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Pentacoordinated copper-sparteine complexes with chelating nitrite or nitrate ligand: Synthesis and catalytic aspects

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ABSTRACT

Copper(II)-sparteine complexes, $[Cu^{II}\{(-)Sp\}(NO_2)CI]$ (1) and $[Cu^{II}\{(-)Sp\}(NO_3)CI]$ (2) (Sp = sparteine) with chelating nitrite and nitrate ligands, respectively, have been synthesized and structurally characterized. The penta-coordinated **1** or **2** exhibits distorted square pyramidal geometry and shows characteristic EPR spectra with g_{II} : 2.27 and g_{\perp} : 2.06. **1** and **2** behave similarly towards the catalytic epoxidation of alkenes as well as oxidation of alcohols. Though the epoxidation of cyclohexene using **1** or **2** as a catalyst and tertiarybutyl hydroperoxide (TBHP) as an oxidant at 298 K in acetonitrile results in 100% cyclohexene oxide product, under identical reaction conditions styrene selectively transforms to benzaldehyde (~90%) instead of any styrene oxide. However, at higher temperature (353 K) the selectivity of cyclohexanol and cyclohexanone are formed. Furthermore, **1** or **2** effectively catalyzes the oxidation of benzyl alcohol to benzoic acid and cyclohexanol to cyclohexanone in presence of molecular oxygen (O₂) as an oxidant at 353 K in acetonitrile.

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1. Introduction

Metal complexes with sparteine (Sp) as a bidentate N,N donor ligand exhibit important physico-chemical, magnetic and structural properties [1–5]. The largely strained structural feature of the alkaloid sparteine and the distance between the two coordinating nitrogen atoms make it an interesting ligand. Consequently a large number of copper-sparteine complexes along with different monodentate anionic ancillary ligands have been reported [1,2,6–14]. However, only one example of Cu(II)–Sp complex with chelating ancillary ligand, maleonitriledithiolato-S,S' has been reported by Choi and co-workers [15]. In all the cases the four coordinated copper complexes exhibit pseudo tetrahedral structure. A five coordinated Cu(II)–Sp complex has also been reported by Masuda et al. but it has a dicopper core with bridging peroxo and carboxylate groups [16].

Monodentate or bridging nitrite and nitrate ligands attached to Cu(I) or Cu(II) center along with ancillary tripodal ligands were reported in the literature [17–19]. However, copper complexes with chelating nitrite or nitrate ligand are rather rare. Hsu reported monomeric and dimeric Cu(I) complexes with nitrite as chelating and bridging ligand [20]. Hubberstey et al. reported one copper(II)

* Corresponding authors. *E-mail addresses:* s-bhaduri@northwestern.edu (S. Bhaduri), lahiri@chem.iitb. ac.in (G.K. Lahiri). nitrite complex where the crystal structure reveals the presence of chelated, non-chelated as well as bridging modes of the nitrite ion in the three independent molecules in the unit cell [21]. Using tris(pyrazolyl)borate as the co-ligand chelating $-NO_2$ group with O,O donors has been reported by Tolman et al. as nitrite reductase model complex [22].

In view of these reports the synthesis of monomeric copper–Sp complex with nitrite or nitrate as a chelating ligand, is synthetically challenging and structurally important as the steric demands for the two ligands (Sp and NO_2^- or NO_3^-) are different. Here we report the synthese and characterizations monomeric copper–sparteine complexes [Cu{(-)Sp}(NO_2)Cl] (1) and [Cu{(-)Sp}(NO_3) Cl] (2) with $-NO_2$ and $-NO_3$ as chelating ligands. The single-crystal X-ray structures of both 1 and 2 have been determined and the catalytic potentials of 1 and 2 towards epoxidation of alkenes and oxidation of alcohols have been investigated.

2. Experimental section

2.1. Chemicals

(–)Sparteine, cyclohexene, cyclohexene oxide, styrene, styrene oxides, benzaldehyde, benzyl alcohol, 3-methylbenzylalcohol, 3-methoxybenzylalcohol, cyclohexanol, cyclohexanone, tertia-rybutyl hydroperoxide (TBHP) (5–6 M in decane), (±)-1-phenylethanol, acetophenone have been obtained from Aldrich. Other





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chemicals and solvents were reagent grade and used as received. The precursor complex $[Cu{(-)Sparteine}Cl_2]$ was prepared according to the literature reported procedure [23].

