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Azide/thiocyanate incorporated cobalt(III)-Schiff base complexes: Characterizations and catalytic activity in aerobic epoxidation of olefins

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ABSTRACT

Reaction of cobalt(II) perchlorate hexahydrate with a potentially tetradentate Schiff base ligand, HL (2-methoxy-6-[(2-diethylaminoethylimino)methyl]phenol) in presence of sodium azide and sodium thiocyanate yields two complexes $[Co(L)(HL)(N_3)]\cdot ClO_4$ (**1**) and $[Co(L)(HL)(NCS)]\cdot ClO_4$ (**2**); both being characterized by different physicochemical methods. Crystal structure of **1** was determined by single crystal X-ray diffraction while that of **2** was reported earlier. In **1**, the central cobalt(III) adopts slightly distorted octahedral geometry with same donor set to that of **2**. Catalytic efficacy of the complexes towards epoxidation of different alkenes under aerobic condition were investigated in homogeneous medium which reveals that **1** is better catalyst than **2** with respect to alkene oxidation, reflected from the turn over frequencies (TOF) measured at an optimum temperature of 60 °C in acetonitrile.

1. Introduction

Cobalt(III) complexes derived from symmetrical and unsymmetrical Schiff bases have drawn extensive attention in the domain of metallo-organic and coordination chemistry due to their synthetic accessibility, fascinating structural features and diverse range of applications covering organic synthesis, photochemistry [1], magnetic and electrochromism [2–8], and catalysis [9,10]. Cobalt(III)-Schiff base complexes also find important biological applications [11–14].

On the other hand, epoxidation of alkenes remains a thrust area of research among the various catalytic processes used industrially as epoxides are important intermediate chemicals for making valuable products [15–17], and also used as precursors for many fine chemicals [18]. Epoxidation of alkenes was performed using different single oxygen donor reagents; each of them possesses certain disadvantages. For example, stoichiometric amount of peracid [19] was used as conventional alkene epoxidation catalyst but its use was limited for its high cost and corrosivity, non-selectivity for the epoxide formed, as well as for the formation of undesirable products, creating a lot of waste. Similarly, several other single oxygen donors such as $NaIO_4$ [20], NaOCl [21], PhIO [22], tert-butyl hydroperoxide (TBHP) [23–25], and H_2O_2 [26–29] were used which also appeared as either expensive or dangerous for environment. Manufacturing methods of epoxides by chlorohydrin and Halcon processes [30] also cause serious environmental pollution. Therefore from both environmental and economic concern, use of O_2 or naturally cheap air over effective catalysts becomes a promising and attractive method for epoxidation of alkenes [31–34].

Many efforts [35,36] have been made for epoxidation of alkenes with molecular O_2 or air however, among them, Mukaiyama epoxidation system [37,38] appeared as very effective [39–41]. In this method, the sacrificial aldehyde, acted as reductant, was transformed to a carboxylperoxo radical *in situ*, facilitating oxygen transfer to the olefin and generated carboxylic acid as a stoichiometric side product. Schiff's base transition metal complexes [42], metalloporphyrins [43], and meta-cyclam complexes [44] also demonstrated high catalytic performance for the aerobic oxidation in the presence of co-reactant aldehyde.

Epoxidation of alkenes with O_2 using simple cobalt salts [38,45] or cobalt(II) Schiff base complexes [31,37,42,46,47] in presence of different sacrificial co-reductant, e.g. ketone [31,37,42], β-ketoester [31,42], ethers [38], and aldehyde [31,42,47] has been investigated. Cobalt(II)-salen derived Jacobsen type complexes were also used as catalysts for aerobic asymmetric epoxidation [48] though the formation of μ-oxo dimers and other polymeric species were the major limitations in homogenous solutions which ultimately led to deactivation of the catalyst. Oxidation of mono-terpenes with O_2

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was also investigated using cobalt(II) chloride and it was observed that allylic oxidation proceeds predominantly [49]. Recently, aerobic oxidation of alkenes over cobalt(II)–catalyst using TBHP initiator in DMF without any co-reductant have been studied [50,51] and in some cases DMF itself also performed the role of sacrificial co-reductant [33,52].

In this paper we report the synthesis of a new cobalt(III) complex $[Co(HL)(L)(N_3)]{\cdot}ClO_4$ (**1**) derived from $Co(ClO_4)_2{\cdot}6H_2O$, NaN_3 and Schiff base ligand, HL, 2-methoxy-6-[(2-diethylaminoethylimino)methyl] phenol, obtained by 1:1 condensation of o-vanillin and 2-diethylaminoethylamine in methanol (Scheme I). Title complex is characterized by elemental analyses, FTIR, UV-Vis, EPR, magnetic, and cyclic voltammetric methods and its crystal structure was established by single crystal X-ray diffraction and compared to that of the reported **2**. Their catalytic potentiality under homogeneous condition towards aerial olefin epoxidations in presence of the sacrificial co-reductant, isobutyraldehyde was also investigated.

2. Experimental

2.1. Materials

Caution! Perchlorate salts of metals in presence of organic ligands are potentially explosive. Even though we did not encounter any problems they should be prepared in small amounts and be handled with caution.

