metallic copper, which appears as a red powder in the “hot” part of the sublimation tube.

Crystallization of Cu(I)TiPB from a weakly coordinating solvent such as o-dichlorobenzene breaks the infinite chain into discrete dimers of 4. Cleavage of an extended CuI chain into smaller copper(I) fragments was also reported for copper(I) 3,5-bis(trifluoromethyl)benzoate, whose infinite double helical chain was broken into hexa-, tetra-, and dinuclear clusters upon sublimation with poliaromatic hydrocarbons such as fluoranthene, pyrene, and coronene.68

Additional solution studies of Cu(I)TiPB were prevented by the ease of its disproportionation, oxidation, and hydrolysis. Although the title compound is readily soluble in anhydrous acetonitrile and tetrahydrofuran, the dissolution process is accompanied by the formation of a red-brownish powder and change of the solution color to green within a few minutes. This is indicative of a rapid disproportionation to a copper(II) carboxylate and metallic copper, a decomposition pathway common for copper(I) carboxylates.75 For example, recrystallization of Cu(I)TiPB from anhydrous acetone yielded the paddlewheel copper(II) complex of TiPB with two molecules of acetone in the axial positions (Fig. 30).
Figure 30. The structure of Cu$_2$(TiPB)$_4$·2OC(CH$_3$)$_2$. Isopropyl groups and hydrogen atoms are omitted for clarity.

The compositions of both 1 and 3 were confirmed by elemental analysis and correspond to the empirical formula [Cu(O$_2$C$_{16}$H$_{23}$)], while the composition of 4 was confirmed to be [Cu$_2$(O$_2$C$_{16}$H$_{23}$)$_2$·2C$_6$H$_4$Cl$_2$]. Crystals of 2, 3, and 4 were produced in good yields and only crystalline material has been used for all characterization experiments. The molecular structures and purity of 2, 3, and 4 have been determined by X-ray diffraction analysis.

II. Structural polymorphs

Crystallization of Cu(I)TiPB (1) from gas-phase by sublimation-deposition techniques under controlled experimental conditions yields two individual structural polymorphs, 2 and 3. Both of them represent a novel structural type for the copper(I) carboxylate family: infinite copper wires held together by bridging carboxylates and further supported by cuprophilic interactions. Complex 2 provides the first example of an extended linear copper chain, while 3 is an infinite zigzag chain.

The individual structural polymorphs of copper(I) 2,4,6-triisopropylbenzoate 2 and 3 have been isolated in pure form and fully characterized. The XRPD data have confirmed the structural identity and purity of both 2 and 3 crystalline materials (Fig. 45 and Fig. 46 in SI). Single crystals of 2 were accessed by sublimation–deposition procedures at elevated temperatures (185 °C) under reduced pressure. Heating a small ampule containing single crystals of 2 in a nongradient furnace at 215 °C resulted in the formation of large colorless block-shaped
crystals of 3. Thus, changes of experimental conditions offers control over accessing the desired structural motif.

Interestingly, when crystals of 2 or 3 are redissolved in benzene or other aromatic solvents, such as toluene or m-xylene, they quantitatively transform back to 1, which under gas phase sublimation conditions can be transformed back to 2 or 3 (all steps confirmed by XRPD). These conversion procedures can be repeated multiple times along a transformation cycle for the linear wire ↔ zigzag wire system, depending on the crystallization conditions (Fig. 31).

![Figure 31](image)

**Figure 31.** Schematic representation of synthetic transformations between the forms of [Cu(O_2C_{16}H_{23})].

### III. Structure-photoluminescence correlation

Considerable effort and attention has been paid to study the origin of the photoluminescent (PL) properties of copper(I) carboxylates. The photophysical properties of Cu^I_ aggregates have previously been discussed in context with cuprophilic interactions, the nature of bridging ligands, and solid state structures.

