Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Structure 751 (2005) 22–28

Journal of MOLECULAR STRUCTURE

www.elsevier.com/locate/molstruc

Structure and heterogeneous catalytic activity of a coordination polymer containing $Cu(NO_3)_2$ and $Cu(H_2O)_2^{2+}$ units bridged alternatively by btp ligands (btp = 2,6-bis(N'-1,2,4-triazolyl)pyridine)

Sung Jin Hong[a], Jin Soo Seo[a], Ji Young Ryu[a], Jung Hwan Lee[a], Cheal Kim[a,*,1], Sung-Jin Kim[b], Youngmee Kim[b,*,2], Alan J. Lough[c]

[a]*Department of Fine Chemistry, Seoul National University of Technology, Seoul 139-743, South Korea*
[b]*Division of Nano Sciences, Ewha Womans University, Seoul 120-750, South Korea*
[c]*Department of Chemistry, University Toronto, Toronto, Ont., Canada M5S 3H6*

Received 24 March 2005; revised 3 May 2005; accepted 3 May 2005
Available online 13 June 2005

Abstract

The reaction of $Cu(NO_3)_2$ containing NH_4PF_6 with btp ligands produced a new polymeric compound **1** containing $Cu(H_2O)_2^{2+}$ and $Cu(NO_3)_2$ units alternatively bridged by btp ligands with H-bonds between copper-bonded water and nitrate oxygen atoms. Crystal Data: $M = 1465.97$, space group $P2/n$, $a = 11.6300(3)$ Å, $b = 12.8000(4)$ Å, $c = 19.2960(6)$ Å, $\beta = 98.6200(19)°$, $V = 2840.03(15)$ Å^3, $Z = 2$, $\mu = 0.926$ mm^{-1}, $Dc = 1.714$ Mg/m^3, $R = 0.0629$, $wR = 0.1614$. The polymeric compound **1** has shown the heterogeneous catalytic activity for the ring opening of epoxides under mild conditions. This catalyst system appears to be an efficient, mild, and easily recyclable method for the alcoholysis of epoxides. In addition, the heterogeneous catalyst **1** has, surprisingly, shown even better catalytic activity than copper salt system in homogeneous condition.

Keywords: Polymeric compound; Copper complex; Crystal structure; Catalyst; Ring opening of epoxide

1. Introduction

Self-assembly of organic ligands and inorganic metal ions is one of the most efficient and widely used approaches for the construction of supramolecular architectures [1]. Owing to their potential as new functional solid materials such as gas or chemical absorption [2], ion-exchange [3], magnetism [4], host–guest chemistry [5], and catalysis [6], interest in self-assembled coordination polymers has grown rapidly. In this field, the coordination chemistry of bidentate rigid or flexible organodiamine ligands has been the main interest. While several types of those organodiamine ligands such as 4,4′-bipyridine [7], 1,2-bis(4-pyridyl)ethene [8], 1,2-bis(4-pyridyl)ethyne [9], 1,2-bis(4-pyridyl)ethane [10], and 1,3-bis(4-pyridyl)propane [11] have been utilized, the angular bifunctional ligands are far less studied [12].

Therefore, in our attempt to investigate the design and control of the self-assembly of coordination polymers with the angular bridging ligands, we initiated a synthetic program for the construction of various supramolecular complexes with interesting extended frameworks based on the angular btp (2,6-bis(N'-1,2,4-triazolyl)pyridine) ligand [13]. We have previously reported that Cu(II) salts with btp ligands produced coordination polymers as well as a monomeric molecule [6d,e]. In all btp-bridged Cu-containing coordination polymers, the geometry of Cu(II) ion has D_{4h} symmetry, and both Jahn–Teller effect and counter anion effect are very important roles for the construction of coordination crystal structures. In addition, the polymeric Cu(II) compounds showed, surprisingly, an unexpected heterogeneous catalytic reactivity and recyclability for alcoholysis of epoxides at ambient temperature. These results have prompted us to design new polymeric compounds as a potential heterogeneous catalyst. Therefore,

---

* Corresponding authors. [1]Tel.: +82 2 970 6693; fax: +82 2 973 9149; [2]Tel.: +82 232 773589; fax: +82 232 772384.

E-mail addresses: chealkim@snut.ac.kr (C. Kim), ymeekim@ewha.ac.kr (Y. Kim).

0022-2860/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2005.05.006

we have synthesized and characterized a new polymeric compound **1** by the reaction of the btp ligand and copper nitrate with NH_4PF_6, and we have examined the reactivity of the polymeric compound **1** as a potential heterogeneous catalyst for the ring opening of epoxides under mild conditions.

Herein, we report crystal structure of another new Cu-containing polymeric compound **1** obtained by the reaction of $Cu(NO_3)_2$ containing NH_4PF_6 with btp ligands, and a systematic study of the heterogeneous catalytic ring opening of epoxides by the polymeric compound **1**.

