

# Oxidation of cyclohexene with *tert*-butylhydroperoxide and hydrogen peroxide catalyzed by Cu(II), Ni(II), Co(II) and Mn(II) complexes of *N,N'*-bis-( $\alpha$ -methylsalicylidene)-2,2-dimethylpropane-1,3-diamine, supported on alumina

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## Abstract

New square-planar manganese(II), copper(II), nickel(II) and cobalt(II) complexes of a tetradentate Schiff-base ligand “*N,N'*-bis-( $\alpha$ -methylsalicylidene)-2,2-dimethylpropane-1,3-diamine”,  $H_2[Me_2salpnMe_2]$  have been prepared and characterized by elemental analyses, IR, UV–vis, conductometric and magnetic measurements. The results suggest that the symmetrical Schiff-base is a bivalent anion with tetradentate ONNO donors derived from the phenolic oxygen and azomethine nitrogen. The formulae was found to be  $[M(Me_2salpnMe_2)]$  for the 1:1 non-electrolytic complexes. Alumina-supported metal complexes (ASMC);  $[M(Me_2salpnMe_2)/Al_2O_3]$ ; catalyze the oxidation of cyclohexene with *tert*-butylhydroperoxide (TBHP) and hydrogen peroxide. Oxidation of cyclohexene with TBHP gave 2-cyclohexene-1-one, 2-cyclohexene-2-ol and 1-(*tert*-butylperoxy)-2-cyclohexene whereas, oxidation with  $H_2O_2$  resulted in the formation of cyclohexene oxide and cyclohexene-1,2-diol. Manganese(II) complex supported on alumina “ $[Mn(Me_2salpnMe_2)/Al_2O_3]$ ” shows significantly higher catalytic activity than other catalysts.

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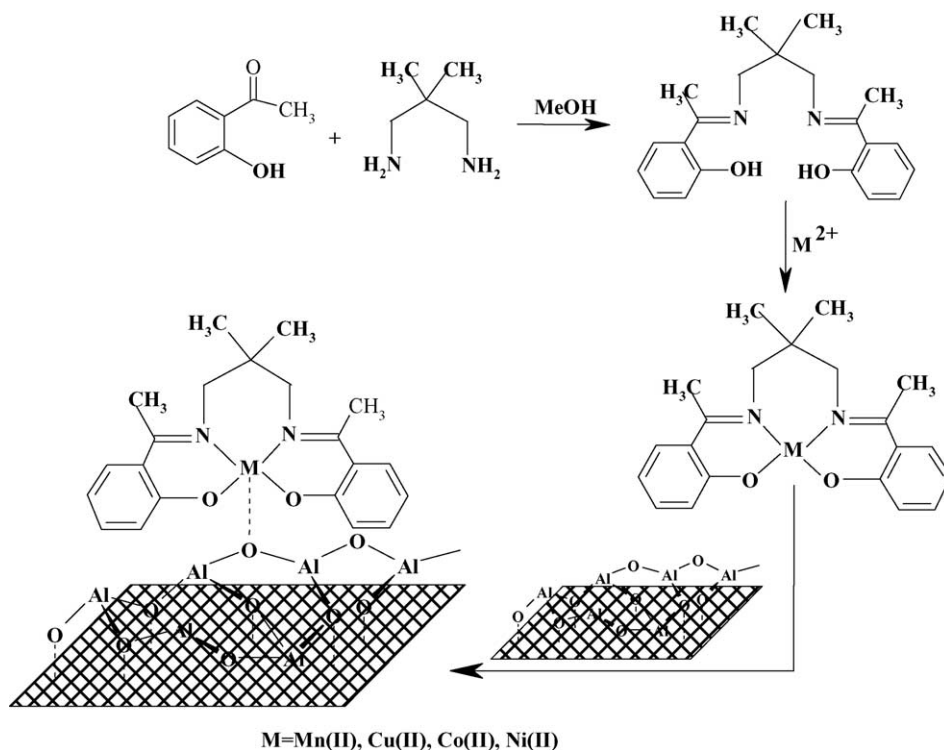
**Keywords:** Schiff-base; Alumina; THBP;  $H_2O_2$ ; Oxidation; Cyclohexene

## 1. Introduction

Selective oxidation of hydrocarbons to give oxygen-containing compounds (alcohols, aldehydes, ketones, acids etc.) is an extremely important and useful reaction in the chemical industry. Normally more than one oxygenate and all products are susceptible to complete combustion to give  $CO_2$  [1]. The search for new selective oxidation catalysts is one of the most important current topics, connected with both industrial and academic research. In this field, the use of homogeneous catalysts has received great attention in the last few years, given that they have shown to be useful in the oxidation of olefins [2]. Despite its interest, this method of

oxidation suffers from some drawbacks from a practical point of view. The low conversion, the catalyst deactivation by  $\mu$ -dimerization through the formation of oxygen bridges, the high cost of the complex and the lack of recycling methods make it difficult for application of this system on a large scale. To avoid these problems, to improve the separation of the catalyst from the reaction medium and to increase its active life, various strategies can be employed. The encapsulation in zeolites [3–8], the grafting on polymers [9–11] or MCM-41 silica [12] and the immobilization in polysiloxane membranes [13] have been used as supporting methods, with moderate to excellent results. Application of alumina-supported catalysis in organic transformation has been receiving attention in recent years [14,15]. Immobilization of homogeneous transition metal catalysts to alumina carriers offers several practical benefits of heterogeneous catalysis, while retaining