The variety of structural polymorphs revealed for copper(I) 2,4,6-triisopropylbenzoate allowed for the first time analysis of the structure-photoluminescence correlations for two different structural forms of the same metal chain. Both polymorphs, 2 and 3, exhibit green-to-orange photoluminescence upon exposure to UV radiation in the solid state (Fig. 32). Specifically, the PL measurements (\(\lambda_{ex} = 350\) nm) carried out at room temperature on crystalline samples in the range of 300-650 nm revealed broad emission bands centered at 563 nm (green region) for 2 and 610 nm (orange region) for 3. Interestingly, the emission intensity is substantially greater in the case of the linear copper wire 2 compared to the zigzag polymorphic form 3. Such a drastic difference in PL properties of 2 and 3 (including both emission wavelengths and intensity) shows that relatively small variations in the position of copper atoms held together by the same bridging ligand may lead to significant changes in photoluminescence.
Figure 32. Solid state photoluminescence spectra of 1 (black), 2 (blue), 3 (red). The emission of 4 is quenched.

An analogous example is the substantial difference in PL emission reported for two polymorphs of copper(I) benzoate: namely the tetranuclear \([\text{Cu}_4(\text{O}_2\text{CC}_6\text{H}_5)_4]\) and the hexanuclear \([\text{Cu}_6(\text{O}_2\text{CC}_6\text{H}_5)_6]\).\(^{76}\) The tetramer revealed an emission significantly red-shifted to 676 nm (\(\lambda_{\text{ex}} = 418\) nm), while the hexamer exhibits solid state photoluminescence at 577 nm (\(\lambda_{\text{ex}} = 350\) nm). It was concluded that the key factors affecting their PL properties are the different nuclearities and solid-state structures. However, the case of Cu(I)TiPB is the first instance when two structurally close polymorphs, that differ only in the way how the same molecular monomers are connected into a polymeric chain, show a very different PL behavior.

The solid sample of 1 brightly emits light with a maximum wavelength of 535 nm. It is well accepted that PL properties are controlled by solid state interactions. While 1, 2 and 3 exhibit strong solid state photoluminescence, the complex 4 is nonluminescent at r.t. in the solid state. The overall structural differences of 4 and the presence of axially coordinated solvent through the heavy Cl atom both seem to affect its emission properties and show a great effect on the electronic communication between the Cu(I) centers in 4.

Thus the consideration of photoluminescent behavior for the structurally diverse copper(I) 2,4,6-triisopropylbenzoate products revealed that emission wavelengths and intensities depend not only on the overall structural type (for example, infinite wires vs. dimeric structures), but also show great sensitivity to the subtle differences in spatial distribution of Cu(I) ions for the
otherwise similar polymeric chains constructed from the same molecular units (linear vs. zigzag wires).

**IV. Structural description**

The single-crystal X-ray structural analysis revealed that \([\text{Cu(O}_2\text{C}_{16}\text{H}_{23})]_{\text{e,linear}} (2)\) has a remarkable structural motif, an infinite linear copper(I) wire. Compound 2, crystallizing in the monoclinic space group P2\(_1\)/c (Z = 4 for the empirical formula), consists of copper(I) ions bridged by carboxylate groups and aligned in an infinite chain (Fig. 33). Attractive interactions between the d\(^{10}\) closed-shell copper centers accounts for the linear, sequential arrangement of copper(I) ions in 2. This is an example of ligand-supported cuprophilic interactions and it is the first case for a copper carboxylate where we encounter this new type of infinite linear chain based on Cu···Cu interactions that is not helical. The other known extended Cu(I) polymers held by cuprophilic Cu···Cu interactions, Cu(I) 3,5-bis(trifluoromethylbenzoate) and Cu(I) pivalate, have extended double-helical structures.

![Figure 33](image)

*Figure 33.* A fragment of molecular structure of \([\text{Cu(O}_2\text{C}_{16}\text{H}_{23})]_{\text{e,linear}} (2)\). Isopropyl groups and hydrogen atoms are omitted for clarity.

