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Synthesis, Characterization and Application of Oxo-Molybdenum(V)- Corrolato Complexes in Epoxidation Reactions

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Abstract: Sharpless *et al.* has described, while performing the molybdenum catalyzed epoxidation reaction of olefins using alkyl hydroperoxides, that molybdenum-oxo moiety is the active catalytic species. Thus there is a continuous effort to synthesize molybdenum-oxo complexes of different ligand environments. While such works of literature on molybdenum porphyrins are plenty but related molybdenum(V)-corrolato complexes are described herein. Both the complexes were fully characterized by several spectroscopic techniques in conjunction with single-crystal X-ray diffraction analysis. The efficacy of the oxo-molybdenum(V)-corrolato complexes have also been explored. The catalytic application of oxo-molybdenum(V)-corrolato complexes in the epoxidation reaction was not reported earlier. A mechanism has been proposed to explain the experimental findings.

KEYWORDS: Corrole / Molybdenum (V) / Oxido-ligand / EPR spectroscopy / Catalysis / Epoxidation reaction

Introduction

Alkene epoxidation has key importance in the chemical industry and often generates useful precursors for commodity chemicals.^{1,2} Industrially relevant Halcón process deals with the epoxidation of propylene and uses molybdenum complexes as catalyst and tertbutylhydroperoxide (t-BuOOH) as oxidant.^{3,4} While performing the molybdenum catalyzed epoxidation of olefins using alkyl hydroperoxides, Sharpless et al. has described the molybdenum-oxo core as an active catalytic moiety.⁵ Thus the syntheses of molybdenum-oxo complexes having different coordination environments are gained valuable insight. ⁶⁻⁸ Due to their superior performance, various aspects of molybdenum porphyrin complexes are extensively studied and their uses as epoxidation catalysts are also described in detail in the literature.⁹⁻¹⁴ Corrole, a contracted porphyrin analogue, has gained a considerable research interest in recent times.¹⁵⁻³¹ The discovery of facile and efficient synthetic protocols for corroles has fueled its rapid growth.³²⁻³³ Being tri-anionic in nature, smaller cavity size, and also having electron-rich core structure, corrole tends to stabilize different metals in their possible higher oxidation states in comparison to their porphyrin counterparts.¹⁵⁻³¹ Thus it is logical to consider that oxomolvbdenum(V)-corrolato complexes will also act as potent epoxidation catalysts. However, similar literatures using corrole as a metal chelator are very limited. Very few research reports indeed highlight the fascinating chemistry of molybdenum-corrole complexes.³⁴⁻⁴⁰ Such reports on their catalytic applications are non-existent. Herein we have reported the synthesis and characterization of two new molybdenum corrole complexes. Both the complexes were thoroughly characterized by ample spectroscopic techniques in conjugation with single-crystal XRD analysis of a representative derivative. The present work thus describes the synthesis of two new oxo-molybdenum(V)-corrolato complexes, namely, oxo[5,10,15-tris(4cyanophenyl)corrolato] molybdenum (V), 1, and oxo[5,15-bis(4-cyanophenyl)-10-(4bromophenyl)-corrolato] molybdenum (V), 2, (Scheme 1). One A₃-corrole and one *trans*-A₂B corrole has been chosen here in order to modulate the electronic and steric factors of the synthesized complexes. This variation of corrole framework (trans-A2B corrole is more versatile) might lead to the changes in the energies of molecular orbitals of the respective metallo-corrole complexes and thus could cause the difference in their spectroscopic properties.⁴¹ Finally one of the representative derivatives has been tested as an epoxidation catalyst using t-BuOOH as an oxidant.



Scheme 1. Structures of the oxo-molybdenum(V)-corrolato complexes: oxo[5,10,15-tris(4-cyanophenyl)corrolato] molybdenum (V), **1**, and oxo[5,15-bis(4-cyanophenyl)-10-(4-bromophenyl)-corrolato] molybdenum (V), **2**.

RESULTS AND DISCUSSION

Synthesis and characterization

Oxo-molybdenum(V)-corrolato complexes were synthesized by a slight modification of a previously reported synthetic protocol.³⁹ The corresponding free base corroles were dissolved in toluene and the molybdenum hexacarbonyl was added and refluxed for 8-10 hours and resulted in the formation of oxo-molybdenum(V)-corrolato derivatives (**1** and **2**) in good yields. Oxygen from the air is the source of oxido ligand here and it also leads to the conversion of Mo (0) to Mo (V) oxidation state and no other co-oxidants are necessary for this purpose. Purity and identity of the oxo-molybdenum(V)-corrolato complexes are demonstrated by their satisfactory elemental analyses and ESI-MS data (Figures S2-S3, see the Supporting Information). As the oxo-molybdenum(V)-corrolato derivatives are paramagnetic in nature thus it was not possible to characterize these complexes *via* NMR spectroscopy. However, all the oxo-molybdenum(V)-corrolato complexes were investigated by X-band EPR spectroscopy.³⁴⁻⁴⁰

Crystal Structure

Single crystals of oxo-molybdenum(V)-corrolato complexes were grown at room temperature. The crystallographic analysis revealed that a representative oxo-molybdenum(V)-corrolato complex, **1** is a mononuclear complex having a penta-coordination and with a distortion from the square-pyramidal geometry around molybdenum ion (Figure 1 and Figure S1). Important crystallographic parameters are summarized in Table S1 (see Supporting Information). The Mo=O bond distance is observed as 1.659 Å, and this distance falls in the range of previously reported other molybdenum-oxo bond distances.⁴² Gross et al. has reported earlier that the Mo=O bond distance in a related oxo-molybdenum(V)-corrolato complex is 1.684 Å and thus it was a bit elongated in comparison to the present case.³⁶ The Mo=O bond distance obtained from other structurally characterized oxo-molybdenum(V)-porphyrinato complex was 1.658 Å.⁴² The Mo atom points out of the N₄ plane axially by 0.74 Å and thus resulted in the dome-shaped of the corrole ring. Similar deviation of molybdenum ion is also observed in a related oxo-molybdenum(V)-corrolato complex molybdenum ion has deviated from the mean N₄ plane by a distance of ~0.73 Å.³⁶ The deviation of the molybdenum atom from the 19-carbon corrolato plane is even more prominent and assumes a value of ~0.93 Å.

