Inorganica Chimica Acta 409 (2014) 202–207

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Single end to end azido bridged adduct of a tridentate schiff base copper(II) complex: Synthesis, structure, magnetism and catalytic studies

Sourajit Banerjee [a], Chandan Adhikary [a,*], Corrado Rizzoli [b], Rammohan Pal [c]

[a] Department of Chemistry, Government College of Education, Burdwan 713102, India
[b] Departimento di Chimica, Parco Area delle Scienze 17/A, 43124 Parma, Italy
[c] Department of Chemistry, Acharya Jagadish Chandra Bose College, Kolkata 700020, India

ARTICLE INFO

Article history:
Received 23 July 2013
Received in revised form 6 September 2013
Accepted 17 September 2013
Available online 30 September 2013

Keywords:
Copper(II)-azido complex
Schiff-base ligand
X-ray crystal structure
Magnetic study
Olefin oxidation

ABSTRACT

Copper(II) azido complex $[CuL(\mu_{-1,3}\text{-}N_3)]_n$ (**1**) of a NNO donor tridentate Schiff base (HL = 2-[1-(methyl-amino-ethylimino)-methyl]-phenol containing single end-to-end $\mu_{-1,3}$-azido bridged 1D infinite chain has been synthesized and characterized by elemental analysis, FT-IR spectroscopy. X-ray single crystal structure analysis reveals that in **1**, the central copper(II) ion displays a distorted square pyramidal coordination geometry and are linked by single EE azide bridges forming chains running parallel to the crystallographic *b* axis. The magnetic interaction revealed that **1** is antiferromagnetic in nature ($J = -19.5\ (\pm 0.2)\ \text{cm}^{-1}$). The catalytic activity of the complex is investigated in a series of solvents for the oxidation of olefins using *tert*-butyl-hydroperoxide as oxidant. The results showed highest selectivity for **1** in acetonitrile medium.

1. Introduction

The Schiff bases derived from the mono-condensation of diamines with carbonyl compounds (salicylaldehyde, o-hydroxy-acetophenone, acetylacetone or benzoylacetone) are a group of mono-negative NNO donor ligands which readily react with transition metal ions and auxiliary ligand to form mono and poly-nuclear complexes with varied functionalities and applications. Depending on the number, nature and relative position of the donor atoms of a Schiff base, the ligand allows a good control over the stereochemistry of the metallic centers in homo- and heteropolynuclear complexes [1–3]. All these advantages make Schiff bases privileged ligands in the effort to synthesize metal complexes having relevance to bioinorganic chemistry, catalysis, encapsulation, transport and separation processes [4]. Copper(II) Schiff base complexes find wide applicability in the field of catalysis, antimicrobial activities, synergistic action on insecticides, plant growth regulator, antitumor and cytotoxic activity, harmonic generation activity etc. [5]. Furthermore copper(II) azido complexes have also received intense attention in the field of molecular magnetism [6]. Keeping such observations in mind we have directed our investigation in synthesizing Schiff base copper(II) complexes and their azido adducts and simultaneous study of their magnetic property and catalytic efficacy. Schiff base copper complexes can now be extensively used as active catalysts in several oxidation reactions both in homogeneous [7–11] and heterogeneous condition [12–16]. So far our knowledge goes, catalytic oxidations involving Schiff base copper azido complexes have been scarcely reported in the literature [17–18]. Although molecular oxygen and hydrogen peroxide (30%, an environmental friendly oxidant) catalyzed epoxidation reactions are well documented in the literature yet due to the explosive nature of hydrogen peroxide, the industrial processes still mainly have to rely on *tert*-butyl-hydroperoxide (TBHP) [19].In industrial epoxidation involving Halcon-Arco and Sumitomo processes [20–23] alkyl-hydroperoxides are used on a large scale. The recycling of co-products *e.g. tert*-BuOOH has been realized in the Sumitomo process. Notably, TBHP has seldom been used as an oxidant in the investigations of the catalytic efficiency of copper(II) complexes towards epoxidation/oxidation reactions in homogeneous medium. Here we report the synthesis, characterization, X-ray single crystal structure and magnetic study of an azido derivative of a Schiff base Cu(II) complex. The catalytic epoxidation acivity of the complex has been investigated in a variety of alkenes using *tert*-butyl-hydroperoxide as an oxidant.

