Inorganica Chimica Acta 375 (2011) 101–105

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Epoxide ring opening in a zinc(II) complex in water without any Lewis acid catalyst: Formation of only one diastereomer out of 2^3

Nirmal K. Shee [a], F.A. Oluwafunmilayo Adekunle [a,1], Debashree Das [a], Michael G.B. Drew [b], Dipankar Datta [a,*]

[a] Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India
[b] Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK

ARTICLE INFO

Article history:
Received 4 November 2010
Received in revised form 19 April 2011
Accepted 20 April 2011
Available online 27 April 2011

Keywords:
Zinc(II)
Epoxide
Epoxide opening
Diastereomer
Diastereoselective

ABSTRACT

The epoxide ring in 5,6-dihydro-5,6-epoxy-1,10-phenanthroline (L) opens up in its reaction with 4-methylaniline and 4-methoxyaniline in water in equimolar proportion at room temperature without any Lewis acid catalyst to give a monohydrate of 6-(4-methyl-phenylamino)-5,6-dihydro-1,10-phenanthrolin-5-ol ($L'\cdot H_2O$) and 6-(4-methoxyphenyl-amino)-5,6-dihydro-1,10-phenanthrolin-5-ol (L'') respectively. Reaction time decreases from 72 to 14 h in boiling water. But the yields become less. Reaction of L with $Zn(ClO_4)_2\cdot 6H_2O$ in methanol in 3:1 molar ratio at room temperature affords white $[ZnL_3](ClO_4)_2\cdot H_2O$. The X-ray crystal structure of the acetonitrile solvate $[ZnL_3](ClO_4)_2\cdot MeCN$ has been determined which shows that the metal has a distorted octahedral N_6 coordination sphere. $[ZnL_3](ClO_4)_2\cdot 2H_2O$ reacts with 4-methylaniline and 4-methoxyaniline in boiling water in 1:3 molar proportion in the absence of any Lewis acid catalyst to produce $[ZnL'_3](ClO_4)_2\cdot 4H_2O$ and $[ZnL''_3](ClO_4)_2\cdot H_2O$, respectively in 1–4 h time in somewhat low yield. In the ^1H NMR spectra of $[ZnL'_3](ClO_4)_2\cdot 4H_2O$ and $[ZnL''_3](ClO_4)_2\cdot H_2O$, only one sharp methyl signal is observed implicating that only one diastereomer out of the 2^3 possibilities is formed. The same diastereomers are obtained when $L'\cdot H_2O$ and L'' are reacted directly with $Zn(ClO_4)_2\cdot 6H_2O$ in tetrahydrofuran at room temperature in very good yields. Reactions of $L'\cdot H_2O$ and L'' with $Ru(phen)_2Cl_2\cdot 2H_2O$ (phen = 1,10-phenanthroline) in equimolar proportion in methanol–water mixture under refluxing condition lead to the isolation of two diastereomers of $[Ru(phen)_2L'](ClO_4)_2\cdot 2H_2O$ and $[Ru(phen)_2L''](ClO_4)_2\cdot 2H_2O$.

1. Introduction

Epoxides (or oxiranes) are highly versatile intermediates in synthetic organic chemistry. Nature also uses them as intermediates in many key biosynthetic pathways. However, there are other functions of epoxides in biological systems. They can impart localised structural rigidity, confer cytotoxicity by alkylation, or be secondary metabolites [1]. The chemistry of epoxides is dominated by the reactions that involve opening of the strained three-membered heterocyclic ring by nucleophiles. Such reactions yield valuable bifunctional compounds. In nature, epoxide ring opening is catalysed by the phenolic proton of a tyrosine moiety [2]. But in laboratory, the cleavage usually occurs in non-aqueous media in presence of a Lewis acid catalyst like Al_2O_3, Li^+, Mg^{2+}, etc. Additionally often elevated temperature and excess of nucleophiles are required. There are a few reports where use of a catalyst has not been necessary [3,4]. For example, aminolysis of epoxide by an α-amino acid ester proceeds smoothly in refluxing trifluoroethanol [3]. The same reactions fail in water. In contrast, aliphatic and aromatic amines are found to cleave an epoxide ring in water at room temperature without any Lewis acid catalyst [4]. Herein we report opening of an epoxide group present in a chelate ring of a metal complex by aromatic amines stoichiometrically in refluxing water in the absence of any catalyst. The ligand chosen is 5,6-dihydro-5,6-epoxy-1,10-phenanthroline (L) and the metal ion is Zn(II).

