



# Solvothermal synthesis, structure and catalytic activity of a mixed-valence Cu<sup>I</sup>/Cu<sup>II</sup> complex with 1-D chain structure

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## ARTICLE INFO

### Article history:

Received 8 March 2012

Accepted 15 May 2012

Available online 24 May 2012

### Keywords:

Mixed-valence complex

1-D chain

Solvothermal synthesis

Catalytic activity

## ABSTRACT

A complex of composition  $[\text{Cu}^{\text{I}}_4\text{Cu}^{\text{II}}(\text{mtpo})_4(\text{H}_2\text{O})_2\text{Cl}_2]_n$  (**1**) was synthesized from reaction of Hmtpo (Hmtpo = 5-methyl-[1,2,4]-triazolo-[1,5-a]-pyrimidin-7-*o*1) with one equivalent of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in water at 100 °C under autogenous pressure. Complex **1** was fully characterized by X-ray single crystal diffraction, elemental analysis and IR spectroscopy. X-ray analysis reveals that complex **1** is a mixed-valence coordination polymer and displays 1-D chain structure. Compound **1** was able to heterogeneously catalyze the ketalization reaction of 2-butanone and ethylene glycol to afford 2-ethyl-2-methyl-[1,3]-dioxolane in excellent yield under mild conditions.

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The chemistry of novel metal–organic coordination polymers continues to attract intensive attention, due to their intriguing topology architectures [1] and potential applications as functional materials in catalysis [2], magnetism [3], gas storage [4] and molecular recognition [5]. The successful strategies in building such polymers include employing appropriate bridging ligands that can bind metal ions in different modes and aggregate metal ions in a polymeric system, and utilizing simple and efficient synthetic methods. We are interested in employing 1,2,4-triazolo[1,5-a] pyrimidine and its derivatives as bridging ligands to construct coordination polymers, because these ligands could provide four nitrogen donors that can foster formation of polymeric structures. There is currently a growing interest in the coordination chemistry of 1,2,4-triazolo[1,5-a] pyrimidine and its derivatives [6]. The interests are driven by a number of considerations, and two of which are the development of new antimicrobial agents [7] and the study of metal–metal interactions [8].

As one of the derivatives of 1,2,4-triazolo[1,5-a] pyrimidine, 5-methyl-[1,2,4]-triazolo-[1,5-a]-pyrimidin-7-*o*1 (Hmtpo) has been recently a popular ligand in coordination chemistry. Hmtpo exhibits a great variety of coordination modes [6] (Scheme 1), and a few coordination complexes with transition metals, e.g.,  $[\text{Cu}_2(\text{NCS})_4(\text{Hmtpo})_2(\text{H}_2\text{O})_2]$  [9],  $[\text{Cu}(\text{mtpo})_2(\text{py})_2(\text{H}_2\text{O})_2]$  [10],  $[\text{Ag}(\text{NO}_3)(\text{Hmtpo})_n]$  [11],  $[\text{Pt}_2(\text{mtpo})_4] \cdot 2\text{DMSO}$  [8a],  $[\text{Pt}(\text{NH}_3)_2(\text{Hmtpo})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  [12],  $[\text{Co}(\text{H}_2\text{O})(\text{Hmtpo})_2]_n$  [13],  $[\text{Ni}(\text{H}_2\text{O})(\text{Hmtpo})_2]_n$  [13], etc., have been reported. However, most of these complexes are mononuclear or dinuclear and only a handful of complexes exhibit polymeric structure [11,13]. Therefore the synthesis

of coordination polymers of this ligand deserves attention. Noticeably, nearly all of the reported complexes have been synthesized via ‘conventional’ coordination chemistry techniques, i.e., solution chemistry under atmospheric pressure and at temperatures limited to the boiling points of common solvents, and the solvothermal techniques [14] have rarely been used in preparing the coordination complex of the Hmtpo ligand [13].

With an idea of employing solvothermal techniques in mind and prompted by the expectation for synthesizing the coordination polymers of the Hmtpo ligand, we carried out a reaction involving  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and the Hmtpo ligand. Gratifyingly, a coordination polymer  $[\text{Cu}^{\text{I}}_4\text{Cu}^{\text{II}}(\text{mtpo})_4(\text{H}_2\text{O})_2\text{Cl}_2]_n$  (**1**) has been synthesized. Herein, we report the preparation and characterization of this complex. The catalytic activity of **1** toward ketalization reaction is also described.