---

* Corresponding author. Tel.: +91 0342 2656853.
E-mail address: cadhikary123@gmail.com (C. Adhikary).

0020-1693/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ica.2013.09.032

2. Experimental

2.1. Materials

All solvents used are of AR grade and were distilled and dried before use. Salicylaldehyde, and copper(II) nitrate trihydrate were purchased from Merck (India) and used as received. Styrene, α-methylstyrene, cyclooctene, cyclohexene, *tert*-BuOOH (70% aq.), N-methylethylenediamine were purchased form Aldrich and used as received.

2.2. Physical measurements

Microanalysis (CHN) was performed in a Perkin Elmer 240 elemental analyzer. IR spectra were recorded on a Bruker Alpha T 200140 FT-IR spectrometer. Absorption spectra were studied on Shimadzu UV2100 UV–Vis recording spectrophotometer. Magnetic measurements of **1** were performed with a Cryogenic SQUID S600 magnetometer operating between 2 and 300 K at an applied field of 1T. Magnetic data were corrected for the diamagnetism of the sample holder, measured in the same range of temperature and field, and for the intrinsic diamagnetism of the samples estimated through Pascal's constants. GC analysis was carried out with an Agilent Technologies 6890N network GC system equipped with a fused silica capillary column (30 m × 0.32 mm) and a FID detector.

2.3. Synthesis

Caution! Although our samples never exploded during handling, azide metal complexes are potentially explosive: only a small amount of material should be prepared and it should be handled with care.

2.3.1. Synthesis of [CuL($\mu_{1,3}$-N_3)] (*1*)

A methanolic solution (20 ml) of N-methylethylenediamine (1 mmol, 0.074 g) was added to a methanolic solution (20 ml) of salicylaldehyde (1 mmol, 0.122 g). The reaction mixture was refluxed for 1 h and evaporated on a water bath until the volume reduced to ca. 5 ml to obtained a viscous yellow orange liquid. Copper(II) nitrate trihydrate (1 mmol, 0.241 g) dissolved in methanol was added and the mixture was refluxed for another 30 min Finally 5 ml aqueous solution of NaN_3 (2 mmol, 0.130 g) was added dropwise to the mixture with continuous stirring and the resulting solution was then filtered. The green filtrate was kept in the open atmosphere. From the green solution block pale yellow crystals were formed within few days. (Yield ca. 80%). *Anal.* Calc. for $C_{10}H_{13}CuN_5O$ (282.79): C, 42.4; H, 4.6; N, 24.8. Found: C, 42.2; H, 4.8; N, 24.9%. FTIR (cm^{-1}): $\nu_{as}(N_3)$, 2030; $\nu_s(N_3)$, 1332 and 1345; $\delta(N_3)$, 620; $\nu(C{=}N)$, 1640 cm^{-1}. λ_{max}/nm (methanol), 299; 266; 360; 621.

2.4. X-ray crystallography

2.4.1. X-ray Crystal data of [CuL($\mu_{1,3}$-N_3)]$_n$ (*1*)

$C_{10}H_{13}CuN_5O$, $M = 282.79$, Orthorhombic, space group $P2_12_12_1$, $a = 7.1631(9)$, $b = 8.3919\ (10)$, $c = 19.652\ (2)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1181.3\ (2)$ Å^3, $Z = 4$, $R_{int} = 0.050$, $D_{calc.} = 1.590$ Mg m^{-3}, $F_{000} = 580$, $\mu = 1.84$ mm^{-1}, dimensions = 0.16 × 0.10 × 0.07 mm, $T = 295$ K.