2. Experimental

2.1. Materials

The btp (2,6-bis(*N*′-1,2,4-triazolyl)pyridine) was synthesized by previous method [13]. 2,6-Dibromopyridine, potassium triazole, methanol and diglyme were purchased from Aldrich and used as received. Epoxides (cyclohexene oxide, cyclopentene oxide, styrene oxide, *cis*-2,3-epoxybutane, *trans*-2,3-epoxybutane) and their products *trans*-diol mono-ethers were also obtained from Aldrich and used without further purification.

2.2. Instrumentation

Elemental analysis for carbon, nitrogen, and hydrogen was carried out by using an EA1108 (Carlo Erba Instrument, Italy) in the Organic Chemistry Research Center of Sogang University, Korea. Product analyses for the ring opening of epoxides were performed on either a Hewlett-Packard 5890 II Plus gas chromatograph interfaced with Hewlett-Packard Model 5989B mass spectrometer or a Donam Systems 6200 gas chromatograph equipped with a FID detector using 30-m capillary column (Hewlett-Packard, HP-1, HP-5, and Ultra 2). PXRD data were obtained using a Rigaku X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å).

2.3. Synthesis of a polymeric compound $[Cu(H_2O)_2–(btp)_2–Cu(NO_3)_2](PF_6)_2$ 1

57.4 mg (0.3 mmol) of $Cu(NO_3)_2$ and 97.8 mg (0.6 mmol) of NH_4PF_6 were dissolved in 20 mL water and carefully layered by 20 mL methanol solution of btp ligand (128.5 mg, 0.6 mmol). Suitable crystals of the compound **1** for X-ray analysis were obtained in a few days. Anal. Calcd. for $C_{36}H_{36}Cu_2F_{12}N_{30}O_{10}P_2$ (1465.97): C, 29.49; H, 2.48; N, 28.67. Found: C, 29.75; H, 2.30; N, 28.58%. IR (KBr): $\nu(\mathrm{cm}^{-1}) = 3446$(brs), 3127(brm), 1615(m), 1527(m), 1481(s), 1384(m), 1282(m), 1218(m), 1141(m), 1223(w), 1070(m), 980(m), 842(s), 799(m), 671(m), 557(m), 468(w).

2.4. Catalytic activity of the polymeric compound 1 and copper salt

Catalytic reaction conditions: epoxides (0.05 mmol) were dissolved in methanol (1 mL), and the polymeric compound (1 mg/FW of $\mathbf{1} = 0.68 \times 10^{-4}$ mmol), which was ground well into appropriate sizes for high surface area but not too small for convenient filtration, was added and shaken at room temperature (450 rpm). Reaction conversion was monitored by GC/GC-Mass analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. All reactions were run at least three times and the average conversion yields are presented. Conversion yield was based on the consumption of the starting epoxide. Reaction conditions for the homogeneous copper salt were the same as above described except that 2×10^{-3} mmol of copper salt was used instead of the polymeric compound **1**.

2.5. Crystallography

Crystal Data: $C_{36}H_{36}Cu_2F_{12}N_{30}O_{10}P_2$, $M = 1465.97$, monoclinic, $T = 150(1)$ K, $a = 11.6300(3)$ Å, $b = 12.8000(4)$ Å, $c = 19.2960(6)$ Å, $\beta = 98.6200(19)°$, $V = 2840.03(15)$ Å^3, space group *P2/n*, $Z = 2$, $\mu(\mathrm{Mo\ K}\alpha) = 0.926\ \mathrm{mm}^{-1}$, $Dc = 1.714\ \mathrm{Mg/m}^3$, $F(000) = 1476$, 20950 reflections measured, 6483 unique ($R_{\mathrm{int}} = 0.0547$) which were used in all calculations, final $R = 0.0629$ ($R_w = 0.1614$) with reflections having intensities greater than 2θ, $\mathrm{GOF}(F^2) = 0.993$. The diffraction data were collected on a Nonius Kappa-CCD diffractometer using Mo Kα ($\lambda = 0.71073$ Å) [14]. The crystal was mounted on a glass fiber under epoxy resin. The CCD data were integrated and scaled using the DENZO-SMN software package [15], and the structures were solved by direct method and refined by using SHEXTL/PC V5.1 [16]. During the refinement it was noticed that one of the PF_6^- anions was highly disordered over several sites and attempts to model the anion were unsuccessful. In addition, what appeared to be a water molecule was also grossly disordered. Ultimately, the contributions from these species were removed using the SQUEEZE option in PLATON [17]. This procedure did not affect the geometry of the rest of the structure, but did improve the precision of the geometric parameters. The contributions of the removed species are included in the empirical formula. All hydrogen atoms were placed in the calculated positions. The crystal and experimental data are given in Table 1. The bond distances and angles are listed in Table 2. The molecular structure was drawn by the Ortep-3 for Windows program [18].

