

# A copper(II) complex with rare $\mu_{1,1,1}$ -azide ligand: Active catalyst for heterogeneous olefin epoxidation

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## Abstract

A copper(II) complex  $[\text{Cu}_2\text{L}(\mu_{1,1}\text{-N}_3)(\mu_{1,3}\text{-N}_3)(\mu_{1,1,1}\text{-N}_3)]$  (**1**) where **HL** = 4-methyl-2,6-bis(phenylmethyliminomethyl)phenol, with  $\text{N}_2\text{O}$  donor ligand was synthesized and characterized by elemental analysis, FT-IR spectra and X-ray crystallography. X-ray crystallographic study reveals that it is a 1D chain along crystallographic *b* axis and the existence of rare  $\mu_{1,1,1}$ -azide bridging mode. The complex was immobilized on mesoporous silica and the immobilized compound was used as the active catalyst for the oxidation of olefins using *tert*-butyl hydroperoxide as oxidant. The results show that corresponding epoxides were produced in high yield with high selectivity. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Cu(II) complex; Azide; Heterogeneous catalysis; Olefin epoxidation

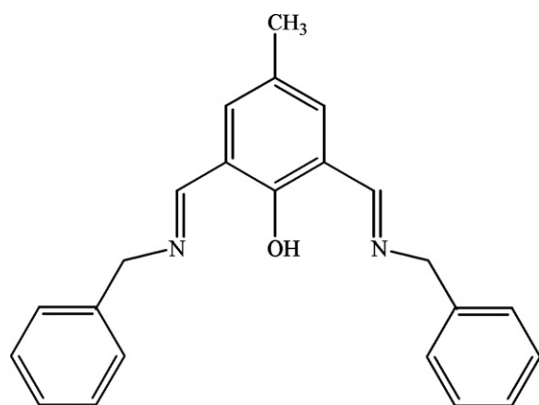
In homogeneous catalysis excellent catalytic efficiencies are noted in the epoxidation of olefin [1] under liquid phase conditions where the catalyst, substrate, oxidant and product(s) are in a single phase with the solvent. But the major problems encountered in homogeneous catalysis are (i) poor recycling efficiencies of the catalysts and (ii) separation of the product(s) from the reaction mixture. A reusable catalyst which would show minimum effort for its separation is the most desirable one in industrial process. For this reason, attention has been triggered on the use of heterogeneous catalysts for over the last few decades [2]. The presence of a heterogeneous catalyst can be achieved in two ways as a separate solid phase under biphasic [3] or triphasic [4] conditions. The heterogenization of transition metal based catalysts onto different supports, e.g. silica [5], polymers [6] and mesoporous materials [7] has been made effectively in recent years. This enables to get advantages of both homogeneous and heterogeneous catalytic systems. Our group has recently synthesized several Ni(II) complexes and explored their application as

the active catalysts in heterogeneous epoxidation reaction of alkenes [8]. In this communication, we report the synthesis and crystal structure of a copper(II) complex  $[\text{Cu}_2\text{L}(\mu_{1,1}\text{-N}_3)(\mu_{1,3}\text{-N}_3)(\mu_{1,1,1}\text{-N}_3)]$  (**1**) where **HL** = 4-methyl-2,6-bis(phenylmethyliminomethyl)phenol. Interestingly, the study of X-ray crystallography reveals that three different binding modes of the azide moiety namely, the  $\mu_{1,1}\text{-N}_3$ ,  $\mu_{1,3}\text{-N}_3$  and  $\mu_{1,1,1}\text{-N}_3$ , occur in complex **1** thereby leading to a rare situation in Cu(II) chemistry [9]. Complex **1** forms 1D chain along the crystallographic *b* axis. The catalytic oxidation of cyclohexene, styrene,  $\alpha$ -methyl styrene and *trans*-stilbene has been carried out heterogeneously with complex **1** immobilized on highly ordered mesoporous silica using *tert*-butyl hydroperoxide as the oxidant. Reasons for the use of copper-containing catalysts are manifold (i) it is very cheap and available abundantly in nature and (ii) it plays tremendous role in biological systems (being the third most abundant trace metal in body) acting as metalloenzymes [10].