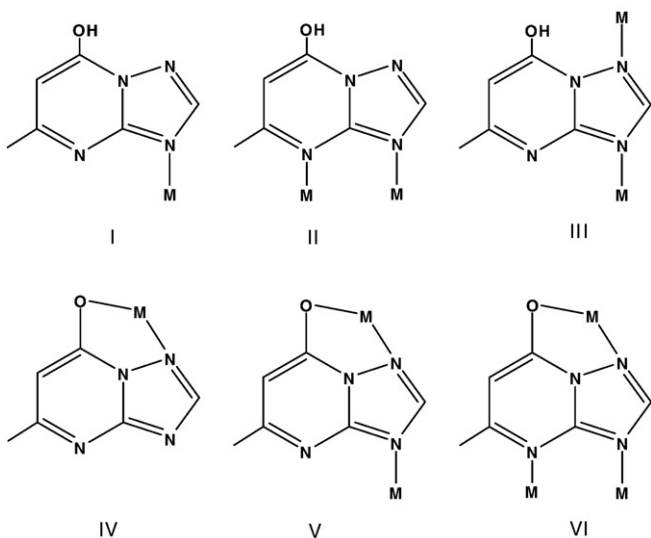
Complex **1** was prepared under solvothermal conditions in  $\text{H}_2\text{O}$ . Treatment of a mixture of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CH}_3\text{ONa}$  with Hmtpo in  $\text{H}_2\text{O}$  results in the formation of **1**. Complex **1** was readily isolated as light brown crystals with moderate yield.

We have explored the importance of the solvothermal techniques in this chemistry by attempting the analogous reaction under ‘conventional’ conditions. The synthetic investigation of the  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{CH}_3\text{ONa}/\text{Hmtpo}$  system in  $\text{H}_2\text{O}$  under ambient reflux conditions gives known compound  $\text{Cu}(\text{mtpo})_2(\text{H}_2\text{O})_4$  [15]. Since **1** is a mixed-valence coordination polymer, it seems that  $\text{Cu}^{\text{II}}$  can be easily reduced to  $\text{Cu}^{\text{I}}$  under solvothermal conditions.

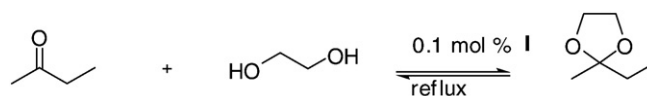
The IR spectrum of **1** (Fig. S2) presents only small changes when compared to free Hmtpo. The broad band appears at 3290–3070  $\text{cm}^{-1}$  in **1** is ascribed to the  $\nu(\text{OH})$  of the two coordinated water molecules. In the spectrum of solid Hmtpo a band is found at 1700  $\text{cm}^{-1}$ , which is ascribed to the C=O stretching vibration [16]. This absorption shifts

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Scheme 1. Coordination modes of Hmtpo.



Scheme 2. Ketalization reaction between 2-butanone and ethylene glycol catalyzed by complex **1**.

arrayed  $\text{Cu}^{\text{II}}\text{N}_2\text{O}_4^{2+}$  polyhedron and tetranuclear  $[\text{Cu}_4(\text{mtpo})_4\text{Cl}_2]^{2-}$  unit (Fig. 1a).

As shown in Fig. 1a, the  $\text{Cu}^{\text{II}}$  ion is coordinated by two oxygen atoms of two water molecules, two nitrogen atoms and two oxygen atoms from the two mtpo<sup>−</sup> ligands of the two  $[\text{Cu}_4(\text{mtpo})_4\text{Cl}_2]^{2-}$  units, forming a slightly distorted octahedron geometry.

In the tetranuclear  $[\text{Cu}_4(\text{mtpo})_4\text{Cl}_2]^{2-}$  unit, two  $[\text{Cu}_2(\text{mtpo})_2]$  moieties are bridged by two  $\text{Cl}^-$  ions. The two mtpo<sup>−</sup> ligands are oriented in a head-to-head disposition; therefore, all four  $\text{Cu}^{\text{I}}$  ions in the  $[\text{Cu}_4(\text{mtpo})_4\text{Cl}_2]^{2-}$  unit display slightly distorted trigonal-planar geometry. The coordination of the two mtpo<sup>−</sup> ligands to two  $\text{Cu}^{\text{I}}$  ions generates an eight-membered  $\text{Cu}_2\text{N}_4\text{C}_2$  ring analogous to those of the ligands with N–C–N motifs [18]. The distance between the two N–C–N bridged Cu atoms in the  $[\text{Cu}_2(\text{mtpo})_2]$  unit is 2.904 Å. The mtpo<sup>−</sup> ligands in **1** adopt two coordination modes (II and VI in Scheme 1).