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Scheme 1.

the advantages of homogeneous catalytic reactions [14–17]. Some of the attractive features of alumina-supported catalysis include: (1) easy separation of the catalysts from the reagents and reaction products; (2) simplification of methods to recycle expensive catalysts; (3) nonvolatile and nontoxic characteristics to high molecular weight alumina backbones; (4) minimization of certain catalyst deactivation pathways by site isolation. These attractive features of these catalysts could possibly help in developing high through put discovery applications as well as in developing continues catalytic processes for industrial scale synthesis. In this paper, we report the synthesis and characterization of transition metal (cobalt(II), manganese(II), nickel(II) and copper(II)) complexes of the Schiff-base ligand; *N,N'*-bis-( $\alpha$ -methylsalicylidene)-2,2-dimethyl propane-1,3-diamine;  $H_2[Me_2salpnMe_2]$ ; and the same complex immobilized in acidic alumina (Scheme 1);  $[M(Me_2salpnMe_2)/Al_2O_3]$ ; and used in the oxidation of cyclohexene with *tert*-butylhydroperoxide and hydrogen peroxide as oxygen donors.

## 2. Experimental

### 2.1. Materials and physical measurements

All the solvents were purchased from Merck (pro-analysis) and were distilled and dried using molecular sieves (Linda 4 Å) [18]. Manganese(II) acetate, copper(II) acetate, nickel(II) acetate, cobalt(II) acetate, 2-hydroxyacetophe-

none, 2,2-dimethyl-1,3-propanediamine, hydrogen peroxide and *tert*-butylhydroperoxide (solution 80% in di-*tert*-butylperoxide) were obtained from Merck Co. Cyclohexene was distilled under nitrogen and stored over molecular sieves (4 Å). Cyclohexanone was used as an internal standard for the quantitative analysis of the product using gas chromatography. Reference samples of cyclohexene oxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one (Aldrich) were distilled and stored in the refrigerator. Acidic alumina was purchased from Merck (Art. no. 1078, aluminum oxide 90 active acidic, 0.063–0.200 mm). It was activated at 500 °C for 8 h before use.

XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation. Elemental analyses were obtained from Carlo ERBA Model EA 1108 analyzer. The metal contents of the samples were measured by Atomic Absorption Spectrophotometer (AAS-Perkin-Elmer 4100-1319) using a flame approach. The products were analyzed by GC-MS, using a Philips Pu 4400 Chromatograph (capillary column: DB5MS, 30 m), Varian 3400 Chromatograph (15 m capillary column of HP-5; FID) coupled with a QP Finnegan MAT INCOF 50, 70 eV. Diffuse reflectance spectra (DRS) were registered on a Shimadzu UV/3101 PC spectrophotometer the range 1500–200 nm, using MgO as reference. The stability of the supported catalyst was checked after the reaction by UV-vis and possible leaching of the complex was investigated by UV-vis in the reaction solution after filtration of the alumina.

## 2.2. Preparation of $N,N'$ -bis( $\alpha$ -methylsalicylidene)-2,2-dimethylpropane-1,3-diamine; $H_2[Me_2salpnMe_2]$

The stoichiometric amount of 2-hydroxyacetophenone (0.02 mol, 2.72 g) in dissolved methanol (25 ml) is added drop by drop to 2,2-dimethyl-1,3-propanediamine solution (0.01 mol, 1.02 g) in 25 ml methanol. The contents were refluxed for 3 h and a bright yellow precipitate of symmetrical Schiff-base ligand ( $H_2L$ ) was obtained. The yellow precipitate was separated by filtration, washed and dried in vacuum. It was then recrystallized from methanol to yield  $H_2[Me_2salpnMe_2]$  (3 g, 89%). Elemental and spectroscopic analysis of neat and alumina-supported complexes confirmed the molecular composition of ligand (Table 1).

## 2.3. Preparation of $[Co(Me_2salpnMe_2)]$

The flask containing a stirred suspension of cobalt(II) acetate tetrahydrate (3.96 g, 0.016 mol) in propanol (100 cm<sup>3</sup>) was purged with nitrogen, and then warmed to 50 °C under a nitrogen atmosphere.  $N,N'$ -bis( $\alpha$ -methylsalicylidene)-2,2-dimethylpropane-1,3-diamine (5.41 g, 0.016 mol) was added in one portion, and the resulting black suspension was then stirred and heated under reflux under a nitrogen atmosphere for 8 h. Then the mixture was cooled and filtered under reduced pressure. The collected solid was washed with diethylether and dried in air to give black crystalline  $[Co(Me_2salpnMe_2)]$  which was purified by recrystallization from chloroform.

