



Catalytic Efficacy of 2,2'-Bipyridine Cobalt(II) Complex: Hydrothermal Synthesis, X-Ray Structure and Aerobic Epoxidation of Alkenes

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A mononuclear cobalt(II) complex, $[\text{Co}(\text{bpy})_2(\text{NO}_3)](\text{NO}_3) \cdot 3\text{H}_2\text{O}$ (**1**) (bpy = 2,2'-bipyridine) has been synthesized hydrothermally and the crystal structure was characterized by X-ray crystallography. Complex **1** is capable of activating aerobic oxygen at atmospheric pressure. $[\text{Co}(\text{bpy})_2(\text{NO}_3)](\text{NO}_3) \cdot 3\text{H}_2\text{O}$ (**1**) was used as an active catalyst for the aerobic epoxidation of various alkenes with isobutyraldehyde as co-reductant in acetonitrile medium. Complex **1** catalyzes the epoxidation reaction efficiently, which reflected in high yield of products with desired selectivity.

Keywords: Cobalt(II), 2,2'-Bipyridine, Hydrothermal synthesis, X-ray crystallography, Epoxidation, Alkene.

INTRODUCTION

The catalytic epoxidation of alkenes is a reaction of great industrial interest given the numerous applications of epoxides as precursors in the production of valuable chemicals [1]. Conventionally, the epoxidation of alkenes is carried out by stoichiometric amount of peracids [2]. However, peracids are expensive, corrosive, non-selective for the epoxide formation, lead to the formation of undesirable products, so create a lot of waste [3]. Therefore, many alternative methodologies using single oxygen donor reagents such as NaIO_4 , NaOCl , PhIO , RCOOOH , KHSO_5 and H_2O_2 have been reported for the epoxidation of alkenes. However, these methods are either expensive or not environment friendly. Another commercial manufacturing method of epoxides is the chlorohydrin process, which causes serious environmental pollution. Hence, from both economic and environmental viewpoint and to avoid co-products, the epoxidation of alkenes with O_2 or naturally cheap air over effective catalysts is a promising and attractive method.

Metal complexes catalyzed homogeneous epoxidation system could produce high yield of epoxide in presence of an aldehyde which acts as a reducing agent for the reductive activation of oxygen [4]. Many efforts have been made to seek methods of epoxidation with molecular oxygen or air [5-13]. Among all

these methods, Mukaiyama epoxidation system [8,10-13] uses metal complexes such as Ni(II), Mn(III), Co(II) or Fe(III) as the homogeneous catalysts, aldehydes or alcohols as the reductants is confirmed to be very effective. Subsequently, many metal catalysts such as manganese complex [14,15], metalloporphyrins [16-19], cobalt-containing molecular sieves [20] demonstrated highly catalytic performance for the aerobic oxidation in the presence of aldehyde.

Cobalt ions and cobalt complexes are used as catalysts for the selective oxidation of alkanes and alkylbenzenes with O_2 [21]. In the recent past, Budnik and Kochi [22] have used cobalt complexes for the epoxidation of alkenes with molecular oxygen. Using a cobalt(II) complex, the catalytic oxidation of terminal olefins, including styrene, by O_2 to the corresponding 2° ketones and 2° alcohols has been reported [23,24]. Cobalt-salen complexes were reported to show catalytic activity for epoxidation of styrene with O_2 , where isobutyraldehyde was used as a sacrificial co-reductant [25]. Again, one of the major drawbacks of using metal salens in homogenous solutions is the formation of μ -oxo dimers and other polymeric species, which leads to irreversible catalyst deactivation. Iqbal *et al.* [26,27] studied various Schiff-base cobalt complexes for the epoxidation of alkenes including steroids and terpenoids in the presence of either aliphatic aldehyde or β -ketoester. Saha

et al. [28] studied the epoxidation of alkenes over a cobalt(III) Schiff-base complex in the presence of molecular oxygen using isobutyraldehyde [28]. Co(II) salen derived Jacobsen type complexes [16] were used as catalysts for aerobic asymmetric epoxidation [29]. Oxidation of monoterpenes with O₂ using CoCl₂ as catalyst has been reported, and it was found that allylic oxidation takes place predominantly [30]. In the presence of propionaldehyde diethyl acetal as the reducing agent, bis-(diketonato)cobalt(II) derivatives, *i.e.* Co(acac)₂ are active in the aerobic epoxidation of alkenes [31]. Cobalt based heterogeneous catalysts for aerobic epoxidation of alkenes are also reported in recent past [32-40].

Herein, the synthesis, characterization, X-ray single crystal structure of a new mononuclear cobalt(II) complex and its catalytic efficacy towards aerobic epoxidation of olefins in presence of isobutyraldehyde as co-reductant are reported.