Cobalt(II) perchlorate hexahydrate, o-vanillin, 2-diethylaminoethylamine, styrene, 1-heptene, 1-octene, cycloheptene, and cyclooctene were purchased from Aldrich Chemical Co. and were used as received. Sodium azide, sodium thiocyanate and solvents were purchased from E. Merck (India). The solvents were distilled and dried before use. Schiff base (HL) and complex **2** were synthesized following the literature procedure [53].

2.2. Syntheses

2.2.1. Synthesis of the Schiff base ligand (HL)

The Schiff base HL was prepared following the literature procedure [53]. Briefly, *o*-vanillin (5 mmol, 0.760 g) and 2-diethylaminoethylamine (5 mmol, 0.710 g) in 20 mL methanol was refluxed for half an hour. The resulting yellow solution containing the Schiff base ligand (HL) was cooled and subjected to TLC which revealed the presence of some starting materials along with the Schiff base product. The Schiff base ligand was isolated by column chromatography over silica gel (SRL) 60–120 mesh size, using a mixture of light petroleum and ethyl acetate (v/v, 2:3); subsequent evaporation of this eluent yielded the pure ligand in liquid form. The purified liquid ligand was then evaporated under reduced pressure to yield a gummy mass, which was dried and stored in *vacuo* over fused $CaCl_2$ for subsequent use. Yield: 0.814 g (65%). *Anal.* Calc. for $C_{14}H_{22}N_2O_2$ (250.34): C, 67.17; H, 8.86; N, 11.19. Found: C, 67.10; H, 8.76; N, 11.15%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (t, J = 7.7 Hz, $6H^1$), 2.72 (t, J = 7.5 Hz, $2H^3$), 3.48 (q, J = 7.7 Hz, $4H^2$), 3.65 (t, J = 7.5 Hz, $2H^4$), 3.93 (s, $3H^9$), 6.97 (t, J = 7.9, $1H^7$), 7.17 (d, J = 7.8 Hz, $1H^6$), 7.21 (d, J = 7.8 Hz, $1H^8$), 8.53 (s, $1H^5$), 11.12 (s, $1H^{10}$) ppm (Scheme II). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4 ($^8C=N$), 152.9 ($^1C{-}OH$), 148.6 ($^2C{-}OMe$), 122.9 ($^6C{-}C=N$), 118.3 (^5CH), 117.4 (^4CH), 113.8 (^3CH), 57.1 ($^{10}CH_2$), 56.0 (O^7CH_3), 53.3 ($^9CH_2$), 47.4 ($^{11}CH_2$) 12.0 ($^{12}CH_3$) ppm (Scheme II).

2.2.2. Synthesis of $[Co(L)(HL)(N_3)]{\cdot}ClO_4$ (1)

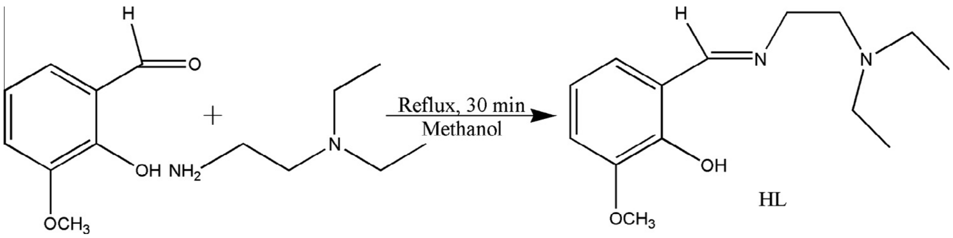
To a stirred methanolic solution (20 mL) of cobalt(II) perchlorate hexahydrate (1 mmol, 0.366 g), methanolic solution (10 mL) of Schiff base (HL) (2 mmol, 0.250 g) was added very slowly with constant stirring, followed by drop wise addition of an aqueous solution (10 mL) of sodium azide (1 mmol, 0.065 g). Reaction mixture was stirred for 30 min. and filtered. The filtrate kept for slow evaporation at room temperature. Deep green crystals of **1** were separated after 10 days. *Anal.* Calc. for $[C_{28}H_{43}ClCoN_7O_8]$: C, 48.04; H, 6.19; N, 14.01; Found, C, 47.99; H, 6.11; N, 13.95%.