The copper(I) centers in 2 are in a distorted square-planar environment of two oxygen and two copper atoms with the two equatorial Cu–O distances being slightly different, 1.843(3) and 1.846(3) Å. There is a deviation from linearity of coordination environment surrounding the copper centers, with a Cu–Cu–Cu angle of 159.42(5)\(^\circ\). Only one Cu(I) atom is crystallographically independent. Notably, the Cu···Cu distances of 2.9398(6) Å are shorter than those in Cu(II)TiPB (3.131(3) Å)\(^72\) and fall within the range of cuprophilic interactions.
The second structural polymorph \([\text{Cu}(\text{O}_2\text{C}_{16}\text{H}_{23})]_{\infty, \text{zigzag}}\) (3) was also crystallographically characterized. The crystal structure of 3 exhibits an extended zigzag chain arrangement having a different spatial distribution of the same structural unit as 2 (Fig. 34). Complex 3 crystallizes in the orthorhombic \(P\text{bcn}\) space group and contains two crystallographically independent Cu(I) atoms in the asymmetric unit. The average intramolecular Cu–O_carb distances in 3 (1.8483(12) Å) are similar to those in 2 (1.8445(3) Å). Moreover, the Cu⋯Cu distance in 3 (2.8843(3) Å) is noticeably shorter than in 2 (2.9398(6) Å). In general, the Cu⋯Cu distances in 2 and 3 are significantly shorter than the sum of their van der Waals radii \((r_{\text{vdW(Cu)}} = 1.92 \text{ Å})\) and fall into the category of metalophilic interactions, similar to those in Au(I) compounds.\(^7\)

*Figure 34.* A fragment of molecular structure of \([\text{Cu}(\text{O}_2\text{C}_{16}\text{H}_{23})]_{\infty, \text{zigzag}}\) (3). Isopropyl groups and hydrogen atoms are omitted for clarity.

There are two types of Cu–Cu–Cu angles in the chain of 3, Cu(2)–Cu(1)–Cu(2A) and Cu(1)–Cu(2)–Cu(1A), 96.22(1)° and 180.00° respectively. In 3, the copper(I) atoms have two types of coordination environments. The geometry around Cu(2) can be viewed as distorted square planar, while the Cu(1) atom possesses a seesaw coordination geometry. Although the two polymorphic forms 2 and 3 crystallize in different space groups their cell volumes, normalized by a number of formula units, are essentially the same (382 and 380 Å\(^3\) per \([\text{Cu}(\text{O}_2\text{C}_{16}\text{H}_{23})]\) in 2 and 3, respectively). The dihedral angles between the carboxylic groups and phenyl ring planes are 74.33° in 2 and 64.29° in 3 in comparison with the ca. 69° in the structure.
of 2,4,6-triisopropylbenzoic acid (Fig. 39 in SI), showing just a minor steric repulsion effect of neighboring isopropyl groups upon formation of copper wires.

Importantly, the XRPD spectrum of 1 recrystallized from benzene did not correlate to the observed pattern for the single crystalline sample of either 2 or 3 (Fig. 44 in SI), which confirms that complexes 2 and 3 are structurally different from the starting bulk copper(I) 2,4,6-triisopropylbenzoate (1). Careful consideration of the carboxylate stretches in the IR spectra showed that 2 and 3 are nearly identical, but distinctly different from 1 (Fig. 41 in SI). All our numerous attempts to isolate single crystals of 1 by solution crystallization resulted in the formation of very thin long colorless needles not suitable for the single crystal X-ray diffraction study. The bulkiness of the isopropyl groups may greatly affect the poor crystallinity of 1.

Although we can not provide a direct crystallographic proof, we can only speculate that the starting copper(I) 2,4,6-triisopropylbenzoate (1) has a crystalline structure similar to copper(I) acetate,78 which exhibits a 1D polymeric chain based on dicopper units linked by intermolecular Cu···O interactions. In support of this, we report the isolation of two dinuclear based compounds with the TiPB ligand, namely [Cu$_2$(O$_2$C$_{16}$H$_{23}$)$_2$·2C$_6$H$_4$Cl$_2$] (4) and [Ag$_2$(O$_2$C$_{16}$H$_{23}$)$_2$]$_\infty$ (Fig. 40 in SI). The 2,4,6-triisopropylbenzoate of Ag(I) exhibits a Cu(I) acetate-like structural type based on metal···oxygen intermolecular interactions. Moreover, the carboxylate stretches in the IR spectra of 1 and [Ag$_2$(O$_2$C$_{16}$H$_{23}$)$_2$]$_\infty$ are almost identical (see Fig. 43 in SI) and that provides experimental evidence in support of the above structural assignment for 1.