2.2. Instrumentation

Bruker AV III 400 MHz FT-NMR spectrometer, Micromass Q-ToF mass spectrometer were used for NMR and mass measurements,

respectively. Magna 550 from Nicolet Instruments, USA was used for recording IR spectra as KBr disk. Elemental analyses were performed by using a Perkin–Elmer 240C elemental analyzer. UV–Vis spectra were taken in a Perkin–Elmer 950 spectrophotometer. The EPR measurements were made with a Varian model 109C E-line X-band spectrometer fitted with a quartz dewar for measurements at 77 K. Solution electrical conductivity was measured in Systronic conductivity bridge-305. Cyclic voltammetric measurements were



Scheme 1. Syntheses of the complexes **1** and **2**.



carried out using a PAR model 273A electrochemistry system. A platinum wire working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE) were used in a standard three-electrode configuration. Tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte and the solution concentration was *ca.* 10^{-3} M; the scan rate used was 100 mV s^{-1} . Electrochemical experiments were carried out under dinitrogen atmosphere. % conversion and the product distribution ratio for the catalytic experiments were established by gas chromatographic technique with the FID detector (Shimadzu GC-2014

Table 1

Crystallographic data and structural refinements for $[Cu(Sp)(NO_2)Cl]$ (1) and $[Cu(Sp)(NO_3)Cl]$ (2).

Molecule	[Cu(Sp)(NO ₂)Cl] (1)	[Cu(Sp)(NO ₃)Cl] (2)	
Molecular formula	C15H26ClCuN3O2	C15H26ClCuN3O3	
Formula weight	379.38	395.38	
T (K)	150(2)	150(2)	
Crystal symmetry	orthorhombic	orthorhombic	
Space group	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2$	
a (Å)	7.8797(3)	16.370(4)	
b (Å)	12.4862(5)	13.334(2)	
c (Å)	17.1936(8)	7.6803(9)	
α (°)	90	90	
β (°)	90	90	
γ (°)	90	90	
$V(Å^3)$	1691.64(12)	1676.4(5)	
Ζ	4	4	
D_{calc} (g/cm ³)	1.490	1.567	
μ (mm ⁻¹)	1.459	1.480	
F(0 0 0)	796	828	
2θ Range (°)	6.56-49.96	6.60-50.00	
Data/restraints/parameters	2978/0/209	2942/0/208	
Goodness-of-fit (GOF)	0.945	0.794	
$R_1, wR_2 [I > 2\sigma(I)]$	0.0416, 0.1004	0.0524, 0.0879	
R_1 , wR_2 (all data)	0.0589, 0.1044	0.1061, 0.0972	
Largest difference in peak/hole $(e \text{ Å}^{-3})$	0.700 and -0.252	0.570 and -0.430	

Table 2

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Selected bond distances and bond angles for $[Cu(Sp)(NO_2)Cl]$ (1) and $[Cu(Sp)(NO_3)Cl]$ (2).

