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Synthesis, characterization, reactivity and catalytic activity of a novel chiral manganese Schiff base complex

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A new chiral linear tetraamine (N^1 -(1-(2-aminophenylamino) propan-2-yl) benzene-1,2-diamine), CLT, and its Schiff base ligand, derived from CLT with 2-hydroxybenzaldehyde was synthesized and transformed to the corresponding manganese (III) complex. The Schiff base ligand was studied by ¹HNMR, ¹³C NMR, COSY, HSQC, DEPT and microanalysis. Density-functional theory (DFT) calculations were performed to determine the structure of [Mn^{III}L]⁺ complex. This manganese complex catalyzes the oxidation of alcohols using 30% H₂O₂ as an oxidant. Over oxidation of aldehydes to carboxylic acid and the formation of by-products were not observed. α - β unsaturated alcohol was oxidized smoothly without oxidation of the double bond.

Keywords: alcohol; oxidation; hydrogen peroxide; Schiff-base complex; manganese (III); tetraamine.

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The oxidation of alcohols to the corresponding aldehydes and ketones is one of the important reactions in organic chemistry both at the laboratory and in industrial synthetic chemistry.¹⁻³ Interest in the coordination chemistry of transition metals with Schiff bases is growing on account of the wide range of applications of the resulting complexes.⁴⁻⁶ Particular attention has been devoted to salicylidene Schiff base derivatives because they can promote chelation and provides extra stability to the metal centers. This type of complexes have been used as catalysts in reactions such as oxidation of olefins,⁷⁻⁸ oxidation of alcohols,⁹⁻¹¹ enantioselective epoxidation of olefins,¹²⁻¹³ enantioselective trimethylsilylcyanation of carbonyl compounds,¹⁴⁻¹⁵ enantioselective ring opening of meso aziridines,¹⁶ asymmetric hetero-Diels Alder reactions,¹⁷ and enantioselective Cyclopropanation of olefins.¹⁸⁻¹⁹

Transition metal-catalyzed oxidation of alcohols is of current interest, and the various effective catalysts have been reported, such as molybdenum²⁰ and tungsten,²¹ ruthenium,²² cobalt,²³ manganese,²⁴ iron²⁵ and rhenium-based catalysts.²⁶ Although many studies have been performed on the oxidation of hydrocarbons using Mn(III) complexes²⁷⁻³² and various peroxide substances as oxidant, only a few have used H₂O₂ as a source of oxygen for the oxidation of alcohols.³³⁻³⁴ Herein, we describe design and synthesis of a new chiral manganese (III) Schiff base complex and its application as selective catalyst for the oxidation of alcohols to the carbonyl compounds.

N'-(1-(2-aminophenylamino)propan-2-yl)benzene-1,2-diamine was synthesized from reaction of 1,2-diaminopropane and 1-chloro-2-nitrobenzene in the presence of potassium carbonate and the product reduced by zinc dust and ammonium chloride. H₂L was characterized by microanalysis, IR, and NMR studies. The IR spectrum of H₂L reveals a strong absorption band at *ca* 1618 cm⁻¹ due to stretching vibrations of C=N bands. [Mn^{III}L]Cl exhibits the (C=N) mode at *ca*. 1630 cm⁻¹ and the (NH) mode at *ca*. 3324 cm⁻¹. The shift of the characteristic imine (C=N) band for the complex, demonstrates the coordination of the azomethine nitrogens to the metal ion.

The ¹H as well as ¹³C{¹H} NMR data for H₂L dissolved in CDCl₃ are surveyed, using the lettering scheme shown in Table 1. The ¹H and ¹³C signals were assigned using one- and two-dimensional ¹H-¹H COSY, ¹H-¹³C HSQC and DEPT spectra. The spectral data were obtained at ambient temperature and are tabulated in Table 1. The ¹H NMR spectrum of the H₂L shows a doublet signal at 1.20 ppm which can be assigned to methyl group (3H), a broad signal at *ca*. 4.11 ppm attributed to secondary amine protons (2H) and H_b (1H), two signals at *ca*. 4.53 and 4.67 ppm attributed to H_c (2H). Two signals corresponding to the methylene protons (H_c) are

observed and these show that the protons are inequivalent, due to asymmetric nature of the compound. In the aromatic region (6.26-7.78 ppm) eight signals were found, and since the protons do not show scalar-coupling we were not able to assign explicitly the signals to each of the aromatic systems present in the molecule. The imine hydrogen signals (CH=N) was observed at 8.46 ppm. The ^{13}C NMR spectrum in the region of aliphatic shows three signals at 19.43, 48.62 and 51.48 ppm attributed to C_a , C_b and C_c , respectively. In the region corresponding to the signals of aromatic ring carbons (110.07–160.67 ppm), 21 peaks are observed. The imine carbon signals (CH=N) was observed at 162.67 ppm. ^1H NMR, ^{13}C NMR, ^1H - ^1H COSY, ^1H - ^{13}C HSQC and DEPT spectra are shown in [Supplementary Figs. 1–5](#), respectively.