3. Results and discussion

3.1. Structure description

The btp ligands have acted as bridging ligands with different copper salts to form different polymeric

Table 1
Crystal and experimental data for $[Cu(H_2O)_2–(btp)_2–Cu(NO_3)_2](PF_6)_2$

Empirical formula	$C_{36}H_{36}Cu_2F_{12}N_{30}O_{10}P_2$
Formula weight	1465.97
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P2/n*
Unit cell dimensions	$a=11.6300(3)$ Å $\alpha=90°$
	$b=12.8000(4)$ Å $\beta=98.620(19)°$
	$c=19.2960(6)$ Å $\gamma=90°$
Volume	2840.03(15) Å^3
Z	2
Density (calculated)	1.714 Mg/m^3
Absorption coefficient	0.926 mm^{-1}
$F(000)$	1476
Crystal size	$0.30\times0.12\times0.08$ mm^3
θ range	2.72–27.47°
Index ranges (h, k, l)	$-15/15$, $-15/16$, $-24/25$
Reflections collected	20950
Independent reflections	6483 [R(int)$=0.0547$]
Completeness to theta$=27.47°$	99.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.975 and 0.930
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6483/2/386
Goodness-of-fit on F^2	0.993
Final R, wR indices [$I>2\sigma(I)$]	0.0629, 0.1614
R, wR indices (all data)	0.1094, 0.1805
Extinction coefficient	0.0055(8)
Largest diff. peak and hole	0.631 and -0.782 eÅ^{-3}

compounds. With nitrate anions, btp-bridged tetranuclear Cu(II) units were weakly connected by nitrate ions to form a polymeric compound [6d], while double zigzag chains and single zigzag chains were formed with perchlorate anions and sulfate anions, respectively [6e]. The btp ligand has also acted as a monodentate ligand to form a discrete molecule with $Cu(O_2CCH_3)_2$ [6d]. To see the anion effect for construction of polymeric compounds, we added PF_6^- anions to the $Cu(NO_3)_2$ solution with btp ligands. The reaction of $Cu(NO_3)_2$ containing NH_4PF_6 with btp ligands produced a new compound containing $Cu(NO_3)_2$ and units bridged alternatively by btp ligands.

Table 2
Bond distances (Å) and angles (°) for $[Cu(H_2O)_2–(btp)_2–Cu(NO_3)_2](PF_6)_2$

Bond lengths			
Cu(1)–N(1)	2.018(3)	Cu(1)–N(14)	2.041(3)
Cu(1)–O(1)	2.360(3)	Cu(2)–N(8)	2.007(3)
Cu(2)–N(7)	2.008(4)	Cu(2)–O(2)	2.399(3)
Bond angles			
N(1)–Cu(1)–N(1)#1	180.0	N(1)–Cu(1)–N(14)	89.3(11)
N(1)#1–Cu(1)–N(14)	90.7(11)	N(14)–Cu(1)–N(14)#1	180.0
N(1)–Cu(1)–O(1)#1	90.7(11)	N(14)–Cu(1)–O(1)#1	88.9(11)
N(1)–Cu(1)–O(1)	89.3(11)	N(14)–Cu(1)–O(1)	91.1(11)
O(1)#1–Cu(1)–O(1)	180.0	N(8)#2–Cu(2)–N(8)	180.0
N(8)#2–Cu(2)–N(7)	87.8(14)	N(8)–Cu(2)–N(7)	92.2(14)
N(7)–Cu(2)–N(7)#2	180.0	N(8)–Cu(2)–O(2)	91.6(12)
N(8)–Cu(2)–O(2)#2	88.4(12)	N(7)–Cu(2)–O(2)#2	87.1(13)
N(7)–Cu(2)–O(2)	92.9(13)	O(2)#2–Cu(2)–O(2)	180.0

Symmetry transformations used to generate equivalent atoms: #1 $-x+1,-y,-z+1$; #2 $-x,-y+1,-z+1$; #3 $-x+1,-y+1,-z+1$.

Asymmetric unit of the new compound **1** without PF_6^- anions is shown in Fig. 1(a). The complete compound structure is generated by the symmetry operations ($-x+1$, $-y$, $-z+1$), ($-x$, $-y+1$, $-z+1$) and ($-x+1$, $-y+1$, $-z+1$) as shown in Fig. 2(b). Two btp ligands bridge $Cu(NO_3)_2$ units and $Cu(H_2O)_2^{2+}$ units alternatively to form an one-dimensional coordination polymer with H-bonds between copper-bonded water and nitrate oxygen atoms (O1(water)–H···O3(nitrate) and O1(water–H···O4(nitrate) distances of 2.886(1) and 3.126(2) Å, respectively). PF_6^- anions connect each one-dimensional polymer to form a two-dimensional compound with noncovalent interchain C–H···F interaction (C11–H11···F1 distance of 2.430(1) Å) and intrachain C–H···F interactions (C8–H8···F2 and C1–H1···F2 distances of 2.730(1) and 2.66(1) Å, respectively) (Fig. 2). The Cu–N(btp) distances range from 2.007(3) to 2.041(3) Å. The Cu1–O1(water) distance is 2.360(3), and the Cu2–O(nitrate) distance is 2.399(3) Å. The O1(water)–Cu1–O1(water) and O2(nitrate)–Cu2–O2(nitrate) angles are 180° (Table 2).

