

# Synthesis, structure and heterogeneous catalytic activity of a coordination polymer containing tetranuclear Cu(II)-btp units connected by nitrates

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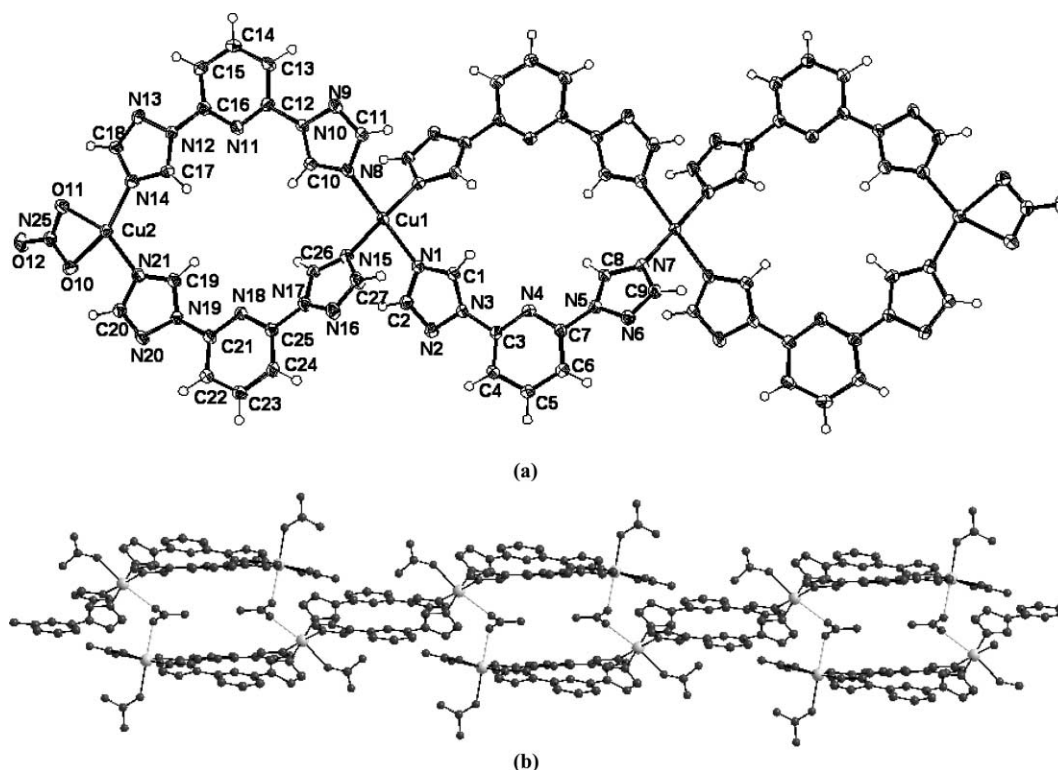
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**A new coordination polymer containing a tetranuclear Cu(II)-btp unit is an effective heterogeneous catalyst for the regioselective ring opening of epoxide by methanol.**

Self-assembly coordination compounds<sup>1,2</sup> have been intensively synthesized as their porous channels have special properties such as gas or chemical absorption, ion-exchange, heterogeneous catalysis, and so on. Since Cu(II) has a Jahn–Teller effect that drives a tetragonally elongated structure and can produce different types of polymers by changing counter anions,<sup>3</sup> Cu(II) complexes have often been used as building blocks for the construction of different polymeric architectures. However, in spite of intensive study of the Cu-containing coordination polymers, to our knowledge, their use as heterogeneous catalysts has not been reported yet.<sup>4</sup> Herein, we report that, with btp [2,6-bis(*N'*-1,2,4-triazolyl)pyridine] ligand, Cu(NO<sub>3</sub>)<sub>2</sub> produces a new btp-bridged tetranuclear unit connected by nitrate anions to form a polymeric compound whereas Cu(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> produces a discrete molecule. Furthermore, preliminary application of the polymeric Cu(II)

compound **1** as a heterogeneous catalyst showed, unexpectedly, very promising results for alcoholysis of epoxides at ambient temperature and this novel catalytic system appears to be very mild, efficient, regioselective, and easily recyclable, while the discrete Cu(II) molecule **2** did not catalyze the alcoholysis.