Table 1 ^1H NMR and ^{13}C NMR{ ^1H } spectral assignments for H_2L recorded in CDCl_3

Hydrogen atom	δ_{H} (ppm)	J (Hz)	Carbon atom	δ_{C} (ppm)
H_a (3H)	1.2	$^3\text{J}(\text{H}_a, \text{H}_b) \approx 6.50$	C_a (1C)	19.43
H_b (1H)	4.11		C_b (1C)	48.62
$\text{H}_{c\alpha}, \text{H}_{c\beta}$ (2H)	4.53, 4.67	$^2\text{J}(\text{H}_{c\alpha}, \text{H}_{c\beta}) \approx 13.35$ $^3\text{J}(\text{H}_c, \text{H}_b) \approx 6.35$	C_c (1C)	51.48
H_d (2H)	8.46		C_d (2C)	162.67
NH	4.11			
OH	12.81			

The structure of $[\text{Mn}^{\text{III}}\text{L}]^+$ was optimized by Density Functional Theory (DFT) calculations using B3LYP/6-31G* basis set. The resulting structure for $[\text{Mn}^{\text{III}}\text{L}]^+$ was used for further calculations using the effective core potential (ECP) standard basis set LanL2DZ³⁵⁻³⁷ for Mn^{3+} ion and the standard 6-31G* basis set for all other atoms. The resulting structural diagrams are shown in [Fig. 1](#) and selected calculated bond distances and angles relating to them are shown in [Table 2](#). The manganese is bound by the two imine nitrogen atoms, two oxygen atoms from two phenolate groups and two secondary amine nitrogen atoms in a distorted octahedral arrangement.

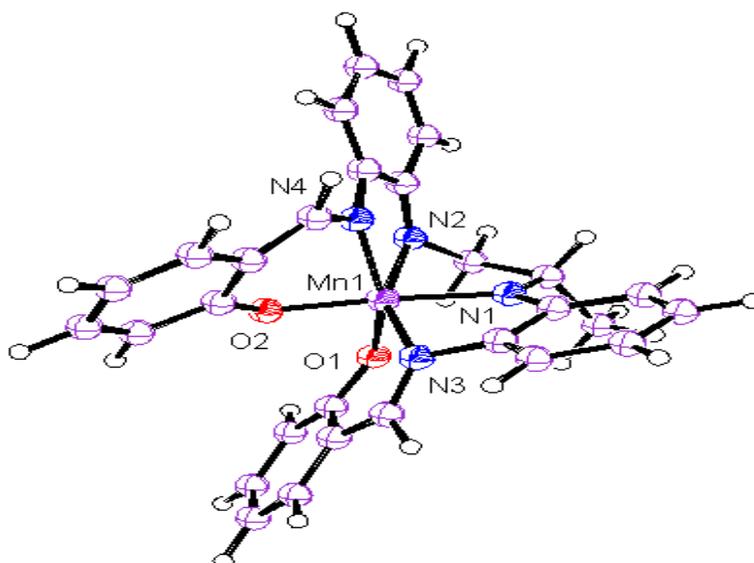


Fig. 1 DFT-optimized structure of $[\text{Mn}^{\text{III}}\text{L}]^+$.

Table 2 The selected bond lengths (Å) and angles (°) for $[\text{Mn}^{\text{III}}\text{L}]^+$

Bond length (Å)		Bond angle (°)	
Mn(1)-N(1)	1.986	N(1)-Mn(1)-N(2)	73.08
Mn(1)-N(2)	2.018	N(2)-Mn(1)-N(3)	151.87
Mn(1)-N(3)	1.934	N(2)-Mn(1)-N(4)	76.79
Mn(1)-N(4)	2.079	N(4)-Mn(1)-O(1)	160
Mn(1)-O(1)	1.782	O(1)-Mn(1)-N(3)	90.27
Mn(1)-O(2)	1.87	O(2)-Mn(1)-O(1)	87.83
		O(2)-Mn(1)-N(4)	79.96
		O(2)-Mn(1)-N(2)	116.55
		O(2)-Mn(1)-N(3)	91.22