The coordination of Cu(II) ion in the new compound **1** has also D_{4h} symmetry as previously reported Cu-containing polymeric compounds. The Cu–N(btp) distances of all these Cu-containing polymeric compounds are about 2.0 Å (1.978(3)–2.061(3) Å for nitrate anions, 2.021(2) Å for perchlorate anions, 1.990(4) Å for sulfate anions, and 2.007(3)–2.041(3) Å for the new compound **1** with nitrate and PF_6^- anions). The distances between Cu(II) ion and axial ligands are enlongated (2.359(2)–2.482(2) Å for nitrate anions, 2.398(17) Å for perchlorate anions, 2.469(16) Å for sulfate anions, and 2.360(3)–2.399(3) Å for the new compound **1**) (Table 3). These results indicate that all of the Cu-containing polymeric compounds show D_{4h} symmetry due to Jahn–Teller effect of the electronic configuration of Cu(II). The Cu···Cu distance of this new compound is 8.647(1) Å, that is the shortest distance in these Cu-containing polymeric compound series (Table 3). This is because of H-bonds between copper-bonded water and nitrate oxygen atoms.

In summary, $Cu(NO_3)_2$ and btp ligands produced a different polymeric structure by adding PF_6^- anions. The new polymeric compound **1** contains $Cu(H_2O)_2^{2+}$and $Cu(NO_3)_2$ units alternatively bridged by btp ligands with H-bonds between copper-bonded water and nitrate oxygen atoms. Our study of these Cu-containing btp-bridged polymeric compounds confirms that both Jahn–Teller effect and anion effect are very important roles for construction of polymeric structures.

3.2. Heterogeneous catalytic activity of the new compound 1

Though a huge number of the polymeric compounds have been developed over the past 10 years, their application as heterogeneous catalysts is very rare [6].

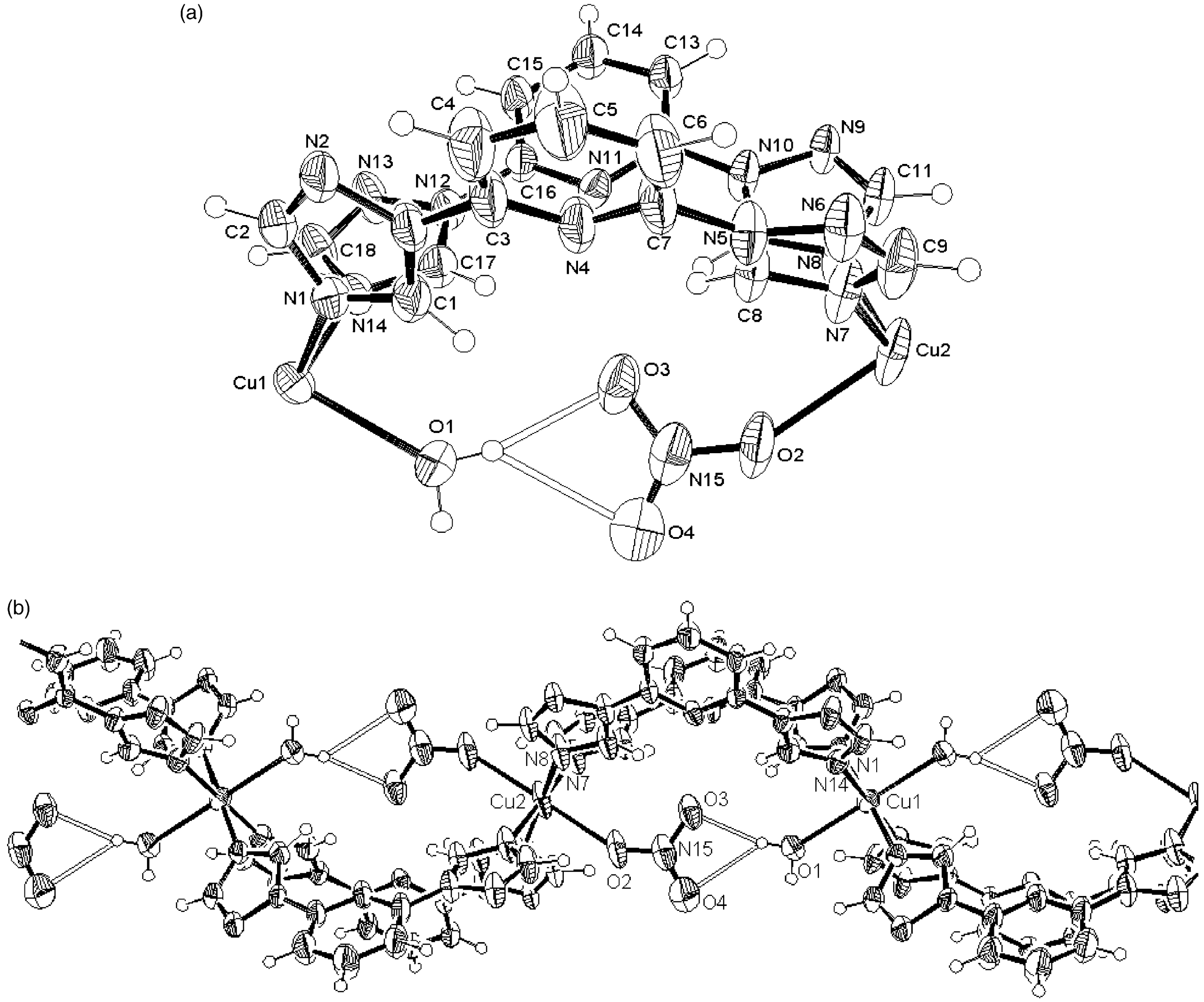
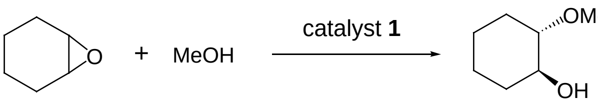


