

A combined experimental and computational investigation on Tetrakis- μ -acetato-bis(acetamido)dicopper(II) and its application as a single source precursor for copper oxide

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ABSTRACT

The physico-chemical properties of the Tetrakis- μ -acetato-bis(acetamido)dicopper(II) $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CONH}_2)]_2$ (**1**), have been thoroughly investigated via an integrated multi-technique experimental–computational approach. In the newly found orthorhombic compound, as revealed by low temperature single-crystal X-ray studies, the complex is present as centrosymmetrical dimeric unit, has a paddle-wheel conformation with four acetate ligands bridging two symmetry-related Cu^{II} ions. The distorted octahedral coordination environment around the Cu^{II} ion is completed by an oxygen atom from an acetamide ligand. The compound sublimates, without premature side decompositions, at 180 °C. The structural, electronic and thermal behavior of the neutral complex (**1**) has been investigated. The present study suggests application of $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CONH}_2)]_2$ (**1**) as a precursor for copper-based materials by Chemical Vapor Deposition.

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Copper and copper oxides (Cu_2O and CuO), especially with nanometer-scale dimensions and morphological specificity, have been studied for various areas of technological interest, including metallic interconnections between circuit devices, heterogeneous catalysts, gas sensors, solar cells, lithium ion electrodes, rectifying and microwave diodes, high temperature superconductors, and transparent conducting oxides for flat panel displays [1–7]. In order to control and engineer the properties of the resulting systems, various physical and chemical methods for the preparation of copper-based thin films, nanoparticles and nanorods with tailored properties have been reported [5,6]. Among them, Chemical Vapor Deposition (CVD) and related routes [2,8] have rapidly expanded into mainstream technological applications, thanks to their flexibility, conformal step coverage even over high-aspect ratio structures and unprecedented control on the morphology of the resulting nanoarchitectures. In this context, several copper(I) and (II) complexes have been used as copper molecular sources. Nevertheless, despite several works in the field, there is still the demand for novel CVD copper source reagents possessing the combined advantages of Cu(I) and Cu(II) compounds, namely the high thermal stability, appreciable volatility at moderate temperatures, long shelf-life in air, and possibly the capacity of depositing Cu(0) in the absence of reducing gases [9–11].

Herein, we wish to report on the preparation and characterization of tetrakis- μ -acetato-bis(acetamido)dicopper(II) $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CONH}_2)]_2$ (**1**). Particular attention is also devoted to highlighting the complex thermal properties by the use of thermal analyses technique, in view of eventual CVD applications. Some of the experimental data reported herein is validated and integrated by computational modeling of the complex aimed at providing a theoretical basis for the interpretation of the chemical behavior of $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CONH}_2)]_2$ (**1**).

Reaction of cuprous cyanide, 1, 3, 5-triazine and acetic acid in ammonia solution hydrothermally yielded a very stable compound $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CONH}_2)]_2$ (**1**) instead of the CuCN , triazine adduct [12]. The acetamide in the compound would have come from the reaction between acetic acid and the ammonia. On performing the reaction between copper acetate and acetamide in methanol solution yielded the same product. The obtained complex is air stable and characterized by elemental analysis, IR, electronic absorption spectroscopy and its structures elucidated by the single crystal X-ray.

Infrared spectrum of **1** in nujol display the bands expected for the acetamide and acetate ligands. In **1**, the carboxyl group of the ligand bridges the copper atoms with both of its oxygen atoms, and group is almost completely symmetric. The $\nu_{\text{as}}(\text{COO})$ of **1** is about 1646 cm^{-1} , which is typical of the bridging carboxylate of the copper(II) carboxylate dimer. A strong IR absorption is observed at 1393 cm^{-1} that corresponds to the $\nu_s(\text{C-O})$ vibration [13].

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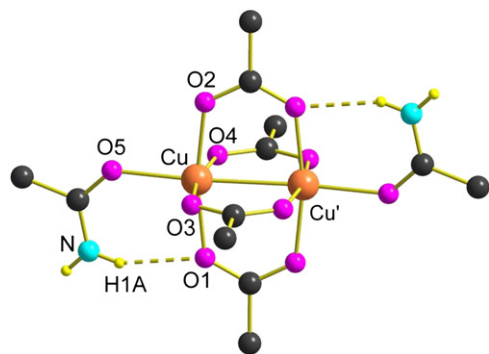
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Table 1
TD-DFT calculated excitations and approximate assignments for **1**.