2.3. Physical measurements

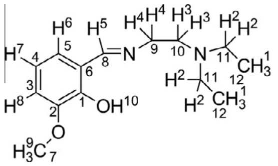
Elemental analyses (carbon, nitrogen and hydrogen) were carried out using a Perkin–Elmer 2400 II elemental analyzer. Infrared spectra were recorded on a Perkin–Elmer Spectrum RX FTIR instrument in the range of 4000–400 cm^{-1} as KBr pellets. The UV-Vis spectra in solution were recorded at room temperature on a Perkin Elmer *Lambda* 40 UV–Vis spectrophotometer using acetonitrile in 1 cm quartz cuvettes. ^{1}H NMR and ^{13}C NMR spectra of HL was recorded on a Bruker 300 MHz FT-NMR spectrometer using tetramethylsilane as internal standard in $CDCl_3$. Electrochemical measurements were performed using a PAR VersaStat- potentiostat/ Galvanostat II electrochemical analysis system under a dry argon atmosphere using conventional three electrode configurations in acetonitrile with tetrabutylammonium perchlorate as the supporting electrolyte. Platinised platinum milli electrode and saturated calomel electrode (SCE) were used as working and reference electrodes, respectively, along with a platinum counter electrode in cyclic voltammetry performed at a scan rate of v = 50 mV sec^{-1}. The room temperature X-band EPR spectra were recorded on an X-band JEOL JES FA200 ESR Spectrometer. Magnetic susceptibilities were measured with a model 155 PAR vibrating sample magnetometer fitted with a Waker Scientific 175 FBAL magnet using $Hg[Co(SCN)_4]$ as the standard. The necessary diamagnetic corrections for the ligand were done using Pascal's table. The products of the catalytic reactions were identified and quantified by Agilent HP 6890 series gas chromatograph using a HP-5 GC column.

2.4. X-ray crystallography

A diffraction quality deep brown plate shaped crystal of **1** (dimension; 0.14 × 0.11 × 0.03 mm) was mounted on 'Xcalibur Eos, Nova' CCD diffractometer equipped with mirror monochromatized Mo X-ray radiation source (Mo Kα = 0.71073 Å) at 298(2) K. CrysAlisPro [54] was used for preliminary determination of the cell constants, data collection strategy, and for data collection.



Scheme I. Synthetic scheme for Schiff base (HL).



Scheme II. Proton and carbon numbering scheme of HL.

Following data collection, CrysAlisPro [54] was also used to integrate the reflection intensities. Multi-scan absorption corrections were applied to the intensity data ($T_{max} = 0.980$, $T_{min} = 0.911$) empirically using spherical harmonics, implemented in SCALE3 ABSPACK [55] scaling algorithm, followed by cell refinement and data reduction. The crystal structure was solved by direct methods using the program SHELXS-97 [56] and refined with full-matrix least-squares based on F^2 using program SHELXL – 97 [56]. All non-hydrogen atoms were refined anisotropically. The ethyl groups (atoms C11–C14) and one carbon atom of the ethylene bridge (atom C10) bound to the N2 nitrogen atom are disordered over two sets of orientations (called A and B) with refined occupancy ratio 0.547(4):0.453(4). During the refinement the N—C and C—C bond lengths involving the disordered atoms were restrained to be 1.50(1) and 1.54(1) Å, respectively. SIMU and EADP restraints [56] were applied to the disorder components. The perchlorate anion was also found to be rotationally disordered about the Cl1—O8 bond over two orientations (called A and B, with refined occupancy ratio 0.547(4):0.453(4)) which were refined with a SADI distance restraint [56], and with the anisotropic displacement ellipsoids of pairs of disordered oxygen atoms equivalenced by the EADP command. The amine H atom was located in a difference Fourier map and refined freely. All other H atoms were placed at calculated positions and refined using a riding model approximation, with C—H = 0.93–0.97 Å, and with $U_{iso}(H) = 1.2\ U_{eq}(C)$ or $1.5\ U_{eq}(C)$ for methyl H atoms. A rotating model was applied to the methyl groups. The publication materials and crystallographic illustrations for **1** were prepared using PLATON [57] and ORTEP [58] programs. Crystallographic parameters, details of data collection and refinement procedures for **1** are summarized in Table 1.

2.5. Catalytic reactions

The catalytic reactions were carried out in a glass batch reactor according to the following procedure. Substrate (10 mmol), isobutyraldehyde (10 mmol), solvent (20 mL) and catalysts (1.5 mg) were first mixed. The mixture was then equilibrated to desired temperature in an oil bath. Reactions were performed in open air. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified by gas chromatography. The turnover frequency (TOF) was calculated as follows:

$$\text{TOF} = \frac{\text{moles converted}}{\text{moles of cobalt(active site)taken for reaction x reaction time}} \times 100$$

3. Results and discussion

3.1. Fourier transform infrared spectra

The infrared spectra of the complexes are consistent with their crystal structure. In the spectra of the complexes azomethine (–CH=N–) stretching frequency is lowered by 14 cm^{-1} compared to that of the free Schiff base ligand (1632 cm^{-1}) and appeared at 1618 cm^{-1}, indicating the coordination of imine nitrogen to the metal center [59–61]. The aromatic –OH stretching vibration of the free ligand (3445 cm^{-1}) disappeared in the spectra of the complexes suggested deprotonation of this phenolic-OH group during complexation. Coordination of the phenolic oxygen is further substantiated by lowering of phenolic C–O stretching vibration of free ligand (1255 cm^{-1}) which appeared at 1226 and 1224 cm^{-1} in the spectra of **1** and **2**, respectively. The bands at 2943 for **1** and 2941 cm^{-1} for **2** may be assigned to alkyl C–H bond stretching of methoxy group [14]. The band for $\nu_{N\equiv N}$ for terminal azide in **1** and $\nu_{C\equiv N}$ of the terminal NCS group in **2** appeared at 2027 and 2081 cm^{-1}. Coordination of nitrogen to cobalt(III) center ($\nu_{Co\text{–}N}$) is also evident by the appearance of weak bands at 492 and 435 cm^{-1} for **1** and 490 and 431 cm^{-1} for **2**, respectively. A sharp strong peak appeared at 1087 and 1086 cm^{-1} in the spectra of **1** and **2** may be assignable to perchlorate stretching vibrations and this single peak without splitting evidenced the presence of non-coordinating perchlorate anion [62].