Fig. 1. (a) Asymmetric unit for the polymeric compound **1** with labeling atoms. (b) One-dimensional structure with strong H-bonds between copper-bonded water and nitrate oxygen atoms. PF_6^- anions were omitted for clarity.

Therefore, the use of the polymeric compounds as catalysts for various organic reactions is important and meaningful. We have previously reported that two Cu-containing polymeric compounds were found to be good heterogeneous catalysts [6d,e] that offers the practical advantages of simplifying the separation and isolation of products, and of the potential for catalyst recycling [19]. These results have prompted us to design new polymeric compounds as a potential heterogeneous catalyst. Therefore, we have synthesized and characterized the polymeric compound **1** by the reaction of the btp ligand and copper nitrate with NH_4PF_6 and we have examined the reactivity of the polymeric compound **1** as a potential heterogeneous catalyst for the ring opening of epoxides under mild conditions. The reaction was complete in 4 days when a mixture of the catalyst and cyclohexene oxide in methanol was shaken at room temperature (Eq. (1) and see entry 1 of the third column in Table 4), while a control reaction carried out in absence of the catalyst **1** showed trace amounts of the conversion of the oxide to the product in the same time period. Importantly, the catalyst **1** shows the best efficiency among the polymeric compounds that we have previously reported.



(1)

Then, we have performed another control reaction before further reactivity study with other substrates, because in the catalysis process of the catalyst **1** the leached copper species might catalyze efficiently the ring-opening reaction instead of the catalyst **1**. To test for this possibility we have filtered the catalyst after the ring-opening reaction of cyclohexene oxide and allowed the filtered catalyst and the filtrate to react with another aliquot of cyclohexene oxide, respectively, as shown in

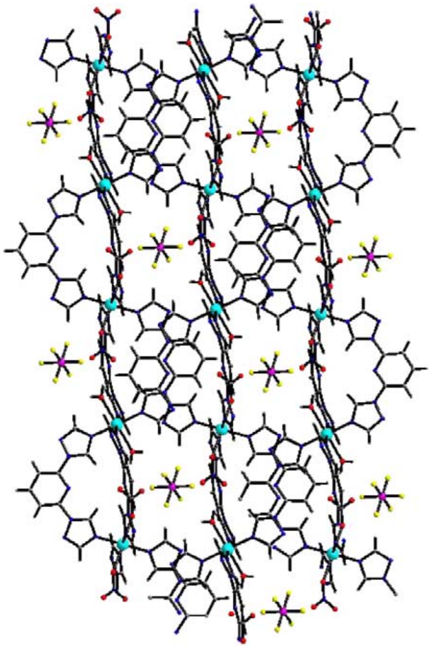


Fig. 2. Two-dimensional structure with noncovalent C–H···F interactions.

the previous study [6d,e]. We have observed that the ring-opening reaction with the filtered catalyst proceeded at 90–95% of the original rate, while the filtrate showed about 5–10% conversion within the same time interval. This result strongly suggests that the dominant reactive species is the heterogeneous catalyst **1**, not the other species. The alcoholysis of other epoxides by the compound **1** was also carried out efficiently, and the results are given in Table 4 (see the third column). Cyclopentene oxide was completely converted by **1**. Moreover, this novel catalyst **1** was active to acyclic epoxides, as *cis*- and *trans*-2-butene oxides were ring-opened to the corresponding products in 10 and 30 days, respectively. All products were found to have a *trans* conformation by NMR, GC and GC/MS analysis, comparing to authentic samples.