## 2.4. Preparation of $[Mn(Me_2salpnMe_2)]$

The Schiff-base ligand (3.72 g, 0.011 mol) was dissolved in 100 ml of refluxing ethanol and a stream of nitrogen was purged for 4 h to eliminate the oxygen. A solution containing 2.69 g (0.011 mol) of manganese(II) acetate tetrahydrate in water was added dropwise to the deoxygenated ligand solution. The resulting mixture was agitated and refluxed under nitrogen with 5 ml of ethanol followed by 5 ml of water. The mixture was then cooled and filtered under reduced pressure. The collected solid was washed with diethyl ether and dried in air to give yellow crystalline  $[Mn(Me_2salpnMe_2)]$  which purified by recrystallization from chloroform.

## 2.5. Preparation of $[Ni(Me_2salpnMe_2)]$

$H_2[Me_2salpnMe_2]$  (4.73 g, 0.014 mol) was dissolved in 100 ml of ethanol, and the solution was refluxed. To this hot solution was added nickel(II) acetate tetrahydrate (0.014 mol, 3.48 g) dissolved in 100 ml of ethanol. Refluxing was continued for 8 h. Upon cooling the solution, a solid crystalline was obtained which was filtered, washed with ethanol, and dried in vacuum and purified by recrystallization from chloroform.

Table 1  
Chemical composition, DRS absorption, UV–vis and IR stretching frequencies of neat and alumina-supported transition metal complexes

Sample	C (%)	H (%)	N (%)	M (%)	C/N	C/M	$\nu_{C=N}^a$ (cm <sup>-1</sup> )	$d \leftrightarrow d$ (cm <sup>-1</sup> )	$\mu_{eff}$ (MB)	$\Delta_M^a$ (Å <sup>-1</sup> cm <sup>-1</sup> mol <sup>-1</sup> )
$H_2Me_2salpnMe_2$	74.52 (74.41)	7.74 (7.65)	8.28 (8.36)	–	9.00 (8.90)	–	1570	–	–	–
$[Mn(Me_2salpnMe_2)]$	64.44 (64.30)	6.18 (6.04)	7.16 (7.22)	14.04 (13.92)	9.00 (8.91)	4.59 (4.62)	1550	21370 <sup>b</sup>	5.94	12
$[Mn(Me_2salpnMe_2)]-Al_2O_3$	8.97	1.69	1.03	2.05	8.73	4.37	1552	21140	–	–
$[Co(Me_2salpnMe_2)]$	63.80 (63.69)	6.12 (6.01)	7.09 (7.16)	14.91 (14.80)	9.00 (8.90)	4.28 (4.30)	1540	20200 <sup>b</sup>	1.79	18
$[Co(Me_2salpnMe_2)]-Al_2O_3$	8.84	1.65	1.02	2.18	8.69	4.06	1538	20040	–	–
$[Ni(Me_2salpnMe_2)]$	63.84 (63.72)	6.12 (6.04)	7.09 (7.18)	14.85 (14.74)	9.00 (8.87)	4.30 (4.32)	1530	24100 <sup>b</sup>	-0.11	6
$[Ni(Me_2salpnMe_2)]-Al_2O_3$	8.88	1.63	1.01	2.16	8.76	4.12	1527	24000	–	–
$[Cu(Me_2salpnMe_2)]$	63.06 (62.95)	6.05 (5.92)	7.00 (7.10)	15.89 (15.77)	9.00 (8.87)	3.97 (3.99)	1525	17540 <sup>b</sup>	1.77	20
$[Cu(Me_2salpnMe_2)]-Al_2O_3$	8.82	1.60	1.02	2.35	8.69	3.76	1523	17390	–	–
$[Zn(Me_2salpnMe_2)]$	62.77 (62.63)	6.02 (5.91)	6.97 (7.08)	16.27 (16.15)	9.00 (8.85)	3.86 (3.88)	1515	–	–	15

Estimated values are given in parentheses.

<sup>a</sup> Infrared spectra measured as KBr pellets.

<sup>b</sup> In chloroform solutions at 25 °C as never specified for neat complexes.

### 2.6. Preparation of $[Cu(Me_2salpnMe_2)]$

The procedure followed was similar to that for  $[Ni(Me_2salpnMe_2)]$ , except that copper(II) acetate hydrate (0.014 mol, 2.79 g) was used instead of nickel(II) acetate tetrahydrate.

### 2.7. Preparation of $[Zn(Me_2salpnMe_2)]$

This complex was prepared by a method similar to that for  $[Ni(Me_2salpnMe_2)]$  except zinc(II) acetate dihydrate (0.014 mol, 3.07 g) was used instead nickel(II) acetate tetrahydrate.

### 2.8. Preparation of $[M(Me_2salpnMe_2)]/Al_2O_3$

A solution of the  $[M(Me_2salpnMe_2)]$  (2.0 g) in  $CHCl_3$  was added to a suspension of  $Al_2O_3$  (10.0 g) in  $CHCl_3$ . The resulting suspension was stirred at 50 °C under Ar atmosphere. The solid was filtered, washed with  $CHCl_3$ . The  $[M(Me_2salpnMe_2)]/Al_2O_3$  catalyst was dried at 70 °C under vacuum overnight prior to use.