In contrast to the extended wire-type structures of 2 and 3, complex [Cu$_2$(O$_2$C$_{16}$H$_{23}$)$_2$·2C$_6$H$_4$Cl$_2$] (4) exhibits a discrete structure based on dicopper(I) unit bridged by carboxylate groups, with a chlorine atom of o-dichlorobenzene axially coordinated at both ends of the dicopper(I) unit (Fig. 35). Compound 4 crystallizes in the monoclinic $P2_1/c$ space group and contains one crystallographically independent Cu(I) atom in the asymmetric unit. The intramolecular Cu···Cu contact is 2.4934(5) Å, which is shorter than the Cu···Cu interactions in both 2 and 3. The axial Cu···Cl contact between the [Cu$_2$] core and o-dichlorobenzene is 2.895 Å.
Figure 35. The structure of \([\text{Cu}_2(\text{O}_2\text{C}_{16}\text{H}_{23})_2\cdot 2\text{C}_6\text{H}_4\text{Cl}_2] (3)\). Isopropyl groups and hydrogen atoms are omitted for clarity.

The X-ray study of copper complexes with the 2,4,6-triisopropylbenzoate ligand revealed a variety of structural motifs. Crystallization of the title compound by gas-phase deposition technique caused the inhibition of Cu···O interactions and resulted in the isolation of the first known copper(I) carboxylate wire in two structural variations, 2 and 3. On the other hand, solution crystallization turned on Cu···O contacts, which hold together a polymeric chain of dinuclear units (1). Thus, the use of the bulky isopropyl groups of copper(I) 2,4,6-triisopropylbenzoate and various crystallization techniques allows for controllably switching on/off the Cu···O interactions.
5. EXPERIMENTAL DETAILS

General procedures

All synthetic reactions and manipulations were carried out under a dry dinitrogen atmosphere using standard Schlenk and vacuum-line techniques. Sublimation–deposition procedures were performed in small glass ampules (approximately 6 cm long with a diameter of 1.1 cm), which were sealed under a vacuum of $10^{-2}$ Torr and then placed in electric furnaces having a small temperature gradient along the length of the tube.

I. Starting materials

Copper(I) acetate (90% purity, purchased from Acros) and 2,4,6-triisopropylbenzoic acid (97% purity, purchased from Alfa Aesar) were both used as received. Metallic copper (>99% purity) was obtained from Fluka. Anhydrous solvents such as $m$-xylene (99% purity) and $o$-dichlorobenzene (99% purity) were purchased in sure-seal bottles from Sigma-Aldrich. Hexanes and benzene were purified by distillation from sodium/benzophenone under an argon atmosphere.

II. Physical measurements

The IR spectra were recorded on a Perkin Elmer FT-IR Spectrometer (Spectrum 100) in the 4000–600 cm$^{-1}$ range, using a universal ATR accessory.

The room temperature photoluminescence (PL) spectra of crystalline powders were collected on a HORIBA Jobin Yvon spectrofluorimeter using front-face detection. Three full scans were recorded in each case and then averaged. Default hardware settings (5 nm slit width and 0.1 sec integration time) were applied.

Elemental analyses for 1, 3 and 4 were performed by Complete Analysis Laboratories, Inc., New Jersey, U.S.

III. Synthesis and crystal growth

$[\text{Cu}_2(\text{O}_2\text{C}_{16}\text{H}_{23})_2]_{\infty}$ (1). The title compound was prepared by a ligand exchange procedure. Copper(I) acetate (0.100 g, 0.408 mmol) and excess 2,4,6-triisopropylbenzoic acid (0.500 g, 2.016 mmol) were loaded in a Schlenk flask inside the glove box together with metallic
copper (0.050g, 0.786 mmol) and 40 mL of anhydrous m-xylene were added to the mixture. The green colored solution was refluxed for 48 hours. The light brown solution was filtered through Celite and evaporated to dryness to afford a brown solid. This was washed with anhydrous hexanes (4 x 10 mL) until a white compound was obtained. Compound was dried under vacuum in a sand bath at 65-70 °C overnight. Yield: 0.252 g, 99%. Elemental analysis calculated% (found%): C 61.81 (61.72); H 7.46 (7.35). PL ($\lambda_{ex} = 350$ nm, solid, $\lambda_{max} = 535$ nm). IR ($\nu_{max}$/cm$^{-1}$): 2957m, 2925w, 2869w, 1609w, 1577w, 1518s, 1476m, 1460m, 1404s, 1382w, 1361w, 1342w, 1320w, 1300w, 1244w, 1157w, 1108w, 1072w, 941w, 873m, 857w, 813w, 781w. The experimental X-ray powder pattern is different from the calculated powder patterns based on the single crystal unit cell parameters for 2 or 3 (see Fig. 4 in SI).

