



A solvothermal and mechanochemical strategy for the construction of chiral N,N-ditopic metalloligands: oxygenation process of a Cu(I)X/quinine system



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ABSTRACT

Oxygenation process of a CuX/QN system (where X = Cl, Br; QN–H = quinine) involving either a solvothermal or mechanochemical approach affords novel chiral N,N-ditopic metalloligands [XCu(μ-QN)]₂. The molecular and crystal structures of the resulting complexes have been determined by single-crystal X-ray diffraction and PXRD.

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The design and synthesis of inorganic–organic hybrid materials based on copper halides (I) have been extensively investigated due to their intriguing topology and interesting physical or chemical properties [1]. To date, a series of copper halides in one, two, or three dimensions have been successfully synthesized such as rhomboid dimers of stoichiometry [Cu₂X₂L₂]_n, the tetranuclear species on cubane or stepped cubane tetramers of stoichiometry [Cu₄X₄L₄]_n and hexagonal [Cu₆X₆]_n grid chains [2]. A variety of structural motifs have also been observed for copper(I)–olefin systems [3]. On the other hand, the reaction of O₂ and copper(I) complexes of appropriate ligands provides a variety of copper–dioxygen complexes [4]. However, the examination of oxygenation processes involving copper(I) halides is a highly undeveloped field and to our knowledge structural analysis of the resulting products has not been thoroughly exploited.

Recently, we turned our attention toward readily available cinchona alkaloids and developed a novel attractive route to chiral bipyridine-type linkers based on cinchona alkaloids' metal complexes [5]. This strategy appeared as an efficient method providing semi-rigid mononuclear and dinuclear chiral N,N-ditopic metalloligands varying in angular disposition of N-donor sites. Following our recent report on a simple combination of quinine and CuI leading to a novel class of homochiral coordination polymer of unique ladderlike framework [6], we were

highly encouraged to use other copper halide salts in this context. Additionally, we extended this study to the examination of the oxygenation process of the resulting CuX/quinine systems. We describe here our results on the synthesis and characterization of the first copper quinine-based metalloligands under both conventional solvothermal and mechanochemical conditions.

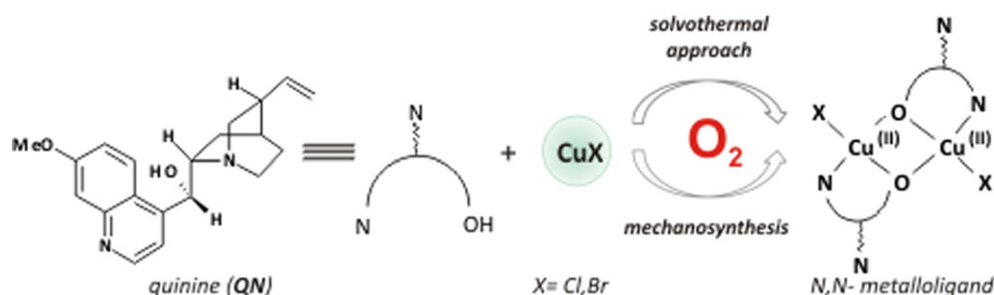
The reaction between quinine (QN) and CuCl or CuBr under solvothermal conditions in MeCN in a sealed tube leads to the formation of pale yellow solution in 5 h (Scheme 1). After cooling the solution to room temperature, the postreaction mixture turned immediately into gel, which may be attributed to the formation of a more extended network through various possible interactions between multifunctional cinchona alkaloid and copper(I) halide [7]. Thus, in the next experiment we carried out the reaction between CuX/QN (X = Cl, Br, I) systems in MeCN solution in the excess of O₂ at 80 °C. The reactions proceeded with a color change of the solution from yellow to green after several hours, which confirms the oxygenation process that was supported by luminescence measurements (Fig. S5). From the post-reaction mixtures green cubic crystals of [ClCu(μ-QN)]₂ (1) and [BrCu(μ-QN)]₂ (2) were isolated at 20 °C (because of a low quality of crystals resulting from the oxygenation of CuI/QN system, we were unable to obtain a proper data set to perform a reliable X-ray analysis).

The molecular structure of 1 is shown in Fig. 1. The dimeric structure of 1 possesses *P* 2₁ symmetry with two four-coordinate copper centers.

The geometry of the Cu atom coordination sphere can be described as a distorted square planar with angles ranging from 75.52° to

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Scheme 1. Schematic representation of the syntheses of N,N-metalloligands.

100.93°. The structural analysis of **2** revealed the presence of isostructural dimeric motif as depicted in Fig. S2 (for experimental and crystallographic details for **1** and **2** see Supplementary information). Complexes **1** and **2** comprise the quinoline moieties oriented in a nearly parallel fashion with the N atoms 8.78 Å and 8.68 Å away from each other, and the links of the potential N,N-ditopic linker form an angle of 49.38° and 44.55° respectively. Thus **1** and **2** represent a new example of chiral N,N-ditopic metalloligands potentially capable of further coordination to metal centers [8]. Our previous studies have revealed that mono- and dinuclear molecular metal complexes derived from cinchona exhibited intrinsic molecular shape-derived properties for noncovalent interaction-driven self-assembly into chiral microporous supramolecular architectures. So we wondered how small structural differences in a cinchona alkaloid ligand, that is, the introduction of the methoxy group of the quinoline ring, can impart changes in the assembly of the corresponding metal complexes [9]. Detailed examination of the crystal structures of **1** and **2** showed that the resulting compounds assemble into the close packing mode with void cavities occupied by acetonitrile molecules (Fig. S3 in the Supplementary information).