Excitation energy (eV)	Wavelength (nm)	Oscillator strength (f)	Composition (%)	Nature of the transition and approximate assignment
1.814	683	0.0080	β HOMO-15 \rightarrow β LUMO (20%) β HOMO-1 \rightarrow β LUMO (31%) β HOMO-5 \rightarrow β LUMO + 1 (15%)	Cu($d_{x^2-y^2}$) + lp(OAc) \rightarrow Cu(d_{xy}) lp(OAc) \rightarrow Cu(d_{xy}) lp(OAc) + lp(amide O) \rightarrow Cu(d_{yz})
3.712	334	0.0038	β HOMO-3 \rightarrow β LUMO (66%) β HOMO \rightarrow β LUMO + 1 (24%)	lp(OAc) + lp(amide O) \rightarrow Cu(d_{xy}) Cu(d_{z^2}) + lp(amide O) \rightarrow Cu(d_{yz})
3.791	327	0.0222	β HOMO-1 \rightarrow β LUMO (56%)	lp(OAc) \rightarrow Cu(d_{xy})
4.320	287	0.0236	β HOMO-10 \rightarrow β LUMO (60%)	lp(OAc) \rightarrow Cu(d_{xy})
4.810	258	0.0758	β HOMO-5 \rightarrow β LUMO + 1 (25%) β HOMO-10 \rightarrow β LUMO + 1 (34%)	lp(OAc) + lp(amide N) \rightarrow Cu(d_{yz}) lp(OAc) + lp(amide) \rightarrow Cu(d_{yz})
5.099	243	0.0271	β HOMO-9 \rightarrow β LUMO (22%) β HOMO-9 \rightarrow β LUMO + 1 (47%) β HOMO-10 \rightarrow β LUMO + 1 (32%)	lp(OAc) \rightarrow Cu(d_{yz}) Cu(d_{z^2}) + lp(amide O) \rightarrow Cu(d_{xy}) Cu(d_{xy}) + lp(OAc) + lp(amide O) \rightarrow Cu(d_{yz})

The electronic excitations involve transitions mainly from metal-ligand bonding MOs to the β -spin LUMO, with dominant Cu d_{xy} character, and to β -LUMO + 1. Since each absorption line in a TD-DFT spectrum can arise from a several single orbital excitations, a description of the transition character is generally not straightforward. However, approximate assignments can be made, although they provide a simplified representation of the transitions. TD-DFT excitations were calculated both on the gas phase and in the solvent using the PCM (dichloromethane) [14]. By comparing the calculated spectra it is evident that calculated transitions do not exhibit significant solvatochromic effects, apart from a small blue-shift (~ 0.2 eV) of the weak feature centred at ~ 3 eV in the gas phase spectrum. In this view, only the PCM model results are presented in the Table 1. The experimental UV-Vis spectrum presents a very weak and broad absorption centered at 680 nm, 335 nm, 287 nm and shoulder at 245 nm. The calculated electronic excitations give rise to the same pattern of bands, at energies in good agreement with the experimental ones. The main difference between the experimental and TD-DFT spectra arises from relative intensities of the two peaks in the UV region, the calculated intensities at 243 nm being higher than that at 245 nm.

Crystals of the $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CONH}_2)]_2$ (**1**) suitable for single crystal X-ray diffraction were obtained hydrothermally [19]. Molecular structure of the complex with atomic numbering scheme is shown in Fig. 1 and hydrogen bond parameters are listed in Table 2. Selected geometrical parameters together with comparative results obtained by DFT calculations are tabulated in Table 3. The complex crystallizes in orthorhombic system with *Pcab* space group. It contains the commonly occurring dinuclear ('paddlewheel') copper(II) unit constructed by four bridging acetate and two acetamide ligands (coordination through the acetamide oxygen atom). The two halves of the dimeric species are related by an inversion centre at the mid-point of the Cu–Cu bond. This arrangement means that the two amide functionalities are oriented in a linear fashion but pointing in opposite directions. Each Cu atom shows

**Fig. 1.** Perspective view of the molecular structure for the $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CONH}_2)]_2$ with atom numbering scheme. All hydrogen atoms except those on the amide group have been removed for clarity. Symmetry operation: $1 - x, -y, 1 - z$.**Table 2**
Hydrogen bond parameters for **1**.