$[\text{Cu}(\text{O}_2\text{C}_{16}\text{H}_{23})]_{\infty, \text{linear}}$ (2): Colorless long thin needles of 2 suitable for the single crystal X-ray diffraction analysis were obtained by sublimation of 1 at 186 °C over 2 months. Yield: 0.028g, 93%. The 70% yield can be achieved over 5 days. PL ($\lambda_{ex} = 350$ nm, solid, $\lambda_{max} = 535$ nm). IR ($\nu_{max}$/cm$^{-1}$): 2956m, 2928w, 2866w, 1606w, 1576w, 1512s, 1482m, 1463m, 1421s, 1380w, 1361m, 1319w, 1240w, 1171w, 1158w, 1109w, 1071w, 1055w, 951w, 940w, 923w, 875m, 859w, 814w, 799w, 769m. The experimental X-ray powder pattern of the bulk material is consistent with the calculated powder pattern based on the single crystal unit cell parameters for 2 (see Fig. 45 in SI).

$[\text{Cu}(\text{O}_2\text{C}_{16}\text{H}_{23})]_{\infty, \text{zigzag}}$ (3). Colorless blocks of 3 suitable for the single crystal X-ray diffraction analysis were obtained by sublimation of 1 at 215 °C in 4 days. Crystals of 3 appear as a mixture with 2 but can be easily mechanically separated. Yield: 0.016g, 53%. Elemental analysis calculated% (found%): C 61.81 (61.84); H 7.46 (7.37). PL ($\lambda_{ex} = 350$ nm, solid, $\lambda_{max} = 610$ nm). IR ($\nu_{max}$/cm$^{-1}$): 2958m, 2926w, 2866w, 1606w, 1574w, 1543s, 1520s, 1478w, 1456m, 1417s, 1379m, 1362w, 1354w, 1319w, 1240w, 1158w, 1109w, 1071w, 1055w, 951w, 940w, 923w, 875m, 859w, 815w, 765m. X-ray powder pattern of the crystalline bulk material was fully consistent with the calculated powder pattern based on the unit cell parameters of a single crystal of 3 (see Fig. 46 in SI).

$[\text{Cu}_2(\text{O}_2\text{C}_{16}\text{H}_{23})_2\cdot 2\text{C}_6\text{H}_4\text{Cl}_2]$ (4). 0.050 g of copper(I)-2,4,6-triisopropylbenzoate was dissolved upon heating in 2 mL of o-dichlorobenzene yielding a light-yellow solution. The hot solution was filtered off through cannula to a Schlenk tube leaving behind white traces of undissolved starting material. The filtered solution was frozen for 6 hours at - 35 °C, after which
the solution was slowly brought to liquid state at +12 °C. Colorless blocks of 4 formed overnight. Yield: 0.030g, 41%. Elemental analysis calculated% (found%): C 57.71 (57.67); H 5.94 (6.03). PL ($\lambda_{ex}$ = 350 nm, solid, $\lambda_{max}$ = 514 nm, very faint detectable emission). IR ($\nu_{max}$/cm$^{-1}$): 2955w, 2925w, 2866w, 1607w, 1574w, 1525s, 1483w, 1453m, 1434w, 1416s, 1380w, 1360w, 1343w, 1318w, 1249w, 1156w, 1124w, 1112w, 1070w, 1029m, 944w, 880w, 857w, 810w, 790w, 781w, 753s, 736w. X-ray powder pattern of the crystalline bulk material was fully consistent with the calculated powder pattern based on the single crystal unit cell parameters of a single crystal of 4 (see Fig. 47 in SI).

**Transformation of 2 to 3.** Crystals of 2 can be sublimed at 214 °C to form 3. See procedure above for the synthesis of 3 from the bulk material.

**Transformation of 2 and 3 to 1.** Recrystallization of 2 or 3 from benzene, toluene, or m-xylene (or from hexanes using solvothermal conditions) provides 1 that, in turn, can be converted to either 2 or 3 using gas-phase sublimation procedures.