Mechanochemistry is becoming an increasingly important strategy in materials synthesis since it is often rapid and convenient and requires little or no solvent for the reaction step [10]. Recently, mechanochemical methods have been investigated in the context of metal complexes [11] and synthesis of coordination polymers [10] as well as conducting the organic syntheses and catalytic processes in ball mills [12]. However, to date, the application and versatility of such mechanochemical methods for the oxygenation reaction of copper(I) systems have been limited, and not been thoroughly investigated. Very recently we and others have revealed the applicability of the liquid-assisted grinding (LAG) to the synthesis of the copper(I) iodide coordination polymers

[6,13]. Therefore, we exploited this approach for the CuCl/QN and CuBr/QN systems. Neat grinding of CuCl (or CuBr) and quinine in the stoichiometric ratio 1:1 for 1 h only provided copper halide salts as was revealed by PXRD. However, 1 h LAG of CuCl (or CuBr) and QN in the presence of small amount of acetonitrile resulted in the formation of dark green powder [14]. PXRD analysis showed that the mechanochemical synthesis produced a material with no detectable amounts of the starting materials present. As shown in Fig. 2 the powder XRD pattern of such obtained material is consistent with the calculated pattern of **1** (corresponding comparison of the XRD patterns for the product between CuBr and QN is shown in Fig. S4) and shows significantly broader peaks due to the smaller crystalline size and possible microstrain. The formation of **1** and **2** is interesting from the aspect of mechanochemistry, as the oxygenation process of Cu(I) to Cu(II) systems in such way has not been observed so far.

In conclusion, the results demonstrate a viable means of constructing novel chiral N,N-ditopic metalloligands by oxygenation process of CuX/QN systems under both solvothermal and liquid-assisted grinding conditions. Efforts to the rational design and preparation of novel chiral homo- or heterometallic supramolecular architectures with tailor-made properties, including enantioselective recognition and separation, are underway.

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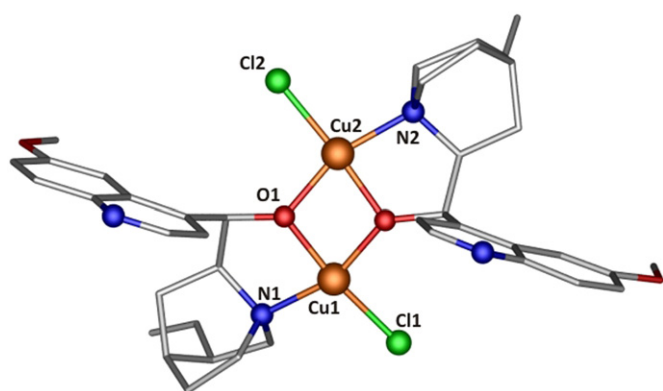


Fig. 1. Molecular structure of **1**; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1–Cl1, 2.201(2); Cu1–O1, 1.909(4); Cu1–N1, 2.009(2); Cu2–Cl2, 2.215(4); Cu2–N2, 1.999(2); Cu1–O1–Cu2, 101.3(5); O1–Cu1–N1, 83.75(8); N1–Cu1–Cl1, 100.0(6).

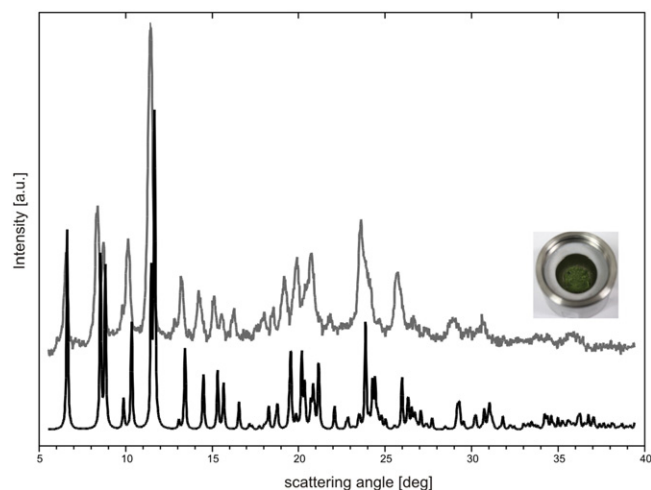


Fig. 2. Comparison of the PXRD patterns of **1** calculated from single-crystal data (lower curve) and measured for the ground sample (upper curve).

Appendix A. Supplementary material

Experimental procedures and details of the structural solutions and X-ray data for **1** and **2**. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.inoche.2014.06.002>. These data include MOL files and InChIKeys of the most important compounds described in this article.

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