Blue block-type crystals were obtained from the direct diffusion technique.<sup>†</sup> The structure of **1** was determined by X-ray crystallography.<sup>‡</sup> An asymmetric unit consists of two Cu atoms, three btp ligands, and four NO<sub>3</sub><sup>−</sup> anions. Four Cu atoms are bridged by btp ligands to form a tetranuclear compound. Chelating nitrate anions to Cu atoms terminate connections for polymerization. The terminal Cu2 atoms have a monodentate nitrate anion, a chelating bidentate nitrate anion, and two btp ligands, and inner Cu1 atoms have four btp ligands and a monodentate nitrate anion. There is a crystallographic center of inversion at the mid-point of the compound. Fig. 1(a) shows the complete structure of a tetranuclear compound containing three bridged rings. Cu1 and Cu2 atoms are also weakly bridged by nitrate anions [Cu–O(bridging nitrate) 2.482(2) and



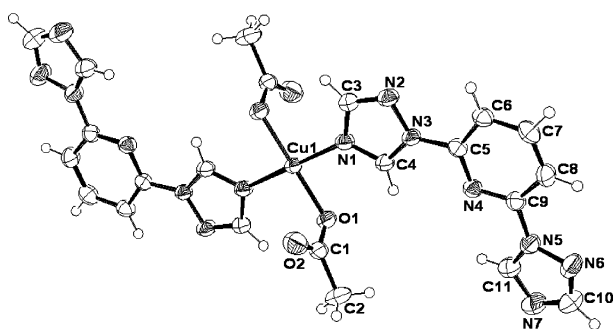
**Fig. 1** (a) ORTEP<sup>9</sup> drawing of the tetranuclear compound containing Cu(II) ions, btp ligands and nitrates. Axial nitrate anions are omitted for clarity. Cu–N(btp) 1.978(3)–2.061(3) Å and Cu2–O(chelating nitrate) 2.014(2), 2.042(2) Å. (b) Nitrate bridged polymeric structure. Cu1–O(monodentate nitrate) 2.359(2) Å and Cu2–(monodentate nitrate) 2.275(2) Å. Cu1–O(bridging nitrate) 2.482(2) Å and Cu2–O(bridging nitrate) 2.420(2) Å.

**Table 1** Ring opening of epoxides by methanol in the presence of catalyst **1**

Entry	Substrate	Time/days	Conversion yield <sup>a,b</sup> (%)
1	Cyclohexene oxide	6	>99
2	Cyclohexene oxide/Cu(NO <sub>3</sub> ) <sub>2</sub> <sup>c</sup>	6	55 <sup>d</sup>
3	Cyclohexene oxide/complex <b>2</b> <sup>e</sup>	6	0
4	Cyclopentene oxide	60	>99
5	<i>cis</i> -2,3-Epoxybutane	20	>99
6	<i>trans</i> -2,3-Epoxybutane	50	>99
7	Styrene oxide	3	>99 (exclusively primary alcohol)

<sup>a</sup> Catalytic reaction conditions: epoxides (0.05 mmol) were dissolved in methanol (1 mL), and the catalyst **1** (1 mg/FW of **1**  $\sim 1 \times 10^{-3}$  mmol) was added and shaken at room temperature (450 rpm). Reaction conversion was monitored by GC/GC-Mass analysis of 20  $\mu$ L aliquots withdrawn periodically from the reaction mixture. All reactions were run at least three times and the average conversion yields are presented. <sup>b</sup> Based on the consumption of the starting epoxide. <sup>c</sup> Reaction conditions were the same as described in *a* except that  $1 \times 10^{-3}$  mmol of Cu(NO<sub>3</sub>)<sub>2</sub> salt was used instead of catalyst **1**. <sup>d</sup> Conversion stopped at 55% and did not proceed even at longer reaction times. <sup>e</sup> Reaction conditions were the same as described in *a* except that  $1 \times 10^{-3}$  mmol of complex **2** was used instead of catalyst **1**.

2.420(2) Å]. The nitrate bridged polymeric structure is shown in Fig. 1(b). If the weak coordination of nitrate is considered, the geometry of each Cu atom is tetragonally elongated octahedral. The Cu1  $\cdots$  Cu2 and Cu1  $\cdots$  Cu1' distances are 9.659(7) and 10.014(7) Å, respectively. Blue needle-type crystals were obtained by the slow evaporation of a mixture of a methanol solution of Cu(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> and a methanol solution of btp ligand. †, ‡ The asymmetric unit cell of mononuclear Cu(II) complex **2** contains half a molecule and a water molecule. A crystallographic center of inversion is located on the Cu atom, and the complete molecule is shown in Fig. 2. When Cu(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> is used in a reaction with btp ligands, btp does not bridge the Cu atoms. Two acetate ions and two btp ligands are coordinated to the Cu(II) ion with O–Cu–O and N–Cu–N angles of 180.0°. Therefore, the geometry of the Cu(II) ion is essentially square planar.