	Bond distance (Å)		Bond angle (°)		
$[Cu(Sp)(NO_2)Cl]$ (1)					
Cu(1)-Cl(1A)	1.998(10)	Cl(1A)-Cu(1)-N(1)	167.1(3)		
Cu(1) - N(1)	2.019(3)	Cl(1A)-Cu(1)-N(2)	95.6(4)		
Cu(1) - N(2)	2.019(4)	N(1)-Cu(1)-N(2)	90.56(18)		
Cu(1) - O(1)	2.033(4)	Cl(1A)-Cu(1)-O(1)	84.8(4)		
Cu(1) - O(2)	2.358(5)	N(1)-Cu(1)-O(1)	94.94(19)		
O(1) - N(3)	1.269(7)	N(2)-Cu(1)-O(1)	152.40(18)		
O(2)-N(3)	1.249(8)	Cl(1A)-Cu(1)-O(2)	77.0(3)		
		N(1)-Cu(1)-O(2)	113.55(17)		
		N(2)-Cu(1)-O(2)	96.64(18)		
		O(1)-Cu(1)-O(2)	56.45(18)		
		N(3) - O(1) - Cu(1)	102.8(4)		
		N(3)-O(2)-Cu(1)	87.7(4)		
		O(2)-N(3)-O(1)	112.7(5)		
[Cu(Sp)(NO ₃)Cl]	(2)				
Cu(1)-Cl(1)	2.238(2)	Cl(1)-Cu(1)-N(1)	135.17(19)		
Cu(1) - N(1)	2.005(6)	Cl(1)-Cu(1)-N(2)	105.26(16)		
Cu(1) - N(2)	1.998(5)	N(1)-Cu(1)-N(2)	89.7(2)		
Cu(1) - O(1)	2.051(6)	Cl(1)-Cu(1)-O(1)	96.06(18)		
Cu(1) - O(2)	2.420(5)	N(1)-Cu(1)-O(1)	92.5(2)		
O(1)-N(3)	1.260(7)	N(2)-Cu(1)-O(1)	147.2(2)		
O(2)-N(3)	1.232(8)	Cl(1)-Cu(1)-O(2)	101.20(15)		
O(3)-N(3)	1.240(7)	N(1)-Cu(1)-O(2)	119.8(3)		
		N(2)-Cu(1)-O(2)	94.5(2)		
		O(1)-Cu(1)-O(2)	56.5(2)		
		N(3)-O(1)-Cu(1)	100.8(5)		
		N(3)-O(2)-Cu(1)	84.1(4)		
		O(2)-N(3)-O(1)	118.4(7)		

gas chromatograph) and using a capillary column (Sigma Aldrich, Supelco, Astec, Chiraldex B-DM; length 50 m, inner diameter 0.25 mm, thickness 0.12μ m).



Fig. 2. UV–Vis spectrum of $[Cu(Sp)(NO_2)Cl]$ (1) in CH₃CN. Inset shows the spectrum of $[Cu(Sp)(NO_3)Cl]$ (2) in CH₃CN.



Fig. 3. X-band EPR spectra of complexes (a) $[Cu(Sp)(NO_2)Cl]$ (1) and (b) $[Cu(Sp)(NO_3)Cl]$ (2) in 1:1 dichloromethane–toluene glass.

2.3. Crystallography

Single crystals of $[Cu\{(-)Sp\}(NO_2)Cl]$ (1) and $[Cu\{(-)Sp\}(NO_3)Cl]$ (2) were grown by slow evaporations of the corresponding acetonitrile:dichloromethane (1:1) solutions. X-ray data were collected using an OXFORD XCALIBUR-S CCD single crystal X-ray diffractometer. The structures were solved and refined by full-matrix least-squares techniques on F^2 using the SHELX-97 program [24]. The absorption corrections were done by the multi-scan technique. All data were corrected for Lorentz and polarization effects, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement process as per the riding model.

2.4. Catalytic experiment

The catalytic runs for the epoxidation reaction were carried out in glass vials with the specified ratios of substrates and catalyst in acetonitrile under magnetic stirring condition (stirring rate \geq 900 rpm). Calculated amount of TBHP was added at regular time intervals in small quantities over the whole span of the reaction time. At the end of the catalytic run the reaction mixture was subjected to GC and the extent of conversion was calculated on the basis of the ratio of the areas of the starting material and the product(s) by using *meta*-xylene as an external standard. All products were initially identified by using authentic commercial samples.

Oxidation reactions with dioxygen were carried out in a twonecked round bottom flask fitted with a gas inlet and a condenser. The mixture of substrate, catalyst, TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] in fixed volume of acetonitrile in the round bottom flask was placed in an oil bath previously heated at 353 K and dioxygen was bubbled through the mixture at ten bubbles per minute. Product was identified by ¹H NMR and gas chromatographic techniques.