EXPERIMENTAL

The chemicals *viz.* Co(NO₃)₂·6H₂O, styrene, cyclooctene, cyclohexene, 1-hexene, 1-octene, limonene, 2,2'-bipyridine were purchased from Aldrich and used as received. The solvents were purchased from Merck (India) and distilled before use.

Synthesis of [Co(bpy)₂(NO₃)](NO₃)·3H₂O (1): Complex [Co(bpy)₂(NO₃)](NO₃)·3H₂O (**1**) was synthesized hydrothermally. Compound **1** was grown as red block crystals in a Teflon-lined Parr acid digestion bomb. For digestion, cobalt(II) nitrate, 2,2'-bpy and aspartic acid were added in the molar ratio of 1:1:1 in 10 mL of distilled water and kept at 160 °C for 3 days followed by slow cooling at the rate of 5 °C/h to room temperature. The crystals thus formed were filtered off, washed first with water and then with a small amount of ethyl alcohol and dried in air (yield 75 %, based on cobalt). Anal. calcd. (found) % for C₂₀H₂₂N₆O₉Co: C, 50.97 (50.50); H, 4.00 (4.20); N, 15.29 (15.50); Co, 10.72 (10.51). The crystal structure of [Co(2,2'-bpy)₂(NO₃)]NO₃·5H₂O has been reported previously [41], however, the synthetic procedure was different.

X-ray single crystal structure determination of 1: X-Ray diffraction data of complex **1** was collected at 293(2) K on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Determination of integrated intensities and cell refinement were performed with the SAINT [42] software package using a narrow-frame integration algorithm. An empirical absorption correction (SADABS) [43] was applied. The structure was solved by direct method and refined using full-matrix least-squares technique against F^2 with anisotropic displacement parameters for non-hydrogen atoms with the programs SHELXS-97 and SHELXL-97 [44]. All hydrogen atoms were located from difference Fourier map and treated as a suitable riding models with isotropic displacement parameters derived from their carrier atoms and were refined with isotropic thermal parameters (except for the hydrogen atoms of water molecules). A summary of crystal data and relevant refinement parameters for complex **1** is collated in Table-1. The molecular graphics softwares used were ORTEP III [45] and MERCURY 1.2.1 [46].

Catalytic epoxidation reaction: The catalytic epoxidation reactions were carried out under air in a batch reactor at 60 °C.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE
REFINEMENT PARAMETERS FOR COMPLEX 1

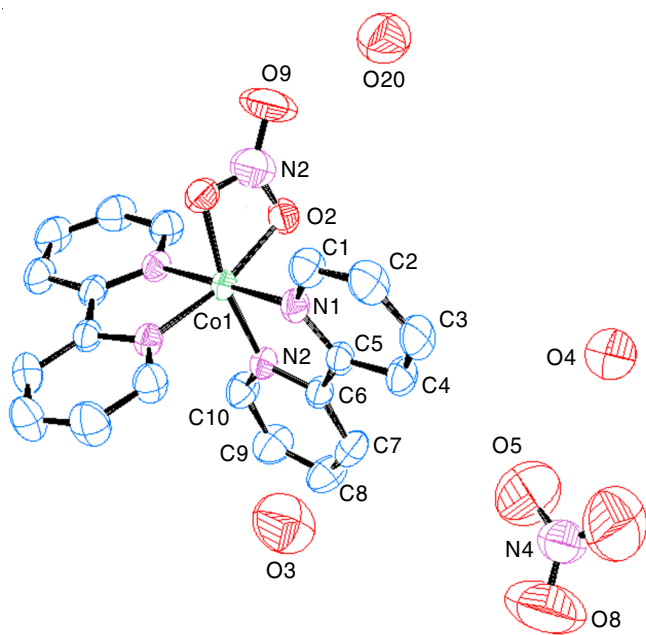
| Parameters | |
|--|--|
| Chemical formula sum | C ₂₀ H ₂₂ N ₆ O ₉ Co |
| Chemical formula weight | 549.36 |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Cell dimensions | a = 10.9317(3) Å; b = 16.0118(3) Å; c = 14.4587(5) Å |
| β (°) | 102.017(2) |
| V (Å ³) | 2475.33(12) |
| Z | 8 |
| Temperature (K) | 293(2) |
| D _c (g cm ⁻³) | 1.571 |
| μ (mm ⁻¹) | 0.765 |
| F(000) | 1212 |
| Intervals of reflection indices | -14 ≤ h ≤ 14, -20 ≤ k ≤ 20, -18 ≤ l ≤ 18 |
| Reflections with I > 2σ(I) | 2863 |
| Independent reflections | 2504 |
| Final R indices [I > 2σ(I)] | R1 = 0.0481, wR2 = 0.1366 |
| R indices (all data) | R1 = 0.0545, wR2 = 0.1426 |
| $\Delta\rho_{\max}$ (e Å ⁻³) | 0.382 |
| $\Delta\rho_{\min}$ (e Å ⁻³) | -0.617 |
| Goodness-of-fit on F ² | 1.076 |
| $R_1 = \sum F_o - F_c / \sum F_o $, $wR_2 = [\sum w(F_o - F_c)^2] / \sum [w(F_o^2)]^{1/2}$ | |