**Fig. 2** ORTEP drawing of compound **2**, Cu(OAc)<sub>2</sub>(btp)<sub>2</sub>. Cu–N(btp) 1.986(2) Å and Cu–O(acetate) 1.943(2) Å.

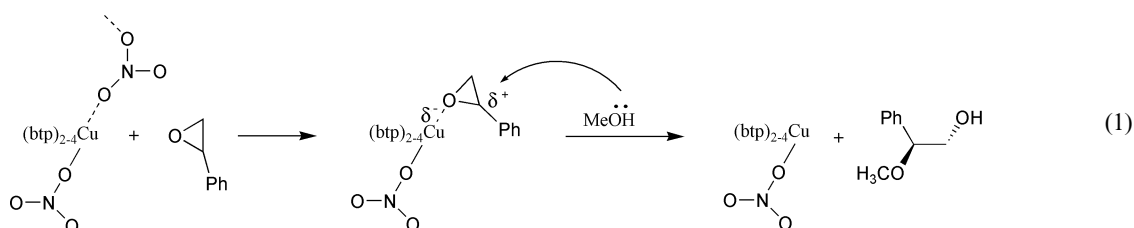
The btp ligand usually bridges transition metal atoms to form a polymeric structure as shown in our previous btp bridged dirhodium(II,II) compounds,<sup>5</sup> but in this study the btp ligands act as monodentate ligands as well as bidentate bridging ligands. A Cu(II) ion having nitrate counteranions produced a btp-bridged Cu(II) tetranuclear compound that was also bridged by nitrate anions to form a polymeric compound. With acetate instead of nitrate as counteranion, the Cu(II) ion produces only a discrete molecule. In the case of compound **1**, the geometry of the Cu(II) ion is tetragonally elongated octahedral, while compound **2** has a square planar geometry. Actually, the

geometry of the Cu(II) ion is also elongated octahedral with Cu–O(OAc) distances of 2.69(5) Å in compound **2**. This result suggests that both the Jahn–Teller effect of the electronic configuration of Cu(II) and the counter anion effect are important for the construction of coordination polymers.

Since copper has recently gained prominence as a catalyst for numerous transformations<sup>6</sup> and heterogeneous catalysts are easy to handle and separate from the reaction solution,<sup>7</sup> the reactivity of the copper-containing polymer **1** as a heterogeneous catalyst was examined in the ring opening of a wide range of epoxides with methanol.<sup>8</sup> The results are summarized in Table 1.

Cyclohexene oxide was effectively converted to *trans*-1,2-diol monomethyl ether (>99% conversion in 6 days), while a control reaction carried out in the absence of catalyst **1** showed only trace amounts of the product over the same time period. More importantly, the catalyst could be easily recovered by a simple filtration and used repeatedly with about a 5% decrease in original catalytic activity. § Furthermore, catalyst **1** has shown even better catalytic activity than Cu(NO<sub>3</sub>)<sub>2</sub> salt under homogeneous conditions (Table 1, entry 2). ¶ This novel catalyst **1** was also very active towards acyclic epoxides, as *cis*- and *trans*-2-butene oxides were ring opened to the corresponding products. All products were determined to have a *trans* stereochemistry by NMR, GC and GC/MS analysis with comparison to authentic samples. Styrene oxide was converted to 2-methoxy-2-phenyl ethanol within 3 days, which was the fastest, and the alkoxy group was incorporated exclusively at the benzylic position ( $\alpha$ -carbon) instead of the less hindered  $\beta$ -carbon center to generate primary alcohol. These results indicate that the regiochemistry of the ring opening by catalyst **1** is dependent on the electronic nature of the substrate rather than steric factors. In addition, exclusive attack at the benzylic position of styrene oxide suggests that the more substituted carbon in the intermediate adduct generated from the substitution of labile bridging nitrate in catalyst **1** by the oxide might have a significant cationic character [eqn. (1)].