2. Results and discussion

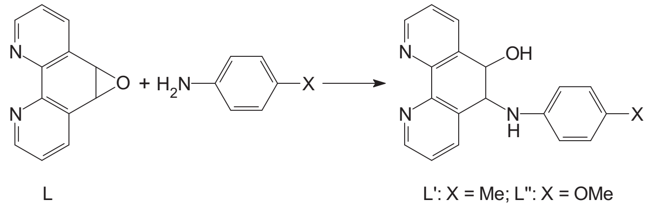
Stirring of L with 4-methylaniline and 4-methoxyaniline in equimolar proportion in water at room temperature for 72 h without any Lewis acid catalyst gives $L'\cdot H_2O$ and L'', respectively (Scheme 1). The yield of $L'\cdot H_2O$ is 90% and that of L'' 70%. These are obtained in 60% yield when the reactants are refluxed in water for 14 h. But the yield goes on decreasing when increasingly more refluxing time is used. Earlier Moody et al. have [5] studied opening of the epoxide ring in L in connection with their total synthesis of the pentacyclic marine alkaloid ascididemin from 1,10-phenanthroline (phen). They used reaction (1) in dichloromethane to obtain L'' in 74% yield. However, unsubstituted aniline can open the

---

[*] Corresponding author. Tel.: +91 33 2473 5374; fax: +91 33 2473 2805.
E-mail address: icdd@iacs.res.in (D. Datta).

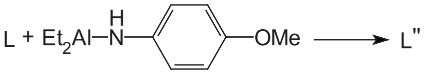
[1] Permanent address: Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, P.M.B. 4000, Ogbomoso, Nigeria.

0020-1693/$ - see front matter
doi:10.1016/j.ica.2011.04.037



Scheme 1.

epoxide ring in L in dichloromethane when alumina is used as a catalyst [5,6].



(1)

Aminolysis of L is potential in generating two chiral centers, i.e. 2^2 isomers. But due to the stereoselectivity of the reaction, formation of only two enantiomers is possible. Hence in a *tris* metal complex of L, Scheme 1 will render four pairs of enantiomers (i.e. 2^3 isomers). This fact when coupled with the optical isomerism of a *tris* chelate indicates that 2^3 diastereomers are possible. Because of our recent interest in diastereoselective synthesis of metal complexes [7], we have prepared the *tris* L complex of Zn(II) and studied its reactions with 4-methylaniline and 4-methoxyaniline.

White $[ZnL_3](ClO_4)_2 \cdot 2H_2O$ is obtained by reacting L with $Zn(ClO_4)_2 \cdot 6H_2O$ in methanol in 3:1 molar proportion at room temperature. Direct diffusion of diethyl ether to an acetonitrile solution of $[ZnL_3](ClO_4)_2 \cdot 2H_2O$ gives single crystals of $[ZnL_3](ClO_4)_2 \cdot MeCN$, the X-ray crystal structure of which has been determined. The structure of the cation $[ZnL_3]^{2+}$ is shown in Fig. 1. The metal atom has a distorted octahedral N_6 coordination sphere. The main cause of distortion is the bite angles of the ligand which are 77.45(13), 76.74(14) and 76.67(14)°. The Zn–N bond lengths show some variations in the range of 2.147(3)–2.202(4) Å. A similar variation is found in the structure of $[Zn(phen)_3](ClO_4)_2$ of 2.122–2.230 Å [8]. As is apparent from Fig. 1, two oxygen atoms O(38), O(58) are directed in one direction and O(18) the other, thus the structure of $[ZnL_3]^{2+}$ lacks C_3 symmetry. Our DFT calculations at the B3LYP/6-311** level show that the symmetric structure is more stable than that found in X-ray crystallography by only 0.2 kJ mol^{-1}.