### 2.9. Heterogeneous oxidation of cyclohexene

A mixture of 1.0 g catalyst, 25 ml solvent and 10 mmol cyclohexene was stirred under nitrogen atmosphere in a 50 ml round-bottom flask equipped with a condenser and a dropping funnel at room temperature for 30 min. Then 16 mmol of TBHP (solution 80% in di-*tert*-butylperoxide) or hydrogen peroxide (30% in water) was added. The resulting mixture was then refluxed for 8 h under  $N_2$  atmosphere. After filtration and washing with solvent, the filtrate was concentrated and then subjected to GC analysis. The concentrations of products were determined using cyclohexanone as internal standard.

### 2.10. Homogeneous oxidation of cyclohexene

To a solution of cyclohexene (1 ml), neat metal complex ( $1.02 \times 10^{-5}$  mol) in dichloromethane (10 ml), TBHP (2 ml) was added. The resulting mixture was then refluxed for 8 h under  $N_2$  atmosphere, the solvent evaporated under reduced pressure and the crude analyzed by GC and GC-MS. The concentrations of products were determined using cyclohexanone as internal standard.

## 3. Results and discussion

### 3.1. Synthesis of complexes

Synthesis of the metal complexes were essentially the same and involved heating and stirring of stoichiometric amounts of  $H_2[Me_2salpnMe_2]$  and metal acetate in methanol.

The desired complexes crystallized upon cooling and recrystallized from chloroform. Elemental analysis indicates that all of the complexes are monomeric species formed by coordination of 1 mol of the metal ion and 1 mol  $[Me_2salpnMe_2]$ . All of the metal chelates in this study are insoluble in water but soluble in most organic solvents. Electrical conductivity measurements of the metal complexes give  $\Lambda_M$  values of 6–20  $\Omega^{-1} cm^{-1} mol^{-1}$  and confirm that they are non-electrolytes. The metal content of the ASMC catalysts were estimated by dissolving the known amounts of the heterogeneous catalyst in concentrated HCl and from these solutions, transition metal contents were estimated by atomic absorption spectrometer. The metal content of the different catalysts synthesized were almost the same in all the supported system and was 0.012 mol g<sup>-1</sup>. The chemical composition (Table 1) confirmed the purity and stoichiometry of the neat and alumina-supported complexes. The chemical analysis of the samples reveals the presence of organic matter with a C/N ratio roughly similar to that of neat complexes (Table 1).

### 3.2. IR spectral study

A partial list of the IR spectral data of Schiff-base and supported complexes along with their respective simple complexes are presented in Table 1. However, significant change in some important bands from free ligand noticed. For example, free ligand exhibits  $\nu_{C=N}$  stretch at 1570  $cm^{-1}$ . In complexes, this band shifts to lower frequency and appears at 1515–1550  $cm^{-1}$ , indicating the coordination of azomethine nitrogen to the metal. The appearance of two to three bands in the low frequency region (between 410 and 527  $cm^{-1}$ ) indicates the coordination of phenolic oxygen in addition to azomethine nitrogen. The presence of several bands of medium intensity in 2700–2960  $cm^{-1}$  region indicates the existence of methyl and propylene group of the amine residue of the ligand.

The intensity of the alumina-supported metal complexes (ASMC) is though weak due to low concentration of the complex, the IR spectra of supported complexes are essentially similar to that of the free metal complexes. The adsorbing tendency of the acidic alumina might arise from the presence of oxygen groups on the surface in order to coordinate to metal ion center (Scheme 1). All metal complexes supported on alumina exhibit band around 1200–740  $cm^{-1}$  due to alumina framework. No significant broadening or shift of the structure sensitive alumina vibrations at 1140  $cm^{-1}$  (due to the asymmetric Al–O stretch).

### 3.3. $^1H$ NMR studies of ligand and neat $[Zn(Me_2salpnMe_2)]$

Comparison of  $^1H$  NMR spectral data of the  $H_2[Me_2salpnMe_2]$  and  $[Zn(Me_2salpnMe_2)]$  recorded in DMSO- $d_6$  further supplements the conclusion drawn from IR data. The  $^1H$  NMR spectrum of  $H_2[Me_2salpnMe_2]$  exhibits the following signals: 11.88 (s, 2H, OH), 2.32 (s, 6H,

–C(CH<sub>3</sub>)=N–), 6.61–7.80 (m, 8H, aromatic), 3.52 ppm (s, 4H, CH<sub>2</sub>) and 1.15 (s, 6H, CH<sub>3</sub>–C–). The disappearance of phenolic signal and down field shift of azomethine signal (3.14 ppm, –C(CH<sub>3</sub>)=N–) indicates the coordination of phenolic oxygen after deprotonation and azomethine nitrogen atoms. <sup>1</sup>H NMR spectrum of other neat complexes could not be recorded due to its partial paramagnetic nature of complex as noticed earlier [19].