2.5. Synthesis of $[Cu{(-)Sp}(NO_2)Cl]$ (1)

The precursor complex $[Cu\{(-)Sparteine\}Cl_2]$ (36.7 mg, 0.1 mmol) was dissolved in 10 mL of (1:1) CH₂Cl₂:CH₃CN. AgClO₄ (20.5 mg, 0.1 mmol) was dissolved in 5 mL of ethanol and added drop wise to the above copper solution with vigorous stirring. Immediate precipitation of AgCl was observed. 11 mg (0.15 mmol) NaNO₂ was added to the above mixture at a time in the solid form and stirred magnetically for 6 h. The solution was filtered and the solvent was removed under reduced pressure to get the green solid. The solid mass thus obtained was redissolved in (1:1) CH₂Cl₂:CH₃CN solvent mixture to get the single-crystals by slow evaporation technique at 253 K. Yield: 32 mg (84%). *Anal.* Calc. for C₁₅H₂₆ClCuN₃O₂ (Mol. wt. 379.38): C, 47.49; H, 6.91; N, 11.08. Found: C, 47.26; H, 6.86; N, 11.12%. Molar conductivity $[\Lambda_{\rm M} (\Omega^{-1} \text{ cm}^2 \text{ M}^{-1})]$ in acetonitrile: 26. ESI(+) Mass spectrum in CH₃CN: m/z = 343.22 corresponding to $[1-C1]^+$ (calcd. 343.13).

2.6. Synthesis of [Cu{(-)Sp}(NO₃)Cl] (2)

The precursor complex $[Cu\{(-)Sparteine\}Cl_2]$ (36.7 mg, 0.1 mmol) was dissolved in 10 mL of (1:1) CH₂Cl₂:CH₃CN. AgNO₃ (17 mg, 0.1 mmol) was dissolved in 5 mL of ethanol and added drop wise slowly to the previous solution with vigorous stirring. Immediate precipitation of AgCl was observed. The solution was filtered and the solvent was removed to get the bluish-green solid. The solid was redissolved in (1:1) CH₂Cl₂:CH₃CN solvent mixture to get the crystal by slow evaporation at 253 K. Yield: 30 mg (76%). *Anal.* Calc. for C₁₅H₂₆ClCuN₃O₃ (Mol. wt. 395.38): C, 45.47; H, 6.63; N, 10.63. Found: C, 45.38; H, 6.49; N, 10.68%. Molar

conductivity $[\Lambda_{\rm M} (\Omega^{-1} \text{ cm}^2 \text{ M}^{-1})]$ in acetonitrile: 30. ESI(+) Mass spectrum in CH₃CN: 359.82 *m*/*z*, corresponding to $[2-\text{Cl}]^+$ (calcd. 359.13).

3. Result and discussion

3.1. Syntheses of the complexes 1 and 2

The synthetic procedures of the complexes **1** and **2** are shown in Scheme 1. Using $[Cu\{(-)Sp\}Cl_2]$ as the starting material the complexes are synthesized in single step reactions. The precursor complex $[Cu\{(-)Sp\}Cl_2]$ has been synthesized according to the literature procedure by the reaction of (-)Sp with $CuCl_2 \cdot 2H_2O$ [23].

The electrically neutral complexes (1 and 2) exhibit satisfactory microanalytical and mass spectral data (see Experimental section).

3.2. X-ray crystal structure

Crystal structures of **1** and **2** are shown in Fig. 1. The selected crystallographic parameters and bond distances and angles are set in Tables 1 and 2, respectively. The CuN_2O_2Cl chromophore in **1** or **2** exhibits a distorted square pyramidal geometry. The nitrite $(-NO_2)$ and nitrate $(-NO_3)$ groups in **1** and **2**, respectively, are bound to the copper ion through two oxygen donors forming four member chelate rings. The bulky sparteine ligand binds to the copper ion through the nitrogen donors forming a six-membered chelate ring in both **1** and **2**. The N1 and N2 donors of sparteine



Fig. 4. 1H NMR spectra of complexes (a) $[Cu(Sp)(NO_2)Cl]$ (1) and (b) $[Cu(Sp)(-NO_3)Cl]$ (2) in CDCl_3.