Table 1
Crystal data and structure refinement parameters for **1**.

	1
Empirical formula	$C_{28}H_{43}ClCoN_7O_8$
Formula weight	700.07
Crystal dimension (mm)	0.14 × 0.11 × 0.03
Crystal system	monoclinic
Space group	*P*21/*c*
a (Å)	9.620(5)
b (Å)	31.00(2)
c (Å)	11.108(8)
β (°)	105.87(6)
V ($Å^3$)	3186(4)
Z	4
T (K)	298(2)
$\lambda_{Mo\ K\alpha}$ (Å)	0.71073
D_c (g cm^{-3})	1.460
μ (mm^{-1})	0.682
F(000)	1472
θ (°)	2.56–25.5
hkl ranges	$-11 \leqslant h \leqslant 11$, $-37 \leqslant k \leqslant 37$, $-13 \leqslant l \leqslant 13$
Total data	25570
Unique data	5764
Observed data [$I > 2\sigma(I)$]	3753
N_{ref}; N_{par}	5764; 443
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0675$, $wR_2 = 0.1611$
R indices (all data)	$R_1 = 0.1083$, $wR_2 = 0.1944$
R_{int}	0.083
Goodness-of-fit (GOF) on F^2	1.027
$\Delta\rho_{max}$ (e $Å^{-3}$)	0.65
$\Delta\rho_{min}$ (e $Å^{-3}$)	−0.51

3.2. UV–Vis spectra

The electronic spectra of the complexes were recorded in acetronitrile at room temperature and are in good agreement with octahedral geometries of the complexes. Generally octahedral cobalt(III) complexes show two strong and broad band around 550 and 360 nm due to spin allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively. In our cases, both complexes show broad band at ca. 555 nm corresponds to $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. However, other characteristic d–d transition ($^1A_{1g} \rightarrow {}^1T_{2g}$) was absent. This high energy band probably was obscured by several ligand to metal charge transfer transition bands [14]. In the high energy region both complexes show several intense bands observed in the region 340–385 nm, attributed to the charge transfer transition from the coordinated unsaturated ligands to the respective metal ions (LMCT) [63]. Two intense high energy bands corresponding to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the lignad were also observed in the spectra of **1** and **2** at 239 and 402 nm, and 230 and 385 nm, respectively.

3.3. Electrochemistry

Cyclic voltammograms of **1** and **2** were recorded at room temperature in acetonitrile within the potential range +1.5 to −1.5 V. On cathodic scan a reductive response due to Co(III) → Co(II) reduction was observed at −0.75 and −0.76 V for **1** and **2**, respectively. On anodic scan an oxidative response for **1** and **2** was observed at −0.26 and −0.25 V correspond to Co(II) → Co(III) oxidation. Peak-to-peak separations of 490 and 510 mV for **1** and **2** with $I_{pc}/I_{pa} > 1$ suggest the irreversible nature of these redox processes. Upon changing the scan rate peak potentials slightly shifted towards more anodic potentials and the peak current increased but I_{pc}/I_{pa} always remained greater than one which also confirmed the irreversible nature of these redox processes. An additional peak at +0.42 and +0.46 V during anodic scan was also observed for **1** and **2** which may be assigned to the oxidation of the ligand on the electrode surface [1].

3.4. EPR and magnetic studies

The X band EPR spectra of polycrystalline samples **1** and **2** were recorded at room temperature to get information about the valence and spin state of cobalt ion. The cobalt ion exhibits two oxidation states (II and III), where cobalt(III) with a t_{2g}^6 configuration is diamagnetic in nature and hence EPR silent, whereas cobalt(II) exist in both low spin ($S = 1/2$) and high spin ($S = 3/2$) states and is paramagnetic, and hence EPR active. In our complexes they appear as EPR silent (Supplementary material: Figs. S1 and S2) confirming the diamagnetic nature (t_{2g}^6 configuration) of the complexes with the +III oxidation state of the cobalt ion. The diamagnetic behavior of the complexes was also supported by room temperature magnetic moment measurements. The room temperature effective magnetic moment incorporating the necessary diamagnetic corrections using Pascal's table for the polycrystalline complexes of **1** and **2** was found to be 0.01 B.M. which indicates the presence of low spin cobalt(III) ions in these complexes.