The ligand, 4-methyl-2,6-bis(phenylmethyliminomethyl)phenol (**Scheme 1**), was prepared according to a published procedure [11]. Complex **1** was prepared by adding a 5 mL methanolic solution of **HL** (0.068 g, 0.2 mmol) to

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HL

Scheme 1.

a solution of copper(II) perchlorate hexahydrate (0.148 g, 0.4 mmol) in 5 mL of methanol under stirring condition. To this 5 mL of an aqueous solution of sodium azide (0.039 g, 0.6 mmol) was added slowly and the mixture was finally stirred for 30 min. It was refluxed for 1 h and then cooled to room temperature and filtered. Needle shaped black single crystals for X-ray diffraction were obtained from the filtrate on slow evaporation after 2 days (Yield: 0.083 g, 70%). The results of C, H, N analysis were in good agreement with the calculated values. (Anal. Calc. for  $C_{23}H_{21}Cu_2N_{11}O$ : C, 46.42; H, 3.56; N, 25.90. Found: C, 46.35; H, 3.37; N, 26.02%). FT-IR (KBr phase) ( $cm^{-1}$ ): 3465 br, 2086 vs, 2057 vs, 1639 s, 1562 s, 1454 w, 1342 m, 825 w, 759 m, 705 m (br, broad; w, weak; m, medium; s, strong; vs, very strong).

Perchlorate and azide salts of metal ions are potentially explosive. Only small quantity of the materials should be handled and should be handled with care.

Complex **1** crystallizes in the monoclinic system, space group  $P2_1/n$  (No. 14). A perspective view of complex **1** with atom numbering scheme, selected bond lengths and bond angles is shown in Fig. 1. The X-ray [12] analyses show that the asymmetric unit consists of two crystallographically independent  $Cu^{2+}$ , one dinucleating ligand, 4-methyl-2,6-bis(phenylmethyliminomethyl)phenolate and three different types of azide ligand, one  $\mu_{1,1}$ , second one  $\mu_{1,3}$  and the other  $\mu_{1,1,1}$  bridging mode. Cu1 adopts distorted octahedral geometry whereas Cu2 is in a distorted square pyramidal geometry. Hexacoordinated Cu1 atom is linked by a  $\mu_2$ -phenoxo oxygen atom (O1) and a nitrogen atom N1 of the binucleating ligand, one nitrogen atom, N6 of  $\mu_{1,1}$ -azide group which also binds to Cu2 atom of the same asymmetric unit, one N9 atom of  $\mu_{1,1}$ -azide group, one N5\_b (symmetry code:  $-x, 1-y, 1-z$ ) atom of  $\mu_{1,3}$ -azide group and one N6\_a (symmetry code:  $-x, -y, 1-z$ ) atom of  $\mu_{1,1,1}$ -azide ligand from another asymmetric unit. O1, N1, N6 and N9 atoms form the square plane and the rest two nitrogen atoms occupy the axial position of the octahedron. The Cu1–O bond length is 2.0001(19) Å. The