D-H...A-X	<i>d</i> H...A Å	<i>D</i> D...A Å	θ D-H...A ^a
N-H(1A)...O(1)	2.18	2.946	156
N-H(1B)...O(2) ^a	2.28	3.066	161
Symmetry equivalents: (a) $1/2 - x, 1/2 + y, 1 - z$.			

distorted octahedral coordination geometry with four carboxyl O atoms in the basal plane [mean Cu–O(carboxyl) = 1.973 (2) Å] and the O atoms of the acetamide ligands in the axial positions, with a significantly longer Cu–O distance [2.119 (2) Å]. All the Cu–O bond distances in the basal plane are in agreement with the bond lengths found in similar complexes [23]. The Cu–Cu distance within dinuclear core in **1** is 2.619(7) Å, and the Cu–Cu distance between adjacent metal-complexes within each hydrogen-bonded chain is 10.0 Å. The shortest through-space inter-chain distance between Cu(II) ions is 6.6 Å. The Cu–Cu separation in $\text{Cu}_2\text{X}_4\text{L}_2$ type systems is usually longer when the axial ligand is nitrogen instead of an oxygen atom. The Cu–Cu distances vary from 2.576 Å to 2.886 Å, for CuO_4N chromophores, and from 2.563 Å to 2.666 Å for CuO_5 chromophores. The Cu–Cu distance in **1** agrees well the distances reported for CuO_5 chromophores [24].

The rigidity of the molecule is reinforced by an intramolecular hydrogen bond between H1A of the amide and O1 or a coordinated carboxylate group [H1A...O1: 2.17(4) Å; \angle N-H1A...O1: 156.0(4)°]. The metal complex becomes part of an infinite 1-D chain as a result of self-complementary homomeric amide...amide dimers, N-H...O, 2.946 (4)–3.067(3) Å (Fig. 2).

In order to gain further insight into the role of intramolecular hydrogen bonding N-H1A...O1 having dimension 2.17(4) Å and angle 156.0(4)° (Table 3), bond order calculations have been performed on

Table 3
Selected geometrical parameters for the complex from X-ray data (Exp) and from the geometry optimization in gas phase (Calc).

	Exp	Calc
<i>Bond lengths (nm)</i>		
Cu–Cu'	2.6190(7)	2.619
Cu–O1	1.983(2)	1.983
Cu–O2	1.986(2)	1.986
Cu–O3	1.962(2)	1.962
Cu–O4	1.959(2)	1.959
Cu–O5	2.119(2)	2.119
H1A...O1	2.17(4)	2.173
<i>Bond angles (°)</i>		
O2–Cu–O1	168.59(9)	168.59
O3–Cu–O4	168.96(9)	168.96
O5–Cu–Cu	175.77(7)	175.76
N–H1A...O1	156.00(4)	155.90
Symmetry operation: $1 - x, -y, 1 - z$		

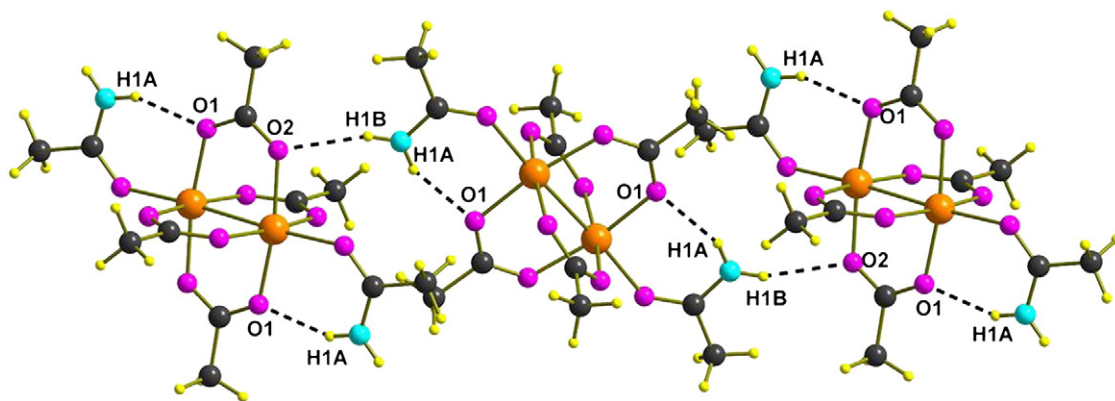


Fig. 2. 1-D chain in the crystal structure of the complex. Each paddlewheel unit comprises two Cu(II) ions (orange) and four acetate ligands (purple). The axial positions are occupied by acetamide ligands with coordination through the oxygen atoms (purple).

the optimized geometry. The H1A...O1 Wiberg bond order is 0.0364 which is quite significant for the hydrogen bonding interactions. The contour diagram showing the overlap of orbitals is presented in Fig. 3. It is apparent from the figure that this overlap is not strong.