Typically, a 50 mL three-neck round-bottomed flask equipped with a water condenser containing 1 g alkene in 10 mL dry acetonitrile and 2 mg of catalyst is kept in a preheated oil bath. Air was bubbled through the reaction mixture at atmospheric pressure at a flow rate of *ca.* 3.0 cm³ min⁻¹. The reaction mixture was magnetically stirred continuously for 8 h. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified by Varian CP 3800 gas chromatograph equipped with an FID detector and a CP-Sil 8 CB capillary column.

RESULTS AND DISCUSSION

X-ray structure of [Co(bpy)₂(NO₃)](NO₃)·3H₂O (1): The complex shows a cationic monomeric unit [Co(bpy)₂(NO₃)] along with three water molecules of crystallization and a discrete nitrate anion. The unique metal center (Co1) is surrounded by two bipyridyl ligand and one bidentate NO₃⁻ ion forming a distorted octahedron. An ORTEP view with atom numbering scheme of complex **1** is shown in Fig. 1. Selected bond lengths and angles of complex **1** are given in Table-2. The basal plane of Co1 center is formed by the two nitrate oxygen atoms O2, O2* and two bipyridine nitrogen atoms N1, N1*; the axial positions are occupied by the two bipyridine nitrogen atoms N2 and N2* [where * = -x, y, 1/2-z]. Among the two nitrate ions, one is chelated with the Co1 center and other nitrate ion is present outside of coordination sphere, thereby balancing the charge of the Co1 center. Three water molecules are also present in the lattice without offering any hydrogen bonding. The bond lengths and bond angles are well in agreement with the reported cobalt(II) complexes [46,47].

Epoxidation reaction: Catalytic activity of the complex was investigated in the epoxidation of both cyclic and straight

Fig. 1. ORTEP diagram of complex **1** with the atom-numbering schemeTABLE-2
SELECTED BOND LENGTHS (Å)
AND ANGLES (°) FOR COMPLEX **1**

| Bond lengths (Å) | | Bond angles (°) | |
|------------------|------------|------------------|------------|
| Co(1)-O(2) | 1.8887(19) | O(2)-Co(1)-O(2) | 70.14(13) |
| Co(1)-N(2) | 1.922(2) | O(2)-Co(1)-N(2)* | 88.31(9) |
| Co(1)-N(1) | 1.932(2) | O(2)-Co(1)-N(2) | 88.31(9) |
| Co(1)-N(3) | 2.286(4) | N(2)-Co(1)-N(2) | 179.42(12) |
| N(2)-C(10) | 1.341(4) | O(2)-Co(1)-N(1) | 98.38(9) |
| N(1)-C(1) | 1.337(3) | O(2)-Co(1)-N(1)* | 167.82(9) |
| O(2)-N(3) | 1.314(3) | N(2)-Co(1)-N(1) | 96.37(9) |
| N(3)-O(9) | 1.230(5) | N(1)-Co(1)-N(1) | 93.35(12) |
| N(3)-O(2) | 1.314(3) | | |