The catalytic performance of $[\text{Mn}^{\text{III}}\text{L}]\text{Cl}$ was first studied in the biphasic oxidation of benzhydrol, used as a model substrate, and hydrogen peroxide as the oxygen donor. In a series of control experiments we evaluated the influence of several solvents. Different solvents such as chloroform, dichloromethane and acetonitrile were used (Table 3); our finding showed that CH_3CN was generally the best of the solvents tested in terms of yield and time. In this study, an

attempt was also made to investigate the effect of temperature. The oxidation yield is very low at lower temperatures (30 °C). Catalytic reactions run at higher temperatures led to a significant increase in the product yield. However, the activity increases considerably with an increase in temperature, so that at 60 and 80 °C, yields of 50% and 72% can be obtained, respectively. (Table 3)

Table 3 Optimization of solvent and temperature in oxidation of benzhydrol to benzophenone

Entry	Solvent	Temperature (°C)	Time (h)	Yield (%) ^{a, b}
1	CH ₂ Cl ₂	30	5	25
2	CH ₂ Cl ₂	37	5	30
3	CHCl ₃	40	5	40
4	CHCl ₃	57	5	45
5	CHCl ₃	57	4	45
6	CH ₃ CN	40	5	50
7	CH ₃ CN	60	4	50
8	CH ₃ CN	80	4	72

^a Yields refer to isolated pure products.

^b Reaction conditions: Alcohol (1 mmol), H₂O₂ (10 mmol), [Mn^{III}L]Cl (0.2 mmol).

For investigation of the effect of different amounts of the catalyst, various amount of catalyst were used and detected that 0.1 mmol of the catalyst, was the best amount of the catalyst (Table 4). The yield was insignificant when the reaction was carried in the absence of catalyst (Table 4, entry 1). Effect of the amount of the oxidant was also investigated. It can be seen from Table 4 that as the amount of oxidant increases, the yield constantly increases and reaches to maximum when 10 mmol of oxidant is used. All the reactions occurred with complete selectivity for oxidation of various alcohols to the aldehydes and ketones and no other products were detected in the reaction mixture.

Table 4 Optimization of catalyst and oxidant for oxidation of diphenylmethanol to benzophenone

Entry	Amount of [Mn ^{III} L]Cl (mmol)	Amount of oxidant (mmol)	Yield (%) ^{a, b}
1	0	10	-
2	0.05	10	43
3	0.07	10	60
4	0.1	10	71
5	0.2	10	72
7	0.1	5	52
8	0.1	8	61
9	0.1	15	72

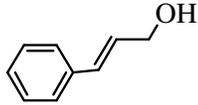
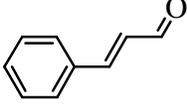
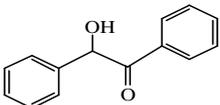
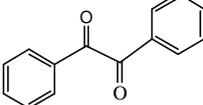
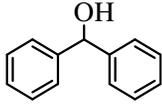
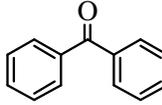
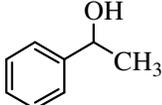
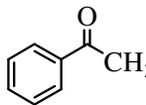
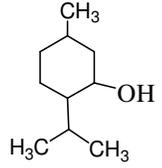
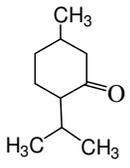
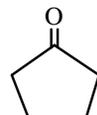
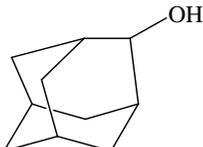
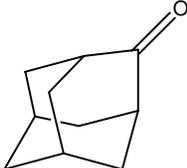
^a Yields refer to isolated pure products.

^b Reaction conditions: Alcohol (1 mmol), different amounts of oxidant and catalyst in CH₃CN under reflux.

The results for the oxidation of a variety of alcohols are summarized in (Table 5). As shown in Table 5, benzyl alcohol and substituted benzyl alcohols are converted to their corresponding aldehydes efficiently. In this oxidation process, the aromatic primary alcoholic groups (Table 5, entries 1–4) were oxidized faster than the secondary aliphatic groups, and the yields were higher than them (Table 5, entries 9–14). A good selectivity observed in the case of cinnamyl alcohol and only alcoholic group is oxidized and formation of epoxide was not observed.