Thermal analyses of the $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{CONH}_2)_2$, performed both under flowing air or nitrogen, provided very similar results, indicating thus that the complex is thermally stable and gives rise to clean vaporization free from undesired side reactions irrespective of the adopted atmosphere. Fig. 4 displays the simultaneous TGA and DSC curves recorded in the presence of oxygen, which is typically employed as reactant gas in CVD routes to copper oxides. The TGA profile displays an initially weak weight loss, which becomes more significant for $T > 130^\circ\text{C}$ and is followed by a marked slope change, leading

ultimately to a constant zero residual weight at temperatures higher than 180°C . These observations highlight a clean and quantitative precursor sublimation in a relatively narrow temperature range, a very promising behavior for possible applications of $[\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{CONH}_2)_2]$ as a CVD precursor. The DSC curve (Fig. 4) is characterized by two exothermic peaks located at 80°C and 180°C , attributed to the compound melting and its subsequent vaporization, respectively. No other signal detected at higher temperatures.

Inspired by the above facts the decomposition experiments in air flow were performed for the complex **1** at 210°C for 5 h and at 500°C for 15 h. The PXRD pattern recorded for product decomposed at 210°C (Fig. 5b) are consistent with $[\text{Cu}(\text{O}_2\text{CCH}_3)_2]$, with lattice parameters $a = 13.312(5) \text{ \AA}$, $b = 13.312(5) \text{ \AA}$ and $c = 15.121(1) \text{ \AA}$ (PDF 271126).

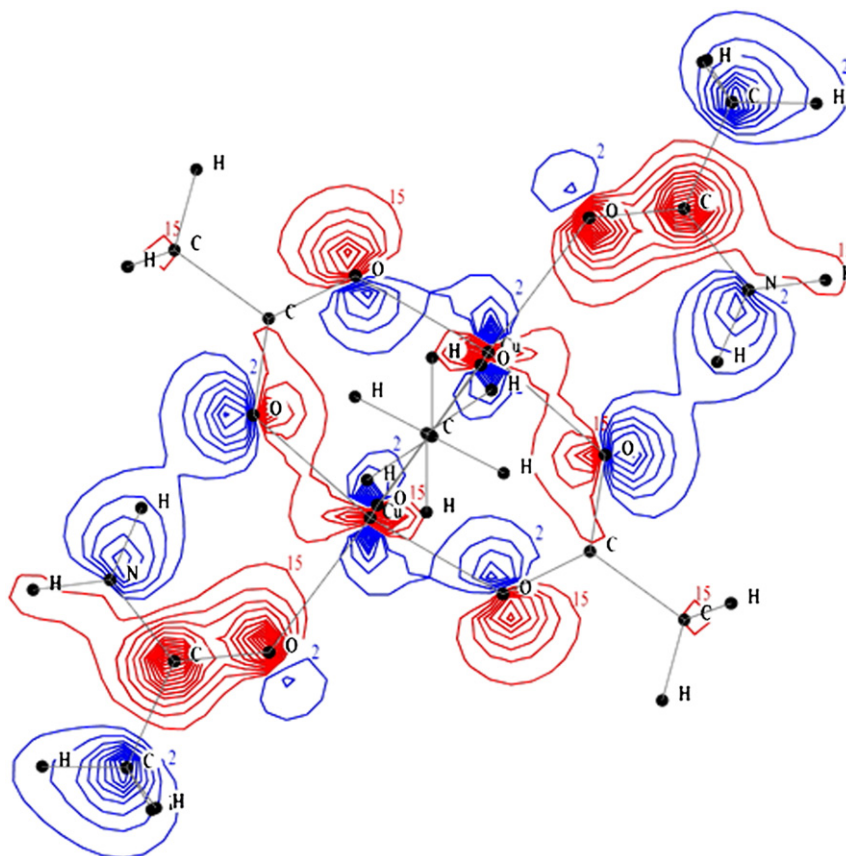


Fig. 3. Contour diagram showing natural bond orbital overlap.