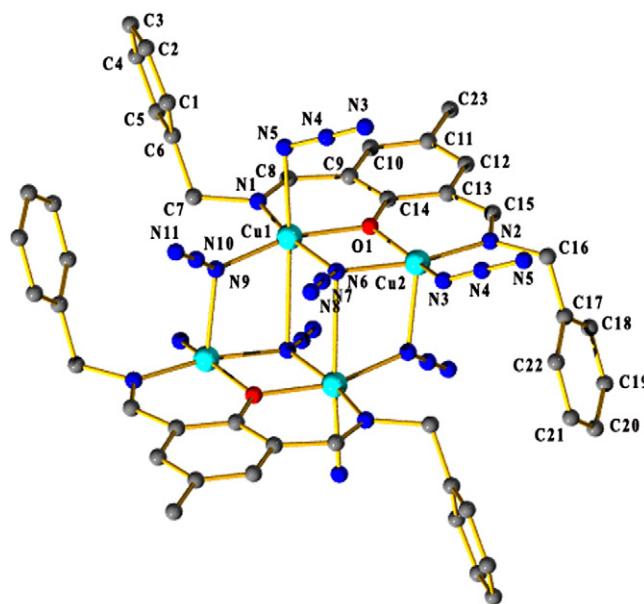


Fig. 1. A perspective view of complex **1** with the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles ( $^\circ$ ): Cu1–O1, 2.0001(19); Cu1–N1, 1.952(3); Cu1–N6, 1.946(3); Cu1–N9, 1.978(3); Cu1–N6\_a, 2.771(3); Cu1–N5\_b, 2.382(4); Cu2–O1, 2.017(2); Cu2–N2, 1.964(3); Cu2–N3, 1.975(3); Cu2–N6, 1.985(3); Cu2–N9\_a, 2.297(3); O1–Cu1–N1, 91.59(12); O1–Cu1–N6, 76.17(12); O1–Cu1–N9, 164.71(12); O1–Cu1–N6\_a, 91.56(10); O1–Cu1–N5\_b, 95.39(11); N1–Cu1–N6, 167.65(15); N1–Cu1–N9, 96.15(14); N1–Cu1–N6\_a, 97.47(12); N1–Cu1–N5\_b, 90.25(13); N6–Cu1–N9, 95.40(14); N6–Cu1–N6\_a, 81.46(12); N5\_b–Cu1–N6, 92.52(13); N6\_a–Cu1–N9, 74.40(12); N5\_b–Cu1–N9, 97.74(13); N5\_b–Cu1–N6\_a, 169.47(11); O1–Cu2–N2, 92.51(11); O1–Cu2–N3, 158.43(12); O1–Cu2–N6, 74.94(11); O1–Cu2–N9\_a, 91.38(11); N2–Cu2–N3, 101.57(14); N2–Cu2–N6, 167.00(15); N2–Cu2–N9\_a, 97.48(13); N3–Cu2–N6, 89.60(14); N3–Cu2–N9\_a, 102.75(13); N6–Cu2–N9\_a, 86.38(13); ( $a = -x, -y, 1-z$ ,  $b = -x, 1-y, 1-z$ ).

Cu1–N bond distances vary from 1.946(3) to 2.771(3) Å. The axial Cu1–N bond distances are longer compared to the other distances. Cu1–N $_{\mu_{1,1,1}}$  distance (2.771(3) Å) is comparable with the reported distance of this type of Cu–N bond [9]. Cu2 atom is coordinated to the same  $\mu_2$ -phenoxo oxygen atom O1 and nitrogen atom N2 of the binucleating ligand, nitrogen atoms N6 of  $\mu_{1,1}$ -azide group, N3 atom of  $\mu_{1,3}$ -azide group and N9\_a atom from another asymmetric unit of the  $\mu_{1,1}$  mode of azide group. The basal plane is formed by the O1, N2, N6 and N3 atoms while the apical position is occupied by the N9\_a. The Cu2–O bond length is 2.017(2) Å. The basal Cu2–N bond distances vary from 1.964(3) to 1.985(3) Å. The apical Cu2–N distance (2.297(3) Å) is quite longer than the basal metal-donor distances. All the Cu–N distances are in good agreement with reported values [9,13]. The atoms of the basal plane are coplanar to within 0.103 Å, with the Cu2 atom being slightly displaced out of the plane towards N9\_a atom by 0.179 Å. Cu2 atom is located in a slightly distorted square pyramidal environment as revealed by the trigonal index,  $\tau = 0.143$ . The value of  $\tau$  is defined as the difference between the two largest donor-metal-donor angles divided

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