The Mo–N bond distances vary from 2.020–2.039 Å and are very much comparable to other related metal-nitrogen bonds of molybdenum coordinated corrolato rings.



Figure 1. Single-crystal X-ray structure of 1. Hydrogen atoms are omitted for clarity.

The Mo–N bond distances are in line with the previously reported similar bond distances (Mo–N: 2.033–2.039 Å) of related complexes by Gross *et al.* ³⁶ The N–Mo–N bite angles vary from 74.71 to 88.82 °.

Electrochemistry

The cyclic voltammetric and differential pulse voltammetric techniques were used in order to analyze the redox properties of complexes **1** and **2**. The measurements were performed in dichloromethane solvent and 0.1 M tetra-*n*-butyl ammonium perchlorate was used as a supporting electrolyte (Figure 2 and Table S2). The oxidation processes at the positive side of the reference electrode (Ag/Ag⁺) were recorded by using a platinum wire working electrode. A glassy–carbon (GC) working electrode was used specifically for recording the reduction processes. Both the molybdenum complexes exhibited one reversible oxidation couple at +0.59 V for **1** ($\Delta E_p = 80$ mV) and +0.41 V ($\Delta E_p = 80$ mV) for **2** respectively (versus Fc/Fc⁺). They also showed one reversible reduction couple at -0.94 V ($\Delta E_p = 80$ mV) for **1** and -1.17 V ($\Delta E_p = 80$

mV) for **2** respectively (versus Fc/Fc^+). Thus the electronic effect of the peripherial *meso*-substituents in the corrole framework on tuning the redox potentials of the oxo-molybdenum(V)-corrolato complexes are significant.³⁶



Figure 2. Cyclic voltammogram (black solid line) and differential pulse voltammogram (black doted line) of (a) **1** and (b) **2** in CH₂Cl₂. The potentials are *vs*. ferrocene/ ferricinium.

EPR and Magnetism

Both the complexes showed similar kinds of EPR spectra thus only one will be discussed here in detail (Figure 3 and Figure S4). Complex **1** shows EPR in fluid solution at room temperature (Figure 3). The spectrum shows nine super-hyperfine lines at the center and the six hyperfine lines at the periphery. The central nine lines can be easily assigned and can be originated due to the coupling of four inner ring nitrogen atoms (^{14}N , I=1) of corrole with the Mo isotopes (75% I = 0, ^{92}Mo , ^{94}Mo , ^{96}Mo , ^{98}Mo and ^{100}Mo). The presence of Mo isotopes (25% I = 5/2, ^{95}Mo and ^{97}Mo) are responsible for the origin of six weaker bands at the wide range of the spectrum.



Figure 3. EPR spectrum of **1** recorded in CH_2Cl_2 at 298 K. Inset shows the enlargement of the central lines (super-hyperfine lines due to four nitrogen nuclei).

Thus the EPR spectrum leads to the conclusion that the oxo-molybdenum(V)-corrolato complexes are indeed monomeric in nature and the ground state is a doublet.³⁴ The EPR signal due to Mo isotopes (75% I = 0) is very intense over a temperature range and thus clearly indicates that unpaired electron largely occupies the d_{xy} orbital of the Mo ion.³⁴ The following

parameters are obtained from EPR measurements of compound 1: $g_{iso} = 1.974$, $A^{95/97}Mo = 4.589$ mT, $A^{14}N = 0.208$ mT (Table S3). The obtained *g* vlaue of 1.97 suggests a strong covalent nature of the coordinate bonds with the metal center. All these parameters match nicely with the previously reported other oxo-molybdenum(V)-corrolato complexes.³⁴⁻⁴⁰

Figure 4 shows the inverse molar magnetic susceptibility (χ_m^{-1}) vs. Temperature (T) plot of compound 1. The curve shows typical Curie-Weiss behavior. We have not observed any appreciable magnetic ordering down to liquid helium temperature. The room temperature magnetic moment was observed as 1.62 μ_B for 1 and 1.72 μ_B for 2 at 300K (Figure S5) corresponds to one unpaired electron in each case. Thus there is no appreciable Mo(V)…Mo(V) interaction in the solid state. The observed magnetic moment tally well with the previously reported other oxo-molybdenum(V) complexes.⁴³





The catalytic efficiency of oxo-molybdenum(V)-corrolato complexes (1 and 2) for the epoxidation of olefins were optimized by performing the experiments under various reaction conditions. The details of the optimization of reaction conditions using cyclohexene as a model substrate for catalyst 1 and 2 are summarized in Table S4 and S5 (see the supporting information). The initial results indicated that the catalyst 1 exhibited superior catalytic performance than catalyst 2. This observation can be corroborated well with the observed redox potential of Mo^V/Mo^{IV} couple. The observed redox potential of Mo^V/Mo^{IV} couple of 2 (-1.17 V) is more negative than 1 (-0.94 V) vs Fc/Fc⁺ in CH₂Cl₂. Thus, we focus our discussion on the compound 1 in the following part (vide infra). All the catalytic reactions of compound 1 were carried out in a closed 10 mL single neck round bottom flask over an ice bath at 0°C and an oil bath at 80°C with constant stirring. Cyclohexene, norbornene, and 3-bromo-1-propene were used as model substrates for optimization of reaction conditions using catalyst 1. The influence of reaction time, types of oxidants, solvent amount, types of solvents and the effect of catalyst loading were also investigated. The optimized reaction conditions for the selective epoxidation of 0.25 mL (2.46 mmol) of cyclohexene are as follows : 0.356 mg (0.0005 mmol) of complex 1 and 0.05 mL (0.5 mmol) of t-BuOOH were taken together in 1.3 mL of benzene and were stirred at 80°C for 15 h. A good conversion with excellent selectivity to cyclohexene oxide was observed. Selectivity for epoxidation is determined from the percent of epoxide in total product. The product identification and the percentage of conversions were determined by analyzing the ¹H NMR spectrum of the crude reaction mixture (Figure S6-S24). The details of the optimization of reaction conditions at 80°C and at 0°C are summarized in Table 1, Table 2, Table S4 and Table S6 respectively. Cyclohexene was used as a model substrate for the optimization of reaction conditions using catalyst 1 at 80°C. While at 0°C, norbornene, cyclohexene, and 3bromo-1-propene were used as model substrates for optimization of reaction conditions.