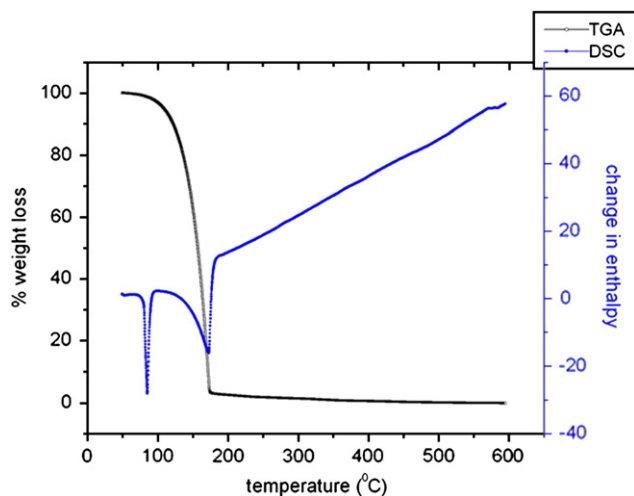


Fig. 4. TGA and DSC profiles of $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CONH}_2)]_2$ recorded under an air flow.

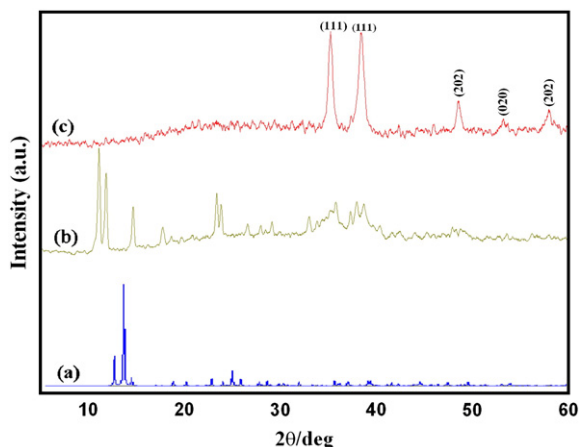


Fig. 5. Powder X-ray diffractogram of Tetrakis- μ -acetato-bis(acetamido)dicopper(II) $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CONH}_2)]_2$ (1): (a) Simulated; (b) at 210 °C for 6 h; (c) at 500 °C for 15 h.

This indicates that complex have lost the axial acetamide ligand which seems to be reasonable. The pattern recorded for product obtained at 500 °C (Fig. 5c) matches with CuO, having lattice parameters $a = 4.561$ (5) Å, $b = 3.379$ (1) Å and $c = 5.1183$ (4) Å (PDF 892530) quite well.

In this work we have presented physico-chemical properties of the Tetrakis- μ -acetato-bis(acetamido)dicopper(II) $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CONH}_2)]_2$ (1) by experimental-computational approach. The complex was volatile and could be sublimed at $T = 180$ °C. In addition, TGA/DSC analyses and PXRD data evidenced the occurrence of a clean vaporization process without premature side decompositions, and of clear PXRD pattern dominated by the loss of the acetamido ligands. A key point of the present investigation was the integrated use of a theoretical and experimental approach, enabling us to validate and integrate the obtained results and to gain a detailed insight into the structure, bonding and chemical behavior of the target compound. Taken together, these results make the $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CONH}_2)]_2$ complex an attractive candidate for a CVD precursor for copper based thin films and nanosystems. The results of such investigations will be the focus for our future studies.

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Appendix A. Supplementary material

The crystallographic data in CIF format has been deposited with CCDC (CCDC deposition number is 806962). This data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internet.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2011.03.031](https://doi.org/10.1016/j.inoche.2011.03.031).

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- [19] Intensity data for **1** was collected at 150(2) K on a Nonius Kappa CCD diffractometer system equipped with graphite monochromated Mo-K α radiation $\lambda = 0.71073$ Å. The final unit cell determination, scaling of the data, and corrections for Lorentz and polarization effects were performed with Denzo-SMN [20]. The structures were solved by direct methods (SIR97) [21] and refined by a full-matrix least-squares procedure based on F2 [22]. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located at calculated positions and refined using a riding model with isotropic thermal parameters fixed at 1.2 times the Ueq value of the appropriate carrier atom. The computer programme PLATON was used for analyzing the interaction and stacking distances. [Cu(O₂CCH₃)₂(CH₃CONH₂)₂]₂, C₁₂H₂₂N₂O₁₀Cu₂, M = 481.40, Orthorhombic, Pcab, a = 9.2906(2) Å, b = 13.5970(3) Å, c = 14.6039(4) Å, $\beta = 90^\circ$, $\gamma = 90^\circ$, V = 1844.83(8) Å³, Z = 4, D_c = 1.733 mg m⁻³, F(000) = 984, T = 150(2) K, R1 = 0.0689, wR2 = 0.0990, GOF = 1.077. A total of 26,296 reflections were collected, 2117 unique (Rint = 0.1094).
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