### 3.4. X-ray diffraction

The X-ray powder diffractograms (XRD) of Al<sub>2</sub>O<sub>3</sub>, NiCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and [Ni(Me<sub>2</sub>salpnMe<sub>2</sub>)]/Al<sub>2</sub>O<sub>3</sub> were recorded to study their crystallinity and to ensure supporting. After careful comparison of XRD patterns of Al<sub>2</sub>O<sub>3</sub> and NiCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, it was observed that, there is one new peak with a *d* value of 1.734 nm in NiCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> this peak was also observed in [Ni(Me<sub>2</sub>salpnMe<sub>2</sub>)]/Al<sub>2</sub>O<sub>3</sub> and [Ni(Me<sub>2</sub>salpnMe<sub>2</sub>)] at the same position. In addition, the [Ni(Me<sub>2</sub>salpnMe<sub>2</sub>)]/Al<sub>2</sub>O<sub>3</sub> exhibits one new signal with value of 8.274 nm, which is a part of the ligand as this signal was also observed in [Ni(Me<sub>2</sub>salpnMe<sub>2</sub>)] but not observed in Al<sub>2</sub>O<sub>3</sub> or NiCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. This information clearly indicates the support of [Ni(Me<sub>2</sub>salpnMe<sub>2</sub>)] on alumina. Very low intensity of other peaks made it difficult to distinguish them from the other peaks in the XRD pattern of the ASMC.

### 3.5. Electronic spectral studies

Within the UV spectrum of the ligand has been observed the existence of two absorption bands assigned to the transition  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  at 41500 and 34500 cm<sup>-1</sup>, respectively. Also these transitions are to be found in the spectra of the complexes, but they are shifted to lower frequencies, confirming the coordination of the ligand to the metal ions [20]. In addition, in the spectra of the some complexes of H<sub>2</sub>Me<sub>2</sub>salpnMe<sub>2</sub> ligand, the new bands observed in the 25,640–23,250 cm<sup>-1</sup> range can be attributed to the charge-transfer bands (ligand to metal or metal to ligand centre) [21]. The magnetic measurement obtained at room temperature (Table 1) for manganese complex in the powder state is 5.94 BM, i.e., close to the spin only value expected for high spin manganese(II) in a tetrahedral environment [21]. The electronic spectrum of [Co(Me<sub>2</sub>salpnMe<sub>2</sub>)] is very similar to that reported for related cobalt(II) complexes [22]. The spectrum of the [Co(Me<sub>2</sub>salpnMe<sub>2</sub>)] exhibits one band at 20,200 cm<sup>-1</sup> that is assigned to  $d \leftrightarrow d$  transitions. This geometry is confirmed by the values of the effective magnetic moment (1.79 BM). The electronic spectrum of the [Ni(Me<sub>2</sub>salpnMe<sub>2</sub>)] exhibit one band at 24,100 cm<sup>-1</sup> that can be assigned to a  $d \leftrightarrow d$  transition of the metal ion. The average energy of this absorption is comparable to  $d \leftrightarrow d$  transitions of other square planar Schiff-base of nickel(II) chelates with nitrogen and oxygen donor atoms [23]. The magnetic moment suggests a square-planar geometry. The spectrum of the [Cu(Me<sub>2</sub>salpnMe<sub>2</sub>)] exhibit one broad band

at 17,540 cm<sup>-1</sup> that is attributed to  $d \leftrightarrow d$  transitions. The spectrum of this complex is similar to those reported for Cu(II) complexes [23]. The magnetic moment (1.77 BM) suggests a square-planar geometry.

### 3.6. Diffuse reflectance spectra

The diffuse reflectance spectra of Mn(II), Co(II), Ni(II) and Cu(II) complexes contain (Me<sub>2</sub>salpnMe<sub>2</sub>) were almost identical before and after supporting, indicating the complexes maintain their geometry even after supported without significant distortion. For example, the UV–vis spectrum of CuCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> does not show any absorption band above 380 nm, while spectrum of [Cu(Me<sub>2</sub>salMe<sub>2</sub>)]/Al<sub>2</sub>O<sub>3</sub> displays one broad band at 380 nm, which is probably due to a symmetry forbidden ligand to metal charge transfer transition, similar to that observed in Cu(CH<sub>3</sub>COO)<sub>2</sub>(H<sub>2</sub>O) [24c] at 370 nm. A very weak but broad absorption at 575 nm is also observed when highly concentrated sample was used to record the spectrum and this is due to  $d-d$  transition in the complex [24c]. These data compare closely with that of pure complex [Cu(Me<sub>2</sub>salMe<sub>2</sub>)] as well as of [Cu(salpn)] and are indicative of a square-planar structure present on the alumina. Other two bands appearing at 250 (sh) and 220 nm can be assigned as intra-ligand transition. The electronic spectral data of ligand, neat [Cu(Me<sub>2</sub>salMe<sub>2</sub>)] and [Cu(Me<sub>2</sub>salMe<sub>2</sub>)]/Al<sub>2</sub>O<sub>3</sub> are presented in Table 1.