In order to optimize the reaction conditions and to investigate the role of catalyst, cyclohexene epoxidation was carried out at 80° C for 17 h under air with a molar ratio of [Mocatalyst]: [*t*-BuOOH]: [alkene] = 1:1000:5000.¹² Using cyclohexene, nearly 99% conversion of the substrate [Table 1, Entry 2] to product was observed showing the effectiveness of the catalyst. However, in absence of the catalyst, only 14% conversion to cyclohexene oxide was observed [Table 1, Entry 1]. While optimizing the reaction time, we get the best conversion

(99%) after running the reaction for 15 h [Table 1, Entry 3]. It was also remarked that the shorter reaction time reduces the reaction yield significantly [Table 1, Entry 4, 5].

A series of various oxidants were screened in order to find out the best possible oxidant for this catalytic reaction. Here, t-BuOOH has been turned out to be the best oxidant with a conversion of 99% [Table 1, Entry 3]. t-BuOOH has a better thermal stability and thus activate the catalyst to participate in the reaction. Using hydrogen peroxide in the oxidation reactions, generates lower yield of epoxides [Table 1, Entry 15]. The solvent volume has also effect in the catlytic reaction and it was also observed that 1.3 mL of solvent gives the best result [Table 1, Entry 3]. Further decrease in solvent amount does not change much in the result [Table 1, Entry 11, 12]. For this study, a series of different solvents, such as benzene, toluene, THF, 1,4-dioxane, acetonitrile and DCE were screened. The most appropriate solvent turned out to be benzene [Table 1, Entry 3]. Although both DCE and benzene gave identical results but benzene is the cheaper alternative. Its enhanced solubility may dictate the good conversion in the reaction. The polar solvents like acetonitrile and tetrahydrofuran give negligible conversion of olefin [Table 1, Entry 6, 10]. 1,4-Dioxane shows a significant conversion of 78% [Table 1, Entry 8]. Similarly, 99% and 57% conversion of cyclohexene was observed in presence of dichloroethane and toluene, respectively [Table 1, Entry 7, 9]. The percent of conversion is maximum, i.e, 99% at a molar ratio of [Mo-catalyst, 1] : [t-BuOOH]: [alkene] = 1:1000:5000 (catalyst loading = 0.02%). While decreasing the catalyst loading to 0.01% {[catalyst]: [t-BuOOH]: [alkene] = 0.5:1000:5000} and 0.005% {[catalyst]: [t-BuOOH]: [alkene] = 0.25:1000:5000} [Table 1, Entry 13, 14], a reduction in reaction yield was observed.

The catalytic epoxidation reaction was optimized thoroughly at 80°C. In most cases, alkenes to alkene oxides conversion are satisfactory under this optimized condition. However, unspecified decomposition probably occured at the end of the reaction and thus resulted in the loss of active catalyst. It was indeed very difficult to isolate and characterize the intermediate species while performing the reaction at 80°C. and thus essentially hinder the study of the reaction mechanism. We have tried to perform the column chromatography in order to recover the catalyst and have obtained a new pink color species as a major end product (Figure S27). In order to sort out these difficultes, the epoxidation reactions were performed at variable temperatures. While studying the catalytic epoxidation reactions at room temperature, it was also observed that the substrate to product conversion was also very much similar to that of the 80°C.

Entry	Catalyst ^c	Solvent	Oxidant	Time	% Conv.
	(mmol)	(mL)	(mmol)	(h)	
1	-	C ₆ H ₆ , 1.3	TBHP, 0.5	17	14
2	0.0005	C ₆ H ₆ , 1.3	TBHP, 0.5	17	99
3	0.0005	C ₆ H ₆ , 1.3	TBHP , 0.5	15	99
4	0.0005	C ₆ H ₆ , 1.3	TBHP, 0.5	14	97
5	0.0005	C ₆ H ₆ , 1.3	TBHP, 0.5	12	96
6	0.0005	CH ₃ CN, 1.3	TBHP, 0.5	15	7
7	0.0005	DCE, 1.3	TBHP, 0.5	15	99
8	0.0005	Dioxane, 1.3	TBHP, 0.5	15	78
9	0.0005	Toluene, 1.3	TBHP, 0.5	15	57
10	0.0005	THF, 1.3	TBHP, 0.5	15	-
11	0.0005	C ₆ H ₆ , 0.5	TBHP, 0.5	15	75
12	0.0005	C ₆ H ₆ , 1	TBHP, 0.5	15	65
13	0.00025	C ₆ H ₆ , 1.3	TBHP, 0.5	15	89
14	0.000125	C ₆ H ₆ , 1.3	TBHP, 0.5	15	86
15	0.0005	C ₆ H ₆ , 1.3	H ₂ O ₂ , 0.5	15	61

Table 1. Optimization of cyclohexene ^{a, b} epoxidation at 80°C under variable reaction conditions using oxo-molybdenum(V)-corrolato complex, **1** as catalyst.

^a Amount of cyclohexene used = 0.25 mL (2.46 mmol). ^b Under air. ^c Oxo-molybdenum(V)corrolato complex, **1**. ^d % of conversion were established by ¹H NMR.

However, the problem associated with the unspecified decomposition still persisits and eventually makes it difficult to study the reaction mechanism. While studying the reaction at 0°C, we have observed almost similar conversion of substrate to product as that of 80°C without any significant decomposition of the catalyst (Figure S25-S27). The facile isolation and characterization of the intermediate species to a certain extent at 0°C thus remain viable.

Table 2. Optimization of norbornene ^{a, b} epoxidation at 0°C under variable reaction conditions using oxo-molybdenum(V)-corrolato complex, **1** as catalyst.