This cationic character can be stabilized by the phenyl group through conjugation, and therefore the nucleophile would attack the more cationic carbon site to give *trans*-2-methoxy-2-phenyl ethanol. To our knowledge, this is the first example that a Cu-containing self-assembly coordination compound can carry out the ring opening of epoxide with methanol, while the



discrete Cu(II) molecule **2** did not catalyze the alcoholysis of epoxide (Table 1, entry 3).

In summary, we have shown a new structure in coordination polymer **1** containing btp-bridged tetranuclear Cu(II) units weakly connected by nitrate ions. With acetate counteranions however, a discrete Cu(II) molecule, **2**, was obtained. This result suggests that both the Jahn–Teller effect of Cu(II) and the counteranion effect are important for the construction of coordination polymers. We have also reported for the first time that Cu-containing **1** is an efficient heterogeneous catalyst for regioselective ring opening of epoxide with methanol. This catalyst system appears to be an efficient, mild, and easily recyclable method for the alcoholysis of epoxides.

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## Notes and references

† A water solution of Cu(NO<sub>3</sub>)<sub>2</sub> was carefully layered with a methanol solution of btp ligand. Anal. calc. for C<sub>27</sub>H<sub>21</sub>Cu<sub>2</sub>N<sub>25</sub>O<sub>12</sub>, **1**: C, 31.96; H, 2.23; N, 34.49. Found: C, 32.95; H, 2.31; N, 34.53%.

For C<sub>22</sub>H<sub>20</sub>CuN<sub>14</sub>O<sub>4</sub>, **2**: C, 43.45; H, 3.32; N, 32.26. Found: C, 43.45; H, 3.30; N, 32.23%.

‡ Crystal data for compound **1**: C<sub>27</sub>H<sub>21</sub>Cu<sub>2</sub>N<sub>25</sub>O<sub>12</sub>, 0.12 × 0.11 × 0.10 mm<sup>3</sup>, FW = 1014.77, triclinic, *a* = 11.1473(3), *b* = 13.3356(3), *c* = 13.4689(3) Å, *a* = 78.475(2), *β* = 70.419(2), *γ* = 76.033(2)°, *V* = 1815.12(8) Å<sup>3</sup>, *Z* = 2, *μ*(Mo-Kα) = 1.274 mm<sup>-1</sup>, 23632 measured reflections [*R*(int) = 0.073] were used in all calculations, final *R* = 0.0751 (*R*<sub>w</sub> = 0.1003) with reflections having intensities greater than 2σ, GOF(*F*<sup>2</sup>) = 1.043. CCDC reference number 196739.

Crystal data for compound **2**: C<sub>22</sub>H<sub>20</sub>CuN<sub>14</sub>O<sub>4</sub>, 0.35 × 0.3 × 0.25 mm<sup>3</sup>, FW = 644.09, triclinic, *a* = 6.867(3), *b* = 9.304(2), *c* = 10.935(4) Å, *a* = 93.40(2), *β* = 102.42(3), *γ* = 97.11(2)°, *V* = 674.3(4) Å<sup>3</sup>, *Z* = 1, *μ*(Mo-Kα) = 0.877 mm<sup>-1</sup>, 2882 measured reflections [*R*(int) = 0.0152] were used in all calculations, final *R* = 0.0405 (*R*<sub>w</sub> = 0.1026) with reflections having intensities greater than 2σ, GOF(*F*<sup>2</sup>) = 1.117. CCDC reference number 196738. See <http://www.rsc.org/suppdata/dt/b3/b301082a/> for crystallographic data in CIF or other electronic format.

§ The decrease in the catalytic activity is presumably due to leaching of

copper metal during the ring opening reaction. To test for leaching we filtered the catalyst after the reaction and allowed the filtered catalyst and the filtrate to react with another aliquot of epoxide. We observed that the ring opening reaction with the filtered catalyst proceeded at 95% of the original rate, while the filtrate showed less than 5% conversion. On the other hand, the powder X-ray diffraction (XRD) pattern of the filtered catalyst after the reaction revealed the same pattern as the original catalyst, suggesting that the original structure of the filtered catalyst has been kept during the reaction.

¶ We will discuss a comparison of homogeneous vs. heterogeneous catalytic activity for the Cu(NO<sub>3</sub>)<sub>2</sub> salt and catalyst **1** elsewhere.

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