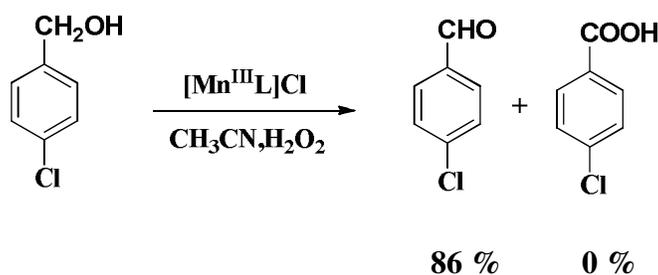
Table 5 Oxidation of alcohols

Entry	Substrate	Product	Yield (%) ^{a, b}	Selectivity (%)	Time (h)
1			82	100	2
2			86	100	3
3			76	100	2:40
4			78	100	3:10

5			65	100	4
6			43	100	7
7			71	100	4
8			70	100	4
9	$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	74	100	3:30
10			68	100	4
11			70	100	5
12			64	100	3:30
13	$\text{CH}_3\text{-CHOH}(\text{CH}_2)_6\text{-CH}_3$	$\text{CH}_3\text{-CO}(\text{CH}_2)_6\text{-CH}_3$	67	100	4:30
14			71	100	4:30

^a Alcohol (1 mmol), H_2O_2 (10 mmol), $[\text{Mn}^{\text{III}}\text{L}]\text{Cl}$ (0.1 mmol), CH_3CN (10 mL), under reflux condition, ^b Yields refer to the isolated pure products.

It is noteworthy that, in this study over oxidation of aldehydes to carboxylic acid and the formation of by-products were not observed (Scheme 1). α - β unsaturated alcohol (Entry 5, Table 5) was oxidated smoothly without oxidation of the double bond.



Scheme 1 Selective oxidation of benzylic group to the aldehyde

In order to establish the catalytic activity of our catalyst ($[\text{Mn}^{\text{III}}\text{L}]\text{Cl}$), we compared our results on the oxidation of diphenyl methanol (as a typical example) with data from the literature (Table 6). As shown in Table 6, the previously reported procedures suffer from one or more disadvantages such as elevated reaction temperatures, longer reaction times, and hard reaction conditions and work up.

Table 6 Comparison of the different methods used for the oxidation of diphenyl methanol

Entry	Reagent	Time (min)	Yield (%) ^a	Reference
1	CuTPP (0.002 mmol), isobutyraldehyde (6 mmol) in O-xylol solvent (10 ml), O ₂	2220	87.8	38
2	Oxone (2.4 equiv.), AlCl ₃ (2.7 equiv.)	240	98	39
3	V ₂ O ₅ (0.05 mmol) aq TBHP (70%, 4 mmol)	480	99	40
4	[Co(L) ₂](NO ₃) ₃ .2CH ₃ OH(0.05 mmol), H ₂ O ₂ (3 mmol)	480	36	41
5	Silica based cobalt (II) interphase catalyst (0.25% mol), NHPI (1 mmol), O ₂	3300	94	42
6	H ₂ O ₂ (10 mmol), [Mn ^{III} L]Cl (0.1 mmol), CH ₃ CN (10 mL)	240	71	This method

^a Isolated yield.

This oxidation procedure offers several major advantages: (1) highly efficient for the selective oxidation of structurally diverse alcohols in good yields; (2) control over the degree of oxidation offers access to aldehydes (and not to acids); (3) excellent chemoselectivity and (4) convenient reaction and easy work up procedure.

In conclusion, oxidation of alcohols using hydrogen peroxide, as a mild oxidant, in the presence of catalytic amounts of synthesized $[\text{Mn}^{\text{III}}\text{L}]\text{Cl}$ provides a simple, safe, and efficient method for the oxidation of alcohols to the corresponding carbonyls compounds with high yields.

Experimental

Materials and instruments

All solvents were of reagent grade quality and purchased commercially. 1,2-diaminopropane, 2-hydroxybenzaldehyde and 1-chloro-2-nitrobenzene were obtained from Merck and were used without further purification. NMR spectra were obtained using a Bruker 500 MHz spectrometer. Infrared spectra were recorded in KBr pellets using a BIO-RAD FTS-40A spectrophotometer ($4000\text{--}400\text{ cm}^{-1}$).