More importantly, the catalyst **1** could be easily recovered by a simple filtration and used repeatedly with about 5–10% decrease of the original catalytic activity. These results suggest that the polymeric compound **1** could also be used as a useful heterogeneous catalyst. Decrease of the catalytic activity is presumably due to leaching of copper metal during the ring-opening reaction. 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 (see Fig. 3). Based on these results, we have concluded that the heterogeneous catalyst **1** could be recycled multiple times without a significant loss of activity.

In the regioselectivity study, styrene oxide was converted to 2-methoxy-2-phenyl ethanol within 1.2 days. That is, the methoxy group was, exclusively, incorporated at the benzylic position (α-carbon) instead of the less hindered β-carbon center to generate primary alcohol, showing no steric preference for the methanol nucleophile. In addition, the reactions with **1** have shown the same product patterns for styrene oxide (primary alcohol only) as

Table 3
Comparison of bond distances of Cu(II)-containing polymeric compounds

	Cu–N(btp)	Cu-axial ligand	Cu···Cu
NO_3^{-}[a]	1.978(3)–2.061(3) Å	Cu–O(monodentate nitrate) 2.359(2), 2.275(2) Å Cu–O(bridging nitrate) 2.482(2), 2.420(2) Å	9.659(7), 10.014(7) Å
ClO_4^{-}[b]	2.021(2) Å	2.398(17) Å	9.871(1) Å
SO_4^{2-}[b]	1.990(4) Å	2.469(16) Å	9.341(9) Å
NO_3^{-} and PF_6^{-}[c]	2.007(3)–2.041(3) Å	Cu–O(water) 2.360(3) Å Cu–O(nitrate) 2.399(3) Å	8.647(1) Å

[a] From Ref. [6d].
[b] From Ref. [6e].
[c] This work.

Table 4
Ring opening of epoxides by methanol in the presence of the polymeric compound **1** and the corresponding copper salt at room temperature

Entry	Substrate	**1** (1 mg) (time/days)	$Cu(NO_3)_2+2NH_4PF_6$ (2 mM) (time/days)
1	Cyclohexene oxide	4	15
2	Cyclopentene oxide	30	100
3	*cis*-2,3-Epoxybutane	10	30
4	*trans*-2,3-Epoxybutane	25	50
5	Styrene oxide	1.2 (primary alcohol only)	5 (primary alcohol only)

All epoxides were completely converted to the corresponding products. See Section 2 for the detailed reaction conditions. The concentrations of the complexes used in this study were 0.68 mM for **1** and 2 mM for $Cu(NO_3)_2$, respectively. Control reactions carried out in absence of the catalyst **1** and copper salt showed trace amounts of conversion of the oxide to the product in the same time period.

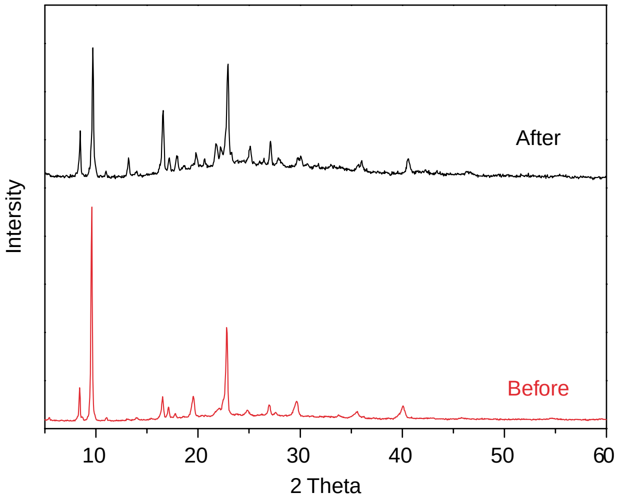
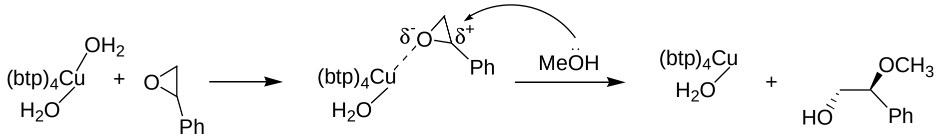


Fig. 3. PXRD patterns of the compound **1** after the catalytic reaction (upper) and before the reaction (down).

the previously reported polymeric compounds [6d,e], indicating that all the catalysts carry out the ring opening of epoxide possibly by the same reaction mechanism. The possible ring-opening mechanism with styrene oxide as a substrate can be proposed as shown in Eq. (2). The more substituted carbon in the intermediate adduct generated from the substitution of the labile water in the catalyst **1** by the oxide might have a significant cationic character which can be stabilized by the phenyl group through conjugation. Then, the nucleophile methanol would attack the more cationic carbon to produce *trans*-2-methoxy-2-phenylethanol.