Entry	Catalyst ^c	Solvent ^d	Oxidant	Time	% Conv. ^e
	(mmol)	(mL)	(mmol)	(h)	
1	-	1.3	TBHP, 0.5	17	3
2	0.0005	1.3	TBHP, 0.5	17	99
3	0.0005	1.3	TBHP , 0.5	15	99
4	0.0005	1.3	TBHP, 0.5	14	96
5	0.0005	1.3	TBHP, 0.5	12	93
6	0.0005	1.3	TBHP, 2.5	15	0
7	0.0005	0.5	TBHP, 0.5	15	70
8	0.0005	1	TBHP, 0.5	15	78
9	0.00025	1.3	TBHP, 0.5	15	80
10	0.000125	1.3	TBHP, 0.5	15	75
11	0.0005	1.3	-	17	0

^a Amount of norbornene used = 231.6 mg (2.46 mmol). ^b Under air. ^c Oxo-molybdenum(V)corrolato complex, **1**. ^d Benzene: Toluene (9:1). ^e % of conversion were established by ¹H NMR.

From the above observations, it can be concluded that the temperature essentially plays an important role in stabilizing various reactive intermediates. A series of different olefins were screened for epoxidation reactions at optimized condition. The catalytic epoxidation reactions were performed at the 0°C and 80°C respectively with a series of substrates. Table 3 describes the catalytic activity with respect to the conversion of substrates into the respective epoxides with turnover numbers (TONs). In general, aliphatic alkenes have been transformed in good yields to epoxide as compared to aryl-substituted alkenes. An excellent conversion was observed in cyclohexene, cyclooctene (except for 80°C) and norbornene [Table 3, Entry 1-3] with a TON > 4820 and thus reveals the effectiveness of the catalyst in the epoxidation of alkenes in both the temperatures. At 80°C, except para-substituted styrene and cyclooctene, other substrates show a good conversion of 60% or more to their respective products with a TON > 2500 [Table 3, Entry 4-8]. However, 3-bromopropene shows a quite good conversion succeeding the cyclic aliphatic alkenes both at 0°C and 80°C [Table 3, Entry 6]. The catalyst is unable to genarate the desired epoxides in case of α,β -unsaturated carbonyl compounds [Table 3, Entry 11, 12]. At 0°C, cyclopentene shows significant conversion [Table 3, Entry 13]. Ledon et al., have reported the rate of cyclohexene oxide formation catalyzed by different molybdenum complexes. Reaction conditions are similar to the present case, however, contrary to the present one, all the reactions they performed were in a strictly inert atmosphere. For Mo(CO)₆, they have observed a turnover number of 283 h⁻¹ and for a molybdenum porphyrin complex, OMo(TPP)OMe, it was observed as 51 h⁻¹.¹² Herein, we have observed the rate of cyclohexene oxide formation is 321 h⁻¹ (at 0° C). The participation of aerial O₂ probably increases the rate of epoxide formation here. In order to confirm the role of aerial O₂, the epoxidation reactions were performed in both aerial and also in strictly nitrogen atmosphere. We have observed a clear difference in the yield of the epoxide formation reactions. For this purpose, the epoxidation reactions were performed for complex 1 at 0°C for 15 h with a molar ratio of [Mo-catalyst]: [t-BuOOH]: [alkene] {alkene = 3bromo-1-propene or cyclohexene} = 1:1000:5000 under air and nitrogen respectively. A significant decrease in reaction yield was observed in the case of nitrogen atmosphere (Table S4, Entry 6 and Table S6, Entry 4). Epoxidation reaction promoted by aerobic O₂ (irradiation by visible light) by a oxo-Mo(V)-porphyrinato complex was reported earlier.44

S.No	Subs.	Product	% Conv	% Conversion ^{a, b}		TONC	
			0 °C	80 °C	0 °C	80° C	
1	\bigcirc	0	98 (82) ^d	99 (83) ^d	4822	4871	
2		$\widetilde{\Box}$	100	22	4920	1082	
3	$\sum_{i=1}^{n}$		100	100	4920	4920	
4			38	99	1870	4871	
5	$\frown \frown \frown \frown$		15	50	738	2460	
6	≫∽ _{Br}	Br	83	66	4084	3247	
7	Br		22	65	1082	3198	
8			21	62 (48) ^d	1033	3050	
9			0	7	0	344	
10			0.01	13	0.49	640	
11			0	-	0	-	
12			0	-	0	-	
10	\square		76	-	3739	-	
13	\square		0.02		0.1		
14	Br	Br	0.02	-	0.1	-	

rrolato

^a Reaction conditions: benzene and toluene (9:1 ratio) at 0°C and pure benzene at 80°C under air. Relative molar ratio [Mo-catalyst]: [*t*-BuOOH]: [alkene] = 1:1000:5000. ^b % of conversion were established by ¹H NMR. ^c Turn Over Number (TON) = (% conversion \times mmol of substrate) / $(100 \times \text{mmol of cat. used})$. ^d The values in the parentheses indicate the isolated yields.

It is well established that the Mo-complexes can catalyze the epoxidation reaction of olefins with the help of hydroperoxides irrespective of the oxidation state of the starting complex.⁴⁵ Sheldon et al. have demonstrated that the catalysts (Mo-complexes) are modified to some active species at the beginning of the reaction. ⁴⁶ EPR studies highlight the oxidation state distribution in various reactive intermediates. At the very beginning of the reaction, the EPR peak arises due to the d^1 Mo(V) species disappeared after the addition of t-BuOOH and thereafter addition of the substrate. The recorded spectrum after the end of the reaction is also devoid of any EPR signal. As we have used the Mo(V) complexes as a catalyst, thus it is highly unlikely that it will be reduced in such oxidizing conditions (in presence of *t*-BuOOH). Thus the active species might be a Mo(V) or a higher oxidation state complex. We have observed that all the oxomolybdenum(V)-corrolato complex is consumed during the catalytic reactions. This is as per the previous literature reports.⁵ The disappearance of the EPR signal clearly indicates that a highvalent Mo species is probably involved in the catalytic cycle. While performing the catalytic reaction at 0°C, we have not observed any traces of free base corrole at the end of the reaction (Figure S25). Here after, we have tried to perform the column chromatography in order to recover the catalyst. But, instead we obtained a new green color compound as a a major end product (Figure S26). The hypsochromic shift of ~14 nm in the Soret band to 425 nm and bathochromic shift of ~100 nm in the Q-bands of UV-Vis spectra of the green species as compared to the oxo-molybdenum(V)-corrolato catalyst is observed (Figure S26). In addition to that, a new band at around 334 nm is also observed. This band probably arises due to the interaction of the π -systems of the two closely spaced macrocycles. The blue-shift of the Soret band with a magnitude of ~ 100 nm in the dimeric corrole complexes are documented earlier.³⁰ ESI-MS (m/z = 714.29) indicates typical molybdenum coordination to the corrole cavity (Figure S28). In addition to that FT-IR spectra indicate the appearance of a very intense stretching vibration at 735 cm⁻¹ (Figure S29). The asymmetric stretch of a bent Mo-O-Mo bridge is typically observed in this region and is characteristic of the μ -oxo-bridged Mo complexes.⁴⁷⁻⁴⁸ But due to the presence of some impurities in the green intermediate, we are unable to assign the NMR data. From all these observations we have proposed a catalytic cycle (Scheme 2). Thus it is proposed that the oxo-Mo(V) corrole catalyst in presence of t-BuOOH gives μ -oxo-bridged oxo-Mo(VI)-corrolato dimeric species as intermediate and tert-butyl alcohol (by-product). However, an alternative structural motif of the μ -oxo-bridged oxo-Mo(VI)-corrolato dimeric species cannot