The presence of four  $\text{Cu}^{\text{I}}$  atoms in the  $[\text{Cu}_4(\text{mtpo})_4\text{Cl}_2]^{2-}$  unit was confirmed by the X-ray photoelectron spectrum (Fig. S3). The spin-orbit component ( $^2\text{P}_{3/2}$  and  $^2\text{P}_{1/2}$ ) of the Cu 2p peak at approximately 932.0 and 952.0 eV with a spin-orbit separation of 20.0 eV suggests the presence of  $\text{Cu}^{\text{I}}$  atom in the complex.

to  $1705\text{ cm}^{-1}$  in **1**, due to the coordination of oxygen atoms to the metal ions.

Single-crystal X-ray diffraction studies reveal that complex **1** [17] crystallizes in the triclinic crystal system of the *P*-1 space group and possesses 1-D chain structure. The infinite chain is composed of alternating

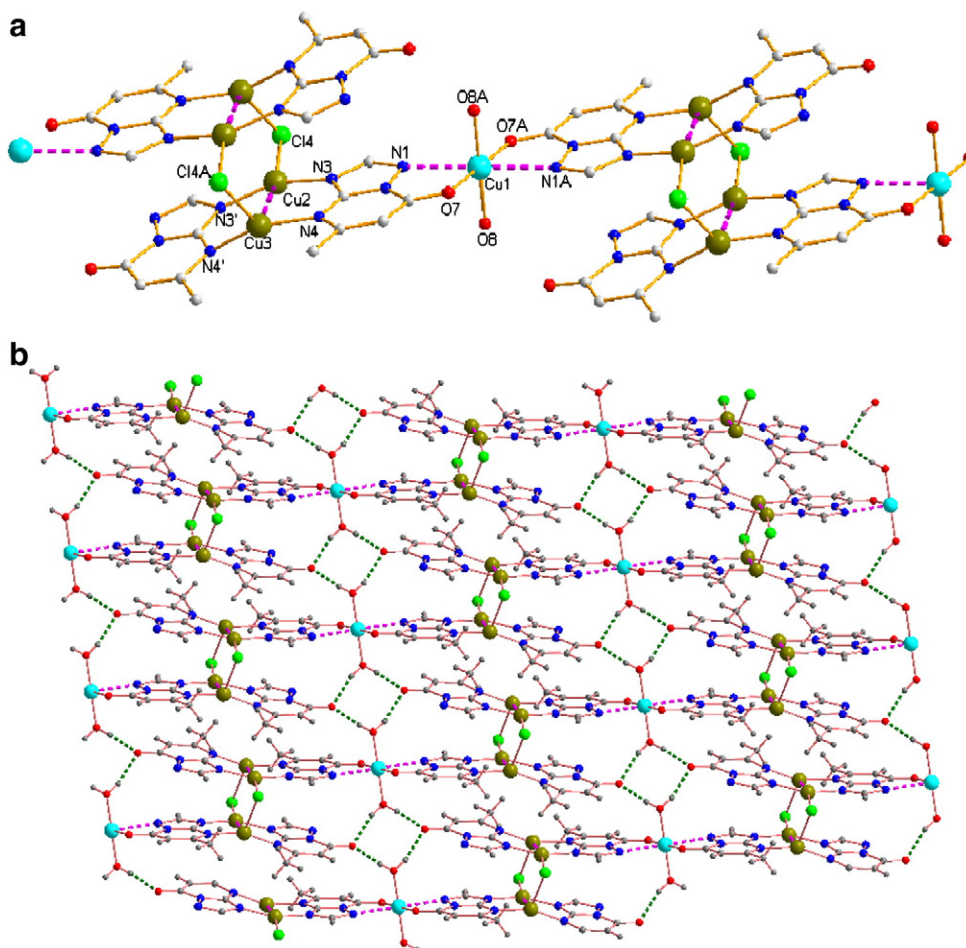


Fig. 1. (a) Coordination environments of the  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$  ions in **1**. (b) Molecular packing in **1** illustrating the hydrogen bond interactions. Colour scheme:  $\text{Cu}^{\text{I}}$ , yellow;  $\text{Cu}^{\text{II}}$ , light blue; O, red; N, blue; Cl, green; C, grey.