*3.5. Structure description of [Co(L)(HL)(N$_3$)]·ClO$_4$ (**1**)*

An ORTEP view of **1** is shown in Fig. 1 and selected bond lengths and angles are listed in Table 2. The structure of **1** consists of mononuclear $[Co(L)(HL)(N_3)]^+$ cation and perchlorate anion. In the cationic unit two Schiff bases coordinate to the cobalt(III) atom in tridentate and bidentate modes. The anionic tridentate Schiff base coordinates to the cobalt(III) center through the phenolato oxygen (O1), the imine nitrogen (N1), and the amine nitrogen (N2) atoms while the neutral bidentate Schiff base, which is protonated at the amine nitrogen atom (N4), coordinates by its phenolato oxygen (O3), and imine nitrogen (N3). The azide ion acts as a terminal coligand and coordinates through one terminal nitrogen (N5) atom. Thus the cobalt(III) ion is hexa-coordinated by a N_4O_2 donor set and its coordination polyhedron is best described as a slightly distorted octahedron. The best equatorial plane (r.m.s. deviation = 0.0094) is formed by the imine nitrogen (N1 and N3) atoms, the azide nitrogen (N5) and the phenolato oxygen (O3) of the bidentate Schiff base ligand while the two apical positions are occupied by the phenolato oxygen (O1) and the amine nitrogen (N2) of the tridentate Schiff base ligand. The metal ion is displaced form the mean equatorial plane by only 0.0046(8) Å toward N5. The bond lengths related to cobalt(III) center range from 1.890(4) to 2.076(4) Å. *Cisoid* and *transoid* angles vary in the range 84.58(17)–95.02(17)° and 174.30(18)–179.78(19)°. The N–N bond distances in the coordinated azide ion are just significantly different (N5–N6 = 1.193(6) Å, N6–N7 = 1.166(7) Å) with an almost linear ∠N5–N6–N7 angle of 176.3(7)°. The percholarte ion is disordered and remains uncoordinated to the cobalt(III). However it is connected to the complex unit through C–H···O interactions (Table 3). An intramolecular N–H···O hydrogen bond is also observed (Table 3).

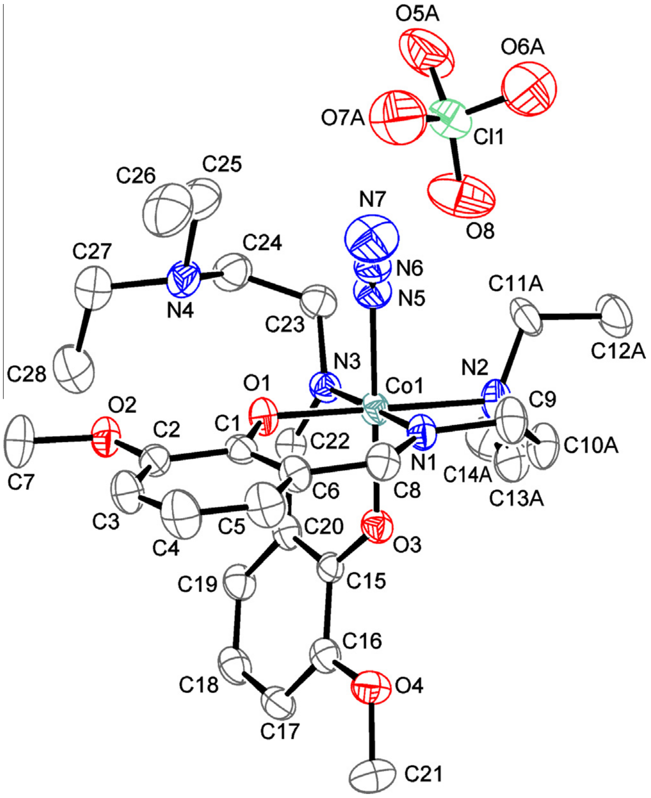


Fig. 1. ORTEP plot of **1** with displacement ellipsoids drawn at the 30% probability level. Only the major components of disorder are shown. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for **1**.

Co1–O1	1.902(3)	Co1–N2	2.076(4)
Co1–O3	1.908(3)	Co1–N3	1.950(4)
Co1–N1	1.889(4)	Co1–N5	1.956(5)
O1–Co1–O3	89.68(14)	O3–Co1–N5	174.31(17)
O1–Co1–N1	94.43(16)	N1–Co1–N2	85.52(18)
O1–Co1–N2	179.77(19)	N1–Co1–N3	178.97(17)
O1–Co1–N3	85.02(15)	N1–Co1–N5	90.19(19)
O1–Co1–N5	88.48(17)	N2–Co1–N3	95.02(17)
O3–Co1–N1	84.59(16)	N2–Co1–N5	91.29(18)
O3–Co1–N2	90.54(16)	N3–Co1–N5	90.67(19)
O3–Co1–N3	94.53(16)	–	–

Table 3
Hydrogen bonding parameters (Å, °) for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(D–H···A)
N4–H4N···O1	0.95(6)	2.21(6)	3.132(7)	164(5)
C8–H8···O4[a]	0.93	2.56	3.376(7)	146
C9–H9B···O5A[b]	0.97	2.52	3.301(13)	138
C22–H22···O6A[b]	0.93	2.56	3.286(16)	136
C23–H23A···O7A	0.97	2.55	3.246(17)	128
C24–H24A···O7A[c]	0.97	2.39	3.28(2)	152
C24–H24A···O6B[c]	0.97	2.57	3.19(2)	121

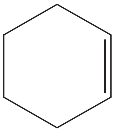
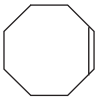
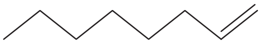
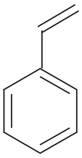
[a] Symmetry code: −x, −y, 1 − z.
[b] Symmetry code: x, 0.5 − y, 0.5 + z.
[c] Symmetry code: x, 0.5 − y, −0.5 + z.