### 3.7. Catalytic activity

We have recently reported the activation of C–H bond with TBHP and H<sub>2</sub>O<sub>2</sub> in the presence of exchanged zeolite NaY with transition metal elements, alumina-supported and zeolite-encapsulation of metal complexes [25]. We showed that some complexes of Mn(II) included in zeolite Y, catalyzed the oxygen transfer from TBHP to cyclohexene and concluded that such simple systems mimic the behavior of cytochrome P-450 type oxidation systems [25b]. We also showed the [Mn(haacac)]/Al<sub>2</sub>O<sub>3</sub>; (haacac = bis(2-hydroxyanyl)acetylacetone), catalyzed cyclohexene oxidation with the highest reactivity and selectivity and 2-cyclohexene-1-one was formed as the main product [25d], and we showed a simple catalyst system of alumina supported Mn(II) complexes with a number of bidentate ligands of N,N; N,O and O,O donors atoms in the oxidation of cyclohexene [25c]. Since, alumina-supported metal systems exhibit catalytic activity in a wide range of the industrially important processes and have been extensively studied, we decided to investigate the effect of transition metal complexes with a tetradentate Schiff-base ligand “*N,N'*-bis-( $\alpha$ -methylsalicylidene)-2,2-dimethylpropane-1,3-diamine”, H<sub>2</sub>[Me<sub>2</sub>salpnMe<sub>2</sub>], supported on acidic alumina in the oxidation of cyclohexene with TBHP.

Results of Table 2 show the catalytic activity of homogeneous catalysts. Comparing between neat and

Table 2  
Oxidation of cyclohexene with TBHP catalyzed by metal complexes in  $\text{CH}_2\text{Cl}_2$

Catalyst	Conversion (%)	Selectivity (%)		
		Ketone <sup>a</sup>	Alcohol <sup>b</sup>	Peroxide <sup>c</sup>
$[\text{Mn}(\text{Me}_2\text{salpnMe}_2)]$	50.9	56.6	21.6	21.8
$[\text{Co}(\text{Me}_2\text{salpnMe}_2)]$	42.7	47.6	27.4	25.0
$[\text{Ni}(\text{Me}_2\text{salpnMe}_2)]$	23.8	31.4	38.7	29.9
$[\text{Cu}(\text{Me}_2\text{salpnMe}_2)]$	36.9	35.2	29.8	35.0

<sup>a</sup> 2-Cyclohexene-1-one.

<sup>b</sup> 2-Cyclohexene-1-ol.

<sup>c</sup> 1-(*tert*-butylperoxy)-2-cyclohexene.

alumina-supported (Tables 3 and 4 and Figs. 1 and 2) complexes as catalyst evidence that ASMC gave higher conversion of cyclohexene than their corresponding neat complexes. The higher activity of supported complexes is because of site isolation of the complexes.

The selectivity and activity results of these ASMC on the oxidation of cyclohexene with TBHP are given in Tables 3 and 4 and Figs. 1 and 2. At the end of the reaction, the catalyst was separated by filtration, thoroughly washed with solvent and reused under similar conditions. Although

Table 3  
Oxidation of cyclohexene with TBHP catalyzed by metal complexes on alumina in  $\text{CH}_2\text{Cl}_2$

Catalyst	Conversion (%)	Selectivity (%)		
		Ketone <sup>a</sup>	Alcohol <sup>b</sup>	Peroxide <sup>c</sup>
$[\text{Mn}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3$	82.8	80.5	14.2	5.3
$[\text{Mn}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3^{\text{d}}$	81.9	79.2	15.6	5.2
$[\text{Mn}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3^{\text{e}}$	81.1	78.6	16.4	5.0
$[\text{Mn}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3^{\text{f}}$	80.3	78.1	17.0	4.9
$[\text{Co}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3$	74.6	74.6	21.0	4.4
$[\text{Ni}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3$	49.6	64.2	26.7	9.1
$[\text{Cu}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3$	60.1	69.6	18.6	11.8

<sup>a</sup> 2-Cyclohexene-1-one.

<sup>b</sup> 2-Cyclohexene-1-ol.

<sup>c</sup> 1-(*tert*-butylperoxy)-2-cyclohexene.

<sup>d</sup> First reuse.

<sup>e</sup> Second reuse.

<sup>f</sup> Third reuse.

Table 4  
Oxidation of cyclohexene with TBHP catalyzed by metal complexes on alumina in  $\text{CH}_3\text{Cl}$

Catalyst	Conversion (%)	Selectivity (%)		
		Ketone <sup>a</sup>	Alcohol <sup>b</sup>	Peroxide <sup>c</sup>
$[\text{Mn}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3$	79.6	76.7	16.9	6.4
$[\text{Mn}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3^{\text{d}}$	78.8	75.7	18.2	6.1
$[\text{Mn}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3^{\text{e}}$	78.1	75.1	19.0	5.9
$[\text{Mn}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3^{\text{f}}$	77.4	74.3	20.1	5.6
$[\text{Co}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3$	69.7	70.6	23.1	6.3
$[\text{Ni}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3$	45.1	60.1	28.8	11.1
$[\text{Cu}(\text{Me}_2\text{salpnMe}_2)]\text{-Al}_2\text{O}_3$	57.4	65.6	22.1	12.3

<sup>a</sup> 2-Cyclohexene-1-one.