ligand attached to the copper ion in endo and exo fashions, respectively, with regard to the pendant cyclohexane ring. The bite angles, N1–Cu–N2 involving the sparteine ligand in **1** and **2** are 90.56° and 89.66°, respectively, which are much higher than that reported for the pseudo-tetrahedral four coordinated copper-Sp complexes, 50–60°. This difference in bite angle develops primarily due to the five coodinated square pyramidal geometry in **1** or **2** which essentially widens the angle between the Cu and the two nitrogen donors of the sparteine ligand. The much shorter bite angles involving the nitrite or nitrate ligand in 1 or 2 of 56.45° or 56.48°, respectively, arises due to the steric constrains originated through the four-membered chelate ring.

3.3. Spectral and redox properties

The complexes, **1** and **2** have been characterized by UV–Vis, IR, NMR, EPR spectroscopic and cyclic voltammetric studies.

The UV–Vis spectrum of **1** exhibits one sharp charge-transfer transition in the UV-region at 299 nm with the molar extinction coefficient (ε) value 1625 M⁻¹ cm⁻¹ and a broad d–d transition in the visible region at 720 nm having ε value 80 M⁻¹ cm⁻¹ (Fig. 2).

The UV–Vis spectrum of **2** shows the corresponding transitions at 321 nm ε : 1685 M⁻¹ cm⁻¹) and at 744 nm (ε : 92 M⁻¹ cm⁻¹).

The IR spectra of **1** and **2** show the characteristic vibrations of N–O of coordinated $-NO_2$ and $-NO_3$ groups at 1465, 1383 and 1302 cm⁻¹ and 1481, 1384 and 1302 cm⁻¹, respectively [17,25].

The X-band EPR spectra of 1 and 2 in the solid state at 300 K exhibit one broad signal with center field g values of 2.12 and 2.14, respectively. The better picture is obtained at 77 K in 1:1 dichloromethane:toluene mixture. The complexes exhibit typical four lines EPR spectra for ⁶³Cu with I = 3/2 showing $g_{\parallel} > g_{\perp} > 2.0023$ (Fig. 3). This indicates a distorted square pyramidal or trigonal bipyramidal geometry with $d_{x^2-v^2}$ as the ground state. The g_{\parallel} values calculated to be 2.28 and 2.26 with $A_{||}$ values of 120×10^{-4} and $132 \times$ 10^{-4} cm⁻¹ and g₁ to be 2.07 and 2.06 for complex **1** and **2**, respectively. For square planar CuN4 chromophore parallel hyperfine splitting is reported always greater than $140 \times 10^{-4} \text{ cm}^{-1}$ [1]. For a five coordinated species the two possible geometries, trigonal bipyramid (tbp) and square pyramid can easily be recognized from the EPR spectral features. For tbp structure parallel hyperfine splitting (A_{II}) value lies between 60×10^{-4} and 100×10^{-4} cm⁻¹ whereas the same A_{\parallel} value for the square pyramidal structure varies in

Table 3

 $Product \ selectivity \ in \ the \ conversion \ of \ cyclohexene \ and \ styrene \ with \ 1 \ and \ 2 \ and \ [Cu{(-)Sp}Cl_2] \ in \ presence \ of \ TBHP.^a$

	\bigcirc			and	$\begin{array}{c} \leftarrow \\ \bullet \\ d \\ \end{array} \\ \begin{array}{c} \leftarrow \\ \bullet \\ e \\ \end{array} \\ \begin{array}{c} \leftarrow \\ \bullet \\ \bullet \\ \end{array} \\ \begin{array}{c} \leftarrow \\ \bullet \\ \bullet \\ \bullet \\ \end{array} \\ \begin{array}{c} \leftarrow \\ \bullet \\ \bullet \\ \bullet \\ \bullet \\ \bullet \\ \end{array} \\ \begin{array}{c} \leftarrow \\ \bullet \\$	<u> </u>
Entry	Substrate	Temperature (K)	Time (h)	1 (% conversion) selectivity	2 (% conversion) selectivity	Cu{(–)Sp}Cl ₂ (% conversion) selectivity
1	\sim	300	24	(86) a = 100	(82) a = 100	(81) a = 52 b = 4 c = 44
2		353	12	(100) a = 61 b = 25 c = 14	(100) a = 54 b = 28 c = 18	L = 44 -
3		300	24	(100) e = 92 f = 8	(100) e = 96 f = 4	(56) d = 20 e = 42 f = 38
4		278	24	(5) d = 32 e = 64 f = 4	(8) d = 41 e = 59	-
5		353	12	(100) e = 100	(100) <i>e</i> = 100	-