**IV. X-ray crystallography**

Data for structural analysis were collected on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda$ = 0.71073 Å) operated at 1800 W power. The crystals were mounted on a goniometer head with silicone grease. A total of 1850 frames were collected with a scan width of 0.3° in $\omega$ and an exposure time of 20 s/frame for each experiment. The frames were integrated with the Bruker SAINT software package (*SAINT*, version 6.02; Bruker AXS, Inc.: Madison, WI, 2001) using a narrow-frame integration algorithm. The final cell constants were based upon the refinement of the XYZ-centroids of several thousand reflections above 20$\sigma(I)$. Analysis of the data showed negligible decay during data collection. The data were corrected for absorption effects using the empirical method SADABS (*SADABS*; Bruker AXS, Inc.: Madison, WI, 2001). The structures were solved and refined using the Bruker SHELXTL (Version 6.1) software package (Sheldrick, G. M. *SHELXTL*, version 6.14; Bruker AXS, Inc.: Madison, WI, 2001). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at idealized positions as a riding model. The X-ray crystal data for 2-4 as well as selected bond lengths and angles are listed in Tables 1 and 2.
Table 1. Selected bond distances (Å) and angles (º) for [Cu(O₂C₁₆H₂₃)]∞, linear (2), [Cu(O₂C₁₆H₂₃)]∞, zigzag (3), and [Cu₂(O₂C₁₆H₂₃)₂·2C₆H₄Cl₂] (4).

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<tr>
<td>Cu···Cu carb-bridged</td>
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<tr>
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<td>-</td>
<td>-</td>
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<tr>
<td>Cu–O carb</td>
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Table 2. Crystallographic data and X-ray experimental conditions for [Cu(O₂C₁₆H₂₃)]∞, linear (2), [Cu(O₂C₁₆H₂₃)]∞, zigzag (3), [Cu₂(O₂C₁₆H₂₃)₂·2C₆H₄Cl₂] (4), and C₁₆H₂₃O₂H.

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<td>C₁₆H₂₃CuO₂</td>
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<td>310.88</td>
<td>915.77</td>
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<td>c (Å)</td>
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<td>Quality-of-fit¹</td>
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<td>1.086</td>
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<td>Largest diff, peak/hole, e/Å³</td>
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<td>1.247, -0.367</td>
<td>0.894, -0.325</td>
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</table>

¹R₁ = Σ ||Fo|| - |Fc| / Σ |Fo|;
²wR² = [Σ[w(Fo²-Fc²)²]/Σ[w(Fo²)²]]½;
³Quality-of-fit = [Σ[w(Fo²-Fc²)²]/(Nobs-Nparams)]½, based on all data.
A colorless needle of \([\text{Cu}(\text{O}_2\text{C}_{16}\text{H}_{23})]_{\infty, \text{linear}} \) \(2\), MW=310.88 g/mol, \((0.27 \times 0.04 \times 0.01\) mm\) was analyzed at 100(2) K and found to be monoclinic, space group \(P2_1/c\), \(a = 17.979(3)\) Å, \(b = 5.785(10)\) Å, \(c = 15.146(3)\) Å, \(\alpha = 90.00^\circ\), \(\beta = 104.285(3)^\circ\), \(\gamma = 90.00^\circ\), \(V = 1526.5(5)\) Å\(^3\), \(Z = 4\). A total of 10313 reflections were collected. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found in the difference Fourier map and refined independently. The final refinement cycle was based on 2688 reflections, 218 parameters, and 36 restraints. The final \(R\) value was 0.0609 \((wR_2 = 0.1664)\) for 2214 reflections \([I > 2\sigma(I)]\). The maximum and minimum peaks in the final difference Fourier map corresponded to 1.339 and −0.626 e/Å\(^3\), with a goodness-of-fit value of 1.062. The crystal was collected as str1213 (Fig. 36).