<sup>b</sup> 2-Cyclohexene-1-ol.

<sup>c</sup> 1-(*tert*-butylperoxy)-2-cyclohexene.

<sup>d</sup> First reuse.

<sup>e</sup> Second reuse.

<sup>f</sup> Third reuse.

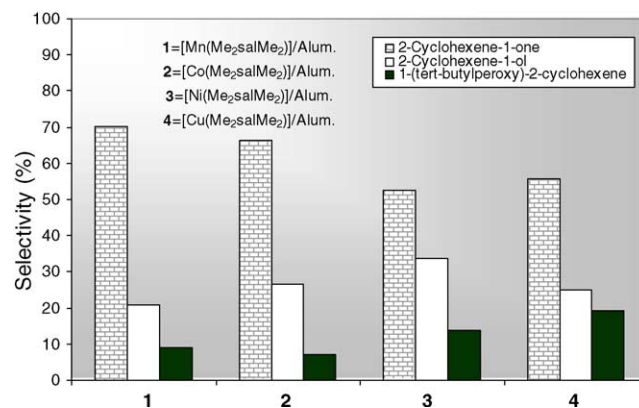


Fig. 1. Oxidation products distribution in methanol with  $[\text{M}(\text{Me}_2\text{salMe}_2)]\text{-Al}_2\text{O}_3/\text{TBHP}$ .

the analysis of the recovered catalysts by atomic absorption spectroscopy showed no reduction in the amount of transition metal ions, they showed a slightly lower catalytic activity (2.5%) (Tables 3 and 4).

The effect of transition metal complexes supported on alumina was studied on the oxidation of cyclohexene with TBHP in dichloromethane and the results are shown in Table 3. As

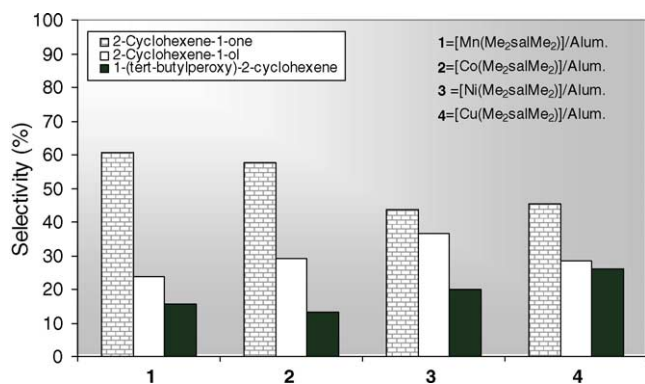


Fig. 2. Oxidation products distribution in acetonitrile with  $[M(\text{Me}_2\text{salMe}_2)]\text{-Al}_2\text{O}_3/\text{TBHP}$ .

shown in Table 3, only allylic oxidation has occurred with the formation of 2-cyclohexene-1-one, 2-cyclohexene-1-ol and 1-(*tert*-butylperoxy)-2-cyclohexene. Oxidation with the same oxidant in the presence of  $\text{MnCl}_2/\text{Al}_2\text{O}_3$  was 29.1% [25c]. The increase of conversion from 29.4% [25c] to 82.8% compared to  $\text{MnCl}_2/\text{Al}_2\text{O}_3$  with  $[\text{Mn}(\text{Me}_2\text{salpnMe}_2)]/\text{Al}_2\text{O}_3$  indicates that the existence of ligand has increased the activity of the catalyst by a factor of 2.84. From the results indicated in Tables 2–4 and Figs. 1 and 2 it is evident that cyclohexene-2-one is selectively formed in the presence of all catalysts.

The trend observed in Tables 2–4 and Figs. 1 and 2 can be explained by the donor ability of ligand available in the complex catalysts. As Wang and co-workers have pointed out recently, the key point in the conversion of cyclohexene to the products is the reduction of  $\text{L-Mn}^{3+}$  to  $\text{L-Mn}^{2+}$ . This reduction to  $\text{L-Mn}^{2+}$  is facilitated with the ligands available around the metal cation [26]. The formation of the allylic oxidation products 2-cyclohexene-1-one and 2-cyclohexene-1-ol shows the preferential attack of the activated C–H bond over the C=C bond. The formation of 1-(*tert*-butylperoxy)-2-cyclohexene shows the presence of radical reactions [27]. That TBHP as oxidant promotes the allylic oxidation pathway and epoxidation is minimized, especially under the highly acidic properties of alumina supported with divalent and trivalent transition metal ions and complexes, has been observed by us and others [25,28]. It should be emphasized that the destructive oxidation of alkenes via epoxidation pathway with  $\text{H}_2\text{O}_2$  under the catalytic effect of alumina-supported Mn(II) complexes seems interesting [25]. Although the two systems are alike, it is the oxidant structure that has changed the fate of the reaction.