Synthesis of nitro-N-(2-(2-nitrophenylamino)propyl)benzenamine (1)

1,2-diaminopropane (0.74 g, 10 mmol), 1-chloro-2-nitrobenzene (3.14 g, 20 mmol) and potassium carbonate (2.76 g, 20 mmol) were mixed in a round-bottomed flask, and then fused at temperatures between $175\text{--}180\text{ }^{\circ}\text{C}$ for 2 h. The resulting solid was washed with water ($\times 3$). Yield (2.57 g, 80%), Scheme 2. Anal. Calc. for $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_4$: C, 56.96; H, 5.10; N, 17.71. Found: C, 57.00; H, 5.15; N, 17.70%. IR (KBr, cm^{-1}) 1343, 1527 (NO_2), 3280 (NH); ^1H NMR δ_{H} (CDCl_3 , ppm) 1.41 (d, 3H, CH_3), 3.50 (m, 2H, CH_2), 4.09 (m, 1H, CH), 6.54-8.16 (m, 8H, Ar + NH).

Synthesis of N^1 -(2-(2-aminophenylamino) propyl)benzene-1,2-diamine (CLT)

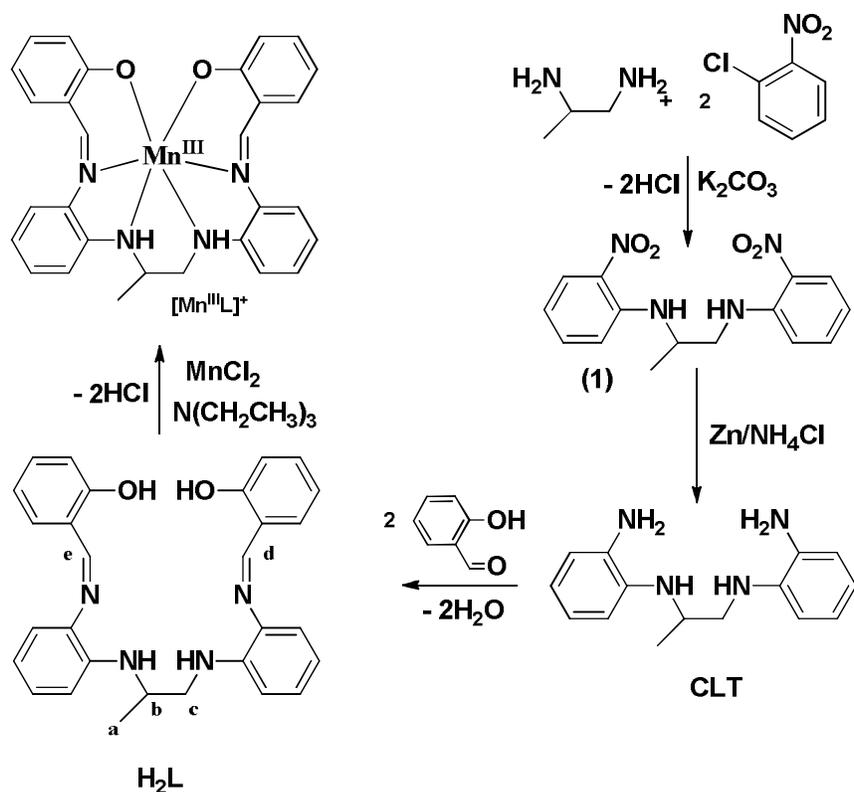
A mixture of 2-nitro-N-(2-(2-nitrophenylamino)propyl)benzenamine (1) (3.16 g, 10 mmol), ammonium chloride (4 g), and water (2 mL) in 100 mL of ethanol was heated to boiling and of zinc dust (3 g) was gradually added. When the solution was colorless it was filtered. The volume was then reduced to 20 mL by rotary evaporation. Excess water was added to the mixture and the

pH was adjusted to 12 with potassium hydroxide. The product was obtained as brown powder precipitate in the solution. Yield (1.3 g, 62%), Scheme 2. Anal. Calc. for C₁₅H₂₀N₄: C, 70.28; H, 7.86; N, 21.86. Found: C, 70.25; H, 7.88; N, 21.81%. IR (KBr, cm⁻¹) 3365, 3382 (NH₂); ¹H NMR δ_H (CDCl₃, ppm) 1.30 (d, 3H, CH₃), 3.17 (b, 9H, CH+ CH₂+NH+ NH₂), 6.71 (b, 6H, Ar).