(2)

In general, since heterogeneous systems for ring opening were reported to show lower reactivity than the corresponding homogeneous systems [20], we compared the heterogeneous and the homogeneous catalytic reactivity with the polymeric compound **1** (1 mg: 0.68 mM) and the corresponding copper salt system, $Cu(NO_3)_2/2NH_4PF_6$ (2 mM), for the ring opening of epoxides in methanol at room temperature. The results from the ring opening of epoxides with the insoluble polymeric compound **1** and the soluble copper salt system are also shown in Table 4 (see the third and fourth columns). As it can be seen, the conversion rates obtained with the polymeric compound **1** were much faster than those of the corresponding copper salt system (9–12 times; the ratio (1:3) of concentration of **1** and copper salt was also considered). That is, the formation of the polymeric compound **1** of the copper salt $Cu(NO_3)_2/2NH_4PF_6$ with btp ligand leads to an increase in reactivity when compared with the corresponding copper salt system. This observation is very significant, since it encourages us to construct new polymeric compounds that could be efficiently used as heterogeneous catalysts friendly to the environment.

4. Supplementary materials

CCDC-266142 for **1** contains the supplementary crystallographic data for this paper. These 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].

Acknowledgements

Financial support from the Korean Science and Engineering Foundation (ABRL R14-2003-014-01-001-0 and R01-2005-000-10490-0(2005)) and the Korea Research Foundation (2002-070-C00053) is gratefully acknowledged.

References

[1] (a) S.R. Batten, R. Robson, Angew. Chem. Int. Ed. 37 (1998) 1460;
(b) D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319;
(c) B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629;
(d) A.N. Khlobystov, A.J. Blake, N.R. Champness, D.A. Lemenovskii, A.G. Majouga, N.V. Zyk, M. Schroder, Coord. Chem. Rev. 222 (2001) 155;
(e) O.R. Evans, W. Lin, Acc. Chem. Res. 35 (2002) 511;
(f) C. Janiak, Dalton Trans. (2003) 2781;
(g) P.J. Hagrman, D. Hagrman, J. Zubieta, Angew. Chem. Int. Ed. 38 (1999) 2638;
(h) S.-L. Zheng, M.-L. Tong, X.-M. Chen, Coord. Chem. Rev. 246 (2003) 185;
(i) S.L. James, Chem. Soc. Rev. 32 (2003) 276.
[2] (a) H. Li, M. Eddaoudi, T.L. Groy, O.M. Yaghi, J. Am. Chem. Soc. 120 (1998) 8571;
(b) M. Kondo, T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, K. Seki, Angew. Chem. Int. Ed. 38 (1999) 140;
(c) S. Noro, S. Kitagawa, M. Kondo, K. Seki, Angew. Chem. Int. Ed. 39 (2000) 2081.
[3] (a) K.S. Min, M.P. Suh, J. Am. Chem. Soc. 122 (2000) 6834;
(b) J. Fan, L. Gan, H. Kawaguchi, W.-Y. Sun, K.-B. Yu, W.-X. Tang, Chem. Eur. J. 9 (2003) 3965.