^a All the reactions were carried out with 1 mmol substrate 0.01 mmol of complex 1, 2 or Cu(-)SpCl₂ in 3 mL of acetonitrile using 1.5 mmol of TBHP.

Table 4

Distribution of the products with time in the epoxidation of cyclohexene at 353 K with 1 and 2.ª

Entry	Time (h)	(h) Complex 1				Complex 2			
		% conversion	0	ОН	O O	% conversion	0	ОН	0
1	2	24	86	12	2	27	88	12	0
2	4	43	82	14	4	38	76	19	5
3	6	62	74	20	6	56	70	21	9
4	8	76	68	23	9	70	62	26	12
5	10	89	64	27	9	86	56	28	16
6	12	100	61	25	14	100	54	28	18

^a All the reactions were carried out at 353 K with 1 mmol of cyclohexene 0.01 mmol of complex 1 or 2 in 3 mL of acetonitrile using 1.5 mmol of TBHP.

the range of $120-150\times10^{-4}~cm^{-1}$ [26]. The EPR spectra of 1 and 2 therefore establish the distorted square pyramidal geometry around the copper ion.

¹H NMR spectrum of free (–)sparteine in CDCl₃ shows the proton resonances within the chemical shift range of 1.0–2.8 ppm. However, the one-electron paramagnetic complexes (μ : 1.91 B.M. (**1**) and 1.95 B.M. (**2**) in the solid state at 298 K) display ¹H NMR resonances over a wide range of chemical shift values, –20 to +12 ppm in CDCl₃ (Fig. 4) due to paramagnetic contact shift effect [27,28].

The irreversible oxidation and reduction processes of **1** and **2** in CH₃CN appear at 1.2, -0.58 V and 0.76, -0.70 V (vs. SCE/Pt/[Et₄N]-[ClO₄]), respectively which are tentatively assigned to copper



Fig. 5. % Conversion and selectivity with time during cyclohexene epoxidation with 1 and 2.



Fig. 6. Change in the concentration of the products with time during the epoxidation of cyclohexene by (a) 1 and (b) 2.

based processes of $[(Sp)Cu^{II}(L)]$ $(1/2) \rightarrow [(Sp)Cu^{II}(L)]^{+} (1^{+}/2^{+})$ and $[(Sp)Cu^{II}(L)]$ $(1/2) \rightarrow [(Sp)Cu^{I}(L)]$ $(1^{-}/2^{-})$, respectively. The potentials vary appreciably based on the nitrite and nitrate ligands.

3.4. Catalytic study

3.4.1. Epoxidation

With complexes **1** and **2** as catalysts epoxidation of the alkenes are first carried out using TBHP as the oxidant. At room temperature cyclohexene is selectively converted to the corresponding epoxide (Table 3, Entry 1). In contrast, styrene is selectively oxidized to benzaldehyde at room temperature. The catalytic activity of reported pseudo tetrahedral complex $[Cu{(-)Sp}Cl_2]$ has also been studied in the similar condition for the comparison purpose. With $[Cu{(-)Sp}Cl_2]$ as the catalyst both cyclohexene and styrene produce a mixture of products at room temperature (Table 3, Entry 1 and 3). The effect of temperature on the reaction has been studied at three different temperatures. At 353 K the product is observed to be benzaldehyde with full selectivity (Table 3, Entry 5). At low temperature (278 K) the same reaction is found to produce low amount of styrene oxide along with benzaldehyde, though the conversion is only 5% and 8% with 1 and 2, respectively (Table 3, Entry 4).