be ruled out by the above mentioned experimental data. This dimeric species upon addition of cyclohexene (substrate) proceeds through a transition state to yield cyclohexene oxide as product along with some probable μ -oxo-bridged Mo(IV)corrolato dimeric species and some unidentified monomeric species.



Scheme 2. Proposed mechanism for alkene epoxidation by oxo-molybdenum(V)-corrolato , 1 in presence of *t*-BuOOH.

Conclusions

In conclusion, we have synthesized two new oxo-molybdenum(V)-corrolato complexes. Single-crystal X-ray structural analysis reveals that the Mo=O bond distance is 1.659 Å and is very close to the previously reported Mo=O bond distances in oxo-molybdenum(V)-porphyrinato complex (1.658 Å). Both the molybdenum complexes exhibited one reversible oxidation couple and one reversible reduction couple *versus* Fc/Fc⁺. The electronic effect of the peripherial *meso*substituents in the corrole ring on tuning the redox potentials of the molybdenum complexes is evident from the observed change in redox potentials of two oxo-molybdenum(V)-corrolato complexes. EPR spectra indicate that the oxo-molybdenum(V)-corrolato complexes are monomeric and the ground state is a doublet. The obtained *g* value of ~1.97 suggests a strong covalent nature of the coordinate bonds with the metal center. The room temperature magnetic moment was observed as (1.62 $\mu_{\rm B}$ for 1 and 1.72 $\mu_{\rm B}$ for 2) corresponds to one unpaired electron. The inverse molar magnetic susceptibility ($\chi_{\rm m}^{-1}$) *vs.* temperature (T) plot shows typical Curie-Weiss behavior. A series of different olefins were tested for epoxidation reaction using the synthesized oxo-molybdenum(V)-corrolato complex, 1 at 0°C and 80°C and showed the catalytic activity of 1 with respect to the conversion of substrates to their respective epoxides and their corresponding TONs. We have also proposed a catalytic cycle for this epoxidation reaction. UV-Vis, IR, EPR and ESI-MS data help us to deduce the catalytic cycle for this epoxidation reaction. The alkene epoxidation reactions mediated by oxo-molybdenum(V)-corrolato complexes in presence of *t*-BuOOH were not reported earlier.

EXPERIMENTAL SECTION

Materials: The precursor's pyrrole, styrene, 4-methylstyrene, 4-chlorostyrene, cyclooctene, 1hexene, 1-octene, norbornene, 6-bromo-1-hexene, 3-bromo-1-propene, Cyclopentene, 5-Bromo-1-pentene, 2-Cyclohexen-1-one, 2-Cyclopenten-1-one, chloranil, *tert*-butylhydroperoxide (*t*-BuOOH) and tetrabutylammonium perchlorate (TBAP) were purchased from Sigma- Aldrich, USA. All the reaction products {7-oxabicyclo[4.1.0]heptane, 9-oxabicyclo[6.1.0]nonane, 2butyloxirane, 2-hexyloxirane, 3-oxatricyclo[3.2.1.02,4]octane, 2-phenyloxirane, 1-Bromo-2,3epoxypropane, 2-(p-tolyl)oxirane, 2-(4-chlorophenyl)oxirane}, 6-Oxabicyclo[3.1.0]hexane, 7-Oxabicyclo[4.1.0]heptan-2-one were purchased from Sigma-Aldrich, USA. Molybdenum hexacarbonyl and cyclohexene were purchased from ACROS Organics. 4-bromobenzaldehyde and 4-cyanobenzaldehyde were purchased from Merck, India. Other chemicals were of reagent grade. All the high temperature experiments were performed in an oil bath and all the low temperature experiments were performed in an ice bath. Hexane and CH_2Cl_2 were distilled from KOH and CaH₂ respectively. 5,10,15-tris(4-cyanophenyl)corrole and 5,15-bis(4-cyanophenyl)-10-(4-bromophenyl)-corrole are synthesized by following earlier reported protocols.³²

Physical Measurements: UV-Vis spectral studies were performed on a Perkin-Elmer LAMBDA-750 spectrophotometer. FT-IR spectra were recorded on a Perkin-Elmer spectrophotometer with samples prepared as KBr pellets. The NMR measurements were carried out using a Bruker AVANCE 400 NMR spectrometer. Tetramethylsilane (TMS) was the internal standard. Electrospray mass spectra were recorded on a Bruker Micro TOF-QII mass spectrometer. Cyclic voltammetry measurements were carried out using a CS350 electrochemical test system (China). A glassy carbon working electrode, a platinum wire as an auxiliary electrode, and an Ag-AgCl reference electrode were used in a three-electrode configuration. Tetrabutylammonium perchlorate (TBAP) was the supporting electrolyte (0.1 M), and the concentration of the solution was 10^{-3} M with respect to the complex. The half-wave potential E_{298}^0 was set equal to 0.5 ($E_{pa} + E_{pc}$), where E_{pa} and E_{pc} are anodic and cathodic cyclic voltammetric peak potentials, respectively. The scan rate used was 100 mV s⁻¹. The magnetic susceptibility of the samples were measured by using a superconducting quantum interference device (SQUID) manufactured by Quantum Design, USA. EPR spectra at X-band frequency (ca. 9.5 GHz) were obtained with a Bruker EMX (ER 073) System. The measurements were carried out in synthetic quartz glass tubes.