Synthesis of

2-((2-(2-(2-(2-hydroxybenzylideneamino)phenylamino)propylamino)phenylimino)methyl)phenol (H₂L)

To a solution of *N*'-(2-(2-aminophenylamino)propyl)benzene-1,2-diamine (0.25 g, 1 mmol) in absolute methanol, 2-hydroxybenzaldehyde (0.24 g, 20 mmol) was added and the reaction was refluxed for 3 hours. The compound which precipitated during refluxing was filtered off and washed several times with methanol, and dried in air at room temperature. Yield (0.37 g, 80%). Anal. Calc. for C₂₉H₂₈N₄O₂: C, 74.98; H, 6.08; N, 12.06. Found: C, 75.01; H, 6.12; N, 12.20 %. IR (KBr, cm⁻¹) 3400 (OH), 1618 (C=N); ¹H NMR δ_H (CDCl₃, ppm) 1.20 (d, 3H, CH₃), 4.11 (b, 3H, CH + NH), 4.53 and 4.67 (m, 2H, CH₂), 6.26-7.78 (16H, Ar), 8.46 (s, 2H, CH=N), 12.81 (s, 2H, OH); ¹³C NMR δ_C (CDCl₃, ppm) 19.43, 48.62, 51.48, 110.07, 110.68, 117.95, 117.85, 118.08, 118.27, 118.99, 119.38, 123.03, 123.45, 123.58, 127.38, 128.19, 130.72, 131.60, 132.23, 132.33, 133.19, 136.24, 140.03, 160.68, 162.67. The mass spectrum shows peak at *m/z* = 464 corresponding to the H₂L (Scheme 2).



Scheme 2 The synthetic route of $[\text{Mn}^{\text{III}}\text{L}]^+$, H_2L and numbering scheme for the proton assignments of H_2L

Synthesis of complex ($[\text{Mn}^{\text{III}}\text{L}]\text{Cl}$)

To a solution of H_2L (0.464 g, 1 mmol) and manganese (II) chloride tetrahydrate (0.2 g, 1 mmol) in methanol (100 mL), a solution of triethylamine (0.2 g, 2 mmol) in absolute MeOH (5 mL) was added. After stirring for 12 h under reflux, the volume was reduced to half by evaporation and the solid formed was filtered, washed with cold methanol (3 mL) and dried under vacuum to give $[\text{Mn}^{\text{III}}\text{L}]\text{Cl}$. Yield (0.4 g, 73%). Anal. Calc. for $\text{C}_{29}\text{H}_{26}\text{ClMnN}_4\text{O}_2$: C, 62.99; H, 4.74; N, 10.13. Found: C, 63.04; H, 4.69; N, 10.17%. IR (KBr, cm^{-1}) 1630 (C=N), 3324 (NH).

Theoretical calculations

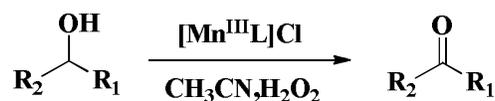
The complex gave fine powders and we were not able to prepare single crystals for structure determination by X-ray spectroscopy. Instead, The geometry of $[\text{Mn}^{\text{III}}\text{L}]^+$ was fully optimized at DFT⁴³⁻⁴⁴ levels of theory using the GAUSSIAN 03 program.⁴⁵

Catalytic reaction

Oxidation of alcohols (general procedure)

Complex $[\text{Mn}^{\text{III}}\text{L}]\text{Cl}$ has been found effecting for catalyzing oxidation of primary alcohols to the corresponding aldehydes and secondary alcohols to the ketones in acetonitrile (Scheme 3).

A typical experimental procedure was as follows: to a solution of $[\text{Mn}^{\text{III}}\text{L}]\text{Cl}$ (0.1 mmol) in acetonitrile (10 mL), the substrate alcohol (1 mmol) was added, then hydrogen peroxide (10 mmol, 30%) was slowly added. The mixture was then stirred at reflux conditions. The progress of reaction was monitored by TLC and, after completion of the reaction, the reaction was filtered. The filtrate was evaporated under reduced pressure and the residual mass was dissolved in a mixture of ethyl acetate/hexane (1:9). The precipitate was filtered off and the product was purified by column chromatography. The corresponding aldehydes and ketones were identified by comparing their physical and spectral data with those of authentic compounds reported in literature. The determination of reaction yield is based on isolated pure products after column chromatography. In some cases lower yields were obtained as the loss of the products could not be avoided during the isolation.



$\text{R}_1, \text{R}_2 = \text{H, Benzylic, Linear, Cyclic, Aryl}$

Scheme 3 Conversion of alcohols to carbonyl compounds

Acknowledgments

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