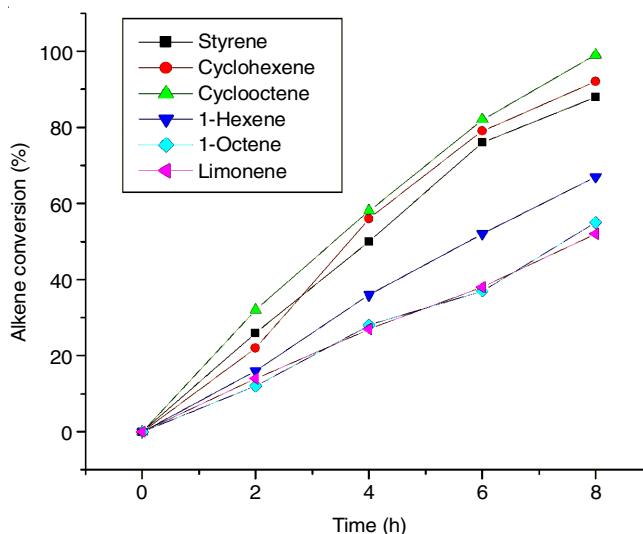
* -x, y, 1/2-z

chain alkenes with air. The resultant conversions, selectivities and turnover number (TONs) are given in Table-3. The reaction profile of the epoxidation of alkenes is shown in Fig. 2. The epoxidation of styrene gives styrene oxide in 76% yield (conversion 88%, selectivity 67%); along with this, benzaldehyde (yield 12%) was also detected. Turnover number of ~2347 has been attained for the epoxide production. Epoxidation of styrene with molecular oxygen over a variety of cobalt catalysts under homogeneous condition has been studied in the recent past. Kureshy *et al.* [29] studied epoxidation of styrene over Co(II) chiral Schiff-base complexes in presence of molecular oxygen using isobutyraldehyde which shows up to 45% conversion. Cobalt(II) calix[4]pyrrole complexes afforded a maximum of 68% yield of styrene oxide in presence 2-ethylbutyr-aldehyde/O₂ in 24h [48]. Opre *et al.* [49] reported that DMF interacts with oxygen, styrene and cobalt containing catalyst according to a complex reaction network, resulting in the formation of 49% styrene oxide with various co-products, such as *N*-formyl-*N*-methylformamide, CO₂ and dimethylamine [49]. They concluded that DMF should be considered as a “sacrificial” solvent that functions as a co-reductant in the epoxidation

TABLE-3
HOMOGENEOUS ALKENE EPOXIDATION
CATALYZED BY COMPLEX **1**^a

| Substrate | Conversion (%) | Yield of product (%) | | TON ^f |
|-----------|----------------|----------------------|-----------------|------------------|
| | | Epoxide | Others | |
| | 88 | 76 | 16 ^b | 2347 |
| | 92 | 80 | 12 ^c | 3111 |
| | 99 | 99 | – | 2495 |
| | 67 | 67 | – | 2211 |
| | 55 | 48 | 7 ^d | 1361 |
| | 52 | 52 ^e | – | 1060 |

^aReaction conditions: alkenes (1 g); catalyst (2 mg); flow rate of air, 3.0 cm³min⁻¹; CH₂CN (10 mL); Temperature (60°C). ^bBenzaldehyde. ^c2-Cyclohexen-1-ol and 2-Cyclohexen-1-one. ^dOther unidentified product. ^eLimonene epoxide. ^fTurn Over Number = moles converted / moles of active site. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified by Varian CP3800 gas chromatograph equipped with an FID detector and a CP-Sil 8 CB capillary column.

Fig. 2. Reaction profile for the aerobic epoxidation of alkenes over complex **1**

reaction. In present study, the reaction in DMF under this condition was performed but no conversion of styrene was observed. O'Neill *et al.* [50] obtained a yield of 74% styrene epoxide using *bis*(2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(II), [Co(thd)₂] under aerobic condition using pivaldehyde as sacrificial reductant.

The epoxidation of endocyclic alkene such as cyclohexene showing a conversion (92%) with 80% epoxide selectivity. Along with the epoxide, a small amount of allylic oxidation products *i.e.* 2-cyclohexen-1-ol and 2-cyclohexen-1-one are also detected. The epoxidation of cyclooctene goes smoothly, showing an excellent conversion of 99% with 100% epoxide selectivity. The linear aliphatic olefins such as 1-hexene and 1-octene converted to the corresponding 1, 2-epoxy alkanes. As shown in Table-3, the conversion of 1-hexene is 67% where epoxide was the sole product. Conversion of 1-octene was 55%, where epoxide selectivity was 87%. Along with 1,2-epoxy alkane, a small amount (7%) of other undetected side product was also obtained. It shows that the catalytic activity decreases along with length of olefin. This may be due to the larger hexyl group of 1-octene connected to double bond sterically hinders it in approaching to the catalyst metal center with respect to 1-hexene which its double bond carries a smaller butyl group. Limonene undergoes a relatively slow conversion and after 8 h of reaction only 52% conversion is noticed. At that time, limonene oxide is the exclusive product. da Silva *et al.* [30] studied the oxidation of limonene with dioxygen in acetonitrile medium over CoCl₂ where the molar ratio of allyl oxidation and epoxidation products was nearly 1:1. However, no allylic oxidation product is noticed in epoxidation reaction catalyzed by complex 1.

Conclusion

A new mononuclear cobalt(II) complex was hydrothermally synthesized and characterized by X-ray crystallography. The complex has shown excellent catalytic efficacy towards the aerobic epoxidation of alkenes in presence of isobutyraldehyde as co-reductant. The complex 1 is new example of cobalt based catalyst that can oxidize olefinic substrates only by bubbling air.

Supplementary material

Crystal data are available from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44-1223-336-033; www: <http://www.ccdc.cam.ac.uk> or E-mail: deposit@ccdc.cam.ac.uk) upon request, quoting the deposition number CCDC 808604.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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