The selective formation of benzaldehyde from styrene is considered to be a challenging catalytic process and only a few reports are known so far. Palladium chloride catalyzed oxidation of styrene to acetophenone in homogeneous medium using molecular oxygen has recently been reported by Gusevskaya and co-workers [29]. Depending on the reaction conditions, formation of varying amounts of benzaldehyde along with acetophenone is mentioned. A water soluble palladium complex has been used by the Hou group to produce benzaldehyde as the major product from styrene

Table 5

Oxidation of alcohols with 1 and 2 by molecular oxygen.^a



^a 1 mmol substrate, 5 mol% catalyst, 10 mol% TEMPO in acetonitrile for 24 h at 353 K in bubbling oxygen.

in the presence of molecular oxygen [30]. More relevant in the present context is the report by Koner et al. of a copper Schiff base complex, where during styrene oxidation with TBHP, formation of both benzaldehyde and styrene oxide was observed [31]. Using heterogeneous catalytic system or polyoxometallate there are reports of selective formation of benzaldehyde from styrene [32-35] but in homogeneous medium the reaction is not very common [36].

When the epoxidation of cyclohexene is carried out at 353 K, the selectivity towards the epoxide decreases and a mixture of cyclohene oxide, cyclohexanol and cyclohexanone are obtained (Table 4, Entry 1). A time monitored profile of the product formation for the cyclohexene at 353 K is shown in Fig. 5 and Table 4. At high temperature even under low conversions all the three products, cyclohexene oxide, cyclohexanol, and cyclohexanone are found to be present. With increasing time selectivity towards cvclohexene oxide decreases and the amounts of cvclohexanol and cyclohexanone increase. Time monitored concentration profile of the products reveals that with time concentrations of all the three products increase till full conversion is reached (Fig. 6). During the reaction formation of the other oxidized species like 2-cyclohexene-1-ol or 2-cyclohexene-1-one or cyclohexane-1.2-diol was not observed.

Epoxidation reactions with metal catalysts are often facilitated through the formation of a high valent metal-oxo intermediate or by polarization of the peroxo moiety by interaction with an electrohilic metal ion in high oxidation state [37-40]. As complex 1 or 2 is five coordinated, the formation of a six co-ordinate oxo intermediate of Cu(IV) is unlikely. However, the labile Cu-Cl site in 1 or 2 can facilitate the formation of the intermediate four coordinated species in the reaction mixture. This labile species may interact with TBHP facilitating the polarization and oxygen atom transfer from the peroxo group. In the oxidizing condition the nitrite species is not stable and removal of the -NO₂ group is clear from the IR spectra of the recovered species after the catalytic run. However, preliminary ESR measurements show that with 1 and **2** radical pathways are also present. Our future work will address these mechanistic points in more detail.

3.4.2. Oxidation

Complexes 1 and 2 have been used for the oxidation of the primary alcohols like benzyl alcohol and cyclohexanol in bubbling oxygen at 353 K using TEMPO. Benzyl alcohols are converted to benzoic acids and cyclohexanol to cyclohexanone (Table 5). An attempt to oxidize secondary alcohols in the same condition is failed where 7 and 11% conversion is achieved for $(\pm)1$ -phenyl ethanol by both **1** and **2**, respectively.

4. Conclusion

Five coordinated copper-sparteine complexes with nitrite (1) and nitrate (2) as chelating ligands have been synthesized. The complexes have been characterized by X-ray crystallography and spectroscopic techniques. The catalytic activities of the complexes for the epoxidation and oxidation reactions have been explored. At room temperature with TBHP as the oxidant cyclohexene oxide with high selectivity is obtained from cyclohexene, whereas under the same conditions oxidation of styrene selectively gives benzaldehyde.

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structural studies were carried out at the National Single Crystal Diffractometer Facility, Indian Institute of Technology, Bombay. EPR experiments were carried out at the Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology Bombay.

Appendix A. Supplementary material

CCDC 810122 and 810123 contain the supplementary crystallographic data for complexes 1 and 2, respectively. 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 doi:10.1016/j.ica.2011.03.027.

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