Synthesis of oxo[5,10,15-tris(4-cyanophenyl)corrolato] molybdenum (V), 1: 1 was prepared by a slight modification of a previously reported synthetic procedure of oxo-molybdenum(V) compound. ³⁹ 50 mg (0.08 mmol) of the 5,10,15- tris(4-cyanophenyl)corrole was dissolved in 25 mL of toluene. 110 mg (0.42 mmol) of the molybdenum hexacarbonyl was added to the reaction vessel under reflux condition over an oil bath and stirring was continued for 8 - 10 h. The color of the reaction mixture gradually changes from green to greenish-red and the consumption of starting material was monitored by TLC. The solvent was evaporated by using a rotary evaporation and pure dark red colored compound was isolated by column chromatography through silica gel bed (100-200 mesh) using CH₂Cl₂ as an eluent. Re-crystallization from CH₂Cl₂/CH₃OH solution yielded dark red X-ray quality crystals of the compound. Yield: 54% (32 mg). Anal. Calcd for C₄₀H₂₀MoN₇O (1): C, 67.61; H, 2.84; N, 13.80; Found: C, 67.45; H, 2.90; N, 13.92. λ_{max}/nm ($x/M^{-1}cm^{-1}$) in dichloromethane: 438 (142400), 506 (12000), 547 (19800), 595 (34900) (Figure S30). FT-IR spectra (as KBr Pellet): ν (Mo^VO) = 966 cm⁻¹ (Figure S31). HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₄₀H₂₁MoN₇O 713.0865; Found 713.1850 (Figure S2).

Synthesis of oxo[5,15-bis(4-cyanophenyl)-10-(4-bromophenyl)-corrolato] molybdenum (V), 2: 50 mg (0.076 mmol) of the 5,15-bis(4-cyanophenyl)-10-(4-bromophenyl)corrole was dissolved in 25 mL of toluene. 110 mg (0.42 mmol) of the molybdenum hexacarbonyl was added to the reaction vessel under reflux condition over an oil bath and stirring was continued for 8- 10 h. The color of the reaction mixture gradually changes from green to greenish-red and the consumption of starting material was monitored by TLC. The solvent was evaporated by using a rotary evaporation and pure dark red colored compound was isolated by column chromatography through silica gel bed (100-200 mesh) using CH₂Cl₂ as an eluent. Re-crystallization from CH₂Cl₂/CH₃OH solution yielded dark red X-ray quality crystals of the compound. Yield: 56% (33 mg). Anal. Calcd for C₃₉H₂₀BrMoN₆O (**2**): C, 61.27; H, 2.64; N, 10.99; Found: C, 61.18; H, 2.75; N, 10.88. λ_{max} /nm (ε /M⁻¹cm⁻¹) in dichloromethane: 437 (118600), 508 (10800), 547 (15300), 596 (29700) (Figure S32). FT-IR spectra (as KBr Pellet): ν (Mo^VO) = 965 cm⁻¹ (Figure S33). HRMS (ESI-TOF) *m*/*z*: [M]⁺ Calcd for C₃₉H₂₀BrMoN₆O 764.9930; Found 765.1447 (Figure S3).

Synthesis of cyclohexene oxide: 2.5 mL (24.6 mmol) of cyclohexene and 3.56 mg (5×10⁻³ mmol) of catalyst were dissolved in 13 mL of mixture of benzene and toluene (9:1). 0.5 mL (5 mmol) of *t*-BuOOH was added to the reaction vessel kept over an ice bath at 0°C with constant stirring for 15 h. The colour of the reaction mixture changes from dark red to reddish-pink. The spot of the desired product, i.e., 1, 2-epoxycyclohexane (colourless) was detected through TLC. The desired compound was then isolated by column chromatography through silica gel bed (100-200 mesh). The solvent was evaporated by using a rotary evaporation and dried in high vacuum to obtain the colourless liquid; yield: 1.98 g, 82%; ¹H NMR (400 MHz, CDCl₃) δ 3.10 (bm, 2H), 1.91(m, 2H), 1.79(m, 2H), 1.38(m, 2H), 1.23(m, 2H) (Figure S34). ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 52.21, 24.52, 19.51 (Figure S35). NMR data is in agreement with authentic sample (commercially available).

Synthesis of styrene oxide: 2.82 mL (24.6 mmol) of styrene and 3.56 mg (5×10^{-3} mmol) of catalyst were dissolved in 13 mL of benzene. 0.5 mL (5 mmol) of *t*-BuOOH was added to the reaction vessel kept over an oil bath at 80°C with constant stirring for 15 h. The colour of the reaction mixture changes from dark red to reddish-pink. The spot of the desired product, i.e., styrene oxide (pale yellow) was detected through TLC. The desired compound was then isolated by column chromatography through silica gel bed (100-200 mesh). The solvent was evaporated

by using a rotary evaporation and dried in high vacuum to obtain the pale yellow liquid. Yield: 1.42 g, 48%; ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.41 (5H, m), 3.86 (1H, dd, J = 3.9, 2.7 Hz), 3.13 (1H, dd, J = 5.6, 4.1 Hz), 2.80 (1H, dd, J = 5.6, 2.6 Hz) (Figure S36).¹³C{¹H} NMR (101 MHz, CDCl₃) δ 137.56, 128.33, 127.99, 125.36, 52.10, 50.93 (Figure S37). NMR data is in agreement with authentic sample (commercially available).

ASSOCIATED CONTENT

Supporting Information

Crystallographic data, UV–Vis, FT-IR, electrochemical data, magnetic susceptibility data, EPR data, ESI-MS data of oxo-molybdenum(V) complexes, ¹H-NMR data of catalysis reactions. UV-Vis, FT-IR and ESI-MS data of green species.