**Figure 36.** An ORTEP drawing of the \([\text{Cu}(\text{O}_2\text{C}_{16}\text{H}_{23})]_{\infty, \text{linear}} \) \(2\) complex fragment showing the Cu labeling scheme with thermal ellipsoids drawn at the 40% probability level. Cu blue, O red, C grey, H light grey.
A colorless plate of \([\text{Cu(O}_2\text{C}_{16}\text{H}_{23})]_{\infty,zigzag} \text{(3)}\), MW=310.88 g/mol, \((0.27 \times 0.22 \times 0.06 \text{ mm})\) was analyzed at 100(2) K and found to be orthorhombic, space group \(Pbcn\), \(a = 34.687(3) \text{ Å}, b = 10.2092(8) \text{ Å}, c = 8.5888(7) \text{ Å}\), \(\alpha = 90.00^\circ, \beta = 90.00^\circ, \gamma = 90.00^\circ\), \(V = 3041.5(4) \text{ Å}^3\), \(Z = 8\). A total of 24294 reflections were collected. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found in the difference Fourier map and refined independently. The final refinement cycle was based on 3638 reflections, 180 parameters, and 36 restraints. The final \(R1\) value was 0.0375 \((wR2 = 0.0966)\) for 3228 reflections \([I > 2\sigma(I)]\). The maximum and minimum peaks in the final difference Fourier map corresponded to 1.247 and \(-0.367 \text{ e/Å}^3\), with a goodness-of-fit value of 1.086. The crystal was collected as str1227 (Fig. 37).

**Figure 37.** An ORTEP drawing of the \([\text{Cu(O}_2\text{C}_{16}\text{H}_{23})]_{\infty,zigzag} \text{(3)}\) complex fragment showing the Cu labeling scheme with thermal ellipsoids drawn at the 40% probability level. Cu blue, O red, C grey, H light grey.
A colorless block of \([\text{Cu}_2(\text{O}_2\text{C}_{16}\text{H}_{23})_2 \cdot 2\text{C}_6\text{H}_4\text{Cl}_2] \text{(4)}\), MW=915.77 g/mol, \((0.28 \times 0.25 \times 0.18 \text{ mm})\) was analyzed at 100(2) K and found to be monoclinic, space group \(P2_1/c\), \(a = 8.4789(9) \ \text{Å}, b = 11.4630(13) \ \text{Å}, c = 22.026(2) \ \text{Å}, \alpha = 90.00^\circ, \beta = 92.125(2)^\circ, \gamma = 90.00^\circ, V = 2139.3(4) \ \text{Å}^3, Z = 2\). A total of 18036 reflections were collected. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found in the difference Fourier map and refined independently. The final refinement cycle was based on 4987 reflections, 250 parameters, and 36 restraints. The final \(R1\) value was 0.0341 \((wR2 = 0.0879)\) for 4341 reflections \([I > 2\sigma(I)]\). The maximum and minimum peaks in the final difference Fourier map corresponded to \(0.894\) and \(-0.325\) \(\text{e/Å}^3\), with a goodness-of-fit value of 1.047. The crystal was collected as str1207 \(\text{(Fig. 38)}\).

**Figure 38.** An ORTEP drawing of the \([\text{Cu}_2(\text{O}_2\text{C}_{16}\text{H}_{23})_2 \cdot 2\text{C}_6\text{H}_4\text{Cl}_2] \text{(4)}\) complex showing the Cu labeling scheme with thermal ellipsoids drawn at the 40% probability level. Cu blue, O red, C grey, H light grey.
6. CONCLUSIONS

We have now prepared a new copper(I) complex, namely copper(I) 2,4,6-triisopropylbenzoate, by ligand exchange procedures. Its single crystal X-ray characterization revealed a novel structural type, which was not known before for this class of compounds: an infinite “copper wire” with short Cu···Cu contacts.

We were also successful in the isolation and structural characterization of another structural polymorph of copper(I) 2,4,6-triisopropylbenzoate: an infinite “zigzag” wire held together by even shorter cuprophilic interactions.

The solution recrystallization from o-dichlorobenzene afforded a dicopper(I) 2,4,6-triisopropylbenzoate unit with two o-dichlorobenzene molecules approaching from the axial directions. Thus, by using even a weakly coordinating solvent such as o-dichlorobenzene we were able to break the copper(I) 2,4,6-triisopropylbenzoate infinite chain and isolate a discrete dicopper(I) complex.

Importantly, the study of photoluminescence of these two copper(I) wire structural polymorphs revealed the effect of structural types on their photophysical properties. Both polymorphs of Cu(I)TiPB exhibit green-to-orange photoluminescence upon exposure to UV radiation in the solid state, but with different emission wavelengths.