The complex reported herein may be compared to that of **2**, reported earlier [53]. Both the complexes were derived from same Schiff base and metal salt with different terminal ligand; N_3^- for **1** while SCN^- for **2**. In both cases, two coordinating Schiff bases exhibit similar ligating properties; one in a tridentate fashion through its phenolato oxygen, imine, and amine nitrogen atoms while the other acts as a bidentate ligand through its phenolato oxygen and imine nitrogen atoms. In both the complexes pseudohalide ions coordinated through nitrogen atoms in monodentate fashion. As a consequence the cobalt(III) atom is six-coordinated by the same N_4O_2 donor set and adopts a slightly distorted octahedral geometry. Though the degree of distortion from the ideal geometry is small in both complexes, it originates from significantly different coordination modes of the pseudohalide ligands. In fact, the Co1–N5–N6 angle in **1** is 122.1(4)° while in **2** the Co–N5–C29 angle is 157.8(5)°, indicating that azide leads to a more relevant steric crowding than thiocyanate. The Co1–O bond (1.908(3) Å) trans to Co1–N5 bond in **1** is slightly longer than the Co1–O bond (1.880(4) Å) trans to Co1–N5 bond in **2**, indicating higher trans influence of azide ion than that of thiocyanate [64].

3.6. Catalytic epoxidation reactions

Catalytic activity of **1** and **2** was investigated in the epoxidation of both cyclic and straight chain alkenes with air. Complete conversion of the substrates such as cyclooctene, cyclohexene, 1-hexene, 1-octene, and styrene required 12 and 18 h, 14 and 22 h, 16 and 24 h, 18 and 26 h, and 13 and 18 h, for **1** and **2**, respectively. Bearing in mind both conversion and time, we have studied the catalytic reaction for 6 h only to get satisfactory results. Catalytic performance of **1** and **2** in the epoxidation of various olefins is summarized in Table 4. The epoxidation results of various olefins differed significantly due to the different activity of the double bonds. In the epoxidation of endocyclic alkene such as for cyclooctene, epoxide selectivity was 100% due to its highly active double bond and relative stability of product, cyclooctene oxide. However, for cyclohexene, only 49% and 38% epoxide selectivity was obtained for **1** and **2** as their active allylic site could also be attacked in the oxidation process. Linear aliphatic olefins such as 1-hexene and 1-octene converted to their corresponding 1,2-epoxy alkanes as an exclusive product. However, the conversion of 1-hexene (72% for **1** and 61% for **2**) was greater than of 1-octene (66% for **1** and 54% for **2**) which showed that catalytic activity decreases along with chain length of olefins. Larger hexyl group of 1-octene connected to double bond sterically hinders its approach to the active site compared to 1-hexene in which its double bond carries a smaller butyl group. In view of the conjugative effect of benzene ring, styrene should show lower activity, but surprisingly it gave styrene oxide with above 54% selectivity; along with this, benzaldehyde and benzoic acid were also detected. Kureshy et al. studied that epoxidation of styrene over cobalt(II) chiral Schiff base complexes in presence of O_2 and isobutyraldehyde showed up to 45% conversion [48]. Yield of styrene oxide is maximized to 68% using cobalt(II) calix [4] pyrrole complexes in presence 2-ethylbutyraldehyde/O_2 in 24 h [65]. Opre et al. studied that DMF interacts with oxygen, styrene, and the 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, CO_2, and dimethylamine [52] and established that DMF as "sacrificial" solvent which also functions as co-reductant. We also performed the reaction in DMF under this condition but no conversion of styrene was detected. Gao et al. obtained 60% styrene epoxide over cobalt(II) containing zeolite imidazolate framework under aerobic condition using isobutyraldehyde as sacrificial reductant [32]. A graphical representation of relative efficacy of **1** and **2** for the epoxidation of various alkenes versus time is shown in Figs. S3 and S4 (Supplementary material), respectively.

Table 4
Epoxidation of olefins catalyzed by **1**[i] and **2**[i].

Substrate	Reaction time (h)	Conversion (wt%)	% Yield of product		TOF[ii]
			Epoxide	Others	(h^{-1})
	a) 6 b) 6	a) 83 b) 70	a) 49 b) 38	a) 22[iii], 12[iv] b) 19[iii], 13[iv]	a) 660 b) 544
	a) 6 b) 6	a) 79 b) 66	a) 79 b) 66	–	a) 628 b) 513
	a) 6 b) 6	a) 72 b) 61	a) 72 b) 61	–	a) 573 b) 474
	a) 6 b) 6	a) 66 b) 54	a) 66 b) 54	–	a) 525 b) 420
	a) 6 b) 6	a) 78 b) 69	a) 43 b) 37	a) 18[v], 17[vi] b) 17[v], 15[vi]	a) 621 b) 537

(a), (b), corresponds to the catalytic performance of compounds **1** and **2**, respectively.