Crystallographic data for compound 1 (CIF). CCDC 2003270 contains the supplementary crystallographic data for 1. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Sienel, G.; Rieth, R.; Rowbottom, K. T. In *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2000**.
- Yudin, A. K. Aziridines and Epoxides in Organic Synthesis, Wiley-VCH, Weinheim, 2006, 185-389.
- (3) Kollar, J. U.S. Patent 3 360 584 (1967) to Halcón International.
- (4) Sheldon, R. A.; Wallau, M.; Arends, I. W. C. E.; Schuchardt, U. Heterogeneous catalysts for liquid-phase oxidations: philosophers' stones or Trojan horses?. *Acc. Chem. Res.* 1998, *31*, 485-493.
- (5) Chong, A. O.; Sharpless, K. B. Mechanism of the molybdenum and vanadium catalyzed epoxidation of olefins by alkyl hydroperoxides. *J. Org. Chem.* **1977**, *42*, 1587-1590.
- (6) Jørgensen, K. A. Transition-metal-catalyzed epoxidations. *Chem. Rev.* **1989**, *89*, 431-458.
- (7) Dickman, M. H.; Pope, M. T. Peroxo and superoxo complexes of chromium, molybdenum, and tungsten. *Chem. Rev.* **1994**, *94*, 569-584.
- (8) Arzoumanian, H. Molybdenum-oxo chemistry in various aspects of oxygen atom transfer processes. *Coord. Chem. Rev.* 1998, *178*, 191-202.
- (9) Rutkowska-Zbik, D.; Tokarz-Sobieraj, R.; Witko, M. Quantum chemical description of oxygen activation process on Co, Mn, and Mo porphyrins. J. Chem. Theory Comput. 2007, 3, 914-920.
- (10) Harada, R.; Matsuda, Y.; Ōkawa, H.; Kojima, T. A Porphyrin Nanotube: Size-Selective Inclusion of Tetranuclear Molybdenum–Oxo Clusters. *Angew. Chem. Int. Ed.* 2004, 43, 1825-1828.
- Baccouche, M.; Ernst, J.; Fuhrhop, J.-H.; Schlözer, R.; Arzoumanian, H. Metallo-porphyrin catalysed epoxidations with molecular oxygen. J. Chem. Soc., Chem. Commun. 1977, 821-822.
- (12) Ledon, H. J.; Durbut, P.; Varescon, F. Selective epoxidation of olefins by molybdenum porphyrin catalyzed peroxy-bond heterolysis. *J. Am. Chem. Soc.* **1981**, *103*, 3601-3603.
- (13) Tachibana, J.; Imamura, T.; Sasaki, Y. Synthesis and characterization of a novel dioxygen complex of molybdenum porphyrin. J. Chem. Soc., Chem. Commun. 1993, 1436-1438.

(14)	Fujihara, T.; Sasaki, Y.; Imamura, T. Preparation of molybdenum porphyrin dioxyger
	complexes without bulky substituents. Chem. Lett. 1999, 28, 403-404.
(15)	Patra, B.; Mondal, S.; Kar, S. Corroles, in: Scott, R. A.; Storr, T. (Eds.) Encyclopedia of
	Inorganic and Bioinorganic Chemistry, John Wiley & Sons, Ltd, Chichester, UK, 2020
	DOI: https://doi.org/10.1002/9781119951438.eibc2729.
16)	Mondal, S.; Naik, P. K.; Adha, J. K.; Kar, S. Synthesis, characterization, and reactivities
	of high valent metal-corrole (M= Cr, Mn, and Fe) complexes. Coord. Chem. Rev. 2019
	400, 213043.
17)	Nardis, S.; Mandoj, F.; Stefanelli, M.; Paolesse, R. Metal complexes of corrole. Coord
	<i>Chem. Rev.</i> 2019 , <i>388</i> , 360-405.
18)	Mahammed, A.; Gross, Z. Corroles as triplet photosensitizers. Coord. Chem. Rev. 2019
	379, 121-132.
(19)	Erben, C.; Will, S.; Kadish, K. M. in: Kadish, K. M.; Smith, K. M.; Guilard, R. (Eds.)
	The Porphyrin Handbook, Vol. 2, Academic Press, San Diego, CA, 2000.
20)	Aviv-Harel, I.; Gross, Z. Aura of corroles. Chem. Eur. J. 2009, 15, 8382-8394.
21)	Ghosh, A. Electronic structure of corrole derivatives: Insights from molecular structures
	spectroscopy, electrochemistry, and quantum chemical calculations. Chem. Rev. 2017
	117, 3798-3881.
22)	Orłowski, R.; Gryko, D.; Gryko, D. T. Synthesis of corroles and their heteroanalogs
	<i>Chem. Rev.</i> 2017 , <i>117</i> , 3102–3137.
23)	Fang, Y.; Ou, Z.; Kadish, K. M. Electrochemistry of corroles in nonaqueous media
	<i>Chem. Rev.</i> 2017 , <i>117</i> , 3377–3419.
24)	Fujino, K.; Hirata, Y.; Kawabe, Y.; Morimoto, T.; Srinivasan, A.; Toganoh, M.; Miseki
	Y.; Kudo, A.; Furuta, H. Confusion and Neo-Confusion: Corrole Isomers with an NNNC
	Core. Angew. Chem. Int. Ed. 2011, 50, 6855–6859.
(25)	Hiroto, S.; Furukawa, K.; Shinokubo; H.; Osuka, A. Synthesis and biradicaloid characte
	of doubly linked corrole dimers. J. Am. Chem. Soc. 2006, 128, 12380-12381.
(26)	Sinha, W.; Sommer, M. G.; Deibel, N.; Ehret, F.; Bauer, M.; Sarkar, B.; Kar, S
	Experimental and theoretical investigations of the existence of Cu ^{II} , Cu ^{III} , and Cu ^{IV} in
	copper corrolato complexes. Angew. Chem. Int. Ed. 2015, 54, 13769-13774.

(27) Sinha, W.; Sommer, M. G.; Deibel, N.; Ehret, F.; Sarkar, B.; Kar, S. Silver Corrole Complexes: Unusual Oxidation States and Near-IR-Absorbing Dyes. *Chem. Eur. J.* 2014, 20, 15920-15932.