[4] (a) J.R. Galan-Mascaros, K.R. Dunbar, Angew. Chem. Int. Ed. 42 (2003) 2289;
(b) H.-Z. Kou, B.C. Zhou, S. Gao, R. Wang, Angew. Chem. Int. Ed. 42 (2003) 3288.
[5] (a) C.-Y. Su, Y.-P. Cai, C.-L. Chen, F. Lissner, B.-S. Kang, W. Kaim, Angew. Chem. Int. Ed. 41 (2002) 3371;
(b) M. Oh, G.B. Carpenter, D.A. Sweigart, Angew. Chem. Int. Ed. 42 (2003) 2025;
(c) C.-Y. Su, Y.-P. Cai, C.-L. Chen, M.D. Smith, W. Kaim, H.C. zur Loye, J. Am. Chem. Soc. 125 (2003) 8595.
[6] (a) T. Sawaki, Y. Aoyama, J. Am. Chem. Soc. 121 (1999) 4793;
(b) J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim, Nature 404 (2000) 982;
(c) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, Chem. Commun. (2001) 509;
(d) S.-K. Yoo, J.Y. Ryu, J.Y. Lee, C. Kim, S.-J. Kim, Y. Kim, Dalton Trans. (2003) 1454;
(e) S.J. Hong, J.Y. Ryu, J.Y. Lee, C. Kim, Y. Kim, S.-J. Kim, Dalton Trans. (2004) 2697;
(f) S. Takizawa, H. Somei, D. Jayaprakash, H. Sasai, Angew. Chem. Int. Ed. 42 (2003) 5711;
(g) O.R. Evans, H.L. Ngo, W. Lin, J. Am. Chem. Soc. 123 (2001) 10395.
[7] (a) S. Noro, S. Kitagawa, M. Kondo, K. Seki, Angew. Chem. Int. Ed. 39 (2000) 2081;
(b) Y. Wang, L. Feng, Y. Li, C. Hu, E. Wang, N. Hu, H. Jia, Inorg. Chem. 41 (2002) 6351;
(c) Y. Xu, W. Bi, X. Li, D. Sun, R. Cao, M. Hong, Inorg. Chem. Commun. 6 (2003) 495.
[8] (a) J.M. Knaust, S.W. Keller, Inorg. Chem. 41 (2002) 5650;
(b) J.Y. Lu, A.M. Babb, Inorg. Chem. 40 (2001) 3261;
(c) J.Y. Lu, K.A. Runnels, C. Norman, Inorg. Chem. 40 (2001) 4516.
[9] (a) Y.-B. Dong, R.C. Layland, M.D. Smith, N.G. Pschirer, U.H.F. Bunz, H.-C. zur Loye, Inorg. Chem. 38 (1999) 3056;
(b) L. Carlucci, G. Ciani, D.M. Proserpio, Chem. Commun. (1999) 449;
(c) L. Carlucci, G. Ciani, D.M. Proserpio, J. Chem. Soc., Dalton Trans. (1999) 1799.
[10] (a) Q.-M. Wang, T.C.W. Mak, Inorg. Chem. 42 (2003) 1637;
(b) P.S. Mukherjee, S. Konar, E. Zangrando, T. Mallah, J. Ribas, N.R. Chaudhuri, Inorg. Chem. 42 (2003) 2695.
[11] (a) L. Pan, E.B. Woodlock, X. Wang, K.-C. Lam, A.L. Rheingold, Chem. Commun. (2001) 1762;
(b) E.-Q. Gao, S.-Q. Bai, Z.-M. Wang, C.-H. Yan, Dalton Trans. (2003) 1759;
(c) Y. Niu, Y Song, H. Hou, Y. Zhu, Inorg. Chim. Acta 355 (2003) 151.
[12] (a) Z. Huang, M. Du, H.-B. Song, X.-H. Bu, Cryst. Growth Des. 4 (2004) 71;
(b) Y.-B. Dong, J.-P. Ma, R.-Q. Huang, Inorg. Chem. 42 (2003) 294;
(c) Y.W. Shin, T.H. Kim, K.Y. Lee, K.-M. Park, S.S. Lee, J. Kim, Inorg. Chem. Commun. 7 (2004) 374;
(d) Y. Zheng, M. Du, J.-R. Li, R.-H. Zhang, X.-H. Bu, Dalton Trans. (2003) 1509;
(e) X.-M. Ouyang, B.-L. Fei, T. Okamura, H.-W. Bu, W.-Y. Sun, W.-X. Tang, N. Ueyama, Eur. J. Inorg. Chem. (2003) 618;
(f) C.V. Krishnamohan, S.T. Griffin, R.D. Rogers, Chem. Commun. (1998) 215.
[13] (a) Y. Kim, S.-J. Kim, A.J. Lough, Polyhedron 20 (2001) 3073;
(b) J.Y. Ryu, J.Y. Lee, J.S. Seo, C. Kim, Y. Kim, Appl. Organomet. Chem. 17 (2003) 805;
(c) W.G. Christopher, M.M. Turnbull, Inorg. Chem. Acta 332 (2002) 92;
(d) J.Y. Ryu, J.Y. Lee, S.J. Hong, H.W. Yang, C. Kim, Y. Kim, S.-J. Kim, A.J. Lough, Appl. Organomet. Chem. 18 (2004) 497.
[14] Nonius. Kappa-CCD Server software, Nonius B.V., Delft, The Netherlands, 1997.
[15] Z. Otowinowski, W. Minor, Methods Enzymol. 176 (1997) 307.
[16] G.M. Sheldrick, SHELXTL/PC, Version 5.1 Windows NT Version, Bruker AXS, Inc., Madison, USA, 1998.
[17] A.L. Spek, J. Appl. Cryst. 36 (2003) 3–17.
[18] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.
[19] (a) T.J. Dickerson, N.N. Reed, K.D. Janda, Chem. Rev. 102 (2002) 3325;
(b) Q.-H. Fan, Y.-M. Li, A.S. Chan, Chem. Rev. 102 (2002) 3385;
(c) D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs, Chem. Rev. 102 (2002) 3615;
(d) D. Rechavi, M. Lemaire, Chem. Rev. 102 (2002) 3467;
(e) C.E. Song, S.-G. Lee, Chem. Rev. 102 (2002) 3495;
(f) Y. Kim, S.K. Choi, S.-M. Park, W. Nam, S.-J. Kim, Inorg. Chem. Commun. 5 (2002) 612;
(g) D.W. Yoo, S.-K. Yoo, C. Kim, J.-K. Lee, J. Chem. Soc., Dalton Trans. (2002) 3931;
(h) J. Suh, Acc. Chem. Res. 36 (2003) 562.
[20] (a) R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, Acc. Chem. Res. 31 (1998) 485;
(b) D.A. Annis, E.N. Jacobsen, J. Am. Chem. Soc. 121 (1999) 4147;
(c) M.D. Angelino, P.E. Laibinis, J. Polym. Sci.: Part A: Polym. Chem. 37 (1999) 3888.