[i] Reaction conditions: alkenes (10 mmol); isobutyraldehyde (10 mmol); catalyst (1.5 mg); flow rate of air *ca.* 5 mL/min; solvent (acetonitrile (20 mL)); temperature 60 °C. 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.

[ii] Turn over frequency (TOF) = moles converted per moles of active site per hour.

[iii] 2-Cyclohexen-1-ol.

[iv] 2-Cyclohexene-1-one.

[v] Benzaldehyde.

[vi] Benzoic acid.

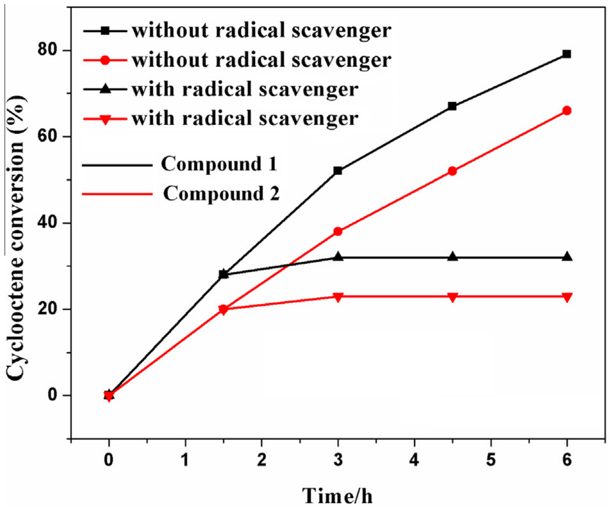
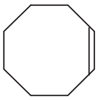


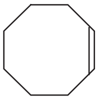
Fig. 2. Plot of % conversion of cyclooctene vs. time for comparison between reaction with radical scavenger (hydroquinone) and a control reaction without adding radical scavenger.

Table 5
Influence of solvent on **1** and **2** catalyzed epoxidation reaction[i].

Substrate	% of conversion (% of epoxide yield) in different solvent				
	CH_3CN	CH_3COCH_3	$CHCl_3$	C_2H_5OH	CH_3OH
	a) 79 (79) b) 66 (66)	a) 58 b) 45	a) 49 b) 36	No conversion	No conversion

[i] Reaction conditions were the same as given in footnote of Table 4.

Table 6
Temperature effect on **1** and **2** catalyzed epoxidation reaction[i].

Substrate	% of conversion (% of epoxide yield) at different temperature					
	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C
	a) 42 (42) b) 30 (30)	a) 48 (48) b) 35 (35)	a) 66 (66) b) 53 (53)	a) 79 (79) b) 66 (66)	a) 82 (82) b) 70 (70)	a) 83 (83) b) 72 (72)

[i] Reaction conditions were the same as given in footnote of Table 4.

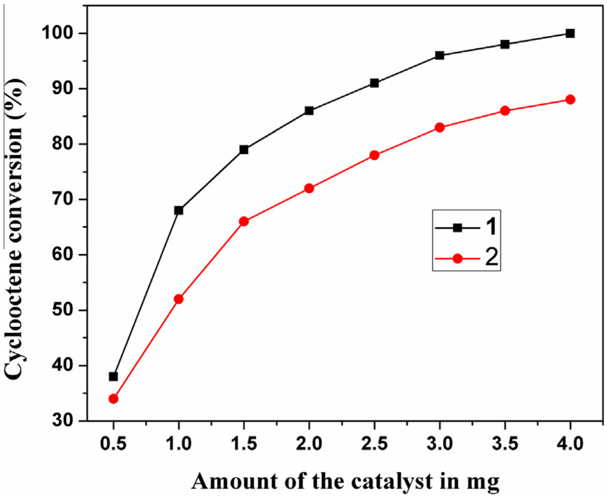
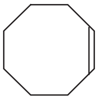
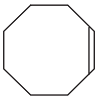


Fig. 3. Plot showing cyclooctene conversion with respect to amount of catalyst.

Table 7
Epoxidation of olefins catalyzed by cobalt salts[i].

Substrate	Catalyst	Conversion (wt%)	% yield of product		TOF[ii] (h^{-1})
			Epoxide	Others	
	$Co(ac)_2{\cdot}4H_2O$	24	24	–	158
	$[Co(acac)_3]$	25	25	–	164

[i] Reaction conditions were the same as given in footnote of Table 4.
[ii] Turn over frequency (TOF) = moles converted per moles of active site per hour.
ac = acetate. acac = acetylacetonate.