- (28) Sinha, W.; Sommer, M. G.; Van der Meer, M.; Plebst, S.; Sarkar, B.; Kar, S. Structural, electrochemical and spectroelectrochemical study on the geometric and electronic structures of [(corrolato)Au^{III}]ⁿ (n= 0,+ 1,- 1) complexes. *Dalton Trans.* 2016, 45, 2914-2923.
- (29) Patra, B.; Sobottka, S.; Sinha, W.; Sarkar, B.; Kar, S. Isovalent Ag^{III}/Ag^{III}, Ag^{II}/Ag^{II}, Mixed-Valent Ag^{II}/Ag^{III}, and Corrolato-Based Mixed-Valency in β, β'-Linked [Bis {corrolato-silver}]ⁿ Complexes. *Chem. Eur. J.* 2017, 23, 13858-13863.
- (30) Sinha, W.; Sommer, M. G.; Hettmanczyk, L.; Patra, B.; Filippou, V.; Sarkar, B.; Kar, S. Ruthenium–Ruthenium-Bonded [Bis {corrolato-ruthenium (III)}]ⁿ (n= 0,+ 1,- 1) Complexes: Model Compounds for the Photosynthetic Special Pair. *Chem. Eur. J.* 2017, 23, 2396-2404.
- (31) Patra, B.; Sobottka, S.; Mondal, S.; Sarkar, B.; Kar, S. Metal coordination induced ring contraction of porphyrin derivatives. *Chem. Commun.* **2018**, *54*, 9945-9948.
- (32) Koszarna, B.; Gryko, D. T. Efficient synthesis of meso-substituted corroles in a H₂O–MeOH mixture. *J. Org. Chem.* 2006, *71*, 3707-3717.
- (33) Gross, Z.; Galili, N.; Simkhovich, L.; Saltsman, I.; Botoshsnsky, M.; Blaser, D.; Boese, R.; Goldberg, I. Solvent-free condensation of pyrrole and pentafluorobenzaldehyde: A novel synthetic pathway to corrole and oligopyrromethenes. *Org. Lett.* 1999, *1*, 599-602.
- (34) Murakami, Y.; Matsuda, Y.; Yamada, S. Preparation and characterization of oxo (2, 3, 17, 18-tetramethyl-7, 8, 12, 13-tetraethylcorrolato) molybdenum (V). *Chem. Lett.* 1977, 6, 689-692.
- (35) Sashuk, V.; Koszarna, B.; Winiarek, P.; Gryko, D. T.; Grela, K. The simple synthesis of stable A₃-and trans-A₂B-molybdenum (V) corrolates. *Inorg. Chem. Commun.* 2004, *7*, 871-875.
- (36) Luobeznova, I.; Raizman, M.; Goldberg, I.; Gross, Z. Synthesis and full characterization of molybdenum and antimony corroles and utilization of the latter complexes as very efficient catalysts for highly selective aerobic oxygenation reactions. *Inorg. Chem.* 2006, 45, 386-394.

(37)	Czernuszewicz, R. S.; Mody, V.; Zareba, A. A.; Zaczek, M. B.; Gałęzowski, M.; Sashuk,
	V.; Grela, K.; Gryko, D.T. Solvent-dependent resonance raman spectra of high-valent
	oxomolybdenum (V) tris [3, 5-bis (trifluoromethyl) phenyl] corrolate. Inorg. Chem. 2007,
	46, 5616-5624.
(38)	Nigel-Etinger, I.; Goldberg, I.; Gross, Z. Intriguing Chemistry of Molybdenum
	Corroles. Inorg. Chem. 2013, 52, 4139-4141.
(39)	Schweyen, P.; Brandhorst, K.; Hoffmann, M.; Wolfram, B.; Zaretzke, M. K.; Bröring, M.
	Viking helmet corroles: activating inert oxidometal corroles. Chem. Eur. J. 2017, 23,
	13897-13900.
(40)	Alemayehu, A. B.; Vazquez-Lima, H.; McCormick, L. J.; Ghosh, A. Relativistic effects
	in metallocorroles: comparison of molybdenum and tungsten biscorroles. Chem.
	Commun. 2017, 53, 5830-5833.
(41)	Sinha, W.; Deibel, N.; Agarwala, H.; Garai, A.; Schweinfurth, D.; Purohit, C. S.; Lahiri,
	G. K.; Sarkar, B.; Kar, S. Synthesis, Spectral Characterization, Structures, and Oxidation
	State Distributions in $[(corrolato)Fe^{III} (NO)]^n$ (n = 0,+ 1,- 1) Complexes. <i>Inorg.</i>
	Chem. 2014, 53, 1417-1429.
(42)	Hamstra, B. J.; Cheng, B.; Ellison, M. K.; Scheidt, W. R. Molybdenum (V) on an Oxide
	String. Synthesis and Structure of the Novel Linear Trinuclear Complex {[MoO
	(TPP)][O- Mo (TPP)- O][MoO (TPP)]} ClO ₄ . Inorg. Chem. 1999 , 38, 3554-3561.
(43)	Janczak, J.; Kubiak, R. Synthesis, Structure, and Characterization of Oxomolybdenum
	(V) Phthalocyaninato (2-) Triiodide. Inorg. Chem. 1999, 38, 2429-2433.
(44)	Matsuda, Y., Koshima, H., Nakamura, K. and Murakami, Y. Photochemical epoxidation
	of olefins with molecular oxygen activated by oxo (tetra-p-tolylporphinato) molybdenum
	(V). Chemistry Letters, 1988, 17, 625-628.
(45)	Sheldon, R. A. Molybdenum-catalysed epoxidation of olefins with alkyl hydroperoxides
	I. Kinetic and product studies. Rec. Trav. Chim. Pays- Bas 1973, 92, 253-266.
(46)	Sheldon, R. A. Molybdenum-catalysed epoxidation of olefins with alkyl hydroperoxides
	II. Isolation and structure of the catalyst. Rec. Trav. Chim. Pays-Bas 1973, 92, 367-373.
(47)	El- Hendawy, A. M.; Griffith, W. P.; Pumphre, C. A. Complexes of osmium, uranium,
	molybdenum, and tungsten with the catechol amines adrenaline, noradrenaline, dopamine, dopa,
	and isoprotoronal I. Cham. Soc. Dalton Tuging 1000 1017 1021

(48) Berg, J. M.; Holm, R. H. Structure proofs of ligated and polymeric dioxomolybdenum (VI)-tridentate complexes: MoO₂ (C₅H₃N-2, 6-(CH₂S)₂)(C₄H₈SO) and [MoO₂ (C₅H₃N-2, 6-(CH₂O)₂)]ⁿ. *Inorg. Chem.* 1983, 22, 1768-1771.