When the oxidant was changed to hydrogen peroxide (Fig. 3), the oxidation occurred on the double bond and cyclohexene epoxide obtained as the sole product. It seems that the diol resulted from the epoxide ring opening under the aqueous acidic conditions. Since both  $\text{H}_2\text{O}_2$  and TBHP oxidize cyclohexene in the presence of alumina-supported metal complexes, but that only  $\text{H}_2\text{O}_2$  and not TBHP gave epoxidation of cyclohexene under the similar conditions leads us to conclude that the two types of reactions do not occur via

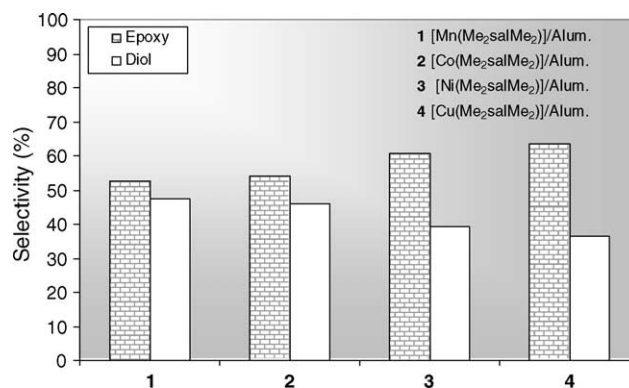


Fig. 3. Oxidation products distribution in acetonitrile with  $[M(\text{Me}_2\text{salMe}_2)]\text{-Al}_2\text{O}_3/\text{H}_2\text{O}_2$ .

a common intermediate. As Valentine and his co-workers have pointed out one possible explanation is that the species responsible for the cyclohexene oxidation are the products formed from cleavage of the O–O bond, whereas, the epoxidation reaction occurs by a direct reaction of olefin with coordinated HOO radical. Since the O–O bond of HOOH is 5 kcal/mol stronger than that of TBHP, an HOO complex is expected to have a higher activation energy for O–O bond cleavage than a TBOO complex and, therefore, to have a longer lifetime [29].

The effect of various solvents for the oxidation of cyclohexene with  $[M(\text{Me}_2\text{salpnMe}_2)]/\text{Al}_2\text{O}_3$  catalysts was also studied (Fig. 4). The oxidation reactions were carried out in protic and aprotic solvents. The results are given in Tables 3 and 4 and Figs. 1 and 2. In all the oxidation reaction, 2-cyclohexene-1-one was formed as the major product. When the reaction was carried out in a coordinating solvent like  $\text{CH}_3\text{CN}$  the conversion decreased by a factor of  $\sim 1.53$  (Fig. 4). This might be attributed to the donor number of acetonitrile (14.1) and, therefore, to its higher ability to occupy the vacant spaces around the metal center and prevent

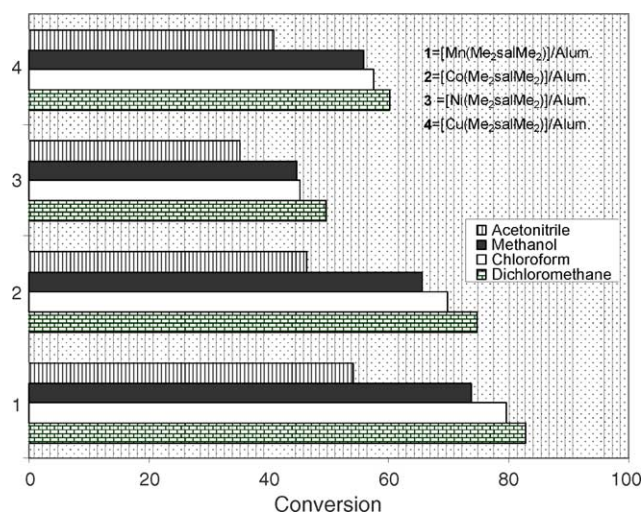


Fig. 4. Effect of solvent on the conversion by  $[M(\text{Me}_2\text{salMe}_2)]/\text{Alum.}/\text{TBHP}$ .

the approaching of oxidant molecules. In dichloromethane and chloroform the yields of 2-cyclohexene-1-ol and 2-cyclohexene-1-one were higher and lower yield of the peroxy species was obtained as compared to the other solvents. The efficiency of the catalysts for oxidation of cyclohexene in different solvents decreases in the order: dichloromethane > chloroform > methanol > acetonitrile.

#### 4. Conclusions

In this study, we have used a rather simple catalysis system of alumina-supported manganese(II), cobalt(II), nickel(II) and copper(II) complexes with a Schiff-base ligand “*N,N'*-bis-( $\alpha$ -methylsalicylidene)-2,2-dimethylpropane-1,3-diamine,  $H_2[Me_2salpnMe_2]$ ” in the oxidation of cyclohexene. Oxidation of allylic site and double bond were resulted with the oxidants of TBHP and  $H_2O_2$ , respectively. The high percentage yield of reactions especially in the presence of alumina-supported manganese(II) complex seems promising. The extension of the method to different olefins is currently under investigation in our laboratory.

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