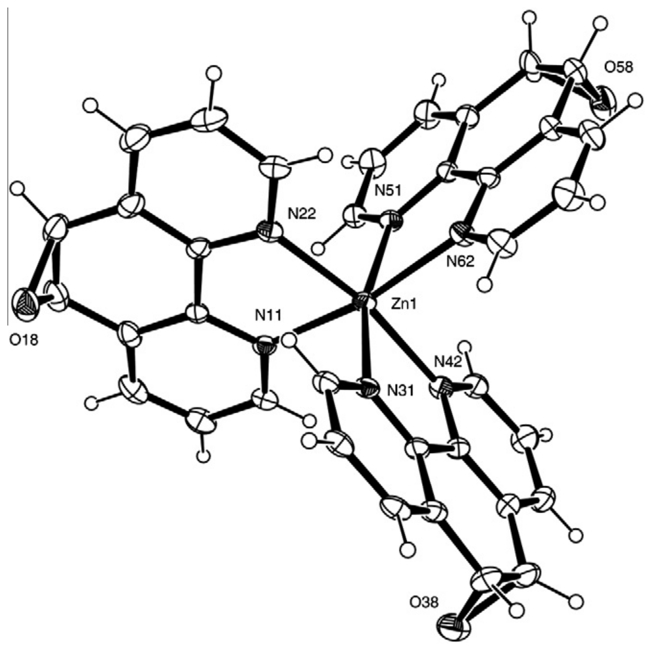


Fig. 1. The structure of the cation in $[ZnL_3](ClO_4)_2 \cdot MeCN$ with ellipsoids at 30% probability. Selected bond distances (Å) and angles (°): Zn1–N31 2.147(3), Zn1–N42 2.155(4), Zn1–N11 2.159(4), Zn1–N51 2.161(3), Zn1–N22 2.171(4), Zn1–N62 2.202(4), N31–Zn1–N42 77.45(13), N31–Zn1–N11 96.89(13), N42–Zn1–N11 95.99(14), N31–Zn1–N51 166.13(14), N42–Zn1–N51 94.80(13), N11–Zn1–N51 95.34(14), N31–Zn1–N22 95.27(13), N42–Zn1–N22 169.17(13), N11–Zn1–N22 76.74(14), N51–Zn1–N22 93.88(13), N31–Zn1–N62 91.92(13), N42–Zn1–N62 91.70(14), N11–Zn1–N62 169.37(13), N51–Zn1–N62 76.67(14), N22–Zn1–N62 96.60(14).

$[ZnL_3](ClO_4)_2 \cdot 2H_2O$ reacts with 4-methylaniline and 4-methoxyaniline in refluxing water in 1:3 molar proportion in the absence of any Lewis acid catalyst to produce $[ZnL'_3](ClO_4)_2 \cdot 4H_2O$ and $[ZnL''_3](ClO_4)_2 \cdot H_2O$, respectively. When the refluxing time is 1 h in the case of 4-methylaniline, the yield is 30%, and when it is 4 h in the case of 4-methoxyaniline, the yield is 45%. The yield goes on decreasing in each case when refluxing time is increasingly more than that specified. Their proton NMR spectra show that in each case only one sharp methyl signal is obtained. The ^1H NMR spectrum of $[ZnL'_3](ClO_4)_2 \cdot 4H_2O$ is shown in Fig. 2. This implies that only one diastereomer out of the 2^3 possibilities is formed. Thus the aminolysis of the epoxide rings in $[ZnL_3]^{2+}$ by 4-substituted anilines is diastereoselective. The same diastereomers are obtained when $L' \cdot H_2O$ and L'' are reacted directly with $Zn(ClO_4)_2 \cdot 6H_2O$ in tetrahydrofuran (THF) at room temperature in 70–80% yield. $L' \cdot H_2O$ yields $[ZnL'_3](ClO_4)_2 \cdot 0.75THF \cdot 5H_2O$ but L'' gives $[ZnL''_3](ClO_4)_2 \cdot 4H_2O$ the same complex obtained by aminolysis of $[ZnL_3](ClO_4)_2 \cdot 2H_2O$ by 4-methoxyaniline in water. Such selectivity is not common in inorganic synthesis [9,10]. We have found that two diastereomers are obtained when $L' \cdot H_2O$ is reacted with $Ru(phen)_2Cl_2 \cdot 2H_2O$ in equimolar proportion in 1:1 (v/v) methanol–water mixture under refluxing condition to synthesise $[Ru(phen)_2L'](ClO_4)_2 \cdot 2H_2O$. This conclusion is based on the observation of two methyl signals in the ^1H NMR spectrum of $[Ru(phen)_2L'](ClO_4)_2 \cdot 2H_2O$ (Fig. 2). Incidentally only two diastereomers are indeed expected from the reaction of $L' \cdot H_2O$ with $Ru(phen)_2Cl_2 \cdot 2H_2O$ because of coupling of the two enantiomers of L′ and the chirality of the hetero tris chelate. Two diastereomers are also obtained in the generation of $[Ru(phen)_2L''](ClO_4)_2 \cdot 2H_2O$ from the reaction of L″ with $Ru(phen)_2Cl_2 \cdot 2H_2O$ in 1:1 molar proportion in refluxing 1:1 (v/v) methanol–water mixture. Evidently the diastereoselectivity observed here is metal dependent.

The role of Zn(II) ion in the opening of the epoxide rings is not clear. Our B3LYP/6-311G** calculations show that while the Mulliken charge on the two C atoms of the epoxide ring in the free L is −0.020, that in the L chelated to Zn(II) −0.015. Thus simple electrostatic considerations cannot explain the observed effect of Zn(II).

3. Experimental

3.1. Materials and physical measurements

5,6-Dihydro-5,6-epoxy-1,10-phenanthroline (L) was procured from Aldrich. $Ru(phen)_2Cl_2 \cdot 2H_2O$ was prepared by a reported procedure [11]. Microanalyses were performed by a Perkin-Elmer 2400II elemental analyser. Molar conductances were measured by a Syntronics (India) conductivity meter (model 306) in acetonitrile. FTIR spectra (KBr) were recorded on a Shimadzu FTIR-8400S spectrometer, UV–Vis spectra in acetonitrile on a Perkin Elmer Lambda 950 spectrophotometer, ESI mass spectra on a Waters Qtof Micro YA263 spectrometer and 300 MHz NMR spectra on a Bruker DPX300 spectrometer in deuterated dimethylsulfoxide (DMSO-d_6).