**Table 1**  
Conversion yields for the ketalization of 2-butanone.

Time (h)	T (°C)	Conv.(%) <sup>a</sup>
24	90	47
24	110	97

<sup>a</sup> Conversion yields were determined by <sup>1</sup>H NMR.

In order to confirm the valence-states of Cu atoms in **1**, bond valence sum (BVS) calculations [19] were performed for each Cu ion; indeed, the BVS calculations for Cu1 (Cu1 = 1.82) agreed with the 2+ valence state, whereas those for Cu2, Cu2A, Cu3 and Cu3A (Cu2 = Cu2A = 1.08; Cu3 = Cu3A = 1.00) confirmed the 1+ valence state.

The X-ray crystal structure analysis of **1** also reveals that two planar triangular copper units coupled via two Cu–Cu interactions (Cu2–Cu3 and Cu2A–Cu3A). Compared to the metal–metal distances in the open-shell metallic copper (2.556 Å) as well as to the estimated sum of van der Waals radii (Cu–Cu) 2.80 Å, the presently documented Cu–Cu distance is closer to the upper van der Waals limit. The question of a cuprophilicity of Cu<sup>I</sup> is still a matter of controversy [20]. However, there are scarce examples of ligand-unsupported Cu<sup>I</sup>–Cu<sup>I</sup> interactions [21].

The hydrogen bonds between the coordinated water molecules and deprotonated hydroxyl oxygen atoms have not affected the geometry of the mtpo<sup>−</sup> ligands. The chains are linked by the above-mentioned hydrogen bonds to form a 2-D structure (Fig. 1b).

To estimate the stability of complex **1**, its thermal behavior was studied by TGA. The TGA curve of **1** (Fig. S4) shows a weight loss of 3.6% from 100 to 190 °C, which corresponds to the removal of the two coordinated water molecules (theoretical value is 3.5%). The second weight loss of 3.3% from 190 to 281 °C is observed, which is possibly due to the loss of one Cl<sup>−</sup> ion (calculated value is 3.4%). The third weight loss occurs (57.5%) from 281 to 685.8 °C, which may be ascribed to the removal of the four mtpo<sup>−</sup> ligands.

As the Cu<sup>I</sup> ion of **1** is coordinatively unsaturated, it may exhibit Lewis acid catalytic properties. We then found **1** is catalytically active in heterogeneous ketal formation. Ketalization is an important method to protect carbonyl groups in organic synthesis and drug design [22,23]. The reaction requires a Lewis acid catalyst to activate the oxygen of the carbonyl group, allowing glycol to substitute the ketone group. The experiment was performed with 2-butanone and ethylene glycol in toluene and catalyst loading is 0.1% mmol (Scheme 2). Our results are summarized in Table 1. As shown in Table 1, when the reaction was performed at 90 °C, the product 2-ethyl-2-methyl-1,3-dioxolane was obtained in 47% yield (Fig. S5). As the temperature is increased to 110 °C, 97% yield (Fig. S6) of the product was resulted, which indicates the ketone could be completely protected under the relatively mild condition. Complex **1** is insoluble in common organic solvent, indicating the heterogeneous nature of the catalysis.

In summary, the use of Hmtpo in reaction with Cu<sup>II</sup> salt has led to the rare coordination polymer **1**. The presence of Cu<sup>II</sup>/Cu<sup>I</sup> in **1** emphasizes the synthetic novelty that arises when solvothermal techniques are used in Cu<sup>II</sup>/Hmtpo chemistry. We are pursuing the ways of producing additional and interesting coordination polymers supported by the Hmtpo ligand. The mechanism studies of complex **1** catalyzed ketalization reaction are also in progress and will be reported soon.

## Acknowledgements

The authors appreciate the financial supports of Hundreds of Talents Program (2005012) of CAS, Natural Science Foundation of China (20872105), “Qinglan Project” of Jiangsu Province (Bu109805), A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institution, and the Scientific Research Project of the Shannxi Province of China (2011K17-07-04).

## Appendix A. Supplementary material

CCDC 767584 contains the supplementary crystallographic data for complex **1**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.inoche.2012.05.023>.

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