2.4.2. X-ray single crystal structure determination of [CuL($\mu_{1,3}$-N_3)]$_n$ (*1*)

Single crystal X-ray diffraction data for **1** were mounted on a Bruker SMART 1000 CCD diffractometer at room temperature using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and were used to measure cell dimensions and diffraction intensities. The crystals were found to belong to the orthorhombic system and the systematic absences identified the correct space group as $P2_12_12_1$. For data collection, data reduction and cell refinement the programs APEX2 and SAINT [24] were used. The structure was solved by direct methods using SIR97 [25] and refined by SHELX97-L [26]. The N-bound H atom was located in a difference Fourier map and refined isotropically. All other H atoms were positioned geometrically and refined using a riding model, with C–H = 0.93–0.97 Å and with *U*iso = 1.2 *U*eq(C) or 1.5 *U*eq(C) for methyl H atoms. A rotating model was used for the methyl group.

2.5. Catalytic reactions

The homogeneous oxidation reactions were carried out under stirring in a two-neck round-bottom flask fitted with a water condenser and placed in an oil bath at 333–353 K. The proportions used were: substrate (10 mmol), solvent (10 ml) and catalyst (0.005 mmol). *tert*-BuOOH (20 mmol) was added immediately before the start of the reaction and the mixture was stirred continuously for 24 h. At different time intervals, the products were collected from the reaction mixture and analyzed by gas chromatography. The products were identified by known standards.

3. Results and discussion

3.1. Description of structure of [CuL($\mu_{1,3}$-N_3)]$_n$ (*1*)

The structure determination reveals that the neutral [CuL($\mu_{-1,3}$-N_3)]$_n$ units in complex **1** are connected by the single $\mu_{-1,3}$-azido ligands to form an infinite 1D polymeric chains. A perspective view of the chain structure running parallel to the crystallographic *b*-axis is depicted in Fig. 1 and an Ortep diagram of the monomer with atom labeling scheme is shown in Fig. 2.

In **1**, each Cu(II) ion is placed in a distorted square pyramidal environment, in which the basal plane is made up by two nitrogens, N(1) and N(2), one deprotonated phenoxo oxygen O(1), of the tridentate Schiff base ligand HL and one azido nitrogen, N(3). A second azido nitrogen, N(5)^{i} from a symmetry related unit (symmetry operation, i = $-x + 1$, $y + 1/2$, $-z + 1/2$) at the apical position occupies the remaining fifth position of the coordinated polyhedron. Thus the azido nitrogen N(5) bridges two copper(II) centers. Selected bond lengths and angles are listed in Table 1.

The basal Cu–N(3)(azido) distance [1.973(4) Å] is an intermediate between the other two basal Cu–N(1) and Cu–N(2) distances [1.940(4), 2.054(4) Å, respectively], while the apical Cu–N(5)^{i} (symmetry operation i = $-x + 1$, $y + 1/2$, $-z + 1/2$) distance [2.506(4) Å] is remarkably longer, indicating a rather weak axial coordinative interaction. The axial Cu–N distance is significantly longer than those observed in other similar single end-to-end azido bridged 1D copper(II) complexes [6].

The diagonal basal angles, N(1)–Cu(1)–N(3) = 165.54(16)° and N(2)–Cu(1)–O(1) = 176.51(15)° and the basal–apical angles, O(1)–Cu(1)–N(5)^{i} = 87.66(12)° and N(1)–Cu(1)–N(5)^{i} = 94.61(5)° (symmetry operation i = $-x + 1$, $y + 1/2$, $-z + 1/2$) significantly deviate from the ideal values. The trigonality index τ (0.18) [$=\Phi_1-\Phi_2$)/60, where Φ_1, Φ_2 are the two largest L–M–L angles of the coordination sphere] as calculated for the pentagonal copper site [27] confirms the square pyramidal environment. The Cu(1)–N(3)···N(5)–Cu(1)^{ii} torsion angle (symmetry operation ii = $1 - x$, $-1/2 + y$, $1/2 - z$) is −90.3(2)° and the angle formed by the lines through the Cu(1)–N(3) and N(5)–Cu(1)^{ii} (symmetry operation ii = $1 - x$, $-1/2 + y$, $1/2 - z$) bonds is 99.73(13)°. The Cu···Cu distance is 5.0748(8) Å.