Buranaprasertsuk et al. [65] proposed a mechanism for the metal complex-catalyzed oxygenation of substrates by O_2 and aldehyde. We also propose a similar mechanism, operative in our case. First, O_2 and aldehyde generated the peroxyacid by a radical mechanism. Then the reaction between metal complex and peroxyacid takes place and metal–peroxy adduct is formed. This metal–peroxy adduct then releases peroxy radical and regenerates metal environment. This is followed by a reaction between peroxy radical and olefin to form a peroxy species which undergoes migration of oxygen to form the epoxide product and acid byproduct. To probe if radicals were involved in our reactions, a radical scavenger, hydroquinone, was added after 1.5 h of the reaction, and the reaction progress was monitored. It was observed that the reaction stopped immediately upon addition of the radical scavenger (Fig. 2), which suggests that the process indeed proceeds via radical epoxidation.

The catalytic reaction was performed in a variety of solvents on cyclooctene to study the catalytic efficacy of **1** and **2** in different solvent. The best performance of the catalyst was observed in acetonitrile (Table 5). The efficiency of catalyst followed the order: acetonitrile > acetone > chloroform > ethanol/methanol. The catalytic reaction on cyclooctene was also performed at different temperature to study the catalytic efficacy of **1** and **2** at different temperature (Table 6). We have studied the effect of temperature up to the boiling point of acetonitrile. Higher temperatures enhanced the reaction rate. The epoxide selectivity as well as conversion for cyclooctene increased with increasing temperature, but above 60 °C, the temperature had little effect on the cyclooctene conversion. From the view point of energy consumption, it is cost effective to perform the catalytic reaction at low temperature. The rate of cyclooctene conversion increases rapidly with the amount of the catalyst at low concentration of the catalyst (Fig. 3). But this progress of conversion decreases with the increases in catalyst concentration and thus for full conversion large amount of catalyst is required. Therefore we have restricted the use of amount of the catalyst (1.5 mg) which is economically beneficial. A comparison of the catalytic efficiency of **1** and **2** with other cobalt salts (cobalt(III) acetylacetonate and cobalt(II) acetate) in homogeneous medium (Table 7) clearly indicates that **1** and **2** perform as a more efficient catalyst than simple cobalt salts.

The catalytic efficacy of the complexes reported herein may be compared (Table 8) to the closely related Co-salen type of complexes reported earlier [34,51,66,67,68] concerning aerobic epoxidation of styrene. This comparison indicates that epoxide selectivity (% wt.) increases when cobalt-salen complexes were

Table 8
A comparison of catalytic efficacy on aerobic styrene epoxidation of **1** and **2** with other related Co-salen systems.

Catalyst	Solvent	Temperature (°C)	Conversion (wt.%)	Epoxide selectivity (wt.%)	TOF (h^{-1})	Refs.
Co-[H_4]Salen-SBA-15[i]	CH_3CN	80	78.5	54.1	196	[66]
Co-ZSM-5(L_1)[ii]	DMF	90	93.9	89.7	–	[51]
Co-ZSM-5(L_2)[iii]	DMF	90	92.6	91.1	–	[51]
Co-ZSM-5(L_3)[iv]	DMF	90	83.7	91.7	–	[51]
(R,R)-Co(II)Salen[v]	Toluene	4	95	30	–	[67]
Co-Salen-graphene oxide	CH_3CN	80	70.1	35.3	83.5	[68]
[Co(HL[vi])$_2$]$NO_3 \cdot H_2O$	CH_3CN	60	100	46	659	[34]
1	CH_3CN	60	78	55	621	This study
2	CH_3CN	60	69	53.6	537	This study

[i] [H_4]Salen-SBA-15 = tetrahydro-salen and salen complex onto amino-functionalized SBA-15.
[ii] L_1 = salicylaldehyde benzoylhydrazone.
[iii] L_2 = vanillic aldehyde benzoylhydrazone.
[iv] L_3 = 4-methyl benzaldehyde benzoylhydrazone.
[v] (R,R)-Salen = (R,R)-(-)-*N,N′*-bis(3,5-di-*tert*butylsalicylidene)-1,2-cyclohexanediamine.
[vi] (H_2L = 1-(N-3-methoxy-salicylideneimino)-ethane-2-ol).

immobilized over ZSM though wt.% conversions in almost all cases are comparable to that of our complexes except one [34]. When the catalytic efficacy of the complexes are compared with respect to their TOF it is observed that our complexes show very high TOF compared to the reported complexes [66,68] and are comparable to that of the other reported complex [34].

4. Conclusions

Herein we report the synthesis and characterizations of two cobalt(III)-Schiff base complexes incorporating azide and thiocyanate as coligands. Structural characterization reveals that in spite of the same coordination mode of the ligand the relative distortion in the geometries of the metal centers in the complexes are different which is due to the relative binding mode of the terminal coligands (azide in **1** and thiocyanate in **2**). Catalytic efficacy of both the complexes towards epoxidation of alkenes in aerobic condition using isobutyraldehyde as co-reductant has been thoroughly investigated which reveals that **1** shows better catalytic activity than **2** with respect to TOF as well as alkene conversion in acetonitrile at an optimum temperature of 60 °C.

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Appendix A. Supplementary material

CCDC 946732 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.02.036.

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