Thus, this study resulted in the preparation, structural analysis, and photoluminescent properties investigation of new copper(I) carboxylates, of which compound 1 ([Cu₂(O₂C₁₆H₂₃)₂]ₙ) is based on dinuclear [Cu₂(O₂C₁₆H₂₃)₂] units that form a polymeric chain through additional Cu···O interactions, polymorph 2 ([Cu(O₂C₁₆H₂₃)]ₙ,linear) has a linear 1D wire structure, while polymorph 3 ([Cu₂(O₂C₁₆H₂₃)₂]ₙ,zigzag) has a 1D zigzag wire structure, and 4 ([Cu₂(O₂C₁₆H₂₃)₂·2C₆H₄Cl₂]) is a discrete dicopper(I) molecule.
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Figure 34. A fragment of molecular structure of [Cu(O₂C₁₀H₂₃)]ₘ-zigzag (3). Isopropyl groups and hydrogen atoms are omitted for clarity.

Figure 35. The structure of [Cu₂(O₂C₁₀H₂₃)₂·2C₆H₄Cl₂] (3). Isopropyl groups and hydrogen atoms are omitted for clarity.

Figure 36. An ORTEP drawing of the [Cu(O₂C₁₀H₂₃)]ₘ-linear (2) complex fragment showing the Cu labeling scheme with thermal ellipsoids drawn at the 40% probability level. Cu blue, O red, C grey, H light grey.

Figure 37. An ORTEP drawing of the [Cu(O₂C₁₀H₂₃)]ₘ-zigzag (3) complex fragment showing the Cu labeling scheme with thermal ellipsoids drawn at the 40% probability level. Cu blue, O red, C grey, H light grey.

Figure 38. An ORTEP drawing of the [Cu₂(O₂C₁₀H₂₃)₂·2C₆H₄Cl₂] (4) complex showing the Cu labeling scheme with thermal ellipsoids drawn at the 40% probability level. Cu blue, O red, C grey, H light grey.

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Figure 45. The observed X-ray powder pattern for the bulk microcrystalline sample of 2 (black) vs. the simulated X-ray powder pattern based on the single crystal diffraction data of 2 (red).

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[Cu$_2$(O$_2$C$_{16}$H$_{23}$)$_2$·2C$_6$H$_4$Cl$_2$] (4) .................................................................................................... 37
10. SUPORTING INFORMATION

Figure 39. a) An ORTEP drawing of 2,4,6-triisopropylbenzoic acid. b) Formation of dimers in the solid state via intermolecular hydrogen bonds.

Figure 40. A fragment of the [Ag₂(O₂C₁₆H₂₃)₂]ₓ polymeric chain. Hydrogen atoms are omitted for clarity.
IR analysis

**Figure 41.** IR spectra of 1 (red), 2 (black), and 3 (blue).

**Figure 42.** IR spectra of 1 obtained by recrystallization from benzene/hexanes at room temperature (black), from hexanes at 95 °C (sealed ampule, red), or from m-xylene 215 °C (sealed ampule, black).
Figure 43. IR spectra of 1 (black) and [Ag₂(O₂C₁₆H₂₃)₂]∞ (red).

X-ray powder diffraction spectra

Figure 44. The observed X-ray powder patterns for the bulk copper(I) 2,4,6-triisopropylbenzoate (1) (black) vs. the bulk microcrystalline samples of 2 (red) and 3 (blue).
Figure 45. The observed X-ray powder pattern for the bulk microcrystalline sample of 2 (black) vs. the simulated X-ray powder pattern based on the single crystal diffraction data of 2 (red).

Figure 46. The observed X-ray powder pattern for the bulk microcrystalline sample of 3 (black) vs. the simulated X-ray powder pattern based on the single crystal diffraction data of 3 (blue).
Figure 47. The observed X-ray powder pattern for the single crystals of 4 (black) vs. the simulated X-ray powder pattern based on the single crystal diffraction data of 4 (red).

Figure 48. The observed X-ray powder pattern for wet copper(I) 2,4,6-triisopropylbenzoate crystals obtained from benzene (in black) and for the same crystals dried overnight at r. t. (in red), and for the same crystals dried overnight in a sand bath at 111 °C (in blue).
1. REFERENCES

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